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Formation of Uranium Sesquicarbide by the Partial Decarburization of Uranium Dicarbide Using Magnesium Oxide

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Formation of U_2C_3 by the reaction of UC_2 with MgO has been studied by means of chemical and X-ray analyses at temperatures 1450—1700°C *in vacuo*. The reaction was found to proceed generating CO and Mg vapor and to produce U_2C_3. The decarburization is represented by

$$2UC_2 + MgO \rightarrow U_2C_3 + CO + Mg.$$

UO_2 and UC were formed as the intermediate compounds. The amount of UO_2 was nearly equal to that formed by the reaction: $UC_2+4MgO=UO_2+2CO+4Mg$. The lattice parameter of U_2C_3 was 8.0890 Å. The lattice parameters of UC_2 and UC varied with the reaction time. The main reaction sequence was suggested to be:

$$1/4UC_2 + MgO = 1/4UO_2 + 1/2CO + Mg$$

$$7/4UC_2 + 1/4UO_2 = U_2C_3 + 1/2CO.$$

The experimental results were in good agreement with those obtained by thermochemical calculation.

In the system uranium-carbon, there are three compounds, monocarbide, sesquicarbide, and dicarbide. Monocarbide UC is NaCl-type face-centered cubic,[1,2] with a lattice parameter of 4.9605 Å. Sesquicarbide U_2C_3 is known to be body-centered cubic (space group I43d) by X-ray[3] as well as neutron diffraction studies[4]. The best parameter seems to be 8.0898 Å[5,6]. Dicarbide UC_2 has two modifications. α-UC_2 is CaC_2-type body-centered tetragonal.[1,2,4,7,8,9] The compound exhibits a non stoichiometric range of composition, $UC_{1.85}$—$UC_{1.96}$. Various lattice parameters are found in literature. They lie in the ranges $a_0=3.515$—3.526 Å, $c_0=5.98$—6.00 Å. It was shown that the values of carbon-saturated UC_2 obtained in equilibrium state are $a_0=3.5256$ Å and $c_0=6.000$ Å[6,10]. Above 1765°C the tetragonal structure is transformed into the cubic structure[8,11], which is considered to be of the NaCl-type with a C_2 group as in the case of CaC_2 and KCN.

Although uranium sesquicarbide is stable below 1780°C[12], it is not formed easily by the carburization of uranium metal or by the carbothermic reaction of uranium dioxide. In both reactions, the carbide phase of the composition $C/U=1.5$ is always found to be a mixture of monocarbide and dicarbide. No sesquicarbide is obtained directly. It was reported that sesquicarbide is formed by adding mechanical stress onto a mixture of monocarbide and dicarbide,[13] or by heating and cooling it repeatedly at about the temperature of decomposition of U_2C_3.[14] It was also reported that U_2C_3 is formed by heating a mixture of UC and UC_2 at 1500—1600°C,[15] or by the reaction of pure UC and graphite *in vacuo*.[16,17] The formation of sesquicarbide is apparently inhibited by the presence of dissolved oxygen in the matrix.[17,18] Self-purification is reported when the carbide of composition $UC_{1.5}$ is annealed at 1500°C in a vacuum of 10^{-5} mmHg, producing U_2C_3.[15,17]

However, it was found that uranium sesquicarbide is easily produced by the reaction of dicarbide with uranium dioxide:[19]

$$7UC_2 + UO_2 = 4U_2C_3 + 2CO.$$

In this reaction, U_2C_3 is formed not only by the direct reaction of UC_2 and UO_2, but also by the reaction of UC, which appears as an intermediate with some quantity of oxygen, with UC_2, which dissolves oxygen from UO_2 : $U(C,O)+U(C_2,O)\rightarrow U_2C_3+CO$. Oxygen has an important role in the formation of sesquicarbide. Thus, if a suitable metal oxide is used instead of uranium dioxide, the oxygen will act to give the product U_2C_3.

