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**THERMODYNAMIC PROPERTIES AND PHASE RELATIONSHIPS
IN THE U-C SYSTEM AND SELECTED U-M-C SYSTEMS**

By

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ABSTRACT

Results of extensive phase and thermodynamic studies made over the last few years strongly suggest only small differences in stability for the different uranium carbides.

Partial phase diagram studies have been made on several U-M-C ternary systems. Studies of the U-Zr-C and the U-Nb-C system indicate improved physical properties and stability for (U,M)C solid solutions in some reactor fuel applications. A relatively large number of compounds of the type UMC_2 exist and may exhibit desirable properties as specific reactor fuels. For example, $UMoC_2$ does not hydrolyze and does not react with C to form UC_2 .

Introduction

During the last few years, refractory uranium compounds have received increasing attention as possible fuels for high temperature reactors. The uranium carbides, in particular, have been investigated in many different Laboratories. However, additional work is still required, not only to resolve a small amount of conflicting data, but also to provide the very detailed knowledge required for actual use of any material as a reactor fuel.

At the Los Alamos Scientific Laboratory, a continuing program has been concerned with determinations of phase relationships and thermodynamic parameters of the different phases in the U-C system. In addition, selected domains of several ternary systems have been investigated in order to find possible methods for increasing the general thermodynamic stability of uranium in carbide phases or for improving specific properties such as melting point, resistance to oxidation or hydrolysis, and high temperature strength. Although the studies have not been completed, interesting results have been obtained.

Experimental

In all of the experimental work, emphasis has been placed on avoiding impurities especially oxygen and nitrogen. Therefore,

starting compositions were prepared by arc-melting pure metals with spectroscopic grade graphite on a water-cooled copper hearth in purified argon. Where a powder was required, the arc-melted material was ground in an inert atmosphere. Heat treatments and annealings were made at pressures between 10^{-5} and 10^{-7} torr. Samples were carefully characterized by means of X-ray diffraction, metallography and chemical analysis.

U-C Phases

Observations made at LASL during studies of the U-C system have been described recently by Witteman and Bowman.⁽¹⁾ These observations, together with results of vaporization studies, were utilized by Bowman and Krupka⁽²⁾ in a discussion of the thermodynamic properties of the uranium carbides. It was concluded that only small differences exist in heats and entropies of formation of the different U-C phases. Thus, relatively small changes in experimental conditions are sufficient to convert one phase into another. For example: the U_2C_3 phase can be formed by the reaction of $UC + C$ at temperatures between $1200^\circ C$ (and probably lower) and $1780^\circ C$. The UC_2 phase can be formed by the reaction of $U_2C_3 + C$ (and by $UC + C$) at temperatures above $1500^\circ C$.[†] Conversely, UC_2

[†] It must be noted that different temperatures have been reported for the decomposition of the UC_2 phase. Additional work may be necessary to fix the temperature.

decomposes to $U_2C_3 + C$ at temperatures below $1500^\circ C$ and U_2C_3 disproportionates at $1780^\circ C$ to $UC + UC_2$.

The various vaporization studies of $UC^{(3,4,5)}$ and $UC_2^{(6,7,8,9,10)}$ have produced a range of values. Perhaps the most significant fact that can be considered in an evaluation of these studies is the congruent vaporization composition redetermined by Krupka⁽²⁾ as $UC_{1.065 \pm 0.025}$ for the temperature range $2100^\circ - 2300^\circ C$. This fact together with some assumptions, permits one to calculate maximum permissible pressures of uranium for UC and UC_2 . In the case of UC , it was assumed that the free energy values for $UC^{(11)}$ could be applied to $UC_{1.065}$. The vapor pressure values are given in Table 1. It would appear that the Langmuir values are better than the Knudsen values in this case. The latter values could be in error due to reactions with the crucible material. For UC_2 the maximum uranium pressure at $2273^\circ K$ which still permits preferential loss of C has been calculated and compiled with literature values in Table 2. In the case of Fujishiro and that of Alcock and Grievson it was necessary to extrapolate their data to this temperature. It can be seen that the first three values permit carbon losses such that the composition shifts from UC_2 toward $UC_{1.065}$. The last two

values require a preferential loss of uranium if the vaporizing species are $U_{(g)}$ and $C_{(g)}$ so that one should end up with UC_2 upon vaporizing a sample.

