TECHNICAL REPORTS SERIES No. 14

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THE URANIUM-CARBON AND PLUTONIUM-CARBON SYSTEMS

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THE URANIUM-CARBON AND PLUTONIUM-CARBON SYSTEMS

A Thermochemical Assessment

A REPORT FROM THE PANEL ON THE THERMODYNAMIC PROPERTIES
OF THE URANIUM-CARBON AND PLUTONIUM-CARBON SYSTEMS
HELD IN VIENNA, 8 - 12 OCTOBER 1962

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA 1963

THE URANIUM-CARBON AND PLUTONIUM-CARBON SYSTEMS,
IAEA, VIENNA, 1963
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FOREWORD

The development of advanced types of nuclear reactor has underlined the importance of two new groups of fuel materials, the uranium carbides and the plutonium carbides. The present degree of interest in these substances was illustrated by the large number of papers about them submitted to the Symposium on Thermodynamics of Nuclear Materials held by the Agency during May 1962 in Vienna. However, a considerable number of discrepancies were found among the results reported by the different investigators. After the Symposium, a few scientists started to evaluate the data more fully in an effort to discover the reasons for the disagreements. Their work was collected by a panel which was set up by the Agency to discuss in detail all the presently available thermodynamic data on these carbides. This panel not only made such a critical evaluation but also recommended a set of thermodynamic values as being the most reliable of those available: they also indicated areas in this field where further exploration was needed. The findings of the panel are presented by the Agency in this issue of the Technical Reports Series in the belief that they will prove of value to scientists and engineers working on this aspect of nuclear technology.

SIGVARD EKLUND
Director General

February 1963

ACKNOWLEDGEMENT

The Panel Meeting on the Thermodynamic properties of nuclear materials was held on 8-12 October 1962 at the Headquarters of the International Atomic Energy Agency in Vienna, to assess the thermodynamic properties of the uranium-carbon and plutonium-carbon systems. The members of the Panel were as follows:

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Professor Edgar F. Westrum,	Department of Chemistry, University of Michigan, Ann Arbor, Michigan, USA
and	
Dr. R. Hara (Scientific Secretary)	Division of Research and Laboratories, International Atomic Energy Agency, Vienna I, Kärntnerring 11

The following reports were submitted to the panel, and the assessment contained in this publication was based on these reports:

1.	O. Kubaschewski:	Chemical thermodynamics of metals: measurements, assessments and applications.
2.	T. Mukaibo and K. Naito:	On the thermochemical properties of uranium carbides.
3.	H. A. Eick, E. G. Rauh and R. J. Thorn:	Thermodynamic properties of carbides at high temperatures.
4.	D. T. Livey:	A review of carbide data in the light of recent phase studies.
5.	M. H. Rand:	Thermodynamic data of uranium carbides.
6.	F. Benesovsky, A. Neckel, H. Nowotny, E. Rudy:	Thermodynamic data on uranium carbides and related compounds.
7.	C. E. Holley, Jr.:	The thermodynamic properties of the uranium and plutonium carbides.
8.	V. V. Achachinsky:	Critical evaluation of thermodynamic data of uranium and plutonium carbides.
9.	Edgar F. Westrum Jr.:	Thermodynamic properties of actinide carbides with special reference to the entropies of uranium mono- and dicarbides. (In collaboration with Dr. H. K. Lonsdale and Mr. E. Suits for the experimental studies).

The introduction was written by Dr. L. E. J. Roberts; Chemistry Division,
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CONTENTS

NOTATION

a, c	Lattice constants (Å).
C_p	Molar heat capacity (cal mole^{-1} $^{\circ}$K^{-1}).
γ	Activity coefficient.
ΔG^0	Gibbs standard free energy of formation or reaction (kcal/mole or cal/mole).
H	Heat content, enthalpy (kcal/mole or cal/mole).
ΔH^0	Heat of formation (or reaction) (kcal/mole or cal/mole).
ΔH^0_{298}	Heat of formation at 25°C.
L_t, L_f	Heats of transformation and of fusion respectively (kcal/mole or cal/mole).
N_A, N_B	Mole fractions ($N_A + N_B = 1$).
p	Pressure (atm or mm Hg).
R	Gas constant (1.986 cal mole^{-1} $^{\circ}$K^{-1}).
S^0_{298}	Standard entropy (cal mole^{-1} $^{\circ}$K^{-1}).
ΔS^0	Entropy of formation (or reaction) (cal mole^{-1} $^{\circ}$K^{-1}).
T	Absolute temperature (°K).
	1 cal = 4.186 joules.

