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Ternary Alloy Systems

Phase Diagrams, Crystallographic and Thermodynamic Data

critically evaluated by MSIT[®]

Subvolume C

Non-Ferrous Metal Systems

Part 4

Selected Nuclear Materials and Engineering Systems

Editors

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Materials Science International Team, MSIT[®]



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Preface

This volume provides basic information to a field that is facing a strong revival of research and engineering in a growing number of countries. The volume can not claim to be comprehensive in covering all systems, and it has to be noted that for nuclear systems the way from phase diagrams to applicable alloys often is much more complicated than in non-nuclear materials. They are special, Plutonium systems in particular, and require great care in the research of material-property relations.

The sub-series *Ternary Alloy Systems of the Landolt-Börnstein New Series* provides reliable and comprehensive descriptions of the materials constitution, based on critical intellectual evaluations of all data available at the time, and it critically weights the different findings, also with respect to their compatibility with today's edge binary phase diagrams. Selected are ternary systems of importance to industrial alloy development and systems which gained scientific interest in the recent years otherwise. In a ternary materials system, however, one may find alloys for various applications, depending on the chosen composition.

Reliable phase diagrams provide scientists and engineers with basic information of eminent importance for fundamental research and for the development and optimization of materials. So collections of such diagrams are extremely useful, if the data on which they are based have been subjected to critical evaluation, like in these volumes. Critical evaluation means: where contradictory information is published data and conclusions are being analyzed, broken down to the firm facts and re-interpreted in the light of all present knowledge. Depending on the information available this can be a very difficult task to achieve. Critical evaluations establish descriptions of reliably known phase configurations and related data.

The evaluations are performed by MSIT[®], Materials Science International Team, a group which has been working together for 20 years now. Within this team skilled expertise is available for a broad range of methods, materials and applications. This joint competence is employed in the critical evaluation of the often conflicting literature data. Particularly helpful in this are targeted thermodynamic calculations for individual equilibria, driving forces or complete phase diagram sections.

Insight in materials constitution and phase reactions is gained from many distinctly different types of experiments, calculation and observations. Intellectual evaluations which interpret all data simultaneously reveal the chemistry of a materials system best. The conclusions on the phase equilibria may be drawn from direct observations e.g. by microscope, from monitoring caloric or thermal effects or measuring properties such as electric resistivity, electro-magnetic or mechanical properties. Other examples of useful methods in materials chemistry are mass-spectrometry, thermo-gravimetry, measurement of electro-motive forces, X-ray and microprobe analyses. In each published case the applicability of the chosen method has to be validated, the way of actually performing the experiment or computer modeling has to be validated and the interpretation of the results with regard to the material's chemistry has to be verified.

An additional degree of complexity is introduced by the material itself, as the state of the material under test depends heavily on its history, in particular on the way of homogenization, thermal and mechanical treatments. All this is taken into account in an MSIT[®] expert evaluation.

To include binary data in the ternary evaluation is mandatory. Each of the three-dimensional ternary phase diagrams has edge binary systems as boundary planes; their data have to match the ternary data smoothly. At the same time each of the edge binary systems A-B is a boundary plane for many ternary A-B-X systems. Therefore combining systematically binary and ternary evaluations can lead to a level of increased confidence and reliability in both ternary and binary phase diagrams. This has started systematically for the first time here, by the MSIT[®] Evaluation Programs applied to the *Landolt-Börnstein New Series*. The degree of success, however, depends on both the nature of materials and scientists!

The multitude of correlated or inter-dependant data requires special care. Within MSIT[®] an evaluation routine has been established that proceeds knowledge driven and applies both human based expertise and electronically formatted data and software tools. MSIT[®] internal discussions take place in almost all evaluation works and on many different specific questions, adding the competence of a team to the work of individual authors. In some cases the authors of earlier published work contributed to the knowledge base by making their original data records available for re-interpretation. All evaluation reports published here have undergone a thorough review process in which the reviewers had access to all the original data.

In publishing we have adopted a standard format that provides the reader with the data for each ternary system in a concise and consistent manner, as applied in the MSIT[®] Workplace: Phase Diagrams Online. The standard format and special features of the Landolt-Börnstein compendium are explained in the Introduction to the volume.

In spite of the skill and labor that have been put into this volume, it will not be faultless. All criticisms and suggestions that can help us to improve our work are very welcome. Please contact us via effenberg@msiwp.com. We hope that this volume will prove to be an as useful tool for the materials scientist and engineer as the other volumes of *Landolt-Börnstein New Series* and the previous works of MSIT[®] have been. We hope that the *Landolt-Börnstein Sub-series Ternary Alloy Systems* will be well received by our colleagues in research and industry.

On behalf of the participating authors we want to thank all those who contributed their comments and insight during the evaluation process. In particular we thank the reviewers - Nathalie Lebrun, Marina Bulanova, Andy Watson, Pierre Perrot, Artem Kozlov, Olga Fabrichnaya, Tamara Velikanova, Anatoliy Bondar, Joachim Gröbner, Yong Du, Ludmila Tretyachenko, Volodymyr Ivanchenko, Hans Leo Lukas, Nataliya Bochar, Matvei Zinkevich and Lazar Rokhlin.

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Günter Effenberg, Svitlana Ilyenko and Oleksandr Dovbenko

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- Links to Literature (up-to-date bibliographic data base)
- Diagrams as Published (not MSIT[®]-evaluated diagrams)
- Research Results (published and proprietary data)
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This service is free of charge for Landolt-Börnstein subscribers and applies for material systems included in the sub-series IV/11. As eligible Springer customer, please contact MSI for access at license@msiwp.com.

Contents and supplementary information to the Landolt-Boernstein sub-series IV/11 are made by MSI, Materials Science International Services, GmbH, Stuttgart and its global team MSIT[®], as part of their ongoing Phase Diagram Evaluation Programs. For details on “MSIT[®] Workplace, Phase Diagrams Online” see: <http://www.matport.com>.

Introduction

Data Covered

The series focuses on light metal ternary systems and includes phase equilibria of importance for alloy development, processing or application, reporting on selected ternary systems of importance to industrial light alloy development and systems which gained otherwise scientific interest in the recent years.

General

The series provides consistent phase diagram descriptions for individual ternary systems. The representation of the equilibria of ternary systems as a function of temperature results in spacial diagrams whose sections and projections are generally published in the literature. Phase equilibria are described in terms of liquidus, solidus and solvus projections, isothermal and pseudobinary sections; data on invariant equilibria are generally given in the form of tables.

The world literature is thoroughly and systematically searched back to the year 1900. Then, the published data are critically evaluated by experts in materials science and reviewed. Conflicting information is commented upon and errors and inconsistencies removed wherever possible. It considers those, and only those data, which are firmly established, comments on questionable findings and justifies re-interpretations made by the authors of the evaluation reports.

In general, the approach used to discuss the phase relationships is to consider changes in state and phase reactions which occur with decreasing temperature. This has influenced the terminology employed and is reflected in the tables and the reaction schemes presented.

The system reports present concise descriptions and hence do not repeat in the text facts which can clearly be read from the diagrams. For most purposes the use of the compendium is expected to be self-sufficient. However, a detailed bibliography of all cited references is given to enable original sources of information to be studied if required.

Structure of a System Report

The constitutional description of an alloy system consists of text and a table/diagram section which are separated by the bibliography referring to the original literature (see Fig. 1). The tables and diagrams carry the essential constitutional information and are commented on in the text if necessary.

Where published data allow, the following sections are provided in each report:

Introduction

The opening text reviews briefly the status of knowledge published on the system and outlines the experimental methods that have been applied. Furthermore, attention may be drawn to questions which are still open or to cases where conclusions from the evaluation work modified the published phase diagram.

Binary Systems

Where binary systems are accepted from standard compilations reference is made to these compilations. In other cases the accepted binary phase diagrams are reproduced for the convenience of the reader. The selection of the binary systems used as a basis for the evaluation of the ternary system was at the discretion of the assessor.

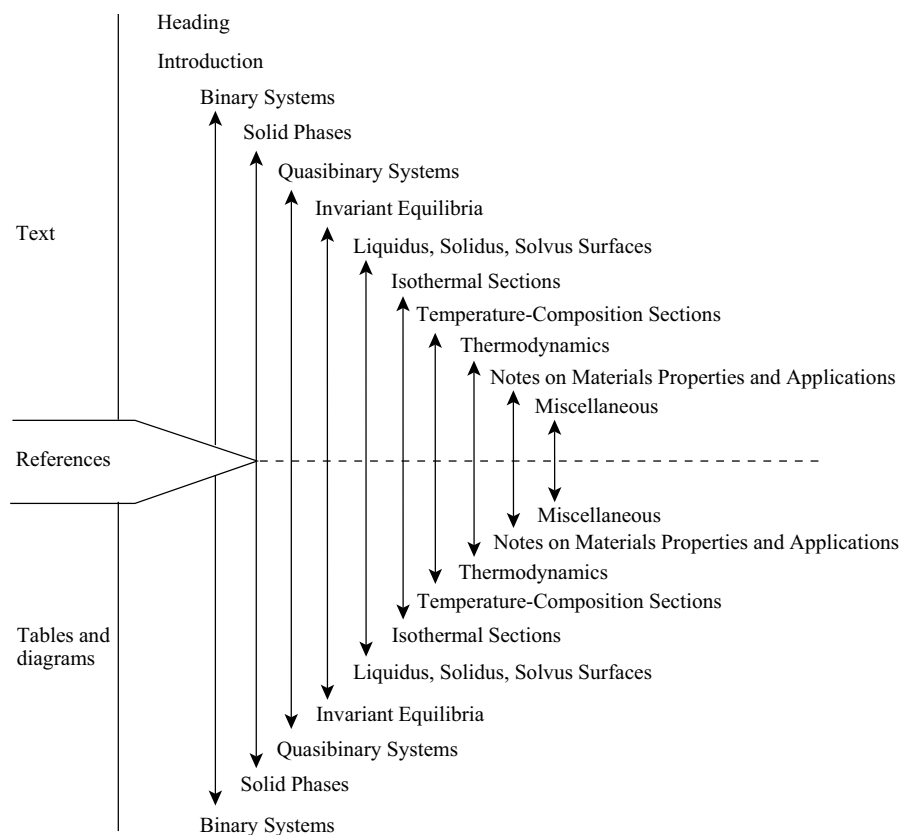


Fig. 1: Structure of a system report

Solid Phases

The tabular listing of solid phases incorporates knowledge of the phases which is necessary or helpful for understanding the text and diagrams. Throughout a system report a unique phase name and abbreviation is allocated to each phase.

Phases with the same formulae but different space lattices (e.g. allotropic transformation) are distinguished by:

- small letters (h), high temperature modification ($h_2 > h_1$)
(r), room temperature modification
(l), low temperature modification ($l_1 > l_2$)
- Greek letters, e.g., ϵ , ϵ'
- Roman numerals, e.g., (I) and (II) for different pressure modifications.

In the table “Solid Phases” ternary phases are denoted by * and different phases are separated by horizontal lines.

Quasibinary Systems

Quasibinary (pseudobinary) sections describe equilibria and can be read in the same way as binary diagrams. The notation used in quasibinary systems is the same as that of vertical sections, which are reported under “Temperature – Composition Sections”.

Invariant Equilibria

The invariant equilibria of a system are listed in the table “Invariant Equilibria” and, where possible, are described by a constitutional “Reaction Scheme” (Fig. 2).

The sequential numbering of invariant equilibria increases with decreasing temperature, one numbering for all binaries together and one for the ternary system.

Equilibria notations are used to indicate the reactions by which phases will be

- decomposed (e- and E-type reactions)
- formed (p- and P-type reactions)
- transformed (U-type reactions)

For transition reactions the letter U (Übergangsreaktion) is used in order to reserve the letter *T* to denote temperature. The letters d and D indicate degenerate equilibria which do not allow a distinction according to the above classes.

Liquidus, Solidus, Solvus Surfaces

The phase equilibria are commonly shown in triangular coordinates which allow a reading of the concentration of the constituents in at.%. In some cases mass% scaling is used for better data readability (see Figs. 3 and 4).

In the polythermal projection of the liquidus surface, monovariant liquidus grooves separate phase regions of primary crystallization and, where available, isothermal lines contour the liquidus surface (see Fig. 3).

Isothermal Sections

Phase equilibria at constant temperatures are plotted in the form of isothermal sections (see Fig. 4).

Temperature – Composition Sections

Non-quasibinary *T*-*x* sections (or vertical sections, isopleths, polythermal sections) show the phase fields where generally the tie lines are not in the same plane as the section. The notation employed for the latter (see Fig. 5) is the same as that used for binary and pseudobinary phase diagrams.

Thermodynamics

Experimental ternary data are reported in some system reports and reference to thermodynamic modelling is made.

Notes on Materials Properties and Applications

Noteworthy physical and chemical materials properties and application areas are briefly reported if they were given in the original constitutional and phase diagram literature.

Miscellaneous

In this section noteworthy features are reported which are not described in preceding paragraphs. These include graphical data not covered by the general report format, such as lattice spacing – composition data, *p*-*T*-*x* diagrams, *etc.*

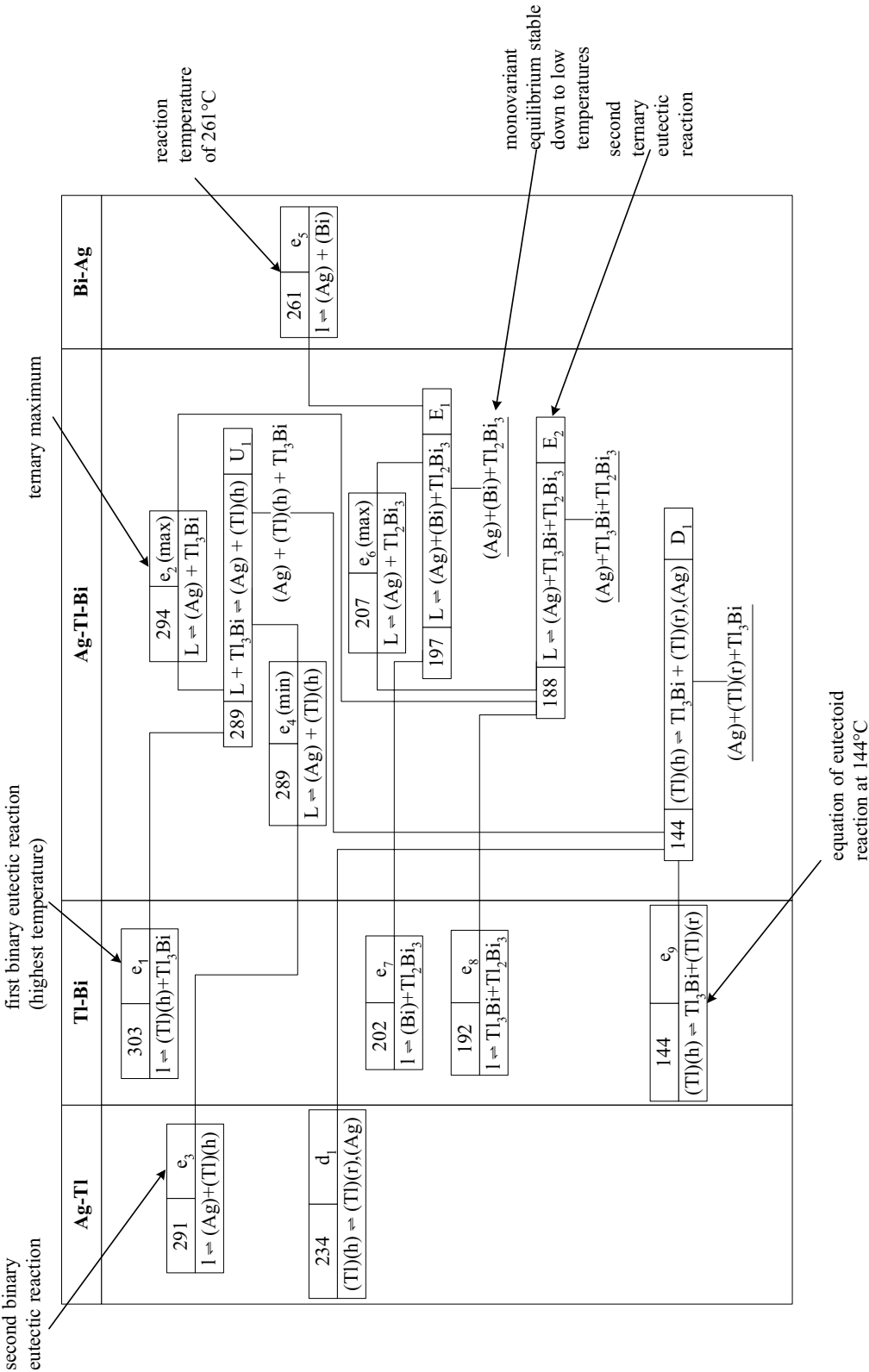
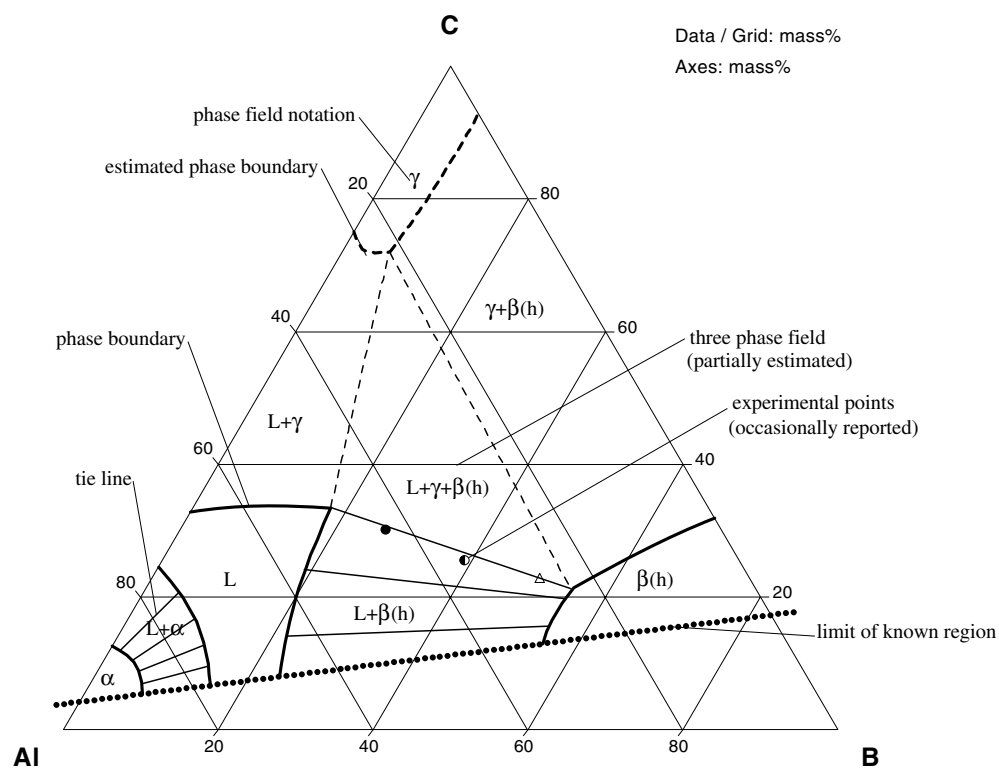
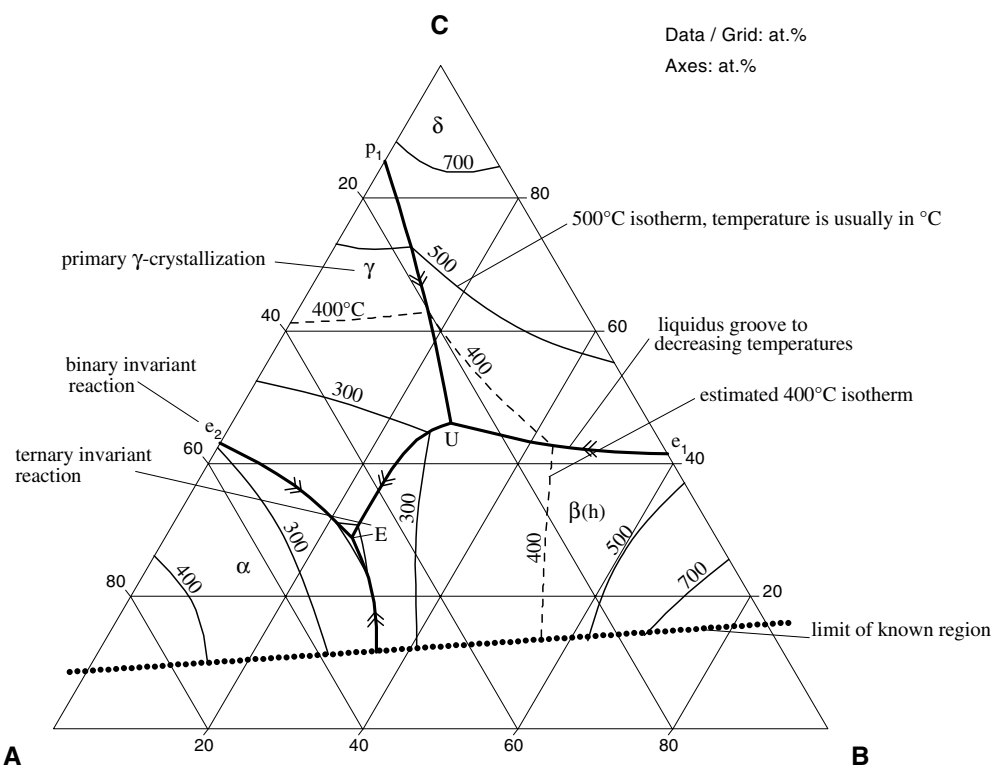


Fig 2: Typical reaction scheme



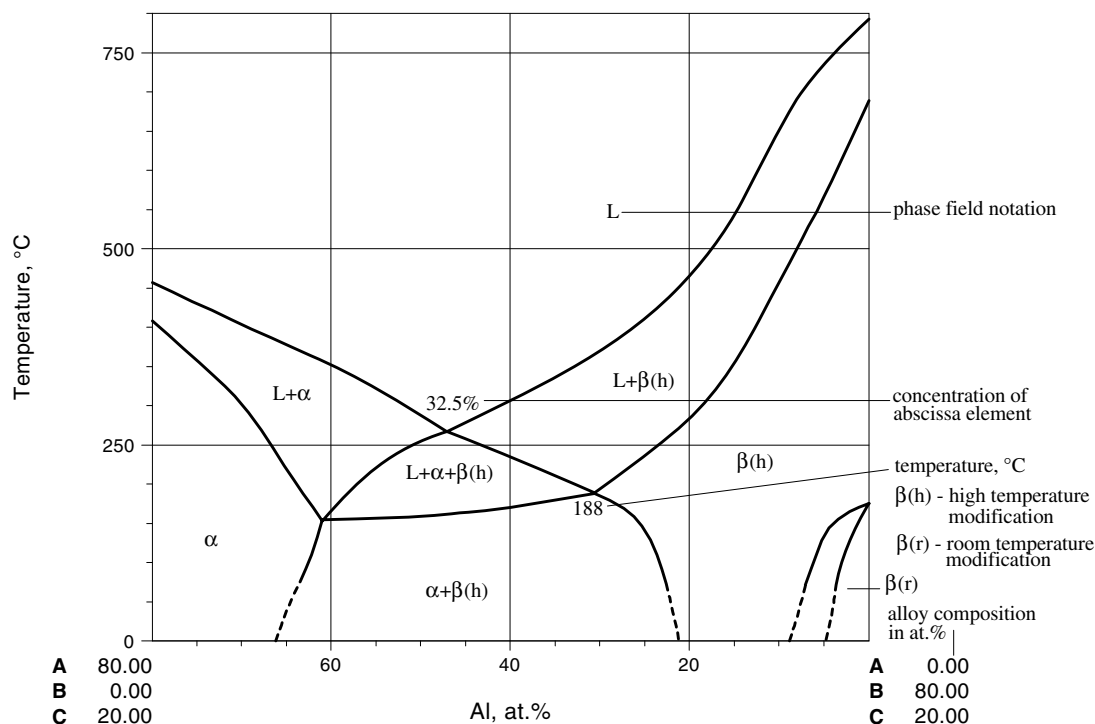


Fig. 5: Hypothetical vertical section showing notation employed

References

The publications which form the bases of the assessments are listed in the following manner:

[1974Hay] Hayashi, M., Azakami, T., Kamed, M., "Effects of Third Elements on the Activity of Lead in Liquid Copper Base Alloys" (in Japanese), *Nippon Kogyo Kaishi*, **90**, 51-56 (1974) (Experimental, Thermodyn., 16)

This paper, for example, whose title is given in English, is actually written in Japanese. It was published in 1974 on pages 51- 56, volume 90 of *Nippon Kogyo Kaishi*, the Journal of the Mining and Metallurgical Institute of Japan. It reports on experimental work that leads to thermodynamic data and it refers to 16 cross-references.

Additional conventions used in citing are:

to indicate the source of accepted phase diagrams

* to indicate key papers that significantly contributed to the understanding of the system.

Standard reference works given in the list "General References" are cited using their abbreviations and are not included in the reference list of each individual system.

General References

- [C.A.] *Chemical Abstracts* - pathways to published research in the world's journal and patent literature - <http://www.cas.org/>
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IV/11 Ternary Alloy Systems

Phase Diagrams, Crystallographic and Thermodynamic Data

Subvolume C: Non-Ferrous Metal Systems

Part 4: Selected Nuclear Materials and Engineering Systems

Al - ... Al - Fe - U Al - O - Pu Al - Si - U	Ce - ... Ce - Mg - O	N - ... N - Pu - U N - Pu - Zr N - Th - U N - U - Zr	Pu - ... Pu - Th - U Pu - U - Zr
C - ... C - Fe - Pu C - Fe - U C - Mo - U C - Pd - Pu C - Pd - Th C - Pd - U C - Pu - Rh C - Pu - Ru C - Pu - U C - Pu - Zr C - Rh - Th C - Rh - U C - Ru - Th C - Ru - U C - Th - U C - Th - Zr C - U - Zr	Cs - ... Cs - Fe - O Cs - Mo - O Cs - O - U Cs - O - Zr	Nb - ... Nb - Si - U	Ru - ... Ru - Si - U
	Fe - ... Fe - N - U Fe - Na - O Fe - O - Pb Fe - O - U Fe - U - Zr	O - ... O - Pb - Zr O - Pu - U O - Pu - Zr O - Th - Zr O - U - Zr	Th - ... Th - U - Zr
	Mo - ... Mo - O - U Mo - Ru - U Mo - Si - U	Pd - ... Pd - Rh - U	

Remarks on the Actinide Alloying Behavior

Riccardo Ferro and Gabriele Cacciamani

Introduction

The actinide metals represent a peculiar group of elements and are constituents of very important materials systems, their dual use in civil and war applications very often generated strong emotional responses which will become more pronounced and controversial in future.

On the other side, from a more fundamental point of view, actinides are located at a crucial point of the Periodic Table, where peculiar properties may be noticed. Actinides, together with lanthanides, are the inner transition metals and form the *f*-block of the Periodic Table. Several characteristics of both families show more or less regular trends which have been widely studied by both experimental and theoretical methods, and often were used for extrapolation and prediction of the alloying behavior of such element combinations. Experimental investigations on actinide systems are indeed extremely difficult, as can be easily verified by examining the experimental papers, and therefore critical assessment of the available data and extrapolation, modelling and calculation techniques are important approaches for investigating constitutional properties of actinide-based alloys.

A few comments on the general alloying behavior of the actinides are reported in this introductory chapter, while more detailed information on selected ternary systems relevant to the nuclear materials technology is reported in the following contributions compiled by several authors of the MSI Team.

The overall information collected in this book, even in the relative scarcity of experimental results reported in the scientific literature, may be an important contribution not only to the development of nuclear materials but also to the science of materials constitution and physical chemistry in general, of this intriguing group of elements.

For the actinide systems we may suggest the Editors to go beyond the possibility of books: making the MSI research platform available for the coming renaissance in Europe of a peaceful nuclear research, including but not limited to phase diagrams.

While compiling this introductory chapter we have been continuously supported by Dr. Günter Effenberg, Dr. Svitlana Ilyenko and the staff at MSI. On this occasion we would like to thank them all for their hard work in planning, organizing and managing this multi-disciplinary, multi-national and multi-component adventure of a multi volume Landolt-Boernstein series.

1. Actinide Elements and Inter-Actinide Binary Systems

1.1 Actinide Elements

A summary of the constitutional properties of the actinide elements is given in Table 1, where crystal structure data (structural types, lattice parameters) and temperature range of stability relevant to the elemental phases are reported.

A different presentation of the same data is shown in Fig. 1, where the temperature ranges of stability of the different allotropic forms are shown as a function of the actinide atomic number. This figure (the history of which is reported in [2000Bor]) highlights the progressive structural changes we have as a function of the atomic number along the actinide series. It can also be underlined that this figure may be used as a first presentation of a group of inter-actinide binary systems: those formed by each element with the adjacent ones in the sequence.

A second interconnected diagram showing phase relations of the actinide metals at room temperature as a function of pressure is reported in Fig. 2. The figure is based mainly on Benedict [1987Ben] and updated with some data by Heathman [1998Hea].

In a comparison between the pressure behavior of actinides and lanthanides Benedict underlined the analogies between the right-hand part of Fig. 2 and the left-hand part of the corresponding inter-lanthanide graph. This comparison between the two diagrams is considered an illustration of the "shifted homologous

relationships" between the trans-plutonium actinides and the light rare earth metals, even if it is not always possible to establish a one-to-one relationship between specific metals of the two series.

In the figure the particular behavior of Cm may be observed: it shows transition temperatures much higher than the neighbouring elements.

It may be noted, both in Table 1 and in the figures, the peculiar complexity of the sequence in vicinity of Pu. This may be related to the trend illustrated in Fig. 3, where the periodic table has been re-arranged by Smith and Kmetko [1983Smi] in order to highlight the separation between elements with "localized" and "delocalized" electrons. This re-arranged periodic table shows the above-mentioned "shifted homologous relationships" qualitatively relating elements in different positions in the original periodic system. In particular borderline elements in this table are characterized by having their properties modified appreciably by small perturbations. Pu, in particular, has six allotropic structures and a seventh under pressure.

These structures are close to each other in energy, so minor changes in the surroundings conditions (temperature, pressure) may result in a change of structure and density. Some unusual crystal properties of Pu may be underlined: its room temperature form has a very low symmetry structure with 16 atoms in the unit cell. Among the other structures the face centred cubic phase (which may be stabilized and retained down to low temperature by alloying with small amounts of partner elements such as Al or Ga) has a very low density and an unusual negative thermal expansion coefficient.

Table 1: Crystal Structure Data for the Actinide Elements

Phase/ Temperature Range [°C]*	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Ac) < 1051	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 531.1$ $a = 567.0$	[Mas2] [V-C2]
(α Th) < 1360	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 508.42$ $a = 508.61$	[Mas2] [V-C2]
(β Th) 1755 - 1360	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 411$	[Mas2, V-C2]
(α Pa) < 1170	<i>tI2</i> <i>I4/mmm</i> α Pa	$a = 394.0$ $c = 324.4$ $a = 392.1$ $c = 323.5$	[V-C2] [Mas2]
(β Pa) 1572 - 1170	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 381.0$	[Mas2]
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	[Mas2, V-C2]
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> β U	$a = 1075.9$ $c = 565.6$ $a = 1052$ $c = 557$	[Mas2] [V-C2]
(γ U) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352.4$ $a = 353.2$	[Mas2] [V-C2]

Phase/ Temperature Range [°C]*	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α Np) < 280	<i>oP8</i> <i>Pnma</i> α Np	$a = 666.3$ $b = 472.3$ $c = 488.7$	[Mas2, V-C2]
(β Np) 576 - 280	<i>tP4</i> <i>P42₁2</i> β Np	$a = 488.3$ $c = 338.9$ $a = 489.7$ $c = 338.8$	[Mas2] [V-C2]
(γ Np) 639 - 576	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352$	[Mas2, V-C2]
(α Pu) < 125	<i>mP16</i> <i>P2₁/m</i> α Pu	$a = 618.3$ $b = 482.2$ $c = 1096.3$ $\beta = 101.97^\circ$	[Mas2, V-C2]
(β Pu) 215 - 125	<i>mC34</i> <i>C2/m</i> β Pu	$a = 928.4$ $b = 1046.3$ $c = 785.9$ $\beta = 92.13^\circ$ $a = 1183.0$ $b = 1044.9$ $c = 922.7$ $\beta = 138.65^\circ$	[Mas2] [V-C2]
(γ Pu) 320 - 215	<i>oF8</i> <i>Fddd</i> γ Pu	$a = 315.87$ $b = 576.82$ $c = 1016.2$	[Mas2, V-C2]
(δ Pu) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 463.71$ $a = 463.47$	[Mas2] [V-C2]
(δ' Pu) 483 - 463	<i>tI2</i> <i>I4/mmm</i> In	$a = 332.61$ $c = 446.30$ $a = 333.9$ $c = 444.6$	[Mas2] [V-C2]
(ϵ Pu) 640 - 483	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 363.43$ $a = 363.75$	[Mas2] [V-C2]
(α Am) < 769	<i>hP4</i> <i>P6₃/mmc</i> α La	$a = 346.81$ $c = 1124.1$ $a = 346.3$ $c = 1123.1$	[Mas2] [V-C2]
(β Am) 1077 - 769	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 489.4$ $a = 465.6$	[Mas2] [V-C2]
(γ Am) 1176 - 1077	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = ?$	[Mas2, V-C2]

Phase/ Temperature Range [°C]*	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(δ Am) high pressure phase	<i>oC4</i> <i>Cmcm</i> α U	$a = 306.3$ $b = 596.8$ $c = 516.9$	at $p = 15.2$ GPa [Mas2, V-C2]
(Am) high pressure phase	<i>mP4</i> <i>P2₁/m</i> Am	$a = 302.5$ $b = 1188.7$ $c = 283.0$ $\beta = 106.11^\circ$	at $p > 12.5$ GPa [V-C2]
(α Cm) < 1277	<i>hP4</i> <i>P6₃/mmc</i> α La	$a = 349.6$ $c = 1133.1$ $a = 350.2$ $c = 1132$	[Mas2] [V-C2]
(β Cm) 1345 - 1277	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 503.9$	[V-C2]
(Cm) high pressure phase	<i>oC4</i> <i>Cmcm</i> α U	$a = 243.6$ $b = 581.0$ $c = 451.5$	at $p = 45.5$ GPa [V-C2]
(α Bk) < 977	<i>hP4</i> <i>P6₃/mmc</i> α La	$a = 341.6$ $c = 1106.9$	[Mas2]
(β Bk) 1050 - 977	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 499.7$	[Mas2]
(α Cf) < 590	<i>hP4</i> <i>P6₃/mmc</i> α La	$a = 339$ $c = 1101.5$	[Mas2]
(β Cf) 900 - 590	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = ?$	[Mas2]
(Cf) high pressure phase	<i>oC4</i> <i>Cmcm</i> α U	$a = 231.3$ $b = 552.6$ $c = 447.2$	at $p = 46.6$ GPa [V-C2]
(α Es) < ?	<i>hP4</i> <i>P6₃/mmc</i> α La	$a = ?$ $c = ?$	[Mas2]
(β Es) 860 - ?	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = ?$	[Mas2]

* Melting point in bold

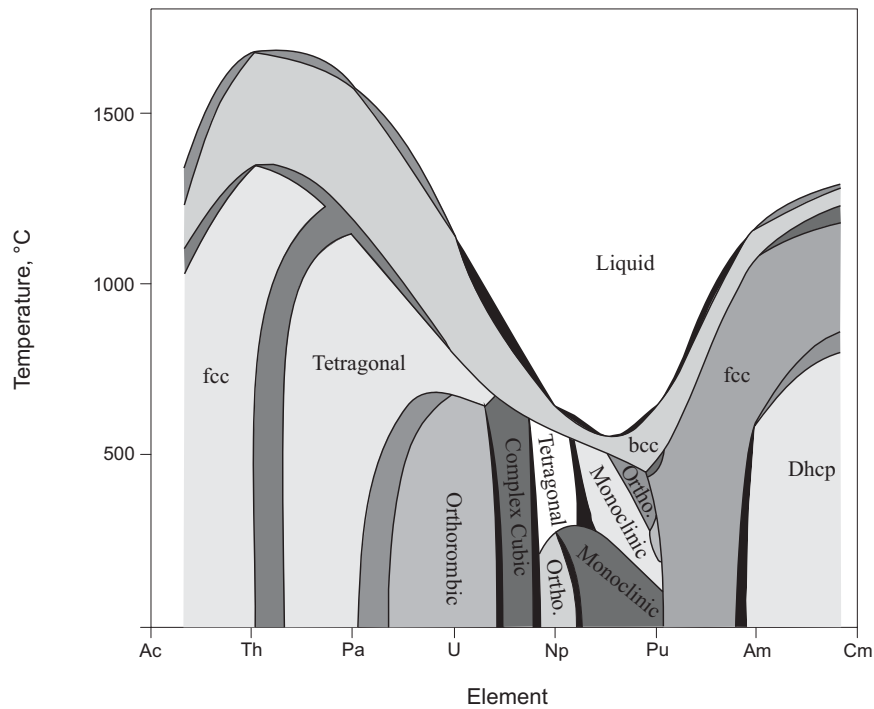


Fig. 1: Interconnected phase diagram of the binary An-An' systems formed by consecutive elements in the actinide series. Stability ranges of the different crystal structures are shown as a function of temperature. Among two-phase fields the black ones have been experimentally determined the others have been predicted. The formation of several low-symmetry structures and the overall destabilisation of the solid phases may be observed in the central part of the diagram, especially between Np and Pu.

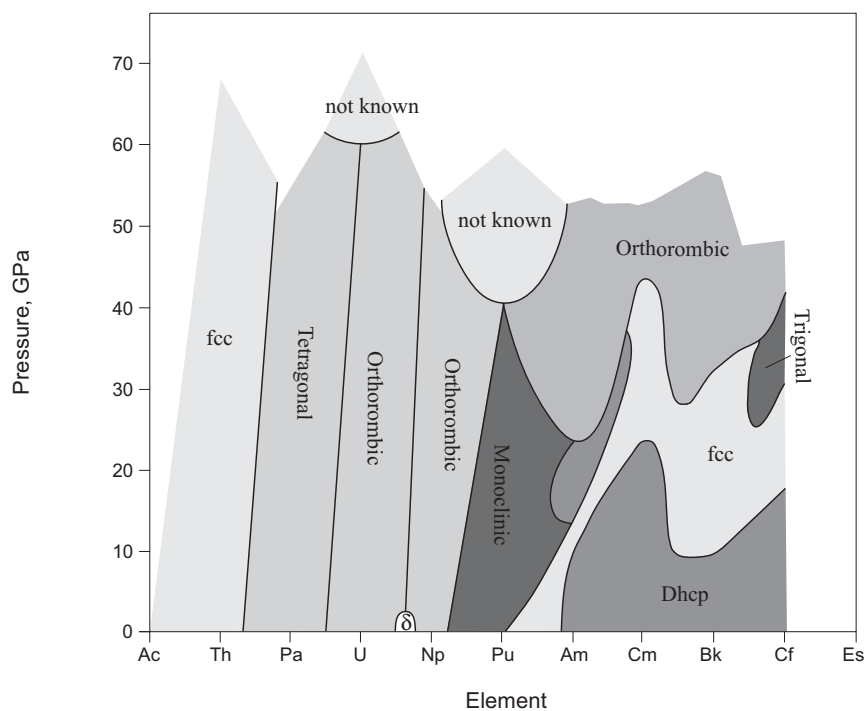


Fig. 2: Interconnected phase diagram of the binary An-An' systems formed by consecutive elements in the actinide series. Stability ranges of the different crystal structures are shown as a function of pressure.

4f	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
5f	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3d	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn				
4d	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd				
5d	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg				

Fig. 3: Modified periodic table of the *f* and *d* series according to Smith and Kmetko [1983Smi]. Elements in the upper right part are characterised by having localised *f* or *d* electrons and became magnetic at low temperature. Elements in the lower left part are characterised by having itinerant *f* or *d* electrons and became superconductor at low temperature. Border line elements, such as Ce, Np, Pu, Mn, Fe, etc., have their properties modified appreciably by small perturbations: for example they show a large number of allotropic structures which can be alternately stabilised by temperature and/or pressure variations.

1.2 Inter – Actinide Binary Systems

The sequence of the binary diagrams (interconnected diagram) between adjacent actinide elements has been shown in Fig. 1. This well-known diagram has been frequently used to highlight general trends inside the actinide series. It may be noted that, due to the high number of allotropic forms assumed by Pu, the graph became particularly complex in vicinity of this element.

Only a few binary inter-actinide phase diagrams have been investigated. The available information reported in literature is here briefly summarized. The systems are sorted according to the atomic number of the component elements. Crystal structure data have been summarized in Table 2.

Table 2: Crystal Structure Data for the Inter-Actinide Binary Systems

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments
Th-U			
(α Th) < 1360	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 508.4$ to 508.7 $a = 514.3$ to 514.7 $a = 508.1$ $a = 514.3$ $a = 508.1$ $a = 513.8$ $a = 516.5$ $a = 513.5$ $a = 516.0$ $a = 515.4$ $a = 515.4$	at $x(\text{U}) = 0$, room T at $x(\text{U}) = 0$, $T = 950^\circ\text{C}$ at $x(\text{U}) = 1.0$ (saturation limit), room T at $x(\text{U}) = 1.0$, $T = 950^\circ\text{C}$ at $x(\text{U}) = 2.0$, room T at $x(\text{U}) = 2.0$, $T = 950^\circ\text{C}$ at $x(\text{U}) = 2.0$, $T = 1250^\circ\text{C}$ at $x(\text{U}) = 5.0$, $T = 950^\circ\text{C}$ at $x(\text{U}) = 5.0$, $T = 1250^\circ\text{C}$ at $x(\text{U}) = 8.0$, room T at $x(\text{U}) = \sim 10.0$, $T = 1250^\circ\text{C}$ [1975Fer]
Th-Pu			
(α Th) < 1360	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 508.5$ $a = 505.5$ $a = 501.3$ $a = 497.0$ $a = 496.3$	at $x(\text{Pu}) = 0$, $d_x = 11.72 \text{ g}\cdot\text{cm}^{-3}$ at $x(\text{Pu}) = 0.1$, $d_x = 11.98 \text{ g}\cdot\text{cm}^{-3}$ at $x(\text{Pu}) = 0.25$, $d_x = 12.36 \text{ g}\cdot\text{cm}^{-3}$ at $x(\text{Pu}) = 0.40$ at $x(\text{Pu}) = 0.43$, $d_x = 12.84 \text{ g}\cdot\text{cm}^{-3}$ [1975Fer]
ζ , Th ₃ Pu ₇ < 615	<i>o*20</i>	$a = 622$ $b = 1162$ $c = 709$	$d_x = 15.35 \text{ g}\cdot\text{cm}^{-3}$; $d_{\text{exp}} = 15.39 \text{ g}\cdot\text{cm}^{-3}$ [1968Mar]
U-Np			
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 283.29$ $b = 586.04$ $c = 493.47$	at $x(\text{U}) = 0.968$ [V-C2]
(α Np) < 280	<i>oP8</i> <i>Pnma</i> α Np	$a = 669.4$ $b = 473.3$ $c = 491.2$	at $x(\text{U}) = 0.15$ [V-C2]
(β Np) 612 - 185	<i>tP4</i> <i>P42₁2</i> β Np	$a = 495.0$ $c = 338.6$	at $x(\text{U}) = 0.15$, $T = 400^\circ\text{C}$ [V-C2]
δ , U _x Np _{1-x} < 668	<i>cP58</i> (?)	$a = 1055$ $a = 1063$	at $x = 0.25$ at $x = 0.50$ [1959Mar]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments
U-Pu			
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 286.24$ $b = 585.61$ $c = 496.27$	at $x(\text{U}) = 0.85$ [V-C2]
$\alpha\text{U}_x\text{Pu}_{1-x}$ 1135 - 480	<i>cI2</i> <i>Im\bar{3}m</i> W	$a = 363.6$ $a = 361.2$ $a = 353$	at $x = 0$ at $x = 0.08$ at $x = 1$
(β Pu) 278 - 121	<i>mC34</i> <i>C2/m</i> β Pu	$a = 1181.8$ $b = 1041.8$ $c = 921.5$ $\beta = 138.68^\circ$ $a = 1190.3$ $b = 1043.9$ $c = 926.4$ $\beta = 138.85^\circ$ $a = 1196.9$ $b = 1044.4$ $c = 930.2$ $\beta = 139.03^\circ$	at $x(\text{U}) = 0.02$, $T = 83^\circ\text{C}$ at $x(\text{U}) = 0.02$, $T = 186^\circ\text{C}$ at $x(\text{U}) = 0.02$, $T = 252^\circ\text{C}$
η , $\text{U}_x\text{Pu}_{1-x}$ 702 - 278	<i>tP52</i>	$a = 1057$ $c = 1076$	$0.04 < x < 0.70$ at $x = 0.25$, $T = 500^\circ\text{C}$
ζ , $\text{U}_x\text{Pu}_{1-x}$ < 590	<i>cP58</i> <i>hR58</i> <i>R\bar{3}m</i>	$a = 1069.2$ $a = 1066.4$ $a = 1065.1$ $a = 1507.64$ $c = 1859.26$	$0.25 < x < 0.77$ at $x = 0.35$, $T = 25^\circ\text{C}$ at $x = 0.50$, $T = 25^\circ\text{C}$ at $x = 0.70$, $T = 25^\circ\text{C}$ rhombohedral settings [1996Law]: $a = b = c = 1068.53$ $\alpha = \beta = \gamma = 89.736^\circ$
Np-Pu			
(α Pu) < 300	<i>mP16</i> <i>P2_1/m</i> α Pu	$a = 612$ $b = 480$ $c = 1095$ $\beta = 101.74^\circ$	$0 < x(\text{Np}) < 0.96$ at $x(\text{Np}) = 0.565$ [V-C2]
η , $\text{Np}_x\text{Pu}_{1-x}$ 508 - 288	<i>o**</i>	$a = 1086$ $b = 1067$ $c = 1043$	$0.03 < x < 0.49$ Uncertain parameters. Structure tentatively related to a $3 \times 3 \times 3$ bcc superstructure [1985She1].
Pu-Am			
$\delta\text{Pu}_x\beta\text{Am}_{1-x}$ < 1077	<i>cF4</i> <i>Fm\bar{3}m</i> Cu	$a = 479.4$	$0 < x < 1$ at $x = 0.50$ [V-C2]

Ac-An

No experimental data are available on these phase diagrams. Ac-Th phase equilibria reported in Fig. 1 have been drawn by assuming complete mutual solubility between Ac and Th in both fcc and bcc structures. This also in analogy with the known La-Th system.

Th-U

The Th-U phase diagram is shown in Fig. 4 according to the critical assessment by [1985Pet2]. Phase equilibria have been determined by a variety of techniques including DTA and, above the monotectic temperature, chemical analysis of equilibrated samples.

No intermediate phases are present in this system. It is characterized by small solid solution in α - and β Th and very small solid solution in the different forms of U. A miscibility gap appears in the liquid phase.

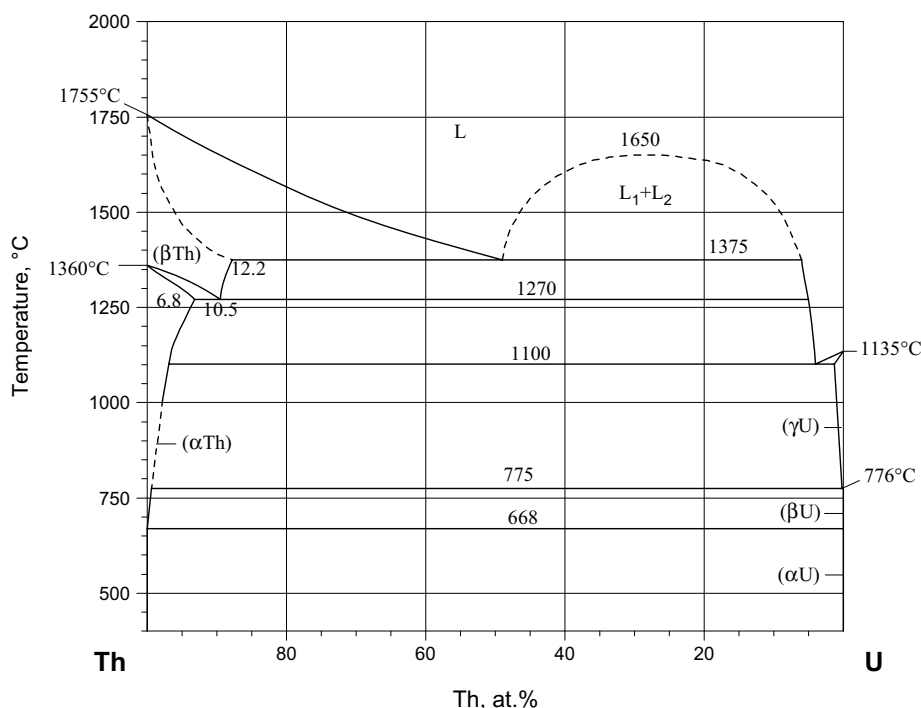


Fig. 4: Phase diagram of the Th-U system

Th-Np

No experimental data are available on this phase diagram. An early Calphad prediction of this system has been performed by Chan *et al.* [1980Cha].

Th-Pu

The Th-Pu phase diagram has been assessed by [1985Pet1] and it is shown in Fig. 5. It has been studied in the entire composition range by metallography, X-ray diffraction, thermal analysis, dilatometry.

It is characterized by the formation of an intermediate compound which has a peritectic decomposition at 615°C. Large solubility regions are given by Pu in α - and β Th while solubility of Th in the different Pu phases ranges from 0 (in α - and β Pu) to 2.6 and 5.6 at.% Th in δ - and ϵ Pu, respectively.

One binary phase is known for this system: it was previously reported as $\text{Pu}_{13}\text{Th}_6$ homogeneous around 67-70 at.% Pu and orthorhombic ($a = 982$, $b = 816.4$, $c = 668.1$). In agreement with [1985Pet1], however, it is indicated as Pu_7Th_3 in Table 2.

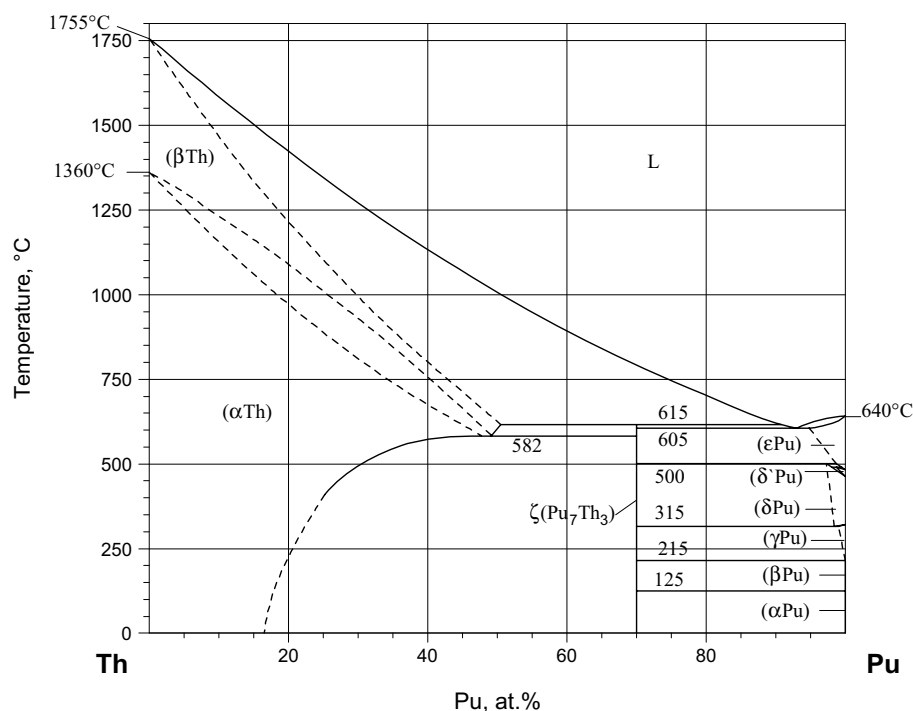


Fig. 5: Phase diagram of the Th-Pu system

Pa-An

No experimental data are available on these phase diagrams. Th-Pa and Pa-U phase diagrams reported in Fig. 1 have been drawn by assuming the simplest combination of equilibria compatible with the elemental phases. In particular, large solid solutions and no intermediate compounds have been predicted.

U-Np

A critical assessment of the U-Np system has been presented by [1985She2], based on the experimental work of [1959Mar]. Figure 6 shows the phase diagram as reported by [1985She2]. The fcc solid solution and its equilibria with liquid are in agreement with a calculation performed by [1993Oga] on the basis of the Brewer valence bond model. It is also in fair agreement with the phase equilibria schematically reported in Fig. 1.

As for the solid state equilibria, further experimental investigation could be useful, considering the shape of the reported phase boundaries, sometime not well defined and eventually unlikely.

Only one intermediate δ phase is reported in this system (see Table 2), characterized by a large solubility range.

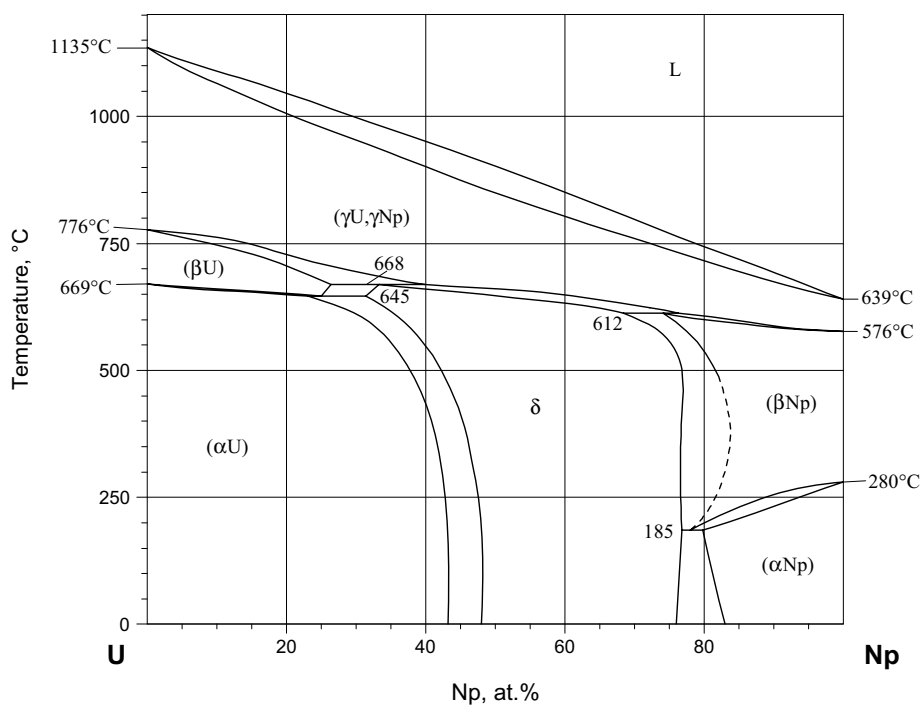


Fig. 6: Phase diagram of the U-Np system

U-Pu

The U-Pu phase diagram was assessed by [1989Pet] on the basis of several experimental data. This diagram was criticized by [1992Oka] considering several thermodynamically unlike features. The diagram reported in Fig. 7 was proposed by [1996Oka], based on the assessment of [1989Pet], new experimental results by [1994Oka] and thermodynamic modelling by [1991Lei].

The bcc solid solution and its equilibria with liquid are in fair agreement also with a calculation performed by [1993Oga] on the basis of the Brewer valence bond model. The crystal structure of the ζ phase was determined by [1996Law].

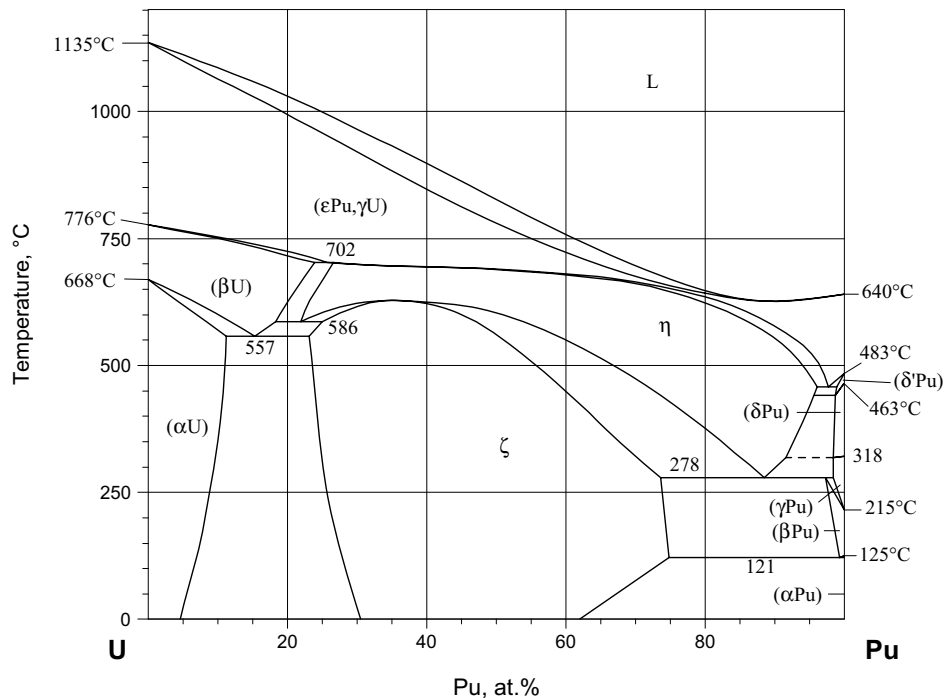


Fig. 7: Phase diagram of the U-Pu system

U-Am

No experimental information is available in literature. In Fig. 8 it is reported the predicted phase diagram calculated by [1993Oga] using interaction parameters obtained on the basis of the Brewer valence bond model.

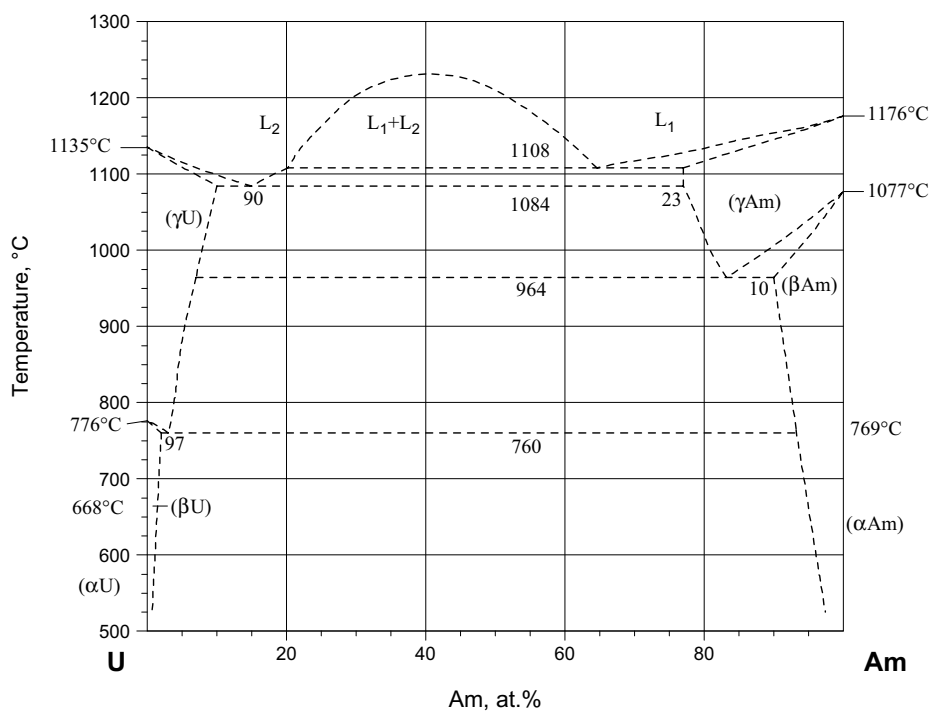


Fig. 8: Predicted phase diagram of the U-Am system (α U and α Am have been omitted in the calculation)

Np-Pu

A critical assessment of the very complex Np-Pu system has been presented by [1985She1], based on the experimental work of [1961Mar].

Lattice parameters of the high temperature solid solution based on β Pu have been reported by [1961Mar]. The cell, however, has been described as orthorhombic instead of monoclinic. For the $c/2$ -(γ Np, ϵ Pu) solid solution $a = 356.5$ was reported for 550°C and $x(\text{Pu}) = 0.5$.

The phase diagram is shown in Fig. 9, in agreement with the assessment of [1985She1]. The bcc solid solution and its equilibria with liquid are in agreement with a calculation performed by [1993Oga] on the basis of the Brewer valence bond model.

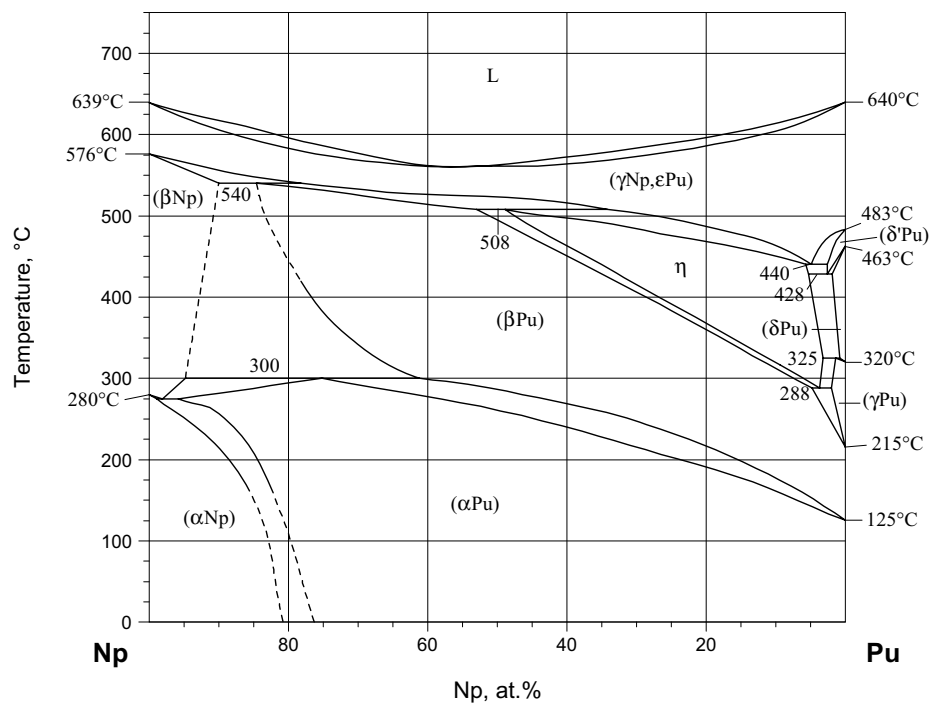


Fig. 9: Phase diagram of the Np-Pu system

Np-Am

A DTA investigation was carried out on a few alloys by [1992Gib]. Measurements on a $\text{Np}_{0.54}\text{Am}_{0.46}$ sample suggested some degree of mutual solubility although terminal solid phases, one Np rich and one Am rich, were found to coexist.

The phase diagram reported in Fig. 10 was calculated by [1993Oga] using regular interaction parameters obtained on the basis of the Brewer valence bond model. Low temperature phases αAm and βNp were not considered. Barely noticeable liquid miscibility gap was suggested. The model predicts greater solubility of Np in Am than *vice-versa*. This seems to be in agreement with the DTA data by [1992Gib].

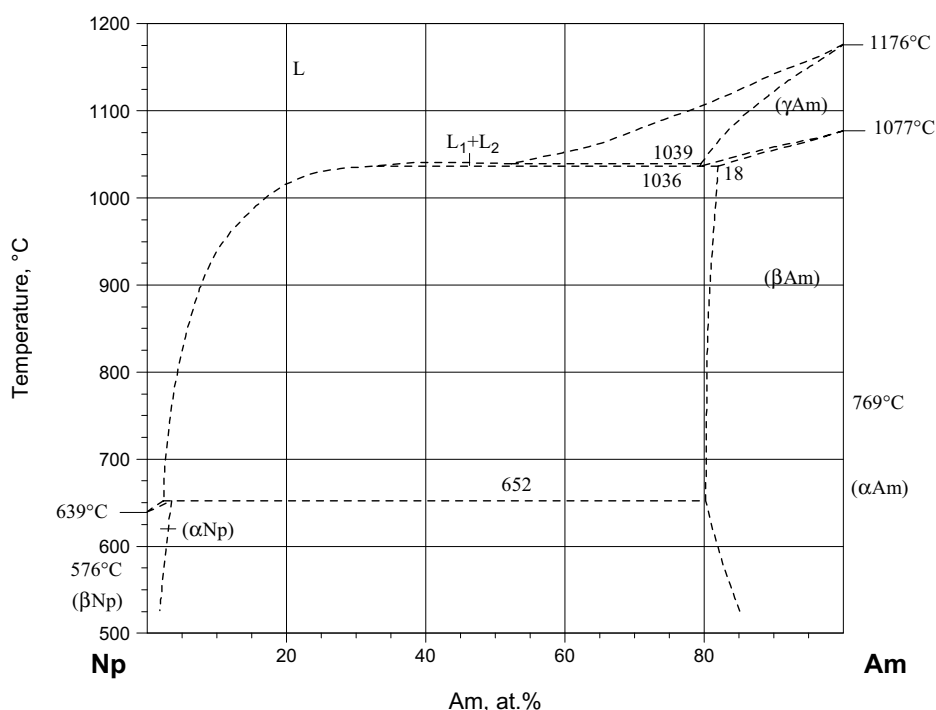


Fig. 10: Predicted phase diagram of the Np-Am system (βNp and αAm have been omitted in the calculation)

Pu-Am

An experimental investigation of the Pu-Am phase diagram was carried out by [1990Shu] by DTA, microscopy, high temperature X-ray analysis, density measurements. The obtained phase diagram, reported in [Eff1], is characterized by continuous ranges of solid solutions (ϵ Pu, γ Am) bcc and (δ Pu, β Am) fcc. The fcc structure is stable to room temperature between 6.2 and 80 at.% Am. Okamoto [1999Oka2] presented a phase diagram in good qualitative agreement with the previous one, which was obtained combining the liquid + (γ Am, ϵ Pu) and (γ Am, ϵ Pu) + (β Am, δ Pu) two-phase fields calculated by [1993Oga] with the boundaries of the low temperature phases (α Am, γ Pu, β Pu, α Pu) previously proposed by Ellinger [1966Ell]. Okamoto tentatively added a small δ' Pu field, which possibly corresponds to the (η Pu) field shown by Ellinger.

The phase diagram reported in Fig. 11 is mainly based on [1990Shu], slightly modified by smoothing the original curves.

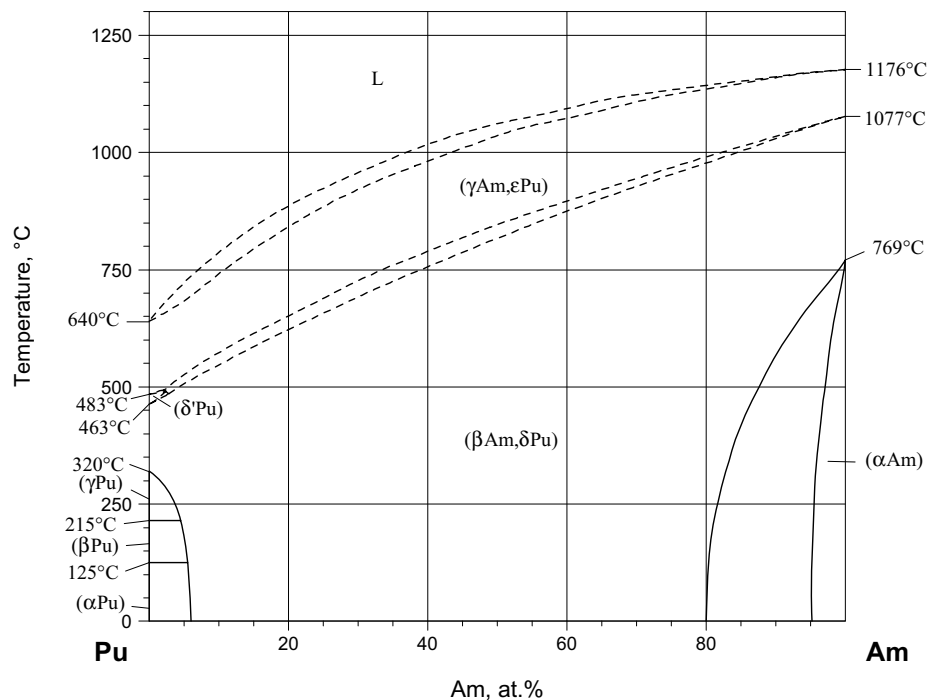


Fig. 11: Phase diagram of the Pu-Am system

Pu-Cm

The phase diagram has been studied by [1995Shu], by using DTA, high temperature X-ray diffraction and microstructural analysis. The phase diagram with experimental points has been reported in [Eff1] and in a slightly smoothed version by [2000Oka]. This is shown in Fig. 12.

The (β Cm) solid solution tends to remain in a metastable state down to room temperature. As a consequence it is difficult to equilibrate the (α Cm) solution. The (α' Cm) region, probably metastable, corresponds to a faulted fcc phase differing from dhcp (α Cm) in the ordering of the close-packed layers.

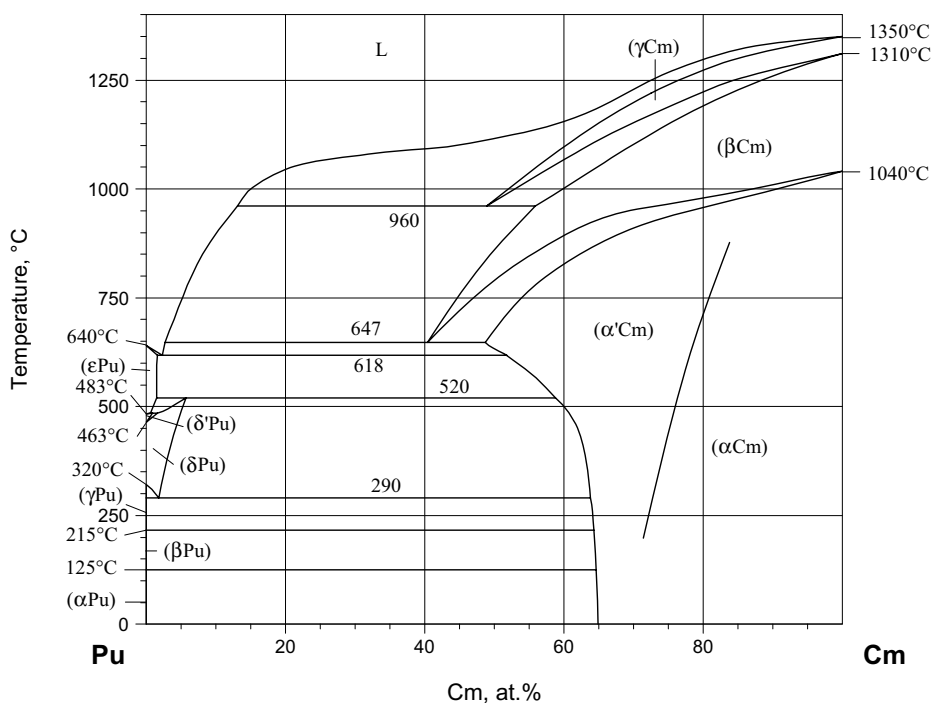


Fig. 12: Phase diagram of the Pu-Cm system

Cm-Bk

Cm-Bk alloys were studied by [1998Hea], by X-ray diffraction up to 53 GPa to probe their structural behavior under pressure. Two Bk-Cm alloys containing 70 and 46 at.% Cm were investigated. These studies resulted in the determination of the transition pressure reported in Fig. 2.

2. General Alloying Behavior of the Actinides

2.1. Notes about the Systems An-Me

For only a few actinides binary phase diagrams with several partner elements are available in literature. Main characteristics of the binary equilibria formed by Th, U and Pu, have been summarized and schematically shown in Fig. 13a, 13b, and 13c, respectively. In these figures the partner elements are represented by their position in the Periodic Table and in the various corresponding “boxes” of the Table a few symbols have been inserted in order to show the characteristic features of the alloying behavior (solubility or miscibility gaps in the solid and/or liquid state, formation of intermediate phases in the solid state, *etc.*).

Solubility in the Liquid State

As for Th-Me systems complete liquid solubility is shown for all partner elements except for a small miscibility gap with O and extended gaps with Eu and Yb.

As for U, miscibility gaps in the liquid state have been observed with rare earth and actinide elements, and with Zn and 11th group elements.

Similar behavior is shown by Pu: miscibility gaps are present in the systems with oxygen, lanthanides, actinides, Mg, Ag, Cd.

Solubility in the Solid State

More or less extended solid solutions are observed with most of the partner elements. In a few cases complete solid solutions are observed at least for one of the actinide solid phases.

For Th complete solid solutions are present only with Zr and rare earths (in particular with La complete solid solution is present in both fcc and bcc structures).

Complete solid solutions are formed by U only with Ti, Zr, Hf and Nb, while Pu shows complete solid solutions with Sc and Zr.

Compound Formation

The binary systems in which we have the formation of intermediate phases form, in the Periodic Table, a nearly well defined pattern, which is similar for the different actinides and shows close analogies also with the corresponding pattern of the lanthanides and, more generally, with those of the elements of the first groups of the Periodic Table.

As a general rule compound formation is found with partner elements on the right of the Periodic Table, typically from the 7th group on. The elements on the left (with some exceptions for the lightest ones: Be, Mg, *etc.*) do not form any intermediate phases; their binary phase diagrams with An are generally of the simple eutectic or monotectic type. For selected actinides however, the formation by solid state reaction of low temperature phases has also been observed.

As an exceptions to this general behavior the compounds formed by U with Ti, Zr and Mo, and by Pu with Sc, Zr and Hf may be mentioned. These phases are generally formed by solid state reaction and are stable only at relatively low temperature.

Considering the general validity of this subdivision, it may be assumed that it is also applicable to the heavy transplutonium actinides. For Am, the data available, even though approximate and incomplete, are in agreement with the mentioned general behavior. An overview of the Am alloying behavior has been recently published [2001Fer].

Th															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
== 2															
	== 1											== 3	== 2	== 2	<> 1
== 1	== 2											== 7	== 4	== 4	== 5
		== ==	== 0	== 0	== 0	== 3	== 5	== 5	== 7	== 4	== 4	== 4	== 6	== 3	== 5
		== ==	== ==	== 0	== 0		== 4	== 7	== 7	== 3	== 6	== 4	== 4	== 3	== 4
	0	== ==	== 0	== 0	== 0	== 1	== 3	== 6	== 8	== 6	== 4	== 5	== 4	== 6	
Ln	== ==	== ==	== ==	== ==	== ==	== ==	<> 0	== ==	== ==	== ==	== ==	== ==	== 0	<> 0	== 0
An	Th		<>			== 1									

Fig. 13a: Systematics of the binary alloying behavior of Thorium. Data relevant to the Th-X system are reported at the cell of the element X in the periodic tables.
Legend:
Empty cell: no information.
Upper part: liquid state behavior; == complete solubility; <> miscibility gap.
Lower part: solid state behavior; == complete solubility (at least in a temperature range);
<> miscibility gap; the number of known intermediate compounds or phases is also reported.

U															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
== 1															
0	◇ 1											== 3	== 3	== 3?	== 6?
== 0	◇ 0											== 3	== 7	== 3	== 6
		◇ 0	== 1	== 0	== 0	== 2	== 2	== 6	== 7	◇ 1	◇ 2	== 5?	== 7	== 3	== 6
		◇ 0	== 1	== 0	== 1		== 5	== 4	== 5	◇ 0	== 1	== 5?	== 5	== 4	== 10
			== 0	== 0	== 0	== 2	== 4	== 5	== 4	◇ 2	== 4	== 1	◇ 2	◇ 3	

Ln	◇ 0	◇ 0	◇ 0		◇ 0	◇ 0								◇ 0	
An	◇		U	0	2	◇ 0									

Fig. 13b: Systematics of the binary alloying behavior of Uranium. Data relevant to the U-X system are reported at the cell of the element X in the periodic tables. See caption of Fig 13a for the legend.

Pu															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
== 2															
== 0	== 1											== 5	== 4	== 1	< 4
== 0	< 3											== 5	== 5	== 1	3
0	== 0	== =1=	== 0	== 0	== 0	== 1	== 2	== 6	== 6	== 4	== 6	== 12	== 3?	== 1	4
	0	== 0	== 1	== 0	== 0		== 5	== 8	== 4	< 2	< 4	== 5	== 7	== 5	2
	0	< 0	== 2	== 0	== 0	== 1	== 4	== 4	== 8	== 8	== 2	== 2	== 6	== 3	
Ln	< 0	< 0	< 0			< 0	< 0	< 0	< 0	< 0	< 0		0	< 0	0
An	< =1=		=2=	==	Pu	< 0									

Fig. 13c: Systematics of the binary alloying behavior of Plutonium. Data relevant to the Pu-X system are reported at the cell of the element X in the periodic tables. See caption of Fig. 13a for the legend. For a few partner elements both intermediate compounds and complete solid solutions are observed.

2.2. Stabilization of the U and Pu Elementary Structures

Another important feature in the alloying behavior of the actinides is the effect of alloying elements on the stability of the different actinide elementary structures. Particular interest has been devoted to U and Pu, also because of their relevance in nuclear technology and the high number of polymorphic forms of these elements.

Uranium

The (γ U) phase ($cI2$ -W type structure) generates continuous solid solutions with the elements having the same structure, and in particular with Ti, Zr, Hf, Nb, at least in a limited high temperature range. With other early-transition elements the gamma field is also stabilized. The solubility of partner elements in (β U) is generally lower than in (γ U).

[2002Bla] studied the phase stabilization of the light actinide phases in binary alloys. They proposed a quantitative evaluation of the stabilization of a selected phase with respect to the other phases stable at lower temperature by considering the initial slope dT/dc of the two-phase boundary between the two phases (β to α transus).

According to this definition the β stabilizing elements are placed in the central part of the d -block. They are Cr and Mn, Mo to Rh, Re to Pt in first, second and third transition series, respectively.

It may be observed that with s -block metals and early transition elements (groups 1 to 6), no intermediate compounds are formed or they are stable only at relatively low temperature and decompose before melting. With the elements from group 7 to 10 an increasing number of compounds are formed and, in particular with elements from Mn to Ni, U rich compounds (typically U_6Mn type) appear which compete with the stability of the β - and γ based solid solutions.

Plutonium and the “Saga” of Ga-Pu System

Among topics related to the stabilization of the actinide allotropic phases the question related to the stability of the fcc (δ Pu) is particularly important. (δ Pu) is malleable and easily shaped, and it is important because of its uses (in nuclear weapons, *etc.*).

This phase may be retained (either in stable or metastable conditions) down to room temperature by the addition of gallium or aluminium. Of particular interest is therefore the Ga-Pu system. The question of the stabilization of delta plutonium and the related investigation of this phase diagram has been the subject of an intense research activity carried out, during the cold war, separately by two teams (the Anglo-American one and that from the Soviet Union) with the production of two different versions, reported in Fig. 14a and 14b, respectively, which only recently came to an agreement.

The two versions, in a way, may now be reconciled: the diagram shown in Fig. 14a represents the metastable conditions and it is adequate for practical applications; the equilibrium diagram of Fig. 14b shows the eutectoid decomposition of the (δ Pu) phase, which however, due to very slow diffusion processes, cannot be directly observed. It was only through long-term annealing treatments (several thousands of hours at 130°C, or at 150°C) with pre-treated (preconditioned) samples subjected to high pressure or compressive plastic deformation, that it was finally possible to deduce (to extrapolate from a slightly higher temperature) the equilibrium phase boundaries and confirm the diagram of Fig. 14b.

As a final comment to this point we may remark that, as observed by Hecker and Timofeeva [2000Hec], the situation in Pu alloys (especially Ga-Pu, Al-Pu) is similar to that in steel where for the C-Fe system two diagrams (stable with graphite and metastable with Fe_3C) must be considered.

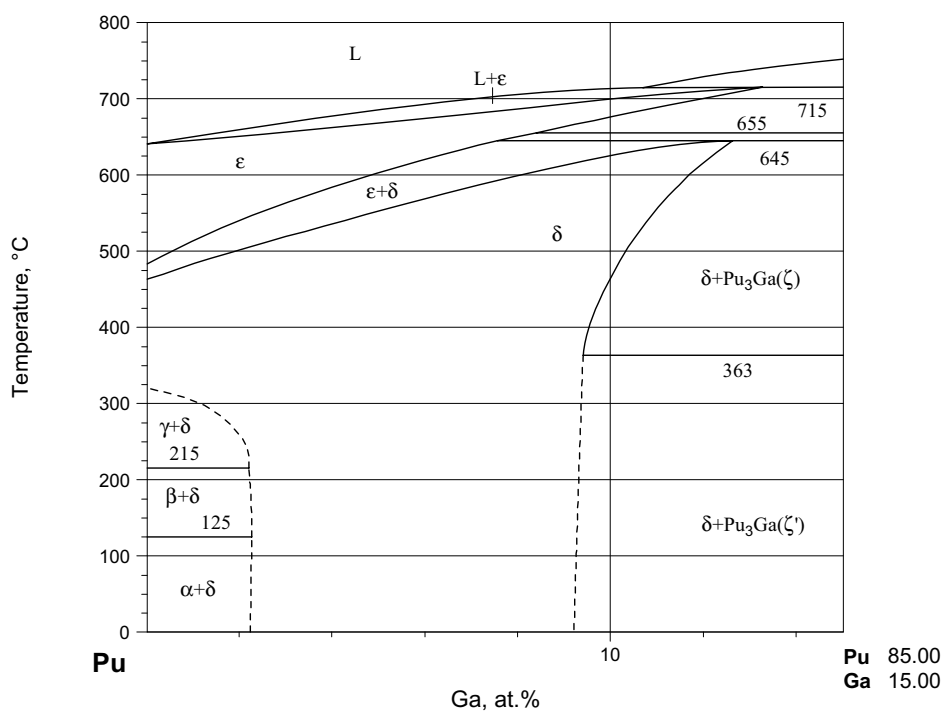


Fig. 14a: Metastable phase diagram of the Ga-Pu system

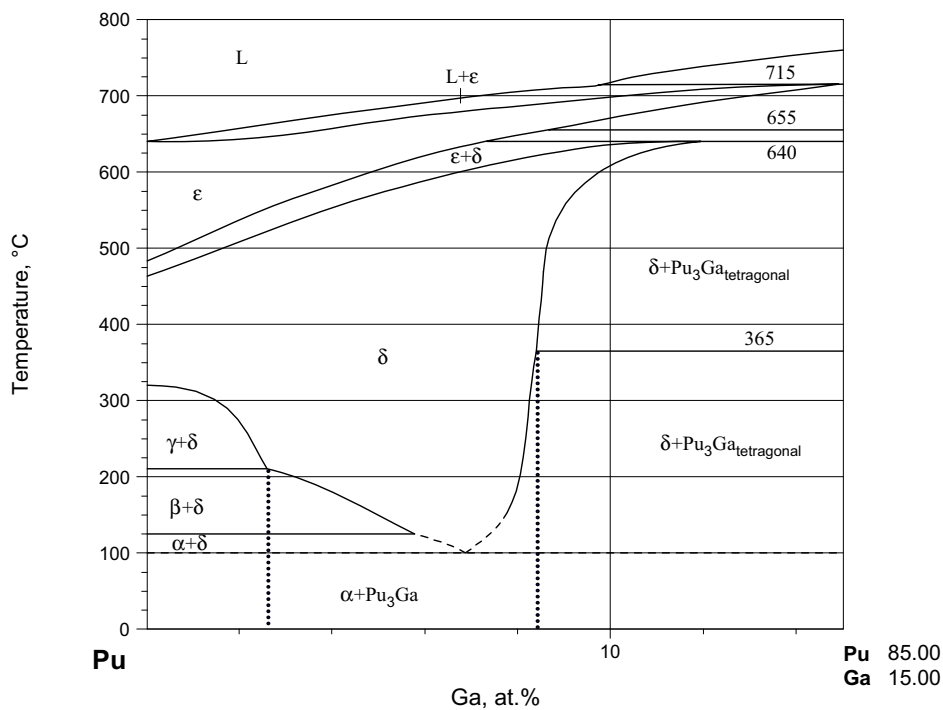


Fig. 14b: Equilibrium phase diagram of the Ga-Pu system

2.3. Notes about the Systems An'-An''-Me

For the ternary alloy systems formed by two actinides with a third element the lack of experimental data available in literature is particularly evident. A short list of these systems is reported in Table 3 with a synopsis of the experimental investigations performed.

No data have been found in literature about experimental investigations on phase equilibria in ternary inter-actinide systems An'-An''-An'''.

Table 3: Notes on Experimental Studies on Phase Equilibria in An'-An''-X Ternary Systems Mainly Based on [TA], [Eff1, Eff2, Eff3, Eff4, Eff5, Eff6, Eff7] and [Vil3]

An'-An'' Elements	-X element	Experimental Information
Th-U	-Al	Partial liquidus projection. Solubility of U in ThAl ₃
	-As	Solid solubility of Th ₃ As ₄
	-B	Partial isothermal section at 800°C (range UB ₂ -Th-U). Solid solubility of (Th _{1-x} U _x)B ₄
	-Be	Complete solid solubility of (Th _{1-x} U _x)Be ₁₃
	-Bi	Partial isothermal section at 1000°C (80-100 at.% Bi)
	-C	Several partial isothermal sections Temperature-composition section ThC ₂ -UC ₂ Complete solid solubility of (Th _{1-x} U _x)C
	-Fe	Partial liquidus projection (range UFe ₂ -Th-U) Partial isothermal section (range UFe ₂ -Th-U) Ternary compound UFe ₂ Th ₂ (no structure data available)
	-Mn	Partial liquidus projection (range UMn ₂ -Th-U)
	-Ni	Partial liquidus projection (range 0-60 at.% Ni)
	-P	Complete solid solubility of (Th _{1-x} U _x) ₃ P ₄
	-Pd	Partial liquidus projection and isothermal section (Pd rich corner) Complete solid solubility of (Th _{1-x} U _x)Pd ₄
	-Re	Solubility of U in ThRe ₂ (MgZn ₂ type) and solubility of Th in URe ₂ (URe ₂ type)
	-S	Complete solid solubility of (Th _{1-x} U _x)S (NaCl type) U ₂ ThS ₅ (U ₃ S ₅ derivative) ternary compound (or solid solution?)
	-Sb	Complete solid solubility of (Th _{1-x} U _x)Sb ₂ (Cu ₂ Sb type)
	-Se	Complete solid solubility of (Th _{1-x} U _x)Se (NaCl type)
	-Te	Solubility of U in ThTe (CsCl type) and solubility of Th in UTe (NaCl type)
	-Zr	Complete liquidus and solidus projections Several isothermal sections
Th-Pu	-C	Partial isothermal sections at 1100, 1300, 1600°C Temperature-composition section (ThC ₂ -PuC ₂)
	-N	Partial isothermal sections. Isothermal section at 1500 (computed) Complete solid solubility of (Th _{1-x} Pu _x)N

An'-An" Elements	-X element	Experimental Information
U-Np	-O	Partial isothermal section at 1000°C Complete solid solubility of $(U_{1-x}Np_x)O_2$
	-Pt	Solubility of Np in UPt_3 (SnNi ₃ and TaPd ₃ type)
	-Zr	Partial isothermal sections at 520, 595 and 700°C
U-Pu	-C	Liquidus projection Several isothermal sections Several temperature-composition sections (UC_2 - PuC_2 , etc.)
	-Mo	Full phase diagram in the range 35-100 at.% U Partial liquidus projection Partial isothermal sections at different T Solid solubility of $(U_{1-x}Pu_x)_4Mo$ (W type) $0 < x < 0.22$ (metastable?).
	-N	Complete solid solubility of $(U_{1-x}Pu_x)N$ (NaCl type) Isothermal section at 1000 (computed)
	-Pt	Solubility of Pu in UPt_3 (SnNi ₃ type)
	-S	Solid solubility of Pu in U_3S_5
	-Sn	Complete solid solubility of $(U_{1-x}Pu_x)Sn_3$ (AuCu ₃ type)
	-Zr	Liquidus and solidus projections Several isothermal sections at different T Zr migration in alloys exposed to a thermal gradient
Np-Pu	-B	Complete solid solubility of $(Np_{1-x}Pu_x)B_2$ (AlB ₂ type)

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Aluminium – Iron – Uranium

Bernd Grieb, updated by Hans Leo Lukas

Introduction

Petzow *et al.* [1962Pet] as well as Lam *et al.* [1962Lam] investigated the quasibinary section $\text{UFe}_2\text{-UAl}_2$. [1963Pet] studied the partial ternary system $\text{U-UFe}_2\text{-UAl}_2$ in detail. 18 alloys for the quasibinary section and 84 ternary alloys were produced by arc melting from the pure elements (Al:99.99%, Armco-Fe, nuclear pure U) and studied by chemical, X-ray, microhardness, density, thermal and differential thermal (DTA) analyses and metallography. U and Fe were prealloyed. Samples were annealed at 1000°C (8 d), 800°C (16 d) and 600°C (24 d) and quenched in water.

[1963Kha, 1963Rus, 1964Dix] and [1966Sch] studied the solubilities of Al and Fe in the three solid modifications of pure U.

The homogeneity ranges and structures of the phases along the $\text{UAl}_2\text{-UFe}_2$ section were investigated by [1963Pet, 1964Ste, 1967Lam, 1971Kim].

In the U poor system structure and lattice parameters of a compound UFe_4Al_8 were determined by [1984Bar, 1984Ste]. In the following years this phase was investigated intensively for its exceptional magnetic properties using magnetic measurements, neutron diffraction at polycrystalline and single crystalline samples by [1986Bar, 1988Pta, 1989Sch, 1992Sus, 1994Gon, 1995God, 1995Gon, 1996God, 1996Wys, 1997Pai, 1997Rec, 1998Gon, 1999Kuz, 2000Car, 2000Rec, 2001Rec, 2001Wae, 2002Car, 2002Gon, 2002Rec, 2003Gon, 2003Li, 2003Tal]. It has an extended homogeneity range along Al-Fe exchange, $\text{UFe}_x\text{Al}_{1-x}$ ($3 < x < 7$ at 850°C [1994Gon]). At high pressure, up to 26 GPa at composition UFe_5Al_7 the phase was found to remain stable [2002Hal]. Later several other phases were detected in the region with less than 33 at.% U, most of them in a systematic investigation of the 850°C isothermal section by [2005Gon]: $\text{U}_2\text{Fe}_{12}\text{Al}_5$ [1995Che], $\text{UFe}_2\text{Al}_{10}$ [2002Mes, 2004Mes, 2004Noe], $\text{U}_2\text{Fe}_{3.6}\text{Al}_{12.4}$ [2005Gon], $\text{U}_3\text{Fe}_4\text{Al}_{12}$ [2005Gon] and $\text{U}_2\text{Fe}_x\text{Al}_{17-x}$ ($6.7 < x < 8.6$) [2005Gon]. Near the Al corner [2005Mes] found a further phase, $\text{U}_2\text{FeAl}_{20}$. No investigations were performed on temperature ranges of stability or on invariant reactions between these U poor phases.

The important experimental investigations are summarized in Table 1.

Binary Systems

[1963Pet] based the ternary investigation on the binaries U-UAl_2 and U-UFe_2 published by [H] with little corrections of the U transition temperatures ($1 \rightarrow \gamma$: 776°C, $\beta \rightarrow \alpha$: 668°C) and the melting point of UAl_2 (1620°C). These are virtually equivalent to those of [Mas2], given in more detail by [1990Kas] and [1993Oka], respectively. In the binary systems UAl_2 and UFe_2 show no homogeneity ranges. UAl_4 was assumed to have some homogeneity range. However, in a very detailed comparison of samples with excess or deficient Al content [2004Tou] concluded from powder and single crystal X-ray diffraction measurements this phase to be strictly stoichiometric. As a third boundary system, the section $\text{UFe}_2\text{-UAl}_2$ after [1962Pet] (Fig. 1) was used by [1963Pet]. For the Al-Fe binary system the assessment adopted by [Mas2] was accepted, which is given in more detail by [1993Kat]. Complete thermodynamic datasets are assessed for the Al-Fe [1998Sei] and Fe-U [2003Cha] systems. For Al-U a partial dataset is given by [1990Kas].

Solid Phases

The solubilities of Fe and Al in the pure modifications of U were investigated by [1963Kha, 1963Rus, 1964Dix, 1964Rus, 1966Sch].

The maximum mutual solubility of the cubic Laves phases UFe_2 and UAl_2 is 19 mol% at 1000°C on both sides [1963Pet]. [1967Lam] gives solubilities of 27 mol% UFe_2 in UAl_2 and 15 mol% UAl_2 in UFe_2 . The lattice parameters deviate from Vegard's law to smaller values. A ternary MgZn_2 type Laves phase

U(Fe,Al)_2 has been found between UFe_2 and UAl_2 , ranging from 22 to 39.67 at.% Al [1964Ste]. It was later characterized to have an ordering of Fe and Al atoms on the different Wyckoff positions of this structure type ($\text{Mg}_2\text{Cu}_3\text{Si}$ type [1971Kim]).

Another phase in the UFe_2 - UAl_2 quasibinary system has a well-defined composition corresponding to the stoichiometric formula UAlFe ; it is stable below 700°C [1967Lam]. Its structure is the Fe_2P -type, but with Al and Fe ordered on the two different Wyckoff positions of P-sites (ZrNiAl type) [1986And]. A phase called UFe_4Al_8 was first studied by X-ray diffraction [1984Ste, 1984Bar]. It has an extended homogeneity range along Al-Fe interchange, $\text{UFe}_x\text{Al}_{12-x}$ ($3 < x < 7$ [2005Gon]). Up to the composition UFe_4Al_8 , the Fe atoms are restricted to the 8f position of the ThMn_{12} type structure. Until $x = 6$ further Fe atoms occupy preferably the 8j position, whereas for $x > 6$ also some Fe atoms go to the 8i position [1995Gon, 2005Gon]. Like other phases of the ThMn_{12} type it is ferromagnetic and exhibits very large magnetic anisotropy with the hard magnetization along the c-axis. By spectroscopic investigation [2003Tal] found domination of the U 5f states at the Fermi level.

Five more ternary phases were identified to be stable at 850°C [2005Gon]. The crystal structure is known for all of them. An additional phase, $\text{U}_2\text{FeAl}_{20}$ was reported without investigation of its stability range or details of its crystal structure [2005Mes].

The crystallographic data of all solid phases are summarized in Table 2.

Quasibinary Systems

The section UFe_2 - UAl_2 was established to be quasibinary by [1962Pet, 1963Pet] and [1967Lam] (Fig. 1). [1967Lam] corrected their own results of 1962 [1962Lam]. [1967Lam] found additionally a ternary stoichiometric phase UFeAl . Above 800°C the phase relationships of [1962Pet] and [1967Lam] differ somewhat in the stability ranges of the phases. The major difference is at approximately 700°C , where UFeAl is formed peritectoidally and a concomitant narrowing of the U(Fe,Al)_2 phase field results. In Fig. 1 the section UFe_2 - UAl_2 is mainly taken as published by [1962Pet], completed by the ternary compound UAlFe published by [1967Lam].

Invariant Equilibria

Five invariant four-phase equilibria are reported in the region U- UFe_2 - UAl_2 [1963Pet] and listed with the phase compositions in Table 3. E_1 and E_2 are solid phase reactions resulting from the polymorphy of uranium. In Fig. 2 the reaction scheme is presented, mainly taken from [1963Pet]. The temperatures of E_1 and E_2 are based on small effects in the DTA curves and are not established exactly by [1963Pet] nor are the concentrations of the participating solid phases. At temperatures below the formation temperature of the stoichiometric phase UFeAl ($700 \pm 10^\circ\text{C}$) the phase equilibria given by [1963Pet] had to be corrected by adding equilibria with the phase UFeAl . As all three phases UAl_2 , UFeAl and U(Fe,Al)_2 are restricted to the line with 33.3 at.% U, thus phase U_6Fe cannot participate in the four-phase reaction D_1 : $\text{UAl}_2 + \text{U(Fe,Al)}_2 \rightleftharpoons \text{UFeAl}$, U_6Fe , which therefore is degenerate.

Liquidus Surface

Figure 3 shows the isotherms of the partial U- UFe_2 - UAl_2 liquidus surface and the melting grooves separating five areas of primary crystallization: (γU), UAl_2 , U(Fe,Al)_2 , UFe_2 and U_6Fe after [1963Pet]. For the part with less than 33 at.% U no liquidus data are published.

Isothermal Sections

Figures 4 and 6 to 8 show isothermal sections of the U- UFe_2 - UAl_2 partial system after [1963Pet] at 1000, 800, 700 and 600°C , respectively. Figure 5 presents the isothermal section at 850°C of the whole system. This is the only temperature, for which equilibria between phases with less than 33.3 at.% U are reported. The U rich part of Fig. 5 is based on [1963Pet], the U poor part on [2005Gon]. Some three-phase equilibria were given incompletely by [2005Gon], they are tentatively completed in Fig. 5. In Fig. 8 the stoichiometric ternary phase UFeAl is implemented into the diagram of [1963Pet]. In the binary systems the solubility

ranges of UFe_2 and UAl_2 are very small, therefore small deviations from exactly 33.3 at.% U, as drawn by [1963Pet] in the ternary system, are very improbable and omitted in Figs. 4 to 8.

Temperature – Composition Sections

Six isopleths (Figs. 9 to 14) at constant contents of 5, 10, 20 at.% Al, 25 at.% Fe, 40 and 60 at.% U are given after [1963Pet]. [1963Kha] published isopleths in the U corner, three at constant Fe:Al ratios (3:1, 1:1, 1:3) up to an amount of Al+Fe of 5 at.% (Figs. 15, 16, 17), one at constant 95 at.% U (Fig. 18) as well as a projection of the curves of double saturation of the (β U) and (γ U) solid solutions (Fig. 19). The temperatures given by [1963Pet] and [1963Kha] differ slightly, but are kept in Figs. 9 to 19 as declared by the respective authors.

Notes on Materials Properties and Applications

The U rich phases were investigated as candidates for nuclear fuel materials. This may still be interesting for research reactors. In U with small amounts of Al and Fe (“adjusted uranium”) small precipitates of UAl_2 or U_6Fe in (α U) diminish swelling [1964Dix].

Although its Curie temperature is near room temperature the phase $\text{UFe}_x\text{Al}_{12-x}$ is of large theoretical interest to study the effect of f electrons (lanthanides and actinides) on magnetic structures and properties.

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Table 1: Key-Investigations of the Al-Fe-U Phase Equilibria and Crystal Structures

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1962Pet] [1963Pet]	DTA, optical microscopy, X-ray diffraction	33-100 at.% U, 600-1150°C
[1962Lam] [1967Lam]	DTA, optical microscopy, X-ray diffraction	33.3 at.% U, 600-1100°C
[1963Kha]	Metallography of annealed and quenched samples	95-100 at.% U, 650-1050°C
[2005Gon]	scanning electron microprobe, X-ray powder diffraction	0-33 at.% U, 850°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ , (γ U)(h ₂) 1132 - 772	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	$a = 352.4$	[Mas2]
β , (β U)(h ₁) 772 - 662	<i>tP30</i> <i>P4</i> ₂ / <i>mnm</i> β U(h ₁)	$a = 1075.9$ $c = 565.6$	[Mas2]
α , (α U)(r) < 662	<i>oC4</i> <i>Cmcm</i> α U(r)	$a = 285.37$ $b = 586.95$ $c = 495.48$	[Mas2]
(γ Fe) 1390 - 910	<i>cF4</i> <i>Fm</i> $\bar{3}m$ Cu	$a = 364.67$	[Mas2]
(α Fe) < 1535	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	$a = 286.65$	[Mas2]
(Al)	<i>cF4</i> <i>Fm</i> $\bar{3}m$ Cu	$a = 404.96$	[Mas2]
U(Fe _x Al _{1-x}) ₂ UAl ₂	<i>cF24</i> <i>Fd</i> $\bar{3}m$ MgCu ₂	$a = 776.6$ $a = 774.85$ $a = 769.6$ $a = 766.9$ $a = 759.5$	$0 \leq x \leq 0.162$ [V-C] maximal solubility of Fe (at 1000°C): 12.67 at.% [V-C2] 0 at.% Fe, quenched from 1000°C, ($x = 0$) [1964Ste] 5 at.% Fe, quenched from 1000°C, ($x = 0.075$) [1964Ste] 8.17 at.% Fe, quenched from 1000°C, ($x = 0.122$) [1964Ste] 10.87 at.% Fe, quenched from 1000°C, ($x = 0.162$) [1964Ste]
UAl ₃	<i>cP4</i> <i>Pm</i> $\bar{3}m$ Cu ₃ Au	$a = 426.5$	[V-C2]
UAl ₄	<i>oI20</i> <i>Imma</i> UAl ₄	$a = 440.14$ $b = 625.52$ $c = 1372.79$	[V-C2], lattice parameters [2004Tou]
U ₆ Fe < 805	<i>tI28</i> <i>I4/mcm</i> U ₆ Mn	$a = 1030.22$ $c = 523.86$	[2005Gon]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
U(Fe _{1-x} Al _x) ₂	<i>cF</i> 24 <i>Fd</i> $\bar{3}m$ MgCu ₂		0 ≤ <i>x</i> ≤ 0.19 [V-C] maximal solubility of Al (at 1000°C): 12.7 at. %
UFe ₂		<i>a</i> = 706.5 <i>a</i> = 704.7 <i>a</i> = 706.96 <i>a</i> = 711.8	0 at. % Al, 1000°C, (<i>x</i> = 0) [1964Ste] 5 at. % Al, 1000°C, (<i>I</i> = 0.05) [1964Ste] 12 at. % Al, 1000°C, (<i>x</i> = 0.18) [1964Ste]
Fe ₄ Al ₅	<i>cI</i> 16?	<i>a</i> = 598.0	at 61 at. % Al, [1993Kat]
FeAl ₂ < 1156	<i>aP</i> 18 <i>P</i> 1 FeAl ₂	<i>a</i> = 487.8 <i>b</i> = 646.1 <i>c</i> = 880.0 α = 91.75° β = 73.27° γ = 96.89°	at 66.9 at. % Al, solid solubility ranges from 65.5 to 67.0 at. % Al [1993Kat]
Fe ₂ Al ₅ < 1169	<i>oC</i> 24 ^a <i>Cmcm</i> Fe ₂ Al ₅	<i>a</i> = 765.59 <i>b</i> = 641.54 <i>c</i> = 421.84	at 71.5 at. % Al [1994Bur]
Fe ₄ Al ₁₃ < 1160	<i>mC</i> 102 <i>C2/m</i> Fe ₄ Al ₁₃	<i>a</i> = 1552.7 to 1548.7 <i>b</i> = 803.5 to 808.4 <i>c</i> = 1244.9 to 1248.8 β = 107.7 to 107.99°	solid solubility ranges from 74.5 to 75.5 at. % Al [1993Kat]
* U(Fe _x Al _{1-x}) ₂ < 1060	<i>hP</i> 12 <i>P</i> 6 ₃ / <i>mmc</i> MgZn ₂	<i>a</i> = 515 <i>c</i> = 798	0.167 ≤ <i>x</i> ≤ 0.292 (22 to 39.67 at. % Al) 41.67 at. % Fe, 25 at. % Al, 1000°C [1964Ste]
	(Mg ₂ Cu ₃ Si)	<i>a</i> = 522 <i>c</i> = 816	30.67 at. % Fe, 36 at. % Al, 1000°C [1964Ste] [1971Kim]
* UFeAl < 700	<i>hP</i> 9 <i>P</i> 6 ₂ $\bar{m}$ Fe ₂ P (ZrNiAl)	<i>a</i> = 667.2 <i>c</i> = 398.1	[1967Lam] water quenched from 675°C; [1986And]
* U ₃ Fe ₄ Al ₁₂	<i>hP</i> 38 <i>P</i> 6 ₃ / <i>mmc</i> Gd ₃ Ru ₄ Al ₁₂	<i>a</i> = 874.51 <i>c</i> = 925.88	[2005Gon]
* U ₂ Fe ₁₂ Al ₁₅	<i>hP</i> 38 <i>P</i> 6 ₃ / <i>mmc</i> Th ₂ Ni ₁₇	<i>a</i> = 856.31 <i>c</i> = 843.8	<i>x</i> = 12 [2005Gon]
* U ₂ Fe _x Al _{17-x}	<i>hR</i> 57 <i>R</i> 3 $\bar{m}$ Th ₂ Zn ₁₇	<i>a</i> = 875.3 <i>c</i> = 1265.8	6.7 < <i>x</i> < 8.6 at 850°C [2005Gon] <i>a</i> , <i>c</i> at <i>x</i> = 8

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* U ₂ Fe _{3.6} Al _{13.4-x}	<i>hP38</i> <i>P6₃/mmc</i> Th ₂ Ni ₁₇	$a = 885.89$ $c = 898.24$	$x = 3.6$ [2005Gon]
* UFe _x Al _{12-x}	<i>tI26</i> <i>I4/mmm</i> ThMn ₁₂	$a = 874.9$ $c = 503.6$	$3 < x < 7$ [2005Gon] a, c at $x = 4$, room temperature [1984Ste]
* UFe ₂ Al ₁₀	<i>oC52</i> <i>Cmcn</i> YbFe ₂ Al ₁₀	$a = 891.46$ $b = 1019.86$ $c = 901.14$	[2004Noe]
		$a = 891.92$ $b = 1020.78$ $c = 901.83$	[2004Mes]
* U ₂ FeAl ₂₀	<i>tI*</i> <i>I42m</i>	$a = 1240$ $c = 1030$	[2005Mes]

^a 12 Al-positions of the 24 total positions denoted in the Pearson symbol are occupied only partially. The mean total number of atoms in the unit cell is about 15.2 [1994Bur].

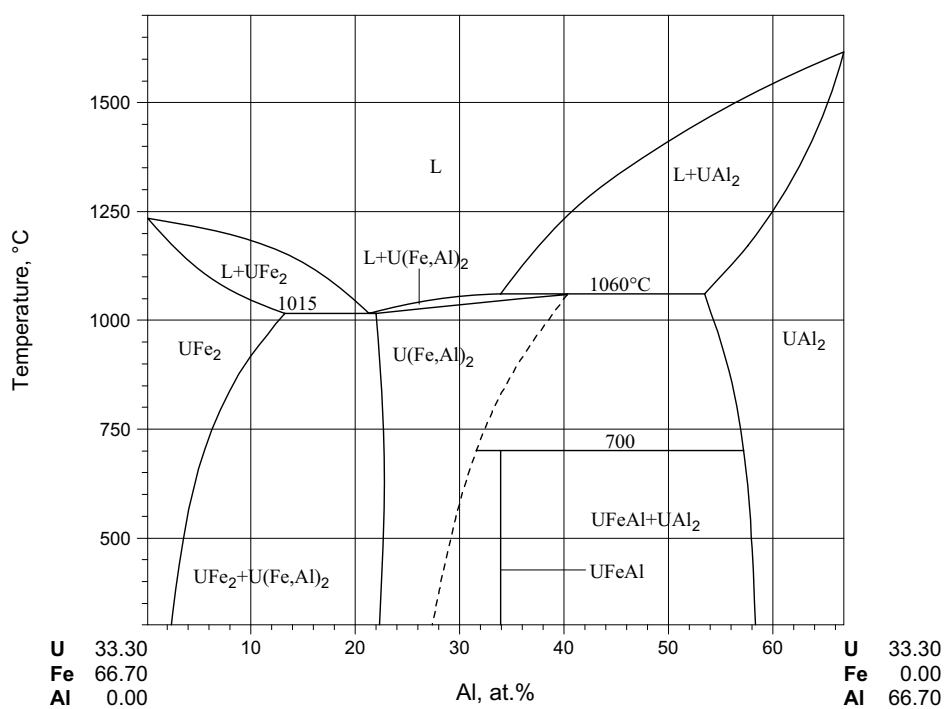
Table 3: Compositions of the Invariant Equilibria in the U-UAl₂-UFe₂ Partial System

Reaction	T [°C]	Type	Phase	Composition* (at.%)		
				Al	Fe	U
L + UAl ₂ $\rightleftharpoons$ U(Fe,Al) ₂	1060	max ₁	L	(33)	(34)	33.3
			UAl ₂	(53)	(14)	33.3
			U(Fe,Al) ₂	40	26.7	33.3
L $\rightleftharpoons$ U(Fe,Al) ₂ + UFe ₂	1015	max ₂	L	20.5	46.2	33.3
			U(Fe,Al) ₂	(22)	(45)	33.3
			UFe ₂	(13)	(54)	33.3
L + (γ U) $\rightleftharpoons$ UAl ₂ + U ₆ Fe	805	U ₁	L	6	19.5	74.5
			(γ U)	3	2	95
			UAl ₂	(64)	(2.7)	33.3
			U ₆ Fe	-	14.3	85.7
L + UAl ₂ $\rightleftharpoons$ U(Fe,Al) ₂ + U ₆ Fe	780	U ₂	L	6	23	71
			UAl ₂	(57)	(9.7)	33.3
			U(Fe,Al) ₂	(33.3)	(33.3)	33.3
			U ₆ Fe	-	14.3	85.7
L + U(Fe,Al) ₂ $\rightleftharpoons$ UFe ₂ + U ₆ Fe	745	U ₃	L	(2)	(33)	65
			U(Fe,Al) ₂	(22.7)	(44)	33.3
			UFe ₂	(4.7)	(62)	33.3
			U ₆ Fe	-	14.3	85.7

Reaction	T [°C]	Type	Phase	Composition* (at.%)		
				Al	Fe	U
$(\gamma\text{U}) \rightleftharpoons (\beta\text{U}) + \text{UAl}_2 + \text{U}_6\text{Fe}$	~ 680	E_1	(γU)	(< 1.5)	(1)	(> 97)
			(βU)	(< 0.5)	(< 1)	(> 98)
			UAl_2	(66)	(0.7)	33.3
			U_6Fe	-	14.3	85.7
$(\beta\text{U}) \rightleftharpoons (\alpha\text{U}) + \text{UAl}_2 + \text{U}_6\text{Fe}$	~ 610	E_2	(βU)	(< 0.2)	(< 0.2)	(> 99)
			(αU)	(< 0.01)	(< 0.1)	(> 99)
			UAl_2	(66.5)	(0.2)	33.3
			U_6Fe	(-)	14.3	85.7

* Values given in brackets are estimated

Fig. 1: Al-Fe-U.
The quasibinary
system UAl_2 - UFe_2



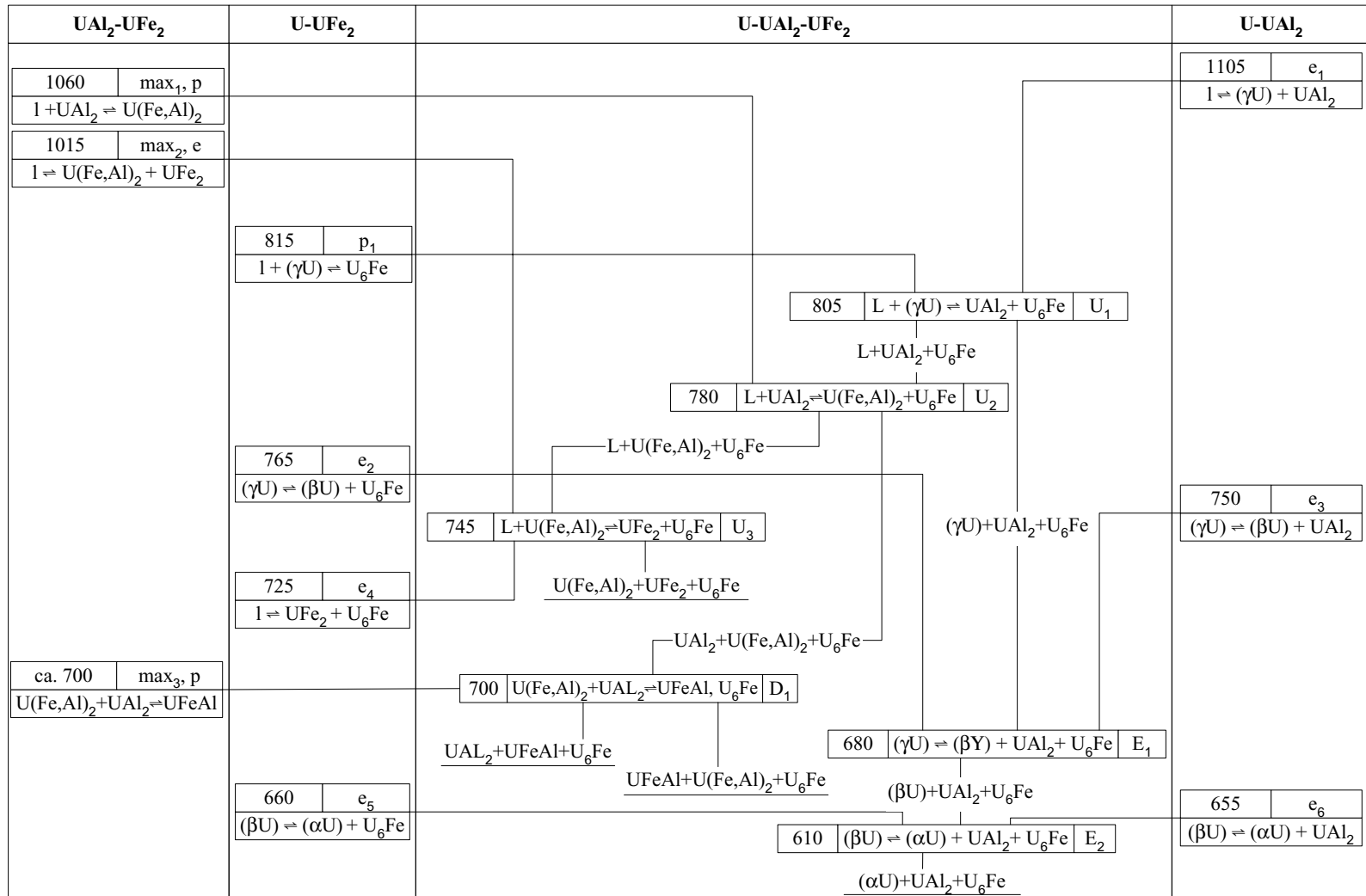


Fig. 2: Al-Fe-U. Partial reaction scheme

Fig. 3: Al-Fe-U.
Partial liquidus
surface projection

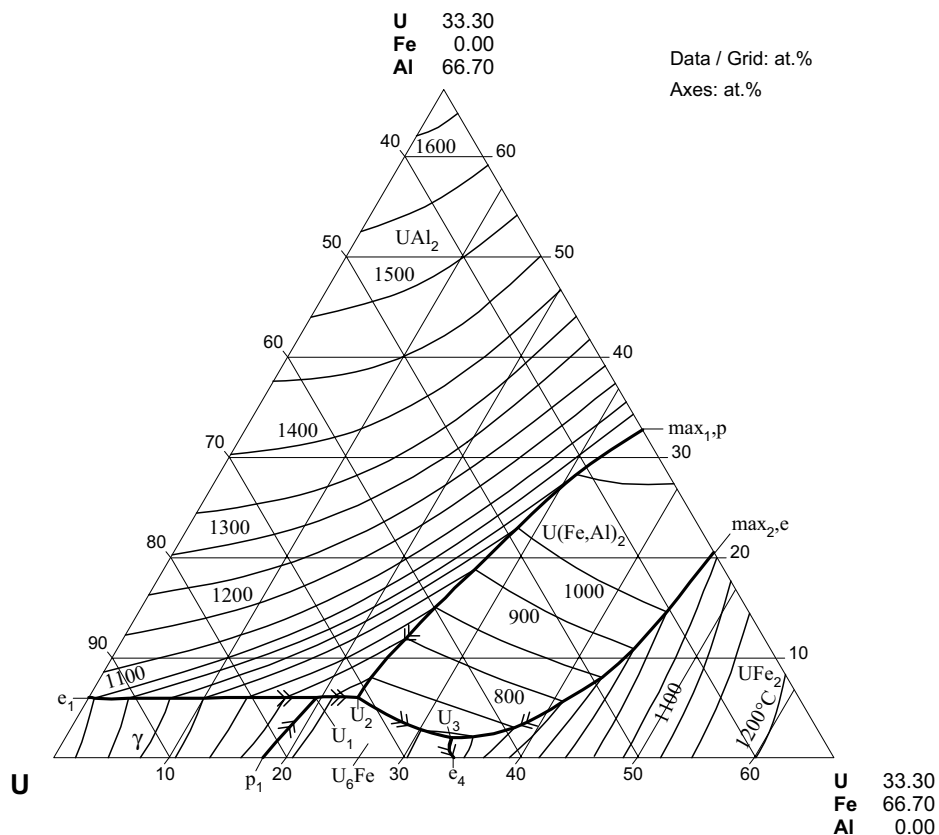


Fig. 4: Al-Fe-U.
Isothermal section at
1000°C

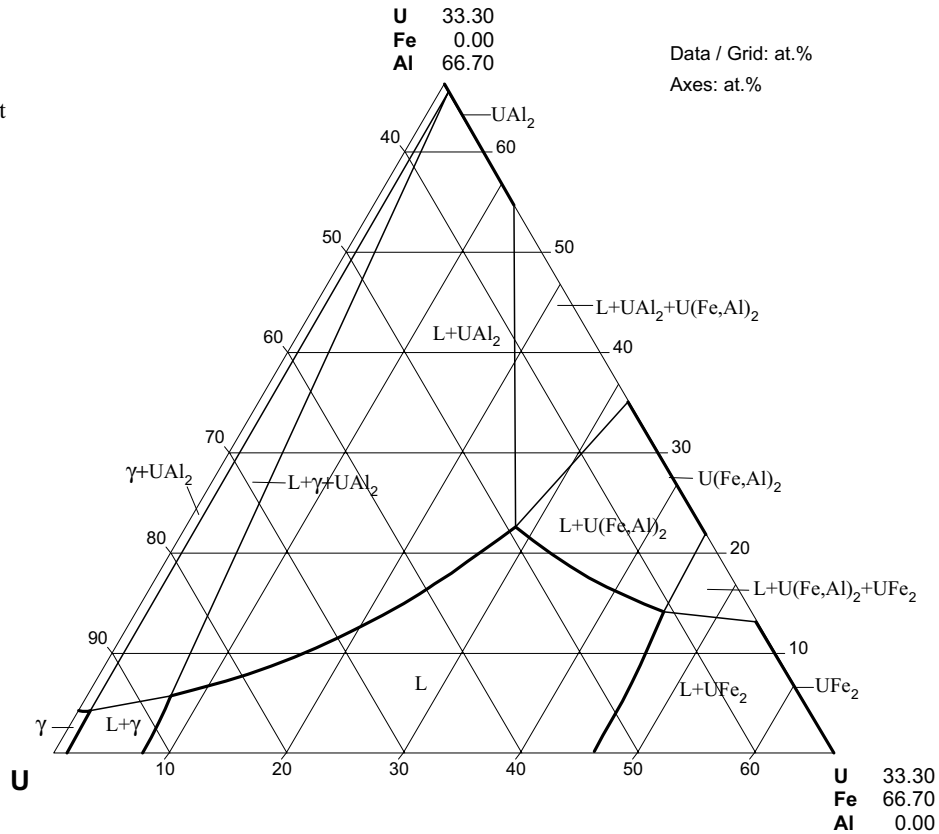


Fig. 5: Al-Fe-U.
Isothermal section at
850°C

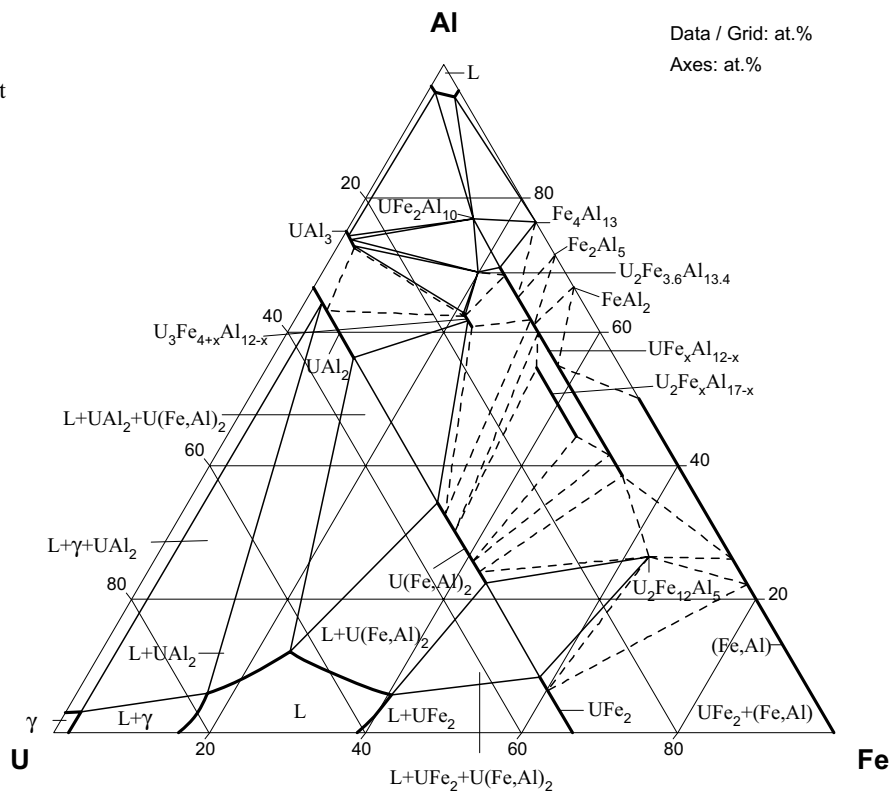


Fig. 6: Al-Fe-U.
Isothermal section at
800°C

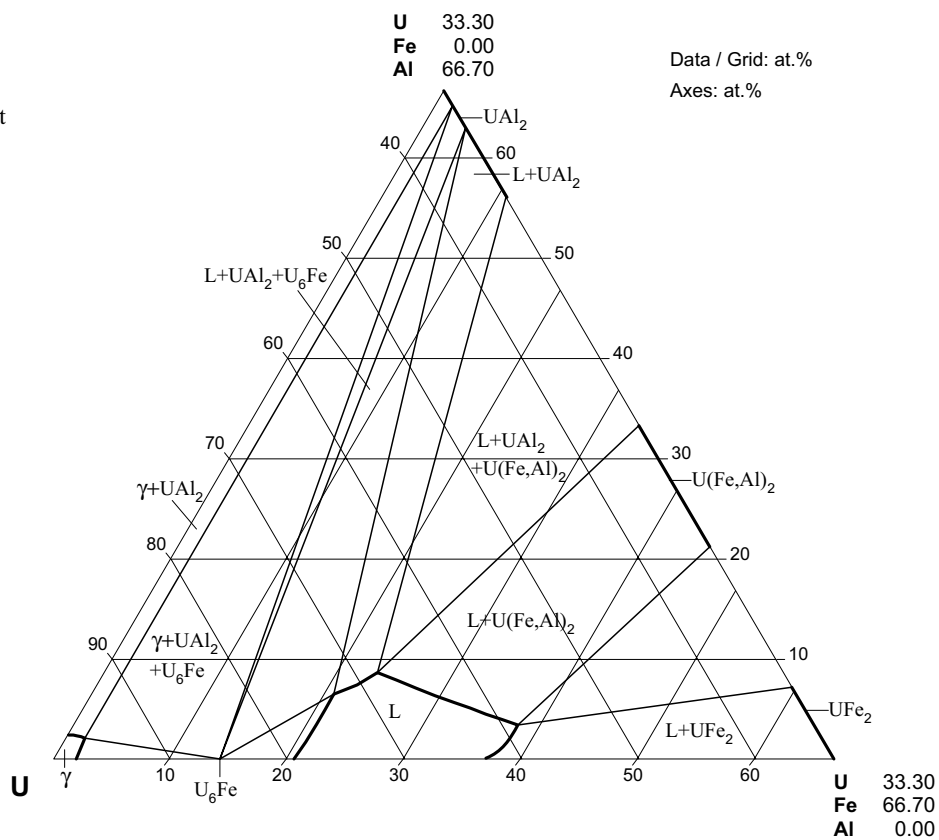


Fig. 7: Al-Fe-U.
Isothermal section at
700°C

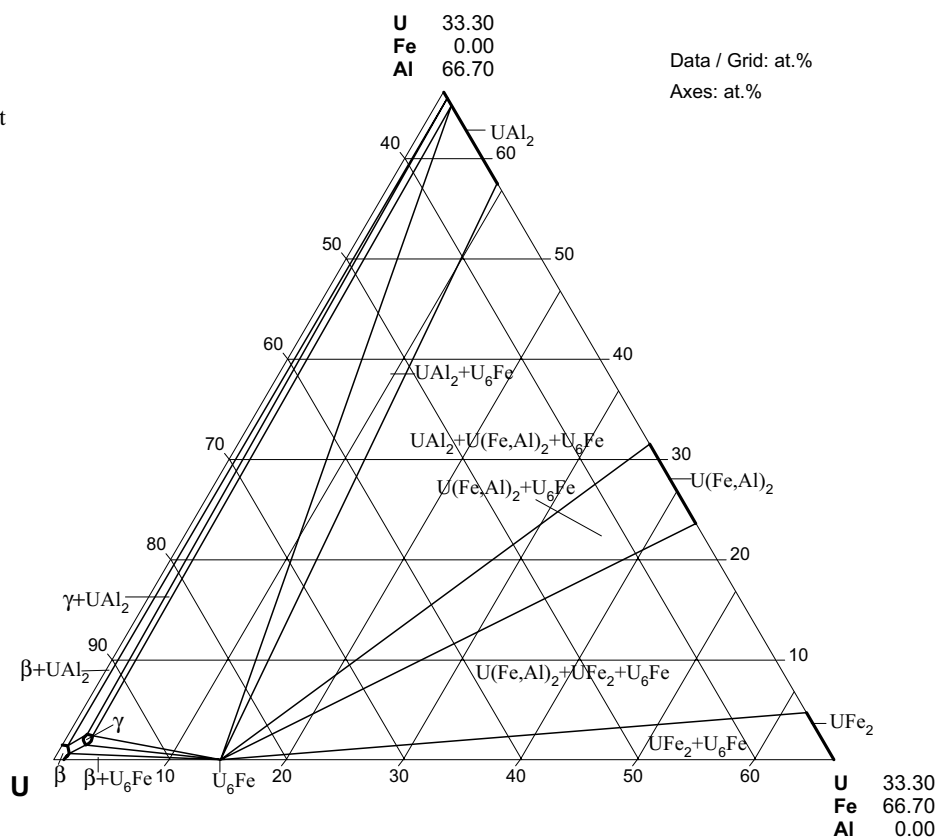


Fig. 8: Al-Fe-U.
Isothermal section at
600°C

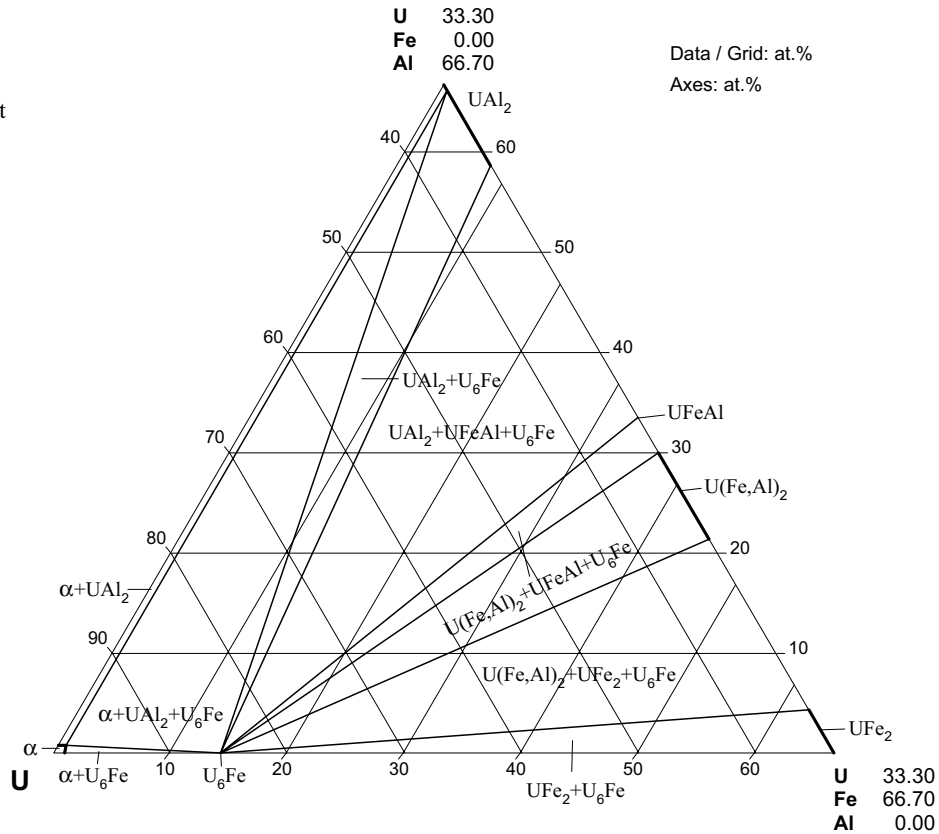


Fig. 9: Al-Fe-U.
Temperature -
composition cut for
5 at.% Al

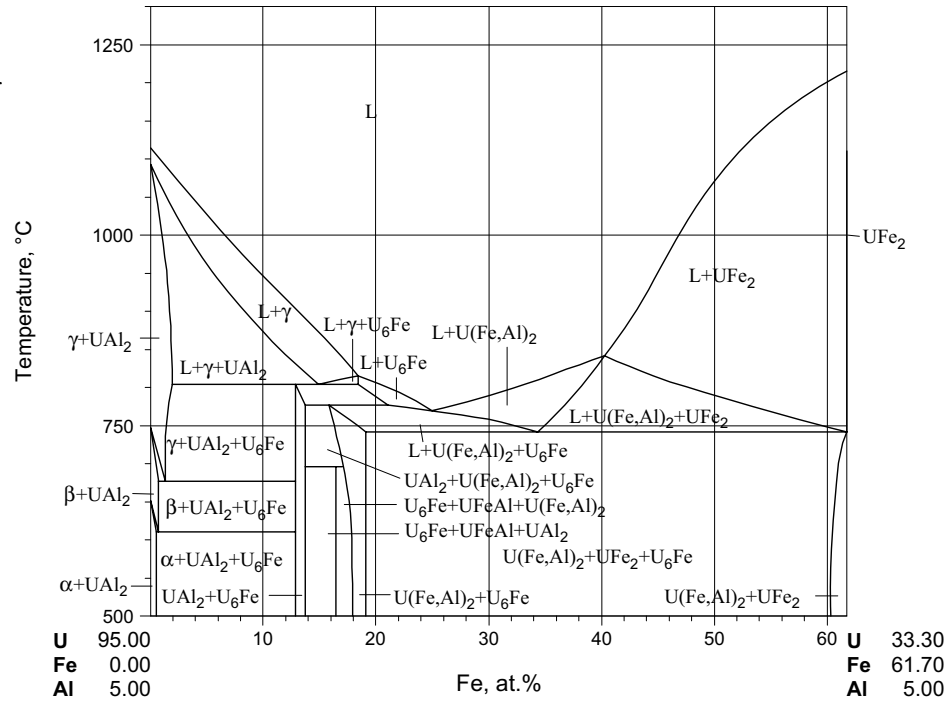


Fig. 10: Al-Fe-U.
Temperature -
composition cut for
10 at.% Al

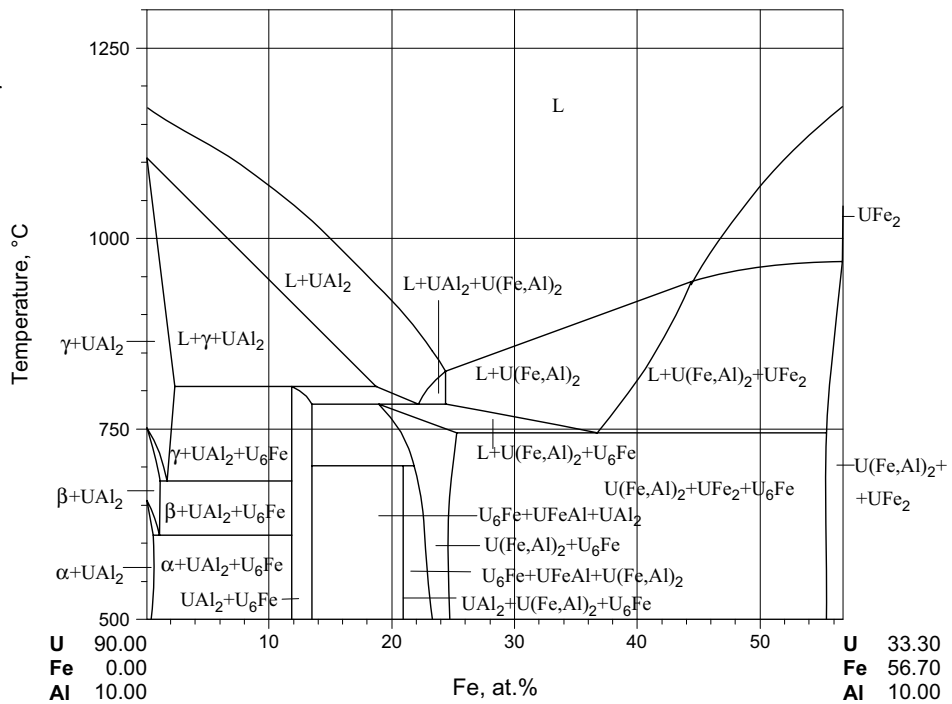


Fig. 11: Al-Fe-U.
Temperature -
composition cut for
20 at.% Al

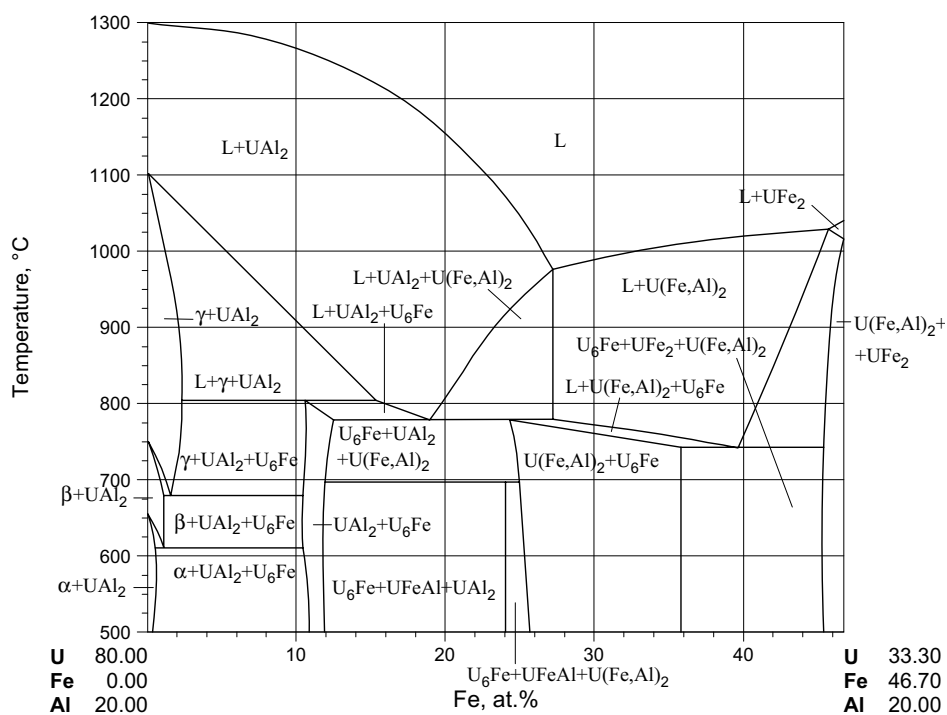


Fig. 12: Al-Fe-U.
Temperature -
composition cut for
25 at.% Fe

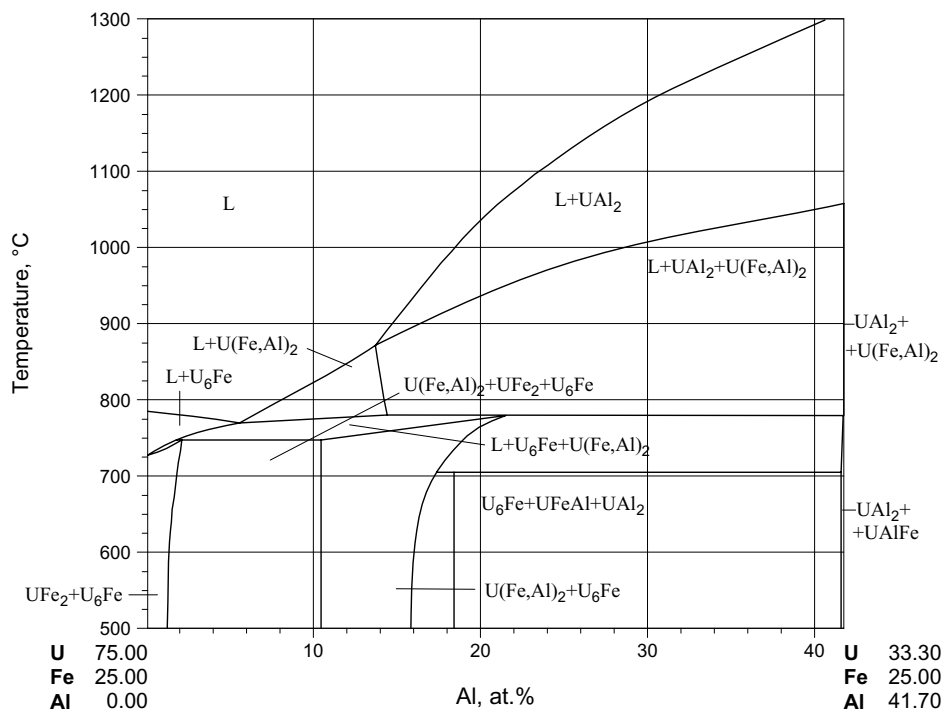


Fig. 13: Al-Fe-U.
Temperature -
composition cut for
40 at.% U

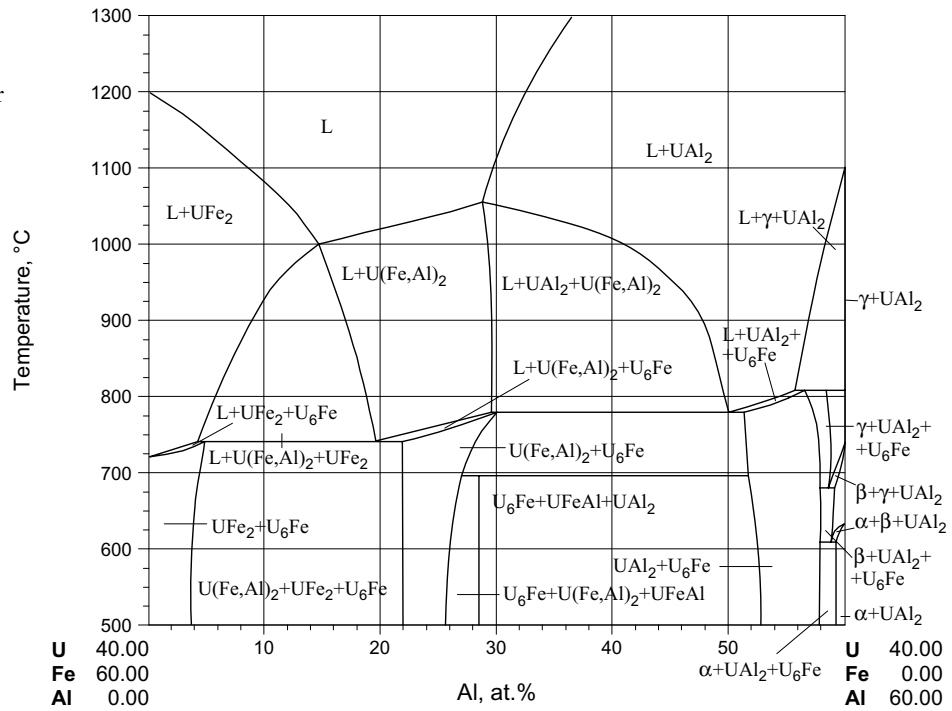


Fig. 14: Al-Fe-U.
Temperature -
composition cut for
40 at.% U

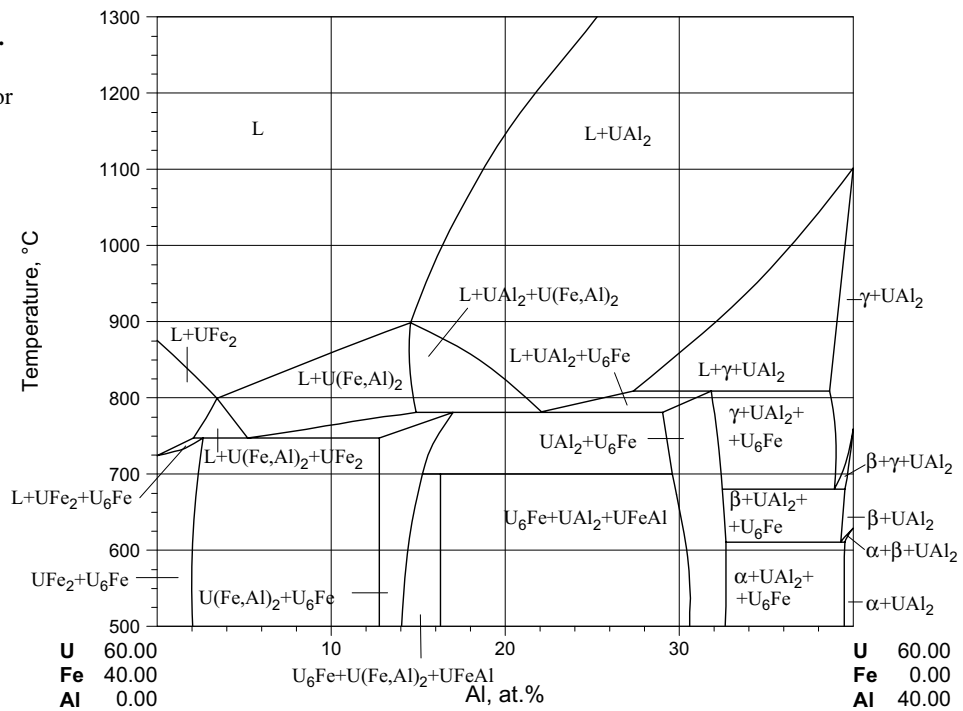


Fig. 15: Al-Fe-U.
Isopleth with constant
ratio Al:Fe = 3:1

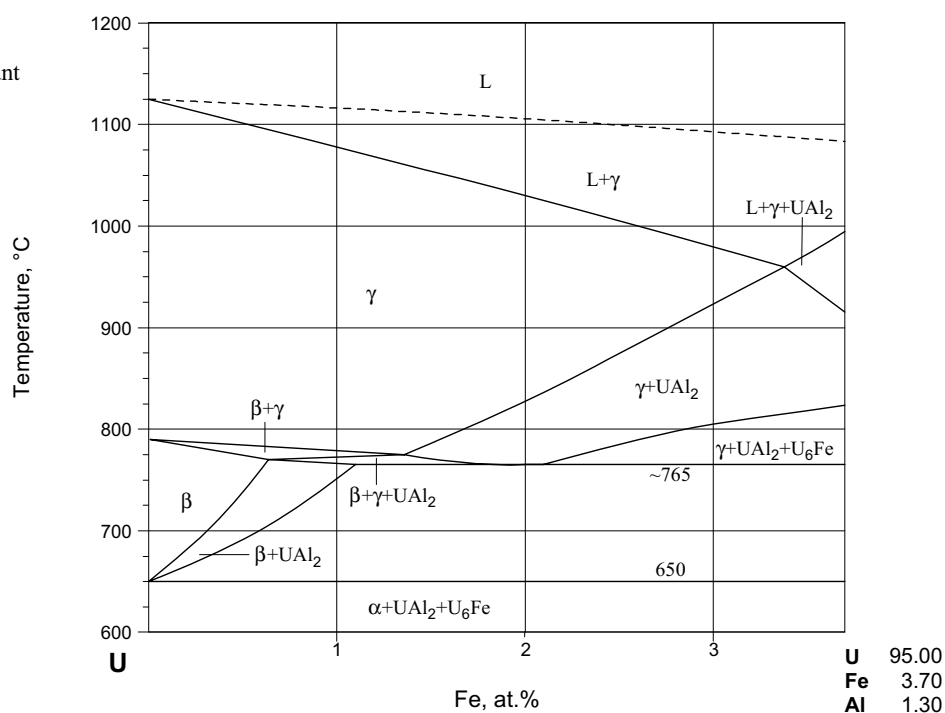


Fig. 16: Al-Fe-U.
Isopleth with constant
ratio Al:Fe = 1:1

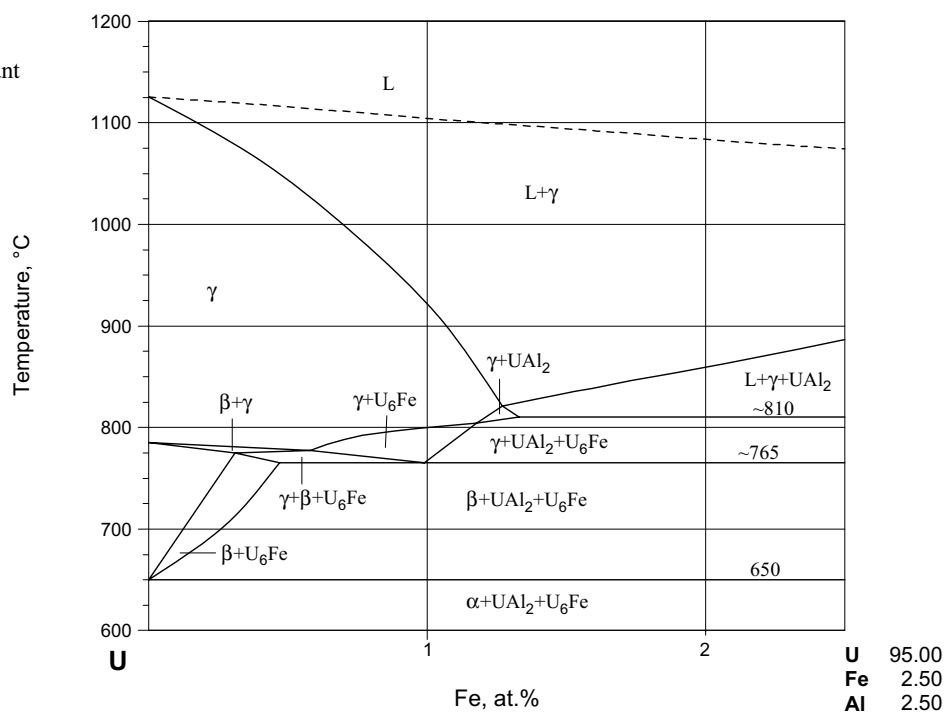


Fig. 17: Al-Fe-U.
Isopleth with constant
ratio Al:Fe = 1:3

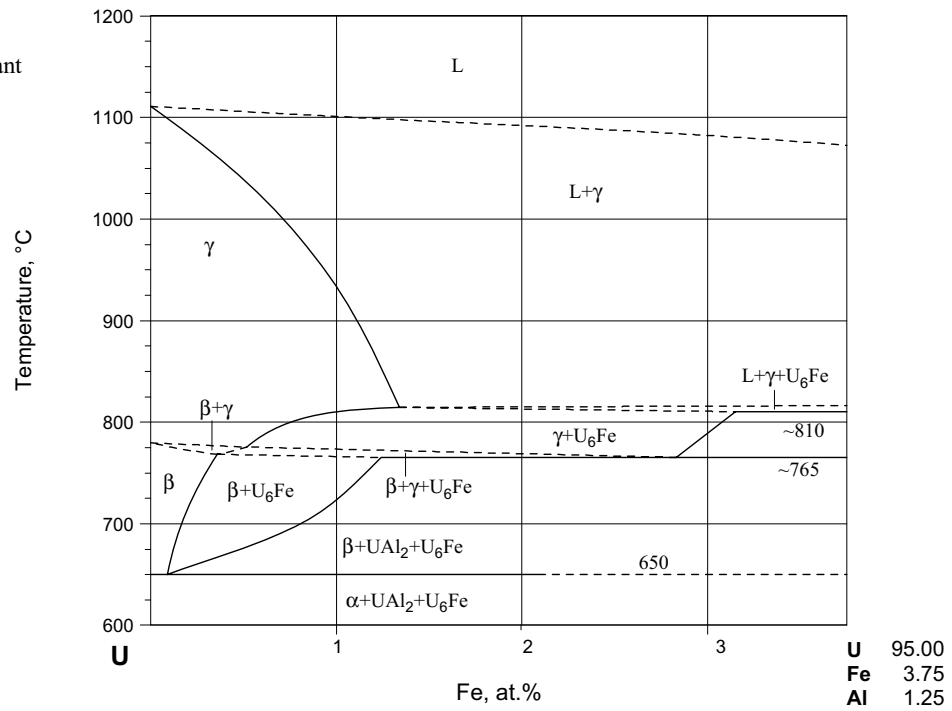


Fig. 18: Al-Fe-U.
Isopleth at constant
95 at.% U

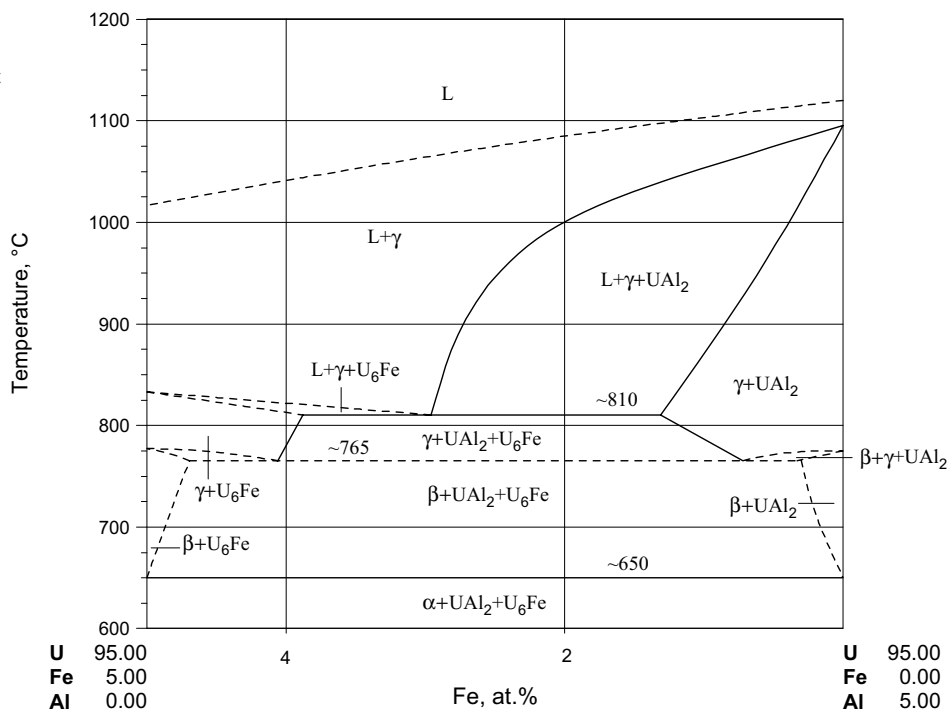
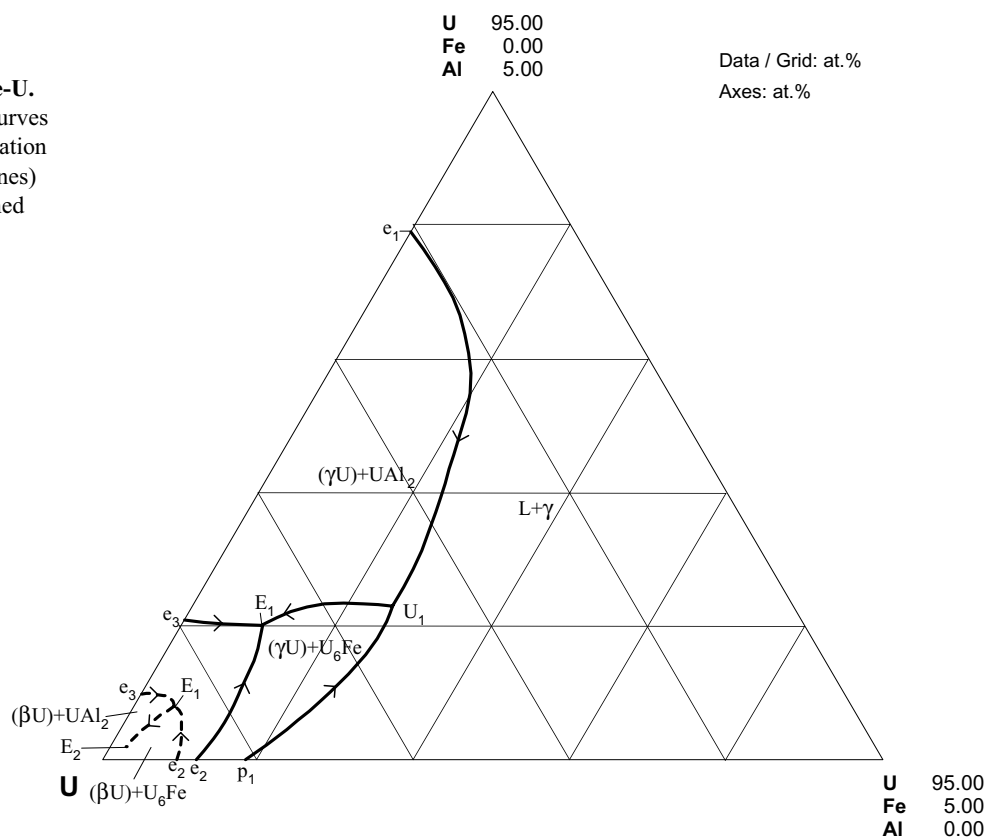


Fig. 19: Al-Fe-U.
Projection of curves
of double saturation
of (γ U) (full lines)
and (β U) (dashed
lines)



Aluminium – Oxygen – Plutonium

Kostyantyn Korniyenko

Introduction

Partitioning and transmutation is considered to be a complementary option in the management of waste from nuclear power generation. In this process, the radionuclides are separated from the spent fuel, followed by fission or transmutations in reactors or accelerators. As the long-term radiotoxicity of the fission products is much less than that of the actinide after about 250 years, a substantial reduction of the waste can be achieved. Plutonium is one of the actinides formed by neutron capture in ^{238}U during irradiation of UO_2 in nuclear power plants. Efficient partitioning of plutonium from the spent fuel has already been realized in present commercial PUREX (plutonium reprocessing and extraction) installations. For the fabrication of fuels for transmutation, two ways are considered: homogeneous mixing in fresh MOx (mixed oxide) fuel, and heterogeneous dispersion in an inert support material [1997Zha]. Aluminium oxide Al_2O_3 is an appropriate candidate inert matrix material for heterogeneous transmutation based on an evaluation of some its physico-chemical and neutronic properties. Among these properties, the melting behavior is extremely important. An inert-matrix fuel should have a high melting temperature to avoid melting the fuel during power ramps. In general, knowledge of the phase equilibria of fuels consisting of plutonium oxides and inert matrix aluminium oxide is of great importance. But up to now, information is incomplete. Results of experimental investigations of phase equilibria in the $\text{PuO}_2\text{-Al}_2\text{O}_3$ quasibinary system are presented in [1964Hou] (as quoted by [1965Far]) and [1965Hou] (reproduced also in [1967Ack]). The authors of [1965Hou] have prepared plutonium dioxide from the oxolate by calcining at 600°C . The used aluminium oxide was chemical reagent grade material. The $\text{PuO}_2\text{-Al}_2\text{O}_3$ powders were sintered in an oxygen atmosphere at 1250°C for 2 hours in thoria crucibles. The melting points of the pellets were determined and high temperature sintering was carried out in oxygen and argon atmospheres. The specimens were studied using metallography, X-ray diffraction and microprobe analysis. The melting behavior of the systems $\text{PuO}_2\text{-Al}_2\text{O}_3$ and $\text{PuO}_{1.61}\text{-Al}_2\text{O}_3$ as well as the character of the phase equilibria in the $\text{Al}_2\text{O}_3\text{-PuO}_{1.61}\text{-PuO}_2$ partial system over the temperature range 1727 to 2177°C were calculated by [1997Zha] using the Calphad method. Future experimental determinations of phase equilibria along the $\text{PuO}_{1.61}\text{-Al}_2\text{O}_3$ and $\text{PuO}_2\text{-Al}_2\text{O}_3$ sections as well as the melting behavior and solid state equilibria in the range of compositions including Al_2O_3 and plutonium oxides are necessary. This new information will become a theoretical basis for new practical applications of Al–O–Pu alloys.

Binary Systems

The Al–O system is accepted from [Mas2]. The constitution of the Al–Pu and O–Pu systems are mainly based on the data of [1989Kas] and [1990Wri], respectively, that serve also as the foundation of the [Mas2] handbook data concerning the corresponding systems. The O–Pu binary was slightly modified in [1997Zha], which accepted a temperature of $2300 \pm 40^\circ\text{C}$ for melting point of the “ PuO_2 ” phase (of composition $\text{PuO}_{1.61}$) and a maximum point in the liquidus and solidus lines at 2475°C for the composition $\text{PuO}_{1.77}$.

Solid Phases

No ternary phases were found. Crystallographic data concerning the known unary and binary phases are listed in Table 1. No visible solubility of the third component in the binary phases was determined.

Quasibinary Systems

The phase diagram of the $\text{PuO}_2\text{-Al}_2\text{O}_3$ quasibinary system is presented in Fig. 1. It is based on the experimental results of [1964Hou] and [1965Hou] that were quoted in [1965Far] and [1967Ack] and was corrected slightly to take into account the accepted melting point of 2475°C for PuO_2 . The $\text{PuO}_2\text{-Al}_2\text{O}_3$ phase diagram calculated by [1997Zha] is identical. This phase diagram was found to be simple eutectic

with very little terminal solid solubility and no ternary compounds. So, the mutual solubilities of PuO_2 in Al_2O_3 and Al_2O_3 in PuO_2 are 0.28 ± 0.2 and 0.14 ± 0.14 (mol%), respectively. The oxygen contents corresponding to the maximum solubilities are 60.019 and 66.661 (at.%), respectively. The eutectic temperature obtained by [1964Hou] and [1965Hou] is accepted as an average of those obtained from a series of specimens. No attempts were made by the authors to determine the liquidus because no crucible material could be found by them which did not react with these substances when molten and which was also stable in oxygen at the temperatures involved ($> 2000^\circ\text{C}$). Thus, the liquidus curves are plotted in Fig. 1 as dotted lines.

Invariant Equilibria

On the basis of experimental investigations, [1964Hou, 1965Hou] found a three-phase invariant equilibrium $\text{L} \rightleftharpoons \alpha + \pi$ at a temperature of $1910 \pm 15^\circ\text{C}$. The temperature of the invariant equilibrium involving the participation of liquid, the α and σ phases and, obviously, a fourth phase, was calculated by [1997Zha] to be 1776°C .

Isothermal Sections

Isothermal sections of the Al_2O_3 - $\text{PuO}_{1.61}$ - PuO_2 partial system were calculated by [1997Zha] for the temperature range from 1727 to 2177°C . During construction of these sections, results of their own calculations of the phase equilibria in the forming O–Pu binary system in the range of compositions 61.68 to 66.67 at.% O (between the σ and π phases) were used. They accepted the maximum point in the liquidus and solidus lines at 2475°C and 63.90 at.% O which contradicts the accepted data of [1990Wri, Mas2], and therefore, the data obtained by [1997Zha] need further experimental verification. The Al_2O_3 - PuO_2 - $\text{PuO}_{1.61}$ (PuO_{2-x} - Al_2O_3 at $0 \leq x \leq 0.39$) isothermal section calculated at 1877°C by [1997Zha] is shown in Fig. 2. The dashed line represents the projection of the eutectic valley.

Temperature – Composition Sections

It was assumed by [1997Zha] that the $\text{PuO}_{1.61}$ - Al_2O_3 system is a simple eutectic like the PuO_2 - Al_2O_3 section and that the liquid phase behaves ideally. With this assumption, the eutectic point was calculated to be at 1776°C and 52 mol% $\text{PuO}_{1.61}$ (60.87 at.% O). However, as at higher temperatures, the composition $\text{PuO}_{1.61}$ lies in the PuO_2 phase field (the CaF_2 type structure), the $\text{PuO}_{1.61}$ - Al_2O_3 section would seem not to be quasibinary, and the eutectic temperature, probably, corresponds to the invariant four-phase process with participation of the liquid phase.

Thermodynamics

The Calphad technique was used by [1997Zha] for the calculation of phase equilibria with involving the plutonium oxides. The thermodynamic data used for Pu_2O_3 , $\text{PuO}_{1.61}$ (solid) and PuO_2 were taken from the ECN-T base [1990Cor, 1997Zha]. The data for the liquid σ phase were estimated while those used for the α phase are from the SGTE database. The least-square optimization programs BINGSS and BINFKT [1995Luk, 1997Zha] were used to perform the thermodynamic phase diagram optimization of the binary systems. Phase diagrams were then generated using the program MTDATA [1994Aea, 1997Zha] with the model parameters obtained in the optimization.

Notes on Materials Properties and Applications

In connection with high temperature reactor systems, the dispersion of plutonium oxides in various ceramic matrices, in particular, in Al_2O_3 , the properties of the diluent (particularly its thermal conductivity) may be expected largely to determine the behavior of the fuel. The corresponding system is the Al–O–Pu.

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Al) (I) < 660.452, 1.013 bar	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 404.96$	at 25°C [Mas2] dissolves less than $3 \cdot 10^{-8}$ at.% O at ~660°C and up to 1.6 at.% Pu at 650°C [Mas2]
(Al) (II) $2.05 \cdot 10^5$ bar	<i>hP2</i> <i>P6$_3$/mmc</i> Mg	$a = 269.3$ $c = 439.8$	at 25°C [Mas2]
(η Pu) (h_5) 640 - 483	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 363.43$	at 483°C [1990Wri] dissolves up to 10.5 at.% Al at 801°C [1989Kas]
(ϵ Pu) (h_4) 483 - 463	<i>tI2</i> <i>I4/mmm</i> In	$a = 332.61$ $c = 446.30$	at 477°C [1990Wri] dissolves up to 0.25 at.% Al at 463°C [1989Kas]
(δ Pu) (h_3) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 463.71$	at 320°C [1990Wri] dissolves up to 14.5 at.% Al at 788°C [1989Kas]
(γ Pu) (h_2) 320 - 215	<i>oF8</i> <i>Fddd</i> γ Pu	$a = 315.87$ $b = 576.82$ $c = 1016.2$	at 235°C [1990Wri]
(β Pu) (h_1) 215 - 125	<i>mC34</i> <i>C2/m</i> β Pu	$a = 928.4$ $b = 1046.3$ $c = 785.9$ $\beta = 92.13^\circ$	at 190°C [1990Wri]
(α Pu) (r) < 125	<i>mP16</i> <i>P2$_1$/m</i> α Pu	$a = 618.3$ $b = 482.2$ $c = 1096.3$ $\beta = 101.97^\circ$	at 21°C [1990Wri]
α , Al ₂ O ₃ 2054 - < 500	<i>hR30</i> <i>R$\bar{3}m$</i> α Al ₂ O ₃	$a = 479$ $c = 1293$	60 at.% O [1977Kri]
γ (Al–O)	<i>cF56</i> <i>Fd$\bar{3}m$</i> MgAl ₂ O ₄		metastable; ~ 60 at.% O; labelled as “ γ Al ₂ O ₃ ” [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
δ (Al–O)	-	-	metastable; ~ 60 at.% O; labelled as “ $\delta\text{Al}_2\text{O}_3$ ” [Mas2]
θ (Al–O)	m^{**} $C2/m$ $\beta\text{Ga}_2\text{O}_3$	-	metastable; ~ 60 at.% O; labelled as “ $\theta\text{Al}_2\text{O}_3$ ” [Mas2]
κ (Al–O)	-	-	metastable; ~ 60 at.% O; labelled as “ $\kappa\text{Al}_2\text{O}_3$ ” [Mas2]
χ (Al–O)	h^{**} $P6_3/mcm$ or $P6/mmm$ or $P6_3/mmc$ $\chi\text{Al}_2\text{O}_3$	-	metastable; ~ 60 at.% O; labelled as “ $\kappa\text{Al}_2\text{O}_3$ ” [Mas2]
$\beta\text{Pu}_3\text{Al}$ (h) 560 - 195	$tP4$ $P4/mmm$ SrPb_3	$a = 449.9$ $c = 453.8$ $a = 453.0$ $c = 447.5$ $a = 449.9$ $c = 453.6$	25 at.% Al [1989Kas] [E] [1959Boc]
$\alpha\text{Pu}_3\text{Al}$ (r) < 195	c^{**}		25 at.% Al [1989Kas]
η , PuAl 590 - 193	$cI58$	$a = 1076$	50 at.% Al [1989Kas] [1959Boc]
β , PuAl_2 < 1540	$cF24$ $Fd\bar{3}m$ Cu_2Mg	$a = 783.1$	66.7 at.% Al [1989Kas] [E]
$\delta\text{Pu}_{0.95}\text{Al}_3$ (h_3) 1420 - 1210	$cP4$ $Pm\bar{3}m$ AuCu_3	$a = 426.2$	~76 at.% Al, labelled as “3H” [1989Kas]
$\gamma\text{Pu}_{0.95}\text{Al}_3$ (h_2) 1210 - 1027	$hP24$ $P6_3/mmc$ PuAl_3	$a = 608.3$ $c = 1441.0$	~76 at.% Al, labelled as “6H” [1989Kas]
$\beta\text{Pu}_{0.95}\text{Al}_3$ (h_1) 1027 - 915	$hR36$ $R\bar{3}m$	$a = 614.85$ $c = 2110.11$	~76 at.% Al, labelled as “9H β ” [1989Kas]
$\alpha\text{Pu}_{0.95}\text{Al}_3$ (r) < 915	$hR36$ $R\bar{3}m$	$a = 615.02$ $c = 2117.44$	~76 at.% Al, labelled as “9H α ” [1989Kas]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
λ , Pu _{0.90} Al ₄ < 925	<i>oI20</i> <i>Imma</i> UAl ₄	$a = 439.6$ $b = 626.6$ $c = 1370.8$	~81.6 at.% Al [1989Kas] undergoes a second order transition at 645°C [1989Kas]
ν , Pu ₂ O ₃ < 2080	<i>hP5</i> <i>P$\bar{3}m1$</i> La ₂ O ₃	$a = 383.88$ $c = 595.94$	59.3 to 60.5 at.% O [1990Wri] [1990Wri]
ρ , PuO _{1.52} < 450	<i>cI80</i> <i>Ia$\bar{3}$</i> Mn ₂ O ₃	$a = 1104.5$	60.2 at.% O [1990Wri]
σ , PuO _{1.61} 1180 - 335	<i>cI80</i> <i>Ia$\bar{3}$</i> Mn ₂ O ₃	$a = 1099.1$	61.7 to 63.0 at.% O [1990Wri] [1990Wri]
π , PuO ₂ < 2425	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF ₂	$a = 539.6$ $a = 539.26$ $a = 539.53$	60 to 66.7 at.% O [1990Wri, 1997Zha] [E] [1962Pap, S] [1963Lea, S]

Fig. 1: Al-O-Pu.
The PuO_2 - Al_2O_3
quasibinary section

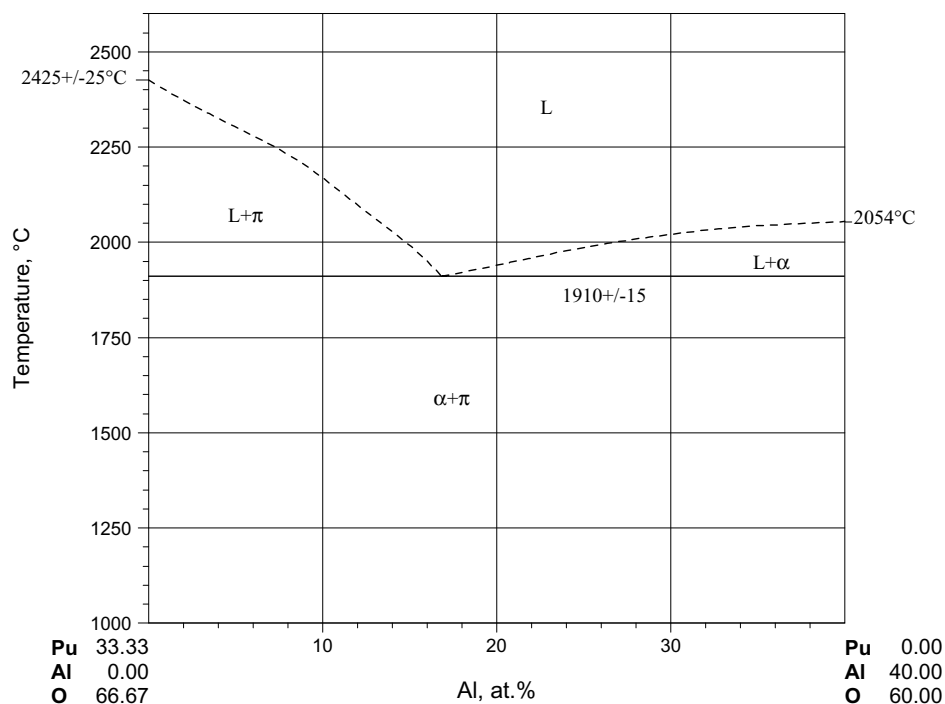
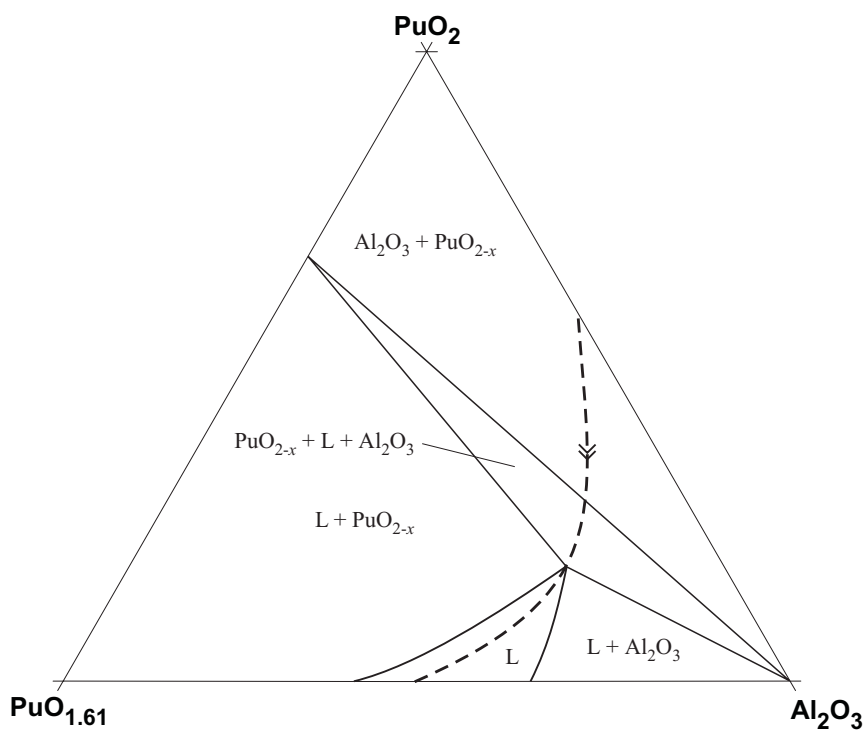


Fig. 2: Al-O-Pu.
Schematic partial
isothermal section
calculated at 1877°C.
Dashed line:
projection of the
eutectic valley



Aluminium – Silicon – Uranium

Peter Rogl, Henri Noél

Introduction

Due to their high potential as low-enriched uranium fuels ($< 20\%$ ^{235}U) in aluminium cladding, U_3Si and U_3Si_2 have directed research activities towards the metallurgy of the ternary system Al-Si-U. A first critical assessment of the Al-Si-U system has been made by [1998Ans]. Although many research groups dealt with the phase equilibria in the U rich part of the system [1961Pet, 1962Pet, 1963Svi, 1986Naz, 1989Ale1, 1991Pet], with the section $\text{UAl}_2\text{-USi}_{2-y}$ [1990Che, 1991Che] as well as with isothermal sections covering the whole composition range [1982Dwi, 1992Wei], there are several inconsistencies regarding phase relations, solution ranges and formation of ternary compounds (see discussion below). Some of the inconsistencies may have been inferred by the use of carbon containing uranium metal. Thus the authors of [1989Ale2] using high-purity electrolytic uranium (99.99 mass%) have demonstrated, that temperatures and reactions of ternary invariant equilibria reported by [1961Pet, 1962Pet] suffer from carbon impurity in uranium and in some aspects rather refer to the Al-C-Si-U quaternary system. Whereas [1977Zyg, 1990Che, 1991Che] reported on a ternary compound “UAlSi”, the investigations of [1982Dwi, 1986Naz, 1992Wei, 1994Wei] did not confirm its existence, but essentially agreed on a compound at or near $\text{U}_{-2}\text{AlSi}_{-2}$. The crystal structures of two further compounds U_3AlSi_3 and $\text{U}_3\text{Al}_2\text{Si}_3$ have been established by [1992Wei, 1994Wei].

