THE PROPERTIES AND IRRADIATION

BEHAVIOR OF U_3Si_2

By
H. Shimizu

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.

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ABSTRACT

A limited study of the compound U_3Si_2 has been made in reference to its use as a prospective nuclear fuel in sodium cooled reactors. Pertinent physical and chemical data for the U-Si system were compiled or obtained and are reported. Special emphasis was directed to the irradiation study of fusion cast compositions which were somewhat deficient in silicon in the range of 7.08 to 7.17 wt % Si (cf. 7.30 wt % Si for U_3Si_2). A 12-in. fuel column consisting of six each 10%-enriched U_3Si_2 specimens, sodium bonded to a stainless steel cladding, was irradiated to an average burnup level of approximately 0.65% of the total uranium. The maximum average operating fuel center-line and surface temperatures were 1750°F and 1290°F, respectively. Except for the top specimen, which was cracked into several pieces, the irradiated fuel slugs were in relatively good condition. Fractional fission gas release of approximately 2.6% and representative density decreases of 6 to 7% were measured. The stainless steel cladding was intact and its microstructure appeared unaffected.

I. INTRODUCTION

Of the several silicide compounds of uranium, only U_3Si and U_3Si_2 , the two with the higher uranium content, have been seriously considered as nuclear fuel prospects. However, U_3Si , commonly designated the epsilon phase, has shown very poor irradiation stability.^(1,2) U_3Si_2 , although of lower uranium content, is more promising but has yet to be suitably tested under irradiation. This report describes the results of a capsule irradiation experiment on slightly sub-stoichiometric U_3Si_2 (7.08 - 7.17 vs. stoichiometric 7.30 wt % Si) and a few out-of-pile studies of U_3Si_2 properties. This study was conducted during the period 1959 - 1962 as part of an advanced fuel development program for the Sodium Graphite Reactor. Over the ensuing period, the subject has been reported in progress reports from Atomics International (AI) and Battelle Memorial Institute (BMI), which conducted the postirradiation examination as a subcontractor. All of the pertinent information, together with other available information, is presented and discussed in this report.

The silicides of uranium have been described in several reviews of non-metallic nuclear fuels.^(3,4,5) On the specific subject of U_3Si_2 , the work reported by Taylor and McMurtry⁽⁶⁾ on the preparation and property determinations is the most comprehensive to date and includes a review of uranium silicide data. Their work, as well as the earlier studies of the uranium-silicon system, is reviewed in the course of this report.

II. THE URANIUM-SILICON PHASE SYSTEM

The first extensive study of the system was conducted by Kaufman and co-workers⁽⁷⁾ as part of the Manhattan Project. This study resulted in the proposal of six compounds, $U_{10}Si_3$, U_5Si_2 , USi , U_2Si_3 , USi_2 , and USi_3 . Subsequently, x-ray studies by Zachariasen⁽⁸⁾ showed that crystal symmetries and unit cell structures required the stoichiometric relationships to be described by the formulas U_3Si , U_3Si_2 , USi , $\alpha-USi_2$, $\beta-USi_2$ and USi_3 . Kaufman, Cullity, and Bitsianes,⁽⁹⁾ with additional work, later published a revised form of the constitutional diagram with the corrected and currently accepted U_3Si and U_3Si_2 . However, the U_2Si_3 phase was maintained since the $\alpha - \beta$ transformation in USi_2 could not be detected. They also re-examined and confirmed the original value for the silicon composition of 23 at. % for U_3Si indicating that the lattice is approximately 8 % deficient in silicon (since interstitial uranium atoms are unlikely). Brown and Norreys^(10,11) later, in conjunction with thorium disilicide investigations, studied the mid-range of the uranium-silicon system. They were unable to detect an $\alpha - \beta$ transformation in hexagonal USi_2 although such a transformation occurs in $ThSi_2$. A hexagonal form of USi_2 was synthesized in liquid bismuth which was unstable above 450°C, decomposing to USi_3 and $USi_{1.88}$, in a proportion of 1:5. The $USi_{1.88}$ was found to be a hypostoichiometric tetragonal form of the disilicide, containing about 65 at. % Si. This combination was also found in like proportions in as-cast material containing 66.7 at. % silicon. The previously reported U_2Si_3 was found to contain 62 to 63 at. % silicon and assigned a formula of U_3Si_5 although it is structurally equivalent to the hexagonal USi_2 but considerably deficient in silicon. Slight differences were found for x-ray powder patterns for $USi_{1.88}$ above and below 650°C which were attributed to differences in ordering. Gross and co-workers,⁽¹²⁾ in preparing uranium silicides for thermodynamic studies, were unable to identify USi and USi_2 according to Zachariasen's x-ray data, indicating the work of Brown and Norreys to be in agreement. More recently, Straatman and Neumann⁽¹³⁾ made a detailed study of the very low silicon portion of the system (up to 0.3 wt % Si) and defined more precisely some of the transformation temperatures and compositional limits. The diagram shown in Figure 1 represents the combined findings of the foregoing investigators. Only U_3Si_2 and USi_2 (65 at. % Si) are thought to melt congruently, the approximate

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Figure 1. The Uranium-Silicon System

melting points being 1665° and 1700°C, respectively. USi , U_3Si_5 and USi_3 are shown to melt peritectically at 1575°, 1610° and 1510°C, respectively. U_3Si decomposes peritectoidally at 925°C into α -U and U_3Si_2 . This thermal instability would undoubtedly be a limiting factor in the high temperature irradiation behavior of U_3Si .