The reaction of uranium dicarbide with magnesium oxide as a metal oxide was examined by means of X-ray and chemical analyses. Magnesium oxide was chosen because the vapor pressure of magnesium pro-

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duced is very large at high temperatures, and magnesium does not form carbide under the experimental conditions, uranium sesquicarbide thus being expected as the product.

Experimental

Materials. Uranium dicarbide was prepared by the carburization of uranium metal. The procedure was the same as that reported.[6] Uranium hydride and spectroscopically pure graphite powder were mixed at a mole ratio 1 : 2, and cold-pressed to cylindrical pellets. The resulting pellets were heated in a graphite crucible at 400°C to decompose the hydride, and then at 1700°C for 3 hr *in vacuo.* Composition of the dicarbide produced: uranium, 90.767 wt%; total carbon, 8.870 wt% (C/U=1.937), with no free carbon. The lattice parameters were $a_0=3.5252$ Å and $c_0=5.999$ Å. Chemically pure magnesium oxide was ignited at 900°C in the air before use.

Procedure. The UC_2 and MgO powders under 200 mesh were mixed together at the ratio 13 : 1 by weight, and cold-compacted at 3 ton/cm^2 into cylindrical pellets, 7 mm in diameter and 7 mm in height. The pellets were heated in a graphite crucible *in vacuo* at 1450—1700°C for 0.5 to 7 hr. The reaction was carried out in a tantalum resistance furnace, evacuated to 1×10^{-5} mmHg or below. The temperature of crucible was measured with a two-color eye pyrometer, calibrated by the melting point of platinum.

Chemical and X-ray analyses. Chemical analysis of amounts of total carbon and uranium was carried out by means of combustion technique.[6] The amount of magnesium oxide unreacted was determined by the photometric method with 8-hydroxyquinoline.[20] The method involves TBP extraction to separate uranium, precipitation of magnesium as 8-hydroxyquinolate, and photometric measurement of combined 8-hydroxyquinoline in hydrochloric acid medium.

X-ray measurements were carried out with a diffractometer, the operation conditions being the same as reported.[10] The lattice parameters were calculated from diffraction lines between 165° and 70° of twice the Bragg angle, by the $\cos^2\theta$ extrapolation method. The standard deviations were within 0.0004 Å for UC, U_2C_3, a_0 of UC_2 and UO_2, and within 0.002 Å for c_0 of UC_2. The amounts of three uranium carbides in the product were determined by comparison of relative intensities. The (311) or (222) reflection for UC, the (521) reflection for U_2C_3 and the (211+202) reflection for UC, the (521) reflection for U_2C_3 and the (211+202) reflections for UC_2 were used. No reflection was found for magnesium oxide. The amount of uranium dioxide as an intermediate was determined by comparison of the reflection (111) for UO_2 with the (111) reflection for UC and (101) for UC_2. The results were compared with those of chemical analysis.

Results

Reaction of UC_2 with MgO. The reaction of a pelletized mixture of uranium dicarbide and magnesium oxide at temperatures 1450—1700°C *in vacuo* was found to proceed generating carbon monoxide and magnesium vapor, which condensed at a cold zone in the furnace. At 1500°C the weight change in the pellets before and after the reaction was 8.27, 8.60, 9.21, and 9.30 wt% corresponding to the heating time 0.5, 1, 2, and 7 hr, respectively. It was shown that most of the weight loss took place within 0.5 hr. The reaction at 1700°C terminated after heating about 1 hr. The results of chemical analysis for the products heated at 1500°C are given in Fig. 1. The change in the carbide composition by X-ray analysis obtained by the summation of the composition of the three carbides, is also given. The difference in the data obtained by X-ray and chemical analyses was taken as the amount of uranium dioxide. This was in good agreement with that obtained directly by X-ray analysis. Magnesium oxide unreacted was detected only in the products obtained by 0.5 hr heating and at 1500°C or below; the amount was 0.95 wt% at 1450°C and 0.09 wt% at 1500°C. Figure 2 shows the change in the phases UC_2, U_2C_3, UC, and UO_2 in the products with the reaction time at 1500°C. The amount of UO_2 showed a maximum in 0.5 hr of heating at all the temperatures. We see that UO_2 (10 mol%) was found in the product by heating for 0.5 hr. The amount was nearly the same as that formed by the reaction: $UC_2+4MgO=UO_2+2CO+4Mg$, *i.e.*, 12.5 mol%. On visual inspection of the cross section of the pellets heated for 0.5 hr, uranium dioxide was found to be scattered throughout the area. Uranium monocarbide was also formd as an intermediate; the amount of UC showed a maximum at all the reaction temperatures for 0.5—1 hr of heating time. The quantity of uranium sesquicarbide increased monotonically with the reaction time, UC_2 being rapidly consumed.

