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Journal of Nuclear Materials 248 (1997) 204–208

journal of nuclear materials

Behavior of neutron-irradiated U_3Si

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Abstract

The behavior of U_3Si-based alloys has been studied under neutron irradiation. Maximum burnup reached ~ 62% of the initially contained 19.6% ^{235}U and irradiation temperatures were in the approximate range of 190–280°C. Postirradiation examinations revealed the following. The dimensional instability of the high uranium-density fuels is attributed to the radiation-induced amorphization and plastic deformation. The occurrence of amorphization is suggested by the liquid-like behavior of U_3Si under irradiation at temperatures well below the melting point of crystalline material. The accelerated swelling of U_3Si due to the large fission-gas-bubble growth can be suppressed by the cladding restraint. The reaction layer is formed at the U_3Si–Al interface. The thickness of the reaction layer of surface-oxidized U_3Si is significantly reduced in comparison with that of non-oxidized U_3Si. This reduction in thickness is caused by the thin film of UO_2 that has been formed at the surface of the U_3Si by oxidation. © 1997 Elsevier Science B.V.

1. Introduction

The uranium silicide U_3Si_2 possesses a uranium density of 11.3 gU/cm^3 with a congruent melting point of 1665°C. This alloy is used in research reactors as a plate-type fuel with low-enriched uranium [1,2]. Another silicide U_3Si has a higher uranium density of 15 gU/cm^3, prompting us to assess its irradiation behavior for applications to any type of reactors. Fuel specimens of two types, Al-clad disks and miniature plates (miniplates), were fabricated and subjected to neutron irradiation. Postirradiation examinations have been carried out to evaluate the fission-gas-bubble swelling of U_3Si-based alloys and their compatibility with the Al metal under irradiation.

2. Fuel preparation and irradiation

U_3Si and U_3Si–50 wt% U_3Si_2 alloys were made by arc-melting the elements and annealing at 850°C for 72 h to complete the peritectoid reaction: $U_3Si_2 + U \rightarrow U_3Si$ at 930°C. The annealed buttons were cut into thin (~ 0.3 mm) plates. Each plate was then clad with two Al disks by hot-pressing at about 25 MPa and at 400–450°C for 30 min in vacuum. The dimensions of disk-type fuel specimens were 22.5 mm diameter and 5 mm thickness. To improve the high-temperature compatibility with aluminum, the surfaces of some of the U_3Si plates were oxidized at 500–800°C under a low oxygen partial pressure in vacuum < 0.1 Pa. This treatment yielded on the U_3Si surface the dense thin layer of $UO_2 + U_3Si_2$. Miniplates containing U_3(Si, Ge) were prepared by the picture-frame method, in which thin (~ 0.2 mm) alloy specimens were embedded in the Al powder and pressed to obtain compacts. Dimensions of the finished miniplates clad with Al–1.0 wt% Mg–0.6 wt% Si alloy (A16061) by rolling were 20 mm wide, 30 mm long and 1.3 mm thick.

The fuels were irradiated in the He-sealed capsules using the JMTR. Burnups were calculated from the results of neutron flux measurements: thermal neutron fluxes (< 0.68 eV) were in the range of $0.9–1.1 \times 10^{14}$ n/cm^2 s. In the disk-type fuels, burnups up to 62% of the initially contained 19.6% ^{235}U were achieved after irradiation for 216 days, while 36% was reached after a 108 days irradiation. The $U_3(Si_{0.8}Ge_{0.2})$ miniplate was irradiated for 216 days to a burnup of 57%. The mean irradiation temperature of each disk, measured at the surface, was in the range of 250–280°C. The surface temperature of the $U_3(Si_{0.8}Ge_{0.2})$

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PII S0022-3115(97)00199-2

miniplate was $\sim 190°C$ which was approximately 100°C higher than the normal temperature of research reactor operation. The temperatures were held within about $\pm 20°C$ by controlling the He gas pressure outside the inner capsule during the entire period of irradiation. Fuel temperatures were estimated to be $\sim 20°C$ higher than the surface temperatures.

3. Results and discussion

3.1. High fuel plasticity due to amorphization

Birtcher et al. [3] studied the structural and dimensional stabilities of unconstrained U_3Si by in situ HVEM observations. They indicated that void growth by plastic flow of U_3Si under Kr ion irradiation occurs when the material is in the amorphous state and not when it is in the crystalline state. Panteleev et al. [4] reported that amorphous U_3Si exhibits superplastic behavior under neutron irradiation.