Solid Solutions of UC

Uranium monocarbide can be dissolved in some of the refractory carbides to form solid solutions which permits lowering the thermodynamic activity of uranium carbide. This can then be used to raise the melting point of the carbon eutectic or suppress UC_2 formation. The carbides best suited for this in thermal reactors are ZrC and NbC.

In addition, these solid solutions when heated with graphite can give pertinent thermodynamic data. The free energy of formation of UC_2 from UC and graphite has been determined by studying the following reaction;⁽¹²⁾

One heats a solid solution with excess graphite a sufficiently long time to achieve equilibrium with C and UC_2 . The UC content of the solid solution is determined at room temperature by inspection of its lattice parameter. Then by assuming UC_2 and C were present at unit activity i. e. were present as the pure solids at temperature, one can calculate free energies.

This reaction was studied using the U-Zr-C system. In

order to approach equilibrium from both sides, two series of samples were used. One set was made up of mixtures of UC_2 , ZrC and C. The other consisted of a mixture of the UC-ZrC solid solution of various concentrations with graphite. These were heated to $1500^\circ C$ under a partial atmosphere of hydrogen for varying times up to a total of 67 hours. It could be seen that the two series were converging toward a common value of approximately 25-75 mol % UC-ZrC. Additional experiments at $1700^\circ C$ also gave similar results but in neither case could it be claimed equilibrium was attained. In connection with this work, thermal analysis was being conducted on mixtures of UC_2 with ZrC and C over the temperature range $1500 - 1900^\circ$. Pure UC_2 undergoes a phase change at $1785^\circ C$ with a heat of transition of 11 cal/g.⁽¹³⁾ If the addition of ZrC has no effect on the cooling curve for UC_2 , then presumably there is no solid solubility at these temperatures. Conversely, if a change does occur, there is solid solubility and one can no longer calculate the thermodynamic values as readily.

The cooling curves were obtained with an apparatus which will be described in a forthcoming publication.⁽¹⁴⁾ Briefly, the

technique was to focus the light from the incandescent sample upon a photo-diode. The output from this was displayed on an oscilloscope screen with temperature as the ordinate and time as the abscissa. Cooling times of the order of 5-10 seconds were used. The cooling curve for UC_2 (Fig. 1, curve labeled A) displayed a well defined thermal arrest at about $1785^\circ C$. The UC_2 -ZrC 80-20 mol % sample (Fig. 2) showed only a change in slope, indicated by an arrow in the figure, over the range of 1720° to 1680° . The 70-30 mol % sample (Fig. 3) showed nothing upon cooling but the heating curve showed a break around $1800^\circ C$ as indicated by an arrow. The 70-30 mol % material was run in another apparatus and a thermal effect was detected over the range 1580° to 1515° . These observations were taken to indicate a eutectoid system in the UC_2 -ZrC pseudo-binary in the temperature range of 1500° to $2000^\circ C$. It is possible that cooling rates were too high to permit equilibrium and that the temperatures observed were therefore in error. It is planned to study this system at temperature using X-ray and neutron diffraction to get more accurate data. Nevertheless it appears that cubic UC_2 can dissolve ZrC at high temperatures and any thermodynamic calculations on this system must take this into account. This also points up the difficulty of interpreting high temperature phenomena based on

room temperature observations.

Ternary Carbides of Uranium

Uranium and carbon can combine with some metals to form ternary compounds of formula UMC_2 .⁽¹⁵⁾ Some of the known compounds are characterized by narrow ranges of homogeneity, slight tendency to hydrolyse, and stable towards melting in graphite. There also appears to be compounds of general formula U_2MC_2 but these are not as well known.

Both $UMoC_2$ and UWC_2 appear to have good resistance to hydrolysis. For example a sample of $UMoC_2$ (-325 mesh) was immersed in distilled water for 51 days with no apparent effect. It was found to dissolve only slowly in concentrated hydrochloric acid at room temperature so that after 18 days approximately 85% still remained.

Values of some melting points are given in Table III.⁽¹⁶⁾ As can be seen, these materials are not too refractory. Both $UCrC_2$ and $UTcC_2$ when melted in graphite go over to another crystal structure (Table IV).⁽¹⁶⁾ The formulae of the latter are not known.