The x-ray studies by Zachariasen⁽⁸⁾ showed the structure of U_3Si_2 to be tetragonal with a primitive space group of $P4/mbm(D^{5}_{4h})$. The following atomic positions provided good agreement between the observed and calculated diffraction intensities:

2 U_I in $(0,0,0)$, $(1/2,1/2,0)$;

4 U_{II} in $\pm (u, u+1/2, 1/2)$, $(1/2-u, u, 1/2)$ with $u = 0.181 \pm 0.006$;

4 Si in $\pm (v, v + 1/2, 0)$, $(1/2-v, v, 0)$ with $v = 0.389$

Unit cell parameters of $a = 7.3299 \pm 0.004$ and $c = 3.9004 \pm 0.0005$ with two molecules per cell lead to a theoretical density of 12.20 gms/cm^3 and a uranium content of 11.31 gms/cm^3 .

III. FUEL PREPARATION

Most of the specimens for the property measurements and irradiation investigations performed on this program were prepared by an inert atmosphere arc-casting technique developed during the early stages of this study. All castings were prepared singly. Starting materials for casting were either elemental uranium and silicon or premelted silicide alloys to which uranium or silicon was added to adjust the composition. The arc-casting process involved a preliminary preparation of arc-melted buttons with a non-consumable tungsten electrode on a water-cooled copper hearth. The buttons were turned and re-melted three or four times for homogenization purposes. The casting operation was performed by melting one or more of these buttons, depending on the size of the casting required, in either a graphite or copper (water-cooled) crucible-mold system. After carefully melting all but a thin bottom layer of the button, the power was increased (typically from 200 amp, 20 v to 600 amp, 28 v) to melt through the bottom allowing the charge to drop into the mold. Although no erosion problems were noted, some carbon pick-up was evident. Representative carbon compositions were 0.08 to 0.21 wt % in the graphite system compared to 0.05 to 0.10 wt % (depending on initial impurities) in the all-copper crucible and mold system. The latter product contained copper impurities in quantities of 0.1 to 0.9 wt %. The major source of this impurity was suspected to be from the initial button preparation. Copper analyses, however, were not made on the arc melted buttons themselves nor on graphite cast materials.

Since the melting point of U_3Si_2 is not extremely high and because the ultimate need for massive specimens or multiple castings was anticipated, induction melting and casting techniques were also studied. U_3Si_2 was found to be easily melted by induction heating in graphite crucibles, but the extreme fluidity of the material made special care necessary to prevent premature leakage around the plug in the bottom-pour crucible. Katz and Binstock⁽¹⁴⁾ have described a parallel development of a vacuum induction melting and casting technique. A pouring temperature of only 1700°C, approximately 35°C above the melting point,^{*} was adequate. To overcome the problem of leakage around the crucible stopper, a crucible design with a tightly-fitting, breakable graphite plug was later developed and used with success.

IV. PHYSICAL, CHEMICAL, AND MECHANICAL PROPERTIES

Some of the important properties which contribute to the usefulness of nuclear fuels are, (a) good thermal conductivity, (b) high uranium density, (c) adequate mechanical strength to withstand thermal stresses, and (d) high melting point. These and other representative properties of U_3Si_2 are compared with those of UC and UO_2 in Table 1.

TABLE 1
SELECTED PROPERTIES OF
 U_3Si_2 , UC AND UO_2

	U_3Si_2	UC	UO_2
Density, total (g/cm^3)	12.20	13.62	10.96
Density, uranium (g/cm^3)	11.31	12.97	9.66
Melting Point ($^{\circ}C$)	1665	2535	2810
Thermal Conductivity at $600^{\circ}C$	0.03	0.055	0.010
($cal/cm\text{-}sec^{\circ}C$) at $1000^{\circ}C$	0.05	0.055	0.006
Corrosion-Oxidation Resistance	Good	Poor	Excellent
Thermal Expansion $0\text{-}1000^{\circ}C$ ($10^{-6}/^{\circ}C$)	14-17	~ 10	~ 10

Most of these properties for U_3Si_2 are intermediate between those for UC and UO_2 . The melting point of U_3Si_2 , however, is considerably below the others, but should be adequate for moderate-temperature reactors in which the maximum fuel temperature is maintained well below $1200^{\circ}C$ ($2150^{\circ}F$). In thermal stress characteristics, U_3Si_2 appears inferior to the carbide. The higher expansion coefficient and lower thermal conductivity correspond to higher thermal stresses for a given power density.

A. ELECTRICAL RESISTIVITY

The electrical resistivities of uranium silicides were measured in this program, in the course of specific heat determinations wherein the resistivity served as the measure of temperature. The samples of uranium silicide used for these measurements were prepared by arc melting and casting. In addition to the U_3Si_2 (7.3 wt % Si), lower Si materials were also studied. Since it was found that resistivity of as-cast materials was not reproducible during early

thermal cycling, the samples were annealed for 24 hours at 800°C, the highest temperature at which resistivities were measured. The lower Si compositions were stabilized by this pretreatment, but the stoichiometric U_3Si_2 continued to drift. The final values for the 3.9 and 6.1 wt % Si samples and the last series of values obtained for the 7.3 wt % Si material are shown in Figure 2.

The results show that the resistivity of U_3Si_2 is greater than that of U_3Si and that mixtures of the two phases vary in resistivity according to the silicon composition. The room temperature resistivity of U_3Si_2 was found to be approximately $1.05 \times 10^{-4} \Omega\text{-cm}$. The resistivity value obtained for sintered material reported by Taylor and McMurtry⁽⁶⁾ was $1.50 \times 10^{-4} \Omega\text{-cm}$.

B. SPECIFIC HEAT

Because the resistivity of the U_3Si_2 specimen failed to stabilize, the specific heat determination for this composition was not made. The specific heats of the lower silicides are shown in Figure 3. Experimental values for the specific heat of U_3Si_2 have not yet been reported. However, Cape and Taylor,⁽¹⁵⁾ whose work is being reported here, calculated the DuLong-Petit specific heat by means of the equation

$$C_p = \frac{6.4 \times \text{no. of atoms (in formula)}}{\text{formula wt.}}, \quad \dots (1)$$

giving 0.0359 and 0.0416 cal/gm C° for U_3Si and U_3Si_2 , respectively.