Various types of bracket have been used to denote states of aggregation:

$\langle$solid$\rangle$, {liquid}, (gaseous), [dissolved].

1. INTRODUCTION

The carbides of uranium and plutonium are potentially valuable fuel materials for nuclear reactors; uranium monocarbide, for example, has been reported to combine a high melting point and high thermal conductivity with good resistance to irradiation damage. Various proposals for the use of carbides have been made; they could be used alone, canned in a suitable material, or dispersed in another phase, such as a metal or graphite or a non-fissile carbide. Carbides could be used to fuel both fast and thermal reactors. The lower carbides, or solid solutions of UC and PuC, are usually considered for fast reactor fuels, while the higher carbides dispersed in graphite have been considered as fuels for various designs of high-temperature, gas-cooled thermal reactors. Different parts of the fuel assembly may be required to operate over a wide range of temperatures, perhaps from 500 to 1500°C.

Three carbides of uranium and three of plutonium have been described. They can be prepared by the reaction of the respective metals with carbon or with hydrocarbons, or by reduction of the oxides with carbon. They are commonly fabricated into fuel element shapes by various sintering or arc-melting procedures, at temperatures of 1500 to above 2500°C.

During preparation, and in use, these carbides will be in contact with a variety of materials over a wide range of temperatures, and, possibly, in different gaseous atmospheres. The stability of the various phases on temperature cycling, and for long times at different temperatures, is an important technical consideration. It is, therefore, desirable to establish the equilibrium phase diagrams accurately and to know the effect of impurities introduced during manufacture on the relative stability of the different structures. Accurate thermodynamic data, including a knowledge of solid solution or non-stoichiometric ranges, are also essential for the assessment of various compatibility problems and the calculation of the composition of phases prepared by different preparative routes.

A large number of papers on these subjects were submitted to the Symposium on Thermodynamics of Nuclear Materials held by the IAEA in Vienna in May, 1962*. Several discrepancies were apparent between the results reported from different laboratories. The Agency therefore called together a discussion panel to investigate the thermodynamic data on these carbides in detail and to resolve the discrepancies if possible.

2. PREPARATION OF URANIUM CARBIDE SAMPLES

METHODS

The two principal methods of preparation are:

(a) Uranium metal is reacted at high temperature with carbon, which may be provided in various forms, e.g. graphite, carbon black, methane.

(b) Uranium oxide is reacted with carbon at high temperature.

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* Proceedings published September 1962 as "Thermodynamics of nuclear materials", IAEA, Vienna (1962)

To obtain pure uranium carbide phases, elimination of oxygen and nitrogen is essential since nitrogen has been shown to be soluble in the sodium-chloride type phase as a UC/UN solid solution [1, 2], and oxygen in the tetragonal phase to form a UC_xO_y solution [3, 4].

For method (a) the materials used must therefore be freed of these elements. If solid carbon is used, it is preferable for the experiment to be carried out in a high vacuum.

Method (b) is only suited to the formation of the highest carbon containing compound of uranium, since control of the reduction reaction at an intermediate stage is a difficult process. The phase formed by method (b) depends on the conditions under which reduction is effected, since experiments have shown [3, 4] that the tetragonal "UC_2" phase is stablized by solution of oxygen, while at a low oxygen potential the sesquicarbide U_2C_3 is preferentially formed. It would be expected therefore that method (b) would result in an oxygen-containing tetragonal "UC_2" phase, unless high vacuum is employed to carry the reaction to a stage of very low oxygen content.

Other impurities which could play a part in the phases which exist under given conditions are silicon and iron. Furthermore the effect of various materials such as tungsten and tantalum used as heating elements, etc. during preparation can be seen from a study of ternary systems, e.g. U-C-Ta [5].

SPECIFICATION

It is common to specify the phases which are used in general studies only by X-ray analysis, but for complete evaluation metallographic work [6] and chemical analysis are essential.

Furthermore even when the impurities discussed above can be reduced to negligible quantities the heat treatment which a specimen has undergone may effect the final form of the material. It has been observed by BUCKLEY [7], for example, that a decrease in the lattice parameter of UC may result from rapid rates of cooling, due, it is suggested, to the existence of a defect structure at high temperature deficient in carbon. At high temperatures, variations in the carbon content of phases above their stoichimetric composition will also lead to varied lattice parameters.