References

1. W. G. Witteman and M. G. Bowman, Fourth Uranium Carbide Meeting, East Hartford, Conn. (USA), May, 1963.
2. M. G. Bowman and M. C. Krupka, *ibid.*
3. M. C. Krupka and M. G. Bowman, LASL, Preliminary Results from Continuing Study.
4. P. A. Vozzella, A. D. Miller, and M. A. DeCrescente, Pratt and Whitney Aircraft Corp. -378, Jan. 15, 1963.
5. J. L. Leitnaker and W. G. Witteman, Los Alamos Scientific Laboratory, private communication.
6. H. Eick, E. G. Rauh, and R. J. Thorn, IAEA Symposium, (1962) SM-26/39.
7. J. L. Leitnaker and W. G. Witteman, J. Chem. Phys. 36, No. 6 (1962) 1445.
8. H. K. Lonsdale and J. N. Graves, IAEA Symposium (1962) 601.
9. J. Fujishiro, J. Atomic Energy Society, (Japan), 3 (1961) No. 12.
10. C. Alcock and P. Grieveson, IAEA Symposium (1962) 563.
11. E. J. Huber, Jr. and C. E. Holley, Jr., IAEA Symposium (1962) 581.
12. E. Rudy and F. Benesovsky, Monatsh. 94 (1963) 204.

13. L. S. Levinson, J. Chem. Phys. 38, No. 9 (1963) 2105.
14. G. N. Rupert, Rev. Sci. Inst., Nov. (1963).
15. F. Benesovsky and E. Rudy, Planseeber. Pulvermetallurgie
9 (1961) 65.
16. C. P. Gutierrez, N. H. Krikorian, M. C. Krupka and T. C.
Wallace, Los Alamos Scientific Laboratory, private communication.

Table I

The Pressure of $U_{(g)}$ over UC at 2273°K

$P_{U_{(g)}}$	Composition	Type of Study	Reference
7.3×10^{-8} atm	$UC_{1.065}$	Calculated	
$5. \times 10^{-8}$	$UC_{1.065}$	Langmuir	3
$1. \times 10^{-7}$	$UC_{1.1}$	Langmuir	4
$4. \times 10^{-7}$	$UC_{1.02}$	Knudsen	5
$8. \times 10^{-7}$	$UC_{1.065}$	Knudsen	3

Table II

The Pressure of $U_{(g)}$ over $UC_2 + C$ at $2273^\circ K$

$P_{U_{(g)}}$	Reference
5.3×10^{-9} atm.	Eick, Rauh and Thorn (6)
9.6×10^{-9}	Leitnaker and Witteman (7)
1.8×10^{-8}	Lonsdale and Graves (8)
5.1×10^{-8}	Computed Maximum Pressure
9.3×10^{-8}	Fujishiro (9)
1.3×10^{-7}	Alcock and Grieveson (10)

Table III

Some Melting Points of U-M-C Compositions

°C

Compound	Melting Point	C-Eutectic
UMoC ₂	2350° ± 30°	2200° ± 30°
UWC ₂	2575° ± 30°	2360° ± 30°
UTcC ₂	~1800°	
UReC ₂		2115° ± 30°
UCrCx		1770° ± 30°
UTcCx		1865° ± 30°

Table IV

Crystallographic Data for Ternary Uranium Carbides

	$a_o \text{ \AA}$	$b_o \text{ \AA}$	$c_o \text{ \AA}$	Structure
UMoC ₂	5.6251 ± 0.0064	3.2407 ± 0.0004	10.9579 ± 0.0128	Orthorhombic
UWC ₂	5.6286 ± 0.0009	3.2514 ± 0.0014	10.9740 ± 0.0014	Orthorhombic
UMnC ₂ [†]	5.04 ± 0.01	3.172 ± 0.002	10.74 ± 0.02	Orthorhombic
UTcC ₂ [†]	5.4	3.22	10.9	Orthorhombic
UReC ₂	5.5489 ± 0.0057	3.2229 ± 0.0004	10.7416 ± 0.0086	Orthorhombic
UCrC _x	3.636 ± 0.006		15.739 ± 0.008	Body-centered Tetragonal
U ₂ IrC ₂	3.4790 ± 0.0003		12.4780 ± 0.0024	" "
U ₂ RhC ₂	3.466 ± 0.001		12.512 ± 0.001	" "

[†] Preliminary structure and lattice constants

FIG. I

FIG. 2

TEMP.

A

FIG. 3

Figure 1. The Cooling Curve of UC_2 .

Figure 2. The Cooling Curve of 80-20 mol % UC_2 -ZrC

Figure 3. The Cooling Curve of 70-30 mol % UC_2 -ZrC