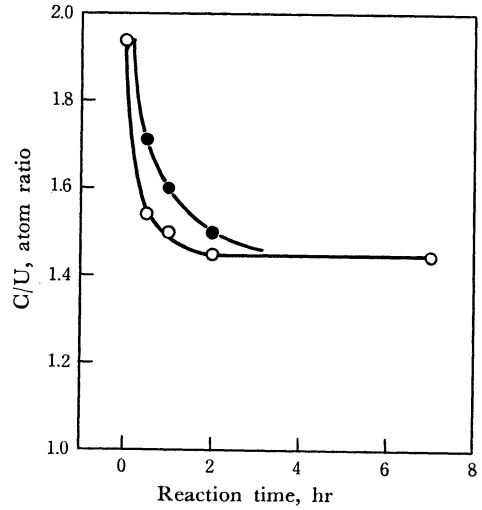

Fig. 1. Variation of the C/U atom ratios of the product at 1500°C by chemical and X-ray analyses with reaction time.

○: chemical analysis

●: X-ray analysis. The difference between X-ray and chemical analysis is taken as UO_2.

Change in the Lattice Parameters. The lattice parameters of the three uranium carbides were found to vary with the reaction time. The results for the products heated at 1500°C are given in Table 1. The lattice parameter of UC at 0.5 hr is slightly smaller

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TABLE 1. THE VARIATION OF THE LATTICE PARAMETERS OF URANIUM CARBIDES AND DIOXIDE WITH THE REACTION TIME IN THE PRODUCT HEATED AT 1500°C

Time	UC	U_2C_3	UC_2		UO_2
			a_0	c_0	
(hr)	(Å)	(Å)	(Å)	(Å)	(Å)
0.5	4.9598	8.0900	3.5198	5.996	5.4715
1	4.9604	8.0897	3.5238	5.998	—
2	4.9606	8.0895	—	—	—
7	4.9604	8.0888	—	—	—

than that at 1 hr or longer heating times, which is the same as that of stoichiometric UC with a small quantity of oxygen[12]. The value at 0.5 hr at 1450°C was 4.9611 Å, and that for longer heating times was about 4.9605 Å. At 1600° and 1700°C, the UC lattice parameter took the nearly constant value 4.9605 Å. When oxygen is dissolved into UC, the lattice parameter has been shown to deviate from 4.9605 Å[21-24]. The change in the lattice parameter observed indicates that oxygen is dissolved in UC to form a $UC_{1-x}O_x$ phase. It is possible to determine the amount of dissolved oxygen from the change in lattice parameter. In the present work, the amount of oxygen dissolved in the UC phase does not seem to be very large. For example, the parameter 4.9611 Å for UC in the product heated at 1450°C for 0.5 hr corresponds to 2000 ppm of dissolved oxygen, according to Magnier et al.[21] By further heating, UC is converted into U_2C_3 by the reaction with UC_2. The oxygen dissolved would have been removed as CO.