The various experimental activities related to the constitution of the ternary Al-Si-U system are summarized in Table 1.

Binary Systems

The binary boundary system Al-Si has been accepted from [2004Gro]. The system Si-U is taken from the reinvestigation by [1992Rem], but the U rich part of the diagram up to 4 at.% Si is from [1965Str, 1991Pet]. The Al-U binary is based on a critical assessment by [1989Kas, 1990Kas], however, taking UAl_4 as a fully ordered, stoichiometric phase [2004Tou]. A listing of the crystallographic and melting data of the phases pertinent to the Al-Si-U system is given in Table 2.

Solid Phases

Although two research groups [1977Zyg] and [1990Che, 1991Che] independently corroborated the existence of the ternary compound UAlSi, investigations of the ternary isotherm by X-ray diffraction, metallography and EMPA [1982Dwi, 1992Wei, 1994Wei] did not reveal an equiatomic compound. Both [1977Zyg] and [1990Che, 1991Che] presented unit cell dimensions for “UAlSi”, however, did not agree on the crystal system: whereas [1977Zyg] reported a hexagonal unit cell with $a = 1077.8 \pm 8$, $c = 843.3 \pm 1.3$, [1990Che, 1991Che] arrived at a tetragonal system with $a = 679.6 \pm 0.3$, $c = 1080.5 \pm 0.3$. No further details were given, but [1977Zyg] presented an indexation for the powder pattern of presumably isotypic UAlGe ($a = 1005 \pm 2$, $c = 854 \pm 2$). In a re-evaluation of these powder data [1994Wei] demonstrated that the X-ray intensity pattern of “UAlGe” could be interpreted as a combination of a tetragonal main phase $\text{U}_3\text{Al}_2\text{Ge}_3$ with small amounts of $\text{U}(\text{Al},\text{Ge})_3$. $\text{U}_3\text{Al}_2\text{Si}_3$ is isotypic with $\text{U}_3\text{Al}_2\text{Ge}_3$ and its composition is close to equiatomic: it is thus conceivable that “UAlSi” of [1977Zyg, 1990Che, 1991Che] in fact should be better represented by $\text{U}_3\text{Al}_2\text{Si}_3$. As part of the section $\text{USi}_{2-y}\text{-UAl}_2$, the compound “UAlSi” was claimed to form in a peritectic reaction at 1355°C [1990Che, 1991Che].

Similarly, it was shown by [1994Wei] that the X-ray spectrum reported for the as-cast compound “ U_2AlSi_2 ” by [1982Dwi] could be reindexed on the basis of the tetragonal main phase $\text{U}_3\text{Al}_2\text{Si}_3$ with small amounts of $\text{U}(\text{Al},\text{Si})_2$ and U_3Si_2 . A small homogeneous range was reported for $\text{U}_3\text{Al}_2\text{Si}_3$ i.e. $\text{U}_{3+y}(\text{Al}_{1-x}\text{Si}_x)_{5-y}$ ranging in as cast alloys from $0.64 < x < 0.68$ and $0 < y < 0.04$ slightly deviating from the stoichiometric composition $\text{U}_3\text{Al}_2\text{Si}_3$ [1994Wei]. It should furthermore be noted that $\text{U}_3\text{Al}_2\text{Si}_3$ is a high-temperature

compound, which was found in as-cast alloys, but which decomposes in a rather sluggish reaction on annealing at 900°C for 100 h [1994Wei]. From experimental evidence it was thus concluded that the high temperature phase $\text{U}_3\text{Al}_2\text{Si}_3$ reported by [1994Wei] corresponds to as-cast “ U_2AlSi_2 ” of [1982Dwi], for which also the annealing experiments of [1982Dwi] attested a phase transformation at about 900°C. The crystal structure of $\text{U}_3\text{Al}_2\text{Si}_3$ was found to be a unique structure type deriving from anti- Cr_5B_3 type. From X-ray single crystal data a space group $I4/mcm$ was assigned [1994Wei], but detailed neutron powder and single crystal studies confirmed Al/Si atom order in the lower symmetric space group $I4$ [1997Rog, 2002Guk].

The compound U_3AlSi_3 was observed at 900°C at stoichiometric composition with full atom order [1992Wei].

The solubility of Al in U_3Si was determined by [1991Pet] to range between 1.94 and 3.2 at.% Al replacing silicon atoms in the lattice. Although [1961Pet, 1982Dwi, 1991Pet] claimed a non-negligible but minor solid solubility of Al in U_3Si_2 , EMPA and XPD revealed solubility of Al of up to 3 at.% Al at 900°C with Al atoms preferentially replacing the U atoms in the 2a-sites *i.e.* at the center of the CsCl type sublattice structure in U_3Si_2 [1992Wei]. Whereas agreement exists on negligible solid solubility at 900°C of Al in USi [1982Dwi, 1992Wei] as well as a small solid solubility of Al in the AlB_2 type based defect structures USi_{2-x} (5 at.% Al [1982Dwi]; < 2 at.% Al [1992Wei]), some controversies concern the solubility of Al in ThSi_2 type and GdSi_2 type USi_{2-x} . According to the reinvestigation of the Si–U binary by [1992Rem], the disilicide richest in Si is USi_{2-x} ($\text{USi}_{1.88}$) with the tetragonal defect- ThSi_2 type, followed at lower Si concentrations by the defect GdSi_2 type (orthorhombic distortion of ThSi_2 type) and at further reduction of Si content by two orthorhombic superstructures of defect AlB_2 type and finally by the simple hexagonal, defect AlB_2 type. In the investigation of [1982Dwi] the USi_{2-x} phase richest in Si (without specification of its structure type) was reported at 900°C to dissolve at least 16 at.% Al, whereas EMPA data of [1992Wei] showed a maximum solubility in $\text{USi}_{1.88}$ (ThSi_2 type) of only about 2 at.% Al. GdSi_2 type USi_{2-x} (not mentioned by [1982Dwi]!), however, was found from EMPA to dissolve at 900°C about 11 at.% Al [1992Wei]. The authors of [1990Che, 1991Che] reported a solubility of about 26 at.% Al in the ThSi_2 type structure, which, however, was shown to transform (second order transformation) into the GdSi_2 type. The understoichiometry of the USi_{2-x} solid solution was said to change on Al substitution from $\text{USi}_{1.97}$ to $\text{U}(\text{Si},\text{Al})_{1.84}$ for alloys with 8 at.% Al and the transformation temperature for the ThSi_2 type to GdSi_2 type transformation as a function of the Si/Al-substitution was given as follows: 215°C at 8 at.% Al, 350°C at 16.7 at.% Al, 290°C at 23 at.% Al, 190°C at 28.7 at.% Al [1990Che, 1991Che]. With respect to the location of the phase $\text{U}_3\text{Al}_2\text{Si}_3$ at 900°C [1994Wei], confirmed by a single crystal [2002Guk], the large solubility limit derived by [1990Che, 1991Che] seems to be doubtful.

Whilst [1982Dwi] reported a complete series of solid solutions at 900°C for the compounds UAl_3 and USi_3 , the investigations of [1992Wei] revealed difficulties to achieve equilibrium or alternatively were interpreted as the appearance of a miscibility gap at 900°C for the compositions $\text{U}(\text{Si}_{1-x}\text{Al}_x)_3$, $0.4 < x < 0.71$. Indications for the formation of a miscibility gap at 600°C were also reported by [1986Naz]. In all cases there is a clear indication for Al/Si-substitution. However, alloys “ UAl_2Si_2 ” made by [1977Zyg] ($a = 414.5$ pm) and [1985Ott] (three unit cell parameters were given for different samples of the same nominal composition: $a = 414.5, 416.3, 417.6$ pm) were claimed to be isotypic with the cubic Cu_3Au type structure. The phase composition was explained by filling the central position of the structure with Al/Si-atoms [1985Ott].

Some discrepancies concern the solubility limit of Si in UAl_2 : [1991Pet] deduced about 1 at.% in the range 1100° to 780°C in agreement with data reported by [1961Pet]. X-ray lattice parameter measurements by [1982Dwi], however, indicated a maximum solubility of 10 at.% Si at 700°C and of 16.5 at.% at 900°C. Also [1990Che, 1991Che] indicated 16 at.% Si solubility (dashed solvus line without temperature dependency between RT and 1000°C), whereas [1992Wei] arrived at about 10 at.% Si at 900°C. Studying the reaction in miniature fuel element plates (U_3Si , $\text{U}_3\text{Si}_2 + \text{Al}$; for U-densities up to 7 Mg U m^{-3} in the dispersion) under equilibrium conditions at 600°C [1986Naz] observed the formation of UAl_2 , UAl_3 , UAl_4 , U_2AlSi_2 and reported solubility limits of ~6 at.% Si in UAl_2 , of ~9 at.% Si in UAl_4 as well as indications for a miscibility gap within the solid solution of USi_3 – UAl_3 .

Crystallographic data concerning solid phases are compiled in Table 2.

Quasibinary Systems

The authors of [1961Pet] determined the phase relations within the quasibinary section $\text{UAl}_2\text{-U}_3\text{Si}_2$ using DTA, metallography, chemical and X-ray analyses. The diagram contains a eutectic transformation (max.) at 1360°C and 26 at.% Si (Fig. 1). The section $\text{USi}_{2-x}\text{-UAl}_2$ was reported by [1990Che, 1991Che] to be quasibinary, claiming a peritectic formation at 1355°C of a compound UAlSi (which has not been confirmed by [1982Dwi, 1992Wei]) and followed by a eutectic reaction at 1330°C and 40 at.% Al: $\text{L} \rightleftharpoons \text{UAlSi} + \text{UAl}_2$. Besides this controversy concerning UAlSi , the section is not perfectly quasibinary as it does not cut through congruently melting USi_{2-x} . Furthermore the solubility limit of Al in USi_{2-x} (at 26 at.% Al) is not in agreement with the limit given by [1982Dwi] at 16 at.% Al or by [1992Wei] at 11 at.% Al.

Invariant Equilibria

The reaction scheme of the $\text{U-UAl}_2\text{-U}_3\text{Si}_2$ partial system, as shown in Fig. 2 was taken from [1989Ale1, 1991Pet] adding the eutectoid decomposition of (βU) from [1962Pet] assuming a degenerate reaction, as the solubility of Al as well as of Si in βU and αU is very small at that temperature [Mas2]. This makes the temperature of 580°C given by [1962Pet] very improbable. A ternary eutectic reaction occurs at 976°C ; containing 10.9 at.% (1.5 mass%) Si and 3.69 at.% (0.49 mass%) Al. The intermetallic phases UAl_2 and U_3Si_2 are virtually stoichiometric at that temperature. U_3Si forms peritectoidally at 973°C from $(\gamma\text{U}) + \text{UAl}_2 + \text{U}_3\text{Si}_2$. At 765°C a transition reaction $(\gamma\text{U}) + \text{U}_3\text{Si} \rightleftharpoons (\beta\text{U}) + \text{UAl}_2$ occurs [1989Ale1, 1991Pet], superseding earlier data of [1963Svi] listing this reaction at 790°C . In the Al rich region [1976Mon] reported on an invariant reaction, $\text{L} + \text{UAl}_4 \rightleftharpoons \text{U}(\text{Al},\text{Si})_3 + (\text{Al})$, at 3 at.% Si, 5-10 at.% U, $\sim 600^\circ\text{C}$; and above 3 at.% Si, aluminium was said to be in equilibrium with $\text{U}(\text{Al},\text{Si})_3$ [1958Rou]. A ternary eutectic, $\text{L} \rightleftharpoons (\text{Al}) + (\text{Si}) + \text{U}(\text{Al},\text{Si})_3$, was suggested to be close to the Al-Si binary [1976Mon].

Table 3 contains all information pertinent to the ternary invariant reactions.

Liquidus Surface

Only a partial liquidus surface is established for the region $\text{U-UAl}_2\text{-U}_3\text{Si}_2$ including three fields of primary crystallization: (γU) , UAl_2 , U_3Si_2 (Fig. 3).

Isothermal Sections

Due to the strong interest in U_3Si , U_3Si_2 -fuel interaction with Al, three groups of authors supplied detailed information on the phase relations in the $\text{U-UAl}_2\text{-USi}_2$ concentration range: [1989Ale1, 1991Pet] reported 9 isothermal sections (at 1120, 980, 977, 975, 970, 950, 930, 780, 740°C), [1962Pet] reported 3 sections (at 950, 850, 650°C) and [1963Svi] reported 4 sections (at 900, 800, 770, 740°C) in the U corner up to 4 at.% Al and Si to determine homogeneity ranges of (αU) and (βU) . Figures 4 and 5 summarize these results in terms of two isothermal sections at 780 and 950°C , taking the area near U_3Si from [1991Pet] and the U corner from [1963Svi, 1962Pet].

In a determination of the growth kinetics of $\text{U}(\text{Al},\text{Si})_2$, $\text{U}(\text{Al},\text{Si})_3$ and diffusion coefficient from diffusion couples $\text{U}_3\text{Si}+\text{Al}$ in the range from 510 to 670°C , [1991Rhe] observed $\text{U}(\text{Al},\text{Si})_2$ along the grain boundaries of U_3Si as the initial stage of reaction after 48 h anneal at 510°C , followed by $\text{U}(\text{Al},\text{Si})_3$ on the Al rich side of the diffusion couple. No evidence was found for the presence of the $\text{U}(\text{Al},\text{Si})_4$ phase in any of the diffusion couples: the composition of the phases were said to be $\text{U}(\text{Al}_{0.17}\text{Si}_{0.83})_2$ and $\text{U}(\text{Al}_{0.11}\text{Si}_{0.89})_3$ for the couple at 670°C [1991Rhe]. These findings are consistent with the phase triangulation as well as indicate large solid solubilities of Si in the phases UAl_2 and UAl_3 .

Two isothermal sections (at 900 and 400°C) over the whole concentration range were given by [1982Dwi], with one ternary compound $\text{U}_{-2}\text{AlSi}_{-2}$ (in high and low-temperature modification; $T_{\text{tr}} \approx 900^\circ\text{C}$). Figure 6 shows the phase equilibria in the isothermal section at 900°C based on the results of [1992Wei] with two ternary compounds: U_3AlSi_3 (W_3CoB_3 type) and $\text{U}_3\text{Al}_2\text{Si}_3$ (ordered anti Cr_5B_3 type), as well as the position of the low temperature phase $\text{U}_{-2}\text{AlSi}_{-2}$.

Temperature – Composition Sections

The isopleth $U_3Si - UAl_2$ is shown in Fig. 7.

Thermodynamics

Low-temperature specific heat data for $U_3Al_2Si_3$ ($2 < T < 70$ K) inferred a small gap of $\Delta = 54$ K in the magnon dispersion in close agreement with the gap of 29 K derived from electrical resistivity data: C_p/T (in $J \cdot K^{-2} \cdot mol^{-1}$) = $0.253 + 7.0 \cdot 10^{-4} T^2 + 17.9 \cdot T^{-0.5} \exp(-\Delta/T)$; $\Delta = 54$ K [2001Tro]. The slightly enhanced gamma-value points towards a medium-heavy fermion character.

Notes on Materials Properties and Applications

Additions of small amounts of Al to U_3Si greatly improved aqueous corrosion resistance [1975Mat]. Thermal stability of Al - “UAlSi” dispersion fuels (“UAlSi” = U - 3.5 mass% Si - 1.5 mass% Al which consists of a matrix of U_3Si containing 0.5 mass% Al in solution and particles of U_3Si_2 and UAl_2) with 55 mass% “UAlSi” and 75 mass% “UAlSi”, respectively, were examined in the temperature range from 250 to 400°C [1982Fer]. Whilst no metallurgical changes were observed after heating to 200°C, between 250 and 400°C the fuel particles reacted via grain boundary diffusion with the Al-matrix to form UAl_3 and UAl_4 [1982Fer]. Extruded rods of Al - “UAlSi” dispersion fuels were said to have an aqueous corrosion resistance similar to Al-U alloys [1980Fer]. Swelling due to irradiation with 0.5 and 2 MeV Ar-ions of an alloy U - 3.5 mass% Si - 1.5 mass% Al at 570-950 K was investigated by [1976Cai, 1975Fer, 1983Dom]. Postirradiation heating tests showed that U_3Si -fuel undergoes gross swelling at temperatures above 900°C [1975Mat]. The manufacture of miniature fuel element plates (U_3Si , $U_3Si_2 + Al$) was described for U-densities up to $7 \text{ Mg} \cdot \text{U} \cdot \text{m}^{-3}$ in the dispersion and the reaction behavior under equilibrium conditions at 600°C was determined [1986Naz]. After 33 days anneal at 600°C various uranium aluminides were detected (see section “Solid Phases”); minor swelling of the plates was obvious at 350°C and major swelling occurred at 550°C [1986Naz]. The exothermic reaction peak in DTA at about 630°C prior to clad melting was not interpreted; irradiation tests of U_3Si_2 -Al fuel show remarkable dimensional stability up to 97% burn-up [1986Naz]. Thermal conductivity of the fuel alloy U-1.5Al-3.5Si (mass%) was studied by [1975Feh]. Hot-hardness and microstructure of an U-350 ppm Si-800 ppm Al alloy was examined; the alloy content was dissolved in (β U) and subsequently precipitated in the (α U) phase; some dispersion hardening was observed [1965Far1]; dissolving Al, Si in liquid uranium and subsequent splat cooling failed to produce any precipitate particles, however on compaction at 600°C and extrusion at 500°C a precipitate with irregular shape (0.1-0.4 μm) was observed; aging of the splat cooled alloy for 100 h at 600°C produced considerable particle agglomeration [1965Far2]. The Vickers hardness of alloys containing 17% U and 2-3.5% Si was reported to be of the order of 350 - 300 $\text{MN} \cdot \text{m}^{-2}$ and rises to 450 - 500 $\text{MN} \cdot \text{m}^{-2}$ with 35% coldwork [1976Mon]. Diffusion of U in Al-Si alloys is much slower than in Al $D_0 = 0.07 \text{ S}$; $Q = 0.55 \text{ eV}$ [1976Mon].

The authors of [1991Rhe] determined the growth kinetics of $U(Al,Si)_2$, $U(Al,Si)_3$ and the diffusion coefficient from diffusion couples $U_3Si + Al$ in the range from 510 to 670°C: the growth of the $U(Al,Si)_3$ interface phase followed a parabolic rate law and was concluded to be controlled by diffusion of Al atoms not by interfacial reactions; furthermore, an activation energy of $Q = 220 \text{ kJ} \cdot \text{mol}^{-1}$ was derived for the temperature range 510 to 670°C, which was said to be approximately equal to the activation energy for the Al diffusion through the $U(Al,Si)_3$ phase (Q was about three times higher than for the diffusion through UAl_3).

Miscellaneous

Magnetic susceptibility and magnetization data for polycrystalline $U_3Al_2Si_3$ showed ferromagnetic order below $T_C = 36 \text{ K}$ and $\mu_s = 0.45 \mu_B/U$; for the paramagnetic region $\mu_{\text{eff}} = 1.99 \mu_B/U$ and $\Theta_p = 11 \text{ K}$ were reported [1994Wei]. Hysteresis loop and susceptibility measurements on a Czochralsky grown single crystal specimen $U_3Al_2Si_3$ revealed a small magnetocrystalline anisotropy between b - and c -axis [1998Mih, 1999Mih]. Magneto-transport data at 0 and 8 Tesla revealed a pronounced maximum below T_C probably

caused by a reduction of effective conduction carriers or by a spin density wave type of spin-disorder scattering of electrons [2001Tro]. Nuclear and magnetic structure of $\text{U}_3\text{Al}_2\text{Si}_3$ were investigated by means of neutron powder [1997Rog, 1999Rog] as well as by single crystal diffractometry additionally employing polarized neutrons in the range from 7 K to 250 K and in external magnetic field up to 6 Tesla parallel $[\bar{1}10]$, $[100]$, $[001]$ [2002Guk]. Refinements of the nuclear structure at 70 K (above the magnetic ordering temperature defined by neutrons at $T_m \approx 33$ K) confirmed the fully ordered distribution of Al and Si atoms in the 8c sites of space group $I4$ ($R_F^2 = 0.054$). Thus isotypism was established with the $\text{U}_3\text{Ga}_2\text{Ge}_3$ type as a low symmetry derivative of the ordered anti type of Cr_5B_3 (space group $I4/mcm$). Refinement of the magnetic four-circle data collected at 7 K was performed in space group $I2$ ($I112$) keeping all atom positions as derived from the nuclear data at 70 K. Uranium moments are all parallel to the a , b plane, but equivalent pairs U3, U4 are non-collinear at an angle of 90° . Experiments with polarized neutrons at 7 K and in an external magnetic field of 6 Tesla along $[\bar{1}10]$, $[100]$, $[001]$ proved the non-collinear spin arrangement: $\Phi(\text{U3}) = 45^\circ$ (in direction $[110]$) and $\Phi(\text{U4}) = 135^\circ$ (in direction $[\bar{1}10]$), resulting in a ferromagnetic net component ($\mu(\text{U1}, \text{U2}) = 0.18(1) \mu_B$; $\mu(\text{U3}, \text{U4}) = 1.39(1) \mu_B$; $R_F^2 = 0.056$). A rather strong local anisotropy field prevents full alignment of the U spins to the external magnetic field of 6 T. However, moments U1 and U2 are small and align along the external magnetic field. Polarized neutron scattering as a microprobe for local anisotropy in the paramagnetic region provided the anisotropic magnetization parameters at 6 Tesla for the paramagnetic state up to 250 K. Size and direction of the uranium moments obtained confirm the strong local anisotropy field on the U3,4 atoms ($\Phi(\text{U3}) \sim 45^\circ$ and $\Phi(\text{U4}) \sim 135^\circ$) persisting even at 250 K [2002Guk]. Calculation of the band structure by the tight binding linear muffin-tin orbital method (TB-LMTO for a simple ferromagnetic order) and X-ray photoemission spectra (XPS) indicate predominantly itinerant 5f-electrons [2005Sza]. Figure 8 presents the magnetic phase diagram for $\text{U}_3\text{Al}_2\text{Si}_3$; the solid line is the phase boundary between the paramagnetic and the (non-collinear) ferromagnetic region. The inset shows the spin orientation for the three uranium atom sites.

Preliminary magnetic susceptibility and magnetization measurements on “ U_2AlSi_2 ” yielded weak ferromagnetism below $T_C = 27$ K and $\mu = 3 \cdot 10^{-2} \mu_B/\text{U}$ under 3T; for the paramagnetic region $\mu_{\text{eff}} = 3.15 \mu_B/\text{U}$ and $\Theta_p = -157$ K were found [1992Wei].

“ UAl_2Si_2 ” with the Cu_3Au type structure ($a = 414.5$ pm) showed superconductivity below $T_{sc} = 1.35$ K; coefficients of specific heat, $C_p = \gamma T + \beta T^3$, were given as $\gamma = 27.9 \text{ mJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$ and $\beta = 0.435 \text{ mJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-4}$ [1985Ott].

The influence of silicon on the reprocessing of aluminium-uranium fuels was studied by [1968Pai] and instantaneous dissolution rates in nitric acid were related to the composition of the alloys *i.e.* to the Si content of the fuel. Analytical atomic spectrometric methods were optimized for detection of metal traces (including silicon) in Al-U samples [1989Arg].

[1993Kon] investigated the corrosion resistance of an alloy U-0.2Al-3.8Si (mass%) against water at 300°C under 90 MPa: the speed of corrosion was measured for various length of time from 10 to 3000 h. After 100 h the speed of corrosion for instance reached a value of saturation at $0.5 \text{ mg} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$.

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Table 1: Investigation of the Al-Si-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1961Pet]	12 samples prepared from 99.99% pure Al, Si and reactor-grade U (containing ca 150 ppm C) via argon arc melting. Samples were annealed in vacuum at 950°C (200 h), 850°C (340 h), 650°C (500 h) and quenched; thermal analyses, DTA; chemical analyses; metallography of as cast and annealed alloys; X-ray powder diffraction.	Quasibinary eutectic section UAl_2 - U_3Si_2 ; eutectic at 26 at.% Si and 1360°C.
[1962Pet]	About 150 samples prepared from 99.99% pure Al, Si and reactor-grade U (containing ca 150 ppm C) via argon arc melting. Samples were annealed in vacuum at 950°C (200 h), 850°C (340 h), 650°C (500 h) and quenched; thermal analyses, DTA; chemical analyses; metallography of as cast and annealed alloys; X-ray powder diffraction; micro-hardness, chemical and thermal etching.	Investigation of the region $U-U_3Si_2-UAl_2$: liquidus surface and solidus; isothermal sections at 650°C, 850°C, 950°C; Isopleths $U-U_3Si_2$, $UAl_2-U_3Si_2$, $U-UAl_2$; isopleths at 3 at.% Al up to 40 at.% Si; at 6 at.% Si up to 55 at.% Al; at 30 at.% Al up to 25 at.% Si; isopleth from 64U36Si to 60Al40U. Scheil diagram.
[1963Svi]	Purity of starting materials: 99.87% U, 99.99% Al, Si. Samples were annealed in evacuated quartz ampoules at 740°C (84 h), 770°C (72 h), 800°C (60 h), 900°C (48 h); chemical analyses; metallography (chemical etching) of as cast and annealed alloys; X-ray powder diffraction.	Investigation of the U rich corner up to U-4 at.% Si-4 at.% Al on three series of alloys with constant ratios Si:Al = 3:1, 1:1 and 1:3. Determination of liquidus and solidus lines; isothermal sections at 740°C, 770°C, 800°C, 900°C. Scheil diagram.
[1977Zyg]	Samples $UAlSi$ and UAl_2Si_2 were prepared from 99.99% pure Al, Si and 99.8% U via argon arc melting. Samples were annealed in Ta containers, sealed in evacuated quartz ampoules at 850-900°C for 170 h; X-ray powder diffraction.	Identification of hexagonal compound (crystal structure unknown). Indexation of the powder pattern of presumably isotypic $UAlGe$ was reported.
[1982Dwi]	About 260 samples prepared from 99.99% pure Al, Si and reactor-grade U (containing ca 100 ppm C) via argon arc melting. Samples were annealed in vacuum at temperatures between 700 and 1040°C and water quenched; thermal analyses, DTA; metallography of as cast and annealed alloys (chemical etching); X-ray powder diffraction;	Investigation of the ternary system (<80 at.% Al and <75 at.% Si). Determination of isothermal sections at 400 and 900°C. Lattice parameter data for solutions $U(Al,Si)_2$ and $U(Al,Si)_{2-x}$. One or two ternary compounds near U_2AlSi_2 (unknown crystal structure).

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1986Naz]	U ₃ Si, U ₃ Si ₂ prepared by arc melting in inert gas. Preparation of fuel plates (U ₃ Si, U ₃ Si ₂ + Al) for U-densities up to 7 Mg·U·m ⁻³ in the dispersion containing 75 mass% fuel < 44 to 150 μm particle size, rest < 44 μm particles. Homogenization at 600°C for 33 days in evacuated pyrex tubes, quench. Metallography, EMPA, X-ray powder diffraction at RT, DTA.	Investigation of chemical reaction with Al. Dimensional thermal stability and stability under irradiation.
[1990Che] [1991Che]	Purity of starting materials: 99.8% U, 99.999% Al, Si. annealed at 1000°C for 5 h under He. DTA; metallography of as cast and annealed alloys; X-ray powder diffraction at RT and high temperatures.	Determination of concentration section UAl ₂ -USi _{2-y} from RT to 1800°C. Lattice parameter data for solutions U(Si,Al) _{2-x} and U(Al,Si) _{2-x} . Peritectic formation of UAlSi at 1355°C.
[1991Pet]	Purity of starting materials: electrolytic 99.98%U, 99.999% Al, Si. Samples were prepared via argon arc melting subsequently were wrapped in Zr foil, delta annealed in evacuated quartz capsules at 800°C for 100 h. Then they were annealed for 5 h at successively higher temperatures (10 K intervals) from 880°C to 980°C. DTA (80 K·min ⁻¹); metallography of as cast and annealed alloys; X-ray powder diffraction.	Investigation of the region U-U ₃ Si ₂ -UAl ₂ : isothermal sections at 1120, 980, 977, 975, 970, 950, 930, 780, 740°C. Isopleths U ₃ Si-UAl ₂ ; isopleth at 75 at.% U up to 25 at.% Al; Scheil diagram.
[1991Rhe]	Preparation of alloy U-3.9 mass% Si in vacuum induction furnace followed by casting and heat treatment at 800°C, 3 days. Depleted U < 0.1% impurities, 99.999% Si. Diffusion couples prepared from 5x5x20 mm ³ U ₃ Si-block dipped into Al-melt at 750°C, sealed in evacuated quartz, anneal 510-670°C up to 300 h, air cooling. X-ray diffraction, metallography, EMPA.	Determination of growth kinetics of U(Al,Si) ₂ , U(Al,Si) ₃ and diffusion coefficient from diffusion couples U ₃ Si+Al. Phase relations.
[1992Wei] [1994Wei]	About 60 samples prepared from 99.99% pure Al, Si and nuclear grade U-platelets (E. Merck) via argon arc melting. Samples were wrapped in Mo foil, annealed in evacuated quartz capsules at 800°C for 150 h (900°C for 100 h, respectively) and water quenched; EMPA, metallography of as cast and annealed alloys (chemical etching); X-ray powder diffraction.	Investigation of the isothermal sections at 900, 800°C. Crystal structure and lattice parameter data.

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Al) < 660.5	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 404.88$	pure Al [Mas2, V-C2]
(Si) < 1414	<i>cF8</i> <i>Fd$\bar{3}m$</i> C _{diamond}	$a = 543.06$	[Mas2]
(γ U) 1135 to 774.8	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 353.35$	[Mas2] refined at 787°C
(β U) 774.8 to 667.7	<i>tP30</i> <i>P4₂/mnm</i> β U	$a = 1075.89$ $c = 565.31$	[Mas2]
(α U) < 667.7	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	[Mas2]
U(Al _{1-x} Si _x) ₂ UAl ₂ < 1620	<i>cF24</i> <i>Fd$\bar{3}m$</i> MgCu ₂	$a = 776.6$ $a = 772.5$ $a = 771.3$ $a = 769.8$	$0 \leq x \leq 0.17$ at 900°C; $0 \leq x \leq 0.10$ at 700°C; linear variation of $a(x)$ [1982Dwi]; at $x = 0$ [1982Dwi] at $x = 0.10$ [1982Dwi] in alloy 40U40Al20Si, 900°C [1992Wei] at $x = 0.17$ [1982Dwi]
U(Al _{1-x} Si _x) ₃ UAl ₃ < 1350 USi ₃ < 1510	<i>cP4</i> <i>Pm$\bar{3}m$</i> Cu ₃ Au	$a = 426.51$ $a = 403.53$	$0 \leq x \leq 1$ at 900°C; nonlinear variation of $a(x)$ [1982Dwi]; miscibility gap at $T < 900^\circ\text{C}$? at $x = 0$ [V-C2] at $x = 1$ [V-C2]
UAl ₄ < 731	<i>oI20</i> <i>Imma</i> UAl ₄	$a = 440.14$ $b = 625.52$ $c = 1372.79$	[1990Kas] [2004Tou]
USi ₂ < 450?	<i>tI12</i> <i>I4₁/amd</i> ThSi ₂	$a = 392.2$ $c = 1415.4$	(metastable) [1992Rem]
U(Si _{1-x} Al _x) _{2-y} α_1 , USi _{2-y} (USi _{1.88}) < 1710	<i>tI12</i> <i>I4₁/amd</i> defect ThSi ₂	$a = 394.23$ $c = 1371.2$	$0 \leq x \leq 0.05$; $y = 0.12$ at 900°C [1992Wei] at $x = 0$; $y = 0.12$; 65 at.% Si

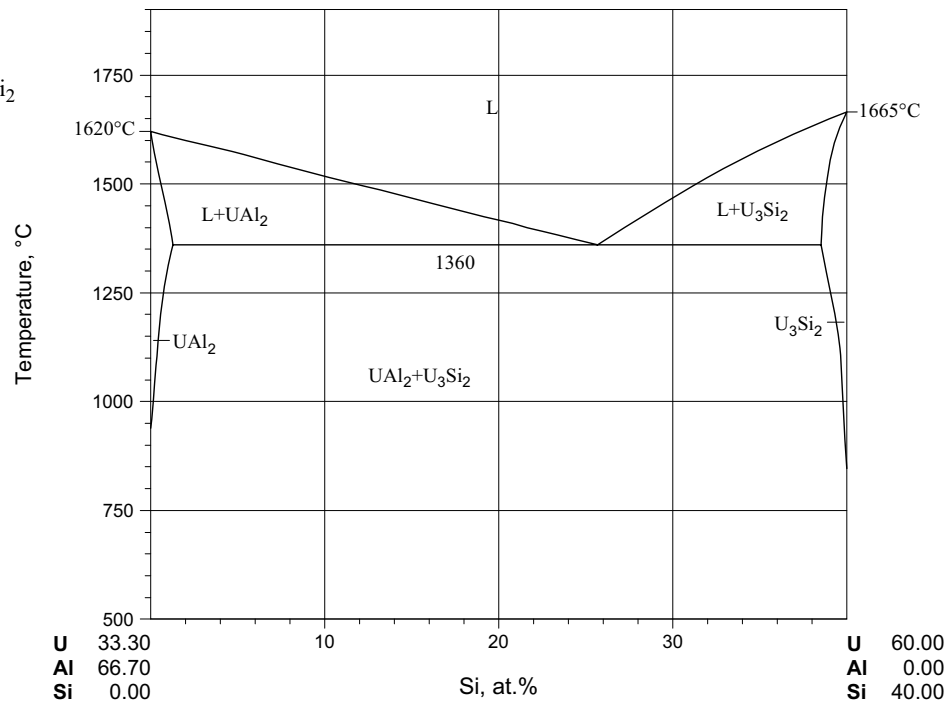
Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
α_2 , $\text{U}(\text{Si}_{1-x}\text{Al}_x)_{2-y}$ USi_{2-y}	<i>oI12</i> <i>Imma</i> defect GdSi_2	$a = 395.45$ $b = 393.02$ $c = 1365.2$	$0 \leq x \leq 0.17$; $y = 0.22$ at 900°C [1992Wei] at $x = 0$; $y = 0.22$; 64 at.% Si [1992Rem]
		$a = 402.88$ $b = 392.02$ $c = 1359.2$	at $x = 0.17$; $y = 0.22$; 64 at.% Si [1992Wei]
α_3 , $\text{USi}_{2-y}(\text{U}_3\text{Si}_5\text{-o2})$	<i>oP6</i> <i>Pmmm</i> (?) distorted AlB_2	$a = 389.3$ $b = 671.7$ $c = 404.2$	at ~ 63 at.% Si [1992Rem]
α_4 , $\text{USi}_{2-y}(\text{U}_3\text{Si}_5\text{-o1})$	<i>oP6</i> <i>Pmmm</i> distorted AlB_2	$a = 386.4$ $b = 666.0$ $c = 407.3$	at 63 at.% Si [1992Rem]
α_5 , $\text{USi}_{2-y}(\text{U}_3\text{Si}_5\text{-hex}$ or $\text{USi}_{1.67})$ < 1770	<i>hP3</i> <i>P6/mmm</i> defect AlB_2	$a = 384.75$ $c = 407.40$	[1992Rem]
USi < 1580	<i>tI138</i> <i>I4/mmm</i> USi	$a = 1058.7$ $c = 2431.0$	[1992Rem, 1993LeB, 1996LeB]
USi	<i>oP8</i> <i>Pnma</i> FeB	$a = 758.5$ $b = 390.3$ $c = 566.3$	probably impurity (O) stabilized [1992Rem, 1993LeB]
U_5Si_4 < 1100	<i>hP18</i> <i>P6/mmm</i> U_5Si_4	$a = 1046.7$ $c = 391.2$	[1998Noe] single crystal study [2006Noe]
$(\text{U}_{1-x}\text{Al}_x)_3\text{Si}_2$ U_3Si_2 < 1665	<i>tP10</i> <i>P4/mbm</i> U_3Si_2	$a = 732.99$ $c = 390.04$	$0 \leq x \leq 0.05$ at 900°C ; [1992Wei] at $x = 0$
		$a = 729.60$ $c = 393.92$	at $x = 0.05$
$\gamma\text{U}_3\text{Si}$ 930 - 759	<i>cP4</i> <i>Pm3m</i> Cu_3Au	$a = 434.6$	[V-C2, 1965Str]
$\beta\text{U}_3\text{Si}$ 762 - -153	<i>tI16</i> <i>I4/mcm</i> $\beta\text{U}_3\text{Si}$	$a = 603.28$ $c = 869.07$	[V-C2, 1965Str]
$\alpha\text{U}_3\text{Si}$ < -153	<i>oF32</i> <i>Fmmm</i> $\alpha\text{U}_3\text{Si}$	$a = 865.4$ $b = 854.9$ $c = 852.3$	[V-C2, 1965Str] at -193°C

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_1 , U_3AlSi_3	<i>oC28</i> <i>Cmcm</i> W_3CoB_3	$a = 399.63$ $b = 1049.7$ $c = 1348.1$	[1992Wei]
* τ_2 , $\text{U}_3\text{Al}_2\text{Si}_3$ $\geq 900^\circ\text{C}$	<i>tI32</i> <i>I4</i> $\text{U}_3\text{Al}_2\text{Ge}_3$	$a = 761.83$ $c = 1077.51$ $a = 764.95$ $c = 1082.21$	[1992Wei, 1994Wei] single crystal $\text{U}_3\text{Al}_{1.76}\text{Si}_{3.24}$ $R_F^2 = 0.057$ from alloy $\text{U}_{45.5}\text{Al}_{22.9}\text{Si}_{31.6}$ [1994Wei]
* τ_3 , $\text{U}_{\sim 2}\text{Al}_{\sim 1}\text{Si}_{\sim 2}$ $\leq 900^\circ\text{C}$	unknown	-	[1982Dwi] at $\text{U}_{\sim 37}\text{Al}_{\sim 24}\text{Si}_{\sim 39}$ in at.% [1992Wei]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Al	Si	U
$\text{l} \rightleftharpoons \text{U}_3\text{Si}_2 + \text{UAl}_2$	1360	e_1	l U_3Si_2 UAl_2	24 ~1 ~66	26 ~39 ~1	50 ~60 ~33
$\text{L} \rightleftharpoons (\gamma\text{U}) + \text{U}_3\text{Si}_2 + \text{UAl}_2$	976	E_1	L (γU) U_3Si_2 UAl_2	~3.6 3.5 ~0.5 ~66.7	10-11 1.8 ~39.5 ~0	~85 94.7 ~60 ~33.3
$(\gamma\text{U}) + \text{U}_3\text{Si}_2 + \text{UAl}_2 \rightleftharpoons \text{U}_3\text{Si}$	973	P_1	U_3Si (γU) U_3Si_2 UAl_2	3 3.5 ~0.5 ~66.7	22 1.8 ~39.5 ~0	75 94.7 ~60 ~33.3
$(\gamma\text{U}) + \text{U}_3\text{Si} \rightleftharpoons (\beta\text{U}) + \text{UAl}_2$	765	U_1	U_3Si (γU) (βU) UAl_2	~2.5 ~1.2 ~0.4 ~66.7	~22.5 ~0.5 ~1.2 ~0	75 ~98.3 ~98.4 ~33.3
$(\beta\text{U}) \rightleftharpoons (\alpha\text{U}) + \text{U}_3\text{Si} + \text{UAl}_2$	665	D_1	-	-	-	-
$\text{L} + \text{UAl}_4 \rightleftharpoons \text{U}(\text{Al},\text{Si})_3 + (\text{Al})$	~600	U_2	L	87-92	3	~5-10
$\text{L} \rightleftharpoons (\text{Al}) + (\text{Si}) + \text{U}(\text{Al},\text{Si})_3$	?	E_2	-	-	-	-

Fig. 1: Al-Si-U.
The quasibinary
section UAl_2 - U_3Si_2



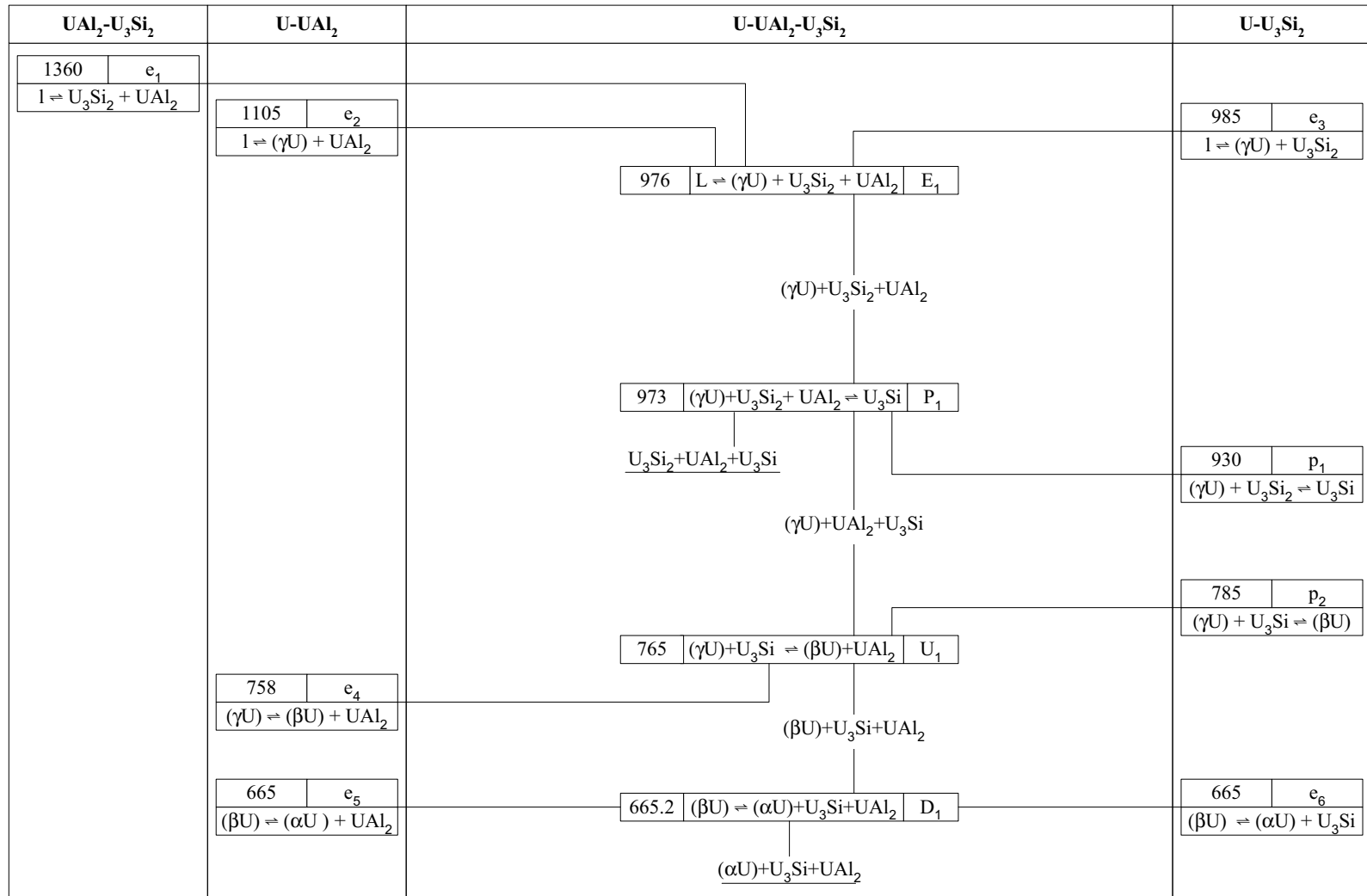


Fig. 2: Al-Si-U. Reaction scheme

Fig. 3: Al-Si-U.
Liquidus surface for
the region
U-UAl₂-U₃Si₂

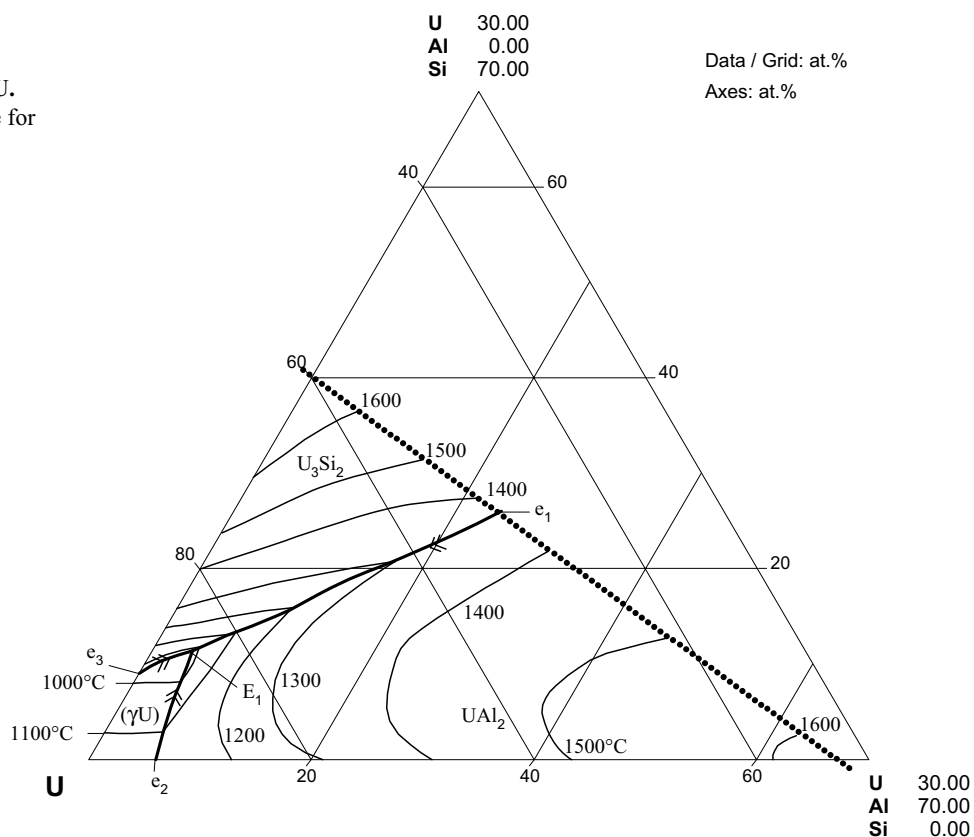


Fig. 4: Al-Si-U.
Isothermal section for
the region
U-UAl₂-U₃Si₂ at
780°C

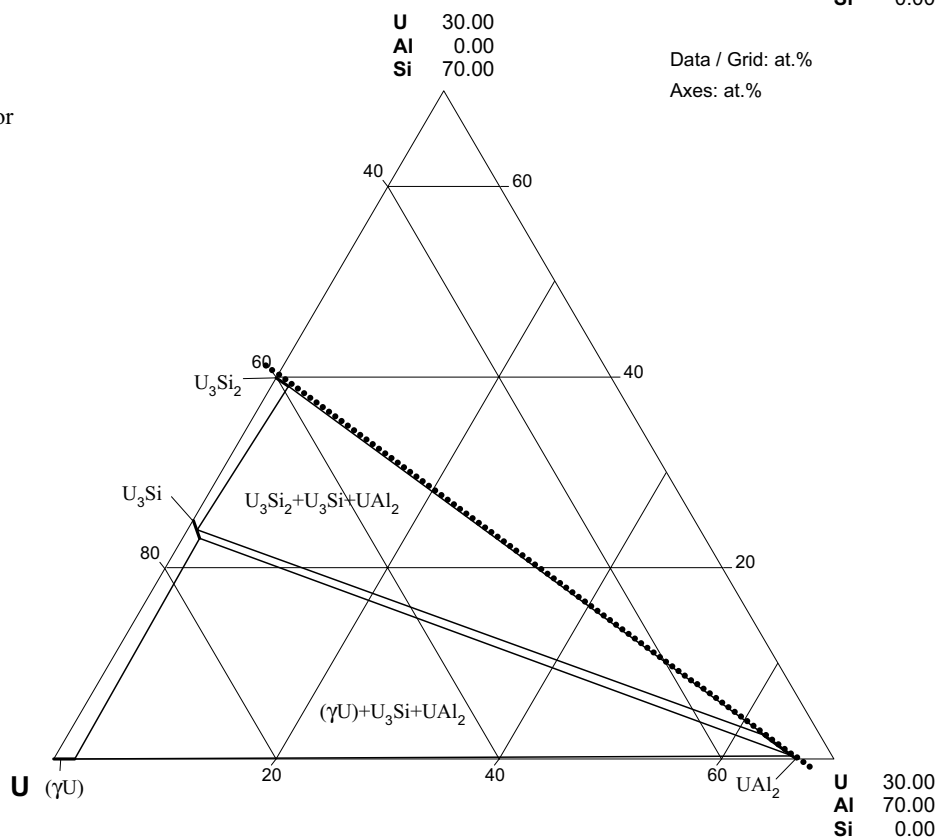


Fig. 5: Al-Si-U.
Isothermal section for
the region
U-UAl₂-U₃Si₂ at
950°C

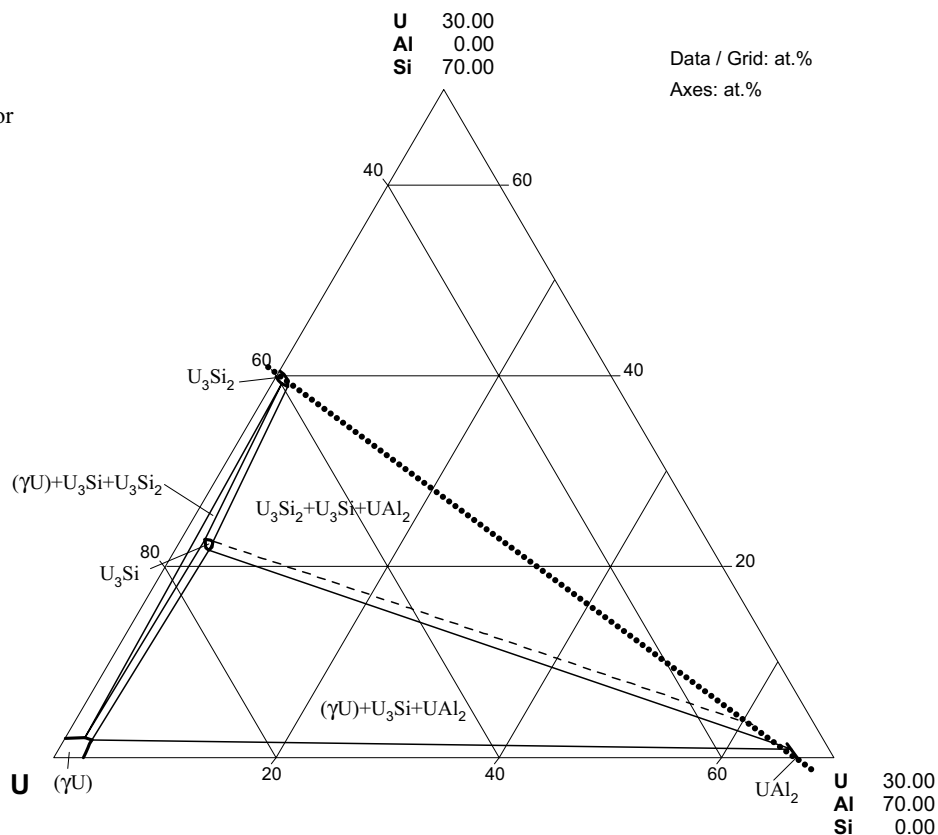


Fig. 6: Al-Si-U.
Isothermal section at
900°C; the position of
the low-temperature
compound τ_3 near
U₂AlSi₂ is labelled
by a filled square

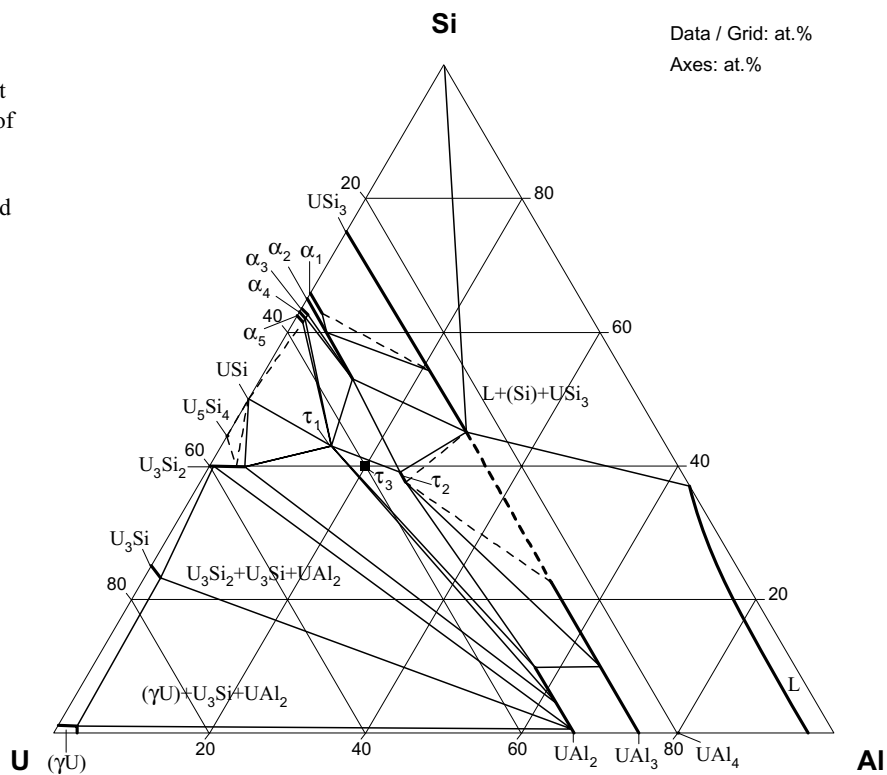


Fig. 7: Al-Si-U.
Isopleth $U_3Si - UAl_2$

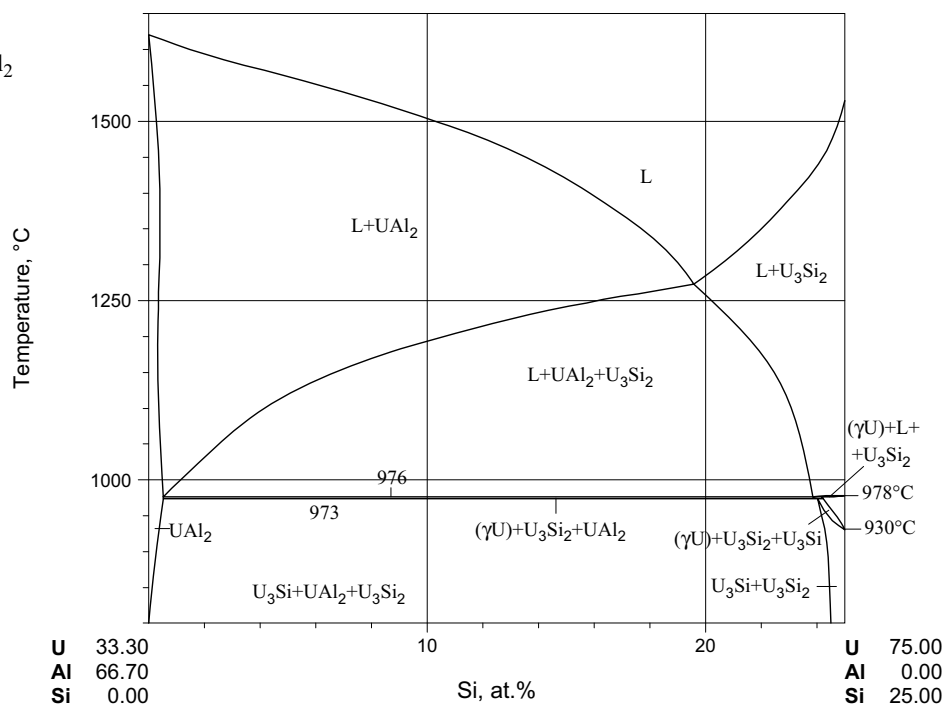
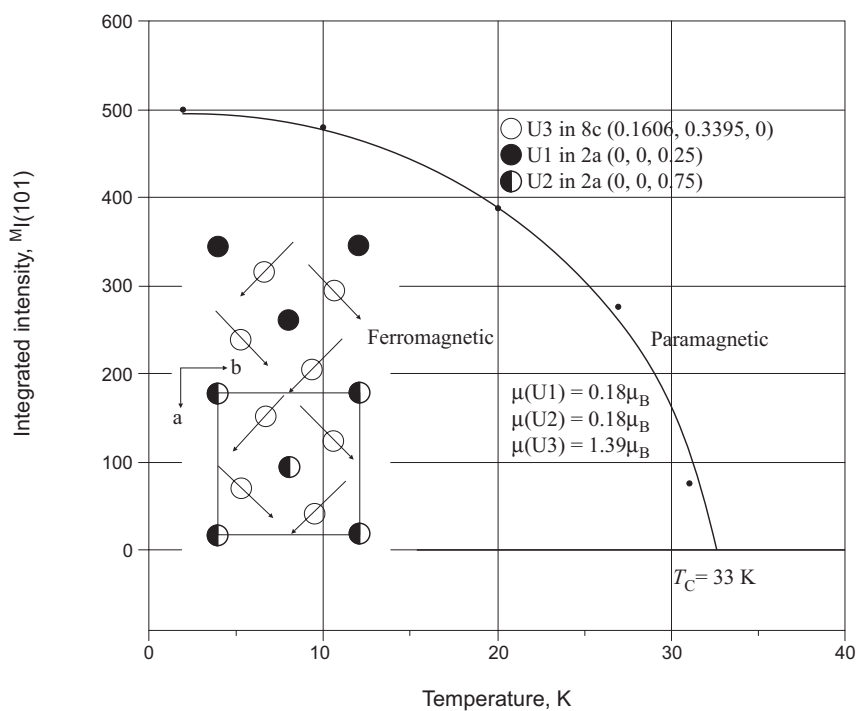


Fig. 8: Al-Si-U.
Magnetic phase diagram for $U_3Al_2Si_3$; the solid line is the phase boundary between the paramagnetic and the (non-collinear) ferromagnetic region. The inset shows the spin distribution and spin orientation for the three uranium atom sites



Carbon – Iron – Plutonium

Viktor Kuznetsov

Introduction

Phase equilibria in the system were studied in the only work [1963Nic] to provide background to studies of compatibility between carbides and steel canning materials as well as metal bonded cermets. Pu used was of 99.7 mass% purity, and C and Fe were spectrally pure. The system was studied only in the region $\text{PuC-Pu}_2\text{C}_3\text{-Fe}_3\text{C-FePu}_2$. Two ternary phases were found: PuFeC_2 (τ_1) and a phase with an approximate stoichiometry $\text{Pu}_3\text{Fe}_4\text{C}_5$ (τ_2). Authors also acknowledged earlier unpublished investigation, results of which were incorporated basing on private communication from the authors of this work.

The crystal structures of both ternary phases are known. For the τ_1 phase [1986Ger] showed it to be isotypic with UCoC_2 whose structure was established in this work using single-crystal X-ray study. For the τ_2 phase [1995Wac] found perfect agreement between X-ray pictures, calculated by the latter author basing on $\text{Th}_{11}\text{Ru}_{12}\text{C}_{18}$ structure type and presented in [1963Nic]. Based on that, he ascribed to the τ_2 phase this structural type and the composition $\text{Pu}_{11}\text{Fe}_{12}\text{C}_{18}$.

Thermodynamic data were obtained for τ_1 phase by [1983Suz] using Knudsen mass spectrometry. They determined the Gibbs energy of formation of this phase at 1147 to 1377°C. In addition, the temperature of the peritectic formation of PuFeC_2 was refined.

The results of [1963Nic] were slightly modified in the review article [1984Hol1] and in the reference book [1984Hol2].

An overview of experimental investigation of the system is given in Table 1.

Binary Systems

All the three binary systems are taken from [Mas2].

Solid Phases

The structure of the PuFeC_2 (τ_1) phase was determined by [1986Ger] to be of UCoC_2 type. It is isotypic with UFeC_2 and a number of other ternary carbides of actinoids and transition metals.

The temperature of peritectic formation of PuFeC_2 is accepted to be 1377°C after [1983Suz], as thermodynamic measurements are usually considered to be closer to equilibrium state.

The composition $\text{Pu}_{11}\text{Fe}_{12}\text{C}_{18}$, suggested by [1995Wac] based on the stoichiometry of the prototype, is accepted in the present evaluation, because real composition of this phase seems not to be determined by [1963Nic] with high precision. However it might be mentioned that a sample C-33Fe-25Pu (at.%), as claimed in the “Discussion” part of [1963Nic], was “almost single-phase” after annealing at 1160°C for 90 h.

The lattice spacing of (Fe) in three-phase sample was found to be essentially identical to that of pure iron, indicating absence of Pu solubility [1963Nic]. The authors also claimed that no marked line shifts were observed on X-ray patterns indicating absence of significant solubilities in solid phases.

Crystallographic data of all phases stable in the studied region of the C-Fe-Pu system are given in Table 2.

Invariant Equilibria

The temperatures of invariant reactions were determined by [1963Nic], based on thermal analysis of about 20 samples (including those studied in previous unpublished work). Data exist only for the region with the Fe content >50 at.%. As noted by the authors, the compositions of liquid in invariant reactions are “rather uncertain”. This seems to be especially true for the reactions of peritectic formation of both ternary carbides, where compositions of liquid, given only in figures, seem to be estimated by extrapolation of liquidus isotherms.

The data for invariant equilibria occurring in the studied region are given in Table 3. The compositions of liquid are taken by the present author from figures.

The temperature of the U_2 reaction is accepted from the “Discussion” part in [1963Nic] (written contribution of one of the authors).

In addition to equilibria listed in Table 3, [1963Nic] mentioned quasibinary eutectic $1 \rightleftharpoons PuFeC_2 + Fe_3C$ which occurs at 1096°C. As Fe_3C is not stable in the C-Fe system, this reaction can not occur in the stable system C-Fe-Pu, though it may belong to a metastable system Fe_3C -Fe-Pu.

Liquidus, Solidus and Solvus Surfaces

Figure 1 presents a tentative partial liquidus contours after [1963Nic]. The equilibria with the participation of the Fe_3C phase are rejected because this phase is not stable in the C-Fe binary system and no Pu solubility, which in principle could stabilize it, was observed. Also rejected are very uncertain connections of the studied part of the system with the C-Pu edge.

Liquidus lines in Fig. 1 were somewhat corrected to bring them into agreement with the accepted binaries.

Isothermal Sections

Figure 2 presents isothermal section for room temperature, accepted from [1963Nic] after removing a metastable phase Fe_3C and tentative addition of a tie line $PuFeC_2$ - PuT_2 . These changes made it essentially identical with a version, suggested in [1984Hol1, 1984Hol2], though the latter author arbitrarily ascribed it to 1000°C. For simplicity a small homogeneity range of the $PuC_{0.92}$ phase is not shown.

A number of “isothermal sections” at temperatures of invariant reactions, suggested by [1963Nic], are not presented here, as those seem to be nothing more than separate liquidus contours from a figure, corresponding to our Fig. 1.

Thermodynamics

$PuFeC_2$ phase was studied [1983Suz] by Knudsen mass spectrometry of vaporization which was accepted to occur by reaction $PuFeC_2(s) \rightleftharpoons 1/2Pu_2C_3(s) + C(gr) + Fe(g)$. The Gibbs energy of formation of $PuFeC_2$, obtained by these authors, is presented in Table 4.

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Table 1: Investigations of the C-Fe-Pu Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1963Nic]	Metallography, thermal analysis and XRD	“room temperature” to app. 1350°C; composition region PuC-Pu ₂ C ₃ -Fe ₃ C-FePu ₂
[1983Suz]	Knudsen mass spectrometry	1147 to 1580°C, PuFeC ₂ (τ_1) phase; samples contained excess C, solid to 1397°C
[1986Ger]	Single crystal X-ray crystal structure study	τ_1 phase (PuFeC ₂)
[1995Wac]	Interpretation of X-ray diffraction data of [1963Nic]	τ_2 phase (Pu ₁₁ Fe ₁₂ C ₁₈)

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (graphite) < 3827	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.90	at 25°C [Mas2] sublimation point
(δ Fe) 1538 - 1394	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 293.15	[Mas2]
(γ Fe) < 1394 - 912	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	<i>a</i> = 364.67	at 915°C [V-C2, Mas2]
(α Fe) < 912	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 286.65	at 25°C [Mas2]
(ϵ Pu) 640 - 483	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 363.43	[Mas2]
(δ' Pu) 483 - 463	<i>tI2</i> <i>I4/mmm</i> In	<i>a</i> = 332.61 <i>c</i> = 446.30	[Mas2]
(δ Pu) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	<i>a</i> = 463.71	[Mas2]
(γ Pu) 320 - 215	<i>oF8</i> <i>Fddd</i> γ Pu	<i>a</i> = 315.87 <i>b</i> = 576.82 <i>c</i> = 1016.2	[Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(β Pu) 215 - 125	<i>mC34</i> <i>C2/m</i> β Pu	$a = 1183$ $b = 1045$ $c = 923$ $\beta = 138.7^\circ$	[V-C2]
		$a = 928.4$ $b = 1046.3$ $c = 785.9$ $\beta = 92.13^\circ$	[Mas2]
(α Pu) < 125	<i>mP16</i> <i>P2₁/m</i> α Pu	$a = 618.3$ $b = 482.2$ $c = 1096.3$ $\beta = 101.97^\circ$	[Mas2]
PuC _{0.92} < 1654	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	$a = 496.19$	[Mas2]
Pu ₂ C ₃ < 2050	<i>cI40</i> <i>I$\bar{4}3d$</i> Pu ₂ C ₃	$a = 813.50$	[Mas2]
PuC ₂ (h) 2350 to 1660	<i>cF36</i> <i>Fm$\bar{3}m$</i> CaF ₂	$a = 569.0$	[Mas2]
PuC ₂ (r) < 1660	<i>tI6</i> <i>I4/mmm</i> CaF ₂	$a = 363$ $c = 609.4$	[Mas2]
PuFe ₂ (h) 1240 - 1020	<i>cF24</i> <i>Fd$\bar{3}m$</i> MgCu ₂	$a = 715.0$	[Mas2]
PuFe ₂ (r) < 1050	-	-	[Mas2]
* τ_1 , PuFeC ₂ < 1377	<i>tP8</i> <i>P4/mmm</i> UCoC ₂	$a = 350.1$ $c = 746.7$	[1983Suz] (temperature of formation) [1986Ger] (crystal structure established based on published data)
* τ_2 , Pu ₁₁ Fe ₁₂ C ₁₈ < 1197	<i>cI82</i> <i>I$\bar{4}3m$</i> Th ₁₁ Ru ₁₂ C ₁₈	$a = 1010.5$	[1963Nic] (temperature of formation, X-ray pattern) [1995Wac] (interpretation of X-ray data)

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				C	Fe	Pu
$L + \text{Pu}_2\text{C}_3 + (\text{C}) \rightleftharpoons \tau_1$	1377	P_1	L	~30	~50	~20
$L + \text{Pu}_2\text{C}_3 + \tau_1 \rightleftharpoons \tau_2$	1197	P_2	L	~35	~43	~22
$L \rightleftharpoons \tau_1 + (\gamma\text{Fe})$	1156	e_1	L	19	69	12
$L + \tau_1 \rightleftharpoons \tau_2 + (\gamma\text{Fe})$	1143	U_1	L	17	68	15
$L \rightleftharpoons \text{Pu}_2\text{C}_3 + \text{PuFe}_2$	1100	e_2	L	19	45	36
$L + \text{Pu}_2\text{C}_3 \rightleftharpoons \text{PuFe}_2 + \text{PuC}_{0.92}$	1090	U_2^a	-	-	-	-
$L + \text{Pu}_2\text{C}_3 \rightleftharpoons \tau_2 + \text{PuFe}_2$	1051	U_3	L	18	55.5	26.5
$L \rightleftharpoons \text{PuFe}_2 + \tau_2 + (\gamma\text{Fe})$	1037	E_1	L	15	63	22

^aNote: no data for composition of liquid provided

Table 4: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Property, per mole of atoms [J·mol ⁻¹]	Comments
PuFeC_2	1147 to 1377	$\Delta_f G = -(6000 \pm 2000) - (5 \pm 0.75)T$	[1983Suz], Knudsen effusion

Carbon – Iron – Uranium

Viktor Kuznetsov

Introduction

The system was studied to provide a background for the description of the interaction between carbide fuels and steel canning materials.

Most attention has been paid to the vertical sections. The quasibinary section UC-Fe was studied by [1961Bar, 1963Bri1, 1963Bri2, 1963Nic, 1971Guh] and the results of [1963Bri2, 1963Nic, 1971Guh] are in good agreement. The UC- UFe_2 quasibinary section was studied by [1961Bar] and [1963Nic]. It was found that the section was of a simple eutectic type, but the eutectic temperature presented by [1961Bar] and the eutectic temperature presented by [1963Nic] differed by more than 120°C. The discrepancies in the results may have arisen from differences in the techniques used. [1961Bar] used metallographic observation of melting of powder mixtures of Fe and UC which had been annealed at various temperatures, whereas [1963Nic] used thermal analysis studies of alloys of higher purity which had been prepared by arc melting under an argon atmosphere on a water cooled copper hearth using a tungsten electrode.

The phase equilibria along the Fe- UC_2 tie line were studied by [1962Bal, 1963Bri2, 1963Nic]. [1962Bal] found that the UFeC_2 ternary carbide was formed peritectically from UC_2 and liquid [1963Bri2]. The existence of a quasibinary eutectic between Fe and UFeC_2 was established by [1963Bri2, 1963Nic]. The UC_2 - Fe section cannot be considered as truly quasibinary because of the eutectoid decomposition of UC_2 at 1516°C in the C-U binary system.

In addition to these sections, thermal analysis studies by [1963Nic] led to the suggestion of a number of invariant four-phase equilibria, but these are very uncertain and in need of further experimental investigation. They also presented a scheme of solid state tie lines for “low temperatures”. Based on these data, [1984Hol1, 1984Hol2] constructed schematic isothermal sections for 1000°C.

Recently, [1990Ale, 1992Ale] investigated the system with special attention to the UC- UC_2 - UFeC_2 composition region through the study of approximately 10 alloys.

Based on the results of X-ray analysis of annealed and quenched alloys, [1990Ale] reported the existence of two new ternary carbides, namely $\text{U}_2\text{Fe}_2\text{C}_3$ and $\text{U}_3\text{Fe}_2\text{C}_5$. Later, [1995Wac] reported that compound called “ $\text{U}_2\text{Fe}_2\text{C}_3$ ” by [1990Ale] is isotypic with $\text{Th}_{11}\text{Fe}_{12}\text{C}_{18}$. [1986Ger] found the UFeC_2 compound to be isostructural with UCoC_2 .

[1992Ale] presented the liquidus projection, partial isothermal section at 1400°C and isothermal section at 1150°C. In addition to UFeC_2 , three more ternary phases were found. The solubility of Fe in UC_{1+x} was studied; for compositions with $x \approx 0$ (near UC composition). The homogeneity region stretches towards a carbon content of ≥ 50 at.%, so this result does not contradict the absence of Fe solubility in UC found in the Fe-UC and UFe_2 -UC sections by earlier investigators. For compositions with $x \approx 1$ (αUC_2), an island phase field of UC_{1+x} is found to exist at both temperatures. [1992Ale] also attempted to make a qualitative description of all topologically different isothermal sections where the liquid phase exists. These results were presented in the review of [2002Rag].

Thermodynamic data exist only for the UFeC_2 phase. Its Gibbs energy of formation was obtained by [1973Tan] using emf measurement of U activity in a $\text{UFeC}_2 + (\text{C}) + (\text{Fe})$ mixture at 722 to 811°C. CaF_2 was used as solid electrolyte with a $\text{U} + \text{UF}_3$ mixture as reference electrode.

The reaction of UC and UC_2 powders with Fe as well as stainless steel at 1000°C was studied by [1962Kat] and [1963Nic]. [1974Mat] studied the influence of Fe on the self-diffusion of C in UC. [1988Jon] determined the products of acid hydrolysis of UFeC_2 and some other carbides as a tool for determining whether C atoms form chains.

Experimental investigations of phase relations, crystal structure and thermodynamics are reviewed in Table 1.

Binary Systems

The three binary systems are taken from [Mas2]. In the C-U binary system, the UC_{1+x} phase ($x \approx 1$) in equilibrium with graphite should be denoted as the βUC_2 phase with a crystal structure of the CaF_2 type.

Solid Phases

In the C-U binary phase UC_{1+x} at temperatures between 2104 and 1769°C, there exists two separate regions with $x \approx 0$ and at $x \approx 1$ which are often considered as separate carbides, UC and βUC_2 [2001Che]. At 1400°C, the phase dissolves about 10 at.% Fe near the “UC” composition and also exists as a separate region at Fe contents of about 4 to 6 at.% and C contents of about 62 to 65 at.%, *i.e.* close to the “ UC_2 ” binary composition [1992Ale]. At 1150°C, the Fe solubility is smaller, but both solid solutions near “UC” and a small separate region near “ UC_2 ” still exist (see below Isothermal Sections).

Four ternary phases are known, denoted here τ_1 to τ_4 . The τ_1 phase with the composition UFeC_2 is formed by a peritectic reaction in the section “ UC_2 ”-Fe [1962Bal, 1963Bri1]. [1986Ger] found it to be isostructural with UCoC_2 . Phase τ_2 was found by [1990Ale] to form peritectoidally at $1500 \pm 100^\circ\text{C}$; a composition close to $\text{U}_3\text{Fe}_2\text{C}_5$ was claimed. Later, [1992Ale] shifted its composition from the section UC-Fe to a higher C content $\text{U}_{32}\text{Fe}_{17}\text{C}_{51}$ (see isothermal section at 1400°C below); this shift is accepted here. X-ray diffraction of this phase suggests it to be a distorted tetragonal solid solution of Fe in UC_{1+x} [1990Ale, 2002Rag]; though no structural studies were performed. The phase τ_3 exists at 1400°C but not at 1150°C in an alloy with a gross composition of $\text{U}_{30.6}\text{Fe}_{8.6}\text{C}_{60.8}$, taken from figure 2 of [1992Ale]; no structural data exist. The phase τ_4 is formed by peritectoid reaction at 1197°C [1992Ale] with a composition close to $\text{U}_2\text{Fe}_2\text{C}_3$; the stoichiometry $\text{U}_{11}\text{Fe}_{12}\text{C}_{18}$ following from its crystal structure was established by [1995Wac]. All of the phases are listed in Table 2.

Quasibinary Systems

The sections between UC-Fe and UC- UFe_2 are quasibinary with simple eutectics [1961Bar, 1963Bri1, 1963Bri2, 1963Nic, 1971Guh]. No solid solubilities were found in either. All data for the eutectic temperature and composition for UC-Fe section are in good agreement. The UC-Fe section is given in Fig. 1. A eutectic temperature of 1117°C was accepted from [1963Nic], where it was measured using TA. The UC- UFe_2 section is presented in Fig. 2 after [1961Bar, 1963Bri1, 1963Bri2, 1963Nic]. A eutectic melting temperature of 1201°C is accepted from [1963Nic]. This value is preferred as the method of observation of melting used by [1961Bar, 1963Bri1] may be too sensitive to admixtures.

The solubility of Fe in UC which was found by [1992Ale] does not lie in either of these sections (see Isothermal Sections below) and so does not contradict these findings.

The UC_2 -Fe section, as presented by [1963Bri2], may be regarded as quasibinary but in the Fe- UFeC_2 composition region only, since the eutectoid decomposition of αUC_2 at 1516°C takes place in the C-U binary system. The peritectic formation of the τ_1 phase UFeC_2 occurs at 1615°C. The region between the τ_1 phase and βUC_2 is unclear. The Fe solid solution (about 3 mass%) is stabilized at low temperatures, and the βUC_2 phase and the τ_3 phase should exist at least around 1400°C according to [1992Ale]. But these results are in contradiction with those presented by [1963Bri2], who reported the decomposition of βUC_2 at temperatures lower than 1516°C. Since additional experimental data in this composition region are absent and the phase equilibria promise to be very complicated and would include the phase relations between solid phases existing at these temperature and composition intervals, the composition region between UFeC_2 and UC_2 was deleted from the section and it was bordered by UFeC_2 compound. The quasibinary section UFeC_2 -Fe is presented in Fig. 3.

Invariant Equilibria

The invariant equilibria are listed in Table 3. They are almost confined to those in the quasibinary sections UC-Fe, UC- UFe_2 and the vertical section Fe-“ UC_2 ” (see below).

Also, according to [1963Nic], two eutectic reactions: E_1 : $\text{L} \rightleftharpoons \text{UC} + (\text{Fe}) + \text{UFe}_2$ at 1037°C and E_2 : $\text{L} \rightleftharpoons \text{UC} + \text{UFe}_2 + \text{U}_6\text{Fe}$ with a melting point of 720°C exist in the system. A series of invariant reactions

proposed in [1992Ale] was omitted since they have not any experimental confirmation and are only speculative constructions.

Liquidus, Solidus and Solvus Surfaces

The liquidus projection presented by [1992Ale] was omitted since the amount of experimental data associated with its construction was not sufficient.

Isothermal Sections

A partial isothermal section for 1400°C is presented in Fig. 4. It is taken mainly from [1992Ale], but redrawn slightly to bring it into agreement with the accepted binary systems.

The UC phase dissolves up to about 10 at.% Fe. This unary region is directed along and somewhat above the line at 50 at.% C. This is the reason for it being missing in early works where the sections studied were directed from UC to Fe and UFe₂. Another stability region for that phase is near the UC₂ composition.

The isothermal section at 1050°C is presented in Fig. 5. It is also based on the data of [1992Ale]. The composition of the τ_4 phase has been changed slightly to bring it into accordance with the accepted stoichiometry U₁₁Fe₁₂C₁₈. Two regions of solid solubility of Fe in UC and β UC₂ still exist at this temperature though with narrower homogeneity ranges. Two three-phase fields with a seemingly identical phase composition of L+UC+UFe₂ are separated by the quasibinary section UC-UFe₂ with a maximum on the monovariant line and so differ in the composition of the participating liquid phases.

Thermodynamics

The Gibbs energy of formation of the τ_1 phase is presented in Table 4 as obtained by emf studies [1973Tan].

Notes on Materials Properties and Applications

Uranium monocarbide has received a good deal of attention as a reactor fuel, particularly for fast reactor applications, since it has the advantage over the dioxide UO₂ of possessing a high thermal conductivity and is, therefore, capable of being used at higher ratings with lower centre temperatures [1961Bar]. To elucidate the interaction between UC-base nuclear fuel and canning materials, the underlying phase equilibrium relationships in the system involved have been studied.

[1962Kat] studied the interaction of UC and UC₂ powders with Fe in samples held at 1000°C for 500 h. At these conditions, UC reacted with Fe; however, the UC₂ showed no signs of interaction. A parabolic time dependence was found for the reaction with UC.

[1963Nic] noticed that UC gives a “eutectic” (*i.e.* begins to form liquid) with stainless steel 100°C lower than with pure Fe.

Both UC and UC₂ quickly react with stainless steel after an induction period of 24 h [1962Kat]. [1966Far] noted that in the three-phase region UC-UFe₂-Fe, a UC-Fe mixture containing less than 50 at.% carbon did not react with type 316 stainless steel after 1500 h at 750°C, whereas unalloyed UC containing less than 50 at.% carbon reacted with stainless steel in 24 h at 750°C.

Miscellaneous

[1988Jon] found that the products of acid hydrolysis of UFeC₂ contain only CH₄ and concluded that no C-C bonds exist in crystals of that phase.

The self-diffusion of uranium in stoichiometric UC which was doped with Fe is increased as compared to undoped UC at all temperatures studied (1380 to 2200°C). The increase was most pronounced (by more than a factor of 100) at low temperatures [1974Mat]. Simultaneously, pronounced grain-boundary penetration was observed at low temperatures.

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Table 1: Investigations of the C-Fe-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1961Bar]	Metallography, XRD	Up to 1800°C, sections UC-Fe and UC- UFe_2 ,
[1962Bal]	Metallography, chemical analysis of single-phase specimen, density and microhardness measurements, thermal analysis, XRD	$UFeC_2$ and close compositions
[1963Bri1]	Metallographical and X-ray investigation of annealed mixtures of powders of UC and UC_2 with Fe	Up to 1800°C, sections UC-Fe and UC- UFe_2
[1963Bri2]	Metallographical and X-ray investigation of annealed mixtures of powders of UC and UC_2 with Fe	Up to 1950°C, sections UC-Fe, UC- UFe_2 and UC_2 -Fe
[1963Nic]	Thermal analysis, metallography	Up to 1700°C, U_6Fe -UC- UC_2 -Fe composition region
[1971Guh]	Metallography, XRD	Section UC-Fe
[1973Tan]	emf	$UFeC_2$ compound, 722 to 811°C
[1986Ger]	Powder XRD	Crystal structure of $UFeC_2$
[1990Ale]	XRD	X-ray data and temperatures of formation of " $U_2Fe_2C_3$ " and " $U_3Fe_2C_5$ "
[1992Ale]	Metallography, XRD, EPMA	UC- UC_2 -Fe region: UC- UC_2 - $UFeC_2$ at 1400°C, other at 1050°C
[1995Wac]	XRD	Crystal structure of " $U_2Fe_2C_3$ " phase

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (graphite) < 3827	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	$a = 246.12$ $c = 670.90$	at 25°C [Mas2] sublimation point
(δFe) 1538 - 1394	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 293.15$	[Mas2]
(γFe) 1394 - 912	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 364.67$	at 915°C [V-C2, Mas2]
(αFe) < 912	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 286.65$	at 25°C [Mas2]
(γU) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352.4$	[Mas2]
(βU) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> βU	$a = 1075.9$ $c = 565.6$	[Mas2]
(αU) < 668	<i>oC4</i> <i>Cmcm</i> αU	$a = 285.37$ $b = 586.95$ $c = 495.48$	at 25°C [Mas2]
UC _{1+x} < 2530 (at $x \approx 0$) 2585 - ~2100 (at $x \approx 1$) NaCl	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	$a = 496.1$ $a = 507.5$ $a = 550.4$	$x = 0$, room temperature [V-C] $x = 0$, at 2100°C $x = 0.9$ at 2100°C [1972Ben]
βUC ₂ ~2100 - 1768	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF ₂ ?	$a = 547.5$	[2001Che] actually, “βUC ₂ ” phase represents the UC phase in equilibrium with graphite [2001Che]
αUC ₂ 1793 - 1516	<i>tI6</i> <i>I4/mmm</i> CaC ₂	$a = 355.2$ $c = 598.8$	[V-C2] may be stabilized by alloying with Fe up to 1050°C [1992Ale]
U ₂ C ₃ 1823 - 850	<i>cI40</i> <i>I$\bar{4}3d$</i> Pu ₂ C ₃	$a = 807.4$	[V-C2]
UFe _{2-x} < 1228	<i>cF24</i> <i>Fd$\bar{3}m$</i> MgCu ₂	$a = 707.2$ $a = 706.3$	$x = -0.137$ $x = 0.048$, [V-C2]
U ₆ Fe < 795	<i>tI28</i> <i>I4/mcm</i> Mn ₆ U	$a = 1028.63$ $c = 524.10$	[V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_1 , UFeC ₂ < 1615 ± 10	<i>tP</i> 8 <i>P4/mmm</i> UCoC ₂	$a = 349.44 \pm 0.06$ $c = 738.9$	[V-C2]
* τ_2 , U _{~32} Fe _{~17} C _{~51} < 1500 ± 100	<i>t</i> **	$a = 500.7$ $c = 508.4$	stoichiometry U ₃ Fe ₂ C ₅ [1990Ale] stoichiometry U _{~32} Fe _{~17} C _{~51} [1992Ale]
* τ_3 , U _{30.6} Fe _{8.6} C _{60.8} (≥1400) - (>1150)	-	-	[1992Ale]
* τ_4 U ₁₁ Fe ₁₂ C ₁₈ < 1197	<i>cI</i> 82 <i>I</i> $\bar{4}$ 3 <i>m</i> Th ₁₁ Ru ₁₂ C ₁₈	$a = 1006.8$	[1990Ale], [1995Wac]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				C	Fe	U
1 + UC ₂ ^{a)} $\rightleftharpoons$ UFeC ₂	1615 ± 10	p ₁	L UFeC ₂	48.8 50	26.8 25	24.4 25
1 $\rightleftharpoons$ UC + UFe ₂	1201	e ₁ (max)	L UC UFe ₂	3.8 ~ 50 ~ 0	61.7 ~ 0 ~ 66.7	34.5 ~ 50 ~ 33.3
1 $\rightleftharpoons$ UFeC ₂ + (γ Fe)	1160	e ₂ (max)	L UFeC ₂ (γ Fe)	14.8 50 ~ 0	70.4 25 ~ 100	14.8 25 ~ 0
1 $\rightleftharpoons$ UC + (γ Fe)	1117	e ₃ (max)	L UC (γ Fe)	48.8 ~ 50 ~ 0	26.8 ~ 0 ~ 100	24.4 ~ 50 ~ 0
L $\rightleftharpoons$ UC + (γ Fe) + UFe ₂	1037	E ₁	UC (γ Fe) UFe ₂	~ 50 ~ 0 ~ 0	~ 0 100 ~ 66.7	~ 50 ~ 0 ~ 33.3
L $\rightleftharpoons$ UC + UFe ₂ + U ₆ Fe	720	E ₂	UC UFe ₂ U ₆ Fe	~ 50 ~ 0 ~ 0	~ 0 ~ 66.7 ~ 7.7	~ 50 ~ 33.3 92.3

a) note: contains some (not determined exactly, probably about 3 mass%) Fe

Table 4: Thermodynamic Data of Reaction or Transformation

Reaction or Transformation	Temperature [°C]	Quantity, per mol [kJ, mol, K]	Comments
(α Fe) + (β U) + 2C(gr) $\rightleftharpoons$ UFeC ₂	722-778	$\Delta G = -139.03 + 0.01448T$	emf [1973Tan]
(α Fe) + (γ U) + 2C(gr) $\rightleftharpoons$ UFeC ₂	778-811	$\Delta G = -146.65 + 0.02172T$	emf [1973Tan]

Fig. 1: C-Fe-U.
The UC - Fe
quasibinary section

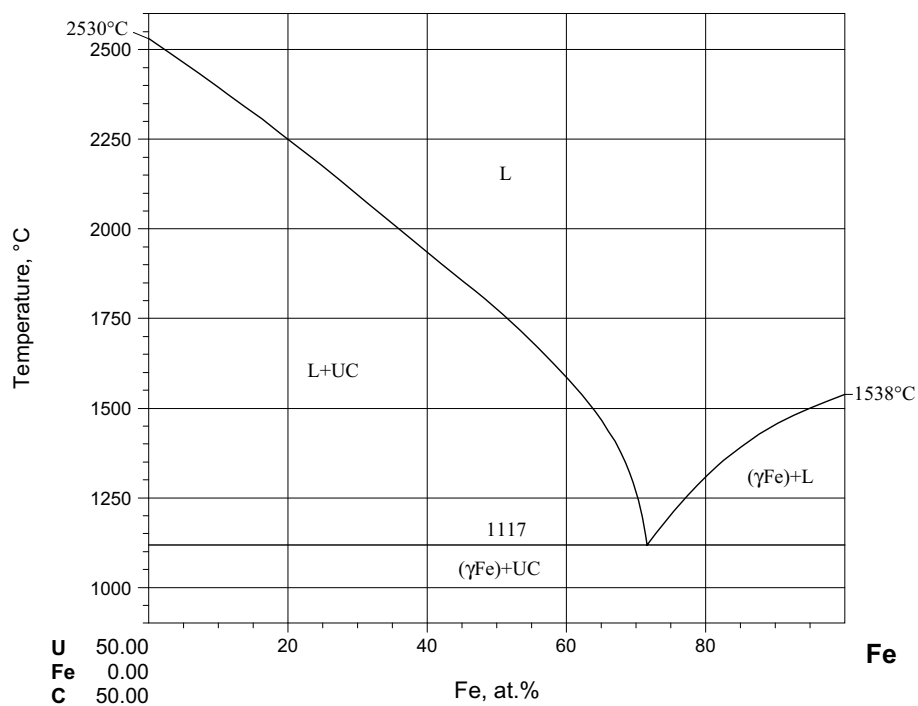


Fig. 2: C-Fe-U.
The UC - UFe₂
quasibinary section

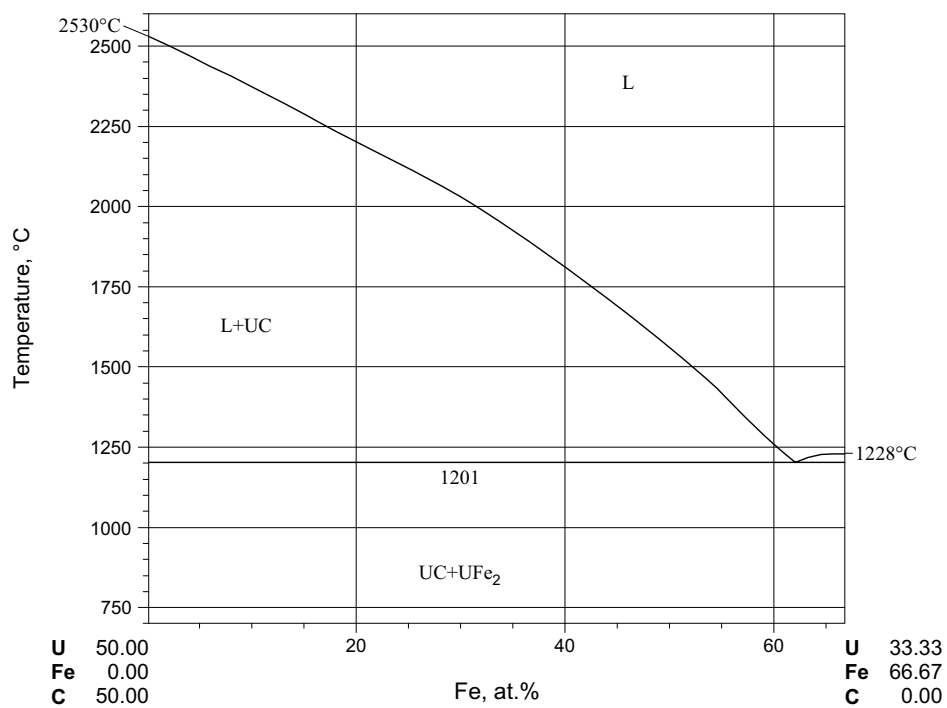


Fig. 3: C-Fe-U.
The UF_6C_2 - Fe
quasibinary section

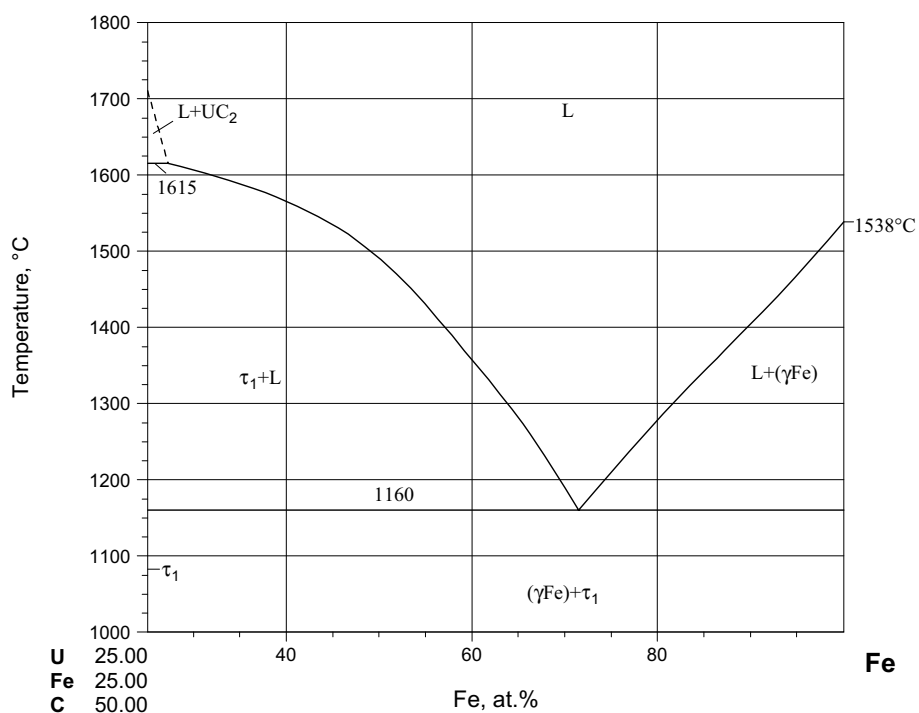


Fig. 4: C-Fe-U.
Partial isothermal
section at 1400°C

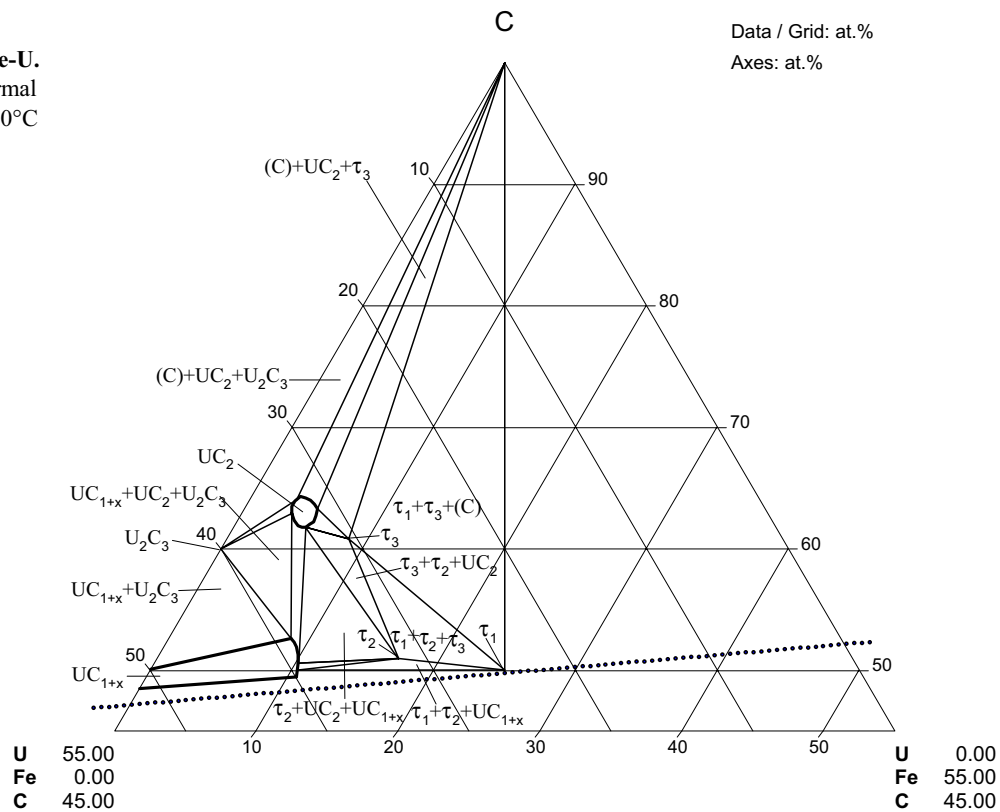
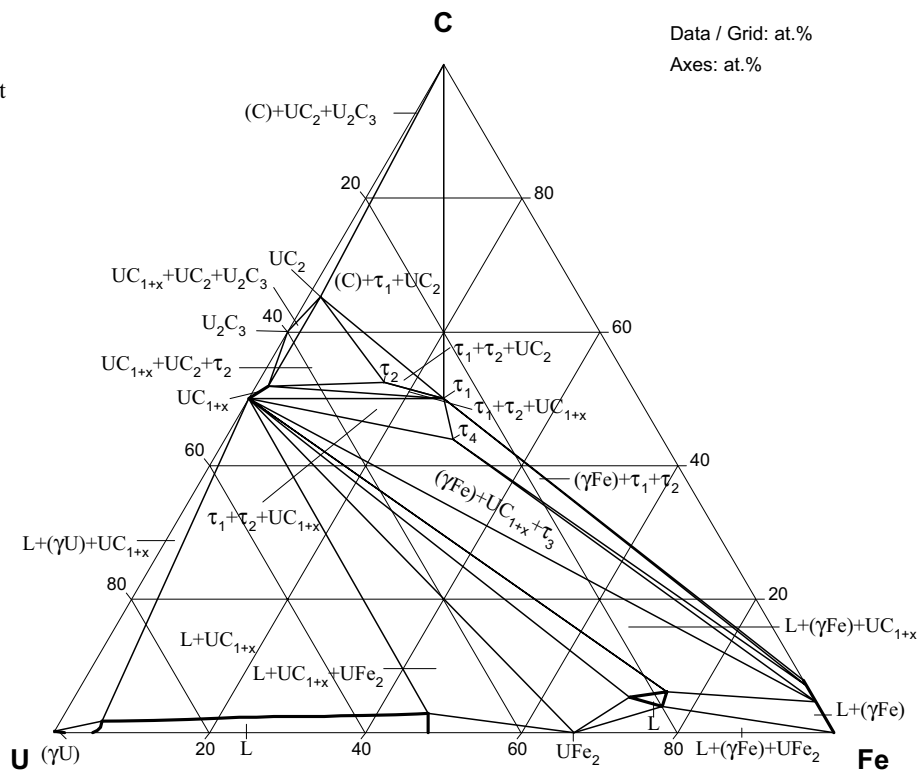


Fig. 5: C-Fe-U.
Isothermal section at
1050°C



Carbon – Molybdenum – Uranium

Kostyantyn Korniyenko

Introduction

Mixed carbides of uranium are candidate fuel materials for fast breeder reactors. The fuel pellets are enclosed in stainless steel clad tubes. During reactor operation, transport of carbon may occur to or from the cladding through the fuel-clad interface. The difference in carbon potential between the fuel and the cladding strongly influences carbon transport. Variation in the carbon content of the stainless steel cladding can adversely affect the mechanical integrity of the steel. Thus, data on the carbon potentials of the fuel and the cladding are useful in understanding and predicting the carbon transport phenomenon. As uranium undergoes fission, a number of fission products are formed with different affinities for formation of binary and ternary carbides. Thus, fission products with high yield, in particular, with participation of molybdenum, may alter the carbon balance as well as the carbon potential of the fuel, and consequently influence cladding carburization [1996Ana]. With a view to the optimization of alloy compositions in the preparation of these materials, information about phase relations in the corresponding ternary system C–Mo–U is of great importance. But up to now, this information has errors and is not complete. It is presented in literature via the invariant equilibrium data [1968Ale, 1973Ale2, 1975Uga2, 1984Ale], liquidus surface projection [1964Chu, 1975Uga2, 1968Ale], a series of isothermal sections [1962Cra, 1963Rud, 1964Chu, 1964Str, 1975Hol, 1975Uga1, 1984Ale, 1984Hol1, 1984Hol2, 1989Lin, 1994Mch] and temperature-composition sections [1964Str, 1967Chu, 1973Ale2, 1973Ale3, 1975Uga2, 1989Lin, 1994Mch]. Phase contents of the alloys and crystal structures of the intermediate phases were studied by [1962Cra, 1962Kat, 1963Rud, 1964Str, 1964Cro, 1965Dec, 1966Ans, 1967Chu, 1968Ale, 1970Bow, 1971Uch, 1973Ale1, 1973Ale2, 1973Ale3, 1973Ale4, 1973–1974Nar, 1974Iva, 1975Ale, 1985Ara, 1986Jei, 1988Jon]. Thermodynamic properties were obtained experimentally by [1974Nar, 1975Uga2, 1996Ana]. The experimental methods used and the temperature and composition ranges studied are shown in Table 1. Physical properties of the C–Mo–U alloys are presented in [1967Chu, 1970Bow, 1971Uch, 1972Lor, 1985Ara]. The C–Mo–U system was reviewed in [1963Bri, 1964Far, 1967Far, 1968Ale, 1975Hol, 1984Hol1, 1984Hol2, 1994Mch]. However, further amendments to the character of the phase equilibria are necessary, in particular concerning the constitution of the liquidus, solidus and solvus surfaces as well as the reaction scheme for the whole range of compositions. Discrepancies between the isothermal and temperature-composition sections need to be solved.

Binary Systems

The C–U and Mo–U constituent binary systems are accepted from [Mas2]. The constitution of the C–Mo system as a whole has been accepted from [Mas2], but with the addition of the β' , Mo_2C (h_1) ordered phase after [1988Epi].

Solid Phases

Crystallographic data relating to the unary, binary and ternary phases are listed in Table 2. The solubilities of the third component in each of the binary C–U, C–Mo and Mo–U phases were found to be no more than 0.1 at.%. Two ternary phases with crystal structures different from any of the unary and binary phases were found, namely τ_1 , UMoC_{2-x} ($x = 0.25$ to 0.5) and τ_2 , UMoC_2 . They melt, respectively, incongruently at $\sim 2227^\circ\text{C}$ [1975Uga2] and congruently at $\sim 2350^\circ\text{C}$ [1967Chu].

Invariant Equilibria

A partial reaction scheme is presented in Fig. 1. It was compiled on the basis of data relating to reactions involving the liquid phase as presented in [1968Ale, 1973Ale2, 1975Uga2], as well solid state reactions from [1984Ale]. Carbon poor and carbon rich compositions of the ϵ , UC phase are labeled as ϵ' and ϵ'' ,

respectively. Invariant reactions in the binary systems are presented according to the accepted versions, with addition of the reaction $(\beta\text{U}) \rightleftharpoons (\alpha\text{U}) + \varepsilon$ in the C–U system (e_{18} , $\sim 668^\circ\text{C}$) taken from [1984Ale], and information relating to invariant temperatures in the C–Mo system from [1985Dan, 1988Vel]. All the four-phase invariant temperatures need experimental determination as they were evaluated on the basis of comparing of phase equilibria at different temperatures.

The compositions of the liquid phase taking part in the invariant equilibria are shown in Table 3. They were determined on the basis of the liquidus surface projection from [1964Chu, 1968Ale, 1973Ale2, 1975Uga2], (see “Liquidus, Solidus and Solvus Surfaces”).

Liquidus, Solidus and Solvus Surfaces

The partial liquidus surface projection is shown in Fig. 2. It is based on the experimental results of [1964Chu, 1968Ale, 1973Ale2] as well as on the data of [1975Uga2], including both their own experimental results and an assessment of the literature data. Corrections to the invariant points in the edge binary systems have been made to maintain consistency with the accepted corresponding phase diagrams. Temperatures of invariant four-phase reactions are corrected according to the accepted reaction scheme (Table 3, Fig. 1). The U_5 point was shifted towards the uranium corner in comparison to [1968Ale] owing to the location of p_4 in the accepted Mo–U phase diagram. The positions of the curves U_1U_4 and U_3U_4 are reproduced according to data of this work. The composition of the phase τ_1 taking part in equilibria with the liquid is given as $\text{UMoC}_{1.7}$ whereas in some publications in the literature it varies from $\text{UMoC}_{1.75}$ to $\text{UMoC}_{1.5}$ (Table 2). Thus, the carbon content of this phase can vary from 42.9 to 46.7 at.%, with a constant U:Mo ratio of 1:1. The τ_1 phase field of primary crystallization is placed outside of its composition range because of the incongruent formation of this phase. The position of the point p_1 is located on the intersection of monovariant curve U_1U_2 with the extension of the $\tau_1\tau_2$ tie line. As a whole, the liquidus surface projection, like the solidus and solvus surface projections need further experimental determination.

Isothermal Sections

An isothermal section at 2000°C for the whole range of compositions is presented in Fig. 3 based on the data of [1967Chu] with amendments to maintain consistency with the accepted binary phase diagrams and in accordance with the reaction scheme and the temperature – composition sections. The extent of the liquid and molybdenum solid solution regions in the Mo–U system as well as the liquid region in the C–U system are enlarged compared with the section given in [1967Chu]. In the C–Mo system the δ and η phases are presented instead of the Mo_3C_2 phase. Both the τ_1 and τ_2 phases are included in Fig. 3, whereas [1967Chu] presented just the UMoC_2 phase with a carbon content ranging from ~ 43.7 to 50 at.% C. The composition of the τ_1 , UMoC_{2-x} phase is about 43.7 at.% C ($x \approx 0.45$). From the reaction scheme one can conclude that at 2000°C the $\tau_2 + \varepsilon + \tau_1$ and $\tau_2 + \tau_1 + \beta$ three-phase as well as the $\tau_2 + \beta$, $\tau_1 + \tau_2$ and $\varepsilon + \tau_2$ two-phase equilibria must exist, while the $\beta + (\text{Mo}) + \tau_1$, $\tau_1 + \varepsilon + (\text{Mo})$ and $(\text{Mo}) + \varepsilon + (\gamma\text{U})$ equilibria cannot (in the corresponding range of compositions the liquid phase region must be presented). The UC_2 phase which is presented in [1967Chu] is replaced by ε'' (the carbon rich ε phase) while the UC phase is labeled as ε' . The liquid phase field in the ternary system in Fig. 3 is widened considerably compared with [1967Chu] owing to the presence of the corresponding field in the UMoC_2 –Mo temperature–composition section [1973Ale2] at 2000°C .

The isothermal section at 1800°C (Fig. 4) is also constructed on the basis of [1967Chu] taking into account the accepted binary phase diagrams, the reaction scheme and the temperature–composition sections. Comparing with [1967Chu], the liquid phase field is widened, the μ phase is added, the UC and UC_2 phases are replaced by ε' and ε'' phases, respectively. In the C–Mo system the Mo_3C_2 -based phase is replaced by the η phase. The composition of the τ_1 , UMoC_{2-x} phase is shown with $x = 0.3$ (about 45.9 at.% C) after [1966Ans] and [1985Ara] (Table 2). The liquid phase region stretches deep inside the ternary system, as found in the UC–Mo at 1800°C (Fig. 4). From the reaction scheme it follows that at this temperature, the $\tau_2 + \varepsilon + \tau_1$, $\tau_2 + \tau_1 + \beta$ and $\beta + (\text{Mo}) + \tau_1$ three-phase fields, as well as the $\tau_2 + \beta$, $\tau_1 + \tau_2$ and $\varepsilon + \tau_2$ must exist while $\tau_1 + \beta + (\text{Mo})$ and $(\text{Mo}) + (\gamma\text{U}) + \varepsilon$ three-phase equilibria cannot be present. Structure modifications of the β phase are designated as β' and β'' , but it was not determined which modification takes

part in the three-phase equilibrium with the τ_1 phase and (Mo). The corresponding phase field is labeled $\tau_1 + \beta + (\text{Mo})$.

[1963Rud] presented a partial isothermal section in the UC–Mo–C corner for 1600°C. Equilibria were presented that involved the metastable ω , UMo_2C_2 phase which formed from the melt being found at temperatures between 1500°C and 1800°C, whilst the existence of the τ_1 phase was not taken into account. Therefore the corresponding figure is not shown in this assessment.

The isothermal section for 1525°C (Fig. 5) is presented after [1989Lin, 1994Mch] with some amendments for consistency with the accepted binary phase diagrams. According to the accepted C–U phase diagram, the ϵ phase possesses a visible homogeneity range (from 48.5 to 50 at.% C) at this temperature, which is not shown in [1989Lin, 1994Mch]. In order to be consistent with the accepted binary phase diagrams the extent of liquid phase field is increased in the both C–U and Mo–U systems somewhat - from 8 to 12 at.% and from 34 to 37 at.%, respectively. The composition of τ_1 is presented as $\text{UMoC}_{1.7}$.

The assessed isothermal section for 1500°C was first published by [1964Chu]. It was compiled on the basis of available literature data. Only one ternary phase, UMoC_2 , was included in the diagram. Equilibria involving the UC_2 and Mo_3C_2 phases were shown, although it was established later that at this temperature, they do not take part in equilibria. An assessed isothermal section for 1500°C was published by [1975Uga1] (with reference to experimental data), [1975Hol] and [1984Hol1, 1984Hol2] (with references to [1966Ans, 1975Ale, 1975Uga2]). The constitution of the section presented in [1975Hol, 1984Hol1, 1984Hol2] is the same, while the data of [1975Uga1] differ from them by the presence of equilibria involving the UC_2 and MoC_{1-x} phases as well as by the extent of liquid phase region in the U rich corner deep into the ternary system. Taking into account the constitution of the accepted binaries, the isothermal section at 1500°C is redrawn in Fig. 6. The character of phase equilibria at this temperature differs from those at 1525°C by the disappearance of the κ phase following its dissociation at $1516 \pm 10^\circ\text{C}$ in the C–U binary system.

The metallographic characteristics of the microstructures of the uranium-based alloys with up to 2 mass% of Mo and up to 2 mass% of C, after annealing at 800°C and step-annealing at 675°C, were obtained by [1962Cra]. The possible effects of the microstructural condition of these alloys during irradiation were discussed. An isothermal section of the U–UC–Mo partial system at 900°C was presented by [1963Rud], Fig. 7. It was established, that a wide $\epsilon + (\gamma\text{U}) + (\text{Mo})$ three-phase field occupies most of this part of the diagram. Isothermal sections in the concentration range of up to 45 at.% C and 25 at.% Mo at temperatures of 650, 585 and 550°C were constructed on the basis of experimental results from [1964Str]. It was concluded that carbon added to Mo–U alloys removes uranium from the metallic matrix through the formation of UC and enriches the matrix in molybdenum. The solubility of molybdenum in UC at 650°C was estimated to be about 1.8 at.%. Isothermal sections in the U–UC–Mo composition range and the temperature range 1100–550°C were constructed theoretically by [1984Ale] to show the development of the phase equilibria. Data relating to the Mo–U and C–U forming edge binary systems as well as the experimentally determined isothermal section for 900°C from [1963Rud] were used.

Temperature – Composition Sections

The UMoC_2 –Mo temperature-composition section is presented in Fig. 8 based on [1973Ale2] with corrections according to the constitution of the accepted boundary binary systems as well as of the reaction scheme, liquidus surface and isothermal sections. In comparison with [1973Ale2], fields containing the β' phase have been added and the positions of the $L + \tau_2$, $L + \tau_1$, $L + \beta$ and $L + (\text{Mo})$ fields have been changed considerably. The $\tau_1 + \beta$ (β') two-phase region is placed in the range of molybdenum content of about 1 at.%. From the isothermal sections for different temperatures it follows that position of this region shifts towards the molybdenum side with increasing temperature.

The UC–Mo temperature-composition section is presented in (Fig. 9) based mainly on [1973Ale2]. Some corrections according to constitution of the forming C–U system are carried out, in particular, the $\epsilon + \mu$, $\epsilon + \mu + (\text{Mo})$, $\epsilon + (\text{C})$ and $\epsilon + (\text{C}) + (\text{Mo})$ fields are added. In contrast to the work of [1967Chu], the authors of [1973Ale2] determined that the UC–Mo system contains the τ_1 phase rather than the τ_2 phase, and consequently, the phase fields have been amended.

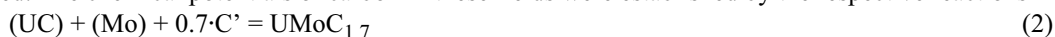
The $U_{50}Mo_{50}$ -C temperature-composition section is shown in Fig. 10. It is based mainly on the data of [1975Uga2] (reproduced in [1989Lin, 1994Mch]) with modifications to be consistent with the accepted Mo-U binary system and the ternary phase diagram. This section was also reported in [1967Chu], but the τ_1 phase was not presented and the τ_2 phase was demonstrated as possessing a visible homogeneity range (up to 3 at.% carbon). In Fig. 10, the narrow by temperature $L + \epsilon$ two-phase field is added; the $L / L + \epsilon$ and $L + \epsilon / L + \epsilon + (Mo)$ fields increase in temperature with increasing carbon content. Following the reaction scheme, the temperatures of the horizontal lines at the Mo-U system side representing the invariants U_4 and U_5 are changed to 1530°C (instead of 1830°C) and 1185°C (instead of ~1265°C), respectively.

Partial temperature-composition sections at 5 and 15 at.% C for molybdenum contents of up to 40 and 30 at.%, respectively, are presented in Figs. 11 and 12 after [1964Str]. They illustrate the character of the phase equilibria in the solid state from the C-U side of the system. Also in this article, schematic partial temperature-composition sections at 2 mass% (up to 25 at.% Mo) and at 4 mass% (up to 10 at.% Mo) for temperatures up to 750°C were shown. However, they need further investigation. The UC_2 - $UMoC_2$ section was presented in [1973Ale3], but it also needs further study owing to contradictions with isothermal sections of the ternary system and the accepted C-U binary system. The authors of this work also have investigated a series of alloys along the U_2C_3 - $UMoC_2$ and $UMoC_2$ - $Mo_{58}C_{42}$ sections. Some of the lattice parameters obtained for the η , MoC_{1-x} phase are presented in Table 2.

Thermodynamics

[1996Ana] measured the carbon potential in the $\epsilon + (Mo) + \tau_1$ and the $\epsilon + \tau_1 + \tau_2$ three-phase fields using the methane-hydrogen gas equilibration technique. Graphite was the standard state and the temperature range used was 700°C to 900°C (973 to 1173 K). The results for these fields are presented in Figs. 13 and 14, respectively. The chemical potential of carbon was calculated from the equilibrium using the expression $\Delta\mu_C = R \cdot T \cdot \ln a_C = \Delta_f G^\circ (CH_4) + R \cdot T \cdot \ln (p_{CH_4}/p_{H_2}^2)$ (1)

From a least squares regression analysis of the data, the expression for $\Delta\mu_C = -52.21 - 19 \cdot T (\pm 7.3) \text{ kJ} \cdot \text{mol}^{-1}$ for the $\epsilon + (Mo) + \tau_1$ three-phase field and $\Delta\mu_C = -17.77 - 2 \cdot T (\pm 4.6) \text{ kJ} \cdot \text{mol}^{-1}$ for the $\epsilon + \tau_1 + \tau_2$ field were obtained. The chemical potentials of carbon in these fields were established by the respective reactions



and



Here C' refers to carbon in a state with an activity less than unity with respect to graphite as the reference state. The thermodynamic properties of the τ_1 and τ_2 phases are given in Table 4. The Gibbs energy of formation of the τ_2 phase was obtained by [1974Nar] from emf measurements using a three phase mixture of $\tau_2 + \epsilon + (Mo)$ as the electrode, but according to later phase equilibrium studies, these phases are not in equilibrium and therefore their data are found to be in error.

Notes on Materials Properties and Applications

Mixed uranium carbides containing molybdenum are the prospective components for nuclear fuel. [1972Lor, 1996Ana] have predicted that about 2 at.% Mo would be produced in a mixed carbide fuel when the burn up exceeds 10 at.%. Further, these authors have indicated that the ternary carbides $UMoC_{1.7}$ and $UMoC_2$ may form in irradiated UC fuel when the concentration of Mo is about 2 at.%. Microhardness of the phase constituents of alloys have been measured by [1967Chu]. Using a high temperature neutron diffractometer, [1970Bow] determined the lattice parameters of the $UMoC_2$ compound in the temperature range from 925 to 2100°C. Some of the data are listed in Table 2. Anisotropic thermal expansion was measured. The coefficients of thermal expansion are equal to (units of 10^{-6} C^{-1}): $\alpha_{11} = 8.6 \pm 0.2$, $\alpha_{22} = 15.5 \pm 0.5$, $\alpha_{33} = 9.9 \pm 2.6$. Thermal expansion coefficients for $UMoC_2$ were also determined by [1971Uch] using X-ray diffraction technique in the temperature range from 20 to 1100°C. The values obtained are (10^{-6} C^{-1} units): $\alpha_{11} = 7.7 \pm 0.6$, $\alpha_{22} = 12.5 \pm 0.7$, $\alpha_{33} = 3.4 \pm 1.0$. They are lower than the data of [1970Bow], and differ most in the behavior of the c -axis (α_{33}), which the authors of [1970Bow] reported as expanding more rapidly than the a -axis (α_{11}). [1971Uch] attributed this to the higher temperature range

covered by [1970Bow], since it is believed that in general the thermal expansion coefficient increases with temperature. [1985Ara] have determined the thermal conductivities of UMoC_2 and $\text{UMoC}_{1.7}$ from thermal diffusivities measured in the temperature range from 477 to 1227°C. The pellets were preliminarily sintered at 1800°C for 5 h. The measured bulk densities were $10.2 \text{ g}\cdot\text{cm}^{-3}$ and $10.6 \text{ g}\cdot\text{cm}^{-3}$ for UMoC_2 and $\text{UMoC}_{1.7}$, respectively. Figure 15 shows the thermal diffusivities. These values are not corrected for porosity. Thermal diffusivities for these compounds increase gradually with increasing temperature. The thermal conductivities were calculated by using the thermal diffusivity data, the heat capacity and the density of the samples. Figure 16 presents the thermal conductivities of $\text{UMoC}_{1.7}$ corrected to 100% theoretical density in the temperature range from 477 to 1227°C. The thermal conductivities also increase as the temperature increases, but their temperature dependence was a little larger than that of the thermal diffusivities, which was mainly due to the heat capacity values estimated in [1985Ara]. The thermal conductivity of UMoC_2 is slightly higher than that of $\text{UMoC}_{1.7}$ especially at lower temperatures.

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Table 1: Investigations of the C-Mo-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1962Cra]	Optical microscopy, replica electron microscopy of slowly cooled alloys	U rich corner
[1962Kat]	Metallography, X-ray diffraction	1000°C; UC-Mo, UC_2 -Mo
[1963Rud]	X-ray diffraction, metallography	Whole range of compositions
[1964Str]	Metallography, X-ray diffraction	500-950°C, isopleths at 5 and 15 at.% C, 2 and 4 mass% C, 0 to 25 at.% Mo
[1964Cro]	Single-crystal X-ray diffraction	$UMoC_2$
[1965Dec]	Metallography	U rich corner
[1966Ans]	X-ray diffraction, metallography	Annealed at 1800°C, $UMoC_{1.7}$
[1967Chu]	Metallography, X-ray diffraction	Whole range of compositions
[1968Ale]	Single-crystal X-ray diffraction, optical microscopy	UC- $UMoC_2$ -Mo-U-UC phase region
[1970Bow]	High-temperature neutron diffractometry	800-2100°C, $UMoC_2$
[1971Uch]	High-temperature X-ray diffraction	$UMoC_2$

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1973Ale1]	Metallography, X-ray diffraction	Isopleths UMoC_2 -C, UMoC_2 -U:Mo = 1:1
[1973Ale2]	Metallography, X-ray diffraction	UC- UMoC_2 - Mo_2C -Mo-U phase region. Partial liquidus surface
[1973Ale3]	Metallography, X-ray diffraction	The UC_2 - UMoC_2 , UMoC_2 - $\text{Mo}_{58}\text{C}_{42}$, U_2C_3 - UMoC_2 sections
[1973Ale4]	X-ray diffraction (single crystal)	UMoC_{2-x}
[1974Nar]	Chemical analysis, X-ray diffraction, electron probe, metallography, standard Gibbs free energy of formation determination (emf studies)	UMoC_{2-x} ($x = 0, 0.25$ to 0.5). $\Delta_f G^\circ$ (UMoC_2)
[1974Iva]	Crystal structure studies	UMoC_2
[1975Ale] as quoted by [1986Jei]	Crystal structure studies	$\text{UMoC}_{1.5}$
[1975Uga1]	Free energy determination, thermodynamic activity calculation	Three-phase and two-phase fields across the system.
[1975Uga2]	Free energy estimation, metallography, X-ray diffraction	1500-2000°C
[1985Ara]	X-ray diffraction, chemical analysis	UMoC_2 , $\text{UMoC}_{1.7}$
[1986Jei]	X-ray Guinier studies	$\text{UMoC}_{1.5}$
[1988Jon]	Mild hydrolysis, thermal analysis, X-ray diffraction, Rietveld neutron powder diffraction	UMoC_2
[1989Lin] as quoted by [1994Mch]	Phase equilibria experimental studying	Whole range of compositions
[1996Ana]	Methane-hydrogen gas equilibrium technique - C activity	700-900°C, $\text{UMoC}_{1.7}$, UMoC_2

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (diamond)	$cF8$ $Fd\bar{3}m$ C (diamond)	$a = 356.69$	at 25°C, 60 GPa [Mas2]
(C) (graphite) < 3827	$hP4$ $P6_3/mmc$ C (graphite)	$a = 246.12$ $c = 670.90$	at 25°C [Mas2] sublimation point

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Mo) < 2623	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 314.70$	at 25°C [Mas2] $x = 0, 0 < y \leq 0.011, T = 2205 \pm 9^\circ\text{C}$ [Mas2]
$\text{U}_x\text{Mo}_{1-x-y}\text{C}_y$		$a = 336.93$	$y = 0, 0 < x \leq 0.03,$ $T = 1284 \pm 2^\circ\text{C}$ [Mas2] $y = 0, x = 0.645$ [2001Pov]
(γ U) 1135 - 776 $\text{U}_{1-x-y}\text{Mo}_x\text{C}_y$	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352.4$ $a = 436$	[Mas2] $x = 0, 0 < y \leq 0.0022$ to 0.0037, $T = 1119 \pm 1^\circ\text{C}$ [Mas2] $y = 0, 0 < x \leq 0.42,$ $T = 1284 \pm 2^\circ\text{C}$ [Mas2] $x = 0.36, y = 0, T = 900^\circ\text{C}$ [1963Rud]
(β U) 776 - 668 $\text{U}_{1-x-y}\text{Mo}_x\text{C}_y$	<i>tP30</i> <i>P4₂/mm</i> β U	$a = 1075.9$ $c = 565.6$	[Mas2] $x = 0, 0 < y \leq 0.0002, T = 772^\circ\text{C}$ [Mas2] $y = 0, 0 < x < 0.02,$ $T = 668^\circ\text{C}$ [Mas2]
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	at 25°C [Mas2] [1963Rud]
$\text{U}_{1-x-y}\text{Mo}_x\text{C}_y$		$a = 285.8$ $b = 587.6$ $c = 494.7$	$x = 0, 0 < y \leq 6 \cdot 10^{-5}, T = 660^\circ\text{C}$ [Mas2] $y = 0, 0 < x \leq 0.007,$ $T = \sim 570^\circ\text{C}$ [Mas2]
$\beta, \text{Mo}_2\text{C} (h_2)$ 2537 - 1650	<i>hP3</i> <i>P6₃/mmc</i> Fe_2N	$a = 299.6$ to 301.2 $c = 473.1$ to 478.6 $a = 299.6$ $c = 473.8$ $a = 300.6$ $c = 473.4$ $a = 299.0$ to 301.0 $c = 473.0$ to 477.8	27 to 36 at.% C [Mas2], [1988Epi], [1988Vel] $T = 255^\circ\text{C}$ [V-C2] at 33.5 at.% C, quenched from $T = 2000^\circ\text{C}$ [1965Rud] at 30 to 34 at.% C, $T = 2200^\circ\text{C}$ [V-C2]
$\beta', \text{Mo}_2\text{C} (h_1)$ 1960 - 1190	<i>hP12</i> <i>P$\bar{3}1m$</i> Mo_2C	$a = 519$ $c = 472.4$ $a = 526$ $c = 480$	ordered β phase, labeled as “ ϵ - Mo_2C ” in [1988Epi] $T = 1700^\circ\text{C}$ [1988Epi]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
β'' , Mo ₂ C (r ₂) ≤ 1380	<i>oP12</i> <i>Pbcn</i> PbO ₂	$a = 473.0$	at ~32.5 at.% C [Mas2], [V-C2]
		$b = 602.7$	
		$c = 519.8$	
		$a = 473.5$ $b = 602.5$ $c = 521.0$	
		$a = 473.2$ $b = 604.8$ $c = 518.8$	labeled as “ β' -Mo ₂ C” [1988Vel] $T = 20^\circ\text{C}$ [1988Epi] $T = 227^\circ\text{C}$ [V-C2]
		$a = 476.2$ $b = 607.2$ $c = 521.6$	$T = 727^\circ\text{C}$ [V-C2]
β''' , Mo ₂ C (r ₁) < 1220	<i>o**</i>	$a = 946.6$ $b = 2415.2$ $c = 4167.5$	at ~33.5 at.% C [Mas2] labeled as “ β -Mo ₂ C” [1988Vel]
δ , MoC _{1-x} 2605 - 1956	<i>oF8</i> <i>Fm$\bar{3}m$</i> NaCl		37 to 43 at.% C [V-C, Mas2] labeled as “ α -MoC _{1-x} ” [1973Ale3]
		$a = 426.6$ to 428.1	39.7 to 43 at.% C [1988Vel]
		$a = 426.7$	at 41 at.% C [1965Rud]
		$a = 428.1$	at 43 at.% C [1965Rud]
U _y Mo _x C _{1-x-y}		$a = 426.2$	in the alloy U _{2.3} Mo ₅₅ C _{42.7} annealed at $T = 2050^\circ\text{C}$ [1973Ale3]
		$a = 426.8$	in the alloy U _{9.85} Mo ₄₅ C _{45.15} annealed at $T = 2050^\circ\text{C}$ [1973Ale3]
		$a = 427.6$	in the as-cast alloy U _{2.3} Mo ₅₅ C _{42.7} [1973Ale3]
		$a = 428.2$	in the as-cast alloy U _{9.85} Mo ₄₅ C _{45.15} [1973Ale3]
η , MoC _{1-x} 2530 - 1647	<i>hP8</i> <i>P6₃/mmc</i> TiAs	$a = 301.2$	37 to 40 at.% C [Mas2]
		$c = 1463.4$	at 39 at.% C [1988Vel]
		$a = 301.2$ $c = 1465$	at 39 at.% C [1965Rud]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ , MoC < 1220	$hP2$ $P\bar{6}m2$ WC	$a = 289.8$ $c = 280.9$ $a = 290.6$ $c = 282.2$	50 at.% C [Mas2] [V-C2] [1988Vel]
ϵ , UC (I) < 2585 1.013 bar	$cF8$ $Fm\bar{3}m$ NaCl	$a = 495.98$ $a = 496.2$	47 to 66 at.% C [Mas2] [E] [1963Rud]
UC (II) > $2.7 \cdot 10^5$ bar	o^{**}	-	[1987Ben]
μ , U_2C_3 1823 - ~850	$cI40$ $\bar{I}43d$ Pu_2C_3	-	60 at.% C [Mas2]
κ , UC_2 1793 - 1516	$tI6$ $I4/mmm$ CaC_2	$a = 351.7$ $c = 598.7$ $a = 352.4$ $c = 599.9$ $a = 351.9$ to 352.41 [S] $c = 597.87$ to 599.62 $a = 352.7$ $c = 598.0$ $a = 352.0$ $c = 598.5$ $a = 352.2$ $c = 598.8$	62 to 65.5 at.% C [Mas2] [E] [H] [1963Rud] [1967Rea] [1987Jon]
UC_2 2434 - 1762	$cF12$ $Fm\bar{3}m$ $CaF_2?$	$a = 545.0$	actually, “ UC_2 ” phase represents the ϵ ,UC phase in equilibrium with graphite [1993But, 2001Che]
λ , U_2Mo ≤ 1252 (?)	$tI6$ $I4/mmm$ $MoSi_2$	$a = 342.7$ $c = 985.4$	32.5 to 34 at.% Mo [Mas2] [E]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_1 , UMoC_{2-x} $\lesssim 2227$	m^{**}	$a = 562.6$ $b = 323.8$ $c = 1166.1$ $\beta = 109.7^\circ$	$x = 0.25$ to 0.5 $x = 0.3$, $T = 1800^\circ\text{C}$ [1966Ans]
		$a = 532$ $b = 324$ $c = 1100$ $\beta = 108.5^\circ$	$x = 0.33$ [1968Ale]
		$a = 562.8$ $b = 323.8$ $c = 1165.5$ $\beta = 109.5^\circ$	$x = 0.5$ [1973Ale4, 1975Ale, 1986Jei]
		$a = 564$ $b = 324$ $c = 1166$ $\beta = 109.8^\circ$	$x = 0.3$, $T = 1800^\circ\text{C}$ [1985Ara]
		$a = 561.8$ $b = 324.35$ $c = 1164.9$ $\beta = 109.63^\circ$	$x = 0.5$ [1986Jei]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_2 , UMoC ₂ ≤ 2350	<i>oP4</i> <i>Pnma</i> UCrC ₂	$a = 562.5$ $b = 324.9$ $c = 1098.0$	[1964Cro]
		$a = 562.6$ $b = 324.0$ $c = 1095.7$	at room temperature [1970Bow]
		$a = 566.5$ $b = 328.5$ $c = 1102.0$	$T = 925^\circ\text{C}$ [1970Bow]
		$a = 571.5$ $b = 334.2$ $c = 1110.0$	$T = 2000^\circ\text{C}$ [1970Bow]
		$a = 563.0$ $b = 325.3$ $c = 1101.0$	[1971Uch]
		$a = 562.5$ $b = 324.9$ $c = 1099.0$	[1974Iva]
		$a = 561.2$ $b = 324.1$ $c = 1095.6$	[1988Jon]
ω , UMo ₂ C ₂ 1800 - 1500	-	-	Metastable [1963Rud]
χ , UMoC > 1800	-	-	Metastable [1964Chu]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				C	Mo	U
$L \rightleftharpoons \tau_2$	~2350	congruent	L τ_2	50 50	25 25	25 25
$l \rightleftharpoons \tau_2 + \beta$	2270	e_5	L	-	-	-
$l \rightleftharpoons \tau_2 + (C)$	2200	e	L	-	-	-
$l + \tau_2 \rightleftharpoons \tau_1$	2170	p_1	L	~ 42	~ 29	~ 29
$l \rightleftharpoons \varepsilon + \tau_2$	2160	e_7	L	-	-	-

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				C	Mo	U
$L + \tau_2 \rightleftharpoons \varepsilon + \tau_1$	?	U_1	L	~ 45	~ 18	~ 37
$L + \tau_2 \rightleftharpoons \tau_1 + \beta$	2100 ± 50	U_2	L	~ 39	~ 44	~ 17
$L + \beta \rightleftharpoons (\text{Mo}) + \tau_1$	1900 ± 20	U_3	L	~ 33	~ 46	~ 21
$L + \tau_1 \rightleftharpoons \varepsilon + (\text{Mo})$	1530	U_4	L	~ 20	~ 43	~ 37
$L + (\text{Mo}) \rightleftharpoons (\gamma\text{U}) + \varepsilon$	1185	U_5	L	~ 3	~ 29	~ 68
$(\beta\text{U}) \rightleftharpoons (\alpha\text{U}) + (\gamma\text{U}) + \varepsilon$	640	E_1	-	-	-	-
$(\gamma\text{U}) \rightleftharpoons \lambda + \varepsilon$	590	e_{20}	-	-	-	-
$(\gamma\text{U}) \rightleftharpoons \lambda + \varepsilon + (\text{Mo})$	580 ± 7	E_2	-	-	-	-
$(\gamma\text{U}) + \varepsilon \rightleftharpoons \lambda + (\alpha\text{U})$	570	U_6	-	-	-	-

Table 4: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Property, per mole of atoms [J, mol, K]	Comments
τ_1 , $\text{UMoC}_{1.7}$	25 - 1827	$\Delta_f G^\circ = -168824 - 2.89 \cdot T$ (± 17000)	[1975Uga2] approximation
	700 - 900	$\Delta_f G^\circ = -146632 - 15.0 \cdot T$ (± 8200)	[1996Ana] methane-hydrogen gas equilibration technique
τ_2 , UMoC_2	727 - 927	$\Delta_f G^\circ = -274658 + 90.0 \cdot T$	[1973-1974Nar] derived from galvanic cell measurements
	25 - 1827	$\Delta_f G^\circ = -193970 - 2.89 \cdot T$	[1975Uga2] approximation
	700 - 900	$\Delta_f G^\circ = -151961 - 13.7 \cdot T$ (± 8100)	[1996Ana] methane-hydrogen gas equilibration technique
	25	$S^\circ = 93.05$	[1975Uga2] estimation

The diagram illustrates the relationship between C-Mo, C-U, and Mo-U isotopes, showing mass numbers, chemical symbols, and various mathematical expressions representing isotopic relationships and uncertainties.

C-Mo

- 2589±9 e_1
 $1 \Rightarrow \delta + (C)$
- ~2525 e_3
 $\delta \Rightarrow 1 + \eta$
- 2515±9 e_4
 $1 \Rightarrow \beta + \eta$
- 2205±9 e_6
 $1 \Rightarrow (Mo) + \beta$
- 1956±15 e_8
 $\delta \Rightarrow \eta + (C)$
- 1647±15 e_{10}
 $\eta \Rightarrow \beta + (C)$

C-U

- 2557 e_2
 $1 \Rightarrow \varepsilon + (C)$
- 1823±10 p_2
 $\varepsilon' + \varepsilon'' \Rightarrow \mu$
- 1793 p_3
 $\mu + \varepsilon \Rightarrow \kappa$
- 1768±5 e_9
 $\varepsilon \Rightarrow \kappa + (C)$

Mo-U

- 2270 e_5
 $L \Rightarrow \tau_2 + \beta$
- 2160 e_7
 $L \Rightarrow \varepsilon + \tau_2$
- 2170 p_1
 $L + \tau_2 \Rightarrow \tau_1$
- 2100±50 $L + \tau_2 \Rightarrow \tau_1 + \beta$ U_2
- 1900±20 $L + \beta \Rightarrow (Mo) + \tau_1$ U_3
- 1530 $L + \tau_1 \Rightarrow \varepsilon + (Mo)$ U_4

Relationships and Expressions:

- $L + (Mo) + \beta$
- $L + \tau_2 + \beta$
- $L + \tau_2 + \tau_1$
- $L + \tau_2 \Rightarrow \varepsilon + \tau_1$
- $\tau_2 + \varepsilon + \tau_1$
- $\tau_2 + \tau_1 + \beta$
- $L + \tau_1 + \beta$
- $\beta + (Mo) + \tau_1$
- $L + (Mo) + \tau_1$
- $L + \varepsilon + \tau_1$
- $\tau_1 + \varepsilon + (Mo)$
- U_5

Fig. 1a: C-Mo-U. Partial reaction scheme

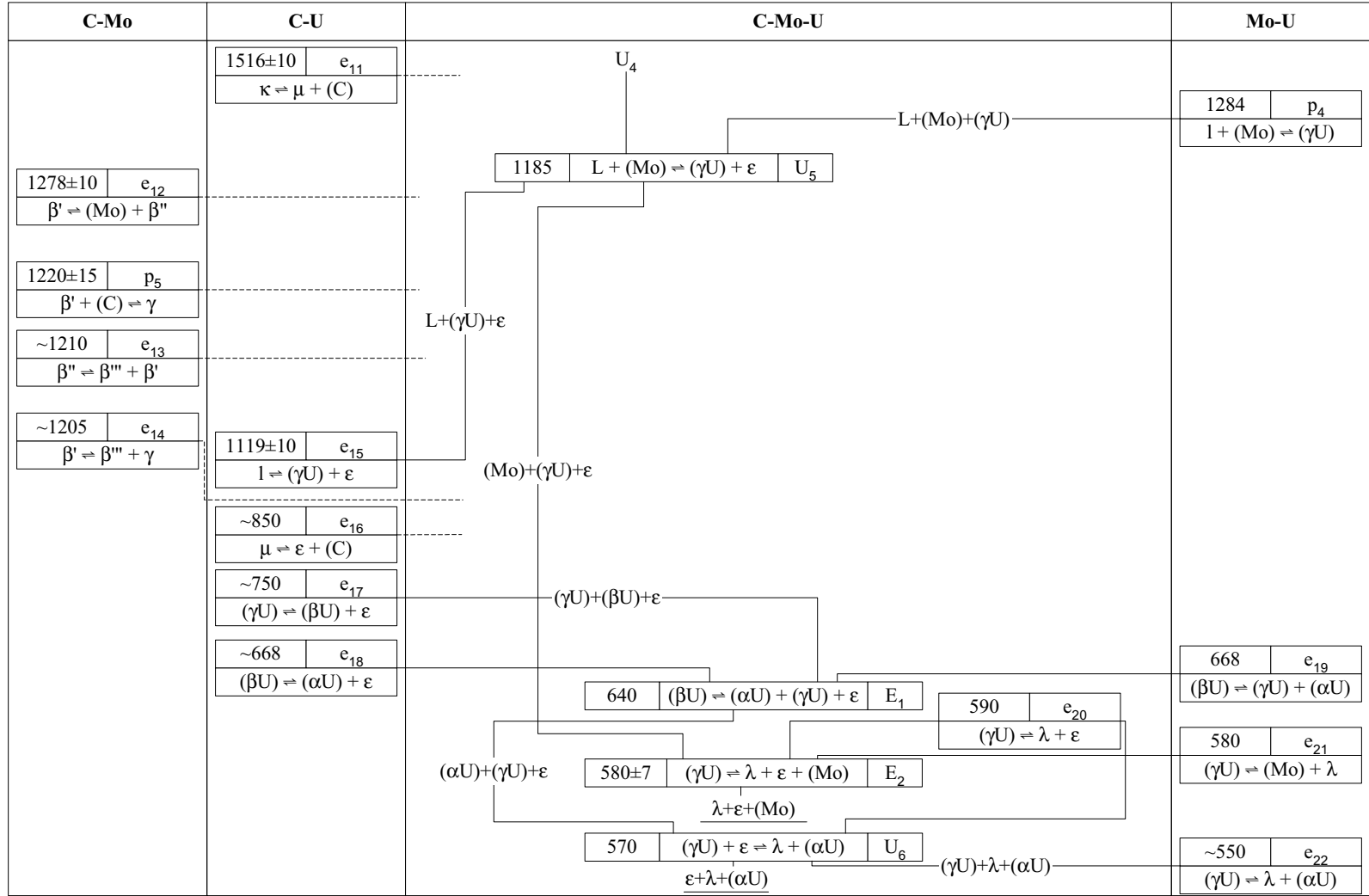
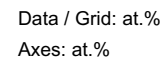


Fig. 1b: C-Mo-U. Partial reaction scheme

Data / Grid: at.%
Axes: at.%



Data / Grid: at. %
Axes: at. %

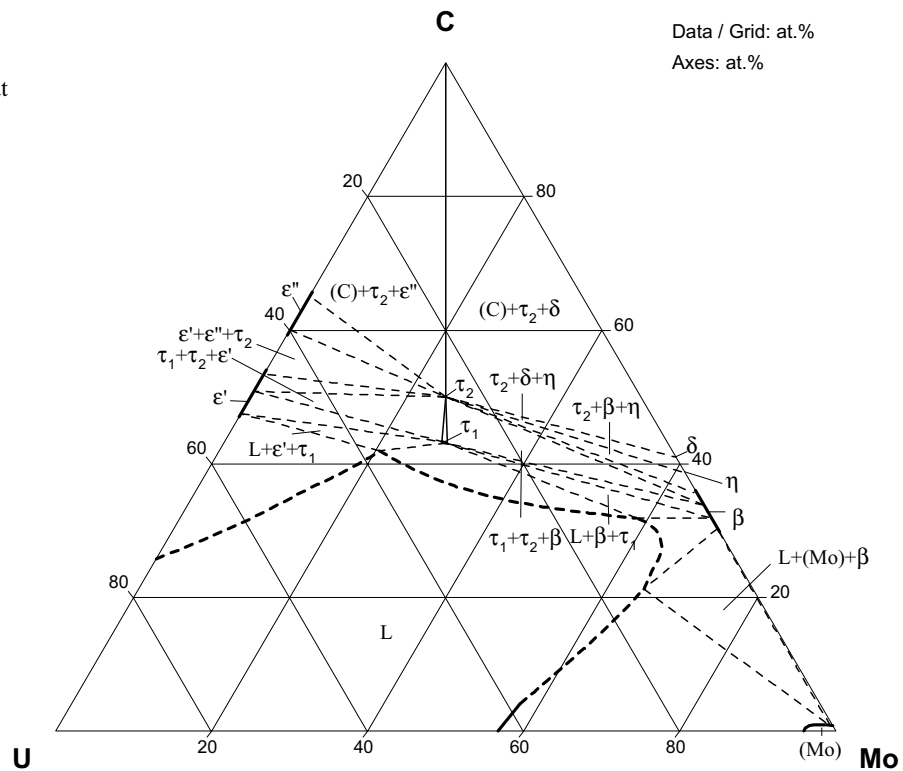


Fig. 4: C-Mo-U.
Isothermal section at
1800°C

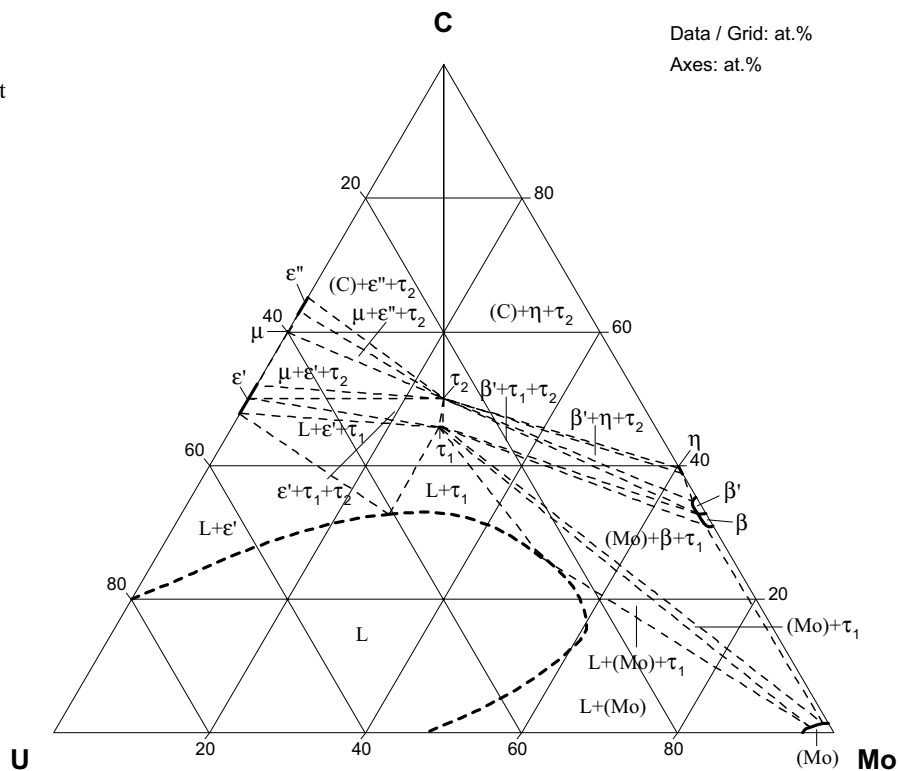


Fig. 5: C-Mo-U.
Isothermal section at
1525°C

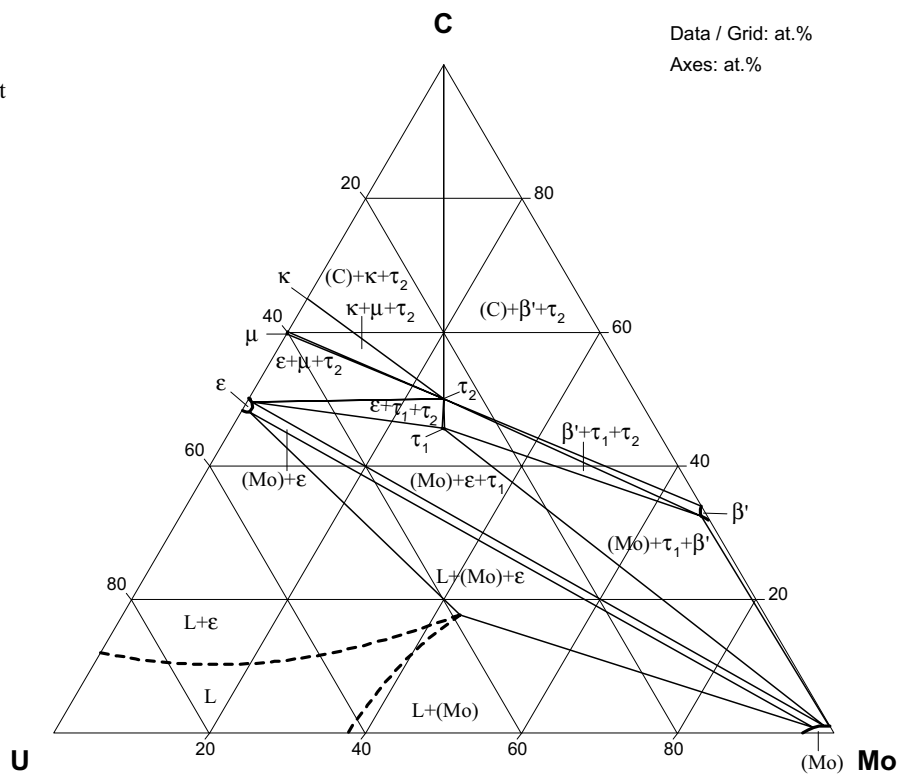


Fig. 6: C-Mo-U.
Isothermal section at
1500°C

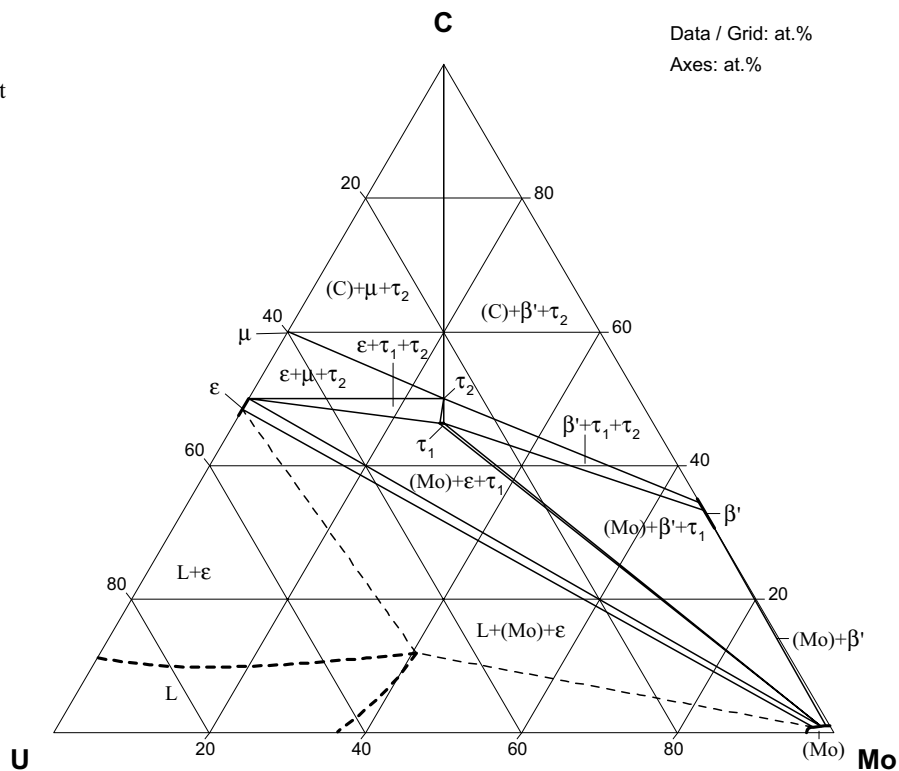


Fig. 7: C-Mo-U.
Partial isothermal
section at 900°C

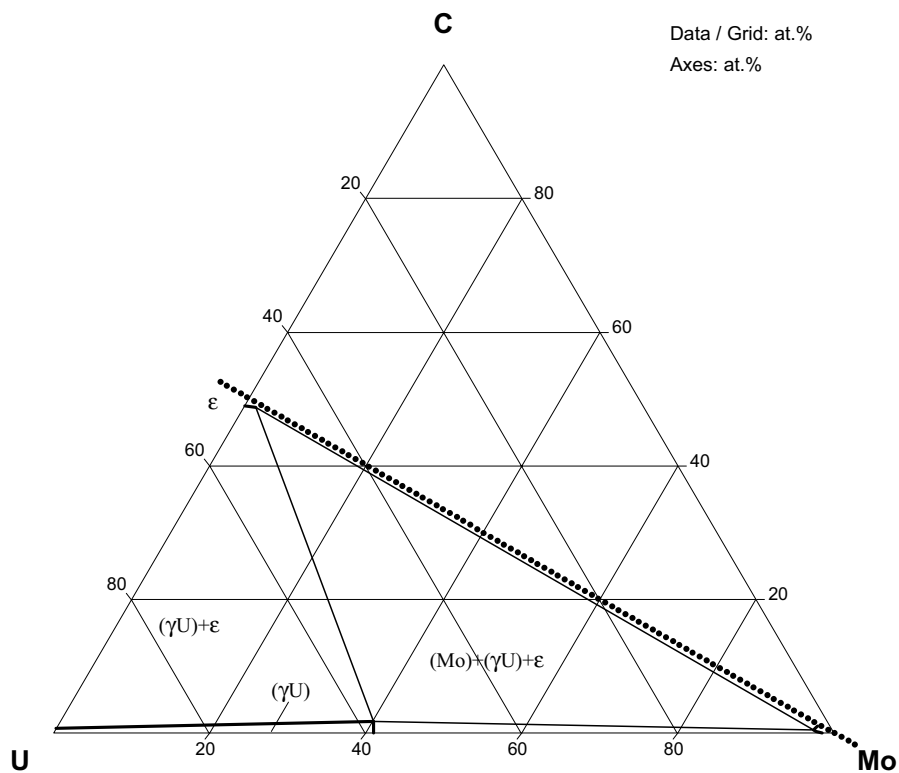


Fig. 8: C-Mo-U.
Temperature -
composition section
UMoC₂ - Mo

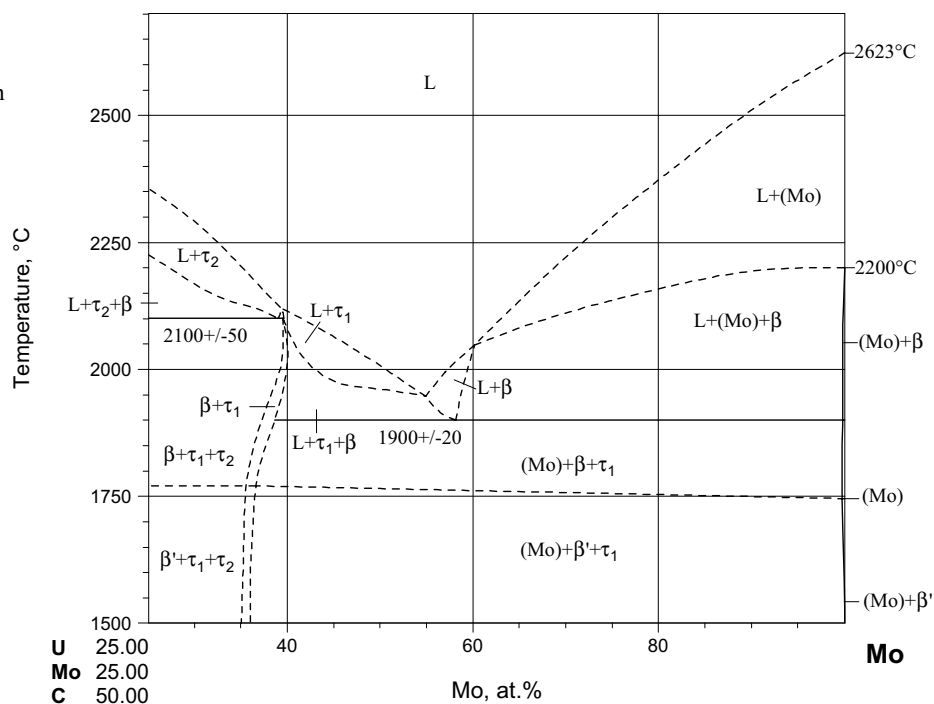


Fig. 9: C-Mo-U.
Temperature -
composition section
UC - Mo

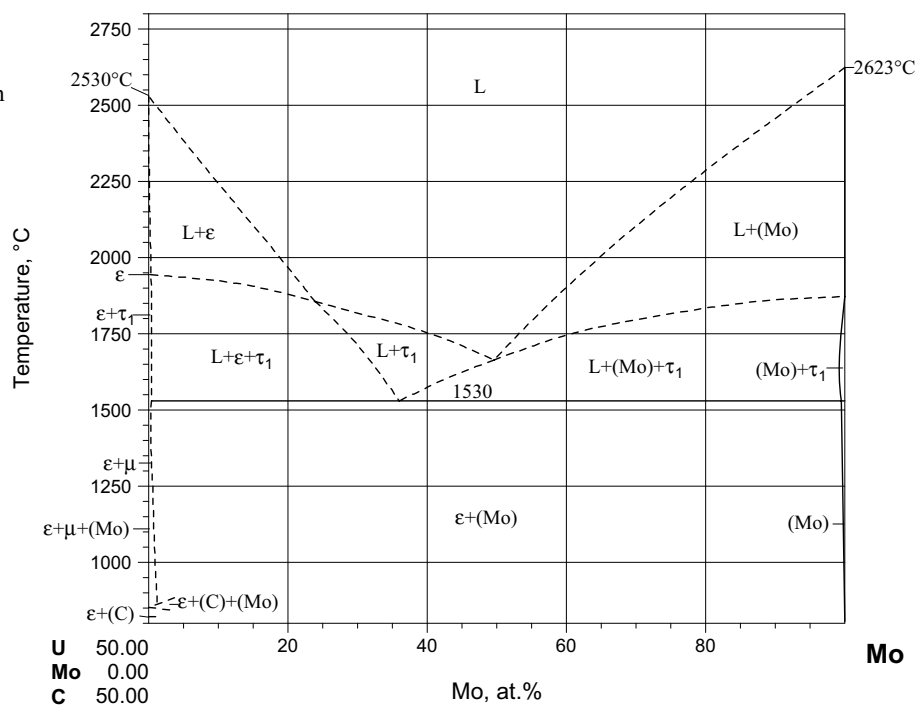


Fig. 10: C-Mo-U.
Temperature -
composition section
 $U_{50}Mo_{50}C$

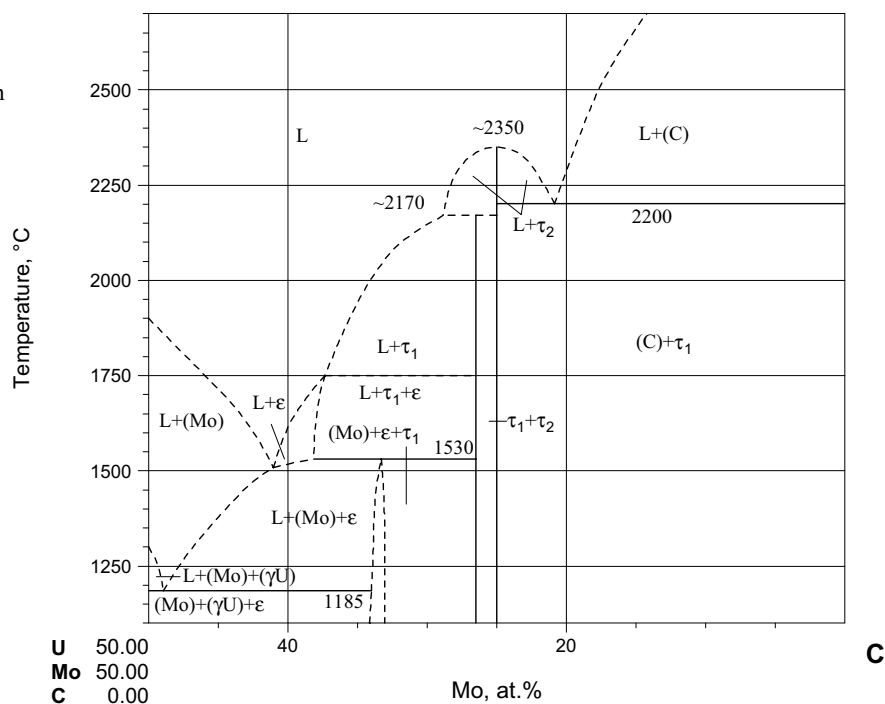


Fig. 11: C-Mo-U.
Partial temperature -
composition section
at 5 at.% C

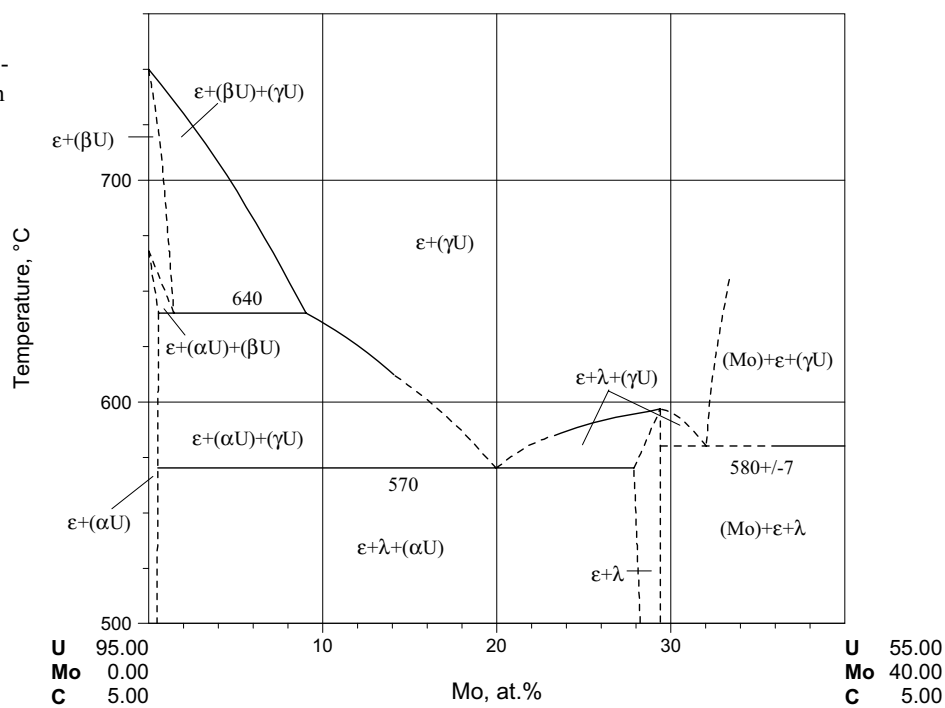


Fig. 12: C-Mo-U.
Partial temperature-
composition section
at 15 at.% C

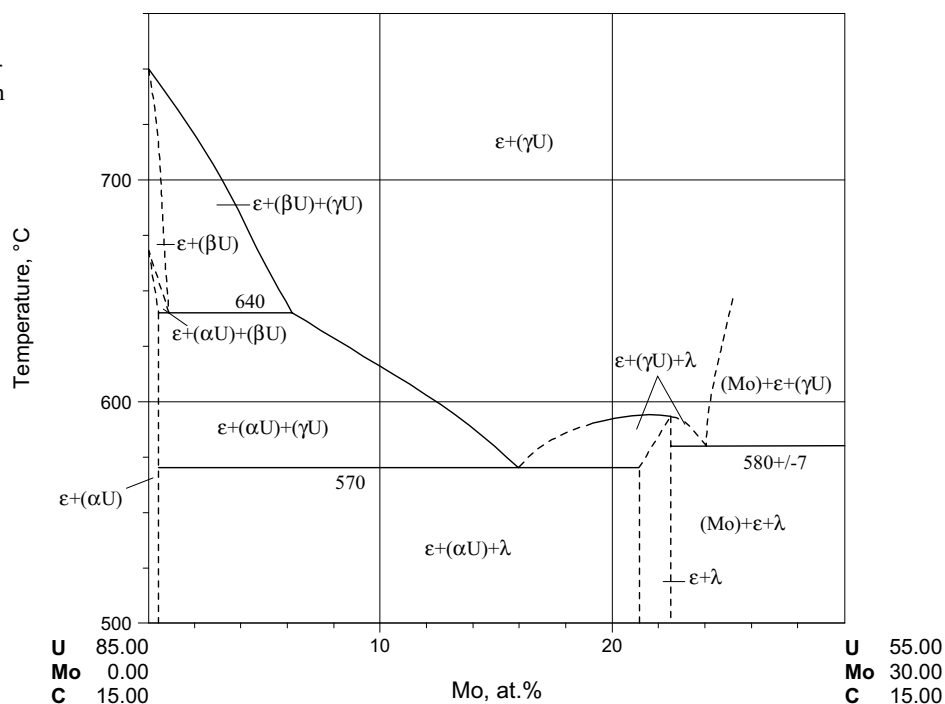


Fig. 13: C-Mo-U.
Temperature
dependence of the
carbon potential in the
three-phase field
 $\epsilon + (Mo) + \tau_1$

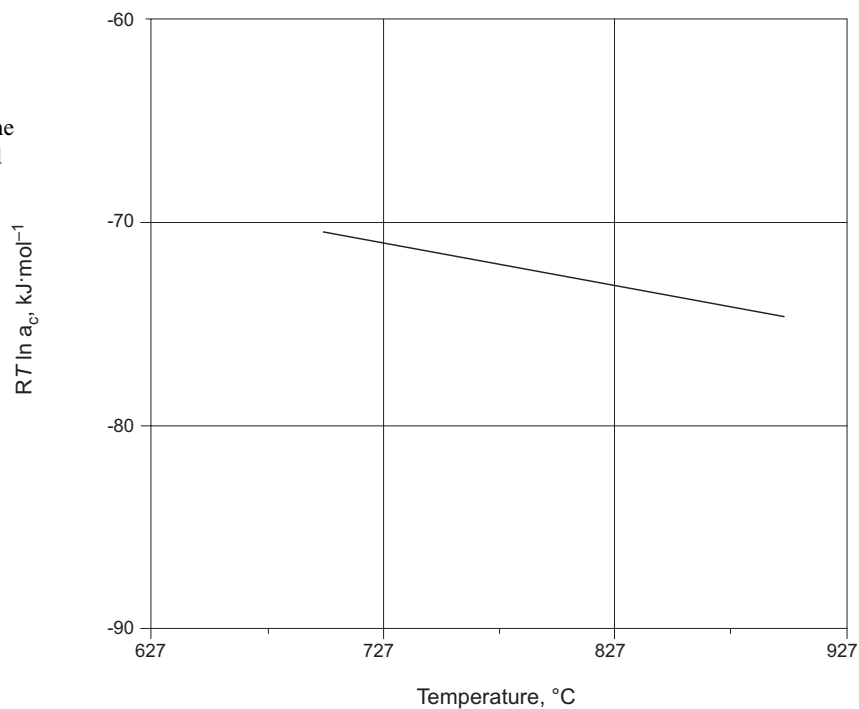


Fig. 14: C-Mo-U.
Temperature
dependence of the
carbon potential in the
three-phase field
 $\epsilon + \tau_1 + \tau_2$

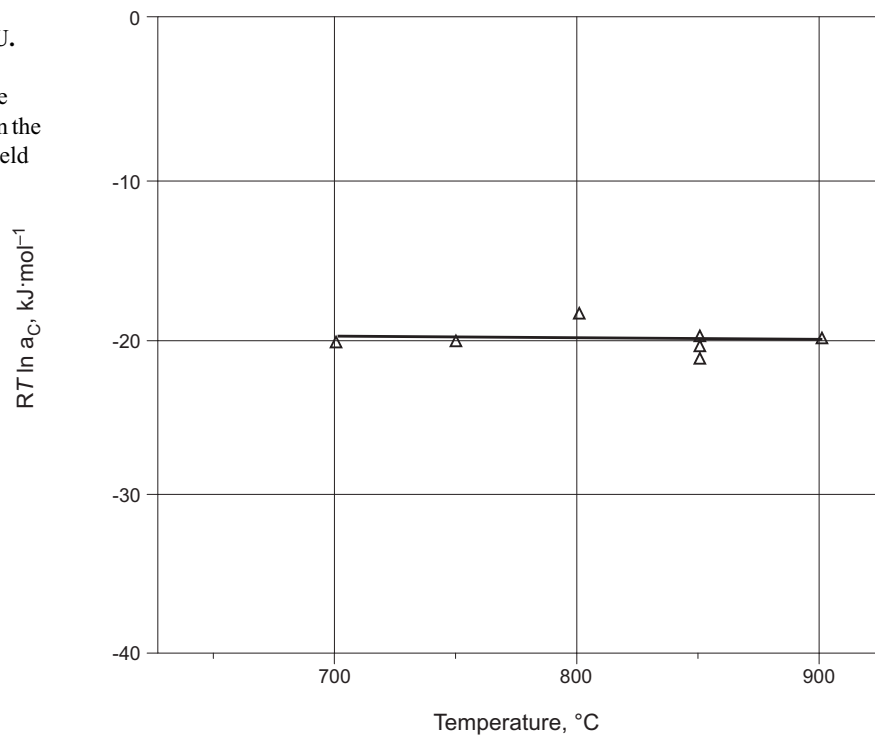


Fig. 15: C-Mo-U.
Thermal diffusivities
of UMoC_2 and
 $\text{UMoC}_{1.7}$

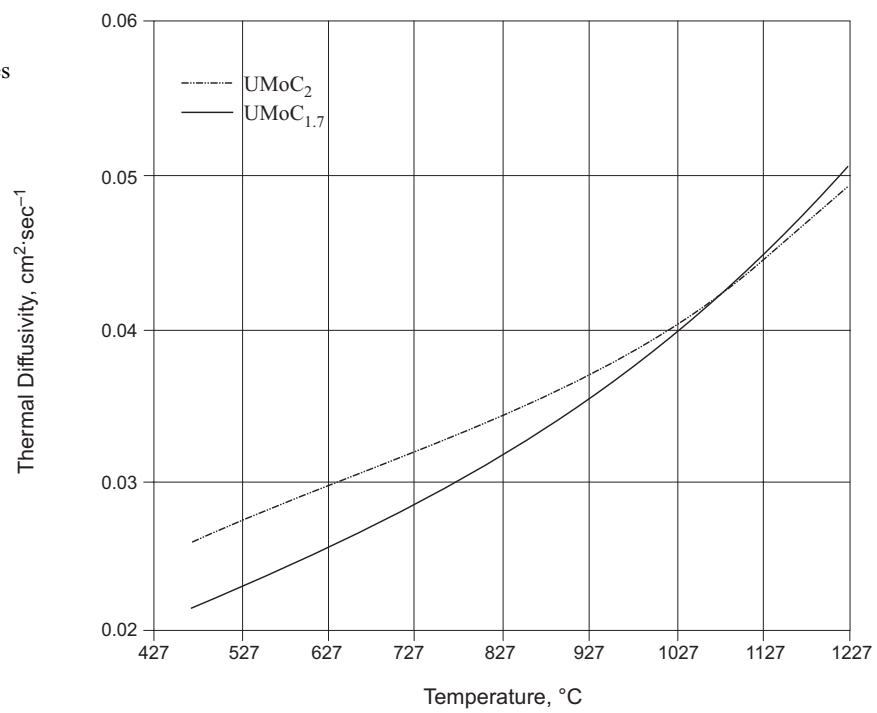
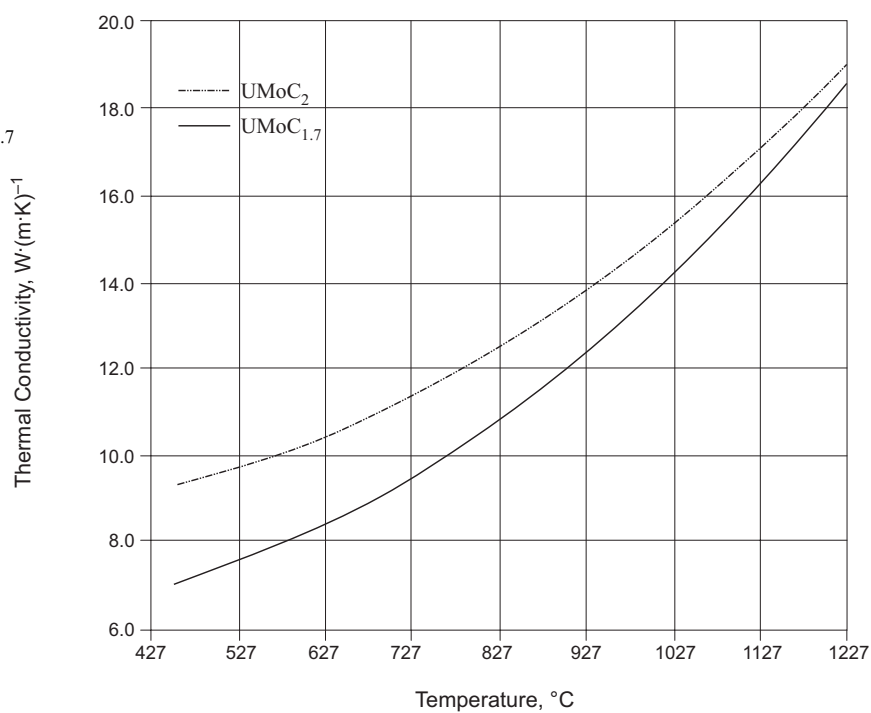


Fig. 16: C-Mo-U.
Thermal
conductivities of
 UMoC_2 and $\text{UMoC}_{1.7}$
normalized to 100%
theoretical density



Carbon – Palladium – Plutonium

Volodymyr Ivanchenko, Tatiana Pryadko

Introduction

For an understanding of the chemical constitution of an irradiation carbide nuclear fuel, a knowledge of the phase relationships of the individual fission product elements with the C-Pu system is required. The list of elements in the fission products includes palladium, and thus there is the interest in studying the C-Pd-Pu system. Experimental studies of this system are restricted to two works only. [1970Hai] performed constitutional studies in U and Pu carbide fission product systems including C-Pd-Pu. [1975Hol] presented an isothermal section for 1200°C based on the experimental results of [1970Hai] and common similarities in the phase equilibria observed in the actinide-platinum group metal-carbon systems. The PuC_2 carbide in the accepted C-Pu phase diagram decomposes eutectoidally at 1700°C, and therefore, does not take part in phase equilibria at 1200°C [1975Hol]. The absence of a two-phase region between PuC_2 and PuPd_3 was experimentally confirmed by [1982Hol]. The isothermal section at 1200°C published in [1977Hol, 1984Hol1, 1984Hol2] is the same as that published in [1975Hol, 1982Hol]. The compositions of alloys, as well as the experimental techniques used to study the C-Pd-Pu system are presented in Table 1.

Binary Systems

The C-Pd binary system is accepted from [Mas2]. The C-Pu system is accepted from [1969Lea] because the C-Pu phase diagram presented by [Mas2], with reference to [1970Gre], shows a polymorphic transformation of PuC_2 at 1660°C and the presence of PuC_2 at room temperature as an equilibrium low-temperature modification. Actually, [1970Gre] showed that low-temperature PuC_2 is a metastable phase. In the accepted C-Pu phase diagram, PuC_2 decomposes eutectoidally to Pu_2C_3 and carbon at 1660°C. The main discrepancies are concerned with the Pd-Pu system. The Pd-Pu system presented by [Mas2] was redrawn from [1967Kut]. [1967Kut] reported the presence of four compounds in this system: Pu_5Pd_4 , PuPd , Pu_4Pd_5 and PuPd_3 . Their crystal structures were not identified. Later, [1975Cro, 1973Cro, 1976Cro] reported the crystal structures of PuPd , Pu_3Pd_4 and Pu_3Pd_5 . The stoichiometry of the Pu_3Pd_4 and Pu_3Pd_5 compounds is different from that reported by [1967Kut]. Hence, the experimental information available is not enough to provide a well defined Pd-Pu system. This uncertainty is not critical in this case because the isothermal section presented by [1982Hol] was constructed for 1200°C, which is higher than the temperature of formation of the intermetallic compounds in the Pd-Pu system apart from PuPd_3 .

Solid Phases

No ternary compounds have been found in the C-Pd-Pu system. Some discrepancies in the literature are concerned with the temperature interval over which the PuC_2 carbide is stable. Room temperature X-ray powder diffraction analysis of PuC_2 samples quenched from above the transition temperature indicated that this compound is isostructural with tetragonal UC_2 [1965Cha]. The high-temperature X-ray diffraction studies have indicated that the equilibrium high-temperature structure is cubic [1970Gre]. As it was shown by [1970Gre], substantial amounts of bct PuC_2 were obtained by quenching from the fcc PuC_2 + graphite field at approximately $500 \text{ K}\cdot\text{s}^{-1}$. It was assumed, that this species was metastable in the C-Pu system and was formed by a diffusionless transformation where the cubic dicarbide is quenched fast enough to kinetically inhibit decomposition. When cooling rates were reduced to approximately $10 \text{ K}\cdot\text{s}^{-1}$, no bct PuC_2 was observed in the quenched samples; however substantial amounts of a material of unknown structure were present. [1970Gre] proposed that this phase was also a kinetically trapped metastable phase, possibly resulting from a massive transformation. The structural data of the unary and binary phases are given in Table 2.

Isothermal Sections

The isothermal section at 1200°C constructed by [1982Hol] is presented in Fig. 1. As was mentioned earlier, [1975Hol, 1982Hol] accepted the C-Pu phase diagram in which PuC_2 decomposes eutectoidally at ~1700°C.