C. HEAT OF FORMATION

Gross, Hayman and Clayton⁽¹²⁾ have determined the heat of formation of various silicides of uranium by direct combination of elements in a bomb calorimeter. The heat of formation of U_3Si_2 was found to be 40.7 ± 0.5 kcal/mole or 8.1 ± 0.1 kcal/gm-atom. This was considered to be in good agreement with the value of 8.6 ± 0.8 kcal/gm-atom calculated by Alcock and Grievson⁽¹⁶⁾ in their vapor pressure studies of various uranium binary systems. The latter investigators also obtained the free energy of formation:

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Figure 2. Resistivity of Uranium Silicide

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Figure 3. Specific Heat Capacity of Uranium Silicide

No determinations of thermodynamic properties were conducted in the present work.

D. THERMAL EXPANSION

The thermal expansion of U_3Si_2 has been measured at various sites. Arc-cast materials measured in this program showed significantly higher expansion than have sintered materials measured at other laboratories. Comparative data are shown in Table 2. It might be expected that the lower values of sintered material may be due to the counteracting effect of continued densification. However, it has been observed by Accary and Caillat⁽¹⁷⁾ that significant shrinkage does not occur until $\sim 1200^\circ C$ which is the highest temperature at which any of the expansion measurements have been made. A more plausible reason for the apparent high expansion coefficient for cast U_3Si_2 is oxidation due to poor vacuum capabilities (8×10^{-3} torr) of the dilatometer used. Poor vacuum conditions during one of the thermal conductivity determinations caused a severe volumetric increase in the specimen before reaching $500^\circ C$. However, the reported value is the result of duplicate, self-consistent runs. No final resolution of the discrepancy is possible at this time.

TABLE 2
THERMAL EXPANSION OF U_3Si_2

AI	$\alpha = 17.3 \times 10^{-6} ^\circ C^{-1}$	100 - $880^\circ C$	arc cast
Carborundum Co	$\alpha = 15.0 \times 10^{-6} ^\circ C^{-1}$	25 - $1200^\circ C$	sintered 92% theoretical density
BMI	$\alpha = 15.0 \times 10^{-6} ^\circ C^{-1}$	25 - $800^\circ C$	sintered
	$\alpha = 14.6 \times 10^{-6} ^\circ C^{-1}$	25 - $950^\circ C$	sintered

E. THERMAL CONDUCTIVITY

Thermal conductivity measurements were made on four specimens. One arc-cast specimen was sent to the National Bureau of Standards for measurements at relatively low temperatures, $100-200^\circ C$. Another arc-cast specimen was sent to Batelle Memorial Institute where measurements were made up to

temperatures near 1200°C. In both cases the axial heat flow method was used. The remaining two conductivity determinations, made at Atomics International, were on induction cast material using a radial heat flow technique. One of these was terminated prematurely at ~500°C because of specimen growth under defective vacuum conditions. However, over the range that useful information was obtained, the results of the two determinations were very much in agreement. The results of all of these tests are shown in Figure 4, together with values reported by Taylor and McMurtry⁽⁶⁾ for sintered U_3Si_2 and a value of 0.035 cal/cm-sec-°C reported by Nichols.⁽¹⁸⁾ Although there were significant differences in thermal conductivity values for fusion cast-materials, it is evident from the graph that these are in better mutual agreement than with the results on the sintered material of Taylor and McMurtry.

Recently, Laubitz,⁽¹⁹⁾ by means of mathematical analysis, has given evidence that the series comparator method can lead to erroneous results if the conductivity characteristics of comparator materials are not similar to those of the materials being tested. When considerable differences exist between the materials, the unknown material apparently tends to take on the characteristics of the standard. In the determinations reported by Taylor and McMurtry, this technique was used with nickel as the comparator material. Nickel has a relatively high thermal conductivity and a negative temperature coefficient. The BMI and NBS measurements of this program were also made by the series comparator method, the latter using the standard material only at one end. The reference materials used were Types 347 and 316 stainless steels, respectively, the conductivity values for which are also shown in the graph.

Whether the differences in the values, determined by the three laboratories on cast material prepared at Atomics International, are due to true differences in the materials or to differences in experimental techniques cannot be accurately assessed. It is probable that both contributed to the lack of agreement. However, it can be reasonably concluded that the thermal conductivity of U_3Si_2 increases with temperature, and that it remains below that of uranium monocarbide and above that of uranium oxide over the useful temperature range. The AI and BMI data were reproducible up to 600°C, but above this temperature, the scatter in the measurements was more than should be encountered. This provides further evidence that changes may have been occurring in the microstructure at the elevated temperatures.

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Figure 4. Thermal Conductivity of U_3Si_2

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F. CHEMICAL STABILITY

No problems of fuel deterioration have been encountered in the handling or during the storage of U_3Si_2 . It is thus considered to be stable indefinitely at room temperature. At higher temperatures, however, U_3Si_2 undergoes reactions with oxygen or water vapor. Loch, Engle, Snyder and Duckworth⁽²⁰⁾ reported that at 400°C in air, sintered U_3Si_2 (7.25 wt % Si) gained 18.5% in weight in 7-1/2 hr; the material having disintegrated into powder by this time. Snyder and Duckworth⁽²¹⁾ later reported an approximate parabolic oxidation rate in oxygen at 300° and 350°C and determined the following relationship for the rate constant:

$$k \text{ (g/cm}^2\text{-sec)} = 3.3 \times 10^5 \exp \left(\frac{-10,600 \text{ cal/mole}}{RT} \right) \quad \dots (3)$$

At 400°C the reaction was exothermic such that an isothermal reaction rate could not be determined.

