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PROPERTIES OF SOME REFRACTORY URANIUM COMPOUNDS

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1

PROPERTIES OF SOME REFRACTORY URANIUM COMPOUNDS

M. Jack Snyder and Winston H. Duckworth

BMI - 1223

Methods of preparing some refractory uranium compounds and of sintering them to high densities are described. Thermal-expansion coefficients, specific heats, microhardnesses, and rates of reaction with oxygen and nitrogen are given for the silicides and UAl_2 .

The thermal-expansion coefficients of the silicides and of UAl_2 were approximately equal and of the same order of magnitude as that of uranium metal. Specific heats ranged from about 0.04 cal/(g°C) for U_3Si to about 0.08 cal/(g°C) for USi_3 . The microhardness of USi_3 was appreciably lower than that of the other silicides.

The initial oxidation of USi_2 , USi_3 , U_3Si_2 , and UAl_2 at 150 to about 400 C resulted in the formation of a protective film. In contrast, nonprotective oxide films were formed on uranium and USi at these temperatures. A protective film was formed in the reaction of all the silicides with nitrogen at temperatures of about 400 to 700 C, but reaction rates were higher than that of nitrogen with uranium.

INTRODUCTION

The properties of a number of refractory binary compounds of uranium that may have potential application as nuclear fuels are being investigated at Battelle. The results of a survey of the literature on these compounds and of initial experimental work were reported in BMI-1124.

Methods of preparing some of the compounds and data on their physical and chemical properties are given in the present report. Data are given on U_3Si , U_3Si_2 , USi , USi_2 , USi_3 , and UAl_2 . Methods of preparing these compounds, as well as UAl_3 , UN , and UBe_{13} , are described.

PREPARATION OF COMPOUNDS

(Work done by W. D. McKee,
A. B. Tripler, Jr., and A. F. Gerds)

Very few of the compounds of interest are available commercially so that it was necessary to prepare them in the laboratory prior to making property measurements. After forming the compounds by a suitable procedure, it was desirable to anneal them to as nearly a single-phase condition as possible and then to fabricate simple shapes for use in property measurements. Minimum porosity was desired, but not essential, in the fabricated specimens. Because of the reactive nature of most of the compounds

and starting materials, it was necessary to exclude air in most of the processing steps.

Two methods were employed in forming the compounds: (1) arc melting of the constituent elements, and (2) solid-solid high-temperature reaction of the elements or of compounds thermally decomposable to the elements.

Arc Melting

Arc melting is a feasible method of preparing those uranium compounds for which the combining element is solid at room temperature and has a vapor pressure sufficiently below the reaction temperature, and in which the dissociation pressure of the compound itself is not excessive at the melting temperature. The arc-melting furnace used is schematically illustrated in Figure 1. A power supply furnishing up to 5000 amp at about 35 v was used with the furnace.

In forming compounds by arc melting, uranium (preferably as sponge chunks) was placed in the water-cooled copper crucible and the other element to be melted was added either as chunks or powder. The system was closed and pumped to a vacuum of less than 5×10^{-3} mm of mercury. Then the arc was struck to the uranium chunks. The arc current was interrupted as soon as the entire charge melted. After cooling, requiring about 1 min, the resulting button was "flipped" by striking the striker plate a sharp blow with a hammer. The charge then was remelted 8 to 10 times to achieve a homogeneous melt.

In many cases, the result of the arc-melting process was a multiphase composite, as shown by X-ray diffraction analysis. Heat treatment was required subsequently to arrive at a single-phase material.

Solid-Solid Reaction

In cases where arc melting is not feasible because of volatility of the combining element or of the compound at the melting temperature, compounds may be formed by solid-solid reaction below the melting or dissociation temperature.