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Table 1: Investigations of the C-Pd-Pu Phase Relations, Structures and Thermodynamics

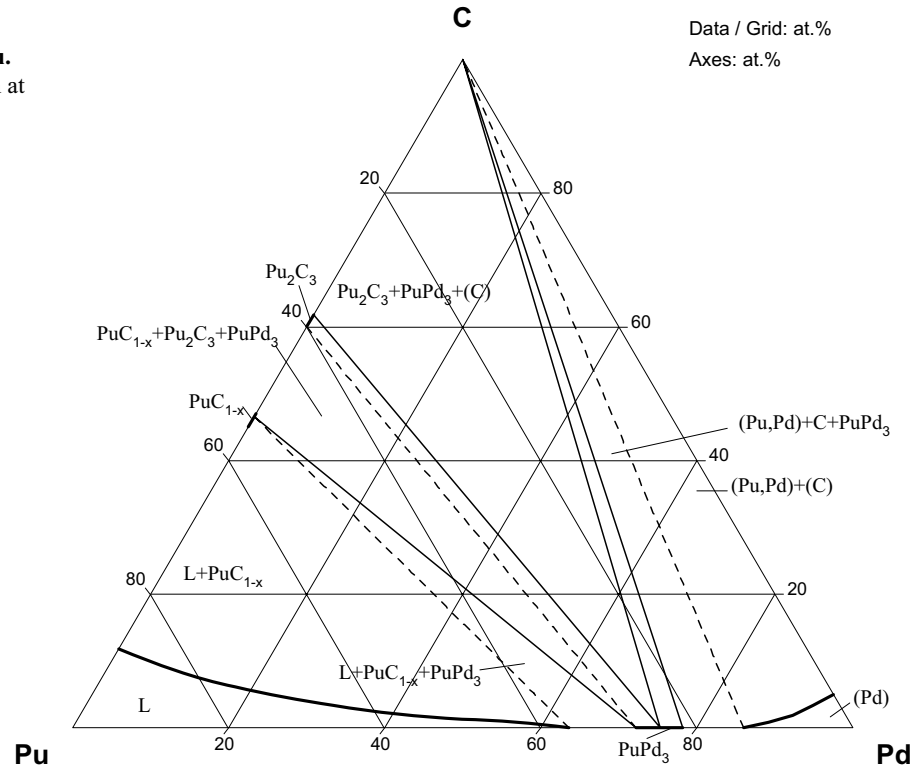
Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1970Hai]	X-ray diffraction, electron micro-probe analysis, ceramographic analysis	annealed at 800°C for 260 h and at 1000°C for 72 h, Pu ₂ PdC ₂ , PuC+Pu ₂ C ₃ +PuPd ₃
[1982Hol]	Optical light microscopy, X-ray diffraction, electron micro-probe analysis	annealed at 1200°C for 40 h, 20 at.% Pu-60 at.% Pd-20 at.% C, PuC _{1-x} +Pu ₂ C ₃ +PuPd ₃

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) ≤ 3827 (S.P.)	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.90	at 25°C [Mas2]
(Pd) < 1555	<i>cF4</i> <i>Fm$\bar{3}$m</i> Cu	<i>a</i> = 389.03	at 25°C [Mas2]
(εPu) 640 - 483	<i>cI2</i> <i>Im$\bar{3}$m</i> W	<i>a</i> = 363.43	[Mas2]
(δ'Pu) 483 - 463	<i>tI2</i> <i>I4/mmm</i> In	<i>a</i> = 332.61 <i>c</i> = 446.30	[Mas2]
(δPu) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}$m</i> Cu	<i>a</i> = 463.71	[Mas2]
(γPu) 320 - 215	<i>oF8</i> <i>Fddd</i> γPu	<i>a</i> = 315.87 <i>b</i> = 576.82 <i>c</i> = 1016.2	[Mas2]
(βPu) 215 - 125	<i>mC34</i> <i>C2/m</i> βPu	<i>a</i> = 1183 <i>b</i> = 1045 <i>c</i> = 923 β = 138.7° <i>a</i> = 928.4 <i>c</i> = 1046.3 <i>b</i> = 785.9 β = 92.13°	[V-C2] [Mas2]
(αPu) < 125	<i>mP16</i> <i>P2₁/m</i> αPu	<i>a</i> = 618.3 <i>b</i> = 482.2 <i>c</i> = 1096.3 β = 101.97°	[Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Pu ₃ C ₂ < 575	-	-	[Mas2]
PuC < 1654	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	<i>a</i> = 497.2	[1975Hai]
Pu ₂ C ₃ < 2050	<i>cI40</i> <i>I$\bar{4}3d$</i> Pu ₂ C ₃	<i>a</i> = 813.13	[1969Lea]
βPuC ₂ ~2230 - 1660	<i>c**</i>	<i>a</i> = 569.0	[1970Gre]
αPuC ₂ < 1660	<i>tI6</i> <i>I4/mmm</i> CaC ₂	<i>a</i> = 363 <i>c</i> = 609.4	[1965Cha] metastable [1970Gre]
Pu ₅ Pd ₄	-	-	[Mas2]
PuPd 1150 - 950	<i>oP8</i> <i>Pnma</i> FeB	<i>a</i> = 703.6 <i>b</i> = 455.0 <i>c</i> = 566.3	[1975Cro]
Pu ₃ Pd ₄	<i>hR42</i> <i>R$\bar{3}$</i> Pu ₃ Pd ₄	<i>a</i> = 1334.4 <i>c</i> = 574.4	[1973Cro]
Pu ₃ Pd ₅	<i>oC32</i> <i>Cmcm</i> Pu ₃ Pd ₅	<i>a</i> = 920.1 <i>b</i> = 715.9 <i>c</i> = 977.1	[1976Cro]
PuPd ₃	<i>cP4</i> <i>Pm$\bar{3}m$</i> AuCu ₃	<i>a</i> = 410.2	[1970Hai]

Fig. 1: C-Pd-Pu.
Isothermal section at
1200°C



Carbon – Palladium – Thorium

Andy Watson, Lesley Cornish

Introduction

Interest in this ternary system is with respect to equilibria between fission products and constituent elements in cladding and structural materials. However, very little work has been carried out on this system. The only phase equilibrium study is the work of [1971Hol], which produced an isothermal section for 1100°C. Fourteen samples were prepared by arc-melting thorium turnings (0.3% O), palladium (purity >99.9%) and spectroscopic grade graphite. The cast samples were then annealed under high vacuum for 50 h before investigation by XRD and optical microscopy. This work has been quoted in a number of reviews [1975Hol, 1984Hol1, 1984Hol2].

Binary Systems

The binary systems are accepted from [Mas2]. The C–Th system has 4 carbide phases, but the monocarbide (designated here as ThC_{1-x}) and γThC_2 are structurally related to (αTh). At high temperatures, the two phase regions between the (αTh) and ThC_{1-x} , and between ThC_{1-x} and γThC_2 disappear. Three alternative versions of the C–Th phase diagram are available in [S], each focussed on the region from 45 - 70 at.% C, but that produced in [Mas2] is preferred as it is based on more recent work.

Solid Phases

Solid phases associated with the system are given in Table 1. No ternary phases have been reported.

Isothermal Sections

The isothermal section for 1100°C given by [1971Hol] is shown in Fig. 1. Some additions (in the Pd corner) and alterations have been made in order to maintain consistency with the C–Pd and C–Th binary phase diagrams.

Miscellaneous

Adding boron has produced a compound $\text{ThPd}_2\text{B}_2\text{C}$ that shows superconductivity with a critical temperature of 14.5 K [1994Sar, 1994Zan].

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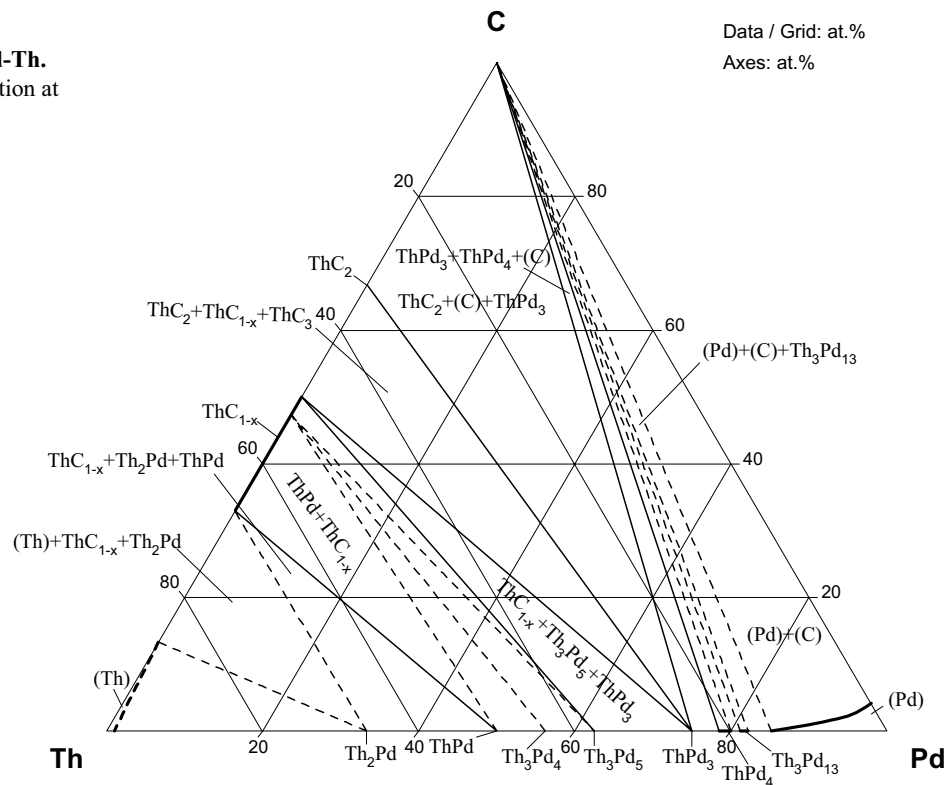
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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (graphite) < 3827	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	$a = 246.12$ $c = 670.90$	at 25°C [Mas2] Sublimation point
(Pd) < 1555	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 389.03$	at 25°C [Mas2] dissolves ~8 at.% C at 1504°C, ~15 at.% Th at 1145°C [Mas2].
(βTh) 1755 - 1360	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 411$	[Mas2] dissolves ~9 at.% C at 1707°C, < 1 at.% Pd
(αTh) < 1360	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 508.42$	at 25°C [Mas2] dissolves < 1 at.% Pd
Th ₃ Pd ₁₃ < 1215	<i>tI*</i>	-	18 - 19 at.% Th [Mas2]
ThPd ₄ < 1340	<i>cP4</i> <i>Pm$\bar{3}m$</i> AuCu ₃	$a = 411.3 \pm 0.3$	[V-C2] 19 (at 1215°C) - 21.5 at.% Th [Mas2]
ThPd ₃ ≤ 1575	<i>hP16</i> <i>P6₃/mmc</i> Ni ₃ Ti	$a = 585.8 \pm 0.3$ $c = 981.4 \pm 0.4$	[V-C2] 22.5 (at 1340°C) - 25 at.% Th [Mas2]
Th ₃ Pd ₅ < 1387	<i>hP8</i> <i>P$\bar{6}2m$</i>	$a = 714.9 \pm 0.3$ $c = 389.9 \pm 0.2$	[V-C2] 37.5 at.% Th [Mas2]
Th ₃ Pd ₄ < 1325	<i>hR42</i> <i>R$\bar{3}$</i>	$a = 1364.6$ $c = 584.7$	[V-C2] 42.9 at.% Th [Mas2]
ThPd < 1412	<i>oP8</i> <i>Pnma</i> FeB	$a = 724.9 \pm 0.5$ $b = 457.1 \pm 0.3$ $c = 585.6 \pm 0.4$	[V-C2] 50 at.% Th [Mas2]
Th ₂ Pd < 1162	<i>tI12</i> <i>I4/mcm</i> CuAl ₂	$a = 731.3 \pm 0.4$ $c = 594.2 \pm 0.4$	[V-C2] 66.7 at.% Th [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ThC_{1-x} < 2500	$cF8$ $Fm\bar{3}m$ NaCl	$a = 532.21 \pm 0.05$	[V-C2] 50 < x < 56 at.% Th at 25°C [Mas2]
γThC_2 2610 - 1470	$cF8$ $Fm\bar{3}m$ NaCl	$a = 580.6$	[V-C2]
βThC_2 1495 - 1255	$tI4$ $I4/mmm$ CoO	$a = 422.1 \pm 0.3$ $c = 539.4 \pm 0.3$	[V-C2]
αThC_2 < 1440	$mC12$ $C2/c$ ThC_2	$a = 668.4 \pm 0.2$ $b = 422.0 \pm 0.1$ $c = 673.5 \pm 0.2$ $\alpha = 103.91 \pm 0.01^\circ$	[V-C2]

Fig. 1: C-Pd-Th.
Isothermal section at
1100°C



Carbon – Palladium – Uranium

Volodymyr Ivanchenko, Tatiana Pryadko

Introduction

The reaction behavior of multicomponent systems containing actinide carbides is of great interest for many problems in nuclear technology. Of particular importance in this respect are ternary systems involving the transition metals, which are the most frequently occurring fission products. The clearest way of surveying the reaction behavior for specific combination of elements at high temperatures is to extract information from the appropriate phase diagrams. The list of elements in fission products includes palladium. This fact triggered the interest to study the C-Pd-U system. Experimental studies of this system are limited to two works only. [1970Hai] performed constitutional studies in U carbide fission product system including the C-Pd-U. A preliminary ternary phase diagram at 1300°C has been given by [1971Hol]. Compositions of alloys, as well as experimental technique used to study the C-Pd-U system are presented in Table 1.

Binary Systems

The C-Pd binary system is accepted from [Mas2]. The Pd-U is accepted from [1992Oka], who took into account results of [1991Kle]. Despite the fact that the C-U system presented in [Mas2] is based on [1967Sto] there is a substantial difference between them. [Mas2] shows a single-phase region between UC and βUC_2 as one phase (δ), that leads to the appearance of the two-phase regions: $\text{I}+\delta$ and $\delta+\text{C}$ on both sides from the borders of the δ phase. Actually, the phase designated by [Mas2] as δ represents a solid solution between UC and βUC_2 with the graded junction from the NaCl type to the CaF_2 type structure realized by a gradual change of the carbon atom fraction located in the tetrahedral interstices for the octahedral ones. In accordance with [1967Sto] such designation is consistent with the existence of a miscibility gap at lower temperatures. This is accepted by in the present evaluation.

Solid Phases

No ternary compounds have been found in the C-Pd-U system [1970Hai, 1971Hol]. Some discrepancies in literature data are concerned with the stoichiometry of compounds existing in the Pd rich region of the Pd-U system. [1968Ter] found, that UPd_3 , UPd_4 and UPd_8 exist in the range of 75 to 100 at.% Pd rather than UPd_3 , UPd_4 , UPd_5 , U_2Pd_{11} and U_2Pd_{17} reported by [1964Pel]. [1991Kle] confirmed the results of [1968Ter]. The “ UPd_5 ” compound with the fcc structure reported by [1987Zol] may be regarded as supersaturated nonequilibrium Pd based solid solution. The transformation of “ UPd_5 ” into the hexagonal UPd_5 compound under high temperature treatment, reported by [1987Zol], may be regarded as a result of nonequilibrium solid state reaction and this phase most likely is metastable. [2003Hea] examined the behavior of the UPd_3 crystal lattice under the pressure up to 53 GPa. The study does not reveal any volume anomaly, which could be associated with a delocalization of the $5f$ electronic states, in the entire pressure range. Crystal structure of unary and binary phases is presented in Table 2.

Isothermal Sections

The isothermal section at 1300°C published by [1971Hol] was constructed basing on his own results of the study of two alloys 25U-25Pd-50C (at.%) and 40U-20Pd-40C (at.%). These results well coincide with those presented by [1970Hai], who studied alloys of the nominal composition U_2PdC_2 and UPdC_2 . This section was reproduced by [1975Hol, 1977Hol, 1982Hol, 1984Hol1, 1984Hol2]. It is presented in Fig. 1 with minor modifications, that take into account the latest results concerning the location of the liquid region and the homogeneity regions of UPd_3 and (Pd) in the binary systems and the absence of the UPd_5 compound in the assessed Pd-U system.

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- [1984Hol1] Holleck, H., “Ternary Carbide Systems of Actinoids with Transition Metals of Other Groups” in “*Binary and Ternary Transition Metal Carbide and Nitride Systems*” (in German), Petzow, G. (Ed.) Gebrueder Borntraeger Berlin, Stuttgart, 92-111 (1984) (Crys. Structure, Phase Diagram, Phase Relations, Review, 91)
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Table 1: Investigations of the C–Pd–U Phase Relations, Structures and Thermodynamics

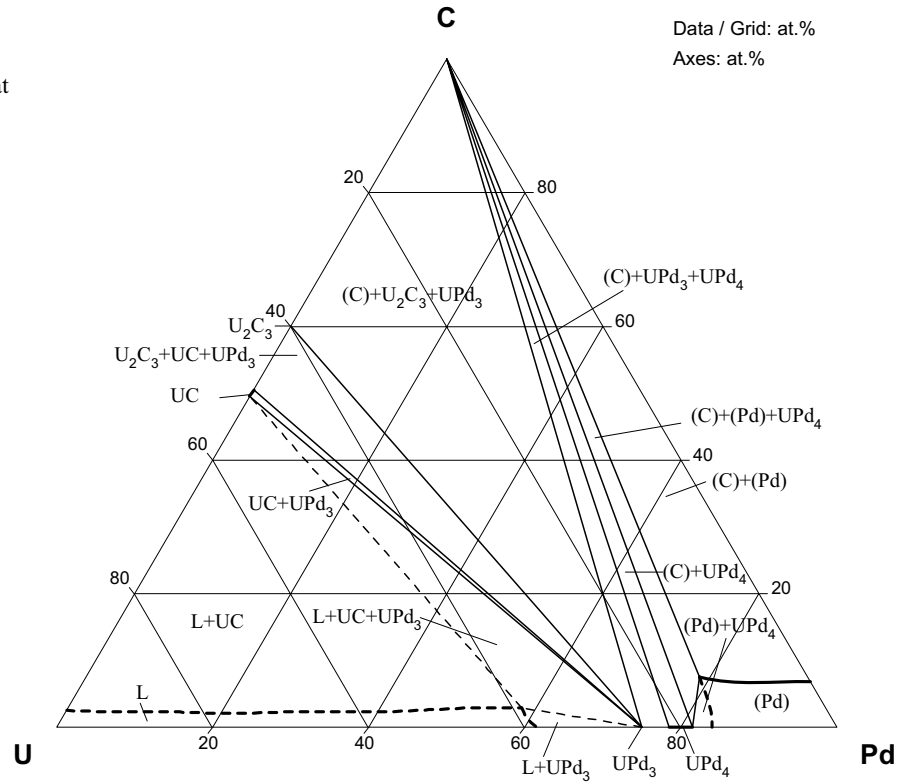
Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1970Hai]	X-ray diffraction, electron probe micro analysis, ceramographic analysis	annealed at 800°C for 200 h and at 1250°C for 60 h, U ₂ PdC ₂ , UPdC ₂
[1971Hol]	X-ray diffraction, optical light microscopy	annealed at 1300°C for 63 h, 25 at.% U+25 at.% Pd+50 at.% C; 40 at.% U+20 at.% Pd+40 at.% C, UC ₂ +UPd ₃ , U ₂ C ₃ +UPd ₃ , UC+U ₂ C ₃ +UPd ₃

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) ≤ 3827 ± 50 (S.P.)	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.90	at 25°C [Mas2] sublimation point
(Pd) < 1555	<i>cF4</i> <i>Fm$\bar{3}$m</i> Cu	<i>a</i> = 389.03 <i>a</i> = 401.1 <i>a</i> = 406.1 ± 0.1	pure Pd, at 25°C [Mas2] 15.0 ± 0.2 at.% U [1991Kle] at 1050°C 16.6 at.% U, may be supersaturated metastable solid solution, [1987Zol]
(γU) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}$m</i> W	<i>a</i> = 352.4	pure U, [Mas2] dissolves ~ 5 at.% Pd at 998°C [1991Kle]
(βU) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> βU	<i>a</i> = 1075.9 <i>c</i> = 565.6	pure U, [Mas2]
(αU) < 668	<i>oC4</i> <i>Cmcm</i> αU	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	pure U, at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
UC < 2515	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	$a = 495.97$ $a = 495.63$	from 47 to 66 at.% C miscibility gap (critical point at 2050°C, 43.8 at.% C) [2001Che] stoichiometric [2001Che] 48 at.% C [2001Che]
β , UC ₂ 2434 - 1762	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF ₂ ?	$a = 545.0$	[2001Che] actually, “ β ,UC ₂ ” phase represents the UC phase in equilibrium with graphite [2001Che]
α , UC ₂ 1762 - 1477	<i>tI6</i> <i>I4/mmm</i> CaC ₂	$a = 351.90$ $c = 597.87$ $a = 352.41$ $c = 599.62$	U rich, [2001Che] C rich, [2001Che]
U ₂ C ₃ < 1833	<i>cI40</i> <i>I$\bar{4}3d$</i> Pu ₂ C ₃	$a = 808.89$	[1969Lea]
UPd 1047 - 970	-	-	50 at.% Pd [1991Kle]
U ₅ Pd ₆ 1110 - 980	-	-	54.54 at.% Pd [1991Kle]
UPd ₃ < 1640	<i>hP16</i> <i>P6₃/mmc</i> Ni ₃ Ti	$a = 577.0 \pm 0.1$ $c = 961.9 \pm 0.4$	[2003Hea]
UPd ₄ < 1585	<i>cP4</i> <i>Pm$\bar{3}m$</i> AuCu ₃	$a = 404.7$ to 407.4	from 19.1 ± 0.2 to 21.6 ± 0.2 at.% U at 1050°C, [1991Kle] defect structure
UPd ₈ < 800	<i>t*</i>	$a = 388.2$ $c = 408.3$	[1968Ter]
UPd ₅	<i>h*</i>	$a = 550.6 \pm 0.2$ $c = 703.4 \pm 0.5$	16.6 at.% U, [1987Zol] most likely is metastable

Fig. 1: C-Pd-U.
Isothermal section at
1300°C



Carbon – Plutonium – Rhodium

Lesley Cornish, Andy Watson

Introduction

The C-Pu-Rh system is of interest because of its links with the fission products when plutonium carbides are used as fuel in nuclear reactors [1970Hai]. Studies were made of the ternary systems comprising the most important actinides (Th, U and Pu), and many of the U- and Pu- systems had perovskite phases of the filled Cu_3Au structure. The latter structures are important because they are found in both irradiated oxide [1968Bra] and carbide [1970Bra] fast reactor conditions. The experimental studies of the system are listed in Table 1.

Binary Systems

The C-Rh and Pu-Rh binary systems are taken from [Mas2]. The C-Pu phase diagram from [Mas2] has been amended and is given in Fig. 1. The αPuC_2 compound shown in the phase diagram given in [Mas2] is omitted from Fig. 1, as according to [1970Gre], the phase is metastable. This compound does not appear in any of the earlier versions of the phase diagram. As well as the six polymorphs of Pu, there are eight intermetallic Pu-Rh compounds, three C-Pu intermetallic compounds, and no miscibility between C and Rh.

Solid Phases

The solid phases are given in Table 2. To date, no true ternary compounds have been reported, only an extension of the (Pu) and PuRh_3 phases into the ternary system [1975Hai, 1975Hol, 1977Hol, 1980Hol, 1984Hol1, 1984Hol2].

Isothermal Sections

In a review and assessment, [1984Hol1, 1984Hol2] gave an isothermal section at 1200°C showing no true ternary phases, but an extension of PuRh_3 as $\text{PuRh}_3\text{C}_{1-x}$. This was redrawn from [1975Hai] and [1980Hol] (Fig. 2). A partial isothermal section for 1300°C was given by [1977Hol]. The phase equilibria shown are virtually identical to those given for the same region at 1200°C. A tentative isothermal section at 800°C is shown in Fig. 3 taken from [1975Hai]. Alterations were made to the isothermal sections to ensure agreement with the accepted binary systems.

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Table 1: Investigations of the C-Pu-Rh Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1975Hai]	XRD, ceramography and EMPA of arc-melted samples, homogenized between 800 and 1250°C for up to 750 h	Isothermal section at 800°C
[1977Hol]	XRD of arc melted samples, homogenized at 1300°C	Rh rich alloys. Partial isothermal section at 1300°C
[1982Hol]	Arc-melted sample, annealed for 40 h at 1200°C. Metallography, atom probe and XRD	20Pu-60Rh-20C (at.%)

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C)	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.9	at 25°C [Mas2]
(εPu) 640 - 483	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 363.43	[Mas2]
(δ'Pu) 483 - 463	<i>tI2</i> <i>I4/mmm</i> In	<i>a</i> = 332.61 <i>c</i> = 446.30	[Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(δ Pu) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 463.71$	[Mas2]
(γ Pu) 320 - 215	<i>oF8</i> <i>Fddd</i> γ Pu	$a = 315.87$ $b = 576.82$ $c = 1016.2$	[Mas2]
(β Pu) 215 - 125	<i>mC34</i> <i>C2/m</i> β Pu	$a = 928.4$ $b = 1046.3$ $c = 785.9$	[Mas2]
(α Pu) < 125	<i>mP16</i> <i>P2₁/m</i> α Pu	$a = 618.3$ $b = 482.2$ $c = 1096.3$	at 25°C [Mas2]
(Rh)	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 380.32$ $a = 380.3$	at 25°C [Mas2] [1980Hol]
Pu ₃ C ₂ < 575	-	-	-
PuC < ~1654	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	$a = 497.25$	[Mas2], [V-C2]
Pu ₂ C ₃ ≈ 2050	<i>cI40</i> <i>I$\bar{4}3d$</i> Pu ₂ C ₃	$a = 813.2$ $a = 813.5$	isotope ²³⁹ Pu [V-C2] isotope ²⁴⁰ Pu [V-C2]
β PuC ₂ 2350 - 1660	-	$a = 569.6$	[Mas2], [V-C2]
α PuC ₂ < 1660	<i>tI6</i> <i>I4/mmm</i> CaC ₂	$a = 363.0$ $c = 609.4$	metastable [1970Gre], [V-C2]
Pu ₂ Rh < 940	-	-	[Mas2]
Pu ₅ Rh ₃ < 980	<i>tP32</i> <i>P4/ncc</i> Pu ₅ Rh ₃	$a = 1094.1$ $c = 602.03$	[Mas2], [V-C2]
Pu ₃₁ Rh ₂₀ < 1020?	<i>tI204</i> <i>I4/mcm</i> Pu ₃₁ Rh ₂₀	$a = 1107.6 \pm 0.4$ $c = 3693.3 \pm 0.12$	[Mas2], [V-C2]
Pu ₅ Rh ₄ < 1180	<i>oP36</i> <i>Pnma</i> Sm ₅ Ge ₄	$a = 726.3$ $b = 1448.0$ $c = 746.4$	[Mas2], [V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
PuRh < 1300	-	-	[Mas2]
Pu ₃ Rh ₄ < 1310	-	-	[Mas2]
PuRh ₂ < 1340	<i>cF</i> 24 <i>Fd</i> $\bar{3}m$ MgCu ₂	<i>a</i> = 748.8	[1961Mul], [V-C2]
PuRh ₃ C _{1-x}	<i>cP</i> 4 <i>Pm</i> $\bar{3}m$ CaTiO ₂	<i>a</i> = 409.8 <i>a</i> = 498.0	at PuRh ₃ C, 1200°C [1975Hai] [1984Hol1, 1984Hol2] possibly misquoting [1975Hai] 0 < <i>x</i> < 1
PuRh ₃ < 1495	<i>cP</i> 4 <i>Pm</i> $\bar{3}m$ Cu ₃ Au	<i>a</i> = 400.9 to 404.0 <i>a</i> = 404.0	[1961Mul], [V-C2] [1980Hol]

Fig. 1: C–Pu–Rh.
Amended C–Pu phase
diagram

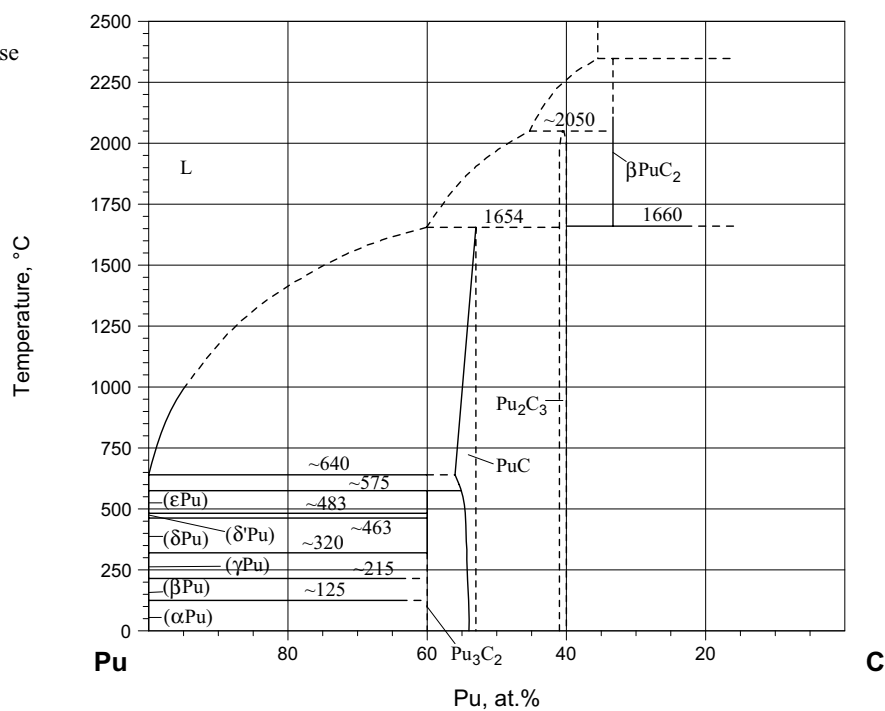


Fig. 2: C-Pu-Rh.
Isothermal section at
1200°C

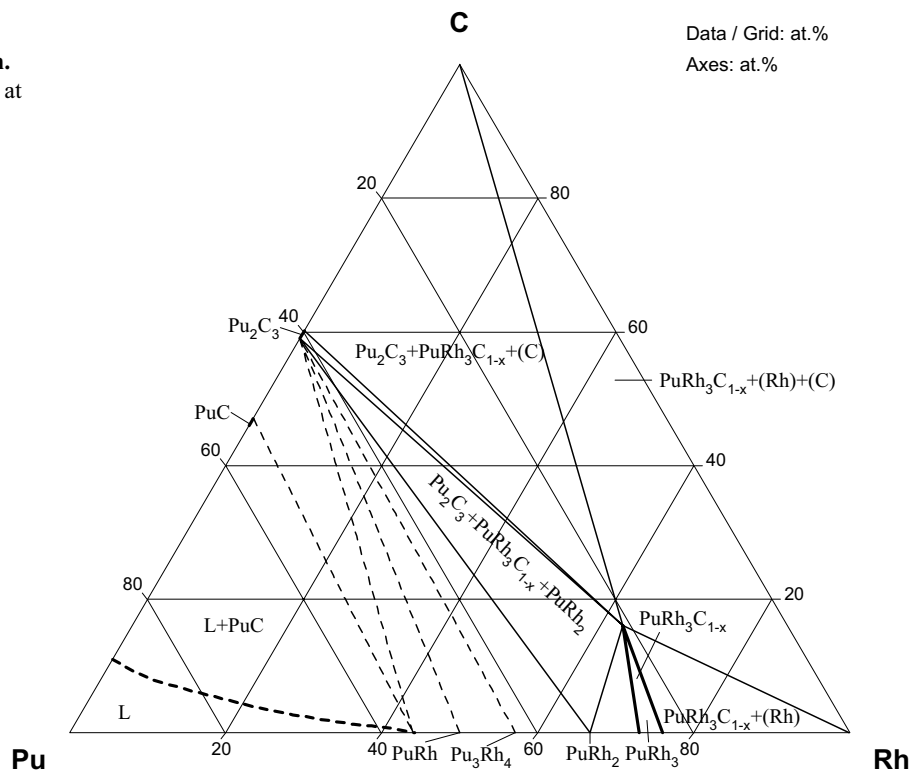
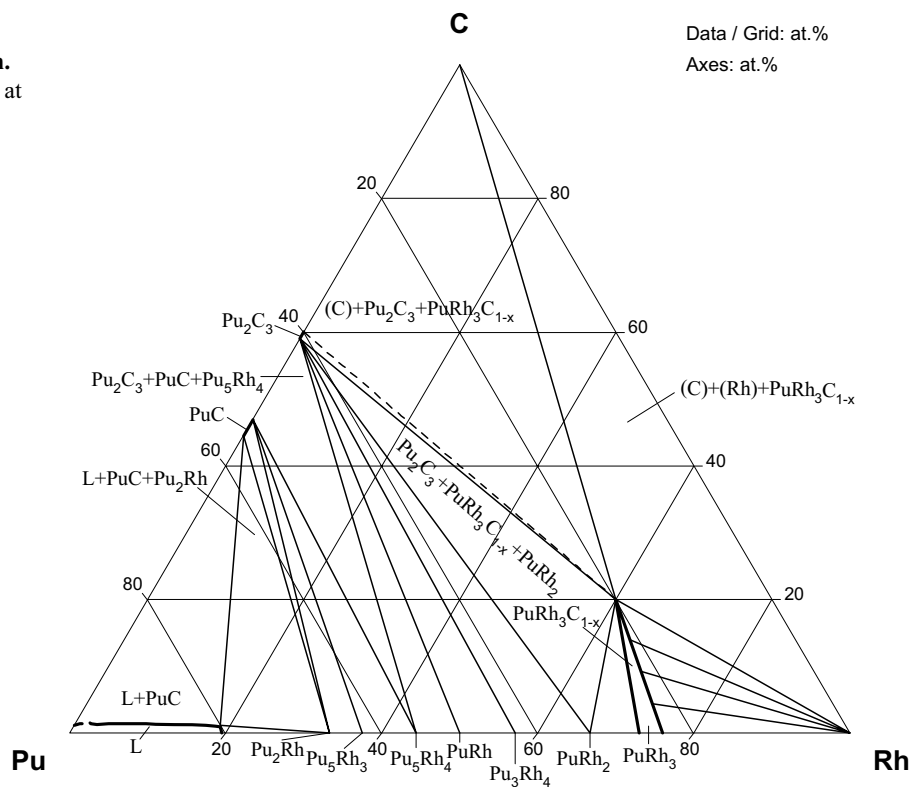


Fig. 3: C-Pu-Rh.
Isothermal section at
800°C



Carbon – Plutonium – Ruthenium

Lesley Cornish, Andy Watson

Introduction

The C-Pu-Ru system is of interest because some of the phases are related to fission products of irradiated plutonium carbides fuels in nuclear reactors [1970Hai]. Studies were made of the ternary systems comprising the most important actinides (Th, U and Pu), and many of the U- and Pu- systems were found to contain petrovskite phases of the filled Cu_3Au structure. These phases are important because they are found in both irradiated oxide [1968Bra] and carbide [1970Bra] fast reactor fuels. Experimental investigations of the system are given in Table 1.

Binary Systems

The C-Ru and Pu-Ru binary systems are taken from [Mas2]. However, the C-Pu phase diagram from [Mas2] is in error. The αPuC_2 compound shown in the phase diagram given in [Mas2] is, according to [1970Gre], metastable. This compound does not appear in any of the earlier versions of the phase diagram. An amended version of this phase diagram is given in the evaluation report for C-Pu-Rh (as Fig. 1) in the present volume. As well as six polymorphs of Pu, there are five intermetallic Pu-Ru compounds, three Pu-C intermetallic compounds, but no miscibility between C and Ru.

Solid Phases

The solid phases are given in Table 2. To date, only one true ternary compound has been reported: PuRu_3C , although (Pu) extends into the ternary system [1975Hai, 1977Hol, 1980Hol, 1984Hol1, 1984Hol2].

Isothermal Sections

In an assessment and review, [1984Hol1, 1984Hol2] gave an isothermal section at 1200°C showing the PuRu_3C ternary phase as a line compound, and (Pu) with an extension into the ternary, using information from [1975Hol] and [1980Hol] (Fig. 1). However, [1984Hol1, 1984Hol2] erroneously showed solid (Pu) in the isothermal section, which is impossible because it melts at 640°C [Mas2]. Figure 1 is similar to, but not in total agreement with, the partial section of [1977Hol] at 1300°C. The diagram of [1980Hol] is taken to be correct since it is later and complete. An isothermal section was also produced at 800°C by [1975Hai], and is shown in Fig. 2. Both the section at 800°C and that at 1200°C disagree with earlier work of [1970Hai] which suggested that Pu_2C_3 and PuRu_2 were in equilibrium with each other at these temperatures. Their later work contradicts this giving equilibrium between Pu_2C_3 and PuRu , presumably benefitting from longer annealing times. Figures 1 and 2 have been amended to ensure consistency with the accepted binary systems, particularly with respect to the homogeneity ranges for Pu_2C_3 and PuRu_2 which appear as having a range of homogeneity in the binary diagrams.

Thermodynamics

The Gibbs energy of formation of PuRu and PuRu_3C were estimated using data for the Pu carbides and PuRu_2 [1968Cam]. For PuRu ;

$$\Delta_f G^\circ (\text{PuRu}) < -78538 + 12.72T \text{ J}\cdot\text{mol}^{-1} \quad (800 < T < 1000^\circ\text{C})$$

For PuRu_3C ;

$$-89789 + 8.79T > \Delta_f G^\circ (\text{PuRu}_3\text{C}) > -218501 + 64.27T \text{ J}\cdot\text{mol}^{-1} \quad (662 < T < 796^\circ\text{C})$$

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Table 1: Investigations of the C-Pu-Ru Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1970Hai]	XRD, ceramography and EMPA of arc-melted samples, homogenised at 800 and 1000°C for up to 43 h	Isothermal section at 1000°C
[1975Hai]	XRD, ceramography and EMPA of arc-melted samples, homogenised between 800 and 1250°C for up to 750 h	Isothermal section at 800°C

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1977Hol]	XRD of arc melted samples, homogenized at 1300°C	Ru rich alloys. Partial isothermal section at 1300°C
[1982Hol]	Arc-melted sample, annealed for 40 h at 1200°C. Metallography, atom probe and XRD	20Pu- 60Ru-20C (at.%)

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C)	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.9	at 25°C [Mas2]
(εPu) 640 - 483	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 363.43	[Mas2]
(δ'Pu) 483 - 463	<i>tI2</i> <i>I4/mmm</i> In	<i>a</i> = 332.61 <i>c</i> = 446.30	[Mas2]
(δPu) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	<i>a</i> = 463.71	[Mas2]
(γPu) 320 - 215	<i>oF8</i> <i>Fddd</i> γPu	<i>a</i> = 315.87 <i>b</i> = 576.82 <i>c</i> = 1016.2	[Mas2]
(βPu) 215 - 125	<i>mC34</i> <i>C2/m</i> βPu	<i>a</i> = 928.4 <i>b</i> = 1046.3 <i>c</i> = 785.9	[Mas2]
(αPu) < 125	<i>mP16</i> <i>P2₁/m</i> αPu	<i>a</i> = 618.3 <i>b</i> = 482.2 <i>c</i> = 1096.3	at 25°C [Mas2]
(Ru)	<i>hP2</i> <i>P6₃/mmc</i> Mg	<i>a</i> = 270.58 <i>c</i> = 428.16	at 25°C [Mas2]
Pu ₃ C ₂ < 575	-	-	-
PuC ≤ 1654	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	<i>a</i> = 497.25	[Mas2], [V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Pu ₂ C ₃ ≤ 2050	<i>cI40</i> <i>I43d</i> Pu ₂ C ₃	<i>a</i> = 813.2 <i>a</i> = 813.5	isotope ²³⁹ Pu [V-C2] isotope ²⁴⁰ Pu [V-C2]
βPuC ₂ 2350 - 1660	<i>cF*</i>	<i>a</i> = 569.6	[Mas2], [V-C2]
αPuC ₂ < 1660	<i>tI6</i> <i>I4/mmm</i> CaC ₂	<i>a</i> = 363.0 <i>c</i> = 609.4	metastable [1970Gre], [V-C2]
Pu ₁₉ Ru < 325	-	-	[Mas2]
Pu ₃ Ru < 600	<i>oP16</i> <i>Pmmm</i> -	<i>a</i> = 621.6 <i>b</i> = 692.4 <i>c</i> = 809.3	[Mas2], [V-C2]
Pu ₅ Ru ₃ < 1025	<i>tI32</i> <i>I4/mcm</i> W ₅ Si ₃	<i>a</i> = 1074.5 ± 0.3 <i>c</i> = 571.9 ± 0.2	[Mas2], [V-C2]
PuRu < 1250	<i>cP2</i> <i>Pm3̄m</i> CsCl	<i>a</i> = 336.35 ± 0.6	[Mas2], [V-C2]
PuRu ₂ < 1600	<i>cF24</i> <i>Fd3̄m</i> Cu ₂ Mg	<i>a</i> = 747.2 ± 0.1	[Mas2], [V-C2]
* PuRu ₃ C	<i>cP4</i> <i>Pm3̄m</i> CaTiO ₃	<i>a</i> = 411.3	[1984Hol1] using [1975Hai, 1980Hol] [V-C2]

Fig. 1: C-Pu-Ru.
Isothermal section at
1200°C

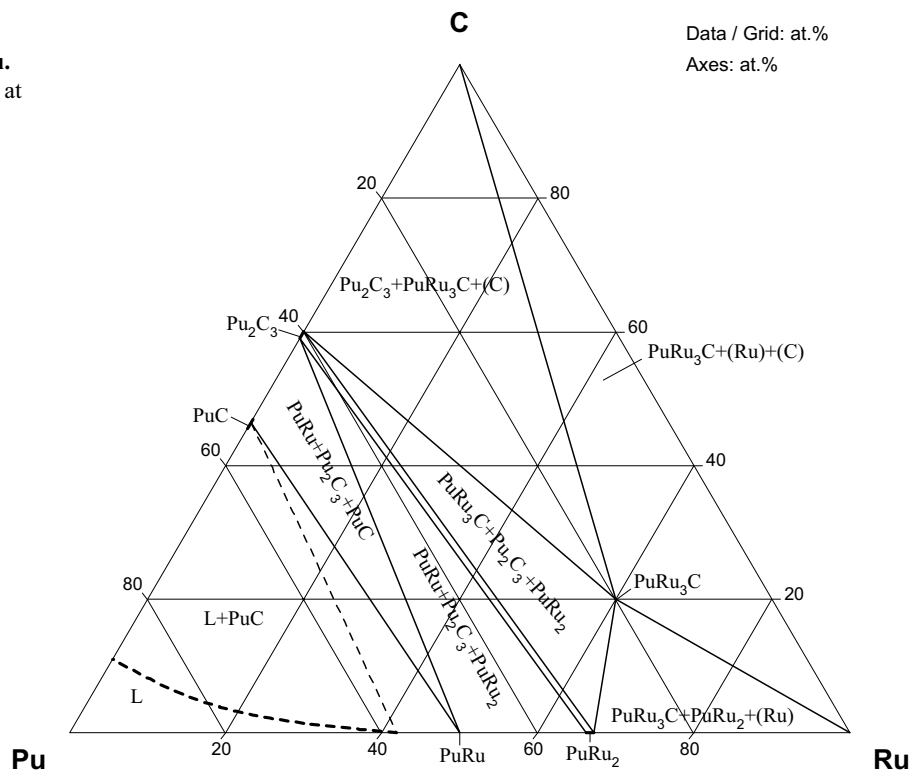
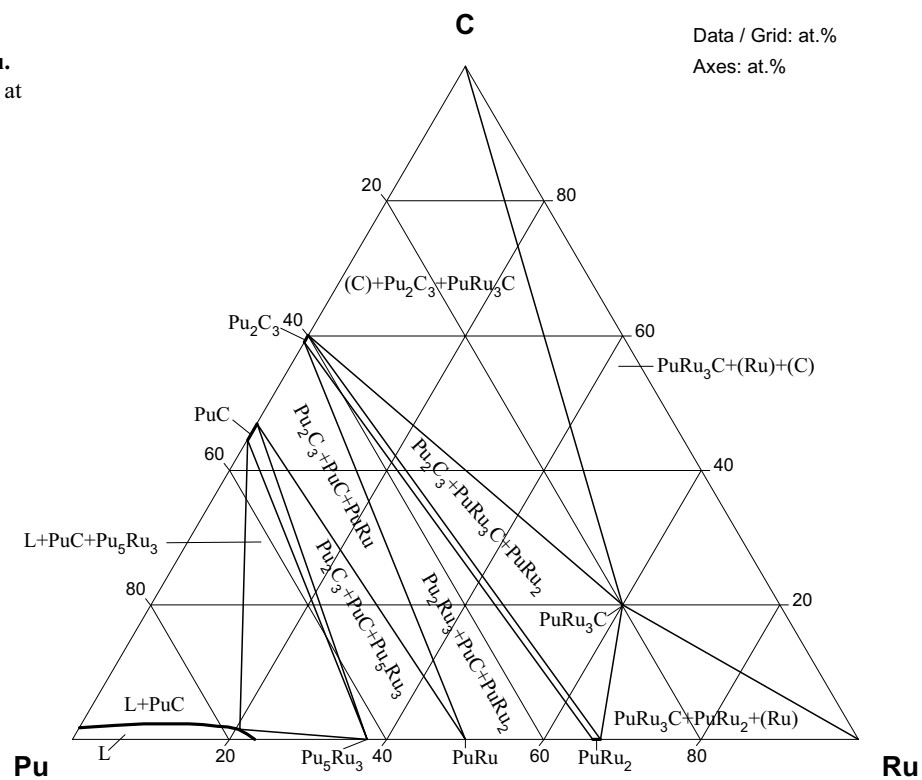


Fig. 2: C-Pu-Ru.
Isothermal section at
800°C



Carbon – Plutonium – Uranium

Kostyantyn Korniyenko, Nathalie Lebrun

Introduction

With a view to optimizing alloy composition for the preparation of plutonium-uranium carbide fuel and its operation in liquid-metal fast breeder reactors (LMFBR), information about phase relations in the corresponding ternary system C–Pu–U is of a great importance. But up to now this information has discrepancies and is not complete. It is presented in the literature as a partial reaction scheme [1963Ros1, 1981Udo, 1982Udo], liquidus and solidus temperatures and surfaces [1964Sta, 1965Far, 1967Rea, 1968Pot, 1969Lea, 1970Mar, 1976Ohs, 1982Udo], a series of isothermal sections [1963Ros1, 1963Ros2, 1970Mar, 1972Ker, 1975Hol, 1976Bro, 1981Udo, 1982Udo, 1984Hol] and temperature – composition sections [1981Udo, 1982Ogo, 1982Udo]. Phase content of the alloys and the crystal structures of the intermediate phases were studied by [1961Pas, 1963Nev, 1963Ros1, 1963Ros2, 1964Sta, 1967Rea, 1969Lea, 1976Bro, 2005Kut]. Thermodynamic properties were determined experimentally by [1964Sta, 1976Bro, 1976Ohs, 1977Fis]. The experimental methods used as well as the temperature and composition ranges studied are presented in Table 1. The literature related to the carbon-plutonium-uranium system was reviewed in [1968Pot, 1969Lea, 1970Mar, 1975Hol, 1978Kot, 1981Udo, 1982Udo, 1984Hol]. However, further amendment of character of the phase equilibria is necessary, in particular, the constitution of the liquidus and solidus surfaces, the reaction scheme and isothermal sections at different temperatures in the range of carbon content of more than 50 at. %.

Binary Systems

The C–Pu system is accepted from [Mas2]. Despite the fact that C–U system presented in [Mas2] is redrawn from [1967Sto] there is difference between them. The difference relates to the single-phase region between βUC and βUC_2 . In [Mas2] the, δ phase leads to appearance of two phase regions: $1 + \delta$ and $\delta + (\text{C})$ either side of the δ phase. Actually, the phase designated by [Mas2] as δ represents the solid solution between βUC and βUC_2 with gradual change from the NaCl type of structure to the CaF_2 type of structure realized by a gradual change in the fraction of carbon atoms located in the tetrahedral interstices with respect to the octahedral sites. In accordance with [1967Sto], such a designation is consistent with the existence of a miscibility gap at lower temperatures. It was accepted by [2001Che] during thermodynamic modeling of the C–U system. The accepted phase diagram of the binary boundary system Pu–U is reported in the chapter “Remarks on the Actinide Alloying Behavior” in the present volume. It is based on the thermodynamic calculation by [1991Lei].

Solid Phases

Crystallographic data about the unary and binary phases are listed in Table 2. No ternary phases with crystal structures different from those inherent in the unary and binary phases were determined. In the forming Pu–U binary system, the existence of a continuous series of solid solutions between isostructural ϵ modification of plutonium and γ modification of uranium takes place (labelled as the μ phase). Also, four continuous series of solid solutions between isostructural binary C–Pu and C–U phases exist (the ν , θ , ρ and ρ' phases).

The (Pu,U)C phase, labelled ν , exists below the melting point of the PuC phase ($\sim 1654^\circ\text{C}$) across the whole range of plutonium and uranium mutual substitution. The experimental evidence of this is presented in [1963Nev, 1963Ros1, 1963Ros2, 1984Hol]. At higher temperatures, liquid-solid and liquid fields are located down to 50 at. % C along the C–Pu binary system. The ν phase is stoichiometric with respect to its carbon content over a composition range from 0 to about 35 at. % Pu. A further increase in the plutonium content induces a deviation from ideal stoichiometry towards greater metal-to-carbon ratios to form the defect ν phase. According to the crystallographic investigation carried out by [1963Ros2], plutonium

expands the unit cell of the monocarbide over the composition range over which it retains its stoichiometric character. In the region of the defect structure, the lattice parameter decreases with increasing plutonium content, the extent of the decrease being dependent upon the carbon content.

The $(\text{Pu,U})_2\text{C}_3$ phase, labelled θ , exists below the melting temperature (1833°C) of the U_2C_3 phase across the whole range of plutonium and uranium mutual substitution. This feature was observed experimentally at 1600°C by [1975Hol] and at 1700 and 1550°C by [1967Rea] with annealed alloys equilibrated with an excess of carbon. The upper and lower limits of the lattice parameter along UC_2 – PuC_2 are reported in Table 2. The θ phase seems to disappear at about 850°C from the C–U binary system.

According to experimental results of an earlier publication presented by H.Holleck in [1984Hol], the $(\text{Pu,U})\text{C}_2$ phase, labelled ρ , is a continuous series of solid solutions between the isostructural βPuC_2 and βUC_2 phases, and exists in the system over the temperature range from ~ 1797 to 2227°C . The KCN type of structure was attributed to the ρ phase, but from crystal structure data accepted in this assessment (Table 2), this is not possible because the βPuC_2 phase structure type is not clear. The ρ phase was also reported by [1978Kot] whereas this phase was questioned in the assessment of published experimental data given by [1981Udo]. This problem has not been resolved.

Complete solid solubility between the tetragonal αPuC_2 and the αUC_2 structures was observed by [1967Rea] and [1969Lea] from plutonium-uranium dicarbide samples equilibrated with excess carbon at high temperature and quenched. But all attempts to prepare the cubic PuC_2 – UC_2 solid solutions were unsuccessful. In view of the fact that the equilibrium structure of βPuC_2 is known to be cubic, the tetragonal $(\text{Pu,U})\text{C}_2$ phase (labelled as ρ' in Table 2) may represent a metastable phase at higher plutonium concentrations [1969Lea].

According to the results of experimental investigations available in the literature, solubilities of the third component in the Pu_3C_2 , η and $(\epsilon\text{Pu},\gamma\text{U})$ phases as well as in solid solutions based on the components were not reported.

Invariant Equilibria

The partial reaction scheme is presented in Fig. 1. It was compiled on the basis of [1963Ros1, 1981Udo, 1982Udo] with some amendments to maintain compatibility with the forming binary systems. The data of [1963Ros1] concerned phase equilibria at temperatures below 750°C while [1981Udo] and [1982Udo] deal with equilibria at higher temperatures, including the participation of the liquid phase. In order to agree with temperatures of invariant processes in the ternary and boundary binary systems, some invariant four-phase equilibria were changed: U_1 at 2250°C , P_1 at 2135°C , D_1 at $1767 \pm 10^\circ\text{C}$ and P_2 at 1750°C instead of a P, U, P and U types proposed by [1982Udo], respectively. Also, the ternary reaction at 594°C proposed by [1963Ros1] has been considered as peritectoid P_3 . According to the data of [1982Udo], the co-ordinates of the U_1 and P_1 points are as follows (in at.%): $66.67\text{C}-27.88\text{Pu}-5.45\text{U}$ and $60\text{C}-17.68\text{Pu}-22.32\text{U}$, respectively. The ternary reaction $\text{L} + \beta\text{UC} + \beta\text{UC}_2 \rightleftharpoons \text{Pu}_2\text{C}_3$ suggested by [1982Udo] at 2440°C which involves the βUC and the βUC_2 phases, cannot lead to a ternary reaction since βUC and βUC_2 form a continuous solid solution v on the binary edge. Consequently, this reaction was not taken into account in the reaction scheme. The corresponding invariant equilibria have been reported in Table 3.

Liquidus, Solidus and Solvus Surfaces

[1964Sta] have determined the values of liquidus and solidus temperatures of a $\text{Pu}_{0.2}\text{U}_{0.8}\text{C}_{0.95}$ alloy as $2480 \pm 20^\circ\text{C}$ and about 2430°C , respectively, while the liquidus temperature of the $\text{Pu}_{0.05}\text{U}_{0.95}\text{C}_{0.98}$ alloy was reported to be about 2500°C . [1965Far] have corrected the last value to $2535 \pm 20^\circ\text{C}$ and reported the solidus temperature as $2520 \pm 25^\circ\text{C}$. [1967Rea] presented the melting points of alloy specimens in the range of compositions from 60 to about 100 at.% C. In the review of [1969Lea], the results of the experimental determination of liquidus and solidus temperatures of the alloys along the section $\text{Pu}:\text{U} = 1:1$ containing from 50 to 60 at.% C. [1976Ohs, 1982Udo] have presented the values of liquidus and solidus temperatures of alloys with 50 at.% C. On the basis of the above data, [1982Udo] assessed the constitution of the C–Pu–U system liquidus surface projection. They also compared their results with a schematic liquidus surface projection plotted by [1970Mar, 1982Udo] and noted that their own data possess a quantitative character.

The liquidus surface projection based on [1982Udo] with corrections according to the constitution of the binary systems accepted in this assessment, is shown in Fig. 2. [1982Udo] reported the existence of a monovariant curve which separates the UC and the βUC_2 phases. Since in the binary C–U these two phases form a continuous solid solution v , the corresponding monovariant curve on the liquidus surface has not been retained and the monovariant reaction $L + \text{UC} + \beta\text{UC}_2 \rightleftharpoons \text{U}_2\text{C}_3$ at 2240 °C has been deleted. The e_5e_8 monovariant curve (dashed line) joins the corresponding points in the C–Pu and C–U systems.

Isothermal Sections

Isothermal sections constructed by different authors on the basis of experimental investigations, with some corrections according to the accepted binary systems, are shown in Figs. 3 to 6. They correspond to the temperatures of 1600, 635, 570 and 400°C, respectively (the last three are in the range of compositions 0–50 at.% C).

The isothermal section at 1600°C (Fig. 3) is based on the calculation of [1975Hol], reported in the review of [1984Hol]. The upper limit of carbon content for the liquid phase field is shifted significantly in the direction of carbon corner. The position of the homogeneity range for the PuC phase is corrected. Two solid solutions, θ and v , take part in the phase equilibria. The carbon rich corner is still questionable and has been indicated with a question mark in Fig. 3. The αPuC_2 was not observed and a two-phase equilibrium $\text{Pu}_2\text{C}_3 + (\text{C})$ has been proposed [1975Hol, 1984Hol, 1982Udo]. [1969Lea] stipulates that αPuC_2 is metastable. More experimental investigations are needed.

The isothermal section at 635°C is presented in Fig. 4 according to the data of [1963Ros1] in the range of carbon contents up to 50 at.% C. The $L + \mu + v$ three-phase regions seem to be narrow by the mutual solubility of plutonium and uranium according to the two-phase $L + \mu$ regions in the Pu–U binary system. Consequently, the solubility of the liquid phase inside the ternary system along the Pu–U edge has been reduced compared with that suggested by [1963Ros1]. The unknown limits of the phase regions are indicated with dashed lines on the drawing (Fig. 4).

The isothermal section at 570°C shown in Fig. 5 is reproduced on the basis of experimental work carried out by [1963Ros1] and [1963Ros2] over the composition range of up to 50 at.% C. The phase equilibria involving the Pu_3C_2 phase were added according to its existence at this temperature along the C–Pu binary system. The $\mu + \eta + v$ region has been considered in this assessment to be narrower than in [1963Ros1] according to the accepted Pu–U binary system (phase equilibria as dashed lines in Fig. 5).

The isothermal section at 400°C is presented in Fig. 6 according to the data of [1963Ros1] in the region up to 50 at.% C. Some discrepancies in the borders of the phase fields are observed as compared with the edges of the accepted Pu–U binary diagram. The new regions are indicated as dashed lines in the Fig. 6.

Isothermal sections were also investigated between 2300 and 2000°C by [1970Mar] as indicated by [1982Udo]. On the basis of the available literature data on phase equilibria in the ternary system and their own C–Pu and C–U binary phase diagrams, [1981Udo] and [1982Udo] have calculated the isothermal sections over the wide temperature range (1200 to 2435°C). They determined the positions of the phase boundaries for the phase equilibria $v / (v + \theta)$, $v / (v + \theta + \rho)$ and $v / (v + \rho)$ with specimens having the ratio Pu:U = 1.4. The isothermal section at 2000°C was calculated by [1984Hol] who proposed the existence of a solid solution ρ between βPuC_2 and βUC_2 . This result is in disagreement with the work done by [1982Udo] who suggested two separate phases βPuC_2 and βUC_2 involving two- and three-phase equilibria with carbon. Moreover, a deeper region for the Pu_2C_3 phase has been proposed in [1982Udo]. All the calculated isothermal sections available in the literature up to 2000°C need further experimental investigation.

Temperature – Composition Sections

The temperature – composition section PuC–UC was constructed by [1981Udo] using the experimental data about liquidus and solidus temperatures presented in [1964Sta], [1976Ohs] and in review [1978Kot], as well as data about the $v / (v + \gamma)$ boundary [1975Hol]. This section is shown in Fig. 7. Slight modifications were done according to the binaries and the liquidus surface accepted in this assessment. The liquidus and solidus

curves were also calculated in this section using thermodynamic assumption [1982Ogo]. This later work is in contradiction with [1981Udo] and was not retained in this assessment.

Other isopleths were also assessed by [1981Udo] and [1982Udo]: Pu_2C_3 - U_2C_3 , PuC_2 - UC_2 and $\text{Pu}_{0.5}\text{U}_{0.5}\text{C}$ - $\text{Pu}_{0.5}\text{U}_{0.5}\text{C}_{1.5}$. The isopleth U_2C_3 - Pu_2C_3 was not retained since the βUC_2 and UC phases form a series of solid solution leading to the non existence of the ternary reaction at 2240 °C. The two others isopleths are reproduced on Figs. 8 and 9 with corrections according to the binaries. In the UC_2 - PuC_2 section, the ternary reaction at 1750 °C has been modified due to the higher transition temperature between the βUC_2 and αUC_2 phases. Moreover, the phase equilibria occurring at temperatures lower than 1700°C have not been retained in this assessment owing to the absence of the αPuC_2 phase which exists in the binary edge.

Thermodynamics

Values of thermodynamic properties for the ν single-phase alloy $\text{Pu}_{0.2}\text{U}_{0.8}\text{C}$ were determined by [1975Tet] and [1977Fis]. The enthalpy was estimated over the range 25 to 2275°C by [1977Fis] using the enthalpy values reported by [1975Tet, 1977Fis] down to 627°C, and in the range 866 to 2148°C. The heat capacity values were deduced using thermodynamic calculations and are quite good in comparison to those reported by [1975Tet]. The values of S°_T and $-(G^\circ_T - H^\circ_{298})/T$ for the ν phase were calculated by [1977Fis] from 25 to 2275°C. All of these data are listed in Table 4. [1972Ker] determined the relationship between free energy of some alloys with compositions between 50 and 60 at.% C.

[1964Sta] estimated the vapor pressure of Pu and U over $\text{Pu}_{0.2}\text{U}_{0.8}\text{C}_{0.95}$. Later, [1976Bro] measured the partial pressure of various species over $(\text{Pu},\text{U})\text{C} + (\text{Pu},\text{U})_2\text{C}_3$, $(\text{Pu},\text{U})\text{C}_2 + (\text{C})$, $(\text{Pu},\text{U})_2\text{C}_3 + (\text{C})$ specimens at 1600°C. All of the major experimental data of vapor pressure are reported in Table 5. The evaporation behavior of uranium-plutonium carbides has been studied in the high temperature phase fields $(\text{Pu},\text{U})\text{C}$, $(\text{Pu},\text{U})\text{C} + (\text{Pu},\text{U})_2\text{C}_3$, $(\text{Pu},\text{U})\text{C} + (\text{Pu},\text{U})\text{C}_2$ over the range of composition $(\text{Pu}_{0.2}\text{U}_{0.8})\text{C}_x$ with $1.014 \leq x \leq 1.30$ and temperature 1730-2230°C [1976Ohs]. A pressure-composition diagram has been deduced from the experimental data and is reported in Fig. 10. The $\log_{10}(p)$ values over $1/T$ are given in Table 5 for the single phase $(\text{Pu},\text{U})\text{C}$ and the two-phase region $(\text{Pu},\text{U})\text{C} + (\text{Pu},\text{U})_2\text{C}_3$. An increase in the heat of sublimation was observed for the different phase fields. For the $(\text{Pu},\text{U})\text{C}$ phase, this value varies from 361.57 kJ·mol⁻¹ to 432.2 kJ·mol⁻¹ for compounds $(\text{Pu}_{0.2}\text{U}_{0.8})\text{C}_x$ with $1.014 \leq x \leq 1.15$. In the two-phase region $(\text{Pu},\text{U})\text{C} + (\text{Pu},\text{U})_2\text{C}_3$, an increase from 382.5 to 455.2 kJ·mol⁻¹ for compounds $(\text{Pu}_{0.2}\text{U}_{0.8})\text{C}_x$ with $1.15 \leq x \leq 1.30$.

Notes on Materials Properties and Applications

Among the fuel materials that have been considered for LMFBR designs, plutonium-uranium carbide, in general, has material properties more conducive to achieving high performance than either the mixed-oxide or metal fuel [1975Bie, 1968Far]. The high density of the heavy metal and low density of the light atom of the carbide allow high breeding ratios. The high thermal conductivity in combination with a sufficiently high allowable fuel temperature permits high linear power. The adoption of the concept of the sodium-bonded fuel rod, in particular, will alleviate the problems of achieving high burnup. By providing sufficient room for the accommodation of fuel swelling, the cladding need not be required to restrain the swelling fuel as in the case with gas-bonded fuel rod designs [1969Sto]. It was found that the swelling rate strongly depends on the temperature for mixed carbides [1982Zim]. At high temperature, it decreases with increasing burnup due to a saturation of the fission gas bubble porosity. The swelling rate of carbide fuel under cladding restraint corresponds with the free swelling at relative low temperature. The irradiation-induced creep rate of carbide fuel seems to be considerably dependent on its porosity [1984Die]. The general information concerning investigations of the properties of C-Pu-U materials is listed in Table 6. [1961Pas] found that the electrical resistivity of a $(\text{Pu},\text{U})\text{C}$ solid solution which is of interest for a fast reactor is $1.5 \cdot 10^{-6} \Omega \text{ m}$. Coefficients of expansion of $\text{Pu}_{0.05}\text{U}_{0.95}\text{C}_{0.98}$ and $\text{Pu}_{0.2}\text{U}_{0.8}\text{C}_{0.95}$, according to the data of [1964Sta], in the temperature range 25-1400°C are equal to $12.6 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $11.9 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$,

respectively. Creep rates in the (Pu,U)C specimens tested by [1971Tok,1973Tok] were higher than those reported for UC tested under similar conditions.

Thermal diffusivity and thermal conductivity dependences of the $\text{Pu}_{0.2}\text{U}_{0.8}\text{C}$ solid solution in the temperature range from 407 to 1327°C obtained by [1989Ara] are presented in Figs. 11 and 12, respectively. The second one is normalized to 100% theoretical density. Both these dependencies gradually increase with the increasing temperature. Electrical resistivity of the $\text{Pu}_{0.2}\text{U}_{0.8}\text{C}$ solid solution depending on the temperature in the range from room temperature up to 727°C, normalized to 100% theoretical density, according to the data of [1989Ara], is shown in Fig. 13. A linear increase with the increasing temperature is observed.

Miscellaneous

In the reviews of [1966Bar1] and [1966Bar2], the results of the development of the technique of plutonium-uranium carbide synthesis are presented. The sintering behavior of $\text{Pu}_{0.55}\text{U}_{0.45}\text{C}$ pellets has been studied up to 1700°C using a dilatometer in an Ar-8% H_2 atmosphere. The mechanism for the initial stage of sintering was determined using a rate controlled sintering technique and it was found to be volume diffusion [2005Kut].

[1972Ker] investigated the phase relations at 1700°C and 1500°C on the two-phase $v + \theta$ samples with Pu : (U + Pu) ratios of 0.2 and 0.5 and proportion of the θ phase varied from 10 to 70%. The distribution coefficients k_U and k_{Pu} were measured where k represents the ratio (amount of U or Pu in v phase) / (amount of U or Pu in θ phase). 14 samples were analyzed and the values of k were found to be independent of temperature and the proportion of the two phases. [1976Bro] calculated the positions of the tie-lines in the $v + \theta$ two-phase region at 1500°C and 1950°C using ideal solution behavior. It was concluded that plutonium was concentrated in the θ phase. At the same time, [1976Ohs, 1982Udo] have determined the positions of the $v / (v + \theta)$, $v / (v + \theta + \rho)$ and $v / (v + \rho)$ phase boundaries in the temperature range from 1730 to 2230°C with specimens with a ratio of Pu:U = 1:4.

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Table 1: Investigations of the C-Pu-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1963Nev]	X-ray diffraction studies, optical metallography	50 at.% C
[1963Ros1]	Metallography, X-ray diffraction Debye-Scherrer studies, melting point beginning measurements, chemical analysis	< 635°C, 0-50 at.% C
[1963Ros2]	Metallography, X-ray diffraction Debye-Scherrer studies, chemical analysis	< 635°C, ~ 50 at.% C
[1964Sta]	Metallography, X-ray diffraction studies, chemical etching, microprobe analysis, Knudsen effusion cell method, melting points determination (black body technique)	Pu _{0.2} U _{0.8} C _{0.95} Pu _{0.05} U _{0.95} C _{0.98}
[1965Far]	Liquidus and solidus temperatures measurements (black body technique)	Pu _{0.05} U _{0.95} C _{0.98}
[1967Rea]	High-temperature DTA, X-ray powder diffraction, metallographic techniques	≤ 2425°C, ≥ 60 at.% C
[1968Pot]	Liquidus and solidus temperatures measurements	2000-2200°C; 50 to 60 at.% C, Pu:U = 1:1
[1969Lea]	X-ray powder diffraction, DTA	50 to 66.67 at.% C
[1970Mar]	Thermal analysis, metallography, X-ray diffraction	Whole range of compositions
[1972Ker]	Microprobe analysis	1500°C, 1700°C, 50 to 60 at.% C
[1976Bro]	Chemical analysis, mechanical polishing, chemical etching, X-ray Debye-Scherrer studies, EMPA, Knudsen effusion mass spectrometry	(Pu,U)C + (Pu,U) ₂ C ₃ phase region
[1976Ohs]	Liquidus and solidus temperatures measurements, vapor pressure measurements	~ 50 at.% C; Pu:U = 1:4
[1977Fis]	Induction-heated drop calorimetry	766-2148°C, Pu _{0.2} U _{0.8} C
[1989Ara]	X-ray diffraction, chemical analysis, density measurements	≤ 1327°C, Pu _{0.2} U _{0.8} C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) ≤ 3827 ± 50 (S.P.)	<i>hP</i> 4 <i>P</i> 6 ₃ / <i>mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.9	at 25°C [Mas2] sublimation point Negligible solubility of U [2001Che]
(δ'Pu) 483 - 463	<i>tI</i> 2 <i>I</i> 4/ <i>mmm</i> In	<i>a</i> = 333.9 <i>c</i> = 444.6	pure, 477°C [1989Pet], dissolves about 1.3 at.% U at 440°C [1991Lei]; exists down to 437°C in the Pu-U binary [1991Lei]
(δPu) 463 - 320	<i>cF</i> 4 <i>Fm</i> $\bar{3}$ <i>m</i> Cu	<i>a</i> = 463.70	pure, 320°C [1989Pet], dissolves about 1.6 at.% U at 318°C [1991Lei]
(γPu) 320 - 215	<i>oF</i> 8 <i>Fddd</i> γPu	<i>a</i> = 315.87 <i>b</i> = 576.82 <i>c</i> = 1016.2	pure, 235°C, [1989Pet], dissolves about 1.6 at.% U at 278°C [1991Lei], negligible solubility of C [Mas2]
(βPu) 215 - 125	<i>mC</i> 34 <i>C</i> 2/ <i>m</i> βPu	<i>a</i> = 928.4 <i>b</i> = 1046.3 <i>c</i> = 785.9 β = 92.13°	pure, 190°C [1989Pet], dissolves about 2.7 at.% U at 278°C [1991Lei], negligible solubility of C [Mas2]
(αPu) < 125	<i>mP</i> 16 <i>P</i> 2 ₁ / <i>m</i> αPu	<i>a</i> = 618.3 <i>b</i> = 482.2 <i>c</i> = 1096.3 β = 101.79°	pure, 21°C [1989Pet], negligible solubility of U and C. [1991Lei, Mas2]
(βU) 776 - 668	<i>tP</i> 30 <i>P</i> 4 ₂ / <i>mnm</i> βU	<i>a</i> = 1075.9 <i>c</i> = 565.6	pure, 720°C, [1989Pet] dissolves about 24 at.% Pu at 702°C [1991Lei], the solubility of C is very small [2001Che]
(αU) (r) < 668	<i>oC</i> 4 <i>Cmcm</i> αU	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	pure, at 25°C [1989Pet] dissolves about 24 at.% Pu at 702°C [1991Lei], the solubility of C is very small [2001Che]
μ, (εPu, γU)	<i>cI</i> 2 <i>Im</i> $\bar{3}$ <i>m</i> W		continuous solid solution which exists between 1135 and 454°C [1991Lei]
(εPu) 640 - 483		<i>a</i> = 363.8	pure, 500°C [1989Pet] dissolves 100 at.% U [1991Lei]
(γU) 1135 - 776		<i>a</i> = 352.4	pure, 805°C [Mas2] dissolves 100 at.% Pu [1991Lei]
Pu ₃ C ₂ ≤ 575	-	-	40 at.% C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
v, (Pu,U)C	$cF8$ $Fm\bar{3}m$ NaCl	$a = 496.47$	continuous solid solution called v in the $\text{Pu}_{0.2}\text{U}_{0.8}\text{C}$ specimen sintered at 1750°C [1989Ara]
PuC $\lesssim 1654$		$a = 497.25$	~ 44 to ~ 48 at.% C [Mas2] sometimes labelled as “ PuC_{1-x} ” (the structure defect by carbon content)
βUC < 2515		$a = 495.97$ $a = 495.63$	[V-C2] stoichiometric [2001Che] 48 at.% C [2001Che] from 47 to 66 at.% C. Miscibility gap (critical point at 2050°C, 43.8 at.% C) [2001Che]
θ , (Pu,U) $_2\text{C}_3$	$cI40$ $I\bar{4}3d$ Pu_2C_3	$a = 808.8$ to 813.3	continuous solid solution called θ ; $(\text{Pu}_{1-x}\text{U}_x)_2\text{C}_3$, $0 \leq x \leq 1$, $T = 1700^\circ\text{C}$, specimen with excess carbon [1967Rea]
Pu_2C_3 $\lesssim 2050$		$a = 812.58 \pm 3$	~ 59 to ~ 60 at.% C [Mas2] [V-C2]
U_2C_3 < 1833		$a = 808.89$	60 at.% C [Mas2] [1969Lea]
ρ , (Pu,U) C_2		$a = 352.0$ to 360.6 $c = 598.5$ to 610.6	continuous solid solution called ρ $T = 2227$ to $\sim 1797^\circ\text{C}$ [1984Hol] $(\text{Pu}_{1-x}\text{U}_x)\text{C}_2$, $0 \leq x \leq 1$, $T = 1700^\circ\text{C}$, specimen with excess carbon [1967Rea]
βPuC_2 $\sim 2350 - 1660$	c^{**}	$a = 569.6$	66.7 at.% C [Mas2]
βUC_2 2435 - 1763	$cF12$ $Fm\bar{3}m$ $\text{CaF}_2?$	$a = 545.0$	[2001Che] actually, “ βUC_2 ” phase represents the UC phase in equilibrium with graphite [2001Che]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ρ' , (Pu,U)C ₂	<i>tI6</i> <i>I4/mmm</i> CaC ₂	$a = 357.5$ $c = 605$ $a = 355$ $c = 603$	continuous solid solution called ρ' reported as metastable in [1969Lea] Pu _{1-x} U _x C ₂ , $x = 0.4$, quenched from high temperature in the presence of excess carbon [1969Lea] Pu _{1-x} U _x C ₂ , $x = 0.7$, quenched from high temperature in the presence of excess carbon [1969Lea]
α PuC ₂ < 1660		$a = 363$ $c = 609.4$	66.7 at.% C [Mas2] [1987Ben]
α UC ₂ 1780 - 1478		$a = 351.90$ $c = 597.87$ $a = 352.41$ $c = 599.62$	U rich [2001Che] C rich [2001Che]
ζ , PuU ≤ 628	<i>t**</i>	$a = 1069.2$ $a = 1065.1$	~26.4 to ~77 at.% U at 25°C, 35 at.% U [1969Lea] at 25°C, 70 at.% U [1969Lea] $c/a \approx 1$
η , PuU 702 - 278	<i>tP52</i>	$a = 1057$ $c = 1076$	~4 to ~78 at.% U at 25 at.% U [1969Lea]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				C	Pu	U
L + (C) $\rightleftharpoons$ β UC ₂ + β PuC ₂	2250	U ₁	L (C) β PuC ₂	66.67 ~ 100 ~ 66.67	27.88 ~ 0.00 ~ 33.33	5.45 ~ 0.00 0.00
L + β UC ₂ + β PuC ₂ $\rightleftharpoons$ θ	2135	P ₁	L β PuC ₂ θ	60.00 ~ 66.67 ~ 60.00	17.68 ~ 33.33 ~ 40.00	22.32 0.00 0.00
β PuC ₂ + β UC ₂ $\rightleftharpoons$ θ , α UC ₂	1767±10	D ₁	β PuC ₂ θ α UC ₂	~ 66.67 ~ 60.00 ~ 66.67	~ 33.33 ~ 40.00 0.00	0.00 0.00 ~ 33.33
α UC ₂ $\rightleftharpoons$ β UC ₂ + β PuC ₂ + (C)	1750	E ₁	β PuC ₂ (C) α UC ₂	~ 66.67 ~ 100 ~ 66.67	~ 33.33 ~ 0.00 0.00	0.00 ~ 0.00 ~ 33.33
α UC ₂ + β PuC ₂ $\rightleftharpoons$ θ + (C)	1725	U ₂	α UC ₂ β PuC ₂ θ (C)	~ 66.67 ~ 66.67 ~ 60.00 ~ 100	0.00 ~ 33.33 ~ 40.00 ~ 0.00	~ 33.33 0.00 0.00 ~ 0.00

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				C	Pu	U
$(\gamma\text{U}) + (\beta\text{U}) + \mu \rightleftharpoons \eta$	712	P_2	(γU)	~ 0	~ 0	~ 100
			(βU)	~ 0	~ 0	~ 100
$(\beta\text{U}) + \eta \rightleftharpoons \zeta + \mu$	594	D_2	(βU)	~ 0.00	~ 0.00	~ 100
$(\beta\text{U}) \rightleftharpoons (\alpha\text{U}) + \zeta + \mu$	549	E_2	(βU)	~ 0.00	~ 0.00	~ 100
			(αU)	~ 0.00	~ 0.00	~ 100
$\eta + \mu \rightleftharpoons (\beta\text{Pu}) + \zeta$	283	U_3	(βPu)	~ 0.00	~ 100	~ 0.00

Table 4: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Property, per mole of atoms [J, mol, K]	Comments
$\text{Pu}_{0.2}\text{U}_{0.8}\text{C}$	25 - 1627	$H(T) - H(298) = -20.0288 \cdot 10^3 + 58.0823 \cdot T + 59.7601 \cdot 10^{-5} T^2 + 95.6713 \cdot 10^{-8} T^3 + 78.7303 \cdot 10^4 / T$	[1975Tet], v phase
	766 - 2148	$H(T) - H(298) = -48.3832 \cdot 10^3 + 121.652 \cdot T - 42.9571 \cdot 10^{-3} T^2 + 10.2309 \cdot 10^{-6} T^3$	[1977Fis] drop calorimeter, v phase
	25 - 2275	$H(T) - H(298) = -12.4866 \cdot 10^3 + 32.5225 \cdot T + 37.2021 \cdot 10^{-3} T^2 + 20.8151 \cdot 10^{-6} T^3 + 43.8487 \cdot 10^{-10} T^4$	[1977Fis] deduced by extrapolation, v phase
	25	$C_p^\circ = 49.62$	calculated value from [1975Tet], v phase
	25	$S^\circ = 61.92$	calculated value from [1977Fis], v phase
	25	$-(G_T^\circ - H_{298}^\circ) / T = 61.92$	calculated value from [1977Fis], v phase

Table 5: Vapor Pressure Measurements

Phases	Temperature [°C]	Pressure [bar]	Comments
$\text{Pu}_{0.2}\text{U}_{0.8}\text{C}_{0.95}$	2347	$p_{\text{Pu}} = 2.49 \cdot 10^{-6}$ $p_{\text{U}} = 8.81 \cdot 10^{-5}$	[1964Sta] Knudsen effusion time of the test: 10 min
	2327	$p_{\text{Pu}} = 3.16 \cdot 10^{-6}$; $3.46 \cdot 10^{-6}$ $p_{\text{U}} = 3.30 \cdot 10^{-4}$; $4.66 \cdot 10^{-4}$	[1964Sta] Knudsen effusion time of the test: 20 min; 10 min
	2237	$p_{\text{Pu}} = 1.35 \cdot 10^{-5}$ $p_{\text{U}} = 1.73 \cdot 10^{-5}$	[1964Sta] Knudsen effusion time of the test: 45 min
	2227	$p_{\text{Pu}} = 2.98 \cdot 10^{-6}$; $4.12 \cdot 10^{-7}$ $p_{\text{U}} = 3.59 \cdot 10^{-5}$; $6.18 \cdot 10^{-5}$	[1964Sta] Knudsen effusion time of the test: 25 min
	2217	$p_{\text{Pu}} = 4.13 \cdot 10^{-7}$ $p_{\text{U}} = 3.59 \cdot 10^{-5}$	[1964Sta] Knudsen effusion time of the test: 25 min
	2127	$p_{\text{Pu}} = 5.32 \cdot 10^{-6}$; $2.35 \cdot 10^{-6}$; $5.53 \cdot 10^{-8}$ $p_{\text{U}} = 2.89 \cdot 10^{-6}$; $5.02 \cdot 10^{-6}$; $4.40 \cdot 10^{-5}$	[1964Sta] Knudsen effusion time of the test: 60 min; 45 min; 30 min
	2117	$p_{\text{Pu}} = 5.57 \cdot 10^{-8}$ $p_{\text{U}} = 9.07 \cdot 10^{-5}$	[1964Sta] Knudsen effusion time of the test: 45 min
	2022	$p_{\text{Pu}} = 3.45 \cdot 10^{-4}$ $p_{\text{U}} = 4.94 \cdot 10^{-4}$	[1964Sta] Knudsen effusion time of the test: 60 min
	2012	$p_{\text{Pu}} = 1.66 \cdot 10^{-8}$; $2.08 \cdot 10^{-4}$ $p_{\text{U}} = 4.74 \cdot 10^{-5}$; $4.83 \cdot 10^{-4}$	[1964Sta] Knudsen effusion time of the test: 60 min
	1997	$p_{\text{Pu}} = 4.65 \cdot 10^{-8}$ $p_{\text{U}} = 3.85 \cdot 10^{-5}$	[1964Sta] Knudsen effusion time of the test: 60 min
	1912	$p_{\text{Pu}} = 3.43 \cdot 10^{-4}$ $p_{\text{U}} = 1.74 \cdot 10^{-4}$	[1964Sta] Knudsen effusion time of the test: 90 min
	1897	$p_{\text{Pu}} = 6.60 \cdot 10^{-4}$ $p_{\text{U}} = 5.83 \cdot 10^{-5}$	[1964Sta] Knudsen effusion time of the test: 90 min
	1797	$p_{\text{Pu}} = 1.22 \cdot 10^{-3}$ $p_{\text{U}} = 2.21 \cdot 10^{-4}$	[1964Sta] Knudsen effusion time of the test: 120 min
	1782	$p_{\text{Pu}} = 1.22 \cdot 10^{-4}$ $p_{\text{U}} = 1.27 \cdot 10^{-4}$	[1964Sta] Knudsen effusion time of the test: 120 min
$\text{Pu}_{0.17}\text{U}_{0.83}\text{C}_{1.5} + (\text{C})$	1589 - 1995	$\log_{10}(p_{\text{Pu}}) = -20.300/T + 3.541$	[1976Bro] Knudsen effusion, all the expressions are given with T in K
$\text{Pu}_{0.335}\text{U}_{0.665}\text{C}_{1.5} + (\text{C})$	1610 - 1984	$\log_{10}(p_{\text{Pu}}) = -20.500/T + 3.841$	[1976Bro] Knudsen effusion, all the expressions are given with T in K
$\text{Pu}_{0.59}\text{U}_{0.41}\text{C}_{1.5} + (\text{C})$	1559 - 1845	$\log_{10}(p_{\text{Pu}}) = -21.429/T + 4.681$	[1976Bro] Knudsen effusion, all the expressions are given with T in K

Phases	Temperature [°C]	Pressure [bar]	Comments
$\text{Pu}_{0.19}\text{U}_{0.81}\text{C}_{1.5} + \text{Pu}_{0.43}\text{U}_{0.57}\text{C}_{1.5}$	1500	$\log_{10}(p_{\text{Pu}}) = -6.58$	[1976Bro] Knudsen effusion
$\text{Pu}_{0.34}\text{U}_{0.66}\text{C} + \text{Pu}_{0.66}\text{U}_{0.34}\text{C}_{1.5}$	1500	$\log_{10}(p_{\text{Pu}}) = -6.12$	[1976Bro] Knudsen effusion
$(\text{Pu}_{0.2}\text{U}_{0.8})\text{C}_{1.014}$ to $(\text{Pu}_{0.2}\text{U}_{0.8})\text{C}_{1.15}$	1730 - 2230	$\log_{10}(p_{\text{Pu}}) = 4.28 - 18700/T$ to $5.66 - 22600/T$	[1976Ohs] Knudsen effusion and mass spectrometry; (Pu,U)C single phase region
$(\text{Pu}_{0.2}\text{U}_{0.8})\text{C}_{1.15}$ to $(\text{Pu}_{0.2}\text{U}_{0.8})\text{C}_{1.30}$	1730 - 2230	$\log_{10}(p_{\text{Pu}}) = 4.32 - 20000/T$ to $5.96 - 23800/T$	[1976Ohs] Knudsen effusion and mass spectrometry; (Pu,U)C + (Pu,U) ₂ C ₃ two-phase field

Table 6: Investigations of the C-Pu-U Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1961Pas]	Electrical resistivity measurements	Electrical resistivity of a solid solution (Pu,U)C
[1964Sta]	Dilatometry	Coefficient of expansion of $\text{Pu}_{0.05}\text{U}_{0.95}\text{C}_{0.98}$ and $\text{Pu}_{0.2}\text{U}_{0.8}\text{C}_{0.95}$
[1971Tok]	Compressive creep and hot hardness studies, ceramographic examination	Compressive creep of $\text{Pu}_{0.2}\text{U}_{0.8}\text{C}$ specimens (1300-1500°C); hot hardness of $\text{Pu}_{0.2-1}\text{U}_{0.8-0}\text{C}$ specimens
[1973Tok]	Compressive creep and hot hardness tests, optical pyrometry	$\text{Pu}_{0.21}\text{U}_{0.79}\text{C}_{1.02}$ specimen at 1300, 1400 and 1500°C
[1982Zim]	Immersion density measurements	Swelling of the (Pu,U)C in the temperature range 300-1750°C
[1984Die]	Irradiation tests	Swelling, irradiation-induced denazification Irradiation-induced creep of the (Pu,U)C fuel
[1989Ara]	Laser flash, dc four probes techniques	Thermal diffusivity, electrical resistivity, thermal conductivity

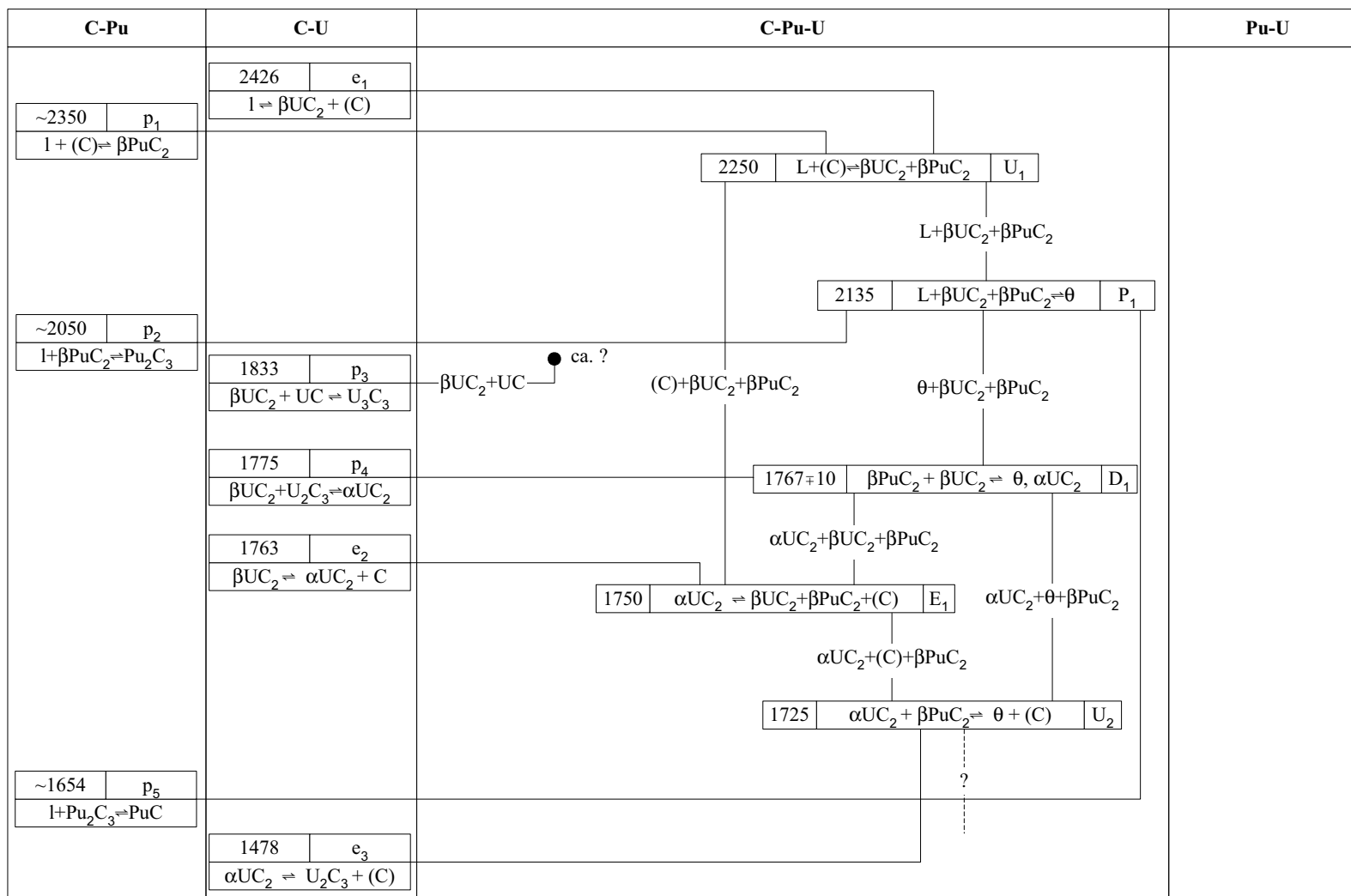


Fig. 1a: C-Pu-U. Partial reaction scheme

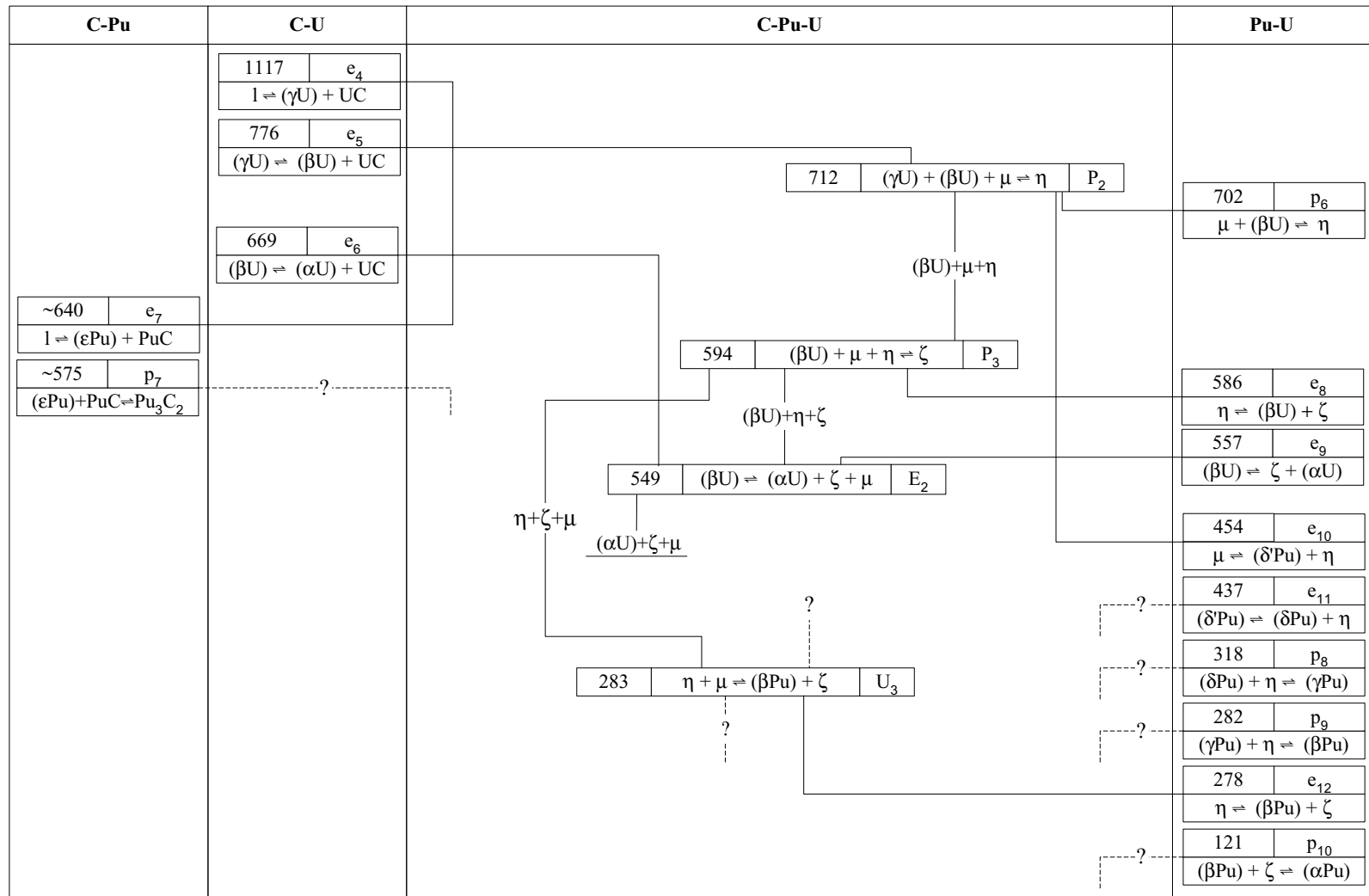


Fig. 1b: C-Pu-U. Partial reaction scheme

Fig. 2: C-Pu-U.
Liquidus surface
projection

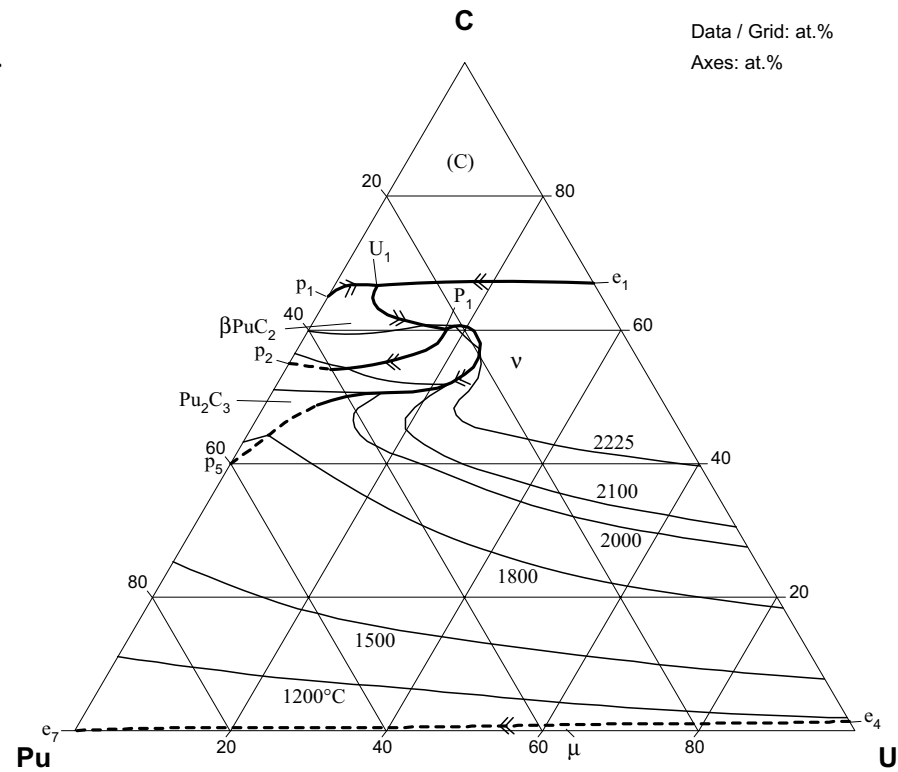


Fig. 3: C-Pu-U.
Isothermal section at
1600°C

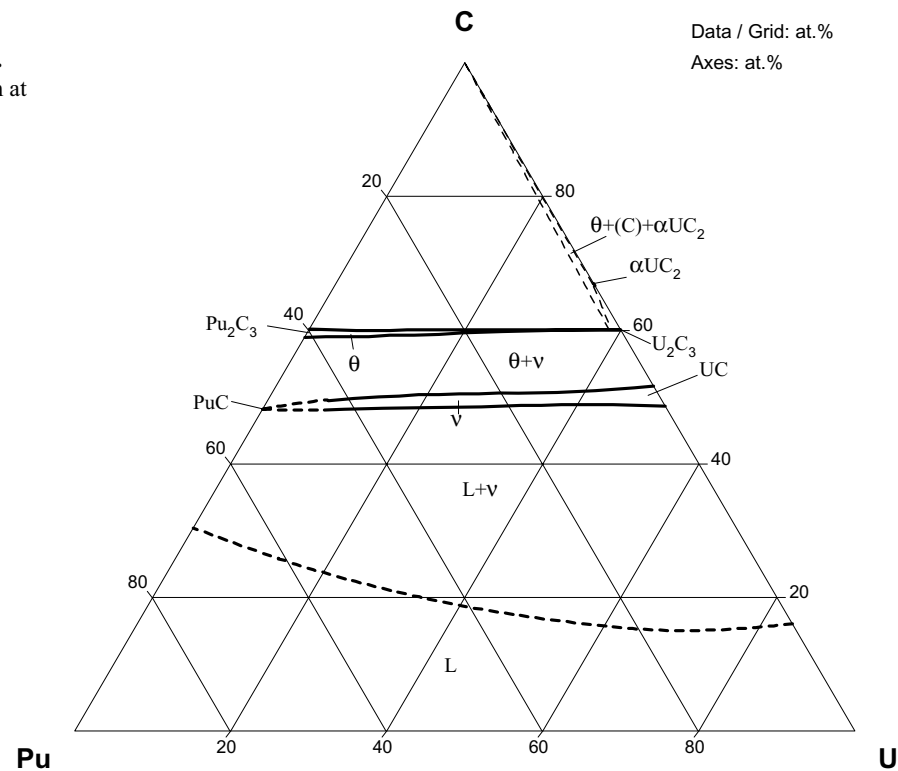


Fig. 4: C-Pu-U.
Partial isothermal
section at 635°C

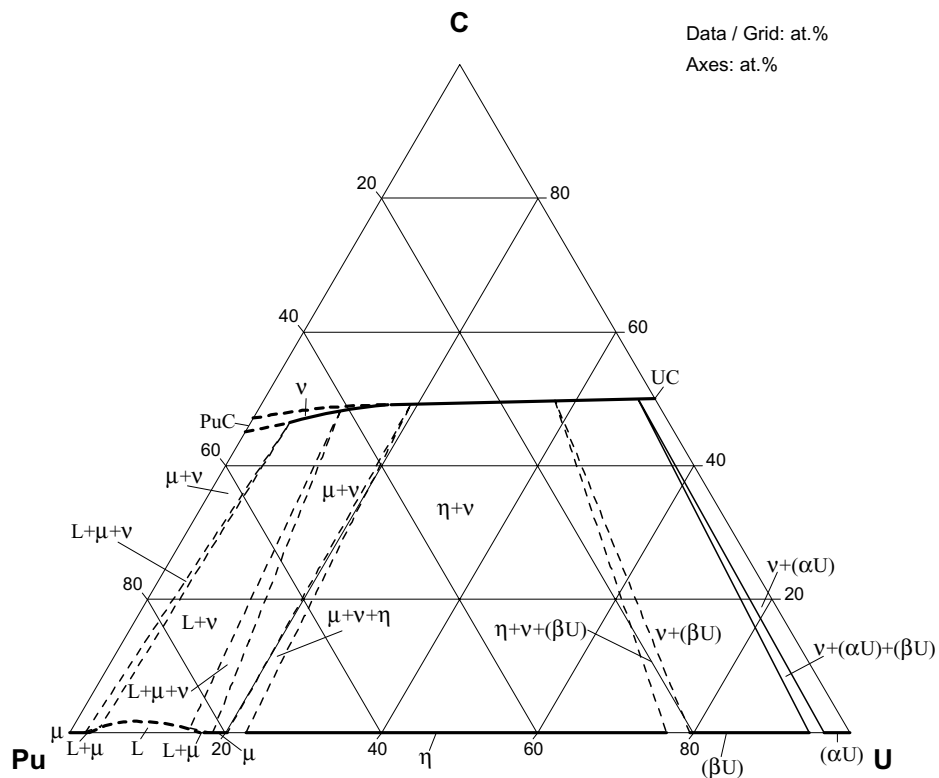


Fig. 5: C-Pu-U.
Partial isothermal
section at 570°C

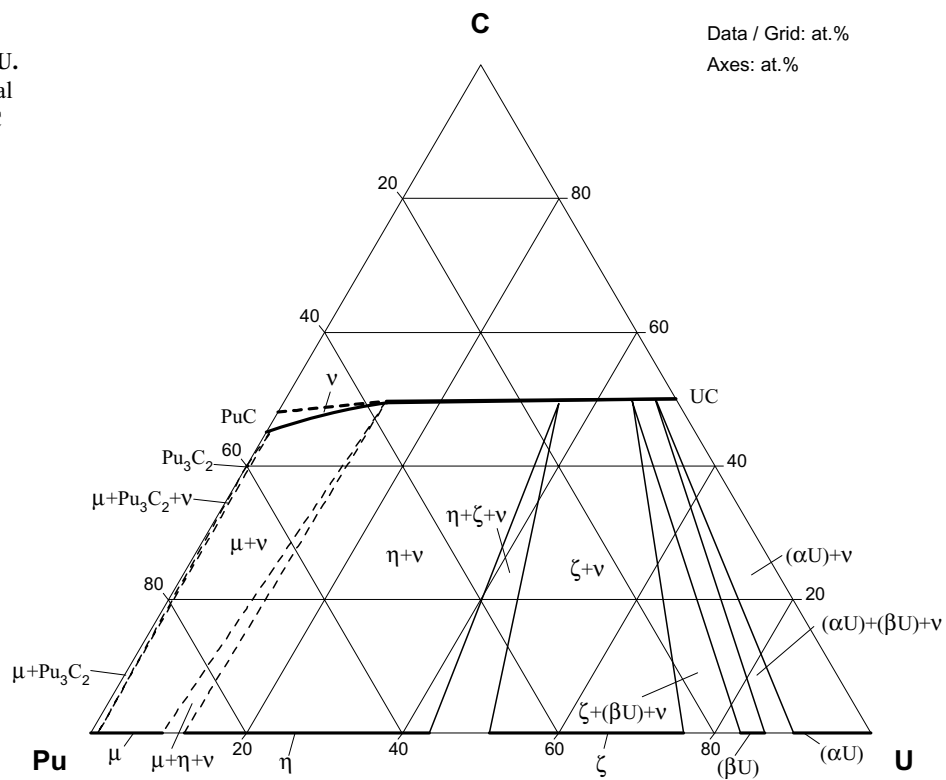


Fig. 6: C–Pu–U.
Partial isothermal
section at 400°C

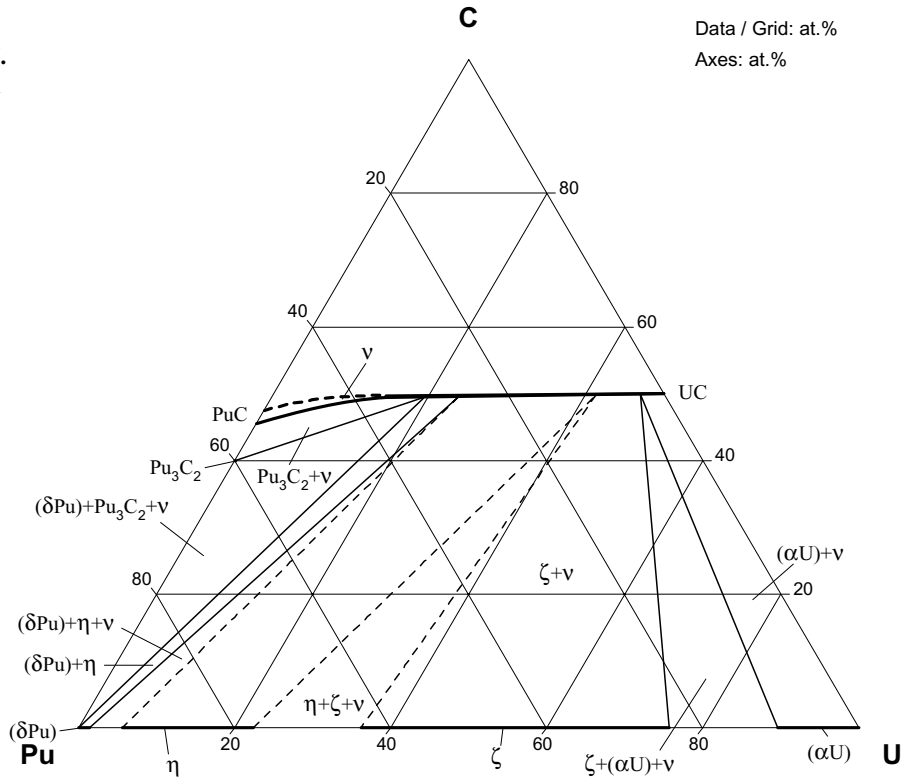


Fig. 7: C–Pu–U.
Temperature -
composition section
PuC–UC

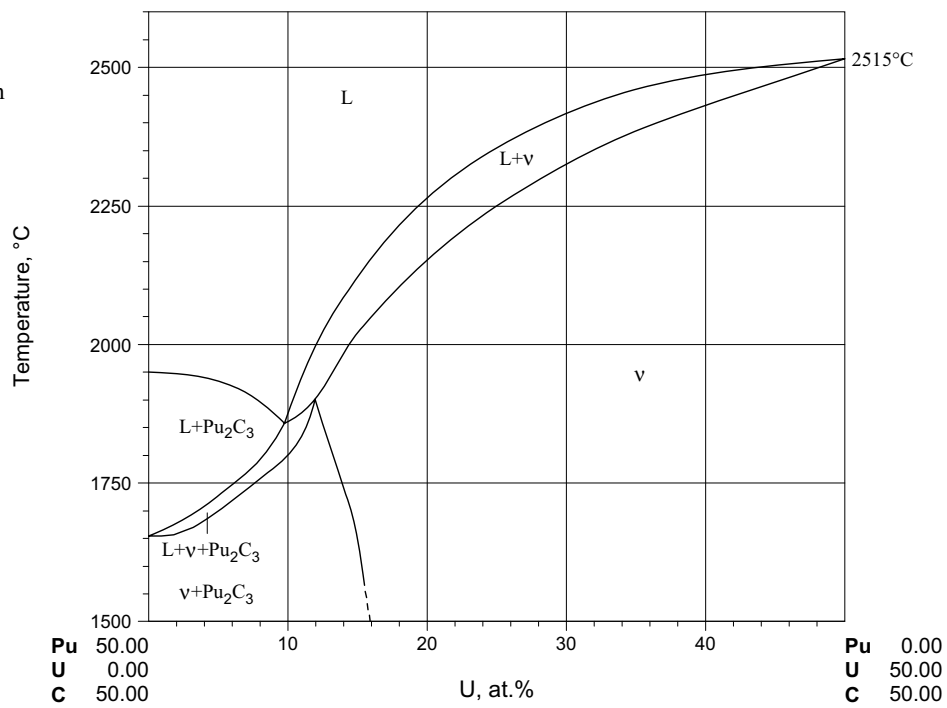


Fig. 8: C-Pu-U.
Temperature -
composition section
 $\text{PuC}_2\text{-UC}_2$

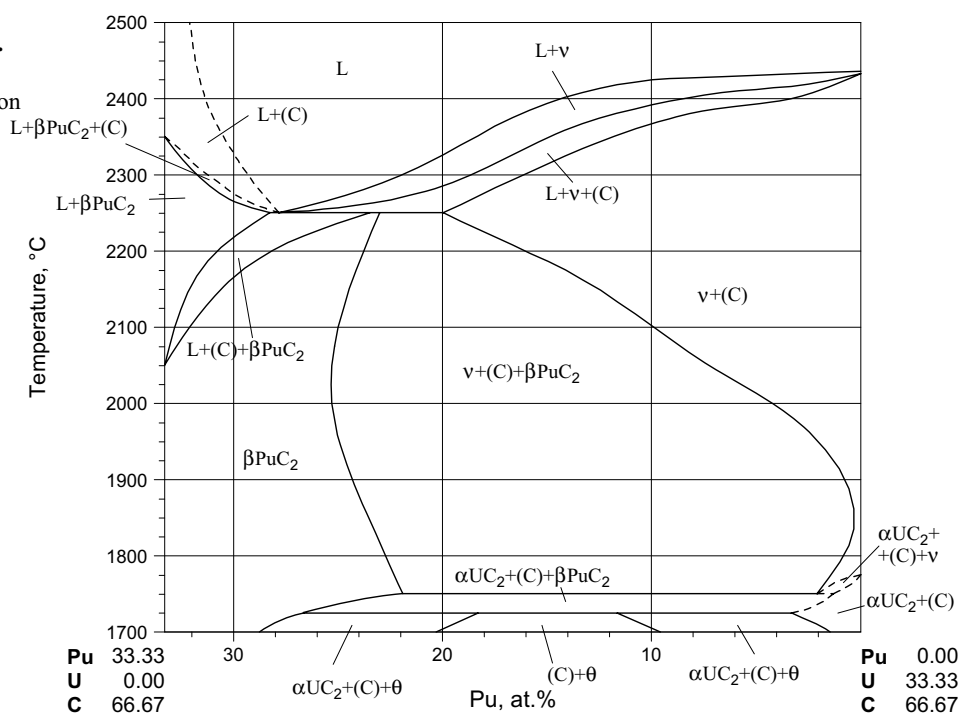


Fig. 9: C-Pu-U.
Temperature -
composition section
 $(\text{Pu,U})\text{C-(Pu,U)}_2\text{C}_3$

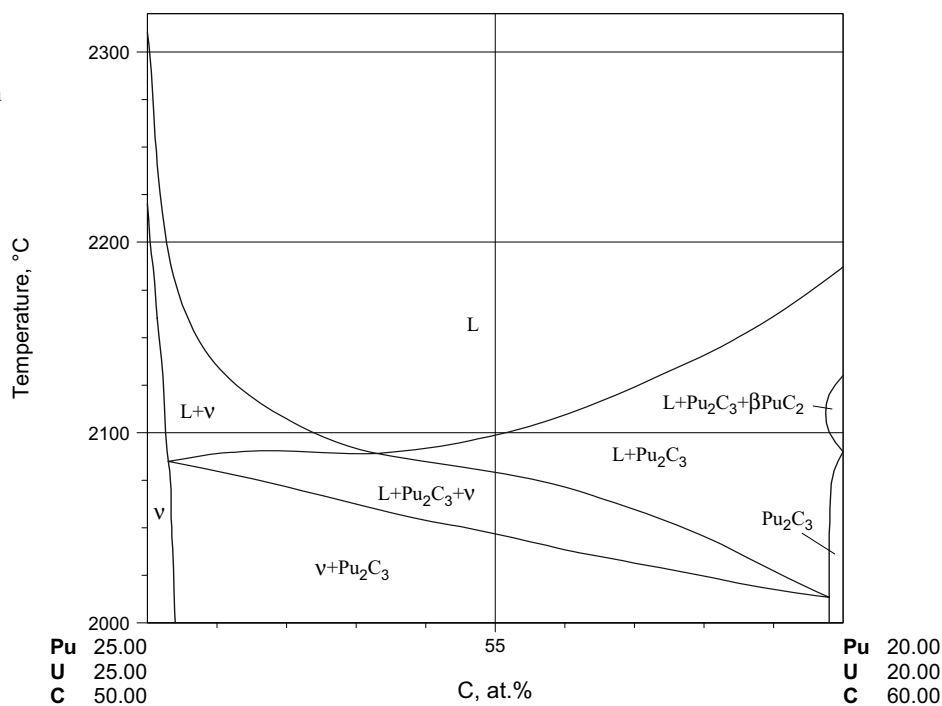


Fig. 10: C–Pu–U.
Pressure-composition
diagram showing the
boundary between the
(Pu,U)C and the
(Pu,U)C + (Pu,U)₂C₃
phase fields

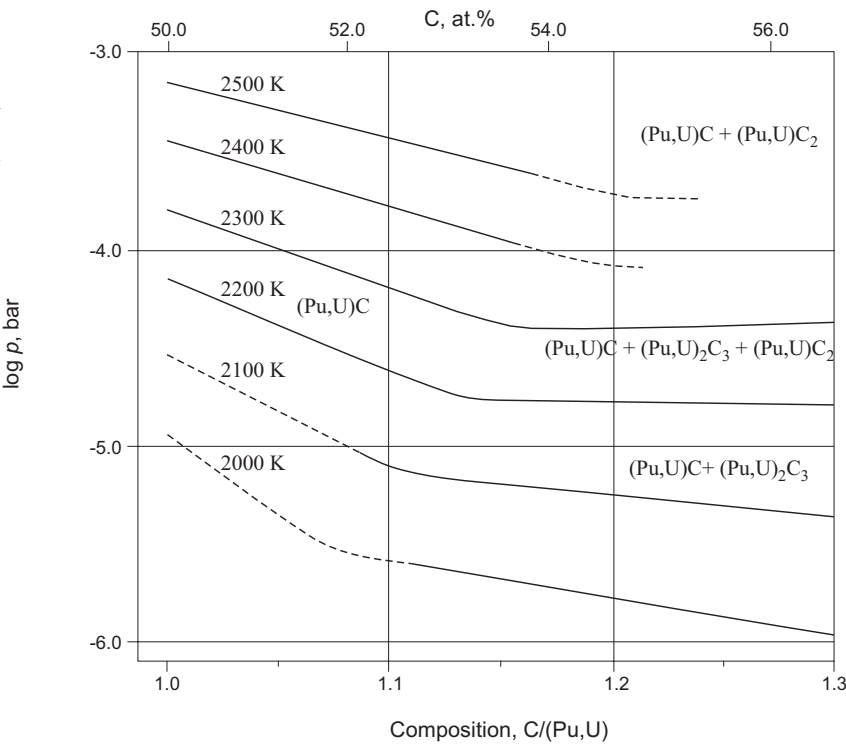


Fig. 11: C–Pu–U.
Thermal diffusivity of
the Pu_{0.2}U_{0.8}C solid
solution

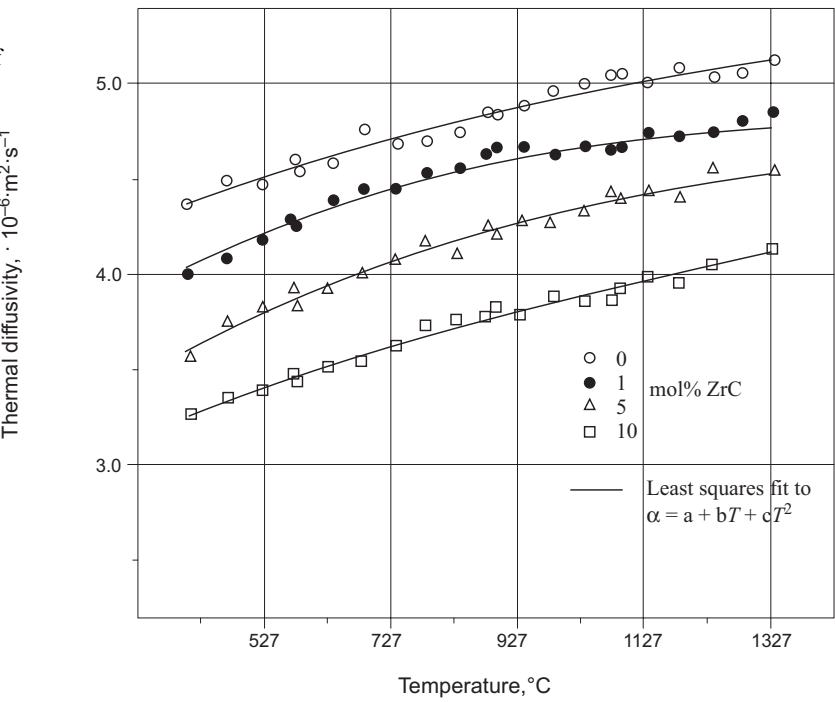


Fig. 12: C-Pu-U.
Thermal conductivity
of the $\text{Pu}_{0.2}\text{U}_{0.8}\text{C}$
solid solution
normalized to 100%
theoretical density

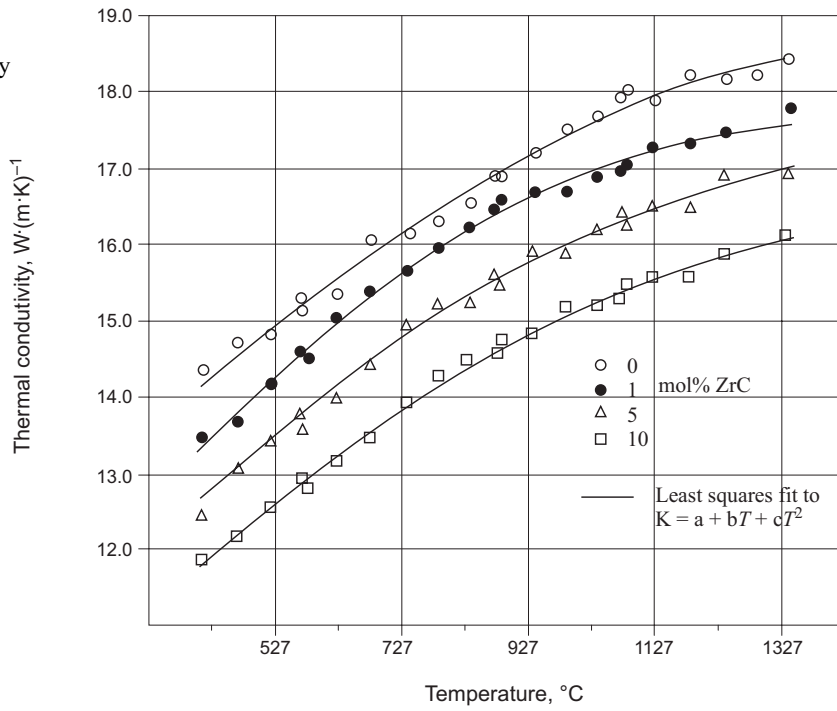
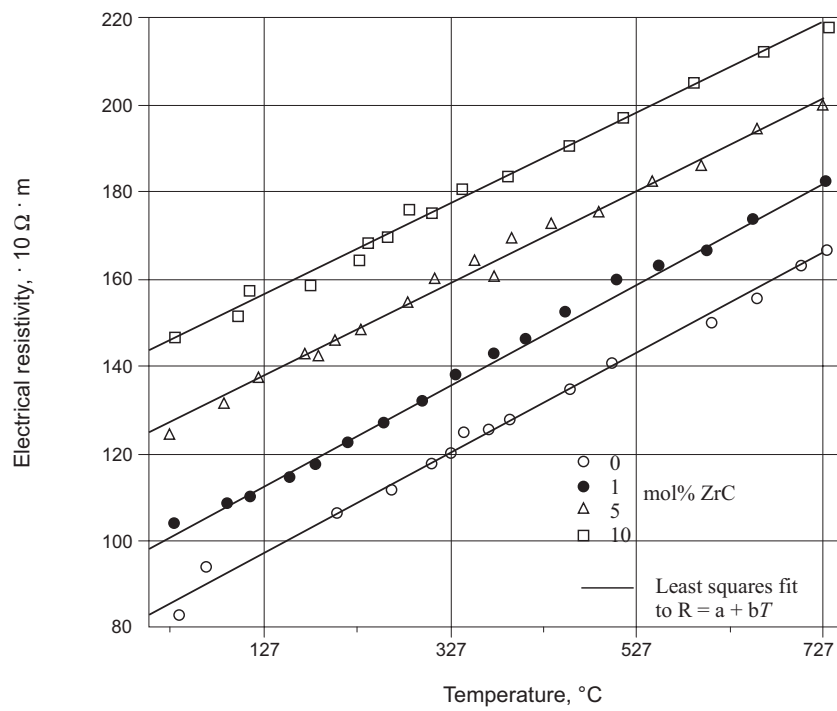


Fig. 13: C-Pu-U.
Electrical resistivity
of the $\text{Pu}_{0.2}\text{U}_{0.8}\text{C}$
solid solution
normalized to 100%
theoretical density



Carbon – Plutonium – Zirconium

Kostyantyn Korniyenko

Introduction

From the 1960s, the development of new plutonium compounds for high specific power, high burn-up applications have been of great interest. And so, mixtures of PuC and refractory carbides, in particular, ZrC became the focus of research. The study of phase relationships in the corresponding multicomponent systems has created a theoretical basis for scientific research in this area. Experimental work relating to the C–Pu–Zr ternary system was carried out by Burnham *et al.* [1964Bur], Haines and Potter [1970Hai] and by Benedict [1978Ben]. The results were reviewed by Holleck [1975Hol, 1984Hol1, 1984Hol2] who presented an isothermal section. The experimental methods used by the above, along with the temperature and composition ranges studied are shown in Table 1. However, the information relating to phase equilibria in the C–Pu–Zr system is at present incomplete being represented only via solid-state phase relationships along the PuC–ZrC section. Thus, future investigations should be concentrated on studies of crystallization paths and the precise determination of compositions of the phases taking part in equilibria with respect to temperature. The new knowledge will provide a basis for the search of new practical applications of carbon-plutonium-zirconium alloys.

Binary Systems

The C–Pu and C–Zr systems are accepted from [Mas2]. The Pu–Zr system is accepted from [1993Oka].

Solid Phases

No ternary phases have been reported. Crystallographic data relating to the known unary and binary phases are presented in Table 2. The μ , PuC and ρ , ZrC phases possess the same type of crystal structure but are distinguished by their paths of crystallization (the ρ phase crystallizes congruently from the melt but the μ phase forms by a peritectic reaction) and do not form a continuous series of solid solutions. The solubility of the μ phase in the ρ phase at 1500°C was studied by [1964Bur]. Later, [1970Hai] reported a solubility of about 4 mol% ZrC in PuC that was derived from the measured lattice parameter for the μ phase in an arc-melted C–Pu–Zr sample, assuming the validity of Vegard's law between PuC and ZrC. The sample contained the μ , ρ and θ phases. The solubility of the ρ phase in the μ phase at 1400°C as well as equilibria between them at 1500°C were investigated by [1978Ben].

Isothermal Sections

A schematic isothermal section for the whole range of compositions at 1250°C was presented by [1970Hai]. The solubility of zirconium in the μ phase was reported to be about 2 at.%. The solubility of Pu in the ρ phase was not shown since it was found to decrease during annealing. The constitution of this section does not seem to be reliable because the investigation was carried out only for two alloys of different composition. The isothermal section presented by [1970Hai] contains a mistake - in the binary Zr–Pu system, the equilibrium $L + (\beta\text{Zr}, \epsilon\text{Pu})$ is missing. The author also carried out the annealing treatments at 1650°C and 1800°C for short periods (30 min and 5 h, respectively) as well as annealing at 1450°C for 288 h. Holleck [1975Hol] has presented an estimated isothermal section of the C–Pu–Zr system for a temperature of 1600°C. The mutual solubilities of the μ and ρ phases are about 1–2 at.% of Pu or Zr. Later, the same author [1984Hol1, 1984Hol2] published an isothermal section compiled using the results of [1978Ben]. However, the declared temperature of 1600°C in [1975Hol, 1984Hol1, 1984Hol2] was erroneous as the data of [1978Ben] actually correspond to 1500°C. Figure 1 shows the isothermal section at 1500°C constructed on the basis of accepted binary systems and the data of [1978Ben]. The character of the phase equilibria involving the αPuC_2 phase, as well as the positions of three-phase regions need to be confirmed.

Temperature – Composition Sections

The partial vertical section ZrC–Pu_{53.8}C_{46.2}, which shows the experimentally determined melting points of arc melted and annealed ZrC–Pu_{53.8}C_{46.2} mixtures was presented by [1964Bur]. Investigations were carried out using a tungsten V-ribbon furnace. This section needs further experimental investigation.

Notes on Materials Properties and Applications

Uranium-plutonium mixed carbide is a possible fuel for future use in fast breeder reactors. However, the properties of the fuel will be strongly affected by the dissolution of Zr which is produced in large amounts among the solid fission products during irradiation [1978Ben]. Hence, it is desirable to know the effect of Zr that is dissolved in the mixed carbide on the thermal conductivity in order to evaluate heat conduction within the fuel. Experimental studies have demonstrated that thermal conductivity decreases with ZrC content in the solid solutions. It was found from electrical resistivity measurements that the decrease was caused mainly by a decrease in the electronic heat conduction.

Arai *et al.* [1989Ara] studied the thermal conductivity of near-stoichiometric (U,Pu,Zr)C solid solutions containing ZrC up to 10 mol% in the temperature range 407–1327°C by a laser flash method.

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Table 1: Investigations of the C-Pu-Zr Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1964Bur]	Arc melting, annealing, X-ray studies, melting points measurements	1500°C, the Pu _{53.8} C _{46.2} -ZrC section
[1970Hai]	Arc melting, X-ray studies	The PuC _{1-x} -ZrC section
[1978Ben]	Arc melting, sintering of pressed pellets, X-ray diffraction, EMPA, chemical analysis	1400°C, 1500°C, the PuC _{1-x} -ZrC section

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (I) < 3827 ± 50 (sublimation point), 1.013 bar	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.9	at 25°C [Mas2]
(C) (II) > 60.78 bar	<i>cF8</i> <i>Fd$\bar{3}m$</i> C (diamond)	<i>a</i> = 356.69	at 25°C [Mas2]

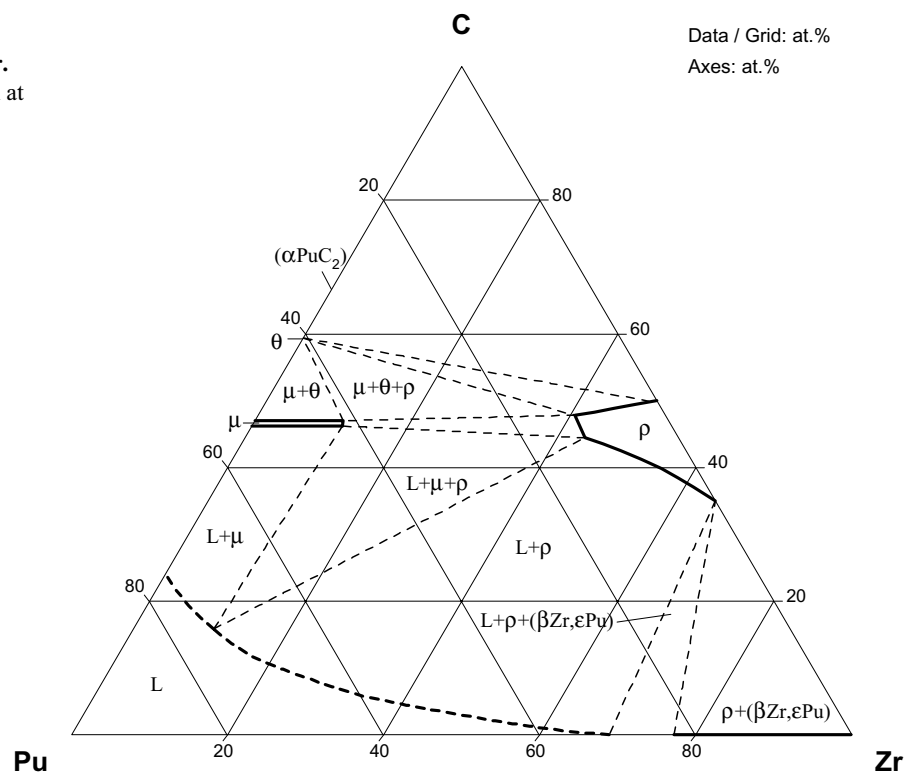
Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(η Pu) (h_5) 640 - 483	$cI2$ $Im\bar{3}m$ W	$a = 363.43$	[Mas2]
(ϵ Pu) (h_4) 483 - 463	$tI2$ $I4/mmm$ In	$a = 332.61$ $c = 446.30$	labelled as “(δ' Pu)” [Mas2]
$Pu_{1-x-y}Zr_xC_y$			$y = 0, x = 0$ to 1 [1993Oka]
(δ Pu) (h_3) 463 - 320	$cF4$ $Fm\bar{3}m$ Cu	$a = 463.71$	[Mas2]
(γ Pu) (h_2) 320 - 215	$oF8$ $Fddd$ γ Pu	$a = 315.87$ $b = 576.82$ $c = 1016.2$	[Mas2]
(β Pu) (h_1) 215 - 125	$mC34$ $C2/m$ β Pu	$a = 928.4$ $b = 1046.3$ $c = 785.9$ $\beta = 92.13^\circ$	[Mas2]
(α Pu) (r) < 125	$mP16$ $P2_1/m$ α Pu	$a = 618.3$ $b = 482.2$ $c = 1096.3$ $\beta = 101.97^\circ$	at 25°C [Mas2]
(β Zr) (h) 1855 - 863	$cI2$ $Im\bar{3}m$ W	$a = 360.90$	pure Zr, $T > 882^\circ\text{C}$ [Mas2]
$Pu_xZr_{1-x-y}C_y$			$y = 0, x = 0$ to 1 [1993Oka]
(α Zr) (r) < 863	$hP2$ $P6_3/mmc$ Mg	$a = 323.16$ $c = 514.75$	pure Zr, $T = 25^\circ\text{C}$ [Mas2]
(ω Zr) (hp)	$hP3$ $P6/mmm$ ω Ti	$a = 503.6$ $c = 310.9$	metastable pure Zr, $T = 25^\circ\text{C}$ [Mas2] high pressure
v, Pu_4Zr < 345	$tP80$ $P4/ncc$	$a = 1039$ $b = 1044$ $c = 1118$	~ 10 to ~ 30 at.% Zr [V-C2] labelled as “ Pu_6Zr ” [1959Boc]
$\kappa, PuZr_3$ < 380(?)	$hP3$ $P6/mmm$ AlB_2	$a = 505.5$ $c = 312.3$	74 at.% Zr [V-C2] [E]
		$a = 506.0$ $c = 311.9$	labelled as “ $PuZr_2$ ” [1959Boc]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
λ , Pu ₃ C ₂ $\lesssim 575$			40 at.% C [Mas2]
μ , PuC $\lesssim 1654$	$cF8$ $Fm\bar{3}m$ NaCl	$a = 495.82$ to 497.37 $a = 495.57$ $a = 497.21$ $a = 496.6$ $a = 495.0$ to 497.38 $a = 496.96$	~ 45 to ~ 48 at.% C [V-C2] sometimes labelled as “PuC _{1-x} ” [E] in the alloy Pu _{62.5} C _{37.5} annealed and quenched from $T = 570^\circ\text{C}$ [S] in the alloy Pu _{52.5} C _{47.5} annealed and quenched from $T = 1500^\circ\text{C}$ [S] [1959Boc] in alloys with 38 to 49 at.% C annealed at $T = 1500^\circ\text{C}$ [1964Bur] [1978Ben]
(Pu _{1-x} Zr _x)C		$a = 496.19$ $a = 496.3$ $a = 496.7$ $a = 491.33$ to 494.37 $a = 491.05$ $a = 491.23$	$x = 0$ to 0.04 , arc melted sample [1970Hai] $x = 0$ to 0.23 , $T = 1500^\circ\text{C}$ [1978Ben] $x = 0$ to 0.2 , $T = 1400^\circ\text{C}$ [1978Ben] $x = 0$, arc melted [1978Ben] $x = 0.25$, arc melted [1970Hai] in the alloy Pu _{0.75} Zr _{0.25} C annealed for 288 h at $T = 1250^\circ\text{C}$ in vacuum, together with the θ and ρ phases [1970Hai] in the alloys Pu _{0.4} Zr _{0.6} C to Pu _{0.8} Zr _{0.2} C sintered for 4 h at $T = 1400^\circ\text{C}$ in vacuum, together with the ρ phase [1978Ben] $x = 0.23$, in the Pu _{0.4} Zr _{0.6} C alloy sintered for 4 h at $T = 1500^\circ\text{C}$ in argon, together with the ρ and θ phases [1978Ben] $x = 0.165$, in the alloy Pu _{0.8} Zr _{0.2} C annealed for 70 h at $T = 1500^\circ\text{C}$ in argon, together with the ρ and θ phases [1978Ben]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
θ , Pu_2C_3 $\lesssim 2050$	$cI40$ $I\bar{4}3d$ Pu_2C_3	$a = 812.58$ to 813.17 $a = 814.5$ $a = 812.10$ $a = 812.56$ $a = 812.56$ to 813.30 $a = 812.8$ $a = 813.0$ $a = 813.0$	~ 59 to ~ 60 at.% C [V-C2] [E] [H] in the alloy $\text{Pu}_{44.3}\text{C}_{55.7}$ [1963Kru] in the alloy $\text{Pu}_{40.4}\text{C}_{59.6}$ [1963Kru] [1978Kot] in the alloys $\text{Pu}_{0.75}\text{Zr}_{0.25}\text{C}$ and $\text{Pu}_{0.25}\text{Zr}_{0.75}\text{C}$ annealed for 288 h at $T = 1250^\circ\text{C}$ in vacuum, together with the μ and ρ phases or with (C) and the ρ phase, respectively [1970Hai] in the alloy $\text{Pu}_{0.75}\text{Zr}_{0.25}\text{C}$ annealed for 30 min at $T = 1650^\circ\text{C}$ in vacuum, together with liquid and the ρ phase [1970Hai] in the alloy $\text{Pu}_{0.25}\text{Zr}_{0.75}\text{C}$ annealed for 5 h at $T = 1800^\circ\text{C}$ in vacuum, together with (C) and the ρ phase [1970Hai]
βPuC_2 (h) > 1660	c^{**}		66.7 at.% C [V-C2]
αPuC_2 (r) < 1660	$tI6$ $I4/mmm$ CaC_2	$a = 363$ to 362 $c = 604$ to 610.5 $a = 363$ $c = 609.4$	66.7 at.% C [V-C2] [1978Kot] [1987Ben]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ρ , ZrC 3540 - (< 500)	$cF8$ $Fm\bar{3}m$ NaCl	$a = 458.2$ to 468.3 $a = 469.5$ $a = 468.4$ to 469.2 $a = 469.41$ $a = 469.83$ $a = 469.34$ to 470.14 $a = 469.7$ $a = 471.5$ $a = 471.0$ $a = 471.3$ $a = 470.0$ $a = 470.1$	33 to 50 at.% C [Mas2] sometimes labelled as “ZrC _{1-x} ” [E] at 50 at.% C [E] [1962Bit] in the alloy Zr _{61.5} C _{38.5} [1965Sar] in the alloy Zr ₅₁ C ₄₉ [1965Sar] [1968Nic] [1978Ben] in the Pu _{0.75} Zr _{0.25} C arc melted alloy together with the μ and θ phases [1970Hai] in the alloy Pu _{0.75} Zr _{0.25} C annealed for 288 h at $T = 1250^\circ\text{C}$ in vacuum, together with the μ and θ phases [1970Hai] in the alloy Pu _{0.75} Zr _{0.25} C annealed for 30 min at $T = 1650^\circ\text{C}$ in vacuum, together with liquid and the θ phase [1970Hai] in the Pu _{0.25} Zr _{0.75} C arc melted alloy together with (C) and the θ phase [1970Hai] in the alloy Pu _{0.25} Zr _{0.75} C annealed for 288 h at $T = 1450^\circ\text{C}$ or during 5 h at $T =$ 1800°C in vacuum, together with (C) and the θ phase [1970Hai]
(Pu _x Zr _{1-x})C		$a = 474.45$ $a = 470.34$	$x = 0$ to 0.24 , $T = 1500^\circ\text{C}$ [1978Ben] $x = 0.21$, in the Pu _{0.6} Zr _{0.4} C alloy annealed for 40 h at $T = 1500^\circ\text{C}$ and cooled under vacuum [1978Ben] $x = 0.03$, in the Pu _{0.4} Zr _{0.6} C arc-melted alloy annealed for 4 h at $T = 1400^\circ\text{C}$ [1978Ben]
ρ' (Zr-C) ≤ 1100	I^{**}	$a = 663$ $c = 1626$ $a = 663.8$ $c = 1626.1$	metastable 39 to 43 at.% C [1979Kha] in the crystalline fragment isolated from the alloy Zr _{59.3} C _{40.7} consequently annealed from 1600°C to 300°C for 1000 h [1983Arb]

Fig. 1: C-Pu-Zr.
Isothermal section at
1500°C



Carbon – Rhodium – Thorium

Kostyantyn Korniyenko

Introduction

Phase relations in the multicomponent systems containing actinide carbides are of great interest in nuclear technology. Of particular importance are ternary systems involving the transition metals, which are the most frequently occurring fission products, the main constituents of the cladding and structural materials and potential alloying elements [1975Hol]. Experimental results relating to the C-Rh-Th system are presented in [1975Hol, 1977Hol, 1984Hol1, 1984Hol2]. To study the phase configurations alloy specimens at 30 different compositions were prepared by arc melting and homogenizing at 1200°C. The alloys were studied by X-ray diffraction, metallography and EMPA in the annealed state. On the basis of the results obtained, an isothermal section covering the whole range of compositions at 1200°C was constructed. [1978Gup] evaluated the free energy and heat content values at different temperatures and obtained the standard value of the atomization energy for the ThRhC₂ molecule. Future investigations of phase relations in the C-Rh-Th system should be concentrated on the study of alloy properties in the equilibrium state at different temperatures. Changes in the character phase equilibria at temperatures higher and lower than 1200°C are needed in particular because of the changes in the compositions and the crystal structures of intermediate phases in the boundary C-Th binary system.

Binary Systems

The C-Rh, C-Th and Rh-Th binary systems are accepted from [Mas2].

Solid Phases

Crystallographic data relating to the known unary and binary phases are listed in Table 1. No ternary phases have been reported. At high temperatures, the C-Th system presents a continuous series of solid solutions between (α Th), the μ phase and the γ ThC₂ phase (labelled as π). All of these phases crystallize into a cubic structure with differing space groups and prototypes.

Isothermal Sections

An isothermal section for the whole range of compositions at 1200°C is shown in Fig. 1. It is presented according to the results of [1975Hol, 1977Hol, 1984Hol1, 1984Hol2] with some corrections for compatibility with the accepted binary systems. Owing to the existence of a continuous series of solid solutions π between (α Th) and the ThC phase at 1200°C, the three-phase region ThC + Th₇Rh₃ + (α Th) is replaced by a two-phase region π + Th₇Rh₃. In the composition range 50 to 100 at.% Th, the two- and three-phase regions are respectively named as ThRh + π and Th₇Rh₃ + ThRh + π . The ThRh₃ phase was shown in [1975Hol, 1977Hol, 1984Hol1, 1984Hol2] as possessing some homogeneity but without any experimental evidence.

Thermodynamics

[1977Hol] noted that dissolving about 5 to 7 at.% C in the κ , ThRh₃ phase stabilizes this phase relative to the neighboring Rh-Th phases and suppresses the α ThRh₂ and λ phases in the ternary region. The free enthalpy of formation of the κ phase in the ternary system at 1200°C was estimated in [1977Hol] from binary data [1975Mur], taking into account the observed phase equilibria. The free enthalpy of formation of the κ phase containing about 5 to 7 at.% C was estimated to be about -305.9 to -268.2 kJ·mol⁻¹. This value is higher than the value measured in the C-Th binary system (-263.6 kJ·mol⁻¹ according to the formula of [1975Mur]). This result confirms the stabilization of the κ phase by carbon.

[1978Gup] observed the gaseous molecule ThRhC₂ in the Knudsen-cell effusate from the C–Rh–Th–U alloys at high temperatures. The thermodynamic properties of ThRhC₂ were evaluated from the various reaction enthalpies determined by the third law method, $\Delta H_{298}^{\circ} = T \cdot \{-R \cdot \ln K_p - \Delta((G_T^{\circ} - H_{298}^{\circ})/T)\}$. The free energy functions $(G_T^{\circ} - H_{298}^{\circ})/T$ were taken from the literature when available or calculated from known or estimated molecular parameters through standard statistical thermodynamic expressions. The calculated values of $-(G_T^{\circ} - H_{298}^{\circ})/T$ and the heat content functions, $H_T^{\circ} - H_{298}^{\circ}$, for ThRhC₂ at various temperatures are listed in Table 2. The values of the $H_{298}^{\circ} - H_0^{\circ}$ heat content functions were obtained as 15.443 kJ·mol⁻¹ for the Rh–Th–C–C structure and 13.748 kJ·mol⁻¹ for the Rh–C–C–Th structure. The atomization energies of gaseous ThRhC₂ were calculated to be 1774 ± 60 kJ·mol⁻¹ and 1763 ± 60 kJ·mol⁻¹ for the temperatures of 25°C and –273.15°C, respectively. After comparison of these data with the estimated value of the heat of formation obtained using the enthalpies of sublimation of C, Rh and Th, the structure Rh–Th–C–C for the ThRhC₂ molecule was proposed. The atomization energy estimated for this structure using the bond additivity method is $H_{at,298}^{\circ} = 1732$ kJ·mol⁻¹.

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (I) < 3827 ± 50	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.9	at 25°C [Mas2] sublimation point at 1.013 bar
(C) (II)	<i>cF8</i> <i>Fd$\bar{3}m$</i> C (diamond)	<i>a</i> = 356.69	at 25°C [Mas2] high pressure phase (> 60.78 bar)
(Rh) < 1963	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	<i>a</i> = 380.32	at 25°C [Mas2] dissolves ~ 1 at.% Th at 1450 ± 12°C [Mas2] dissolves ~ 1.5 at.% C at 1694 ± 17°C [Mas2] and ~ 1.4 at.% C at 1250°C [Mas2]
(βTh) (h) 1755 - 1360	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 411	[Mas2] dissolves ~ 1 at.% Rh at ~1360°C and ~9 at.% C at 1707°C [Mas2]
γ, Th ₇ Rh ₃ < 1362 ± 12	<i>hP20</i> <i>P6₃mc</i> Th ₇ Fe ₃	<i>a</i> = 1003.1 <i>c</i> = 628.4	30 at.% Rh [Mas2]
		<i>a</i> = 1002 <i>c</i> = 629	[V-C2] in the Th _{68.8} Rh _{31.2} alloy [1961Fer]
		<i>a</i> = 1003.1 <i>c</i> = 628.7	[1963Tho]
δ, ThRh < at least ~ 1500	<i>oC8</i> <i>Cmcm</i> CrB	<i>a</i> = 383.4 <i>b</i> = 1120 <i>c</i> = 424.1	50 at.% Rh [Mas2] [V-C2]
		<i>a</i> = 386.6 <i>b</i> = 1124 <i>c</i> = 422	[1962Tho, 1963Tho]
ε, Th ₃ Rh ₄ < 1487	<i>cF*</i>	<i>a</i> = 508.5 ± 2	57 at.% Rh [Mas2] in the annealed alloys Th ₄₄ Rh ₅₆ , Th ₄₃ Rh ₅₇ and Th ₄₂ Rh ₅₈ [1963Tho]

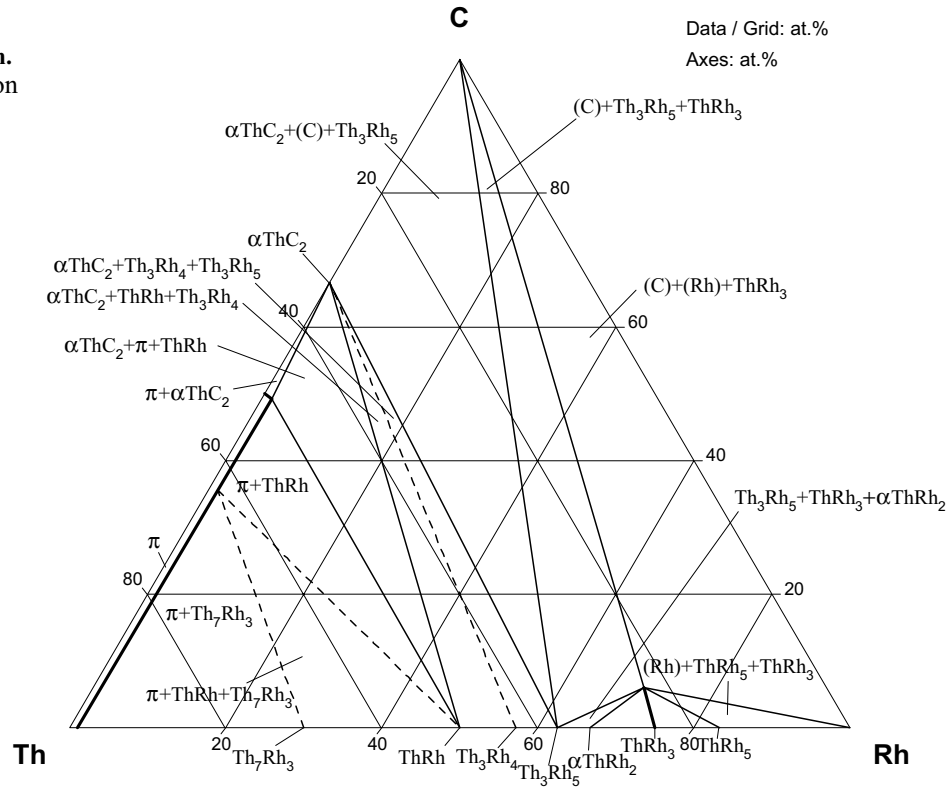
Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
η , Th ₃ Rh ₅ < 1450	<i>t</i> **	$a = 482$ $c = 1460$	~ 61.5 at.% Rh [Mas2] at 1200°C [1977Hol]
β ThRh ₂ (h) < at least ~ 1500 - 1250	<i>hP</i> 6 <i>P</i> 6 ₃ / <i>mmc</i> InNi ₂	$a = 462.9 \pm 2$ $c = 584.9 \pm 3$	~ 66.5 at.% Rh [Mas2] in the as-cast alloy Th ₃₅ Rh ₆₅ [1963Tho]
α ThRh ₂ (r) < 1250	-	-	~ 66.5 at.% Rh [Mas2]
κ , ThRh ₃ < at least ~ 1500	<i>cP</i> 4 <i>Pm</i> $\bar{3}$ <i>m</i> AuCu ₃	$a = 417.3$ $a = 413.9$	75 at.% Rh [Mas2] at 1200°C [1977Hol]. Up to ~ 5 to 7 at.% C, $T = 1200^\circ\text{C}$ [1977Hol] [1961Dwi]
λ , ThRh ₅ < at least ~ 1500	-	-	~ 83 at.% Rh [Mas2]
β ThC ₂ (h ₁) 1495 - 1255	<i>tP</i> 6 <i>P</i> 4 ₂ / <i>mmc</i>	$a = 423.5$ $c = 540.8$	63 to 66 at.% C [Mas2] [S]
α ThC ₂ (r) < 1440	<i>mC</i> 12 <i>C</i> 2/ <i>c</i> α ThC ₂	$a = 669.2$ $b = 422.3$ $c = 674.4$ $\beta = 103.0^\circ$ $a = 653$ $b = 424$ $c = 656$ $\beta = 104^\circ$	66 at.% C [Mas2] [H]
ω , Th ₂ C ₃		$a = 856.09$ to 865.13	metastable [1996Vel] high pressure phase (at 1325°C, $3.5 \cdot 10^{-4}$ bar)

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
π , Th _{1-x-y} Ru _x C _y			$x = 0, 0.22 \leq y \leq 0.66$, 2000°C [Mas2] $x = 0, 0.04 \leq y \leq 0.50, 0.62 \leq y \leq 0.66$, 1500°C [Mas2] $x = 0, 0.33 \leq y \leq 0.50$, 1100°C [Mas2] $x = 0, 0.41 \leq y \leq 0.50$, 800°C [Mas2] $x = 0, y = 0.355$ [S]
(α Th) (r) < 1360	$cF4$ $Fm\bar{3}m$ Cu	$a = 508.42$	at 25°C [Mas2]
μ , ThC < 2500	$cF8$ $Fm\bar{3}m$ NaCl	$a = 530.1$ $a = 530.3$ $a = 534.6$ $a = 534.6$ $a = 533.8$ $a = 534$	$x = 0, y = 0.382$ [1996Vel] $x = 0, y = 0.495$ [1996Vel] $x = 0, y = 0.5$ [1962Kem] $x = 0$ [E] $x = 0$ [H]
γ ThC ₂ (h ₂) 2610 - 1470	$cP12$ $Pa\bar{3}$ FeS ₂	$a = 580.8$	at 1500°C [1964Hil]

Table 2: Thermodynamic Properties of the ThRhC₂ Molecule in a Gaseous State

Structure of the Molecule	Temperature [°C]	Free Energy Function $-(G_T^\circ - H_{298}^\circ)/T$ [J·mol ⁻¹ ·K ⁻¹]	Heat Content Function $H_T^\circ - H_{298}^\circ$ [kJ·mol ⁻¹]
Rh-Th-C-C	25	311.76	0.00
	1827	395.87	147.41
	1927	399.15	156.01
	2027	402.32	164.63
	2127	405.38	173.25
	2227	408.34	181.89
	2327	411.20	190.53
	2427	413.98	199.17
Rh-C-C-Th	25	303.16	0.00
	1827	383.52	144.13
	1927	386.74	152.70
	2027	389.84	161.27
	2127	392.83	169.86
	2227	395.74	179.46
	2327	398.55	187.07
	2427	401.27	195.69

Fig. 1: C-Rh-Th.
Isothermal section
at 1200°C



Carbon – Rhodium – Uranium

Kostyantyn Korniyenko

Introduction

Phase relations in multicomponent systems containing actinide carbides are of great interest in nuclear technology. In particular, the failure of metallic fuels to meet the requirements of nuclear power reactors is gradually leading to their replacement by ceramic fuels. A great deal of interest has consequently been centred on uranium carbide and its solid solutions. During fission, the composition of the fuel will change, with the result that at about 10% burn-up approximately 16% of the atoms will be foreign atoms [1974Nar]. A knowledge of the behavior of these fission products is obviously very important. Consequently, phase relation and thermodynamic studies of C-U fission product systems are necessary to ascertain the stability of the fuel during operating conditions. Among the metals presenting metallic fission products, rhodium has been identified. Results of experimental studies of the C-Rh-U system are presented as isothermal sections at 1300°C [1973Hol, 1975Hol, 1984Hol1, 1984Hol2] and 700°C ([1973Wes], quoted by [1974Nar]). The crystal structure of the U_2RhC_2 phase and its stability were studied by [1964Far, 1968Hol, 1969Hai, 1985Ara]. A brief survey of the literature on the C-Rh-U system has been presented by [1975Hol, 1984Hol1, 1984Hol2].

Experimentally determined thermodynamic properties were obtained by [1973Hol, 1974Nar, 1978Gup]. The thermal conductivity of the U_2RhC_2 phase was determined by [1985Ara]. Magnetic properties of the U_2RhC_2 phase were studied by [1996Ebe]. The experimental methods employed along with the temperature and composition ranges studied are presented in Table 1. Information about phase equilibria in the C-Rh-U system is incomplete. In particular, experimental data relating to phase equilibria in the U rich region need further refinement. Information about the conditions of crystallization of the alloys is lacking. Future investigations of phase relations in the C-Rh-U system should be concentrated on the continuation of the study of alloy properties in the equilibrium state at different temperatures.

Binary Systems

Data relating to the forming binary C-Rh, C-U and Rh-U systems are accepted from [Mas2].

Solid Phases

Crystallographic data of the known unary and binary phases as well as the ternary τ phase are compiled in Table 2. The ternary compound was discovered as a product of the solid-state reaction between uranium carbide and rhodium at a temperature of about 1700°C, and was subsequently prepared by arc melting together the three elements [1964Far, 1967Kri]. The ternary τ phase was supposed to form by a peritectic reaction at a temperature above 1700°C [1967Kri]. According to [1973Hol], the binary URh_3 compound dissolved up to 5 at.% C in a cast alloy and 3 at.% C after annealing at 1300°C. [1968Far] noted that UC reacts with a small amount of rhodium to form the τ phase, and the reaction of UC with more than the stoichiometric amount of rhodium required to form this ternary phase causes the formation of graphite and the ϵ phase.

Isothermal Sections

Isothermal sections for the whole composition range at temperatures of 1300°C and 700°C are shown in Figs. 1 and 2, respectively. The section at 1300°C is presented based on the data of [1973Hol] reproduced in [1975Hol, 1984Hol1, 1984Hol2]. Some corrections have been made to ensure agreement with the accepted boundary binary systems. Thus, the extension of the liquid phase field in the uranium corner is increased due to a higher extension in the boundary C-U system (up to 6 at.% C). The (Rh) single-phase range is drawn due to the existence of solubilities at 1300°C of uranium (about 1.5 at.%) and carbon (about

0.5 at.%) in rhodium. The position of the τ phase is shown in Fig. 1 at the stoichiometric composition without a homogeneity range because there is no information on its composition range given in [1973Hol]. The isothermal section at 700°C (Fig. 2) is shown following the data of [1973Wes], presented in [1974Nar], with corrections in accordance with the accepted binary systems. Because the ε and ζ phases do not take part in equilibria at 700°C in the C–U binary system, the corresponding fields are replaced by the $\delta + (C) + \tau$ field. As the U_2Rh and URh phases do not exist in the binary Rh–U system their phase fields are replaced by corresponding fields including the αU_4Rh_3 phase. The U rich corner of the section is speculative, taking into account the γ and β modifications of U.

Thermodynamics

The Gibbs energies of formation of the “ URh_3C_x ” and U_2RhC_2 compounds were determined by [1973Hol] and [1974Nar], respectively, by means of solid-state electrolytic cells, using CaF_2 as the electrolyte. The temperature dependence of ΔG_T° “ URh_3C_x ” for the temperature range 597–827°C is expressed as ΔG_T° (“ URh_3C_x ”) = $-239000 - 23 \cdot T \pm 1676$ (J, mol, K). At 827°C, the values of the thermodynamic properties of the $(URh_3)_{1-x}C_x$ compound are: $\Delta G^\circ = -264389 \pm 1676$ J·mol⁻¹; $\Delta H^\circ = -238830 \pm 18855$ J·mol⁻¹; $\Delta S^\circ = -23045 \pm 16760$ J·K⁻¹·mol⁻¹. All of these data correspond to the ε phase in equilibrium with (Rh) and (C). [1973Hol] noted that the stability of the ε phase in the C–Rh–U ternary system is only negligibly higher than in the binary Rh–U system. The Gibbs energy of formation of the U_2RhC_2 compound at 827°C was estimated in [1973Hol] as being between -528000 and -268000 J·mol⁻¹. According to the experimental results of [1974Nar], the value of this parameter at 827°C is similar to the limiting value in the presented interval being equal to -267190 J·mol⁻¹. The temperature dependence of the Gibbs energy of formation of the U_2RhC_2 compound for the temperature range 727–927°C is as follows: ΔG_T° (U_2RhC_2) = $-303380 - 32.9 \cdot T$ (J, mol, K) [1974Nar]. These results were determined using a $U_{43}Rh_{22}C_{35}$ alloy containing the τ phase together with the δ and U_3Rh_5 phases. [1978Gup] observed the gaseous molecule $URhC_2$ in the Knudsen-cell effusate from a C–Rh–Th–U alloy at high temperatures. The thermodynamic properties of $URhC_2$ were evaluated from the various reaction enthalpies determined by the third law method, $\Delta H_{298}^\circ = T \cdot \{-R \cdot \ln K_p - \Delta((G_T^\circ - H_{298}^\circ)/T)\}$. The free energy functions $(G_T^\circ - H_{298}^\circ)/T$ were taken from the literature when available or calculated from known or estimated molecular parameters through standard statistical thermodynamic expressions. The calculated values of $-(G_T^\circ - H_{298}^\circ)/T$ and the heat content functions, $H_T^\circ - H_{298}^\circ$, for the $URhC_2$ molecule at various temperatures are listed in Table 3. The values of the $H_{298}^\circ - H_0^\circ$ heat content functions were obtained as 15378 J·mol⁻¹ for the Rh–U–C–C structure and 13700 J·mol⁻¹ for the Rh–C–C–U structure. The average value of the atomization energy, $\Delta H_{at, 298}^\circ$ ($URhC_2$) = 1757 ± 50 kJ·mol⁻¹, which is closer to the value of 1775 ± 46 kJ·mol⁻¹ estimated for the structure Rh–U–C–C than the corresponding value, $\Delta H_{at, 298}^\circ$ ($URhC_2$) = 1789 ± 50 kJ·mol⁻¹ to the value of 1704 ± 50 kJ·mol⁻¹ estimated for the Rh–C–C–U structure from bond additivity considerations. The authors proposed that the linear structure Rh–U–C–C represents the molecule $URhC_2$. The atomization energies of gaseous $URhC_2$ were calculated to be 1757 ± 50 kJ·mol⁻¹ and 1746 ± 50 kJ·mol⁻¹ for temperatures of 25°C and -273.15°C , respectively. A summary of the third law reaction enthalpies and the derived atomization energies for $URhC_2$ are given in Table 4.

Notes on Materials Properties and Applications

The C–Rh–U alloys are the prospective materials for applications in nuclear technology as the alloys contain uranium carbide and the transition metal rhodium. The temperature dependence of the thermal diffusivity of the U_2RhC_2 phase measured by [1985Ara] over the temperature range from 477 to 1227°C is shown in Fig. 3. The temperature dependence of the thermal conductivity obtained for the U_2RhC_2 phase normalized to a 100% theoretical density ($12.7 \text{ g}\cdot\text{cm}^{-3}$) was measured over the temperature range from 477 to 1227°C and is presented in Fig. 4. The magnetic susceptibility of the U_2RhC_2 phase was investigated by [1996Ebe] using a SQUID magnetometer and magnetic flux densities of up to 5.5 T over the temperature range from 2 and 300 K (-271°C to 27°C). A temperature dependent paramagnetism was shown (Fig. 5). This property is compatible with one unpaired electron per transition metal site. The U_2RhC_2 phase also exhibits complex

magnetic behavior below a Néel temperature of $T_N = 18 \pm 1$ K (the inset of Fig. 5). At still lower temperature, the reciprocal susceptibility of U_2RhC_2 decreases suggesting ferromagnetic ordering with a Curie temperature of $T_C = 13 \pm 2$ K. This is confirmed by the magnetization measurements (Fig. 6) which clearly show a hysteresis in the plot recorded at 5 K. Between the different measuring cycles, the sample was heated to above 50 K (-223°C) and cooled to the temperatures indicated in Fig. 6 in a zero magnetic field.

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Table 1: Investigations of the C-Rh-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1964Far] as quoted by [1969Hai]	X-ray studies	U_2RhC_2
[1968Far]	Studies of UC (I) interaction with rhodium	The $\text{U}_2\text{RhC}_2 + (\text{C}) + \text{URh}_3$ phase region
[1968Hol]	X-ray Debye-Scherrer and Guinier studies	1300-1600°C, $\sim \text{U}_2\text{RhC}_2$
[1969Hai]	X-ray Debye-Scherrer studies	U_2RhC_2
[1973Hol]	X-ray Guinier studies, metallography, emf measurements	598-877°C, 1300°C, 1500°C, whole range of compositions
[1974Nar]	Metallography, EMPA, emf measurements	700, 727-927°C, whole range of compositions
[1975Hol]	Experimental techniques	1300°C, whole range of compositions
[1978Gup]	High temperature mass spectrometry	U_2RhC_2
[1984Hol1]	Experimental techniques	1300°C, whole range of compositions
[1984Hol2]	Experimental techniques	1300°C, whole range of compositions
[1985Ara]	X-ray diffraction, chemical analysis, bulk density and thermal conductivity measurements	477-1227°C, 1550°C, U_2RhC_2
[1996Ebe]	X-ray Guinier studies, SQUID magnetic susceptibility measurements	2-300 K (–271-27°C), U_2RhC_2

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (I) < 3827 ± 50 (sublimation point), 1.013 bar	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	$a = 246.12$ $c = 670.9$	at 25°C [Mas2]
(C) (II) > 60.78 bar	<i>cF8</i> <i>Fd$\bar{3}m$</i> C (diamond)	$a = 356.69$	at 25°C [Mas2]
(Rh) < 1963	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 380.32$	dissolves 1.5 at.% C at 1694°C and 2 at.% U at 1393°C [Mas2] at 25°C [Mas2]
$U_xRh_{1-x-y}C_y$			$x = 0, 0 \leq y \leq 0.015, 1694 \pm 17^\circ\text{C}$ [Mas2] $x = 0, 0 \leq y \leq 0.005, 1300^\circ\text{C}$ [Mas2] $y = 0, 0 \leq x \leq 0.02, 1393^\circ\text{C}$ [Mas2] $y = 0, 0 \leq x \leq 0.015, 1300^\circ\text{C}$ [Mas2]
(γ U) (h_2) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352.4$	dissolves ~9 at.% Rh at 855°C and 0.22 to 0.37 at.% C at 1119°C [Mas2] [Mas2]
$U_{1-x-y}Rh_xC_y$			$x = 0, 0 \leq y \leq 0.0022$ to 0.0037, 1119 ± 1°C [Mas2] $y = 0, 0 \leq x \leq 0.01, 855^\circ\text{C}$ [Mas2]
(β U) (h_1) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> β U	$a = 1075.9$ $c = 565.6$	dissolves ~2 at.% Rh at 683°C [Mas2] [Mas2]
$U_{1-x-y}Rh_xC_y$			$x = 0, 0 \leq y \leq 0.0002, 772^\circ\text{C}$ [Mas2] $y = 0, 0 \leq x \leq 0.02, 683^\circ\text{C}$ [Mas2]
(α U) (r) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	dissolves about 1 at.% Rh at 625°C [Mas2] at 25°C [Mas2]
$U_{1-x-y}Rh_xC_y$			$x = 0, 0 \leq y \leq 6 \cdot 10^{-5}, 660^\circ\text{C}$ [Mas2] $y = 0, 0 \leq x \leq 0.01, 625^\circ\text{C}$ [Mas2]
αU_4Rh_3 (h) 1155 - 720	-	-	43 at.% Rh [V-C2]
βU_4Rh_3 (r) 720 - at least < 400	-	-	43 at.% Rh [V-C2]
U_3Rh_4 1450 - at least < 400	-	-	57 at.% Rh [V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
U ₃ Rh ₅ 1550 - at least < 400	-	-	~ 63 at.% Rh [V-C2]
URh ₃ < 1700	<i>cP4</i> <i>Pm$\bar{3}m$</i> AuCu ₃	<i>a</i> = 399.2 <i>a</i> = 399.1 <i>a</i> = 401.5 <i>a</i> = 400.8 <i>a</i> = 399.0 <i>a</i> = 399.3 <i>a</i> = 399.1	75 at.% Rh [V-C2] Labelled as “URh ₃ C _{0.1} ” [1975Hol, 1984Hol1, 1984Hol2] or “URh ₃ C _x [1973Hol] dissolves up to 5 at.% C in cast alloy and 3 at.% C at 1300°C [1973Hol] [E] [1961Dwi] for URh ₃ in ternary cast alloy [1973Hol] for URh ₃ in equilibrium with τ and (C) at 1300°C [1973Hol] for URh ₃ in equilibrium with (Rh) at 1300°C [1973Hol] for URh ₃ in equilibrium with (Rh) and (C) at 1300°C [1973Hol] for URh ₃ in equilibrium with (Rh) and (C) at 800°C [1973Hol]
δ , UC (I) 2585 - 1119 1.013 bar	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	<i>a</i> = 495.98 <i>a</i> = 495.63 <i>a</i> = 495.1 <i>a</i> = 496 to 496.2 <i>a</i> = 507 <i>a</i> = 495.6 <i>a</i> = 496.05	47 to 66 at.% C [Mas2] [E] at 48 at.% C [S] [1957Kie] [1961Ben] at 2100°C [1972Ben] at 1400°C [S] at 25°C [1972Ben]
UC (II) > 2.7·10 ⁵ bar	rhombic	-	[1987Ben]
ζ , U ₂ C ₃ 1823 - ~ 850	<i>cI40</i> <i>I$\bar{4}3d$</i> Pu ₂ C ₃	<i>a</i> = 808.8 <i>a</i> = 808.90 <i>a</i> = 808.89	60 at.% C [Mas2] [H] [S] [1972Ben]
ϵ , UC ₂ 1793 - 1516	<i>tI6</i> <i>I4/mmm</i> CaC ₂	<i>a</i> = 351.7 <i>c</i> = 598.7 <i>a</i> = 352.4 <i>c</i> = 599.9 <i>a</i> = 351.9 to 352.41 <i>c</i> = 597.87 to 599.62 <i>a</i> = 352.7 <i>c</i> = 598	62 to 62.5 at.% C [Mas2] [E] [H] [S] [1961Ben]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
UC ₂ 2434 - 1762	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF ₂ ?	$a = 545.0$	actually, “UC ₂ ” phase represents the δ ,UC phase in equilibrium with graphite [2001Che]
* τ , U ₂ RhC ₂ ≤ 1717	<i>tI10l</i> <i>I4/mmm</i> U ₂ IrC ₂	$a = 346.6$ $c = 1251.2$	[1964Far]
		$a = 346.4$ $c = 1251.3$	at 1300°C [1968Hol, 1973Hol]
		$a = 346.6$ $c = 1251.5$	in the single-phase alloy annealed at 1500°C [1969Hai]
		$a = 347$ $c = 1253$	sintered at 1550°C, with traces of UC [1985Ara]

Table 3: Thermodynamic Properties of the URhC₂ Molecule in a Gaseous State [1978Gup]

Structure of the Molecule	Temperature [°C]	Free Energy Function, $-(G_T^\circ - H_{298}^\circ)/T$ [J·mol ⁻¹ ·K ⁻¹]	Heat Content Function, $H_T^\circ - H_{298}^\circ$ [J·mol ⁻¹]
Rh-U-C-C	25	310.60	0.00
	1827	394.61	147330
	1927	397.89	155940
	2027	401.06	164550
	2127	404.12	173180
	2227	407.08	181810
	2327	409.94	190450
	2427	412.71	199100
Rh-C-C-U	25	302.66	0.00
	1827	382.96	144080
	1927	386.17	152640
	2027	389.27	161220
	2127	392.27	169810
	2227	395.17	178410
	2327	397.98	187020
	2427	400.71	195640

Fig. 1: C-Rh-U.
Isothermal section at
1300°C

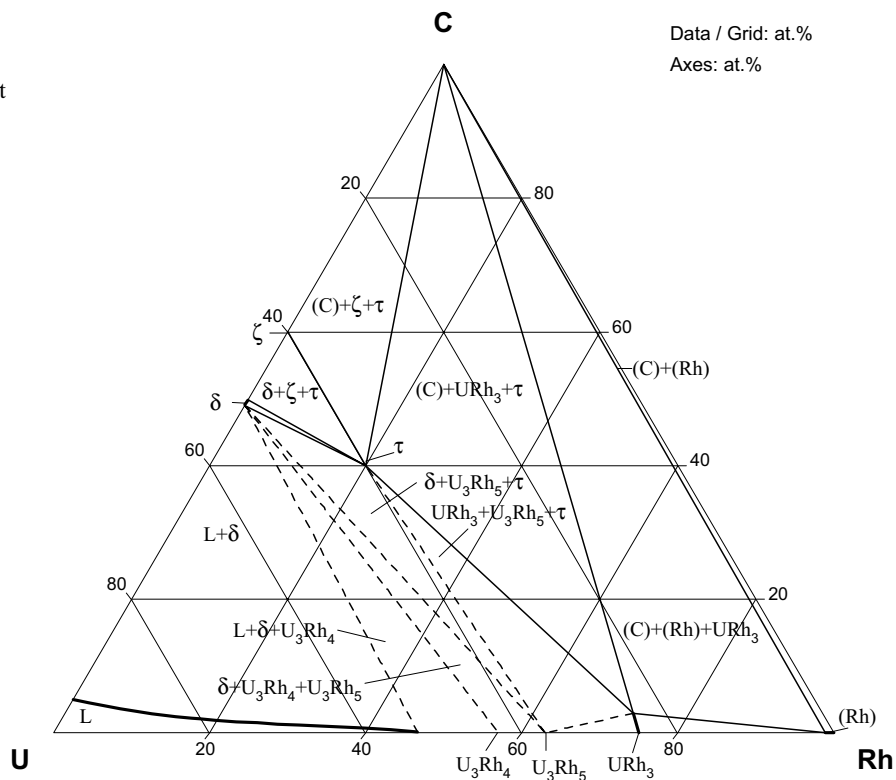


Fig. 2: C-Rh-U.
Isothermal section at
700°C

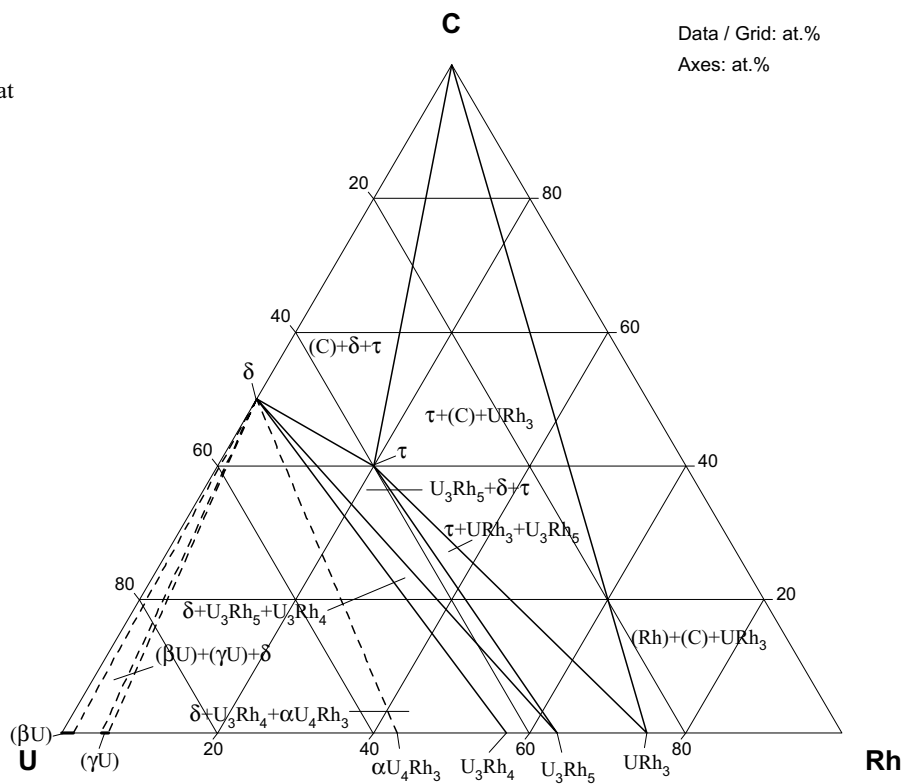


Fig. 3: C-Rh-U.
Thermal diffusivity of
the U_2RhC_2 phase
measured over the
temperature range
from 477 to 1227°C

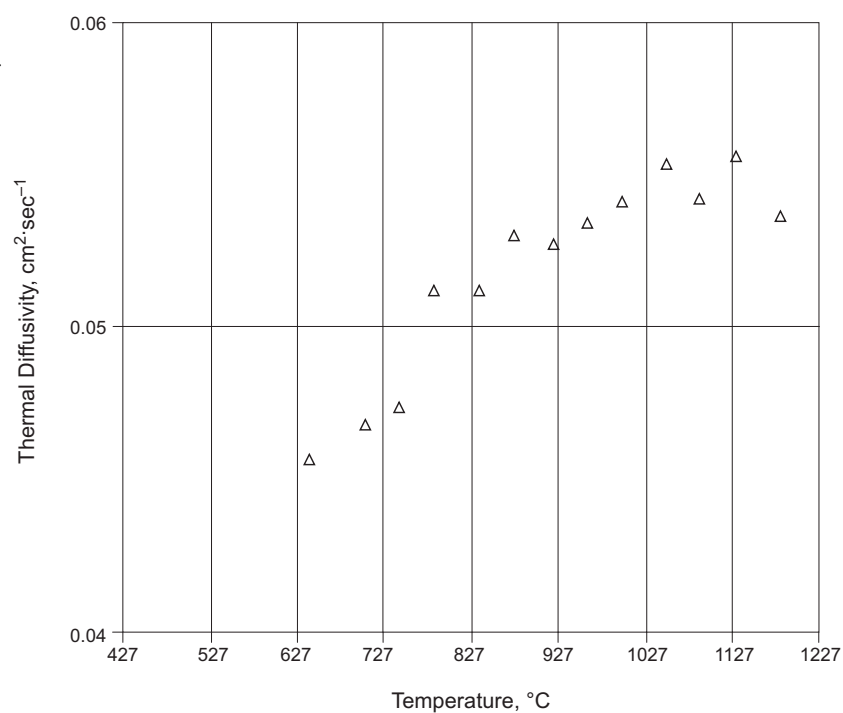


Fig. 4: C-Rh-U.
Thermal conductivity
of the U_2RhC_2 phase
normalized to 100%
theoretical density
measured over the
temperature range
from 477 to 1227°C

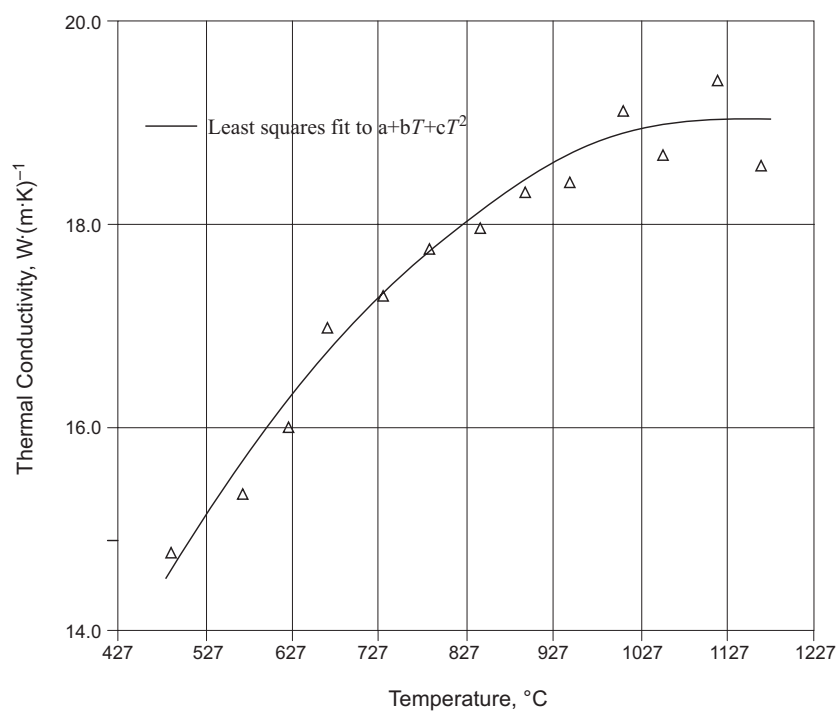


Fig. 5: C-Rh-U.
Temperature dependence of the reciprocal susceptibility of U_2RhC_2 . Low temperature behaviour of the reciprocal susceptibility in magnetic fields of 1 T and 5 T (the inset)

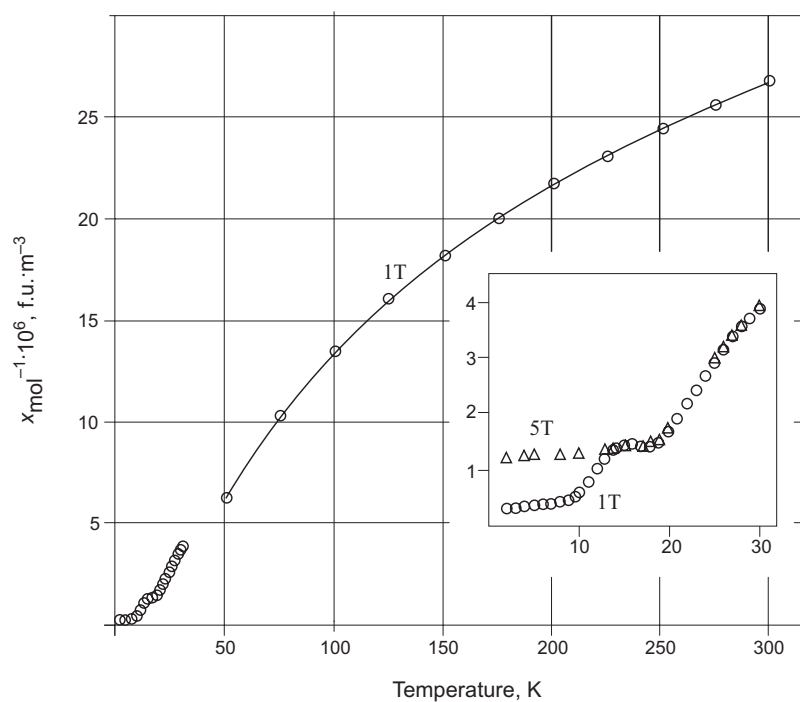
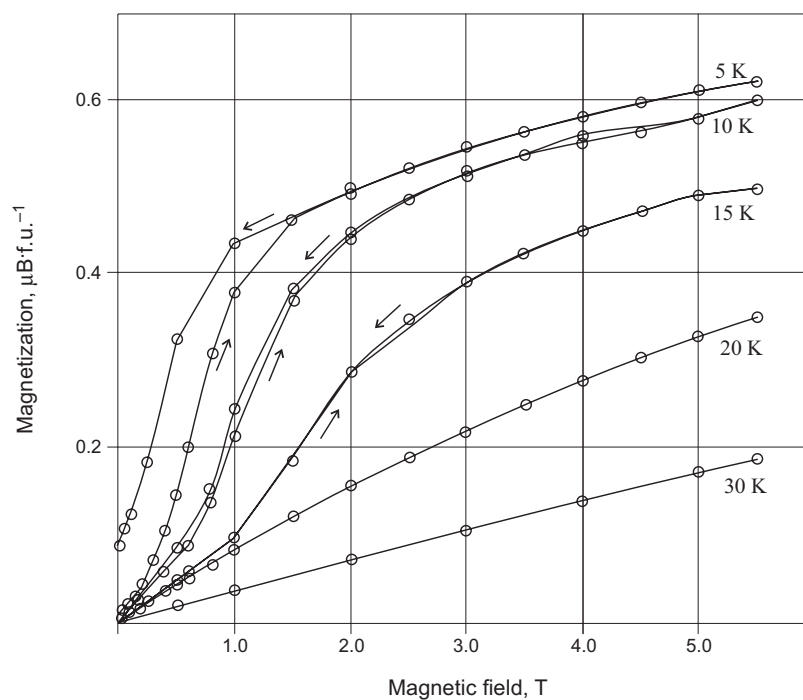


Fig. 6: C-Rh-U.
Magnetisation vs magnetic flux densities B of U_2RhC_2 at different temperatures



Carbon – Ruthenium – Thorium

Kostyantyn Korniyenko

Introduction

For many problems in nuclear technology, information about phase relations in multicomponent systems containing actinide (in particular, thorium) carbides is of a great interest. Of particular importance in this context are ternary systems involving the transition metals, which are the most frequently occurring fission products, the main constituents of the cladding and structural materials and potential alloying elements [1975Hol]. Experimental results concerning the ternary C–Ru–Th system are represented by isothermal sections at 1200°C [1975Hol, 1977Hol, 1984Hol1, 1984Hol2] and 900°C [1995Wac] and the crystal structures of the ternary phases [1971Hol, 1977Hol, 1990Aks1, 1990Aks2, 1995Wac]. The experimental methods used together with the temperature and composition ranges studied are presented in Table 1. Information relating to the phase equilibria of the C–Ru–Th system is incomplete. In particular, experimental data for the Th corner are in need of further refinement. Future investigations of phase relations in the C–Ru–Th system need to be concentrated on obtaining information relating to the conditions of alloy crystallization as well as continuing the study of alloy behavior in the equilibrium state at different temperatures.