Oxidation tests were also performed in this program by Koenig⁽²²⁾ at temperatures of 100°, 200°, and 315°C. The tests at 100°C in ambient air were conducted for periods up to 192 hr with very little visual evidence of oxidation although some non-systematic weight changes were noted. In tests conducted at 200°C in air, also for periods up to 192 hr, approximately parabolic reaction rates were observed for both as-cast and heat treated (1000°C, 24 hr) U_3Si_2 . The weight gains were described by the relationship $0.07t^{0.568}$ and $0.06t^{0.52}$ mg/cm², for two tests, where time is expressed in hours. At 315°C, the material oxidized at a linear rate for about 4 hr, at which time cracks appeared and oxidation proceeded at an accelerating rate with complete deterioration occurring in about 8 hr. Taylor and McMurtry⁽⁶⁾ conducted stability tests in water at room temperature, 100° and 200°C. They observed no evidence of reaction at room temperature and only slight reaction after 16 days at 100°C (0.029 - 0.042% loss), and after four days at 200°C, measured only 0.020% loss in weight.

G. HARDNESS, MODULI, AND STRENGTH CHARACTERISTICS

The information available on the mechanical properties of U_3Si_2 is sparse. Snyder and Duckworth⁽²¹⁾ reported a Knoop hardness value of 796 kg/mm^2 with a 100-gm load. Taylor and McMurtry⁽⁶⁾ determined the modulus of rupture by transverse tests on materials of 90 to 98% density, the results of which are presented in Table 3.

TABLE 3
MODULUS OF RUPTURE BY TRANSVERSE TESTS

Temp. °C	Density % Theoretical	Modulus of Rupture	
		Average, psi	Range, psi
25	92-98	12,500	10,300-17,600
600	90-94	11,300	8,700-17,700
800	93-98	Bars deformed under load	

They also determined the Young's and shear moduli for U_3Si_2 over a range of densities by the sonic technique, reporting room temperature values of 11.3×10^6 psi and 4.8×10^6 psi, respectively, for material of 92% density. From these values, a Poisson's ratio of 0.17 was calculated.

In this program, compression tests were conducted at room temperature on arc cast and induction cast U_3Si_2 specimens which were machined to an approximate $L/D \cong 3$. On three samples taken from a single arc cast rod, an average static modulus of elasticity of 7.6×10^6 was obtained. The specimens fractured in a brittle manner at nearly the same stress level, an average value of 32,760 psi. For the induction cast samples, the modulus of elasticity varied between 9.1×10^6 and 20.3×10^6 psi with an average of 13.9×10^6 psi for eight determinations. The stress at fracture varied between 20,000 psi and 40,000 psi.

V. IRRADIATION STUDY OF U_3Si_2

A. OBJECTIVES

The primary objective of the U_3Si_2 irradiation experiment, which was designated AI-7-1, was to determine the irradiation behavior characteristics, i. e., dimensional stability and fission gas release at maximum central and surface temperatures of 1920°F and 1420°F respectively, to a burnup of 10,000 Mwd/MTU. Associated objectives included the in-pile compatibility of U_3Si_2 -Na-304 SS and fuel phase stability at high temperatures in a sodium environment.

B. EXPERIMENT DESCRIPTION

Longitudinal and radial section views of the capsule are shown in Figure 5. The 12 in. fuel column consisted of six 0.350-in. diameter slugs of 10% U^{235} enriched uranium silicide. The slugs were centered in a 0.436 in. dia, 0.020 in. wall Type 304 stainless steel tube with three longitudinal 0.022 in. dia. equally spaced stainless steel wires. The annular space was filled with sodium to provide efficient heat transfer from the fuel. The fuel rod was placed in a secondary capsule of heavy walled stainless steel tube which was NaK filled, to provide heat barriers to prevent boiling of the reactor coolant water while maintaining design fuel temperature conditions.

The fuel rod was instrumented with eight Type K (chromel-alumel) thermocouples, seven of which were tack-welded to the cladding while the eighth was inserted into the center of the top fuel slug, one inch from the top of the column. The cladding temperatures were monitored at positions 1 (two thermocouples), 3, 5, 7, 9, and 11 in. from the top of the fuel column.

The capsule was designed to provide a maximum fuel surface heat flux of 580,000 BTU/hr-ft² at a linear power of 15.5 kw/ft of fuel.

The fuel composition for this test was originally intended to be stoichiometric U_3Si_2 . However, the loss of silicon by vaporization during the melting and casting process was greater than expected and substoichiometric material resulted. Although the presence of the U_3Si phase was recognized to be a possible detriment to the irradiation stability of the fuel, the decision was

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Figure 5. Capsule Longitudinal and Transverse Section View

made to proceed with the capsule assembly and irradiation. The compositions of the six fuel specimens ranged from 7.08 to 7.17 wt % Si (cf. 7.30% for stoichiometric U_3Si_2). Photographs of the slugs before encapsulation are shown in Figure 6. Typical preirradiation microstructures are shown in Figures 7-a, b, c, d, and e.

C. IRRADIATION HISTORY

The experiment was inserted in the General Electric Test Reactor on April 20, 1960, in position Y-9. It was irradiated through seven cycles (GETR #12-#18) and discharged into the canal on December 12, 1960, where it was allowed to cool for six weeks before shipment to Atomics International.

Four of the eight thermocouples, including the in-fuel thermocouple, functioned properly during the entire eight month irradiation period. A typical plot of calculated (from thermocouple data) fuel center and surface temperatures is shown in Figure 8. The thermocouple which was 5 in. from the fuel column top malfunctioned on initial reactor startup; the thermocouples which were 9 and 11 in. from the fuel top operated only two of the seven reactor cycles, and the thermocouple

3-30-60 7519-51217C
Figure 6. Pre-irradiation Specimen Photographs

which was 7 in. from the fuel top failed after the fourth reactor cycle. The fuel temperature data shown in Table 4 were derived from the burn-up profile and the thermocouple histories, where complete, or from a combination of burnup profile and extrapolations or interpolations of thermocouples histories where incomplete.