Uranium, as the finely divided hydride, and the combining element in powder form were employed as the starting materials. The materials in the proper proportions were mixed together with a mortar and pestle and were transferred to a beryllia crucible in an argon-atmosphere dry box. The contents of the crucible were protected from air during transfer to the furnace for subsequent heating in vacuo by placing a small chunk of freshly broken solid CO_2 in the crucible with the mixture and covering the crucible with a lid. The lid was removed when the crucible was placed in the furnace, and evacuation of the system was started at once. The vacuum furnace used is shown in Figure 2.

A "good" vacuum was not maintained during the degassing operation, since decomposition of the uranium hydride would require many hours if the attempt was made to maintain pressure below 50×10^{-3} mm of mercury. The chamber first was evacuated to about 5×10^{-5} mm of mercury to assure removal of air. Heating then was started,

Legend

1. Water inlet
2. - to electrode
3. To vacuum pump
4. Water-cooled spacer
5. Main vacuum line
6. Gas inlet
7. Water outlet
8. Water inlet
9. + to rectifiers
10. Striking block
11. Tungsten electrode tip
12. Copper crucible
13. Neoprene gaskets
14. Sight glass
15. Compression spring
16. Water-cooled electrode
17. Water outlet

A-25119

FIGURE 1. CHARGE-FLIPPING ARC FURNACE

FIGURE 2. VACUUM-SINTERING FURNACE

and the temperature raised to about 350 C. The pressure increased to several mm of mercury at this temperature, although pumping was continued. (Since the pressure rise was due only to hydrogen, released from the hydride, no deleterious effects resulted.) The temperature was maintained at 350 C until the pressure could be reduced below 1×10^{-4} mm of mercury, and pressure then was maintained at this value while the temperature was gradually increased to the desired reaction temperature.

The compounds resulting from the solid-solid reaction were in the form of porous cakes. If mixing had been thorough, the material was primarily a single phase. Further treatment was required for obtaining high density.

Compacting and Sintering

As mentioned previously, both the arc-melted compounds and those prepared by solid-solid reaction required further treatment to obtain material suitable for physical and chemical measurements. The arc-melted compounds usually were multiphase materials, whereas the sintered cakes resulting from solid-solid reactions were too porous for most uses. Both types of materials were treated in the same manner to obtain dense pieces of single-phase material.

The arc-melt button, or sinter cake, was broken into chunks, and crushed to approximately 20-mesh size in a small "diamond" mortar. Next, the crushed material was ground wet for 4 hr in a 1/2-pt porcelain mill, using alumina grinding balls and petroleum ether as the fluid medium. Tungsten carbide balls were used in some instances, with slightly greater contamination.

The discharge from the ball mill was screened through 200 mesh, and the petroleum ether was removed from the slurry by evaporation in a flowing argon atmosphere. The residue was powdered, and compacted hydrostatically^{(1)*} at 100,000 psi, usually into rough cylinders approximately 3/8 in. in diameter and 2 in. long. The material then was ready for sintering.

The compacts were sintered in the same furnace used in the solid-solid reactions (Figure 2). The chamber was pumped down to a pressure of less than 1×10^{-4} mm of mercury before heating was started, and the temperature was raised at a rate below that causing the pressure to rise above 1×10^{-4} mm of mercury. This usually required degassing over a period of about 2 hr before reaching about 600 C. From this point, the temperature could usually be increased at about 400 C per hr without causing the pressure to rise above 1×10^{-4} mm of mercury. The furnace usually was cooled at the natural rate by shutting off the furnace input at the end of the sintering time. The furnace cooled to below 600 C in about 15 min, and to room temperature in 1 hr. Temperature was determined by means of an optical pyrometer, correcting for the sight glass in the top of the bell jar.

Examination of Compacts

The suitability of the sintered compacts for use in physical and chemical measurements was assessed by measurement of bulk density, by metallographic examination, and, in some cases, by X-ray diffraction and chemical analysis.

*References at end.