Binary Systems

Data relating to the forming C–Ru, C–Th and Ru–Th systems are accepted from [Mas2].

Solid Phases

Crystallographic data relating to the known unary, binary and ternary phases are listed in Table 2. In the C–Th system at high temperatures, a continuous series of solid solutions between (α Th), the μ phase and the γ ThC₂ phase are present (labelled as π). All of these phases possess a cubic structure but of differing space groups and prototypes. It was established that at temperatures of 1200 and 900°C, three ternary phases, τ_1 , τ_2 and τ_3 , exist [1971Hol, 1975Hol, 1977Hol, 1984Hol1, 1984Hol2, 1995Wac], but the temperature ranges of their stability were not determined. These phases do not possess visible homogeneity ranges.

Isothermal Sections

Figure 1 presents an isothermal section for 1200°C covering the whole range of compositions, taken from the data of [1975Hol, 1977Hol, 1984Hol1, 1984Hol2] with amendments in accordance with the refinement of the compositions of the τ_1 and τ_2 phases ([1990Aks1, 1990Aks2, 1995Wac] data compared with the data from earlier publications). In the boundary binary C–Th system, homogeneity region of the π phase stretches from 50 to 100 at.% Th, but in the ternary system, this phase probably does not possess a visible homogeneity with respect to ruthenium content; as in the boundary binary Ru–Th system. The positions of the three-phase regions $\pi + \gamma + \delta$ and $\pi + \delta + \epsilon$ need to be refined.

The isothermal section for a temperature of 900°C covering the whole composition range taken from [1995Wac] is shown in Fig. 2. The constitution of the boundary Ru–Th binary system, according to the accepted [Mas2] data, is well established for temperatures above 1000°C. For this reason, it is accepted that the stoichiometries and homogeneity regions of the Ru–Th binary phases at 900°C are the same as those at 1000°C. In the C–Th system, a two-phase field between (α Th) and μ phases is present, but its position was corrected after comparing with [1995Wac] data. Therefore, the positions of the (α Th) + $\mu + \gamma$, $\mu + \gamma + \delta$ and $\mu + \delta + \epsilon$ three-phase fields were also corrected (marked by dashed lines).

Thermodynamics

The free enthalpies of formation of the τ_1 and τ_3 phases in the ternary system at 1473 K (1200°C) were estimated by [1977Hol] using binary Ru–Th data for 1020 to 1170 K (747 to 897°C) [1974Kle], binary C–Th data [1975Kub, 1977Hol] and by taking into account the observed phase equilibria. From the reactions $4\varepsilon + 6(\alpha\text{ThC}_2) = 7\mu + \tau_1$ and $\tau_1 + 6\text{Th} = 5\mu + 4\varepsilon$, the free enthalpy of formation of the τ_1 phase at 1200°C was estimated to be -824.80 to -464.73 kJ·mol⁻¹. From the reactions $\mu + 3\eta = 3\varepsilon + \tau_3$ and $\tau_3 + 3\delta = 9\varepsilon + \mu$, the free enthalpy of formation of the τ_3 phase at 1200°C was estimated to be -226.09 to -117.23 kJ·mol⁻¹.

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Table 1: Investigations of the C-Ru-Th Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1971Hol]	Arc melting, annealing, X-ray studies, metallography, microanalysis	1200°C, the $\text{Th}_{20}\text{Ru}_{40}\text{C}_{40}$ alloy
[1975Hol]	Experimental techniques	1200°C, whole range of compositions
[1977Hol]	Arc melting, annealing, X-ray studies, metallography, microanalysis	1200°C, 1300°C, whole range of compositions
[1984Hol1]	Experimental techniques	1200°C, whole range of compositions
[1984Hol2]	Experimental techniques	1200°C, whole range of compositions
[1990Aks1]	Laue, rotation and lines layers scanning techniques	$\text{Th}_2\text{Ru}_6\text{C}_5$
[1990Aks2]	Annealing; Laue, rotation and lines layers scanning techniques, powder X-ray diffraction	$\text{Th}_{11}\text{Ru}_{12}\text{C}_{18}$
[1995Wac]	Arc melting, annealing, EDX, Guinier X-ray diffraction	900°C, whole range of compositions

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (I) < 3827 ± 50 (sublimation point), 1.013 bar	$hP4$ $P6_3/mmc$ C (graphite)	$a = 246.12$ $c = 670.9$	at 25°C [Mas2]
(C) (II) > 60.78 bar	$cF8$ $Fd\bar{3}m$ C (diamond)	$a = 356.69$	at 25°C [Mas2]
(Ru) < 2334 $\text{Th}_x\text{Ru}_{1-x-y}\text{C}_y$	$hP2$ $P6_3/mmc$ Mg	$a = 270.58$ $c = 428.16$	at 25°C [Mas2] $x = 0, 0 \leq y \leq 0.03, 1940^\circ\text{C}$ [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(βTh) (h) 1755 - 1360	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 411$	[Mas2]
Th _{1-x-y} Ru _x C _y			$x = 0, 0 \lesssim y \lesssim 0.09, 1707^\circ\text{C}$ [Mas2]
γ, Th ₇ Ru ₃ 1412 - at least < 1000	<i>hP20</i> <i>P6₃mc</i> Th ₇ Fe ₃	$a = 996.9$ $c = 630.2$	30 at.% Ru [V-C2] [1963Tho]
		$a = 997.1$ $c = 628.8$	Ru rich side [1974Kle]
δ, Th ₃ Ru ₂ 1425 - at least < 1000	-	-	40 at.% Ru [V-C2]
ε, ThRu 1462 - at least < 1000	<i>oC8</i> <i>Cmcm</i> CrB	$a = 387.8$ $b = 1129$ $c = 407.1$	50 at.% Ru [V-C2] [1963Tho]
		$a = 390.3$ $b = 1127$ $c = 404.6$	Th rich side [1974Kle]
		$a = 387.8$ $b = 1126$ $c = 406.9$	Ru rich side [1974Kle]
η, ThRu ₂ 1500 - at least < 1000	<i>cF24</i> <i>Fd$\bar{3}m$</i> MgCu ₂	$a = 764.9$	66.7 at.% Ru [V-C2] [E]
		$a = 765.7$	[1963Tho]
		$a = 765.4$	[1974Kle]
βThC ₂ (h ₁) 1495 - 1255	<i>tP6</i> <i>P4₂/mmc</i>	$a = 423.5$ $c = 540.8$	63 to 66 at.% C [V-C2] [S]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
αThC_2 (r) < 1440	<i>mC</i> 12 <i>C</i> 2/ <i>c</i> αThC_2	$a = 653$ $b = 424$ $c = 656$ $\beta = 104^\circ$	66 at.% C [V-C2] [H] [1987Ben] [1964Gan]
ω , Th_2C_3 1325, $3.5 \cdot 10^{-4}$ bar	-	$a = 856.09$ to 865.13	Metastable [1996Vel]
π , $\text{Th}_{1-x-y}\text{Ru}_x\text{C}_y$			$x = 0, 0.22 \leq y \leq 0.66, 2000^\circ\text{C}$ [Mas2] $x = 0, 0.04 \leq y \leq 0.50, 0.62 \leq y \leq 0.66, 1500^\circ\text{C}$ [Mas2] $x = 0, 0.33 \leq y \leq 0.50, 1100^\circ\text{C}$ [Mas2] $x = 0, 0.41 \leq y \leq 0.50, 800^\circ\text{C}$ [Mas2] $x = 0, y = 0.355$ [S]
(αTh) (r) < 1360	<i>cF</i> 4 <i>Fm</i> $\bar{3}m$ Cu	$a = 508.42$	at 25°C [Mas2]
μ , ThC < 2500	<i>cF</i> 8 <i>Fm</i> $\bar{3}m$ NaCl	$a = 530.1$ $a = 530.3$ $a = 534.6$ $a = 534.6$ $a = 533.8$ $a = 534$	$x = 0, y = 0.382$ [1996Vel] $x = 0, y = 0.495$ [1996Vel] $x = 0, y = 0.5$ [1962Kem] $x = 0$ [E] $x = 0$ [H]
γThC_2 (h_2) 2610 - 1470	<i>cP</i> 12 <i>Pa</i> $\bar{3}$ FeS_2	$a = 580.8$	at 1500°C [1964Hil]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_1 , Th ₁₁ Ru ₁₂ C ₁₈	cI^* $\bar{I}43m$ Th ₁₁ Ru ₁₂ C ₁₈	$a = 1078$	at 1200°C, labelled as “Th _{~0.27} Ru _{~0.30} C _{~0.43} ” and “Th _{3+x} Ru _{4-x} C ₅ ” ($x \approx 0.3$) [1971Hol], “Th _{~3} Ru _{~4} C _{~5} ” [1977Hol]
		$a = 1076.4$	X-ray powder diffraction [1990Aks2]
		$a = 1075.4$	single crystal [1995Wac]
* τ_2 , Th ₂ Ru ₆ C ₅	tP^* $P4/mbm$ Th ₂ Ru ₆ C ₅	$a = 911.3$ $c = 418.6$	labelled as “ThRu ₃ C _{1.5} ” [1971Hol, 1977Hol] single crystal [1990Aks1]
		$a = 909.6$ $c = 417.74$	single crystal [1995Wac]
* τ_3 , ThRu ₃ C	$cP5$ $Pm\bar{3}m$ CaTiO ₃	$a = 421.0$	labelled as “ThRu ₃ C _{1-x} ” ($0 < x < 0.1$) [1971Hol, 1977Hol]
		$a = 422.7$	single crystal [1995Wac]

Fig. 1: C–Ru–Th.
Isothermal section at
1200°C

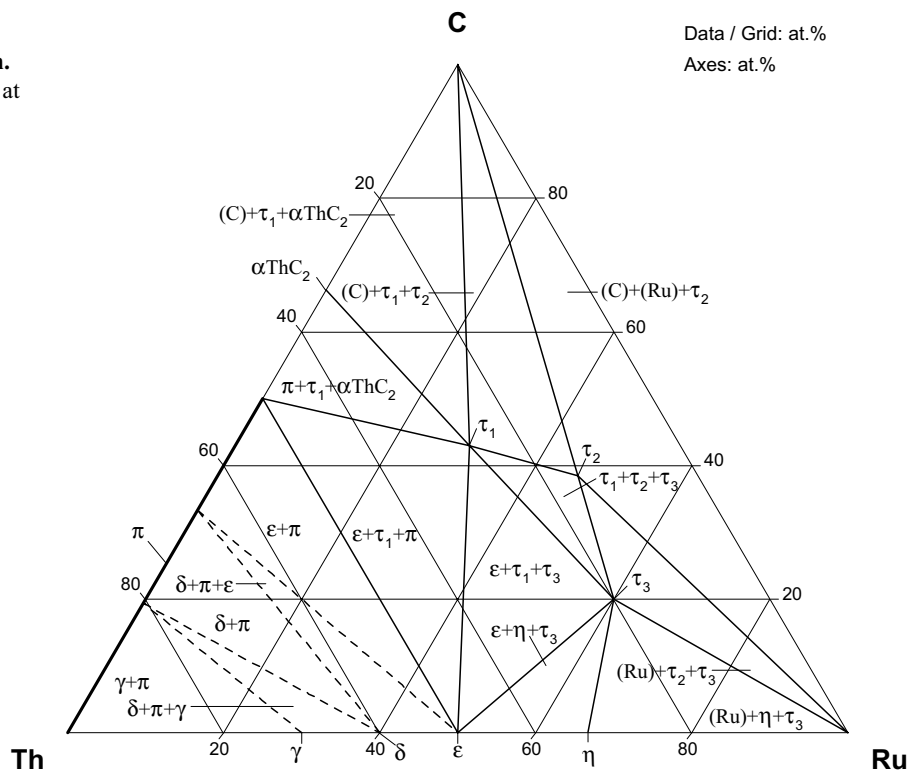
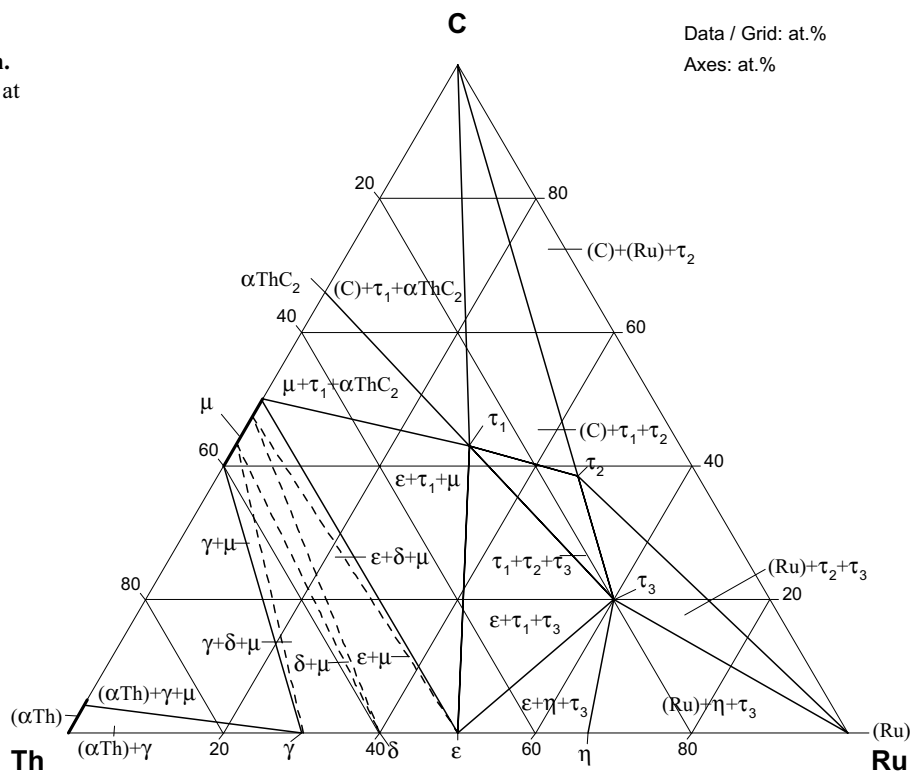


Fig. 2: C–Ru–Th.
Isothermal section at
900°C



Carbon – Ruthenium – Uranium

Kostyantyn Korniyenko

Introduction

Much attention has been paid to the C–Ru–U system because Ru is a product of nuclear fission and a knowledge of the phase relationships of U and C with Ru is of fundamental importance in the interpretation of irradiation experiments involving carbide fuel materials. Table 1 summarizes investigations of the phase relations and thermodynamics of the C–Ru–U system with the experimental techniques and the observed temperature and composition ranges are indicated.

Experimental phase equilibrium data for the C–Ru–U system were presented as isothermal sections at 1300°C [1970Hol, 1975Hol, 1984Hol1, 1984Hol2] and 1000°C [1970Hai, 1991Ale] along with a liquidus surface projection [1970Hai, 1991Ale]. The C–Ru–U isothermal section at 1300°C was established by [1970Hol]. [1970Hol] arc-melted and sintered samples of different compositions that were then characterized by X-ray powder photography, metallography and microanalysis. The system contains one ternary solid phase, U_2RuC_2 that is formed peritectically. The C–Ru–U isothermal section at 1300°C was later refined by the same group of authors [1975Hol, 1984Hol1, 1984Hol2]. [1970Hai] investigated the phase equilibria in the C–Ru–U system using as-cast and equilibrated alloys. The peritectic temperature for the decomposition of U_2RuC_2 was determined to be close to 1500°C by heating a sample of this compound at various temperatures, and then rapidly quenching and examining ceramographically to determine whether liquid had been formed. A schematic diagram of the primary crystallizing phases in the C–Ru–U system, which was indicated with different symbols for different alloys, was also presented by [1970Hai]. It should be noted that the binary phase U_2Ru , which is unstable at 1000°C according to the accepted Ru–U phase diagram, is indicated on the isothermal section at 1000°C by [1970Hai].

From an analysis of the literature data on the binary boundary systems and the C–Ru–U ternary alloys, about 30 topologically nonequivalent isothermal sections in the temperature range from 850 to 2430°C were presented by [1991Ale]. They used a systematic approach that provided a means of establishing the topology of the C–Ru–U phase diagram. Fifteen four-phase equilibria were proposed and the reaction temperatures for these invariant equilibria were estimated. [1991Ale] presented the isothermal section at 1000°C and the liquidus surface projection of the C–Ru–U system in terms of the experimental data obtained by [1970Hai].

A ternary compound U_2RuC_2 was first reported by [1968Hol, 1969Hai]. The crystal structure of the U_2RuC_2 ternary phase and its stability range were investigated by [1968Hol, 1969Hai, 1970Hai, 1970Hol]. [1969Hai] prepared U_2RuC_2 by arc-melting the elements side by side using a carbon electrode under an argon atmosphere (pressure 30 kNm^{−3}) previously gettered with molten zirconium. The as-cast alloy with a nominal composition of U_2RuC_2 showed a complex structure consisting of a U carbide, a U-metal binary alloy phase and the ternary compound. The alloy became single-phase if annealed at temperatures of up to 1500°C in vacuum for longer than 100 h. In view of the experimental observation that U_2RuC_2 decomposed to a U carbide and liquid on heating to ~1700°C, it is suggested that this ternary compound is formed peritectically. The crystal structure and lattice parameters of U_2RuC_2 [1969Hai] were determined via X-ray powder photography using an 11 cm Debye-Scherrer camera.

Thermodynamic properties of the U_2RuC_2 and URu_3C_x phases was reported by [1970Hol, 1991Kle1] following electromotive force studies and were reviewed by [1991Kle2].

Information about phase equilibria in the C–Ru–U system is still incomplete. In particular, the existence of the proposed invariant four-phase equilibria [1991Ale] needs experimental verification. Available data regarding the solidus and solvus surfaces are also very limited. More work is required to establish the phase equilibrium relationships at different temperatures and a complete reaction scheme.

Binary Systems

The binary systems C–Ru, C–U and Ru–U are accepted from [Mas2].

Solid Phases

Solid phase data are listed in Table 2. The η phase (URu_3) exhibits a considerable solubility for carbon (up to about 15 at.% C at 1300°C). The ternary phase τ does not possess a visible homogeneity range and is formed peritectically at a temperature of about 1727°C [1984Hol1, 1984Hol2].

Invariant Equilibria

The invariant reactions are listed in Table 3 according to [1991Ale] who used the experimental data of [1970Hai]. Corrections have been made according to the constitution of the accepted binary systems. A partial reaction scheme is presented in Fig. 1.

Liquidus, Solidus and Solvus Surfaces

The partial liquidus surface projection is shown in Fig. 2, which is based mainly on the work of [1991Ale]. Some corrections have been made according to the constitution of the accepted binaries. It should be noted that, unlike the data of [1991Ale], the μ phase does not exist in the liquid state according to [Mas2].

Isothermal Sections

The isothermal section at 1300°C presented in Fig. 3 is based on [1970Hol, 1975Hol, 1984Hol1, 1984Hol2] with the amendment of up to 6 at.% C in the liquid phase in U rich corner in order to be consistent with the accepted C–U phase diagram. According to the accepted Ru–U phase diagram, the η phase does not possess a visible homogeneity range, whereas in [1970Hol], it is shown with a homogeneity range of about 74 to 75 at.% Ru falling with the addition of the third element C.

The isothermal section for 1000°C according to [1970Hai, 1991Ale] is shown in Fig. 4 with the phase boundaries of the binary phases altered or corrected, especially for U_2Ru , which is unstable at 1000°C according to the accepted Ru–U binary phase diagram.

Thermodynamics

The Gibbs energies of formation of URu_3 and URu_3C_x were determined by [1970Hol] using the emf method employing a solid CaF_2 electrolyte. The standard entropy of URu_3 and the Gibbs free energy of formation of U_2RuC_2 were estimated. [1991Kle1] performed thermodynamic measurements for the binary phases (URu_3 and U_3Ru_5) and the ternary carbides ($\text{URu}_3\text{C}_{0.7}$ and U_2RuC_2) between 950 and 1200 K (677 to 927°C) using galvanic cells employing CaF_2 single crystal electrolytes: U, $\text{UF}_3|\text{CaF}_2|\text{UF}_3$, URu_3 , Ru; U, $\text{UF}_3|\text{CaF}_2|\text{UF}_3$, U_3Ru_5 , URu_3 ; Ru, URu_3 , $\text{UF}_3|\text{CaF}_2|\text{UF}_3$, $\text{URu}_3\text{C}_{0.7}$, Ru, C; U, $\text{UF}_3|\text{CaF}_2|\text{UF}_3$, $\text{URu}_3\text{C}_{0.7}$, U_2RuC_2 , C. The Gibbs energies of formation of URu_3 , U_3Ru_5 , $\text{URu}_3\text{C}_{0.7}$ and U_2RuC_2 were evaluated from the measured emf. According to the work of [1991Kle1], the reaction of UC_{1+x} with the fission product ruthenium is possible according to the reaction $2\text{UC} + \text{Ru} \rightleftharpoons \text{U}_2\text{RuC}_2$, where relative partial molar Gibbs energy of ruthenium is $\Delta G_{\text{Ru}} = -108000 \text{ J}\cdot\text{mol}^{-1}$ at 827°C. Further reaction of Ru follows the equation $\text{U}_2\text{RuC}_2 + \text{Ru} \rightleftharpoons 2\text{URu}_3\text{C}_{0.7} + 0.6\text{C}$, where $\Delta G_{\text{Ru}} = -11450 \text{ J}\cdot\text{mol}^{-1}$. Both types of phases were observed in irradiated nuclear carbide fuels.

Experimentally measured thermodynamic data for several reactions and those for the η and τ phases are listed in Tables 4 and 5, respectively.

Notes on Materials Properties and Applications

The C–Ru–U alloys are the prospective materials for nuclear technology applications as alloys consisting of uranium carbide containing the transition metal ruthenium.

The thermal diffusivity of the U_2RuC_2 phase was measured by [1985Ara] over the temperature range 750 to 1500 K (477 to 1227°C). The temperature dependence obtained is shown in Fig. 5. These values are not corrected for porosity. The thermal conductivity of U_2RuC_2 was calculated using the thermal diffusivity data, the heat capacity and the density of the samples. Because thermal expansion and heat capacity data for U_2RuC_2 were not available, the thermal expansion data of UC were used and heat capacity values were estimated from the sum of those for the individual components as a first approximation. Fig. 6 presents the thermal conductivity of U_2RuC_2 over the temperature range 750 to 1500 K (477 to 1227°C) corrected to 100% theoretical density. The solid line in Fig. 6 was obtained by fitting the experimental data to second order equations using the least squares method.

The magnetic susceptibility of the U_2RuC_2 phase was investigated by [1996Ebe] using a SQUID magnetometer with magnetic flux densities of up to 5.5 T over the temperature range 2 and 300 K (–271°C to 27°C). This phase shows temperature-dependent paramagnetism (Fig. 7) with a room temperature susceptibility of $\chi_{\text{mol}} = (27 \pm 1) \cdot 10^{-9} \text{ m}^3 (\text{f.u})^{-1}$. The magnitude of this susceptibility is considerably higher (at least by a factor of 10) than the Pauli paramagnetism of ordinary metals.

Miscellaneous

[1970Hol] measured the lattice parameter of the URu_3C_x phase with respect to C content, which is shown in Fig. 8.

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Table 1: Investigation of the C-Ru-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1968Hol]	X-ray Debye-Scherrer and Guinier	1300-1600°C, $\sim \text{U}_2\text{RuC}_2$
[1969Hai]	X-ray Debye-Scherrer	< 1500°C, U_2RuC_2
[1970Hai]	Metallography, microanalysis	Primary crystallizing phases Limited data in the temperature range of 1000 to 1500°C. Solid solubility of Ru in UC and U_2C_3 . Solid solubility of C in URu_3
[1970Hol]	Arc melting, sintering, X-ray Debye - Scherrer studies, metallography, Microanalysis, emf measurements	587-797°C, 1300-1500°C, whole composition range
[1985Ara]	Sintering, X-ray diffraction studies, chemical analysis, density and thermal diffusivity measurements	477 to 1227°C, U_2RuC_2
[1991Kle1]	Emf measurements	747 to 927°C, $\text{URu}_3\text{C}_{0.7}$, U_2RuC_2

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1991Kle2]	Emf measurements	747 to 927°C, URu ₃ C _{0.7} , U ₂ RuC ₂
[1996Ebe]	Arc melting, annealing, X-ray Guinier studies, SQUID magnetic susceptibility measurements	–271 to 27°C, 900°C, U ₂ RuC ₂

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (I) < 3827 ± 50	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.9	at 25°C [Mas2] sublimation point at 1.013 bar
(C) (II)	<i>cF8</i> <i>Fd$\bar{3}m$</i> C (diamond)	<i>a</i> = 356.69	at 25°C [Mas2] high pressure phase (>60.78 bar)
(Ru) < 2334	<i>hP2</i> <i>P6₃/mmc</i> Mg	<i>a</i> = 270.58 <i>c</i> = 428.16	at 25°C [Mas2] dissolves 3 at.% C at 1940°C; ~1.3 at.% C at 1850°C [Mas2]
(γU) (h ₂) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 352.4	[Mas2] dissolves 0.22 at.% C at 1119 ± 1°C [Mas2] dissolves ~4.5 at.% Ru at 886°C [Mas2]
(βU) (h ₁) 776 - 668	<i>tP30</i> <i>P4₂/mmn</i> βU	<i>a</i> = 1075.9 <i>c</i> = 565.6	[Mas2] dissolves 0.02 at.% C at 772°C [Mas2] dissolves 2 at.% Ru at 681°C [Mas2]
(αU) (r) < 668	<i>oC4</i> <i>Cmcm</i> αU	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	at 25°C [Mas2] dissolves ~ 6·10 ^{–3} at.% C at 660°C [Mas2] dissolves ~ 1.1 at.% Ru at 625°C [Mas2]
γ, U ₂ Ru 937 - at least <400	<i>mP12</i> <i>P2/m</i> or <i>P2₁/m</i> U ₂ Ru	<i>a</i> = 1310.6 <i>b</i> = 334.3 <i>c</i> = 520.2 β = 96.16°	33.3 at.% Ru [Mas2] [1961Ber]
βURu (h ₂) 1158 - 795	-	-	47.2 at.% Ru [Mas2]
αURu (h ₁) 795 - at least <400	-	-	47.2 at.% Ru [Mas2]
δ, U ₃ Ru ₄ 1163 - at least <400	-	-	57 at.% Ru [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ϵ , U_3Ru_5 1182 - at least <400	-	-	62.5 at.% Ru [Mas2]
η , URu_3 1850 - at least <400	$cP4$ $Pm\bar{3}m$ AuCu_3		75 at.% Ru [Mas2]
URu_3C_x		$a = 398.8$ to 406	$x = 0$ to 0.7 (0 to 14.9 at.% C), 1300°C [1970Hol]
κ , UC (I) 2585 - 1119	$cF8$ $Fm\bar{3}m$ NaCl	$a = 495.98$ $a = 495.63$ $a = 495.1$ $a = 496$ to 496.2 $a = 507$ $a = 495.6$ $a = 496.05$	47 to 66 at.% C [Mas2] [E] at 48 at.% C [S] [1957Kie] [1961Ben] at 2100°C [1972Ben] at 1400°C [S] at 25°C [1972Ben]
UC (II) > $2.7 \cdot 10^5$ bar	r^{**}	-	[1987Ben]
λ , U_2C_3 1823 - ~850	$cI40$ $\bar{I}43d$ Pu_2C_3	$a = 808.8$ $a = 808.90$ $a = 808.89$	60 at.% C [Mas2] [H] [S] [1972Ben]
μ , UC_2 1793 - 1516	$tI6$ $I4/mmm$ CaC_2	$a = 351.7$ $c = 598.7$ $a = 352.4$ $c = 599.9$ $a = 351.9$ to 352.41 $c = 597.87$ to 599.62 $a = 352.7$ $c = 598$	62 to 62.5 at.% C [Mas2] [E] [H] [S] [1961Ben]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
UC ₂ 2434 - 1762	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF ₂ ?	$a = 545.0$	actually, “UC ₂ ” phase represents the κ ,UC phase in equilibrium with graphite [2001Che]
* τ , U ₂ RuC ₂ ≤ 1727	<i>tI*</i> <i>I4/mmm</i> U ₂ IrC ₂	$a = 344.5$ $c = 1252$	[1968Hol]
		$a = 344.89$ $c = 1257.08$	annealing up to 1500°C in vacuum during 100 h [1969Hai]
		$a = 344.5$ to 345.5 $c = 1256.3$ to 1259.2	annealing at 1300°C in vacuum [1970Hol]
		$a = 344$ $c = 1256$	sintering at 1550°C about 7 h in argon [1985Ara]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				C	Ru	U
L + (Ru) $\rightleftharpoons$ η + (C)	~1700	U ₁	L	~17	~61	~22
L + (C) $\rightleftharpoons$ η + τ	1475 $\pm$ 25	U ₂	L	~17	~58	~25

Table 4: Thermodynamic Data of Reactions

Reaction	T [°C]	Quantity, per mole of atoms [kJ, mol, K]	Comment
URu ₃ + 2Ru + (2 + x)C $\rightleftharpoons$ URu ₃ C _{x} + 2Ru + 2C	587 - 797	$\Delta G = -222.32 - 0.029 \cdot T \pm 4.187$	[1970Hol], emf
URu ₃ + 0.7C $\rightleftharpoons$ URu ₃ C _{0.7}	767 - 867	$\Delta G = -192.6 + 0.025 \cdot T \pm 4.1$	[1991Kle1], emf
1/3 {5U + 5.3C + URu ₃ C _{0.7} $\rightleftharpoons$ 3U ₂ RuC ₂ }	747 - 927	$\Delta G = -380.2 + 0.0525 \cdot T \pm 3.6$	[1991Kle1], emf

Table 5: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Quantity, per mole of atoms [kJ, mol, K]	Comment
URu ₃ C _{x}	727	$^f\Delta H^\circ = -222319 \pm 12560.4$	[1970Hol], emf
	727	$^f\Delta S^\circ = -29.3 \pm 8.4$	[1970Hol], emf
	727	$^f\Delta G^\circ = -251627 \pm 4186.8$	[1970Hol], emf
	827 ($x = 0.7$)	$^f\Delta G^\circ = -189800$	[1991Kle1], emf
U ₂ RuC ₂	827	$^f\Delta G^\circ = -155540$	[1991Kle1], emf

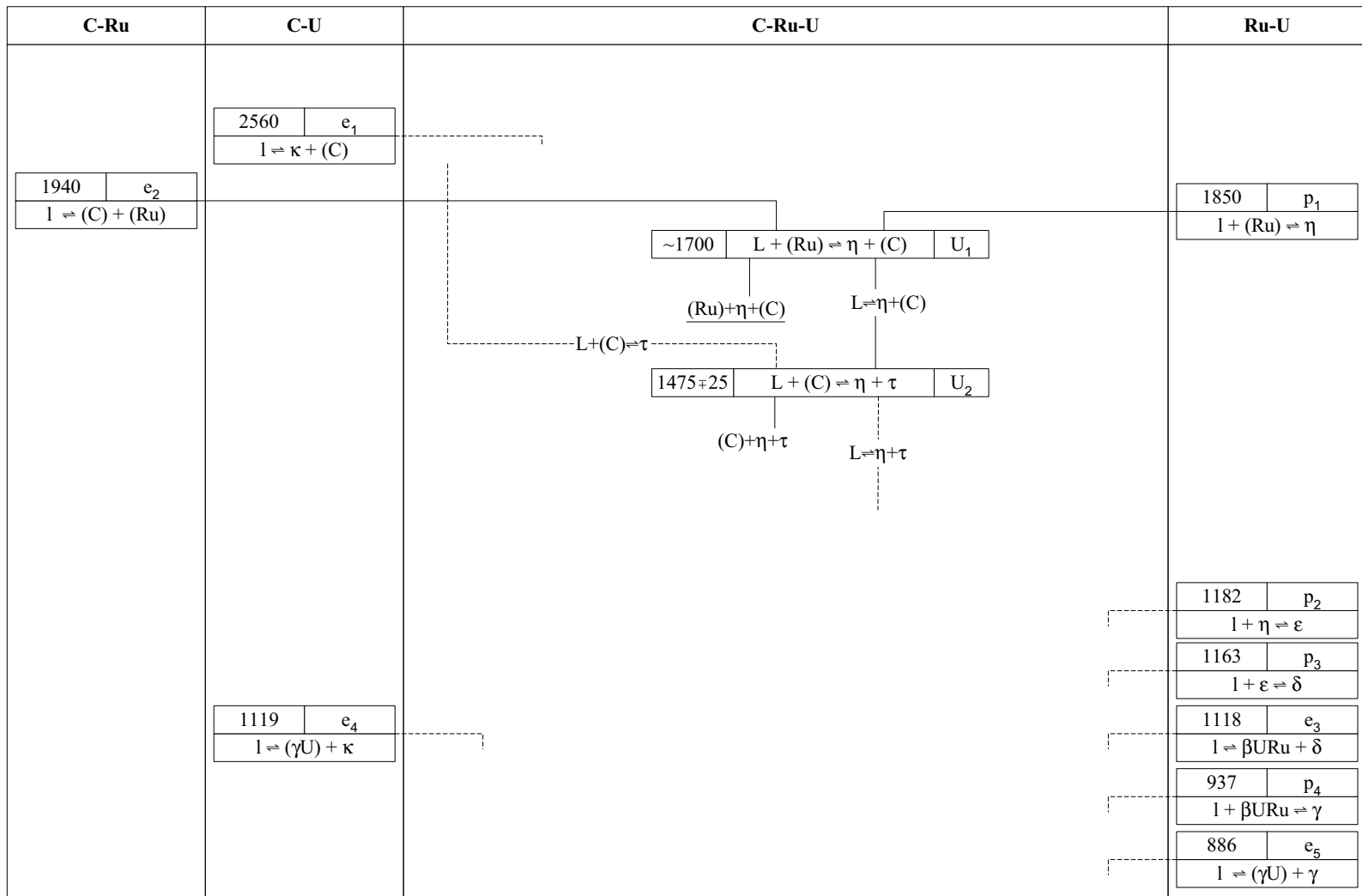


Fig. 1: C-Ru-U. Partial reaction scheme

Fig. 2: C-Ru-U.
Partial liquidus
surface projection

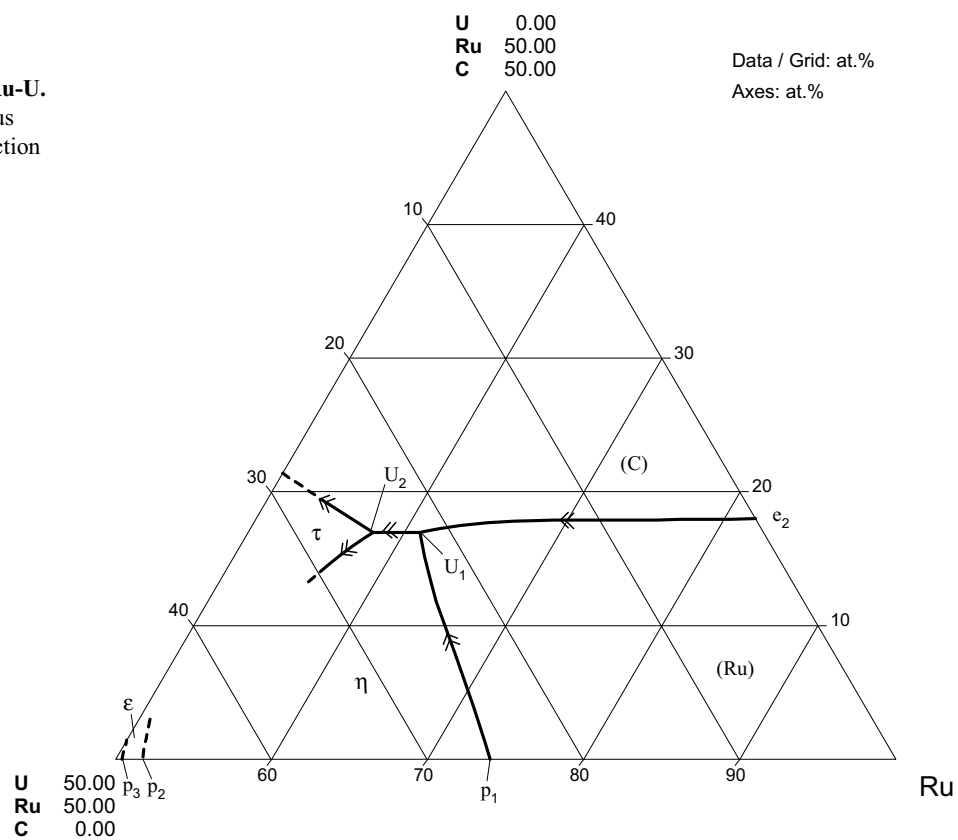


Fig. 3: C-Ru-U.
Isothermal section at
1300°C

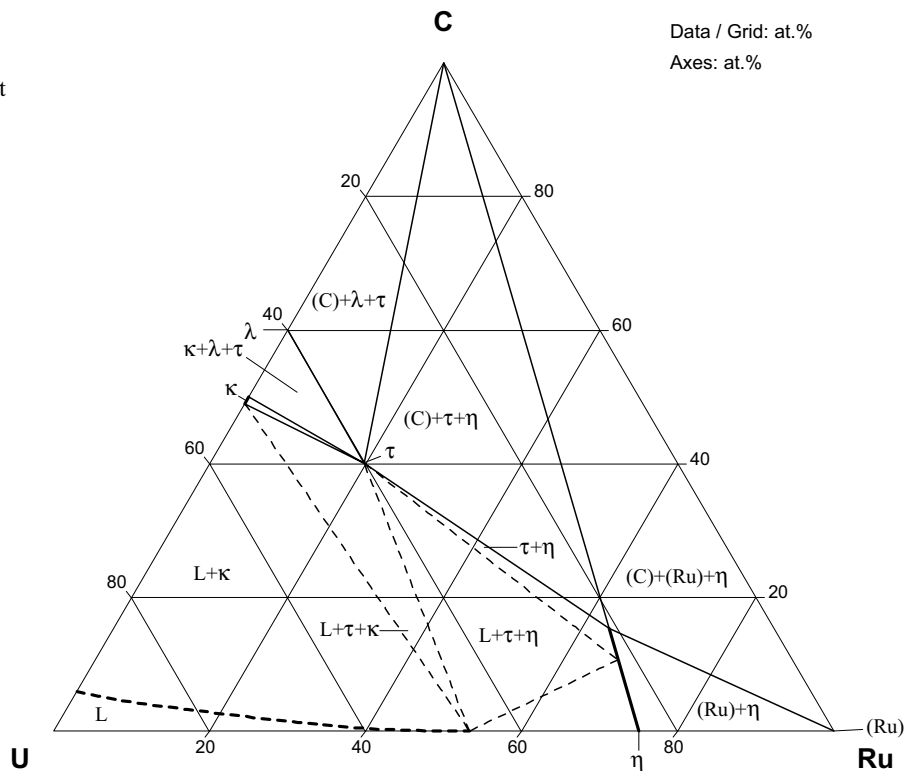


Fig. 4: C–Ru–U.
Isothermal section at
1000°C

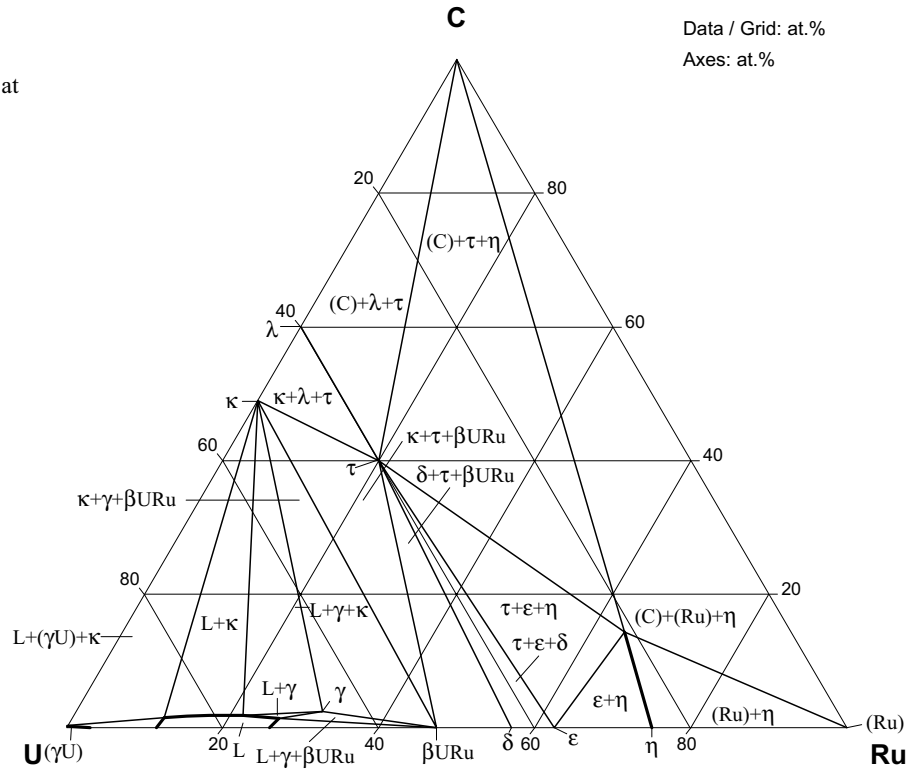


Fig. 5: C–Ru–U.
Thermal diffusivity of
 U_2RuC_2

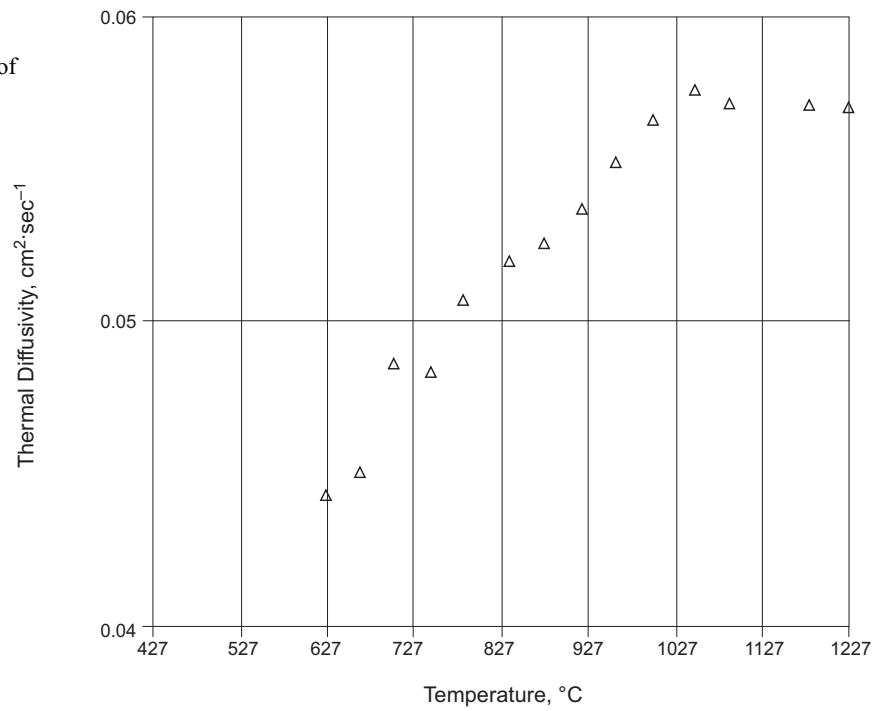


Fig. 6: C-Ru-U.
Thermal conductivity
of U_2RuC_2
normalized to 100%
theoretical density

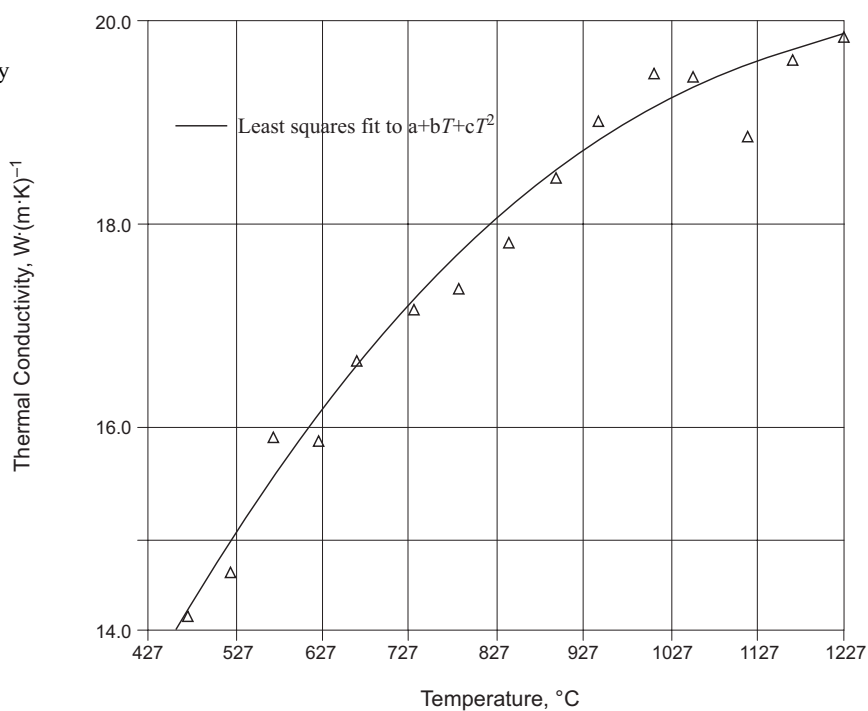


Fig. 7: C-Ru-U.
Magnetic
susceptibility of
 U_2RuC_2 as a function
of temperature,
measured with a
magnetic flux density
of 5 T

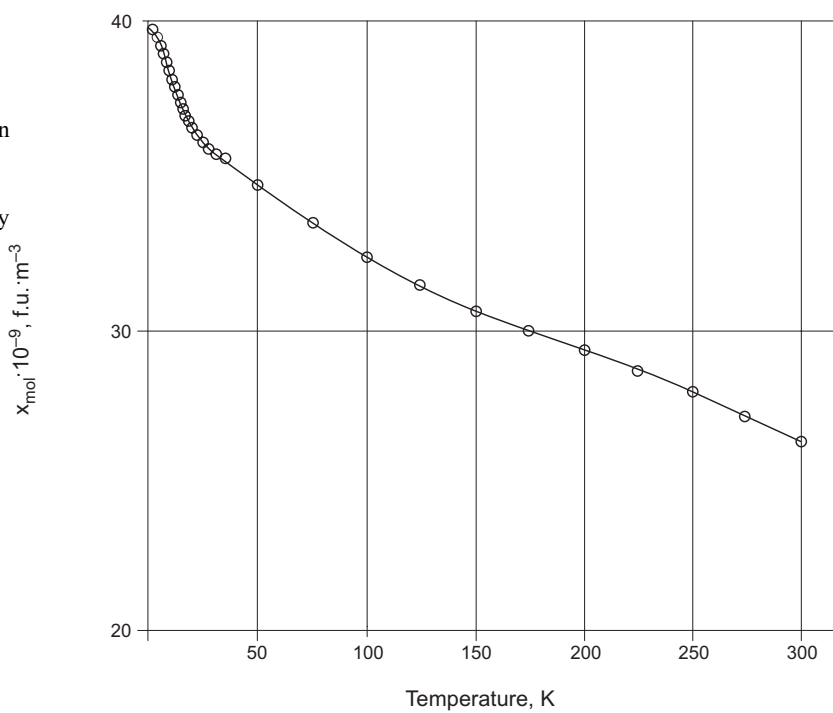
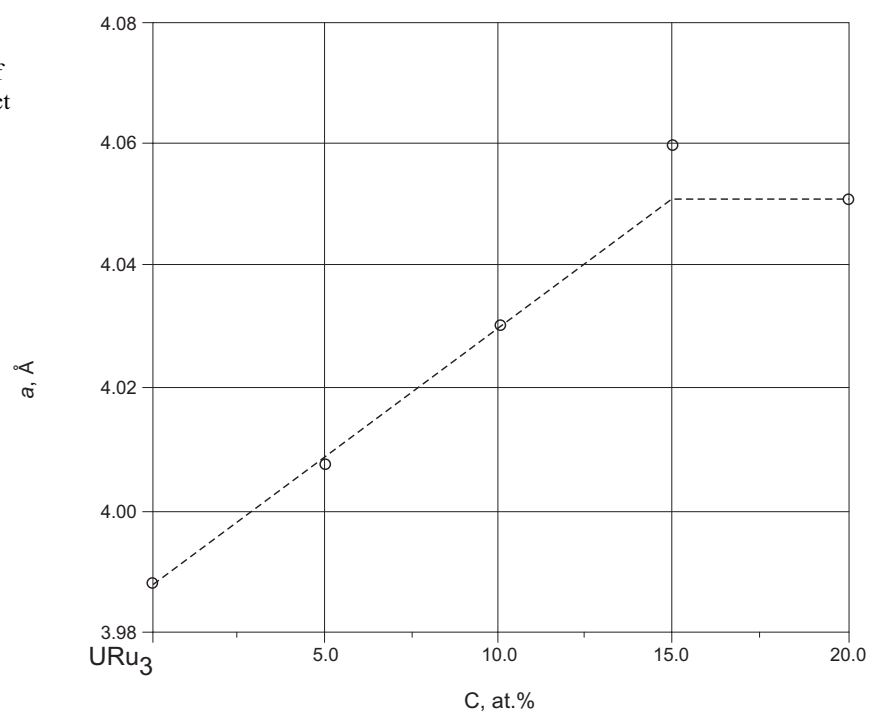


Fig. 8: C-Ru-U.
Lattice parameter of
 URu_3C_x with respect
to C content



Carbon – Thorium – Uranium

Kostyantyn Korniyenko, Nathalie Lebrun

Introduction

Thorium carbide is one of the most favorable chemical forms of fuel for nuclear reactors because of its high thermal conductivity and high thorium density, while the mixture with uranium carbide is considered to be a practical chemical form for use in a reactor [1987Nam]. Therefore, the study of the phase relations in the corresponding ternary system C–Th–U is of great interest. Information about phase equilibria in this system is presented in the literature via a quasibinary section ThC–UC [1982Ogo], isothermal sections at 1800°C [1975Hol, 1984Hol], 1700°C [1961Ben], 1330°C [1984Hol] and 1000°C [1961Ben, 1984Hol] as well as by a temperature-composition section for ThC₂–UC₂ [1966Hen]. Phase content of the alloys and crystal structures of the intermediate phases were studied by [1957Now, 1958Cir, 1958Iva, 1958Lau, 1959Now, 1960Bre, 1961Ben, 1961Iva1, 1961Iva2, 1962Kat, 1966Hen, 1966Lan, 1971Pet, 1987Jon]. Data on thermodynamic properties were obtained experimentally by [1962Kat, 1989Koy, 1991Yam]. Electrical properties of the thorium carbide–uranium carbide solid solutions were reported by [1969Aus]. The morphology of the C–Th–U alloys was studied by [1964Keg]. [1965Kel, 1965Pet, 1965Wym] studied aspects of the application of sol–gel processing to the production of carbon–thorium–uranium particles. The synthesis of thorium–uranium carbides using the method of carbothermic reduction was carried out by [1987Nam]. Experimental methods used in the above works are presented in Table 1. Short assessments of the literature information related to the C–Th–U system were published by [1966Bar, 1975Hol, 1984Hol]. However, knowledge of the phase equilibria in the C–Th–U system is incomplete. In particular, the conditions of the invariant four-phase equilibria need to be established. Information about the constitution of the liquidus, solidus and solvus surfaces is lacking. Future investigations of phase relations in the C–Th–U system should be concentrated on the continuation of studies of alloy properties in the equilibrium state at different temperatures.

Binary Systems

Data related to the boundary C–Th and Th–U systems are accepted from [Mas2]. The constitution of the C–U system is accepted from [2001Che], who presents essentially the same phase diagram as [Mas2].

Solid Phases

Crystallographic data relating to the known unary and binary phases are listed in Table 2. No ternary phases having crystal structures different from those inherent in the unary and binary phases have been found. At high temperatures in the C–Th boundary binary system, a continuous series of solid solutions between (α Th), the δ ThC phase and the γ ThC₂ phase are found. All of these phases possess a cubic structure but of different space groups and prototypes. In the ternary system, a continuous series of solid solutions exists between these phases and the normal pressure modification of the δ UC and δ UC₂ phase (labeled as λ).

Quasibinary Systems

The crystal structure of the alloys along the ThC–UC section have been studied by [1957Now, 1958Cir, 1958Lau, 1959Now, 1961Iva1, 1961Iva2] revealing the presence of a continuous series of solid solutions between the ThC and UC phases. The interaction parameters and the energies of mixing in the quasibinary ThC–UC system have been calculated by [1982Ogo] from the atomization energies, melting points and lattice parameters. From the energies of mixing thus obtained, the liquidus, solidus and solid solution decomposition lines have been calculated applying the regular solution approximation. The formation of a continuous series of solid solutions is confirmed. It was calculated that the liquidus and solidus curves in the quasibinary section possess a minimum at 2195°C and 26.19 at.% U, and decomposition of the λ solid solution takes place at temperatures lower than 1593°C. This section is presented in Fig. 1. Some further

experimental studies are needed because the melting temperature accepted by [1982Ogo] is higher than that accepted by [Mas2] (2670°C and 2500°C, respectively).

Isothermal Sections

Several isothermal sections have been determined over the temperature range 1800–1000°C [1961Ben, 1975Hol, 1984Hol]. The isothermal section reported at 1800°C is based on experimental results obtained by [1966Hen] and [1971Pet]. In order to maintain consistency with the accepted binary systems, the isothermal sections at 1800°C (Fig. 2), 1700°C (Fig. 3), 1330°C (Fig. 4) and 1000°C (Fig. 5) were redrawn. The presence of a miscibility gap in the λ solid solution has been also taken into account at 1330 and 1000°C along the quasibinary system ThC–UC. The corresponding phase equilibria associated with this miscibility gap along the binary edge have been presented as dashed lines. The partial isothermal section for 1000°C proposed by [1961Ben] for the carbon-poor region was not retained in this assessment since the C–Th binary system proposed by [1961Ben] does not reflect the formation of a continuous series of solid solutions between the (α Th) and the δ ThC phases. All the presented isothermal sections are in need of further experimental verification.

Temperature – Composition Sections

The results of X-ray diffraction and microstructural studies of the alloys located along the Th–UC and ThC₂–UC₂ sections are presented in [1958Iva, 1961Iva1] and [1960Bre, 1966Lan], respectively. The reaction of thorium with the UC and UC₂ compounds at 1000°C were studied by [1962Kat] using the diffusion couple method. The formation of the λ phase and uranium was noted. The temperature-composition section constructed as a result of an investigation of alloys with about 66.67 at.% C in the presence of about 1 mass% free carbon was reported by [1966Hen]. The excess carbon was added to reduce the presence of oxide impurities in the uranium and thorium powder starting materials. This section needs further experimental study, in particular, at the UC₂ side because at the temperatures below ~1500°C, the UC₂ phase does not exist in the C–U boundary binary system, according to the accepted data of [2001Che].

Thermodynamics

Calculations of the Gibbs energy of formation ΔG of the λ phase in three-phase equilibria involving the participation of metal-rich phases were carried out by [1961Ben]. Good agreement with the literature was noted. [1962Kat] carried out a comparison between the observed reactivity of the UC–Th and UC₂–Th systems and thermodynamic predictions based on simple displacement reactions whose products were uranium and a metal carbide. Thermodynamic predictions were based on the corresponding standard state reactions and values of free energies of formation of the carbides. According to the results, both phases must react with thorium, as is observed experimentally. Vapor pressures over the λ phase were measured by [1989Koy, 1991Yam] using Knudsen effusion mass spectrometry at temperatures ranging from about 2000 to 2200 K (1727 to 1927°C) (Table 3). The activities of thorium and carbon in the ThC_{1±x} phase were derived from the measured vapor pressures of thorium. Based on the vapor pressure measurement over the λ phase, the Gibbs energy of formation of the phase was derived as a function of uranium fraction. The values obtained are plotted in Fig. 6 as white circles. The $\Delta_f G^\circ$ of the λ phase decreases continuously with decreasing uranium content and was smoothly extrapolated to the values of $\Delta_f G^\circ$ of the δ phase previously obtained by M. Yamawaki *et al.* These values are shown in Fig. 6 by filled circles.

Notes on Materials Properties and Applications

Carbides of thorium can serve as alternative fissile materials for nuclear breeder reactor systems. The monocarbide is particularly interesting on account of its high metal-to-carbon atomic ratio, high thermal conductivity and wide compositional homogeneity range. The uranium-thorium mixed monocarbide (U,Th)C, according to the opinion of [1991Yam], may be a better choice than pure thorium carbide. [1969Aus] have investigated alloys of the ThC-UC quasibinary system with uranium contents of 3, 8 and 15 at.%. Plates were pressed and annealed under vacuum at 1800°C for 6 to 10 h. The compositional dependence of absolute thermoelectric power, Hall coefficient and electrical resistivity are shown in Figs. 7, 8 and 9, respectively. An estimation of the chemical state of various fission products in irradiated uranium-thorium mixed monocarbide fuel pins was performed by [1991Yam] using the SOLGASMIX computer code. In carbide fuel pins, more fission product-containing secondary phases were predicted to form than in oxide fuel pins. Thus, the chemical interaction between fuel and cladding will be much less in thorium carbide fuel pins as compared to oxide fuel pins.

Miscellaneous

[1964Keg] prepared metallographic specimens consisting of pyrolytic carbon coated as-cast alloys with a carbon content of about 66.67 at.% and different contents of thorium and uranium. Both vibratory and mechanical polishing techniques were used. The etchant comprised a solution of HNO₃ and H₂O in a volume ratio of 1:1. [1965Wym, 1966Bar] proposed the application of sol-gel processing for the production of (U,Th)C spheres. An analogous process for the preparation of the (U,Th)C₂ spheroidal particles has been developed by [1965Kel, 1965Wym, 1966Bar]. This process consists of four steps: preparation of the oxide sol; incorporation of carbon in the sol; formation of gel spheroids; firing of the spheroids. [1965Pet, 1966Bar] prepared dense particles of (U,Th)C₂ from dense sol-gel ThO₂ or (U,Th)O₂ microspheres by dispersing the spheres in graphite flour or lampblack and heating the mixture in a graphite crucible. They also have developed a process for coating (U,Th)C₂ particles with carbon films to protect the carbide against attack by water. [1969Aus] proposed a scheme of changes in the band structure of thorium monocarbide after the addition of uranium. The result seems to be a lower Fermi level and an increase in the ratio of holes to electrons. Carbothermic reduction of mechanically mixed ThO₂ + UO₂ + C compacts to (U,Th)C has been studied by [1987Nam] over the temperature range 1470 and 1770°C with an emphasis on the study of reaction kinetics. The rate-limiting step of this reaction was attributed to the diffusion of CO gas in the outermost layer of the reaction products. ThO₂ and UO₂ were found to react with graphite to produce two nearly separate dicarbide phases, both of which then reacted with residual ThO₂ to form a monocarbide phase. An apparent activation energy of about 320 kJ·mol⁻¹ was obtained for this carbothermic reduction.

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Table 1: Investigations of the C-Th-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1957Now]	X-ray diffraction studies	1900°C, 50 at.% C
[1958Cir] as quoted by [1961Ben]	X-ray diffraction studies	50 at.% C
[1958Iva]	X-ray diffraction studies, microstructural investigations	1000°C, 700°C, the Th-UC section
[1958Lau] as quoted by [1959Now]	X-ray diffraction studies	1800°C, 50 at.% C
[1959Now]	X-ray diffraction studies, microstructural investigations	1700-1800°C, 50 at.% C
[1960Bre]	X-ray Debye-Scherrer powder diffraction studies, microstructural investigation, stability tests (moisture, air, oxygen)	1800°C, 66.67 at.% C

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1961Ben]	X-ray powder diffraction studies	1900 - 1000°C, whole composition range
[1961Iva1]	X-ray diffraction studies, microstructural investigations	1000°C, 700°C, the Th-UC and ThC-UC sections
[1961Iva2]	X-ray powder diffraction studies, microstructural analysis	50 at.% C
[1962Kat]	Metallography, X-ray diffraction, diffusion couples	1000°C, the Th-UC and Th-UC ₂ sections
[1964Keg]	Optical microscopy	Pyrolytic carbon coated with as-cast ThC ₂ or (U,Th)C ₂
[1965Kel] as quoted by [1966Bar]	Sol-gel preparation of particles	66.67 at.% C
[1965Pet] as quoted by [1966Bar]	Sol-gel preparation of particles, carbon films coating	66.67 at.% C
[1965Wym] as quoted by [1966Bar]	Sol-gel preparation of particles	66.67 at.% C
[1966Hen]	Thermal analysis, high-temperature X-ray diffraction	> 500°C, 66.67 at.% C in the presence of about 1 mass% free carbon
[1966Lan] as quoted by [1984Hol]	X-ray diffraction studies	66.67 at.% C
[1969Aus]	X-ray diffraction, conventional dc methods, density measurements, chemical analysis	50 at.% C
[1971Pet] as quoted by [1975Hol]	X-ray diffraction studies	66.67 at.% C
[1984Hol]	Phase relations investigation	1800°C, whole range of compositions
[1987Jon]	Neutron powder diffraction	66.67 at.% C
[1987Nam]	X-ray diffraction, carbothermic reduction	1470 - 1770°C
[1989Koy]	Knudsen effusion mass spectrometry	1723 - 1923°C, about 50 at.% C
[1991Yam]	Knudsen effusion mass spectrometry	About 50 at.% C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (I) < 3827 ± 50	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.9	at 25°C [Mas2] sublimation point at 1.013 bar
(C) (II) > 60.78 bar	<i>cF8</i> <i>Fd$\bar{3}m$</i> C (diamond)	<i>a</i> = 356.69	at 25°C [Mas2] high pressure phase (> 60.78 bar)
(βTh) (h) 1755 - 1360	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 411	[Mas2] dissolves ~9 at.% C at 1707°C [Mas2] dissolves 12.2 at.% U at 1375°C [Mas2]
(γU) (h ₂) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 352.4	[Mas2] dissolves ~1 at.% Th at 1100°C [Mas2] dissolves 0.22 to 0.37 at.% C at 1119 ± 1°C, 1 at.% C at 1100°C, 0.3 at.% C at 900°C [Mas2]
(βU) (h ₁) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> βU	<i>a</i> = 1075.9 <i>c</i> = 565.6	[Mas2] dissolves 0.02 at.% C at 772°C and 0.05 at.% C at 700°C [Mas2]
(αU) (r) < 668	<i>oC4</i> <i>Cmcm</i> αU	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	at 25°C [Mas2] dissolves ~6·10 ⁻³ at.% C at 660°C [Mas2]
βThC ₂ (h ₁) 1495 - 1255	<i>tP6</i> <i>P4₂/mmc</i> βThC ₂	<i>a</i> = 423.5 <i>c</i> = 540.8	63 to 66 at.% C [Mas2]
αThC ₂ (r) < 1440	<i>mC12</i> <i>C2/c</i> αThC ₂	<i>a</i> = 669.2 <i>b</i> = 422.3 <i>c</i> = 674.4 β = 103.0°	66 at.% C [Mas2]
ωTh ₂ C ₃	-	<i>a</i> = 856.09 to 865.13	metastable [1996Vel] high pressure phase (at 1325°C, 3.5·10 ⁻⁴ bar)
ζ, U ₂ C ₃ < 1833	<i>cI40</i> <i>I$\bar{4}3d$</i> Pu ₂ C ₃	<i>a</i> = 808.9	60 at.% C [2001Che]
εUC ₂ 1780 - 1478	<i>tI6</i> <i>I4/mmm</i> CaC ₂	<i>a</i> = 351.90 <i>c</i> = 597.87	62 to 62.5 at.% C [2001Che] U rich [2001Che]
		<i>a</i> = 352.41 <i>c</i> = 599.62	C rich [2001Che]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
δUC_2 2435 - 1763	$cF12$ $Fm\bar{3}m$ $\text{CaF}_2?$	$a = 545.0$	[2001Che] actually, “ δUC_2 ” phase represents the UC phase in equilibrium with graphite [2001Che]
δUC (II)	o^{**}	-	high pressure phase ($> 2.7 \cdot 10^5$ bar)
λ , (U,Th)C			solid solution
(αTh) (r) < 1360	$cF4$ $Fm\bar{3}m$ Cu	$a = 508.42$	at 25°C [Mas2] dissolves 6.8 at.% U at 1270°C [Mas2]
γThC_2 (h_2) 2610 - 1470	$cP12$ $Pa\bar{3}$ FeS_2	$a = 580.8$	at 1500°C [1964Hil]
ThC < 2500	$cF8$ $Fm\bar{3}m$ NaCl	$a = 534.6$ $a = 533.8$	$x = 0$ [E] $x = 0$ [H]
UC (I) < 2515		$a = 495.97$	from 47 to 66 at.% C, miscibility gap (critical point at 2050°C, 43.8 at.% C) [2001Che]

Table 3: Partial Vapor Pressures Measurements of U (gaseous) and Th (gaseous) over the λ Phase

Phase(s)	Temperature [K (°C)]	$\log(p \text{ [Pa]})$	Comments
$\text{U}_{0.1}\text{Th}_{0.9}\text{C}_{0.855}$ U (g)	1960 - 2250 (1687 - 1977)	$-(28290 \pm 445) / T$ $+ (9.4793 \pm 0.0093)$	[1989Koy, 1991Yam] Knudsen effusion
Th (g)	2020 - 2250 (1747 - 1977)	$-(30875 \pm 400) / T$ $+ (10.3382 \pm 0.0085)$	
$\text{U}_{0.2}\text{Th}_{0.8}\text{C}_{0.973}$ U (g)	1960 - 2270 (1687 - 1997)	$-(25879 \pm 339) / T$ $+ (8.3584 \pm 0.0073)$	
Th (g)	2080 - 2270 (1807 - 1997)	$-(30174 \pm 239) / T$ $+ (9.6639 \pm 0.0052)$	
$\text{U}_{0.4}\text{Th}_{0.6}\text{C}_{0.973}$ U (g)	1950 - 2170 (1677 - 1897)	$-(24346 \pm 237) / T$ $+ (7.7685 \pm 0.0064)$	
Th (g)	1950 - 2170 (1677 - 1897)	$-(28932 \pm 312) / T$ $+ (8.9489 \pm 0.0064)$	

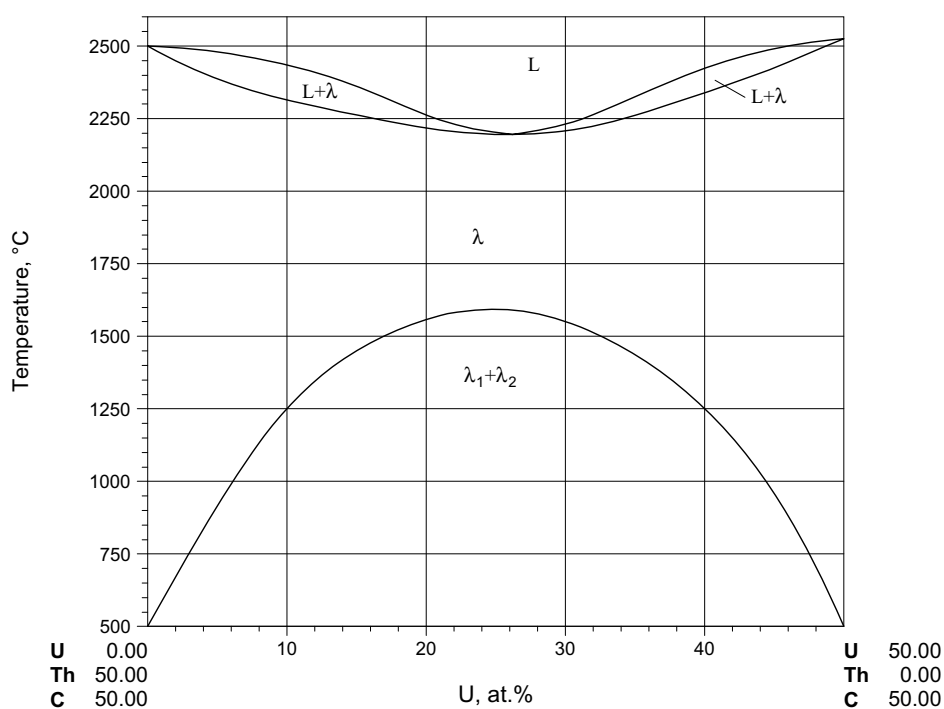
Fig. 1: C–Th–U.
The ThC–UC
quasibinary section

Fig. 2: C-Th-U.
Isothermal section at
1800°C

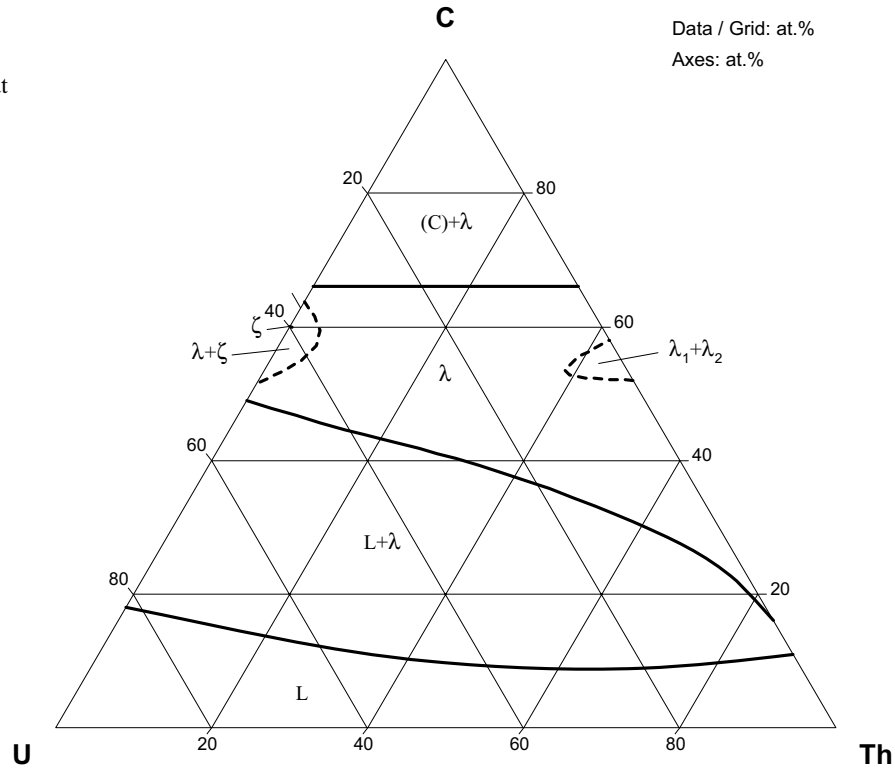


Fig. 3: C-Th-U.
Isothermal section at
1700°C in the range
of compositions
50-100 at.% C

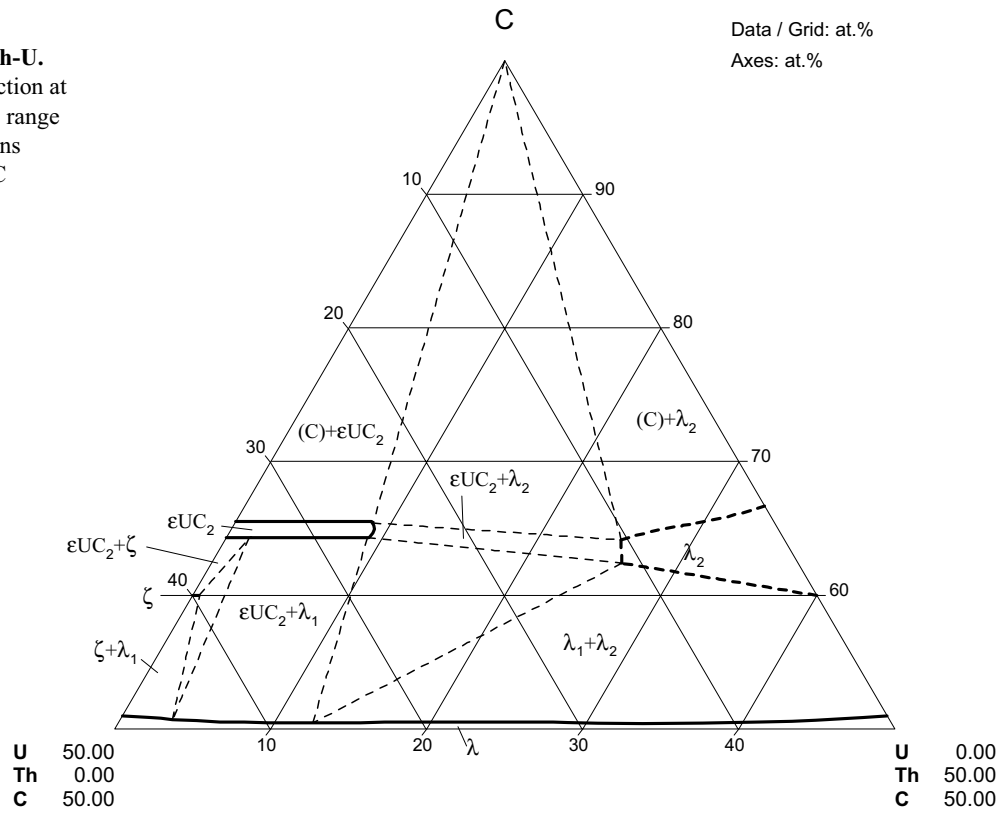


Fig. 4: C-Th-U.
Isothermal section at
1327°C

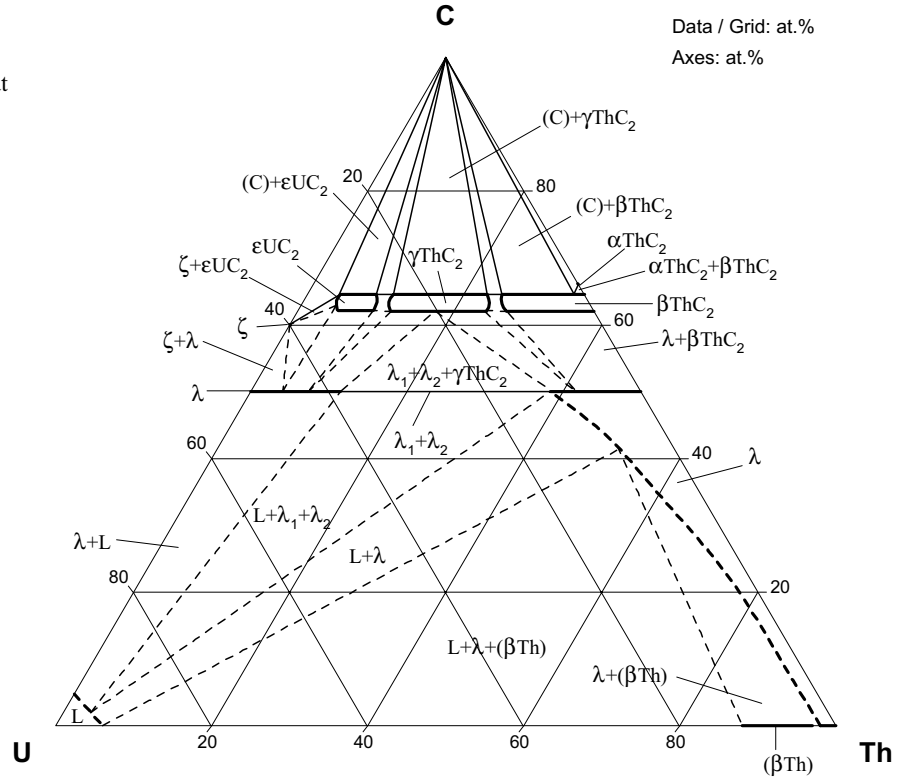


Fig. 5: C-Th-U.
Isothermal section at
1000°C

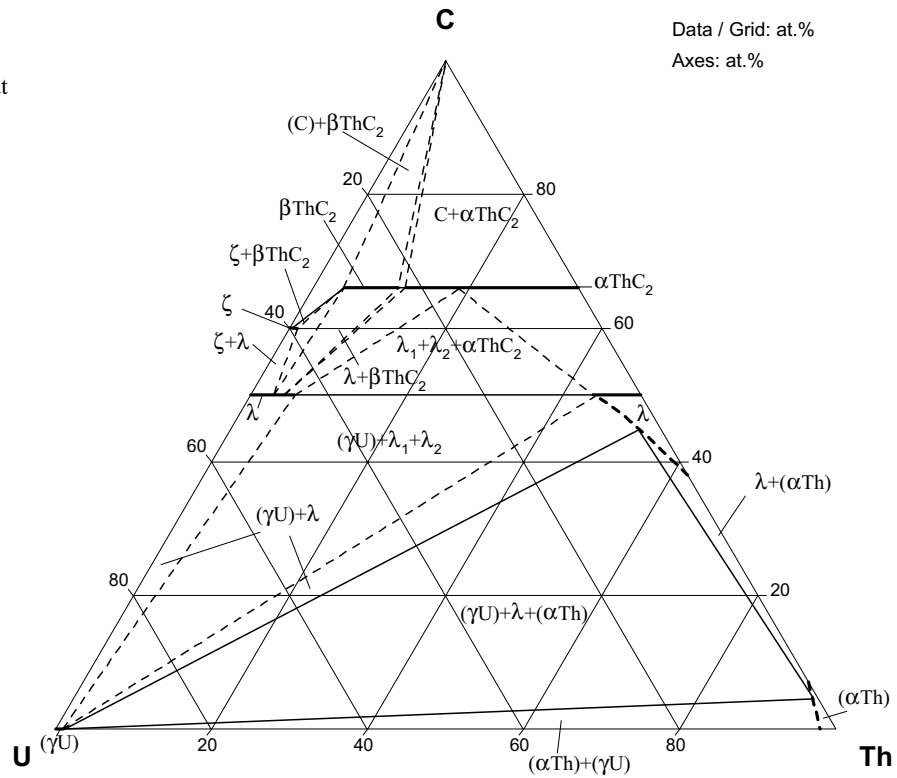


Fig. 6: C-Th-U.
Compositional
dependence of Gibbs
energy of formation
of the λ , $U_xTh_{1-x}C$
phase ($x = 0$ to 0.5)

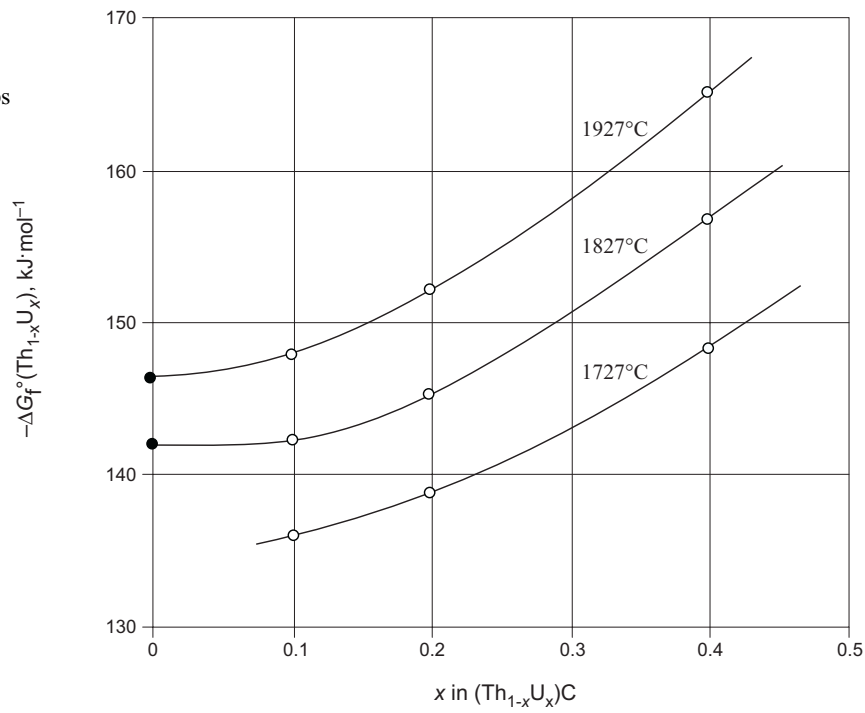


Fig. 7: C-Th-U.
Absolute
thermoelectric power
of alloys of the
ThC-UC section

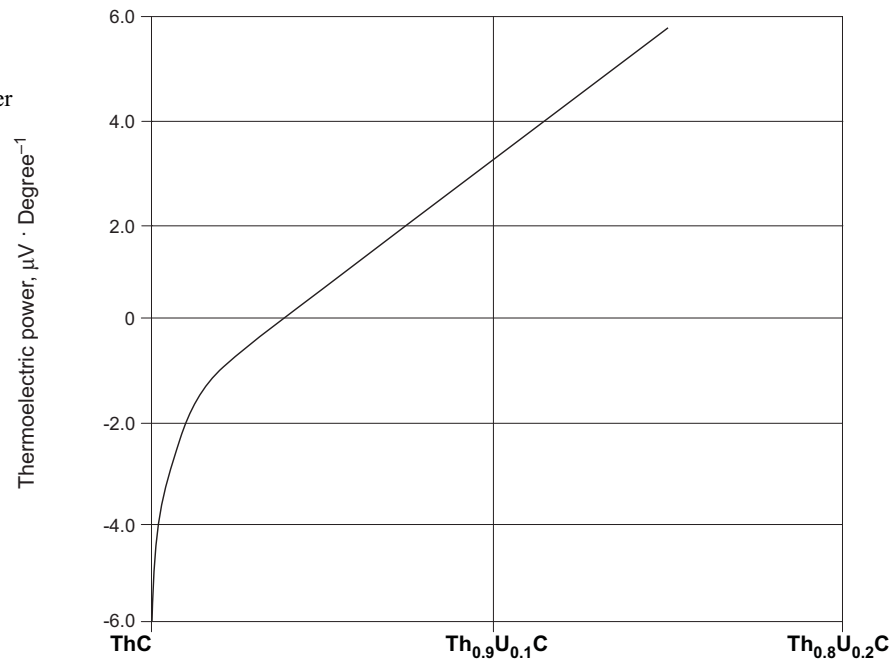


Fig. 8: C-Th-U.
Hall coefficient of
alloys of the ThC-UC
section

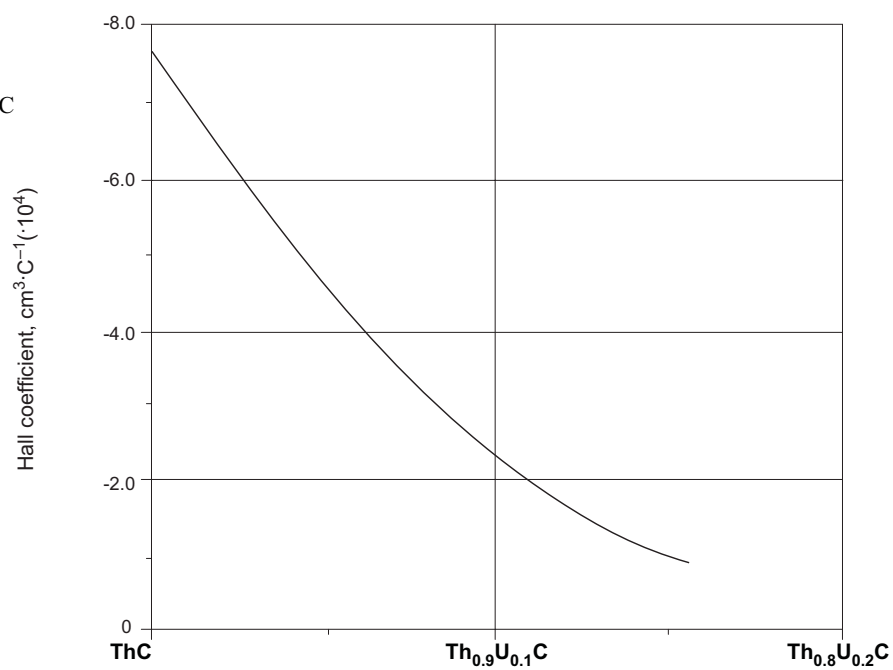
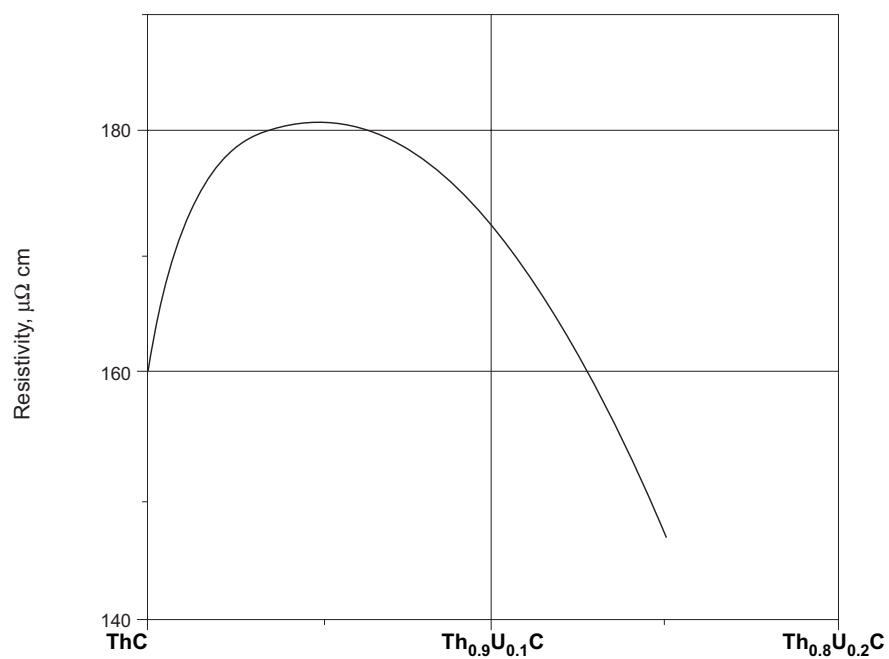


Fig. 9: C-Th-U.
Electrical resistivity
of alloys of the
ThC-UC section



Carbon – Thorium – Zirconium

Pierre Perrot

Introduction

Investigations of the C–Th–Zr system by X-ray diffraction [1958Iva, 1961Iva] showed that ThC and ZrC present a very low mutual solubility, even in the cast state after 5 days of annealing at 1000°C. The first diagram was presented by [1962Rud] which showed that non stoichiometric ZrC may be in equilibrium with (Th), ThC and ThC₂. Mixtures (Th) + ZrC and (Zr) + ThC have been investigated respectively by [1963Bad] and by [1968Ale]. A more complete investigation carried out at 1500°C by [1975Hol] agrees qualitatively with the preceding one, but gives more accurate information concerning equilibria between ZrC and the Th–Zr alloys. Further reviews [1977Hol, 1984Hol1, 1984Hol2] present the same diagram at 1500°C without any modifications.

Binary Systems

The C–Zr system has been assessed by [1995Fer] which proposes for ZrC a melting point of 3427°C, that is 123 K lower than the melting point accepted by [Mas2]. The C–Th and Th–Zr diagrams are accepted from [Mas2].

Solid Phases

The solid phases are presented in Table 1. ThC may dissolve up to 8 mol% ZrC [1958Iva, 1961Iva] whereas ZrC does not dissolve any measurable amount of ThC even in the cast state after a 5 days period of annealing at 1000°C. These results were confirmed by [1963Bad] which investigated by microscopic and X-ray examination mixtures (Th) + ZrC annealed at 1000°C. This mixture behaves as a quasibinary system of the eutectic type with a eutectic composition at 89 at.% Th. The solubility of ZrC in (Th) does not exceed 0.5 at.%. On the other hand, mixtures (Zr) + ThC has been investigated by [1968Ale] in the solid state, unfortunately without giving the working temperature. The (Zr) + ThC mixture reacts by forming ZrC + Zr–Th alloys at low ThC content (< 20 at.% Th). Pure ZrC appears at higher ThC content in the mixture.

Isothermal Sections

The isothermal section at 1500°C is given in Fig. 1. The diagram, mainly from [1975Hol] has been corrected to take into account the accepted binaries and the solubility of ZrC in ThC observed by [1958Iva, 1961Iva].

Notes on Materials Properties and Applications

Natural Thorium (100 % ²³²Th), three times more abundant than uranium in earth crust may be used as nuclear fuel. Although not fissile itself, Th-232 will absorb slow neutrons to produce ²³³U which is fissile. Refractory thorium carbide has been used as fuel element in high temperature (700–800°C) fast breeder reactor. The behavior of ThC with Zr is of greatest interest because Zr is one of the main constituent of cladding materials.

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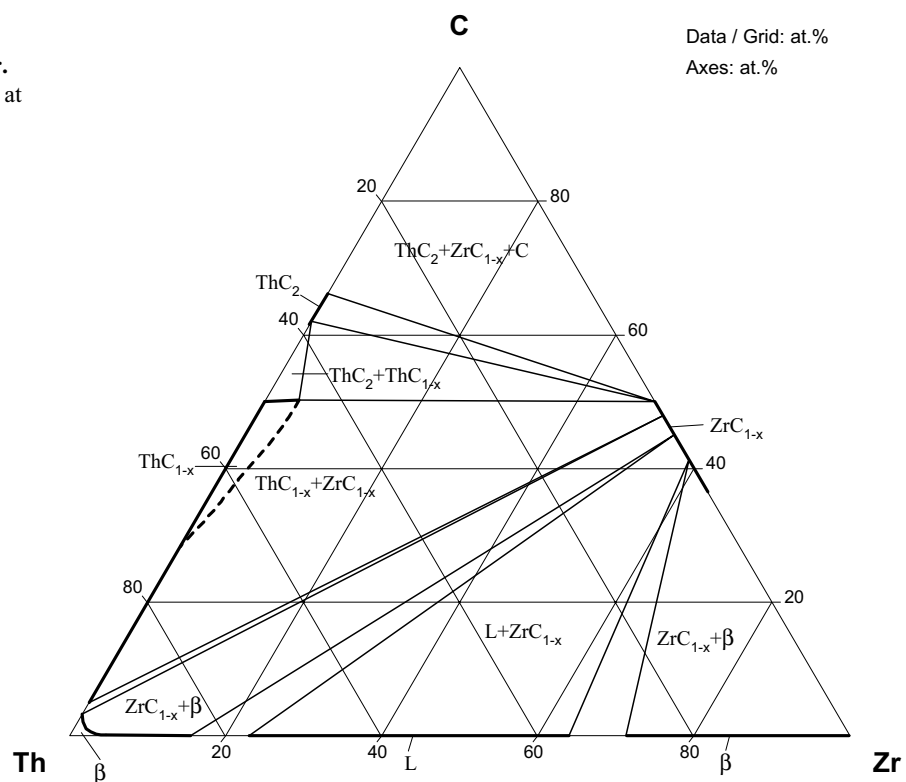
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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
C (graphite) < 3827	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.9	at 25°C [Mas2]
C (diamond)	<i>cF8</i> <i>Fd$\bar{3}m$</i> C (diamond)	<i>a</i> = 356.69	high pressure phase
(α Th) < 863	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	<i>a</i> = 508.42	at 25°C [Mas2] Dissolves up to 14.8 at.% Zr at 908°C
(α Zr) < 1360	<i>hP2</i> <i>P6₃/mmc</i> Mg	<i>a</i> = 323.16 <i>c</i> = 514.75	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
β (β Th) 1755 - 1360	$cI2$ $Im\bar{3}m$ W	$a = 411.0$	β Th _{0.54} Zr _{0.46} stable between 908 and 1350°C [Mas2] (β Th) dissolves ~9 at.% C at 1707°C
(β Zr) 1855 - 863		$a = 360.90$	(β Zr) dissolves ~1 at.% C at 1805°C
ThC _{1-x} < 2500	$cF8$ $Fm\bar{3}m$ NaCl	$a = 534.0$	ThC [1977Hol] Solid solution with (α Th) (critical point at 1140°C, 23 at.% C) and with γ ThC ₂ (critical point at 1850°C, 55 at.% C) [Mas2]
α ThC ₂ < 1440	$mC12$ $C2/c$ α ThC ₂	$a = 669.2$ $b = 422.3$ $c = 674.4$ $\beta = 103.0^\circ$	66 at.% C [Mas2]
β ThC ₂ 1495 - 1255	$tP6$ Pa_2/mmc β ThC ₂	$a = 423.5$ $c = 540.8$	63 to 66 at.% C [Mas2]
γ ThC ₂ 2610 - 1470	$cP12$ $Pa\bar{3}$ FeS ₂	$a = 580.9$	Presents a solid solution with (α Th). Two miscibility gaps. Critical points at 1140°C, 23 at.% C and 1850°C, 55 at.% C [Mas2]
ZrC _{1-x} < 3427	$cF8$ $Fm\bar{3}m$ NaCl	$a = 467.0$ $a = 472.2$	33 to 50 at.% C [1995Fer] at 33 at.% C [1962Rud] at 50 at.% C [1977Hol]

Fig. 1: C-Th-Zr.
Isothermal section at
1500°C



Carbon – Uranium – Zirconium

Pierre Perrot

Introduction

Investigations of the phase equilibria up to 2200°C by [1957Kie, 1957Now1, 1958Bro, 1958Now, 1963Rud1] using X-ray diffraction showed that UC and ZrC form a continuous solid solution. The solid solution is observed both from rapid cooling of the liquid mixture and from annealing at temperatures above 500°C [1958Iva]. According to early investigations [1957Now2, 1958Now], lattice parameter of this solid solution shows a slightly negative deviation from Vegard's law. However, subsequent work [1961Iva, 1963Rud1, 1965Kut, 1968Nic] indicated that Vegard's law holds for this phase within experimental uncertainties. Using a disappearing-filament optical pyrometer, [1958Bro] measured the liquidus curve along the UC–ZrC section. The partial isothermal section at 1700°C within the composition range bounded by C, UC, and ZrC was determined by [1961Ben] using XRD technique. The whole isothermal section at 1700°C was constructed by [1975Hol] using the literature data, supplemented with approximate thermodynamic calculation. Based on XRD technique, [1968Nic] measured the phase relations at 1700, 1900 and 2000°C within the U–Zr–UC–ZrC subsystem.

Binary Systems

The adopted C–Zr phase diagram is due to [1995Fer] who considered the experimental data of [1993But]. The C–U and U–Zr phase diagrams are taken from [2001Che] and [2004Che], respectively. It should be noted that C–U diagram essentially the same as in [Mas2] and U–Zr diagram differs from the one presented in [Mas2]. In the temperature range relevant to the known C–U–Zr equilibria it differs by the position of the L+ β two phase domain.

Solid Phases

The solid phases are presented in Table 1.

Quasibinary Systems

The quasibinary system UC–ZrC_{0.81} established by [1993But, 1994But] is shown in Fig. 1. The miscibility gap at temperatures below 1378°C calculated by [1982Ogo] has not been confirmed experimentally.

Isothermal Sections

The isothermal section at 1700°C presented in Fig. 2 is mainly based on [1961Ben, 1968Nic, 1975Hol]. In order to be consistent with the accepted binaries, the presented isothermal section is slightly modified. This section is in qualitative agreement with the observations of [1968Ale] who measured lattice parameters of the carbides resulting from the reaction between UC and Zr. In the work of [1968Ale], the reaction temperature is not specified. The isothermal sections at 1900 and 2000°C presented by [1968Nic] and the section at 2027°C by [1973Sto] differ from the section at 1700°C in that the ZrC contents of the solid solution (U,Zr)C in equilibrium with the C and UC₂ are reported to be relatively large (68 ± 2 mol% ZrC at 1900°C, 77 ± 2 mol% ZrC at 2000°C, and 78 mol% ZrC at 2027°C), compared with the value of 61 ± 3 mol% ZrC at 1700°C. Several isothermal sections above 2200°C are presented by [1993But], who performed graphical and numerical curve fitting of self-consistent thermodynamic and phase diagram data available in the literature. Figures 3 to 8 show the isothermal sections at 2200, 2410, 2480, 2600, 2850, and 3000°C established by [1993But], respectively. The isothermal section at 3420°C [1993But] shows that C would be in equilibrium with a liquid phase containing approximately 80 at.% C, below which there is a single liquid phase region.

Temperatue – Composition Sections

The vertical section UC₂–ZrC reported by [1973Sto, 1993But] is presented in Fig. 9.

Thermodynamics

The excess Gibbs energy of mixture for the solid solution (U,Zr)C has been evaluated by [1963Rud1, 1963Rud2] using a regular solution model applied to the observed phase relationship. The following expression may be used in the temperature range 1700–1900°C: $\Delta_{\text{mix}}G^{\text{XSJ}} = \alpha x_{\text{UC}}x_{\text{ZrC}}$ with $\alpha = 25.2 \text{ kJ}\cdot\text{mol}^{-1}$. A more precise measurement using the time-of-flight mass spectrometer [1971Hoc] yields a value of $28.0 \pm 2.4 \text{ kJ}\cdot\text{mol}^{-1}$ at 1960°C for α . This value is close to that for the (γ U, β Zr) body centered solid solution. This later value for α leads to a critical point of 1411°C for the solid solution (U,Zr)C, which agrees reasonably with the value of 1378°C calculated by [1982Ogo]. High temperature mass spectrometry was used by [1973Sto] to measure the activities of U and Zr in the (U,Zr)C solid solution in equilibrium with C and UC₂. The solid solution between ZrC and UC was found to be ideal at 1917°C with an increasingly positive enthalpy of mixing as temperature increases. The stability of the solution apparently results from the metal-carbon interactions with a repulsive contribution from the metal-metal interactions above 1917°C.

The heat content of the solid solution U_{1-x}Zr_xC ($x < 0.05$) between 500 and 2500°C has been measured by [1969Boc]. The dissolution of Zr in UC increases slightly the heat content of the solid solution. A more precise description of the solid solutions is obtained by [1982Oga] who took into account the homogeneity ranges of the carbides.

Notes on Materials Properties and Applications

Because of its excellent nuclear and high temperature properties, the C–U–Zr system is attractive as a basis for high temperature nuclear fuels. The (U,Zr)C solid solution and (U,Zr)C + C composite materials may be materials of choice for the manned mission to Mars because of their excellent nuclear properties and thermal stability.

The penetration rate of UC in various metals at 400°C has been investigated by [1962Kat]. The UC–Zr system is considered as a “rapid” reacting system, because the penetration depth is higher than 50 μm in 10 days.

The influence of small additions of C on the morphology and mechanical properties of U–Zr alloys has been investigated by [1962Cra]. In view of application of such alloys as nuclear fuels, the effect of irradiation is also discussed.

Miscellaneous

The average thermal linear expansion coefficients in the temperature range of 25 to 1000°C has been measured for different compositions of the solid solution [1965Kem, 1969Boc] and were found to be $6.4\cdot 10^{-6} \text{ K}^{-1}$ for pure ZrC, $7.28\cdot 10^{-6} \text{ K}^{-1}$ for the composition U_{0.3}Zr_{0.7}C_{0.97} [1965Kem], $10.64\cdot 10^{-6} \text{ K}^{-1}$ for the composition U_{0.9}Zr_{0.17}C and $10.8\cdot 10^{-6} \text{ K}^{-1}$ for pure UC [1969Boc].

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
C (graphite) < 3827	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.9	at 25°C [Mas2]
C (diamond)	<i>cF8</i> <i>Fd$\bar{3}m$</i> C (diamond)	<i>a</i> = 356.69	high pressure phase
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	at 25°C [Mas2] dissolves ~1 at.% Zr at 617°C
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> β U	<i>a</i> = 1075.9 <i>c</i> = 565.6	at 25°C [Mas2] dissolves ~2 at.% Zr at 693°C

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α Zr) < 1360	<i>hP2</i> <i>P6₃/mmc</i> Mg	$a = 323.16$ $c = 514.75$	at 25°C [Mas2]
(γ U, β Zr)	<i>cI2</i> <i>Im$\bar{3}m$</i> W		solid solution (γ U, β Zr)
(γ U) 1135 - 776		$a = 352.4$	[Mas2]
(β Zr) 1855 - 863		$a = 360.90$	β Zr dissolves ~1 at.% C at 1805°C
η , UZr ₂ < 617	<i>hP3</i> <i>P6/mmm</i> AlB ₂	$a = 503$ $c = 308$	65 to 78 at.% Zr [2004Che]
(U,Zr)C	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl		
U _{0.5} Zr _{0.5} C		$a = 482.2$	[1984Hol1, 1984Hol2]
δ , UC < 2515		$a = 495.97 \pm 0.4$	stoichiometric UC from 47 to 66 at.% C miscibility gap (critical point at 2050°C, 45 at.% C) [1993But, 2001Che]
ZrC < 3427		$a = 469.6$	33 to 50 at.% C [1995Fer] at 50 at.% C [1961Ben]
ζ , U ₂ C ₃ < 1833	<i>cI40</i> <i>I$\bar{4}3d$</i> Pu ₂ C ₃	$a = 808.9$	60 at.% C [1993But, 2001Che]
ϵ , UC ₂ 1762 - 1477	<i>tI6</i> <i>I4/mmm</i> CaC ₂	$a = 351.90 \pm 0.11$ $c = 597.87 \pm 0.17$	62 to 65.5 at.% C [Mas2] UC _{1.78} [2001Che]
		$a = 352.41 \pm 0.05$ $c = 599.62 \pm 0.08$	UC _{2.00} [2001Che]
δ , UC ₂ 2434 - 1762	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF ₂ ?	$a = 545.0$	actually, “ δ ,UC ₂ ” phase represents the δ ,UC phase in equilibrium with graphite [1993But, 2001Che]

Figure 1 is a phase diagram of the U-Zr-C system. The y-axis represents Temperature in °C, ranging from 1250 to 3500. The x-axis represents the composition in at.% U, ranging from 50.00 to 0.00. The diagram shows three main regions: L (Liquid), L+(U,Zr)C (Liquid + (U,Zr)C), and (U,Zr)C. The (U,Zr)C phase is a solid solution of U and Zr in carbon. The L+(U,Zr)C region is the two-phase region between the liquid and the solid solution. The L region is the liquid phase. The diagram shows the phase boundaries between these regions as a function of temperature and composition.

U, at.%	Temperature (°C)	Phase Region
50.00	2500	L
40.00	2500	L+(U,Zr)C
30.00	2500	(U,Zr)C
20.00	2500	(U,Zr)C
10.00	2500	(U,Zr)C
0.00	2500	(U,Zr)C

Fig. 3: C-U-Zr.
Isothermal section at
2200°C

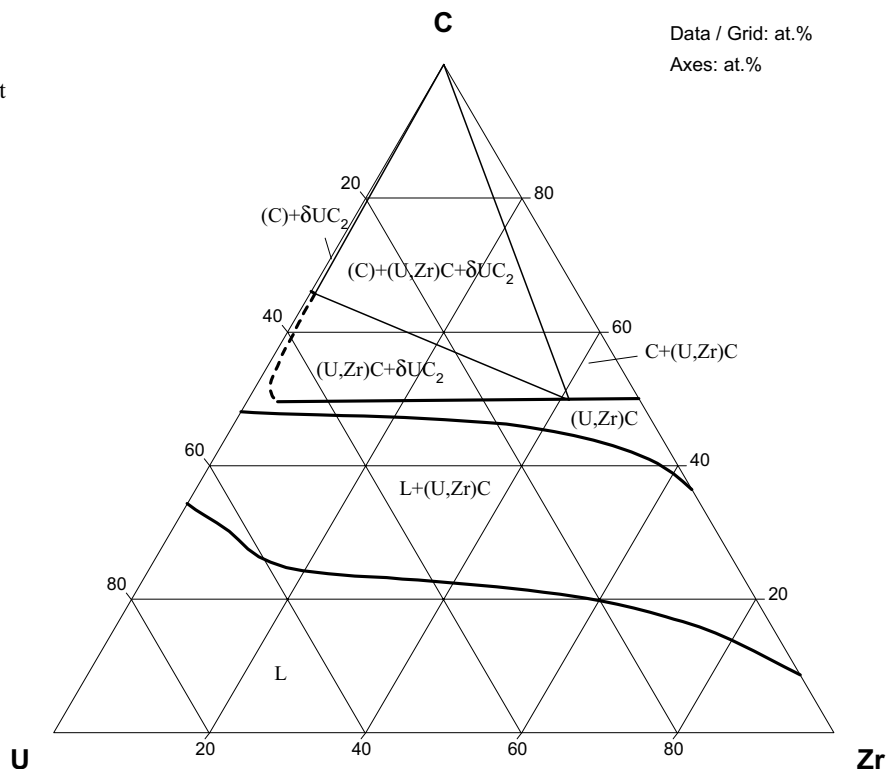


Fig. 4: C-U-Zr.
Isothermal section at
2410°C

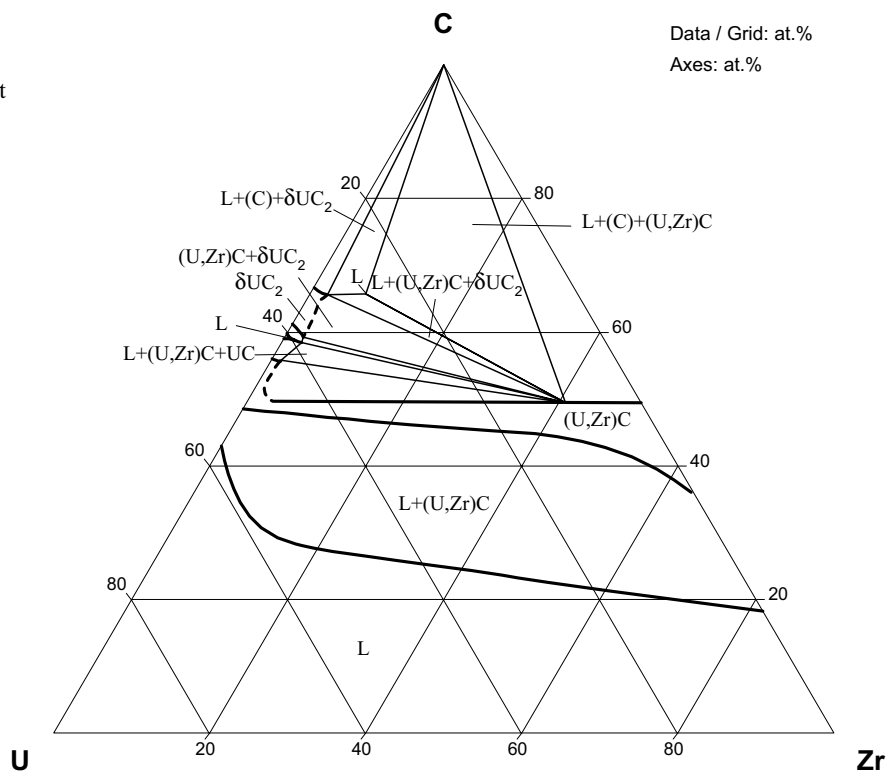


Fig. 5: C-U-Zr.
Isothermal section at
2480°C

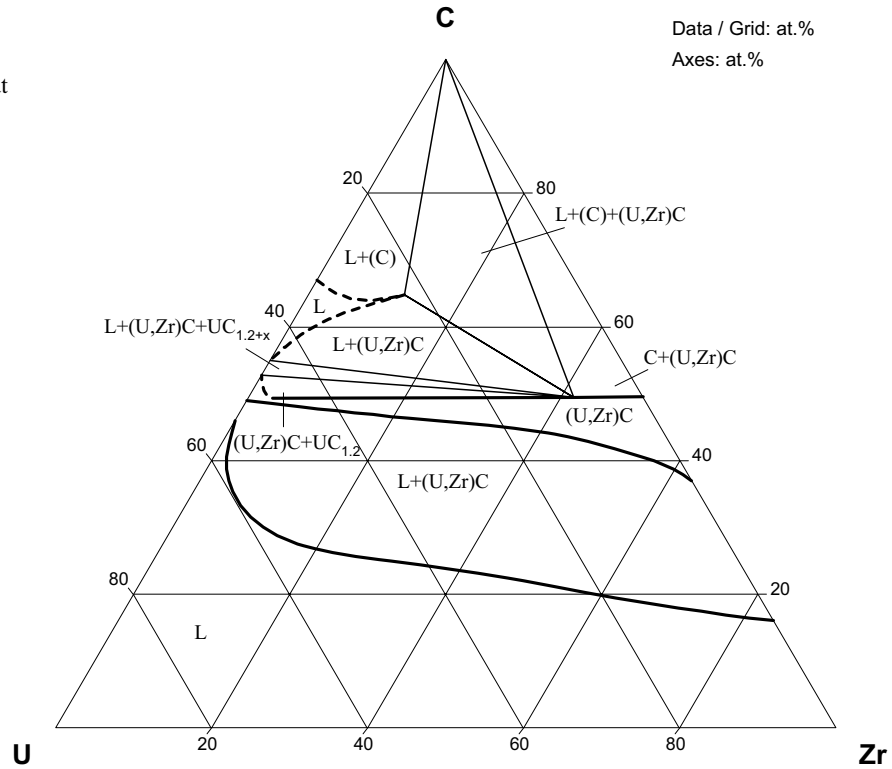


Fig. 6: C-U-Zr.
Isothermal section at
2600°C

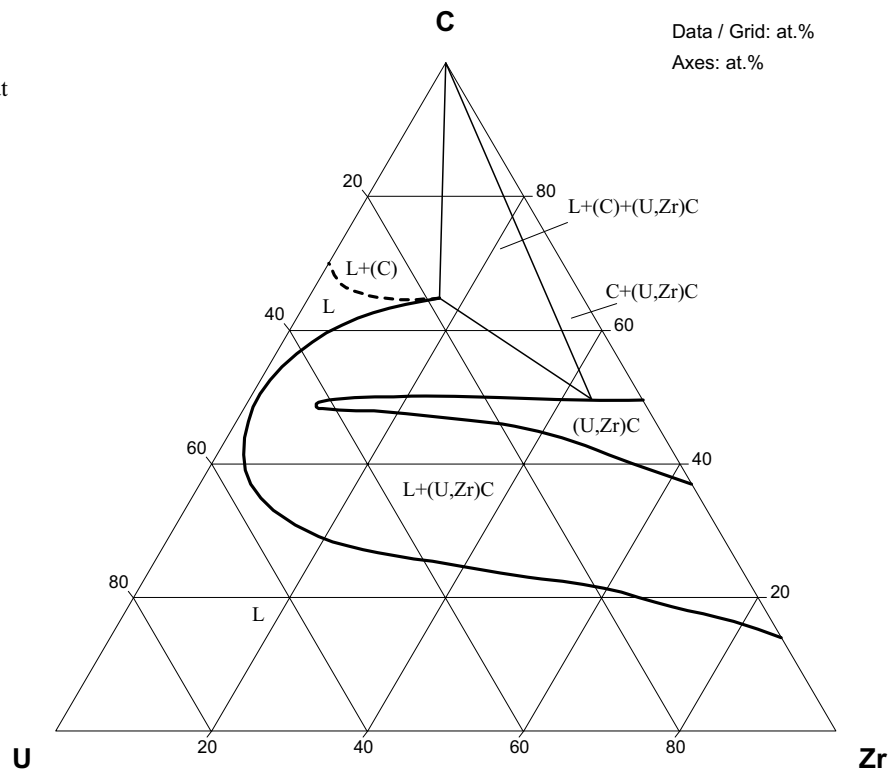


Fig. 7: C-U-Zr.
Isothermal section at
2850°C

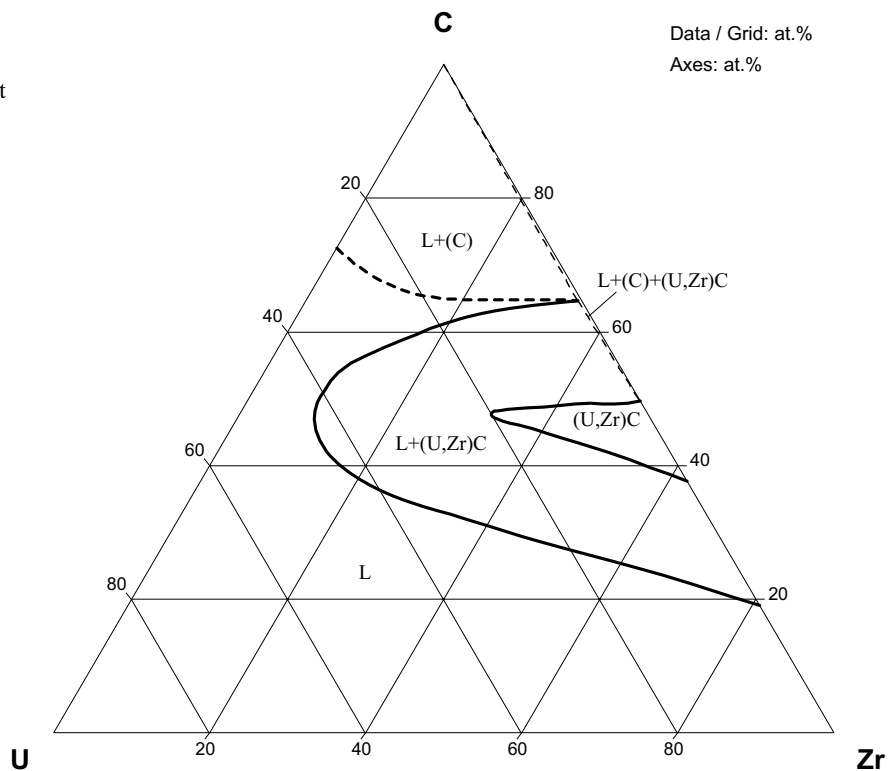


Fig. 8: C-U-Zr.
Isothermal section at
3000°C

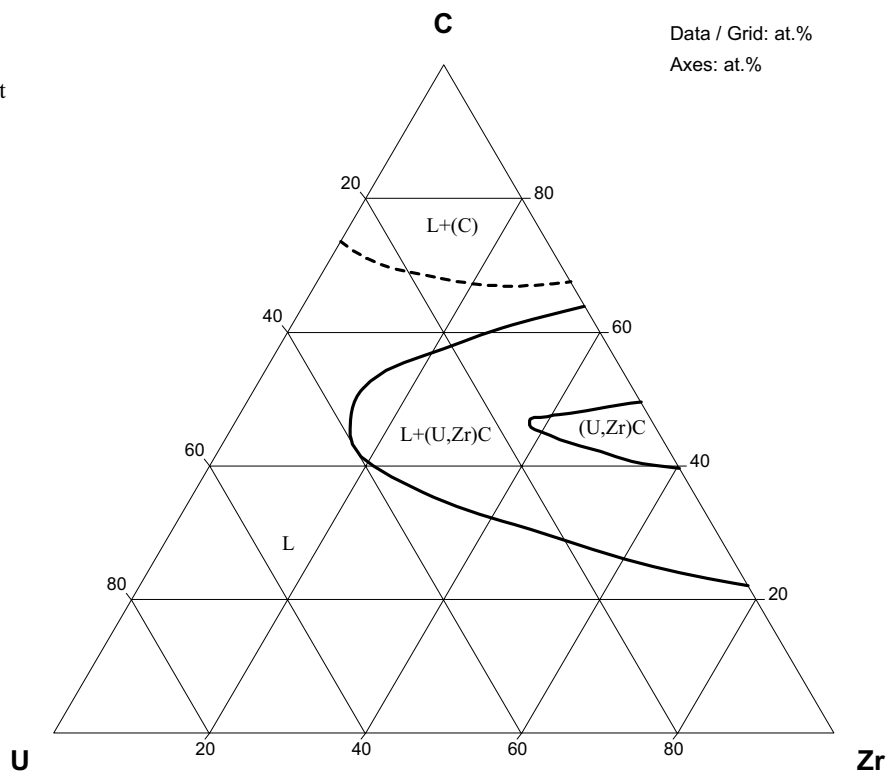
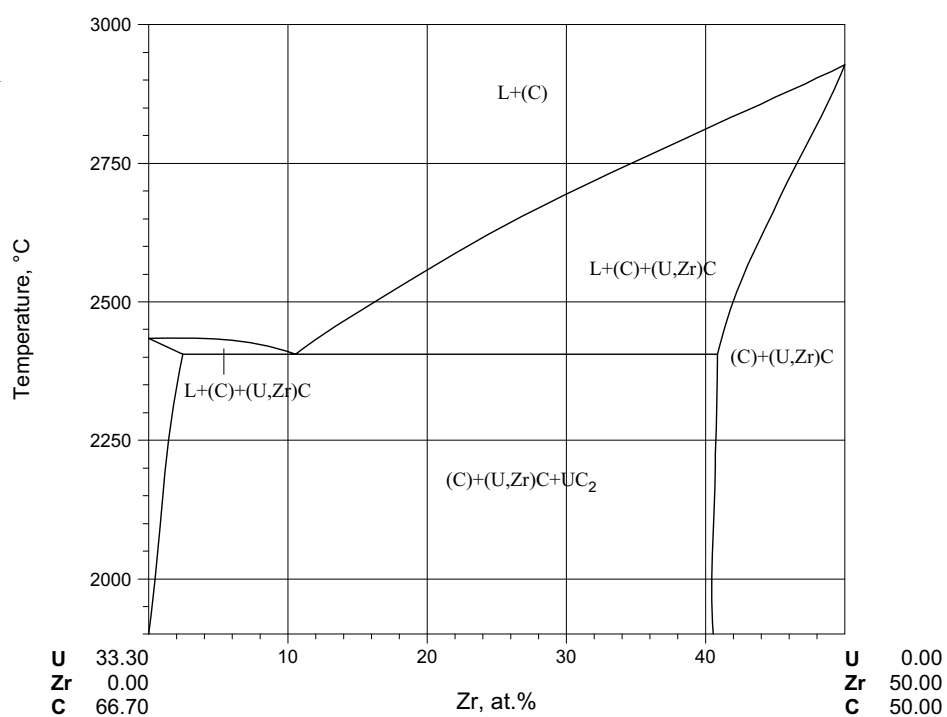


Fig. 9: C-U-Zr.
The vertical section
 $\text{UC}_2\text{-ZrC}$



Cerium – Magnesium – Oxygen

Nataliya Bochvar, Yuriy Liberov, updated by Olga Fabrichnaya

Introduction

The liquidus line in the system MgO–CeO₂ which is part of the liquidus surface of the ternary Ce–Mg–O system was experimentally obtained by [1932War] for the first time. [1976Pre] used X-ray diffraction and optical pyrometry to establish phase configurations and liquidus temperatures of alloys along the same MgO – CeO₂ section. They synthesized their specimens from chemically pure cerium dioxide and magnesium carbonate. By wet ball milling they obtained a homogeneous mixture of the component powders from which their specimens were formed by a heat treatment in the temperature range of 1200–1600°C with subsequent and rapid cooling. According to [1976Pre], no ternary compound exists in the system but a eutectic reaction occurs between MgO and CeO₂. In the Ce₂O₃–MgO system [1971Lop] investigated specimens of 4:1, 1:1 and 1:2 compositions by XRD and DTA techniques. New phases were not observed in this system and the additions of MgO did not change the temperature of the polymorphic transformations in Ce₂O₃. The mixtures of MgO with 5 and 10 mass% of CeO₂ were investigated at 1800–2000°C by measurement of vapor pressure in the study of [1983Gvo]. The specimens were heat treated at 1570°C and characterized by XRD and electron microprobe analysis. Again no ternary compounds were found but the formation of a solid solution was indicated. Thermodynamic parameters to describe the CeO₂–MgO system by the CALPHAD method were assessed by [1997Zha]. In the year 2005 solid solutions based on CeO₂ were synthesized and characterized by [2005Che, 2005Iva].

Details on the experimental and theoretical investigations of the ternary Ce–Mg–O system are summarized in Table 1.

Binary Systems

The edge binary systems of the ternary Ce–Mg–O are accepted from different works. The Ce–Mg phase diagram is accepted from the critical evaluation made by [2002Gro] in the MSIT Evaluation Program. For Mg–O the phase diagram from thermodynamic assessments of [1993Hal] is considered to be best. The phase diagram of the Ce–O system is accepted from the thermodynamic assessment by [2006Zin] up to a temperature of 1800°C. In the Ce₂O₃–CeO₂ region the melting behavior is not well determined. For CeO₂ a melting temperature of 2750°C results from the evaluation of experimental data by [2006Zin]. However, thermodynamic calculations using the Calphad technique show a peritectic melting of CeO₂ with the formation of gas at 2293°C [2006Zin]. The reason for this discrepancy could be in both, in the Calphad modeling of liquid phase and in the experimental uncertainty. It was noticed by several investigators that the CeO₂ compound became oxygen deficient under heating [1932War, 1976Pre, 2006Zin] and neither the type of melting nor the actual composition could be determined [2006Zin].

Solid Phases

The crystallographic characteristics of the binary phases are given in Table 2, ternary phases are not reported in this system. [1976Pre] found CeO₂ to dissolve up to 8 mol% MgO at 2100°C by measuring the lattice parameters. The formation of CeO₂ based solid solutions was also confirmed by [2005Che, 2005Iva]. The investigation of [1983Gvo] demonstrated that vapor pressures of Mg and Ce cations over mixtures containing 5 and 10 mass% CeO₂ were smaller than over pure MgO and CeO₂. This indicates the formation of a solid solution which is more stable than mechanical mixtures of oxides. The formation of the solid solution was also confirmed by microprobe analysis and XRD investigation which indicated the increase of MgO lattice parameters. However, the solubility of CeO₂ was probably less than 5 mass% MgO. Electron microprobe analysis indicates that the CeO₂ phase segregates along the grain boundaries and the pore surfaces.

Quasibinary Systems

The MgO-CeO₂ quasibinary system was experimentally studied by [1932War, 1976Pre]. [1983Gvo] studied the MgO rich compositions of the system. The phase diagram of the MgO - CeO₂ system is presented in Fig. 1 according to [1976Pre] accounting data of [1983Gvo]. The diagram is of simple eutectic nature. Because [1983Gvo] did not determine how much CeO₂ will actually dissolve in MgO the solubility limit is shown by a dashed line in Fig. 1. According to [1976Pre] the invariant equilibrium $L \rightleftharpoons \text{MgO} + \text{CeO}_2$ exists at 2100°C, the eutectic composition is 70 mol% MgO and 30 mol% CeO₂. The temperature of the eutectic reaction obtained earlier by [1932War] was 140°C higher, while the composition was the same. There is no indication for the formation of a CeO₂-based solid solution in the early work of [1932War]. In the present evaluation we rely on the data of [1976Pre] because these authors provided a more detailed description of an appropriate experimental procedure.

[1971Lop, 1976Lop] state that the MgO-Ce₂O₃ phase diagram is also of eutectic type. The temperature and the composition of the eutectic were experimentally determined by [1971Lop, 1976Lop] to be 1920°C and 50 mol% Ce₂O₃. Obviously Ce₂O₃ does not form a solid solution with MgO since the temperatures of polymorphic transformations were not changed by additions of MgO.

Thermodynamics

A thermodynamic modeling of the MgO-CeO₂ system was performed by [1997Zha]. These authors described the CeO₂ based solid solution by a Substitutional Model and applied the Associate Model with 2MgO·CeO₂ species to describe the liquid phase. The eutectic composition and temperature, were reproduced in the calculations very well, as well as the composition of CeO₂ solid solution. However the concave shape of the liquidus line in the MgO rich region can not be reproduced by the associate model and not by the substitutional model with Redlich-Kister polynomials.

Notes on Materials Properties and Applications

Ce-Mg-O is seen as a candidate system to deliver inert matrix material processing nuclear waste. This process of separating the radionuclides from the spent fuel with subsequent fission or transmutation in reactors or accelerators can lead to a considerably reduced long term radiotoxicity. One way to handle the fuel for transmutation is its dispersion in inert matrix material of appropriate properties, in particular of high melting temperatures. Ce and Pu form as fission products in nuclear reactors. High refractory oxides such as aluminium oxide and MgO are appropriate candidate matrix materials for heterogeneous transmutation. Ce substitutes Pu in its compounds, such as PuO₂, forming solid solutions [1997Zha]. That is why phase relations in the Pu-Ce-Mg-O system are important for the waste management from nuclear power generation.

Ce-Mg-O is of interest as catalyst and catalyst support for methane combustion reaction [2005Che, 2005Iva]. The CeO₂ based solid solutions were synthesized and characterized using XRD and adsorption spectroscopy (X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy) by [2005Iva]. The Mg⁺² ions enter the cubic lattice of the CeO₂ to form solid solution. This structure (fluorite) according to [2005Che] is favorable to enhance catalytic activity. The formation of nano size particles and good redox ability of Ce-Mg-O materials are also key factors supporting catalytic properties [2005Che].

Miscellaneous

New material made from Ce-Mg-O nanoparticles with high thermal stability and high surface area was synthesized by [2004Che, 2005Che]. The average crystalline size was from 10 to 20 nm. It was demonstrated by XRD that at all studied Mg/Ce ratios, from 1/9 to 9/1, only fluorite type of solid solutions form. The cell parameters decrease slightly with increasing Mg contents. The smaller Mg⁺² ions entering the CeO₂ lattice decrease the lattice parameter and increase the peaks intensity. It is obvious from the phase diagram of the MgO-CeO₂ system that fluorite solid solutions are metastable at the studied conditions. However they are thermally stable and do not decompose under heating at the studied temperatures up to 1000°C [2004Che].

[1995Gvo] theoretically calculated the solubility of ceria in MgO and the critical temperature at which the solid solution decomposes. These calculations were based on theoretical semi-quantitative approaches introducing cerium cations into the crystal lattice of magnesium oxide.

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Table 1: Investigations of the Ce-Mg-O Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1932War]	pyrometry	2240-2600°C MgO-CeO ₂ 0-91 mol% MgO
[1971Lop]	XRD, DTA	1500-2300°C Ce ₂ O ₃ -MgO 4:1, 1:1 and 1:2
[1976Pre]	DTA, XRD, optical pyrometry	CeO ₂ (DTA 20-900°C), CeO ₂ solid solution at 1200-1600°C (XRD of quenched samples), the MgO-CeO ₂ system (melting determination by optical pyrometry) at 2100-2700°C
[1983Gvo]	XRD, electron microprobe, mass-spectrometry	MgO with 5 and 10 mass% CeO ₂ , heat treatment at 1750°C, vapor pressure measurement at 1800-2000°C
[1997Zha]	CALPHAD	Phase diagram MgO-CeO ₂ 1800-2900°C
[2004Che]	Thermal analysis TG-DTA, transmission electron microscopy (TEM), XRD, Raman spectroscopy, BET surface area technologies	25-700°C TG-DTA, 600-1000°C calcination, compositions Mg/Ce=1/9, 1/1, 9/1.
[2005Che]	XRD, thermo-gravimetric analysis (TG), DTA, atom force microscopy (AFM), catalytic activity test	25-700°C TG-DTA, 650°C calcination, compositions Mg/Ce=1/9, 1/1, 9/1
[2005Iva]	XRD, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR)	5-25 mol% Ce ₂ O ₃ at 450 and 750°C

Table 2: Crystallographic Data of Solid Phases

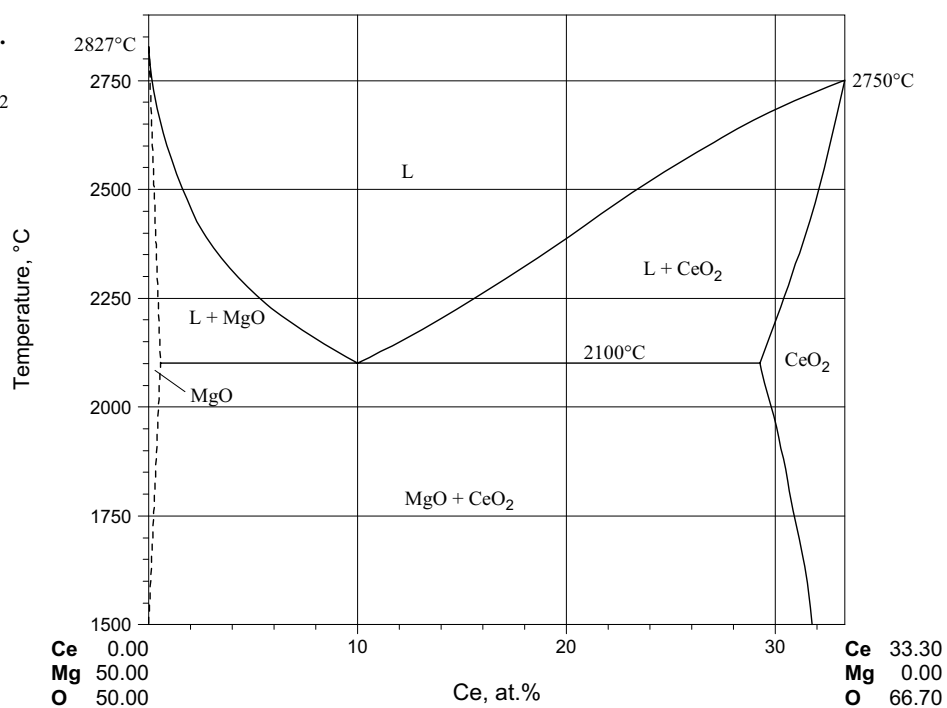
Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Mg) < 650	<i>hP2</i> <i>P6₃/mmc</i> Mg	<i>a</i> = 320.944 <i>c</i> = 521.07	at 25°C [Mas2] 0.066 at.% Ce at 540°C, 0.014 at.% Ce at 400°C [2002Gro]
(δCe) 798 - 726	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 412	[Mas2]
(γCe) 726 - 61	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	<i>a</i> = 516.10	[Mas2] from 0 to 8.2 at.% Mg [2002Gro]
(βCe) 61 - (-177)	<i>hP4</i> <i>P6₃/mmc</i> αLa	<i>a</i> = 386.10 <i>c</i> = 1185.7	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α Ce) < –177	$cF4$ $Fm\bar{3}m$ Cu	$a = 485$	at –196°C [Mas2]
MgO < 2827 ± 10	$cF8$ $Fm\bar{3}m$ NaCl	$a = 421.12$	[1993Hal]
CeO	$cF8$ $Fm\bar{3}m$ NaCl	$a = 508.9$	[V-C2] 1.5 GPa, 700°C
A-Ce ₂ O _{3–x} < 2065	$hP5$ $P\bar{3}2/m1$ A-La ₂ O ₃	$a = 389.1 \pm 1$ $c = 605.9 \pm 1$	O/Ce = (3–3)/2, stoichiometric composition Ce ₂ O ₃ in [2006Zin] transition temperature from [2006Zin] lattice parameters and space group from [1985Bae]
H-Ce ₂ O ₃ 2065–2140	$hP5$ $P6_3/mmc$ H-La ₂ O ₃		[2006Zin] transition temperature from [2006Zin]
X-Ce ₂ O _{3–x} 2240 – 2140	$cI26$ $Im\bar{3}m$ LaYbO ₃		[2006Zin] melting point from [1985She] Exist up to 2140°C [2006Zin]
C-Ce ₂ O _{5±x} 612–1403	$cI96$ $Ia\bar{3}$ Mn ₂ O ₃	$a = 1111.1 \pm 2$	O/Ce=(5±x)/3, stoichiometric composition Ce ₃ O ₅ in [2006Zin]
Ce ₇ O ₁₂ < 1048	$hR57$ $R\bar{3}$ UY ₆ O ₁₂	$a = 1035.09 \pm 0.02$ $c = 963.85 \pm 0.02$	lattice parameters recalculated from [2006Zin]
Ce ₉ O ₁₆ < 632	-	-	[2006Zin]
Ce ₁₉ O ₃₄ < 607	triclinic	$a = 662.7$ $b = 1147.8$ $c = 1012.3$ $\alpha = 100.9^\circ$ $\beta = 90.0^\circ$ $\gamma = 95.5$	[2006Zin]
Ce ₄₀ O ₇₂ < 582	-	-	[2006Zin]
Ce ₆₂ O ₁₁₂ < 487	-	-	[2006Zin]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Ce ₁₁ O ₂₀ < 459	<i>aP</i> 31 <i>P</i> $\bar{1}$ Tb ₁₁ O ₂₀	$a = 675.7 \pm 3$ $b = 1026.0 \pm 5$ $c = 673.2 \pm 3$ $\alpha = 90.04 \pm 4^\circ$ $\beta = 99.80 \pm 4^\circ$ $\gamma = 96.22 \pm 4^\circ$	[2006Zin]
CeO _{2-x} 2750	<i>cF</i> 12 <i>Fm</i> $\bar{3}m$ CaF ₂	$a = 541.12 \pm 10$ $a = 532.0$	[2006Zin] at 4 at.% Mg [1976Pre]
Mg ₁₂ Ce (I) < 616	<i>tI</i> 26 <i>I4/mmm</i> Mn ₁₂ Th	$a = 1033$ $c = 596$	[2002Gro]
Mg ₁₂ Ce (II)	<i>oI</i> 338 <i>Immm</i> Mg ₁₂ Ce(II)	$a = 1033$ $b = 1033$ $c = 7750$	[Mas2, 2002Gro]
Mg _{10.3} Ce 621 - 611	<i>hP</i> 38 <i>P</i> 6 ₃ / <i>mmc</i> Ni ₁₇ Th ₂	$a = 1031$ $c = 1032$	[V-C2, 2002Gro] composition is given as Ce ₂ Mg ₁₇
Mg ₄₁ Ce ₅ < 635	<i>tI</i> 92 <i>I4/m</i> Mg ₄₁ Ce ₅	$a = 1478$ $c = 1043$	[V-C2, 2002Gro]
Mg ₃ Ce < 796	<i>cF</i> 16 <i>Fm</i> $\bar{3}m$ BiF ₃	$a = 744.3$	[V-C2, 2002Gro]
Mg ₂ Ce < 750	<i>cF</i> 24 <i>Fd</i> $\bar{3}m$ Cu ₂ Mg	$a = 873.3$	[V-C2, 2002Gro]
MgCe < 711	<i>cP</i> 2 <i>Pm</i> $\bar{3}m$ CsCl	$a = 391.2$	[V-C2, 2002Gro]

Fig. 1: Ce-Mg-O.

The quasibinary
system MgO - CeO₂



Cesium – Iron – Oxygen

Pierre Perrot

Introduction

Basic oxides such as Cs_2O are known to stabilize the highest oxidation states (IV and VI) of iron. There is a growing interest to the ferrate (VI) compounds due to their potential as powerful oxidizing agents [2001Ded]. It has also been suggested that dry extraterrestrial environments promote the formation of higher oxidation states of iron. Investigations on ferrates (IV and VI) of Cs has been carried out by Mössbauer spectroscopy [1994Kop, 1995Ran, 1999Kul, 2001Ded], which is one of the most appropriate approach to characterize iron containing materials. The Cs–Fe–O system could be important to oxide fuel and cladding interactions in the LMFBR (Liquid Metal Fast Breeding Reactor) systems [1981Lin]. The latest experimental works carried out on the Cs–Fe–O system are summarized in Table 1.

Binary Systems

Cs and Fe present no mutual solubility in the solid and in the liquid state [Mas2]. The Fe–O system is accepted from thermodynamic assessment of [1991Sun]. This diagram is in a very good agreement with evaluation of [Mas2] mainly based on the fundamental work of [1945Dar, 1946Dar]. The Cs–O system has never been thermodynamically assessed. There data on phase equilibria in the Cs–O system are scarce and contradictory. The latest phase diagram is from [1979Kni], where it was claimed that phase diagram data between Cs_7O and Cs_3O were not correct. According to [1979Kni] Cs_4O melts incongruently at 53°C that is higher than 10.5°C given by [Mas2]. According to [Mas2] Cs_3O has homogeneity range, while [1979Kni] show this phase as stoichiometric. The Cs_2O_3 phase [V-C2] was not found in [1979Kni]. Probably this phase is metastable. The accepted Cs–O phase diagram from [1979Kni] is presented in the evaluation of the Cs–Mo–O system in the present volume. Crystallographic data are from [V-C2].

Solid Phases

Crystallographic data of all unary phases and binary and ternary oxides are listed in Table 2. The mixed oxides of Cs and Fe lie mainly on the joint Cs_2O – Fe_2O_3 . All these phases are easily synthesized by solid-state reaction between Fe_2O_3 and a cesium salt such as Cs_2CO_3 or CsNO_3 . The compound $\text{CsFe}_{11}\text{O}_{17}$ whose structure is the “magnetoplumbite” type is decomposed above 800°C by heating under N_2 , air or O_2 [1987Ito]. It is also easily reduced and gives $\text{Fe}_3\text{O}_4 + \text{CsFeO}_2$.

The mixed oxide Cs_2FeO_4 in which iron is in the oxidation state VI can be synthesized via the oxidation of $\text{Fe}(\text{OH})_3$ in concentrated alkaline media by Cl_2 or using the interaction between solid Fe_2O_3 and CsO_2 in dry oxygen flow at high temperatures [1995Kul]. It may also be obtained by reacting a mixture ($\text{Fe} + \text{CsO}_2$) with the ratio $\text{Cs}/\text{Fe} = 4$, at 200°C during 10 hours under an oxygen atmosphere [1999Kul]. Cs_2FeO_4 decomposes above $500 - 600^\circ\text{C}$ with the formation of $\text{CsFeO}_{2.5}$ in which iron is in the state of oxidation IV [1992Kop]. Mössbauer studies [1995Kul] detected iron IV in Cs_2FeO_4 , which is explained by the result of electron capture decay of ^{57}Co in the solid matrix of Cs_2FeO_4 . A slight non stoichiometry has been proposed for $\text{CsFeO}_{2.5}$ which is sometimes labelled $\text{Cs}_x\text{FeO}_{2+0.5x}$ (with $x \sim 1$). However, Mössbauer investigation and magnetic measurements carried out by [1994Kop] failed to detect iron with an oxidation state different from IV. Further lattice of $\text{CsFeO}_{2.5}$ is indexed in a P cubic structure perovskite like. A superstructure may be observed, which is due to the ordering of the oxygen vacancies. By taking into account the superstructure, $\text{CsFeO}_{2.5}$ may be indexed in a F cubic structure with a parameter twice. The ferrate CsFeO_2 in which iron is in the oxidation state III may be obtained by decomposition of the mixed oxalate $\text{Cs}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$ in a shorter time and a lower temperature (700°C) than by the conventional ceramic method [1995Ran].

The compound $\text{Cs}_8\text{Fe}_2\text{O}_7$ in which Fe has a mean oxidation state of 2.33 is obtained by reacting Fe_2O_3 with metallic Cs under Ar at 500°C [2004Fri]. It is probable that the phases $\text{Cs}_8\text{Fe}_2\text{O}_7$ and $\alpha\text{Cs}_5\text{FeO}_4$ with the same structure $P2_1/c$ and whose compositions are very close belong to the same solid solution $P2_1/c$.

Isothermal Section

The Cs-Fe-O diagram in the solid state given in Fig. 1 is taken from the informations given in [1981Lin] related to ferrates in which iron is in a state of oxidation lower than 3. First, they pointed out the fact that no reference to the compounds Cs_4FeO_3 and Cs_2FeO_2 could be found. Nevertheless, they assumed the existence of these compounds and evaluated their properties. In the Fig. 1, the compound Cs_4FeO_3 has been identified with $\text{Cs}_4\text{FeO}_{3.5}$ (or $\text{Cs}_8\text{Fe}_2\text{O}_7$) and the compound Cs_2FeO_2 (or $\text{Cs}_6\text{Fe}_3\text{O}_6$) have been identified with $\text{Cs}_5\text{Fe}_3\text{O}_6$, both compounds being described by [2004Fri]. The main characteristics of the diagram is the existence of the triangle Cs-Fe- $\text{Cs}_5\text{Fe}_3\text{O}_6$, which means that the mixture Cs+Fe oxidize more easily than pure Cs, that is under oxygen pressures lower than the oxygen pressure at Cs- Cs_2O equilibrium. This diagram may be used in the temperature range between 600 and 1000°C; below 570°C, FeO is never stable and the tie lines between FeO and CsFeO_2 have to be deleted. The ferrate (VI) Cs_2FeO_4 stable in highly basic medium [2004Lic] loses its oxygen by heating and thus, is not shown in Fig. 1.

Thermodynamics

The thermodynamic properties of some cesium ferrates given in Table 3 are mainly taken from the evaluation of [1981Lin]. However, as seen above, the compounds Cs_4FeO_3 and Cs_2FeO_2 whose existence was assumed by these authors were identified respectively with the compounds $\text{Cs}_8\text{Fe}_2\text{O}_7$ and $\text{Cs}_5\text{Fe}_3\text{O}_6$ described by [2004Fri]. The entropies were estimated by the same authors with the hypothesis that the entropy of formation of ferrates from pure oxides equals zero, which is fairly unrealistic. The entropies given in Table 2 are thus corrected by using a more probable value of 3 J per mole of metal observed with analogous chromium compounds. [1981Lin] propose a tentative Ellingham (p_{O_2} - T) diagram comparing the stability domains of iron oxides, $\text{Cs}_5\text{Fe}_3\text{O}_6$ and CsFeO_2 . However, this diagram is very unlikely, because the authors assumed that FeO does not exists below 200°C, while this temperature is commonly accepted to be 570°C.

Notes on Materials Properties and Applications

The ferrite $\text{CsFe}_{11}\text{O}_{17}$ is an excellent ionic conductor. However its conductivity, electronic and ionic, measured between 300 and 600°C by [1987Ito] is lower than that of analogous compounds $\text{RbFe}_{11}\text{O}_{17}$ and $\text{KFe}_{11}\text{O}_{17}$ because of the higher ionic radius of the Cs^+ ion. The ferrate VI Cs_2FeO_4 present a high solid state stability, is hardly soluble in concentrated KOH and may be used as an alkali cathode able to sustain current densities similar to that of conventional MnO_2 cathodes [2004Lic].

Miscellaneous

Mössbauer spectra are given for Cs_2FeO_4 [1999Kul], CsFeO_2 [1995Ran] and $\text{CsFeO}_{2.5}$ [1994Kop]. $\text{CsFeO}_{2.5}$ presents a simple symmetrical line with an isomer shift $\delta = 0.15 \text{ mm}\cdot\text{s}^{-1}$ corresponding to Fe^{IV} in an octahedra oxygen environment. The ferrate (VI) presents also a simple line with an isomer shift $\delta = -0.59 \text{ mm}\cdot\text{s}^{-1}$ corresponding to Fe^{VI} in an octahedral environment and an antiferromagnetic transition at 2.8 K.

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Table 1: Recent Investigations of the Cs–Fe–O System

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1986Mor]	X-Ray diffraction analysis	20°C, CsFe ₁₁ O ₁₇
[1987Ito]	Ionic conductivity measurements	300 - 600°C, CsFe ₁₁ O ₁₇
[1992Kop]	Thermal analysis, X-Ray determination	20 - 600°C, Cs ₂ FeO ₄ –CsFeO _{2.5}
[1994Kop]	Thermal analysis, Mössbauer	20 - 600°C, Cs ₂ FeO ₄ –CsFeO _{2.5}
[1995Kul]	Synthesis, Mössbauer	–196°C, +20°C, Cs ₂ FeO ₄
[1995Ran]	Synthesis, Mössbauer	20 - 700°C, CsFeO ₂
[1999Kul]	Synthesis, Mössbauer	200°C, Cs ₂ FeO ₄
[2001Ded]	Mössbauer, Magnetic measurements	2 - 6 K, 20°C, Cs ₂ FeO ₄
[2004Fri]	Synthesis, X-Ray diffraction analysis	500°C, Cs ₈ Fe ₂ O ₇ , Cs ₅ Fe ₃ O ₆ , CsFeO ₂
[2004Lic]	Electrochemistry, IR measurement	20°C, Cs ₂ FeO ₄
[2005Fri]	X-Ray diffraction analysis	20°C, Cs ₅ FeO ₄ , Cs ₇ Fe ₂ O ₈

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cs) < 28.39	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	<i>a</i> = 614.1	at 25°C [Mas2]
(α Fe) 1538 - 1394, 912	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	<i>a</i> = 286.65	at 25°C [Mas2]
(γ Fe) 1394 - 912	<i>cF4</i> <i>Fm</i> $\bar{3}m$ Cu	<i>a</i> = 364.67	at 25°C [Mas2]
Cs ₇ O < 3	<i>hP24</i> <i>P6m2</i> Cs ₇ O	<i>a</i> = 1639.3 <i>c</i> = 919.3	at 0°C [Mas2, V-C2]
Cs ₄ O < 53	<i>oP*</i> <i>Pna2</i> ₁	<i>a</i> = 1682.3 <i>b</i> = 2052.5 <i>c</i> = 1237.2	[1979Kni, V-C2]
Cs ₇ O ₂ < –10.5	<i>mP56</i> <i>P2</i> ₁ / <i>c</i> Cs ₁₁ O ₃	<i>a</i> = 1761.0 <i>b</i> = 921.8 <i>c</i> = 2404.7 β = 100.14°	[1979Kni, V-C2] labelled Cs ₁₁ O ₃ in [Mas2],
Cs ₃ O < 164	-	-	23 to 25 at.% O [Mas2]

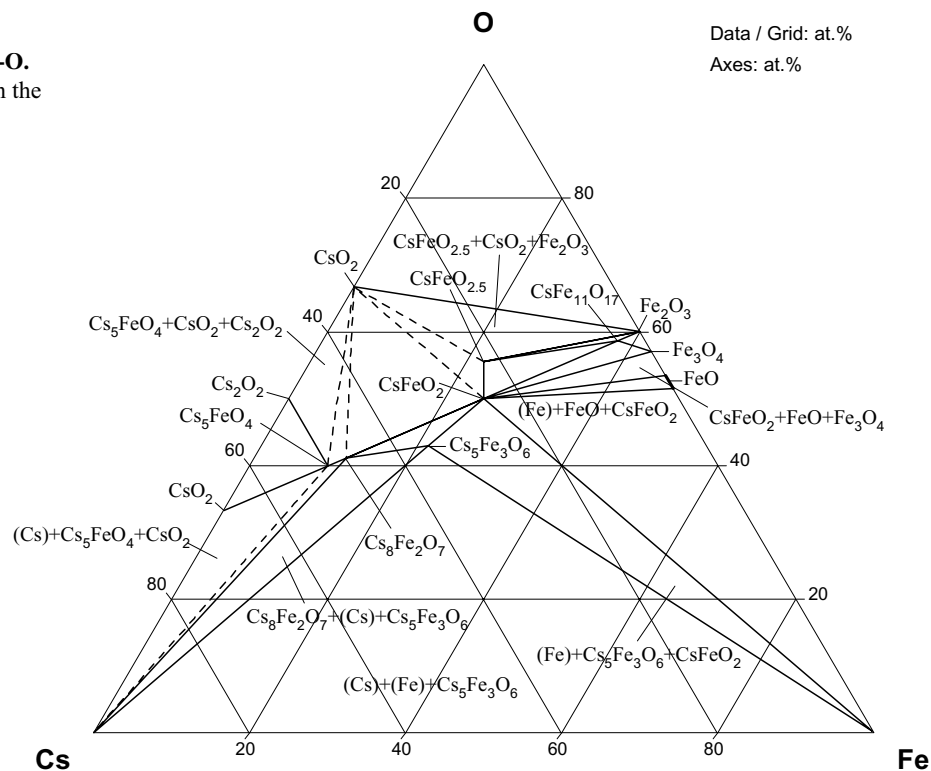
Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Cs ₂ O < 495	<i>hR9</i> <i>R$\bar{3}m$</i> WN ₂	<i>a</i> = 425.6 <i>c</i> = 1899.2	[1979Kni, 2005Gem]
CsO < 590	<i>oI8</i> <i>Immm</i> CsO	<i>a</i> = 432.2 <i>b</i> = 751.7 <i>c</i> = 643.0	[1979Kni, V-C2]
Cs ₂ O ₃ < 502	<i>cI28</i> <i>I$\bar{4}3d$</i> Th ₃ P ₄	<i>a</i> = 988	[Mas2, V-C2]. Not given in [1979Kni]. Probably metastable
α CsO ₂ (r) < 200	<i>tI6</i> <i>I4/mmm</i> CaC ₂	<i>a</i> = 446.2 <i>c</i> = 732.6	[Mas2, V-C2]
β CsO ₂ (h) 450 - 200	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	<i>a</i> = 662	[Mas2, V-C2]
CsO ₃ < 70	<i>mP16</i> <i>P2₁/c</i> RbO ₃	<i>a</i> = 670.9 <i>b</i> = 624.4 <i>c</i> = 899.7	[1979Kni, V-C2]
Fe _{1-x} O (wüstite) 1422 - 569	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	<i>a</i> = 431.0 <i>a</i> = 429.3	0.05 < <i>x</i> < 0.12 [1991Sun] <i>x</i> = 0.05 <i>x</i> = 0.12
Fe ₃ O ₄ (r) < 580	<i>oP56</i> <i>Pbcm</i> Fe ₃ O ₄ (r)	<i>a</i> = 1186.8 <i>b</i> = 1185.1 <i>c</i> = 1675.2	[V-C2]
Fe ₃ O ₄ (h) (magnetite) 1597 - 580	<i>cF56</i> <i>Fd$\bar{3}m$</i> MgAl ₂ O ₄	<i>a</i> = 839.6 <i>a</i> = 854.5	at 25°C at 1000°C [V-C2]
α Fe ₂ O ₃ (hematite) < 1451	<i>hR30</i> <i>R$\bar{3}c$</i> Al ₂ O ₃	<i>a</i> = 503.42 <i>c</i> = 1374.83	at 600°C [Mas2, V-C2]
β Fe ₂ O ₃	<i>cI80</i> <i>Ia$\bar{3}$</i> Mn ₂ O ₃	<i>a</i> = 939.3	metastable phase [V-C2]
γ Fe ₂ O ₃ (maghemite)	<i>tP60</i> <i>P4₁2₁2</i> Mn ₅ Si ₂ (?)	<i>a</i> = 833.96 <i>c</i> = 832.21	metastable phase [V-C2]
* CsFe ₁₁ O ₁₇	<i>hP64</i> <i>P6₃/mmc</i> NaAl ₁₁ O ₁₇ (β alumina)	<i>a</i> = 592.3 <i>c</i> = 2415.8	[1986Mor]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* CsFeO _{2.5}	<i>cP36</i> <i>Pm$\bar{3}m$</i> CaTiO ₃ (perovskite)	<i>a</i> = 419.9	[1992Kop, 1994Kop]
* CsFeO ₂	<i>cF32</i> <i>Fd$\bar{3}m$</i> β cristobalite	<i>a</i> = 839.2	[2004Fri]
* Cs ₅ Fe ₃ O ₆	<i>oP56</i> <i>P2₁2₁2₁</i> Cs ₅ Fe ₃ O ₆	<i>a</i> = 867.1 <i>b</i> = 872.9 <i>c</i> = 1670.1	at – 22°C [2004Fri]
* Cs ₂ FeO ₄	<i>oP28</i> <i>Pnma</i> β K ₂ SO ₄	<i>a</i> = 843.43 <i>b</i> = 629.23 <i>c</i> = 1112.74	[1992Kop] Complete conversion of K ₂ FeO ₄ by CsOH [2004Lic]
* Cs ₇ Fe ₂ O ₈	<i>mP68</i> <i>P2₁/c</i> Rb ₇ Fe ₂ O ₈	<i>a</i> = 666.0 <i>b</i> = 1097.4 <i>c</i> = 2156.6 β = 92.83°	at 22°C [2005Fri]
* Cs ₈ Fe ₂ O ₇	<i>mP68</i> <i>P2₁/c</i> Cs ₈ Fe ₂ O ₇	<i>a</i> = 722.32 <i>b</i> = 1789.0 <i>c</i> = 733.9 β = 118.98°	at – 28°C [2004Fri]
* α Cs ₅ FeO ₄ (r)	<i>mP40</i> <i>P2₁/c</i> α Cs ₅ FeO ₄	<i>a</i> = 1133.9 <i>b</i> = 1269.5 <i>c</i> = 725.05 β = 99.07°	at 22°C [2005Fri]
* β Cs ₅ FeO ₄ (l)	<i>mP40</i> <i>P2₁/c</i> β Cs ₅ FeO ₄	<i>a</i> = 880.78 <i>b</i> = 1067.4 <i>c</i> = 1115.7 β = 97.35°	at – 25°C [2005Fri]

Table 3: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Property, per mole of atoms [J, mol, K]	Comments
1/17 (Cs ₈ Fe ₂ O ₇)	25	<i>S</i> [°] = 47.2 ± 1 $\Delta_f H^\circ = -138\,500 \pm 500$	see text [1981Lin]
1/14 (Cs ₅ Fe ₃ O ₆)	25	<i>S</i> [°] = 44.4 ± 1 $\Delta_f H^\circ = -148\,500 \pm 500$	see text [1981Lin]
1/4 (CsFeO ₂)	25	<i>S</i> [°] = 32.3 ± 1 $\Delta_f H^\circ = -175\,000 \pm 500$	see text [1981Lin]

Fig. 1: Cs-Fe-O.
The equilibria in the
solid state



Cesium – Molybdenum – Oxygen

Olga Fabrichnaya

Introduction

Cs and Mo are important large yield fission products formed in a nuclear fuel during burn up. Molybdenum is a fission product whose chemical state in the oxide fuel changes from metal to oxide with increasing oxygen potential of the fuel. Cesium molybdate (Cs_2MoO_4) is considered to be one of the typical fission product compound in the fuel-cladding gap at high burnup. That is why thermodynamic properties of Cs_2MoO_4 were extensively studied. The review of phase diagram, crystallographic data and thermodynamic data is presented in [1990Cor].

Phase diagram of the Cs_2MoO_4 - MoO_3 system was studied by [1951Spi] using thermal analysis. Later the phase diagram of this system was studied by [1969Sal] and [1973Hoe]. [1969Sal] examined the Cs_2MoO_4 - MoO_3 system by solid state reactions. The products were analyzed by XRD and DTA. There are some inconsistencies between the diagrams obtained by [1951Spi], [1969Sal] and [1973Hoe]. The most reliable is diagram from [1973Hoe]. The obtained compounds were characterized by XRD, IR and Raman spectroscopy. Later the results of [1973Hoe] were confirmed by [1990Baz] using XRD, DTA, IR-spectroscopy. The structure of the compounds $\text{Cs}_2\text{Mo}_2\text{O}_7$, $\text{Cs}_2\text{Mo}_3\text{O}_{10}$, $\text{Cs}_2\text{Mo}_4\text{O}_{13}$, $\text{Cs}_2\text{Mo}_5\text{O}_{16}$ and $\text{Cs}_2\text{Mo}_7\text{O}_{22}$ was studied by XRD and lattice parameters were determined [1970Koo, 1973Gon, 1975Gat, 1995Mar, 1997Ish, 1999Enj]. The phase diagram of the Cs_2O - Cs_2MoO_4 system is not known. The phase with the hexagonal structure $\text{Cs}_6\text{Mo}_2\text{O}_9$ was found by [1977Wec] and its lattice parameters were calculated. Another kind of compounds, where Mo atoms have charge +6 and +5, were obtained: $\text{Cs}_{0.14}\text{MoO}_3$, $\text{Cs}_{0.25}\text{MoO}_3$, $\text{Cs}_{0.3}\text{MoO}_3$, $\text{Cs}_{0.33}\text{MoO}_3$ and $\text{CsMo}_{4-x}\text{O}_{12}$ ($x = 0.13$). The structure of those compounds (bronzes) was studied by [1970Mum, 1970Rei, 1984Sch, 1987Abr, 1987Tsa, 1998Eda].

Thermodynamic data are available for Cs_2MoO_4 and $\text{Cs}_2\text{Mo}_2\text{O}_7$. The Cs_2MoO_4 phase was studied by vapor pressure measurement [1975Joh, 1989Tan, 1992Cor, 1993Yam, 1997Kaz] and calorimetrically [1974Osb, 1974Fre, 1975Den, 1982Koh, 1988Kon]. The $\text{Cs}_2\text{Mo}_2\text{O}_7$ phase was studied by differential scanning calorimetry (DSC) in [1994Koh] and by aqueous solution calorimetry in [1975OHa]. Potential diagrams were calculated by [1978Tak] and [2005Wal] using thermodynamic data available for compounds.

Thermal conductivity of Cs_2MoO_4 was measured in [1996Ish, 1996Min, 1997Ish, 1997Min]; thermal expansion was determined in [1996Min, 1997Min]. The electric properties of $\text{Cs}_2\text{Mo}_2\text{O}_7$, $\text{Cs}_2\text{Mo}_3\text{O}_{10}$, $\text{Cs}_2\text{Mo}_4\text{O}_{13}$, $\text{Cs}_2\text{Mo}_5\text{O}_{16}$ and $\text{Cs}_2\text{Mo}_7\text{O}_{22}$ were measured by [1990Baz]. Bronzes were found to be semiconductors. Their electric properties were studied in [1981Str, 1984Sch, 1987Abr].

The experimental studies in the Cs-Mo-O system are summarized in Table 1.

Binary Systems

Phase diagram for the binary system Mo-O is accepted from [1980Bre, Mas2]. The phase diagram for the Cs-O is accepted from [1979Kni]. Crystallographic data for phases are from [V-C2] (Table 2). The data on phase equilibria in the Cs-O system are scarce and contradictory. The latest phase diagram is from [1979Kni], where it was claimed that phase diagram data between Cs_7O and Cs_3O presented by [Mas2] were not correct. It should be mentioned that formulas Cs_7O_2 from [1979Kni] and Cs_{11}O_3 [V-C2, Mas2] present the same phase. According to [1979Kni] this phase melts at -10.5°C contrary to 53°C given by [V-C2, Mas2]. According to [Mas2] Cs_3O has a homogeneity range, while [1979Kni] show this phase as stoichiometric. The Cs_2O_3 phase [V-C2] was not found in [1979Kni]. Probably this phase is metastable. In [V-C2] two polymorphic modifications of CsO_2 phase are presented. The phase diagram of the Cs-Mo system was not studied experimentally. The calculated diagram for the Cs-Mo system is accepted from [Mas2]. The Cs-O phase diagram from [1979Kni] is presented in Fig. 1.

Solid Phases

Several solid phases of constant composition were found in the $\text{Cs}_2\text{MoO}_4\text{--MoO}_3$ system by [1973Hoe]. The crystallographic study of Cs_2MoO_4 was performed by [1970Koo, 1973Gon, 1997Min], $\text{Cs}_2\text{Mo}_3\text{O}_{10}$ [1999Enj], $\text{Cs}_2\text{Mo}_4\text{O}_{13}$ [1995Mar], $\text{Cs}_2\text{Mo}_5\text{O}_{16}$ and $\text{Cs}_2\text{Mo}_7\text{O}_{22}$ [1975Gat]. Several studies [1973Hoe, 1974Fre, 1988Kon, 1996Min, 1997Min] demonstrated that orthorhombic Cs_2MoO_4 transforms to a hexagonal phase at 568°C . However, crystallographic data for this phase are not available. The lattice parameters of $\text{Cs}_2\text{Mo}_2\text{O}_7$ are available from [1973Hoe]. [1977Wec, 1981Sou] reported the hexagonal phase $\text{Cs}_6\text{Mo}_2\text{O}_9$ in the $\text{Cs}_2\text{O--Cs}_2\text{MoO}_4$ system. Polymorphism in this compound was not found [1981Sou]. The parameters of $\text{Cs}_6\text{Mo}_2\text{O}_9$ were determined by XRD in [1977Wec].

Another kind of compounds found in the Cs–Mo–O system are bronzes. The peculiarity of bronzes is that their structure contains both Mo^{+6} and Mo^{+5} [1987Abr]. The method to prepare bronzes is electrolysis from the $\text{Cs}_2\text{MoO}_4\text{--MoO}_3$ melts [1970Mum, 1970Rei, 1981Str]. The review of crystallographic data for bronzes was presented by [1998Eda].

Quasibinary Systems

The $\text{Cs}_2\text{MoO}_4\text{--MoO}_3$ system was studied experimentally in [1951Spi, 1969Sal, 1973Hoe]. The compounds with the general formula $\text{Cs}_2\text{Mo}_x\text{O}_{3x+1}$ were found in this system. The compounds $\text{Cs}_2\text{Mo}_3\text{O}_{10}$ and $\text{Cs}_2\text{Mo}_4\text{O}_{13}$ were found by [1951Spi]. Two other compounds with $x = 6$ and 8 indicated by [1951Spi] were not confirmed by latter investigations. The $\text{Cs}_2\text{Mo}_2\text{O}_7$ compound was found by [1969Sal]. The solid solutions $\text{Cs}_2\text{Mo}_9\text{O}_{28}$ indicated by [1969Sal] were not confirmed by latter studies. It should be noted that phase diagram presented by [1969Sal] contradicts the phase rule in the range of melting of $\text{Cs}_2\text{Mo}_9\text{O}_{28}$. In this work the phase diagram of [1973Hoe] is accepted. It should be also noted that in spite of some differences in melting relations the liquidus line of [1973Hoe] is in reasonable agreement with the previous studies of [1951Spi, 1969Sal]. [1990Baz] synthesized all solid phases found by [1973Hoe]. Their crystallographic parameters and IR spectra were obtained and electric properties were studied. The phase diagram from the study of [1973Hoe] is presented in Fig. 2. A phase transition in $\text{Cs}_2\text{Mo}_2\text{O}_7$ indicated by a very small DTA maximum is shown by a dashed line, because there was no major structural reorganization confirmed by XRD [1973Hoe] and this transformation was not mentioned in latter studies.

Isothermal Sections

Isothermal section at temperatures valid between 160 and 425°C was calculated by [1981Lin] based on estimates of thermodynamic properties for $\tau_1\text{--}\tau_7$. It is shown in Fig. 3. Bronzes were not taken into account.

Potential Diagrams

Potential phase diagrams are calculated by [1978Tak, 1981Lin, [2005Wal]]. Only one ternary compound Cs_2MoO_4 was taken into account by [2005Wal]. Two compounds Cs_2MoO_4 and $\text{Cs}_2\text{Mo}_2\text{O}_7$ were considered by [1978Tak]. However, at the temperature of the calculation (727°C) the dimolybdate phase is not stable. [1981Lin] took into account all phases found in the $\text{Cs}_2\text{O--MoO}_3$ system. Figures 4 and 5 present potential diagrams from [1978Tak] and [2005Wal], respectively. Potential diagrams from [1981Lin] are presented in Figs. 6, 7. Potential diagrams presented here should not be considered as equilibrium diagrams, because not all ternary phases were taken into account.

Thermodynamics

The standard enthalpy of Cs_2MoO_4 was derived from aqueous solution calorimetry measurements by [1973OHa]. Based on low-temperature C_p data obtained by adiabatic calorimetry standard entropy of Cs_2MoO_4 at 25°C was derived by [1974Osb]. The C_p of Cs_2MoO_4 at $77\text{--}500^\circ\text{C}$ was measured by differential scanning calorimetry by [1982Koh] and the enthalpy increment at $142\text{--}427^\circ\text{C}$ was measured by drop calorimetry [1988Kon]. [1974Fre] studied enthalpy increment by drop calorimetry method in the temperature range of $283\text{--}918^\circ\text{C}$. The enthalpy increment was also measured for the Cs_2MoO_4 in the liquid

state using drop calorimetry at 980–1227°C by [1975Den]. The DSC measurements performed by [1988Kon] indicated transformation from orthorhombic to hexagonal structure at 568°C and melting at 956°C. The enthalpy of α - β phase transformation was determined to be 4.6 kJ·mol⁻¹ from the DSC measurements. This value is in a good agreement with data of [1974Fre]. The enthalpy of fusion was measured by drop calorimetry in [1975Den]. The thermodynamic properties for Cs₂MoO₄ are accepted from [1988Kon] who analyzed all available thermodynamic data for this compound and combined the most reliable data with his own measurements. The C_p data of [1974Fre] was discarded because they do not fit the low-temperature data of [1974Osb].

The thermodynamic properties of the Cs₂Mo₂O₇ phase were studied in [1975OHa, 1994Koh]. The enthalpy of formation of this compound was obtained from aqueous solution calorimetry measurements [1975OHa]. The heat capacity of Cs₂Mo₂O₇ was measured by DSC in the temperature range 37–427°C by [1994Koh]. There is only estimate of standard entropy for Cs₂Mo₂O₇ as 340 J·(mol·K)⁻¹ made by [1975OHa], because experimental data are not available so far. The thermodynamic functions for Cs₂Mo₂O₇ are accepted from [1994Koh] who combined his own measurements and estimates with data of [1975OHa]. The thermodynamic data for the compounds Cs₂MoO₄ and Cs₂Mo₂O₇ are presented in Tables 3 and 4. Estimates of thermodynamic properties from [1981Lin] are not presented here, because they are not based on any physical considerations.

The vapor pressure of Cs₂MoO₄ (gas) was studied by Knudsen effusion mass spectrometry over solid and liquid phases of Cs₂MoO₄ in [1993Yam]. It was proved [1975Joh, 1993Yam, 1997Kaz] that Cs₂MoO₄ evaporates congruently in the form of the Cs₂MoO₄ molecules. The results of [1993Yam] are in a reasonable agreement with previous vapor pressure data [1975Joh, 1989Tan, 1992Cor]. The new determinations of vapor pressure over solid Cs₂MoO₄ by high-temperature mass-spectrometry [1997Kaz] are in a very good agreement with the data of [1993Yam] presented in Table 5. The enthalpy of vaporization calculated by the third-law at 25°C is presented in Table 3.

Notes on Materials Properties and Applications

As it was mentioned in the *Introduction* chapter, Cs and Mo are important fission products and their behavior at various oxygen partial pressure is important to understand migration phenomena and interaction between fuel and clad. [1972Nei] studied stainless-steel - clad mixed-oxide fuel elements after irradiation to burnup of 11 at.%. The separation of the fuel and cladding at high burnup is related to the deposition of Cs–Mo–O at the interface. At low O/M (oxygen-to-metal ratio) in which Mo did not migrate to the interface, the fuel and cladding remain in contact. The axial migration of cesium in the low O/M ratio element resulted in apparently nondetrimental reaction with the UO₂ blanket and insulator pellet.

Thermal expansion and thermal conductivity of Cs₂MoO₄ are necessary to analyze and predict the fuel-clad mechanical interaction and fuel temperature. Thermal diffusivity of Cs₂MoO₄ was experimentally measured by laser flash method and the thermal conductivity was calculated in [1996Ish, 1997Ish, 1997Min]. The temperature dependence of the lattice parameters of Cs₂MoO₄ was measured using high-temperature XRD from 25 to 500°C in [1996Min, 1997Min]. Thermal expansions were obtained nearly isotropic. The geometric mean of thermal expansion of orthorhombic Cs₂MoO₄ was compared with the thermal expansion of UO₂ in [1996Min]. The thermal diffusivity of Cs₂MoO₄ was found to present discontinuity because of the transformation to the hexagonal structure [1996Min, 1997Min]. The thermal conductivity of UO₂ is much larger than that of Cs₂MoO₄, while thermal expansion is considerably larger for Cs₂MoO₄ [1996Min]. Thermomigration of Cs was experimentally studied in oxide fuel systems *i.e.* Cs–O–U and Cs–Mo–O by [1973Ada]. Cesium molybdate, Cs₂MoO₄, appears to be the only ternary Cs–Mo–O compound that can form in oxide fuels (O/M ≤ 2). It is stable at oxygen potentials above the equilibrium $\mu_{\text{O}_2}(\text{Mo}/\text{MoO}_2)$, but it does not form in liquid Cs at 800°C. Thermal gradient tests show that Cs₂MoO₄ is slightly less stable than Cs–O–U compounds in the presence of excess fuel at 700 to 1000°C, but it is considerably more volatile. The Cs₂MoO₄ (gas) molecule may be sufficiently stable to provide additional transport path for Cs, Mo and O in oxide fuel at high burnup.

The temperature dependence of resistivity of compounds in the Cs₂MoO₄–MoO₃ system and their electron transport numbers were studied by [1990Baz]. At high temperature the single crystals of Cs₂MoO₄ and

$\text{Cs}_2\text{Mo}_3\text{O}_{10}$ possess essentially electronic conductance. It was shown that the resistivity increases with increasing MoO_3 content, but there is no correlation between activation energy of ionic conductance and the MoO_3 content. The activation energy of ionic conductance is related to crystal structure of the compounds.

The molybdenum oxide bronzes attract attention, because many of them are semiconductors. The electric and magnetic properties of the $\text{Cs}_{0.33}\text{MoO}_3$ and $\text{Cs}_{0.19}\text{MoO}_{2.85}$ bronzes were measured by [1984Sch]. The $\text{Cs}_{0.33}\text{MoO}_3$ (red bronze) is a diamagnetic semiconductor at all temperatures. The $\text{Cs}_{0.19}\text{MoO}_{2.85}$ (blue bronze) is also semiconductor, but an anomaly in the magnetic susceptibility at 200 K suggesting a phase transition was observed. The resistivity of $\text{CsMo}_{4-x}\text{O}_{12}$ (the same phase as $\text{Cs}_{0.19}\text{MoO}_{2.85}$) was also measured by [1987Abr] and anisotropy was found. The electric resistivity of Cs_xMoO_3 ($x = 0.31$ red bronze) was measured by [1981Str].