The fuel was irradiated to a maximum average burnup of 7300 Mwd/MTU at a power output of 14.1 kw/ft with center and surface temperatures of 1750 and 1290°F, respectively. The peak-to-average burnup ratio was approximately 1.14.

D. POST-IRRADIATION EXAMINATION

The examination of the AI-7-1 capsule was conducted at the hot cell facilities of the Battelle Memorial Institute under the direction of Atomics International. The capsule was taken from storage at the AI Hot Laboratory (AIHL) and shipped to BMI during the second quarter of calendar year 1962. The hot cell operations were conducted in the following order:

- a) Puncturing of the outer capsule, sampling and analysis of gases for detection of fission gas products.

Mag: 250X

1477-4T

Mag: 250X

1477-9T

Mag: 250X

1477-3T

Mag: 250X

1477-4B

A. Sample E-6

Mag: 250X

1477-9B

B. Sample E-14

Mag: 250X

1477-3B

C. Sample E-4

7519-15281

Figure 7. Typical Fuel Preirradiation Microstructure
(Sheet 1 of 2)

Mag: 250X

1477-8T

Mag: 250X

1477-5T

1477-8B

1477-5B

7519-15282

D. Sample E-13

E. Sample E-7

Figure 7. Preirradiation
Microstructure
(Sheet 2 of 2)

NAA-SR-10621

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- b) Removal and gamma scanning of inner capsule to measure longitudinal profile of fission product (Ce-144).
- c) Dimensional measurements of inner capsule.
- d) Puncturing and determination of fission gas content of inner capsule.
- e) Removal of sodium and recovery of fuel specimens.
- f) Cleaning of fuel specimens by reaction of sodium with butyl alcohol and by vacuum distillation.
- g) Dimension and density measurements of fuel specimens.
- h) Selection of three specimens for isotopic burnup analysis.
- i) Silicon analysis of fuel specimens.
- j) Metallography.
- k) X-ray diffraction (after observation of increased amounts of second phase near periphery of specimens).

The external surface of the capsule showed some areas of darkening but this was not considered unusual. Since the capsule surface appearance was not noted at the time of discharge from GETR, it cannot be stated with certainty whether the discoloration occurred during the irradiation or during storage and shipment. The discoloration was considered to be only a surface phenomenon and to have very little effect on integrity of the tube.

No fission gas was detected by gamma spectrometric analysis in the gas collected on drilling through the outer capsule. After opening of the outer capsule and removal of the NaK by reaction with butyl alcohol, the inner capsule containing the fuel was removed. The surface of the cladding in the vicinity of the bottom of the fuel column gave evidence of having experienced high temperatures. The distribution of temperatures and burnup is shown in Figure 8, which includes the gamma activity profile, burnup analysis of selected specimens, and the longitudinal profile of average fuel-center temperature. The gamma activity profile was obtained by moving the capsule vertically

TABLE 4

Specimen No.	Fuel Composition w/o Si	Calculated Fuel Temperatures, °F				Ave. Linear Power, kw/ft	(a) Burnup Mwd/MTU	-%Δp	+%ΔL	+%ΔD	%FGR(c) Kr+Xe
		Ave. T _{CL}	Ave. T _S	Peak T _{CL}	Peak T _S						
6 (top)	7.15	1200	900	1620	1200	9.4	5300	11.7		4.6	} 2.6
14	7.08	1430	1070	1800	1330	11.4	6000	12.6	3.0	6.0	
11	7.12	1610	1190	1980	1460	12.9	6800	5.1(7.3) ^b	3.4	4.3	
4	7.13	1730	1280	1990	1470	13.9	7200	7.2	4.3	2.6	
13	7.15	1750	1290	2000	1480	14.1	7300	6.4	1.8	2.3	
7 (btm)	7.17	1710	1260	1960	1450	13.8	7100	6.1	2.5	3.4	

(c) Shows gas release datum for complete fuel column

across a 1/4 in. collimator hole through the thick hot cell wall with a shielded sodium iodide scintillation crystal placed at the outer end of the hole. The gamma intensity was based on the Ce^{144} peak with an energy of 0.134 Mev. The Ce^{144} peak was selected because of its prominence and isolation from the strong characteristic peaks of other long-lived fission products (e. g., Zr^{95} and Mn^{54}) after a decay period of over one year.

The appearance of a deposit on part of the surface of the capsule was attributed to oxides, possibly of residual NaK. Exterior dimensional measurements of the inner capsule showed it to be uniform and relatively unchanged within the accuracy of the measurement.

The gases from the inner capsule were collected using the same vacuum pumping technique used in the outer capsule sampling. Gamma spectrometry was conducted on small aliquots of the gas; larger aliquots were analyzed by mass spectroscopy. The results, based on an average burnup of 0.63 at. % total uranium, are given in Table 5. The fractional release for most of the isotopes measured varied from 2.2 to 2.8% of the total produced, including the approximately 0.1% expected due to recoil. The concentration of Xe^{136} was exceptionally high, showing an apparent fractional release of 3.7%. This, however, can be attributed to the formation of additional Xe^{136} from the n, γ reaction of Xe^{135} during irradiation. The large relative value for Kr^{83} may have been subject to greater error because of the smaller absolute quantities of this constituent involved. Kr^{85} , analyzed also by gamma spectrometry, indicated 2.2% release. This represents good agreement with the 2.6% obtained by mass spectroscopy, but the latter is considered to be more reliable because of the larger volume sampled for analysis.