TABLE 1. METHOD OF PREPARATION AND SINTERING

Sample	Compounds	Starting Materials	Proportions	Reaction Method	Final Sintering Temperature, C
11726-63	U_3Si_2	U + Si	Stoichiometric	Arc melt	1450
11726-71					1470
11726-87					1500
11726-75	USi	U + Si	Stoichiometric	Arc melt	1500
11726-53					1400
11726-69	USi_2	U + Si	Stoichiometric	Arc melt	1450
11726-88					1600
11726-89					1560
11726-62	USi_3	U + Si	Stoichiometric	Arc melt	1320
11726-73					1310
11726-77					1280
11726-80					1500
11726-54	UAl_2	U + Al	Stoichiometric	Arc melt	1175
11726-81					1350
12829-24	UAl_3	U + Al	Stoichiometric	Arc melt	1200
12829-28	UBe_{13}	UH_3 + Be	Be in 3 w/o excess	Solid-solid	1750
12829-47					1875
12829-53					1500
Various	UN	U + NH_3	NH_3 in excess	Solid-gas (850 C)	Up to 2300

(a) Dissociates.

CONDITIONS FOR URANIUM COMPOUNDS

Reported Melting Point, C	X-Ray Density, g per cm ³	Sintered Bulk Density, g per cm ³	Percentage of Theoretical Density	Figure in Which Metallograph Appears	Remarks
~1665	12.2	9.98(?) 12.05 11.82	81.9(?) 98.6 97.0	3 - -	Metallograph indicated low porosity - -
~1600	10.4	9.89 8.14	95.0 78.2	4 -	- -
~1600	8.98	8.91 9.02 8.98	99.4 >100 100	5 - -	- Metal volatilized during sintering Ditto
~1650	8.15	7.21 7.19 6.91 7.58	88.6 88.2 84.8 93.0	- 6 - 6	- - - -
1590	8.14	6.13 7.16	75.2 88.0	7 -	- -
1250(a)	-	-	-	-	Extensive decomposition at 1150-1200 C
2000	4.37	4.69 4.46 3.93	>100 >100 90.0	- - -	Compact melted Ditto -
2650 ± 100	14.3	-	-	-	All compacts porous

250X Etchant: 2 Drops HNO₃, N36843
 2 Drops HF in 100 Ml H₂O

Shows Dense Major Phase, Containing
Numerous Cracks, and Discrete Particles
of a Second Gray Phase Resembling Oxide

FIGURE 3. MICROSTRUCTURE OF U₃Si₂ (11726-63)

250X

Etchant: 1 Volume
Per Cent HF

N40006

Shows Light-Etching Matrix Phase and
Darker Etching Grain-Boundary Phase
(Possibly U_5Si_3)

FIGURE 4. MICROSTRUCTURE OF USi (11726-75)

Shows Light-Etching Grain-Boundary
Phase, Slightly Darker Etching Matrix
Phase, Gray Inclusions Resembling
Oxide, and Black Voids

FIGURE 5. MICROSTRUCTURE OF USi_2 (11726-69)

250X

Unetched

N40008

Sample No. 11726-73 Sintered at 1310 C;
Shows Many Black Voids

250X

Etchant: 1 Volume
Per Cent HF

N40009

Sample No. 11726-80 Sintered at 1500 C;
Shows Light-Etching Matrix Phase and a
Second Darker Etching Phase (Second
Phase Believed to be Result of Melting
During Sintering)

FIGURE 6. MICROSTRUCTURE OF USi_3

250X Etchant: 30 Ml HNO_3 , N36848
30 Ml Lactic Acid, 10 Ml HF

Shows Light-Etching Matrix and
Very Many Black Voids

FIGURE 7. MICROSTRUCTURE OF UAl_2 (11726-54)

TABLE 2. MAJOR IMPURITIES IN ARC-MELTED
COMPOUNDS AFTER MILLING^(a)

Compound	Analysis, ppm					
	Fe	Al	Mn	Cu	Cr	W
U ₃ Si ₂	500	100	100	—	—	—
USi	500	200	—	—	—	4000
USi ₂	800	700	—	300	—	—
USi ₃	3000	900	—	—	500	10,000
UAl ₂	800	—	—	200	—	2000

(a) Includes only extraneous elements present in amounts of 100 ppm or greater.