Miscellaneous

The structure of Cs_2MoO_4 molecule in gas phase was studied by electron-diffraction in [1973Uga]. Principal parameters (internuclear distances and vibration amplitudes) were derived. Adsorption of cesium and co-adsorption of cesium and oxygen on Mo surface at room temperature was studied by electron spectroscopy [1984Riw] and by electron-loss and photoemission spectroscopy using synchrotron radiation by [1984Sou, 1985Sou]. The IR absorption spectra of Cs_2MoO_4 in nitrogen matrix were obtained at 12 K by [1981Spo]. Matrix-isolated anion vibrational frequencies were obtained from IR spectra.

The crystal lattice energy and enthalpy of formation of Cs_2MoO_4 and many other solid compounds were calculated by empirical method based on effective charges of atoms in molecules and ions (calculated by adjusting some special potentials of atoms) by [1984Kaz]. However, the predicted value for the enthalpy of formation of Cs_2MoO_4 are $30 \text{ kJ}\cdot\text{mol}^{-1}$ more negative than experimentally measured by [1973OHa].

Solid state reactions between UO_2MoO_4 and Cs_2MoO_4 up to 750°C were investigated by [1995Mis]. Two phases of $\text{Cs}_2\text{UO}_2(\text{MoO}_4)_2$ and single phase compound $\text{Cs}_2(\text{UO}_2)_2(\text{MoO}_4)_3$ were isolated and characterized by thermal analysis, XRD, chemical and IR method. The reactions in the U–Cs–Mo–I–O were experimentally studied as a function of oxygen potential using CO–CO₂ gas equilibration method by [1996Uga]. The chemical constitution and the morphology were examined mainly for reaction products containing volatile element Cs. Thermodynamic calculations were performed to verify the experimental results. Predominance of Cs_2MoO_4 over Cs_2UO_4 was proved at oxygen potentials between -380 and $-420 \text{ kJ}\cdot\text{mol}^{-1}$. Calculations suggested that Cs_2UO_4 should coexist with Cs_2MoO_4 at such potentials unless the excess of Mo over Cs is guaranteed. The relative stability of Cs_2MoO_4 to Cs_2UO_4 would be altered at oxygen potential of $-530 \text{ kJ}\cdot\text{mol}^{-1}$. Calculations of Cs–I–Mo–O and Cs–I–O–U potential diagrams were performed by [2005Wal]. The results are presented on the basis of three dimension potential diagrams, calculated at 350°C . It was shown that the iodine partial pressure could be controlled by formation of Cs_2UO_4 from CsI in the fuel. If formation of Cs_2MoO_4 would take place the iodine partial pressure is expected to increase.

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Table 1: Investigations of the Cs–Mo–O Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1951Spi]	Thermal analysis	450-925°C, Cs ₂ MoO ₄ –MoO ₃
[1967Cai, 1969Sal]	Solid state reactions, XRD, DTA	300-940°C, Cs ₂ MoO ₄ –MoO ₃
[1970Mum]	XRD, electrochemistry	530°C, 0.3 Cs ₂ MoO ₄ –0.7 MoO ₃ , lattice parameters for Cs _{0.25} MoO ₃
[1970Rei]	XRD, electrochemistry	530°C, 0.3 Cs ₂ MoO ₄ –0.7 MoO ₃ , lattice parameters for Cs _{0.33} MoO ₃
[1973Gon]	Single crystal X-ray	Cs ₂ MoO ₄ lattice parameters
[1973Hoe]	XRD, thermal analysis (DTA-TGA), IR, Raman spectroscopy	300-940, Cs ₂ MoO ₄ –MoO ₃
[1973OHa]	Aqueous solution calorimetry (enthalpy of formation)	25°C, Cs ₂ MoO ₄
[1973Uga]	Electron-diffraction	1050°C, Cs ₂ MoO ₄ in gas
[1974Fre]	Drop calorimetry	283-918°C, Cs ₂ MoO ₄
[1974Osb]	Adiabatic calorimetry (heat capacity, entropy)	5-350°C, Cs ₂ MoO ₄
[1975Den]	Drop calorimetry	969-1227°C, Cs ₂ MoO ₄
[1975Gat]	XRD	Cs ₂ Mo ₅ O ₁₆ , Cs ₂ Mo ₇ O ₂₂ lattice parameters
[1975Joh]	Mass spectrometric study of vapor pressure over solid and liquid phase	797-897°C, Cs ₂ MoO ₄ solid
[1975OHa]	Aqueous solution calorimetry (enthalpy of formation)	25°C, Cs ₂ Mo ₂ O ₇
[1977Wec]	Solid state reaction at 350°C, XRD at 20°C	Cs ₆ Mo ₂ O ₉ lattice parameters
[1978Tak]	Calculation of potential diagrams based on thermodynamic data	727°C $\mu(\text{O}_2)$ vs $\mu(\text{Cs})$
[1981Lin]	Calculation of potential diagrams based on thermodynamic data	100-700°C, $\mu(\text{O}_2)$ vs T
[1981Str]	XRD, electrical resistivity	Cs _{0.31} MoO ₃ crystal growth by electrolysis from Cs ₂ MoO ₄ –MoO ₃ melts with 70-77 mol% MoO ₃ at 540°C
[1982Koh]	DSC (heat capacity)	27-527°C, Cs ₂ MoO ₄
[1984Sch]	XRD	Cs _{0.33} MoO ₃ , lattice parameters
[1987Abr]	XRD	CsMo _{4-x} O ₁₂ ($x = 0.13$) lattice parameters
[1987Tsa]	Single crystal XRD	Cs _{0.33} MoO ₃ , lattice parameters

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1988Kon]	Drop calorimetry (enthalpy increment) DSC (phase transition)	142-427°C, Cs ₂ MoO ₄ 523-1227°C, Cs ₂ MoO ₄
[1989Tan]	Vaporization over liquid by transpiration technique, chemical and XRD analysis	957-1037°C, Cs ₂ MoO ₄ liquid
[1990Baz]	XRD, DTA, IR-spectroscopy	450-500°C, Cs ₂ MoO ₄ -MoO ₃
[1992Cor]	Vapor pressure over solid phase by entrainment method	844-917°C Cs ₂ MoO ₄ solid
[1993Dep]	Synthesis from CsCl, WO ₂ and MoO ₃ , XRD	560°C, vacuum 10 ⁻⁴ mbar, Cs _{0.14} MoO ₃ , lattice parameters
[1993Yam]	Vaporization by Knudsen effusion mass spectrometry	862-947°C, Cs ₂ MoO ₄ solid 957-972°C Cs ₂ MoO ₄ liquid
[1994Koh]	DSC (heat capacity)	37-427°C Cs ₂ Mo ₂ O ₇
[1995Mar]	Solid state reaction, XRD, pycnometry	Cs ₂ Mo ₄ O ₁₃ synthesis at 627°C, lattice parameters
[1997Kaz]	Vapor pressure measurements by high-temperature mass-spectrometry	753-875°C Cs ₂ MoO ₄ solid
[1997Min]	XRD, DTA	25-500°C, Cs ₂ MoO ₄ , lattice parameters, phase transformation
[1998Eda]	XRD	Cs _{0.3} MoO ₃ , lattice parameters
[1999Enj]	Solid state reaction, XRD	Cs ₂ Mo ₃ O ₁₀ , lattice parameters
[2005Wal]	Calculation of potential diagrams based on thermodynamic data	Cs-Mo-O 127- 427°C, $\mu(\text{O}_2)$ vs T

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cs) < 28.39	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	$a = 614.1$	at 25°C [Mas2]
(Mo) < 2623	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	$a = 314.7$	[V-C2]
CsO < 590	<i>oI8</i> <i>Immm</i> CsO	$a = 432.2$ $b = 751.7$ $c = 643$	[V-C2]
$\alpha\text{CsO}_2(\text{r})$ < 200	<i>tI6</i> <i>I4/mmm</i> CaC ₂	$a = 446.2$ $c = 732.6$	[V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\beta\text{CsO}_2(\text{h})$ 200 - 450	$cF8$ $Fm\bar{3}m$ NaCl	$a = 662$	[V-C2]
CsO_3 < 70	$mP16$ $P2_1/c$ RbO_3	$a = 670.9$ $b = 624.4$ $c = 899.7$	[V-C2]
Cs_2O < 495	$hR9$ $R\bar{3}m$ WN_2	$a = 425.6$ $c = 1899.2$	[2005Gem]
Cs_2O_3 < 502	$cI28$ $I\bar{4}3d$ Th_3P_4	$a = 986$	[V-C2], probably metastable
Cs_7O < 3	$hP24$ $P6m2$ Cs_7O	$a = 1639.3$ $c = 919.3$	[V-C2]
Cs_{11}O_3 also Cs_7O_2 < -10.5	$mP56$ $P2_1/c$ Cs_{11}O_3	$a = 1761$ $b = 921.8$ $c = 2404.7$ $\beta = 100.14^\circ$	[V-C2]
Cs_4O < 53	oP^* $Pna2_1$	$a = 1682.3$ $b = 2052.5$ $c = 1237.2$	[V-C2]
Cs_3O < 164	-	-	[1979Kni]
MoO_3 < 804 (subl.)	$oP16$ $Pbnm$ MoO_3	$a = 396.28$ $b = 1385.5$ $c = 369.64$	[1980Bre]
MoO_2 < 2300 (dec.)	$mP12$ $P2_1/c$ VO_2	$a = 561.08$ $b = 485.62$ $c = 562.85$ $\beta = 120.953^\circ$	[1980Bre]
Mo_4O_{11} < 818	$oP60$ $Pnma$ Mo_4O_{11}	$a = 2449.0$ $b = 545.7$ $c = 675.2$	[1980Bre]
Mo_8O_{23}	$mP62$ $P2/a$ Mo_8O_{23}	$a = 1688$ $b = 450.2$ $c = 1339$ $\beta = 106.19^\circ$	[1980Bre]
Mo_9O_{26}	$mP70$ $P2/c$ Mo_9O_{26}	$a = 1674$ $b = 401.9$ $c = 1453$ $\beta = 95.45^\circ$	[1980Bre]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Mo ₁₇ O ₄₇	<i>oP</i> 128 <i>Pba</i> 2 Mo ₁₇ O ₄₇	<i>a</i> = 2161.5 <i>b</i> = 1963.2 <i>c</i> = 395.15	[1980Bre]
* τ_1 , α Cs ₂ MoO ₄ (l) < 568	<i>oP</i> 28 <i>Pcmn</i> β K ₂ SO ₄	<i>a</i> = 1159 <i>b</i> = 656 <i>c</i> = 850	[1970Koo, 1973Gon, 1997Min] at 25°C
		<i>a</i> = 1183 <i>b</i> = 673 <i>c</i> = 865	at 500°C [1997Min]
* τ_1' , β Cs ₂ MoO ₄ (h) 957 - 568	<i>h</i> *	<i>a</i> = 719 <i>c</i> = 926	[1990Cor, 1997Min]
* τ_2 , Cs ₂ Mo ₂ O ₇	<i>o</i> *	<i>a</i> = 1554 <i>b</i> = 721.6 <i>c</i> = 1561	[1973Hoe]
* τ_3 , Cs ₂ Mo ₃ O ₁₀	<i>mC</i> 64 <i>C2/c</i>	<i>a</i> = 1446.5 <i>b</i> = 839.97 <i>c</i> = 946.14 β = 97.74°	[1999Enj]
* τ_4 , Cs ₂ Mo ₄ O ₁₃	<i>mC</i> 228 <i>C2/c</i>	<i>a</i> = 4592 <i>b</i> = 1041.8 <i>c</i> = 792.3 β = 92.94°	[1995Mar]
* τ_5 , Cs ₂ Mo ₅ O ₁₆	<i>mC</i> 72 <i>C2/c</i>	<i>a</i> = 2144 <i>b</i> = 555.9 <i>c</i> = 1433.8 β = 122.74°	[1975Gat]
* τ_6 , Cs ₂ Mo ₇ O ₂₂	<i>mC</i> 124 <i>C2/c</i>	<i>a</i> = 2154 <i>b</i> = 553.7 <i>c</i> = 1891 β = 122.71°	[1975Gat]
* τ_7 , Cs ₆ Mo ₂ O ₉	<i>h</i> *	<i>a</i> = 1310 <i>c</i> = 851	[1977Wec]
* τ_8 , Cs _{0.14} MoO ₃	<i>hP</i> * <i>P6</i> ₃ / <i>m</i>	<i>a</i> = 1062 <i>c</i> = 372.2	[1993Dep], dark blue
* τ_9 , Cs _{0.25} MoO ₃	<i>mP</i> * <i>P2</i> ₁ / <i>m</i>	<i>a</i> = 642.5 <i>b</i> = 754.3 <i>c</i> = 816.9 β = 96.3°	red [1970Mum]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_{10} , $\text{Cs}_{0.19}\text{MoO}_{2.85}$ or $\text{CsMo}_{4-x}\text{O}_{12}$	mC^* $C2/m$	$a = 1906.3$ $b = 558.27$ $c = 1211.47$ $\beta = 118.94^\circ$	blackish-blue [1984Sch] $x = 0.132$ [1987Abr]
* τ_{11} , $\text{Cs}_{0.33}\text{MoO}_3$	mC^* $C2/m$	$a = 1586.2$ $b = 772.8$ $c = 640.8$ $\beta = 94.37^\circ$	red [1987Tsa], [1970Rei]
* τ_{12} , $\text{Cs}_{0.3}\text{MoO}_3$	m^*	$a = 1936.2$ $b = 756.7$ $c = 1050.6$ $\beta = 121.07^\circ$	blue [1998Eda]

Table 3: Thermodynamic Data of Reaction or Transformation

Reaction or Transformation	Temperature [°C]	Quantity, per mol of atoms [kJ, mol, K]	Comments
$1/7\{2(\text{Cs}) + (\text{Mo}) + 2\text{O}_2(\text{gas}) \rightleftharpoons \text{Cs}_2\text{MoO}_4(\alpha)\}$	25	$\Delta H = -216.37$	recommended by [1988Kon]
$1/7\{\text{Cs}_2\text{MoO}_4(\alpha) \rightleftharpoons \text{Cs}_2\text{MoO}_4(\beta)\}$	568	$\Delta H = 0.657$	[1988Kon]
$1/7\{\text{Cs}_2\text{MoO}_4(\beta) \rightleftharpoons \text{Cs}_2\text{MoO}_4(\text{L})\}$	956	$\Delta H = 4.543$	recommended by [1988Kon]
$1/7\{\text{Cs}_2\text{MoO}_4(\beta) \rightleftharpoons \text{Cs}_2\text{MoO}_4(\text{L})\}$	25	$\Delta H = 42.2$	[1993Yam]
$1/11\{2(\text{Cs}) + 2(\text{Mo}) + 7/2\text{O}_2(\text{gas}) \rightleftharpoons \text{Cs}_2\text{Mo}_2\text{O}_7(\text{s})\}$	25	$\Delta H = -209.31$	recommended by [1994Koh]

Table 4: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Property, per mole of atoms [J, mol, K]	Comments
$\alpha\text{Cs}_2\text{MoO}_4$	25	$S = 35.48$	[1974Osb]
$\alpha\text{Cs}_2\text{MoO}_4$	25 - 568	$C_p = 16.6291 + 0.01546 \cdot T$	[1988Kon]
$\beta\text{Cs}_2\text{MoO}_4$	568 - 956	$C_p = 17.471 + 0.013864 \cdot T$	[1988Kon]
$\text{Cs}_2\text{MoO}_4(\text{L})$	> 956	$C_p = 30.022$	[1988Kon]
$\text{Cs}_2\text{Mo}_2\text{O}_7$	37 - 427	$C_p = 24.211 + 0.06521T - 5.137 \cdot 10^5 \cdot T^{-2}$	[1994Koh]
$\text{Cs}_2\text{Mo}_2\text{O}_7$	25	$S = 30.82$	[1975OHa], estimated

Table 5: Vapor Pressure Measurements

Phase(s)	Temperature [°C]	Pressure [Pa], T [K]	Comments
$\beta\text{Cs}_2\text{MoO}_4$	862 - 957	$\log_{10}(p/\text{Pa}) = 11.02 - 1.36 \cdot 10^4 \cdot T^{-1}$	[1993Yam]
$\text{Cs}_2\text{MoO}_4(\text{L})$	957 - 982	$\log_{10}(p/\text{Pa}) = 9.80 - 1.21 \cdot 10^4 \cdot T^{-1}$	[1993Yam]

Table 6: Investigations of the Cs-Mo-O Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1981Str]	Resistivity	electric properties of $\text{Cs}_{0.31}\text{MoO}_3$ (red)
[1984Sch]	Resistivity, Faraday method	electric properties, magnetic susceptibility $\text{Cs}_{0.19}\text{MoO}_{2.85}$ and $\text{Cs}_{0.33}\text{MoO}_3$
[1987Abr]	Resistivity	electric properties of $\text{CsMo}_{4-x}\text{O}_{12}$ ($x = 0.13$)
[1990Baz]	Resistivity in direct and alternating current	electric properties of $\text{Cs}_2\text{Mo}_n\text{O}_{3n+1}$ ($n = 1-5, 7$)
[1996Min] [1997Min]	XRD, laser flash	thermal expansion and thermal diffusivity of Cs_2MoO_4
[1996Ish] [1997Ish]	laser flash	thermal diffusivity of Cs_2MoO_4
[1998Eda]	Magnetometer	susceptibility, para-diamagnetic transition at 180 K

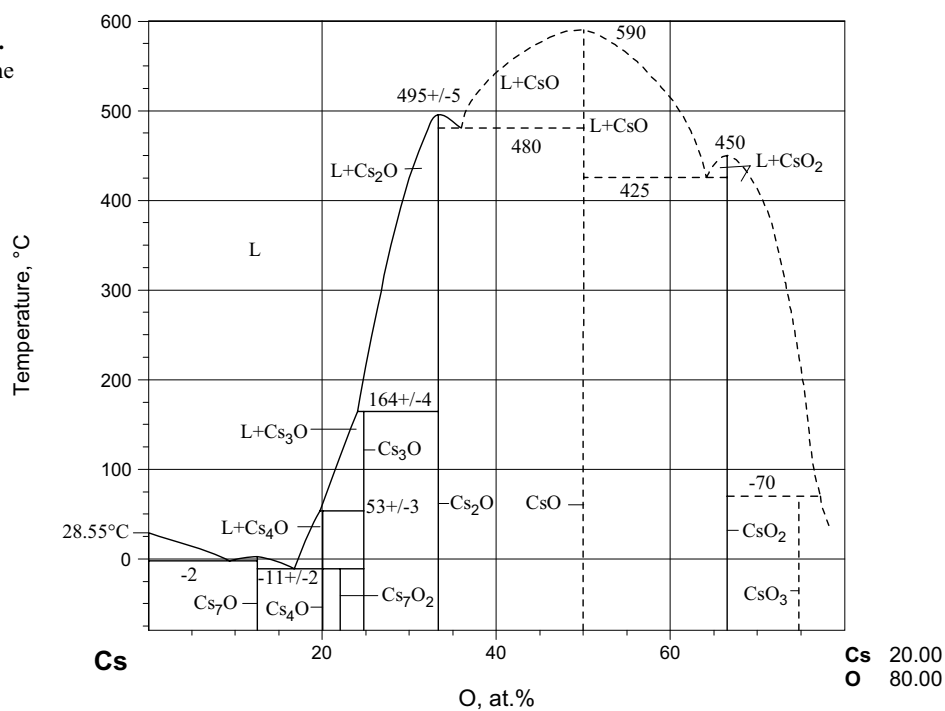
Fig. 1: Cs–Mo–O.
Phase diagram of the
Cs–O system

Fig. 2: Cs-Mo-O.
Phase diagram of the
 Cs_2MoO_4 - MoO_3
quasibinary system

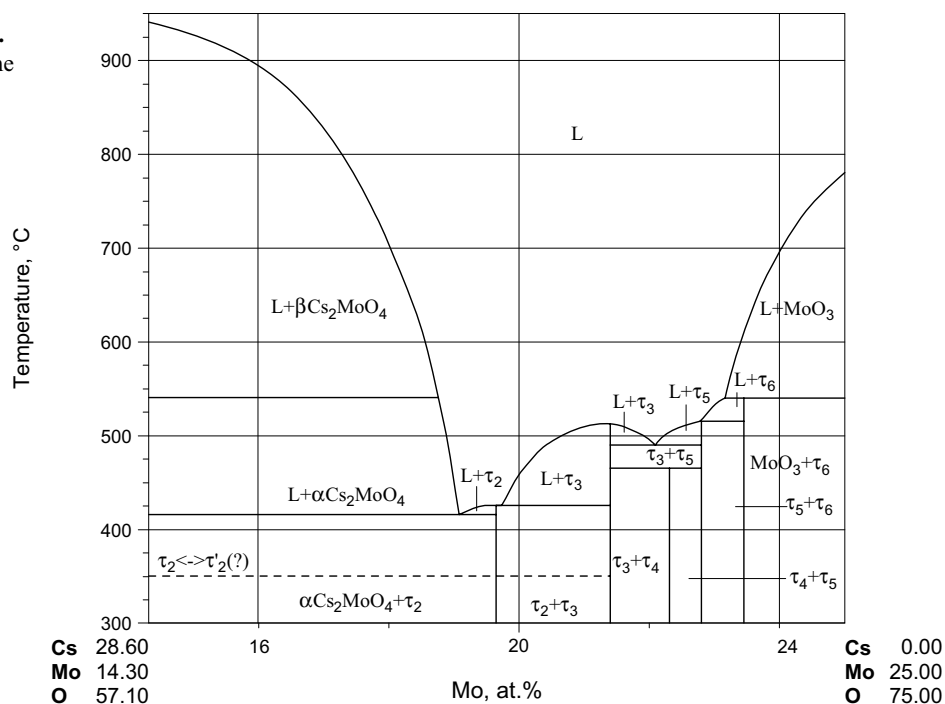


Fig. 3: Cs-Mo-O.
Calculated isothermal
section; valid in the
range 160-425°C

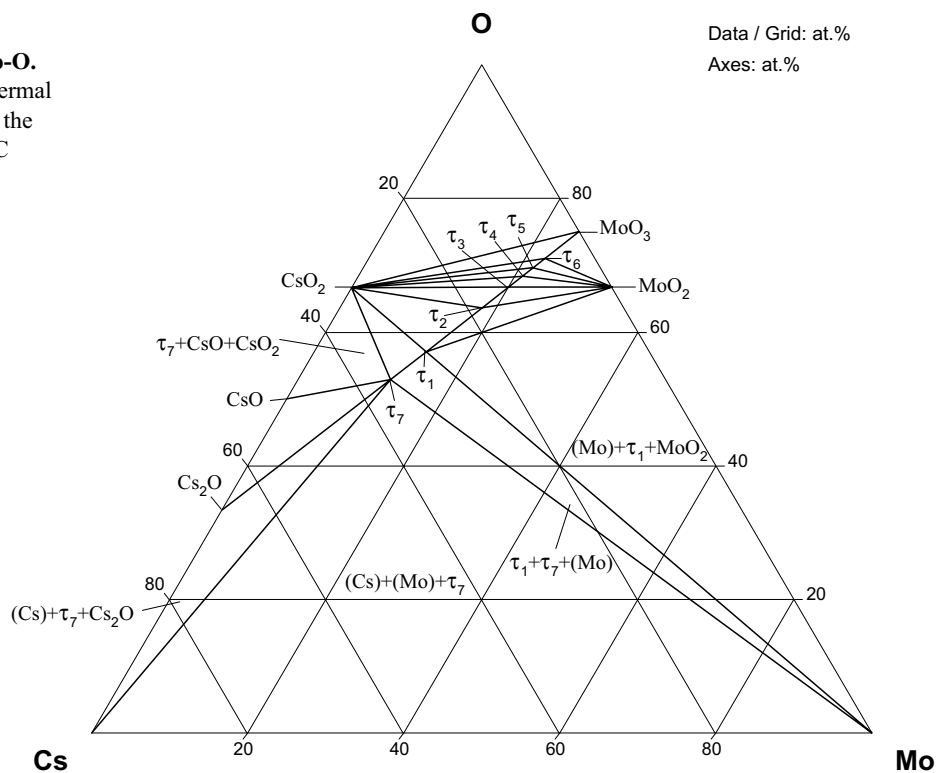


Fig. 4: Cs-Mo-O.
Potential diagram at
727°C

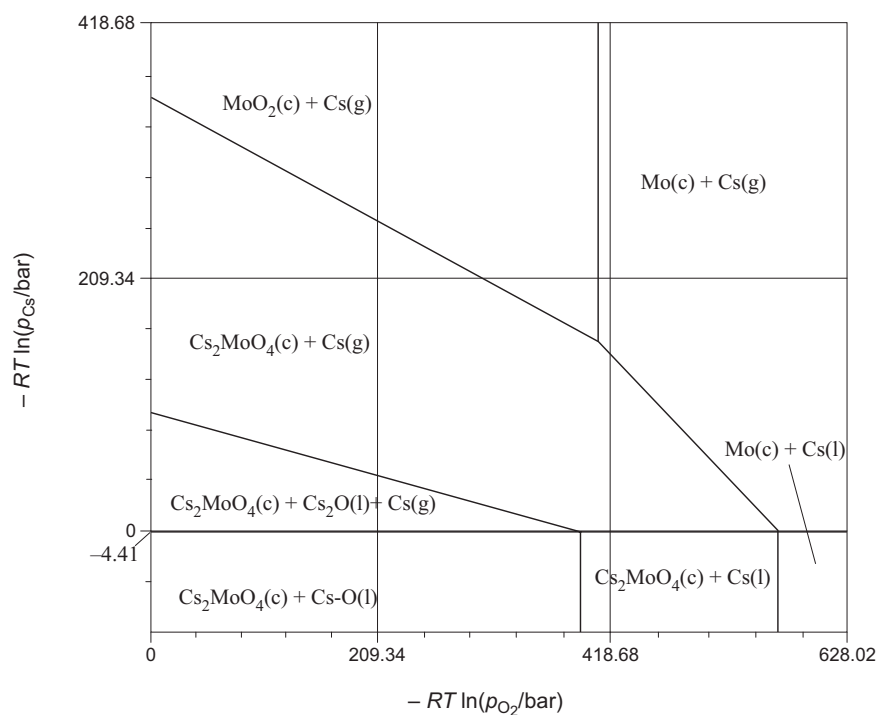


Fig. 5: Cs-Mo-O.
Oxygen potential
diagram

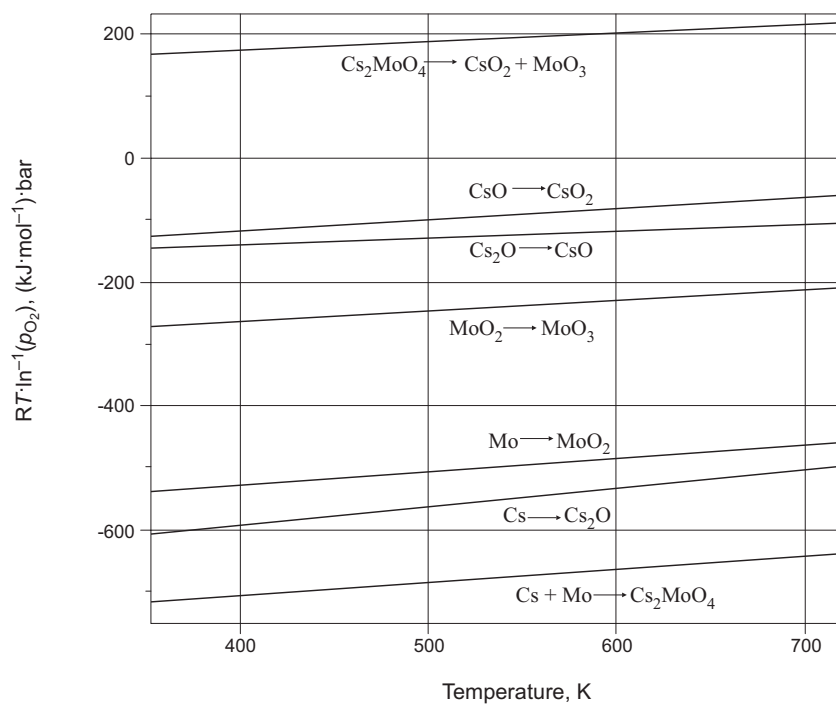


Fig. 6: Cs-Mo-O.
Potential diagram for
compositions
between Cs and
MoO₃. Isobars for Cs
pressure are shown by
dashed line

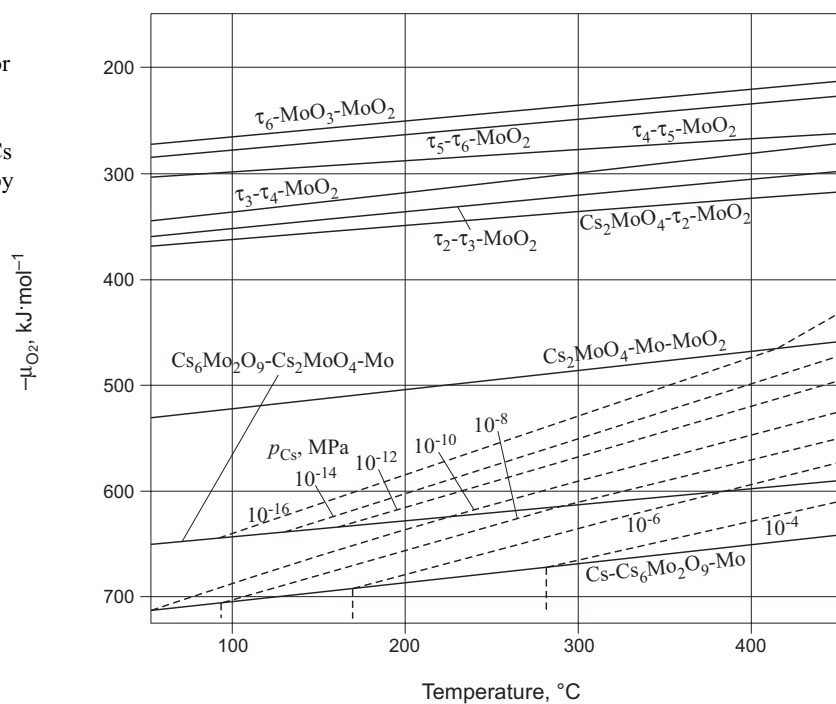
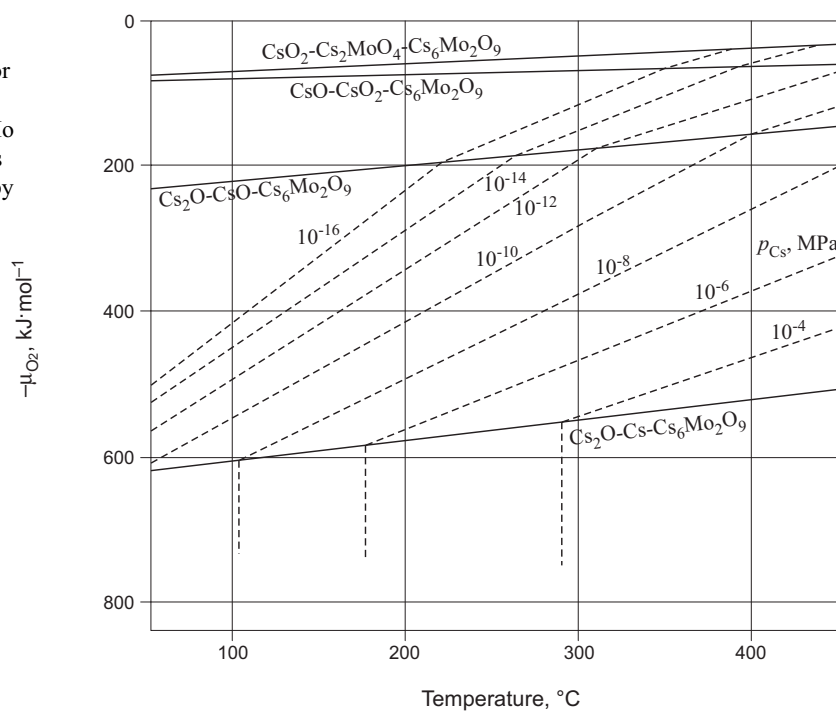


Fig. 7: Cs-Mo-O.
Potential diagram for
compositions
between Cs and O/Mo
< 9:2. Isobars for Cs
pressure are shown by
dashed line



Cesium – Oxygen – Uranium

Pierre Perrot

Introduction

The phase equilibria in the Cs-U-O system and the thermodynamic properties of cesium uranates have been extensively investigated in the past decades, because cesium is one of the main volatile elements synthesized in the fission products of uranium. Experimental investigations are listed in Table 1.

Binary Systems

The phase diagram of the Cs-U binary system is unknown. However, no mutual solubility has been reported. The O-U system is accepted from the Calphad assessment of [2004Che]. A precise model of the solid and liquid oxide solutions taking into account the oxygen vacancies in the O-U system may be found in [2002Gue]. The Cs-O binary system is taken from [Mas2].

Solid Phases

Crystallographic data of binary and ternary oxides are listed in Table 2. Uranium has the unusual property of forming with oxygen strong covalent bonds in one dimension and weak electrostatic bonds in the two other dimensions [2002Kin]. This directional anisotropy leads to low dimensional materials consisting of chains or layers constructed from oxygen-uranium networks and explains the easy volatilization of compounds such as $\text{Cs}_2\text{U}_4\text{O}_{12}$ [1999Hua]. Although UO_2 presents a large stability domain in the oxygen potential-temperature diagram, Cs_2O which is known as a basic oxide stabilizes the higher oxidation states of uranium, so that the cesium uranates known to be stable, namely Cs_2UO_4 , $\text{Cs}_2\text{U}_2\text{O}_7$, $\text{Cs}_4\text{U}_5\text{O}_{17}$ and $\text{Cs}_2\text{U}_4\text{O}_{13}$ lie on the Cs_2O - UO_3 line in which uranium is in a state of oxidation VI. These compounds may be easily obtained by heating a mixture $\text{U}_3\text{O}_8 + \text{Cs}_2\text{CO}_3$ during 48 to 72 h under an air atmosphere at 800°C [2000Ber]. Cs_2UO_4 is non stoichiometric and may loose oxygen with formation of $\text{Cs}_2\text{UO}_{3.56}$ [1981Lin, 2000Ber, 2005Wal]. Cs_2UO_4 is stable under dry air up to 950°C . It decomposes at 630°C ($2 \text{Cs}_2\text{UO}_4 \rightleftharpoons \text{Cs}_2\text{U}_2\text{O}_7 + \text{Cs}_2\text{O}$) only if some moisture is present [1983Dha]. The role of moisture is to displace the decomposition equilibrium with formation of volatile CsOH . This compound may also be obtained by heating a mixture $4\text{U}_3\text{O}_8 + 3\text{Cs}_2\text{CO}_3$ during 12 h at 1100°C under a CO_2 atmosphere [2000Ber]. The formation of $\text{Cs}_4\text{U}_5\text{O}_{17}$ has also been reported and its thermodynamic properties have been measured [1997Jay]. In open air atmosphere, $\text{Cs}_4\text{U}_5\text{O}_{17}$ decomposes around 1000°C with formation of the mixture $\text{Cs}_2\text{U}_4\text{O}_{13} + \text{Cs}_2\text{U}_2\text{O}_7$ [2000Ber]. The structures of the compounds $\text{Cs}_2\text{U}_4\text{O}_{13}$ and $\text{Cs}_2\text{U}_4\text{O}_{12}$ are closely related to that of UO_2 and it is not clear whether $\text{Cs}_2\text{U}_4\text{O}_{13}$ and $\text{Cs}_2\text{U}_4\text{O}_{12}$ may be considered as the two end members of the same solid solution. The formation of $\text{Cs}_4\text{U}_5\text{O}_{17}$ is not observed in the fuel pellets and this compound is often considered as metastable, which is not confirmed by the emf measurements of [1997Jay]. The existence of compounds with high uranium content, namely $\text{Cs}_2\text{U}_5\text{O}_{16}$, $\text{Cs}_2\text{U}_6\text{O}_{18}$, $\text{Cs}_2\text{U}_7\text{O}_{22}$, $\text{Cs}_2\text{U}_9\text{O}_{27}$, $\text{Cs}_2\text{U}_{15}\text{O}_{46}$, and $\text{Cs}_2\text{U}_{16}\text{O}_{49}$ suggested by [1974Cor, 1981Lin] has not been confirmed [2005Wal], notwithstanding that [1978Fee, 1981Lin] proposes an evaluation of the thermodynamic parameters of these phases. [1976Egm1] states that the structure of the so-called $\text{Cs}_2\text{U}_5\text{O}_{16}$ compound is very similar to that of $\text{Cs}_2\text{U}_4\text{O}_{13}$ and shows the existence of a series of solid solution at 600 - 1000°C with a Cs/U ratio ranging from 0.375 and 0.500.

Quasibinary Systems

The solubility of Cs_2O in UO_2 was measured at 1900°C [1993Kle] by annealing an UO_2 -3 mass% Cs_2O pellet in a ThO_2 crucible inserted in a Ta capsule. The chemical potential of oxygen in the capsule was estimated lower than $-450 \text{ kJ}\cdot\text{mol}^{-1}$, which corresponds to the $\text{Ta}/\text{Ta}_2\text{O}_5$ equilibrium. The solubility of cesium was evaluated by quantitative X-ray microanalysis at 0.07 mass% Cs, which corresponds to

0.08 mol% Cs₂O. No thermodynamic equilibrium was attained between Cs₂O and UO₂ in the annealing experiments at 1000°C.

Isothermal Sections

The Cs–O–U diagram in the solid state given in Figs. 1a, 1b is taken from [2005Wal]. This diagram may be used in the temperature range between 25 and 727°C, in which no transformation occurs and all the phases remain solid. Each triangle labelled with a small letter (*a*, *b*, ...*p*) on the diagram is characterized by an oxygen pressure at equilibrium depending on the temperature. These oxygen pressures between 0 and 500°C are shown in Fig. 2. There is a correspondence between the letters (*a*, *b*, ...*m*) in both figures. The equilibrium *i* (oxidation of Cs₂U₂O₇ + Cs₂U₄O₁₂ in Cs₄U₅O₁₇), taken from [1997Jay] is characterized by an oxygen pressure higher than that of equilibrium *e* (oxidation of Cs₂UO₄ + UO₂ in Cs₂U₄O₁₂), which is a strong argument for the stability of Cs₄U₅O₁₇. The oxygen pressures at equilibrium inside the triangles *n* (oxidation of Cs₂U₂O₇ in CsO₂ + Cs₄U₅O₁₇), *o* (oxidation of Cs₄U₅O₁₇ in CsO₂ + Cs₂U₄O₁₃) and *p* (oxidation of Cs₂U₄O₁₃ in CsO₂ + UO₃) are much higher than 1 bar. They have not been determined experimentally and thus are not shown in Fig. 2. The triangles in Figs. 1a, 1b which are not labelled with a letter represent a solid solution in equilibrium with a variable oxygen pressure. Under very high oxygen pressures, higher than those given by equilibrium *p*, gaseous oxygen is in equilibrium with CsO₂ and UO₃.

Thermodynamics

The thermodynamic properties of pure uranates are given in Table 3. These data were first measured by [1974OHa, 1975OHa], but a more recent evaluation of [1981OHa, 1986Cor], give the more acceptable results which are presented in Table 3. The thermodynamic properties of the compound Cs₄U₅O₁₇ has been measured by [1997Jay] from the oxygen pressure at equilibrium in the triangle Cs₄U₅O₁₇–Cs₂U₂O₇–Cs₂U₄O₁₂. Another evaluation of the thermodynamic properties of cesium uranates may be found in [1978Fee]. They have not been reported in Table 3 because they do not well agree with later evaluations [1997Jay, 2005Wal]. The enthalpies of formation and entropies of the mixed oxides Cs₂U₅O₁₆, Cs₂U₆O₁₈, Cs₂U₇O₂₂, Cs₂U₉O₂₇ and Cs₂U₁₅O₄₆, estimated by [1981Lin] are reported in Table 3; however, their stability has never been proved experimentally. The enthalpy of the αCs₂U₄O₁₂/βCs₂U₄O₁₂ transition at 625°C was measured at 190 J per mole of atom [1980Cor]. The stability domain of cesium uranates in the (*p*_{O₂}, *p*_{Cs}) diagram at 727°C (1000 K), calculated by [1980Cor] are reproduced in Fig. 3.

Miscellaneous

Pure cesium uranate phases (Cs₂U₂O₇, Cs₄U₅O₁₇, Cs₂U₄O₁₃ and Cs₂U₄O₁₂) were prepared and analyzed by X-ray photoelectron spectroscopy (XPS), a technique which is in principle able of discerning the different oxidation states [2000Ber] of the same element. The last compound (Cs₂U₄O₁₂) in which the mean oxidation state of uranium is +5.5 has been shown to hold an equal quantity of U(V) and U(VI). It may thus be written Cs₂U₂^(V)U₂^(VI)O₁₂.

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Table 1: Investigations of the Cs-O-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1974Cor]	X-ray diffraction, DTA, emf measurements,	600-1000°C, $p(\text{O}_2) < 10$ MPa $\text{UO}_3\text{-Cs}_2\text{UO}_4$
[1974OHa]	Enthalpies measurements by solution calorimetry in HCl	25°C, Cs_2UO_4
[1975Cor]	X-ray analysis, thermal analysis	$< 1000^\circ\text{C}$, $\text{UO}_3\text{-Cs}_2\text{UO}_4$
[1975OHa]	Enthalpies measurements by solution calorimetry in HCl	25°C, $\text{Cs}_2\text{U}_2\text{O}_7$
[1976Egm1]	X-ray diffraction	$< 1000^\circ\text{C}$, $\text{Cs}_2\text{U}_5\text{O}_{16}\text{-Cs}_2\text{U}_4\text{O}_{13}$
[1976Egm2]	X-ray diffraction	$< 1000^\circ\text{C}$, $\text{Cs}_2\text{U}_2\text{O}_7$
[1976Osb]	Heat capacity, entropy and Gibbs energy measurements	5-350 K, Cs_2UO_4
[1978Fee]	Powder X-ray analysis	600-1000°C, $\text{Cs-Cs}_2\text{O-UO}_2$
[1980Cor]	Heat capacity, entropy and enthalpies measurements	5-1070 K, α and $\beta\text{Cs}_2\text{U}_4\text{O}_{12}$
[1981OHa]	Heat capacity, entropy and enthalpies measurements	5-350 K, $\beta\text{Cs}_2\text{U}_2\text{O}_7$
[1983Dha]	Thermogravimetric analysis, vapor pressure evaluations	$\text{Cs}_2\text{UO}_4\text{-Cs}_2\text{U}_2\text{O}_7$ 725-1125°C
[1986Cor]	Enthalpies measurements by solution calorimetry with H_2SO_4 and with HF	25°C, Cs_2UO_4
[1993Kle]	Solubility measurements by X-Ray diffraction	1900°C, 200 bar ($p(\text{O}_2) < 10$ MPa) $\text{UO}_2\text{-3 mass\% Cs}_2\text{O}$
[1997Jay]	Emf and calorimetric measurements	$< 1000^\circ\text{C}$ $\text{Cs}_4\text{U}_5\text{O}_{17}\text{-Cs}_2\text{U}_2\text{O}_7\text{-Cs}_2\text{U}_4\text{O}_{12}$
[1999Hua]	Mass spectrometric measurements with Knudsen' effusion cell	1000-1300°C $\text{Cs}_2\text{U}_4\text{O}_{12}$

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[2000Ber]	X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS)	25°C, Cs ₂ U ₂ O ₇ , Cs ₄ U ₅ O ₁₇ , Cs ₂ U ₄ O ₁₃ , Cs ₂ U ₄ O ₁₂
[2002Ber1]	Powder neutron and X-ray diffraction	25°C, α Cs ₂ U ₄ O ₁₂
[2002Ber2]	XRD, XPS, Extended X-ray Absorption Fine Structure (EXAFS)	25°C, Cs ₂ UO ₄ , Cs ₂ U ₂ O ₇ , Cs ₄ U ₅ O ₁₇ , Cs ₂ U ₄ O ₁₂
[2005Wal]	Solid phase equilibria	350°C, Cs–O–U

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cs) < 28.39	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 614.1	at 25°C [Mas2]
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	at 25°C [Mas2]
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> β U	<i>a</i> = 1075.9 <i>c</i> = 565.6	at 25°C [Mas2]
(γ U) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 352.4	[Mas2]
Cs ₇ O < 4.33	<i>hP24</i> <i>P$\bar{6}m2$</i> Cs ₇ O	<i>a</i> = 1639.3 <i>c</i> = 919.3	at 0°C [Mas2, V-C2]
Cs ₄ O < 11.5	-	-	[Mas2]
Cs ₁₁ O ₃ < 52.5	<i>mP56</i> <i>P2₁/c</i> Cs ₁₁ O ₃	<i>a</i> = 1761.0 <i>b</i> = 921.8 <i>c</i> = 2404.7 β = 100.14°	[Mas2, V-C2]
Cs ₃ O < 166	-	-	23 to 25 at.% O [Mas2]
Cs ₂ O < 490	<i>hR9</i> <i>R$\bar{3}m$</i> Sm	<i>a</i> = 425.6 <i>c</i> = 1899.2	[Mas2, V-C2]
Cs ₂ O ₂ < 590	<i>oI8</i> <i>Immm</i> Cs ₂ O ₂	<i>a</i> = 432.2 <i>b</i> = 751.7 <i>c</i> = 643.0	[Mas2, V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Cs ₂ O ₃ < 502	<i>cI</i> 28 <i>I</i> $\bar{4}$ 3 <i>d</i> Th ₃ P ₄	<i>a</i> = 988	[Mas2, V-C2]
αCsO ₂ (r) < 200	<i>tI</i> 6 <i>I</i> 4/ <i>mmm</i> CaC ₂	<i>a</i> = 446.2 <i>c</i> = 732.6	[Mas2, V-C2]
βCsO ₂ (h) 432 - 200	<i>cF</i> 8 <i>Fm</i> $\bar{3}$ <i>m</i> NaCl	<i>a</i> = 662	[Mas2, V-C2]
UO ₂	<i>cF</i> 12 <i>Fm</i> $\bar{3}$ <i>m</i> CaF ₂	<i>a</i> = 547.0	from 62.5 to 66.7 at.% O [2002Gue]
U ₃ O ₈ < 1870	<i>oC</i> 44 <i>Cmcm</i>	<i>a</i> = 706.9 <i>b</i> = 1144.5 <i>c</i> = 830.3	[2004Che]
UO ₃ < 669	<i>cP</i> 4 <i>Pm</i> $\bar{3}$ <i>m</i> ReO ₃	<i>a</i> = 414.6	[2004Che]
* Cs ₂ UO ₄ < 950	<i>tI</i> * <i>I</i> 4/ <i>mmm</i>	<i>a</i> = 439.1 <i>c</i> = 1482.3	[2002Ber2] [1983Dha]
* Cs ₂ UO _{3.56}	-	-	Structure unknown [2000Ber]
* αCs ₂ U ₂ O ₇ (r) < 300	<i>mC</i> 22 <i>C</i> 2/ <i>m</i>	<i>a</i> = 1452.8 ± 0.3 <i>b</i> = 426.38 ± 0.07 <i>c</i> = 760.5 ± 0.1 β = 112.93°	[1975Cor, 1976Egm2]
* βCs ₂ U ₂ O ₇ (h) 900 - 300	<i>mC</i> 22 <i>C</i> 2/ <i>m</i>	<i>a</i> = 1452.93 <i>b</i> = 432.33 <i>c</i> = 748.99 β = 113.852°	[2002Ber2]. decomposes at 900°C in open atmosphere [2000Ber]
* γCs ₂ U ₂ O ₇	<i>hP</i> 11 <i>P</i> 6 ₃ / <i>mmc</i>	<i>a</i> = 410.8 ± 0.1 <i>c</i> = 1464.6 ± 0.5	metastable. Gives rapidly βCs ₂ U ₂ O ₇ at 800°C [1976Egm2]
* Cs ₄ U ₅ O ₁₇	<i>oP</i> 104 <i>Pbcn</i>	<i>a</i> = 1875.99 <i>b</i> = 706.38 <i>c</i> = 1495.48	[2002Ber2]
* Cs ₂ U ₄ O ₁₃ < 1000	<i>oC</i> 95 <i>Cmcm</i>	<i>a</i> = 1349.4 ± 0.2 <i>b</i> = 1547.6 ± 0.2 <i>c</i> = 791.1 ± 0.2	[1975Cor] above 1000°C, gives an orthorhombic solid solution with Cs ₂ U ₅ O ₁₆ [1976Egm1]
* αCs ₂ U ₄ O ₁₂ (r) < 625	<i>hR</i> 108 <i>R</i> $\bar{3}$ RbNiCrF ₆	<i>a</i> = 1542.32 <i>c</i> = 1918.16	modified pyrochlore structure [2002Ber1]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* β -Cs ₂ U ₄ O ₁₂ (h1) 695 - 625	<i>m</i> **	-	[1974Cor]
* γ -Cs ₂ U ₄ O ₁₂ (h2) > 695	<i>cF72</i> <i>Fd$\bar{3}m$</i>	$a = 1122.95$	[1974Cor]
* Cs ₂ U ₅ O ₁₆	<i>mC92</i> <i>C2/m</i>	$a = 1346.5 \pm 0.2$ $b = 1556.1 \pm 0.2$ $c = 796.4 \pm 0.2$ $\beta = 92.78^\circ$	[1975Cor] above 1000°C, gives a solid solution with Cs ₂ U ₄ O ₁₃ [1976Egm1]
* Cs ₂ U ₆ O ₁₈ 1050 - ~900	<i>mP26</i> <i>P2₁/c</i>	$a = 413.7 \pm 0.1$ $b = 1347.1 \pm 0.1$ $c = 808.9 \pm 0.2$ $\beta = 90.37^\circ$	[1975Cor, 1976Egm1]
* Cs ₂ U ₇ O ₂₂ < 720	<i>oP62</i> <i>Pbam</i>	$a = 694.9 \pm 0.1$ $b = 1971.1 \pm 0.2$ $c = 739.55 \pm 0.08$	[1975Cor]
* Cs ₂ U ₉ O ₂₇ 900 - 720	<i>oP38</i> <i>P</i> **	$a = 1495.6 \pm 0.4$ $b = 1057.1 \pm 0.3$ $c = 398.56 \pm 0.07$	[1975Cor]
* Cs ₂ U ₁₅ O ₄₆ < 720	<i>oC252</i> <i>Cmca</i>	$a = 1469.0 \pm 0.3$ $b = 1343.5 \pm 0.2$ $c = 1974.1 \pm 0.4$	[1981Lin] labelled Cs ₂ U ₁₆ O ₄₉ in [1975Cor]

Table 3: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Property, per mole of atoms [J, mol, K]	Comments
1/7 (Cs ₂ UO ₄)	25	$C_p = 21.82 \pm 0.05$ $S^\circ = 31.38 \pm 0.06$ $\Delta_f S^\circ = -58.70 \pm 0.10$ $\Delta_f H^\circ = -275\,500 \pm 500$ $\Delta_f G^\circ = -275\,150 + 31.57\,T$	[1976Osb] [1976Osb] [1976Osb] [1986Cor] [1997Jay]
	750-900		
1/6.65 (Cs ₂ UO _{3.56})	25	$S^\circ = 36.43 \pm 0.06$ $\Delta_f H^\circ = -265\,200 \pm 500$ $\Delta_f G^\circ = -267\,540 + 52.31\,T$	[1981Lin] [1981Lin] [1997Jay]
	750-900		
1/11 (α -Cs ₂ U ₂ O ₇)	25	$C_p = 21.02 \pm 0.04$ $S^\circ = 29.80 \pm 0.06$ $\Delta_f H^\circ = -292\,750 \pm 500$ $\Delta_f G^\circ = -290\,800 + 59.64\,T$	[1981OHa] [1981OHa] [1981OHa] [1997Jay]
1/11 (β -Cs ₂ U ₂ O ₇)	750-900		
1/26 (Cs ₄ U ₅ O ₁₇)	25	$C_p = 21.15 \pm 0.05$ $S^\circ = 29.90 \pm 0.06$ $\Delta_f H^\circ = -294\,000 \pm 500$ $\Delta_f G^\circ = -297\,270 + 64.65\,T$	[1997Jay] [1997Jay] [1997Jay] [1997Jay]
	750-900		

Phase	Temperature Range [°C]	Property, per mole of atoms [J, mol, K]	Comments
1/19 (Cs ₂ U ₄ O ₁₃)	25	$S^\circ = 28.21 \pm 0.06$	[1981Lin]
	750-900	$\Delta_f H^\circ = -300\,700 \pm 500$ $\Delta_f G^\circ = -310\,580 + 73.21\,T$	[1981Lin] [1997Jay]
1/18 (Cs ₂ U ₄ O ₁₂)	25	$C_p = 21.33 \pm 0.05$ $S^\circ = 29.25 \pm 0.06$	[1980Cor] [1980Cor]
	25-625	$\Delta_f H^\circ = -309\,660 \pm 500$ $\Delta_f G^\circ = -318\,100 + 69.72\,T$	[1980Cor] [1997Jay]
1/23 (Cs ₂ U ₅ O ₁₆)	25	$S^\circ = 27.65$ (evaluation) $\Delta_f H^\circ = -302\,500$ (evaluation)	[1981Lin] [1981Lin]
1/26 (Cs ₂ U ₆ O ₁₈)	25	$S^\circ = 27.04$ (evaluation) $\Delta_f H^\circ = -311\,000$ (evaluation)	[1981Lin] [1981Lin]
1/31 (Cs ₂ U ₇ O ₂₂)	25	$S^\circ = 26.90$ (evaluation) $\Delta_f H^\circ = -304\,300$ (evaluation)	[1981Lin] [1981Lin]
1/38 (Cs ₂ U ₉ O ₂₇)	25	$S^\circ = 26.26$ (evaluation) $\Delta_f H^\circ = -310\,800$ (evaluation)	[1981Lin] [1981Lin]
1/63 (Cs ₂ U ₁₅ O ₄₆)	25	$S^\circ = 25.83$ (evaluation) $\Delta_f H^\circ = -306\,000$ (evaluation)	[1981Lin] [1981Lin]

Fig. 1a: Cs–O–U.
Phase equilibria in the
solid state

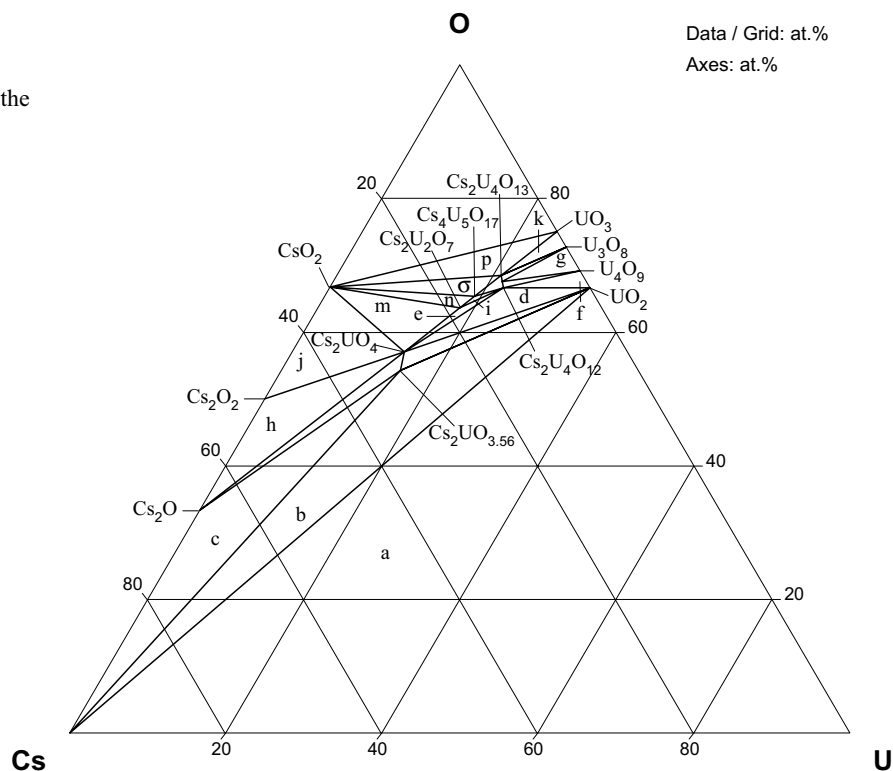


Fig. 1b: Cs-O-U.
Enlargement of
Fig. 1a showing the
"i" domain

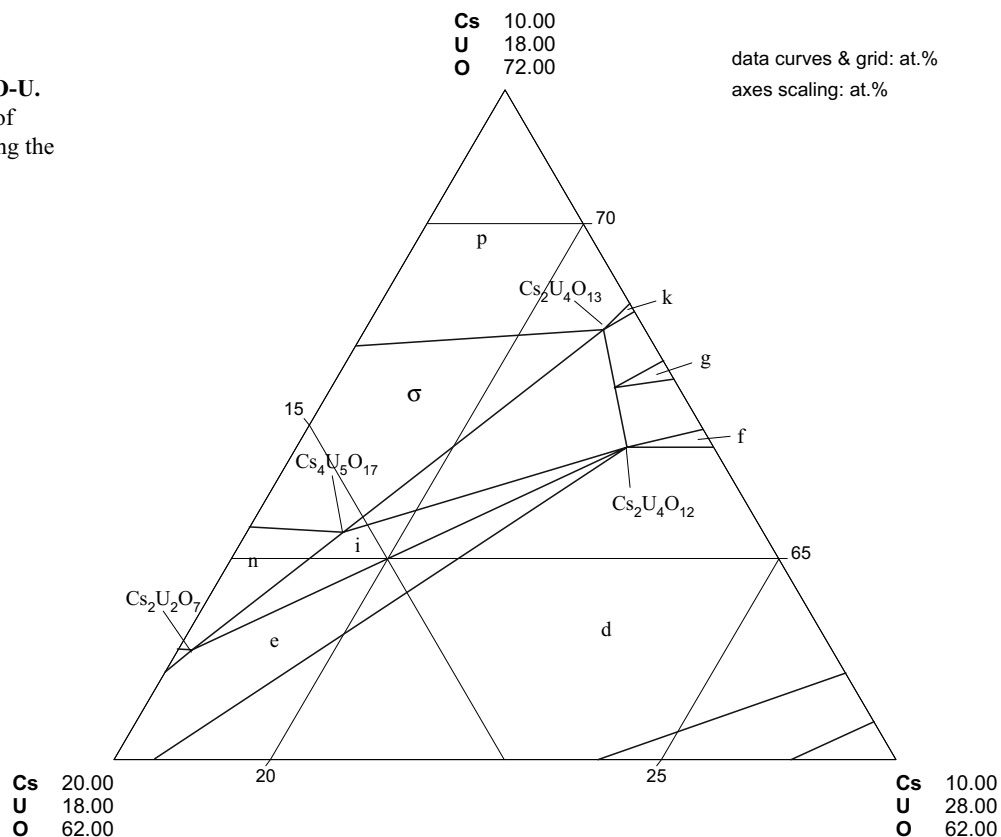


Fig. 2: Cs-O-U.
Oxygen pressures at
equilibrium in the
solid state

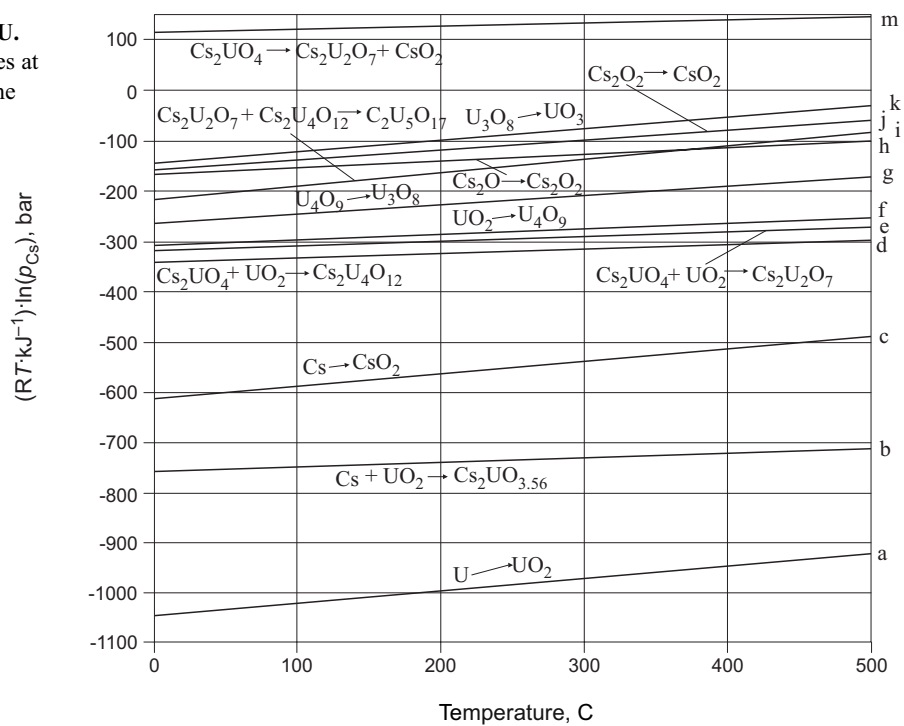
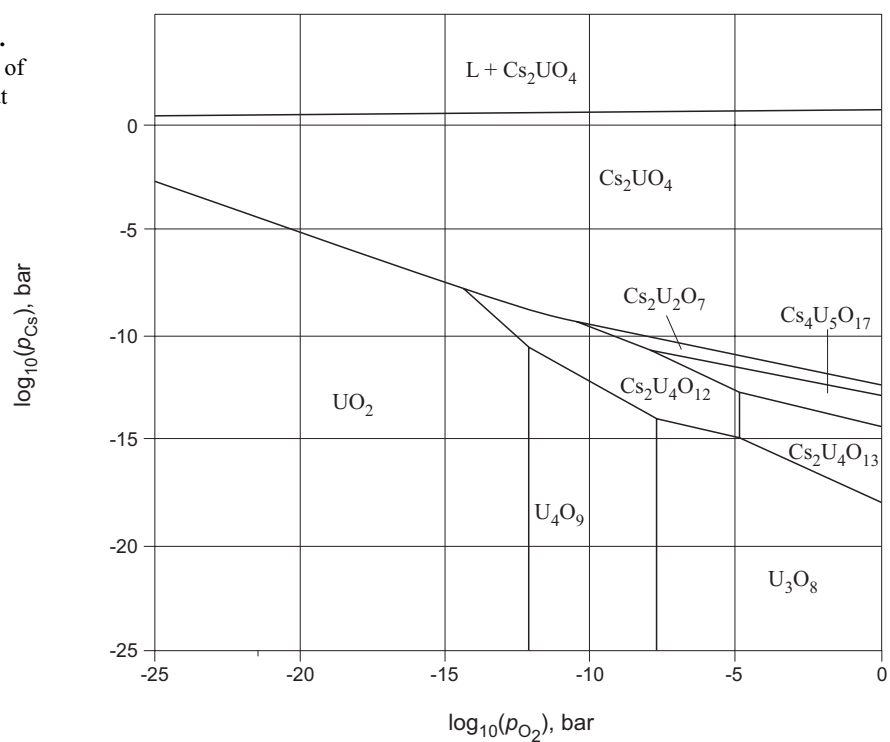


Fig. 3: Cs-O-U.
Stability domains of
cesium uranates at
727°C (1000 K)



Cesium – Oxygen – Zirconium

Jean Claude Tedenac, Pierre Perrot

Introduction

Cs is one of the main fission product of uranium and Zr is one of the main constituent of cladding materials. Several cesium zirconates have been reported in the Cs–O–Zr system [1996Das], but only one compound Cs_2ZrO_3 is known to be stable and its thermodynamic properties have been carefully investigated to make detailed predictions of fission products interactions in a fuel rod. A first evaluation of the thermodynamic properties of Cs_2ZrO_3 was carried out by [1983Koh, 1994Koh]. Experimental measurements are summarized in Table 1. Calculations of the equilibrium at 427°C in the Cs–O–Zr system taking into account the oxygen and cesium potential using the Solgasmix program were proposed by [1996Das]. Calculated isothermal sections at 727 and 1727°C were presented by [1999Pou].

Binary Systems

The Cs–O system which has never been thermodynamically assessed, is accepted from [1979Kni]. Using previous experimental determinations, the system O–Zr was assessed by [2004Wan] according to the Calphad method. Cs and Zr are immiscible as well in the solid than in the liquid phases [1996Das].

Solid Phases

Crystallographic data of solid phases are reported in Table 2. In this system only one mixed oxide is well known: Cs_2ZrO_3 which is of the Cs_2PbO_3 type structure. Other compounds, namely Cs_4ZrO_4 , $\text{Cs}_4\text{Zr}_7\text{O}_{16}$ and $\text{Cs}_6\text{Zr}_7\text{O}_{17}$ have been reported [1996Das]. However, their crystal structure is unknown. Cs_4ZrO_4 decomposes with formation of $\text{Cs}_2\text{ZrO}_3 + 2 \text{Cs}_2\text{O}$, at 275°C under high vacuum and at 730°C in a sealed container. Cs_2ZrO_3 is stable at least up to 915°C.

Isothermal Sections

Two isothermal sections are proposed by [1999Pou] at the temperatures of 727°C (1000K) and 1727°C (2000 K). These sections were calculated using the Thermocalc package with the nuclear materials databases. The calculation is based on the hypothesis of an ideal behavior of Cs in the (Zr,O) solid solutions. However, such an ideal behavior leads to calculate a slight solubility of Cs in (Zr) and ZrO_2 , which contradicts the experimental observations that liquid Cs does not react with Zr, neither with ZrO_2 [1996Das]. Figures 1 and 2 present isothermal sections at 727 and 1727°C under 0.1 MPa pressure, mainly from [1999Pou]. However, the original diagrams have been corrected to take into account the accepted binary diagrams and the lack of any solubility of Cs in zirconium metal and zirconium oxides. According to the thermodynamic modelling [1999Pou] the Cs_2ZrO_3 ternary phase is formed between the room temperature and 900°C by reaction of Cs with zirconia.

Thermodynamics

[1987Cor] measured the standard molar enthalpy of formation of Cs_2ZrO_3 . The value $\Delta_f H^\circ(298.15) = -1584.8 \pm 1.9 \text{ kJ}\cdot\text{mol}^{-1}$ was obtained by measuring its enthalpy of solution in $\text{HF}\cdot 100\text{H}_2\text{O}$ by calorimetry. Same value is reported by [1993Bal] and it is in good agreement with calculated value obtained by [1994Koh] ($\Delta_f H^\circ(298.15) = -1764.2 \text{ kJ}\cdot\text{mol}^{-1}$). It was obtained by measuring $\Delta_f H^\circ$ as a function of temperature from 178°C (451 K) to 378°C (651 K). The resulting value of $\{H(T)-H(298.15 \text{ K})\}$ is presented in Table 3. Gibbs energy of formation of the ternary compound Cs_2ZrO_3 have been obtained by [2001Ali] from vapor pressure of Cs_2O measurements. The value is presented in Table 3. The low temperature heat capacity of Cs_2ZrO_3 was measured between 5 and 393 K by [1999Sch]. The standard entropy at 298.15 K is $199.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

Notes on Materials Properties and Applications

Ytria stabilized zirconia (YSZ) is studied as an inert matrix for an advanced nuclear fuel [1999Pou]. This new fuel generation is foreseen for burning plutonium excesses in light water reactors. Radiocesium is a safety relevant fission product, and both its solubility and retention must be assessed in the fuel. Cesium is known as a volatile fission product which diffuses from the UO_2 pellets towards the gap between the fuel and cladding.

The fission product iodine which is formed in significant amounts combines with another fission product cesium giving CsI [1982Got, 1982Koh, 1985Hof] inside the nuclear fuel pin. In the presence of oxygen, even at its low potential of about 2400 kJ/mol, CsI dissociates to form ternary compounds of cesium such as $\text{Cs}_2\text{U}_4\text{O}_{12}$, Cs_2UO_4 , Cs_2ZrO_3 , etc. and releases elemental iodine [1982Got, 1982Koh, 1985Hof]. The migration of the released iodine to the clad surface and its subsequent reaction with clad material (e.g. zircalloy) causes stress corrosion cracking [1982Got, 1982Koh, 1985Hof] which is detrimental to the long-term stability of the nuclear fuel pins. In this context the knowledge of thermochemistry of the compounds of Cs with the other fission products, fuel matrix and the clad materials are important [2001Ali].

Miscellaneous

The synthesis of Cs_2ZrO_3 by a sol-gel procedure following the nitrate-citrate route [2001Mis] leads to nanocrystallites whose average size is 25 nm. Cs_2ZrO_3 vaporizes incongruently with evolution of Cs_2O (gas) and formation of ZrO_2 .

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Table 1: Investigations of the Cs-O-Zr Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1987Cor]	Dissolution calorimetry in aqueous HF; X-ray measurements	298.15 K / Cs_2ZrO_3
[1993Bal]	Calorimetry /vapor pressure measurements	451-651 K / Cs_2ZrO_3
[1994Koh]	Calorimetry / DSC	310-780 K / Cs_2ZrO_3
[1999Koh]	Heat capacity measurements	310-800 K / Cs_2ZrO_3
[1999Pou]	Implantation / RBS	Cs diffusion in ZrO_2
[1999Sch]	Adiabatic calorimetry and drop calorimetry	5-393 K and 542-703 K / Cs_2ZrO_3
[2001Ali]	Vapor pressure / Knudsen effusion	1142-1273 K / Cs_2ZrO_3

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cs) < 28.39	$cI2$ $Im\bar{3}m$ W	$a = 614.1$	at 25°C [Mas2]
(αZr) < 2129	$hP2$ $P6_3/mmc$ Mg	$a = 323.16$ $c = 514.75$	at 25°C [Mas2] dissolves up to 31.0 at.% O at 2071°C [2004Wan]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(β Zr) 1968 - 866	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 360.90$	β Zr dissolves up to 10.5 at.% O at 1968°C [2004Wan]
α ZrO ₂ < 1203	<i>mP12</i> <i>P2₁/c</i>	$a = 522$ $b = 527$ $c = 538$ $\beta = 99.46^\circ$	66.6 at.% O [2004Wan]
β ZrO ₂ 2333 - 1203	<i>tP6</i> <i>P4₂/nmc</i> HgI ₂	$a = 511.9$ $c = 526.0$	66.5 to 66.6 at.% O [2004Wan]
γ ZrO ₂ 2974 - 1526	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF ₂	$a = 509$	61 to 66.6 at.% O [2004Wan]
Cs ₂ O < 490	<i>hR9</i> <i>R$\bar{3}m$</i> Anti-CdCl ₂	$a = 425.6$ $c = 1899.2$	[2005Gem]
Cs ₂ O ₂ < 590	<i>oI8</i> <i>Immm</i> Cs ₂ O ₂	$a = 432.2$ $b = 751.7$ $c = 643.0$	[Mas2, V-C2]
Cs ₂ O ₃ < 502	<i>cI28</i> <i>I$\bar{4}3d$</i> Th ₃ P ₄	$a = 987 \pm 1$	[Mas2, V-C2]
α CsO ₂ (r) < 200	<i>tI6</i> <i>I4/mmm</i> CaC ₂	$a = 446.2$ $c = 732.6$	[Mas2, V-C2]
β CsO ₂ (h) 432 - 200	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	$a = 662$	[Mas2, V-C2]
* Cs ₂ ZrO ₃ < 915	<i>oC*</i> <i>Cmcm</i> Cs ₂ PbO ₃	$a = 1127.1 \pm 0.7$ $b = 774.3 \pm 0.4$ $c = 595.6 \pm 0.5$	[1989Min]
* Cs ₄ ZrO ₄	-	-	[1996Das]
* Cs ₄ Zr ₇ O ₁₆	-	-	[1996Das]
* Cs ₆ Zr ₇ O ₁₇	-	-	[1996Das]

Table 3: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Property, per mole of atoms [J, mol, K]	Comments
Cs ₂ ZrO ₃	869 - 1000	$\Delta_f G^\circ = (-1671.6 + 0.44T (\pm 18)) \cdot 10^3$	[2001Ali]
Cs ₂ ZrO ₃	25	$\Delta_f H^\circ = -1748.2 \cdot 10^3$ $\Delta_f G^\circ = -1647.2 \cdot 10^3$ $S^\circ = 197.6$ $C_p = 132.05$	[1999Pou]
Cs ₂ ZrO ₃	25 - 900	$H(T) - H(298.15 \text{ K}) = 167.3315 T - 2.6252 \cdot 10^{-3} T^2 + 35.954 \cdot 10^5 / T - 61715.5$	[1993Bal]

Fig. 1: Cs-O-Zr.
Isothermal section at
727°C under 1 bar
pressure

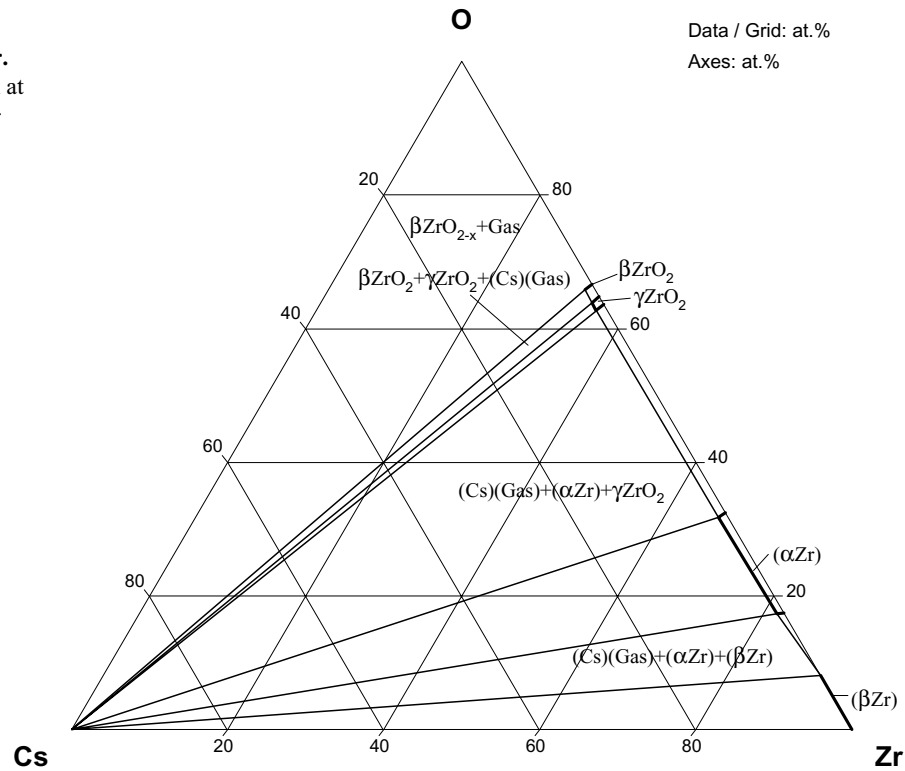
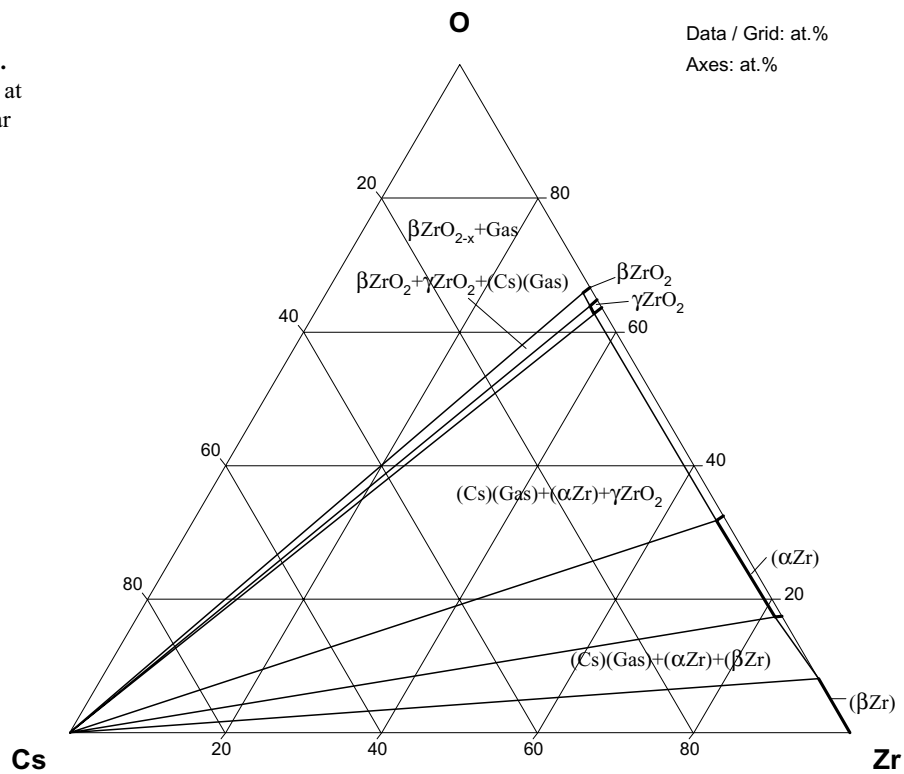


Fig. 2: Cs-O-Zr.
Isothermal section at
1727°C under 1 bar
pressure



Iron – Nitrogen – Uranium

Vasyl Tomashik

Introduction

The investigations of this ternary system are devoted only to the phase diagram of the quasibinary system Fe-UN [1962Kat, 1963Bri, 1966Pri, 1971Guh, 1974Imo].

According to the thermodynamic calculations UN does not react with Fe. The solid-solid reactions of Fe with UN were investigated at elevated temperatures by [1962Kat, 1966Pri]: UN samples showed no signs of reaction after 500 h at 1000°C. [1963Bri] indicated that the system Fe-UN was found to be of simple eutectic type and the eutectic contains 48.5 mass% Fe and crystallizes at $1430 \pm 10^\circ\text{C}$. The later investigations showed that the eutectic temperature is equal to $1395 \pm 5^\circ\text{C}$, eutectic composition being at 49 mass% Fe [1971Guh].

[1974Imo] confirmed that Fe and UN are compatible under the following conditions: at 1000°C in 0.4–33.3 kPa of nitrogen, and at 1400°C in 44 kPa of nitrogen. As the lattice parameter of UN remained unchanged it was suggested that the solubility of Fe in UN is very small. By heating a mixed powder of Fe and UN at 1400°C in a vacuum of 0.013 Pa for 5 h, UFe_2 was formed, but the reaction did not occur at 1220°C by heating for 25 h [1974Imo].

Powdered UFe_2 interacts with UN at 1000°C in 40 kPa of nitrogen for 5 h forming U_2N_3 and Fe [1974Imo]: $4\text{UFe}_2 + 3\text{N}_2 \rightleftharpoons 2\text{U}_2\text{N}_3 + 8\text{Fe}$. Thus there seem to exist as equilibrium the next reactions: $\text{UN} + 2\text{Fe} \rightleftharpoons \text{UFe}_2 + 1/2\text{N}_2$ (1) and/or $2\text{U}_2\text{N}_3 + 8\text{Fe} \rightleftharpoons 4\text{UFe}_2 + 3\text{N}_2$ (2). The equilibrium pressure for the reaction (1) was estimated to be 0.003 Pa at 1220°C and 0.133 Pa at 1400°C. Therefore the formation of UFe_2 is practically impossible below 1400°C and the liquid appears in the Fe-UN quasibinary system at higher temperature [1971Guh].

Investigations of the system are listed in Table 1.

Binary Systems

Binary systems Fe-N, Fe-U and N-U are accepted from [Mas2].

Solid Phases

There are no data about existence of ternary compounds in the Fe-N-U system. Crystallographic data of all unary phases and binary compounds are listed in Table 2.

Quasibinary Systems

The Fe-UN system was constructed using the data of [1963Bri] and [1971Guh] and it is seen that this quasibinary system is of simple eutectic type with no evidence of solid solubility (Fig. 1).

Invariant Equilibria

The temperature of 1395°C and the liquid composition of 49 mass% Fe (68.44Fe-15.79U(at.%)) are accepted from [1971Guh] for the three-phase invariant eutectic reaction $\text{L} \rightleftharpoons \text{UN} + (\gamma\text{Fe})$.

Notes on Materials Properties and Applications

Dispersions of UN in Fe have been examined as potential fuel elements for high-temperature nuclear applications [1963Bri]. To localize fission-product damage it is usually required that the structure consists essentially of discrete particles of the uranium compounds dispersed in a metallic uranium-free matrix.

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Table 1: Investigations of the Fe-N-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1962Kat]	XRD, metallography	1000°C / Fe-UN
[1963Bri]	XRD, metallography	1250-1900°C / Fe-UN
[1966Pri]	Metallography	400-1350°C / Fe-UN
[1971Guh]	XRD, metallography	Fe-UN
[1974Imo]	XRD, measurements of equilibrium pressures of nitrogen	up to 1400°C / Fe-UN

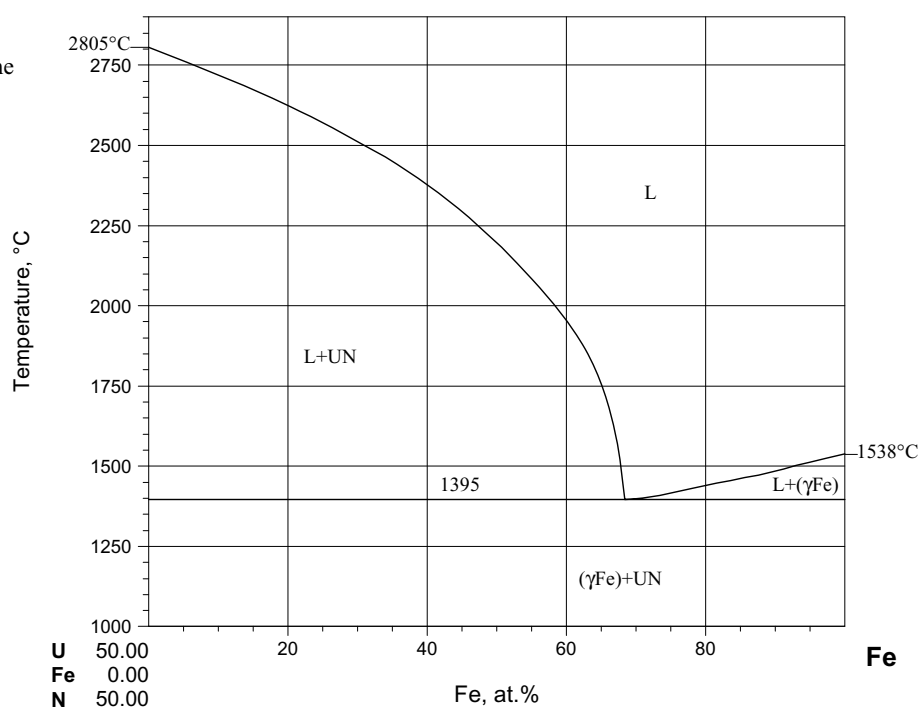
Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(εFe)	<i>hP</i> 2 <i>P</i> 6 ₃ / <i>mmc</i> Mg	<i>a</i> = 246.8 <i>c</i> = 396.0	at 25°C, 13 GPa [Mas2]
(δFe) 1538 - 1394	<i>cI</i> 2 <i>Im</i> $\bar{3}m$ W	<i>a</i> = 293.15	[Mas2]
(γFe) 1394 - 912	<i>cF</i> 4 <i>Fm</i> $\bar{3}m$ Cu	<i>a</i> = 364.67	at 915°C [V-C2, Mas2]
(αFe) < 912	<i>cI</i> 2 <i>Im</i> $\bar{3}m$ W	<i>a</i> = 286.65	at 25°C [Mas2]
(γU) 1135 - 776	<i>cI</i> 2 <i>Im</i> $\bar{3}m$ W	<i>a</i> = 352.4	[Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(βU) 776 - 668	<i>tP</i> 30 <i>P</i> 4 ₂ / <i>mm</i> βU	<i>a</i> = 1075.9 <i>c</i> = 565.6	[Mas2]
(αU) < 668	<i>oC</i> 4 <i>Cmcm</i> αU	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	at 25°C [Mas2]
Fe ₂ N ≤ 500	<i>hP</i> 9 <i>P</i> 3̄1 <i>m</i> V ₂ N	<i>a</i> = 478.7 <i>c</i> = 441.8	[V-C2, Mas2]
Fe ₃ N	<i>hP</i> 4 <i>P</i> 6 ₃ / <i>mmc</i> NiAs	<i>a</i> = 270.5 <i>c</i> = 437.6	[V-C2] Mineral siderazot
Fe ₄ N	<i>cP</i> 5 <i>Pm</i> 3̄ <i>m</i> TiCaO ₃	<i>a</i> = 389.6 ± 0.2	[V-C2] Mineral roaldite
Fe ₄ N < 680	<i>cF</i> 8 <i>Fm</i> 3̄ <i>m</i> NaCl	<i>a</i> = 379.0 ± 0.1	[V-C2, Mas2]
Fe ₅ N ₂ (ε-phase)	<i>hP</i> 4 <i>P</i> 6 ₃ / <i>mmc</i> NiAs	<i>a</i> = 274.42 ± 0.04 <i>c</i> = 440.25 ± 0.11	[V-C2]
Fe ₈ N ?	<i>I</i> 18 <i>I</i> 4/ <i>mmm</i> Fe ₈ N	<i>a</i> = 572.0 <i>c</i> = 629.2	[V-C2]
Fe ₂ U < 1228	<i>cF</i> 24 <i>Fd</i> 3̄ <i>m</i> MgCu ₂	<i>a</i> = 706.29	[V-C2, Mas2]
FeU ₆ < 795	<i>I</i> 28 <i>I</i> 4/ <i>mcm</i> MnU ₆	<i>a</i> = 1024.99 ± 0.01 <i>c</i> = 525.00 ± 0.01 <i>a</i> = 1025.36 ± 0.01 <i>c</i> = 524.84 ± 0.01 <i>a</i> = 1026.25 ± 0.01 <i>c</i> = 524.58 ± 0.01 <i>a</i> = 1027.24 ± 0.01 <i>c</i> = 524.36 ± 0.01 <i>a</i> = 1028.63 ± 0.01 <i>c</i> = 524.10 ± 0.01 <i>a</i> = 1030.22 ± 0.01 <i>c</i> = 523.86 ± 0.01	at 20 K at 50 K at 100 K at 150 K at 220 K at 295 K [V-C2, Mas2]
UN < 2805	<i>cF</i> 8 <i>Fm</i> 3̄ <i>m</i> NaCl	<i>a</i> = 488.87 ± 0.03	[V-C2, Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
UN(hp)	hR^* $R\bar{3}m$?	$a = 316.9 \pm 0.4$ $c = 864.0 \pm 1.4$	high-pressure phase at 34 GPa [V-C2]
UN ₂	$cF12$ $Fm\bar{3}m$ CaF ₂	$a = 529.9$	[V-C2, Mas2]
β U ₂ N ₃ 1352-940	$hP5$ $P\bar{3}m1$ La ₂ O ₃	$a = 369.77 \pm 0.01$ $c = 583.3 \pm 0.1$	[V-C2, Mas2]
α U ₂ N ₃ < 1132	$cI80$ $Ia\bar{3}$ Mn ₂ O ₃	$a = 1068.4 \pm 0.1$	[V-C2, Mas2]
U ₄ N ₇	$cI96$ $Ia\bar{3}$ U ₄ N ₇	$a = 1062.8 \pm 0.1$	[V-C2]

Fig. 1: Fe-N-U.
Phase diagram of the
quasibinary system
Fe-UN



Iron – Sodium – Oxygen

Kostyantyn Korniyenko, Hans Leo Lukas

Introduction

Knowledge of the phase equilibria in the iron-sodium-oxygen system and free energies of formation of sodium ferrites at elevated temperatures is necessary, in the first instance, with a view to analyze the corrosion behavior of sodium in nuclear reactors and to address the problem of scabbing and scaffolding in blast furnaces that is due to high alkali content. Information about phase relations in the Fe–Na–O system is presented in literature by the Fe_3O_4 – NaFeO_2 quasibinary section [1984Dai2], liquidus surface of the partial FeO – Fe_2O_3 – NaFeO_2 system [1984Dai2], isothermal sections and phase relations at different temperatures and composition ranges [1975Cla, 1976Bal2, 1977Kni, 1981Lin, 1984Dai2, 1986Igu, 1993Sri, 1999Kal, 2003Hua2, 2003Lyk] and temperature-composition sections [1940Kni, 1960The, 1962The, 1984Dai1, 1984Dai2]. Crystal structure data obtained by powder- or single crystal X-ray diffraction are published by [1959Col, 1960The, 1962Roo, 1962The, 1963Sch, 1967Rom, 1970Gro, 1971Tsc, 1974Bar, 1974Rie, 1975Cla, 1975Kol, 1976Bal1, 1976Bal2, 1977Bra, 1977Kni, 1978Bra1, 1978Bra2, 1978Bra3, 1980Kes, 1981Kes, 1981Oka, 1985Fru, 1986Igu, 1997Ded, 2002Ama, 2003Sob1, 2003Sob2]. Thermodynamic aspects of the Fe–Na–O system are reflected in [1970Gro, 1977Kni, 1977Sha, 1981Lin, 1984Ban, 1984Dai1, 1984Dai2, 1985Ban1, 1985Ban2, 1987Yam, 1988Bha, 1996Zha, 1999Kal, 2003Hua1, 2003Hua2, 2003Lyk]. The applied experimental techniques as well as the studied temperature and composition ranges are listed in Table 1. Reviews of literature data present information concerning phase equilibria and crystal structures [1989Rag], thermodynamics [1981Lin, 1999Kal] as well as systematics of crystal structures of the Fe–Na–O phases [1978Zve, 1982Bau, 1998Wu, 2000Mat, 2003Mue].

In future further studies are desirable on the liquidus and solidus surfaces in the area FeO – Na_2O – NaO_3 – Fe_2O_3 as well as on invariant equilibria. More details of isothermal sections at different temperatures would be useful. New informations may help to find new practical applications of sodium ferrites.

Binary Systems

The Fe–Na, Fe–O and Na–O binary systems are accepted as compiled in [Mas2]. The assessment of the Na–O system is published with more details by [1987Wri]

Solid Phases

Crystallographic data of all known unary, binary and ternary solid phases are compiled in Table 2. Compositions of the all reported ternary phases, except the τ_9 and τ_{12} phases, lie along the Na_2O – FeO or Na_2O – Fe_2O_3 sections. The composition of the τ_6 phase, established by [1959Col, 1962The, 1999Kal] as “ $\text{Na}_{10}\text{Fe}_{16}\text{O}_{29}$ ”, was later refined by [1962Roo, 1967Rom, 1987Yam, 1996Zha, 1999Kal] to be “ $\text{Na}_3\text{Fe}_5\text{O}_9$ ”. For the τ_2 phase the standard Gibbs energy of formation was determined by [1984Dai1] using emf, but no crystal structure data are known. For many of the ternary phases the temperature range of stability is not known, except the temperature of preparation. The crystal structures of the phases τ_{11} , τ_{12} and τ_{13} also are unknown and need further experimental clarification.

Quasibinary Systems

The section Fe_2O_3 – Na_2O is quasibinary, at least in solid state at lower temperatures. In the range Fe_2O_3 – NaFeO_2 [1940Kni, 1984Dai1] assume a simple eutectic near 1150°C and $\text{Na}/(\text{Na}+\text{Fe}) = 0.36$, whereas [1960The, 1962The] found in solid state the τ_6 phase, stable between 1100 and 755°C. Additionally they found a metastable solid solution of Na_2O in $\gamma\text{Fe}_2\text{O}_3$, decomposing on heating above 650°C. The pure Fe_2O_3 before melting decomposes into Fe_3O_4 and O_2 gas. Thus the two-phase field $\text{L} + \text{Fe}_2\text{O}_3$ must end before it reaches the Fe_2O_3 side of the section. The liquidus temperature of NaFeO_2 is

assumed as 1330°C [1940Kni, 1984Dai1]. Between NaFeO_2 (τ_1''' - τ_1') and Na_2O there are at least five more phases in this quasibinary section, well established by the determination of their crystal structures: $\text{Na}_4\text{Fe}_2\text{O}_5$ (τ_4), $\text{Na}_{14}\text{Fe}_6\text{O}_{16}$ (τ_8), Na_3FeO_3 (τ_{10}), $\text{Na}_8\text{Fe}_2\text{O}_7$ (τ_5) and Na_5FeO_4 (τ_7). On the temperature ranges of stability and on equilibria with melt no experimental data are published for these phases. A further phase, τ_{13} , between τ_6 and τ_1' , postulated by [1981Lin], was denied by [1962The, 1999Kal]. In Fig. 1 the Fe rich part of this section is constructed. The equilibria between gas, liquid, Fe_2O_3 and Fe_3O_4 must be taken as tentative only. The Fe rich liquid, due to Fe^{+2} ions does not reach the section and Na rich liquid may dissolve more O than corresponding to the section, due to peroxide or ozonide ions known in the binary Na–O liquid. On the transition between both cases data are lacking.

The section FeO - Na_2O is quasibinary in the range Na_2FeO_2 - Na_2O [1984Dai1, 1984Dai2]. Between Na_2FeO_2 and FeO it is clearly a not quasibinary isopleth, Fig. 2. At lower temperatures also the range Na_2O to Na_4FeO_3 loses the quasibinary character. [2003Hua2] calculated an invariant reaction: $\text{Na}(\text{liq}) + \text{Na}_4\text{FeO}_3 \rightleftharpoons \text{Na}_2\text{O} + (\alpha\text{Fe})$ at 421°C. This temperature may be a reasonable estimate. [1993Sri] found this reaction experimentally and located it somewhere between 353 and 487°C.

The Fe_3O_4 - NaFeO_2 section is approximately quasibinary. The Fe_3O_4 phase has some homogeneity range towards a composition NaFe_5O_8 , corresponding to the spinel structure of $\gamma\text{Fe}_3\text{O}_4$, in which the divalent Fe^{+2} ions may be replaced by $0.5(\text{Fe}^{+3} + \text{Na}^{+1})$. Due to the difference between this direction and the section plane the tie lines of the two-phase fields containing $\gamma\text{Fe}_3\text{O}_4$ are slightly outside the section plane. Contrary to a strictly quasibinary section all these fields contain a trace of FeO and thus are three-phase fields. Figure 3 shows this approximately quasibinary section as published by [1984Dai2] with correction of a typing error. The horizontal lines at ca. 1150 and 980°C correspond to the invariant four-phase equilibria $\text{L} \rightleftharpoons \gamma\text{Fe}_3\text{O}_4 + \alpha\text{FeO} + \tau_1'''$ and $\tau_1''' \rightleftharpoons \tau_1'', \gamma\text{Fe}_3\text{O}_4, \alpha\text{FeO}$, respectively.

Invariant Equilibria

[1984Dai2] constructed the liquidus surface of the FeO - Fe_2O_3 - NaFeO_2 partial system. These authors mention four invariant four-phase reactions. In Fig. 4 the corresponding reaction scheme is tentatively constructed. It covers the area Fe - Na_2FeO_2 - NaFeO_2 - Fe_2O_3 . The τ_6 phase is tentatively included, assuming no participation in an invariant equilibrium. The three-phase equilibria of the quasibinary part Na_2O - Na_2FeO_2 can be approximated as degenerate four-phase equilibria with Fe in equilibrium. By this consideration the congruent melting point of Na_2FeO_2 in the quasibinary part of the Na_2O - FeO section is also a degenerate maximum of the three-phase equilibrium $\text{L} + \text{Fe} + \text{Na}_2\text{FeO}_2$. Thus only the formation of the three-phase equilibrium $\text{L} + \tau_1 + \tau_2$ remains unsolved in the reaction scheme. The compositions of liquid in the invariant equilibria are too unprecise to justify a tabulation. In Fig. 4 the polymorphic transformations of (Fe) and NaFeO_2 (τ_1) are neglected. As at both compositions all phases are nearly stoichiometric, all these transformations are degenerate with the equations $(\delta\text{Fe}) \rightleftharpoons (\gamma\text{Fe})$, $(\gamma\text{Fe}) \rightleftharpoons (\alpha\text{Fe})$, $\tau_1''' \rightleftharpoons \tau_1''$ or $\tau_1'' \rightleftharpoons \tau_1'$. All other phases participating remain in equilibrium at higher and lower temperatures without taking part at the reactions. Phase τ_{12} was not mentioned by [1984Dai2] and is not implemented in Fig. 4. Outside the range of Fig. 4 the existence of the invariant four-phase equilibrium $\text{L}(\text{Na}) + \text{Na}_4\text{FeO}_3 \rightleftharpoons (\text{Fe}) + \text{Na}_2\text{O}$ is well established, its temperature is inside the interval 487-353°C [1993Sri], but could not be located more precisely.

Liquidus, Solidus and Solvus Surfaces

The liquidus surface projection of the partial FeO - Fe_2O_3 - NaFeO_2 system is shown in Fig. 5, based on [1984Dai2]. Isotherms at the temperatures of 1300, 1400 and 1500°C are plotted. No data concerning solidus or solvus surfaces were found in literature.

Isothermal Sections

The isothermal section of the partial Fe - Fe_2O_3 - NaFeO_2 system at 1000°C is shown in Fig. 6, as constructed by [1986Igu], based on experimental studies of the FeO - Na_2O solid solution in equilibrium with Ar - H_2 - H_2O mixtures. The shapes of the single phase fields of the FeO - Na_2O and Fe_3O_4 - Na_2O solid

solutions agree well with the findings of [1975Cla, 1976Bal2, 2003Lyk], except, that [1976Bal2, 2003Lyk] postulate the existence of τ_{12} , which is not mentioned by [1975Cla, 1984Dai2, 1986Igu]. [1986Igu] also ignored the τ_6 phase, which is reported to be stable at 1000°C [1962The, 1999Kal].

Participation of the τ_6 phase in equilibria at 1000°C was also reported in the works of [1960The] and [1962The, 1999Kal] devoted to constitution of the NaFeO₂-Fe₂O₃ temperature-composition section. The partial isothermal section at 1000°C in the FeO-Fe₃O₄-NaFe₅O₈-NaFeO₂ range was also experimentally constructed by [2003Lyk]. These authors report the τ_{13} phase, but do not show the τ_6 phase. In general, their data conform to the data of [1986Igu] satisfactorily. In their studies of corrosion of steel by liquid Na [1977Kni] found at 650°C the τ_3 phase in equilibrium with (α Fe) and liquid sodium, while at 400°C the tie line Na- τ_3 is replaced by an equilibrium between Na₂O and (α Fe). In the calculations of [2003Hua2] the corresponding four-phase reaction was located at 421°C. [1993Sri] experimentally confirmed this four-phase reaction to happen between 353 and 487°C. [1981Lin] used the SOLGAMIX-PV computer program to calculate phase equilibria in the temperature range from 447 to 607°C in the partial Na-Na₂O-Fe₂O₃-Fe system. They reported the ternary phases τ_1 , τ_2 , τ_3 , τ_5 , τ_6 , τ_7 , τ_{10} and τ_{13} to take part in equilibria in this temperature interval. However, they do not mention the eutectoid decomposition of FeO at 570°C, due to which FeO should not take part in equilibria far below 570°C. The 595°C isothermal section, constructed by [1984Dai2] from their experimental data (Fig. 7), differs as far as the three iron oxides FeO, Fe₃O₄ and Fe₂O₃ all are in equilibrium with NaFeO₂ (τ_1), whereas [1981Lin] show them in equilibrium with Na₃Fe₅O₉ (τ_6) or Na₄Fe₆O₁₁ (τ_{13}). [1984Dai2] left the phases τ_4 , τ_8 , τ_{10} , τ_5 and τ_7 outside their investigated range. [2003Hua2] published six calculated isothermal sections between 25 and 727°C. In this calculation they did not include the phases τ_2 , τ_4 , τ_6 , τ_8 , τ_9 , τ_{11} , τ_{12} and τ_{13} . The thermodynamic dataset used for the calculation is published. Apart from the excluded phases these sections agree well with Fig. 7. The phase τ_5 appears to be stable only above 364°C and the invariant reaction $L(\text{Na}) + \text{Na}_4\text{FeO}_3 \rightleftharpoons \text{Fe} + \text{Na}_2\text{O}$ is located at 421°C. Some of the dashed lines in the O rich part of Fig. 7 may be replaced by equilibria with Na- and O rich liquid.

Temperature – Composition Sections

Besides the partially or approximately quasibinary sections shown in Figs. 1 to 3 the temperature-composition section NaFeO₂-FeO is shown in Fig. 8 based on data of [1984Dai1, 1984Dai2]. The authors qualify this section as qualitative representation of the phases in this section.

Thermodynamics

Information about thermodynamic properties of the Fe-Na-O alloys is widely represented in the literature. Data concerned the reactions are listed in Table 3. The chemical equilibria of gas-slag reactions have been studied by [1984Ban, 1985Ban1, 1985Ban2] to clarify the effect of soda on the thermodynamic properties of slags in the hot metal treatment. The FeO-Na₂O slags were studied at 1610°C being equilibrated with $p_{\text{CO}_2} = 1.013$ bar by using a platinum crucible. The influence of slag composition on the activity of iron oxide and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios has been determined. It has been clarified, that the results can be expressed in terms of the Lumsden's regular solution model over a wide range of compositions. [1984Dai1], besides the results presented in Table 3, also have estimated the standard Gibbs energies of formation of the compounds Na₂FeO₄, Na₂FeO₂ and Na₄FeO₃ referred to the pure elements iron, sodium and oxygen.

Table 4 presents results of vapor pressure measurements. The oxygen and sodium partial pressures were calculated by [1984Dai1] from the Gibbs energy functions. [1984Dai2] obtained an expression for the oxygen partial pressure of the three-phase equilibrium $\alpha + (\text{Fe}) + \text{Na}_2\text{Fe}_2\text{O}_4$ in the temperature range 760 to 910°C. Oxygen and sodium potential ranges at 650°C for the stability of selected equilibria in the Fe-Na-O system were determined by [1977Kni].

[2003Lyk] proposed a thermodynamic model for solid solutions of sodium in the α phase, that provides a possibility to establish a relation between the equilibrium oxygen pressure, composition of the α phase and temperature.

Thermodynamic calculations of isothermal sections of the Fe-Na-O system at the temperatures up to 727°C were carried out by [2003Hua2] using the Thermo-Calc code. Thermodynamic data of the ternary phases

$\text{Na}_4\text{FeO}_3(\text{s})$, $\text{Na}_3\text{FeO}_3(\text{s})$, $\text{Na}_5\text{FeO}_4(\text{s})$ and $\text{Na}_8\text{Fe}_2\text{O}_7(\text{s})$ have been assessed and compiled to a database by reviewing literature data together with DSC and vapor pressure measurements conducted by the authors themselves.

Notes on Materials Properties and Applications

Sodium ferrites have been used, in particular, as reference electrodes in conjunction with sodium-iron-conducting solid electrolytes and, more recently, in sodium and antimony sensors, because of their good electronic conductivity [1996Kal, 1996Zha, 1999Kal], which produces a rapid response of the sensor. Literature data about properties of the Fe–Na–O alloys concern mainly the magnetic properties (Table 5). The magnetic interaction in the structural units $\{\text{Fe}_2\text{O}_7\}^{8-}$, built of two corner-sharing FeO_4 tetrahedra, in the τ_5 phase was studied by [1981Kes] in the temperature range from 4.2 to 500 K (–269 to 27°C). The hypothesis of magnetically isolated $\{\text{Fe}_2\text{O}_7\}^{8-}$ groups was corroborated by Mössbauer spectroscopy between 1.5 and 77 K (–271.7 and –196°C). Authors of [1967Rom] have determined that the τ_6 phase crystals possess antiferromagnetic properties and a possible arrangement of magnetic spins was discussed. Magnetic properties of the τ_7 phase are reported in [1980Kes] and [1985Fru]. The susceptibility obeys a Curie–Weiss law down to 4.2 K, within experimental error, with effective magnetic moment $\mu_{\text{eff}} = 5.83 \cdot \mu_{\text{B}}$, very close to the spin-only value $5.92 \cdot \mu_{\text{B}}$, and the Curie temperature is $\theta = -13$ K. At low temperature the magnetic ordering takes place (the Néel temperature $T_{\text{N}} = 5.40$ K). Authors of [1975Cla] and [1976Bal2] have investigated magnetic properties of alloys from the Fe– Fe_2O_3 – NaFeO_2 partial system annealed at 1000°C. It was established, in particular, that with increasing sodium content of the alloys the Néel temperature values decrease. In opinion of [1997Ded], the Fe–Na–O system is prospective for the study of derivatives of iron in higher oxidation states. The use of oxidizer in abundance in solid-state oxidation synthesis can get novel information about valent possibilities of transition metals. For the first time the data about quadrupole and magnetic interactions of iron in higher oxidation state in the Fe–Na–O system (the Na_2O_2 – Fe_2O_3 section) were obtained by [1997Ded].

Miscellaneous

The mechanism of iron transport by liquid sodium in non-isothermal loop system was studied by [1975Kol]. The loop system was constructed from an AISI Type 316 steel. The sodium was heated from 400°C to 700°C in the heated zone of the system and cooled down reversibly in the cooled zone. In the cooled zone four specimen holders were invariably mounted, the exposition temperatures being 650, 600, 500 and 400°C. Based on the obtained results a model for the transport of iron from the heated zone to the cooled zone was proposed.

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Table 1: Investigations of the Fe–Na–O Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1940Kni] as quoted by [1984Dai1]	Thermal analysis	The NaFeO ₂ -Fe ₂ O ₃ section
[1960The]	X-ray diffraction	300-700°C, NaFeO ₂ -Fe ₂ O ₃ section
[1962Roo] as quoted by [1999Kal]	Crystal structure studies	Na ₃ Fe ₅ O ₉
[1962The]	Dilatometry, X-ray diffraction	≤ 1300°C, NaFeO ₂ -Fe ₂ O ₃ section
[1963Sch]	X-ray diffraction, solubility tests	room temperature, NaFeO ₂ -Fe ₂ O ₃ section
[1967Rom]	X-ray diffraction (single crystals, Weissenberg goniometer), Patterson methods, heavy-atom technique	1100°C, room temperature, complete crystal structure of Na ₃ Fe ₅ O ₉
[1970Gro]	X-ray diffraction, solution calorimetry	500-600°C, Δ <i>H</i> of Na ₄ FeO ₃
[1971Tsc]	X-ray diffraction	450°C, 650°C, three phases in the Na ₂ O-NaFeO ₂ section
[1974Bar]	X-ray diffraction	> 600°C, Na ₄ FeO ₃ as corrosion product of Na steel
[1974Rie]	Guinier X-ray diffraction	crystal structure of Na ₄ FeO ₃
[1975Cla]	X-ray diffraction, chemical analysis	1000°C, Fe-Fe ₂ O ₃ -NaFeO ₂ partial system
[1976Bal1] as quoted by [2003Lyk]	Crystal structure studies	NaFe ₂ O ₃
[1976Bal2]	X-ray diffraction, chemical analysis	1000°C, the Fe-Fe ₂ O ₃ -NaFeO ₂ partial system
[1977Bra]	X-ray diffraction	crystal structure of Na ₄ Fe ₂ O ₅
[1977Kni]	Bendix “time of flight” mass spectrometer vapor pressure measurements (Knudsen cell unit attachment)	Partial pressures of Na and O, 350-600°C, 0 to 60 at.% O
[1977Sha] as quoted by [1981Lin, 1999Kal]	Emf	522-775°C, NaFeO ₂
[1978Bra1]	X-ray Guinier-Simon diffraction technique (single crystals)	crystal structure of Na ₅ FeO ₄
[1978Bra2]	X-ray diffraction (rotation of single crystal, Weissenberg, precision filming techniques)	crystal structure of Na ₁₄ Fe ₆ O ₁₆
[1978Bra3]	X-ray Guinier-Simon diffraction technique (single crystals)	crystal structure of Na ₈ Fe ₂ O ₇

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1981Oka]	X-ray diffraction, kinetics of transformation	NaFeO ₂
[1984Ban]	Slag-iron equilibria studies	FeO-Fe ₂ O ₃ -Na ₂ O partial system
[1984Dai1]	Emf, acid-solution calorimetry	500-1400°C, whole range of compositions
[1984Dai2]	X-ray diffraction, DTA, high-temperature microscopy, emf	500-1400°C, whole range of compositions, phase diagram and thermodynamics
[1985Ban1]	Gas-slag reactions studying	1610°C, FeO-Fe ₂ O ₃ -Na ₂ O partial system
[1985Ban2]	Gas-slag reactions studying	1610°C, FeO-Fe ₂ O ₃ -Na ₂ O partial system
[1985Fru]	Magnetic structure by neutron diffraction	≤ -173°C, Na ₅ FeO ₄
[1986Igu]	Reduction and fire flame techniques	1000°C, FeO-Fe ₂ O ₃ -Na ₂ O partial system
[1987Yam]	Emf	577-1227°C, Fe ₂ O ₃ -Na ₂ O section
[1988Bha]	Emf	350-600°C, Na ₄ FeO ₃
[1993Sri]	Pseudo-isopiestic equilibrations, in-sodium equilibrations, DTA, solid state reactions, X-ray diffraction	< 700°C, 0 to 60 at.% O
[1996Zha] as quoted by [1999Kal]	Emf	≤ 1050°C, Fe ₂ O ₃ -Na ₃ Fe ₅ O ₉ section
[1997Ded]	Mössbauer spectroscopy, EPR, X-ray diffraction	≤ 480°C, Na ₂ O ₂ -Fe ₂ O ₃ section
[1999Kal]	Emf, isothermal equilibration, X-ray diffraction	NaFeO ₂ -Fe ₂ O ₃ section
[2002Ama]	X-ray diffraction (rotation of single crystal)	Na ₉ Fe ₂ O ₇
[2003Hua1]	High temperature mass spectrometry (Knudsen effusion), X-ray diffraction	25-447°C, Na ₄ FeO ₃
[2003Lyk]	Emf	827-1027°C, FeO-Fe ₃ O ₄ -NaFeO ₂ partial system
[2003Sob1]	X-ray diffraction (single crystal)	Na ₃ FeO ₃
[2003Sob2]	X-ray diffraction (single crystal)	Complete crystal structure of Na ₃ FeO ₃

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(δ Fe) (h_2) 1538 - 1394	$cI2$ $Im\bar{3}m$ W	$a = 293.15$	[Mas2], dissolves 0.029 at.% O at 1528°C
(γ Fe) (h_1) 1394 - 912	$cF4$ $Fm\bar{3}m$ Cu	$a = 364.67$	[Mas2], dissolves 0.0098 at.% O at 1392°C
(α Fe) (r) < 912	$cI2$ $Im\bar{3}m$ W	$a = 286.65$	$T = 25^\circ\text{C}$ [Mas2], dissolves 0.00008 at.% O at 912°C
(ϵ Fe) (hp) > $1.3 \cdot 10^5$ bar	$hP2$ $P6_3/mmc$ Mg	$a = 246.8$ $c = 396$	$T = 25^\circ\text{C}$ [Mas2] High pressure phase
(β Na) (r) 97.8 - (-233)	$cI2$ $Im\bar{3}m$ W	$a = 428.865$	$T = 25^\circ\text{C}$ [1987Wri]
(α Na) (l) < -233	$hP2$ $P6_3/mmc$ Mg	$a = 376.7$ $c = 615.4$	$T = -268^\circ\text{C}$ [1987Wri]
α , $\text{Fe}_{1-x}\text{O}_x$ (wüstite) 1424 - 570	$cF8$ $Fm\bar{3}m$ NaCl	$a = 430.88$ $a = 428.00$ $a = 431$	$x = 0.5126$ to 0.5457 [Mas2], dissolves 8 at.% Na (as Na_2O) at 1000°C [1976Bal] $\text{Fe}_{48.5}\text{O}_{51.5}$, 20°C [E] $\text{Fe}_{47.2}\text{O}_{52.8}$, 20°C [E] $\text{Fe}_{47.35}\text{O}_{52.65}$, 1000°C , $p_{\text{O}_2} = 1.2 \cdot 10^{-15}$ bar [1975Cla]
$\text{Na}_y(\text{Fe}_{1-x}\text{O}_x)_{1-y}$		$a = 433$ $a = 434.5$	$x = 0.5265$, $y = 0.0537$, $T = 1000^\circ\text{C}$, $p_{\text{O}_2} = 1.2 \cdot 10^{-15}$ bar [1975Cla] $x = 0.5265$, $y = 0.1020$, $T = 1000^\circ\text{C}$, $p_{\text{O}_2} = 1.2 \cdot 10^{-15}$ bar [1975Cla]
$\gamma\text{Fe}_3\text{O}_4$ (h) 1596 - 580	$cF56$ $Fd\bar{3}m$ MgAl_2O_4	$a = 843.96$	57.1 to 58.02 at.% O [Mas2] at 25°C [V-C2] Fe replaced by 0 to 3.5 at.% Na, at 1000°C in equilibrium with Ar- H_2 - H_2O mixture [1986Igu]
$\beta\text{Fe}_3\text{O}_4$ (r) < 580	$mC224$ Cc $\beta\text{Fe}_3\text{O}_4$	-	~57.1 at.% O [Mas2]
$\alpha\text{Fe}_3\text{O}_4$ (hp) > $2.5 \cdot 10^5$ bar	$m*14$	-	~57.1 at.% O [Mas2] High pressure phase

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
β , Fe ₂ O ₃ < 1457	<i>hR</i> 30 <i>R</i> $\bar{3}c$ Al ₂ O ₃	$a = 503.42$ $c = 1374.73$ $a = 503.5$ $c = 1372$	59.82 to ~60 at.% O [Mas2] $p = 1$ bar [V-C2] [1981Oka]
ϵ (Fe-O)	c^{**}	-	metastable; ~51.3 to ~53.5 at.% O [Mas2]; labelled as “P’ (wüstite)” [Mas2]
η (Fe-O)	<i>mP</i> 500? <i>P</i> 2 ₁ / <i>m</i>	-	metastable; ~52 to ~54 at.% O [Mas2]; labelled as “P’’ (wüstite)” [Mas2]
κ (Fe-O)	<i>hR</i> 6 <i>R</i> $\bar{3}$ NiO (I)	-	metastable; 51.3 to 53.2 at.% O [Mas2]; labelled as “wüstite (low-temperature)” [Mas2]
λ (Fe-O)	<i>cI</i> 80 <i>Ia</i> $\bar{3}$ Mn ₂ O ₃	-	metastable; ~60 at.% O; labelled as “ β Fe ₂ O ₃ ” [Mas2]
γ Fe ₂ O ₃	<i>tP</i> 60 <i>P</i> 4 ₃ 2 ₁ 2	$a = c = 833$ $a = c = 833.9$ $a = c = 840.7$	metastable; ~60 at.% O; labelled also as μ (Fe-O) [1981Oka] $T = 300^\circ\text{C}$ [1960The] $T = 380^\circ\text{C}$ [1960The]
ν (Fe-O)	<i>m</i> *100	$a = 1299$ $b = 1021$ $c = 844$ $\beta = 95.33^\circ$	metastable; ~60 at.% O; labelled as “ ϵ Fe ₂ O ₃ ” [Mas2] [S]
γ , Na ₂ O < 1134 $\pm$ 4	<i>cF</i> 12 <i>Fm</i> $\bar{3}m$ CaF ₂	$a = 556$	33.3 at.% O [Mas2] [E]
β Na ₂ O ₂ (h) 675 - (~512)	<i>cF</i> 12 <i>Fm</i> $\bar{3}m$ CaF ₂	$a = 666$ $c = 993$	~50 at.% O; labelled as “Na ₂ O ₂ -II” [Mas2] [1989Rag]
α Na ₂ O ₂ (r) $\lesssim$ 512	<i>hP</i> 9 <i>P</i> $\bar{6}2m$ Fe ₂ P	$a = 620.7$ $c = 447.1$ $a = 620.8$ $c = 446.9$	~50 at.% O; labelled as “Na ₂ O ₂ -I” [Mas2] [E] [1989Rag]
γ NaO ₂ (r) 552 - (–50)	<i>cF</i> 8 <i>Fm</i> $\bar{3}m$ NaCl	$a = 549$	~66.7 at.% O; labelled as “NaO ₂ (I)” [Mas2] $T = 25^\circ\text{C}$ [E]
β NaO ₂ (I ₁) (–50) - (–77)	<i>cP</i> 12 <i>Pa</i> $\bar{3}$ FeS ₂ (pyrite)	$a = 546$	~66.7 at.% O; labelled as “NaO ₂ (II)” [Mas2] $T = -70^\circ\text{C}$ [E]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
αNaO_2 (l_2) < –77	<i>oP6</i> <i>Pnnm</i> FeS ₂ (marcasite)	$a = 426$ $b = 554$ $c = 344$	~66.7 at.% O; labelled as “NaO ₂ (III)” [Mas2] $T = -100^\circ\text{C}$ [E]
θ (Na–O) < –77	<i>oP6</i> <i>Pnnm</i> FeS ₂ (marcasite)	-	metastable; ~50 at.% O; labelled as “Na ₂ O ₂ -Q” [Mas2]
ρ , NaO ₃	<i>I4</i> * <i>I4/mmm</i>	$a = 1043$ $c = 688$ $a = 1165$ $c = 766$	~75 at.% O [Mas2] [1962Kuz] [1964Kuz]
τ_1''' , NaFeO ₂ (h_2) 1330 - 1010	-	-	by dilatometry distinguished from τ_1'' [1962The]
τ_1'' , βNaFeO_2 (h_1) 1010 - 760	<i>oP16</i> <i>Pna2</i> ₁	$a = 567.2$ $b = 731.6$ $c = 537.7$	[1981Oka]
τ_1' , αNaFeO_2 (r) < 760	<i>hR12</i> <i>R$\bar{3}m$</i> CsICl ₂	$a = 301.9$ $c = 1593.4$ $a = 302.5$ $c = 1609.4$	[1981Oka] [2000Mat]
τ_2 , Na ₂ FeO ₂ < 801	-	-	[1984Dai1]
τ_3 , Na ₄ FeO ₃	<i>mC32</i> <i>Cc</i> Na ₄ FeO ₃	$a = 1096$ $b = 582$ $c = 822$ $\beta = 114^\circ$	single crystals prepared at 630°C, 10 d [1974Rie]
τ_4 , Na ₄ Fe ₂ O ₅	<i>mP44</i> <i>P2</i> ₁ / <i>n</i> Na ₄ Fe ₂ O ₅	$a = 1187$ $b = 567$ $c = 917$ $\beta = 104.5^\circ$	single crystals prepared at 600°C, 6 d [1977Bra]
τ_5 , Na ₈ Fe ₂ O ₇	<i>mP68</i> <i>P2</i> ₁ / <i>c</i> Na ₈ Ga ₂ O ₇	$a = 872$ $b = 1102$ $c = 1010$ $\beta = 107.7^\circ$ $a = 870$ $b = 1101$ $c = 1009$ $\beta = 107.6^\circ$	[1977Bra] single crystals prepared at 600°C, 7 d [1978Bra1]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
τ_6 , $\text{Na}_3\text{Fe}_5\text{O}_9$ 1100 - 755	<i>mC</i> 68 <i>C2/c</i> $\text{Na}_3\text{Fe}_5\text{O}_9$	$a = 1339$ $b = 1207$ $c = 529$ $\beta = 89.17^\circ$	single crystals prepared at 1100°C [1967Rom] labelled as “ $\text{Na}_{10}\text{Fe}_{16}\text{O}_{29}$ ” [1959Col, 1962The, 1999Kal]
τ_7 , Na_5FeO_4	<i>oP</i> 80 <i>Pbca</i> Na_5FeO_4	$a = 1033$ $b = 597$ $c = 1808$ $a = 1026.7$ $b = 591.3$ $c = 1780$ $a = 1027.9$ $b = 592.3$ $c = 1791.4$	single crystals prepared at 650°C, 7 d [1978Bra2] $T = -173^\circ\text{C}$ [1985Fru] $T = -270.5^\circ\text{C}$ [1985Fru]
τ_8 , $\text{Na}_{14}\text{Fe}_6\text{O}_{16}$	<i>aP</i> 36 $P\bar{1}$ $\text{Na}_{14}\text{Fe}_6\text{O}_{16}$	$a = 1142$ $b = 827$ $c = 595$ $\alpha = 109.3^\circ$ $\beta = 87.7^\circ$ $\gamma = 111.4^\circ$	single crystals prepared at 650°C, 7 d [1978Bra3]
τ_9 , $\text{Na}_9\text{Fe}_2\text{O}_7$	<i>oP</i> 72 <i>Pca</i> 2 ₁ $\text{Na}_9\text{Fe}_2\text{O}_7$	$a = 956.2$ $b = 999.1$ $c = 1032.3$	single crystals prepared at 450°C [2002Ama]
τ_{10} , Na_3FeO_3	<i>mP</i> 28 <i>P2</i> ₁ / <i>n</i> Na_3FeO_3	$a = 579.9$ $b = 1265.9$ $c = 582.8$ $\beta = 116.02^\circ$	single crystals prepared at 650°C, 14 d, no single phase product available [2003Sob1, 2003Sob2]
τ_{11} , NaFe_5O_8	<i>cF</i> 56 ? <i>Fd</i> $\bar{3}m$? MgAl_2O_4 ?	-	[1975Cla, 1976Bal2, 1986Igu]. Inside metastable solid solution of $\gamma\text{Fe}_2\text{O}_3$ after [1960The]
τ_{12} , NaFe_2O_3 < 1047	-	-	[1976Bal1, 2003Lyk]
τ_{13} , $\text{Na}_4\text{Fe}_6\text{O}_{11}$	-	-	[1981Lin]. Phase does not exist after [1999Kal]

Table 3: Thermodynamic Data of Reactions or Transformations

Reaction or Transformation	Temperature [°C]	Quantity, per mole of atoms [kJ, mol, K]	Comments
$\text{FeO(s)} + 2\text{Na}_2\text{O(s)} \rightarrow \text{Na}_4\text{FeO}_3\text{(s)}$	25°C	$\Delta H = -13.12 \pm 0.3 \text{ kJ}\cdot\text{mol}^{-1}$	[1970Gro] acid solution calorimetry
$3\text{Na}_2\text{O(s)} + \text{Fe(s)} \rightarrow \text{Na}_4\text{FeO}_3\text{(s)} + 2\text{Na(l)}$	500-600	$\Delta G = 49.89 - 0.07\cdot T$	[1970Gro] derived from acid solution calorimetry

Reaction or Transformation	Temperature [°C]	Quantity, per mole of atoms [kJ, mol, K]	Comments
$\text{Na}_4\text{FeO}_3(\text{s}) \rightarrow \text{NaFeO}_2(\text{s}) + \text{Na}_2\text{O}(\text{s}) + \text{Na}(\text{l})$	500-600	$\Delta G = 93.02 - 0.01 \cdot T$	[1970Gro] derived from acid solution calorimetry
$\text{Ca}(\text{s}) + 2\text{NaF}(\text{s}) + 2\text{FeO}(\text{s}) \rightarrow \text{Na}_2\text{FeO}_2(\text{s}) + \text{CaF}_2(\text{s}) + \text{Fe}(\text{s})$	522-775	$\Delta G = -776.6 + 0.208 \cdot T$	[1977Sha, 1981Lin, 1999Kal] emf
$\text{Na}_2\text{O}(\text{s}) + \text{Fe}_2\text{O}_3(\text{s}) \rightarrow \text{Na}_2\text{Fe}_2\text{O}_4(\text{s})$	522-775 500-1400 657-774 774-1005 1005-1132 362-512 561-731 657-725	$\Delta G = -171.970 - 0.009456 \cdot T$ $\Delta G = -86 - 61.89 \cdot 10^{-3} \cdot T$ $\Delta G = -160.2 - 0.003909 \cdot 10^{-3} \cdot T$ $\Delta G = -157.2 - 1.332 \cdot 10^{-3} \cdot T$ $\Delta G = -147.3 - 13.37 \cdot 10^{-3} \cdot T$ $\Delta G = -237.425 + 83.1 \cdot 10^{-3} \cdot T$ $\Delta G = -247.086 + 89.435 \cdot 10^{-3} \cdot T$ $\Delta G = -232.582 + 69.61 \cdot 10^{-3} \cdot T$	[1977Sha, 1999Kal] emf [1984Dai1] emf [1987Yam] emf [1987Yam] emf [1987Yam] emf [1996Zha, 1999Kal] emf [1996Zha, 1999Kal] emf [1999Kal] emf
$\text{FeO}(\text{s}) + \text{Na}_2\text{O}(\text{s}) \rightarrow \text{Na}_2\text{FeO}_2(\text{s})$	500-1400	$\Delta G = -119.106 + 0.114 \cdot T$	[1984Dai1] acid-solution calorimetry
$\text{FeO}(\text{s}) + 2\text{Na}_2\text{O}(\text{s}) \rightarrow \text{Na}_4\text{FeO}_3(\text{s})$	500-1400	$\Delta G = -147.998 + 0.165 \cdot T$	[1984Dai1] acid-solution calorimetry
$1/2 \{5\text{Fe}_2\text{O}_3(\text{s}) + 3\text{Na}_2\text{O}(\text{s})\} \rightarrow \text{Na}_3\text{Fe}_5\text{O}_9(\text{s})$	< 1132 752-864	$\Delta G = -(248.6 \pm 1.1) - (2.447 \pm 1.188) \cdot 10^{-3} \cdot T$ $\Delta G = -153.978 + 32.32 \cdot 10^{-3} \cdot T$	[1987Yam] emf [1999Kal] emf
$4\text{Na}(\text{l}) + \text{Fe}(\text{s}) + 3/2\text{O}_2(\text{g}) \rightarrow \text{Na}_4\text{FeO}_3(\text{s})$	450-600	$\Delta G = -1212.202 + 0.3511 \cdot T$	[1988Bha] emf
$\text{Na}_4\text{FeO}_3(\text{s}) \rightarrow \text{Na}_3\text{FeO}_3(\text{s}) + \text{Na}(\text{g})$	317-444	$\Delta G (\text{Na}_4\text{FeO}_3) = -11168.629 + 0.33834 \cdot T$	[2003Hua1] Knudsen cell effusion

Table 4: Vapor Pressure Measurements

Phase(s)	Temperature [°C]	Pressure [bar]	Comments
$\text{Fe}(\text{s}), \text{FeO}(\text{s}), \text{Na}_2\text{Fe}_2\text{O}_4(\text{s})$	600 600 900 900	$\log_{10} (p_{\text{O}_2}) = -25.27$ $\log_{10} (p_{\text{Na}}) = -7.14$ $\log_{10} (p_{\text{O}_2}) = -19.6$ $\log_{10} (p_{\text{Na}}) = -1.24$	[1984Dai1] tabulated data
$\text{Fe}(\text{s}), \text{Na}_2\text{Fe}_2\text{O}_4(\text{s}), \text{Na}_2\text{FeO}_2(\text{s})$	600 600	$\log_{10} (p_{\text{O}_2}) = -29.85$ $\log_{10} (p_{\text{Na}}) = -2.56$	
$\text{Fe}(\text{s}), \text{Na}_2\text{FeO}_2(\text{s}), \text{Na}_4\text{FeO}_3(\text{s})$	600	$\log_{10} (p_{\text{O}_2}) = -29.95$ $\log_{10} (p_{\text{Na}}) = -2.50$	
$\text{Na}_2\text{Fe}_2\text{O}_4(\text{s}), \text{Na}_4\text{FeO}_3(\text{s}), \text{Na}_2\text{FeO}_2(\text{s})$	600	$\log_{10} (p_{\text{O}_2}) = -29.69$ $\log_{10} (p_{\text{Na}}) = -2.56$	
$\text{Fe}(\text{s}), \text{Na}(\text{l}), \text{Na}_4\text{FeO}_3(\text{s})$	600	$\log_{10} (p_{\text{O}_2}) = -32.55$ $\log_{10} (p_{\text{Na}}) = -1.53$	

Table 5: Investigations of the Fe–Na–O Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1967Rom]	Magnetic property studies, Mössbauer spectroscopy	Magnetic susceptibility, magnetic ordering of the τ_6 phase
[1975Cla]	Faraday magnetic technique	Magnetic susceptibility of the Fe-Fe ₂ O ₃ -NaFeO ₂ partial system phases
[1976Bal2]	Faraday magnetic technique	Magnetic susceptibility of the Fe-Fe ₂ O ₃ -NaFeO ₂ partial system phases
[1980Kes]	Magnetic property studies, Mössbauer spectroscopy	Magnetic susceptibility, magnetic ordering of the τ_7 phase
[1981Kes]	Magnetic property studies, Mössbauer spectroscopy	Magnetic susceptibility, magnetic ordering of the τ_5 phase
[1985Fru]	Neutron diffraction	Magnetic structure of the τ_7 phase
[1997Ded]	Mössbauer spectroscopy	Magnetic structure of Na ₂ O ₂ -Fe ₂ O ₃ section phases, quadrupol interactions

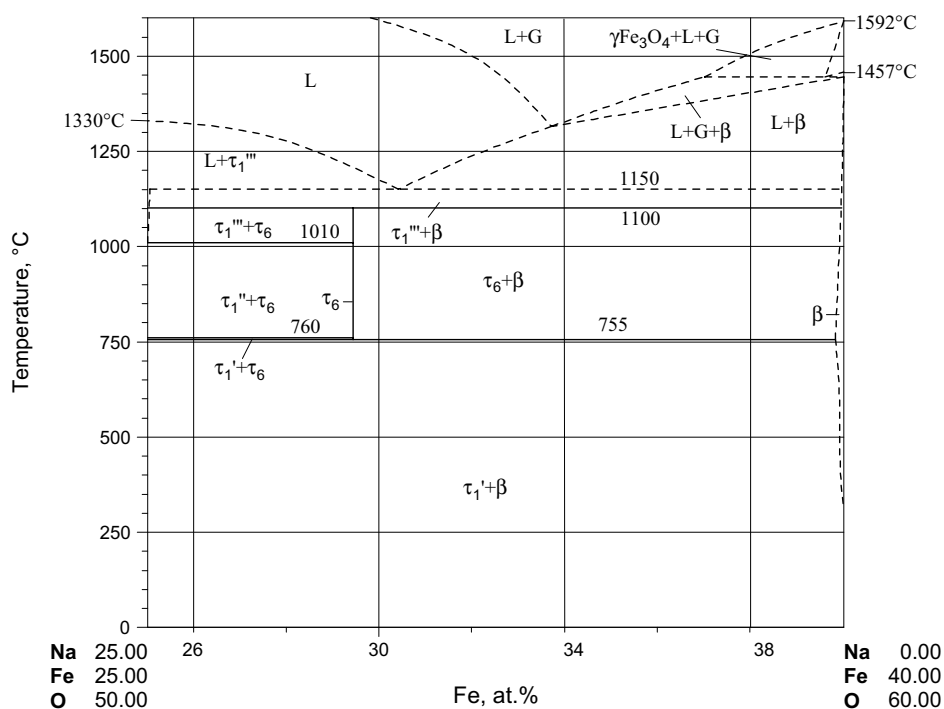
Fig. 1: Fe–Na–O.
The partially quasibinary section NaFeO₂ - Fe₂O₃

Fig. 2: Fe-Na-O.
The partially
quasibinary section
Na₂O - FeO

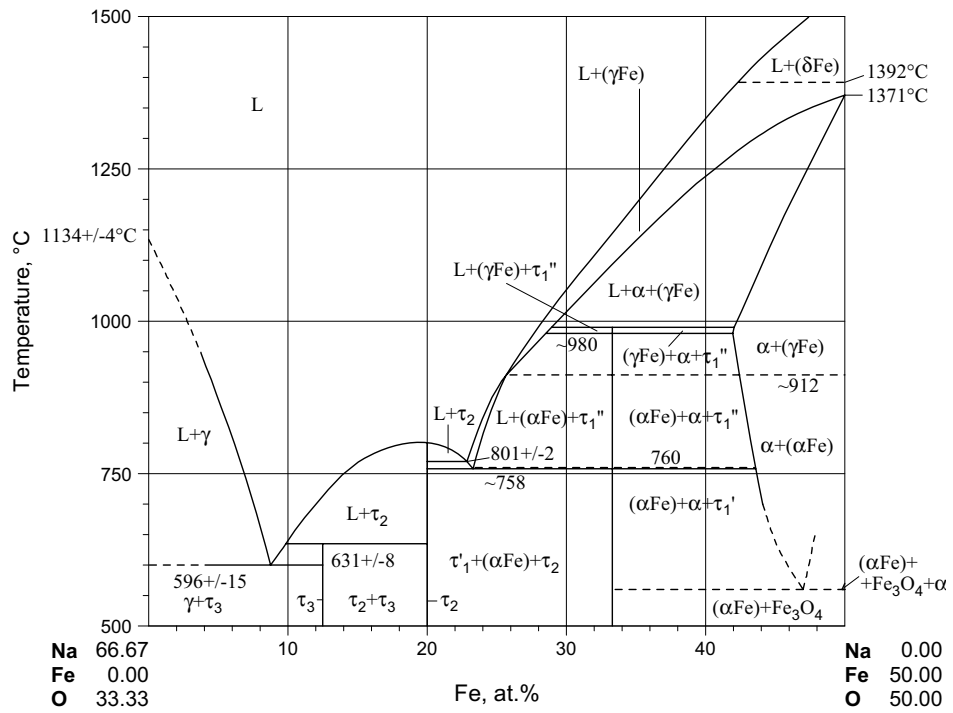
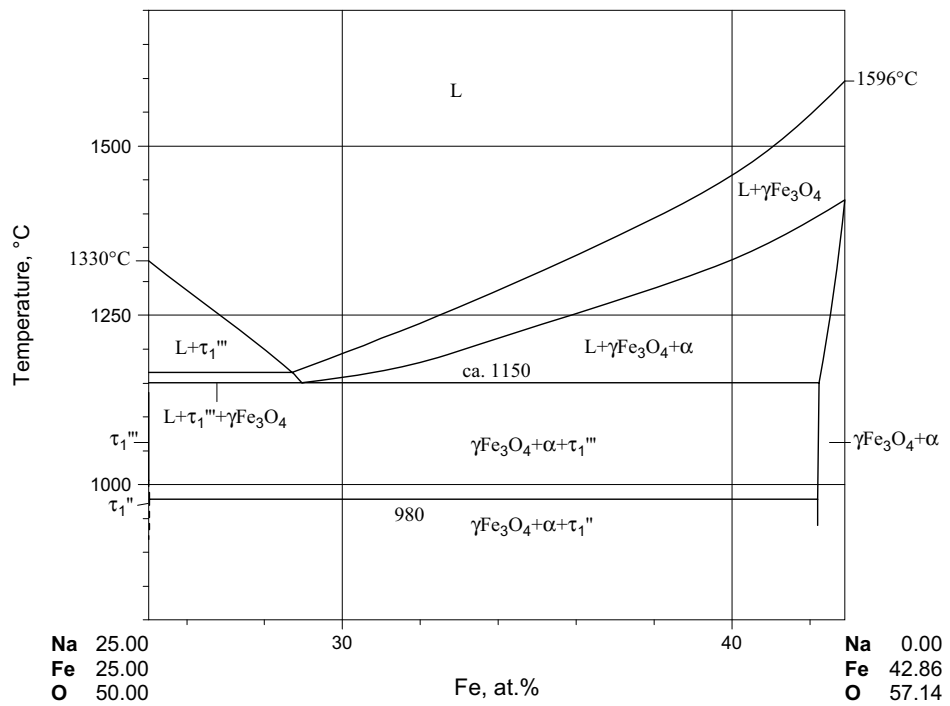


Fig. 3: Fe-Na-O.
The approximately
quasibinary section
Fe₃O₄-NaFeO₂



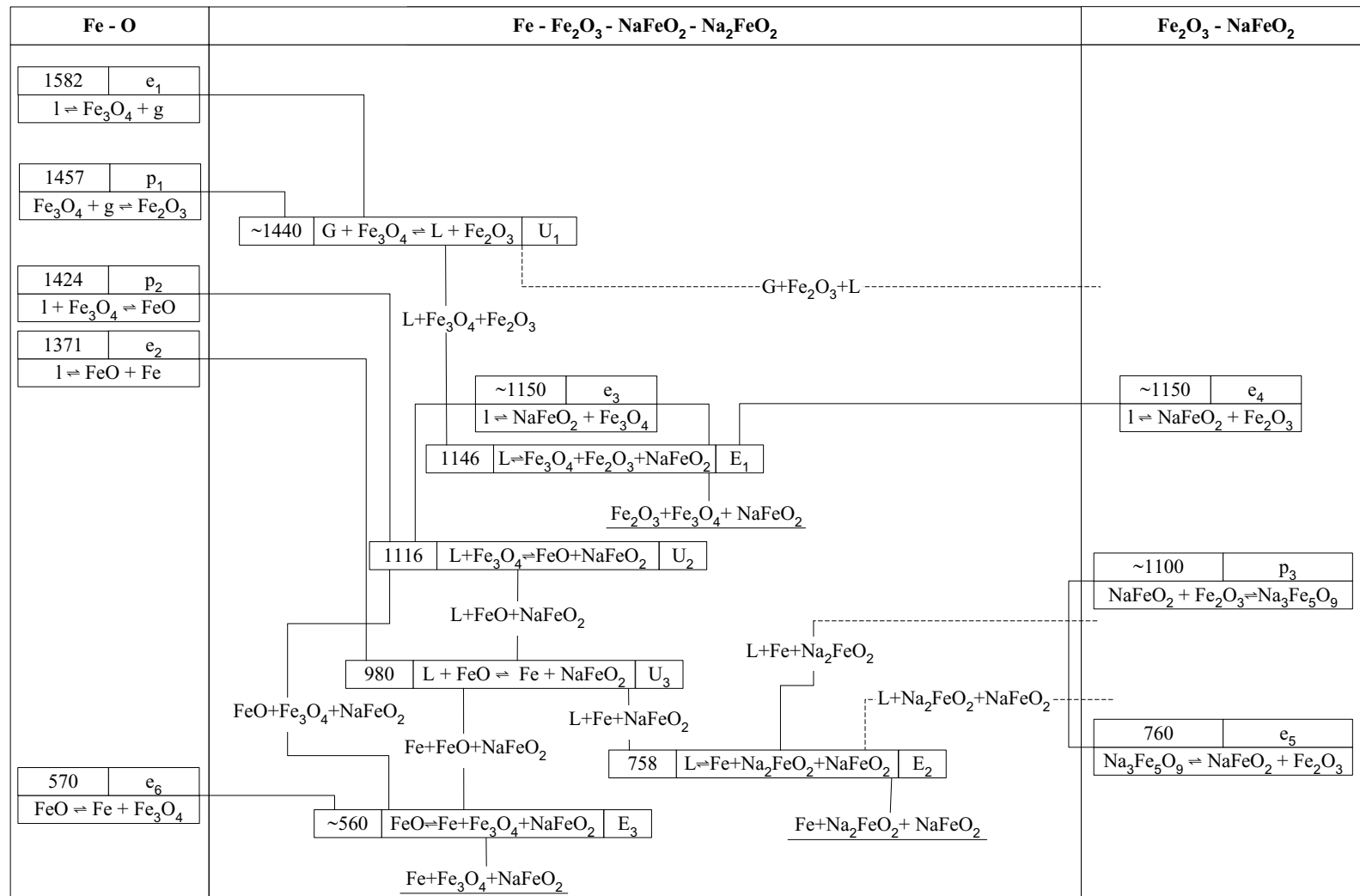
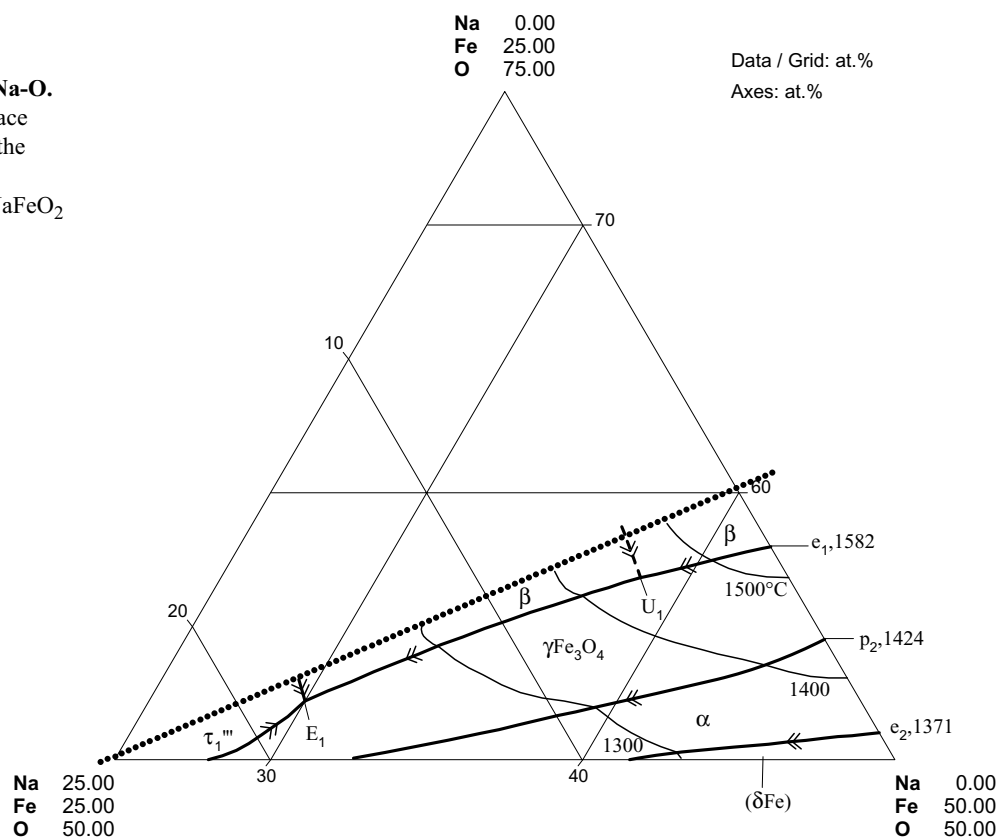


Fig. 4: Fe-Na-O. Reaction scheme of the partial system Fe-Fe₂O₃-NaFeO₂-Na₂FeO₂. The phases (αFe), (γFe) and (δFe) are not distinguished and called Fe. Also τ₁', τ₁" and τ₁" are not distinguished and called NaFeO₂.

Fig. 5: Fe-Na-O.

Liquidus surface
projection of the
partial
FeO-Fe₂O₃-NaFeO₂
system

**Fig. 6: Fe-Na-O.**

Isothermal section of
the partial
Fe-Fe₂O₃-NaFeO₂
system at 1000°C;
equilibrated with
Ar-H₂-H₂O mixtures

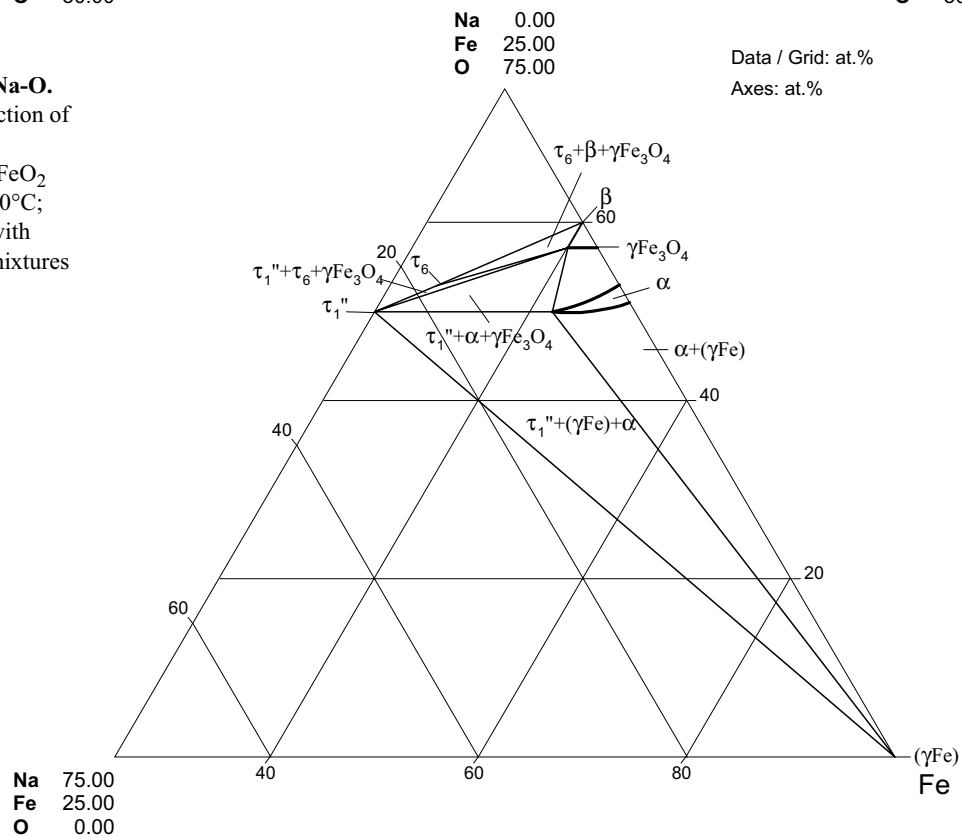


Fig. 7: Fe-Na-O.
Isothermal section at
595°C

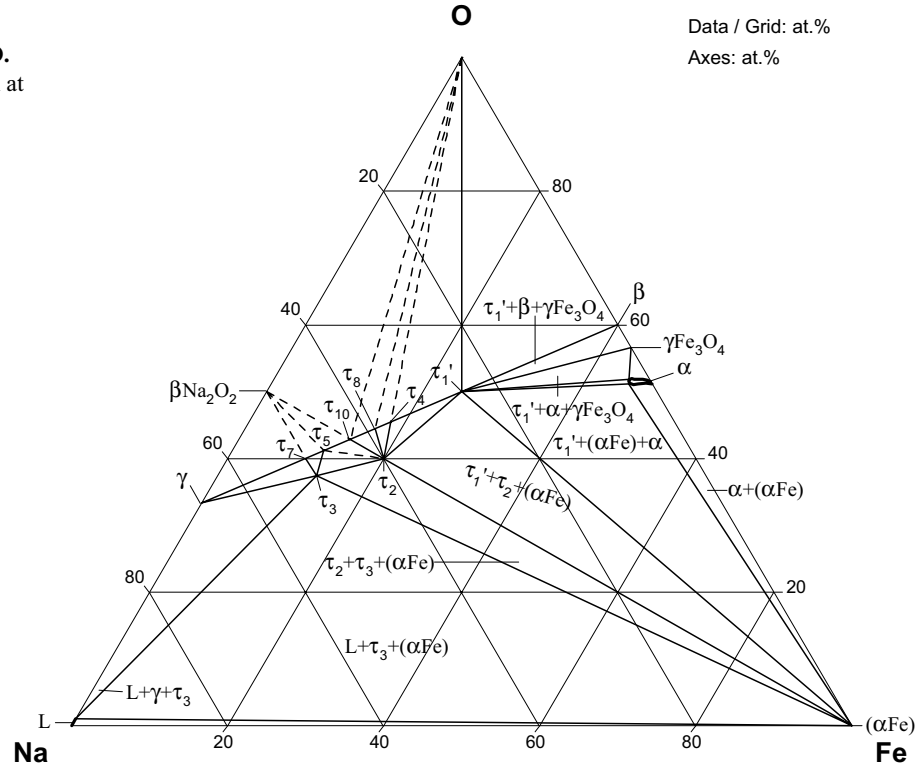
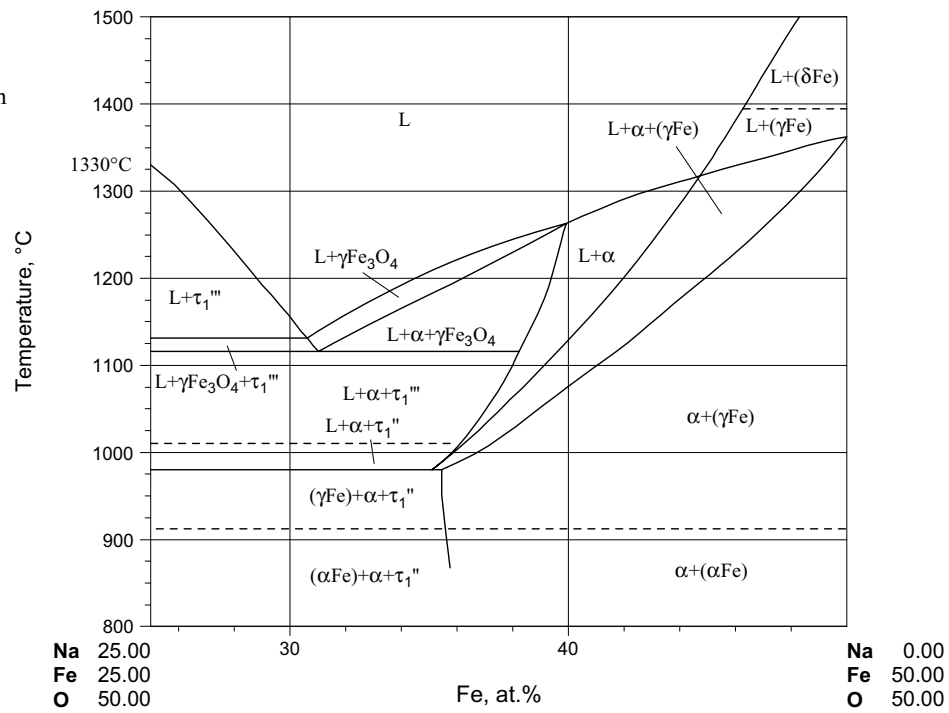


Fig. 8: Fe-Na-O.
Temperature -
composition section
NaFeO₂-FeO



Iron – Oxygen – Lead

Kostyantyn Korniyenko

Introduction

Ferrites, non-metallic solid magnetic materials, are the complex compounds of the iron oxide Fe_2O_3 with oxides of other metals by their chemical compositions. By their magnetic properties the ferrites are the analogues of ferromagnetics but they possess lower densities and lesser losses on the eddy currents. That's why ferrites are widely used in radio engineering, electronics and super high frequent technology productions. With a view to optimization of alloys compositions selection for preparation of ferrites information about phase relations in the corresponding ternary and multicomponent systems is of a great importance. Among these systems the Fe–O–Pb system plays a considerable role, but information concerning phase relations is quite scanty. It is presented in literature by a partial isobaric section in air [1984Sha], the solubility of lead in liquid iron in the presence of oxygen [1995Li] and the constitution of the PbO – Fe_2O_3 temperature-composition section [1955Coc, 1957Ber, 1960Mar, 1962Mou, 1978Mex, 1984Sha, 1986Nev]. Phase contents of the alloys and crystal structures of the identified intermediate phases were studied by [1928Joh, 1938Ade, 1955Coc, 1957Ber, 1960Mar, 1962Mou, 1978Mex, 1984Sha, 1986Nev, 1988Ara, 1997Dor, 1998Cla, 1998Hua, 2000Dia, 2001Dia, 2002Car, 2002Mar, 2003Cas, 2004Dia, 2005Pal]. Data on thermodynamic properties were experimentally obtained by [1986Nev] and [1995Li]. The applied experimental methods as well as the studied temperature and composition ranges are presented in Table 1. Literature information concerning the Fe–O–Pb system was reviewed in [1989Rag]. Further determination of the phase equilibria character is necessary, in particular, on the constitution of the temperature-composition sections formed by Fe_2O_3 with lead oxides Pb_3O_4 , $\text{Pb}_{12}\text{O}_{17}$, $\text{Pb}_{12}\text{O}_{19}$ and PbO_2 .

Binary Systems

Phase diagrams of the Fe–O and Fe–Pb systems are accepted from [Mas2]. Constitution of the O–Pb system is accepted on the basis of [1998Ris] assessment data (Fig. 1).

Solid Phases

Crystallographic data about known unary, binary and ternary phases are compiled in Table 2. Compositions of the all reported ternary phases lie along the PbO – Fe_2O_3 section. Existence of the τ_1 , τ_2 and τ_3 phases was established certainly during both crystal structures and phase relations studies. In particular, data about the τ_1 phase were reported by [1955Coc, 1957Ber, 1962Mou, 1978Mex, 1984Sha, 1986Nev], about the τ_2 phase - by [1928Joh, 1957Ber, 1960Mar, 1962Mou, 1984Sha, 1986Nev], as well as concerned the τ_3 phase - by [1938Ade, 1957Ber, 1960Mar, 1962Mou, 1978Mex, 1984Sha, 1986Nev, 1997Dor, 1998Cla, 2000Dia, 2001Dia, 2002Mar, 2003Cas, 2004Dia, 2005Pal]. Also information about the τ_4 and τ_5 existence was presented by [1955Coc], but later it was shown by [1962Mou] that the τ_2 and τ_3 phases possess homogeneity ranges covering the compositions of the τ_4 and τ_5 phases. Data about the existence of the τ_6 and τ_7 phases ([1960Mar] and [1978Mex, 1999Hsu], respectively) were not confirmed by investigations of phase relations along the PbO – Fe_2O_3 temperature-composition section [1984Sha, 1986Nev].

Invariant Equilibria

On the basis of a dissociation process studies it was established by [1984Sha] that equilibria with the participation of the following phases take place: $\text{L} + \tau_2 + \tau_3 + \beta$ at 1315°C , $\text{L} + \beta\text{Pb}_3\text{O}_4 + \alpha\text{PbO} + \tau_1$ at 455°C , $\text{L} + \beta\text{Pb}_3\text{O}_4 + \tau_1 + \tau_2$ at 430°C and $\text{L} + \beta\text{Pb}_3\text{O}_4 + \tau_3 + \beta$ at 410°C . Also equilibria with the participation of the PbO_x -based phase with inexact stoichiometry were reported. The character of all the respective invariant reactions is not established.

Liquidus, Solidus and Solvus Surfaces

Phase relations at subsolidus temperatures in the range of compositions adjacent to the PbO-Fe₂O₃ section were schematically shown by [1984Sha]. It was established that the β Pb₃O₄ phase takes part in equilibria with the τ_1 , τ_2 and τ_3 phases and with the β phase.

Isothermal Sections

The solubility of lead in the liquid iron in the presence of oxygen was studied by [1995Li] at the temperatures of 1550, 1600 and 1650°C and various oxygen contents. The obtained dependences are shown in Fig. 2. A rise in lead solubility with increasing oxygen content and temperature was observed. Using the method of linear regression, the following functions $\lg(\text{at.}\% \{\text{Pb}\})$ were evaluated as $-0.51 + 0.50 \cdot \{\text{at.}\% \text{O}\} \pm 0.025$ at 1550°C, $-0.43 + 0.67 \cdot \{\text{at.}\% \text{O}\} \pm 0.089$ at 1600°C and $-0.36 + 0.76 \cdot \{\text{at.}\% \text{O}\} \pm 0.038$ at 1650°C.

Temperature – Composition Sections

The PbO-Fe₂O₃ temperature - composition section being named as quasibinary in many publications, does not possess quasibinary character on the Fe₂O₃ side because this phase melts incongruently in the boundary binary Fe–O system. The section shown in Fig. 3 after [1989Rag] is based on the data of [1986Nev] in the PbO rich part and [1962Mou] in the Fe₂O₃ rich side. Another version of the PbO-Fe₂O₃ phase diagram was constructed by [1984Sha] on the basis of dissociation curves projections. The character of the phase relations at low temperatures needs further verification using different physico-chemical experimental techniques.

Thermodynamics

Enthalpies of melting ΔH_{melt}^S of the τ_1 , τ_2 and τ_3 phases were calculated by [1986Nev] using the solution of equations following from the equilibrium conditions of coexisting phases. These values were obtained as 22.24 kJ·mol⁻¹, 49.92 kJ·mol⁻¹ and 61.67 kJ·mol⁻¹, respectively. The enthalpies of formation of the τ_3 phase from oxides ($\Delta_f H$) or from simple substances ($\Delta_f H_{298}$) were calculated by [1992Rez] by approximate methods using the enthalpies of the change of cation coordination in the formation of the compounds from simple oxides. The reported values are 37 kJ·mol⁻¹ and -5115 kJ·mol⁻¹, respectively. In the study of lead solubility in liquid iron, [1995Li] have calculated the activity coefficient f_{Pb}^0 and the interaction parameter e_{Pb}^0 at the temperatures of 1550, 1600 and 1650°C (Table 3).

Notes on Materials Properties and Applications

In case Pb is used as heat exchanger liquid in steel tubes of a nuclear reactor, the system is interesting in case of oxygen contamination of the cooling system producing oxide compounds which are radioactive and may be deposited in cool parts of the tubing system causing unwanted levels of radiation in the outer parts of the reactor system.

Because of their particular magnetic properties, ferrites, in particular, lead-containing, find many industrial applications, in the first instance as magneto-electric materials. Information concerning investigations of the Fe–O–Pb materials properties is collected in Table 4. [1957Ber] studied dependence of magnetic energy on the temperature of sintering for alloys with different PbO:Fe₂O₃ ratios [1957Ber] and observed a maximum energy values at the composition PbO-4Fe₂O₃. The corresponding dependences of the residual magnetic induction and the coercive force were also constructed by [1957Ber]. Magnetic measurements on the epitaxial films with the composition Fe_{12.9}PbO_{22.9} were carried out by [1997Dor]. These objects exhibit magnetically isotropic behavior in the film plane with magnetic remanence to saturation magnetization divided by 4π ratio $M(r)/M(s) = 88 \pm 2.9\%$ and coercive field $H_c = 198.94 \pm 7.72 \text{ kA} \cdot \text{m}^{-1}$. However, the films were anisotropic with respect to the film normal such that the c crystallographic axis is a magnetically hard direction and all directions normal to the c axis are magnetically easy. The saturation magnetization ($4\pi M(s)$) value for the films is 0.063 T at room temperature. Magnetic properties of thin films with the

composition of $\text{Fe}_{12}\text{PbO}_{19}$ prepared by deposition on Si/SiO_2 and sapphire substrates were studied by [2000Dia] and [2001Dia], respectively. The influence of the substrate temperature (550–775°C) and the oxygen pressure (1–3 mbar) on the magnetic properties during the deposition was reported by [2000Dia]. The χ type lead hexaferrite films with high saturation magnetization and high coercive field (302.39 $\text{kA}\cdot\text{m}^{-1}$) were grown using a substrate temperature of 700°C and a pressure of 3.0 mbar of oxygen, while moderate value of coercive field of the thin films deposited on sapphire substrate at 700°C under 3.0 mbar partial pressure of high purity oxygen was 198,94 $\text{kA}\cdot\text{m}^{-1}$ [2001Dia]. The optimum value of coercive field of the $\text{Fe}_{12}\text{PbO}_{19}$ powder obtained by [2004Dia] using modifications to the traditional ceramic route was 318.31 $\text{kA}\cdot\text{m}^{-1}$ at 900°C. It was concluded that at temperatures higher than 900°C the magnetic properties are drastically affected as a consequence of the volatility of PbO. Phase formation during self-propagating high-temperature synthesis of ferrites was studied by [2002Mar]. The combustion temperature was 1267°C, the average front velocity was $9\cdot 10^{-4} \text{ m}\cdot\text{s}^{-1}$, the obtained intermediate phases were FeO, Fe_3O_4 and Fe_4PbO_7 . The value of coercivity was 48 $\text{kA}\cdot\text{m}^{-1}$. Results of tunneling magnetoresistance effect studies in the Fe–O–Pb granular films were presented by [1998Cla, 1999Hsu, 2000Hsu]. The dynamics of the 2b site in the $\text{Fe}_{12}\text{PbO}_{19}$ compound was investigated by [1998Cla] on polycrystalline and oriented single-crystal samples above the Curie temperature.

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Table 1: Investigations of the Fe-O-Pb Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1928Joh] as quoted by [1962Mou]	X-ray diffraction	Fe ₄ PbO ₇
[1938Ade]	X-ray Laue and rotation techniques	Fe ₁₂ PbO ₁₉
[1955Coc] as quoted by [1960Mar] and [1989Rag]	optical microscopy	The PbO-Fe ₂ O ₃ section
[1957Ber]	X-ray Debye-Scherrer studies, thermal analysis, magnetic steel tester measurements	875-1275°C, the PbO-Fe ₂ O ₃ section
[1960Mar]	Thermal analysis, metallography, powder X-ray diffraction	The PbO-Fe ₂ O ₃ section
[1962Mou]	X-ray diffraction (Norelco diffractometer), DTA	600-1400°C, the PbO-Fe ₂ O ₃ section
[1978Mex]	Solid state reactions studying, thermogravimetry, X-ray diffraction	The PbO-Fe ₂ O ₃ section
[1984Sha]	Thermobalance, X-ray diffraction	The PbO-Fe ₂ O ₃ section
[1986Nev]	DTA, X-ray diffraction, crystal growth studying	The PbO-Fe ₂ O ₃ section
[1995Li]	Gas-light Tammann furnace measurements of solubility	1550, 1600, 1650°C, the Fe rich corner
[1997Dor]	X-ray diffraction (standard and grazing incidence), Rutherford back-scattering spectrometry	600°C, room temperature, the Fe _{12.9} PbO _{22.9} thin films
[1998Cla]	Comparative Fe-57 Mössbauer spectroscopy (polycrystalline and oriented single-crystal samples)	477-707°C, Fe ₁₂ PbO ₁₉
[1998Hua]	Method of manufacturing granular films	whole range of compositions

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[2000Dia]	Pulsed laser ablation deposition	550-775°C, Fe ₁₂ PbO ₁₉
[2001Dia]	Pulsed laser ablation deposition, X-ray diffraction	700°C, Fe ₁₂ PbO ₁₉
[2002Car]	Optical microscopy, scanning electron microscopy, electron probe microanalysis, X-ray diffraction, Mössbauer spectroscopy	476°C, Fe–O–Pb thin layers
[2002Mar]	Self-propagating high-temperature synthesis, X-ray diffraction, thermal analysis, chemical analysis, magnetic properties determination, density measurements, arrested front method	Fe ₁₂ PbO ₁₉
[2003Cas]	Laser ablation deposition	700°C, Fe ₁₂ PbO ₁₉ thin films
[2004Dia]	Mössbauer spectroscopy, X-ray diffraction	> 800°C, Fe ₁₂ PbO ₁₉
[2005Pal]	Ceramic method, Rietveld refinement X-ray diffraction	Fe ₁₂ PbO ₁₉

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(δFe) (h ₂) 1538 - 1394 Fe _{1-x-y} Pb _x O _y	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	$a = 293.15$	[Mas2] $x = 0, 0 < y \leq 2.9 \cdot 10^{-4},$ $T = 1528^\circ\text{C}$ [Mas2]
(γFe) (h ₁) 1394 - 912 Fe _{1-x-y} Pb _x O _y	<i>cF4</i> <i>Fm</i> $\bar{3}m$ Cu	$a = 364.67$	[Mas2] $x = 0, 0 < y \leq 9.4 \cdot 10^{-5}, T = 1371^\circ\text{C}$ [Mas2]
(αFe) (r) < 912 Fe _{1-x-y} Pb _x O _y	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	$a = 286.65$	at 25°C [Mas2] $x = 0, 0 < y \leq 8 \cdot 10^{-6}, T \approx 912^\circ\text{C}$ [Mas2]
(εFe) > 1.3·10 ⁵ bar	<i>hP2</i> <i>P6</i> ₃ / <i>mmc</i> Mg	$a = 246.8$ $c = 396$	at 25°C [Mas2]
(βPb) < 327.502 Fe _x Pb _{1-x-y} O _y	<i>cF4</i> <i>Im</i> $\bar{3}m$ Cu	$a = 495.02$	at 25°C [Mas2] $x = 0, 0 < y \leq 10^{-6}, T \approx 327^\circ\text{C}$ [Mas2] $y = 0, 0 < x \leq 2.5 \cdot 10^{-4}, T \approx 910^\circ\text{C}$ [E]
(αPb) > 1.03·10 ⁵ bar	<i>hP2</i> <i>P6</i> ₃ / <i>mmc</i> Mg	$a = 326.5$ $c = 538.7$	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
α , $\text{Fe}_{1-x}\text{O}_x$ (wüstite) 1424 - 570	$cF8$ $Fm\bar{3}m$ NaCl	$a = 430.88$ $a = 428.00$	$x = 0.5126$ to 0.5457 [Mas2] in the alloy $\text{Fe}_{48.5}\text{O}_{51.5}$, $T = 20^\circ\text{C}$ [E] in the alloy $\text{Fe}_{47.2}\text{O}_{52.8}$, $T = 20^\circ\text{C}$ [E]
$\gamma\text{Fe}_3\text{O}_4$ (h) 1596 - 580	$cF56$ $Fd\bar{3}m$ MgAl_2O_4	$a = 840$	57.1 to 58.02 at.% O [Mas2] [E]
$\beta\text{Fe}_3\text{O}_4$ (r) < 580	$mC224$ Cc $\beta\text{Fe}_3\text{O}_4$	-	~57.1 at.% O [Mas2]
$\alpha\text{Fe}_3\text{O}_4$ (hp) > $2.5 \cdot 10^{-5}$ bar	m^*14	-	~57.1 at.% O [Mas2]
β , Fe_2O_3 < 1457	$hR30$ $R\bar{3}c$ Al_2O_3	$a = 503.42$ $c = 1374.83$	59.82 to ~60 at.% O [Mas2] at 600°C [Mas2, V-C2]
ϵ (Fe-O)	c^{**}	-	metastable; ~51.3 to ~53.5 at.% O [Mas2]; labelled as “P” (wüstite)” [Mas2]
η (Fe-O)	$mP500?$ $P2_1/m$	-	metastable; ~52 to ~54 at.% O [Mas2]; labelled as “P” (wüstite)” [Mas2]
κ (Fe-O)	$hR6$ $R\bar{3}$ NiO (I)	-	metastable; 51.3 to 53.2 at.% O [Mas2]; labelled as “wüstite (low-temperature)” [Mas2]
λ (Fe-O)	$cI80$ $Ia\bar{3}$ Mn_2O_3	-	metastable; ~60 at.% O; labelled as “ $\beta\text{Fe}_2\text{O}_3$ ” [Mas2]
μ (Fe-O)	$tP60$ $P4_32_12$	-	metastable; ~60 at.% O; labelled as “ $\gamma\text{Fe}_2\text{O}_3$ ” [Mas2]
ν (Fe-O)	m^*100	$a = 1299$ $b = 1021$ $c = 844$ $\beta = 95.33^\circ$	metastable; ~60 at.% O; labelled as “ $\epsilon\text{Fe}_2\text{O}_3$ ” [Mas2] [S]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
β PbO (h) ~887 - ~489	<i>oP8</i> <i>Pbma</i> or <i>Pbcm</i> β PbO	$a = 547.6$ $b = 474.3$ $c = 587.6$ $a = 548.9$ $b = 475.5$ $c = 589.1$	50 at.% O, labelled as “PbO-M” [Mas2, 1998Ris] [1961Lec1] at $T = 27^\circ\text{C}$ [H]
α PbO (r) $\lesssim 489$	<i>tP4</i> <i>P4/nmm</i> α PbO	$a = 396$ $c = 501$ $a = 397.59$ $c = 502.3$ $a = 397.2$ $c = 501.8$	50 at.% O, labelled as “PbO-L” [Mas2, 1998Ris] [1961Lec2] at $T = 27^\circ\text{C}$ [H] [1989Rag]
β Pb ₃ O ₄ (r) 595 - (-103)	<i>tP28</i> <i>P4₂/mbc</i> β Pb ₃ O ₄ (r)	$a = 881.5$ $c = 656.5$ $a = 880.6$ $c = 656.4$	57.1 at.% O, labelled as “Pb ₃ O ₄ -T” [Mas2, 1998Ris] at $T = 25^\circ\text{C}$ [S] [1989Rag]
α Pb ₃ O ₄ (l) < -103	<i>oP28</i> <i>Pbam</i>	$a = 912.4$ $b = 846.7$ $c = 656.7$ $a = 881.89$ $b = 880.68$ $c = 656.36$	57.1 at.% O, labelled as “Pb ₃ O ₄ -R” [Mas2] at $T = -268^\circ\text{C}$ [1988Wri, 2001Guz] [1989Rag]
γ , Pb ₁₂ O ₁₇ 361 - < 0	<i>oP28</i> <i>Pmc2₁</i> ?	$a = 778$ $b = 1098$ $c = 1148$	58.6 at.% O [Mas2, 1998Ris] [1988Wri, 2001Guz]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
δ , $\text{Pb}_{12}\text{O}_{19}$ 335 - 54	<i>mP62</i> <i>Pc?</i> or <i>P2₁/c</i>	$a = 773$ $b = 1083$ $c = 1147$ $\beta = 88.77^\circ$	61.3 at.% O [Mas2, 1998Ris] in the alloy $\text{PbO}_{1.57}$ [E]
		$a = 775.3$ $b = 1084.8$ $c = 1150.2$ $\beta = 88.93^\circ$	[S]
		$a = 1150$ $b = 1084.3$ $c = 777.3$ $\beta = 91.08^\circ$	[1988Wri, 2001Guz]
βPbO_2 251 - < 0	<i>tP6</i> <i>P4₂/mnm</i> TiO_2 (rutile)	$a = 491$ $c = 336$	66.1 to 66.7 at.% O, with a small amount of hydrogen; labelled as “ PbO_2 -I” [Mas2, 1998Ris] [E]
		$a = 495.5$ $c = 338.3$	[S]
		$a = 495.56$ $c = 338.67$	1988Wri, 2001Guz]
		$a = 495.78$ $c = 338.78$	[1989Rag]
αPbO_2 (hp)	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF_2	-	metastable; about 66.7 at.% O; contains a small amount of hydrogen; labelled as “ PbO_2 -III” [Mas2]
θ (Pb-O)	<i>m**</i> <i>P2₁ or 2₁/m</i>	-	metastable; 50 at.% O [Mas2]
ρ (Pb-O)	<i>o**</i>	-	metastable; 50 at.% O; labelled as “ $\text{PbO}\alpha$ ” [Mas2]
σ (Pb-O)	<i>o**</i>	-	metastable; 57.1 at.% O [Mas2]
ξ (Pb-O)	<i>o**</i>	-	metastable; 57.1 to 61.1 at.% O; labelled as “ PbO_n ” [Mas2]
ζ (Pb-O)	Pseudocubic	-	metastable; 58.6 at.% O [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Δ , Pb ₂ O ₃ , 1 bar hydrostatic pressure	<i>mP20</i> <i>P2₁/a</i>	$a = 781.4$ $b = 562.5$ $c = 846.6$	metastable; 60 at.% O [1961Whi] [1988Wri, 2001Guz]
q (Pb-O)	Pseudocubic	-	metastable; 61.3 at.% O [Mas2]
q' (Pb-O)	<i>m**</i>	-	metastable; 61.3 at.% O [Mas2]
ϕ (Pb-O)	<i>oP12</i> <i>Pbcn</i> Nb ₂ FeO ₆	-	metastable; about 66.7 at.% O; contains a small amount of hydrogen; labelled as “PbO ₂ -II” [Mas2]
* τ_1 , Fe ₂ Pb ₂ O ₅ 870 - ~650	<i>l**</i>	$a = 779$ $c = 1585$ $a = 780$ $c = 1582$	[1957Ber, 1962Mou] [1978Mex] labelled as “ δ ” [1962Mou]
* τ_2 , Fe ₄ PbO ₇ 880 - 750	<i>h**</i>	$a = 1186$ $c = 4714$	[1928Joh, 1962Mou] labelled as “ γ ” [1962Mou]
* τ_3 , Fe ₁₂ PbO ₁₉ ~1315 - ~760	<i>hP64</i> <i>P6₃/mmc</i>	$a = 588$ $c = 2302$ $a = 512$ $c = 2367$ $a = 588.5$ $c = 2306.6$ $a = 592$ $c = 2322$ $a = 587$ $c = 2312$	[1938Ade] in the Fe _{12.9} PbO _{22.9} epitaxial films deposited at $T = 600^\circ\text{C}$ [1997Dor] in the Fe ₁₂ PbO ₁₉ thin films deposited at $T = 700^\circ\text{C}$ [2001Dia] [2002Mar] [2002Mar] labelled as “ β ” [1962Mou]
* τ_4 , Fe ₁₀ Pb ₂ O ₁₇	-	-	[1955Coc]
* τ_5 , Fe ₁₀ PbO ₁₆	-	-	[1955Coc]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_6 , $\text{Fe}_8\text{PbO}_{13}$	h^{**}	$a = 662$ $c = 1019$	[1960Mar]
* τ_7 , $\text{Fe}_6\text{PbO}_{10}$	h^{**}	$a = 591$ $c = 2352$	[1978Mex]

Table 3: Values of Activity Coefficient and Interaction Parameters Referring to O [1995Li]

T [°C]	% {Pb} ^{Fe-Pb}	f°_{Pb}	e°_{Pb}
1550	0.31	3.23	– 0.50
1600	0.38	2.66	– 0.67
1650	0.43	2.31	– 0.76

Table 4: Investigations of the Fe–O–Pb Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1957Ber]	Magnet steel tester measurements	Residual magnetic induction, coercive force, magnetic energy
[1997Dor]	Vibrating sample magnetometer, SQUID magnetometer static magnetic techniques	Magnetic anisotropy, magnetic remanence, coercive field, saturation magnetization
[1998Cla]	Comparative Fe-57 Mössbauer spectroscopy	Dynamics of the 2b site
[1998Hua]	Magnetic resistivity measurements	Magnetic resistivity
[1999Hsu]	Magnetic resistivity measurements	Magnetic resistivity
[2000Dia]	Saturation magnetization and coercive field measurements	Saturation magnetization, coercive field
[2000Hsu]	Tunneling magnetoresistance measurements	Tunneling magnetoresistance
[2001Dia]	Saturation magnetization and coercive field measurements	Saturation magnetization, coercive field
[2002Mar]	Coercive field measurements	Coercive field
[2004Dia]	Saturation magnetization and coercive field measurements	Saturation magnetization, coercive field

Fig. 1: Fe-O-Pb.
The O-Pb phase diagram

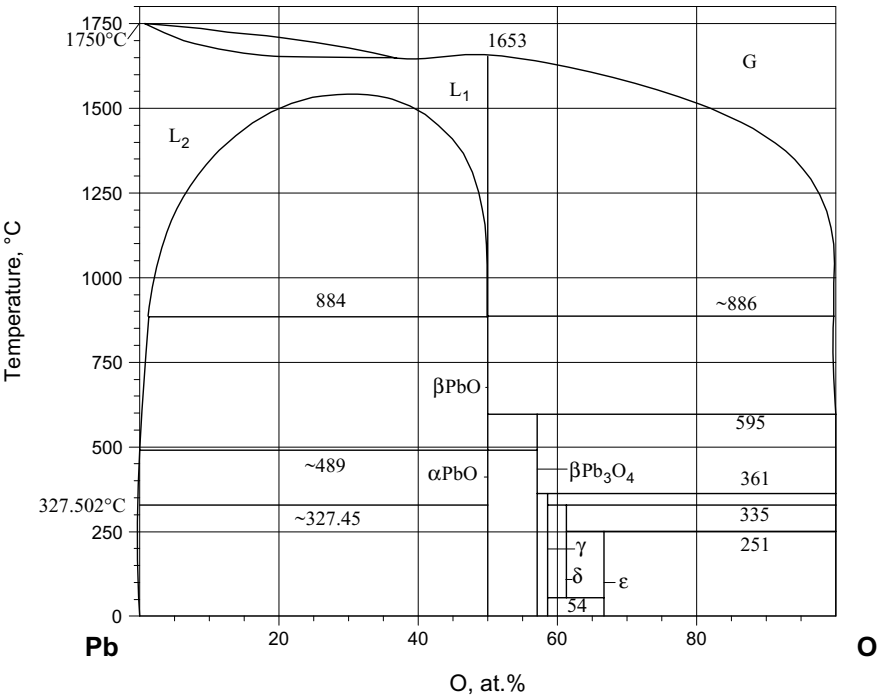


Fig. 2: Fe-O-Pb.
Lead solubility as a function of oxygen content in liquid iron at 1550, 1600 and 1650°C

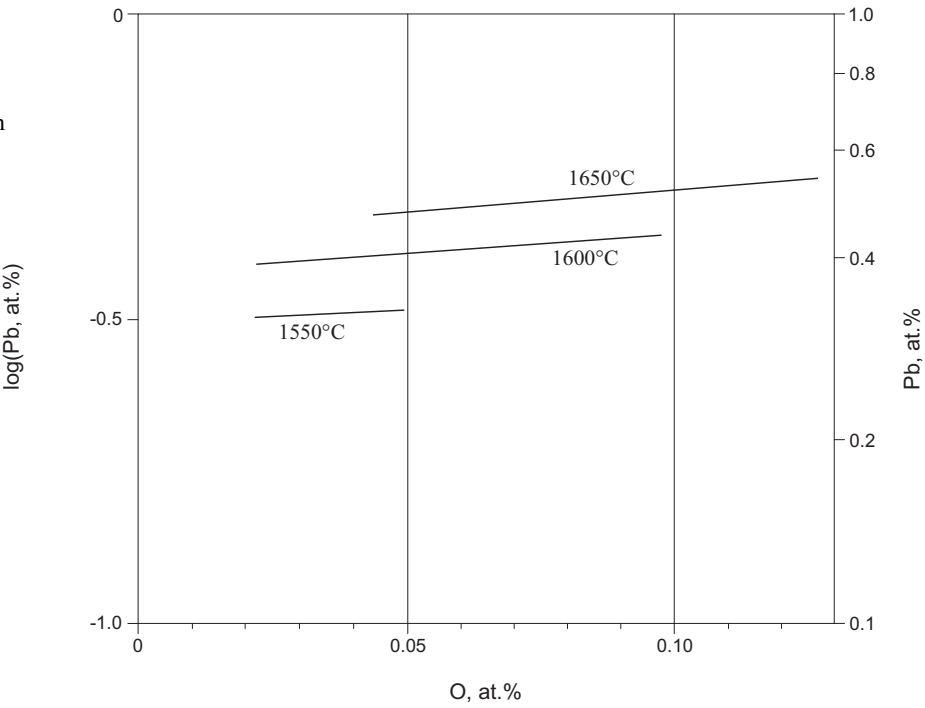
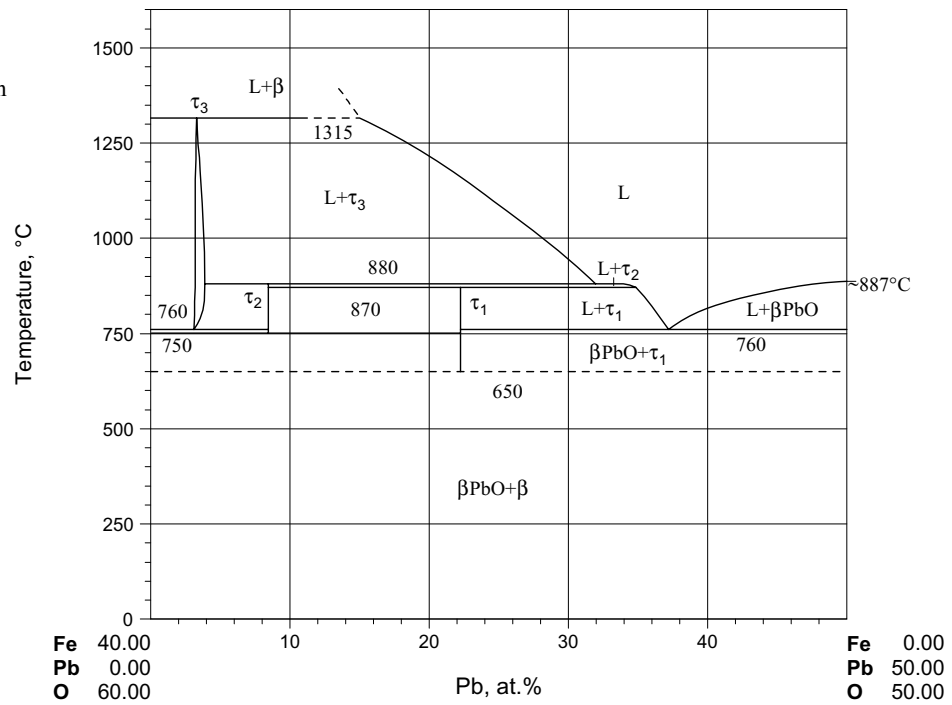


Fig. 3: Fe-O-Pb.
Temperature -
composition section
PbO-Fe₂O₃



Iron – Oxygen – Uranium

Pankaj Nerikar, Hans Jürgen Seifert, Pierre Perrot

Introduction

The Fe–O–U system is a key system in the disposal of nuclear waste where iron oxide is used with uranium waste and finds relevance in the prediction of high temperature phase behavior of corium. Two ternary compounds have been reported for the Fe–O–U system: UFeO_4 and UFe_2O_6 which seems to be stable only under high pressures [1978Col]. The experimental work is summarized in Table 1. The Fe–O–U ternary system was reviewed by [1989Rag]. [1964Eva] and [1983Smi] have constructed isothermal sections at different temperatures and partial pressures. [1973Buz] has reported the solubility of oxygen in (Fe,U) liquid alloys at 1600°C.