URANIUM MONOCARBIDE, UC

Various lattice parameters have been reported as in Table I. Much of the reported variations may be due to impurities, particularly nitrogen as UN or oxygen as UO. The lattice parameter of UN is reported to be 4.8897 ± 0.0003 Å [1], and the UC-UN system shows a complete range of solid solutions [1, 2]. No comparable systematic study of the role of oxygen has been made, nor of the U-C-O-N system.

General experience indicates that when UC is prepared by the vacuum sintering of uranium and graphite powders (10^{-5} mm Hg) then the lattice parameter at room temperature is given by a = 4.961 ± 0.001 Å after annealing at approximately 1200°C in vacuum. Subsequent analysis [3] of such a phase has shown that the nitrogen content is $<$ 100 ppm and this parameter therefore appears to be the nearest approach to the true value for UC.

TABLE I

LATTICE PARAMETERS OF URANIUM MONOCARBIDE (UC)
(Heat treatments not always known)

Parameter (Å)	Reference
4.9554 ± 0.0003	[8]
4.9614 ± 0.0005	[9]
4.961) (other values are between 4.968) 4.961 - 4.968)	[10]
4.951	[11]
4.955	[12]
4.9598 ± 0.0003	[13]
4.951 ± 0.001	[14]
4.962	[5]
4.955	[15]
4.960 ± 0.0002	[16]
4.9600 ± 0.0005	[17]
4.9605 ± 0.0004	[2]
4.961 ± 0.001	[3]

The required conditions of pure components and a pure atmosphere can be realized with other methods of preparation such as arc-melting. For this particular case the above lattice parameter may not be observed unless a subsequent high-temperature anneal is also carried out to allow equilibrium to be attained after the quench usually involved with this process. Since it is very difficult to prepare pure UC, some dicarbide or uranium normally being present, erroneous values of lattice parameter may result on quenching, unless some special techniques are applied. There is some indication of this in the high value, e.g. a = 4.968 Å, reported by BURDICK et al. for a quenched sample [10] . It is suggested that such a high value has to be attributed to a higher carbon content at high temperature.

URANIUM SESQUICARBIDE, U_2C_3

From recent experiments [3] it has been shown that U_2C_3 appears to have a very low solubility for oxygen and nitrogen. Furthermore the homogeneity range for this phase appears to be very narrow in the binary system. This is indicated, as in Table II, by the small deviation in the lattice parameter of U_2C_3 reported by many workers.

TABLE II

LATTICE PARAMETERS OF URANIUM SESQUICARBIDE (U_2C_3)

Parameter (Å)	Reference
8.0870 ± 0.0005	[9]
8.089 ± 0.001	[10]
8.088 ± 0.001	[18]
8.0885 ± 0.0005	[13]
8.088 ± 0.001	[3]

URANIUM DICARBIDE, "UC_2"

Uranium dicarbide exists in a tetragonal form up to ~ 1800°C and in a cubic form above that temperature. This section is concerned with the preparation of the tetragonal form since the cubic structure has never been retained at low temperatures.

A relatively large scatter in the measured lattice parameter of this phase appears to exist depending principally on oxygen which shows solubility in the tetragonal structure [3, 4]. Lattice parameters noted under two different conditions are shown in Table III. Various other reported parameter figures are shown in Table IV, which gives a wider range of values than that noted in Table III. This is perhaps caused by variations in heat treatment resulting in different carbon contents for the examined phase.

TABLE III

LATTICE PARAMETERS OF THE TETRAGONAL PHASE AFTER ANNEALING AT 1500°C [3]

Conditions	Parameter (Å)
Vacuum: 10^{-5} mm Hg UO_2 present	a = 3.525 ± 0.001 c = 6.00 ± 0.01 in equilibrium with U_2C_3
	a = 3.517 ± 0.001 c = 5.98 ± 0.01