The present study has demonstrated high plasticity of U_3Si due most likely to its amorphization under irradiation. Fig. 1 shows metallography of part of a cross-section of the U_3Si disk irradiated to 62% (3.9×10^{21} fissions/cm^3) at 280°C. Splitting of the Al cladding in this disk resulted from the mechanical forces due to the gas-bubble buildup within the U_3Si and to the fuel thickness increase through the U_3Si–Al reaction. (It should be noted that the splitting tendency may also depend on the strength of metallurgical bonding that was formed by hot-pressing prior to irradiation.) The liquid-drop shape is apparent at the chip of the U_3Si that has been pushed into the gap caused by the splitting. The plastic flow of U_3Si is more clearly seen in Fig. 2, in which the direction coincides with that of the deformation of the gas bubbles. Namely, softening of the U_3Si matrix is proved by bubble interlinking and flattening (lenticular gas-bubble formation) near the region of the breakdown of the reaction layer.

Since the melting point of crystalline U_3Si is 985°C [5], the liquid-like behavior near 280°C (or, even at the estimated maximum fuel temperature of $\sim 300°C$) strongly suggests the amorphization of U_3Si under irradiation. The crystallographic X-ray data of the irradiated fuels have not yet been obtained. Therefore, although the metallographic evidence is not definitive, it may provide support for the amorphization of U_3Si. Hofman et al. [6] have already suggested the gas-bubble growth by plastic flow for reactor-irradiated U_3Si. Direct evidence has now been obtained to confirm this suggestion under the conditions of likely reactor operation. What is more important is that the gas bubble growth assisted by plastic flow can be suppressed in the U_3Si disk, if the Al cladding is kept intact under similar irradiation conditions (Fig. 3). The rates of plastic flow of the U_3Si and gas-bubble growth thus depend on the local restraint forces imposed to the fuel matrix, as described in Section 3.2.

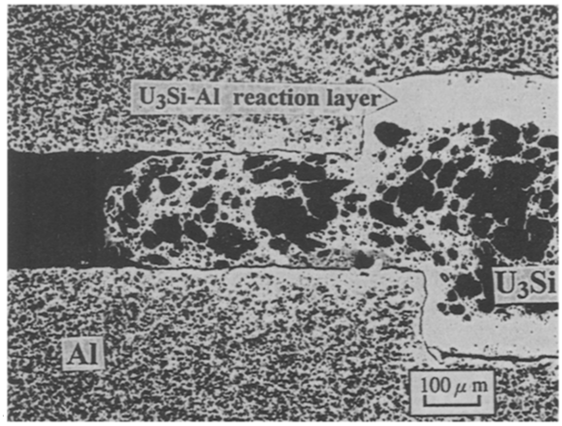

Fig. 1. As-polished cross-section of disk-type U_3Si irradiated to 62% at 280°C for 216 days, where the cladding restraint was lost during irradiation.

Amorphization of U_3Si is caused by the accumulation of defects due to irradiation damage. Enhanced defect annihilation could occur to restore U_3Si crystalline at high temperatures. This may be supported by the results of Panteleev et al. that U_3Si becomes amorphous at 210°C after irradiation of 7×10^{18} fissions/cm^3: however, amorphization was not observed at temperatures above 240°C at the same burnup. It is shown that the Kr ion fluence required to fully amorphize U_3Si increases with irradiation temperature [3]. The feasibility of simulating fission damage in U_3Si by means of Ar ion bombardment has been proved [7,8]; 1 ion/cm^2 is approximately equivalent to 1000 fissions/cm^3. Calculations using the EDEP-1 (ext.) code developed by Aruga et al. [9] indicate that Kr ions cause a damage energy approximately twice than that by Ar ions, suggesting 1 Kr/cm^2–2000 fissions/cm^3. An extrapolation of the data [3] allow us to predict that $\sim 4 \times 10^{19}$ fissions/cm^3 would be required to amorphize U_3Si at 300°C, which is two-orders of magnitude lower than the present level of neutron fluence. Recently, Birtcher et al. [10] reported that the temperature limit for complete amorphization is 290°C for U_3Si. Considering the errors in experiments and estimations, our results of the occurrence of amorphization at the higher temperatures (280–300°C) and at higher burnups may not conflict with these facts and prediction.