Binary Systems

The Fe–U and O–U binary systems are accepted from the critical assessments of [2003Cha] and [2004Che], respectively. A precise model of the solid and liquid oxide solutions taking into account the oxygen vacancies in the O–U system may be found in [2002Gue]. The O–U binary phase diagram from [2004Che] is presented in Fig. 1. The Fe–O phase diagram is accepted from the assessment by [1991Sun].

Solid Phases

The crystallographic data for the phases present in the Fe–O–U system and their ranges of stability are summarized in Table 2.

Invariant Equilibria

Table 3 lists the invariant reactions of the Fe–O–U ternary system from investigation of [1964Eva]. They have identified two ternary eutectic points which occur at oxygen partial pressures of 0.028 and 0.011 bar, respectively.

Isothermal Sections

[1989Rag] gave the Fe–O–U isothermal section at 400°C from the experimental investigations of [1983Smi]. This diagram, shown in Fig. 2, is compatible with the well known fact that Fe_3O_4 oxidizes into Fe_2O_3 at lower oxygen pressures than UO_2 oxidizes into U_4O_9 . Unfortunately, neither [1964Eva] nor [1983Smi] took into account the ternary compound UFeO_4 obtained from the reaction:

$$2\text{U}_3\text{O}_8 + 3\text{Fe}_2\text{O}_3 \rightleftharpoons \text{UFeO}_4 + 0.5\text{O}_2.$$

Temperature – Composition Sections

[1964Eva] have carefully investigated the equilibrium relationships between uranium and iron oxides as a function of oxygen pressure (586–21300 Pa) and temperature (1200–1460°C). Figures 3 to 8 show the projected isobaric sections under oxygen pressures of 21300 (air atmosphere), 7093, 3456, 1773, 892 and 586 Pa, respectively. It must be pointed out that the diagrams presented are not vertical sections because the phases in equilibrium are strongly dependent of the oxygen pressure. For instance, under air atmosphere Fe_2O_3 , stable under 1415°C loses its oxygen to give Fe_3O_4 above that temperature as shown in Fig. 3. The transition $\text{Fe}_2\text{O}_3 \rightleftharpoons \text{Fe}_3\text{O}_4$ occurs at 1359, 1328, 1306, 1289 and 1273°C under 7093, 3456, 1773, 892 and 586 Pa of oxygen pressure, respectively. In the same way, the transition $\text{U}_3\text{O}_8 \rightleftharpoons \text{UO}_2$ occurs at 1448, 1385, 1358, 1316 and 1296°C under 7093, 3456, 1773, 892 and 586 Pa of oxygen pressure, respectively. The three phases UO_2 – Fe_2O_3 – Fe_3O_4 coexist in the solid state at 1248°C under 200 Pa of oxygen pressure.

Notes on Materials Properties and Applications

The ferric-ferrous buffer (mixture $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3$) found naturally may be used to stabilize the state of oxidation IV of uranium [1983Smi].

Fe-U oxides can be used in an energetically efficient way as catalysts for the partial oxidation of propane and propene into formaldehyde which is an industrially important intermediate [2003Tay] in addition to the applications mentioned in the Introduction.

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Table 1: Investigations of the Fe-O-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1964Eva]	Thermogravimetric analysis under controlled oxygen pressures	$\text{UO}_2\text{-U}_3\text{O}_8\text{-Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$, 1260-1460°C, 586 to 21300 Pa of oxygen pressure
[1973Buz]	Interaction parameters measurements	Liquid Fe-O-U alloy (< 10 mass% U, <2 mass% O), 1600°C

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1978Col]	High pressure synthesis, X-ray diffraction	UFe ₂ O ₆ , 600°C, 3 GPa
[1983Smi]	X-ray diffraction	UO ₂ -U ₃ O ₈ -Fe ₂ O ₃ -Fe ₃ O ₄ , 400°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	at 25°C [Mas2]
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> β U	$a = 1075.9$ $c = 565.6$	at 25°C [Mas2]
(γ U) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352.4$	[Mas2]
(Fe) 1538 - 1394 < 912	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 286.65$ $a = 293.15$	at 25°C [Mas2] at > 1394°C [Mas2]
(γ Fe) 1394 - 912	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 364.67$	at 25°C [Mas2]
Fe ₂ U < 1235	<i>cF24</i> <i>Fd$\bar{3}m$</i> Cu ₂ Mg	$a = 705.5$	[2003Cha]
FeU ₆ < 829	<i>tI28</i> <i>I4/mcm</i> MnU ₆	$a = 1024.99$ $c = 525.00$	[2003Cha]
Fe _{1-x} O (wüstite) 1422 - 569	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	$a = 431.0$ $a = 429.3$	0.05 < x < 0.12 [1991Sun] $x = 0.05$ $x = 0.12$
Fe ₃ O ₄ (r) < 580	<i>oP56</i> <i>Pbcm</i> Fe ₃ O ₄ (r)	$a = 1186.8$ $b = 1185.1$ $c = 1675.2$	[V-C2]
Fe ₃ O ₄ (h) (magnetite) 1597 - 580	<i>cF56</i> <i>Fd$\bar{3}m$</i> MgAl ₂ O ₄	$a = 839.6$ $a = 854.5$	at 25°C at 1000°C [V-C2]
α Fe ₂ O ₃ (hematite) < 1451	<i>hR30</i> <i>R$\bar{3}c$</i> Al ₂ O ₃	$a = 503.42$ $c = 1374.83$	at 600°C [Mas2, V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\beta\text{Fe}_2\text{O}_3$	$cI80$ $Ia\bar{3}$ Mn_2O_3	$a = 939.3$	metastable phase [V-C2]
$\gamma\text{Fe}_2\text{O}_3$ (maghemite)	$tP60$ $P4_12_12$ Mn_5Si_2 (?)	$a = 833.96$ $c = 832.21$	metatable phase [V-C2]
UO_2 < 2852	$cF12$ $Fm\bar{3}m$ CaF_2	$a = 547.0$	from 62.7 to 66.7 at.% O [2004Che]
U_4O_9 < 1123	$cI832$ $I\bar{4}32$ or $I4_132$	$a = 2176$	[2004Che]
U_3O_8 < 1870	$oC44$ $Cmcm$	$a = 706.9$ $b = 1144.5$ $c = 830.3$	[2004Che]
UO_3 < 669	$cP4$ $Pm\bar{3}m$ ReO_3	$a = 414.6$	[2004Che]
* UFeO_4	oP^* $Pbcn$	$a = 488.80$ $b = 1193.7$ $c = 511.0$	[1989Rag]
* UFe_2O_6	hP^* $P\bar{3}1m$ PbSb_2O_6	$a = 504.0 \pm 0.1$ $c = 469.2 \pm 0.1$	[1978Col] High pressure phase (600°C, 3 GPa)

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				U	Fe	O
$\text{L} \rightleftharpoons \text{U}_3\text{O}_8 + \text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$	1318	E ₁	L	13.50	21.76	64.74
$\text{L} \rightleftharpoons \text{U}_3\text{O}_8 + \text{UO}_2 + \text{Fe}_3\text{O}_4$	1326	E ₂	L	14.65	20.75	64.60

Fig. 1: Fe-O-U.
Isothermal section at
400°C

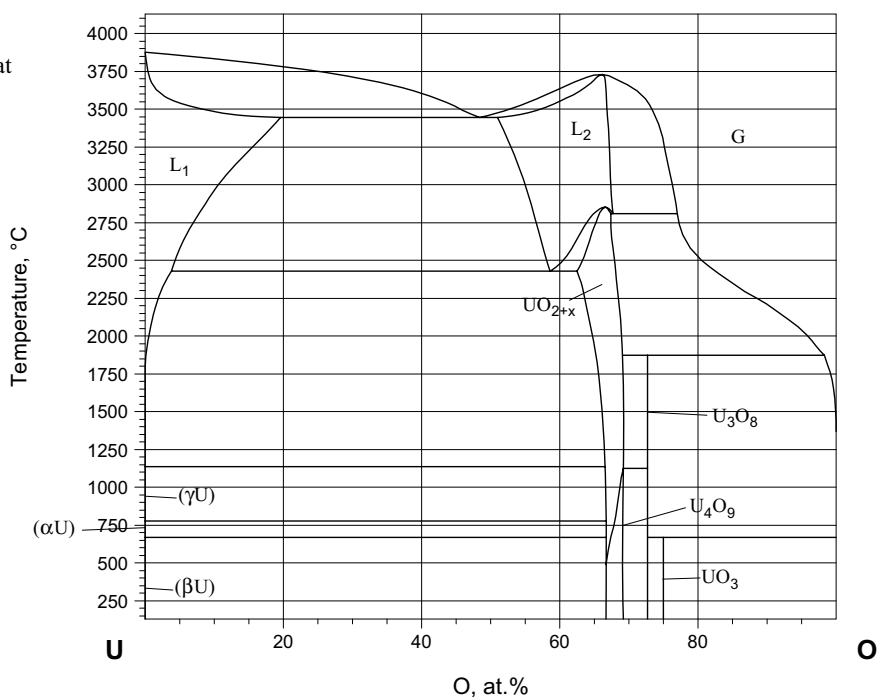


Fig. 2: Fe-O-U.
Isothermal section at
400°C

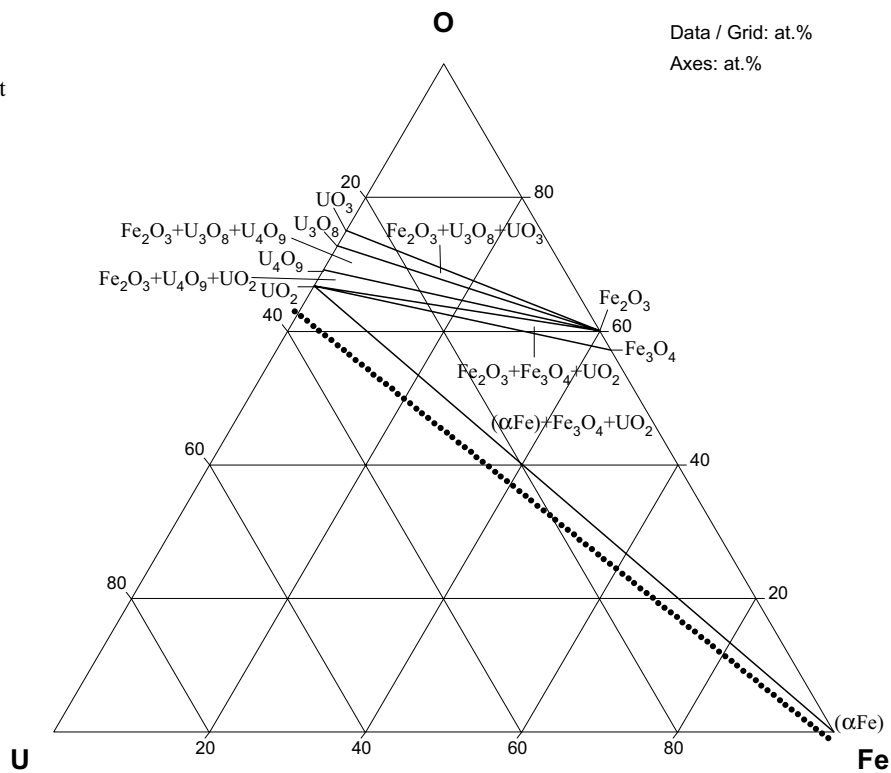


Fig. 3: Fe-O-U.
Isobaric section under
21300 Pa of oxygen
(1355 and 1415°C)

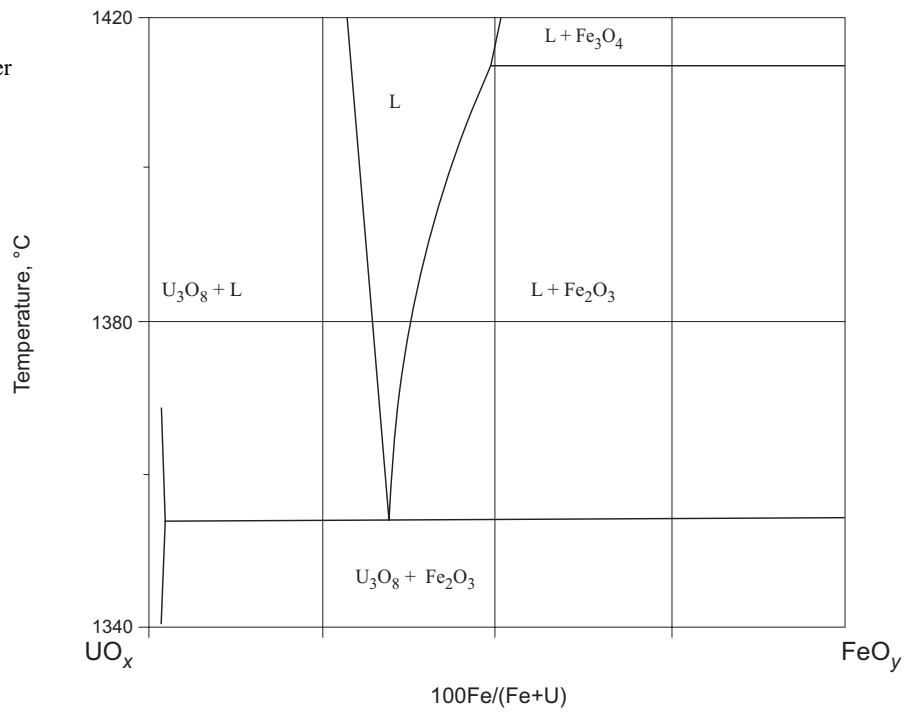


Fig. 4: Fe-O-U.
Isobaric section under
7093 Pa of oxygen
(1328, 1359 and
1448°C)

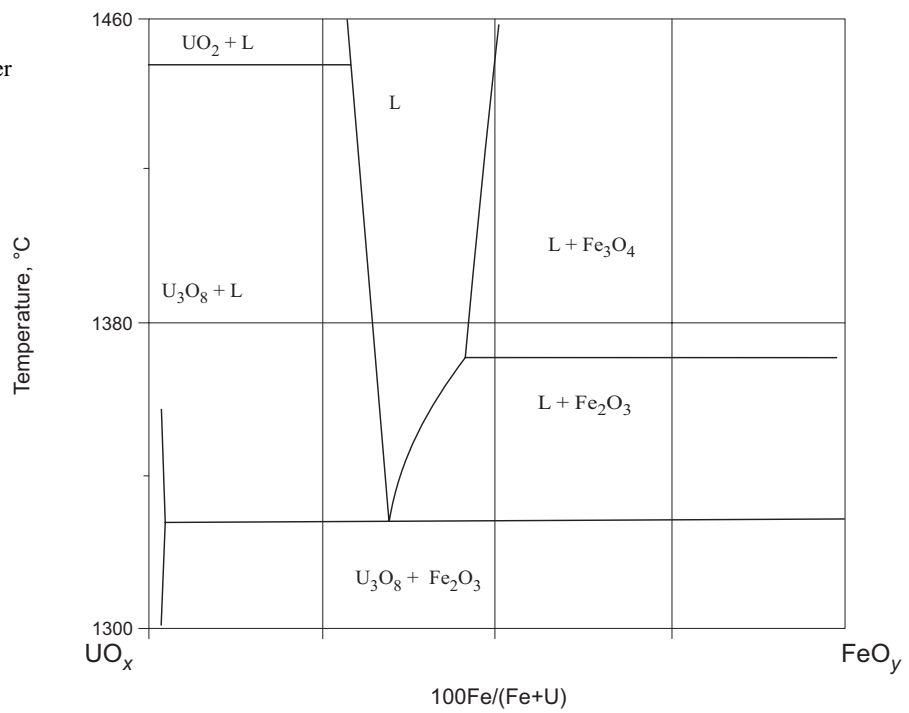


Fig. 5: Fe–O–U.
Isobaric section under
3456 Pa of oxygen
(1322, 1328 and
1385°C)

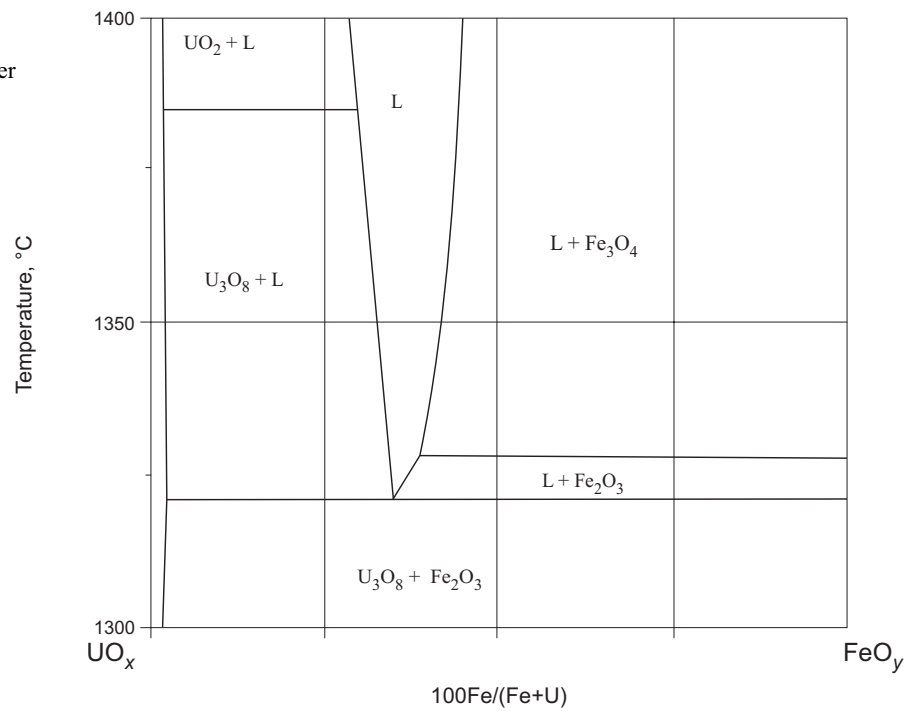


Fig. 6: Fe–O–U.
Isobaric section under
1173 Pa of oxygen
(1306, 1334 and
1358°C)

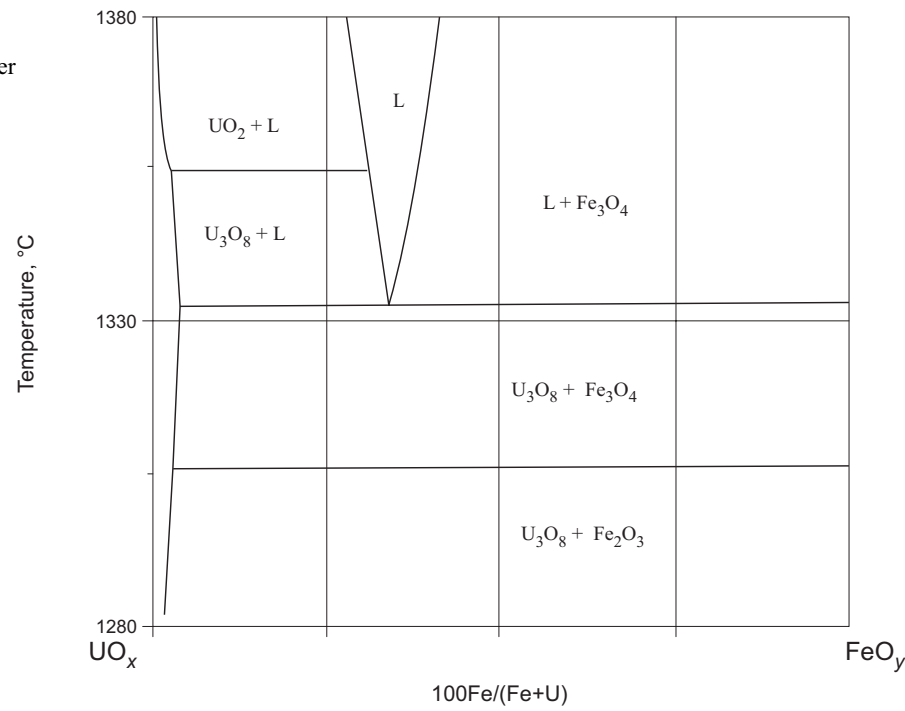


Fig. 7: Fe-O-U.
Isobaric section under
892 Pa of oxygen
(1289, 1316 and
1334°C)

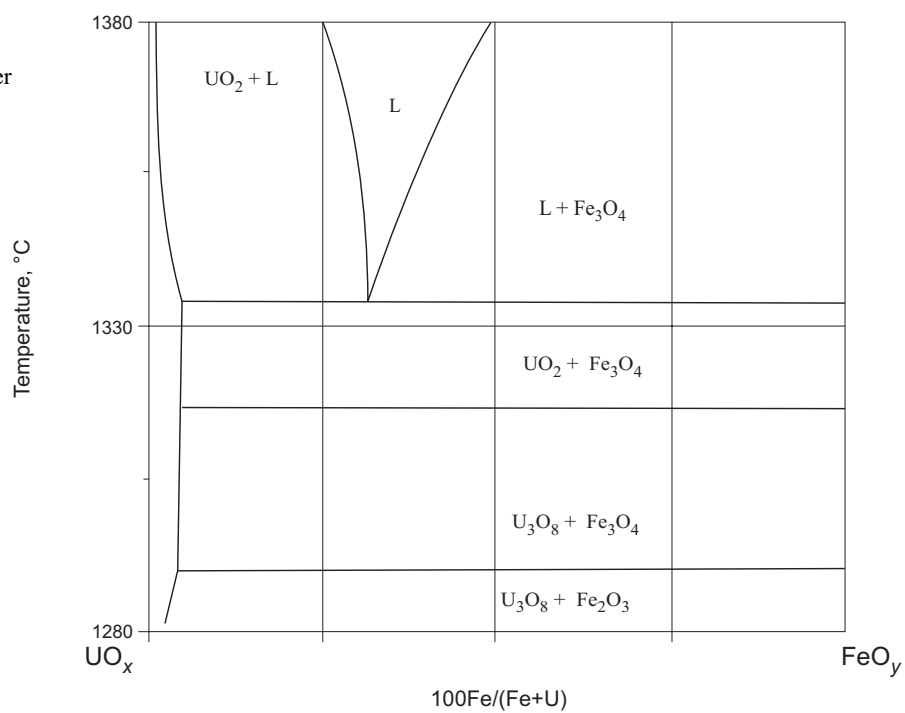
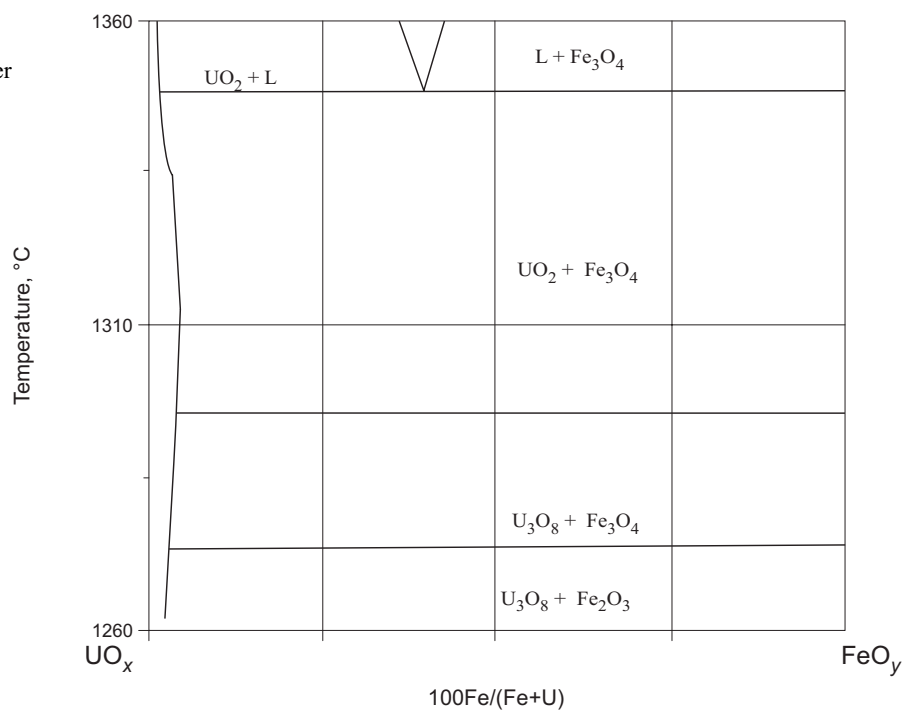


Fig. 8: Fe-O-U.
Isobaric section under
586 Pa of oxygen
(1273, 1296 and
1350°C)



Iron – Uranium – Zirconium

Olga Fabrichnaya

Introduction

The first experimental study of the Fe–U–Zr system was performed by [1965Wal] and partial isothermal section at 800°C was constructed. The detailed investigation of phase equilibria in the Fe–U–Zr system was undertaken by [1999Nak1]. The authors [1999Nak1] melted 17 alloy compositions in arc furnace under Ar atmosphere. The alloys were annealed between 800 and 580°C for 6–180 d and quenched in water. The phase equilibria were investigated by electron probe microanalysis (EPMA). The temperatures of phase transformations were determined by differential thermal analysis (DTA). [1999Nak2] carried out diffusion couple experiments at 635–715°C and determined phases that form in the reaction zone.

The first assessment of thermodynamic functions was performed by [1994Pel]. However occurrence of ternary phases in the system was not taken into account. [1998Kur] derived thermodynamic parameters for the Fe–U–Zr system based on binary description and adjusted parameters for two ternary phases (one ternary phase was not known at the time). His description was improved by [1999Nak1] by involving more experimental data obtained in their own work and taking into account all ternary phases.

The available experimental data and calculations were reviewed and critically evaluated by [2003Rag]. The information about experimental and theoretical investigation of the Fe–U–Zr system is presented Table 1.

Binary Systems

The phase diagram of the Fe–U binary system is accepted from the thermodynamic assessment of [2003Cha]. This diagram is derived by Calphad method taking into account experimental phase equilibrium data and measured thermodynamic properties. The calculated phase diagram agrees with the diagram from the review of [1993Oka]. The Fe–Zr binary system is accepted from experimental study of [2002Ste]. In this study it was shown that previously reported phase $\text{Fe}_{23}\text{Zr}_6$ in fact is stabilized by oxygen and is not an equilibrium phase. The U–Zr phase diagram accepted from [Mas2] originates from review of [1989She].

Solid Phases

The polymorphic modifications of Fe practically do not dissolve any U and Zr. The bcc continuous solid solution of (γU) and (βZr) can dissolve up to 8 at.% Fe in Zr reach area. In the Fe_2U cubic C15 Laves phase can be dissolved up to 5 at.% Zr. The cubic Fe_2Zr C15 Laves has homogeneity range of 27.5–34.4 at.% Zr in the binary Fe–Zr system and dissolves up to 7 at.% U. The FeU_6 tetragonal phase can dissolve up to 5 at.% Zr. The tetragonal phase FeZr_2 stable between 780 and 951°C in the binary Fe–Zr system can dissolve up to 10 at.% U. The FeZr_3 orthorhombic phase practically does not dissolve U and it is stable below 851°C.

There are three ternary compounds in the Fe–U–Zr system (τ_1 , τ_2 , τ_3) according to experimental data of [1999Nak1, 1999Nak2]. The crystal structure data for these phases are not known. The homogeneity ranges of τ_1 and τ_2 phases were determined by [1999Nak1] as 33–50 at.% Zr at constant Fe content of 33 at.% for τ_1 phase and as 21–25 at.% Zr at constant Fe content of 6 at.% for τ_2 phase. The τ_3 phase has practically constant composition of $\text{Fe}_{0.5}\text{U}_{0.18}\text{Zr}_{0.32}$ and it is stable up to at least 895°C. The τ_2 phase decomposes to τ_1 and ($\gamma\text{U}, \beta\text{Zr}$) at 726°C and the τ_1 phase melts at 933°C [1999Nak1].

Crystallographic data of all solid phases are given in Table 2.

Invariant Equilibria

Invariant equilibria in the Fe–U–Zr system were calculated by [1994Pel] for two limiting cases of mutual solubility of Fe_2U and Fe_2Zr . Experimental study of [1999Nak1] showed that ternary phases, which were not taken into account by [1994Pel] form equilibria with the liquid phase and therefore equilibria calculated by [1994Pel] do not correspond to the equilibrium state.

Liquidus, Solidus and Solvus Surfaces

Liquidus surface of the Fe-U-Zr system was calculated by [1994Pel]. However, two liquidus surfaces derived by [1994Pel] for the above mentioned cases are not reproduced in the present evaluation because they are in contradiction with experimental data of [1999Nak1] (see also chapter “Thermodynamics”).

Isothermal Sections

Isothermal sections at 580, 700 and 800°C were constructed based on experimental investigation by [1999Nak1]. The isothermal sections at these temperatures are presented in Figs. 1-3. They are redrawn from review of [2003Rag]. In this work [2003Rag] deleted the $\text{Fe}_{23}\text{Zr}_6$ phase taking into account data of [2002Ste] for the binary Fe-Zr system. The FeZr_2 phase was omitted at 580°C also based on the results of [2002Ste]. Experimentally indicated solubility of U in FeZr_2 at 800°C by [1999Nak1] is taken into account. The isothermal section at 700°C (Fig. 2) is redrawn here from [1999Nak1] making the same corrections as [2003Rag] made at 580°C. The main difference between the phase diagram at 580 and 700°C relates to phase transformations in the U-Zr system. The δ phase is not stable at 700°C and $(\gamma\text{U},\beta\text{Zr})$ solid solution decomposes into two phases (γ' and γ_2'') of different compositions (miscibility gap).

[1994Pel] calculated isothermal sections at 1000 and 1300°C considering two possible cases of complete solubility and zero mutual solubility between Fe_2Zr and Fe_2U . The isothermal sections at 1000 and 1300°C are presented at Figs. 4 and 5. They are tentatively redrawn from [1994Pel] taking into account limited mutual solubility of Fe_2Zr and Fe_2U and excluding Fe_3Zr as a non-equilibrium phase.

Thermodynamics

[1994Pel] computed ternary phase equilibria in the ternary system using the thermodynamic description from their own works. The intermediate phase δ in the U-Zr system was omitted, while the Fe_3Zr phase was included. The solubility of U in (Fe) and of Fe in (αZr) was neglected. The excess Gibbs energies in ternary liquid and solid phases were calculated from binary values using the Kohler and Toop equations, respectively. The liquidus surface and isothermal sections were calculated considering two limiting cases of complete solubility and zero solubility between Fe_2Zr and Fe_2U . Ternary phases were not considered by [1994Pel]. According to experimental data of [1999Nak1] ternary phases come to an equilibrium with liquid, thus the liquidus calculated by [1994Pel] seems to be in contradiction with data of [1999Nak1]. Also, Fe_3Zr is not an equilibrium phase according to the binary Fe-Zr system of [2002Ste] accepted in the present evaluation.

In the thermodynamic assessment of [1998Kur] two ternary phases τ_1 and τ_2 were taken into account. The calculations were based on the thermodynamic description of the binary systems. The Gibbs energies of τ_1 and τ_2 phases were adjusted to reproduce exactly the experimental tie lines in the ternary system. The phase τ_3 was not known when the work of [1998Kur] was performed. The experimental data of [1965Wal] for the partial isothermal section at 800°C and the results obtained at the first stages of experimental investigation of [1999Nak1] were used. The new thermodynamic calculations of isothermal sections was performed by [1999Nak1] using experimental results obtained in their own work. The τ_3 phase found by [1999Nak1] was included in calculations. The calculated results are in a good agreement with experimental data except for the Zr rich corner. Authors assumed that annealing time was not enough to reach equilibrium in experiments with Zr rich alloys.

Notes on Materials Properties and Applications

A metallic Pu-U-Zr alloy fuel has been recognized as a candidate for advanced fast reactor fuel. One of the key issue is a compatibility of fuel alloy with Fe based cladding materials. During irradiation the fuel alloy swells and comes into a contact with the cladding and metallurgical reactions occur at the fuel alloy - cladding interface. The authors of [2000Oga] conducted diffusion couple experiments at 650°C to study the influence of Pu content to liquid phase formation in the reaction zone. If a liquid phase is formed, it can degrade cladding integrity. The experiments showed the Pu content in $(\text{U,Pu})_6\text{Fe}$ phase is crucial factor in determining the conditions of liquid formation. Using Calphad technique a thermodynamic database for the

quaternary Fe–Pu–U–Zr system was derived by [2001Kur]. [2002Nak] presented phase relation data in the U rich region of the Fe–Pu–U–Zr system from annealing studies of quaternary alloys at 650°C. The samples were studied metallographically and by EPMA. Phase compositions were measured using energy dispersive X-ray detector (EDX). The thermodynamic description of the quaternary system was improved by [2002Nak] by including new experimental data (obtained in the same work) and by introducing the three-sublattice model accounting the solubility of Pu in the τ_2 phase. Predicted phase relations at other temperatures than 650°C are compared with the results of DTA and the applicability of calculated phase diagrams in other temperature regions was confirmed. [2005Nak] calculated phase diagrams for the U–Pu–Zr–Fe system at 800°C based on the established thermodynamic description [2002Nak].

The metallurgical interdiffusion zones at the interface between irradiated or unirradiated U–Pu–Zr metal fuel and stainless steel cladding at elevated temperatures in literature [1990Tsa, 1993Coh, 1994Sar] were analyses and interpreted using the calculated phase diagrams.

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Table 1: Investigations of the Fe-U-Zr Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1994Pel]	CALPHAD	Isothermal sections at 1100, 1300°C, liquidus surfaces for case ideal and zero solubility between Fe ₂ U and Fe ₂ Zr
[1998Kur]	CALPHAD	Isothermal section and potential diagram (activity of U vs activity Zr) at 700°C
[1999Nak1]	Arc-melting and annealing for 6-180 days, EPMA (electron probe micro-analysis), DTA (differential thermal analysis), CALPHAD	580, 700 and 800°C isothermal sections
[1999Nak2]	Diffusion couple, EPMA, CALPHAD	635, 650, 700, 715°C U-23at.% Zr/Fe

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(δFe) (h ₂) 1538 - 1394	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	<i>a</i> = 293.15	[Mas2]
(γFe) (h ₁) 1394 - 912	<i>cF4</i> <i>Fm</i> $\bar{3}m$ Cu	<i>a</i> = 364.67	at 915°C [V-C2, Mas2]
(αFe) < 912	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	<i>a</i> = 286.65	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(εFe)	<i>hP2</i> <i>P6₃/mmc</i> Mg	<i>a</i> = 246.8 <i>c</i> = 396.0	at 25°C, 13 GPa [Mas2]
(αU) < 668	<i>oC4</i> <i>Cmcm</i> αU	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	up to 0.05 at.% Fe and up to 0.5 at.% Zr at 25°C, pure U [Mas2]
(βU) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> βU	<i>a</i> = 1075.9 <i>c</i> = 565.6	up to 0.3 at.% Fe and up to 1.1 at.% Zr at 720°C, pure U [V-C2]
γ, (γU,βZr) (γU) 1135 - 762 (βZr) 1855 - 775	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 352.4 <i>a</i> = 360.9	up to 1.3 at.% Fe in U rich area and up to 4.2 at.% Fe in Zr rich area, maximal Fe ~7 at.% pure U [Mas2] pure Zr [Mas2]
(αZr) < 863	<i>hP2</i> <i>P6₃/mmc</i> Mg	<i>a</i> = 323.16 <i>c</i> = 514.75	up to 0.4 at.% U at 25°C pure Zr [Mas2]
Fe ₂ Zr < 1673	<i>cF24</i> <i>Fd$\bar{3}m$</i> Cu ₂ Mg	<i>a</i> = 702 to 709	27.5-34.4 at.% Zr, 0-7 at.% U [2002Ste]
Fe ₂ Zr 1345 - 1240	<i>hP24</i> <i>P6₃/mmc</i> MgNi ₂	<i>a</i> = 495 <i>c</i> = 1614	26.5-27 at.% Zr [2002Ste]
FeZr ₂ 951 - 780	<i>tI12</i> <i>I4/mmc</i> Al ₂ Cu	<i>a</i> = 638 <i>c</i> = 560	66.7-67.2 at.% Zr and up to ~10 at.% U at 66.7 at.% Zr and 0% U [2002Ste]
FeZr ₃ ≤ 851	<i>oC16</i> <i>Cmcm</i> BRe ₃	<i>a</i> = 332 <i>b</i> = 1100 <i>c</i> = 882	74.8-75.4 at.% Zr [2002Ste]
FeZr ₂	<i>cF96</i> <i>Fd$\bar{3}m$</i> NiTi ₂	<i>a</i> = 1221	O-stabilized [2002Ste]
Fe ₂₃ Zr ₆	<i>cF116</i> <i>Fm$\bar{3}m$</i> Mn ₂₃ Th ₆	<i>a</i> = 1172	O-stabilized 20.6-21.6 at.% U [2002Ste]
Fe ₂ U < 1236	<i>cF24</i> <i>Fd$\bar{3}m$</i> Cu ₂ Mg	<i>a</i> = 705.5	[V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
FeU ₆ < 831	<i>tI</i> 28 <i>I4/mcm</i> MnU ₆	<i>a</i> = 1024.99 <i>c</i> = 525	[V-C2]
δ, UZr ₂ < 617	<i>hP</i> 3 <i>P6/mmm</i> AlB ₂	<i>a</i> = 503 <i>c</i> = 308	63-78 at.% Zr at 66.67 at.% Zr [1989She]
* τ ₁ , Fe ₃₃ U _{67-x} Zr _x < 933	-	-	33-50 at.% Zr [1999Nak1]
* τ ₂ , Fe ₆ U _{92-x} Zr _x ? - 726	-	-	21-25 at.% Zr [1999Nak1]
* τ ₃ , Fe ₅₀ U ₁₈ Zr ₃₂ < 895	-	-	[1999Nak1]

Fig. 1: Fe-U-Zr.
Isothermal section at
580°C

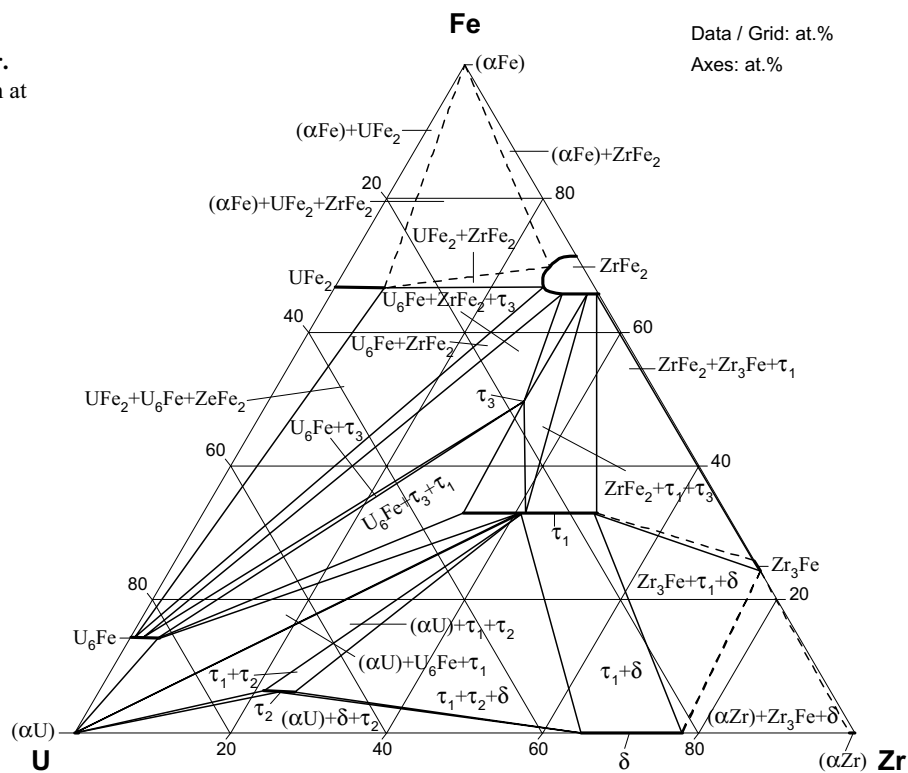


Fig. 2: Fe-U-Zr.
Isothermal section at
700°C

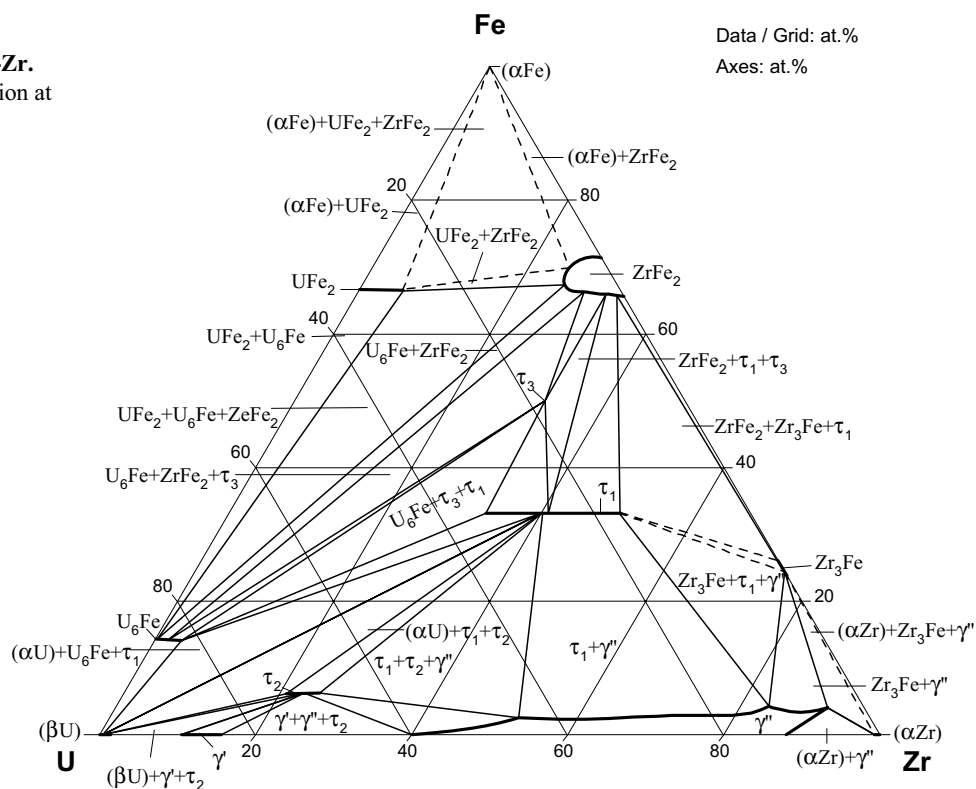


Fig. 3: Fe-U-Zr.
Isothermal section at
800°C

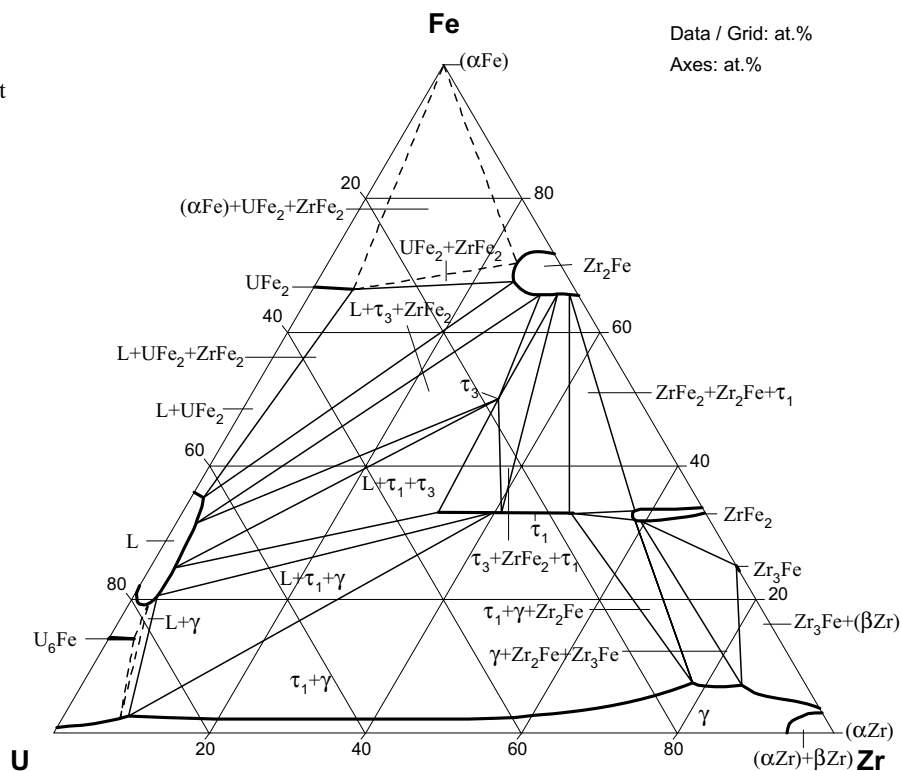


Fig. 4: Fe-U-Zr.
Isothermal section at
1000°C

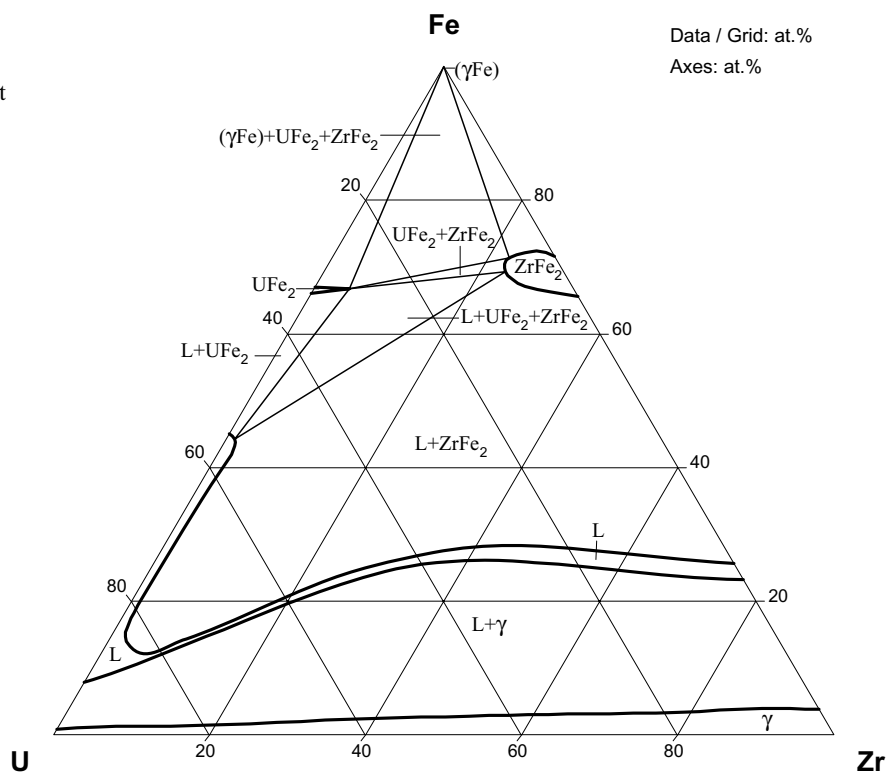
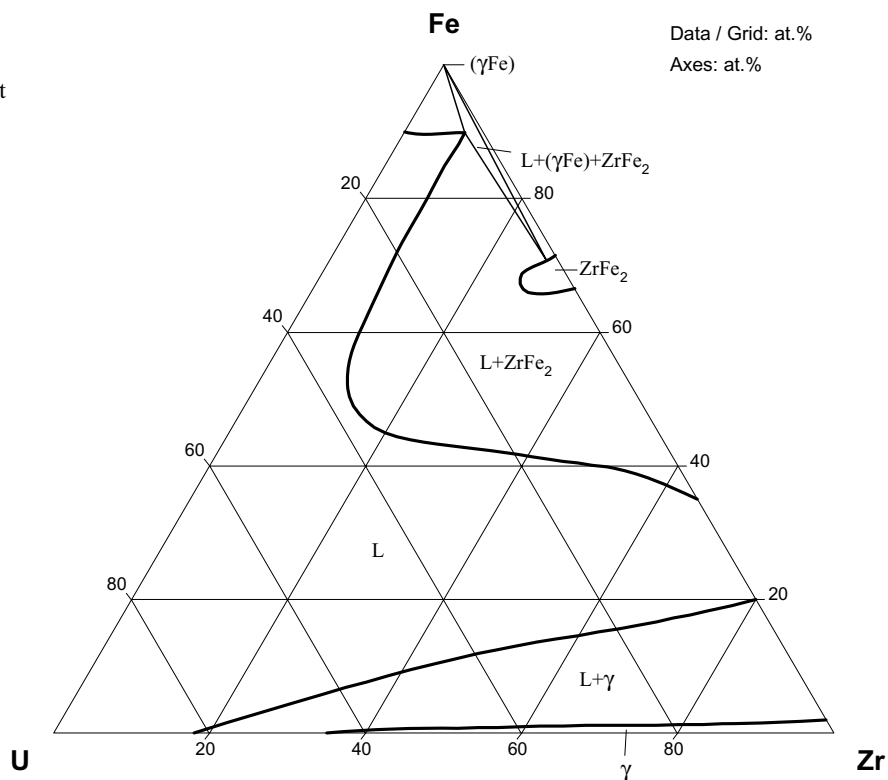


Fig. 5: Fe-U-Zr.
Isothermal section at
1300°C



Molybdenum – Oxygen – Uranium

Viktor Kuznetsov

Introduction

The interest to this system arose mainly from the fact that Mo is one of most abundant products of fission. So it plays an important role in the chemistry of reactor fuel [1984Cha, 1997Nic]. The interaction of Mo with uranium oxides was studied by [1964Geb1, 1964Geb2, 1974Jen, 1993Kle, 2004Mar] experimentally and also by [1997Nic] from more theoretical point of view. [1974Jen] tested possibility to obtain UO_{2+x} -Mo composite materials by unidirectional growth from the melts.

Another point of interest to the system is solid state chemistry of ternary oxides containing both U and Mo. [1965Kov] studied section UO_2 - MoO_2 - MoO_3 . 18 samples were annealed at various temperatures between 700 and 1000°C and studied by XRD. The results are presented in tabular form and as schematic section for 700 to 750°C. Three ternary phases were found and their crystal chemistry discussed basing on their X-ray characteristics (mainly lattice spaces); no detailed structure data were obtained. For the UMo_2O_8 phase a transformation at 1000°C was found by [1966Tru].

[1973Ser], [1974Ser1, 1974Ser2] performed analogous study of crystal chemistry (interrelation of structures through replacing U by Mo and formation of structural vacancies in the structure of $\beta\text{UMo}_2\text{O}_8$) of phases found in the section U_3O_8 - MoO_2 - MoO_3 , though in this case no data on phase equilibria seem to exist.

Crystal structures and complicated crystal chemistry of various mixed oxide phases were studied also by [1990Sun, 1994Sun, 1995Tab, 1996Dya, 2004Kri]. These authors also studied mainly synthesis and structure of particular compounds, and virtually no data on phase equilibria are provided. For structural studies high resolution electron microscopy (HREM) was widely used.

Two vertical sections in oxide part of the system are studied. [1967Efr] investigated by thermal analysis part of the section between UO_2 and MoO_3 (50 to 100 mol% of the latter, *i.e.* UMoO_5 - MoO_3). Two intermediate phases were found, in agreement with [1965Kov, 1966Tru].

The section UO_3 - MoO_3 was investigated by [1973Ust]. Samples were prepared from MoO_3 and U_3O_8 and heated to 600 to 1000°C on air. The presence of phase “ UO_2MoO_4 ” (= UMoO_6) indicated oxidation of U, so results were referred to the aforementioned section.

The review of crystal structures and phase relations of double oxides of U and Mo may be found in [1975Kel].

[1984Cha] investigated partial isothermal section at 1000 K in the region MoO_2 - UO_2 -O. They used XRD as well as emf measurement of O activity as a tool for investigation of composition of U oxide phases. Six ternary oxide phases were found.

Much attention was paid to determination of thermodynamic properties of some ternary oxides. [1984Cha] used their emf data for determination of the Gibbs energy of formation of UMoO_5 . Using phase diagram data they estimated $\Delta_f G$ at 1000 K also for UMoO_6 , U_2MoO_8 and UMo_2O_8 . [1985Tri] studied reaction of vaporization of UMoO_6 by transpiration method at 1110 to 1250 K and derived $\Delta_f G$ for that compound. [1986Dha] tried to do the same using thermogravimetric analysis for determining the beginning temperature of reversible reaction of UMoO_6 with CaO. [1987Swa] also performed emf investigation of O activity in the mixture of UMoO_5 and UMoO_6 . Basing on data of [1985Tri] for the latter, they derived thermodynamic properties of the former phase at 503 to 854°C. [2000Das] measured enthalpy increments for UMoO_6 at 26 to 727°C using high temperature Calvet microcalorimeter. Comparing the data of various authors for $\Delta_f H$ of UMoO_6 against proven empirical estimates, they chose the data of [1985Tri] for calculation of full set of thermodynamic properties of UMoO_6 including, in addition to $\Delta_f H$ and $\Delta_f G$, C_p , entropy, reduced Gibbs energy and reduced enthalpy for 25.15 to 1227°C.

[1985Tri] used own thermodynamic data to estimate a possibility of formation of a number of mixed U oxides during storage of nuclear wastes in the presence of lime.

[2000Abr] mentioned $\alpha\text{UMo}_2\text{O}_8$ amongst potential ferroelectrics which crystallize in the space group $P3$ and satisfy to other criteria of ferroelectricity.

[2002Kan] measured rate of oxidation of alloy U-10 mass% Mo on air at 200 to 500°C.

[2003Tay] did not found any catalytic effect of U/Mo mixed oxide for propane or propene oxidation.

Binary Systems

All the three binary systems are accepted from [Mas2].

Solid Phases

The solubility of Mo in uranium oxides is essentially zero in both solid and liquid state [1964Geb1, 1964Geb2, 1974Jen, 1993Kle]. The same seems to be true for the mutual solubility of U and Mo oxides.

The formation of at least 16 ternary phases (double oxides) is known. Unfortunately, rather few data for phase equilibria seem to exist. In particular, the range of thermal stability for most phases remains unknown. For the $\gamma\text{UMo}_2\text{O}_8$ phase obtained under hydrothermal conditions at low temperature [2004Kri] it is difficult to judge whether it is truly stable and present in the phase diagram.

For UMoO_5 the structural type UVO_5 was widely accepted in early works (including review [1975Kel]), but [1996Dya] established for this phase own structural type.

The known solid phases are listed in Table 2.

Isothermal Sections

The “schematic isothermal section for 700-750°C”, suggested by [1965Kov], as well as section at 727°C from [1984Cha], do not contain numerous phases, synthesized and investigated by [1990Sun, 1994Sun, 1995Tab, 1996Dya] at nearly the same temperature and therefore are not presented here.

Quasibinary Systems

Figure 1 presents a partial section $\text{UMoO}_5\text{--MoO}_3$ (part of section $\text{UO}_2\text{--MoO}_3$) from [1967Efr]. UMoO_5 decomposes peritectically to liquid and UO_2 at 1087°C. Two more ternary phases exist in the section in addition to UMoO_5 , namely UMo_2O_8 , formed by a peritectic reaction at 1040°C in a high temperature α modification, and $\text{UMo}_{10}\text{O}_{32}$. The $\alpha\text{UMo}_2\text{O}_8$ transforms into the $\beta\text{UMo}_2\text{O}_8$ at 1000°C. The $\text{UMo}_{10}\text{O}_{32}$ phase forms by peritectic reaction at 830°C. The temperature of the eutectic $\text{L} \rightleftharpoons \text{UMo}_{10}\text{O}_{32} + \text{MoO}_3$ is 780°C; its composition is estimated to be close to 1.5 mol% UO_2 . We accepted the change of composition from $\text{UMo}_{11}\text{O}_{35}$, as was suggested for that phase in [1967Efr], to $\text{UMo}_{10}\text{O}_{32}$ as was derived in structural works of the same group [1973Ser, 1974Ser1]).

Figure 2 presents the section $\text{MoO}_3\text{--UO}_3$ after [1973Ust]. The phase UMoO_6 forms by a peritectic reaction at 980°C. The eutectic reaction $\text{L} \rightleftharpoons \text{MoO}_3 + \text{UMoO}_6$ takes place at 740°C and about 14.6 mol% UO_3 (in the text of original work this value is claimed to be in mass%, but as seeing in the figure, this must be mol%).

Thermodynamics

Table 4 presents accepted values of the Gibbs energies of formation for UMoO_5 , UMoO_6 , U_2MoO_8 and $\beta\text{UMo}_2\text{O}_8$.

For the UMoO_5 phase results of [1984Cha] and [1987Swa], both obtained by emf, are in good agreement. The data for UMoO_6 include measurement of vapor pressure of $(\text{MoO}_3)_3$ above mixture of this phase with U_3O_8 [1985Tri], estimation of Gibbs energy at 1000K from that of UMoO_5 and phase equilibria data [1987Swa] and enthalpy increments, measured by [2000Das]. These data exhibit good mutual agreement and are accepted here; the results of [1986Dha] differ significantly and were rejected. The equation for enthalpy increments $H(T) - H(298.15)$ suggested by [2000Das] is given in Table 5; full table for 298.15 to 1500 K may be found in the original work.

The Gibbs energies of formation of U_2MoO_8 and $\beta\text{UMo}_2\text{O}_8$ at 1000 K are estimated by [1984Cha] from their data for UMoO_5 and phase equilibria.

Notes on Materials Properties and Applications

[1974Jen] tried to obtain eutectic composites UO_2 with several metals, including Mo, by unidirectional growth from melt. This failed for mixtures $\text{Mo}+\text{UO}_{2.21}$ as neither solubility nor even wetting was observed, but succeeded for $\text{Mo}+\text{UO}_{2.08}$.

[2002Kan] measured the rate of oxidation of Mo–U alloys on air.

Miscellaneous

[1985Tri] used their thermodynamic data for investigation of possibility of formation of double oxides of U and Mo during storing of nuclear wastes in presence of lime.

[2000Abr] predicted ferroelectric properties for $\alpha\text{UMo}_2\text{O}_8$.

[1997Nic] and [2004Mar] studied the state of Mo in UO_2 fuels.

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Table 1: Investigations of the Mo–O–U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1964Geb1, 1964Geb2]	XRD, metallography	800 to 2600°C, section Mo–UO _{2+x}
[1965Kov]	XRD	700 to 1000°C, UO ₂ –MoO ₂ –MoO ₃
[1966Tru]	XRD, lattice spacing	α UMo ₂ O ₈
[1967Efr]	Thermal analysis	Section UO ₂ –MoO ₃ (50 to 100 mol% of the latter)
[1973Ser]	XRD	UMo ₁₀ O ₃₂ and modifications of U ₃ Mo ₂₀ O ₆₄
[1973Ust]	Thermal analysis, XRD	Section UO ₃ –MoO ₃ (samples prepared from MoO ₃ and U ₃ O ₈ and heat treated on air)
[1974Jen]	Unidirectional growth from melt	UO _{2.14} –5 mass% Mo and UO _{2.07} –7 mass% Mo
[1974Ser1]	XRD	UMo ₁₀ O ₃₂ and modifications of U ₃ Mo ₂₀ O ₆₄
[1974Ser2]	XRD, crystal structure	α UMo ₂ O ₈
[1984Cha]	XRD, emf	The region MoO ₂ –UO ₂ –O, 727°C
[1985Tri]	Transpiration	UMoO ₆ , 827 to 977°C
[1986Dha]	Thermogravimetry, XRD	Temperature of beginning of reaction of UMoO ₆ with CaO for thermodynamic properties of the former
[1987Swa]	Emf with ZrO ₂ /CaO electrolyte	Mixture UMoO ₆ + UMoO ₅ , 503 to 854°C
[1990Sun]	HREM, XRD	UMo ₅ O ₁₆ phase
[1993Kle]	EPMA	Solubility of Mo in UO ₂ at 900°C
[1994Sun]	HREM, XRD	Samples of UMo ₅ O ₁₇ and UMo ₈ O ₂₆ gross composition, 970K, anneal for 4 d
[1995Tab]	XRD, HREM	Mixtures of UO ₂ +MoO ₂ +MoO ₃ 1:1:1.25 (annealed at 800°C) and 3:2:18 (hydrothermal synthesis at 5400°C, 500 bar plus re-heating of product at 800°C)
[1996Dya]	XRD and HREM	UMoO ₅ , crystal structure
[2000Das]	Calvet calorimetry	UMoO ₆ , 26 to 727°C
[2004Kri]	XRD	UMoO ₆ , after hydrothermal synthesis at 220°C, 65 h

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Mo) < 2623	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 314.70$	at 25°C [Mas2]
(γ U) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352.4$	[Mas2]
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> β U	$a = 1075.9$ $c = 565.6$	[Mas2]
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	at 25°C [Mas2]
MoO ₂ < 2300	<i>mP12</i> <i>P2₁/c</i> VO ₂	$a = 560.7 \pm 0.1$ $b = 486.0 \pm 0.1$ $c = 562.4 \pm 0.1$ $\beta = 120.94^\circ$	[Mas2, V-C2]
Mo ₄ O ₁₁ < 818	<i>oP60</i> <i>Pna2₁</i> Mo ₄ O ₁₁	$a = 2449$ $b = 675.2$ $c = 545.7$	[Mas2, V-C2]
Mo ₈ O ₂₃ < 818	<i>mP62</i> <i>P2/c</i> Mo ₈ O ₂₃	$a = 1340$ $b = 404$ $c = 1680$ $\beta = 106.1^\circ$	[Mas2, V-C2]
Mo ₉ O ₂₆ < 815	<i>mC280</i> <i>C2/c</i> Mo ₉ O ₂₆	$a = 2929.4 \pm 0.3$ $b = 808.3 \pm 0.1$ $c = 1681.6 \pm 0.3$ $\beta = 95.47 \pm 0.01^\circ$	[Mas2, V-C2]
MoO ₃ < 810	<i>oP16</i> <i>Pnma</i> MoO ₃	$a = 1385.5$ $b = 370.1$ $c = 396.2$	[Mas2, V-C2]
UO ₂	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF ₂	$a = 547.0$	[Mas2, V-C2]
U ₄ O ₉ < 1135	<i>cI832</i> <i>I4₁32</i> U ₄ O ₉	$a = 2176$	[Mas2, V-C2]
U ₃ O ₈	<i>hP11</i> <i>P$\bar{6}2m$</i> U ₃ O ₈	$a = 681.2 \pm 0.1$ $c = 414.2 \pm 0.1$	[Mas2, V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
UO ₃	<i>I</i> 64 <i>I</i> 4 ₁ / <i>amd</i> UO ₃	$a = 690.13 \pm 0.05$ $c = 1997.54 \pm 0.18$	[Mas2, V-C2]
* UMoO ₅ < 1087	<i>o</i> P28 <i>P</i> baa UMoO ₅	$a = 1274.6 \pm 0.1$ $b = 734.94 \pm 0.07$ $c = 412.52 \pm 0.02$	[1965Kov, 1967Efr, 1996Dya]
* UMoO ₆ < 980	<i>m</i> P32 <i>P</i> 21/ <i>c</i> UMoO ₆	$a = 720.0$ $b = 548.0$ $c = 1359$ $\beta = 104^\circ 36'$	[1973Ust]
* α UMo ₂ O ₈ 1040 - 1000	<i>h</i> P99 <i>P</i> 3 α UMo ₂ O ₈	$a = 1730$ $c = 614.5$	[1967Efr, 1974Ser2] ^{a)}
* β UMo ₂ O ₈ < 1000	<i>o</i> P44 <i>P</i> 2 ₁ 2 ₁ 2 β UMo ₂ O ₈	$a = 411.5$ $b = 732.7$ $c = 2008$	[1967Efr, 1973Ser] ^{a)}
* UMo ₇ O ₂₂	<i>o</i> *90	$a = 1975$ $b = 1436$ $c = 410.4$	[1965Kov]
* UMo ₁₀ O ₃₂ < 830	<i>o</i> C344 <i>C</i> ccm UMo ₁₀ O ₃₂	$a = 1618$ $b = 1448$ $c = 1974$	[1967Efr, 1973Ser, 1974Ser1]
* α U ₃ Mo ₂₀ O ₆₄	<i>o</i> C348 <i>C</i> ccm α U ₃ Mo ₂₀ O ₆₄	$a = 824.6$ $b = 2876$ $c = 1978$	[1973Ser, 1974Ser1]
* β U ₃ Mo ₂₀ O ₆₄	<i>o</i> P87 <i>P</i> ccm β U ₃ Mo ₂₀ O ₆₄	$a = 411.9$ $b = 1438$ $c = 1976$	[1973Ser, 1974Ser1]
* γ U _{1.5} Mo ₁₀ O ₃₂	<i>o</i> P43.5 <i>P</i> bmm γ U ₃ Mo ₂₀ O ₆₄	$a = 413.4$ $b = 1433$ $c = 987.3$	[1973Ser, 1974Ser1]
* UMo ₅ O ₁₆ (mon.)	<i>m</i> P22 <i>P</i> 2 UMo ₅ O ₁₆ (mon.)	$a = 990.26$ $b = 718.23$ $c = 413.40$ $\beta = 90.20^\circ$	[1990Sun, 1994Sun]
* UMo ₅ O ₁₆ (orth.)	<i>o</i> P22 <i>P</i> 222 UMo ₅ O ₁₆ (orth.)	$a = 988.50 \pm 0.07$ $b = 716.72 \pm 0.07$ $c = 413.32 \pm 0.03$	[1994Sun] structure determined on sample obtained under hydrothermal conditions and re-heated at 800°C
* U ₂ MoO ₈	<i>o</i> P44 <i>P</i> 2 ₁ 2 ₁ 2 U ₂ MoO ₈	$a = 673.4 \pm 0.6$ $b = 2324 \pm 1$ $c = 411.5 \pm 0.3$	[1975Kel] superstructure to U ₃ O ₈

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* U _{0.5} Mo ₄ O ₁₃	<i>o</i> *	$a = 726.2 \pm 0.3$ $b = 3223 \pm 2$ $c = 402.9 \pm 0.2$	[1994Sun]
* U _{0.5} Mo ₅ O ₁₆	-	-	structure is close to UMo ₅ O ₁₆ but with half of U positions vacant [1994Sun]
* U _{0.75} Mo ₅ O ₁₆	<i>oP</i> 21.75 <i>P</i> 222	$a = 990.00 \pm 0.08$ $b = 718.89 \pm 0.06$ $c = 410.74 \pm 0.04$	[1994Sun]
* U _{1.5} Mo ₁₃ O ₄₂	<i>o</i> *	$a = 720$ $b = 5220$ $c = 400$	[1994Sun]
* γ UMo ₂ O ₈	<i>oP</i> 11 <i>Pbca</i> UW ₂ O ₈	$a = 1019.09 \pm 0.07$ $b = 958.57 \pm 0.07$ $c = 1427.41 \pm 0.11$	[2004Kri] synthesized at 220°C by hydrothermal method; probably metastable

a) note: in [1967Efr] high-temperature modification is called β , in all other works α

Table 4: Thermodynamic Data of Reaction or Transformation

Reaction or Transformation	Temperature [°C]	Quantity, per mol of atoms [kJ, mol, K]	Comments
U + Mo + 5/2O ₂ $\rightleftharpoons$ UMoO ₅	503 - 854	$\Delta G = -1816.9 + 0.3748T$	[1987Swa], emf
U + Mo + 3O ₂ $\rightleftharpoons$ UMoO ₆	298.15	$\Delta H = -1975.2$ $\Delta G = -1824.0$	[1985Tri, 2000Das] tabulated for 298.15 to 1500K in [2000Das]
2U + Mo + 4O ₂ $\rightleftharpoons$ U ₂ MoO ₈	727	$\Delta G = -2433 \pm 8$	[1984Cha], estimated from data for UMoO ₅ , oxides of U and Mo and phase equilibria
U + 2Mo + 4O ₂ $\rightleftharpoons$ β UMo ₂ O ₈	727	$\Delta G = -1928 \pm 10$	[1984Cha], estimated from data for UMoO ₅ , oxides of U and Mo and phase equilibria

Table 5: Thermodynamic Properties of Single Phases

Phase	Temperature Range [K]	Property, per mole of atoms [J, mol, K]	Comments
UMoO ₆	298.15 to 1500	$H(T) - H(298.15) = -53928.8 + 158.65T + 21.443 \cdot 10^{-3}T(K) + 14.077 \cdot 10^5/T$	[2000Das]

Fig. 1: Mo-O-U.
The partial
quasibinary section
UO₂-MoO₃ for 50 to
100 mol% MoO₃
(UMoO₅-MoO₃)

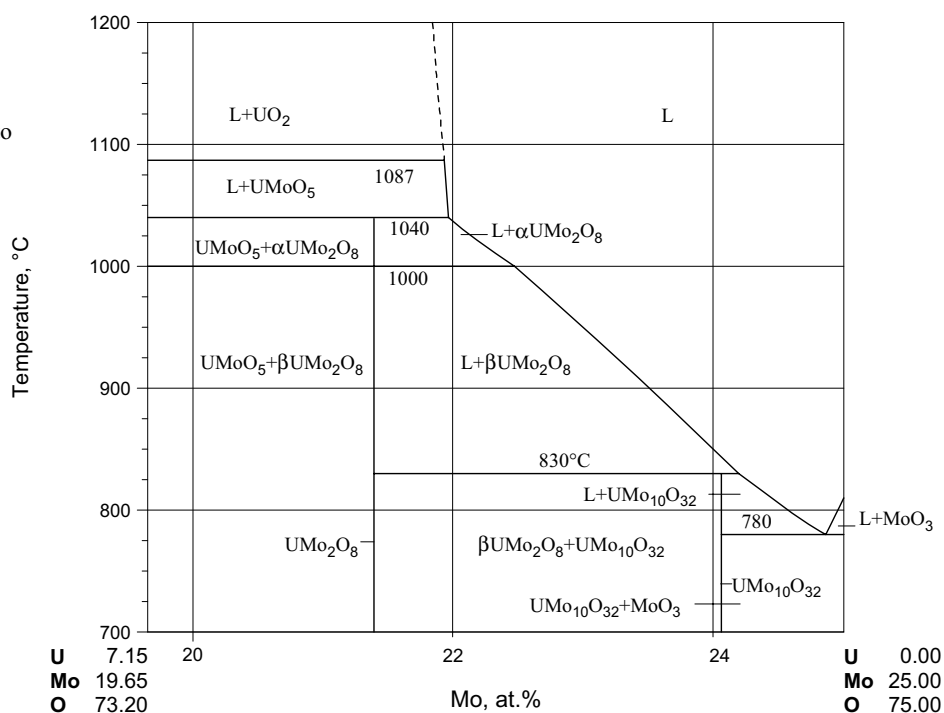
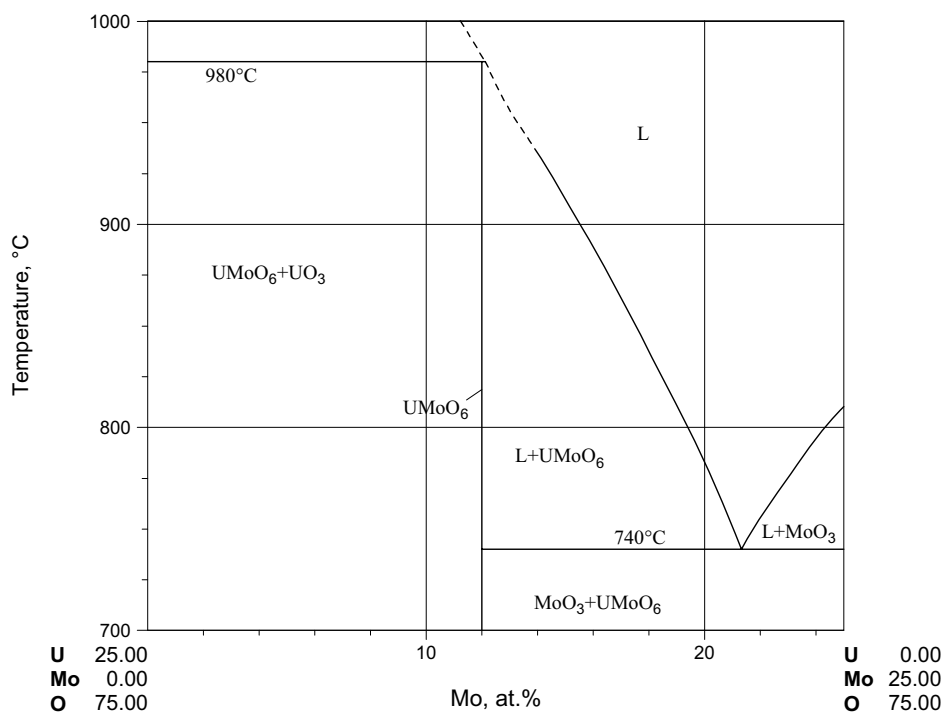


Fig. 2: Mo-O-U.
The quasibinary
section MoO₃-UO₃



Molybdenum – Ruthenium – Uranium

Gabriele Cacciamani

Introduction

Very scarce information is available on this system. A partial vertical section in the U rich corner has been reported by [1959Nev] and quoted as “unpublished work by Dwight”. [1959Nev] investigated the system Uranium-Fissium (where “Fissium” is a mixture of fission products the main components of which are just Molybdenum and Ruthenium). Isothermal equilibria in the U rich corner at 600 and 900°C have been have been reported by [1959Chi] as “unpublished information, Metallurgy Division ANL” and, successively, by [1972Iva].

Solid Phases

Crystallographic data and temperature interval of existence for the solid phases pertinent to the known ternary information are given in Table 1.

Isothermal Sections

The two partial isothermal sections reported by [1959Chi] and [1972Iva] are shown in Figs. 1 and 2. All equilibria are represented by dashed lines because they have to be considered uncertain. Their consistency with the vertical section reported by [1959Nev] is only approximate.

Temperature – Composition Sections

The only known temperature-composition section, reported by [1959Nev], is limited to the U rich region. It is shown in Fig. 3, slightly corrected with respect to the original diagram which presented a small phase rule inconsistency. This figure, as the previous ones, has to be considered with care.

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Mo) < 2623	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 314.70	at 25°C [Mas2]
(γ U) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 352.4	[Mas2]
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> β U	<i>a</i> = 1075.9 <i>c</i> = 565.6	[Mas2]
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	at 25°C [Mas2]
(Ru) < 2334	<i>hP2</i> <i>P6₃/mmc</i> Mg	<i>a</i> = 270.58 <i>c</i> = 428.16	at 25°C [Mas2]
U ₂ Ru < 937	<i>mP12</i> <i>P2/m</i> or <i>P21/m</i> U ₂ Ru	<i>a</i> = 1310.6 <i>b</i> = 334.3 <i>c</i> = 520.2 β = 96.16°	[V-C2]
MoU ₂ < ?	<i>tI16</i> <i>I4/mmm</i> MoSi ₂	<i>a</i> = 342.7 <i>c</i> = 983.4	[V-C2]

Fig. 1: Mo-Ru-U.
Partial isothermal
section at 600°C

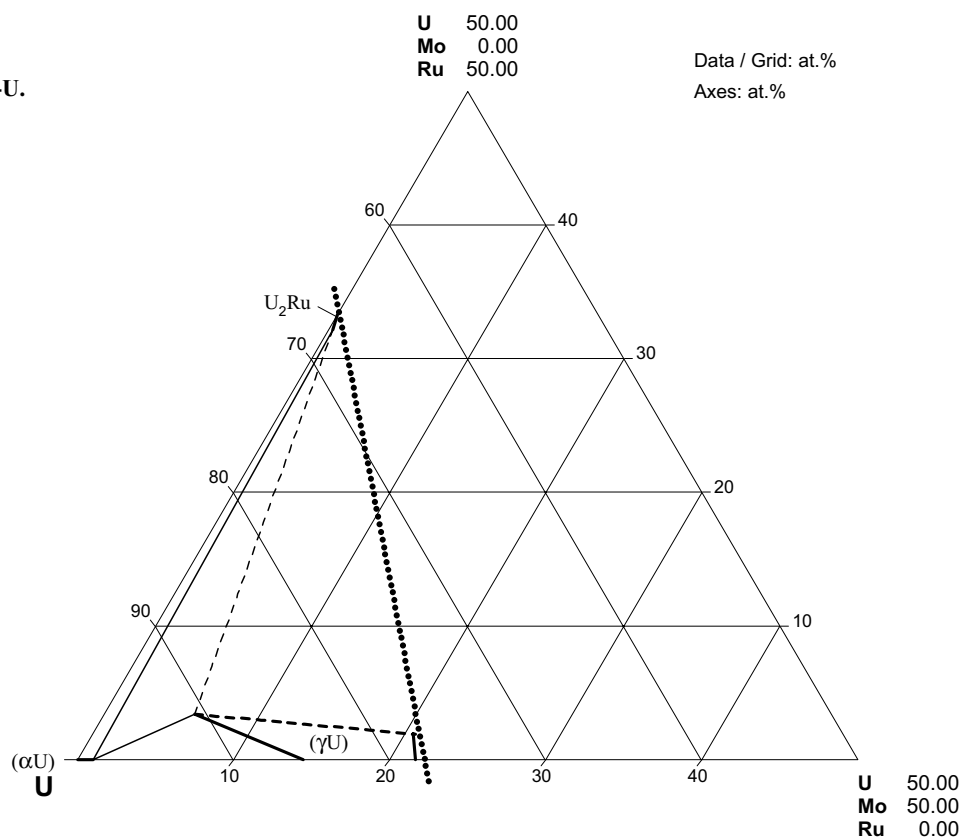


Fig. 2: Mo-Ru-U.
Partial isothermal
section at 900°C

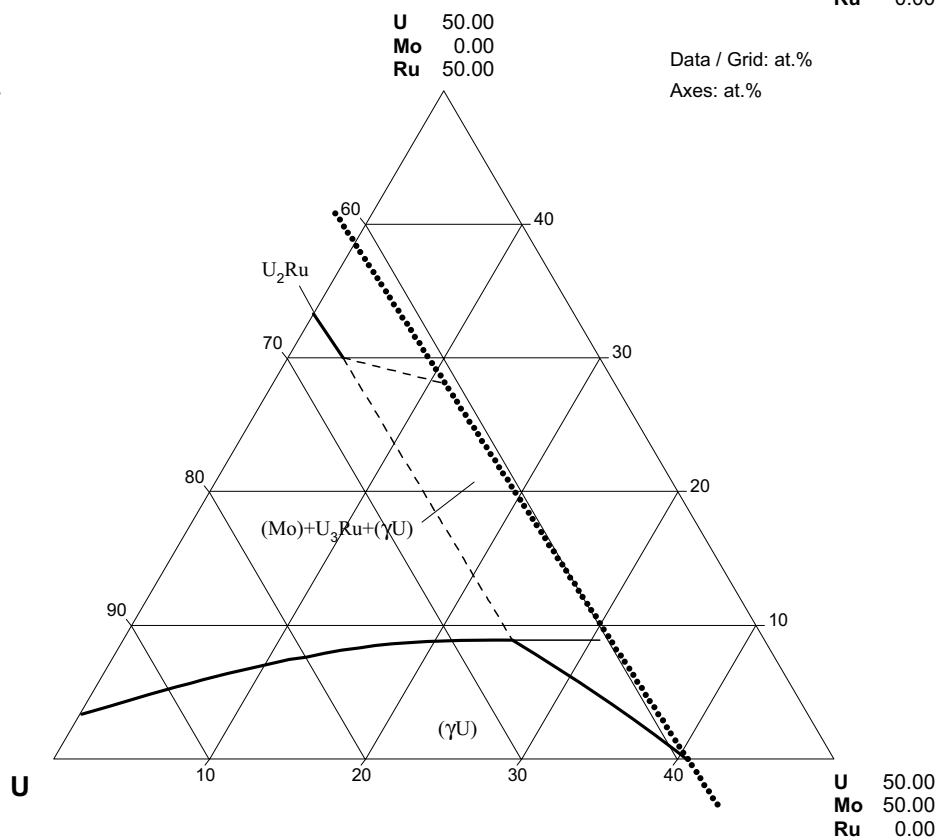
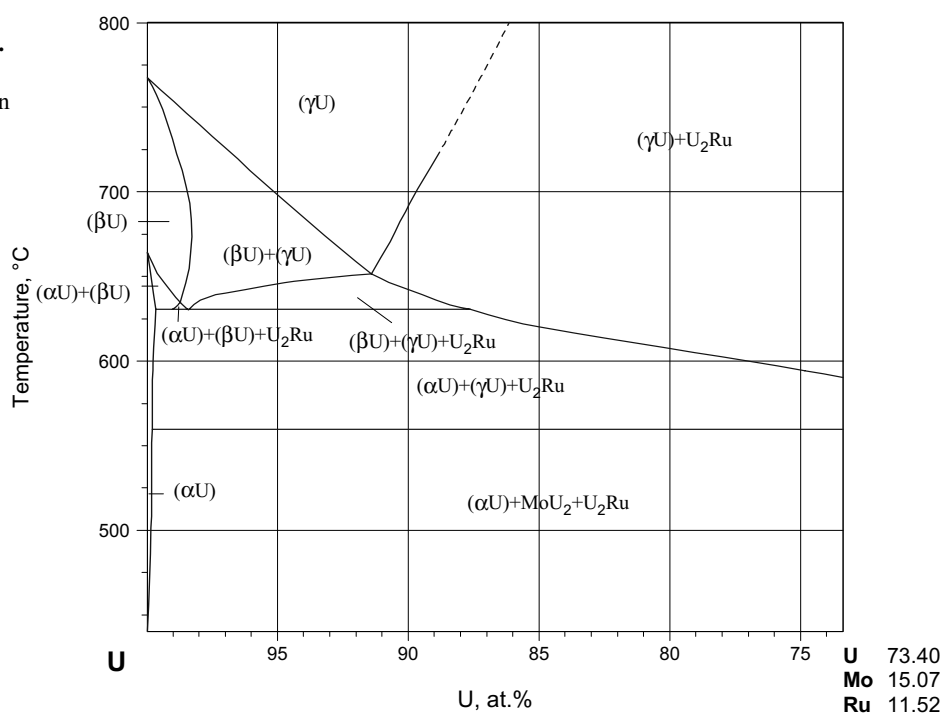


Fig. 3: Mo–Ru–U.
Partial temperature
-composition section
at 1:0.8 Mo:Ru
weight ratio



Molybdenum – Silicon – Uranium

Peter Rogl, Henri Noël

Introduction

Interest in low enriched uranium (LEU) proliferation resistant reactor fuel systems triggered investigations on phase equilibria and compatibility of U_3Si and U_3Si_2 with Mo-metal. Irradiation tests on U-4Mo-0.1Si (mass%) alloys discovered high swelling resistance in solution-quenched structures with effective control of fission-gas nucleation and bubble growth [1968Far].

Early reports on the ternary system mentioned the existence and crystal structure of two ternary compounds: a Laves-phase $\text{UMo}_{1.25}\text{Si}_{0.75}$ with the MgZn_2 type [1963Sik] and $\text{U}_2\text{Mo}_3\text{Si}_4$ with a unique structure type [1978Sik]. The crystal structures of both compounds were confirmed from X-ray single crystal counter data [1993LeB, 1995LeB, 1996LeB1]. To supplement the fission product chemistry in U_3Si_2 -fuel burn-up, partial phase equilibria in the U rich part of the diagram at 850°C were studied by [1994Uga] reporting the existence of three ternary compounds: $\text{U}_2\text{Mo}_3\text{Si}_4$, “ U_3MoSi_2 ”, “ U_4MoSi_3 ”, without defining the crystal structures of “ U_3MoSi_2 ” and “ U_4MoSi_3 ”. Based on a phase diagram investigation at 1400°C [1993LeB], phase relations were reinvestigated by [2001Rog] providing (i) a partial isothermal section at 1400°C for concentrations smaller than 70 at.% U, (ii) a partial isothermal section at 850°C for concentrations smaller than 70 at.% Si; and (iii) an evaluation of crystal structures from X-ray data. Physical properties (*i.e.* magnetic susceptibility and electrical resistivity) of the ternary compounds were reported from several sources [1988Ali, 1993LeB, 1994Was, 1995LeB, 1996LeB1, 1996Pat, 2001Rog]. The various experimental activities related to the constitution of the ternary Mo-Si-U system are summarized in Table 1.

Binary Systems

The binary boundary systems, Mo-U and Mo-Si, have been accepted from [Mas2]. The system U-Si is taken from reinvestigations by [1992Rem, 1993LeB, 1998Noe], but the U rich part of the diagram up to 4 at.% Si is from [1965Str]. A listing of the crystallographic and melting data pertinent to the Mo-Si-U system is given in Table 2.

Solid Phases

Three ternary compounds have been characterized by means of X-ray diffraction techniques: (i) stoichiometric $\text{U}_2\text{Mo}_3\text{Si}_4$ ($\text{Y}_2\text{Mo}_3\text{Si}_4$ type [1978Sik, 1993LeB, 1995LeB]), (ii) a ternary MgZn_2 type Laves phase $\text{U}(\text{Mo}_{1-x}\text{Si}_x)_2$ [1963Sik, 1993LeB, 1996LeB1] with a homogeneous region extending at 1400°C from $\text{UMo}_{1.25}\text{Si}_{0.75}$ to $\text{UMo}_{1.5}\text{Si}_{0.5}$ [1993LeB, 2001Rog], but with a rather small field of existence at 850°C ranging from $\text{UMo}_{1.32}\text{Si}_{0.68}$ to $\text{UMo}_{1.4}\text{Si}_{0.6}$ [2001Rog] and (iii) a novel ternary compound $\text{U}(\text{Mo}_y\text{Si}_{1-y})_2$ extending at 850°C from $y = 0.25$ to $y = 0.33$. For the latter compound a proper structural chemical formula, $\text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2$ ($0 < x < 0.33$), was derived from X-ray powder and single crystal data proving isotypism with the W_5Si_3 type and with statistical Mo/Si substitution only on the 4a sites [2001Rog]. Furthermore, it became obvious, that the phases labeled “ U_3MoSi_2 ”, “ U_4MoSi_3 ”, by [1994Uga], are both part of the same homogeneity region $\text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2$ ($0 < x < 0.33$) [2001Rog]. Accordingly, the X-ray powder pattern, reported by [1998Uga] for U_3MoSi_2 (and tentatively indexed by [1998Uga] as cubic with $a = 1069$ pm), was successfully re-indexed on the basis of the tetragonal W_5Si_3 type unit cell ($a = 1071.0$, $c = 533.6$ pm) [2001Rog]. The X-ray pattern of single phase U_3MoSi_2 after various heat treatments (1100°C for 5 days, 650°C for 5 days and 500°C for 22 days) was said to be unchanged, suggesting the absence of phase transitions in this temperature interval [2001Uga].

Unsuccessful attempts to prepare single-phase composition U_4MoSi_3 even after 8 days of annealing at 850°C were said to stem from the sluggishness of the reaction kinetics at this low temperature [1998Uga]. Although the ternary Laves phase, $\text{U}(\text{Mo}_{1-x}\text{Si}_x)_2$ ($0.25 < x < 0.375$), comprises the composition $\text{UMo}_{1.25}\text{Si}_{0.75}$ for which full atom order is expected, single crystal X-ray data refinement for $\text{UMo}_{1.25}\text{Si}_{0.75}$

showed a random distribution of Mo/Si atoms on both the 2a and 6h sites, but with slight preference of Mo atoms for the 6h site (1Mo + 1Si in 2a, 4Mo + 2 Si in 6h; $R = 0.018$) [1996LeB1]. The X-ray powder pattern of $\text{UMo}_{1.25}\text{Si}_{0.75}$ annealed at 1000°C and slowly cooled were said to be unchanged with respect to that from an alloy quenched from the melting point (ca. 2000°C) [1963Sik]. Furthermore, a DTA experiment from RT to 1000°C confirmed the absence of any signs for atom ordering or phase transition [1963Sik] in good agreement with Rietveld refinements of an X-ray powder spectrum of $\text{UMo}_{1.25}\text{Si}_{0.75}$ annealed at 850°C [2001Rog]. Lattice parameter data given for $\text{UMo}_{1.25}\text{Si}_{0.75}$ ($a = 537.0$, $c = 858.2$ pm) [1963Sik], however, seem to match rather the Mo rich part of the phase field [2001Rog] (see also Table 2). Whereas $\text{U}(\text{Mo}_{1-x}\text{Si}_x)_2$ ($0.25 < x < 0.375$) and $\text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2$ ($0 < x < 0.33$) exhibit solution ranges with Mo/Si substitution, the compound $\text{U}_2\text{Mo}_3\text{Si}_4$ only exists at its stoichiometric composition with full atom order [1978Sik, 1993LeB, 1994Was, 1995LeB].

Minor variations of unit cell dimensions of the boundary phases in ternary multiphase alloys annealed at 850°C or at 1400°C indicate negligible mutual solid solubility among binary uranium and binary molybdenum silicides (see also Fig. 1). This is particularly true for U_3Si_2 , which showed insignificant solubility for molybdenum (0.1 mass% Mo = 0.16 at.% Mo [1994Uga, 1998Uga], ≤ 0.5 at.% Mo [2001Rog]. Even in arc melted alloys the solubility of Mo in U_3Si_2 was measured (EMPA) to be less than ~ 1.6 at.% Mo [2001Rog]. Most of the binary boundary phases engage in two-phase equilibria with $\text{U}_2\text{Mo}_3\text{Si}_4$ inferring a relatively high thermodynamic stability of the ternary compound.

Invariant Equilibria

A peritectic formation of U_3MoSi_2 was proposed by [1994Uga, 1998Uga] via the invariant reaction $\text{U}_4\text{MoSi}_3 + \text{U}_2\text{Mo}_3\text{Si}_4 + \text{L} \rightleftharpoons \text{U}_3\text{MoSi}_2$ at $1480 \pm 30^\circ\text{C}$; the corresponding composition of the peritectic liquid was given as 74U16Mo10Si (in at.%). However, with the conclusion that the phases labeled “ U_3MoSi_2 ”, “ U_4MoSi_3 ”, by [1994Uga, 1998Uga], are both part of the same homogeneity region $\text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2$ ($0 < x < 0.33$) [2001Rog], the peritectic reaction given by [1998Uga] needs to be corrected. Playing on the facts, that the microstructures of both as-cast alloys, U_4MoSi_3 and U_3MoSi_2 , contain primary precipitates of U_3Si_2 [2001Rog], the peritectic formation of the phase $\text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2$ was reformulated as $\text{L} + \text{U}_3\text{Si}_2 + \text{U}_2\text{Mo}_3\text{Si}_4 \rightleftharpoons \text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2$, x being close to $x = 0.33$ [2001Rog]. $\text{U}_2\text{Mo}_3\text{Si}_4$ was described as congruently melting compound [1993LeB, 1995LeB, 1998Uga].

Liquidus, Solidus and Solvus Surfaces

No information is available on liquidus, solidus or solvus surfaces. Silicon-poor alloys with less than 20 at.% Si at 1400°C appeared partially molten [2001Rog]. Eutectic islands in the as-cast microstructure of U_4MoSi_3 , evaluated by EMPA area scans, were reported at a composition 74U10Mo14Si [2001Rog], rather close to the peritectic liquid claimed by [1998Uga].

Isothermal Sections

Phase equilibria have been established in an isothermal section at 1400°C for the region with less than 70 at.% U and at 850°C for the region with less than 70 at.% Si [2001Rog]. The isothermal sections are presented in Figs. 1 and 2.

At 1400°C two ternary compounds were encountered: stoichiometric $\text{U}_2\text{Mo}_3\text{Si}_4$ and the Laves phase extending in a homogeneity region $\text{U}(\text{Mo}_{1-x}\text{Si}_x)_2$ from $x = 0.25$ to $x = 0.375$. Si poor alloys (< 20 at.% Si) were found to be molten. Mutual solid solubilities between binary uranium and molybdenum silicides from EMPA were said to be negligible, and solubility of Mo in U_3Si_2 was less than 0.5 at.% Mo [2001Rog].

Phase equilibria at 850°C are characterized by three ternary compounds: $\text{U}_2\text{Mo}_3\text{Si}_4$, the ternary Laves phase $\text{U}(\text{Mo}_{1-x}\text{Si}_x)_2$ with a reduced homogeneity region from $x = 0.30$ to $x = 0.33$, and the ternary phase $\text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2$ with a homogeneity region from $x = 0$ to $x = 0.33$. The detailed investigation [2001Rog] showed that the phases “ U_3MoSi_2 ”, “ U_4MoSi_3 ” - reported by [1994Uga, 1998Uga] as individual compounds - were in fact part of one single-phase region $\text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2$. The microstructure data of a set of alloys (annealed at 850°C) listed by [1998Uga], i.e. 25U25Mo50Si, 50U10Mo40Si, $\text{U}_3\text{Si}_2 + 0.5$

(2.0, 3.0, respectively) mass% Mo and $\text{U}_3\text{Si} + 5$ mass% Mo, were all compatible with the phase triangulation in the isothermal section at 850°C as given by [2001Rog]. Due to the formation of ternary phases, U_3MoSi_2 and $\text{U}(\text{Mo}_{0.67}\text{Si}_{0.33})_2$, within the join U_3Si_2 - Mo no equilibrium exists between Mo and U_3Si_2 [1998Uga, 2001Rog]. Similarly, the observed two-phase equilibria, $\text{U}_2\text{Mo}_3\text{Si}_4 + (\gamma\text{U},\text{Mo},\text{Si})$, $\text{U}(\text{Mo}_{0.67}\text{Si}_{0.33})_2 + \gamma(\text{U},\text{Mo},\text{Si})$, $\text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2 + (\gamma\text{U},\text{Mo},\text{Si})$, excluded thermodynamic compatibility between Mo and U_3Si [2001Rog]. Below about 925°C U_3Si ties with the Si poor end of $\text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2$ [1994Uga, 2001Rog]. It should be mentioned, that $(\gamma\text{U},\text{Mo},\text{Si})$ in quenched alloys was easily retained at room temperature, although binary $(\gamma\text{U},\text{Mo})$ is metastable below about 550°C [2001Rog]. The vertex of the three-phase equilibrium $(\text{U}) + \text{U}_3\text{Si} + \text{U}_3\text{MoSi}_2$ at the U-metal at 850°C was given by [1998Uga] as 0.4 mass% Mo and 0.1 mass% Si (98.2U1.0Mo0.8Si in at.%).

Miscellaneous

[1964Kam] studied various analytical methods for chemical analysis of U, Mo, Si in nuclear materials. Metallographic studies and hot-hardness measured on an alloy U-350 ppm Fe - 350 ppm Si - 800 ppm Al - 1000 ppm Mo, aged 100 h at 600°C , revealed the formation of $\text{UMo}_{1.25}\text{Si}_{0.75}$ (no further details given) [1965Far]; the addition of Mo to the base alloy U-350 ppm Fe - 350 ppm Si - 800 ppm Al was said to cause an insignificant hardness change. It was observed that $\text{UMo}_{1.25}\text{Si}_{0.75}$ is relatively insoluble in (γU) at 800°C [1965Far]. From various irradiation tests on U - 4mass% Mo - 0.1mass% Si alloys, metal fuels with high swelling resistance were envisaged: the solution-quenched structures (24 h 1100°C or 1050°C , respectively and water quenched) resulted in effective control of fission-gas nucleation and bubble growth [1968Far]. The effect of 0.1 to 0.5 mass% Mo-additives on the corrosion resistance of U_3Si against water at 300°C under 90 MPa was investigated by [1993Kon]. The speed of corrosion was measured for various length of time from 100 to 1000 h. After 300 h the speed of corrosion for instance for the alloys with 0.4 mass% Mo was given as $0.3 \text{ mg}/(\text{cm}^2\text{h})$. Molybdenum seems to decrease the rate of corrosion with amount (from 0.1 to 0.4 mass% Mo) and with time.

Physical properties (*i.e.* magnetic susceptibility and electrical resistivity) of the ternary compounds were reported from several sources [1988Ali, 1993LeB, 1994Was, 1995LeB, 1996LeB1, 1996Pat, 2001Rog], which all agree on a weakly almost temperature independent paramagnetism of all the three ternary compounds. $\text{U}_2\text{Mo}_3\text{Si}_4$ is temperature independent paramagnetic below 30 K but weakly paramagnetic above 50 K with $\mu_{\text{eff}} = 2.30 \text{ } \mu\text{B}/\text{U}$, $\Theta_{\text{p}} = -240 \text{ K}$ and $\chi_0 = 1.4 \cdot 10^{-3} \text{ emu}\cdot\text{mol}^{-1}$ [1993LeB]. These data supersede earlier measurements of [1988Ali] claiming weak paramagnetism in the range $100 < T < 250 \text{ K}$ with $\mu_{\text{eff}} = 0.42 \text{ } \mu\text{B}/\text{U}$. The small abrupt increase in magnetic susceptibility at 40 K (however, no transition to magnetic ordering seen in resistivity data) was attributed to an impurity phase [1988Ali]. Alternatively, the authors of [1996Pat] attributed the “anomalous” susceptibility behavior to crystal field influences. All authors [1988Ali, 1993LeB, 1994Was, 1996Pat] agree on the fact, that no intrinsic magnetic order arises in $\text{U}_2\text{Mo}_3\text{Si}_4$ above 1.5 K. $\text{UMo}_{1.25}\text{Si}_{0.75}$ is temperature independent paramagnetic for the temperature range from 5 to 300 K with $\chi_0 = 4.3 \cdot 10^{-3} \text{ emu}\cdot\text{mol}^{-1}$ [1993LeB]. $\text{U}_4\text{Mo}(\text{Mo}_{0.33}\text{Si}_{0.67})\text{Si}_2$ is temperature independent paramagnetic with $\chi_0 = 2.7 \cdot 10^{-3} \text{ emu}\cdot\text{mol}^{-1}$ exhibiting a slight increase of susceptibility below 180 K [2001Rog].

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Table 1: Experimental Investigations of the Mo-Si-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1963Sik]	Electron beam melting of cold-compacted elemental powder mixtures yielded single phase $UMo_{1.25}Si_{0.75}$. Heat treatment at 1000°C with slow cooling to 300°C for 170 h DTA from RT to 1000°C.	X-ray powder refinement for $U(Mo,Si)_2$ at 33U42Mo25Si (in at.%); $MgZn_2$ type
[1964Kam]	Determination of U, Mo, Si in various U-Mo-silicides by chemical analyses.	For analysis, the silicide was decomposed by (i) with sodium peroxide, (ii) dissolved in a mixture of $HF+H_2SO_3$; (iii) dissolved in a mixture of $HF+HNO_3$.
[1965Far]	Alloy U-350 ppm Fe - 350 ppm Si - 800 ppm Al - 1000 ppm Mo, aged 100 h at 600°C.	Metallography and measurement of hot-hardness.
[1968Far]	Alloys U- 4mass% Mo - 0.1 mass%, were heat treated for 24 h at 1100°C, water-quenched, annealed for 240 h at 670°C, air cooled prior to irradiation (at 550°C and 645°C, respectively) up to 0.8 at.% and 1.4 at.% burnup, respectively. Selected specimens were irradiated at 400 to 510°C to 0.5 at.% burnup. Metallography and measurement of volume increase.	Investigation of swelling after various irradiation treatments. Control of fission gas bubble nucleation.
[1978Sik]	Arc melted alloy $U_2Mo_3Si_4$	Determination of the crystal structure of $U_2Mo_3Si_4$ from X-ray single crystal data
[1988Ali]	No details given on alloy preparation. Measurement range for ρ and χ : $4.2 < T < 300$ K	Electrical resistivity and magnetic susceptibility of $U_2Mo_3Si_4$

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1993LeB]	Arc melting of elemental ingots; heat treatment at 1400°C. A single crystal of $\text{U}_2\text{Mo}_3\text{Si}_4$ was obtained from an alloy annealed for long time at 1450°C in an argon-sealed Mo-crucible. Prolonged annealing of an as cast alloy yielded a single crystal of $\text{UMo}_{1.25}\text{Si}_{0.75}$. X-ray single crystal counter data for structure determination. Measurement range for ρ and χ : $2 < T < 300$ K; magnetization at 5 K up to 6 Tesla.	Partial phase equilibria at 1400°C for compositions < 60 at.% U. Determination of the crystal structures of $\text{U}_2\text{Mo}_3\text{Si}_4$ ($R_F = 0.07$) and $\text{UMo}_{1.25}\text{Si}_{0.75}$ ($R_F = 0.018$) Magnetic susceptibility $2 < T < 300$ K; magnetization < 2.5 Tesla at 5 K for $\text{U}_2\text{Mo}_3\text{Si}_4$ and $\text{UMo}_{1.25}\text{Si}_{0.75}$.
[1993Kon]	Arc-melted alloys U_3Si annealed at 800°C for 100 h. Starting materials 99.8 mass% U, chemical analysis, XPD, metallography.	Investigation of the effect of 0.1 to 0.5% Mo-additives on the corrosion resistance of U_3Si in water at 300°C under 90 MPa (in an autoclave) from 100 to 1000 h.
[1994Uga]	Argon-arc melting of elemental ingots; heat treatment for 3 to 10 days in muffle furnaces at 800° to 1100°C; water quench. Starting materials 99.8 mass% U, 99.95%Mo,Si. Metallography, EMPA, X-ray powder diffraction.	Partial phase equilibria at 850°C. 0.1 mass% Mo solubility limit of Mo in U_3Si_2 . Identification of ternary compounds $\text{U}_2\text{Mo}_3\text{Si}_4$, U_3MoSi_2 and U_4MoSi_3 . Proposition of a ternary peritectic invariant reaction at some temperature $T > 1100^\circ\text{C}$: $\text{U}_4\text{MoSi}_3 + \text{U}_2\text{Mo}_3\text{Si}_4 + \text{L} \rightleftharpoons \text{U}_3\text{MoSi}_2$. Peritectic liquid at 74U16Mo10Si (in at.%). No tie-line between U_3Si and Mo.
[1994Was]	Argon-arc melted alloy $\text{U}_2\text{Mo}_3\text{Si}_4$. Metallography and X-ray PD.	Magnetic susceptibility of $\text{U}_2\text{Mo}_3\text{Si}_4$ for $1.5 < T < 300$ K indicates paramagnetism.
[1995LeB]	A single crystal of $\text{U}_2\text{Mo}_3\text{Si}_4$ was obtained from an arc-melted alloy annealed for long time at 1450°C in an argon-sealed Mo-crucible.	Determination of the crystal structure of $\text{U}_2\text{Mo}_3\text{Si}_4$ from X-ray single crystal data. Temperature independent paramagnetism in the range $2 < T < 300$ K
[1996LeB1]	A single crystal of $\text{UMo}_{1.25}\text{Si}_{0.75}$ was obtained from an arc-melted alloy after prolonged annealing.	Determination of the crystal structure of $\text{UMo}_{1.25}\text{Si}_{0.75}$ from X-ray single crystal data. Temperature independent paramagnetism in the range $10 < T < 300$ K. Small increase of the magnetic susceptibility below 10 K due to impurities.
[1996Pat]	No details given on alloy preparation	Study of the magnetic behavior of $\text{U}_2\text{Mo}_3\text{Si}_4$ $2 < T < 300$ K.

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1998Uga]	Alloys prepared by arc melting under argon. Heat treatment in sealed quartz capsules at 500 to 1100°C for 4 to 22 days, followed by water quenching. Starting materials: 99.8 mass% U, 99.95% Mo 99.99% Si. Metallography, EMPA, X-ray powder diffraction.	Determination of melting point of U_3MoSi_2 at $1480 \pm 30^\circ C$ in a W-mesh heater (Seeger-cone technique); ternary peritectic invariant reaction $U_4MoSi_3 + U_2Mo_3Si_4 + L \rightleftharpoons U_3MoSi_2$. Peritectic liquid at 74U16Mo10Si (in at.%). Density measurements by immersion in metaxylene. Electric resistivity of U_3MoSi_2 measured by four-point technique $1.8 < T < 300$ K. Magnetic susceptibility measurements for U_3MoSi_2 in 0.1 Tesla. Partial phase diagram at $850^\circ C$. Confirmation of ternary compounds U_3MoSi_2 , U_4MoSi_3 and $U_2Mo_3Si_4$. Tentative unit cell ($a = 1069$ pm) for U_3MoSi_2 . Congruent melting of $U_2Mo_3Si_4$.
[2001Rog]	Alloys prepared by arc melting or levitation melting under argon. Heat treatment at $1400^\circ C$ on tungsten substrates in a high vacuum W-sheet furnace for 200 h. For equilibria at $850^\circ C$, samples within alumina crucibles were vacuum-sealed in quartz capsules and heat treated for 250 h and water quenched. Starting materials: 99.9 mass% U, 99.9% Mo, 99.9999% Si. Metallography, EMPA, X-ray powder diffraction. A single crystal of $U_4Mo(Mo_{0.33}Si_{0.67})Si_2$ was obtained from an arc melted alloy U_3MoSi_2 after treatment in an alumina crucible at $1150^\circ C$ under argon for 6 h and slow cooling. Measurement range for χ : $2 < T < 300$ K; magnetization at 5 K up to 6 Tesla.	Partial phase equilibria at $1400^\circ C$ for compositions < 60 at.% U. Partial phase equilibria at $850^\circ C < 70$ at.% Si. Determination of the crystal structure of $U_4Mo(Mo_xSi_{1-x})Si_2$. Determination of atom order as $f(x)$ in $U(Mo_{1-x}Si_x)_2$ from Rietveld refinements. Magnetic susceptibility $2 < T < 300$ K; magnetization < 2.5 Tesla at 5 K for $U_2Mo_3Si_4$ and $UMo_{1.25}Si_{0.75}$.

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Mo) < 2623	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 314.70$	[Mas2]
(Si) < 1414	<i>cF8</i> <i>Fd$\bar{3}m$</i> C _{diamond}	$a = 543.06$	[Mas2]
(γ U) 1135 to 774.8	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 353.35$	refined at 787°C [Mas2]
(β U) 774.8 to 667.7	<i>tP30</i> <i>P4₂/mnm</i> β U	$a = 1075.89$ $c = 565.31$	[Mas2]
(α U) < 667.7	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	[Mas2]
Mo ₃ Si < 2025	<i>cP8</i> <i>Pm$\bar{3}n$</i> Cr ₃ Si	$a = 489.7$	[Mas2, V-C2]
Mo ₅ Si ₃ < 2180	<i>tI38</i> <i>I4/mcm</i> W ₅ Si ₃	$a = 964.25$ $c = 490.96$	37.5 to 40 at.% Si [Mas2, V-C2]
β MoSi ₂ 2020 - 1900	<i>hP9</i> <i>P6₃22</i> CrSi ₂	$a = 464.2$ $c = 652.9$	[Mas2, V-C2]
α MoSi ₂ < 1900	<i>tI6</i> <i>I4/mmm</i> MoSi ₂	$a = 320.6$ $c = 784.6$	[Mas2, V-C2]
USi ₃ < 1510	<i>cP4</i> <i>Pm$\bar{3}m$</i> Cu ₃ Au	$a = 403.53$	[1992Rem]
USi ₂ < 450	<i>tI12</i> <i>I4₁/amd</i> ThSi ₂	$a = 392.2$ $c = 1415.4$	(metastable) [1992Rem]
α_1 , USi _{2-x} < 1710	<i>tI12</i> <i>I4₁/amd</i> def-ThSi ₂	$a = 394.23$ $c = 1371.2$	65 at.% Si [1992Rem]
α_2 , USi _{2-x}	<i>oI12</i> <i>Imma</i> def-GdSi ₂	$a = 395.3$ $b = 392.9$ $c = 1365.6$	at 64 at.% Si [1992Rem]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
α_3 , U_3Si_5 (o_2)	<i>oP6</i> <i>Pmmm</i> (?) distorted AlB_2	$a = 389.3$ $b = 671.7$ $c = 404.2$	at ~ 63 at.% Si [1992Rem]
α_4 , U_3Si_5 (o_1)	<i>oP6</i> <i>Pmmm</i> distorted AlB_2	$a = 86.4$ $b = 666.0$ $c = 407.3$	at 63 at.% Si [1992Rem]
α_5 , U_3Si_5 (hex) < 1770	<i>hP3</i> <i>P6/mmm</i> def- AlB_2	$a = 384.75$ $c = 407.40$	[1992Rem]
USi < 1580	<i>tI138</i> <i>I4/mmm</i> USi	$a = 1058.7$ $c = 2431.0$	[1992Rem, 1993LeB, 1996LeB2]
USi (metastable)	<i>oP8</i> <i>Pnma</i> FeB	$a = 758.5$ $b = 390.3$ $c = 566.3$	probably impurity (O) stabilized [1992Rem, 1993LeB]
U_5Si_4 < 1100	<i>hP18</i> <i>P6/mmm</i> U_5Si_4	$a = 1046.7$ $c = 391.2$	Single crystal study [2006Noe]
U_3Si_2 < 1665	<i>tP10</i> <i>P4/mbm</i> U_3Si_2	$a = 732.99$ $c = 390.04$	[V-C2, Mas2]
$\gamma\text{U}_3\text{Si}$ 930 - 759	<i>cP4</i> <i>Pm\bar{3}m</i> Cu_3Au	$a = 434.6$	[V-C2, 1965Str]
$\beta\text{U}_3\text{Si}$ 762 - -153	<i>tI16</i> <i>I4/mcm</i> $\beta\text{U}_3\text{Si}$	$a = 603.28$ $c = 869.07$	[V-C2, 1965Str]
$\alpha\text{U}_3\text{Si}$ < -153°C, at -193°C	<i>oF32</i> <i>Fmmm</i> $\alpha\text{U}_3\text{Si}$	$a = 865.4$ $b = 854.9$ $c = 852.3$	[V-C2, 1965Str]
* τ_1 , $\text{U}_2\text{Mo}_3\text{Si}_4$	<i>mP18</i> <i>P2_1/c</i> $\text{Y}_2\text{Mo}_3\text{Si}_4$	$a = 687.6$ $b = 688.3$ $c = 676.0$ $\beta = 109.79^\circ$	[1993LeB, 1995LeB] $R_F = 0.074$ $\rho_{\text{Xray}} = 8.76 \text{ Mgm}^{-3}$

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_2 , $\text{U}(\text{Mo}_{1-x}\text{Si}_x)_2$	$cP12$ $P6_3/mmc$ MgZn_2	$a = 537.30$	for $\text{UMo}_{1.25}\text{Si}_{0.75}$ [2001Rog]
		$c = 853.34$	at $x = 0.375$, 1400°C; Mo poor
		$a = 537.35$	for $\text{UMo}_{1.5}\text{Si}_{0.5}$ [2001Rog]
		$c = 859.58$	at $x = 0.250$, 1400°C; Mo rich
		$a = 536.70$	for $\text{UMo}_{1.34}\text{Si}_{0.66}$ [2001Rog]
		$c = 859.01$	at $x = 0.33$, 850°C; Mo poor
* τ_3 , $\text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2$ < 1480 [1998Uga]	$tI38$ $I4/mcm$ W_5Si_3	$a = 536.63$	for $\text{UMo}_{1.40}\text{Si}_{0.60}$ [2001Rog]
		$c = 854.17$	at $x = 0.30$, 850°C; Mo rich
		$a = 537.29$	for $\text{UMo}_{1.25}\text{Si}_{0.75}$ [1996LeB2]
		$c = 852.7$	
		$a = 537.0$	for $\text{UMo}_{1.25}\text{Si}_{0.75}$
		$c = 858.2$	$\rho_{\text{exp}} = 11.56 \text{ Mgm}^{-3}$ [1963Sik]
* τ_3 , $\text{U}_4\text{Mo}(\text{Mo}_x\text{Si}_{1-x})\text{Si}_2$ < 1480 [1998Uga]	$tI38$ $I4/mcm$ W_5Si_3	$a = 1069.42$	for U_4MoSi_3 [2001Rog]
		$c = 532.40$	at $x = 0.0$, 850°C; $R_F = 0.029$
		$a = 1071.00$	for $\text{U}_4\text{Mo}_{1.11}\text{Si}_{2.89}$ [2001Rog]
		$c = 533.65$	at $x = 0.11$, 850°C; $R_F = 0.049$
			$\rho_{\text{exp}} = 12.1 \text{ Mgm}^{-3}$ for U_3MoSi_2 [1998Uga]

Fig. 1: Mo-Si-U.
Partial isothermal
section at 1400°C

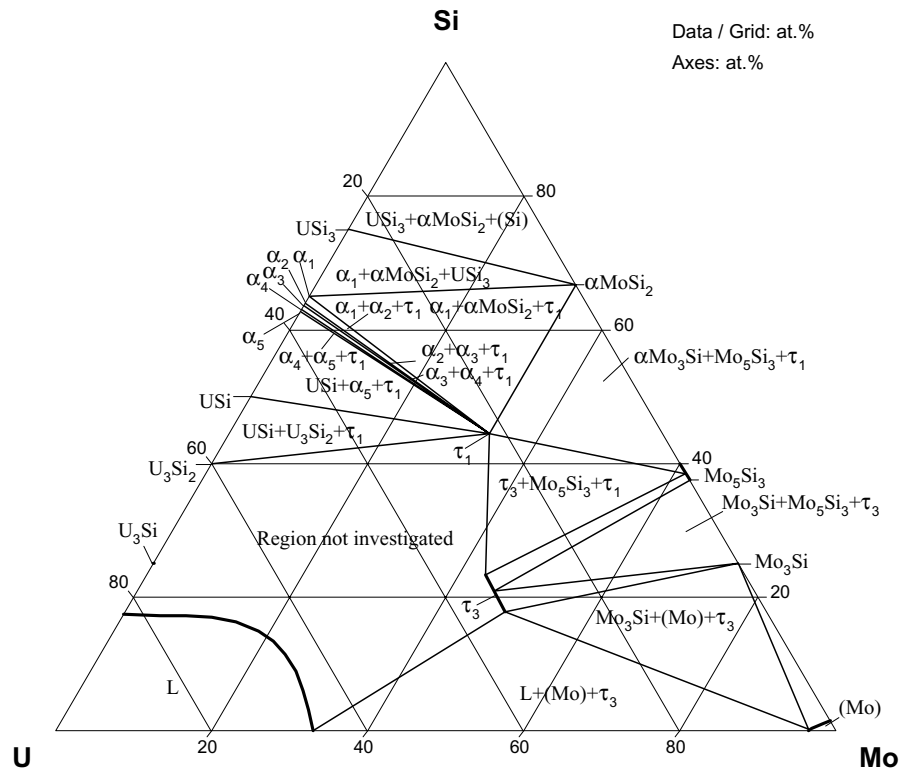
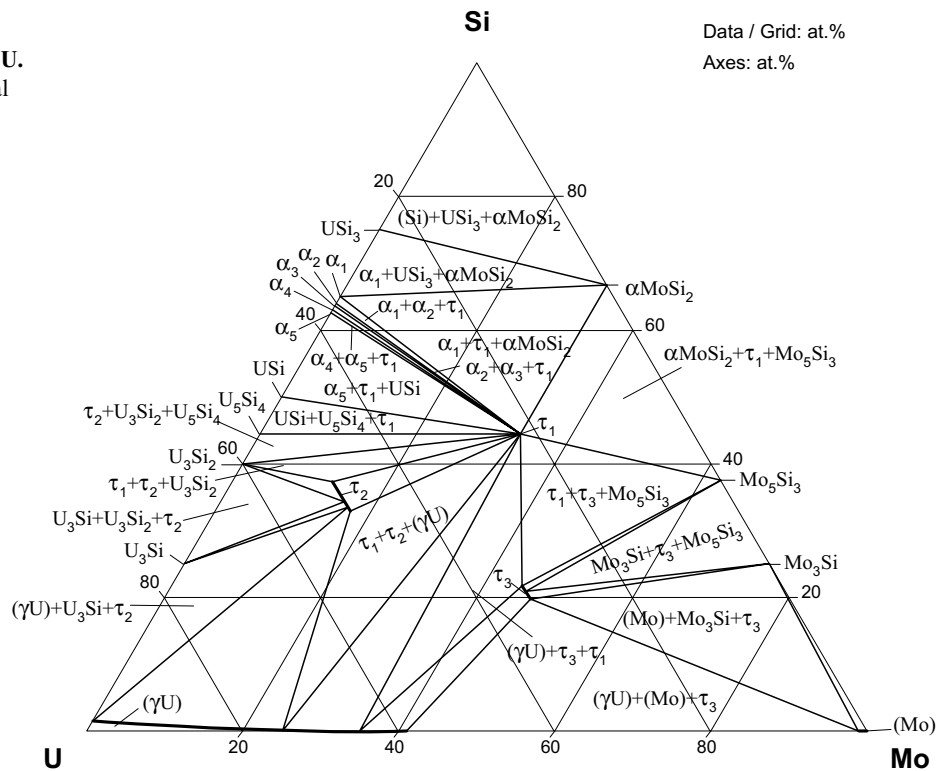


Fig. 2: Mo-Si-U.
Partial isothermal
section at 850°C



Nitrogen – Plutonium – Uranium

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Introduction

Mixed plutonium-uranium mononitrides are universally recognized as advanced fuels for liquid metal cooled fast breeder reactors due to their thermal conductivity, ease of fabrication, complete dissolution in nitric acid, good compatibility with cladding and non-pyrophoric nature. The nitrides of uranium, plutonium and uranium-plutonium mixture may be even more attractive than the carbides from the point of view of higher mechanical strength and higher solubility of solid fission products. Thermodynamic properties and phase equilibria are of great importance to evaluate the fuel performance under normal and abnormal reactor conditions, but also in the fabrication process. The phase relations of the N-Pu-U have not been studied in detail and most studies have been confined to those on the solid solution between UN and PuN with Pu/(U+Pu) ratios of 0.15-0.20 from the technological interest for the possible fast reactor fuel materials. Structural studies on the system have been carried out by [1971Ten] and [1991Suz]. Experimental investigations have been carried out on $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ by [1963Ans]. [1987Mat1, 1987Mat2] have critically evaluated the thermodynamic properties of the PuN-UN subsystem. Numerous thermodynamic properties were calculated and measured, especially on vapor pressure of species [1971Ale, 1992Suz, 1993Oga, 1973Pot, 2001Kur]. Only calculated isothermal sections are available in the literature [1973Pot, 1975Hol, 1976Pot, 1980Udo, 1993Oga]. All the data are summarized in Table 1.

Binary Systems

The accepted phase diagram of the binary boundary system Pu-U is reported in the chapter “*Remarks on the Actinide Alloying Behavior*” in the present volume. It is based on the thermodynamic calculation by [1991Lei].

The N-U system has been taken from the thermodynamic assessments of [2000Che]. This assessment gives a consistent description of thermodynamic data and phase diagram data and therefore is accepted here. The binary system N-Pu has been taken from [Mas2] as assessed by [1989Wri].

Solid Phases

PuN and UN form a complete range of solid solutions [1971Ten] with the rock salt structure in the whole composition range. [1963Ans] first reported the lattice parameters of $(\text{Pu,U})\text{N}$ which widely varied following the heat treatment of the samples and reported a monotonous increase of the lattice parameter, obeying Vegard’s law with increasing Pu content. Values and composition dependence of the lattice parameter are not consistent with those measured by [1971Ten]. Consequently [1991Suz] carried out experiments in order to determine precisely the composition dependence of the lattice parameters of UN-PuN solid solutions. Results are in fairly agreement with those of [1971Ten], especially in the Pu rich composition. The solid solutions do not obey Vegard’s law [1971Ten, 1991Suz]. This deviation may be attributed to a change of the nature of electron population in the solid solution. Disagreements were observed concerning the position of the maximum which is at $(\text{U}_{0.28}\text{Pu}_{0.72})\text{N}$ in [1971Ten] and $(\text{U}_{0.1}\text{Pu}_{0.9})\text{N}$ in [1991Suz]. Further investigations are needed in order to determine precisely the location of this maximum value of the lattice parameter. Small discrepancies in the UN rich region is certainly due to the presence of a small amount of carbon in the UN samples.

As for UN and PuN, $(\text{Pu,U})\text{N}$ melting temperature strongly depends on the nitrogen pressure [1987Mat1, 1987Mat2].

Plutonium sesquinitride is an unstable compound and is reported to be stabilized in a $\text{UN}_{1.5}$ matrix by dissolution up to 15 mol% $\text{PuN}_{1.5}$ [1997Soo]. However, the thermodynamic properties of $\text{PuN}_{1.5}$ are not

available and its stabilization in solution with $\text{UN}_{1.5}$ at high temperatures, particularly in the absence of high nitrogen pressure, appears doubtful.

The crystallographic data for the N–Pu–U phases and their ranges of stability are summarized in Table 2.

Quasibinary Systems

Although the non stoichiometric region of the single phase $(\text{Pu},\text{U})\text{N}$ has not been well determined as a function of temperature, UN and PuN are considered to form a continuous solid solution in the temperature range from room temperature to 1650°C. [1987Mat1, 1987Mat2] compared their calculated partial pressures based on the ideal solution assumption with experimental results and concluded that the UN–PuN system behaves like an ideal solution.

Invariant Equilibria

[1980Udo] carried out thermodynamic calculations and proposed the existence of a ternary four-phase equilibrium $\beta\text{U}_2\text{N}_3 + (\text{Pu},\text{U})\text{N} + \text{N}_2 \rightleftharpoons \alpha\text{U}_2\text{N}_3$ at about $1250 \pm 100^\circ\text{C}$. Since the $\alpha\text{U}_2\text{N}_3$ appears at much lower temperature in the binary 1135°C, the crystallization of this phase inside the ternary at a temperature of $1250 \pm 100^\circ\text{C}$ is certainly improbable. Consequently this reaction has not been retained here and the schematic reaction scheme proposed by [1980Udo] has not been reported here. Further experimental investigations and thermodynamic calculations are needed.

Isothermal Sections

Isothermal sections were only estimated from thermodynamic calculations [1973Pot, 1975Hol, 1976Pot, 1980Udo, 1993Oga]. [1973Pot, 1980Udo] suggested that the solubility of Pu in $\alpha\text{U}_2\text{N}_3$ is up to the ratio $\text{Pu}/(\text{Pu}+\text{U}) = 0.15$ at around 1000°C. Since only one experimental data of solubility is available in literature for $\alpha\text{U}_2\text{N}_3$, [1973Pot] shows two different version of the isothermal section at 800°C. According to [1973Pot] a decision can not be made. Later [1980Udo] calculated isothermal sections at 795, 805, 960 and 1135°C taking into account the experimental results of the solubility range of $\alpha\text{U}_2\text{N}_3$. According to the accepted binary N–U phase diagram, only the low temperature phase $\alpha\text{U}_2\text{N}_3$ exists at this temperature. Consequently the phase equilibria involving the $\beta\text{U}_2\text{N}_3$ phase could not be retained in the calculated isothermal sections at 800°C and 805°C proposed respectively by [1973Pot] and [1980Udo]. [1980Udo] expected that at $1250 \pm 100^\circ\text{C}$ a four-phase reaction would occur: $\beta(\text{Pu},\text{U})_2\text{N}_{3-y} + \text{N}_2 + (\text{Pu},\text{U})\text{N} \rightleftharpoons (\text{Pu},\text{U})_2\text{N}_{3+x}$. According to the binary phase diagram N–U it is improbable that the $\alpha(\text{Pu},\text{U})_2\text{N}_{3+x}$ could exist in this temperature range. Consequently, modifications have been made on the isothermal section at $1250 \pm 100^\circ\text{C}$ presented by [1980Udo]. The accepted calculated isothermal sections are reported in Figs. 1 to 4. Some modifications have been made according to the binary systems. The liquid phase along the Pu–U and N–U system present a solubility range at 795°C and has been taken into account in the drawing at 795°C. The solubility of $\alpha\text{U}_2\text{N}_3$ has been suppressed and the (γU) phase has been added at 1135°C since this temperature is identical to the melting temperature of this phases. Moreover the nitrogen rich part of the Pu–N phase diagram is not established, specially the phase equilibria between PuN and N and as well as the limit solubility of PuN on the nitrogen rich side. All these slight modifications are indicated as dashed lines in the figures. [1993Oga] predicted isothermal phase boundaries between the mixed mononitrides and liquid alloys at 1727°C from modeling of the free Gibbs energies of mixed nitrides $(\text{Pu},\text{U})\text{N}$ using a sublattice formalism. An increase of the N_2 pressure leads to an enrichment in Pu of the nitride and in U of the metal liquid. [1975Hol] calculated invariant points of the three-phase equilibria for various nitrogen pressure in the nitrogen rich part of the phase diagrams. $\alpha\text{U}_2\text{N}_3$ and $\beta\text{U}_2\text{N}_3$ coexist at 1000°C and 1 bar N_2 . At 0.1 bar N_2 , only $\beta\text{U}_2\text{N}_3$ occurs.

More systematic experimental work is necessary.

Thermodynamics

There are only two sets of vapor measurements [1971Ale, 1992Suz] on the mixed nitrides, which contradict each other on some crucial points. [1971Ale] showed that the vaporization behavior of (Pu,U)N was governed by the preferential loss of PuN as elemental plutonium and molecular nitrogen. It stipulated that the vapor pressure of Pu(g) over (U_{0.8}Pu_{0.2})N was nearly 20% of that over PuN, indicating that (U_{0.8}Pu_{0.2})N is a nearly ideal solution of UN and PuN. [1993Oga] predicts by calculation that U(g) pressure is significantly suppressed with a small addition of PuN to UN. The behavior observed by [1971Ale] agrees with this prediction. [1993Oga] found also that the apparent temperature dependence of U(g) pressure over the mixed nitrides is larger than that over the pure uranium nitride. On contrary to this prediction, [1992Suz] found that the temperature dependences of U(g) pressures of (U_{0.8}Pu_{0.2})N and (U_{0.65}Pu_{0.35})N do not differ appreciably from that of UN. Possible causes of the discrepancy may be the carbon contamination occurring in the carbothermic reduction process used for the sample preparation done by [1992Suz]. Thus the question of impurity effects remains open. [1971Ale] suggested the existence of a steady state of the weight loss rate of (U_{0.8}Pu_{0.2})N. Due to high vapor pressure of U(g), the condensate is consisted of Pu, U, PuN after vaporization of (U_{0.4}Pu_{0.6})N and (U_{0.2}Pu_{0.8})N [1987Mat1, 1987Mat2]. The Pu pressures and total pressures above the congruently vaporizing U_{0.8}Pu_{0.2} mononitride calculated by [1973Pot] are in good agreement with the measured values of [1971Ale]. The vapor pressure of U(g), Pu(g), N₂(g), PuN(g) and UN(g) over liquid (Pu,U)N and U(g), Pu(g), N₂(g) and PuN(g) over solid (Pu,U)N were calculated by [1987Mat1, 1987Mat2]. [1987Mat1, 1987Mat2] concluded that (U_{0.8}Pu_{0.2})N is effectively a nearly ideal solution of UN and PuN up to 2127°C. Experimental data on vapor pressure measurements are indicated on Table 3.

The high temperature enthalpy and heat capacity of (U_{0.8}Pu_{0.2})N have been measured by [1971Ale] from room temperature to 1527°C. These measurements seem to be unreliable from the point of view of an ideal solution model, since the heat capacity of mixed nitrides is given lower than those of UN and PuN. This assumption is in contradiction with the vapor pressure measurements of [1971Ale] who concluded that (U_{0.8}Pu_{0.2})N has an ideal solution behavior. [2001Kur] calculated the heat capacity of (U_{0.8}Pu_{0.2})N as the sum of the contribution of lattice vibration and dilatation in the temperature range 27–2227°C. Results show a slight difference with experimental data leading to the fact that other contributions have to be considered in the calculation as for example the Frenkel defect effect.

There has been no reports on the enthalpy of formation for (Pu,U)N. The enthalpy of formation for (U_{0.8}Pu_{0.2})N was estimated by [1987Mat1, 1987Mat2] to be $-296.5 \text{ kJ}\cdot\text{mol}^{-1}$ on the basis of an ideal solid solution model from the enthalpy of solution of UN and PuN at 27°C.

Notes on Materials Properties and Applications

[1992Ara] found that the thermal conductivity of (U_{0.8}Pu_{0.2})N system decreases with increase in porosity and the temperature dependence does not change with porosity. Results agreed fairly well with those of [1970Ale, 1971Ale] but gave slightly higher values than those of [1967Pas] over the temperature range investigated. Moreover addition of Pu in (Pu,U)N pellets decreases the thermal conductivity except for the case of PuN indicating a little higher thermal conductivity than the PuN rich (Pu,U)N solid solutions below 727°C. [1992Ara] also noticed that the decreasing rate of thermal conductivity with Pu content is prominent in the UN rich region. The Pu content dependence of thermal conductivity of [1992Ara] agrees well with results of [1991Gan] for pellets of (U_{0.8}Pu_{0.2})N. The big differences observed for the (U_{0.45}Pu_{0.55})N between [1992Ara] and [1991Gan] is not clear for the moment. Further experiments are needed. [2001Kur] calculated the thermal conductivity of (Pu_{0.2}U_{0.8})N using Green-Kubo relations in the temperature range 27–1727°C. These calculated results from Monte-Carlo simulation are systematically lower than the experimental data [1970Ale, 1971Ale, 1992Ara, 1967Pas].

[1969Par] demonstrated that the mixed nitrides have extremely good irradiation resistance and a potential for burnups with appropriate fuel element design. Data are summarized in Table 4.

Miscellaneous

[1974Ten] have conducted sintering experiments of $(\text{Pu}_x\text{U}_{1-x})\text{N}$ as a function of temperature and nitrogen pressure. They found reducing the nitrogen pressure caused an enhancement in sintering. After diffusion in the solid state of PuN-UN mixture, the solid solution obtained can be sintered to 90% of theoretical density [1963Ans].

At a pressure of $0.1 \cdot 10^{-8}$ bar, [2001Kur] have performed a molecular dynamics study and evaluated the thermal expansion and the compressibility coefficients of $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$.

The most common method for the preparation of mixed nitride fuels is the carbothermic reduction of $\text{UO}_2 + \text{PuO}_2 + \text{C}$ mixture in a nitrogen atmosphere. Phase diagram N-Pu-U of the nitride fuels, in the composition range of interest for fuel manufacture, have been extensively calculated with carbon and oxygen impurities [1973Pot, 1976Pot, 1993Oga, 1997Soo, 1999Aga]. Considering calculation based on ideal solution behavior, it was found that the oxygen impurity of the nitride fuel affects plutonium partial pressure [1999Aga]. [1998Jai] have commented on the paper of [1997Soo] that they have wrongly inferred the presence of a phase $\text{UN}_{1.5}$.

Carbon and oxygen contents ranging from 400-6000 ppm and 2000-9000 ppm, respectively do not significantly affect the melting behavior of $(\text{Pu,U})\text{N}$ fuels [1968Web].

[1992Bar] have conducted kinetic experiments on the mechanism of sintering of $(\text{Pu}_x\text{U}_{1-x})\text{N}$. It was found that the rate of reaction follows an Arrhenius law as a function of temperature. The apparent activation energy for the $(\text{Pu,U})\text{N}$ synthesis is lower than the value of the UN formation. This can be explained by the higher ionic character of PuN which enhances probably the transformation of PuO_2 in PuN. The apparent activation energy ($66 \text{ kJ} \cdot \text{mol}^{-1}$) is lower under N_2 -6% H_2 than the one ($244 \text{ kJ} \cdot \text{mol}^{-1}$) observed with pure N_2 and the kinetic parameter is independent on the gas flow rate.

It was found that the nitride Pu-U mixtures are generally more reactive than the Pu-U oxides mixtures [1975Bie].

[1965Far, 1966Far, 1968Far1, 1968Far2, 1969Fac, 1969Far, 1970Bar] undertook a review of mechanical properties, method of fabrication and irradiation influence on mixed plutonium-uranium nitrides.

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Table 1: Investigations of the N-Pu-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1963Ans]	Metallography X-ray powder diffraction, chemical analysis	900°C/ (Pu _x U _{1-x})N
[1971Ale]	Oelsen calorimeter, massspectrometry	27 - 2127°C / (Pu,U)N
[1971Ten]	X-ray measurements, chemical analysis	1400 - 1800°C for 325 minutes / (Pu _x U _{1-x})N
[1991Suz]	X-ray diffraction	1752°C/ (Pu _x U _{1-x})N
[1992Suz]	Knudsen effusion mass spectrometry, X-ray diffraction	1477 - 1727°C / (Pu _x U _{1-x})N

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(εPu, γU)	<i>cI2</i> <i>Im$\bar{3}m$</i> W		continuous solid solution which exists between 1135 and 454°C [1991Lei]
(εPu) 640 - 483		$a = 363.8$	pure, 500°C, [1989Pet]
(γU) 1135 - 776		$a = 352.4$	pure, 805°C, [Mas2]
(δ'Pu) 483 - 463	<i>tI2</i> <i>I4/mmm</i> In	$a = 333.9$ $c = 444.6$	pure, 477°C, [1989Pet] dissolves about 1.3 at.% U at 440°C [1991Lei]; exists down to 437°C in the Pu-U binary [1991Lei]
(δPu) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 463.70$	pure, 320°C, [1989Pet] dissolves about 1.6 at.% U at 318°C [1991Lei]
(γPu) 320 - 215	<i>oF8</i> <i>Fddd</i> γPu	$a = 315.87$ $b = 576.82$ $c = 1016.2$	pure, 235°C, [1989Pet] dissolves about 1.6 at.% U at 278°C [1991Lei];
(βPu) 215 - 125	<i>mC34</i> <i>C2/m</i> βPu	$a = 928.4$ $b = 1046.3$ $c = 785.9$ $\beta = 92.13^\circ$	pure, 190°C, [1989Pet] dissolves about 2.7 at.% U at 278°C [1991Lei]
(αPu) < 125	<i>mP16</i> <i>P2₁/m</i> αPu	$a = 618.3$ $b = 482.2$ $c = 1096.3$ $\beta = 101.79^\circ$	pure, 21°C, [1989Pet] the solubility of U is nearly absent [1991Lei]
(βU) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> βU	$a = 1075.9$ $c = 565.6$	pure, 720°C, [1989Pet] dissolves about 24 at.% Pu at 702°C [1991Lei] exists down to 557°C along the Pu-U binary [1991Lei]
(αU) < 668	<i>oC4</i> <i>Cmcm</i> αU	$a = 285.37$ $b = 586.95$ $c = 495.48$	pure, at 25°C [1989Pet] dissolves about 11 at.% Pu at 557°C [1991Lei]
(U _x Pu _{1-x})N	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	$a = 488.918$ to 490.386	$0 \leq x \leq 1$ [1971Ten]
UN < 2789		$a = 488.87$	UN melts congruently at 2835°C at 2.5 MPa N ₂ [2000Che], lattice parameters from [V-C2]
PuN < 2830		$a = 490.5$	[2003Min]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\beta\text{U}_2\text{N}_3$ 1349 - 955	$hP5$ $P\bar{3}m1$ La_2O_3	$a = 370.0$ $c = 582.5$	58.7 at.% N [2000Che] [V-C2]
$\alpha\text{U}_2\text{N}_3$ < 1135	$cI80$ $Ia\bar{3}$ Mn_2O_3	$a = 1068.2$	60 to 64 at.% N. Gradually change to CaF_2 type with increasing N content [2000Che], lattice parameters from [V-C2]
η , PuU 702 - 278	$tP52$	$a = 1057$ $c = 1076$	~4 to ~78 at.% U at 25 at.% U [1969Lea]
ξ , PuU ≤ 628	t^{**}	$a = 1069.2$ $a = 1065.1$	~26.4 to ~77 at.% U at 25°C, 35 at.% U [1969Lea] at 25°C, 70 at.% U [1969Lea] $c/a \approx 1$

Table 3: Vapor Pressure Measurements

Phase(s)	Temperature [°C]	Pressure [bar]	Comments
$\text{N}_2(\text{g})$	1127 to 2127	$p_{\text{N}_2(\text{g})} = 3 \cdot 10^{-11}$ to $5.5 \cdot 10^{-5}$	Over $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ [1971Ale]
$\text{Pu}(\text{g})$	1127 to 2127	$p_{\text{Pu}(\text{g})} = 2 \cdot 10^{-10}$ to $3.1 \cdot 10^{-4}$	Over $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ [1971Ale]
$\text{U}(\text{g})$	1127 to 2127	$p_{\text{U}(\text{g})} = 1 \cdot 10^{-14}$ to $8.1 \cdot 10^{-6}$	Over $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ [1971Ale]
$\text{U}(\text{g})$	1520 - 1640	$\log p_{\text{U}(\text{g})} = -(26.4 \pm 0.9) \cdot 10^{-2} / T$	Over 0.8UN-0.2PuN [1992Suz]
$\text{Pu}(\text{g})$	1380 - 1660	$\log p_{\text{Pu}(\text{g})} = -(20.5 \pm 0.2) \cdot 10^{-2} / T$	Over 0.8UN-0.2PuN [1992Suz]
$\text{U}(\text{g})$	1540 - 1560	$\log p_{\text{U}(\text{g})} = -26.9 \cdot 10^{-2} / T$	Over 0.65UN-0.35PuN [1992Suz]
$\text{Pu}(\text{g})$	1320 - 1560	$\log p_{\text{Pu}(\text{g})} = -(19.6 \pm 0.2) \cdot 10^{-2} / T$	Over 0.65UN-0.35PuN [1992Suz]
$\text{Pu}(\text{g})$	1280 - 1500	$\log p_{\text{Pu}(\text{g})} = -(22.0 \pm 0.2) \cdot 10^{-2} / T$	Over 0.4UN-0.6PuN [1992Suz]
$\text{Pu}(\text{g})$	1280 - 1500	$\log p_{\text{Pu}(\text{g})} = -(21.1 \pm 0.2) \cdot 10^{-2} / T$	Over 0.2UN-0.8PuN [1992Suz]

Table 4: Investigations of the N-Pu-U Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1967Pas]	Transient methods	Thermal conductivity
[1971Ale]	Laser pulse method	Thermal conductivity, thermal expansion, Transport rate
[1991Gan]	Transient heat flow method	Thermal conductivity
[1992Ara]	Laser flash method	Thermal conductivity

Fig. 1: N-Pu-U.
Calculated isothermal
section at 795°C

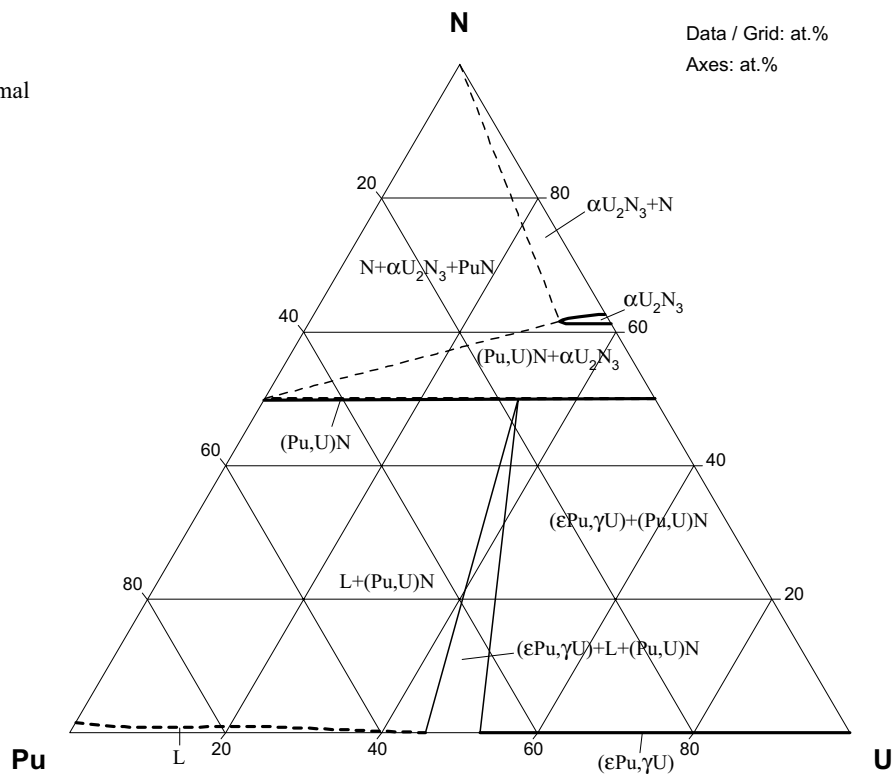


Fig. 2: N-Pu-U.
Calculated isothermal
section at 1135°C

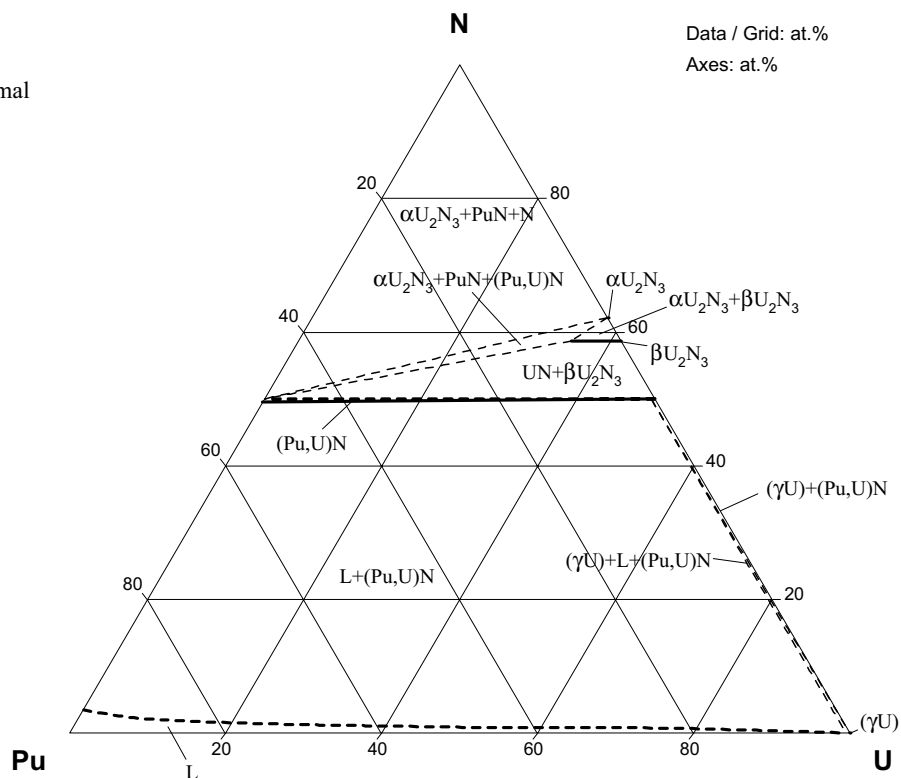


Fig. 3: N-Pu-U.
Calculated isothermal
section
at $1250 \pm 100^\circ\text{C}$

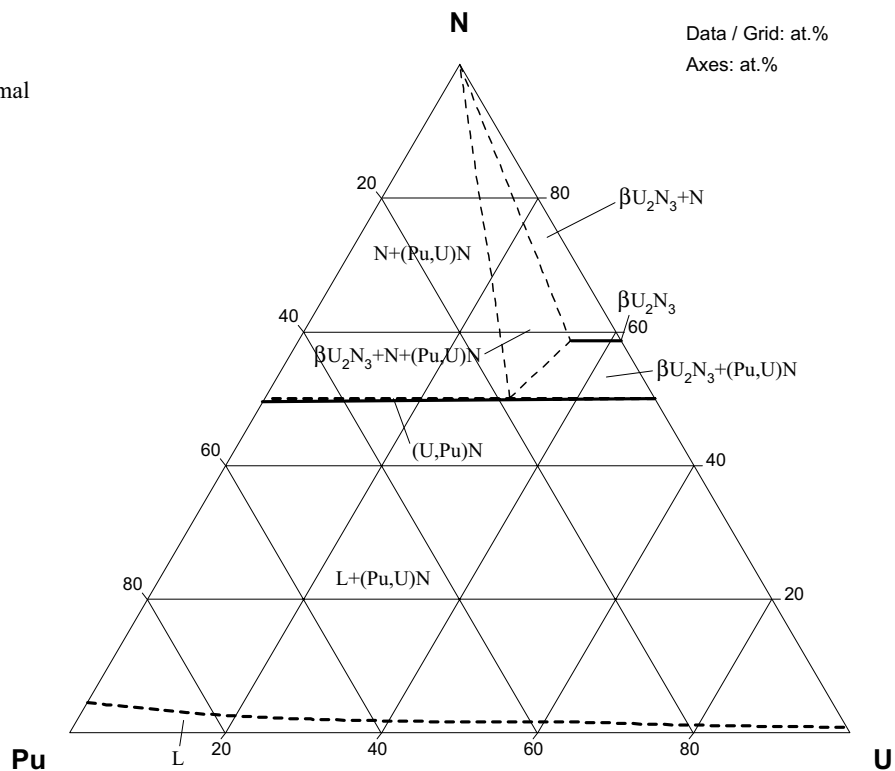
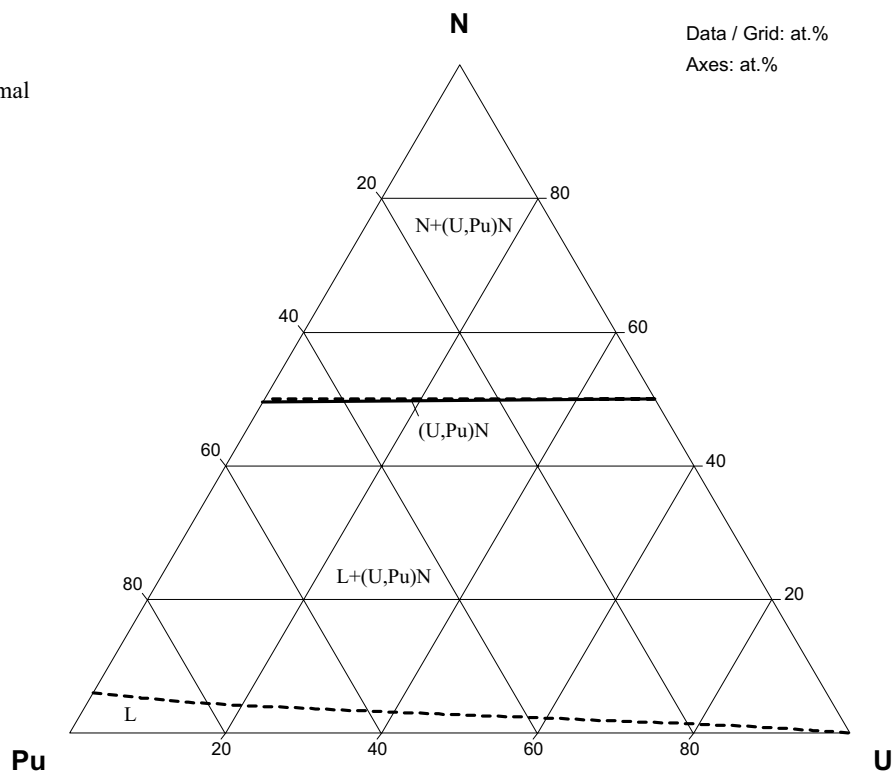


Fig. 4: N-Pu-U.
Calculated isothermal
section at 1355°C



Nitrogen – Plutonium – Zirconium

Pierre Perrot

Introduction

Investigations of the N–Pu–Zr system carried out at 1500°C by X-ray diffraction [1975Hol] showed that PuN and ZrN are soluble in the whole composition range. The properties of the (Pu,Zr)N solid solution, heat capacity (up to 1500°C), thermal conductivity and thermal expansion (up to 2500°C) were experimentally determined by [2005Bas] for ZrN and the solution $\text{Pu}_{0.25}\text{Zr}_{0.75}\text{N}$.

Binary Systems

The N–Zr system has been assessed by [1994Gri] which proposes for ZrN a sublimation point of 3410°C and a melting point of 3670°C under 6 MPa of nitrogen pressure, which is 700 K higher than the melting point estimated by [Mas2]. The N–Pu diagram is accepted from [Mas2] and has been assessed by [1989Wri]. The Pu–Zr diagram is accepted from the Calphad assessment of [1999Kur].

Solid Phases

The solid phases are presented in Table 1. The solid solution (Pu,Zr)N are prepared by mixing and compacting the powders under 100 MPa [2000Ara, 2003Min]. The discs, heated at 1400°C under an $\text{H}_2\text{-N}_2$ gas stream for homogenization are shown to obey the Vegard's law.

Isothermal Sections

The isothermal section at 1500°C is given in Fig. 1. The diagram, mainly from [1975Hol], has been modified to be coherent with the accepted binaries. The position of the tie lines in the two-phase domain (Pu,Zr) liquid solution – (Pu,Zr)N solid solution confirms the well known fact that Zr has a stronger affinity for N than Pu.

Notes on Materials Properties and Applications

The solid solution of PuN having dissolved ZrN has been proposed as a potential fuel for transmutation use [2000Ara, 2003Min, 2005Str]. However, oxygen impurities deteriorate the irradiation behavior and has to be maintained below 0.2 mass% by adding small amount of carbon before the initial mixing.

Actinide mononitrides has been considered as an advanced fuel for fast reactors because of major thermal and neutronic properties [2005Ara]. Mononitrides are also candidates fuel material in the accelerator driven systems for minor actinides transmutation, being coupled with pyrotechnical treatment of spent nuclear fuel.

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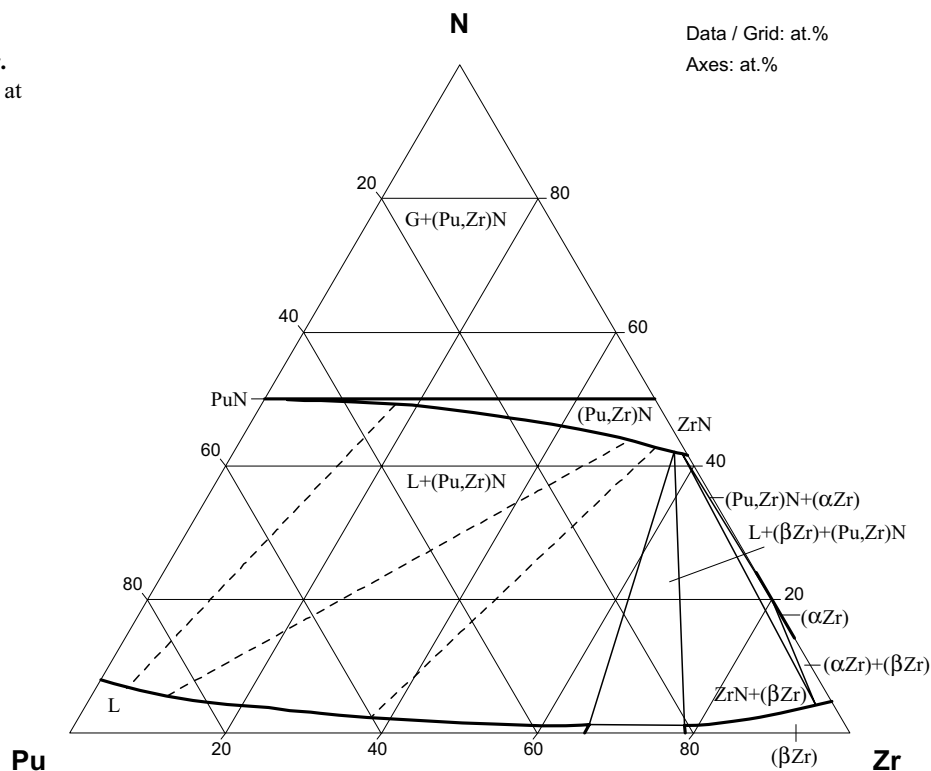
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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α Pu) < 125	<i>mP16</i> <i>P2₁/m</i> α Pu	$a = 618.3$ $b = 482.2$ $c = 1096.3$ $\beta = 101.97^\circ$	at 25°C [Mas2] dissolves ~1.5 at.% Zr at 115°C
(β Pu) 215 - 125	<i>mC34</i> <i>C2/m</i> β Pu	$a = 928.4$ $b = 1046.3$ $c = 785.9$ $\beta = 92.13^\circ$	[Mas2] dissolves ~7 at.% Zr at 280°C
(γ Pu) 320 - 215	<i>oF8</i> <i>Fddd</i> γ Pu	$a = 315.87$ $b = 576.82$ $c = 1016.2$	[Mas2] dissolves ~3 at.% Zr at 280°C
(δ Pu) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 463.71$	[Mas2] dissolves up to 60 at.% Zr at 618°C [1999Kur]
(δ' Pu) 483 - 463	<i>I2</i> <i>I4/mmm</i> In	$a = 332.61$ $c = 446.30$	[Mas2] dissolves ~2 at.% Zr at 483°C
(α Zr) < 1360	<i>hP2</i> <i>P6₃/mmc</i> Mg	$a = 323.16$ $c = 514.75$	at 25°C [Mas2] dissolves up to 13 at.% Pu at 618°C and 25 at.% N at 1985°C

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(εPu,βZr)	$cI2$ $Im\bar{3}m$		solid solution (εPu,βZr) [1995Oka, 1999Kur].
(εPu) 640 - 483	W	$a = 363.43$	The solubility of N in Pu is very small [1989Wri]
(βZr) 1855 - 863		$a = 360.90$	(βZr) dissolves ~5 at.% N at 1880°C
θ, Pu ₄ Zr < 345	$tP80$ $P4/ncc$	$a = 1089.3$ $c = 1488.9$	13 to 17 at.% Zr [1999Kur]
κ, PuZr ₃ < 380	$hP3$ $P6/mmm$ AlB ₂	$a = 505.5$ $c = 312.3$	74 at.% Zr [Mas2]. May be metastable [1995Oka]
(Pu,Zr)N	$cF8$ $Fm\bar{3}m$		solid solution
PuN < 2830	NaCl	$a = 490.5$	[2003Min]
ZrN < 3410		$a = 457.6$	ZrN: 40 to 50 at.% N. Melts congruently at 3670°C, 6 MPa N ₂ pressure [1994Gri]

Fig. 1: N-Pu-Zr.
Isothermal section at
1500°C



Nitrogen – Thorium – Uranium

Pierre Perrot

Introduction

Investigations of the N–Th–U system by X-ray diffraction have been carried out at 1000°C under nitrogen pressures varying from 10^{-4} to 1 bar [1968Far, 1968Ven] and reproduced by [1975Hol]. The UN–ThN quasibinary system presents a solid solution in the whole composition range, which confirms the observations of [1967Ven].

Binary Systems

The N–Th systems is accepted from [Mas2]. The N–U diagram given by [Mas2] has been updated by [1997Oka], then thermodynamically assessed by [2000Che]. The Th–U system is accepted from the assessment of [1985Pet], reproduced by [Mas2].

Solid Phases

The solid phases are presented in Table 1. The Vegard's law is well obeyed by the (U,Th)N solid solution [1967Ven]. At 1000°C, U may be dissolved into pure ThN ($a = 516.19$ pm) up to the formation of a solid solution $\text{Th}_{0.96}\text{U}_{0.02}\text{N}_{0.96}$ whose crystal parameter is $a = 514.1$ pm [1968Ven].

Isothermal Sections

The isothermal section at 1000°C is given in Fig. 1. The diagram, mainly from [1975Hol], has been modified to be coherent with the accepted binaries. The most uranium rich (U,Th)N solid solution in equilibrium with metallic (Th) was found to be $(\text{U}_{0.056}\text{Th}_{0.944})\text{N}_{0.866}$ at 1000°C [1969Fac]. However, taking into account the stoichiometric character of ThN and UN at 1000°C, the composition $(\text{U}_{0.056}\text{Th}_{0.944})\text{N}$ is more probable. Each three-phase triangle in the isothermal section is characterized by a nitrogen pressure at equilibrium. The nitrogen pressure in equilibrium with $\beta\text{U}_2\text{N}_3$, Th_3N_4 and $\text{U}_{0.9}\text{Th}_{0.1}\text{N}$ is ~ 0.1 bar at 1000°C; the nitrogen pressure in equilibrium with $\alpha\text{U}_2\text{N}_3$, $\beta\text{U}_2\text{N}_3$ and Th_3N_4 is ~ 1 bar at the same temperature.

Thermodynamics

The (U,Th)N solid solution has been described at 1000°C with a regular model: $\Delta_{\text{mix}} G^{\text{xs}} = \alpha x_{\text{UN}} x_{\text{ThN}}$ with $\alpha = 11.7$ kJ·mol $^{-1}$. The solid solution probably presents a miscibility gap under a critical point estimated at 430°C [1968Far, 1975Hol].

Notes on Materials Properties and Applications

Alloys N–Th–U are applied as fuel in a fast transmutation reactor in meeting several fuel criteria [1968Ven] such as an operating capability at central fuel temperature of about 800°C.

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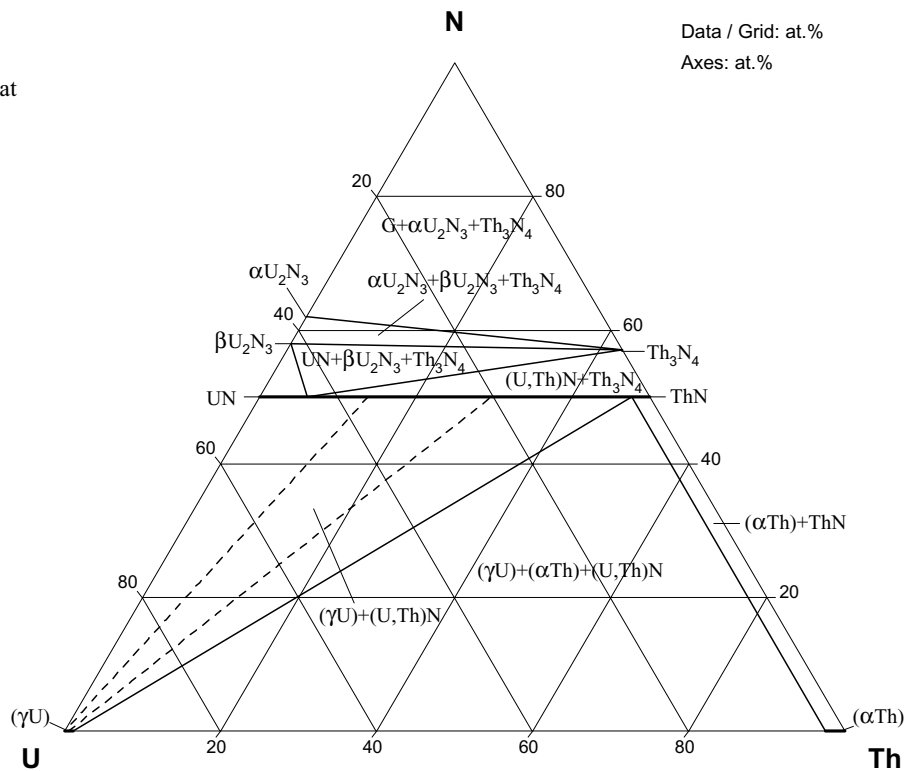
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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(βTh) 1755 - 1360	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 411.0	(βTh) dissolves up to 12.2 at.% U at 1375°C [Mas2]
(αTh) < 1360	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	<i>a</i> = 508.42	at 25°C [Mas2] dissolves up to 6.8 at.% U at 1270°C
(γU) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 352.	(γU) dissolves up to ~2 at.% Th at 1100°C [Mas2]
(βU) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> βU	<i>a</i> = 1075.9 <i>c</i> = 565.6	at 25°C [Mas2]
(αU) < 668	<i>oC4</i> <i>Cmcm</i> αU	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(U,Th)N $U_{0.5}Th_{0.5}N$	$cF8$ $Fm\bar{3}m$ NaCl	$a = 503.2$	solid solution [1968Ven]
UN < 2789		$a = 488.83$	UN melts congruently at 2835°C, 2.5 MPa N_2 [2000Che]
ThN < 2820		$a = 516.19$	ThN: 46 to 50 at.% N [1967Ven, Mas2]
βU_2N_3 1349 - 776	$hP5$ $P\bar{3}m1$ La_2O_3	$a = 370.0$ $c = 582.5$	58.7 at.% N [2000Che]
αU_2N_3 < 1134	$cI80$ $Ia\bar{3}$ Mn_2O_3	$a = 1068.2$	60 to 64 at.% N. Gradually changes to CaF_2 type with increasing N content [2000Che]
Th_3N_4 < 1900	$hR21$ $R\bar{3}m$ Al_4C_3	$a = 387.5$ $c = 2739$	57 at.% N [Mas2, V-C2]

Fig. 1: N-Th-U.
Isothermal section at
1000°C



Nitrogen – Uranium – Zirconium

Pierre Perrot

Introduction

Investigations of the N–U–Zr system by X-ray diffraction [1965Far] showed that the UN–ZrN quasibinary gives a solid solution up to at least 10 mass% Zr whereas [1968Hol1] observed at 1800 and 2000°C a continuous solid solution between pure ZrN and $U_{0.8}Zr_{0.2}N$. The (U,Zr)N solid solution was observed in the whole composition range [1968Hol2] by heating mechanical mixtures during 72 h at 2000°C. The UN–Zr and the (U,Zr)–N₂ reactions at 1000°C were investigated respectively by [1962Kat] and [1994Aka, 1997Oga, 2001Aka].

Binary Systems

The N–Zr system has been assessed by [1994Gri] which proposed for ZrN a sublimation point of 3410°C and a melting point of 3670°C under 6 MPa of nitrogen pressure, which is 427°C higher than the melting point estimated by [Mas2]. Later, the N–Zr system was optimized by calculation using Calphad method [2004Ma], leading to a lower melting point of the ZrN phase. Consequently, the phase diagram proposed by [1994Gri] has been retained in this assessment. The N–U diagram has been updated by [1997Oka], and then thermodynamically assessed by [2000Che]. The U–Zr diagram is accepted from the Calphad assessment of [2004Che].

Solid Phases

The solid phases are presented in Table 1. The (γ U, β Zr) solid solution is stable above the eutectoid point at 606°C and 80 at.% Zr. Nitrogen has the effect to increase the (α Zr)–(β Zr) equilibrium temperature. The nitrogen solubility in the (β Zr) phase at 660°C presents a maximum at a composition of 80 at.% U and 425 ppm N [1958Bau]. The nitrogen content of the (α Zr) phase in equilibrium with the (β Zr) phase is 19 ppm N at the same temperature.

Quasibinary Systems

The solidus and liquidus temperatures of the (U,Zr)N quasibinary system are shown in Fig. 1. The figure is drawn from the diagram proposed by [2003The] modified to take into account two facts: the accepted melting temperature of UN is 2789°C and the temperature of 3410°C is not the true melting temperature of ZrN, but the temperature at which ZrN loses its nitrogen under 1 bar of nitrogen pressure.

Isothermal Sections

The isothermal section at 1000°C showing some isobaric curves is given in Fig. 2. A three-phase triangle in the diagram is characterized by a nitrogen pressure at equilibrium. The nitrogen pressure in equilibrium with the mixture αU_2N_3 – βU_2N_3 – $U_{0.1}Zr_{0.9}N$ is between 0.1 and 1 bar at 1000°C. The diagram, mainly from [1975Hol] has been modified to be coherent with the accepted binary systems. This diagram agrees with the observations of [1962Kat, 1994Aka]. An UN–Zr mixture heated during 168 h at 1000°C shows the formation of a ZrN phase identified by metallographic examination [1962Kat]. The reactions between (U,Zr) alloys and nitrogen was investigated by electron-probe microanalysis and X-ray diffraction between 800 and 1000°C under nitrogen pressures of 0.19 and 20 kPa [1994Aka]. The scales are mainly composed of U_2N_3 , ZrN and (α Zr) having dissolved N. Similar observations are also reported by [1997Oga]. The solubility of U in ZrN or in Zr having dissolved N is negligible [2001Aka].

Thermodynamics

The (U,Zr)N solid solution has been described at 1000°C with a regular model: $\Delta_{\text{mix}} G^{\text{xs}} = \alpha x_{\text{UN}} x_{\text{ZrN}}$ with $\alpha = 18.4 \text{ kJ}\cdot\text{mol}^{-1}$. The solid solution may exhibit a miscibility gap under a critical point estimated at 830°C [1975Hol].

Notes on Materials Properties and Applications

UN used as fuel in a fast transmutation reactor, or (U,Zr)N when ZrN is used as a diluent, offers enhanced performances compared to the conventional oxide fuel [2003The]. It presents higher thermal conductivity, good sodium compatibility and, in case of fuel reprocessing, higher solubility in nitric acid.

The compatibility of UN with cladding materials such as Zr and zircaloy has been tested by [1966Pri] by compressing UN and Zr discs between 400 and 1350°C for periods up to 5000 h. Below 700°C, the reaction products have a low rate of growth and were identified as a mixture of (U,Zr)N solid solution and U rich alloy.