TABLE IV

LATTICE PARAMETERS OF TETRAGONAL URANIUM DICARBIDE AT ROOM TEMPERATURE

Lattice parameters		Reference
a (Å)	c (Å)	
3.515	5.990	[15]
3.523 ± 0.002	5.996 ± 0.003	[19]
3.516	5.972	[9]
3.517	5.987	[11]
3.54	5.99	[12]
3.509 ± 0.003	5.980 ± 0.005	[1]
3.517 ± 0.001	5.987 ± 0.001	[14]
3.517 ± 0.002	5.987 ± 0.002	[20]
3.5266 ± 0.0005	6.0023	[21]

3. PHASE DIAGRAM

From the data available at the present time no complete equilibrium diagram can yet be established for the pure binary system. The major transformations and reactions which have been observed with various phases are reproduced in Fig. 1 and are considered separately below. Recent experiments [3, 4, 19, 22], have shown that the tetragonal dicarbide phase always appears to exist with a carbon content less than the stoichiometric ratio. This phase is therefore referred to as "UC_2" on this understanding.

It has also been shown that oxygen [3, 4] and nitrogen [3] play a considerable part in controlling the appearance of various phases. It is emphasized therefore that this is an aspect which requires detailed and extensive study.

MELTING POINTS

Uranium monocarbide (UC) appears to melt congruently and some of the various values reported for the melting point are given in Table V. Further work is required to determine the melting point more precisely, particularly as nothing is known at the present time of the effect of various impurities of which oxygen and nitrogen are of special interest.

Agreement exists that uranium sesquicarbide (U_2C_3) does not melt congruently but decomposes at high temperature (see later) to UC and "UC_2"

The uranium dicarbide ("UC_2") phase has been reported to form peritectically at 2500°C from a uranium-carbon melt (~ 8.5%C) plus graphite.

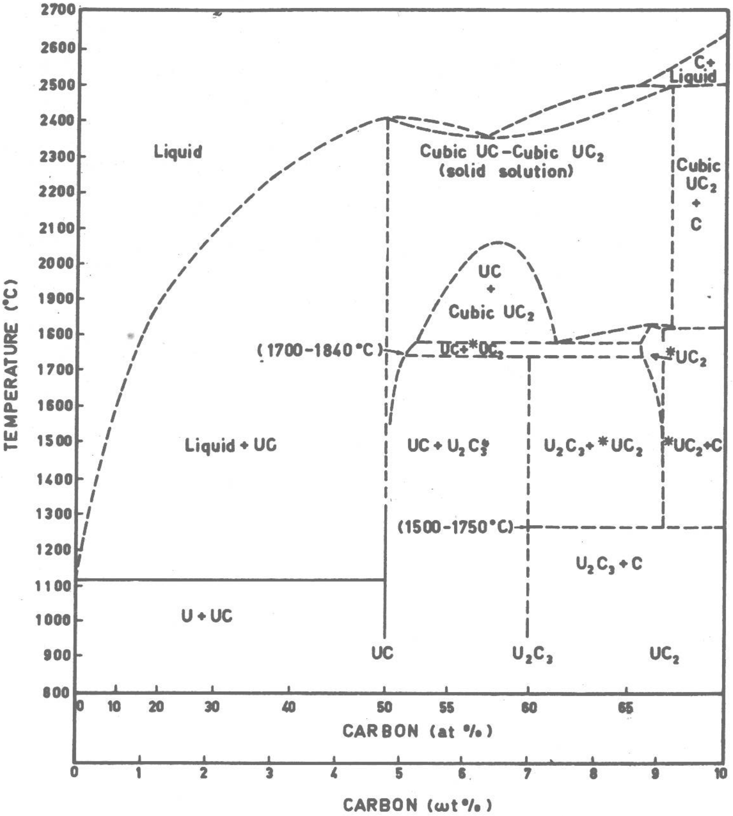

Fig. 1

Phase diagram of the uranium-carbon system
($^*UC_2$ represents tetragonal UC_2)

TRANSFORMATIONS

UC. No transformation in crystal structure has been reported for UC, the cubic structure remaining stable up to the melting point. The range of homogeneity for this phase appears to increase markedly above the stoichiometric ratio at high temperature and also to some extent below the stoichiometric ratio [7].

U_2C_3. No transformation in crystal structure has been reported for this phase. The constancy in lattice parameter referred to in section 2 also suggests that the homogeneity range is very narrow.

"UC_2". The tetragonal "UC_2" phase is reported [12] to transform to a cubic form at 1820°C, a diffusionless transformation being found by CHANG [29]. The tetragonal form has been shown to have some solubility for oxygen [3]