The specific method of preparation of the compounds, the sintering conditions, and the resultant densities are summarized in Table 1. Metallographs representative of the various silicide samples and of UAl_2 are presented in Figures 3 through 7. Data on the purity of the powders prepared from the arc-melted materials prior to sintering are given in Table 2.

These data show that the silicide and aluminide samples used in the physical and chemical measurements were essentially single-phase materials. Most of the samples had low porosity, as evidenced by bulk densities in the range of 95 to 98 per cent of the theoretical density.

Preparation of UBe_{13} by sintering mixtures of UH_3 and beryllium in a vacuum appears to be satisfactory on the basis of results obtained so far. The optimum sintering temperature has not been established as yet, however.

Although UN powder of suitable purity was readily prepared, attempts to obtain a dense compact have not been successful as yet.

PHYSICAL PROPERTIES

(Work done by E. A. Eldridge,
H. W. Deem, and A. F. Gerds)

Data were presented in BMI-1124 on the melting or decomposition temperatures and the uranium contents of the refractory uranium compounds under consideration. In view of the limited data available on the properties of the compounds, laboratory work was undertaken to measure them. Data were obtained on the thermal expansion and specific heats of the uranium silicides. Measurements of thermal conductivity are incomplete and will be presented in a subsequent report. Measurements were made of the microhardness of the silicides incidental to metallographic examination of sintered specimens.

Thermal Expansion

Linear thermal expansions of the uranium silicides and of UAl_2 were measured in a recording, vertical quartz-tube dilatometer with the specimen protected during the measurements by a vacuum of 5×10^{-5} mm of mercury. The thermal-expansion curves during heating and cooling are shown in Figures 8 through 11. Values for the mean coefficients of linear thermal expansion over several temperature ranges were calculated, and are given in Table 3.

The thermal-expansion coefficients of the silicides and of UAl_2 were approximately equal. All were appreciably higher than that of UO_2 (about 10×10^{-6} per C) and of the same order of magnitude as that of uranium metal (about 15×10^{-6} per C).

FIGURE 8. THERMAL EXPANSION OF SINTERED USI

FIGURE 9. THERMAL EXPANSION OF SINTERED USi_2

FIGURE 10. THERMAL EXPANSION OF SINTERED USi_3

FIGURE 11. THERMAL EXPANSION OF SINTERED UAl_2

TABLE 3. THERMAL-EXPANSION COEFFICIENTS

Temperature Range, C	Mean Linear-Thermal-Expansion Coefficient, 10^{-6} per C							
	USi		USi ₂		USi ₃		UAl ₂	
	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling
20-100	20.0	18.8	15.9	15.1	15.5	15.5	14.9	15.2
20-200	18.8	18.1	15.6	14.9	15.3	15.6	14.8	15.2
20-300	17.8	18.2	15.5	15.8	15.4	16.3	14.7	16.0
20-400	17.4	17.9	15.6	15.8	15.7	16.7	15.0	16.1
20-500	16.9	17.7	15.5	15.9	15.8	17.1	15.1	16.4
20-600	16.4	17.7	15.5	16.3	15.6	17.8	15.2	16.7
20-700	16.1	17.6	15.7	16.6	15.3	18.4	15.4	17.0
20-800	15.9	17.6	16.2	16.7	15.1	18.8	15.6	17.3
20-900	15.8	17.4	16.8	16.7	15.0	18.9	16.1	17.1
20-950	15.7	17.3	16.9	16.6	14.9	19.1	16.2	17.1

Microhardness

Knoop hardnesses were determined on polished samples used in the metallographic examinations. Measurements were made both with a 100-g load and a 25-g load on the indenter. The results of the measurements are given in Table 4.