The lattice parameter of U_2C_3 varied between 8.0900 and 8.0885 Å. The values at 7 hr at 1450—1700°C were 8.0890±0.0003 Å.

The lattice parameter of UC_2 varied considerably with the reaction temperature and time. The starting UC_2 phase disappeared within 2 hr in the products heated at temperatures higher than 1500°C. It was found that the lattice parameters varied with the reaction time in the same manner as that reported previously,[19] *viz.*, the parameters, a_0 and c_0, showed minimum values at about 0.5 hr. The change in the UC_2 lattice parameter with time indicates that oxygen is transferred into the carbide phase from MgO and/or UO_2 and then removed gradually.

Discussion

It was reported that the formation of uranium sesquicarbide is inhibited in the presence of dissolved oxygen[17,18]. However, the reaction of UC_2 with UO_2 was found to yield U_2C_3, even when the carbide phase coexisted with unreacted UO_2 and/or dissolved oxygen.[19] We found that partial decarburization of UC_2 with MgO produced U_2C_3 when magnesium oxide was used instead of uranium dioxide. The characteristic in this reaction is the formation of UO_2 as an intermediate. Figure 2 shows that the content of UO_2 in the product heated at 0.5 hr at 1500°C is 10 mol%, and that of UC_2 60 mol%. It is suggested that the reaction of UC_2 with MgO is predominant as compared with the other reactions and the formation of UO_2 by the reaction is complete within 0.5 hr, since the content of UO_2 is 12.5 mol% at a maximum. Uranium monocarbide was also formed as an intermediate dissolving a small amount of oxygen. From the results in Figs. 1 and 2, it is deduced that the reaction of UC_2 with MgO proceeds in three steps:

(1) MgO is consumed by UC_2 to form UO_2 : $UC_2 + 4MgO \rightarrow UO_2 + 2CO + 4Mg$, and UC_2 dissolves oxygen;

(2) U_2C_3 is produced by the reaction of UC_2 with UO_2 formed: $7UC_2 + UO_2 \rightarrow 4U_2C_3 + 2CO$, and at the same time UC is also formed by the paralled reaction: $3UC_2 + UO_2 \rightarrow 4UC + 2CO$; and

(3) UC_2 with dissolved oxygen reacts with UC: $U(C,O) + U(C_2,O) \rightarrow U_2C_3 + CO$.

Figures 1 and 2 show that step (1) terminates within 0.5 hr, step (2) takes place at reaction times between 0.5 and 2 hr or a little longer, and step (3) after 2 hr. The main reaction sequence is given by

$$1/4UC_2 + MgO = 1/4UO_2 + 1/2CO + Mg$$
$$7/4UC_2 + 1/4UO_2 = U_2C_3 + 1/2CO$$

$$2UC_2 + MgO = U_2C_3 + CO + Mg$$

The formation of U_2C_3 should be examined from a thermochemical standpoint. For the various reactions of UC_2-MgO system accompanied by the release of CO and Mg, the following reactions are probable:

$$2UC_2 + MgO = U_2C_3 + CO + Mg \qquad (1)$$
$$UC_2 + MgO = UC + CO + Mg \qquad (2)$$

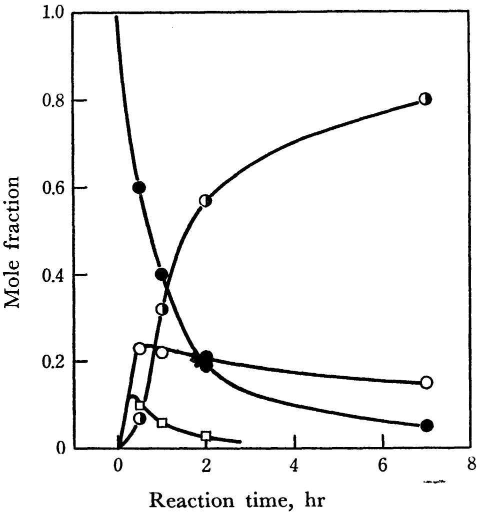

Fig. 2. Variation of mole fractions of UC_2, U_2C_3, UC, and UO_2 in the product at 1500°C with reaction time.
●: UC_2; ◑: U_2C_3; ○: UC; □: UO_2.