The top of the capsule was cut off and the sodium poured out after heating in a mineral oil bath to 250°F. Part of the sodium was retained for silicon analysis. Figure 9 shows the open end of the capsule with the top fuel specimen and the three spacer wires exposed. It proved necessary to slit the cladding longitudinally along two opposite sides in order to remove the fuel specimens, which had lodged tightly against the wire spacers and the cladding. The specimens were removed from the cladding tube and soaked in hot mineral oil to remove the adhering sodium. Four of the six specimens broke during this treatment. Cracking had probably occurred during the irradiation, while the pieces had remained bonded by the solidified sodium after removal from the capsule.

TABLE 5
FISSION GAS RELEASE

Isotope	Number of Atoms Produced in the Specimens ^(a) $\times 10^{19}$	Number of Atoms Released From the Specimens $\times 10^{18}$	Fraction of Total Atoms Released, (%)	Calculated Released Due to Recoil ^(e) , %
Xe-131	10.0	2.2 (c)	2.2	0.115
Xe-132	15.1	3.3 (c)	2.2	0.115
Xe-134	25.6	6.4 (c)	2.5	0.115
Xe-136	21.6 (b)	8.0 (c)	3.7 (b)	0.115
Kr-83	1.7	0.57 (c)	3.3	0.115
Kr-84	3.8	1.1 (c)	2.6	0.115
Kr-85	1.0	2.6 (c)	2.6	0.115
Kr-85	1.0	2.2 (d)	2.2	0.115
Kr-86	7.2	2.0 (c)	2.8	0.115

(a) Based on an average fission burnup of 6.3 a/o of the uranium-235.

(b) A considerable portion of the Xe^{135} atoms is converted to Xe^{136} during irradiation depending on the flux level. Therefore a correction should be added to the number of Xe^{136} atoms produced.

(c) Determined by mass spectroscopy.

(d) Determined by gamma spectrometry.

(e) Assuming a recoil range of 10.

Although it had been anticipated that some or all of the fuel would have severely cracked or pulverized, because of an apparent increase in thermal conductivity of the fuel during irradiation, most of the fuel specimens remained relatively intact and generally good in appearance. The specimens are shown in Figure 10, and some surface details are shown in Figure 11, including a typical impression of the spacer wires in the fuel and an example of lateral and longitudinal cracking.

Dimensional and density measurements are shown in Table 6 together with the corresponding preirradiation values. The changes in dimensions are compared graphically with one-third of the density change (based on the assumption of isotropic growth) in Figure 12 as functions of the silicon

6X

HC 9552

Top specimen and the three spacer wires exposed

6X

HC 9553

7519-15284

Bottom specimen with droplets of oxidized sodium

Figure 9. Exposed Fuel Specimens Before Removal of Cladding

1X

HC 9555

Specimen 6

1X

HC 9557

Specimen 14

1X

HC 9561

Specimen 11

1X

HC 9563

Specimen 4

1X

HC 9565

Specimen 13

1X

HC 9567

Specimen 7

7519-15285

Figure 10. Postirradiation Specimen Photographs

6X

HC 9564

Specimen 4
Showing crack

6X

HC 9559

Specimen 14

NOTE

Groove attributed to growth of fuel around
guide wire. Large depressions were in
original specimen.

7519-15286

Figure 11. Surface Details of Fuel Specimens

NAA-SR-10621

TABLE 6
DIMENSIONS AND DENSITIES OF AI-7-1 FUEL

Specimen No.	Length ^(a)			Diameter ^(a)			Density		
	Before Irradiation, in.	After Irradiation, in.	Percent Change	Before Irradiation, in.	After Irradiation, in.	Percent Change	Before Irradiation, g/cc	After Irradiation, g/cc(c)	Percent Change
6	2.320			0.350	0.366	4.6	12.153	10.86(d)	-11.7
14	1.670	1.720	3.0	0.350	0.371	6.0	12.259	10.72	-12.6
11	2.270	2.348(b)	3.4	0.350	0.365	4.3	{ (12.22) ^(e) 12.503	11.59	{ (- 5.2) 7.3
4	2.358	2.459(b)	4.3	0.350	0.359	2.6	12.149	11.27	7.2
13	1.040	1.059	1.8	0.350	0.358	2.3	12.186	11.41	6.4
7	2.315	2.373(b)	2.5	0.350	0.362	3.4	12.160	11.42	5.1

(a) Accuracy of measurements estimated to be ± 0.0005 .

(b) Specimens had cracked into two pieces and were fitted together for length measurement.

(c) Accuracy of measurement is ± 0.03 g/cc.

(d) Only the 4 largest pieces were used for the determination.

(e) Corrected for composition (see discussion).

7519-15286

Figure 12. Dimensional and Density Changes as Functions of Silicon Composition

composition. The length measurements on three of the broken specimens were made by fitting the parts together. The length of the top specimen, for which all pieces were not available, could not be measured. All traces of sodium were removed from each fuel specimen by vacuum distillation before density measurements were made. Trial heatings which were conducted on two of the specimens in a vacuum furnace at 400°F for 11 hr showed white surface deposits, most of which disappeared after successive treatments at 500 and 600°F. The residual deposit, believed to be sodium oxide, was removed by soaking in water. The remaining four specimens were vacuum distilled directly at 600°F and washed with water to remove traces of sodium oxide. The appearance of additional cracks after these treatments was believed to be the result of sodium removal from pre-existing cracks. The density measurements were made by weighing the specimens in air and in carbon tetrachloride.

The soaking in carbon tetrachloride was continued until an equilibrium weight was reached. Specimens 6 and 14, with the largest degree of cracking, required the longest soaking periods to reach this equilibrium weight.