TABLE 4. MICROHARDNESS OF URANIUM SILICIDES

Sample	Compound	Average Knoop Hardness(a)	
		25-G Load	100-G Load
11726-71	U ₃ Si ₂	—	796
11726-75	USi	645	745
11726-69	USi ₂	745	700
11726-73	USi ₃	485	445

(a) Average of 4 to 22 measurements.

The hardness of USi₃ was appreciably lower than that of the other silicides. Although the data indicate a trend toward an increase in hardness with an increase in the uranium content, the differences between the hardness values for USi₂ and U₃Si₂ are not believed to be significant on the basis of the relatively wide variation in individual hardness measurements on the same sample. The apparent difference in hardness values with the 25- and 100-g loads possibly was caused by local inhomogeneities in the compounds or by chipping of the brittle compounds under the heavier load.

Specific Heats

The specific heats of the silicides were determined by enthalpy measurements using an ice calorimeter with the specimens sealed in capsules in helium. The enthalpy-temperature data are given in Table 5.

Equations of the enthalpy-temperature curves were obtained by least-squares calculations. Instantaneous specific-heat equations were obtained by differentiation with respect to temperature. The specific-heat equations for the silicides calculated in this manner are (over the temperature range 0 to 302 C):

$$\text{USi}_2 \quad C_p = 6.4 \times 10^{-2} - 2.1 \times 10^{-4}T + 2.8 \times 10^{-6}T^2 - 7.5 \times 10^{-9}T^3$$

$$\text{USi}_3 \quad C_p = 7.7 \times 10^{-2} - 1.5 \times 10^{-4}T + 1.4 \times 10^{-6}T^2 - 2.8 \times 10^{-9}T^3$$

$$\text{U}_3\text{Si} \quad C_p = 4.3 \times 10^{-2} - 3.4 \times 10^{-4}T + 3.0 \times 10^{-6}T^2 - 6.5 \times 10^{-9}T^3,$$

where

C_p = instantaneous specific heat, cal/(g)(C)

T = temperature, C.

TABLE 5. ENTHALPY-TEMPERATURE DATA FOR URANIUM SILICIDES

USi ₂		USi ₃		U ₃ Si	
Temperature, C	Enthalpy, cal/(g)(C)	Temperature, C	Enthalpy, cal/(g)(C)	Temperature, C	Enthalpy, cal/(g)(C)
66.6	3.86	72.7	5.29	72.4	2.57
68.6	4.16	74.0	5.43	74.6	2.61
69.3	4.38	148.1	11.14	149.5	5.18
147.9	9.50	148.4	10.92	152.0	5.36
148.6	9.65	150.0	11.29	197.2	7.03
197.2	12.39	195.8	14.27	200.5	7.10
200.4	13.48	196.7	14.73	247.3	9.27
249.4	16.82	244.9	18.59	250.9	9.43
249.7	16.54	248.9	19.38	320.2	11.42
252.8	17.66	302.8	23.37	302.3	11.35
302.1	20.07	303.1	23.67		
302.4	20.09				

Specific-heat values at selected temperatures, as calculated from these equations, are given in Table 6.

TABLE 6. SPECIFIC HEATS OF URANIUM SILICIDES^(a)

Temperature, C	Specific Heat, cal/(g)(c)		
	USi ₂	USi ₃	U ₃ Si
0	0.064	0.077	0.043
50	0.060	0.073	0.033
100	0.064	0.073	0.033
150	0.071	0.077	0.037
200	0.075	0.081	0.042
250	0.070	0.083	0.043
300	0.051	0.083	0.034

(a) Calculated from specific-heat equations derived from enthalpy measurements.