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TABLE 2. STANDARD FREE ENERGIES OF FORMATION

Reaction	ΔG°(cal)	Validity Range (°K)	Reference
$U(l)+C(s)=UC(s)$	$-26160+0.4T$	1400—2100	25
$2U(l)+3C(s)=U_2C_3(s)$	$-48500-2.4T$	1400—2000	25
$U(l)+1.93C(s)=UC_{1.93}(s)$	$-21433-2.89T$	1400—2100	25
$U(l)+O_2(g)=UO_2(s)$	$-269700+97.0T-15.4T\log T$	1400—2000	26
$Mg(g)+1/2O_2(g)=MgO(s)$	$-181600+75.7T-7.37T\log T$	1380—2500	27
$C(s)+1/2O_2(g)=CO(g)$	$-26700-20.95T$	298—2500	27

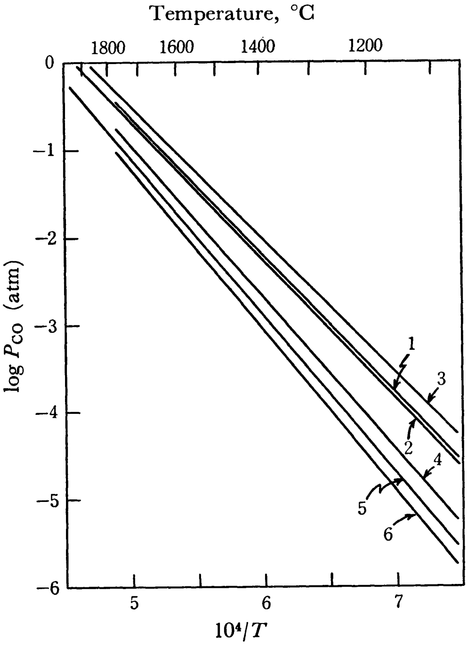

Fig. 3. Calculated equilibrium CO pressures in atm as a function of temperature.
1: $2UC_2+MgO=U_2C_3+CO+Mg$
2: $UC_2+MgO=UC+CO+Mg$
3: $UC_2+4MgO=UO_2+2CO+4Mg$
4: $7UC_2+UO_2=4U_2C_3+2CO$
5: $3UC_2+UO_2=4UC+2CO$
6: $3U_2C_3+UO_2=7UC+2CO$

$$UC_2 + 4MgO = UO_2 + 2CO + 4Mg \qquad (3)$$

UO_2 is formed by the reaction of UC_2 and MgO. Consequently, it is necessary to consider the reactions of UC_2-UO_2 system:

$$7UC_2 + UO_2 = 4U_2C_3 + 2CO \qquad (4)$$

$$3UC_2 + UO_2 = 4UC + 2CO \qquad (5)$$

$$3U_2C_3 + UO_2 = 7UC + 2CO \qquad (6)$$

The equilibrium CO pressures for the equations were calculated with use of the standard free energies of formation for UC,[25] U_2C_3,[25] UC_2,[25] UO_2,[26] MgO[27] and CO[27] listed in Table 2. The calculated values are given in Fig. 3. The figure shows that the CO pressure of reaction (3) is the highest at all temperatures. Thus, in the earlier stage of the reaction of UC_2 with MgO, the formation of uranium dioxide quite possibly takes place before that of uranium sesquicarbide. Once UO_2 is produced, U_2C_3 rather than UC is formed preferentially in the reaction of UC_2 with UO_2. The experimental results are in good agreement with those obtained by thermochemical calculation.

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