The isotopic burnup analyses were performed at the AEC Chemical Processing Plant, NRTS, Idaho, on sections from three specimens selected from the top, middle, and bottom of the fuel column. (The positions are shown with the gamma activity profile curve in Figure 8.) Because control specimens of the original fuel were no longer available, the pre-irradiation uranium isotopic ratios for U^{234} and U^{236} were estimated for a 10.02% U^{235} enrichment from a graph plotted from all previous pre-irradiation mass spectroscopic data compiled at BMI. The U^{238} content was obtained by difference. The burnups of the three specimens were calculated from the analytical data according to the following relationship:

$$B. U. = 100 \left(1 - \frac{E_1 W_o}{E_o W_1} \right), \quad \dots (5)$$

where:

$$\begin{aligned} E_1 &= \text{post-irradiation fraction } U^{235} \\ E_o &= \text{pre-irradiation fraction } U^{235} \\ W_1 &= \text{post-irradiation fraction } U^{238} \\ W_o &= \text{pre-irradiation fraction } U^{238}. \end{aligned}$$

The isotopic data and burnup results are shown in Table 7.

On the basis of correlation of the gamma activity profile with isotopic burnup values of Specimens 4 and 14, the average burnup was determined to be 6.3 at. % of U^{235} atoms or 0.63 at. % of total uranium, corresponding to 1.8×10^{20} fissions/cc. If the burnup value for Specimen 7 had been weighted equally with the others, the burnup profile would be correspondingly greater.

The results of chemical analyses for silicon in the fuel specimens, in the sodium, and in the cladding, are shown in Table 8. There appear to be large inconsistencies in the relative changes in silicon content. The validity of some of the analyses is questioned, especially for those which resulted in a gain in Specimen 4 and a large loss in Specimen 7.

TABLE 7
MASS SPECTROMETRIC BURNUP ANALYSES

Specimen No.	U ²³⁴	U ²³⁵	U ²³⁶	U ²³⁸	Burnup		
					at. % of U ₂₃₅	Fissions/ccx10 ²⁰ (b)	at. % of Uranium
14	0.07	9.44	0.16	90.33	5.3	1.5	0.53
4	0.07	9.28	0.18	90.47	6.8	2.0	0.68
7	0.07	9.17	0.19	90.57	7.8	2.2	0.78
Control (a)	0.07	10.02	0.06	89.85			

(a) The isotopic ratios of U²³⁴ and U²³⁶ for the control were estimated from analyses performed on specimens from other programs which had an enrichment of 10%; U²³⁸ determined by difference.

(b) Based on the densities of the specimens as given in Table 6.

TABLE 8
SILICON ANALYSES OF FUEL AND CAPSULE COMPONENTS

Specimen	Silicon Content, wt %	
	Preirradiation	Postirradiation
6	7.15	6.95
14	7.08	6.79
11	7.12	6.95
4	7.13	7.17
13	7.15	(b)
7	7.17	5.18
Sodium	Not Known	0.5
Type 304 S. S.	(a)	0.3

(a) Range of values 0-1 %. Not determined on original stock.

(b) Data not obtained due to error in analysis.

Metallographic examinations were conducted on all of the six specimens as well as on selected regions of the stainless steel cladding. Metallographic specimens were prepared by mounting in bakelite, grinding through 240, 400 and 600 grit SiC paper, and polishing with 1-micron diamond paste on cashmere cloth and with Linde-B in 2% chromic acid on microcloth. All fuel specimens exhibited increased concentrations of a second phase, probably U_3Si , in the grain boundaries around the outer regions of the transverse cross-section of the fuel, as seen in Figure 13. The inner area was nearly single-phase. This indicates that if the starting material was homogeneous and of silicon-deficient composition, the loss of silicon from the surface was by migration toward the central region and by loss to the sodium. There is no suitable explanation for an increase in silicon concentration as indicated by Sample 4, Table 8. It is suspected that "hot" chemical analyses for silicon were easily subject to errors.

Although x-ray diffraction examination of the surface region was made, a satisfactory identification of the second phase material was not obtained. There is no reason, however, to expect it to be other than U_3Si . The redistribution of silicon by loss to the sodium environment follows previously recognized behavior of silicon solution in sodium, but the redistribution by migration in the direction of positive thermal gradient cannot be readily explained. A discussion of this phenomenon is presented in Section E.

The interior regions of the fuel (Figure 14) can be seen to have undergone considerable grain boundary movement, with solid or gaseous fission products being swept along by the grain boundary. The sweeping action was discontinuous, with arrests occurring each time the temperature dropped to the base level during scheduled or unscheduled shutdown periods. Most of the observable residual gas bubbles or pockets were in or attached to the final grain boundary positions.

In Specimen 13, which operated at the highest temperatures, the amount of the second phase near the surface was especially large. Within this grain boundary material there was also an unidentified third phase material which was distinguishable by the difference in shading of the etched specimen as seen in Figure 15.

250X Etched HC-9788

a. Edge of Fuel Showing the Presence
of the Second Phase

250X Etched HC-9789

b. Half-Way Between Center and Edge
Showing Fission Gas Bubbles and
Second Phase at Grain Boundaries

7519-15288

Figure 13. Postirradiation Fuel Microstructure Showing
Increase in the Grain Boundary Phase in the
Peripheral Area

250X Etched HC-9768

Near Center of Specimen 14 Showing Apparent
Fission Gas Bubble Formation at
Grain Boundaries

Figure 14. Postirradiation Microstructure of the
Stainless Steel Cladding

500X Etched HC-9799

Edge of Fuel Showing the Presence of a
Second Phase

7519-15289

Figure 15. Postirradiation Fuel Microstructure Showing
Grain Boundary Movement in the Central Region

Data regarding the extent of silicon solubility in sodium and its dependence on temperature are not yet available. However, silicide compounds, NaSi_2 and NaSi , have been reported,⁽²³⁾ the latter dissociating at 420°C in vacuum. It is also known, moreover, that sufficient solubility of silicon in sodium exists to allow massive transfer of silicon to steel parts. The silicon lost from the fuel specimen probably either deposited in the stainless steel surface or was precipitated out as a compound and was discarded with the sodium. The metallographic examination of the stainless steel cladding did not reveal any unusual microstructural characteristics (see Figure 16).