CHEMICAL REACTIONS

(Work done by W. M. Albrecht and B. G. Koehl)

The reactivity of the uranium compounds toward gases, liquids, and structural materials with which they might come in contact in a nuclear reactor is of interest in the study of the compounds. Thermodynamic estimates of the reactivity of many of the compounds were reported in BMI-1124. The estimates showed that the silicides would not be expected to be resistant to oxygen, nitrogen, or water vapor. However, thermodynamic calculations reveal only the equilibrium conditions and do not give any information on the rate of reaction. There is always the possibility that a protective film may be formed initially that would prevent or retard further reaction. Accordingly, the kinetics of the reactions of the silicides and of UAl₂ with oxygen and nitrogen were investigated.

Experimental Method

Rates of reaction of the uranium compounds with oxygen and nitrogen were determined from weight-gain measurements using a Sartorius Electrona microbalance. Essentially, this balance is an electronically controlled null-type instrument. The amount of current necessary to maintain balance is measured on a microammeter which is calibrated directly in micrograms.

The balance was evacuated by a three-stage mercury-diffusion pump, backed by a mechanical vacuum pump. A liquid-nitrogen cold trap was placed between the pumping system and the microbalance to prevent back diffusion of mercury into the balance section. An ionization gage between the cold trap and balance was used to measure

pressures in the system. A large system volume was used to minimize the pressure changes which resulted during the reactions.

Irregular polyhedral samples, about 3/16 in. across and roughly equiaxed, cut from sintered compacts were used. Specimen weights ranged from 0.1 to 0.3 g. The samples were dry abraded with 240-, 400-, and 600- grit silicon carbide paper prior to reaction. Individual samples were placed in a 1/4-in.-square platinum boat to prevent loss of material should flaking of the sample occur during reaction. The boat was suspended from the beam of the balance inside the reaction tube by a platinum wire, 0.005 in. in diameter and 24 in. long. A resistance-wound furnace was used to heat the sample. Temperatures were controlled to ± 5 C.

Specimens were heated to temperature in a vacuum at a pressure of $< 0.05 \mu$ of mercury. The reaction was initiated by the addition of 1 atm of gas to the reaction tube. Rate data were not taken until at least 1 min after the reaction was started to allow for adsorption of the gas by the platinum suspension wire, the platinum boat, and the balance beam of the microbalance. Preliminary experiments showed this time to be sufficient to establish equilibrium within the apparatus. Weight-gain measurements were made at 2 to 20 min intervals, depending on the rate of reaction, for 3 hr.

The oxygen used in the oxidation reactions was obtained from the thermal decomposition of degassed potassium permanganate, as described by Hoge⁽²⁾. Matheson pre-purified nitrogen was used, and was dried by passing through a dry ice-acetone cold trap.

The external geometrical surface area was used in calculating weight gain per unit area.

Reactions With Oxygen

Reaction rates of U_3Si_2 , USi , USi_2 , USi_3 , and UAl_2 with oxygen were measured from 150 to 400 C. Representative data obtained for each material are shown in Figure 12. With the exception of U_3Si_2 , the reaction rates of the silicides increase with uranium content. The data reported by Cubicciotti⁽³⁾ for the oxidation of uranium at 237 C and an oxygen pressure of 20 cm of mercury are also shown. It is seen that the rate of uranium oxidation increases rapidly with time, and follows no simple rate law.

The reaction of oxygen with the uranium compounds may be expressed by an equation of the following form:

$$w = kt^n$$

where

w = weight gain, μg per cm^2

k = rate constant

t = time, sec

n = a constant depending on the rate law that is followed:

$n = 1$ for the linear law

$n = 0.5$ for the parabolic law

$n = 0.33$ for the cubic law.

Values of n can be obtained by plotting the logarithm of w against the logarithm of t . Values of k are obtained from the slope of the linear (w versus t), parabolic (w^2 versus t), or cubic (w^3 versus t) plots of w against t , using the appropriate type of plot for the reaction in question.