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	at 25°C [Mas2] dissolves ~1 at.% Zr at 617°C [2004Che]
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> β U	$a = 1075.9$ $c = 565.6$	at 25°C [Mas2] dissolves ~2 at.% Zr at 693°C [2004Che]
(α Zr) < 863	<i>hP2</i> <i>P6₃/mmc</i> Mg	$a = 323.16$ $c = 514.75$	at 25°C [Mas2] dissolves ~0.5 at.% U at 593°C [2004Che] dissolves 24.7 at.% N at 1988°C [1994Gri]
(γ U, β Zr) (γ U) 1135 - 776 (β Zr) 1855 -863	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352.4$ $a = 360.90$	solid solution (γ U, β Zr) [Mas2] [Mas2]
δ , UZr ₂ < 617	<i>hP3</i> <i>P6/mmm</i> AlB ₂	$a = 502.5$ $c = 308.6$	64.7 to 77.9 at.% Zr [2004Che] [V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(U,Zr)N	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	$a = 488.83$	50 to 66.3 at.% U at 2427 °C [2000Che] UN melts congruently at 2850°C, 2.5 MPa N ₂ [2000Che]
UN < 2789			
ZrN < 3410		$a = 457.5$	ZrN: 40 to 50 at.% N. Melts congruently at 3670°C, 6 MPa N ₂ pressure; [1994Gri]
β U ₂ N ₃ 1349.1 - 955.2	<i>hP5</i> <i>P$\bar{3}m1$</i> La ₂ O ₃	$a = 370.0$ $c = 582.6$	58.7 at.% N [2000Che]
α U ₂ N ₃ < 1135	<i>cI80</i> <i>Ia$\bar{3}$</i> Mn ₂ O ₃	$a = 1068.8$	60 to 64 at.% N. Gradually changes to CaF ₂ type with increasing N content [2000Che]
UN ₂	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF ₂	$a = 521.0$	high nitrogen pressure phase

Fig. 1: N-U-Zr.
The UN-ZrN
quasibinary system

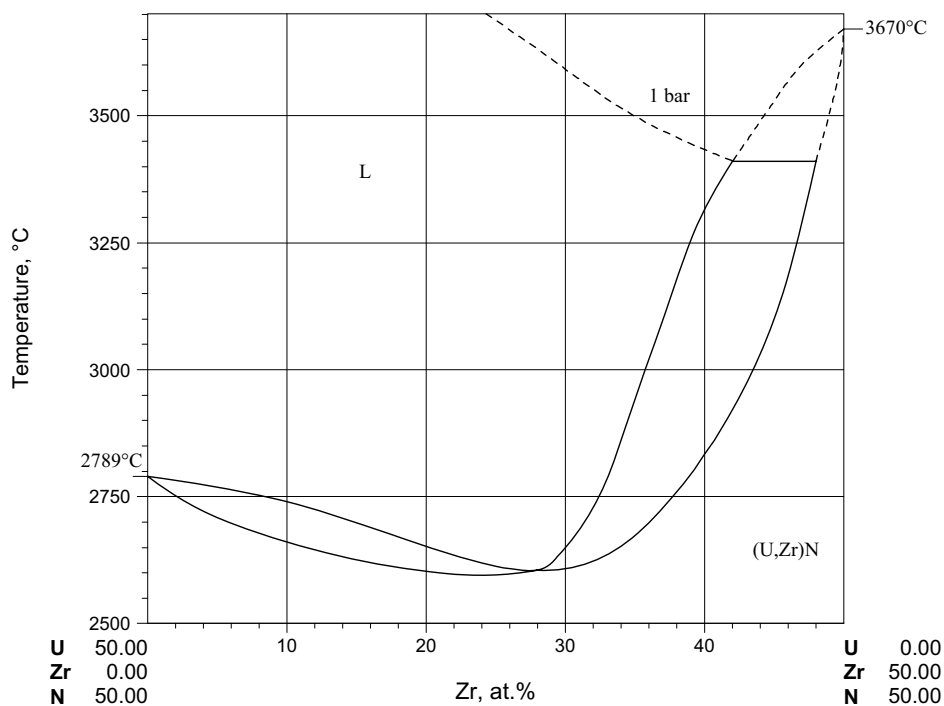
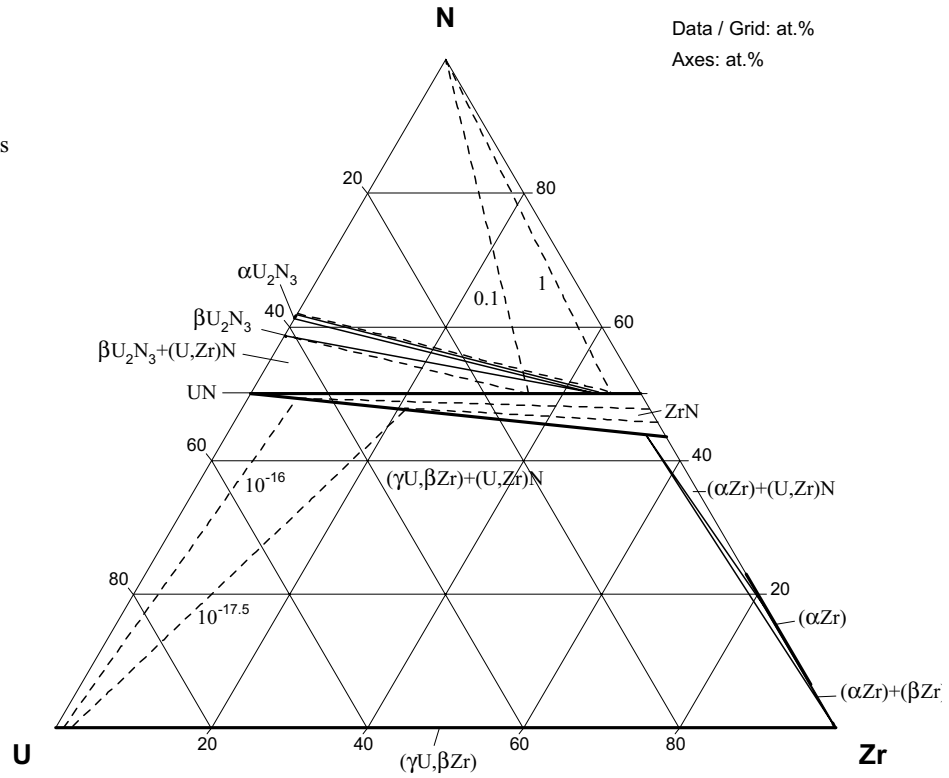


Fig. 2: N-U-Zr.
Phase equilibria at
1000°C showing
some isobaric curves
(dashed lines -
pressures in bar)



Niobium – Silicon – Uranium

Peter Rogl, Henri Noël

Introduction

Missing knowledge on the interaction of uranium silicide fuel and niobium from the burn-up triggered investigation of the Nb-Si-U ternary system.

Information on the constitution of the Nb-Si-U system was provided by two cooperating research groups [1993LeB, 2000Leb] reporting phase relations for the isothermal sections at 1000°C and 850°C, which are characterized by the existence of two ternary compounds: (1) $U_2Nb_3Si_4$ ($Sc_2Re_3Si_4$ type) and (2) closely related $U_{2-x}Nb_{3+x}Si_4$, $x \approx 0.25$, with partially ordered Sm_5Ge_4 type ($Ce_2Sc_3Si_4$ type). Magnetic susceptibility and magnetization data were reported for weakly ferromagnetic $U_2Nb_3Si_4$ [1993LeB, 2000Leb]. The various experimental activities related to the constitution of the ternary Nb-Si-U system are summarized in Table 1.

Binary Systems

The binary boundary system Nb-U is from [Mas2]. The Nb-Si phase diagram was accepted in the version of [1995Sch], which was used in [2002Fer] as a base for thermodynamic assessment. The α - β polymorphic transformation of Nb_5Si_3 takes place in the temperature range 1645 to 1935°C. Nb_3Si was proposed to exist in the temperature range from 1765 to 1975°C. The system Si-U is taken from reinvestigations by [1992Rem, 1993LeB, 1998Noe], but the uranium rich part of the diagram up to 4 at.% Si is from [1965Str]. Crystallographic and melting data pertinent to the Nb-Si-U system are listed in Table 2.

Solid Phases

The crystal structures of the two ternary compounds were established from X-ray Rietveld refinements. Fully ordered and stoichiometric $U_2Nb_3Si_4$ is isotypic with the $Sc_2Re_3Si_4$ type (ordered ternary version of the Zr_5Si_4 type) additionally confirmed from neutron powder data recorded at 1.4 K [1993LeB, 2000Leb]. Single phase $U_2Nb_3Si_4$ was obtained from melted alloys annealed at 1350 to 1400°C. The second ternary phase was obtained at an off-stoichiometric formula $U_{19.3}Nb_{37.4}Si_{43.3}$ (*i.e.* $U_{2-x}Nb_{3+x}Si_4$, $x \approx 0.25$, from EMPA and Rietveld data) with the partially ordered Sm_5Ge_4 type ($Ce_2Sc_3Si_4$ type) [2000Leb]. Retarded reaction kinetics prevented the formation of a single-phase product for $U_{2-x}Nb_{3+x}Si_4$ even after long term annealing treatments (up to 3000 h) still revealing significant amounts of $U_2Nb_3Si_4$ with the $Sc_2Re_3Si_4$ type and of αNb_5Si_3 . The structures of both compounds are closely related and in as-cast alloys they were observed to crystallize in long needles or plates, which separate along a common crystallographic plane [2000Leb].

Liquidus, Solidus and Solvus Surfaces

No information is available on liquidus, solidus or solvus surfaces. Alloys near the Si-U boundary with 10 at.% Si at 1000°C appeared partially molten [2000Leb]. Microstructures of as-cast alloys indicate primary precipitation of the ternary compounds $U_2Nb_3Si_4$ and $U_{2-x}Nb_{3+x}Si_4$.

Isothermal Sections

Phase equilibria have been established in an isothermal section at 1000°C [1993LeB, 2000Leb] and at 850°C [2000Leb]. The isothermal sections are presented in Figs. 1 and 2.

At 1000°C both ternary phases were observed without a homogeneity region and to form a narrow two-phase equilibrium. From the variation of lattice parameters in ternary multiphase alloys annealed at 1000°C small and in most cases negligible mutual solid solubilities among binary uranium and binary niobium silicides were concluded. This was particularly true for αNb_5Si_3 and U_3Si_2 , which from XMA

showed practically no solubility for uranium and niobium, respectively at 1000°C. Even in the as-cast alloys XMA revealed less than 0.6 at.% U in $\alpha\text{Nb}_5\text{Si}_3$ and less than 1.5 at.% Nb in U_3Si_2 . ($\gamma\text{U,Nb}$) was never present in quenched alloys due to rapid decomposition below the monotectoid/eutectoid reaction temperature of the Nb–U binary revealing αU instead. According to the Si–U binary, a small region of liquid phase appears near 90U10Si at 1000°C, which solidifies on quenching the samples giving rise to non-equilibrium structures. $\alpha\text{Nb}_5\text{Si}_3$ was reported to be in equilibrium with the full range of the ($\gamma\text{U,Nb}$) solid solution (see Fig. 1).

Phase equilibria at 850°C are characterized by the two ternary compounds: $\text{U}_2\text{Nb}_3\text{Si}_4$ and closely related $\text{U}_{2-x}\text{Nb}_{3+x}\text{Si}_4$, $x \approx 0.25$, both without homogeneity regions. There is practically no solid solubility of Nb in U_3Si_2 (maximal solubility from EMPA: 59.5U0.1Nb40.4Si), in U_3Si (maximal solubility from EMPA: 75.3U0.1Nb24.6Si) and there is virtually no Si, Nb dissolved in the uranium matrix (maximal solubility from EMPA: 99.3U0.6Nb0.1Si) in contact with the ternary phase $\text{U}_2\text{Nb}_3\text{Si}_4$. The observed two-phase equilibria: ($\gamma\text{U,Nb}$) + $\text{U}_2\text{Nb}_3\text{Si}_4$ and $\alpha\text{Nb}_5\text{Si}_3$ + ($\gamma\text{U,Nb,Si}$) prove, that there is no compatibility between U_3Si_2 fuel and niobium metal at 1000°C and at 850°C, respectively.

Thermodynamics

No experimental thermodynamic data are presently available for the ternary system. As most of the binary boundary phases engage in two-phase equilibria with stoichiometric $\text{U}_2\text{Nb}_3\text{Si}_4$, a relatively high thermodynamic stability of this ternary compound could be inferred.

Miscellaneous

The effect of 0.1 to 0.5 mass% Nb-additives on the corrosion resistance of U_3Si against water at 300°C under 90 MPa was investigated by [1993Kon]. The speed of corrosion was measured for various length of time from 100 to 1000 h. After 300 h the speed of corrosion, for instance, for the alloys with 0.4 mass% Nb was given as $0.2 \text{ mg} \cdot (\text{cm}^{-2} \cdot \text{h})^{-1}$. Niobium seems to decrease the rate of corrosion with amount (from 0.1 to 0.4 mass% Nb) and with time.

Magnetic properties of $\text{U}_2\text{Nb}_3\text{Si}_4$ in the temperature range of 5–300 K and in fields up to 2 Tesla were described with an effective paramagnetic moment $\mu_{\text{eff}} = 2.34 \mu_{\text{B}}/\text{U}_{\text{atom}}$, $\Theta_{\text{p}} = -21 \text{ K}$ and a temperature independent term $\chi_o = 33.9 \cdot 10^{-9} \text{ m}^3 \cdot \text{mol}^{-1}$. $\text{U}_2\text{Nb}_3\text{Si}_4$ was said to be weakly ferromagnetic below $T_c \approx 35 \text{ K}$ with a rather small remanence of only $0.0088 \mu_{\text{B}} \cdot \text{U}_{\text{atom}}^{-1}$. A neutron powder diffraction experiment at 1.4 K failed to reveal any magnetic contribution, which suggested that the magnetic moments were certainly smaller than $\sim 0.3 \mu_{\text{B}}$ [2000Leb].

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Table 1: Experimental Investigations of the Nb-Si-U Phase Relations, Structures and Properties

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1993LeB]	Arc melting of elemental ingots under argon; heat treatment at 1000-1050°C. A single phase material of U ₂ Nb ₃ Si ₄ was obtained from an alloy annealed at 1300-1400°C for 48 h in a W-sheet vacuum furnace. Measurement range for χ : $2 < T < 300$ K; magnetization at 5 K up to 2 Tesla.	Phase equilibria at 1000°C. Determination of the crystal structures of U ₂ Nb ₃ Si ₄ from X-ray powder data. Neutron powder diffraction of U ₂ Nb ₃ Si ₄ ($\lambda = 0.24268$ nm, $T = 1.4$ K). Magnetic susceptibility $2 < T < 300$ K; magnetization < 2 Tesla at 5 K for U ₂ Nb ₃ Si ₄ and UMo _{1.25} Si _{0.75} .
[1993Kon]	Arc-melted alloys U ₃ Si annealed at 800°C for 100 h. Starting materials 99.8 mass% U, chemical analysis, XPD, metallography.	Investigation of the effect of 0.1 to 0.5 % Nb-additives on the corrosion resistance of U ₃ Si in water at 300°C under 90 MPa (in an autoclave) from 100 to 1000 h.
[2000Leb]	Alloys prepared by arc melting or levitation melting in argon. Heat treatment at 1000°C on tungsten substrates in a high vacuum W-sheet furnace for 200 h. For equilibria at 850°C, samples within alumina crucibles were vacuum-sealed in quartz capsules and heat treated for 300 h and water quenched. Starting materials: 99.9 mass% U, 99.9% Nb, 99.9999% Si. Metallography, EMPA, X-ray powder diffraction. Neutron powder diffraction of U ₂ Nb ₃ Si ₄ . Measurement range for χ : $2 < T < 300$ K; magnetization at 5 K up to 6 Tesla.	Phase equilibria at 1000°C and at 850°C. Determination of the crystal structure of U ₂ Nb ₃ Si ₄ and of U _{2-x} Nb _{3+x} Si ₄ , $x \approx 0.25$ from Rietveld refinements. Magnetic susceptibility $2 < T < 300$ K; magnetization < 2.5 Tesla at 5 K for U ₂ Nb ₃ Si ₄ .

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(γU,Nb)	<i>cI2</i> <i>Im$\bar{3}m$</i>		[Mas2]
(γU) 1135 - 774.8	W	$a = 353.35$	pure U; refined at 787°C, [Mas2]
(Nb) < 2469		$a = 330.04$	pure Nb [Mas2]
(Si) < 1414	<i>cF8</i> <i>Fd$\bar{3}m$</i> C _{diamond}	$a = 543.06$	[Mas2]
(βU) 774.8 - 667.7	<i>tP30</i> <i>P4₂/mnm</i> βU	$a = 1075.89$ $c = 565.31$	[Mas2]
(αU) < 667.7	<i>oC4</i> <i>Cmcm</i> αU	$a = 285.37$ $b = 586.95$ $c = 495.48$	[Mas2]
Nb ₃ Si 1975 - 1765	<i>tP32</i> <i>P4₂/n</i> Ti ₃ P	$a = 1022.4$ $c = 518.9$	[1995Sch]
βNb ₅ Si ₃ 2515 - 1645	<i>tI32</i> <i>I4/mcm</i> W ₅ Si ₃	$a = 997$ $c = 508$	37.5 to 40.5 at.% Si, [1995Sch] Si rich [1995Sch]
		$a = 1004.0$ $c = 508.1$	Si poor [1995Sch]
αNb ₅ Si ₃ < 1935	<i>tI32</i> <i>I4/mcm</i> Cr ₅ B ₃	$a = 657.1$ $c = 1188.9$	36.7 to 39.8 at.% Si [1995Sch]
NbSi ₂ < 1935	<i>hP9</i> <i>P6₂22</i> CrSi ₂	$a = 481.9$ $c = 659.2$	[1995Sch]
USi ₃ < 1510	<i>cP4</i> <i>Pm$\bar{3}m$</i> Cu ₃ Au	$a = 403.53$	[1992Rem]
USi ₂ < 450	<i>tI12</i> <i>I4₁/amd</i> ThSi ₂	$a = 392.2$ $c = 1415.4$	(metastable), [1992Rem]
α ₁ , USi _{2-x} < 1710	<i>tI12</i> <i>I4₁/amd</i> def-ThSi ₂	$a = 394.23$ $c = 1371.2$	USi _{1.88} 65 at.% Si, [1992Rem]
α ₂ , USi _{2-x}	<i>oI12</i> <i>Imma</i> def-GdSi ₂	$a = 395.3$ $b = 392.9$ $c = 1365.6$	at 64 at.% Si, [1992Rem]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
α_3 , USi_{2-y}	<i>oP6</i> <i>Pmmm</i> (?) distorted AlB_2	$a = 389.3$ $b = 671.7$ $c = 404.2$	($\text{U}_3\text{Si}_5\text{-o2}$) at ~ 63 at.% Si, [1992Rem]
α_4 , USi_{2-y}	<i>oP6</i> <i>Pmmm</i> distorted AlB_2	$a = 386.4$ $b = 666.0$ $c = 407.3$	($\text{U}_3\text{Si}_5\text{-o1}$) at 63 at.% Si, [1992Rem]
α_5 , USi_{2-y} < 1770	<i>hP3</i> <i>P6/mmm</i> defect AlB_2	$a = 384.75$ $c = 407.40$	($\text{U}_3\text{Si}_5\text{-hex}$ or $\text{USi}_{1.67}$) [1992Rem]
USi < 1580	<i>tI138</i> <i>I4/mmm</i> USi	$a = 1058.7$ $c = 2431.0$	[1992Rem, 1993LeB, 1996LeB]
USi (metastable)	<i>oP8</i> <i>Pnma</i> FeB	$a = 758.5$ $b = 390.3$ $c = 566.3$	probably impurity (O) stabilized [1992Rem, 1993LeB]
U_5Si_4 < 1100	<i>hP18</i> <i>P6/mmm</i> U_5Si_4	$a = 1046.7$ $c = 391.2$	Single crystal study [2006Noe]
U_3Si_2 < 1665	<i>tP10</i> <i>P4/mbm</i> U_3Si_2	$a = 732.99$ $c = 390.04$	[V-C2, Mas2]
$\gamma\text{U}_3\text{Si}$ 930 - 759	<i>cP4</i> <i>Pm\bar{3}m</i> Cu_3Au	$a = 434.6$	[V-C2, 1965Str]
$\beta\text{U}_3\text{Si}$ 762 - -153	<i>tI16</i> <i>I4/mcm</i> $\beta\text{U}_3\text{Si}$	$a = 603.28$ $c = 869.07$	[V-C2, 1965Str]
$\alpha\text{U}_3\text{Si}$ < -153°C, at -193°C	<i>oF32</i> <i>Fmmm</i> $\alpha\text{U}_3\text{Si}$	$a = 865.4$ $b = 854.9$ $c = 852.3$	[V-C2, 1965Str]
* τ_1 , $\text{U}_2\text{Nb}_3\text{Si}_4$	<i>tP36</i> $P4_12_12$ $\text{Sc}_2\text{Re}_3\text{Si}_4$ (ordered Zr_5Si_4 type)	$a = 703.89$ $c = 1298.4$	stoichiometric [2000Leb] $R_F = 0.046$
* τ_2 , $\text{U}_{2-x}\text{Nb}_{3+x}\text{Si}_4$	<i>oP36</i> <i>Pnma</i> $\text{Ce}_2\text{Sc}_3\text{Si}_4$ (ordered Sm_5Ge_4 type)	$a = 0.6760$ $b = 1314.1$ $c = 693.2$	at 19.3U37.4Nb43.3Si (at.%) [2000Leb]

Fig. 1: Nb-Si-U.
Isothermal section at
1000°C

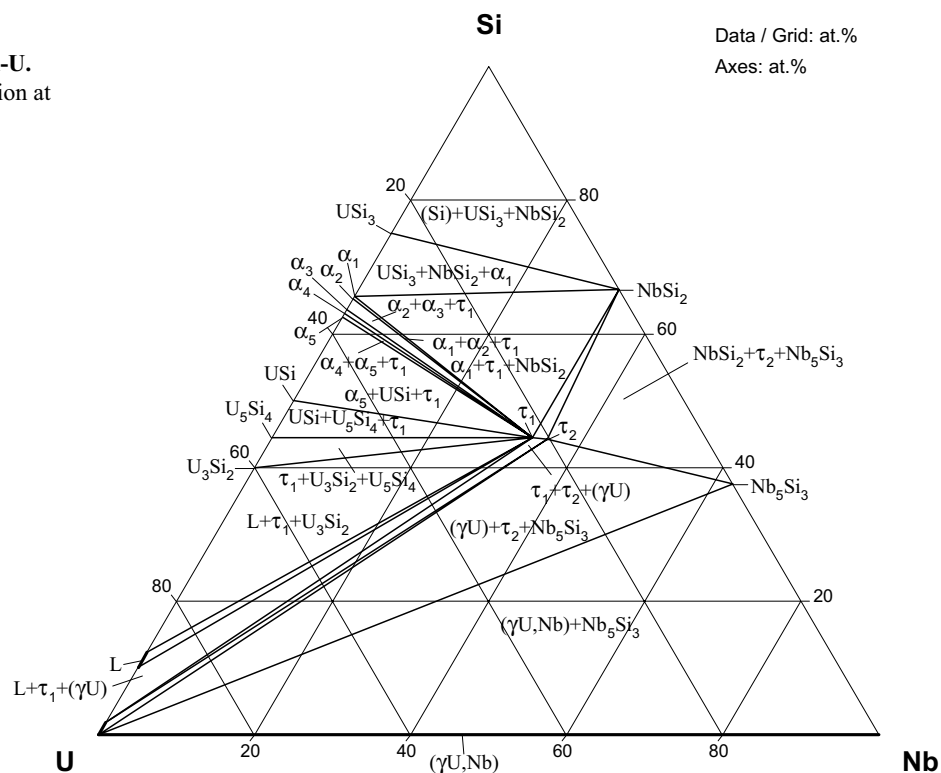
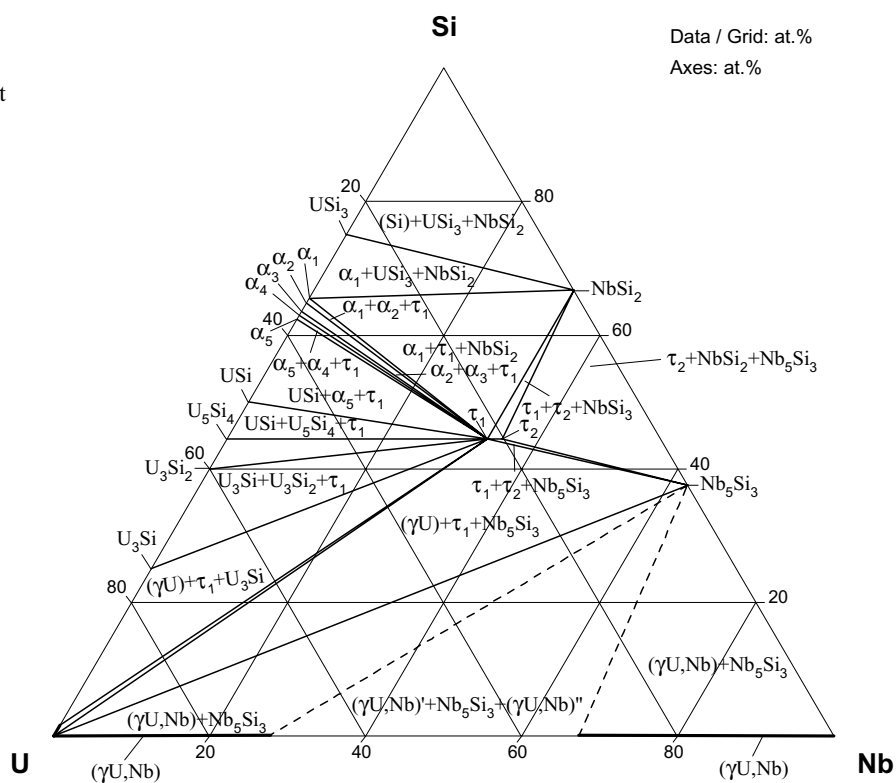


Fig. 2: Nb-Si-U.
Isothermal section at
850°C



Oxygen – Lead – Zirconium

Marija Cancarevic, Matvei Zinkevich, Fritz Aldinger

Introduction

Experimental studies of the O–Pb–Zr system are confined to the investigation of ZrPbO_3 and the PbO–ZrO_2 section [1962Ike, 1967Fus, 1967Har, 1981Jac]. Thermodynamic properties and the phase diagram of the PbO–ZrO_2 system have been critically assessed by [1999Koo]. Extensive studies on the crystal structure, thermodynamic properties and phase transitions in lead zirconate are listed in Table 1.

Binary Systems

The binary O–Zr phase diagram is adopted from [Mas2]. The thermodynamic assessment of the O–Zr system reported by [2001Lia] is consistent with the accepted phase diagram.

The binary O–Pb phase diagram (Fig. 1) is taken from the critical assessment [1998Ris], with some modifications in the liquid phase region [2005Can]. There are no reports about the oxygen saturation limit in solid Pb, but it is certainly extremely small and could never be detected [1988Wri]. The liquid phase exhibits a large miscibility gap.

The accepted Pb–Zr phase diagram (Fig. 2) is taken from the critical evaluation of [1996Ari] later reviewed by [1999Oka]. This diagram is not definitively established due to very limited experimental information. There is no experimental information regarding the melting temperature of Zr_5Pb_3 . This temperature was estimated to be $\sim 1650^\circ\text{C}$ by [1996Ari]. The value of $\sim 2000^\circ\text{C}$ was accepted by [1986Dal].

Solid Phases

Data pertinent to the PbO–ZrO_2 section are listed in Table 2.

Three stable perovskite type phases have been found at the ZrPbO_3 composition: the orthorhombic low temperature (up to 231°C) phase is antiferroelectric, the intermediate (from 231 to 234°C) is ferroelectric, and the cubic high temperature (up to the melting point $T_m = 1570^\circ\text{C}$) phase is paraelectric [1979Wha] (Table 2). The paraelectric $\rightleftharpoons$ ferroelectric $\rightleftharpoons$ antiferroelectric phase transition temperatures depend on the oxygen nonstoichiometry and on the compositional deviations caused by the sublimation of PbO [1985Ujm]. Until now, the basic structure parameters have mainly been investigated for the antiferroelectric phase.

It was under debate for many years whether the room temperature phase of lead zirconate, $\alpha\text{ZrPbO}_3(\text{r})$ is ferroelectric or antiferroelectric and hence whether the crystal structure belongs to the centrosymmetric or non-centrosymmetric space group. The crystal structure of the lead zirconate modifications was first proposed by [1951Saw] and the space group of the antiferroelectric phase was reported to be *Pbam* or *Pba2*. The authors were unable to locate the position of Zr or O ions, or to detect any displacement of the Pb ions out of the (001) planes. [1957Jon] made a more detailed study. Positions of the Zr and O ions were located to some extent, but they were not sure if the cations were displaced out of the (001) plane. The structure of $\alpha\text{ZrPbO}_3(\text{r})$ has been reinvestigated by [1982Fuj, 1984Fuj]. These authors found a better reliability factor for space group *Pbam* than for *Pba2*. Also [1982Tan1, 1982Tan2] suggested the *Pbam* space group and determined the oxygen coordinates. In all these crystal studies it was assumed that the structure is fully ordered. However, according to [1993Gla] $\alpha\text{ZrPbO}_3(\text{r})$ exhibit a disorder in the oxygen sites, whereas the ZrO_6 octahedra are considerably more regular. Later [1997Cor] found the true ordered oxygen structure, while [1998Tes] characterized structure by distortion of the ZrO_6 octahedra which is smaller than in the previous study [1993Gla]. The space group *Pbam* was also confirmed by [1997Cor, 1998Tes]. Moreover, the disorder in Pb ions displacements along *z* axis [1997Cor, 1997Sic, 1998Tes, 2000Fuj, 2001Fuj, 2002Fuj, 2003Fuj1, 2003Fuj2] and Zr-displacements were observed [1998Yam, 1997Soe]. There is a possibility, however, that the observed disorder is simply an artifact of pseudosymmetry. Whatever the space group is, one of the main problems in an accurate structure determination is the strong

pseudosymmmertic character of the Pb and Zr sites and the relatively high scattering factor of the cations compared to the oxygen anions [1996Cor]. The difficulties to grow high quality large single crystals poses an additional problem. Thus, questions regarding the existence of polarization and the true crystal structure of lead zirconate are still open.

The structural instabilities and electronic properties of antiferroelectric $\alpha\text{ZrPbO}_3(\text{r})$ were investigated by local-density total-energy calculations [1995Sin] using the atomic positions of [1982Fuj, 1984Fuj]. Results of [1995Sin] demonstrated the coexistence of both ferroelectric and antiferroelectric instabilities in lead zirconate, with a very delicate balance between them and correctly predicted a centrosymmetric *Pbam* group as the most stable structure, but a ferroelectric rhombohedral structure was very close in energy. Based on the new experimental data of [1997Fuj] a reexamination of crystal structure of antiferroelectric $\alpha\text{ZrPbO}_3(\text{r})$ using density functional calculation [2002Rod, 2005Joh] showed small, but significant changes in cation positions compared to [1995Sin]. The relative stability of the antiferroelectric and ferroelectric phases in lead zirconate was also studied by [1998Ley], where the antiferroelectric dipole configuration was reported to be energetically more favorable than the ferroelectric one.

There is very little structural information about the paraelectric phase [1951Saw, 1979Koc, 1995Sin, 2001Kwa, 2002Aoy]. [1979Koc] found the existence of two phase transitions at 325 and 390°C in cubic paraelectric lead zirconate. [2002Aoy] detected the distinct disorder of Pb at twelve sites toward the neighboring O, which proves the existence of electron hybridization between O and disordered Pb in cubic $\beta\text{ZrPbO}_3(\text{h}_2)$. [2001Kwa] preformed experiments and model calculations reporting the strong indication of the displacement of Pb in cubic high temperature lead zirconate. The local density calculations by [1995Sin] showed a very strong instability of the cubic perovskite structure, which involve the changes in Pb–O distances with substantial hybridization between O and Pb. Results of [2002Rod] are very close to those obtained by [1995Sin]. Covalent nature of Pb and O bonds is also revealed in first principles study of [2005Wan].

Many authors reported the presence of a transient phase, $\gamma\text{ZrPbO}_3(\text{h}_1)$ [1951Saw, 1984Fuj, 1985Ism, 1986Rol, 1989Rol, 1992Fuj, 1998Tes] apart from the orthorhombic antiferroelectric and cubic paraelectric phases. However, the results and conclusions vary in details. [1951Saw] described the intermediate phase as antiferroelectric one with the tetragonal symmetry and occurring on cooling only. [1979Wha] reported the rhombohedral symmetry of the ferroelectric transient phase. [1984Fuj, 1992Fuj] supposed that the intermediate phase has an antiferroelectric character, while [1989Dec, 1982Tan2] reported that the transient phase has a ferroelectric character. Ferroelectric character of the intermediate phase was confirmed by dielectric measurements of [1986Rol, 1989Rol]. Authors of [1982Tan2] were the first who determined the space group of the transient phase as *F2mm*. At the same time, Rietveld analyses with *Pba2* and *Pbam* settings made by [1998Tes] gave poor fits with large thermal factors on all atomic sites, what excluded these space groups.

In the purest samples of ZrPbO_3 the stability range of the intermediate phase is very narrow. Usually it has been detected between 230 and 235°C on heating and between 234 and 225°C on cooling. This temperature range depends on the purity of reagents or solvent used [1979Wha], but within the given class of reagents also on the preparation conditions [1989Dec]. Effect of preparation conditions, *i.e.*, sintering temperature, on phase transitions in lead zirconate was also investigated by [2004Puc1, 2004Puc2], while [1996Fes] reported the effect of the chemical etching on the phase transition and electrical hardening. It was also found that external DC electric field broadened and stabilized the transient ferroelectricity but that hydrostatic pressure rapidly removed it [1981Han].

The temperature dependence of permittivity and remaining polarization in monocrystalline and ceramic ZrPbO_3 and the temperature of the phase transitions between ferro-, antiferro-, and paraelectric phases are influenced by applied electric field and hydrostatic pressure. Under external electric field, ZrPbO_3 undergoes a series of phase transitions [1979Fes]. Although many studies have been performed [1981Han, 1978Fes, 1979Fes, 1984Leo, 1985Ism, 1992Shu, 1996Shu] no complete structural analysis of the field induced phases has been made so far. The lack of structural information on these phases is hindering the elucidation of the mechanisms of phase transition of this kind. [1984Leo] and [1992Shu, 1996Shu] reported the existence of a ferroelectric phase arising at room temperature under electric field of about 220 kV/cm.

The space group of this EFI (Electric Field Induced) phase is $Cm2m$ and its ferroelectric properties are due to the ordering of Pb displacements relative to the oxygen framework along the polar axis [1996Shu]. Before 1995, there were only few studies focused on the influence of hydrostatic pressure on the phase transitions in lead zirconate [1981Han, 1985Ujm]. The ferroelectric phase was found to occur only at pressures less than 26 MPa for monocrystals and 40 MPa for the ceramics [1981Han]. Recently, the behavior at room temperature and much higher pressures has been studied in terms of structure and dielectric properties [1994Men, 1999Kob, 1999Fur1, 1999Fur2]. [1994Men] performed the high pressure experiments on the nanocrystalline $ZrPbO_3$ (with grain size of 94 nm). The transition pressure from ferro- to antiferroelectric as well as from para- to ferroelectric phases was found to be 0.79 and 4.12 GPa, respectively. [1999Kob] found that the orthorhombic phase ($\alpha ZrPbO_3$) transforms into the monoclinic one with almost no volume change at 37 GPa. This study also suggested a subtle structural change occurring in the monoclinic phase at about 75 GPa. On the other hand, dielectric constant measurements showed two anomalies at around 3 and 19 GPa for the polycrystalline samples, which suggested the existence of two transitions in the orthorhombic phase. Two phase transitions at about 2.3 and 17.5 GPa were confirmed by [1999Fur1, 1999Fur2]. Results of *ab initio* molecular dynamics and pseudopotentials calculations for the pressure influence on phase transitions [2002Leu] are in reasonable agreement with experiments. Local density calculations of [2000Coc] show that all the modes determining the orthorhombic antiferroelectric phase become more unstable in the range of lattice parameters corresponding to positive pressures.

Quasibinary Systems

The PbO– ZrO_2 section was first investigated by [1962Ike] and published by [1967Fus]. Decomposition of cubic $\beta ZrPbO_3(h_2)$ to tetragonal βZrO_2 and a liquid phase containing 93 mol% PbO at 1570°C [1967Fus] was also confirmed by [1981Jac]. A few investigations has been performed in the PbO rich part of PbO– ZrO_2 system [1967Fus, 1981Jac, 1967Har] but results are contradictory. [1967Har] reported that X-ray analysis of the samples PbO + ZrO_2 in 1:1 molar ratio heated to 1294°C indicated the presence of $ZrPbO_3$, αZrO_2 , and αPbO . The last phase had a tetragonal structure of the red αPbO rather than the orthorhombic structure of the yellow βPbO . This finding was confirmed by [1981Jac] by heating an equimolar mixture of βPbO and αZrO_2 up to 955°C, followed by cooling in air and X-ray analysis. This observation is not in accord with the phase diagram by [1967Fus], but consistent with the assessed phase diagram by [1999Koo] which is accepted in the present assessment (Figs. 3a, 3b). A detailed study of the PbO rich side of the PbO– ZrO_2 phase diagram is required to check the temperature boundaries and phase composition of the various phase fields.

Invariant Equilibria

Table 3 lists the three-phase equilibria in the PbO– ZrO_2 system calculated using the thermodynamic description of [1999Koo]. The temperatures of the peritectic formation of $\beta ZrPbO_3(h_2)$, αPbO solid solution and that of the PbO rich eutectic were measured by [1967Fus] and are reproduced very exactly by calculations. No other invariant equilibria are known. The temperature of the $L + ZrO_2 \rightleftharpoons \beta ZrPbO_2$ reaction was calculated to be 1538°C [1999Koo], that is lower than experimental value of 1570°C [1967Fus, 1981Jac].

Thermodynamics

Thermodynamic properties of $ZrPbO_3$ were investigated by several groups [1969Hae, 1973Hol, 1979Sch, 1981Jac, 1993Gos, 1996Ono]. The experimental investigations were mainly performed on the high temperature cubic modification, β (Tables 4, 5 and 6) except the study of [1993Gos] on the low temperature orthorhombic modification, α . [1996Ono] measured the heat capacity of single crystals of antiferroelectric $\alpha ZrPbO_3(r)$ in a wide temperature region (from room temperature to 377°C) by AC calorimetry, but have drawn the curve in arbitrary units. Heat capacity curve showed a sharp change at 231.5°C, due to transformation into the high temperature modification. [1993Gos] reported the thermodynamic functions (C_p , S , $H_T - H_{298}$) of the low temperature orthorhombic modification (α) from room temperature to 207°C.

The low temperature heat capacity data of $\alpha\text{ZrPbO}_3(\text{r})$ are missing. The Gibbs energy of formation of lead zirconate calculated from the vapor pressure studies (assuming that the vapor phase consists entirely of monomeric PbO molecules) [1969Hae, 1973Hol, 1979Sch] is inconsistent with the emf measurements reported by [1981Jac] and the PbO-ZrO_2 phase diagram, which suggests decomposition of lead zirconate to tetragonal ZrO_2 and a liquid phase containing 93 mol% PbO at 1570°C . Since the vapor phase over pure solid and liquid PbO consist of polymeric species of type Pb_nO_n ($1 < n < 6$) results based on the vapor pressure measurements differ significantly from those obtained by EMF measurements [1981Jac]. Recently, the enthalpy of formation of $\beta\text{ZrPbO}_3(\text{h}_2)$ was measured by [2001Ran]. The heat content and entropy of $\beta\text{ZrPbO}_3(\text{h}_2)$ are not known. Thermodynamic data for the other phases in the O-Pb-Zr system (liquid, PbO solid solutions, (αZr), (βZr), etc.) are completely missing.

[1999Koo] reported the thermodynamic assessment of the PbO-ZrO_2 system, where ZrPbO_3 was modeled as a stoichiometric compound based on the results of [1981Jac]. However, the only cubic high temperature phase $\beta\text{ZrPbO}_3(\text{h}_2)$ was included in the assessment. The Gibbs energy of cubic lead zirconate was described as $G_{\text{m}}^{\text{ZrPbO}_3} = G(\text{h})_{\text{PbO}_2} + G_{\alpha\text{ZrO}_2} - 4540 - 676T \text{ (J}\cdot\text{mol}^{-1}\text{)}$. The calculated heat capacity ($C_p = 110.6 + 2.5 \cdot 10^{-2} T - 7.8 \cdot 10^5 T^{-2} \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), molar enthalpy and entropy for the cubic ZrPbO_3 are presented in Figs. 4 - 6. Figure 7 shows the calculated PbO vapor pressures compared with experimental data [1979Sch, 1973Hol, 1969Hae]. The standard enthalpy and the Gibbs energy of formation of $\beta\text{ZrPbO}_3(\text{h}_2)$ from elements and its entropy at 298 K, which were calculated using the thermodynamic description of [1999Koo] are presented in Table 7.

Notes on Materials Properties and Applications

Because of dielectric, pyroelectric and electro-optical properties lead zirconate ceramics has long been studied from both physical and technical point of view (Table 8). Especially, lead zirconate thin films have been studied extensively [1992Wan, 1999Bha, 2000Bae, 2000Bha, 2001Dob, 2004Ste]. Intensive research work has been carried out on ferroelectric and paraelectric thin films for commercial applications such as memory devices, infrared detectors and non-linear optoelectronics. Recently, antiferroelectric thin films [1992Wan, 1999Bha, 2000Bha] have been proposed for the new generations of “smart” systems such as high charge coupled devices (MEMs) consisting of sensors and actuators. Antiferroelectric materials are characterized by the antiparallelly aligned adjacent dipoles with zero polarization in equilibrium. The transformation of antiferroelectric to ferroelectric phase by a sufficient applications of electric field could be utilized for the high charge coupled devices and transducer applications. In addition, the highly oriented antiferroelectric ZrPbO_3 thin films were investigated in view of their possible application as a temperature sensitive element in an alternative bolometer system for fusion devices such as the International Thermonuclear Experimental Reactor to quantitatively determine the total power of incident radiation over a wide range of wavelengths [2004Bit, 2004Ste].

Miscellaneous

The E - T phase diagram of lead zirconate and schematic isothermal dependences of the dielectric polarization on the electric field are presented in Fig. 8 [1978Fes, 1979Fes]. [1989Hau] reported the thermodynamic theory to model the phase transition and properties of lead zirconate where its free energy was expressed as a power series of the ferroelectric and antiferroelectric polarization including all possible terms up to the sixth power and first-order cross-coupling terms and couplings to elastic stress. Morphologies of thin films and single crystals were also studied. Preferred orientation in ZrPbO_3 thin films prepared by sol-gel technique was studied by [2000Bae], while [1992Top] investigated the S type of twinning boundaries in ferro- and antiferro- ferroelectric ZrPbO_3 crystals.

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Table 1: Investigation of the O–Pb–Zr Phase Relations, Structures and Thermodynamics

References	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1951Saw]	Polarization microscopy X-ray diffraction	Single crystals of the antiferroelectric and cubic ZrPbZrPbO_3
[1962Ike]	Solid state reactions X-ray diffraction	PbO to ZrO_2 , fired at 1150–1200°C, > 850°C for PbO rich compositions, 1300°C for ZrO_2 rich ones
[1967Fus]	Quenching X-ray diffraction DTA	1100, 1200 and 1300°C Phase relations in PbO rich side of the PbO– ZrO_2 phase diagram
[1967Har]	Solid state reactions X-ray diffraction	1290°C, $\text{PbO}:\text{ZrO}_2 = 1:1$
[1973Hol]	Knudsen effusion mass spectroscopy	850 to 1150°C PbO vapor pressure over the $\text{ZrPbO}_3 + \alpha\text{ZrO}_2$ and $\text{ZrPbO}_3 + \text{PbO(l)}$ region
[1979Nur]	Knudsen effusion mass spectroscopy	712 to 1023°C Pb vapor pressure over the $\text{ZrPbO}_3 + \alpha\text{ZrO}_2$ region
[1979Sch]	Dynamic thermobalance method (transportation technique) and EMF measurements	400, 450, 650 and 1027°C PbO vapor pressure over the $\text{ZrPbO}_3 + \alpha\text{ZrO}_2$ and $\text{ZrPbO}_3 + \text{PbO(l)}$ region
[1979Wha]	X-ray (continuously recording X-ray diffraction)	20 to 228°C Crystal structure of the antiferroelectric, ferroelectric and paraelectric ZrPbO_3 phases
[1979Koc]	X-ray diffraction	230 and 480°C Crystal structure of the paraelectric ZrPbO_3 phase
[1981Jac]	EMF measurements	527 and 1127°C PbO potential over the $\text{ZrPbO}_3 + \alpha\text{ZrO}_2$ region
[1982Fuj]	X-ray diffraction Neutron diffraction	25°C Crystal structure of the antiferroelectric ZrPbO_3 phase
[1982Tan1]	X-ray diffraction Electron microscopy (JEM, CBED)	25°C Crystal structure of the antiferroelectric ZrPbO_3 phase
[1982Tan2]	X-ray diffraction Electron microscopy (JEM)	25°C Crystal structure of the antiferroelectric ZrPbO_3 phase

References	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1984Fuj]	Neutron diffraction	25°C Crystal structure of the antiferroelectric ZrPbO ₃ phase
[1984Leo]	X-ray diffraction	25°C Crystal structure of the electric field induced ferroelectric lead zirconate
[1989Dec]	Polarization microscopy X-ray diffraction	25, 460 and 550°C Single crystals of the antiferroelectric and cubic ZrPbO ₃
[1992Fuj]	X-ray diffraction Neutron diffraction Rietveld method	230°C Crystal structure of the intermediate ZrPbO ₃ phase
[1992Shu]	X-ray diffraction	25°C Crystal structure of the electric-field induced ferroelectric lead zirconate
[1993Gos]	X-ray diffraction Gravimetry Differential scanning calorimetry	127 to 207°C The molar heat capacity of the antiferroelectric ZrPbO ₃
[1993Gla]	Polarization microscopy X-ray diffraction	24°C Crystal structure of the antiferroelectric ZrPbO ₃ phase
[1994Men]	Raman scattering method TEM	25°C Structure of the pressure-induced phase transition in nanocrystalline antiferroelectric ZrPbO ₃ phase
[1996Ono]	AC calorimetry	25 to 377°C The heat capacity of the single crystals of lead zirconate
[1996Shu]	X-ray diffraction EXAFS	25°C Crystal structure of the electric-field induced ferroelectric lead zirconate
[1996Cor]	X-ray diffraction Neutron diffraction	25°C Crystal structure of the antiferroelectric ZrPbO ₃ phase
[1997Fuj]	Neutron diffraction Rietveld method	25°C Crystal structure of the antiferroelectric ZrPbO ₃ phase
[1997Sic]	X-ray (XAFS)	–100 to 550°C Crystal structure of antiferroelectric, intermediate and paraelectric ZrPbO ₃ phases
[1997Cor]	X-ray diffraction Neutron diffraction	–173°C Crystal structure of the single crystals of antiferroelectric ZrPbO ₃ phase
[1997Soe]	X-ray diffraction	25°C Single crystals of the antiferroelectric ZrPbO ₃

References	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1998Tes]	Pulsed neutron diffraction	–253, 25, 200 and 235°C Crystal structure of antiferroelectric, intermediate and paraelectric ZrPbO ₃ phases
[1998Yam]	X-ray diffraction	25°C Crystal structure of the antiferroelectric ZrPbO ₃
[1999Fur1]	Raman spectroscopy	25°C, pressure up to 30 GPa Structure and phase transitions of ZrPbO ₃
[1999Fur2]	Raman spectroscopy	25°C, pressure up to 30 GPa Pressure-induced phase transition in ZrPbO ₃
[1999Kor]	NMR	At 25°C, pressure up to 30 GPa Pressure-induced phase transition in ZrPbO ₃
[1999Kob]	X-ray diffraction	25°C, pressure up to 75 GPa Crystal structure and phase transition of ZrPbO ₃
[2000Fuj]	X-ray diffraction Neutron diffraction (Rietveld method)	25 to –188°C Crystal structure of the antiferroelectric ZrPbO ₃ phase
[2001Fuj]	X-ray diffraction Neutron diffraction (Rietveld method)	25 to –265°C Crystal structure of the antiferroelectric ZrPbO ₃ phase
[2001Ost]	IR reflectivity measurements	623 to –263°C Structure of the antiferroelectric ZrPbO ₃ phase
[2001Kwa]	X-ray diffraction	250 to 600°C Crystal structure of the cubic ZrPbO ₃ phase
[2002Aoy]	X-ray diffraction Rietveld method	247°C Crystal structure of the cubic ZrPbO ₃ phase
[2003Fuj1]	X-ray diffraction	25 to –265°C Crystal structure of the antiferroelectric ZrPbO ₃

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γZrO_{2-x} 2710 - ~1525	<i>cF12</i> <i>Fm3m</i> CaF ₂	$a = 494.72$ $a = 509$	61.0 to 66.6 at.% 63.6 at.% at 1525°C 62 at.% at 2052°C [1986Abr, Mas2] [2000Bou] [1986Abr]
βZrO_{2-x} 2377 - 1205	<i>tP6</i> <i>P4₂/nmc</i> HgI ₂	$a = 359.482$ $c = 518.247$ $a = 358.82$ $c = 518.82$	66.5 to 66.6 at.% O [1986Abr, Mas2] [2000Bou] [1986Abr]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
αZrO_2 < 1205	<i>mP12</i> <i>P2_1/c</i>	$a = 514.513$ $b = 520.234$ $c = 532.194$ $\beta = 99.153^\circ$	[Mas2, 1986Abr] baddeleyite [2002Win]
		$a = 516.9$ $b = 523.2$ $c = 534.1$ $\beta = 99.15^\circ$	[1986Abr]
βPbO 886 - 489	<i>oP8</i> <i>Pbcm</i> βPbO	$a = 589.31$ $b = 549.04$ $c = 475.28$	[1998Ris] massicot [1985Hil, V-C2]
		$a = 561.12$ $b = 560.91$ $c = 499.35$	[V-C2]
αPbO < 489	<i>tP4</i> <i>P4/nmm</i> αPbO	$a = 397.44$ $c = 502.20$	[1998Ris, V-C2] dissolves up to 3.41 at.% Zr (7.058 mol% ZrO_2) [1999Koo] dissolves 4 mol% ZrO_2 [1967Fus] at 25°C [V-C2]
* βZrPbO_3 (h_2) 1570 - 234	<i>cF*</i> <i>Fm$\bar{3}m$</i>	$a = 415$	[1967Fus, 1979Wha] [1951Saw]
* γZrPbO_3 (h_1) 234 - 231	<i>cF*</i> <i>F2mm</i>	-	[1979Wha, 1982Tan1, 1982Tan2]
* αZrPbO_3 (r) < 231	<i>oP40</i> <i>Pbam</i>	$a = 588.194$ $b = 1178.206$ $c = 822.946$	at 25°C [1979Wha, 1998Tes]
* δZrPbO_3 (I) < 234	<i>oC10</i> <i>Cm2m</i>	$a = 589.01$ $b = 589.71$ $c = 413.41$	at 25°C [1992Shu, 1996Shu] Electric field induced phase
* ϵZrPbO_3 (II) < 210	<i>hR*</i> <i>R$\bar{3}m$</i>	-	[1979Fes, 1996Fes] Electric field induced phase
* ϕZrPbO_3 (III) < 20	<i>hR*</i> <i>R$\bar{3}c$</i>	-	[1979Fes, 1996Fes] Electric field induced phase

Table 3: Invariant Three-Phase Equilibria

Reaction	T [°C]	Type	Phase	Composition, (at.%)		
				Pb	Zr	O
$L + \beta\text{ZrO}_2 \rightleftharpoons \beta\text{ZrPbO}_3(\text{h}_2)$	1538	p	L	47.504	1.664	50.832
			βZrO_2	0.0	33.333	66.667
			$\beta\text{ZrPbO}_3(\text{h}_2)$	20.00	20.00	60.00
$L + \beta\text{ZrPbO}_3(\text{h}_2) \rightleftharpoons \alpha\text{PbO}$	909.8	p	L	49.992	0.0054	50.003
			$\beta\text{ZrPbO}_3(\text{h}_2)$	20.00	20.00	60.00
			αPbO	44.887	3.409	51.704
$L \rightleftharpoons \alpha\text{PbO} + \beta\text{PbO}$	885.8	e	L	49.998	0.0014	50.000
			αPbO	47.82	1.45	50.73
			βPbO	50.00	0	50.00

Table 4: Thermodynamic Data of Reaction or Transformation

Phase	T [°C]	Quantity per mole of atoms H , G : [kJ·mol ⁻¹]; S : [J·mol ⁻¹ ·K ⁻¹]	Comments
$\alpha\text{ZrPbO}_3(\text{r}) \rightleftharpoons \beta\text{ZrPbO}_3(\text{h}_2)$	231.5	$\Delta S = 1.65$	[1996Ono], AC calorimetry
$\beta\text{PbO} + \alpha\text{ZrO}_2 \rightleftharpoons \beta\text{ZrPbO}_3(\text{h}_2)$	25	$\Delta H = 5.24$ $\Delta S = 19$ $\Delta G = 0.5$	[1979Sch] derived from EMF measurements
$\beta\text{ZrPbO}_3(\text{h}_2) \rightleftharpoons \alpha\text{ZrO}_2 + \text{Pb}(\text{g}) + 0.5\text{O}_2(\text{g})$	712 - 1023	$\Delta H = 191.36 \pm 12.48$	[1979Nur], mass-spectrometry
$\alpha\text{ZrO}_2 + \beta\text{PbO} \rightleftharpoons \beta\text{ZrPbO}_3(\text{h}_2)$	527 - 1127	$\Delta G = -4.54 - 6.76 \cdot 10^{-3} T (\pm 0.8)$	[1981Jac], derived from emf measurements
$\alpha\text{ZrO}_2 + \beta\text{PbO} \rightleftharpoons \beta\text{ZrPbO}_3(\text{h}_2)$	973	$\Delta H = -2.63 \pm 4.22$	[2001Ran], solution calorimetry

Table 5: Thermodynamic Properties of Single Phases

Phase	Temperature [°C]	Property per mole of atoms H : [J·mol ⁻¹]; S , C_p : [J·mol ⁻¹ ·K ⁻¹]	Comments
$\alpha\text{ZrPbO}_3(\text{r})$	25 - 207	$C_p = 1845 - 2.244 T - 1.045 \cdot 10^8 T^{-2} (\pm 0.23)$	[1993Gos] DSC at $T = 480$ K
	25	$^\circ S = 119.7$	
	25 - 207	$H_T - H_{298} = 47224.35$	

Table 6: Vapor Pressure Measurements

Phase(s)	Temperature Range [°C]	Pressure [bar]	Comments
$\beta\text{ZrPbO}_3(\text{h}_2) + \alpha\text{ZrO}_2$	712	$p_{\text{Pb}} = 0.188 \cdot 10^{-4}$	[1979Nur] mass-spectrometry
	785	$p_{\text{Pb}} = 0.466 \cdot 10^{-4}$	
	832	$p_{\text{Pb}} = 0.912 \cdot 10^{-4}$	
	852	$p_{\text{Pb}} = 0.101 \cdot 10^{-3}$	
	872	$p_{\text{Pb}} = 0.152 \cdot 10^{-3}$	
	912	$p_{\text{Pb}} = 0.249 \cdot 10^{-3}$	
	935	$p_{\text{Pb}} = 0.284 \cdot 10^{-3}$	
	1023	$p_{\text{Pb}} = 0.679 \cdot 10^{-3}$	
$\beta\text{ZrPbO}_3(\text{h}_2) + \alpha\text{ZrO}_2$	1077	$p_{\text{PbO}} = 8.10532 \cdot 10^{-4}$	[1979Sch] dynamic thermobalance method
	1061	$p_{\text{PbO}} = 6.38543 \cdot 10^{-4}$	
	1029	$p_{\text{PbO}} = 3.67096 \cdot 10^{-4}$	
	984	$p_{\text{PbO}} = 1.64153 \cdot 10^{-4}$	
$\beta\text{ZrPbO}_3(\text{h}_2) + \alpha\text{ZrO}_2$	1133	$p_{\text{PbO}} = 1.86 \cdot 10^{-3}$	[1973Hol] Knudsen effusion
	1105	$p_{\text{PbO}} = 1.38 \cdot 10^{-3}$	
	1094	$p_{\text{PbO}} = 9.87131 \cdot 10^{-4}$	
	1073	$p_{\text{PbO}} = 7.34905 \cdot 10^{-4}$	
	1053	$p_{\text{PbO}} = 2.089 \cdot 10^{-4}$	
	992	$p_{\text{PbO}} = 5.48935 \cdot 10^{-5}$	
$\beta\text{ZrPbO}_3(\text{h}_2) + \alpha\text{ZrO}_2$	935	$p_{\text{PbO}} = 6.70008 \cdot 10^{-5}$	[1969Hae] Knudsen effusion
	923	$p_{\text{PbO}} = 5.04917 \cdot 10^{-5}$	
	897	$p_{\text{PbO}} = 3.03886 \cdot 10^{-5}$	
	883	$p_{\text{PbO}} = 2.2327 \cdot 10^{-5}$	
	874	$p_{\text{PbO}} = 1.67641 \cdot 10^{-5}$	
	862	$p_{\text{PbO}} = 1.24062 \cdot 10^{-5}$	
	849	$p_{\text{PbO}} = 8.35468 \cdot 10^{-6}$	
	830	$p_{\text{PbO}} = 6.94496 \cdot 10^{-6}$	
	826	$p_{\text{PbO}} = 5.06501 \cdot 10^{-6}$	

Table 7: Calculated Thermodynamic Functions of $\beta\text{ZrPbO}_3(\text{h}_2)$ at 298 K

$\Delta_f^\circ H$ [kJ·mol ⁻¹]	$^\circ S$ [J·mol ⁻¹ ·K ⁻¹]	$\Delta_f^\circ G$ [kJ·mol ⁻¹]
–1322.960	126.147	–1360.552

Table 8: Investigations of the O–Pb–Zr Materials Properties

References	Method/Experimental Technique	Type of Properties
[1979Wha]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric constant
[1979Koc]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric constant
[1981Han]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric permittivity

References	Method/Experimental Technique	Type of Properties
[1985Ujm]	Inductance-Capacitance-Resistance measurements (LCR meter)	Electric permittivity
[1985Ism]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric permittivity
[1986Rol]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric and pyroelectric
[1989Rol]	Polarization microscopy Inductance-Capacitance-Resistance measurements (LCR meter)	Optic, dielectric and pyroelectric
[1989Cie]	Capacitance measurement	Dielectric permittivity
[1992Fuj]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric constant
[1992Wan]	Phase detection technique in transmission mode	Electro-optic (thin films)
[1993Rol]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric permittivity
[1995Dai]	Inductance-Capacitance-Resistance measurement (LCR meter) Sawyer-Tower circuit	Dielectric permittivity Polarization
[1995Sin]	Local density calculation	Electric
[1999Bha]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric
[1999Kob]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric
[2000Bha]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric constant
[2000Coc]	Local density calculation	Electric
[2001Dob]	Metal-isolator-metal configuration; Optical microscopy;	Dielectric (dielectric impedance) electric and polarization
[2001Fuj]	Inductance-Capacitance-Resistance measurements (LCR measurements)	Dielectric constant
[2001Ost]	Microwave dielectric spectrometry Terahertz transmission measurements	Dielectric
[2004Ost]	HF dielectric spectrometry	Dielectric permittivity
[2004Puc2]	Vickers and Koop microhardness test Inductance-Capacitance-Resistance measurement (LCR meter)	Hardness, fracture toughness and dielectric properties
[2004Ste]	Inductance-Capacitance-Resistance measurement (LCR meter)	Dielectric permittivity
[2004Bit]	Inductance-Capacitance-Resistance measurements	Dielectric permittivity
[2005Wan]	Local density calculation	Electric

Fig. 1: O-Pb-Zr.
Assessed phase diagram of the O-Pb system

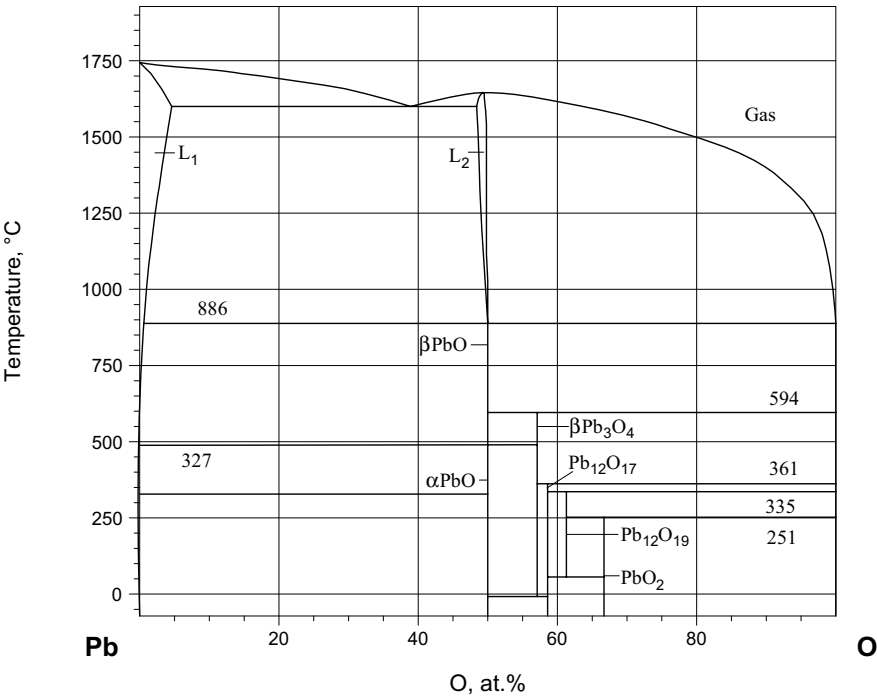


Fig. 2: O-Pb-Zr.
Assessed phase diagram of the Pb-Zr system (solid lines) compared with the calculated one (dotted lines)

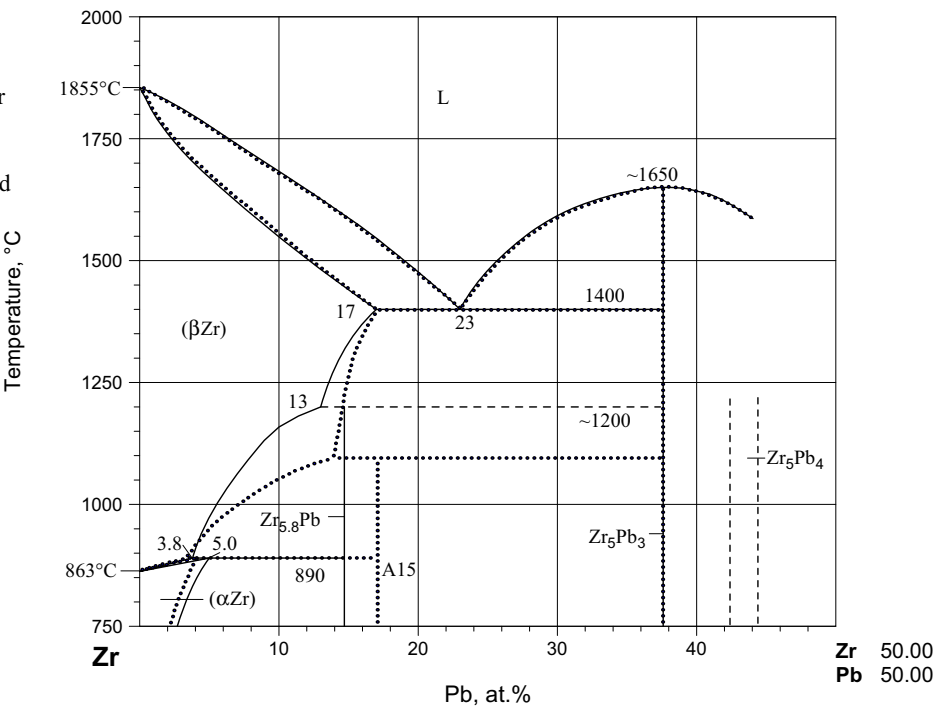


Fig. 3a: O-Pb-Zr.
Phase diagram of the
PbO-ZrO₂ system

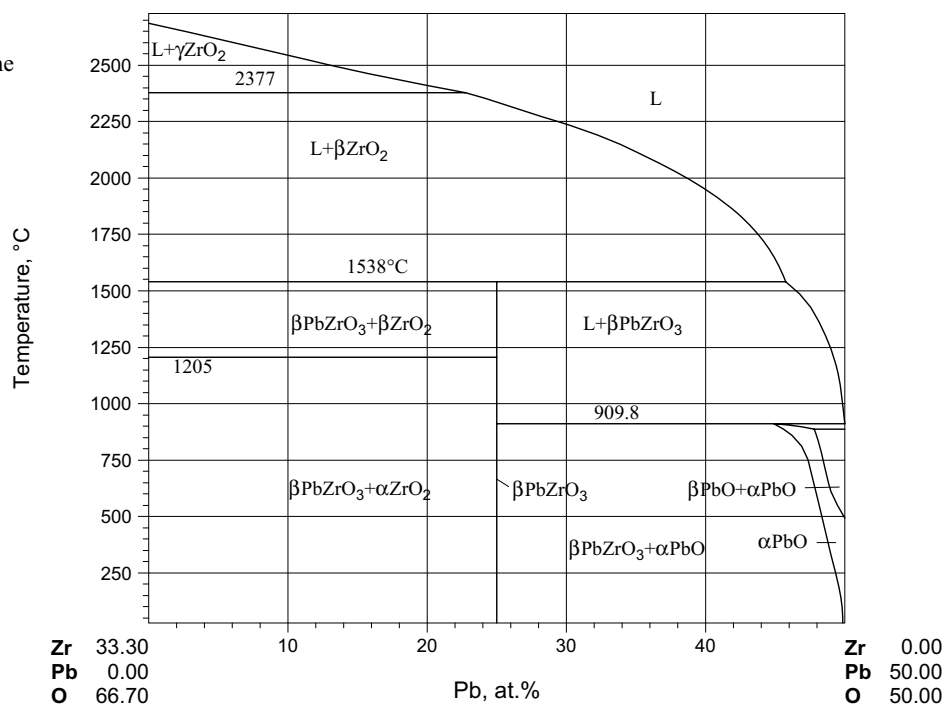


Fig. 3b: O-Pb-Zr.
Enlarged view of the
PbO rich region

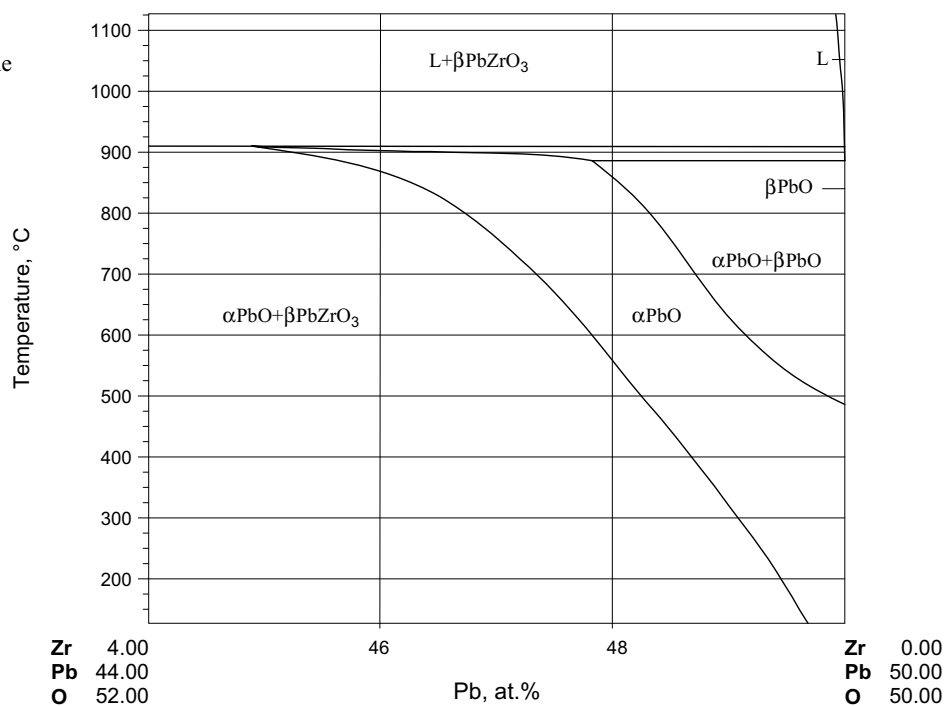


Fig. 4: O-Pb-Zr.
Calculated heat
capacity of the cubic
 βZrPbO_3

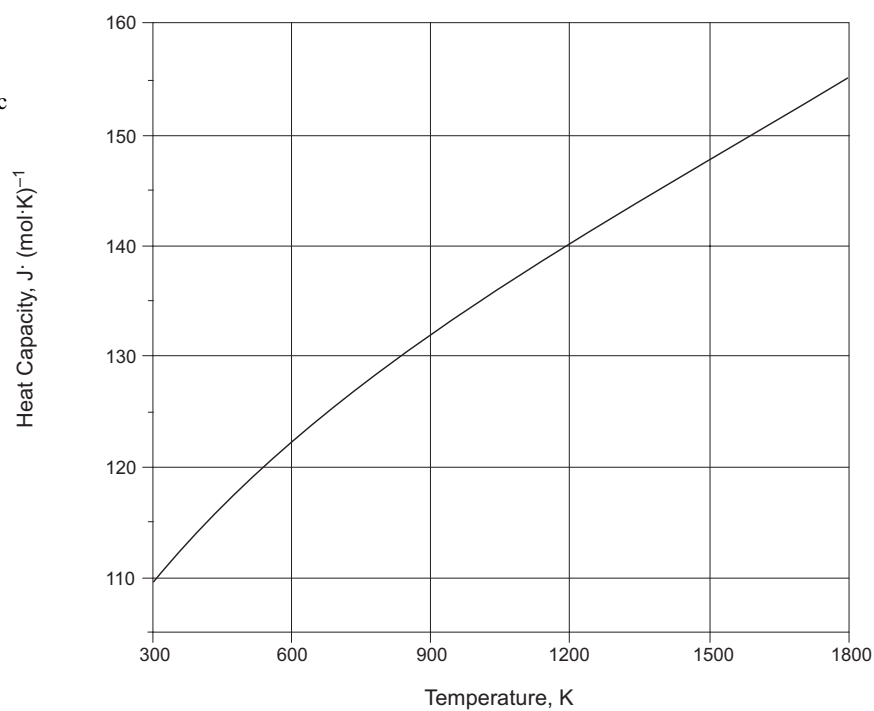


Fig. 5: O-Pb-Zr.
Calculated enthalpy
increment of cubic
 βZrPbO_3

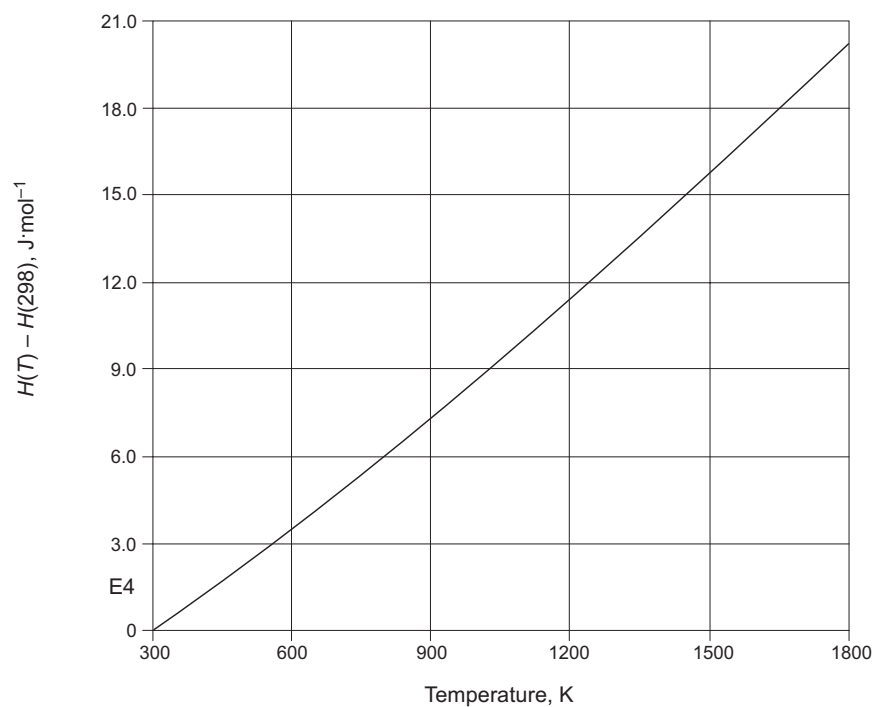


Fig. 6: O-Pb-Zr.
Calculated entropy of
cubic βZrPbO_3

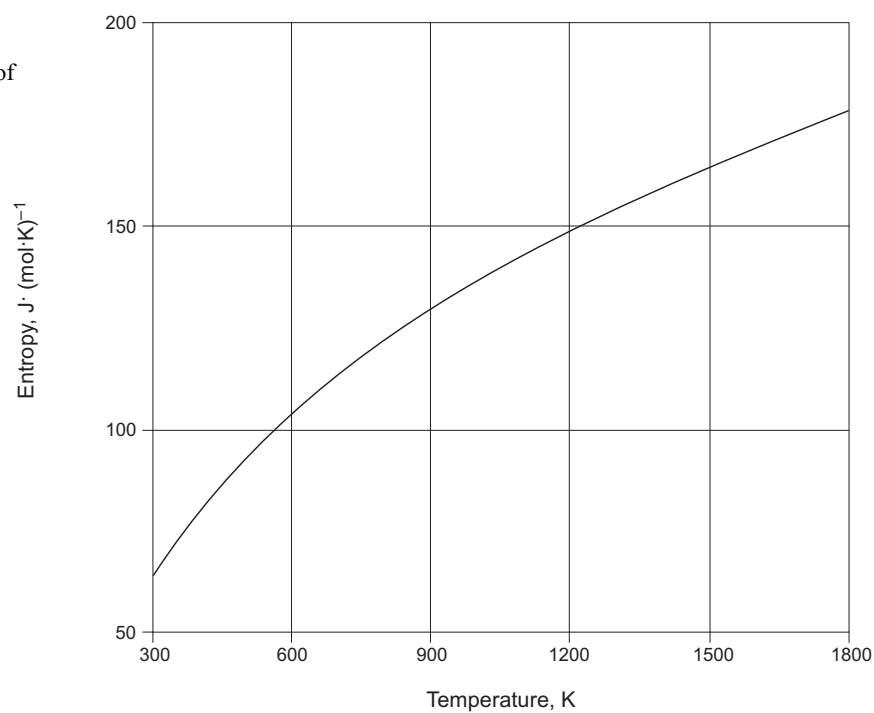
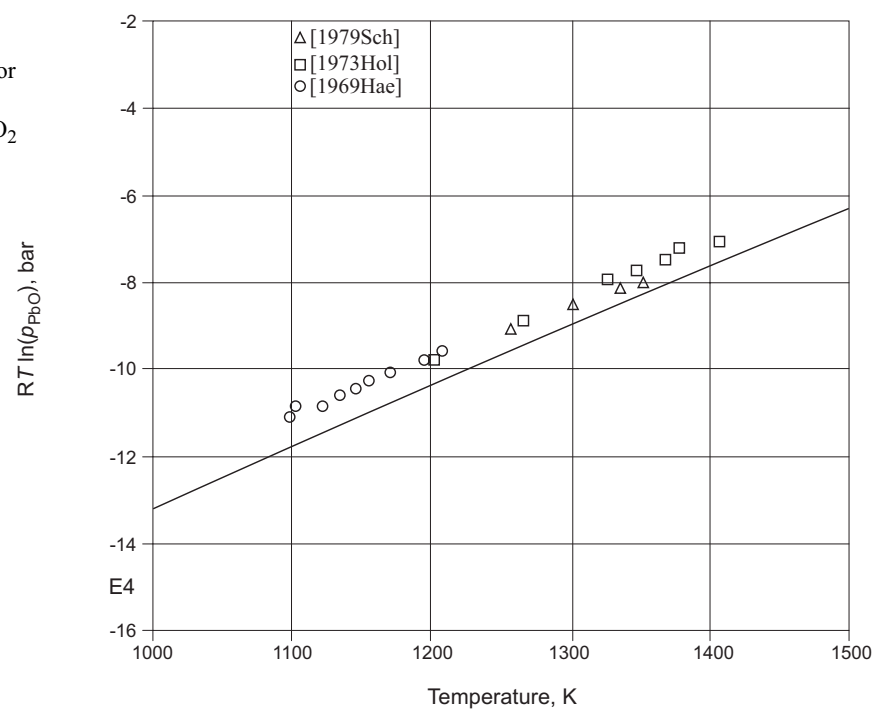


Fig. 7: O-Pb-Zr.
Calculated PbO vapor
pressure over
 $\beta\text{ZrPbO}_3(\text{h}_2) + \alpha\text{ZrO}_2$
in comparison with
experimental data



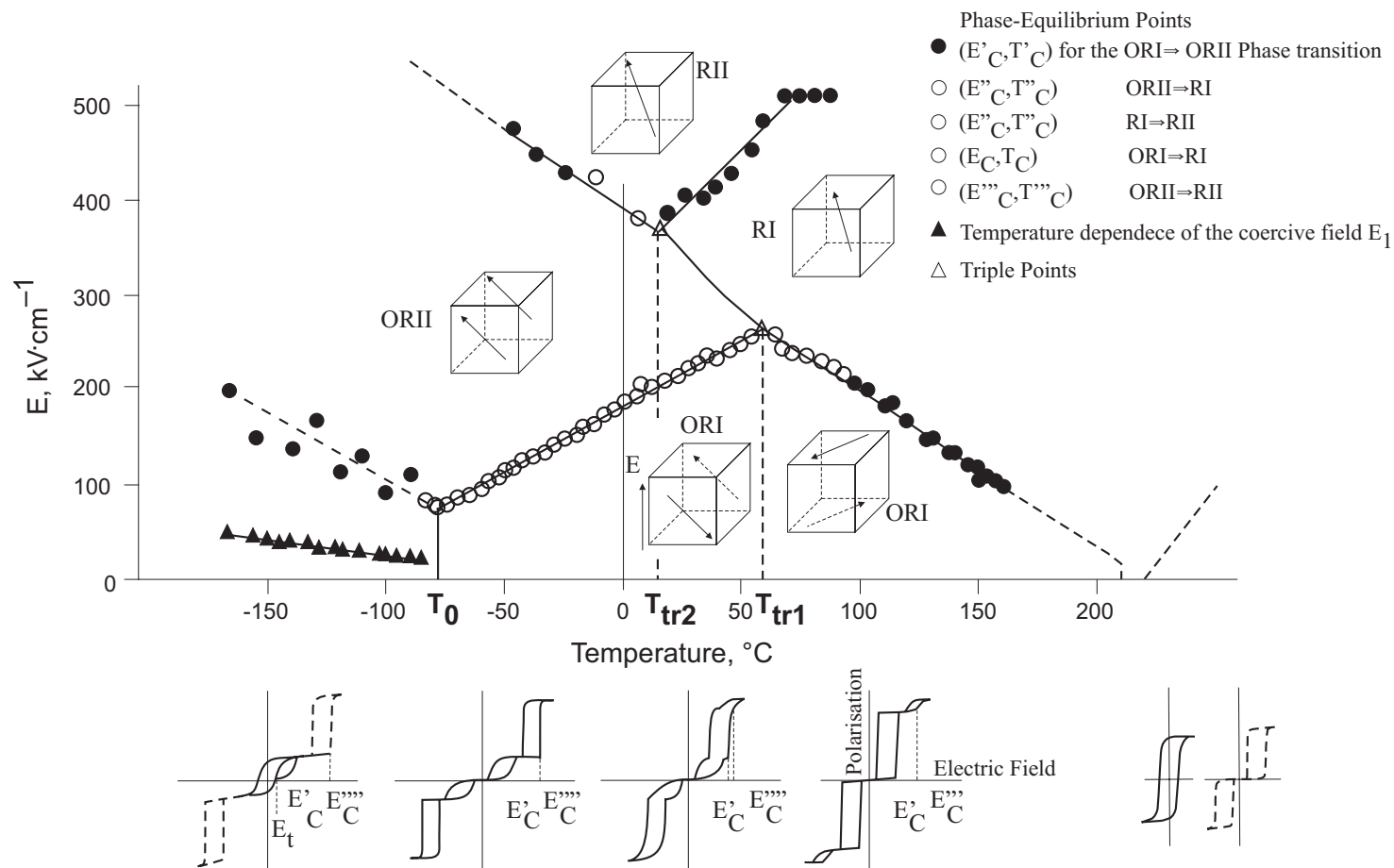


Fig. 8. O-Pb-Yr. The E - T phase diagram and schematic isothermal dependences of the dielectric polarization on the electric field; $\text{ORII} = \delta\text{ZrPbO}_3$ (I), $\text{RI} = \epsilon\text{ZrPbO}_3$ (II), $\text{RII} = \phi\text{ZrPbO}_3$ (III).

Oxygen – Plutonium – Uranium

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Introduction

The interest in the O–Pu–U system arises from the fact that these oxides are of great importance in fuel applications for power reactors. Mixed plutonium-uranium oxides containing about 13–30% PuO₂ have been used as fuels for fast reactors in many countries. Uranium-plutonium mixed oxides containing 40% and higher amounts of PuO₂ are being considered potential fuels for the plutonium burner reactors [2004Kan]. Consequently, the knowledge of thermodynamic properties for these materials is of great importance.

Experimental investigations and calculations have been performed on the O–Pu–U system. The system has also been thermodynamically assessed. All the experimental and calculated investigations are reported in Table 1. [2001Car] have carried out a comprehensive review of the thermophysical properties of UO₂ and MOX fuels.

Binary Systems

[1998Che] has modeled the O–U binary system after performing a critical assessment of the available literature. Experimental incoherency found was the solubility of O in liquid uranium affecting the shape of the liquidus curve as well as the extension of the miscibility gap. Moreover the model used for the solubility of the UO_{2±x} phase did not correspond to the real structure and the model of diatomic gas was considered in the calculation of the phase diagram. More recently, a progress in the thermodynamic modeling was presented by [2002Che] based on recent experimental data concerning the miscibility gap and the solubility of oxygen in liquid uranium. The model for the description of the UO_{2±x} was also improved. However differences have been noticed in a later assessment done by [2002Gue]. It concerns the temperature of the invariant $L_2 \rightleftharpoons \text{UO}_{2\pm x} + \text{Gas}$ at 1 atm, varying from 2427°C [2002Gue] to 2800°C [2002Che]. No agreement was also observed concerning the shape of the miscibility gap in the hyperstoichiometry field which may exist up to the vaporization or be closed before. Due to these uncertainties, [2004Che] recently re-assessed the phase diagram taking into account recent experimental data. [1998Che] have calculated two different phase diagrams taking into account the small and large solubilities of oxygen. The assessment with small solubility of oxygen is accepted here as it is in agreement with [1998Gue] and also due to the fact that other accepted phase diagrams [2004Yam] take this assessment into account. As pointed out by [2004Che], the calculation of phase equilibria is not affected as the limit conditions are respected.

After [Mas2], a Calphad assessment of the O–Pu binary was carried out by [2003Kin] using thermodynamic modeling for the phase behavior and thermodynamic properties. This last version of the phase diagram is accepted in this assessment.

The binary boundary system Pu–U has been modeled by [1991Lei] and [1999Kur] and compared to the first version of the phase diagram presented by [1958Eli]. The phase diagram of [1999Kur] agrees well with experimental data but the calculated liquidus curve is shifted lower. Since version of [1999Kur] was used in the calculation of the ternary diagrams [2004Yam], which are accepted in the present evaluation this binary system has been accepted from [1999Kur]. The accepted binary phase diagrams of the Pu–U and O–Pu are shown in Fig. 1 and 2.

Solid Phases

The crystallographic data for the phases present in the O–Pu–U system and their ranges of stability are summarized in Table 2. Several space groups have been proposed in the literature for the U₃O₈ phase: *P6̄2m*, *Cmcm* and *C222*. The most probable is certainly the space group *Cmcm* determined from the largest number of reflections (85 instead of 11 and 39 measured in other works [V–C2]). The major oxides of the respective binary systems PuO₂ and UO₂ form a complete range of solid solutions [2004Yam] with the

fluorite structure in the whole composition range and the ionic radii of Pu^{4+} and U^{4+} are very similar in the fluorite structure. It was found that the lattice parameters of stoichiometric uranium dioxide doped with plutonium ions decreased linearly with increasing plutonium up to 20 at.% [1998Tsu].

Quasibinary Systems

[1967Lyo] first studied the quasibinary system $\text{PuO}_2\text{--UO}_2$ showing the existence of complete miscibility between the two intermediate compounds. No later experimental work is available in the literature. The UO_2 fuel melts at a higher temperature than PuO_2 , with values for UO_2 ranging from 2730°C to 2876°C [2001Car]. [2001Car] noticed also a large variation of the literature data for the melting temperatures of PuO_2 ranging from 2238°C to 2445°C. [1967Lyo] measured a melting temperature of PuO_2 at about $2390 \pm 20^\circ\text{C}$, lower than the calculated value given by [2003Kin] (2467°C) in agreement with the calculated one proposed in the Calphad calculation of [1997Zha]. Experimental investigations are needed in order to estimate more precisely the melting point of PuO_2 fuels.

Recently, [2004Yam] have also calculated the $\text{PuO}_2\text{--UO}_2$ quasibinary system. The resulting thermodynamic dataset reproduces experimental data in the best possible way. This is also internally consistent with other accepted phase diagrams. Therefore, the calculated phase diagrams are accepted here. $\text{PuO}_2\text{--UO}_2$ are completely miscible in the entire composition range. Accurate determination of heat capacity of PuO_2 experimentally is difficult at high temperatures and this caused problems in the exact location of solidus and liquidus lines. [2004Yam] have made the calculation assuming ideal behavior. It concluded that the deviation from ideality is small as previously suggested by [1992Bea, 2001Car]. This is shown in Fig. 3.

Isothermal Sections

Phase studies on (Pu,U) oxides were carried out from 25 to 800°C [1967Ack, 1968Sar, 1969Koi1] within the limits $\text{UO}_{1.88}\text{--U}_3\text{O}_8$ and $\text{PuO}_2\text{--PuO}_{1.5}$. It was suggested that PuO_2 and Pu_2O_3 above 400°C could form a continuous solid solution. This is in disagreement with the large difference observed on the crystal structure for the two intermediate compounds. Moreover the intermediate compounds $\text{PuO}_{1.51}$ and $\text{PuO}_{1.62}$ are not indicated on the partial isothermal sections. Consequently, further experimental investigations are needed in order to determine precisely the phase equilibria in this composition range. Recently, [2004Yam] have modeled the ternary O–Pu–U system after careful analysis of the crystallographic data and thermophysical quantities. Isothermal sections have been calculated at 500 and 1000°C. This includes the calculation of interaction parameters and takes the non-stoichiometry into account. The data were verified by calculation of the oxygen potential of the fluorite phase in the hyper stoichiometric region. These calculated isothermal sections are shown on Figs. 4 and 5. Slight modifications have been made to bring them to agreement with the accepted binary systems. The calculated isothermal section at 1000°C has been modified along the U–Pu binary edge and the shape of the homogeneity range for the (Pu,U) O_2 solution has been also changed. The three- and two-phase equilibria involving the UO_3 phase have been suppressed since at 1000°C this phase does not crystallize according to the O–U phase diagram. Consequently, changes have been done and the three phase equilibrium $\text{U}_3\text{O}_8 + \text{Gas} + \text{PuO}_2$ has been added.

Thermodynamics

Thermodynamic data for the mixed (Pu,U) oxides have been obtained [1967Ack]. Several experimental data on the heat capacity and enthalpy increments of uranium-plutonium mixed oxides have been reported [1972Lei, 1973Aff, 1974Gib, 1992Bea]. There is general agreement between the data except the data of [1972Lei] which are higher than the others. Agreement is observed in the correlations proposed by [1982Fin, 2000Fin, 2001Car, 2004Kan, 2004Yam] for the enthalpy increment and heat capacity data for uranium-plutonium mixed oxides. The details are reported in Table 3. [2004Kan, 2001Car] concluded that the enthalpies of (Pu,U) O_2 solid solutions in the temperature range 25–1527°C obey to the Neumann-Kopp molar additivity rule.

Oxygen potentials as a function of temperature were calculated for the mixed uranium-plutonium oxide at various O/M ratios and plutonium contents. A comparison of the calculated oxygen potential data of [1984Kri] with the measurements of [1977Tet, 1981Woo, 1979Woo] indicated fair agreements.

Vapor pressures of the various gaseous species above $\text{Pu}_{1-x}\text{U}_x\text{O}_{2-y}$ have been calculated or measured [1970Bat, 1976Osh1, 1976Osh2, 1977Bab, 1976Tet, 1978Ohs, 1982Bab, 2001Vis].

Notes on Materials Properties and Applications

[1973Ola] have carried out oxygen diffusion studies in the hypostoichiometric $(\text{Pu,U})\text{O}_{2-x}$ system. This is important for the mutual segregation of fissile materials. [1999Kut, 2000Kut] have studied the shrinkage behavior and sintering kinetics of UO_2 for varying amounts of PuO_2 . Thermal conductivity of mixed oxides $(\text{Pu,U})\text{O}_2$ has been extensively reviewed [2001Car, 1982Mar, 1992Phi, 2000Dur] and mainly concerned high Pu content (about 20% Pu) mixed oxides for fast breeder reactors. The thermoconductivity of fuels strongly depends on temperature, porosity, composition, burnup and deviation from stoichiometry. [2001Car] noticed that the thermal conductivity decreases with temperature up to 1727°C and then increases with temperature. Addition of PuO_2 to the fuel or increasing porosity reduces the thermal conductivity. Burnup and/or deviations from stoichiometry have similar effects but they are negligible above 1927°C. Magnetic susceptibility of $(\text{Pu,U})\text{O}_2$ has been investigated by [2002Kol] who have determined the ordering and Curie temperatures.

Miscellaneous

The behavior of $(\text{Pu,U})\text{O}_2$ in a steady state temperature gradient between the liquidus and the solidus was investigated [2005Kle, 2001Kle]. The UO_2 and PuO_2 concentrations at the liquid-solid interface are discontinuous [2001Kle]. A severe redistribution phenomena of oxygen is observed in the temperature gradient of hypostoichiometric mixed oxides $(\text{Pu,U})\text{O}_{2-x}$ which is enabled by intrinsic defects in the anion sublattice. It was concluded that the oxygen concentration gradient is controlled by the oxygen vacancy flux in direction to higher temperatures [2005Kle]. This process is quantified by the heat of transport which ranges from $-10 \text{ kJ}\cdot\text{mol}^{-1}$ at the central void and about $-230 \text{ kJ}\cdot\text{mol}^{-1}$ near the fuel surface [2001Kle]. For low temperature fuels in the absence of fission products, the steady state profile of the O/M ratio in the solid is established by flow of H_2O or CO_2 in the gas phase balanced by solid state diffusion of oxygen in the opposite direction [1973Ola]. The influence of this process upon oxygen distribution depends on the diffusion coefficients, densities and flow areas of solid and gaseous phases. [1973Ola] showed analytically how these factors affect oxygen redistribution in a closed axial thermal gradient geometry.

After irradiation of UO_2 fuel with about 3% ^{235}U enrichment, [1993Kle] observed that approximately 0.25% PuO_2 were produced per percent burnup. PuO_2 goes into the $(\text{U,Pu,fp})\text{O}_2$ (fp means fission product) solid solution which results in an additional lattice contraction of $\Delta a = -18.5 \text{ fm}$ per percent burnup. The post-irradiation state of U,Pu mixed oxides nuclear fuels at 2% burnup was simulated by mixing 25 inactive fission products elements [1969Koi2].

[2001Vis] studied the vaporization chemistry of hypo-stoichiometric $(\text{Pu,U})\text{O}_2$. The oxygen coefficient for hyper-stoichiometric uranium-plutonium oxide was measured and a slow oxidation was observed during a three month storage [1989Tes].

[2004Gib] has synthesized small ternary oxide clusters of uranium and plutonium oxide in order to study plutonium chemistry.

[1965Far1, 1965Far2, 1965Far3, 1965Far4, 1966Bar1, 1966Bar2, 1966Far1, 1966Far2, 1967Far1, 1967Far2, 1968Far1, 1968Far2, 1968Far3, 1968Far4, 1968Far5, 1969Fac1, 1969Fac2, 1969Far, 1970Bar] undertook a review of mechanical properties, method of fabrication and irradiation influence on mixed plutonium-uranium mixed oxides.

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Table 1: Investigations of the O-Pu-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1958Eli]	Chemical analysis, heat treatment, thermal analysis, dilatometry, X ray diffraction, metallography	600-700°C for 300 h / Pu-U
[1967Ack]	X-ray diffraction, metallography examination, emf	up to 1000°C / 64 to 73 at.% O and 40 to 33 at.% Pu
[1967Lyo]	Standard gravimetric analyses, X ray fluorescence and X ray diffraction	2300 - 2900°C / 5 to 85 mol% PuO ₂
[1968Sar]	Metallography, X-ray diffraction	up to 1600°C / PuO _{2-x} , 1.62 ≤ x ≤ 2.00 (Pu,U)O ₂
[1969Koi1]	Differential thermal analysis, X-ray diffraction	25 - 800°C/ (Pu _y U _{1-y})O _{2-x} , 0.17 ≤ y ≤ 0.40, 1.92 ≤ x ≤ 2.00

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1970Bat]	Mass-loss and mass-spectrometric Knudsen effusion	1632 - 2138°C / $\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_{2-x}$
[1972Lei]	Calorimetry	2075 - 2732°C / $(\text{Pu}_{0.2}\text{U}_{0.8})\text{O}_{1.97}$
[1973Aff]	Pulse heating method	up to 2727°C / $(\text{Pu}_{0.2}\text{U}_{0.8})\text{O}_{2\pm x}$
[1976Osh1]	Laser pulse heating	up to 4727°C / 20 mol% PuO_2
[1976Osh2]	Laser pulse heating	up to 6727°C / 20 mol% PuO_2
[1976Tet]	Transpiration method	1877 - 2177°C / $(\text{Pu}_{0.2}\text{U}_{0.8})\text{O}_{2-x}$
[1977Bab]	Laser surface heating method	up to 4727°C / liquid UO_2 and $(\text{Pu}_{0.2}\text{U}_{0.8})\text{O}_2$
[1977Tet]	Equilibration technique	1777°C / $(\text{Pu}_y\text{U}_{1-y})\text{O}_{2-x}$, $0.15 \leq y \leq 0.30$, $1.92 \leq x \leq 2.00$
[1978Ohs]	Laser surface heating method	up to 4727°C / liquid UO_2 and $(\text{Pu}_{0.2}\text{U}_{0.8})\text{O}_2$
[1979Woo]	Thermogravimetric analysis, solid-electrolyte galvanic cell technique	800-1000°C / $\text{Pu}_{0.25}\text{U}_{0.75}\text{O}_{2\pm x}$
[1981Woo]	Mass spectrometry analyses, oxygen potential-composition measurements	1000-1200°C / $\text{Pu}_{0.1}\text{U}_{0.9}\text{O}_{2-x}$, $\text{Pu}_{0.4}\text{U}_{0.6}\text{O}_{2-x}$, PuO_{2-x}
[2004Kan]	Inverse drop calorimetry technique	727-1507°C / $(\text{Pu}_y\text{U}_{1-y})\text{O}_2$ ($y = 0.21, 0.28$ and 0.4)

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
($\epsilon\text{Pu}, \gamma\text{U}$)	$cI2$ $Im\bar{3}m$ W		continuous solid solution which exists between 1135 and 459°C [1999Kur]
(ϵPu) 640 - 483		$a = 363.8$	pure Pu, 500°C, [1989Pet] dissolves 100 at.% U [1999Kur] and 5.6 at.% Th at $605 \pm 10^\circ\text{C}$ [1985Pet1]
(γU) 1135 - 776		$a = 352.4$	pure U, 805°C, [Mas2] dissolves 100 at.% Pu [1999Kur] and 1.5 at.% Th at 1100°C [1985Pet2]
($\delta'\text{Pu}$) 483 - 463	$tI2$ $I4/mmm$ In	$a = 333.9$ $c = 444.6$	pure Pu, 477°C, [1989Pet] the solubility of U is nearly absent [1999Kur] exists up to 443°C along the Pu-U binary [1999Kur]
(δPu) 463 - 320	$cF4$ $Fm\bar{3}m$ Cu	$a = 463.70$	pure Pu, 320°C, [1989Pet] the solubility of U is nearly absent [1999Kur]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(γ Pu) 320 - 215	<i>oF8</i> <i>Fddd</i> γ Pu	$a = 315.87$ $b = 576.82$ $c = 1016.2$	pure Pu, 235°C, [1989Pet] dissolves 0.8 at.% U at 280°C [1989Pet]
(β Pu) 215 - 125	<i>mC34</i> <i>C2/m</i> β Pu	$a = 928.4$ $b = 1046.3$ $c = 785.9$ $\beta = 92.13^\circ$	pure Pu, 190°C, [1989Pet] dissolves 2.0 at.% U at 272°C [1999Kur]
(α Pu) < 125	<i>mP16</i> <i>P2₁/m</i> α Pu	$a = 618.3$ $b = 482.2$ $c = 1096.3$ $\beta = 101.79^\circ$	pure Pu, 21°C, [1989Pet], the solubilities of U is nearly absent [1999Kur]
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> β U	$a = 1075.9$ $c = 565.6$	pure, 720°C, [1989Pet] dissolves 25.5 at.% Pu at 702°C [1999Kur] exists down to 567°C along the Pu-U binary [1999Kur]
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	pure, at 25°C [1989Pet] dissolves 14.2 at.% Pu at 567°C [1999Kur]
(Pu,U)O ₂ UO ₂ < 2852	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF ₂	$a = 547.0$	from 62.7 to 66.7 at.% O [2002Gue] lattice parameter at 25°C from [V-C2]
 PuO ₂ < 2467		$a = 539.5$	62.8 to 66.7 at.% O [2003Kin] lattice parameters [1990Wri]
U ₃ O ₈ < 1870	<i>oC44</i> <i>Cmcm</i>	$a = 706.9$ $b = 1144.5$ $c = 830.3$	melting point from [2004Che] lattice parameters from [V-C2]
U ₄ O ₉ < 1123.5	<i>cI832</i> <i>I$\bar{4}$32</i> or <i>I4₁32</i>	$a = 2177$	lattice parameter from [1989Rag]
UO ₃ < 667.88	<i>oF128</i> <i>Fddd</i> UO ₃	$a = 981.8$ $b = 1993$ $c = 971.1$	[2004Che] lattice parameters from [V-C2]
Pu ₂ O ₃ < 2020	<i>hP5</i> <i>P$\bar{3}m1$</i> La ₂ O ₃	$a = 383.88$ $c = 595.94$	lattice parameters from [1990Wri] existence of a ordered superstructure [1967Ack]
PuO _{1.61} 1069 - 353	<i>cI80</i> <i>Ia$\bar{3}$</i> Mn ₂ O ₃	$a = 1099.1$	from 61.7 to 63 at.% O [1990Wri] considered stoichiometric PuO _{1.61} by [2003Kin]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
PuO _{1.52} < 417	<i>cF80</i> <i>Ia$\bar{3}$</i> Mn ₂ O ₃	$a = 1104.5$	at 60.3 at.% O [2003Kin] lattice parameter from [1990Wri]
η , PuU 702 - 272	<i>tP52</i>	$a = 1057$ $c = 1076$	2.12 to 73.4 at.% U at 25 at.% U [1969Lea]
ξ , PuU < 625	<i>I</i> **	$a = 1069.2$ $a = 1065.1$	25.9 to 74.6 at.% U at 25°C, 35 at.% U [1969Lea] at 25°C, 70 at.% U [1969Lea] $c/a \approx 1$

Table 3: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Property, per mole of atoms [kJ, mol, K]	Comments
Pu _{0.21} U _{0.79} O ₂	25 - 1527	$H^\circ_T - H^\circ_{298} = 79.895 \cdot T + 39.05 \cdot 10^{-4} T^2 + 160 \cdot 10^4 T^{-1} - 29534$	[2004Kan]
Pu _{0.28} U _{0.72} O ₂	25 - 1527	$H^\circ_T - H^\circ_{298} = 77.841 \cdot T + 56.06 \cdot 10^{-4} T^2 + 149.17 \cdot 10^4 T^{-1} - 28710$	[2004Kan]
Pu _{0.4} U _{0.6} O ₂	25 - 1527	$H^\circ_T - H^\circ_{298} = 78.263 \cdot T + 58.81 \cdot 10^{-4} T^2 + 151.66 \cdot 10^4 T^{-1} - 28944$	[2004Kan]

Table 4: Investigations of the O–Pu–U Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1992Bea]	X-ray diffraction, electrical conductivity measurements, microcalorimetry	20-2000°C / (Pu _y U _{1-y})O _{2-x} with 30 at.% Pu
[1999Kut]	Dilatometry	Density variation
[2000Kut]	Dilatometry	Sintering behavior
[2000Dur]	Laser Flash Method	Thermal conductivity
[2002Kol]	Superconducting Quantum Interference Device	Magnetic properties

Fig. 1: O-Pu-U.
The calculated Pu-U
phase diagram
[1999Kur]

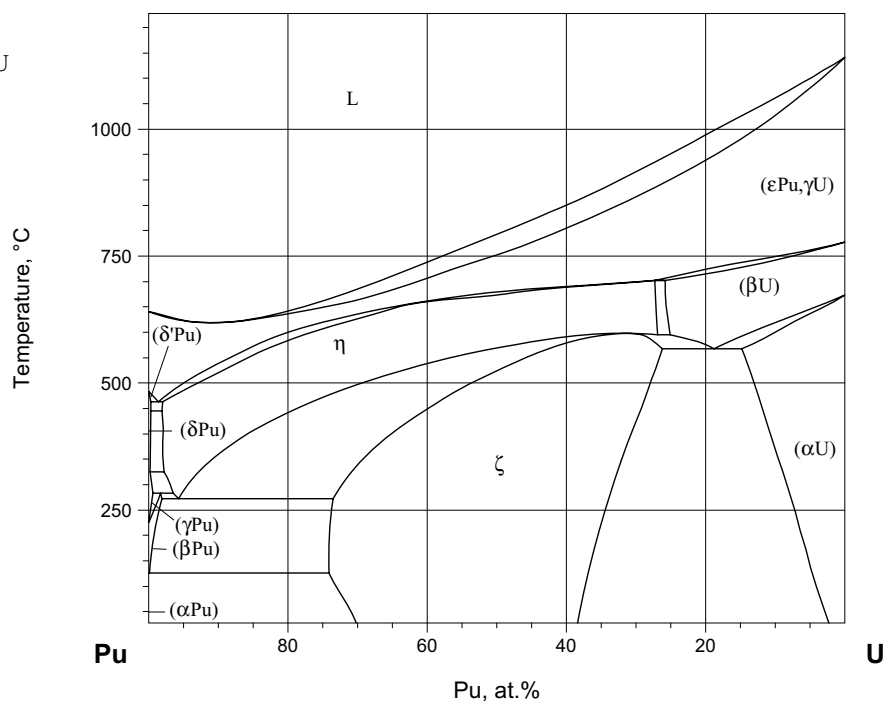


Fig. 2: O-Pu-U.
The calculated O-Pu
phase diagram
[2003Kin]

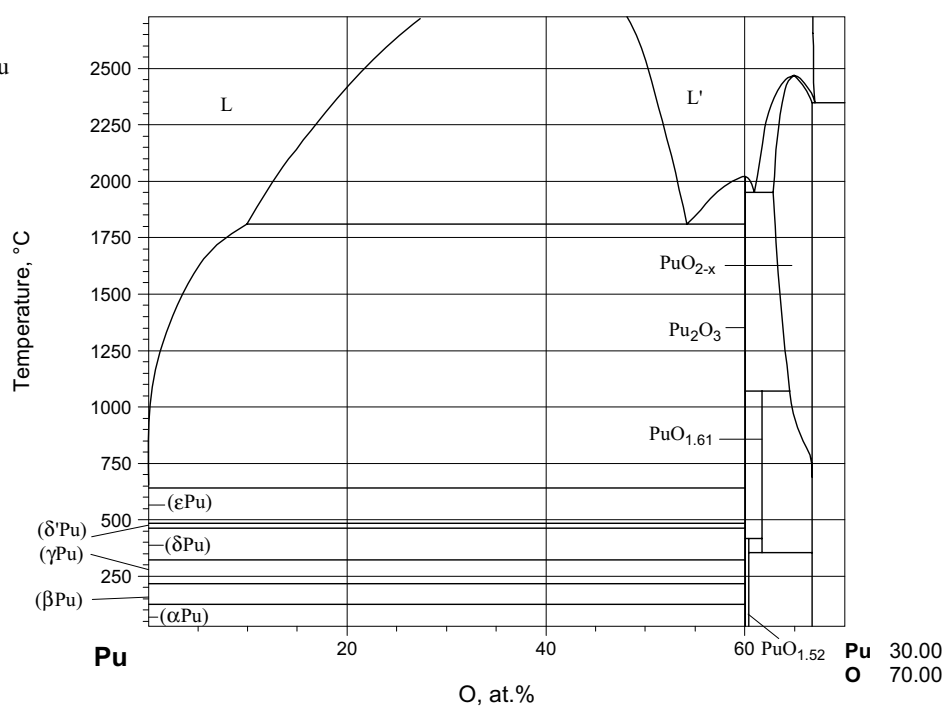


Fig. 3: O-Pu-U.
The calculated
 $\text{PuO}_2\text{-UO}_2$ phase
diagram

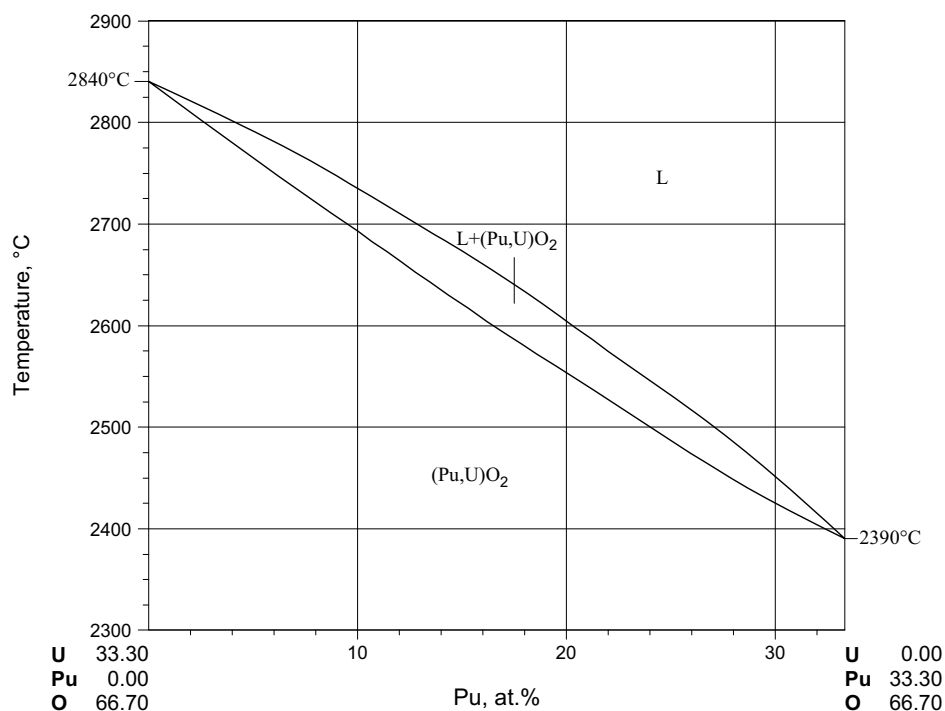


Fig. 4: O-Pu-U.
The calculated
isothermal section at
500°C

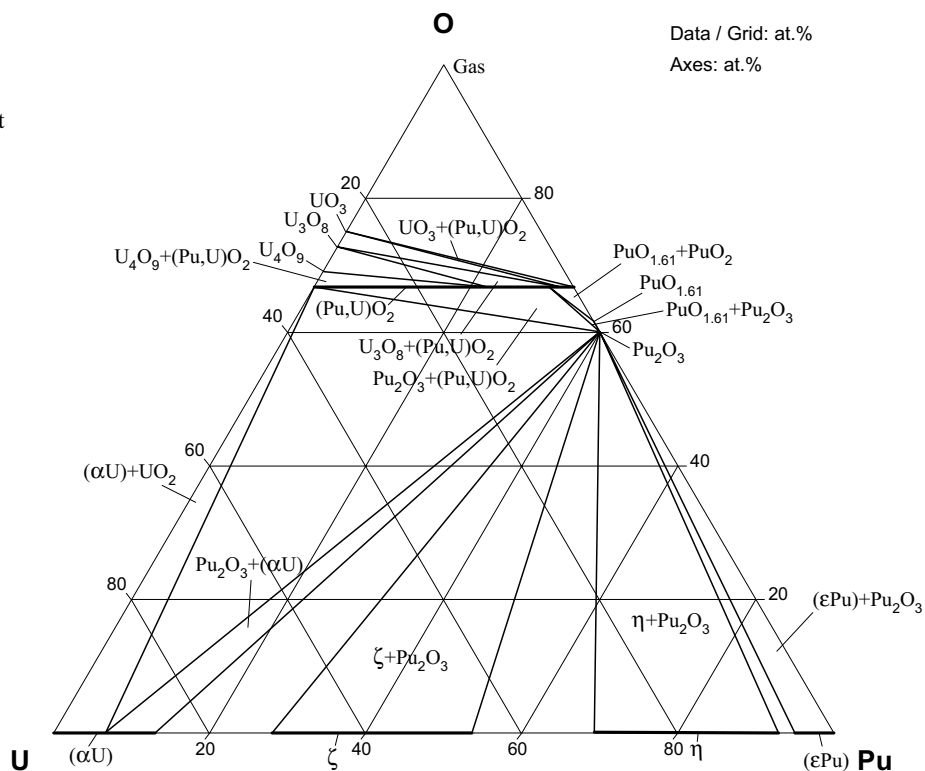
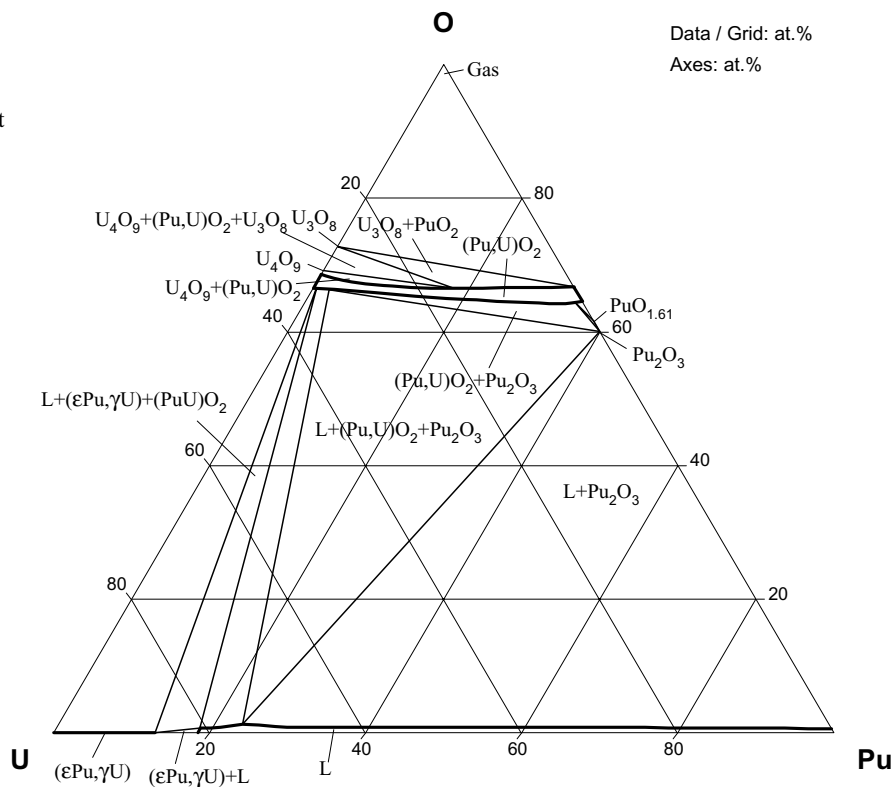


Fig. 5: O-Pu-U.
The calculated
isothermal section at
1000°C



Oxygen – Plutonium – Zirconium

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Introduction

The O–Pu–Zr system is a key system in the nuclear waste and fuel applications where zirconium oxide is used to dilute the fissile ceramic material PuO_2 as ZrO_2 has a low thermal neutron absorption cross section and a high melting point. In addition, it is resistant to fission fragment, ion irradiation and neutron irradiation. The knowledge of the phase equilibria of zirconia forming solid solutions with lanthanides and actinides is of great importance in fuel systems and plutonium disposition. However, there exists very limited experimental information about systems containing plutonium oxides. Experimental investigations on the present system have been carried out by [1963Car], [1969Mar] and [2001Ser]. This is summarized in Table 1.

Binary Systems

The binary boundary system O–Zr is accepted from the thermodynamic assessment of [1998Che] since it was used to calculate ternary O–Pu–Zr diagrams by [2003Kin], which are accepted in the present evaluation. [1999Kur] have performed thermodynamic modeling on the Pu–Zr binary boundary system taking into account the phase behavior and thermodynamic data after performing a critical assessment of the available literature. The calculated results are in very good accordance with experimental data and the Pu–Zr system has been accepted from [1999Kur]. This is shown in Fig. 1. Despite a number of studies, the phase equilibrium in the O–Pu system is not well established. After [Mas2], a Calphad assessment of the O–Pu binary was carried out by [2003Kin] using thermodynamic modeling for the phase behavior and thermodynamic properties. The results are in very good agreement with experimental data in this assessment. This phase diagram is included in the O–Pu–U evaluation report in the present volume.

Solid Phases

The crystallographic data for the O–Pu–Zr phases and their ranges of stability are summarized in Table 2. With regards to the O–Zr system, both the allotropes of Zr show large solubilities of oxygen. ZrO_2 is stable up to a temperature of 2707°C with the cubic modification showing a homogeneity range towards oxygen deficiency formed by the vacancies of oxygen sublattice. The other two allotropes have no significant range of solubility. The amount of experimental data available on the Pu–Zr system is limited. PuO_2 and ZrO_2 are the major oxides formed in the respective systems.

Quasibinary Systems

[1963Car] proposed the first version of the PuO_2 – ZrO_2 quasibinary phase diagram through experimental techniques but the solubility limit of PuO_2 in ZrO_2 was arbitrarily assigned. Moreover, they only considered two allotropes of ZrO_2 . [1969Mar] experimentally determined the quasi binary system in the range ($1.61 < \text{O/M} < 2$). They observed that in the fully oxidized state, the solubility of PuO_2 in βZrO_2 passes through a maximum at about 1000°C and then decreases rapidly. In addition, at high temperatures, βZrO_2 is stabilized over a wide range of PuO_2 contents. But there still remains an uncertain region. The phase relationships in the low PuO_2 region were examined by [2001Ser]. They have concluded from their experiments the presence of a eutectoid point in the composition range of less than 3.1 mol% PuO_2 . [2003Kin] have calculated the phase diagram for PuO_2 – ZrO_2 quasibinary system and presented a consistent thermodynamic database for the O–Pu–Zr system. The resulting thermodynamic dataset reproduces experimental data in the best possible way. Therefore, the calculated quasibinary diagram is accepted here, Figs. 2a and 2b. This diagram differs from the experimental investigations of [1969Mar] but reflects the one suggested by [2001Ser]. The calculated diagram also shows similarity with the UO_2 – ZrO_2 and CeO_2 – ZrO_2 systems as should be the case because all of these phases have the same crystal structure.

Isothermal Sections

No experimental data for the ternary system are known besides the quasibinary section $\text{PuO}_2\text{-ZrO}_2$. [2003Kin] have performed thermodynamic modeling to assess the phase relation in the O–Pu–Zr system. In the first stage, they attempted a preliminary thermodynamic modeling for the O–Pu system with thermodynamic data and phase diagram information available in the literature. The assessed data reproduced the general feature of the system with respect to phase diagram, oxygen potential and heat capacity. In the second stage, a possible set of phase diagrams for the O–Pu–Zr system was calculated using obtained data for the O–Pu system together with those for the O–Zr [1998Che] and Pu–Zr [1999Kur] subsystems available in the literature. In general, the ternary system starts forming oxides when the oxygen composition in the system increases. Moreover, plutonium tends to oxidize more readily than zirconium as is concluded by the presence of Pu_2O_3 rather than ZrO_2 at the calculated ternary sections. All the accepted diagrams are internally consistent as they are based upon the same database for calculation. These are shown in Figs. 3–5. However it should be noted that the $(\alpha\text{Zr})' + (\alpha\text{Zr})'' + \text{Pu}_2\text{O}_3$ three-phase equilibrium in Fig. 3 seems to be doubtful considering the shape of the (αZr) field, which is shifted very close to the binary sides. Therefore tie-lines $(\alpha\text{Zr})' - (\alpha\text{Zr})''$ are shown by dashed lines in Fig. 3.

Notes on Materials Properties and Applications

[2004Gib] have synthesized small ternary oxide clusters of zirconium and plutonium oxide in order to study plutonium chemistry. In other cases, zirconia based ceramics are used in high temperature applications such as engine components due to their low thermal conductivity and high fracture toughness [2002Arr]. The O–Zr system is also important in solid oxide fuel cells. [1965Far1, 1965Far2, 1965Far3, 1965Far4, 1966Bar1, 1966Bar2, 1966Far1, 1966Far2, 1967Far1, 1967Far2, 1968Far1, 1968Far2, 1968Far3, 1968Far4, 1968Far5, 1969Fac1, 1969Fac2, 1969Far] undertook a review of mechanical properties, method of fabrication and irradiation influence on plutonium oxides.

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Table 1: Investigations of the O-Pu-Zr Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1963Car]	X-ray diffraction Metallography	1550°C PuO ₂ -ZrO ₂
[1967Ack]	X-ray diffraction, metallography examination, emf	up to 1000°C from 64 to 73 at.% O and 40 to 33 at.% Pu
[1969Mar]	X-ray powder diffraction dilatometry	1500°C to 1900°C
[2001Ser]	High temperature X-ray diffraction	1000°C to 1200°C 3.1 to 11.2 mol% PuO ₂

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α Pu) < 125	<i>mP</i> 16 <i>P</i> 2 ₁ / <i>m</i> α Pu	<i>a</i> = 618.30 <i>b</i> = 482.20 <i>c</i> = 1096.3	[V-C2]
(β Pu) 215 - 125	<i>mC</i> 34 <i>C</i> 2/ <i>m</i> β Pu	<i>a</i> = 1183.0 <i>b</i> = 1044.9 <i>c</i> = 922.70	[V-C2]
(γ Pu) 320 - 215	<i>oF</i> 8 <i>Fddd</i> γ Pu	<i>a</i> = 315.87 <i>b</i> = 576.82 <i>c</i> = 1016.2	[V-C2]
(δ Pu) 463 - 320	<i>cF</i> 4 <i>Fm</i> $\bar{3}$ <i>m</i> Cu	<i>a</i> = 463.47	[V-C2]
(δ' Pu) 483 - 463	<i>tI</i> 2 <i>I</i> 4/ <i>mmm</i> In	<i>a</i> = 333.90 <i>c</i> = 444.67	[V-C2]
(ϵ Pu, β Zr) (ϵ Pu) 640 - 483 (β Zr) 1855 - 863	<i>cI</i> 2 <i>Im</i> $\bar{3}$ <i>m</i> W	<i>a</i> = 365.70 <i>a</i> = 356.80	[V-C2] [Mas2]
(α Zr) < 863	<i>hP</i> 2 <i>P</i> 6 ₃ / <i>mmc</i> Mg	<i>a</i> = 323.17 <i>c</i> = 514.83	[V-C2] [Mas2]
Pu ₂ O ₃ < 2020	<i>hP</i> 5 <i>P</i> $\bar{3}$ <i>m</i> 1 La ₂ O ₃	<i>a</i> = 383.88 <i>c</i> = 595.94	lattice parameters from [V-C2] existence of an ordered superstructure [1967Ack]
α ZrO ₂ < 1205	<i>mP</i> 12 <i>P</i> 2 ₁ / <i>c</i> CoSb ₂	<i>a</i> = 515.05 <i>b</i> = 521.16 <i>c</i> = 531.73	[V-C2] [Mas2]
β ZrO ₂ 2377 - 1205	<i>tP</i> 6 <i>P</i> 4 ₂ / <i>mm</i> <i>m</i> TiO ₂	<i>a</i> = 529.28 <i>c</i> = 365.26	[V-C2] [Mas2]
γ , (Pu,Zr)O ₂ PuO ₂ < 2467 γ ZrO ₂ 2710 - 2377	<i>cF</i> 12 <i>Fm</i> $\bar{3}$ <i>m</i> CaF ₂	<i>a</i> = 539.7 <i>a</i> = 509.00	continuous solid solution 62.8 to 66.7 at.% O [2003Kin] lattice parameters [V-C2] [V-C2] [Mas2]

Fig. 1: O-Pu-Zr.
The calculated Pu-Zr
equilibrium phase
diagram

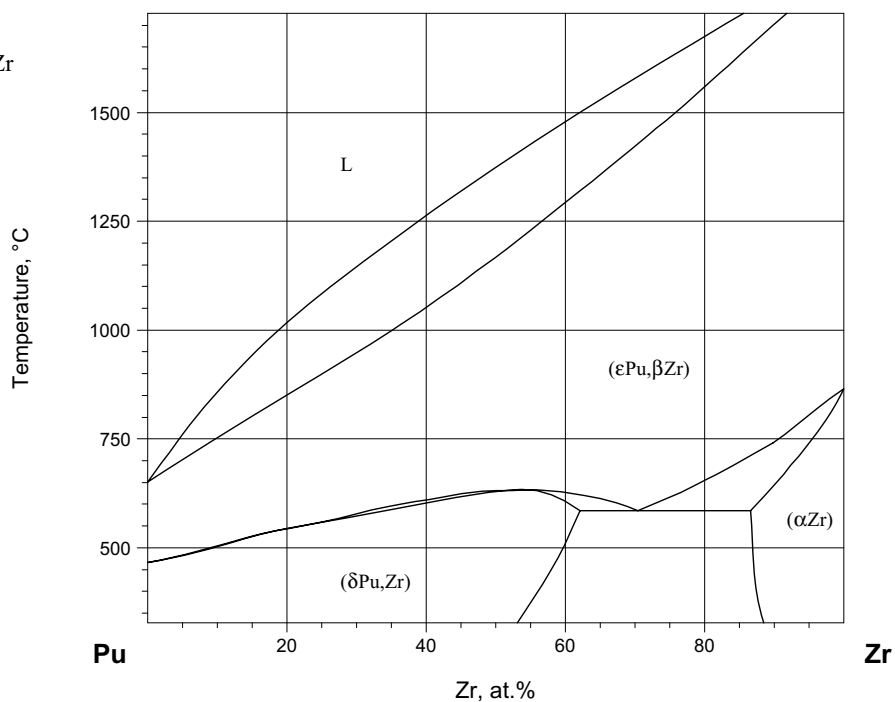


Fig. 2a: O-Pu-Zr.
The calculated
 $\text{PuO}_2\text{-ZrO}_2$
quasibinary phase
diagram in the entire
composition range

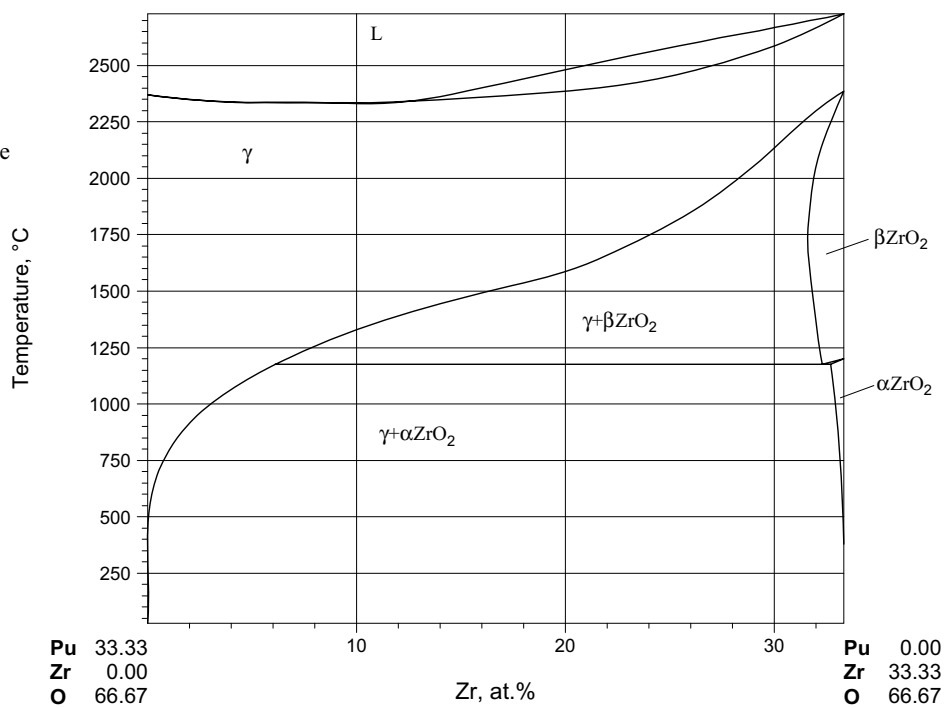
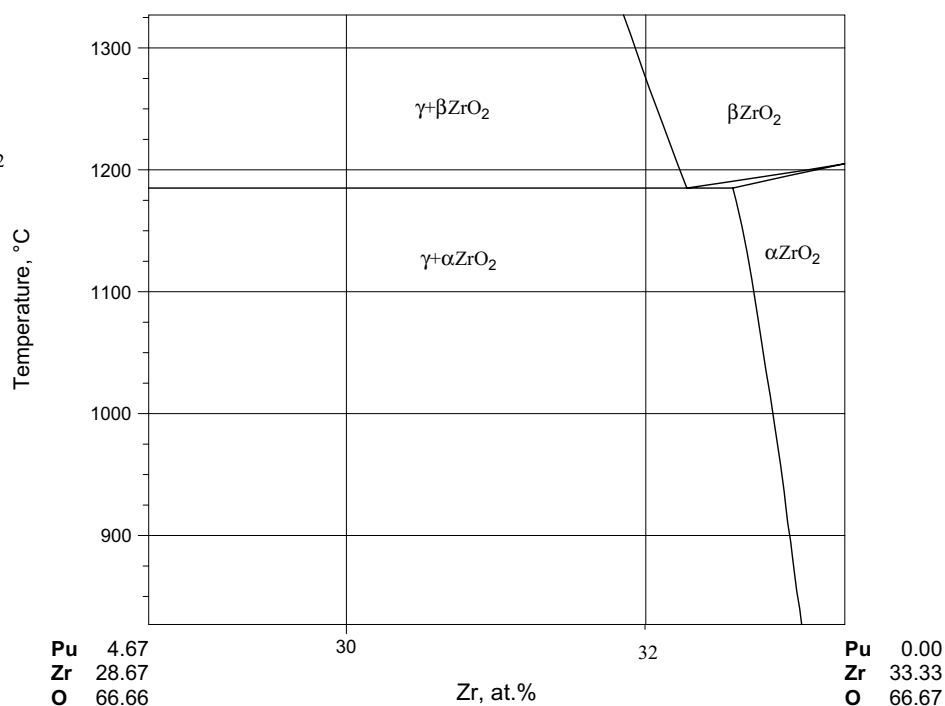


Fig. 2b: O-Pu-Zr.

The calculated
 $\text{PuO}_2\text{-ZrO}_2$
 quasibinary phase
 diagram at the ZrO_2
 rich end; enlarged
 part of Fig. 2a

**Fig. 3: O-Pu-Zr.**

The calculated
 isothermal section
 500°C

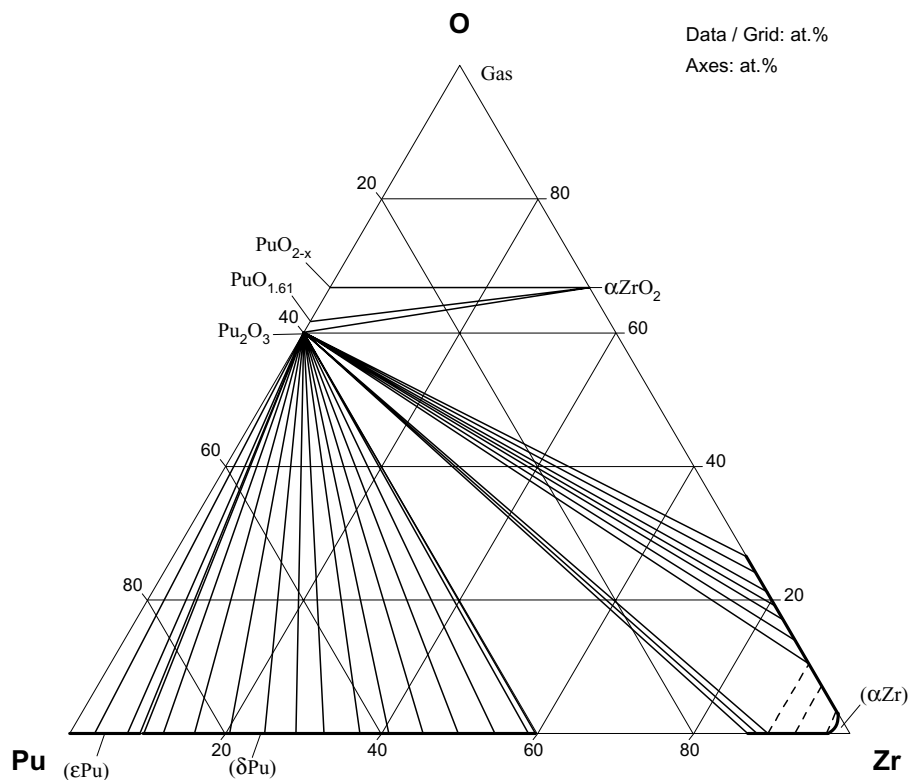


Fig. 4: O-Pu-Zr.
The calculated
isothermal section at
1000°C

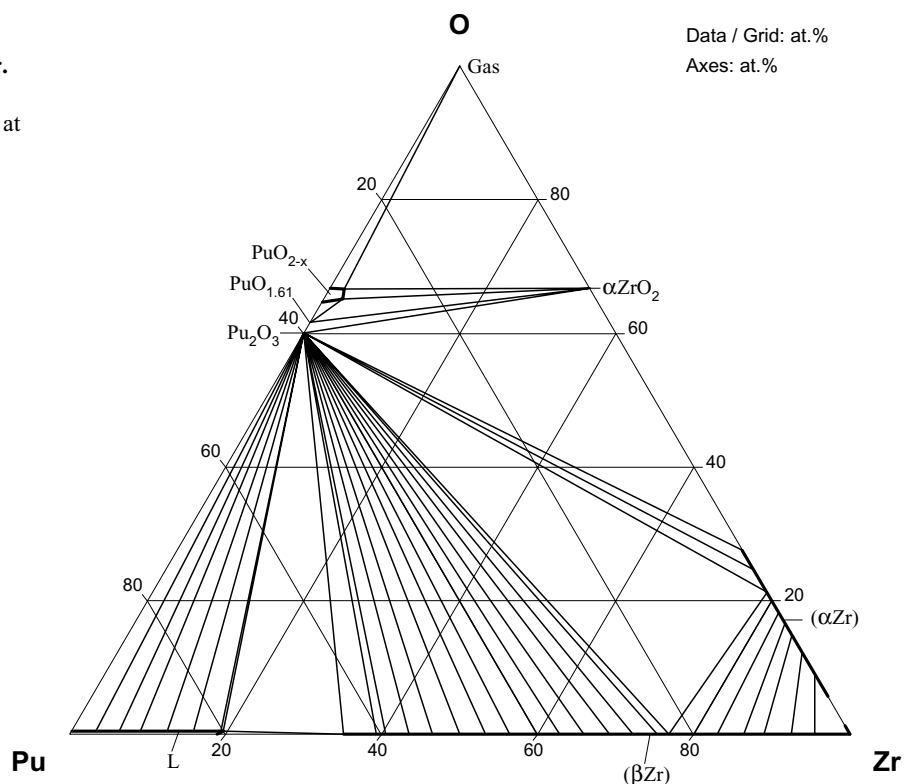
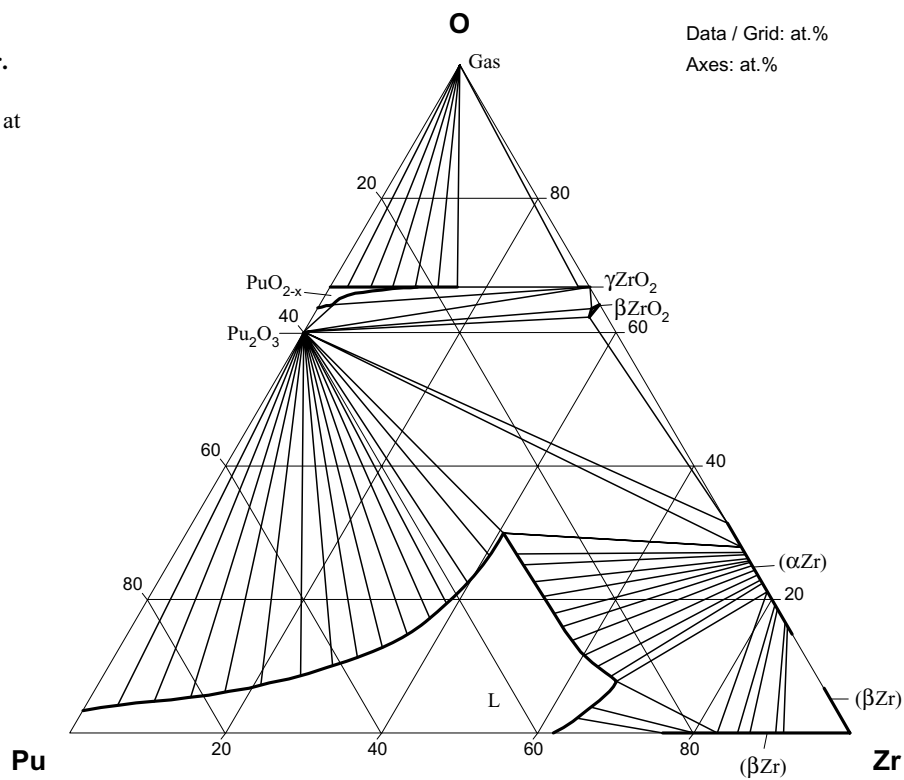


Fig. 5: O-Pu-Zr.
The calculated
isothermal section at
1500°C



Oxygen – Thorium – Zirconium

Pierre Perrot

Introduction

A first tentative ThO₂-ZrO₂ phase diagram was proposed by [1929Ruf], which presented a cigar shaped liquidus and solidus together with a miscibility gap in the γ solid solution with a critical point of 2600°C. However, these features are inconsistent from a thermodynamic point of view. A more careful investigation of this system [1975Sak] using a solar furnace confirms the miscibility gap in the γ phase, but demonstrates the existence of a minimum in the solidus and liquidus lines and both features are thermodynamically consistent. These features were confirmed by [1978Ara] which evaluates the position of the critical point (2400°C and 50 mol% ThO₂), the position of the minimum (2480°C and 28 mol% ThO₂) and precises the shape of the tetragonal domain. The reciprocal solubility of γ ThO₂ and β ZrO₂ at 1400°C has been investigated by [2002Gro]. However, a more recent Calphad assessment [2004Kin] shows that the miscibility gap in the γ solid solution must be metastable and presents a diagram with a large $\beta + \gamma$ two-phase domain.

Binary Systems

The Th-Zr system is accepted from [Mas2]. The O-Zr system is accepted from the Calphad assessment of [1998Che, 2004Che]. The O-Th system is accepted from [1998Che].

Solid Phases

The solid phases are presented in Table 1.

Quasibinary Systems

The ThO₂-ZrO₂ phase diagram shown in Fig. 1 is mainly from [2004Kin]. The diagram proposed by [1978Ara] has not been taken into account because it presents, without any experimental evidence, two biphased domains $\gamma + \gamma'$. Actually, the only miscibility gap recognized is metastable with a critical point at 2400°C and 50 mol% ZrO₂. At low temperature, it is acknowledged [1981Pep] that ThO₂ and ZrO₂ shows slight mutual solubility, probably no more than 2 mol% in each end-member.

The solubility of ZrO₂ in γ ThO₂ and that of ThO₂ in β ZrO₂ has been investigated by X-ray diffraction of mixtures Th_{1-x}Zr_xO₂ annealed at 1400°C following by a slow cooling [2002Gro]. The crystal parameter of cubic γ ThO₂ remains constant for $x > 0.05$, which agrees with [2004Kin]. For the higher values of x , [2002Gro] observes the presence of a monoclinic phase α Th_{0.05}Zr_{0.95}O₂ together with that of γ Th_{0.95}Zr_{0.05}O₂, which contradicts the known behavior of α ZrO₂. It is probable that the monoclinic α phase observed comes from the slow cooling of the β quadratic phase which is stable at 1400°C.

Thermodynamics

The solid solution γ , (Th,Zr)O₂, has been described by [1978Ara] with the approximation of regular solutions: $\Delta_{\text{mix}}G^{\text{xs}} = \alpha x_{\text{ThO}_2} x_{\text{ZrO}_2}$ with $\alpha = 42890 \text{ J}\cdot\text{mol}^{-1}$ for the γ solid solution. Such a value leads for the γ solid solution to a miscibility gap at 50 at.% ZrO₂ and 2306°C, which is 100°C lower than the value proposed by [1978Ara]. An evaluation of the α parameter by [2004Kin] leads to the following values: 8427, 39234, 38717 and 32385 J·mol⁻¹, respectively for the liquid solution, the cubic, tetragonal and monoclinic solid solutions.

Notes on Materials Properties and Applications

Early review of nuclear fuel cycles tended to conclude that uranium fuel cycle currently used in nuclear power plants was more preferable than thorium cycle [2000Bus]. However, Th based fuels are of interest

due to the efficiency of creating new fissile materials with high burnup, the abundance of Th and the chemical stability of thorium. Thorium could be considered as a potential base for diluting plutonium. On another hand, opposite to uranium, thorium can not react with zirconium cladding because the standard enthalpy of formation of ZrO_2 ($-1100 \text{ kJ}\cdot\text{mol}^{-1}$ at 25°C) is of the same order than that of UO_2 ($-1085 \text{ kJ}\cdot\text{mol}^{-1}$ at 25°C) and higher than that of ThO_2 ($-1226 \text{ kJ}\cdot\text{mol}^{-1}$ at 25°C).

Miscellaneous

Zirconium alloys containing thorium oxide were prepared by arc melting [1971Ske]. The refractory ThO_2 dissolved in the molten zirconium precipitates as a dispersed phase on solidification. The resulting composite presents high temperature (650°C) tensile strength up to twice that of Zircaloy-2.

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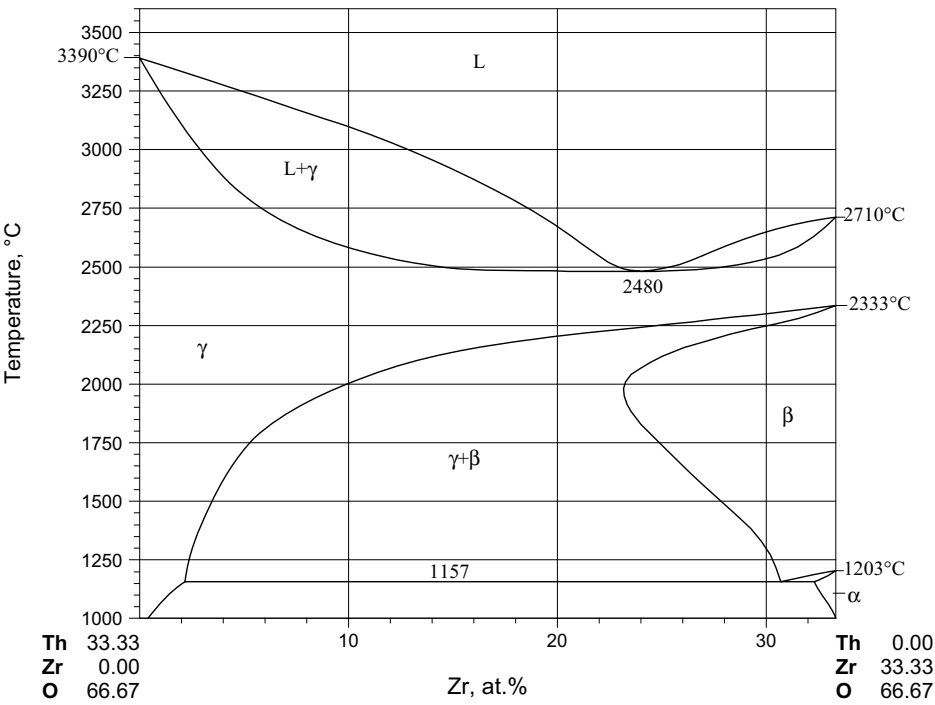
Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α Th) < 1360	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 508.42$	at 25°C [Mas2] dissolves up to 14.8 at.% Zr at 908°C
(α Zr) < 2127	<i>hP2</i> <i>P6₃/mmc</i> Mg	$a = 323.16$ $c = 514.75$	at 25°C [Mas2] dissolves up to 31.3 at.% O at 2097°C [2004Che]
(β Th, β Zr) (β Th) 1755 - 1360	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 411.0$	(β Th _{0.54} Zr _{0.46}) stable between 908 and 1350°C [Mas2]
(β Zr) 1855 - 866		$a = 360.90$	(β Zr) dissolves up to 10.4 at.% O at 1970°C [2004Che]
α , α ZrO ₂ < 1203	<i>mP12</i> <i>P2₁/c</i> ZrO ₂	$a = 522$ $b = 527$ $c = 538$ $\beta = 99.46^\circ$	66.6 at.% O [2004Che]
β , β ZrO ₂ 2333 - 1203	<i>tP6</i> <i>PA₂/nmc</i> HgI ₂	$a = 511.9$ $c = 526.0$	66.5 to 66.6 at.% O [2004Che]. dissolves ~30 at.% ZrO ₂ at 2000°C [2004Kin]
γ , (Th,Zr)O ₂	<i>cF12</i> <i>Fm$\bar{3}m$</i>	$a = 558.7$	Th _{0.95} Zr _{0.05} O ₂ [2002Gro]
γ ZrO ₂ 2710 - 1483	CaF ₂	$a = 509$	61 to 66.6 at.% O [2004Che]
ThO ₂ < 3390		$a = 559.57$	65 to 66.6 at.% O [2003Kin]

Table 2: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				O	Th	Zr
$L \rightleftharpoons \gamma$	2480	min	L	9.19	24.14	66.67
			γ	9.19	24.14	66.67
$\beta \rightleftharpoons \gamma + \alpha$	1157	e	β	2.68	30.65	66.67
			γ	31.03	2.30	66.67
			α	0.96	32.37	66.67

Fig. 1: O-Th-Zr.
The quasibinary
system ThO₂-ZrO₂



Oxygen – Uranium – Zirconium

Pierre Perrot

Introduction

The O-U-Zr system is an important part of the corium, mixture formed at high temperatures between nuclear fuel and other materials (steel, zircaloy, control rods) which may interact with the concrete during an hypothetical severe nuclear accident [1990Rel]. The mixture $\text{U}_{0.6}\text{Zr}_{0.4}\text{O}_2$ which corresponds to 23 mass% ZrO_2 is generally used to model the behavior of corium at high temperatures [2004Asm] and, for this reason, the UO_2 - ZrO_2 system has been thoroughly investigated. A first tentative UO_2 - ZrO_2 phase diagram was proposed by [1953Lam], reproduced by [1956Lan], and then by [1960Eva] which melted the oxides in a solar furnace then annealed the mixture at 1350°C. An extended range of solid solution of each component was observed, but the stabilisation of fluorite like γZrO_2 by UO_2 was not recognised. The hypothesis of a continuous solid solution in the whole composition range above 1950°C was introduced by [1958Wol]. However, the existence of the high temperature modification of ZrO_2 (the fluorite type γZrO_2) was clearly established by [1963Coh] and the stability of the $\gamma(\text{U,Zr})\text{O}_2$ solid solution was put into evidence in the high temperature range. Using experimental informations available to date, [1996Yas] presented a Calphad assessment of the UO_2 - ZrO_2 system. More precise experimental determinations of the O-U-Zr phase equilibria at 1000 and 1400°C were presented by [1985Yam, 1990Yam] and [1987Yam], respectively. In order to understand the reactions between the UO_2 fuel and the zircaloy cladding, the Zr- UO_2 reactions have been investigated at 1000-1400°C by [1988Miy], at 2000-2200°C by [1994Hay, 1997Ola], 2300-2500°C by [1996Hay] and 2500-2975°C by [1998Gue] leading to the representation of the O-U-Zr phase equilibria between 1000 and 2500°C used in the thermodynamic assessment carried out by [2004Che]. Experimental investigations are summarized in Table 1.

A first thermodynamic assessment using all the available experimental informations has been carried out by [1998Che]. Unfortunately, experimental information was not fully consistent. Using new activity measurements and experimental results on the O-U binary system, [2004Che] carried out a critical assessment on which the present report is based. The tentative diagram at 2227°C (2500 K) proposed by [1985Hag] analyzing the Three Mile Island core accident is in a good qualitative agreement with the calculations of [2004Che].

Binary Systems

The three binary systems are accepted from the Calphad assessment of [1998Che, 2004Che]. A precise model of the solid and liquid oxide solutions taking into account the oxygen vacancies in the O-U system may be found in [2002Gue]. This model is used in the thermodynamic description of the O-U-Zr system presented by [2004Che]. It should be noted that the U-Zr diagram calculated in [2004Che] differs from the one presented in [Mas2], however, in the temperature range relevant to the known O-U-Zr equilibria, it is basically the same.

Solid Phases

The solid phases are presented in Table 2. UO_2 dissolves 0.38 mol% αZrO_2 at the eutectoid temperature of 1110°C [1967Rom, 1990Das]. The solubility of UO_2 in βZrO_2 presents a retrograde behavior, increasing from 2.8 mol% at 1110°C up to a maximum of 20 mol% around 1750°C. The reactions between ZrO_2 and U_3O_8 have been investigated by [1970Ver]. The presence of U_3O_8 lowers the α - β transition temperature of ZrO_2 . Besides, under 150 bar of oxygen pressure and 650°C during 200 h, the following phases are formed: UO_{3-x} , having an orthorhombic lattice and a hexagonal $(\text{U,Zr})\text{O}_x$ ones whose compositions are unfortunately not given.

Quasibinary Systems

The quasibinary system $\text{UO}_2\text{--ZrO}_2$ assessed by [2004Che] is shown in Fig. 1 with characteristics of the invariant phase equilibrium indicated in Table 3. The former $\text{UO}_2\text{--ZrO}_2$ phase diagrams [1953Lam, 1960Eva] presented a miscibility gap in the liquid region, which is not acknowledged in the assessment carried out by [1996Yas] and other authors [1998Gue, 2004Asm].

Isothermal Sections

The isothermal section at 1100, 1600, 2000, 2200, 2400, 2600 and 2800°C as proposed by [2004Che] are given in Figs. 2, 3, 4, 5, 6, 7 and 8, respectively. The sections may be used to explain the observations reported by [1970Bar] on the behavior of $\text{UO}_2\text{--Zr}$ mixtures between 1600 and 2500°C. The results indicate the presence of the $(\text{U,Zr})\text{O}_2$ solid solution, U–Zr alloys and liquid phases.

Temperature – Composition Sections

Figure 9 presents the vertical section $\text{UO}_2\text{--Zr}$ [2004Che] which is an important tool for predicting the behavior of UO_2 based nuclear fuel on Zr based cladding material.

Thermodynamics

The heat of solution of O in U–Zr liquid alloys have been measured at 2000°C by [1995Ola1]. The stronger binding of O in the solid oxides compared to that of the liquid metals results in heat of solution of O larger than the heat of fusion of pure metals or pure oxides. The activity of oxides in the solid solution $\gamma(\text{Zr,U})\text{O}_2$, was measured by mass spectrometry coupled with a Knudsen' effusion cell between 1930 and 2375°C [1997Sto] for the ZrO_2 rich mixtures, and between 1727 and 2225°C in the whole concentration range [2001Bai]. The solid solutions present, above 2225°C an ideal behavior and below that temperature, a positive deviation towards ideality. At lower temperature (1100°C), the $(\text{Zr,U})\text{O}_2$ solutions may also be described by a regular model: $\Delta G^{\text{xs}} = \alpha x_{\text{UO}_2} x_{\text{ZrO}_2}$ [2004Kin]. The interaction parameters α are respectively 8428, 32234, 32717 and 31386 J·mol^{−1} for the liquid, cubic (fluorite), tetragonal and monoclinic solutions.

Notes on Materials Properties and Applications

Liquefaction of UO_2 by molten Zircaloy is one of the signal events in a severe fuel damage accident in a light water reactor [1997Ola] and considerable efforts have been devoted to the modelling of the process. By quenching the $\text{UO}_2\text{--ZrO}_2$ melts at 2500°C, [2004Asm] showed that no separation of the corium melts can be observed under conditions of heavy accident. The vaporization of $\text{U}_3\text{O}_8\text{--ZrO}_2$ mixtures in a Knudsen' cell towards 2100°C [1984Bel] leads mainly to the formation of the gaseous species UO_2 .

The system $\text{U}_x\text{Zr}_{1-x}\text{O}_2$ ($0.1 < x < 0.9$) has been found [1962Joh] to exhibit two modes of electrical conductivity: in low temperature region ($< 1200^\circ\text{C}$), the conductivity is mainly electronic and in high temperature region (1200–2000°C), the conductivity is mainly ionic and proceeds by oxygen vacancies. The electrical conductivity in both regions obeys the Arrhenius' law:

$$\sigma_{\text{L}} / (\Omega^{-1} \text{ cm}^{-1}) = (0.1 \text{ to } 1) \exp(-3000 / T) \quad (T \leq 1200^\circ\text{C})$$

$$\sigma_{\text{H}} / (\Omega^{-1} \text{ cm}^{-1}) = (10^3 \text{ to } 10^6) \exp(-18500 / T) \quad (1200 < T < 2000^\circ\text{C})$$

The thermal conductivity of these solid solutions is also described by [1967Far] with two different equations, depending on the temperature range, above or below 1650°C. These equations take also into account the irradiation supported by the solid solution.

The solid solutions $\text{U}_x\text{Zr}_{1-x}\text{O}_2$ ($x > 0.78$) show an antiferromagnetic transition [1985Hin] with a linear dependence of the Neel temperature on concentration and a critical concentration of 22 mol% ZrO_2 .

The density of the $\text{U}_{0.6}\text{Zr}_{0.4}\text{O}_2$ melts, measured between 2700 and 3100°C [2003Asm] is given by the following expression: $\rho(T) / \text{g}\cdot\text{cm}^{-3} = 7.0 - 4.5 \cdot 10^{-4} [(T/\text{K}) - 2973]$. This particular mixture, which corresponds to 23 mass% ZrO_2 is generally used for modelling the corium.

Miscellaneous

Reinterpreting former observations [1961Eva] showed that the α - β transition of the (U,Zr)O₂ solid solution is of the martensitic type. A mixture $\beta + \gamma$ of the (U,Zr)O₂ solid solution was shown to be transformed into an homogeneous, metastable cubic form γ (U,Zr)O₂ under irradiation [1965Ber]. The process of homogenization can be described by a diffusion constant $D = 3.32 \cdot 10^{-14} \text{ cm}^2 \cdot \text{s}^{-1}$, which indicates that a single fission event homogenizes a volume containing $1.66 \cdot 10^7$ atoms. Irradiation is known to have a marked influence on the physical properties of materials [1965Far], for instance, it may decrease the melting point of oxides by several tens of degrees.

When heated in an accident, UO₂ begin to react with the Zr cladding resulting in formation of the multilayer structure consisting of U, Zr and their oxides [1991Ves]. The diffusion of O is the limiting process of the reaction. The kinetics of dissolution of UO₂ in liquid Zr at 2000°C has been described [1995Ola2] by a two-stage model. In the first stage, the saturation is approached by natural convection mass transfer; in the following stage, where (U,Zr)O_{2-x} precipitates from the melt, oxygen enters the melt as the oxide is reduced to UO_{2-x}. A new method for obtaining high quantities (3 to 10 kg) of ZrO₂-UO₂ melts was proposed by [2003Hon]. Called the "Cold crucible method" or the "Skull melting method", this technique allows the separation of gases, the preparation of high purity material and decrease the heat loss during melting. Induction melting under 50 Hz is possible because the electrical resistivity of a mixture UO₂-ZrO₂ lies around $\sim 4 \cdot 10^{-3} \Omega \text{ cm}$ at the melting point.

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Table 1: Investigations on the O–U–Zr Phase Relations, Structure and Thermodynamics

Reference	Experimental Technique	Temperature/Composition/Phase Range Studied
[1957Och]	X-ray diffraction	U ₃ O ₈ –ZrO ₂ (tentative)
[1958Bau]	Metallographic examination	O–U–Zr system at 660°C (< 66.7 at.% O)
[1958Wol]	X-ray diffraction on samples quenched from 2300°C	UO ₂ –ZrO ₂ (tentative)
[1960Dou]	Chemical analysis, partitioning of U and O between α and β Zr	1095°C, > 85 at.% Zr
[1960Eva]	X-ray diffraction after melting and annealing	UO ₂ –ZrO ₂ at 1350 and 2500°C (tentative phase diagram)
[1962Joh]	Electrical conductivity measurements	UO ₂ –ZrO ₂ , 500–2000°C
[1963Coh]	X-ray and metallographic techniques	UO ₂ –ZrO ₂ , 1200–2350°C, cubic-tetragonal equilibrium
[1967Rom]	Chemical analysis	UO ₂ –ZrO ₂ , 600–1130°C, phase equilibria
[1970Ver]	X-ray diffraction	U ₃ O ₈ –ZrO ₂ , 650°C, oxidation under 150 bar O ₂
[1984Bel]	Mass spectrometry measurements	U ₃ O ₈ –ZrO ₂ , 2100°C
[1985Hin]	Magnetic susceptibility measurements	UO ₂ –ZrO ₂ , 2–298 K
[1985Yam, 1990Yam]	X-ray diffraction	O–U–Zr diagram at 1000°C
[1987Yam]	X-ray diffraction of Zr–ZrO ₂ –UO ₂ mixtures	O–U–Zr diagram at 1400°C
[1988Miy]	X-ray diffraction of Zr–UO ₂ mixtures	O–U–Zr diagram at 1000 and 1400°C
[1994Hay]	X-ray diffraction of Zr–UO ₂ mixtures	O–U–Zr diagram, 2000–2200°C
[1995Ola1]	Dissolution calorimetry	Liquid alloy - oxide equilibrium, 2000°C
[1996Hay]	Metallography, SEM and EDX analysis of Zr–UO ₂ mixtures	U–Zr–O equilibria at 2300–2500°C Schematic Zr(O)–UO ₂ diagram
[1997Sto]	Activity measurements by Knudsen' effusion cell	ZrO ₂ –UO ₂ (< 50 at.% UO ₂) 1930–2375°C
[1998Che, 2004Che]	Calphad assessment	The whole diagram up to 2800°C, 0.1 MPa
[1998Gue]	Quenched from the melts, SEM, EDS, WDS analysis	O–U–Zr equilibria at 2500–2975°C
[1998Ves]	Morphological observations, mechanism analysis	Liquid Zr–solid (Zr,U)O ₂ reactions 1900–2000°C
[2001Bai]	Multiple Knudsen Cell mass spectrometric method	ZrO ₂ –UO ₂ , 1727–2225°C

Reference	Experimental Technique	Temperature/Composition/Phase Range Studied
[2003Asm]	Density measurements by a pycnometric method	UO ₂ -ZrO ₂ , 2700-3100°C
[2004Asm]	Quenching from the melts	UO ₂ -ZrO ₂ (1.2 < U/Zr < 1.6) at 2500°C
[2004Kin]	Calphad assessment	UO ₂ -ZrO ₂ , 1000-3200°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	dissolves up to 1.5 at.% Zr at 660°C [1998Che] pure α U at 25°C [Mas2]
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mm</i> β U	$a = 1075.9$ $c = 565.6$	dissolves up to 2 at.% Zr at 695°C [1998Che] pure β U at 25°C [Mas2]
(α Zr) < 2173	<i>hP2</i> <i>P6₃/mmc</i> Mg	$a = 323.16$ $c = 514.75$	dissolves up to 31.3 at.% O at 2097°C [2004Che] pure α Zr at 25°C [Mas2]
(γ U, β Zr) 1970 - 612	<i>cI2</i> <i>Im$\bar{3}m$</i> W		continuous solid solution between γ U and β Zr. β Zr dissolves 10.4 at.% O at 1970°C [2004Che]
(γ U) 1135 - 776		$a = 352.4$	pure γ U [Mas2]
(β Zr) 1885 - 866		$a = 360.90$	pure β Zr [Mas2]
δ , UZr ₂ < 617	<i>hP3</i> <i>P6/mmm</i> AlB ₂	$a = 503$ $c = 308$	65 to 78 at.% Zr [2004Che]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ , $(\text{UO}_2)_{1-x}(\gamma\text{ZrO}_2)_x$ < 2852	$cF12$ $Fm\bar{3}m$ CaF_2	$a = 547.0$	continuous solid solution between UO_2 and γZrO_2 . $0 \leq x \leq 1$ $x = 0$
UO_2 < 2852		$a = 547 - 26.0 x$	UO_2 contains from 62.5 (at 2425°C) to 66.7 at.% O [2004Che]
γZrO_2 2710 - 1483		$a = 527.2$	$(\text{UO}_2)_{1-x}(\gamma\text{ZrO}_2)_x$ annealed at 1700°C ($x < 0.5$) [1993Kle] γZrO_2 contains from 61.6 (at 2097°C) to 66.7 at.% O [1963Coh, 2004Che] $x = 1$
U_4O_9 < 1123	$cI832$ $I\bar{4}3d$ or $I4_132$	$a = 2176$	[2004Che]
U_3O_8 < 1870	$oC44$ $Cmcm$	$a = 706.9$ $b = 1144.5$ $c = 830.3$	[2004Che]
UO_3 < 669	$cP4$ $Pm\bar{3}m$ ReO_3	$a = 414.6$	[2004Che]
αZrO_2 < 1205	$mP12$ $P2_1/c$ αZrO_2	$a = 517$ $b = 522$ $c = 533$ $\beta = 99.46$	[1963Coh, 2004Che] dissolves 0.2 mol% UO_2 at $\sim 1110^\circ\text{C}$ [1967Rom]
βZrO_2 2377 - 1126	$tP6$ PA_2/nmc HgI_2	$a = 508.4$ $c = 517.0$	[1963Coh, 2004Che] dissolves 2.8 mol% UO_2 at $\sim 1110^\circ\text{C}$ [1967Rom]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				O	U	Zr
$\text{L} \rightleftharpoons \gamma$	2562	congruent	L	66.7	13.3	20.0
			γ	66.7	13.3	20.0
$\beta\text{ZrO}_2 \rightleftharpoons \gamma + \alpha\text{ZrO}_2$	1126	e	βZrO_2	66.7	4	29.3
			γ	66.7	32.1	1.2
			αZrO_2	66.7	0	33.3

Fig. 1: O-U-Zr.
The UO_2 - ZrO_2
quasibinary system

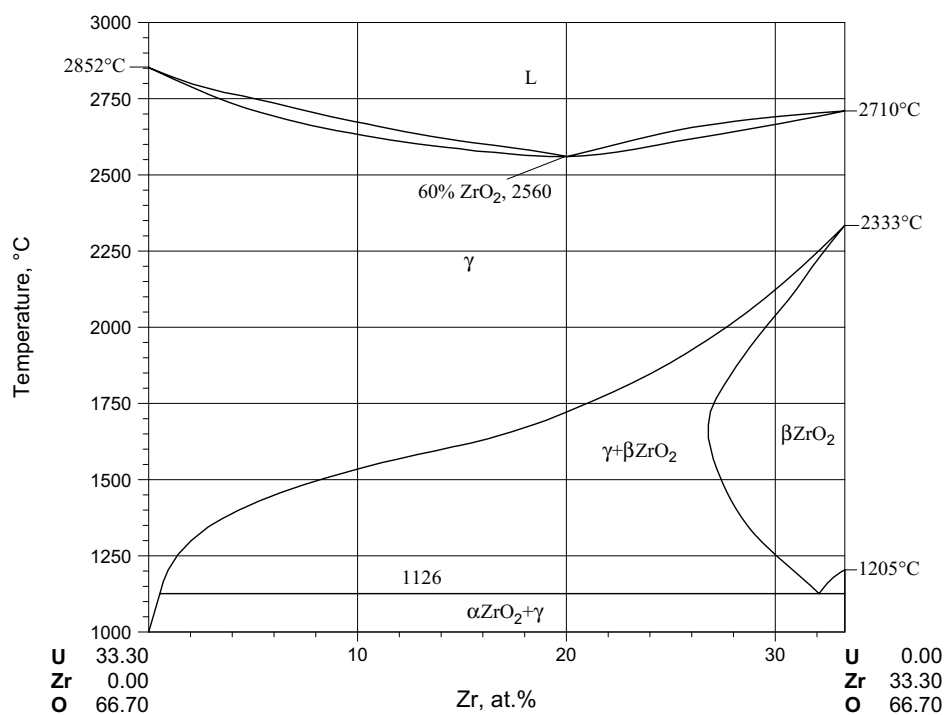


Fig. 2: O-U-Zr.
Isothermal section at
1100°C

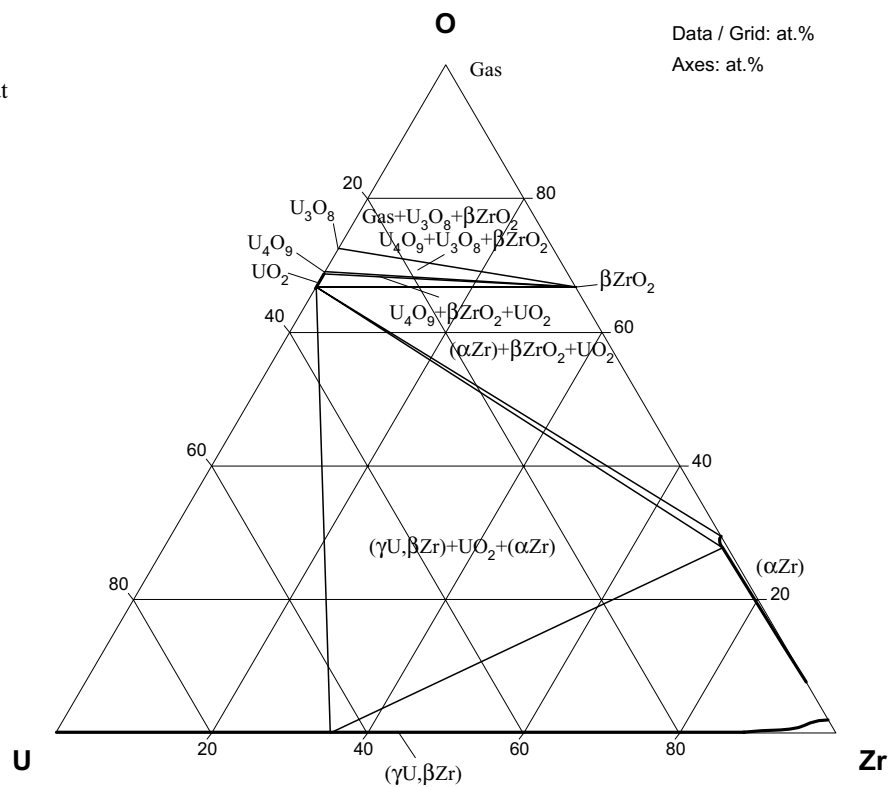


Fig. 3: O-U-Zr.
Isothermal section at
1600°C

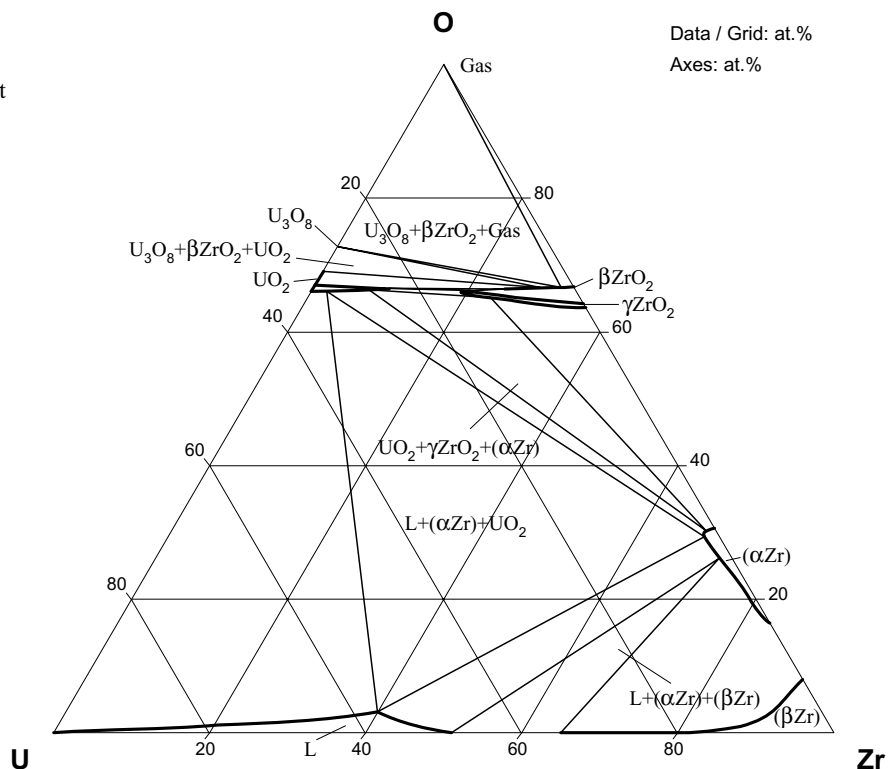


Fig. 4: O-U-Zr.
Isothermal section at
2000°C

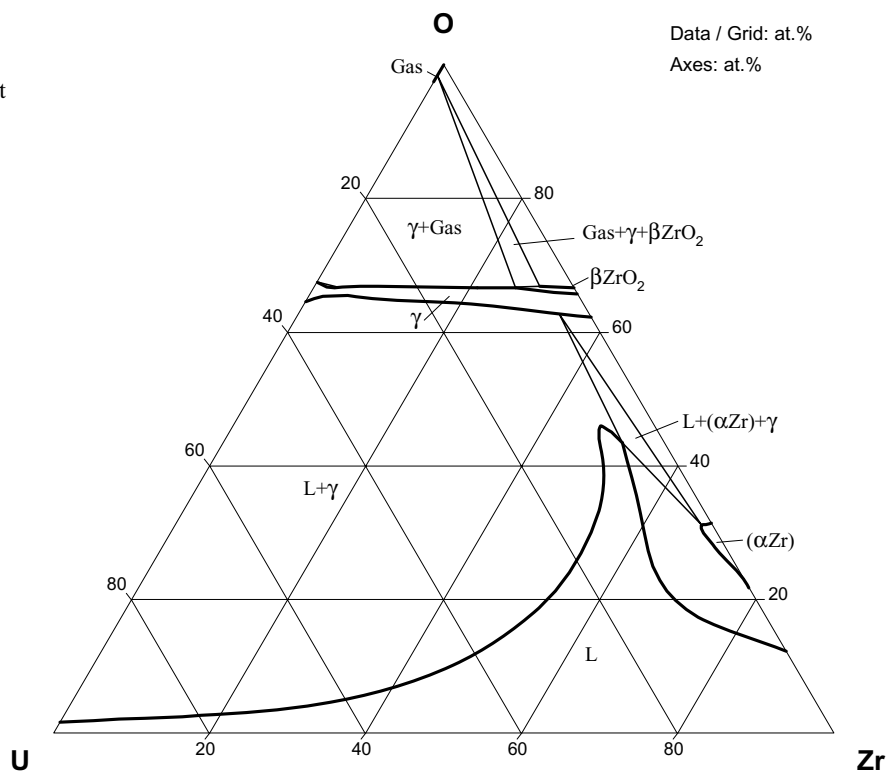


Fig. 5: O-U-Zr.
Isothermal section at
2200°C

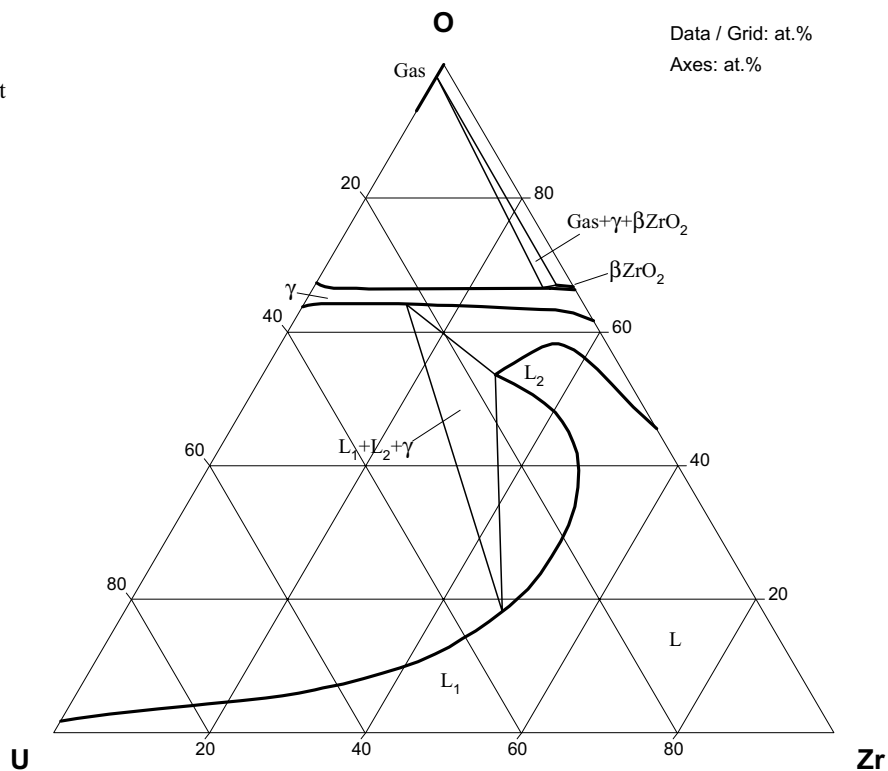


Fig. 6: O-U-Zr.
Isothermal section at
2400°C

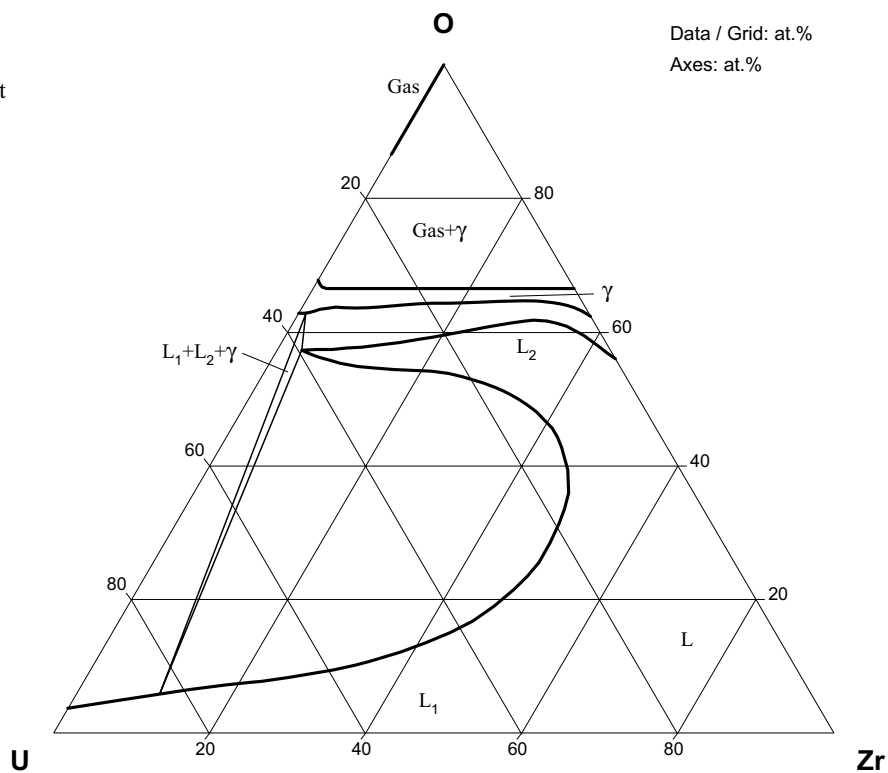


Fig. 7: O-U-Zr.
Isothermal section at
2600°C

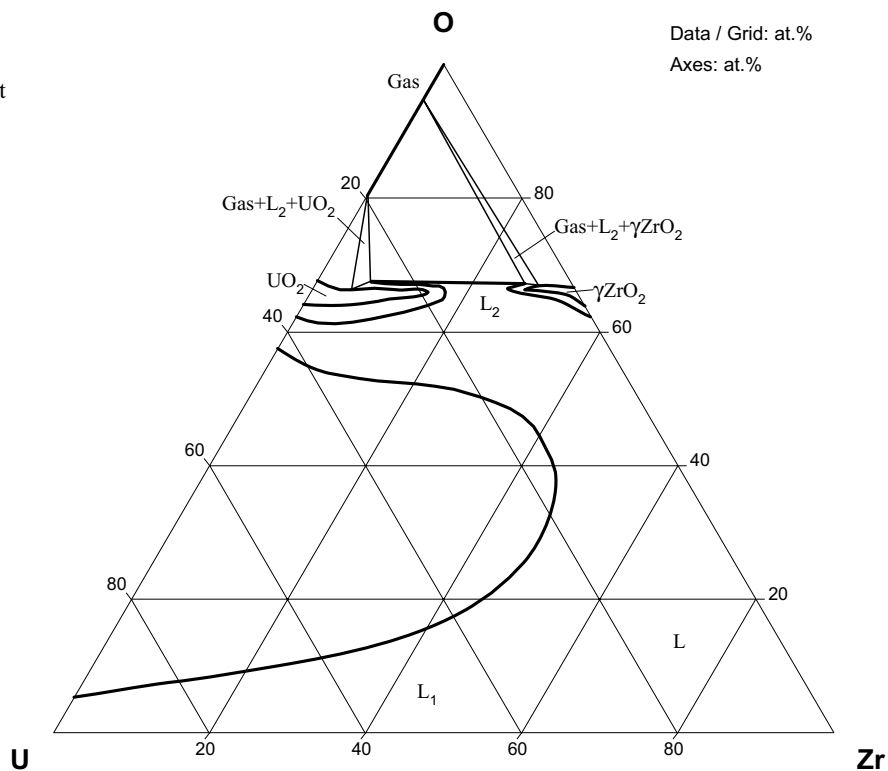


Fig. 8: O-U-Zr.
Isothermal section at
2800°C

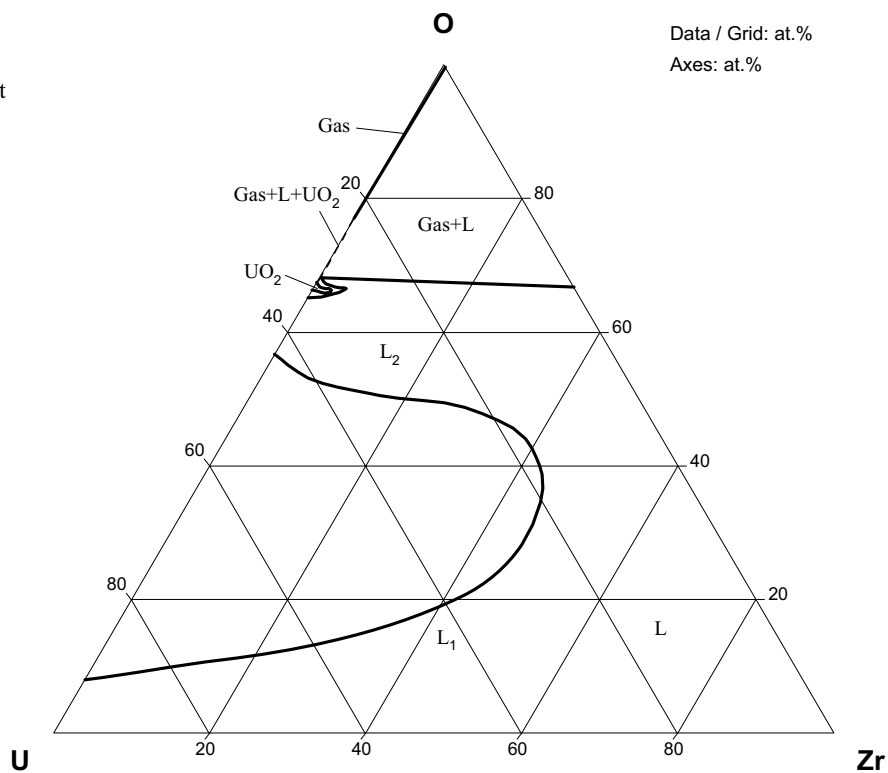
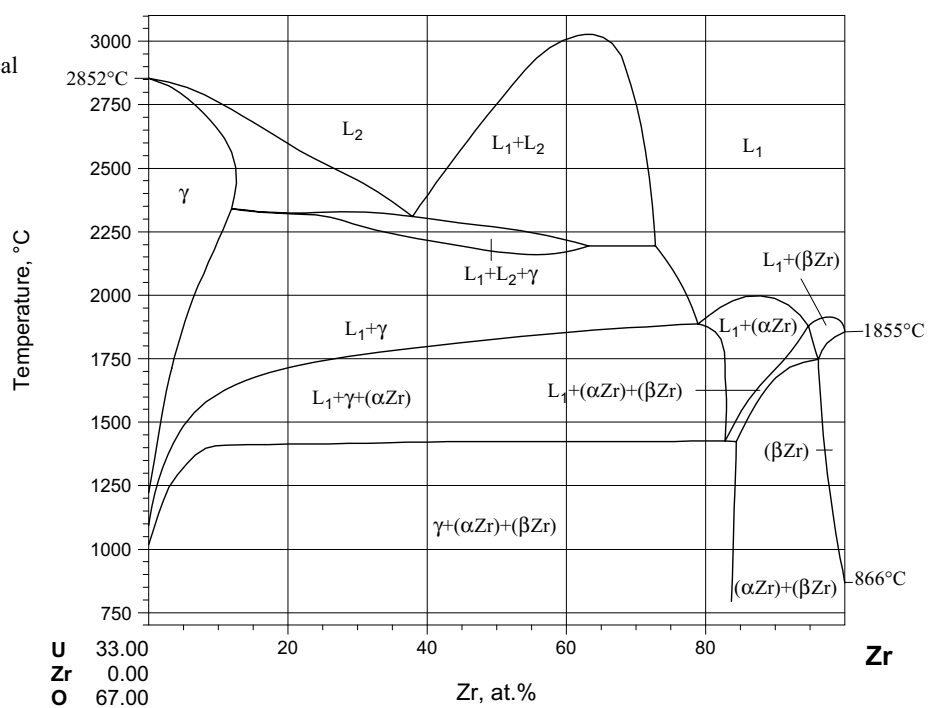


Fig. 9: O-U-Zr.
The UO_2 - Zr vertical
section



Palladium – Rhodium – Uranium

Gabriele Cacciamani, Riccardo Ferro

Introduction

The only phase diagram investigation of this system has been carried out by [1991Kle]. They studied the isothermal section at 1050°C. Alloys were prepared by using Rh and Pd powders (99.7 and 99.9 mass% pure, respectively) and U filings containing 120 ppm oxygen and 120 ppm nitrogen as impurities. U was cleaned for superficial oxide by nitric acid. Pellets of the component powders and filings were arc-melted under reduced argon pressure, crushed and pressed again, and finally annealed at 1050°C for 500 h under static Ar atmosphere. Samples were analyzed by metallography, electron probe microanalysis, X-ray diffraction and DTA (the last one only on selected binary Pd–U alloys).