E. DISCUSSION OF RESULTS

One of the most noticeable irregularities in the results of the irradiation test is the extent of swelling of the two fuel specimens at the top of the column, which experienced the lowest temperatures according to the burnup data. For the second specimen from the top (No. 14), this may be attributable to the lower original silicon content. When dimensional and density changes are shown only as functions of silicon content, as in Figure 12, the trend of lower stability with lower Si composition can be recognized. The results for the top specimen (No. 6), however, cannot be explained by this reason. This fuel specimen had the lowest burnup level and, therefore, presumably operated at the lowest temperature. A possibility exists that part of the sodium thermal bonding was lost from the top specimen by evaporation and redeposition on the colder upper regions of the capsule. Such transfer has been definitely observed in recent irradiation tests of individually encapsulated uranium carbide specimens.⁽²⁴⁾ Such an occurrence would result in an undetermined temperature rise in the top fuel slug. Thus, if the fuel specimen had been partially uncovered, a longitudinal thermal gradient would result, accompanied by longitudinally varying transverse strains, which in turn could have been responsible for the extensive lateral cracking shown by the top specimen. Other mechanisms may have been responsible for the observed behavior, but this is not immediately evident.

The length and diameter measurements are expected to be somewhat erratic since some measurements may be made over large cracks or accumulated microcracks. Density measurements are therefore considered to be the best

250X

HC-9736

Transverse Section

250X

HC-9747

Longitudinal Section

7519-15290

Figure 16. View of Unidentified Third Phase in Grain Boundary of Irradiated Microstructure

measure of swelling. In Figure 12, the density decrease values appear to show the most consistent swelling pattern, excluding the top specimen for the reasons discussed.

One of the most sensitive means of checking fuel composition is by determining corresponding densities. Figure 17 shows the density of some of the fuel slugs which were prepared for the AI-7-1 experiment. Of those used in the experiment, it is shown that specimen No. 11 falls drastically out of line to the extent that it indicates a density which is greater than 100% of theoretical. If this had been noted at the outset, the fuel specimen would have been replaced or reanalyzed. If a correction were to be applied at this stage, the density would be corrected to ~ 12.2 since alteration of silicon concentration would lead to improbable or impossible situations in light of post-irradiation observations.

The silicon-deficient U_3Si_2 fuel column irradiated in this experiment does not, on the surface, compare favorably with typical capabilities of uranium carbide. Under equivalent conditions the fission gas release from uranium carbide would be an order of magnitude lower, and density changes would be

7519-15291

Figure 17. Variation of Density With Composition

less by perhaps a factor of three. However, in this test, the bulk of the fission gases collected may have originated from the top specimen as indicated by the extensive cracking and large density change.

It should be noted, in connection with the apparent redistribution of the U_3Si phase toward the surface during irradiation, that the interior portion of the fuel was above the peritectoid transformation ($2U_3Si \rightarrow U_3Si_2 + 3U$) temperature of $925^\circ C$ ($1697^\circ F$). Under conditions of thermal gradient in which the relative thermodynamic stability of U_3Si and U_3Si_2 changes across a physical boundary defined by the transformation temperature, it can be expected that atomic interchanges may occur in the direction of establishing a steady state condition. Thermal gradient tests, conducted under well controlled conditions on mixed $U_3Si_2 - U_3Si$ material in a temperature range which brackets the transformation temperature, may be fruitful in reproducing and explaining the effects observed in the AI-7-1 fuel. The electron microprobe, which in recent years has become increasingly available to most investigators, is a tool well suited to following of localized changes in silicon concentrations.

The presence of U_3Si and its increase during irradiation, especially in the high burnup, outer region of the fuel, can only be detrimental to the irradiation stability of the fuel. It is thus important, not only to start with stoichiometric or silicon-rich U_3Si_2 , but also to provide excess silicon to satisfy the solution requirement of silicon in sodium. Further, an adequate study of compatibility of the fuel-sodium-cladding system is needed to determine whether a steady state stability can be achieved.

Although compatibility tests have shown interactions between U_3Si_2 and stainless steel at $1450^\circ F$ and a transfer of silicon to stainless steel by sodium at $1600^\circ F$, the AI-7-1 test has given good evidence that stainless steel is unaffected by the fuel at temperatures below $\sim 1200^\circ F$ for several thousand hours in a sodium environment. Even at $1450^\circ F$, the extent of interaction was limited to a small surface region; thus, allowances for operation up to such temperatures for limited periods may possibly be designed into U_3Si_2 fuel elements.

VI. CONCLUSIONS

To draw complete conclusions on the capabilities of U_3Si_2 on the basis of a single irradiation test, which produced one fission gas release datum point and only a few inter-related swelling data, would be premature and possibly misleading. The second irradiation experiment which had been initiated, but subsequently suspended on the basis of increased priority of other work, would be necessary to evaluate the material, U_3Si_2 . Other longer term tests would be required to establish the full capabilities and limitations of U_3Si_2 . That the AI-7-1 experiment was completed with the cladding and the fuel generally intact provides sufficient promise to justify continued irradiation and out-of-pile activities.

The inherent irradiation stability of U_3Si_2 may not match that of UC or UO_2 which may be implied by their relative melting points. However, the advantages of atmospheric stability and compatibility with stainless steel over UC and the advantages of thermal conductivity and fissile density over UO_2 may serve to make the application of U_3Si_2 feasible and to offer practical solutions to some of the difficulties encountered in the use of carbide or oxide fuels.

The presence of any U_3Si phase in a uranium silicide fuel is to be avoided because of the extreme mobility of silicon in this phase at or near the transformation temperature of $925^{\circ}C$ ($1697^{\circ}F$).

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