The reaction rates of oxygen with USi followed the linear law while the rates with USi_2 , USi_3 , and U_3Si_2 followed most nearly a parabolic law. The UAl_2 oxidation followed the cubic law. Representative parabolic plots (w^2 versus t) for USi_2 , USi_3 , and U_3Si_2 are shown in Figure 13. The values of the rate constant, k , were obtained from these plots. Values for k and n are given in Table 7.

All materials reacted nonisothermally with oxygen above 400 C except USi_3 , that is, the rate of reaction increased with time. This was evidenced by a spontaneous heating of the samples. Even at the lower temperatures in some cases, nonisothermal reaction occurred after the initial slow reaction, depending on the temperature of the run. For example, the U_3Si_2 reacted nonisothermally after about 70 min at an initial temperature of 350 C.

The variations of the parabolic rate constants with temperature for U_3Si_2 , USi_2 , and USi_3 are shown in Figure 14. The Arrhenius-type plot, logarithm of rate constant against reciprocal temperature (which should result in a straight-line relationship), was used. In the case of U_3Si_2 , where several rate constants were measured at several temperatures, a good straight line was obtained. Values of the constants for the Arrhenius equation,

$$K = A \exp (-E/RT),$$

calculated from the rate constants for each uranium compound are also given in Table 7. It should be pointed out that in most cases only two points were used to obtain the constants. Therefore, there may be considerable error in the values reported.

At the end of the reaction experiment, several of the specimens were cut in half and examined metallographically. In each case a thin discontinuous oxide layer was seen on the outer surface. The film may only appear to be discontinuous because of the porosity of the base materials. X-ray analysis of the oxide films on the uranium silicides showed only the presence of UO_2 . Within the sensitivity of the analysis, no SiO_2 was detected in any film.

These data indicate that the initial oxidation of U_3Si_2 , USi_2 , USi_3 , and UAl_2 results in the formation of a protective film at temperatures up to about 400 C. The compounds listed in order of increasing oxidation rates are USi_3 , USi_2 , U_3Si_2 , and UAl_2 . At about the same temperatures the initial uranium oxidation follows an increasing rate without the formation of a protective film. Therefore, in the initial reaction, these

FIGURE 12. REACTIONS OF VARIOUS URANIUM COMPOUNDS WITH OXYGEN AT 1 ATM

FIGURE 13. PARABOLIC PLOTS OF THE REACTIONS OF VARIOUS URANIUM COMPOUNDS WITH OXYGEN

TABLE 7. RATE DATA FOR REACTION OF VARIOUS URANIUM COMPOUNDS
WITH OXYGEN

Compounds	Sample	Density, per cent of theoretical	Temperature, C	Rate Constant, k	n, slope of log-log plot	Constants in k = A exp (-E/RT)	
						A	E, cal per mole
<u>Linear, $\mu\text{g}/(\text{cm}^2)(\text{sec})$</u>							
USi	11726-75	95.0	150	4.2×10^{-2}	0.92	1.2×10^3	8,600
	11726-53	78.2	300	6.2×10^{-2}	0.71		
<u>Parabolic $(\mu\text{g}/\text{cm}^2)^2/\text{sec}$</u>							
USi ₂	11726-69	99.4	250	38	0.66	—	—
USi ₃	11726-62	88.6	300	3	0.45	3.0×10^9	23,600
	11726-62	88.6	400	65	0.35		
U ₃ Si ₂	11726-63	81.9 ^(a)	300	31	0.53	3.3×10^5	10,600
	11726-63	81.9 ^(a)	350	56	0.46		
	11726-71	98.6	350	58	0.58		
	11726-63	81.9 ^(a)	400	(b)	—		
	11726-71	98.6	400	(b)	—		
<u>Cubic $(\mu\text{g}/\text{cm}^2)^3/\text{sec}$</u>							
UAl ₂	11726-54	75.2	200	2.6×10^3	0.32	2.7×10^{15}	26,000
	11726-54	75.2	250	37×10^3	0.30		

(a) Believed to be in error. True value is probably >90 per cent.

(b) Reacted nonisothermally.