Binary Systems

Rh–U binary subsystem is accepted after [Mas2]. The phase diagram Pd–Rh is taken from [1994Tri]. As for Pd–U it is here preferred the phase diagram reported by [1991Kle], shown in Fig. 1, which is in agreement with [Mas2] in the range 0–75 at.% Pd and different at higher Pd concentration. In particular, with respect to [Mas2], the existence of the UPd₅ and U₂Pd₁₁ phases is not confirmed, while the Pd richest phase at about 88 at.% Pd is reported as UPd₈ instead of U₂Pd₁₇. Moreover, the UPd₄ phase, previously considered as peritectic forming, is reported by [1991Kle] as congruent melting at 1585°C.

Solid Phases

The Pd–Rh–U solid phases are reported in Table 1. It may be observed that one ternary line compound U(Rh_{1–x}Pd_x)₂ with the MgZn₂ Laves structure is formed and several binary phases show more or less extended ternary solutions. For the fcc and AuCu₃ solid solutions, isoparametric curves according to [1991Kle] are reported in Fig. 2.

Isothermal Sections

The isothermal section at 1050°C investigated by [1991Kle] is reported in Fig. 3. Main features of this section are the following: the continuous (Pd–Rh) based fcc solid solution, extending up to about 18 at.% U (with 9.5 at.% Rh and 72 at.% Pd), includes a large miscibility gap; isostructural URh₃ and UPd₄ AuCu₃ type phases form a continuous solid solution crossing the composition triangle; the U(Rh_{1–x}Pd_x)₂ ternary line compound extends between $x = 0.04$ and $x = 0.25$; the binary-based U₃(Rh_{1–x}Pd_x)₄ solution extends up to $x = 0.47$; most of the U rich part of the section, not investigated, is occupied by the liquid phase.

It may be observed that, according to the accepted binary, U₅Pd₆ should appear in the section: it has been added in Fig. 3 and related equilibria are tentatively indicated by interrupted lines.

Thermodynamics

According to [1991Kle], the fcc region at 1050°C splits into two conjugate solid solutions when more than 0.6 at.% U is dissolved in binary Pd–Rh solution. In other words the critical temperature of the fcc miscibility gap, which is about 915±5°C in the Pd–Rh binary, is steeply raised by U additions. The closed region of immiscibility within the fcc solid solution range was evaluated by use of binary interaction parameters in a ternary regular solution model. The isothermal spinodal curves at 1050°C and the critical temperature were calculated using different values of the interaction parameters (α_{M-M}). The results, taken from [1991Kle], are shown in Fig. 4. From these calculations relative partial molar Gibbs energies of U in Rh and Pd at infinite dilution were evaluated as –290 and –390 kJ·mol^{–1}, respectively.

The heat capacities of U(Rh_xPd_{1–x})₃ at $x = 0$ and $x = 0.15$ were measured by [1997Ari] over the 290–1500 K temperature range by direct heating pulse calorimetry and reported in small graphs in the original paper.

The heat capacity of UPd₃ measured by [1997Ari] was smaller than the literature data up to 900 K. The heat capacity of U(Rh_{0.15}Pd_{0.85})₃ was a little larger than that of UPd₃, with a similar temperature dependence. On the basis of the measured heat capacities and the literature data concerning enthalpy and entropy of formation of the binary UPd₃ phase, the Gibbs energy of the U(Rh_{0.15}Pd_{0.85})₃ solution was calculated by [1997Ari] as $\Delta_f G^\circ = -497.6 + 3.01 \cdot 10^{-3} \cdot T$ (with $\Delta_f G^\circ$ in kJ·mol⁻¹ and T in K).

Miscellaneous

Electronic structure of the U(Rh_xPd_{1-x})₃ phase has been studied by [1988Eri], while X-ray photoelectron spectroscopy studies on the same phase have been carried out by [1998Fuj].

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(γU) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352.4$	[Mas2]
(βU) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> βU	$a = 1075.9$ $c = 565.6$	[Mas2]
(αU) < 668	<i>oC4</i> <i>Cmcm</i> αU	$a = 285.37$ $b = 586.95$ $c = 495.48$	at 25°C [Mas2]
α, (Rh _x Pd _{1-x})	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu		0 < x < 1 dissolves up to 18 at.% U at 9.5 at.% Rh see Fig. 2 for the variation of the lattice parameters inside the solid solution
(Pd) < 1555		$a = 389.03$	at 25°C [Mas2]
(Rh) < 1963		$a = 380.32$	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ , (URh ₃ ,UPd ₄)	<i>cP4</i> <i>Pm$\bar{3}m$</i> AuCu ₃		$0 < x < 1$ see Fig. 2 for the variation of the lattice parameters inside the solid solution
URh ₃ < 1700		$a = 399.2$	[1991Kle]
UPd ₄ < 1585		$a = 407.4$ $a = 404.7$	defective structure at 1050°C and UPd _{3.6} at 1050°C and UPd _{4.3} [1991Kle]
U(Rh _x Pd _{1-x}) ₃	<i>hP16</i> <i>P6₃/mmc</i> TiNi ₃	$a = 578.8 \pm 0.3$ $c = 954.7 \pm 1.4$	$0 < x < 0.09$ at $x = 0.09$ (max Rh solubility, U rich side) [1991Kle]
UPd ₃ < 1640		$a = 577.5 \pm 0.1$ $c = 965.4 \pm 0.3$	at $x = 0$, U rich side [1991Kle]
		$a = 576.3 \pm 0.2$ $c = 954.1 \pm 0.9$	at $x = 0$, Pd rich side [1991Kle]
U ₅ Pd ₆ 1110 - 980	-	-	54.54 at.% Pd [1991Kle]
UPd 1047 - 970	-	-	50 at.% Pd [1991Kle]
U ₃ (Rh _{1-x} Pd _x) ₅ < 1550	-	-	$0 < x < 0.05$ [1991Kle]
U ₃ (Rh _{1-x} Pd _x) ₄ < 1450	-	-	$0 < x < 0.47$ [1991Kle]
β U ₄ Rh ₃ 1155 - 720	-	-	at 43 at.% Rh [Mas2]
α U ₄ Rh ₃ < 720	-	-	at 43 at.% Rh [Mas2]
* τ_1 , U(Rh _{1-x} Pd _x) ₂	<i>hP12</i> <i>P6₃/mmc</i> MgZn ₂	$a = 534.3 \pm 0.5$ $c = 869.4 \pm 2.7$	$0.04 < x < 0.25$ [1991Kle] at $x = 0.04$

Fig. 1: Pd-Rh-U.
The accepted Pd-U
phase diagram

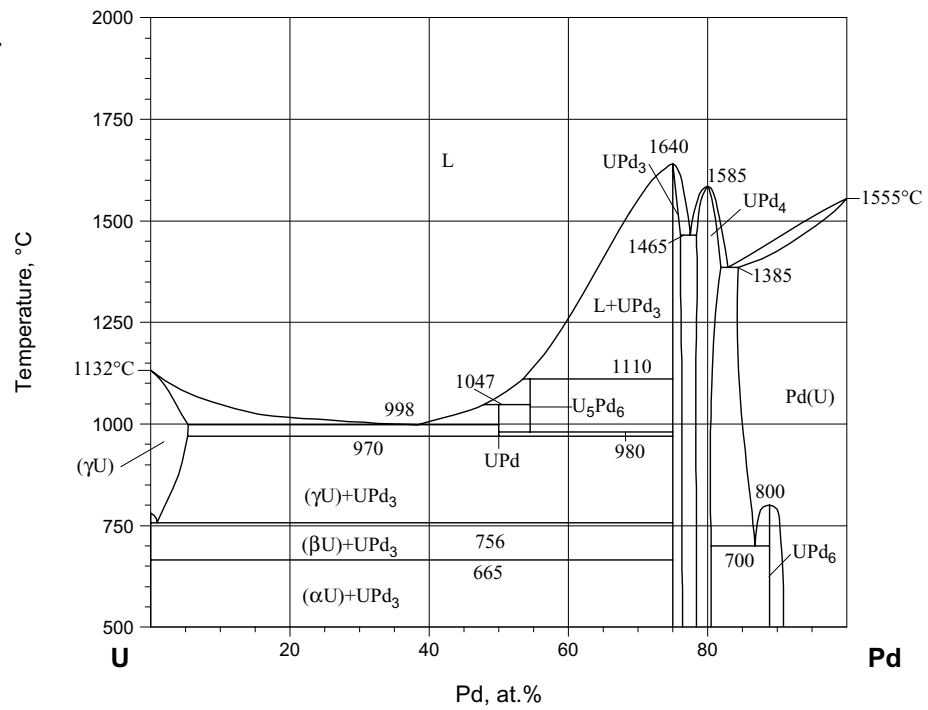


Fig. 2: Pd-Rh-U.
Isoparametric curves
showing the variation
of the lattice
parameter a in α and γ
solid solutions

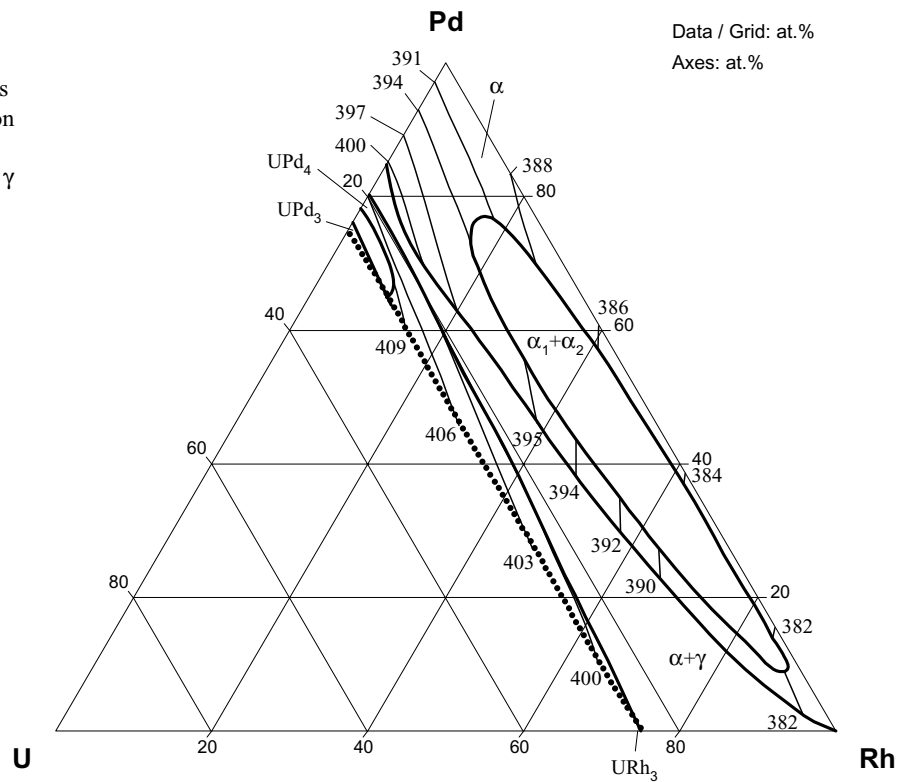


Fig. 3: Pd-Rh-U.
Isothermal section at
1050°C

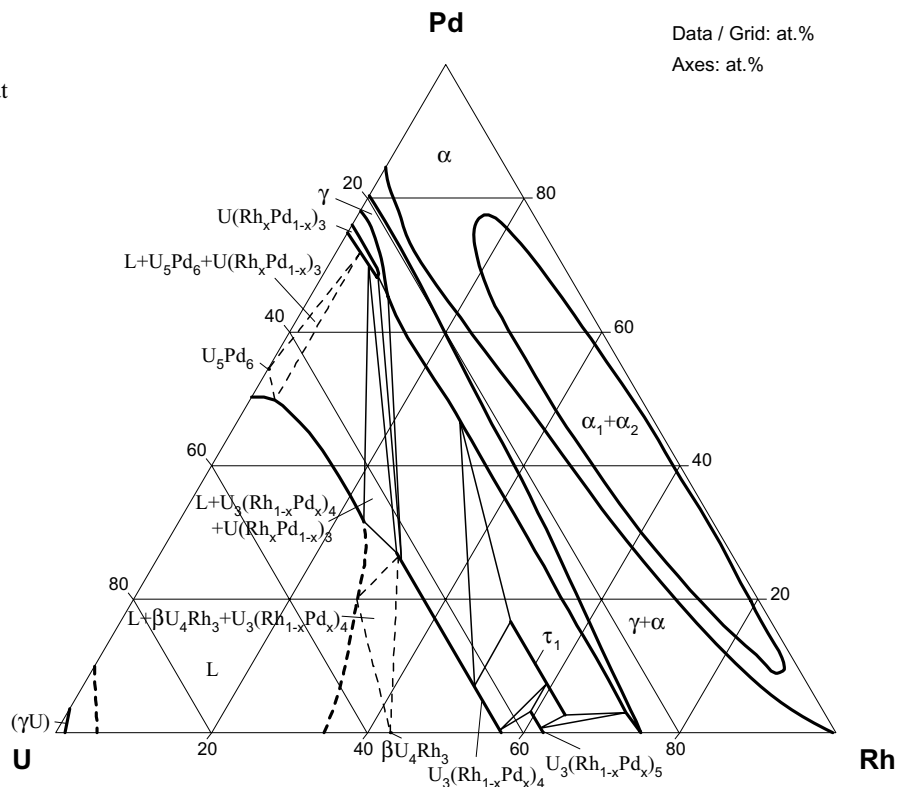
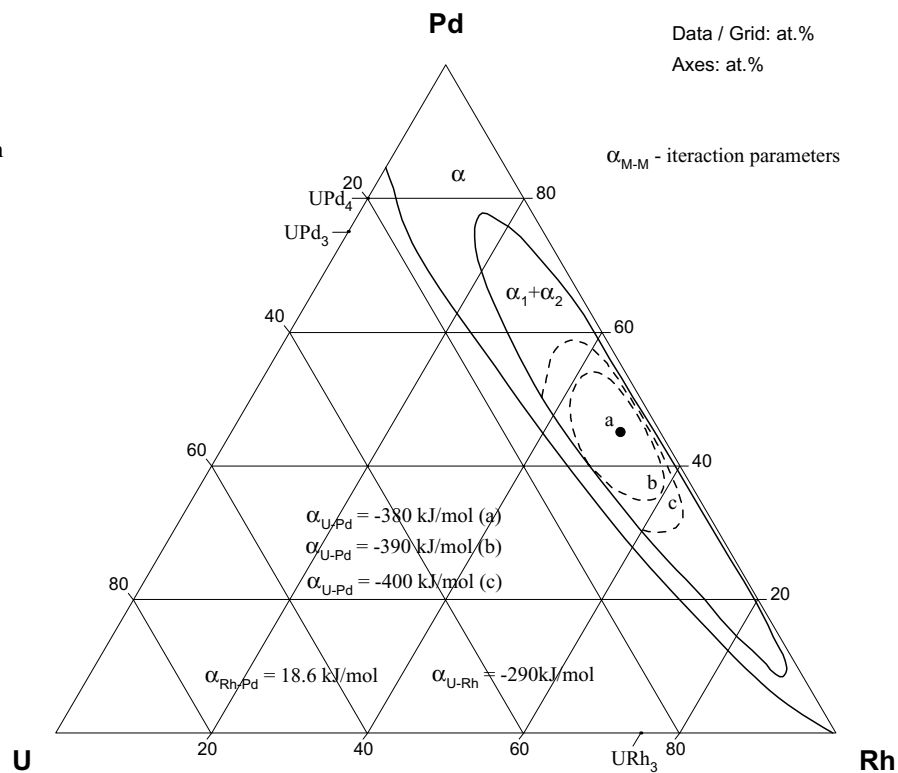


Fig. 4: Pd-Rh-U.
Calculated spinodal
curves in the fcc
immiscibility region
at 1050°C



Plutonium – Thorium – Uranium

Volodymyr Ivanchenko, Tatiana Pryadko

Introduction

Works on the Pu–Th–U system were initiated as a contribution to the development of plutonium-bearing fuels for fast power-breeder reactors. [1965Far] presented the 700 and 900°C sections of the ternary Pu–Th–U phase diagram that have been worked out by investigators at Argonne [1964Ric]. Phase boundaries between (α Th) and (β Th) were determined using mainly X-ray diffraction. [1968Blu] attempted to construct a series of isothermal sections as well as an isopleth at 10 at.% Pu. [1968Far, 1969Blu] reported about experiments with Pu–Th–U fuel alloys. Objectives of these experiments were to determine the restraint characteristics of the V-20 mass% Ti jacket, the relative swelling behavior of the fuels, and the maximum attainable burnup before jacket failure. Works on phase relations and structure are summarized in Table 1.

Binary Systems

The Th–U and Pu–Th phase diagrams are taken from [1985Pet2] and [1985Pet1], respectively. The thermodynamic optimization of the Pu–U phase diagram was carried out by [1991Lei] using a CALPHAD method. Since the results between data and calculation are satisfactory, the diagram proposed by [1991Lei] has been retained in this assessment. It is shown in the chapter “*Remarks on the Actinide Alloying Behavior*” in the present volume.

Solid Phases

No ternary phases are formed in the Pu–Th–U system. Crystal structures of unary and binary phases are presented in Table 2.

Invariant Equilibria

Some ternary reactions were found by [1968Blu] using complementary experimental investigations. In the solid state three four-phase reactions have been reported at 710, 614 and 595°C involving the (α Th) phase and the U rich Pu–U phases. More experimental investigations on the ternary reactions are needed since the high temperature phase (β Th) should be observed at the above temperatures. Consequently these reactions could not be accepted in the present evaluation. The absence of the crystalline phase (β Th) is certainly due to the shift of the nominal composition observed in the alloys after annealing at 900 and 700°C. This change of composition to higher Th content was detected in alloys containing more than 40 at.% Th.

Liquidus Surface

A liquidus surface was proposed by [1968Blu]. No ternary phase was detected. A ternary peritectic reaction was found involving the (α Th), (ϵ Pu) and Pu₇Th₃ phases at 630°C. This liquidus surface needs experimental amendments since normally the (β Th) should participate in these ternary reaction as indicated in the accepted binary Pu–Th.

Isothermal Sections

In the review of [1965Far], partial isothermal sections at 700 and 900°C were reported and taken from the experimental work of [1964Ric]. Later [1968Blu] investigated the ternary system and proposed isothermal sections. Discrepancies were observed along the binary edge Pu–Th since the (β Th) phase have not been detected by [1968Blu]. Disagreements have also been observed concerning the borders of the phase fields. Nevertheless, the schematic isothermal sections at 900 and 700°C were reproduced in Fig. 1 and Fig. 2, respectively, modified in agreement with the accepted binary systems. The Th rich region up to 50 at.% Pu was taken from [1964Ric] and reproduced as dashed lines. The borders of the phase fields inside the ternary

system have been indicated as tentative by dashed lines and some of them were taken from [1968Blu]. These tentative isothermal sections need further experimental investigations. As indicated by [1968Blu] the η phase certainly presents a small solubility range inside the ternary. Consequently the three-phase equilibria $(\alpha\text{Th})+(\beta\text{U})+\eta$ and $(\alpha\text{Th})+\eta+(\gamma\text{U})$ proposed by [1968Blu] should not exist. This has been replaced by a small three-phase field $(\beta\text{U})+\eta+(\gamma\text{U})$ and a large three-phase field $(\alpha\text{Th})+(\beta\text{U})+(\gamma\text{U})$, with a very narrow two-phase field $(\beta\text{U})+(\gamma\text{U})$ in between.

Temperature – Composition Sections

The isopleth for Pu–Th–U system at 10 at.% Pu has been constructed by [1968Blu] and is presented in Fig. 3. Some modifications have been done concerning the binary edges to be in agreement with the accepted binary systems Pu–Th and Pu–U. [1968Blu] suggested the existence of the Pu–U binary phases η and ζ along the isopleth. The presence of these phases is certainly due to the segregation in the alloys since the existence of these phases is not reported at 10 at.% Pu in the binary phase diagram up to 400°C. Consequently the phase equilibria involving the ζ and η phases are not included in the accepted isopleth. Some additional phase equilibria were added at the Pu–Th side.

Notes on Materials Properties and Applications

The ternary Pu–Th–U alloys with 10 and 20 mass% U, and 10 mass% Pu are potentially useful fast reactor fuels.

They have attained high burnups by using strong cladding to restrain swelling. The combination of the isotropic properties of fcc thorium and the high melting temperatures of Th base alloys looked attractive, as they should make possible metallic fuels that have excellent thermal properties. They are easily fabricated by rolling or injection casting, are compatible with liquid sodium, and are reprocessable by pyrometallurgical methods [1968Blu]. The alloys compared favorably with other metal fuels in thermal cycling experiments. Only minor density and length changes were observed after 100 cycles in NaK between 450 and 800°C. The alloys are compatible with vanadium-base cladding materials up to 650°C, but not with stainless steel.

Alloys of the following compositions 80%Th–10%U(93.18% enriched)–10%Pu (94.96% ^{239}Pu , 4.56% ^{240}Pu , 0.48% ^{241}Pu) and 70%Th–10.66%U(93.18% enriched)–9.34% U(normal)–10% Pu (94.96% ^{239}Pu , 4.56% ^{240}Pu , 0.48% ^{241}Pu) have been studied by [1968Blu]. Alloys were annealed at 850°C for 24 h, water quenched, reheated to 700°C for 1 h, furnace cooled. The intermediate inspection by neutron radiography after 2 at.% burnup showed that the alloys had an average elongation of 8%. The inspection after 5.6 at.% burnup showed that no additional elongation had taken place between 2 and 5.6% burnup. The total increase in volume at the end of the irradiation experiments was an average of 40%. Fuel swelling, measured after irradiation, was about 7.2% per atomic percent burnup. Fission-gas releases into the plenum were 72%.

Metallographic examination of the specimens before and after irradiation showed no significant change in microstructure. Lack of visible void formation in the ternary alloys suggested that interconnected microporosity, not readily resolved by optical microscopy, accounted for the high fission-gas release, in agreement with the behavior of other metal fuels.

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Table 1: Investigations of the Pu-Th-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1964Ric]	X-ray diffraction, metallography, microprobe analysis	700°C Th-up to 20 at.% U-up to 50 at.% Pu (α Th), (α Th)+(β Th), (β Th) (α Th)+(β U), (α Th)+(β U)+(γ U) (α Th)+(γ U), (α Th)+(γ U)+L (α Th)+L, (α Th)+(β Th)+L, (β Th)+L 900°C Th-up to 20 at.% U-up to 40 at.% Pu (α Th), (α Th)+(β Th), (β Th) (α Th)+(γ U), (α Th)+(γ U)+L (α Th)+L, (α Th)+(β Th)+L, (β Th)+L
[1968Blu]	Room-temperature X-ray diffraction, metallography, high-temperature X-ray diffraction, electrical resistance, dilatometry, DTA	Th-20U-60Pu 700°C, 900°C

Table 2: Crystallographic Data of Solid Phase

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(εPu, γU)	<i>cI2</i> <i>Im$\bar{3}m$</i> W		continuous solid solution which exists between 1135 and 454°C [1991Lei]
(εPu) 640 - 483		$a = 363.8$	pure, 500°C, [1989Pet] dissolves 5.6 at.% Th at 605 ± 10°C [1985Pet1]
(γU) 1135 - 776		$a = 352.4$	pure, 805°C, [Mas2] dissolves 1.5 at.% Th at 1100°C [1985Pet2]
(δ'Pu) 483 - 463	<i>tI2</i> <i>I4/mmm</i> In	$a = 333.9$ $c = 444.6$	pure, 477°C, [1989Pet] dissolves about 1.3 at.% U at 440°C [1991Lei]; dissolves about 1.4 at.% Th at 490°C [1985Pet1]; exists down to 437°C along the Pu-U binary [1991Lei] and down to 490°C along the Pu-Th binary [1985Pet1]
(δPu) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 463.70$	pure, 320°C, [1989Pet] dissolves about 1.6 at.% U at 318°C [1991Lei] and 2.6 at.% Th at 500°C [1985Pet1] exists up to 500°C along the Pu-Th binary [1985Pet1]
(γPu) 320 - 215	<i>oF8</i> <i>Fddd</i> γPu	$a = 315.87$ $b = 576.82$ $c = 1016.2$	pure, 235°C, [1989Pet] dissolves about 1.6 at.% U at 278°C [1991Lei]; dissolves 1.2 at.% Th at 315°C [1985Pet1]
(βPu) 215 - 125	<i>mC34</i> <i>C2/m</i> βPu	$a = 928.4$ $b = 1046.3$ $c = 785.9$ $\beta = 92.13^\circ\text{C}$	pure, 190°C, [1989Pet] dissolves about 2.7 at.% U at 278°C [1991Lei] the solubility of Th is nearly absent [1985Pet1]
(αPu) < 125	<i>mP16</i> <i>P2₁/m</i> αPu	$a = 618.3$ $b = 482.2$ $c = 1096.3$ $\beta = 101.79^\circ\text{C}$	pure, 21°C, [1989Pet], the solubilities of U and Th are nearly absent [1991Lei, 1985Pet1]
(βTh) 1755 - 1360	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 411$	pure, 1450°C [1985Pet1] dissolves 50 at.% Pu at 615°C [1985Pet1] and 12.2 at.% U at 1375°C [1985Pet2] exists up to 582°C along the Pu-Th binary [1985Pet1] and up to 1270°C along the Th-U binary [1985Pet2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α Th) < 1360	$cF4$ $Fm\bar{3}m$ Cu	$a = 508.45$	pure, 25°C [1985Pet1] dissolves 48 at.% Pu at 582°C [1985Pet1] and 6.8 at.% U at 1270°C [1985Pet2]
(β U) 776 - 668	$tP30$ PA_2/mnm β U	$a = 1075.9$ $c = 565.6$	pure, 720°C, [1989Pet] dissolves about 24 at.% Pu at 702°C [1991Lei] the solubility of Th is very small [1985Pet2] exists down to 557°C along the Pu-U binary [1991Lei]
(α U) < 668	$oC4$ $Cmcm$ α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	pure, at 25°C [1989Pet] dissolves about 11 at.% Pu at 557°C [1991Lei] the solubility of Th is very small [1985Pet2]
Pu ₇ Th ₃ < 615	o^*	$a = 622$ $b = 1162$ $c = 709$	30 at.% Th [1985Pet1]
η , PuU 702 - 278	$tP52$	$a = 1057$ $c = 1076$	~4 to ~78 at.% U at 25 at.% U [1969Lea]
ζ , PuU ≤ 628	$cP58$	$a = 1069.2$ $a = 1065.1$ $a = 1066.4$	~26.4 to ~77 at.% U at 25°C, 35 at.% U [1969Lea] at 25°C, 70 at.% U [1969Lea] at 25°C, 50 at.% U [V-C2]

Table 3: Investigations of the Pu-Th-U Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1969Blu]	Optical microscopy, measurements of density, neutron radiography	Swelling after irradiation

Fig. 1: Pu-Th-U.
Isothermal section at
900°C

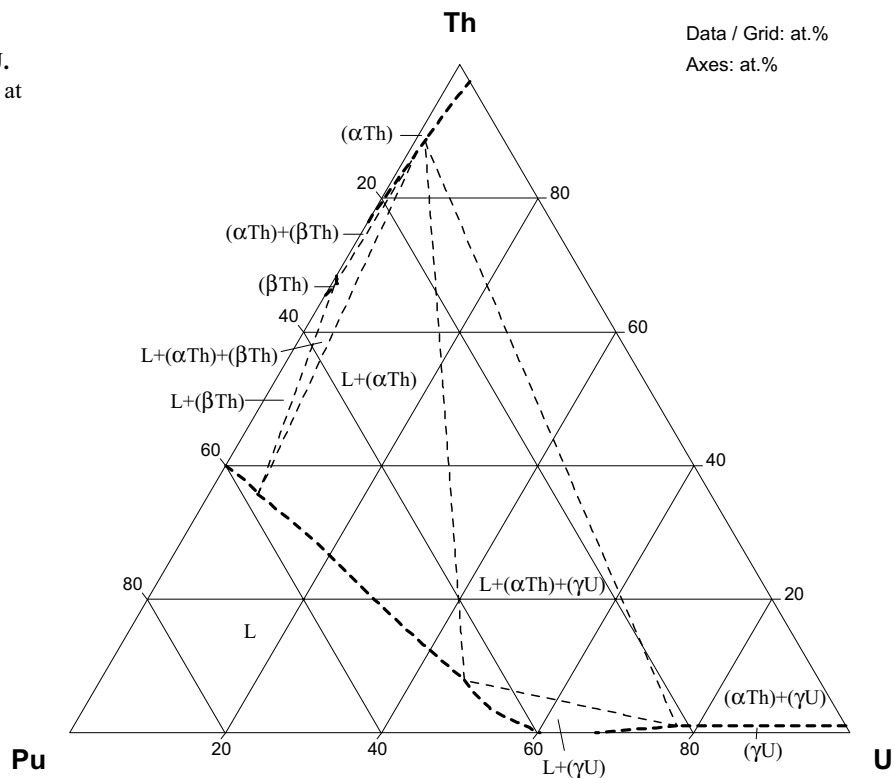


Fig. 2: Pu-Th-U.
Isothermal section at
700°C

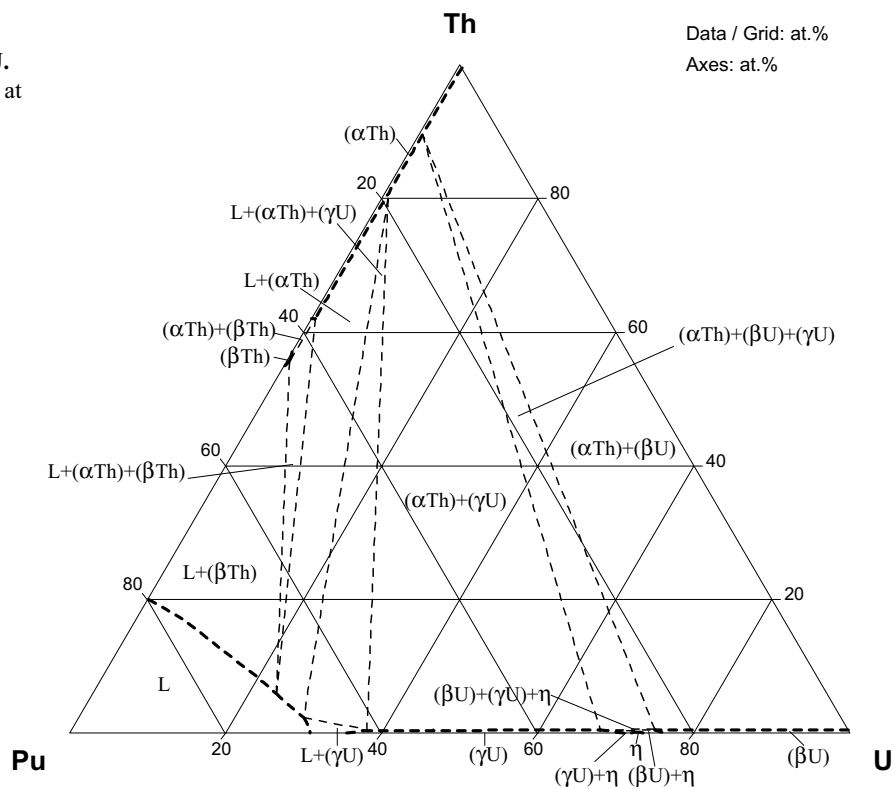
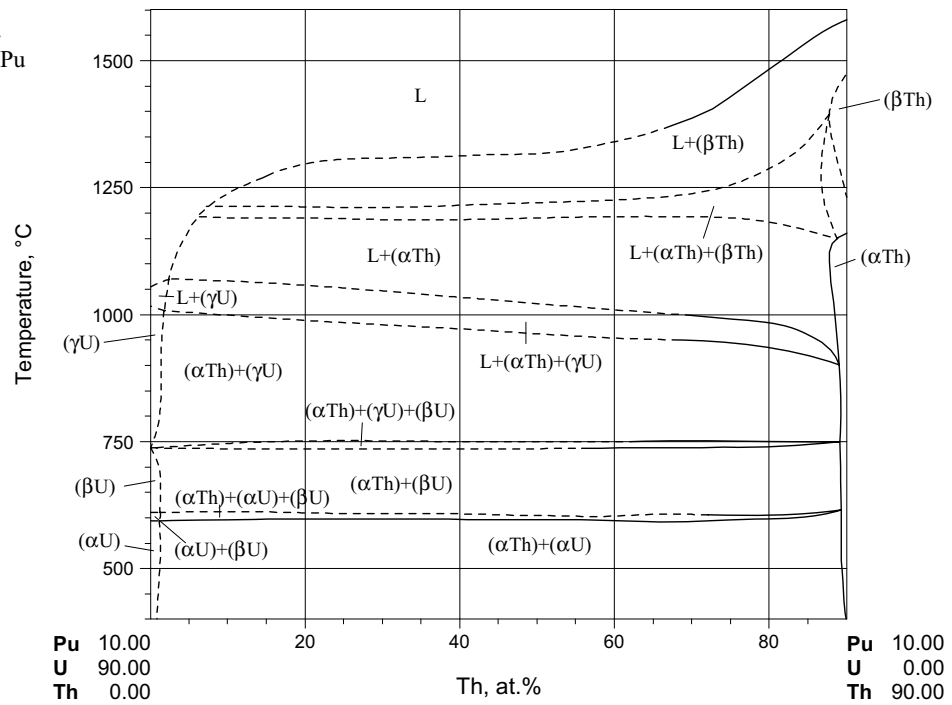


Fig. 3: Pu-Th-U.
Isopleth at 10 at.% Pu



Plutonium – Uranium – Zirconium

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Introduction

Pu-U-Zr system offers potential fuel materials for liquid-metal fast breeder reactor. Their compatibility with Type-304 stainless steel at temperatures up to 800°C makes them particularly valuable for this purpose. The applicability of particular Pu-U-Zr alloy compositions as fuel materials depends partially on properties related to the phase equilibria in the system. Furthermore, the temperatures of liquidus and solidus are important in assessing the possibility of fuel melting under abnormal reactor conditions. [1966Far1] reported results, obtained in Argonne National Laboratory on the study of phase relations in the U-12.9Pu-22.5Zr (at.%) alloy in temperature interval from 25°C to melting point. [1968Tuc] presented the (γ U, ϵ Pu, β Zr) solid solution surface. [1968Far1] and [1968Far4] reported results of phase equilibrium studies conducted at Mound Laboratory. The liquidus and solidus surfaces of the ternary system are known at high Pu concentrations showing that additions of Zr markedly increase the solidus and liquidus temperatures. Extensive studies were made by [1970Obo] presenting isothermal sections at 700, 670, 660, 650, 640, 595, 580, 550, and 500°C. [1988Lei] attempted to construct solidus and liquidus surfaces employing a state of the art approach that couples thermodynamic calculation with experimental determination of solidus and liquidus temperatures, in this case for three selected alloys. For the alloy compositions close to binary edges of the ternary diagram the calculated results agreed reasonably well with measured values. Using the experimental results of [1970Obo], [1999Kur] performed another thermodynamic assessment of the Pu-U-Zr system with reasonable agreement between calculated and experimental data. The publication of [2005Nak] shows that the Pu-U-Zr calculations by [1999Kur] can be applied to analyze the multicomponent interdiffusion zones of the metal fuel and the iron-based cladding. [1965Far] reported the thermal expansion coefficient measured on U-14Pu-30Zr (at.%) alloys. Thermodynamic properties of U-12.2Pu-21.8Zr (at.%) alloy were presented by [1967Far2]. The information available on phase relations, structure and thermodynamic studies is summarized in Table 1.

Binary Systems

There are more than one version for the Pu-U and Pu-Zr phase diagrams. The first assessment of the Pu-U system based on experiments was presented by [1989Pet] and redrawn by [Mas2]. Later, [1991Lei] performed a thermodynamic assessments of this system. The main discrepancies between the calculated and the experimentally constructed phase diagram consists in the appearance of a maximum on the $\eta/(\eta+\zeta)$ phase border, that was in a serious contradiction with experimental results of thermal analysis presented by [1989Pet], which show the absence of a maximum. Some later [1999Kur] repeated the thermodynamic assessment of the Pu-U system and found a maximum too, at lower temperatures. But new problems arose from inconsistencies between the experimentally constructed and calculated slopes of the phase boundaries (α U) / (α U)+ ζ / ζ . For these reasons here the Pu-U system is accepted as constructed by [1989Pet]. The Pu-Zr phase diagram was accepted in accordance with [1993Oka], who took into account results of [1967Lau] and [1992Suz] stabilizing the κ -phase by oxygen. The U-Zr phase diagram is accepted as reported in [Mas2].

Solid Phases

No ternary phases are formed in the Pu-U-Zr system. The crystal structures of unary and binary phases are presented in Table 2. Since all the phases in the ternary system are common to one of the limiting binary systems, the same nomenclature has been used to identify both the binary and ternary system phases in accordance with [1970Obo]. Phase designations used in the present evaluation are as follows: γ is the α body-centred-cubic allotropic modification of U that has complete solid solubility with bcc (ϵ Pu) and bcc

(β Zr). γ_1 is the U rich, γ_2 the Zr rich modification of γ participating in the monotectoid reaction in the U-Zr system. (α U) and (β U) are orthorhombic and tetragonal allotropic modifications of U that dissolve up to 15 and 20 at.% Pu, respectively, but have limited solid solubility of Zr. η is a high-temperature intermediate Pu-U phase that is believed to be tetragonal and has limited solubility for Zr. ζ is a complex cubic U-Pu intermediate phase that dissolves up to 5 at.% Zr. δ stands for a hexagonal intermediate phase in the U-Zr binary system that occurs approximately at the composition UZr_2 and has extensive solubility for Pu. (δ Pu) is the fcc allotropic modification of Pu that has extensive solid solubility for Zr but very limited solubility for U.

Invariant Equilibria

The scheme of solid-state reactions is given in Fig. 1, based on [1970Obo] but modified in the peritectoid reaction $(\alpha\text{U}) + (\gamma\text{U,Zr}) \rightleftharpoons (\delta\text{U,Zr})$ according to the accepted U-Zr binary system.

Liquidus, Solidus and Solvus Surfaces

Liquidus and solidus temperatures in the Pu corner are presented in Fig. 2 based on work by [1968Far1] and [1968Far4] that was conducted at Mound Laboratory and again slightly corrected in accordance with the accepted Pu-Zr binary phase diagram. In the part of reaction scheme including δ , γ , (α Zr) and ζ phases the (ϵ Pu, γ U, β Zr) solid solution surface presented by [1968Tuc] was neglected as it is inconsistent with the results of [1970Obo].

Isothermal Sections

Isothermal sections at 700, 670, 660, 650, 640, 595, 580, 550 and 500°C experimentally constructed by [1970Obo] are given in Figs. 3 to 11. These section were corrected according to the accepted binary systems. Isothermal sections at 670 (Fig. 4), 650 (Fig. 6), 595, 580 and 550°C (Figs. 8 to 10) correspond to the temperatures of the nonvariant reactions P, U_1 , U_2 , U_3 and U_4 . The related four-phase planes are included in the figures.

Thermodynamics

The limited number of experimental data on thermodynamic properties is listed in Table 3 and Table 4.

Notes on Materials Properties and Applications

Thermal expansion coefficient α of the U-12.9Pu-30Zr (at.%) alloy is $18.2 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ in the temperature interval 25 to 596°C. During the phase transformation, in the interval of 596 to 665°C $\Delta l = 0.58\%$ and after the transformation is completed, in the temperature interval of 665 to 950°C, $\alpha = 22.3 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ [1965Far]. [1966Far1] reported data on thermal conductivity measured on U-15Pu-1Zr (at.%) alloys at 100 to 900°C. Thermal conductivity of the alloy U-15Pu-15Zr (at.%) is $K = 0.111 \text{ watt}\cdot(\text{cm})(^\circ\text{C})^{-1}$ at 100°C and rises to $0.301 \text{ watt}\cdot(\text{cm})(^\circ\text{C})^{-1}$ at 900°C. For U-15Pu-25Zr (at.%) K equals $0.0021 \text{ watt}\cdot(\text{cm})(^\circ\text{C})^{-1}$ at 100°C and $0.260 \text{ watt}\cdot(\text{cm})(^\circ\text{C})^{-1}$ at 900°C. Mechanical properties of some Pu-U-Zr alloys [1968Far1] are presented in Tables 6 to 8.

[1967Bec] studied the performance of advanced Pu-U-Zr alloy fuel element under fast reactor conditions. Information about investigations of the Pu-U-Zr materials properties is summarized in Table 5.

Miscellaneous

Various ceramics have been evaluated to find a suitable container material for melting and casting U-Zr and Pu-U-Zr alloys, and most of them proved to be totally inadequate. To date the U - 10Zr (mass%) alloy melted in Gd_2O_3 crucibles has come out with the smallest pickup of oxygen. [1969Far], basing on the results obtained at Los Alamos Scientific Laboratory, reported, that the most promising crucible coating appears to be colloidal suspension of Y_2O_3 spread onto the crucible surface. Very good results were obtained, when water-cooled metallic crucible were used. In this case a frozen alloy skin next to the crucible prevents

impurity pickup from the crucible. The technological route used in Argonne National laboratory included the production of U base and Pu base master alloys alloyed with Zr, using thoria, zirconia or magnesia crucibles coated with yttria. Alloy chunks were melted in yttria-coated graphite crucible using induction furnace. Pins were produced by injection casting into large-L/D-ratio Vycor mold [1978Hin].

The ultimate criteria for fuel pin design is the overall integrity up to the planned life time or target burnup of irradiation. Here, burnup is defined by the fraction of total heavy metal constituents (U+Pu), which have undergone fission and, hence, transferred thermal power to the sodium reactor coolant medium flowing around the pins. Achievement of burnup near 15 at.% is desirable for large scale commercialization of liquid-metal reactors (LMR). The fuel itself is a solid cylinder which has been injection-casted into quartz molds and loaded into the cladding jacket with no prior thermomechanical treatment required. The as cast density of these alloys is $\sim 15.8 \text{ g}\cdot\text{cm}^{-3}$. Sodium fills annulus around the slug and provides the high conductivity heat path to the cladding prior to fuel slug swelling. The plenum space (initially filled with inert gas) above the fuel slug is provided to contain the large volume of stable fission gas (Xe/Kr) which is produced in these fuel slugs at a rate of $\sim 16 \text{ cm}^3$ per percent burnup. The ends of the jacket are hermetically sealed with an automatic tungsten inert gas welder and a helical wire is welded in place to maintain pin spacing and mix coolant flow upward through the close-packed hexagonal pin bundle during irradiation [1990Pah]. Prior to making contact with the cladding tube, metallic alloy fuel swells rapidly due to its high fission-enhanced creep rate and irradiation growth. It has been determined that fission rate, temperature, and plutonium concentration influence the observed macroscopic swelling rate [1990Ger].

The key phenomena which are significant in controlling the fuel pin behavior and reliability are summarized in Table 9.

These swelling phenomena have been subject of many investigations.

It was shown, that U-14.4Pu-29.3Zr (at.%) alloy jacketed in a V - 20Ti (mass%) alloy and irradiated to burnups of 12.5% at 665°C elongated 3% at 4.2% burnup. No further change in length was observed throughout the remaining irradiation. The fission-gas pores were interconnected and the fuel cracked radially [1967Far1]. Density measurements of annual sections of fuels after burnups of 4.6 at.% show that the least-dense fuel is consistently found in the middle zone and the most-dense fuel is in the center zone [1968Far3]. Analyses of irradiated U-15Pu-10Zr (mass%) (U-12.2Pu-21.8Zr (at.%)) showed that considerable amounts of Zr and Tc migrated from the middle of the three annular zones noted in these fuel elements. There was also evidence of some depletion of fission products in the middle zone, and changes in the original alloy composition [1968Far2, 1969Rhu]. The fuel restructuring has been traced carefully as a function of fuel burnup by [1990Por]. The results indicated that the porosity distributions would lead to significant changes in the fuel operating temperature. Concurrent observations concerning composition redistribution indicated that a significant redistribution of constituents proceeded the developing of porosity. [1969Smi] shortly considered the problems concerned with fission products release from Pu-U-Zr ternary alloy fuel element.

Constituent redistribution in a metallic alloy fuel can occur by solid state diffusion under gradients of temperature and concentration. The redistribution is also influenced significantly by irradiation and phase transformation. As a result, an originally uniformly mixed alloy can change to an inhomogeneous alloy. Inhomogeneity in a metallic nuclear fuel alloy can cause phase transformations, solidus temperature change, and local change in the density of fissionable atoms, which can alter the physical and mechanical properties of the alloy fuel affecting its behavior and performance. As it was shown by [2000Soh], the flux contributions by the gradients of U and Zr are similar in magnitude but have opposite signs. The U migration to the colder regions of the sample is driven by both gradients of temperature and Zr concentration. Similarly, the Zr migration to the hot end of the sample is driven by both gradients of temperature and U concentration. Pu-U-Zr metallic alloy fuel irradiated to the end-of-life burnup of 1.9 at.% exhibits three distinct phase regions. For a fuel composition of U-15.5Pu-21.9Zr (at.%), the center region was composed of γ (above 650°C), the intermediate region of $\gamma+\zeta$ (600-650°C), and the outer region of $\delta+\zeta$ (500-600°C) phases [2004Kim]. Thermally activated constituent migration took place in the initially homogeneous fuel, and then, as the concentration gradient builds up, migration due to concentration gradients is followed.

Fuel/cladding chemical interaction involves the interdiffusion of fuel and cladding constituents at operating temperatures. Isothermal experiments at 650°C of U-21Pu-23Zr/HT9 and U-21Pu-23Zr/D9 (at.%) diffusion

couples were performed by [1996Kei] to assess the role of Ni on interdiffusion behavior. It was shown, that the number of observed phases and the diffusion zone size is higher for couples with negligible Ni (U-21Pu-23Zr/HT9) than for the couples with 16 mass% Ni (U-21Pu-23Zr/D9 (at.%)).

The interdiffusion is characterized by diffusion of Fe and Ni, when available as cladding constituents into the fuel, with corresponding diffusion of lanthanide fission products (La, Ce, Nd, Sm, Pr) into cladding [1990Pah]. At minor degrees of interaction, metallography examination often does not reveal the area of interaction in the fuel. The interaction in the cladding, however follows a very defined interaction front, leaving a layer of cladding which contains nearly 20 mass% of the lanthanides [1990Pah]. Rare earth with the Fe and Ni constituents of stainless steel interact to form compounds that melt below 1000 K. U preferentially interacts with Fe, whereas the rare earth interact with Ni. In the absence of U, Fe interact with the rare earths and in this case the formed Fe and Ni interaction compounds melt at a temperature around 890 K [1994Sar].

To decrease the fuel/cladding interaction a Zr coating may be used. Zr-sheet fuel elements irradiated to 2 at.% burnup exhibit significantly less axial growth than standard-cast fuel elements (1.3 to 1.8 versus 4.9 to 8.1%). A 0.2 mm thick Zr sheet around U-20.5Pu-3Zr (mass%) fuel alloy does not provide a reliable barrier against fuel/cladding chemical interaction under irradiation [1993Cra].

[1966Huf] showed, that anion exchange-partition chromatography can be applied to trace the impurity in ternary Pu-U-Zr alloys.

The results of the postirradiation examination of U-14.4Pu-29.3Zr (at.%) alloy performed in Argonne National Laboratory were presented by [1967Far1, 1968Far2, 1968Far3, 1968Far4]. Emphasis at Argonne was centred upon the U-15Pu-10Zr (mass%) (U-12.2Pu-21.8Zr (at.%)) and U-15Pu-15Zr (mass%) (U-11.5Pu-30.7Zr (at.%)) alloys. They were tested as the most promising alloys for fast breeder application [1969Fac]. Results of development of alloying and casting techniques, fabrication of test fuel elements, fuel element performance during irradiation and solid state reactions are shortly reported by [1968Far4, 1969Far, 1977Lam, 1978Hin]. Microstructural changing in fuel, redistribution of components and nucleation and growth of the Xe/Kr fission gas bulbs were analyzed by [1988Lah, 1988Hof, 1988Pah]. An analysis of fission gas release and induced swelling in steady state irradiated Pu-U-Zr metal fuels was performed by [1989Ste] using computer modelling. Irradiation and fission related phenomena in metallic Pu-U-Zr fuels resulted in fuel swelling and in redistribution of the constituents, as studied by [1990Por]. The results of experimental studies of Pu-U-Zr fast reactor fuel pins irradiated to >15 at.% burnup, including fission gas retention & release as well as fuel/cladding chemical interaction have been reported by [1990Pah]. A model for the constituents' migration behavior in Pu-U-Zr metallic fast reactor fuel has been proposed by [1993Ish]. The model can predict the experimentally observed radial three-zone structure and the zirconium and uranium redistribution, however the predicted radial location of zirconium-depleted middle zone disagreed with the experimental result. The swelling mechanisms in the (α U) phase has been modelled by [1993Res]. The results of this study demonstrate that the relatively long incubation times characteristic for the Integral Fast Reactor swelling and the gas release can be understood in terms of a reduced gas-bubble nucleation rate at the α/δ phase boundaries. [1993Cra] reported the behavior of Pu-U-Zr fuel cast in zirconium moulds with relation to chemical interaction of fuel and cladding. Redistribution behavior of lanthanide fission products as well as their chemical interaction with cladding have been reported by [1990Pah, 1994Kur, 1994Sar]. [1996Kei] reported results from diffusion couples annealed at 650°C for 100 h between a Pu-U-Zr alloy and stainless steel, with and without Ni. Isothermal diffusion couple experiments were performed by [1997Pet] at 750°C and [1998Ale] at 800°C to investigate diffusion phenomena in body-centred cubic Pu-U-Zr alloys. Microstructural development and constituent redistribution were investigated by [2000Soh] in rods of a 62U-15.5Pu-21.9Zr (at.%) annealed at a temperature gradient of 220°C·cm⁻¹. Appreciable diffusional interaction were identified between Zr and U. An enrichment of Zr with concurrent depletion of U was observed on the hot-end side (~ 740°C). These results were confirmed by [2004Kim], who measured the postirradiation redistribution profiles of the fuel components. The interdiffusion fluxes of Zr, U and Pu in Pu-U-Zr fuel were calculated.

The metallic fuel anode in the molten salt electro-refining during pyrometallurgical reprocessing was modelled by [2005Iiz] based on the findings from the anodic dissolution tests of Pu-U-Zr ternary alloys.

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Table 1: Investigations of the Pu-U-Zr Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1966Far1]	not reported	25 - 1150°C, U-29Pu-22.5Zr (at.%) 654 - 1150°C, (γ U); 596-654°C, (α U)+(γ U); 25-596°C, (α U)+(U,Zr)
[1966Far2]	Dilatometry and DTA	670 - 25°C, U-12.9Pu-22.6Zr (at.%), (α U), (γ Pu,U,Zr), (U,Zr)
[1967Far2]	Calorimetry	25 - 1150, U-12.2Pu-21.8Zr (at.%) (α U) + (U,Zr); (α U) + (γ U)
[1968Tuc]	DTA, optical metallography	Pu-U-Zr, < 865°C, solid solution surface
[1968Far1] [1968Far4]	DTA, optical metallography	< 1000°C, from 100 to 65 at.% Pu, solidus and liquidus surfaces
[1988Lei]	EPMA, optical metallography, DTA, thermodynamic calculations	Solidus and liquidus surfaces
[1990Ger]	not reported	Isothermal sections at 700, 670, and 500°C
[1970Obo]	EMPA, X-ray diffraction, optical metallography	Isothermal sections at 700, 670, 660, 650, 640, 595, 580, 550, and 500°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ (ϵ Pu, γ U, β Zr) 1855 - 455	<i>cI2</i> <i>Im$\bar{3}m$</i> W		100%Pu - 100% U - 100% Zr
(ϵ Pu) 640 - 463		$a = 363.8$	pure, 500°C, [1989Pet] dissolves 100 at.% U [1989Pet] and 100 at.% Zr in Pu-U system
640 - 455			
(γ U) 1135 - 776		$a = 352.4$	pure, 805°C, [Mas2] dissolves 100 at.% Pu [1989Pet] and 100 at.% Zr in U-Zr system
1135-693			
(β Zr) 1855 - 863		$a = 360.90$	pure, at 863°C [Mas2]
1855 - 606			in U-Zr system
(δ' Pu) 483 - 463	<i>tI2</i> <i>I4/mmm</i> In	$a = 333.9$ $c = 444.6$	pure, 477°C, [1989Pet] dissolves 1.3 at.% U at 455°C [1989Pet] and 2 at.% Zr at 463°C [Mas2] in Pu-U system
483 - 442			
(δ Pu) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 463.7$	pure, 320°C, [1989Pet] dissolves 0.3 at.% U at 442°C [1989Pet] and 70 at.% Zr at 640-267°C [Mas2] in Pu-Zr system
463 - 280			
(γ Pu) 320 - 215	<i>oF8</i> <i>Fddd</i> γ Pu	$a = 315.87$ $b = 576.82$ $c = 1016.2$	pure, 235°C, [1989Pet] dissolves 0.8 at.% U at 280°C [1989Pet] and 3 at.% Zr at 320-218°C [Mas2]
(β Pu) 215 - 125	<i>mC34</i> <i>C2/m</i> β Pu	$a = 928.4$ $b = 1046.3$ $c = 785.9$ $\beta = 92.13^\circ\text{C}$	pure, 190°C, [1989Pet] dissolves 2.0 at.% U at 280°C [1989Pet] and ~5 at.% Zr at ~260°C [Mas2]
~270 - ~115			in Pu-Zr system
(α Pu) < 125	<i>mP16</i> <i>P2₁/m</i> α Pu	$a = 618.3$ $b = 482.2$ $c = 1096.3$ $\beta = 101.79^\circ\text{C}$	pure, 25°C, [1989Pet], the solubilities of U is negligible, dissolves 1.5 at.% Zr at 125°C [Mas2]
(β U) 776 - 560	<i>tP30</i> <i>P4₂/mnm</i> β U	$a = 1075.9$ $c = 565.6$	pure, 720°C, [Mas2] dissolves ~18 at.% Pu at 705°C [1989Pet] and ~2 at.% Zr at 693°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	pure, at 25°C [Mas2] dissolves 15 at.% Pu at 560°C [1989Pet], and 0.5 at.% Zr at 668°C [Mas2]
(α Zr) < 863	<i>hP2</i> <i>P6₃/mmm</i> Mg	$a = 323.16$ $c = 514.75$	pure, at 25°C [Mas2] dissolves 13 at.% Pu at 863°C [Mas2] and 0.4 at.% U at 863°C [Mas2]
(ω Zr)(hp) 25	<i>hP2</i> <i>P6₃/mmm</i> ω Ti	$a = 503.6$ $c = 310.9$	at 25°C [Mas2] metastable
η , (Pu-U) 705 - 278	<i>tP52</i>	$a = 1057$ $c = 1076$	4 -70 at.% U 25 at.% U at 500°C [1989Pet]
ζ , (Pu-U) < 590	<i>t**</i>	$a = 1069.2$ $c/a \cong 1$ $a = 1066.4$ $c/a \cong 1$ $a = 1065.1$ $c/a \cong 1$	25-74 at.% U, dissolves 5 at.% Zr at 25°C, 35 at.% U [1989Pet] at 25°C, 50 at.% U [1989Pet] at 25°C, 70 at.% U [1989Pet]
υ , Pu ₄ Zr < 345	<i>tP80</i> <i>P4/ncc</i>	$a = 1089$ $c = 1489$	[VC2]
κ , PuZr ₃ < 380	<i>hP3</i> <i>P6₃/mmm</i> AlB ₂	$a = 506.0$ $c = 311.9$	oxygen-stabilized [1967Lau, 1992Zuz]
δ , UZr ₂ < 617	<i>hP3</i> <i>P6₃/mmm</i> AlB ₂	$a = 503$ $c = 308.0$	[1989She] at UZr ₂ composition

Table 3: Thermodynamic Data of Reaction or Transformation

Reaction or Transformation	Temperature [°C]	Quantity, per mol of atoms [kJ, mol, K]	Comments
(α U) + (δ U,Zr) $\rightleftharpoons$ (α U) + (γ U)	600 - 650	$\Delta H = 8.32 \text{ kJ}\cdot\text{mol}^{-1}$	Phase transformation, [1967Far2]

Table 4: Thermodynamic Properties of Alloys

Phase	Temperature Range [°C]	Property, per mole of atoms [J, mol, K]	Comments
65.96U-12.23Pu-21.81Zr (at.%)	25 - 600	$\Delta H(T) = -6833.1 + 18.76T + 0.0129 T^2$ $C_p(T) = 18.76 + 0.0258 T$	Two phase alloy: (α U) + (U,Zr), [1967Far2]
65.96U-12.23Pu-21.81Zr (at.%)	650 - 1150	$\Delta H(T) = 8560.1 + 14.15T + 0.01265 T^2$ $C_p(T) = 8.55 + 0.0253 T$	Two phase alloy: (α U) + (γ U), [1967Far2]

Table 5: Investigations of the Pu-U-Zr Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1965Far]	Dilatometry	Temperature expansion coefficient at temperatures from 25 to 950°C
[1966Far1]	Thermoconductivity	Thermoconductivity coefficient at temperatures from 100 to 900°C
[1966Far2]	Mechanical properties, compressive and tensile tests at room and high temperatures, creep	Ultimate compressive strength, Yield tensile strength, Ultimate tensile strength, Young's modulus, Time, min, to attain 2% strain
[1967Far1]	Neutron radiography, optical metallography	Elongation and porosity after irradiation
[1967Far2]	Calorimetry	Heat content, specific heat, solid state heat of transformation
[1969Rhu]	Microprobe scan, optical metallography	Redistribution of elements in cross section of fuel-pin under irradiation
[1990Por]	Optical metallography, neutron radiography, isotopic dilution mass spectrometry, spectrophotometric analysis	Fuel constituent redistribution, fuel swelling
[1990Pah]	Optical metallography, EMPA, neutron radiography, immersion density	Fuel constituent redistribution, fuel swelling, fission gas retention and release, fuel/cladding chemical interaction
[1990Ger]	Optical metallography, scanning electron microscopy employing secondary electron microscopy and backscattered electron detection.	Fuel pin swelling
[1993Cra]	Neutron radiography, contact profilometry, Gamma scan, fission gas analysis, optical metallography	Axial growth under irradiation, fuel-cladding chemical interaction
[1994Kur]	Optical metallography, α -autoradiography, EMPA	Fuel-cladding chemical interaction
[1994Sar]	Optical metallography, EMPA, dilatometry	Fuel-cladding chemical interaction
[1996Kei]	Diffusion couples, SEM/EDX analysis	Interdiffusion behavior in Pu-U-Zr fuel versus stainless steel

Reference	Method/Experimental Technique	Type of Property
[1997Pet]	Diffusion couples, SEM/EDX analysis, mass spectrometry	Isothermal diffusion in Pu-U-Zr alloys
[1998Ale]	Diffusion couples, X-ray microanalysis	Interdiffusion in the BCC phase of the Pu-U-Zr system
[2000Soh]	SEM, EMPA, scanning Auger microscopy	Constituent redistribution under gradients temperature and concentrations
[2004Kim]	Optical microscopy, SEM, EMPA	Constituent redistribution during irradiation

Table 6: Ultimate Compressive Strength of Pu-U-Zr Alloys at Selected Temperatures

Alloy composition (at.%)	Heat-treatment	Ultimate Compressive Strength at Indicated Temperature [MPa]				
		25°C	500°C	625°C	675°C	750°C
U-9.5Pu-14.4Zr	Hom.*	1608.84		117.72	39.24	
U-9.5Pu-29.2Zr	Hom.	1628.46			67.69	41.20
	As cast	1608.84	>539.55	117.72	51.01	
U-12.2Pu-21.8Zr	As cast	1245.87	539.55	107.91	24.53	
U-14.2Pu-14.5Zr	As cast	1265.49	470.88	107.91	54.94	
U-14.4Pu-29.3Zr	Hom.	1137.96			54.94	

* Homogenizing heat-treatment: 1050°C for one week, oil quench for the alloys with more than 22 at.% Zr; and 950°C for one week, oil quench for the alloys with less than 22 at.% Zr

Table 7: Variations of Tensile Properties with Temperature in Homogenized and Quenched* Uranium-Plutonium-Zirconium Alloys

Alloy, at.%	T [°C]	Tensile strength		Yong's modulus (E) [GPa]	Type failure
		Ultimate [MPa]	Yield** [MPa]		
U-9.5Pu-14.4Zr	25	177.56		170.69	Brittle
	675	11.77	10.79	13.73	Ductile
U-14.2Pu-14.5Zr	25	39.24		103.99	Brittle
	675	11.77	10.79	15.70	Ductile
U-14.4Pu-29.5Zr	25	75.54		127.53	Brittle
	675	28.45	27.47	18.64	Ductile

* All specimens were tested in creep prior the tensile tests and therefore contain some (<5%) hot work.

** Yield strength at 0.2% offset. Brittle specimens did not attain this before fracturing

Table 8: Time (min) To Attain 2% Strain in Pu-U-Zr Alloys

Alloy composition (at.%)	Load [MPa]	Temperature [°C]				
		600	625	650	675	700
U-9.5Pu-14.4Zr	4.91				15	
	9.81				5	
	19.62				3	
	39.24		5		1	
U-14.2Pu-14.5Zr	4.91				10	
	9.81		5.000		1	
	19.62		210			
	39.24		10			
U-12.2Pu-21.8Zr	4.91			5.000		
	9.81		5.000	80		
	19.62		210	1		
	39.24		10			
U-14.4Pu-29.5Zr	4.91	100.000		5.000	45	40
	9.81	10.000		80	5	5
	19.62	800		1	1	1
	39.24	70				

Table 9: Key Phenomena that Control Fuel Performance

Phenomena	Experimental Observations	Consequences
Fuel swelling	irradiation growth and grain boundary tearing; Xe/Kr bubble growth; solid fission product accumulation; alloy and burnup rate effects	reactivity loss; rate of gas release; fuel/clad interaction stresses; thermal conductivity loss
Fuel constituent migration	U/Zr interdiffusion; critical Pu threshold	lowered solidus; complexities of properties modeling
Fuel/cladding chemical interaction	penetration into cladding by U, Pu, and lanthanide series fission products; diffusion of cladding constituents into fuel; extensive nickel loss in austenitics	cladding wall thinning; ductility degradation of interaction layer in cladding; eutectic composition approached in fuel
Cladding deformation	irradiation/thermal creep by fission gas pressure loading; some fuel contact pressure loading; void swelling in austenitics	stress-rupture lifetime determines ultimate burnup achieved; high cladding strains can lead to element/bundle interaction stresses

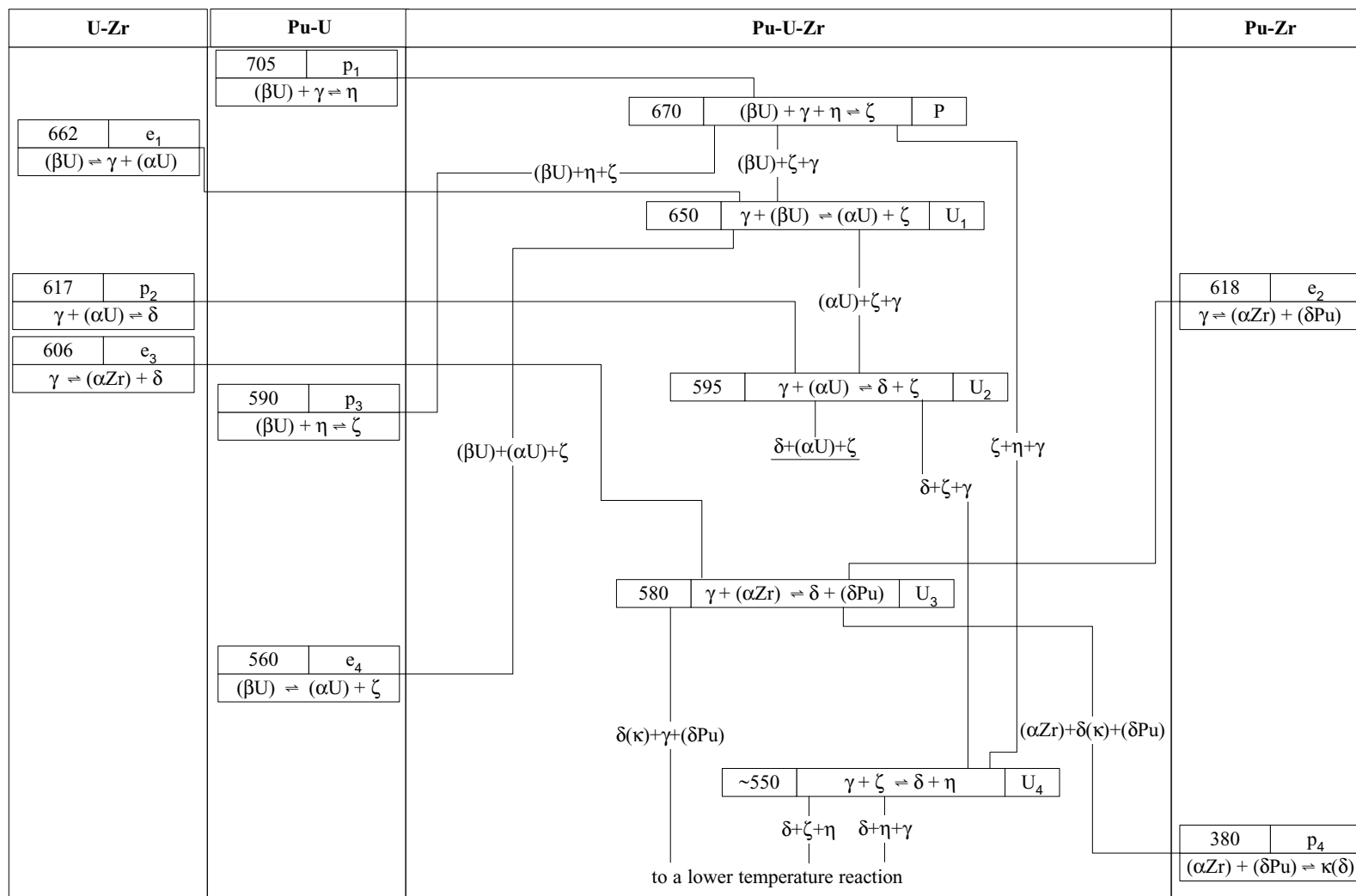


Fig. 1: Pu-U-Zr. Partial reaction scheme

Fig. 2: Pu-U-Zr.
Liquidus (dashed lines) and solidus (solid lines) temperature in the Pu rich corner

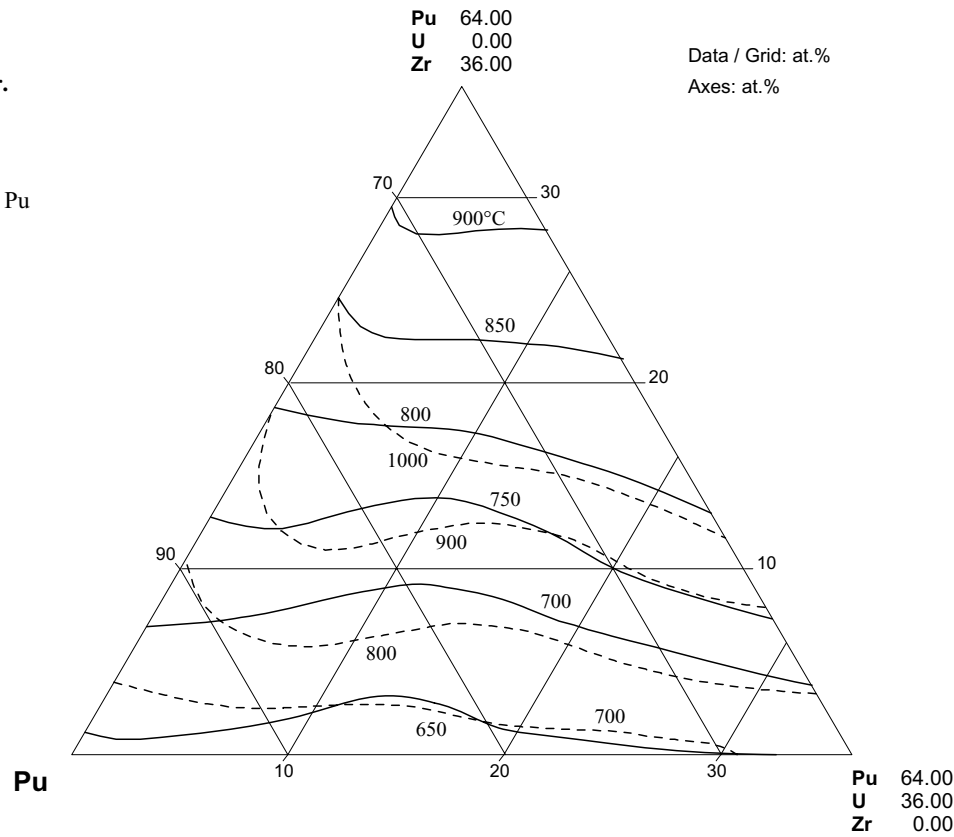


Fig. 3: Pu-U-Zr.
Isothermal section at 700°C

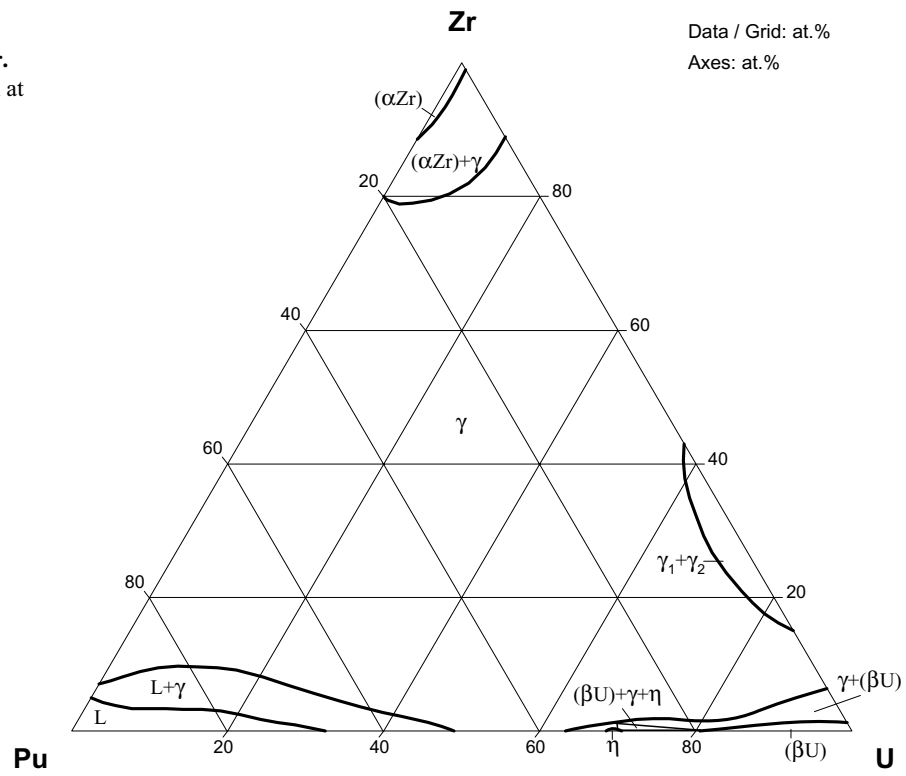


Fig. 4: Pu-U-Zr.
Isothermal section at
670°C

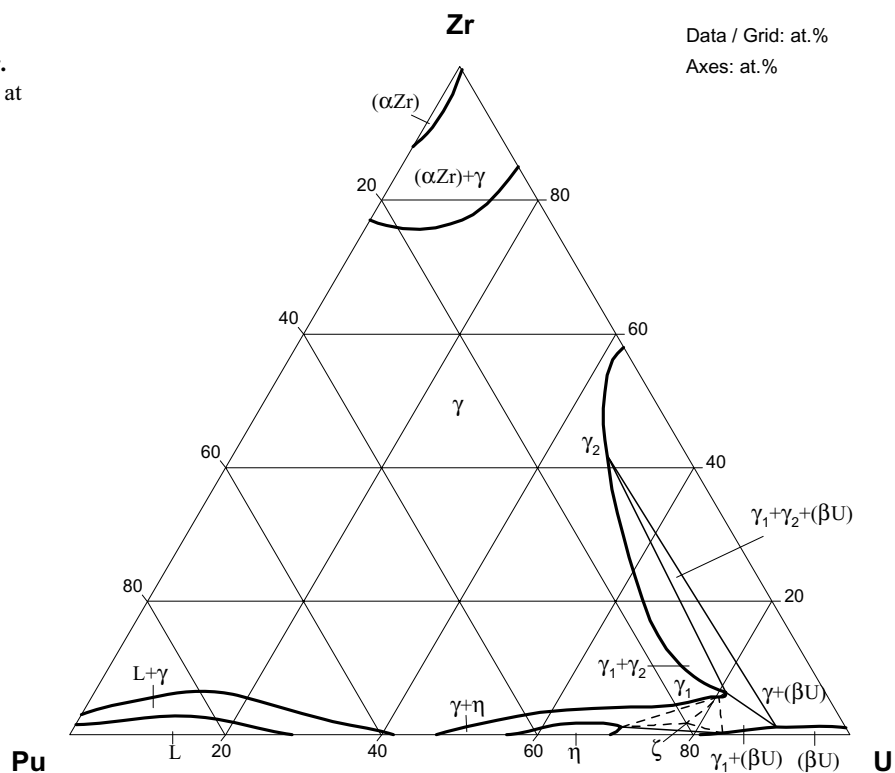


Fig. 5: Pu-U-Zr.
Isothermal section at
660°C

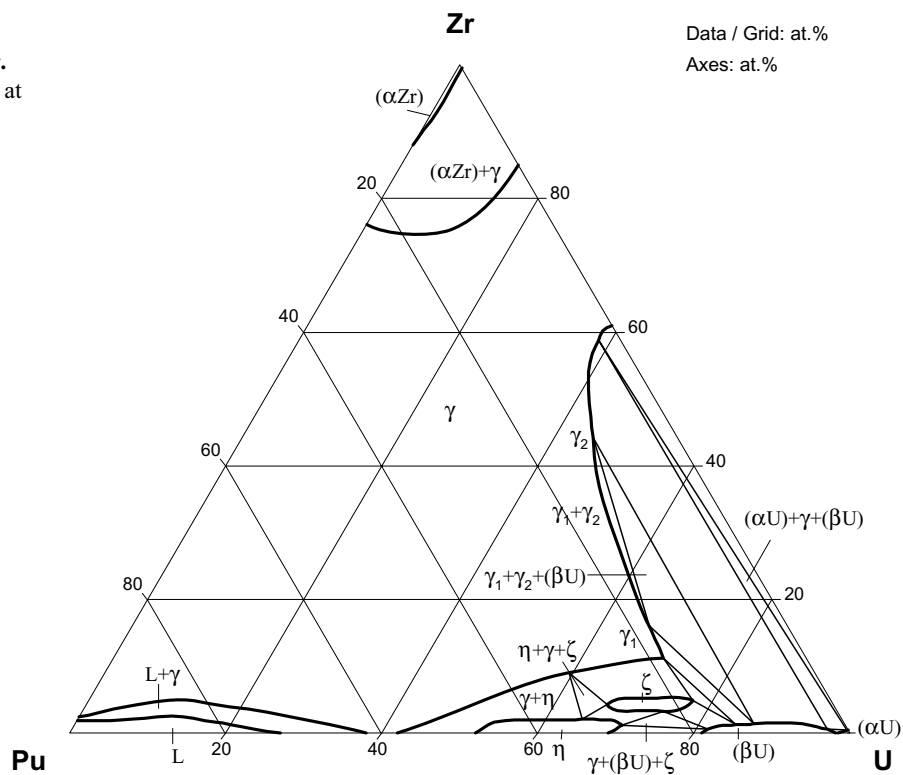


Fig. 6: Pu-U-Zr.
Isothermal section at
650°C

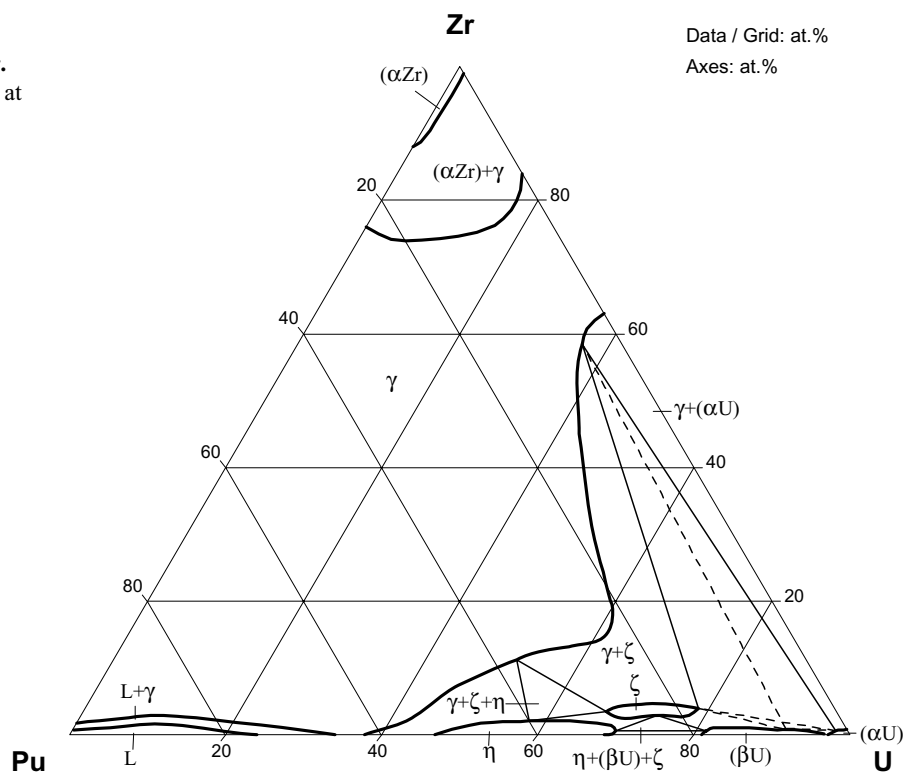


Fig. 7: Pu-U-Zr.
Isothermal section at
640°C

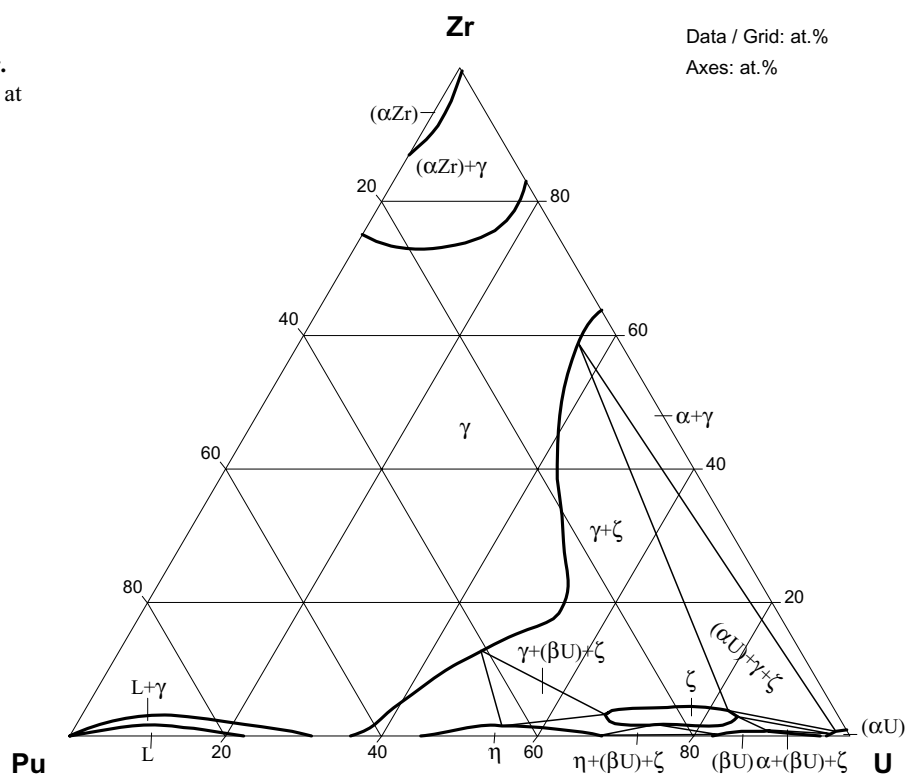


Fig. 8: Pu-U-Zr.
Isothermal section at
595°C

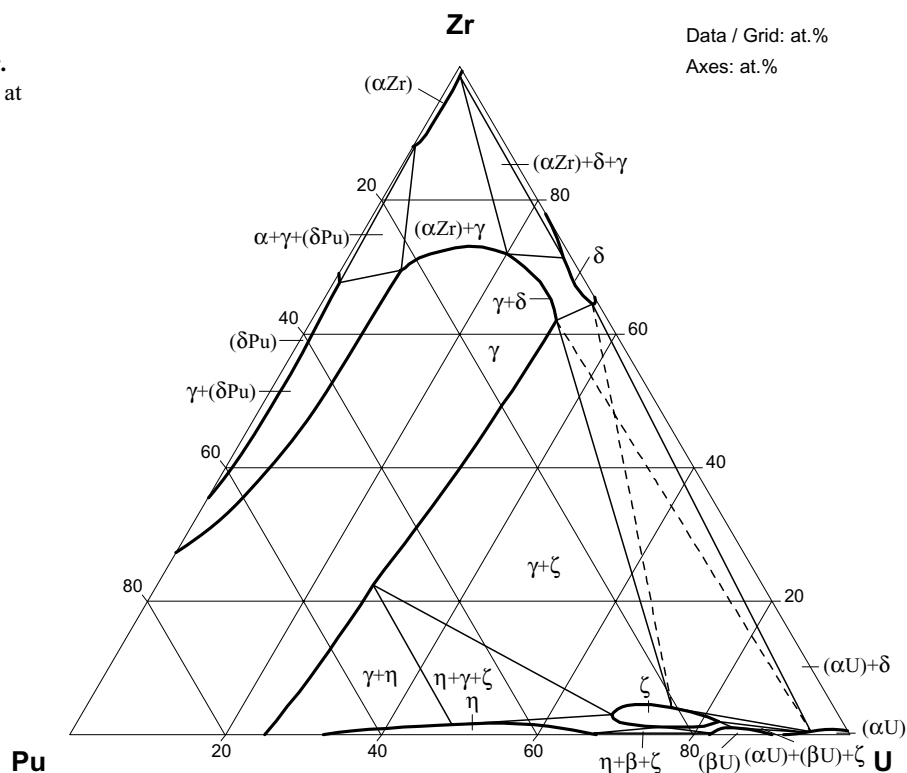


Fig. 9: Pu-U-Zr.
Isothermal section at
580°C

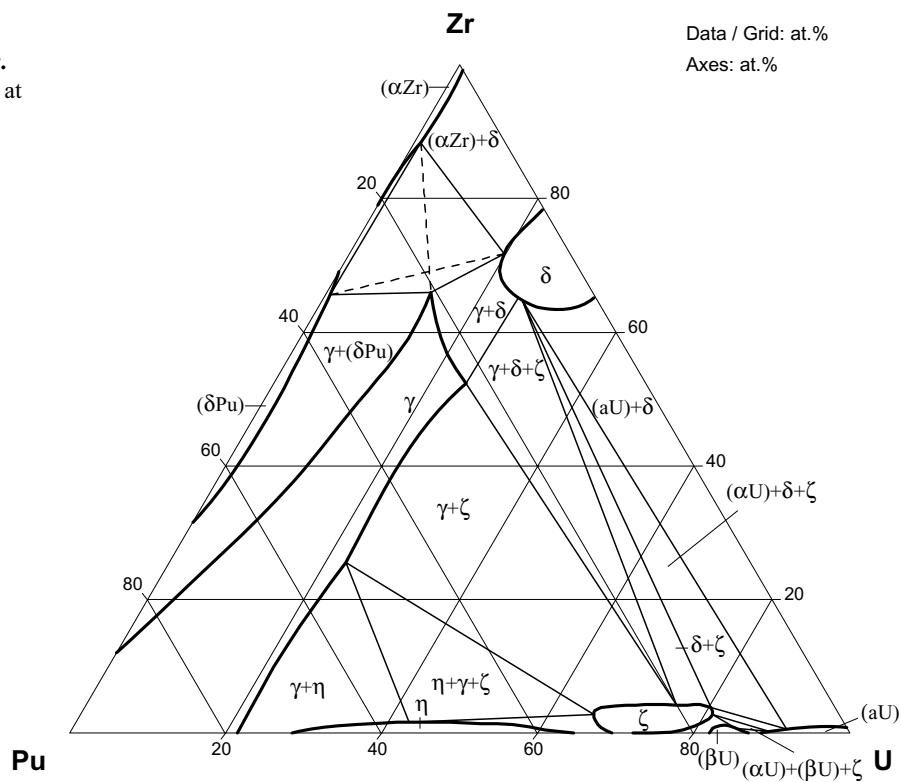


Fig. 10: Pu-U-Zr.
Isothermal section at
550°C

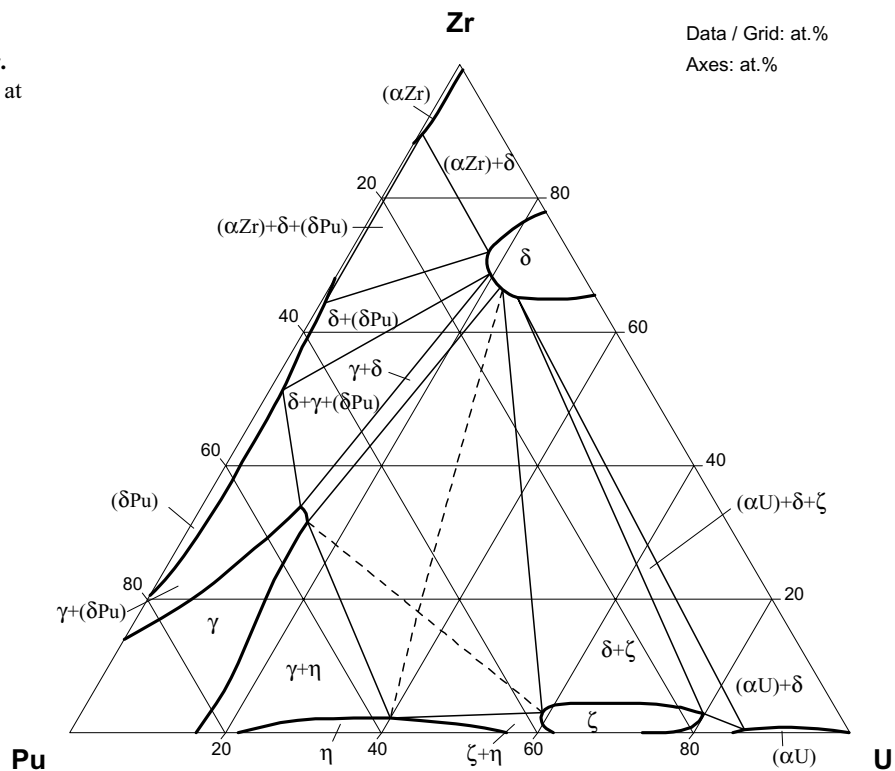
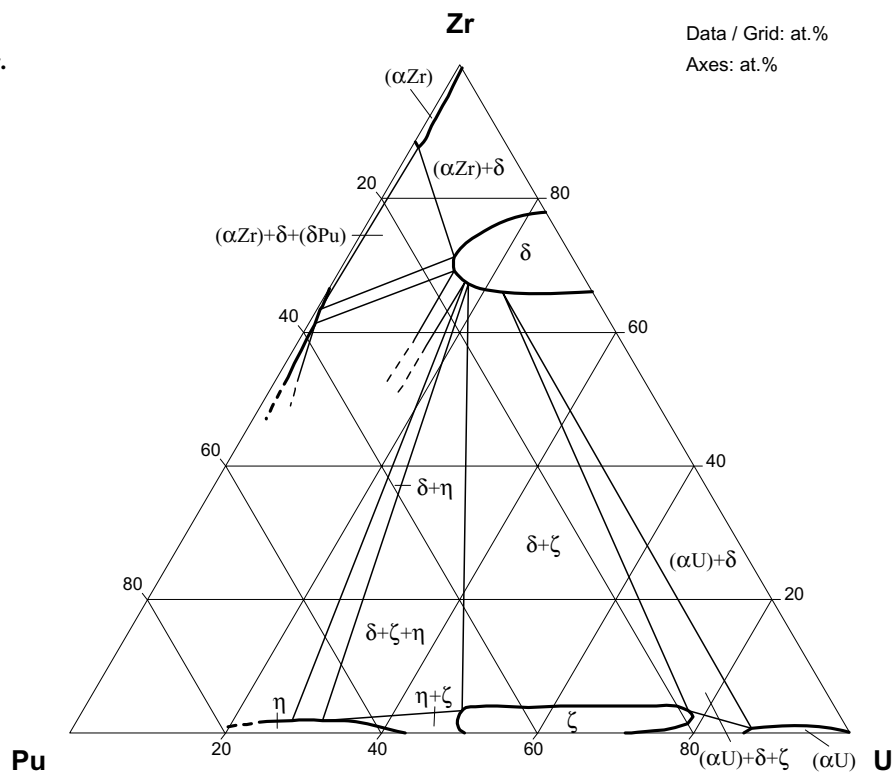


Fig. 11: Pu-U-Zr.
Partial isothermal
section at 500°C



Ruthenium – Silicon – Uranium

Artem Kozlov

Introduction

In the recent years, a great deal of interest has been taken in those U based intermetallic compounds which shown a highly correlated state of the electronic system at low temperature. Discovery of URu₂Si₂ as the superconducting heavy fermion system, made the Ru–Si–U system and particularly the URu₂Si₂ compound the subject of intensive experimental and theoretical investigations because of the unusual interplay between superconducting and magnetic interactions at low temperature. The observation of antiferromagnetic order below ~17.5 K and of superconductivity below ~1 K brings the URu₂Si₂ compound to the center of discussions concerning the coexistence of magnetic order and superconductivity. Despite the fact that a large number of articles are devoted to understand the unusual properties of this heavy-fermion superconductor and to determine crystal structure of compounds, information concerning phase relations is very pure. Partial phase diagram of the Ru–Si–U system at 820°C has been constructed by [1994Uga]. Phase compositions of the alloys and crystal structures of the identified intermediate phases were studied by [1977Aks, 1980Bar, 1985Cor, 1985Rau, 1986Vis, 1993Poe, 1994Poe, 1994Uga, 1994Ver, 1995Lej, 1996Che, 2001Hof, 2002Zel]. Data on thermodynamic properties were studied by [1985Pal, 1986Vis, 1987Myd, 1990Fis, 1993Pir, 1994Bri, 1998Tak, 2003Jai]. A summary of physical properties is given below in the section “Notes on Materials Properties and Applications”. Information on phase relations, structures and thermodynamics is summarized in Table 1.

Binary Systems

The Si–U and Ru–U binary systems are accepted from [Mas2]. The Ru–Si binary phase diagram has been assessed by [2000Oka] based on the experimental results of [1999Per]. More recently, thermodynamic optimization was carried out by [2001Du] and [2001Liu]. Since then, [2002Oka] assessed this system. The Si rich part of the Ru–Si phase diagram has been updated by [2002Iva]. A new phase, RuSi₂, has been observed in the form of inclusions in Ru₂Si₃ single crystals. Ru₂Si₃ single crystals have been grown by the zone melting technique with radiation heating. These crystals contain inclusions, about 500 nm in size, which consist of monocrystalline ruthenium disilicide. Crystal structure has not been determined. Endothermic peaks detected at $T = 962^{\circ}\text{C}$ in the DTA measurement have been interpreted as decomposition of RuSi₂ to Ru₂Si₃ and (Si).

Solid Phases

The crystallographic details of all solid phases are listed in Table 2. Eight ternary compounds have been found in the Ru–Si–U system. Heavy fermion superconductor URu₂Si₂ with the ThCr₂Si₂ structure type has attracted most attention. Single-crystals of URu₂Si₂ have been determined by [1985Cor]. The temperature dependence of the lattice parameters for URu₂Si₂ was studied by [1986Vis] for the temperature interval between 1.4 and 100 K. [1980Bar] synthesized URu₃Si₂ ternary compound. This compound crystallized in hexagonal LaRu₃Si₂ structure and electrical resistivity of this compound has been measured by [1985Rau]. However crystal structure and lattice parameters of URu₃Si₂ are not described by [1980Bar] and [1985Rau]. A new ternary silicide U₂Ru₁₂Si₇ has been discovered by [2002Zel]. The crystal structure has been solved on a single crystal. [1995Lej] reports about the crystal structure and physical properties of a new ruthenium-based ternary silicide, neighbor of URu₂Si₂: U₆Ru₁₆Si₇. The research of new materials was carried out by cross-checking X-ray diffraction pattern and microprobe analysis. The U₆Ru₁₆Si₇ compound has been detected as parasitic phase in as-cast URu₂Si₂ when shifting the composition. Heat treatments (at 1100 and 900°C) led to multiphase samples. No trace of the URu₃Si₂ phase mentioned earlier by [1980Bar] could be detected before and after annealing. The crystal structure has been solved by X-ray and neutron powder refinement using a Rietveld calculation method and according to a Mg₆Cu₁₆Si₇ structural model

with the cubic space group $Fm\bar{3}m$ ($a = 1220.7 \pm 0.2$ pm). Study of the U_2RuSi_3 compound by electron diffraction reveals that this silicide adopts interesting superstructures of the AlB_2 type [1993Poe, 1994Poe, 1996Che, 2001Hof]. The Ru and Si atoms are perfectly ordered in U_2RuSi_3 which leads to the occurrence of a new hexagonal superstructure having the unit cell parameters a twice as great as that observed for the ideal AlB_2 type. U_2Ru_3Si has been discovered by [1994Ver] and crystal structure has been determined by X-ray single crystal and powder diffraction analysis. Existence of this phase was confirmed by [1995Lej]. $U_2Ru_3Si_5$ has been discovered by [1977Aks]. It crystallizes in the monoclinic $Lu_2Co_3Si_5$ type structure which is a deformation variant of $U_2Co_3Si_5$. The $URuSi$ ternary compound has been identified by [1994Uga]. Arc-melted alloys were heat treated in muffle furnaces at temperatures of 800–1100°C. Alloy specimens were water quenched to room temperature after heating for 3–10 d. Phases present before and after the heat treatments were examined by electron probe microanalysis and X-ray powder diffractometry. Compound crystallized in orthorhombic $TiNiSi$ structure type.

Invariant Equilibria

According with [1994Uga], in the Ru–Si–U system, the $URuSi$ ternary compound melts congruently. The following ternary transition reaction (U type) $U_3Si + URuSi \rightleftharpoons U_3Si_2 + L$ has been proposed by [1994Uga]. The invariant reaction temperature was found to be at a temperature between 820 and 850°C. Invariant plane corresponding to this reaction is shown in the isothermal section at 820°C in Fig. 1. The peritectic liquid may undergo the transformation on rapid cooling from the liquid state of the alloy: $L \rightleftharpoons URuSi + (U)$. It was found that the U_3Si compound does not have tie lines with (Ru) but forms those with the $URuSi$ ternary compound.

Isothermal Sections

The partial isothermal section of the Ru–Si–U system at 820°C, as shown in Fig. 1, based on the investigation by [1994Uga].

Thermodynamics

The low temperature specific heat for URu_2Si_2 has been studied by [1985Pal, 1986Vis, 1987Myd, 1990Fis, 1994Bri, 2003Jai], for U_2RuSi_3 ternary compound by [1998Tak] and for $U_2Ru_3Si_5$ - by [1993Pir].

Notes on Materials Properties and Applications

Physical properties data known for URu_2Si_2 , $U_2Ru_3Si_5$, U_2Ru_3Si and U_2RuSi_3 are discussed below.

URu_2Si_2 :

Information concerned investigations of the Ru–Si–U materials properties, particularly URu_2Si_2 compound, are generalized in Table 3. The intermetallic compound URu_2Si_2 has been classified as a heavy-fermion system because of its large linear specific-heat coefficient $\gamma = 180 \text{ mJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$. Susceptibility, magnetization, and specific-heat measurements on single-crystal samples indicate both a magnetic phase transition at ~ 17.5 K and a superconducting transition at ~ 1 K. Ordered moment is unusually small (0.03 ± 0.01) μ_B . The magnetic and superconducting properties are highly anisotropic. The thermoelectric properties of URu_2Si_2 were studied by [2001Ari]. The Seebeck coefficient of URu_2Si_2 was obtained to be $-48.9 \mu\text{V K}^{-1}$ at 1100 K and the compound showed poor thermoelectric properties above room temperature. Correlation between superconductivity and magnetism in the URu_2Si_2 heavy fermion compound has been reviewed by [2003Sat]. High magnetic field studies of the hidden order transition in URu_2Si_2 have been investigated by [2002Jai, 2002Cha1, 2002Cha2, 2002Ami, 2003Ami1, 2003Ami2, 2003Mot1, 2003Mot2, 2003Myd, 2004Bel, 2004Jai, 2004Har, 2004Bou, 2005Min, 2005Ten, 2005Bou, 2005Ber]. Thermal transport in the hidden-order state of URu_2Si_2 has been studied by [2005Beh]. A narrow selection of the important experimental observations of inhomogeneous magnetism and hidden order in URu_2Si_2 has been reviewed by [2002Ami, 2002Cha1, 2002Cha2, 2003Ami1, 2003Ami2]. The theoretical implications of two recent NMR experiments on the hidden order have been discussed by [2003Cha]. Crystal field model of the

magnetic properties of the URu_2Si_2 compound have been proposed by [1987Nie, 1987Fra, 1992Rad, 1994San, 2005Nag]. Theoretical model for magnetic ordering in the heavy-fermion metal URu_2Si_2 has been suggested by [2005Min]. High field magnetic (B, T) phase diagram of URu_2Si_2 with superconducting and magnetically ordered phases was constructed basically combining experimental and literature data by [2003Kim]. Quantum criticality and multiple phase transitions in URu_2Si_2 are evidenced in Fig. 2. Region I refers to the hidden order phase, while II, III, and V constitute newly discovered phases. Region IV was proposed to be a field-induced recovery of the normal metallic phase. The p – T phase diagram has been investigated by [2003Mot1, 2003Mot2, 2003Sus, 2004Bou, 2005Bou,]. The p – T phase diagram (Fig. 3) deduced by [2005Bou] from the resistivity measurements by [1993Sch] and neutron-scattering measurements under pressure by [2004Bou, 2005Bou] shows two distinct phases for $p > p_M$, where $p_M \approx 4.9$ kbar. The small-moment antiferromagnetic phase (SMAF), observed below the second-order phase transition at $T_m = 17.5$ K, is the same as that observed at $p = 0$ and is characterized by a small moment $\sim 0.03 \mu_B$. The transition between the paramagnetic phase and the SMAF phase at T_m is second order and is accompanied by large anomalies in bulk properties. The low temperature antiferromagnetic phase (LMAF), observed below the transition T_M , which seems to be a first-order transition, is characterized by a large moment $\sim 0.33 \mu_B$ and small anomalies in the macroscopic properties. [2005Bou] found that the absence of magnetic scattering at the $(0, 0, 21 + 1)$ reflections shows that the ordered moments are along the c -axis at all pressures, *i.e.* the SMAF and LMAF phases have the same AFM structure. A first-order transition line between the SMAF and the LMAF phases is also found in the thermal expansion measurements by Motoyama *et al.* [2003Mot1, 2003Mot2] under pressure along the a and the c axis. Their p – T phase diagram is similar, but not identical with [2005Bou]. The position of the line $T_m(p)$ is quite sensitive to the sample quality, and the onset pressure p_M for the LMAF phase varies from 4 to 8 kbar. They conclude that transition temperatures join at a critical point. This is in contrast to neutron-scattering measurements of [2005Bou], where the first-order character is preserved all the way up to 11.8 kbar.

$\text{U}_2\text{Ru}_3\text{Si}_5$:

Electrical resistivity, thermoelectric power, thermal conductivity, specific heat and magnetic susceptibility of the polycrystalline $\text{U}_2\text{Ru}_3\text{Si}_5$ silicide have been measured by [1988Ali, 1993Pir]. $\text{U}_2\text{Ru}_3\text{Si}_5$ behaves like a nonmagnetic compound and displays distinct anomalies in the low-temperature domains of resistivity and thermoelectric power. The thermoelectric properties of this compound also have been studied by [2001Ari]. The Seebeck coefficient of $\text{U}_2\text{Ru}_3\text{Si}_5$ was obtained to be $-32.8 \mu\text{V}\cdot\text{K}^{-1}$ at 1100 K and compound showed poor thermoelectric properties above room temperature.

U_2RuSi_3 :

Magnetic susceptibility, low-temperature electrical resistivity and specific heat of the polycrystalline U_2RuSi_3 have been measured by [1998Tak]. The Weiss temperature for U_2RuSi_3 is 139 K and is very close to the values reported by [1996Che]. The reciprocal magnetic susceptibility of this compound follows a Curie-Weiss law above 60 K and effective magnetic moment for uranium $3.02 \mu_B \cdot (\text{U atom})^{-1}$ [1994Poe, 1996Che].

$\text{U}_2\text{Ru}_3\text{Si}$:

Magnetization and resistivity of $\text{U}_2\text{Ru}_3\text{Si}$ compound on a single crystal along the $\{001\}$ direction of the hexagonal cell have been measured by [1994Ver]. $\text{U}_2\text{Ru}_3\text{Si}$ exhibits an enhanced Pauli paramagnetic behavior and no anomalies in the magnetization and in the resistivity curves occur in this material. The resistivity of the single crystal decreases from $153 \mu\Omega$ at room temperature to a saturated value of $7.6 \mu\Omega$ at 4.2 K. The high residual resistivity measured at low temperature reflects the disorder between ruthenium and silicon.

URu_3Si_2 :

The resistivity of URu_3Si_2 has been studied by [1985Rau]. Resistivity is very high and has a negative slope between 70 K and room temperature.

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Table 1: Investigations of the Ru-Si-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1977Aks]	XRD, crystal structure investigations	Formation, structure of U ₂ Ru ₃ Si ₅
[1985Cor]	X-ray single crystal four-circle data	Formation, structure of URu ₂ Si ₂
[1985Rau]	XRD, EPMA, electrical resistivity	Formation, structure of URu ₃ Si ₂
[1987Myd]	Menovsky single-crystal growth, XRD, metallography, electron microprobe	Formation, structure of URu ₂ Si ₂
[1987Hie]	Arc melting, XRD	Formation, structure of Ru ₂ Si ₂ U
[1993Poe]	X-ray diffraction (XPD), crystal structure investigations	Formation, structure of U ₂ RuSi ₃
[1994Poe]	XPD, X-ray single-crystal four-circle data	Formation, structure of U ₂ RuSi ₃ , physical properties
[1994Uga]	XPD	Formation, structure of URuSi, partial isothermal section at 820°C

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1994Ver]	Czochralski single-crystal growth, X-ray single-crystal four-circle data, XPD,	Formation, structure of U_2Ru_3Si , physical properties
[1995Lej]	Czochralski single-crystal growth, Rietveld refinement method, microprobe analysis	Formation, structure of U_2Ru_3Si and $U_6Ru_{16}Si_7$, magnetic properties
[1996Che]	XPD, TEM, SEM	Formation, structure of U_2RuSi_3
[2002Zel]	XPD, Rietveld refinement method, crystal structure investigations	Formation, structure of $U_2Ru_{12}Si_7$

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Ru) < 2334	<i>hP2</i> <i>P6₃/mmc</i> Mg	$a = 270.58$ $c = 428.16$	at 25°C [Mas2]
(δ Si)	<i>hP4</i> <i>P6₃/mmc</i> α La	$a = 380$ $c = 628$	at 25°C, 16 GPa ~ 1 atm [Mas2]
(γ Si)	<i>cI16</i> <i>Im$\bar{3}m$</i> γ Si	$a = 663.6$	at 25°C, 16 GPa [Mas2]
(β Si)	<i>tI4</i> <i>I4₁/amd</i> β Sn	$a = 468.6$ $c = 258.5$	at 25°C, 9.5 GPa [Mas2]
(α Si) < 1414	<i>cF8</i> <i>Fd$\bar{3}m$</i> C (diamond)	$a = 543.06$	at 25°C [Mas2]
(γ U) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352.4$	[Mas2]
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> β U	$a = 1075.9$ $c = 565.6$	[Mas2]
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	at 25°C [Mas2]
Ru_2Si 1544 - 1240	<i>oP12</i> <i>Pnma</i> Co_2Si	$a = 528.35$ $b = 400.44$ $c = 741.86$	[V-C2]
		$a = 528.7 \pm 0.2$ $b = 400.5 \pm 0.1$ $c = 741.3 \pm 0.1$	[1999Per]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Ru ₅ Si ₃ 1550 - 1330	<i>oP16</i> <i>Pbam</i> Rh ₅ Ge ₃	$a = 524.57$ $b = 981.90$ $c = 402.36$	[V-C2]
Ru ₄ Si ₃ < 1560	<i>oP28</i> <i>Pnma</i> Rh ₄ Si ₃	$a = 1713.43 \pm 0.31$ $b = 402.16 \pm 0.05$ $c = 519.36 \pm 0.09$	[V-C2]
		$a = 518.7 \pm 0.1$ $b = 402.1 \pm 0.1$ $c = 1712.8 \pm 0.1$	[1999Per]
RuSi < 1850	<i>cP8</i> <i>P2₁3</i> FeSi or <i>cP2</i> <i>Pm$\bar{3}m$</i> CsCl	$a = 470.75$ $a = 470.0 \pm 0.1$ $a = 290.73$ $a = 291.0 \pm 0.1$ $a = 290.2 \pm 0.1$	[V-C2] [1999Per] [V-C2] 47.1 at.% Si [1999Per] 48.2 at.% Si [1999Per]
Ru ₂ Si ₃ < 1703	<i>oP40</i> <i>Pbcn</i> Ru ₂ Si ₃	$a = 1106.0 \pm 0.2$ $b = 895.2 \pm 0.2$ $c = 553.0 \pm 0.1$	[V-C2]
		$a = 1105.2 \pm 0.4$ $b = 893.7 \pm 0.1$ $c = 552.5 \pm 0.1$	[1999Per]
RuSi ₂ < 962	-	-	[2002Iva]
U ₂ Ru < 937	<i>mP12</i> <i>P2/m</i> or <i>P2₁/m</i>	$a = 1310.6 \pm 0.2$ $b = 334.3 \pm 0.1$ $c = 520.2 \pm 0.1$ $\beta = 96.17 \pm 0.05$	[V-C2]
α URu < 1158	-	-	[Mas2]
β URu < 795	-	-	[Mas2]
U ₃ Ru ₄ < 1148	-	-	[Mas2]
U ₃ Ru ₅ < 1163	-	-	[Mas2]
U ₂ Ru ₃	<i>cF120</i> <i>Fd$\bar{3}m$</i>	$a = 1289.5 \pm 0.1$	[V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
URu ₃ < 1850	<i>cP4</i> <i>Pm$\bar{3}m$</i> AuCu ₃	<i>a</i> = 398.0	[V-C2]
USi ₃ < 1510	<i>cP4</i> <i>Pm$\bar{3}m$</i> AuCu ₃	<i>a</i> = 403.6 <i>a</i> = 403.53	[V-C2] at 78 at.% Si [1992Rem] as cast
USi ₂ < 450	<i>hP3</i> <i>P6/mmm</i> AlB ₂	<i>a</i> = 402.8 ± 0.1 <i>c</i> = 385.2 ± 0.1	[V-C2]
USi ₂ metastable	<i>tI12</i> <i>I4₁/amd</i> defect ThSi ₂	<i>a</i> = 399.0 <i>c</i> = 1315.0 <i>a</i> = 394.06 <i>c</i> = 1377.8	[V-C2] [1992Rem] heat treatment 1400°C
USi _{1.88} < 1710	<i>tI12</i> <i>I4₁/amd</i> defect ThSi ₂	<i>a</i> = 394.57 <i>c</i> = 1373.9 <i>a</i> = 393.78 <i>c</i> = 1372.9 <i>a</i> = 394.23 <i>c</i> = 1371.2	[1992Rem] heat treatment 1400°C [1992Rem] heat treatment 1000°C at 64 at.% Si [1992Rem] heat treatment 1000°C
U ₃ Si ₅ < 1770	<i>hP3</i> <i>P6/mmm</i> defect AlB ₂ distortion AlB ₂	<i>a</i> = 384.75 <i>c</i> = 407.4 <i>a</i> = 384.2 <i>c</i> = 403.6 <i>a</i> = 389.3 <i>b</i> = 671.8 <i>c</i> = 403.5 <i>a</i> = 389.7 <i>b</i> = 673.5 <i>c</i> = 403.5 <i>a</i> = 389.3 <i>b</i> = 671.7 <i>c</i> = 404.2	at 62.5 at.% Si [1992Rem] heat treatment 1400°C at 62.5 at.% Si [1992Rem] heat treatment 1400°C at 62.5 at.% Si [1992Rem] heat treatment 1000°C at 63.2 at.% Si [1992Rem] heat treatment 1000°C at 63.2 at.% Si [1992Rem] heat treatment 1400°C
USi < 1580	<i>tI138</i> <i>I4/mmm</i> USi	<i>a</i> = 1058.7 <i>c</i> = 2431.0	[1992Rem, 1996Bih]
USi (metastable)	<i>oP8</i> <i>Pnma</i> FeB	<i>a</i> = 758.5 <i>b</i> = 390.3 <i>c</i> = 566.3	probably impurity (O) stabilized [1992Rem, 1993LeB]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
U ₅ Si ₄ < 1100	<i>hP</i> 18 <i>P</i> 6/ <i>mmm</i> U ₅ Si ₄	<i>a</i> = 1046.7 <i>c</i> = 391.2	Single crystal study [2006Noe]
U ₃ Si ₂ < 1665	<i>tP</i> 10 <i>P</i> 4/ <i>mbm</i> U ₃ Si ₂	<i>a</i> = 732.99 <i>c</i> = 390.04	[V-C2, Mas2]
γU ₃ Si 930 - 759	<i>cP</i> 4 <i>Pm</i> $\bar{3}m$ Cu ₃ Au	<i>a</i> = 434.6	[V-C2, 1965Str]
βU ₃ Si 762 - -153	<i>tI</i> 16 <i>I</i> 4/ <i>mcm</i> βU ₃ Si	<i>a</i> = 603.28 <i>c</i> = 869.07	[V-C2, 1965Str]
αU ₃ Si < -153°C, at -193°C	<i>oF</i> 32 <i>Fmmm</i> αU ₃ Si	<i>a</i> = 865.4 <i>b</i> = 854.9 <i>c</i> = 852.3	[V-C2, 1965Str]
* URu ₂ Si ₂	<i>tI</i> 10 <i>I</i> 4/ <i>mmm</i> ThCr ₂ Si ₂	<i>a</i> = 412.6 ± 0.2 <i>c</i> = 956.8 ± 0.4	[V-C2]
		<i>a</i> = 412.6 <i>c</i> = 956.8	[1985Cor]
* U ₂ Ru ₁₂ Si ₇	<i>oP</i> 84 <i>Pnma</i> Mg ₂ Co ₁₂ As ₇	<i>a</i> = 1116.9 <i>b</i> = 398.9 <i>c</i> = 2618.5	[2002Zel]
* U ₆ Ru ₁₆ Si ₇	<i>cF</i> 116 <i>Fm</i> $\bar{3}m$ Th ₆ Mn ₂₃	<i>a</i> = 1220.7	[1995Lej]
* U ₂ RuSi ₃	<i>hP</i> 3 <i>P</i> 6/ <i>mmm</i> AlB ₂	<i>a</i> = 407.5 <i>c</i> = 383.8	[1993Poe]
	<i>hP</i> 3 <i>P</i> 6/ <i>mmm</i> U ₂ RuSi ₃	<i>a</i> = 814.8 <i>c</i> = 385.5	[1994Poe]
* U ₂ Ru ₃ Si	<i>hR</i> 6 <i>R</i> $\bar{3}m$ MgCu ₂	<i>a</i> = 550.1 <i>c</i> = 1136.7	[1994Ver], [1995Lej]
* U ₂ Ru ₃ Si ₅	<i>mC</i> 40 <i>C</i> 2/ <i>c</i> Lu ₂ Co ₃ Si ₅	<i>a</i> = 1109.2 <i>b</i> = 1176.2 <i>c</i> = 570.7	[1977Aks]
* URuSi	<i>oP</i> 12 <i>Pnma</i> TiNiSi	<i>a</i> = 637.0 <i>b</i> = 399.0 <i>c</i> = 725.0	[1994Uga]

Table 3: Investigations of the Ru-Si-U Materials Properties

Reference	Method/Experimental Technique	Type of Property
[2005Ten]	Magnetic measurements under high pressures	Magnetization
[2005Bou]	Magnetic measurements	Neutron-scattering and specific-heat
[2005Ber]	Magnetic measurements	^{29}Si NMR in powdered URu_2Si_2
[2005Beh]	Electrical measurements	Thermal conductivity
[2004Bel]	Electrical measurements	Thermoelectricity
[2004Jai]	Magnetic and electrical measurements	Magnetization and resistivity in continuous and pulsed magnetic fields up to 45 T
[2004Har]	Magnetic and electrical measurements	Magnetization, electrical transport, specific heat
[2003Jai]	Magnetic measurements	Specific heat, magnetocaloric effect
[2003Ami1]	Zero-field μSR technique under hydrostatic pressures	static magnetic order under high pressure
[2003Yok]	Magnetic measurements, elastic neutron scattering	Effects of uniaxial stress on the AF state
[2003Mat]	Magnetic measurements	^{29}Si NMR under pressure.
[2003Sus]	Magnetic measurements	Ultrasonic properties
[2002Jai]	Magnetic measurements	Specific heat, magnetocaloric effect, and magnetoresistance
[2002Tsu]	Magnetic measurements	^{29}Si NMR in powdered URu_2Si_2
[2002Par]	High energy inelastic neutron scattering	Magnetic excitations
[2002Sou]	Magnetic measurements	Ultrasonic properties
[1999Sug]	Magnetic measurements	Magnetization
[1999Ina]	Magnetic and electrical measurements	Electrical resistivity, magnetic susceptibility
[1999Ami]	Elastic neutron-scattering experiments, magnetic measurements	Neutron-scattering at high pressure
[1997Dij]	Elastic and inelastic neutron-scattering measurements	Ordered moment and the magnetic gap
[1996Sak]	Electrical measurements, transport Phenomena	Thermoelectric power
[1995Nai]	Electrical measurements	Electrical resistivity
[1994Bri]	Magnetic and electrical measurements	Specific heat, superconductivity
[1994Esc]	Electrical measurements, point-contact spectroscopy	Spin-density wave behavior
[1994Kin]	Magnetic measurements	Electron spin resonance
[1993Ido]	Electrical measurements	Resistivity at high pressure
[1992Rad]	Magnetic measurements	Magnetic susceptibility

Reference	Method/Experimental Technique	Type of Property
[1992Iki]	Electrical measurements	Electrical resistivity measured up 80 kbar
[1992Bak]	Magnetic measurements, superconductivity	Effect of uniaxial stress on the superconducting and magnetic transition
[1992Has]	Electrical measurements, point-contact measurements	Interplay of superconductivity, magnetic order and magnetic excitations
[1992Uwa]	Magnetic and electrical measurements	Effect of pressure and magnetic field on the electrical resistivity
[1991Ali]	Electrical measurements	Thermal conductivity, electrical resistivity
[1991Roz]	Electronic structure	Positron-Annihilation study of the electronic structure of URu ₂ Si ₂ , measurements of the two-dimensional angular correlation of annihilation radiation
[1990Fis]	Magnetic and electrical measurements	Effect of pressure and magnetic field on the magnetic and superconducting transition
[1991Bro]	Neutron scattering measurements	Antiferromagnetic order and fluctuations
[1990Sug]	Magnetic measurements	High-field magnetization, magnetoresistance
[1990Mas]	Magnetic and electrical measurements, neutron scattering measurements	Temperature and magnetic field dependence of the antiferromagnetic Bragg peak
[1989Daw]	Magnetic and electrical measurements	Magnetic susceptibility, transport properties
[1987Myd]	Magnetic and electrical measurements	Magnetization susceptibility, high-field magnetization, thermal expansion, resistivity
[1987Nie]	Magnetic measurements	Crystal-fields calculation
[1987Fra]	Magnetic measurements	Crystal-fields calculation
[1987Hie]	Magnetic measurements	Magnetization
[1987Bro]	Magnetic measurements, neutron scattering experiment	Magnetic excitation, superconductivity
[1987Kay]	Magnetic measurements	Magnetostriction
[1987Onu]	Magnetic and electrical measurements	Electrical resistivity, thermoelectric power, magnetic susceptibility, magnetoresistance under hydrostatic pressure, magnetization
[1986Vis]	Electrical measurements	Thermal expansion
[1986Koh]	Magnetic measurements	Magnetic susceptibility
[1980Bar]	Electrical measurements	Superconductivity

Fig. 1: Ru-Si-U.
Partial isothermal
section at 820°C

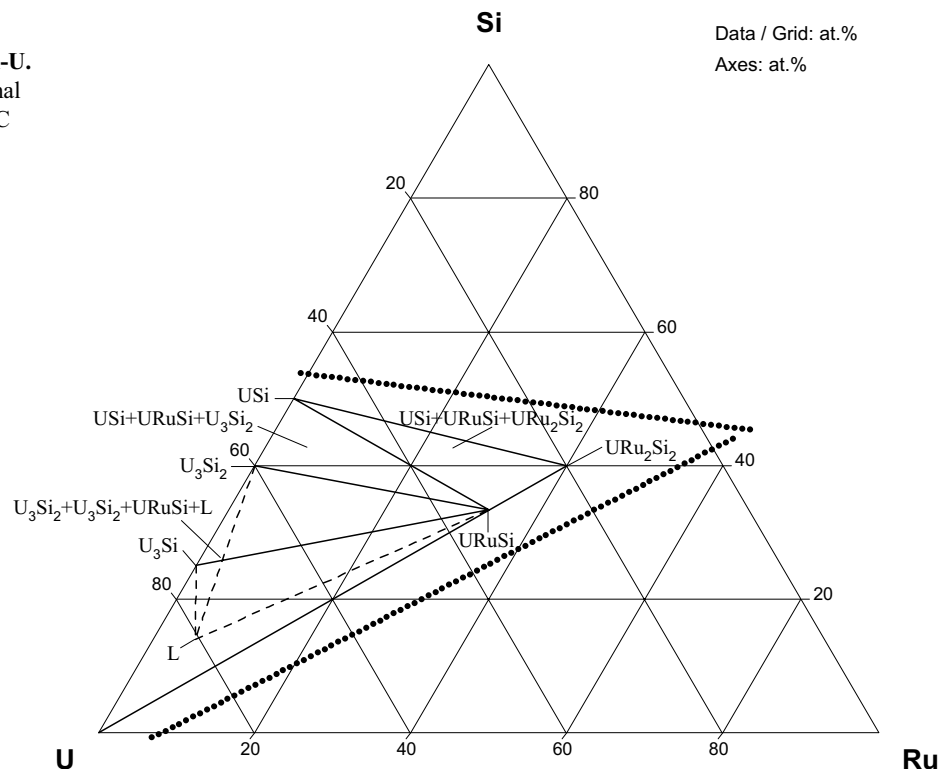


Fig. 2: Ru-Si-U.
Schematic magnetic
(B,T) phase diagram
of URu₂Si₂ with
different
magnetically ordered
phases. Region I
refers to the hidden
order phase, while II,
III, and V constitute
newly discovered
phases. Region IV
was proposed to be a
field-induced
recovery of the
normal metallic
phase

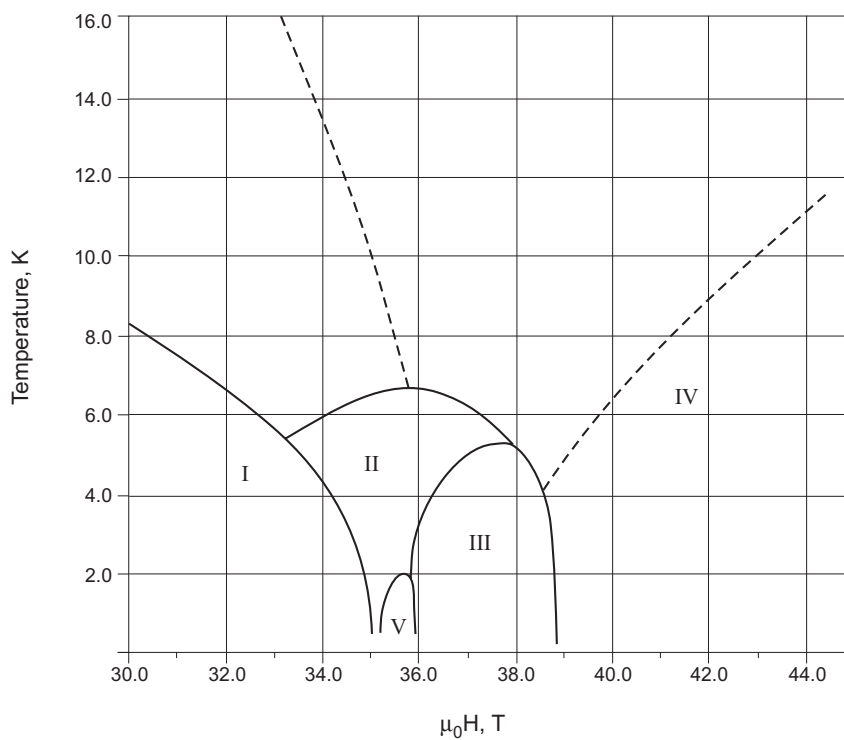
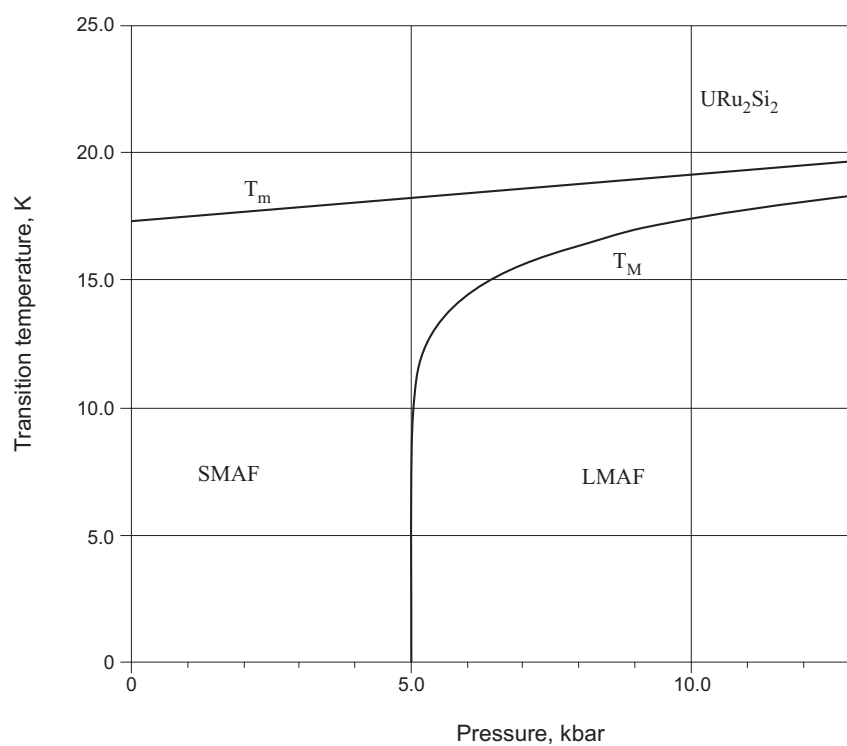


Fig. 3: Ru-Si-U.
p-T phase diagram of
 URu_2Si_2 with
magnetic ordered
phases:
small-moment
antiferromagnetic
phase (SMAF) and
low temperature
antiferromagnetic
phase (LMAF)



Thorium – Uranium – Zirconium

Olga Fabrichnaya

Introduction

Th-U-Zr alloys are important materials for fuel of nuclear reactors [1959Iva, 1967Far, 1968Far1, 1968Far2, 1969Far]. Thorium fuel cycle system has great advantages of resource abundance, less production of transuranium elements and applicability to thermal breeder reactor [1995Yam]. A substantial increase in the ^{233}U isotopic content of the fuel during irradiation demonstrated the attractiveness of Th as a fertile material [1967Far]. Among the systems of ordinary uranium alloys, attention was attracted by metals that possess a high solubility in (γU) and a relatively small cross section for capturing thermal neutrons, such as Zr [1958Iva]. That is why phase relations between solid phases in the Th-U-Zr system are of particular interest. The experimental studies made in the Th-U-Zr system are summarized in Table 1. Carlson [1950Car] investigated the liquidus surface in the concentration range adjacent to the Th-U binary system with Zr contents up to 33 mass%. According to the results of [1950Car] there is no ternary eutectic in the uranium corner of the Th-U-Zr system. Murray [1958Mur] studied the effect of Zr (up to 19 at.%) on the extension of a miscibility gap in the liquid and eutectic temperature found in the Th-U binary system. [1960Mur] studied influence of 2 at.% U addition on the miscibility gap in the bcc phase of the Th-Zr system and demonstrated that U increases the maximal temperature of the miscibility gap and widens its size. Detailed experimental investigations of phase diagrams in the Th-U-Zr system were performed by [1958Iva, 1959Iva, 1961Bad, 1972Bad, 1972Iva] using XRD, microstructural and thermal analysis and hardness measurements. Phase relations between solid phases in the Th-U-Zr system were studied by [1961Bad] at 550-1000°C. The details of this experimental study are reported in [1972Iva]. Liquidus and solidus surfaces were constructed by [1972Bad] using thermal analysis. An early review of phase relations and properties of Zr alloys including the Th-U-Zr alloys can be found from [1963Dou].

Binary Systems

The binary Th-U phase diagram is accepted from the evaluation of [1985Pet]. For the U-Zr system the evaluation of [1989She] is accepted in the present work. The phase diagram of the Th-Zr system is accepted as presented by [1959Bad, 1972Bad] with corrections applied for the temperature of the α - β transition of Th. The phase diagrams of the U-Zr and Th-Zr systems are presented in Figs. 1 and 2.

Solid Phases

The (βZr) forms a continuous solid solution with γU in the U-Zr binary system and with βTh in the Th-Zr binary system. Th and U themselves have limited mutual solubility in solid state. The only binary phase δ is found in the U-Zr system. The summary of solid phases is given in Table 2, showing that no ternary phases have been reported for the Th-U-Zr system.

Invariant Equilibria

The invariant reactions involving solid phases, Table 3, were derived from [1958Iva, 1959Iva, 1961Bad] From their experimental data it was possible to suggest a reaction scheme, taking into account modified temperatures of U_1 and E_3 reactions and the U-Zr binary phase relations as accepted in the present work. The corrected reaction scheme is shown in Fig. 3.

Liquidus, Solidus and Solvus Surfaces

The liquidus and solidus surfaces were experimentally obtained by [1972Bad] using thermal analysis with subsequent study of the microstructure. The results show a three-phase equilibrium $L+(\alpha\text{Th})+(\gamma\text{U})$ which extends from binary Th-U system into a ternary as temperature increases. There should be another

three-phase equilibrium $L+(\beta\text{Th})+(\alpha\text{Th})$ which extends from binary system into a ternary as the temperature increases. However, this reaction was not indicated by [1972Bad]. The liquidus surface shown in Fig. 4 is from [1972Bad] with univariant reaction $L+(\beta\text{Th})+(\alpha\text{Th})$ tentatively indicated by dash lines. [1958Mur] presented a part of the liquidus surface in the U rich corner up to 50 at.% Th which is in a good agreement with the results of [1972Bad].

The solidus surface of the Th-U-Zr ternary system is constructed by [1972Bad] based on experimental studies. The region of Zr rich γ solid solution decreases continuously from the Zr corner to concentration of about 60 at.% Zr. Below this Zr composition the γ -surface contracts and comes close to the binary U-Zr and Th-Zr systems. The remainder of the solidus surface is characterized by the presence of the three-phase equilibrium $L+(\alpha\text{Th})+(\gamma\text{U})$. The boundary of this surface is shown by a dashed line, as obtained from thermal and microstructural analysis. The solidus surface is presented in Fig. 5. A projected solvus surface can be found at [1958Iva, 1959Iva, 1961Bad] constructed on the base of their experimental phase studies.

Isothermal Sections

The isothermal sections were constructed by [1961Bad] based on data of microstructural, X-ray diffraction analysis and hardness measurements of alloys quenched from 1000, 960, 930, 915, 800, 750, 700, 640 and 550°C. The results of [1961Bad] are included in Figs. 6 to 14.

Temperature – Composition Sections

[1960Mur] found a miscibility gap in the γ phase for the binary Th-Zr system and in the Th-U-Zr system at 2 at.% U. It was demonstrated that U as well as other additives resulted in expanding the miscibility gap and in raising its maximum temperature, Fig. 15.

Notes on Materials Properties and Applications

The Th-2.5U-1.0Zr (mass%) alloy fuel elements were being irradiated under water-cooled power-reactor conditions [1968Far1, 1968Far2, 1969Far]. After 403 thermal cycles, the fuel exhibited a 3.8% swelling, as determined by measuring weight and volume of fuel elements in water. The fuel temperatures were maintained between 350 and 600°C with surface temperature of 295°C. No evidence of warpage, bowing or distortion was noted [1969Far]. When given a postirradiation anneal at 800°C for 100 h, the fuel incurred 22.5% total swelling because of the release of fusion gas [1968Far2].

Hydrogen absorption properties of Th-U-Zr alloys were investigated for the purpose of developing of a new hydride nuclear fuel [1994Yam, 1995Yam, 1997Yam1, 1997Yam2, 1998Yam]. The hydrogen absorption properties of four Th-U-Zr alloys with composition of 2:1:6, 1:1:4, 1:2:6 and 1:4:10 (U:Th:Zr ratios) were examined at temperatures from 500 to 900°C and hydrogen pressures from 100 to 10^5 Pa. Regarding the microstructure, the alloy hydrides consisted of three phases: (αU), ZrH_{2-x} and $\text{ThZr}_2\text{H}_{7-x}$, which were finely and homogeneously mixed with each other probably due to formation from one solid solution phase stable at high temperatures [1997Yam1, 1997Yam2]. To get the properties of H-Th-U-Zr alloys, which are needed to utilize them for nuclear fuel, changes in the dimensions and weights of the alloys on hydrogenation and in microstructure and hardness on neutron irradiation to $7.4 \cdot 10^{23} \text{ n} \cdot \text{m}^{-2}$ were examined. The hydrogenated alloys show high apparent densities and high durability for irradiation, which promotes the use of these alloys for a new type of nuclear fuel [1998Yam].

The hardness of Th-U-Zr alloys quenched from 640°C was studied by [1961Bad] to determine the two-phase field boundaries. It is worth noting that γ solid solutions quenched from stable state harden when tempered at 400-550°C, due to the decay of phases formed. The maximum hardness is reached on tempering at 400°C. Increasing the tempering temperature leads to a decrease in hardness of the alloys [1958Iva]. Information about investigations of the Th-U-Zr materials properties is summarized in Table 4.

Miscellaneous

A metastable ω phase with hexagonal structure forms in the Zr rich region [1958Iva, 1972Iva]. On hardening from 1000°C the γ phase undergoes different transformations depending on compositions.

The (α U) phase forms in U rich compositions, the (α Zr) phase forms in Zr rich regime along with metastable ω phase, which is characteristic of hardened alloys of binary U–Zr system. By increasing the Th and U contents the γ phase is preserved on hardening.

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Table 1: Investigations of the Th-U-Zr Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1950Car]	Thermal analysis	Liquidus surface adjacent to Th-U system at Zr up to 33 at. %
[1958Mur]	Thermal analysis, metallographic study, XRD of arc melted alloys and thermal couples after annealing	Annealing at 1000 and 1050°C, thermal analysis up to 1450°C. Influence of Zr (up to 19 at. %) to liquid miscibility gap and eutectic in Th-U system (up to 50 at. % Th)
[1960Mur]	Metallographic method	920-1000°C 40-65 at. % Zr, bcc miscibility gap at 2 at. % U

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1961Bad]	Equilibration and quenching, characterization by XRD and microstructural analysis	1000, 960, 930, 915, 800, 750, 700, 640, 550°C - isothermal sections
[1972Bad]	Thermal analysis, microstructural analysis	Liquidus and solidus surfaces 1075-1800°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α Th) < 1360°C	<i>cF2</i> <i>Fm$\bar{3}m$</i> Cu	$a = 508.45$	at $x = 0$ and $y = 0$ [1985Pet]
(Th _{100-x-y} U _x Zr _y)			dissolves up to 14 at.% Zr and 6.8 at.% U
γ , (Th _{100-x-y} U _x Zr _y)	<i>cI2</i> <i>Im$\bar{3}m$</i> W		(β Th) dissolves up to 12.2 at.% U and from 0 to 100 at.% Zr (γ U) dissolves up to 2.5 at.% Th and from 0 to 100 at.% Zr
(β Th) 1755 - 1360		$a = 411$	at $x = 0$ and $y = 0$ [1985Pet]
(β Zr) 1855 - 863		$a = 360.9$	at $y = 100$ and $x = 0$ [1989She]
(γ U) 1135 - 776		$a = 352.4$	at $x = 100$ and $y = 0$
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	pure U, at 25°C [Mas2] dissolves up to 0.5 at.% Zr and < 0.05 at.% Th
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mm</i> β U	$a = 1075.9$ $c = 565.6$	pure U [Mas2] dissolves up to 1.1 at.% Zr and 0.1 at.% Th
(α Zr) < 863	<i>hP2</i> <i>P6₃/mmc</i> Mg	$a = 323.17$ $c = 514.76$	pure Zr dissolves 0.4 at.% U and 2 at.% Th
δ (U _{100-x} Zr _x) < 617°C	<i>hP3</i> <i>P6/mmm</i> AlB ₂	$a = 503$ $c = 308$	63-78 at.% Zr at 66.67 at.% Zr [1989She] dissolves up to 4 at.% Th
ω	<i>h*</i>	-	Metastable. Form in the Zr rich region [1958Iva, 1972Iva]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Th	U	Zr
$\gamma_U \rightleftharpoons (\alpha\text{Th}) + \gamma_{\text{Zr}} + (\beta\text{U})$	~680	E ₁	-	-	-	-
$(\beta\text{U}) \rightleftharpoons (\alpha\text{U}) + (\alpha\text{Th}) + \gamma_{\text{Zr}}$	~650	E ₂	-	-	-	-
$(\alpha\text{Zr}) + \gamma_{\text{Zr}} \rightleftharpoons (\alpha\text{Th}) + \delta$	~605	U ₁	-	-	-	-
$\gamma_{\text{Zr}} \rightleftharpoons (\alpha\text{U}) + (\alpha\text{Th}) + \delta$	~600	E ₃	-	-	-	-

Table 4: Investigations of the Th-U-Zr Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1961Bad]	Quenched alloys at 640°C	Hardness
[1968Far1, 1968Far2, 1969Far]	Test in thermal cycling 350-600°C by weighing in water; alloys Th-2.5U-1.0Zr (mass%)	Swelling
[1998Yam]	Hydrogen pressure 100 kPa and 800°C Micro-hardness and density measurement for H-Th-U-Zr alloys	Vickers microhardness, density

Fig. 1: Th-U-Zr.
Phase diagram of the
U-Zr system

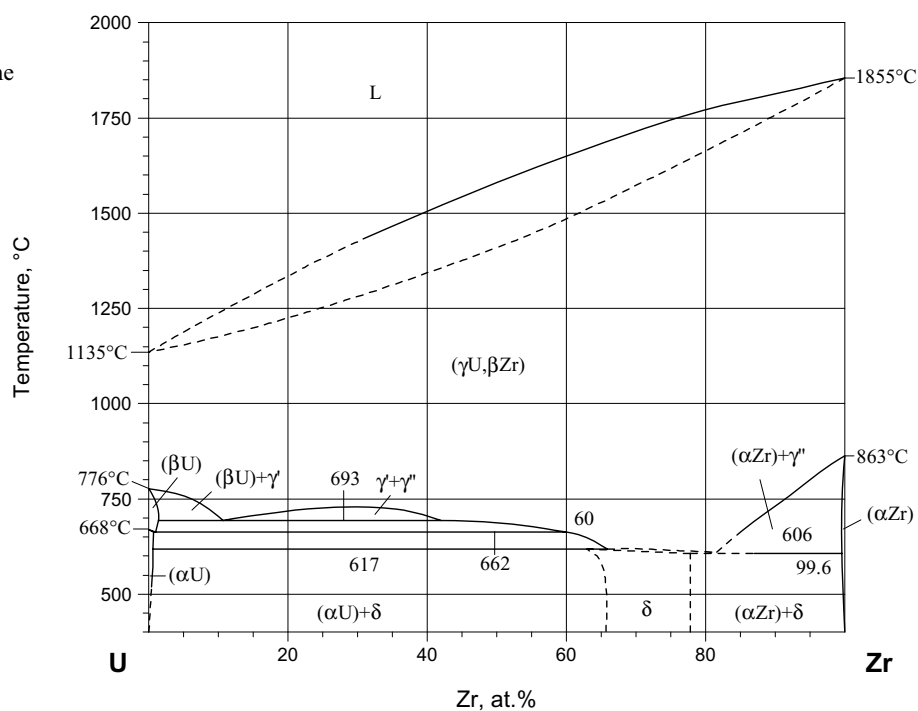
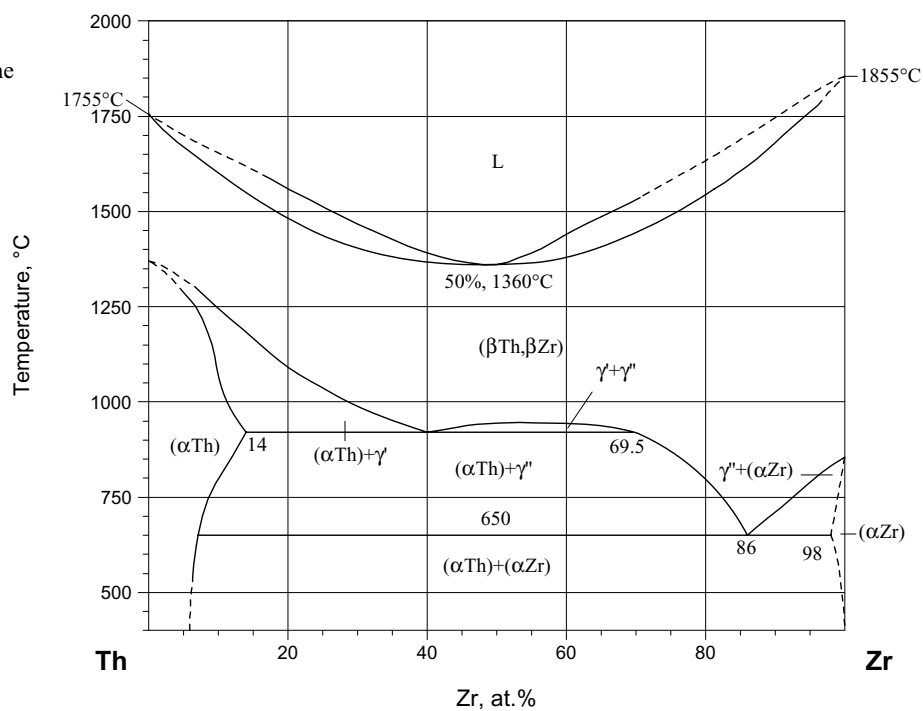


Fig. 2: Th-U-Zr.
Phase diagram of the
Th-Zr system



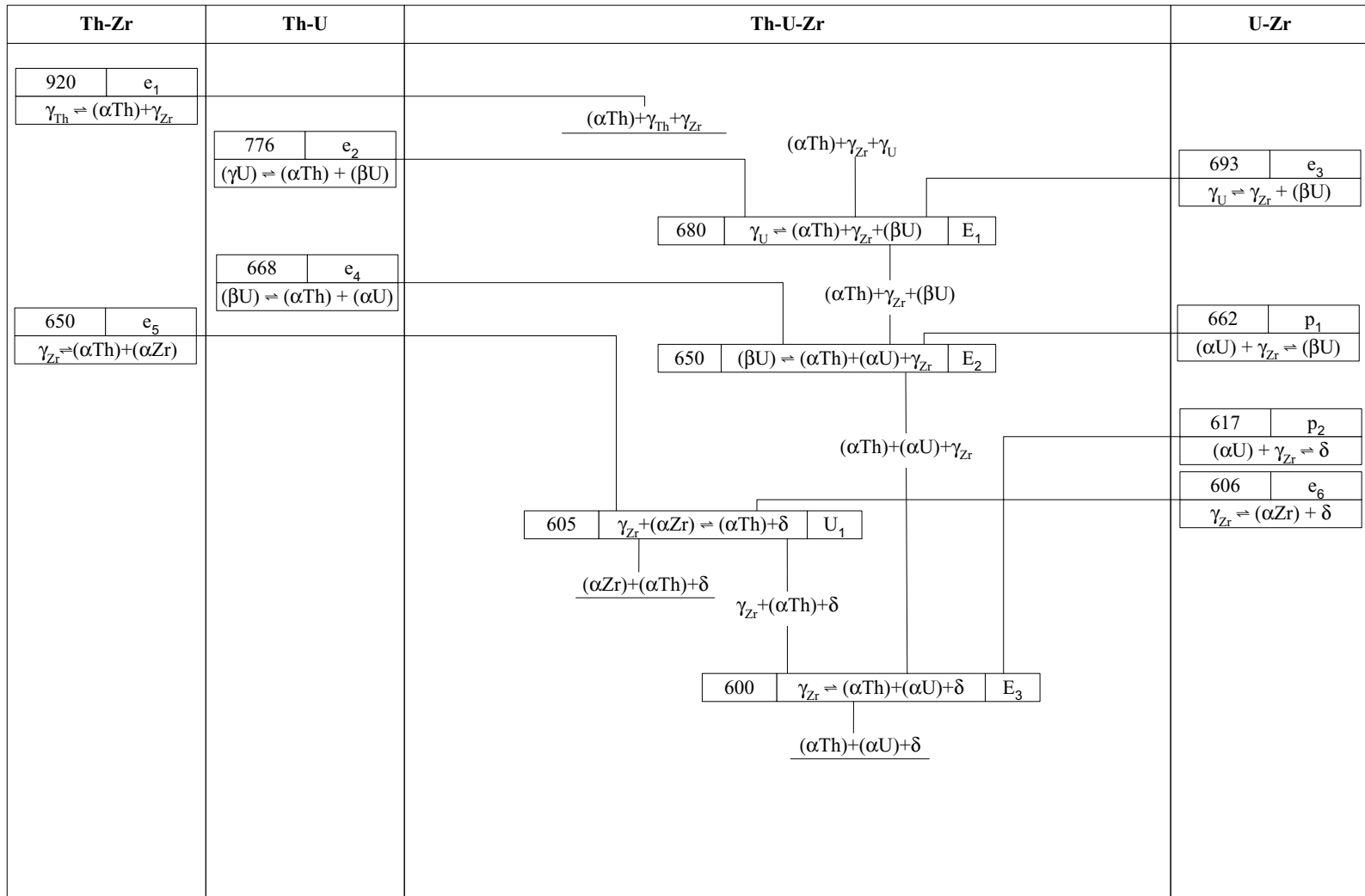


Fig. 3: Th-U-Zr. Partial reaction scheme

Fig. 4: Th-U-Zr.
Liquidus surface
projection

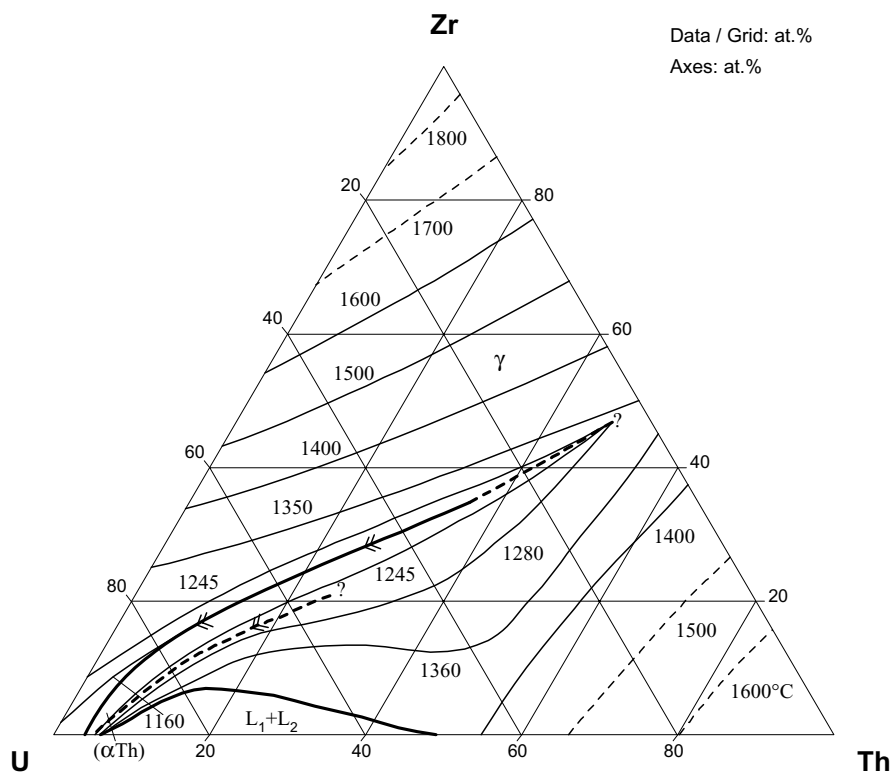


Fig. 5: Th-U-Zr.
Solidus surface
projection

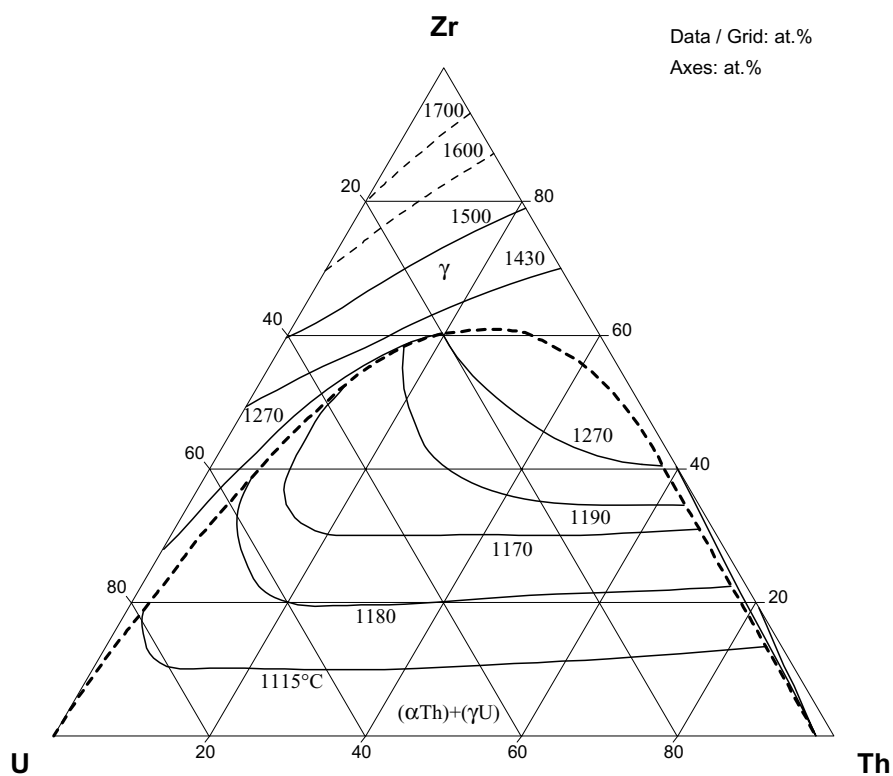


Fig. 6: Th-U-Zr.
Isothermal section at
1000°C

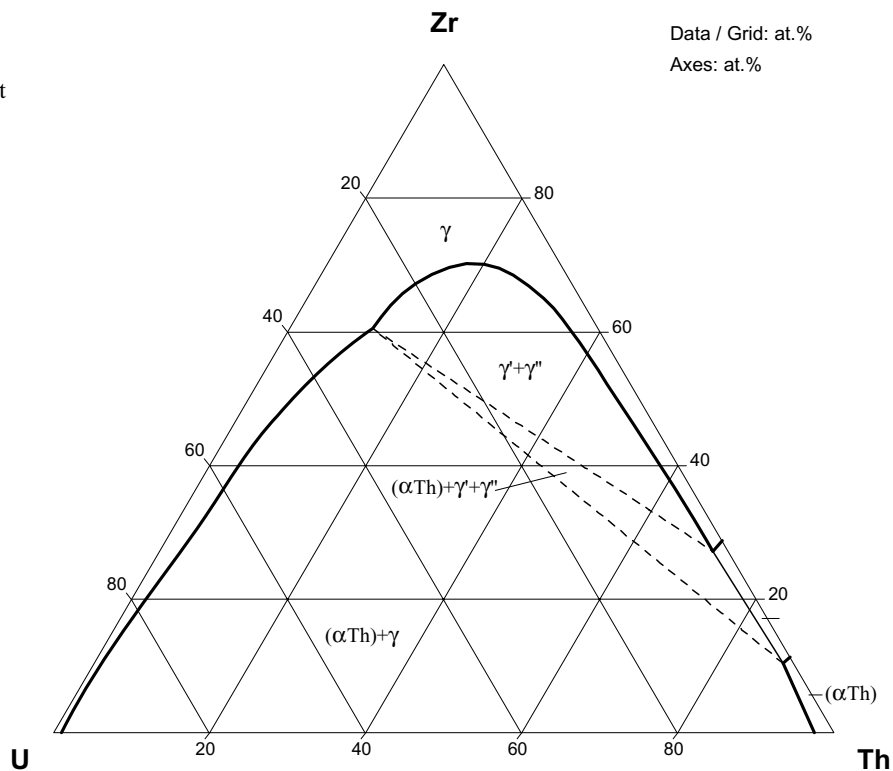


Fig. 7: Th-U-Zr.
Isothermal section at
960°C

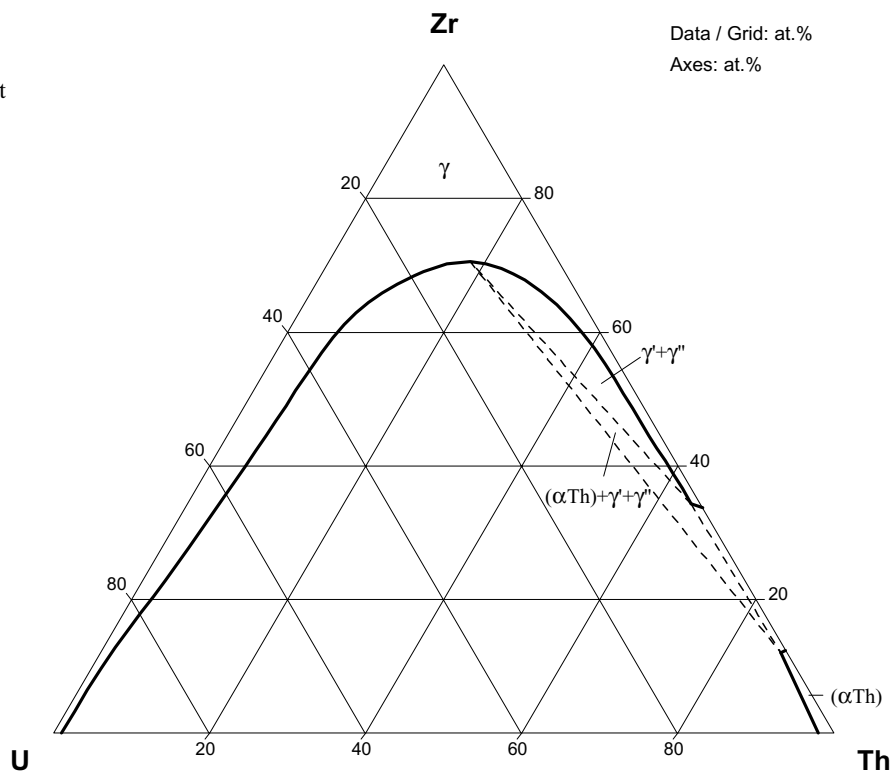


Fig. 8: Th-U-Zr.
Isothermal section at
930°C

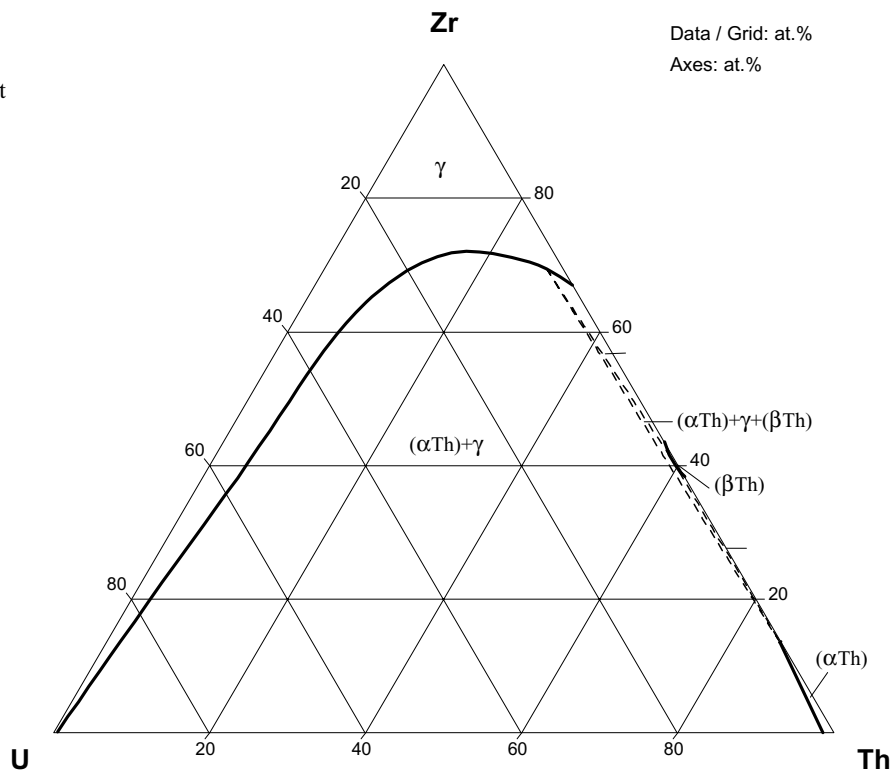


Fig. 9: Th-U-Zr.
Isothermal section at
915°C

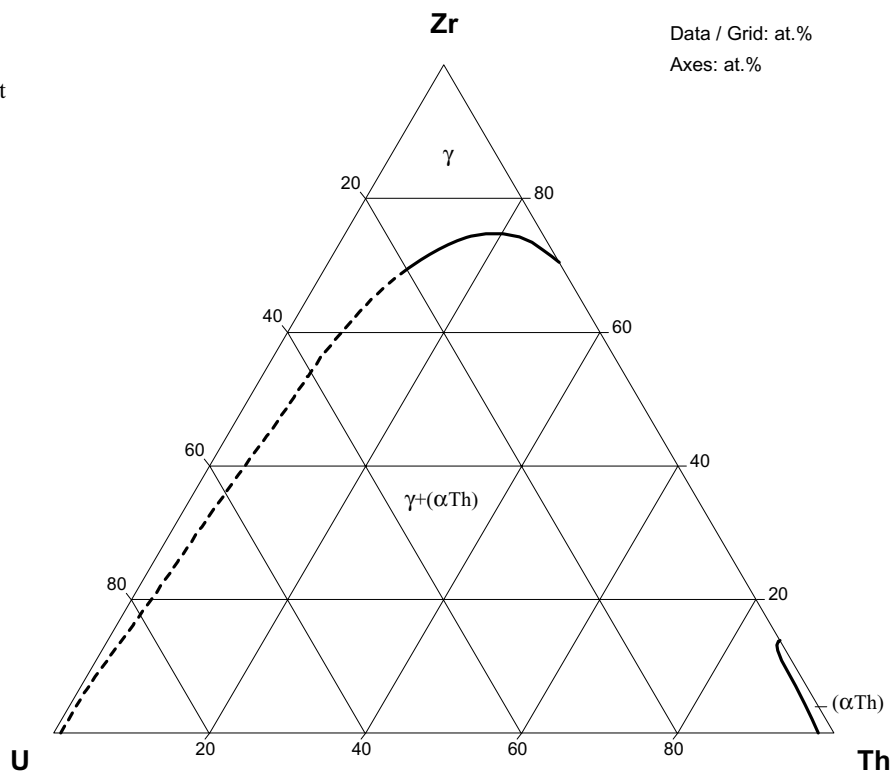


Fig. 10: Th-U-Zr.
Isothermal section at
800°C

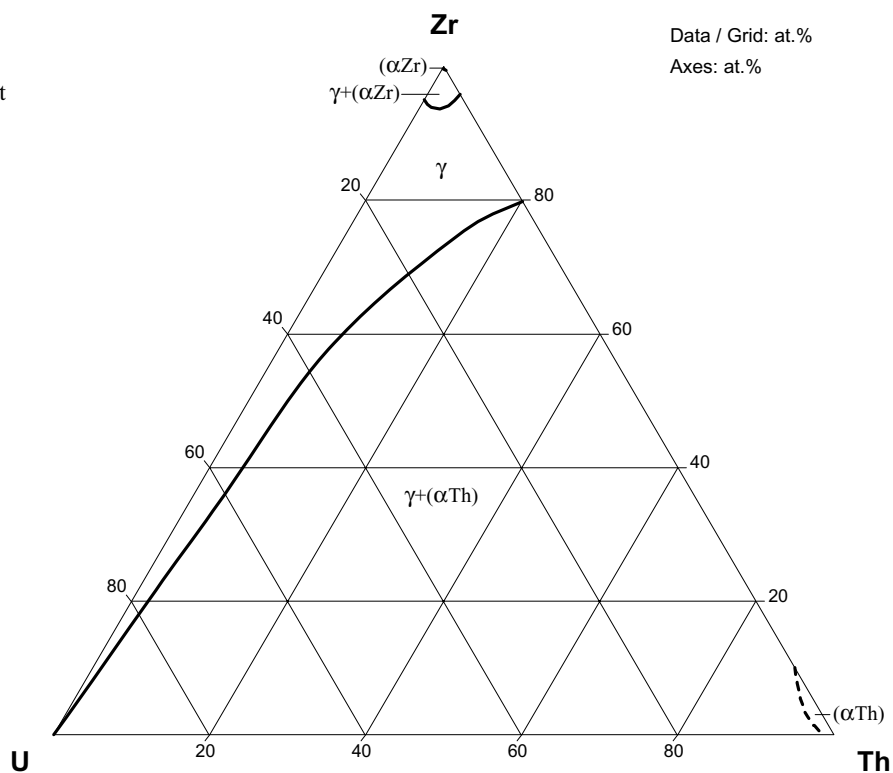


Fig. 11: Th-U-Zr.
Isothermal section at
750°C

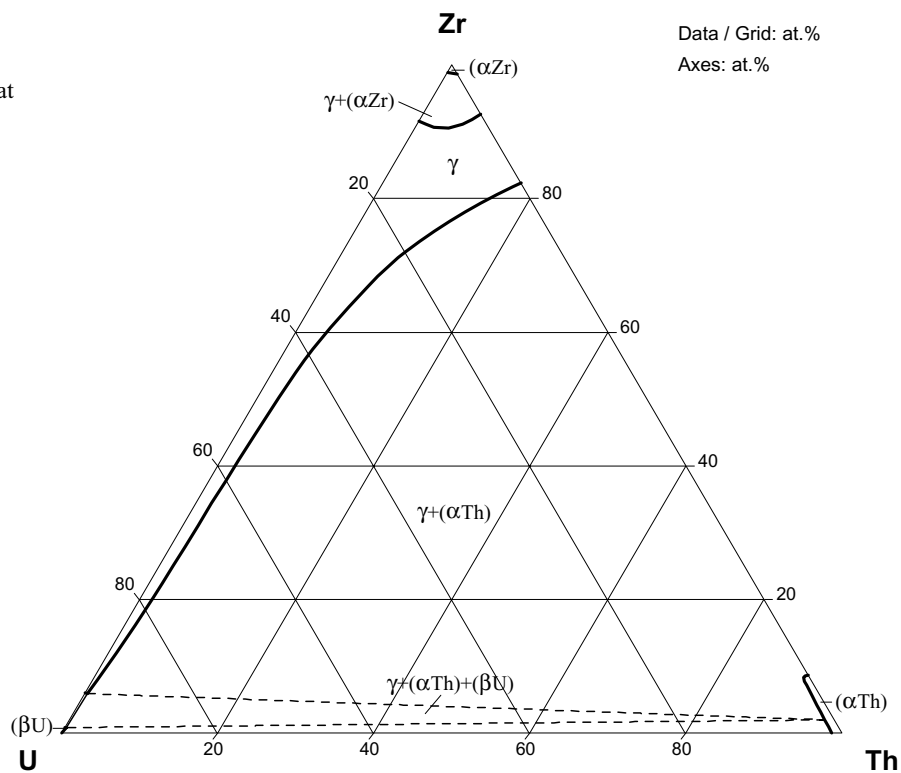


Fig. 12: Th-U-Zr.
Isothermal section at
700°C

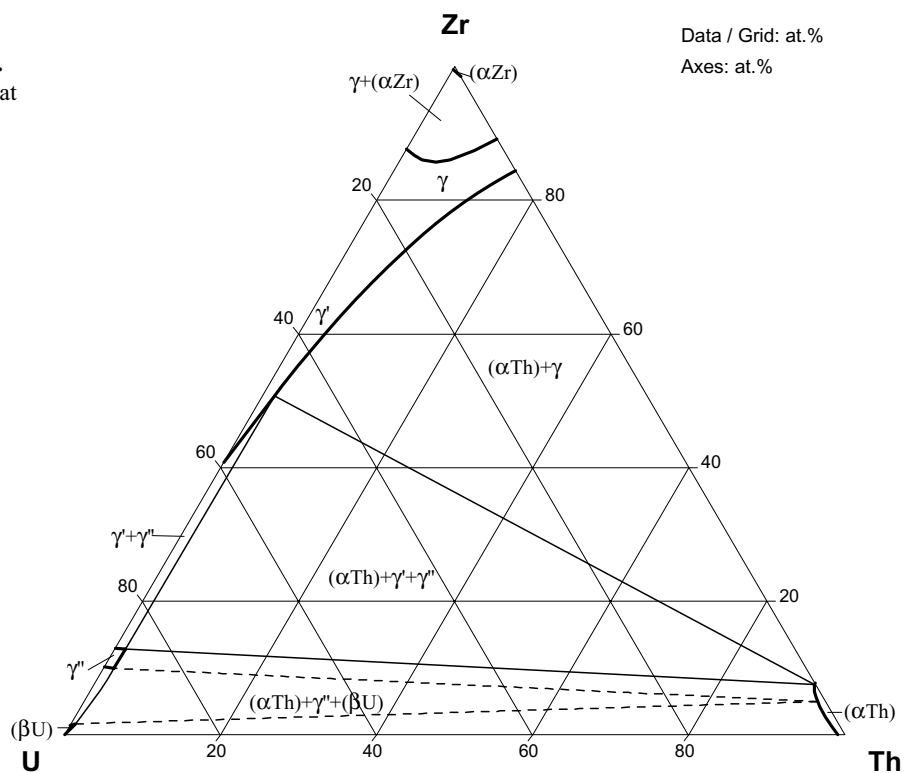


Fig. 13: Th-U-Zr.
Isothermal section at
640°C

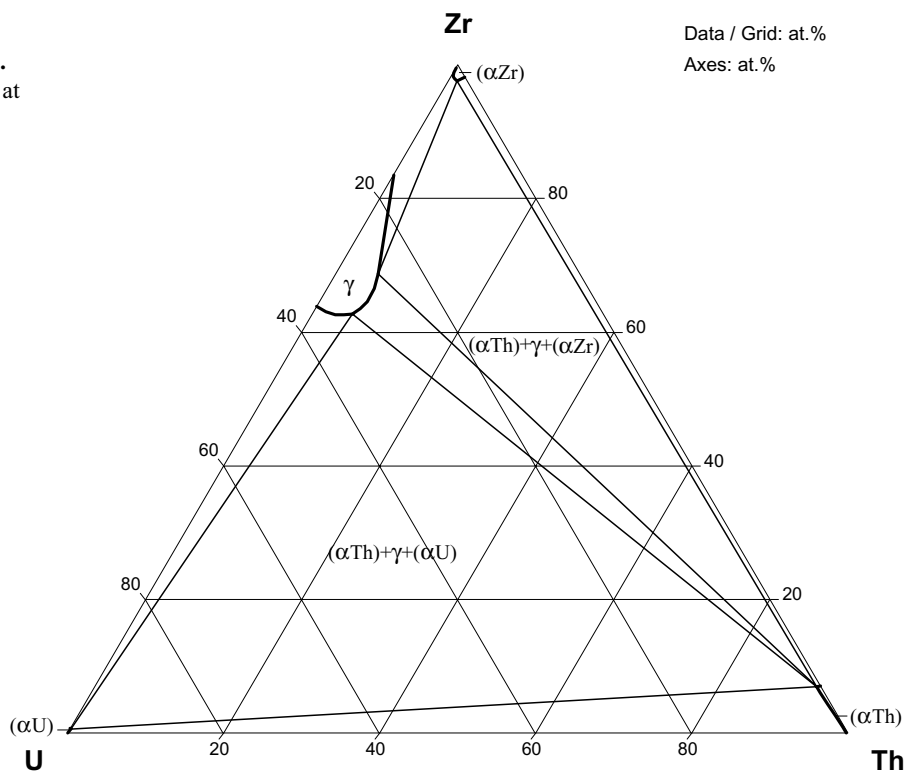


Fig. 14: Th-U-Zr.
Isothermal section at
550°C

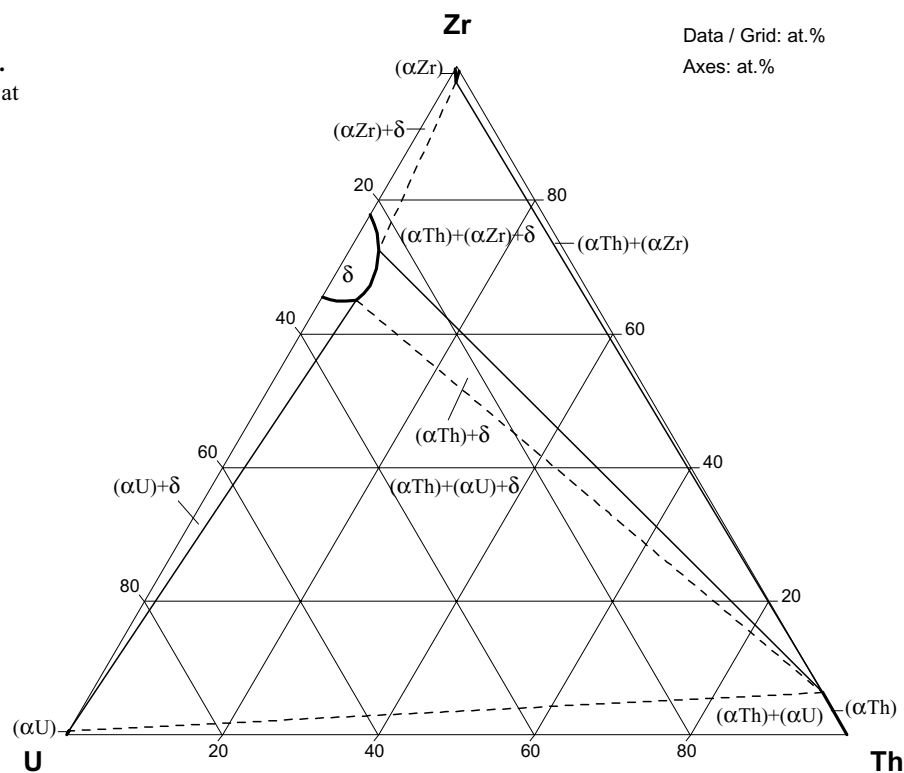


Fig. 15: Th-U-Zr.
Miscibility gap in the
 γ phase at 0 and 2
at.% U