FIGURE 14. VARIATION OF PARABOLIC RATE CONSTANT WITH TEMPERATURE IN REACTIONS OF OXYGEN WITH URANIUM-SILICON COMPOUNDS

FIGURE 15. REACTIONS OF VARIOUS URANIUM-SILICON COMPOUNDS WITH NITROGEN AT 500 C

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TABLE 8. PARABOLIC RATE CONSTANTS FOR THE REACTION OF
VARIOUS URANIUM SILICIDES WITH NITROGEN

Compounds	Sample	Density, per cent of theoretical	Temperature, C	Rate Constant, k, ($\mu\text{g}/\text{cm}^2$) ² /sec	n, slope of log-log plot	Constants in $k = A \exp (-E/RT)$	
						A	E, cal per mole
U	—	—	500	17.9 ^(a)	—	3.15×10^8	25,500
USi	11726-75	95.0	400	163	0.46	3.9×10^{13}	35,000
	11726-75	95.0	500	4820	0.64		
USi ₂	11726-69	99.4	400	99	0.49	1.1×10^4	6,300
	11726-69	99.4	500	177	0.53		
	11726-69	99.4	600	293	0.48		
USi ₃	11726-77	84.8	400	—	—	7.0×10^2	3,700
	11726-77	84.8	500	62	0.64		
	11726-73	88.2	500	21	0.56		
	11726-77	84.8	600	92	0.55		
	11726-73	88.2	600	83	0.56		
	11726-73	88.2	700	100	0.50		
U ₃ Si ₂	11726-71	98.6	400	39	0.67	1.8×10^6	14,300
	11726-71	98.6	450	82	0.65		
	11726-71	98.6	500	— ^(b)	—		

(a) Calculated from work of Mallett and Gerds.

(b) Sample reacted nonisothermally.

FIGURE 16. PARABOLIC PLOTS OF THE REACTIONS OF VARIOUS URANIUM COMPOUNDS WITH NITROGEN AT 500 C

FIGURE 17. VARIATION OF PARABOLIC RATE CONSTANTS WITH TEMPERATURE IN REACTIONS OF NITROGEN WITH URANIUM-SILICON COMPOUNDS

compounds are more oxidation resistant than uranium. Oxidation of USi followed a linear rate with weight increases much greater than for uranium.

Reactions With Nitrogen

The rates of reaction of uranium silicides with nitrogen at 1 atm were determined in the range 400 to 700 C. Representative data obtained at 500 C for each material are shown in Figure 15. The data are compared with those for the reaction of nitrogen at 1 atm with uranium, extrapolated from the parabolic rate reported by Mallett and Gerds⁽⁴⁾. It is seen that the uranium-nitrogen reaction is much slower than those for any of the uranium silicides. With the exception of that for U_3Si_2 , the rates of reaction increased with uranium content of the silicides. The U_3Si_2 reaction with nitrogen was initially slower than that of USi_2 , but after about 16 min the rate increased very rapidly. In all cases, the initial reaction of the silicides with nitrogen followed a parabolic rate. A few parabolic rate constants and the values of n for all the reactions are given in Table 8. Parabolic plots for USi, USi_2 , and USi_3 are shown in Figure 16.

A plot of the logarithm of the rate constants against reciprocal temperature for the various silicides is shown in Figure 17. The constants for the equations of these lines are also given in Table 8.

Metallographic examination of cross sections of reacted specimens of the silicides indicated the presence of a thin discontinuous film on the surface. As mentioned previously, the apparent discontinuity probably resulted from the porosity of the materials. X-ray analysis of these films at room temperature were inconclusive since no nitride patterns could be detected.

In the case of the nitrogen reactions, it is concluded that uranium is less reactive than any of the uranium silicides. The nitrogen reactions are slower than the oxidation reactions, as the silicides burned nonisothermally in oxygen at the times and temperatures where the nitrogen reaction was parabolic.

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