3.2. Gas-bubble swelling and restraint effect

In the U_3Si–Al dispersion plate-type fuel, break-away swelling occurs at high burnups [1,2]. It was noted that the associated total void-volume fraction is orders of magnitude greater than one can account for on the basis of existing fission-gas concentrations [3]. So, we make a rough estimate of the fuel volume swelling due to fission-product gases.

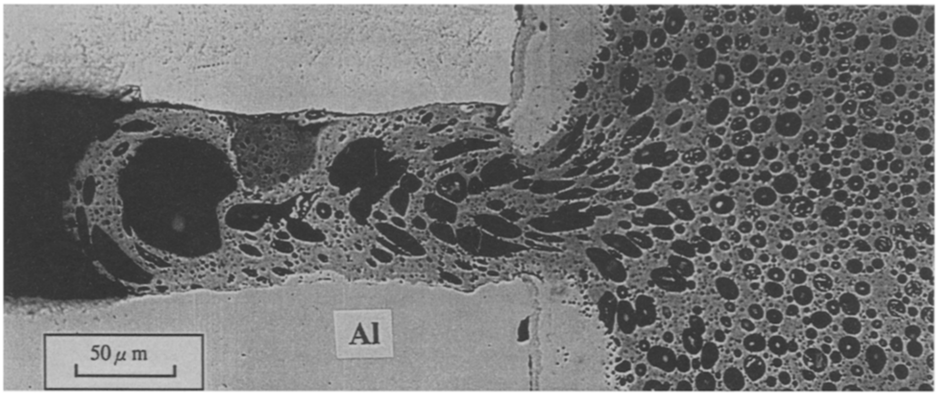

Fig. 2. As-polished cross-section of disk-type U_3Si irradiated to 61% at 280°C for 216 days, where the cladding restraint was lost presumably at the later stage of irradiation.

A compression force may be applied to the fuel by the cladding of Al plates that keep metallurgical bonding during irradiation. Bubbles are assumed to grow and coalesce spherically and maintain a narrow distribution of sizes. If the compressive stress in the vicinity of a bubble is σ, the condition for equilibrium is:

$$P - \sigma = 2\gamma/r,$$

where P is the gas pressure inside a bubble, σ is the fuel self-restraint (intrinsic strength of the fuel) + cladding restraint, γ is the surface energy of the fuel and r is the bubble radius. For a first approximation at a temperature around 280°C, we assume: $\gamma \sim 300$ dyn/cm and $r = 2$–5 μm. The fuel self-restraint is unknown and estimated to be small because of the liquid-like state of U_3Si. So, we put σ = Al cladding restraint = 1–2 kgf/mm^2 (the tensile strength of Al). Then,

$$\sigma \gg 2\gamma/r.$$

Thus, for simplicity

$$P \sim \sigma.$$

All amounts of fission gas atoms (Xe + Kr) are assumed to evenly distribute in each gas bubble, neglecting their radiation-induced solution in the U_3Si matrix. We use the van der Waals equation:

$$V = nRT/P + nb,$$

where $b = 0.051$ l/mol and $n = 0.002$ mol after a fluence of $\sim 4 \times 10^{21}$ fissions/cm^3 taking an approximate concentration of 30 atoms of (Xe + Kr) per 100 fissions. We obtain the total gas volume $V = 1.0$–0.5 cm^3 per original 1 cm^3 of U_3Si. Calculations suggest that the fuel-volume increase due to gas-bubble swelling is approximately 50–100%. This result is in reasonable agreement with the experimental observations [2,11,12], considering the fuel temperature as $\sim$ 150°C higher than in the literature. Thus, it is confirmed that fission-gas-bubbles are directly responsible for the swelling of highly-irradiated U_3Si. Void swelling (i.e., homogeneous nucleation and growth of voids resulting from fission-induced defects) described by Birtcher et al. will occur only at lower burnups up to $\sim 10^{19}$ fissions/cm^3.

Table 1 lists approximate maximum sizes of fission-product gas bubbles in the U_3Si-based alloys irradiated for 216 and 108 days. The effectiveness of the cladding restraint on the bubble-size reduction is seen in the high-burnup disk fuels, which depends on whether the plate splitting has taken place during irradiation (Figs. 1–3). In Fig. 2 the growth of fission-gas bubbles is clearly shown to be enhanced under the unrestraint condition. Gas-filled bubbles at the central part of the disk are still small and spherical indicating equilibrium with the surface tension under the hydrostatic stress. If the stress gradient exerted, however, they could migrate down along its direction with the bubble deformation that occurred near the neck of the U_3Si flow. Approaching the chip of the U_3Si flow, the

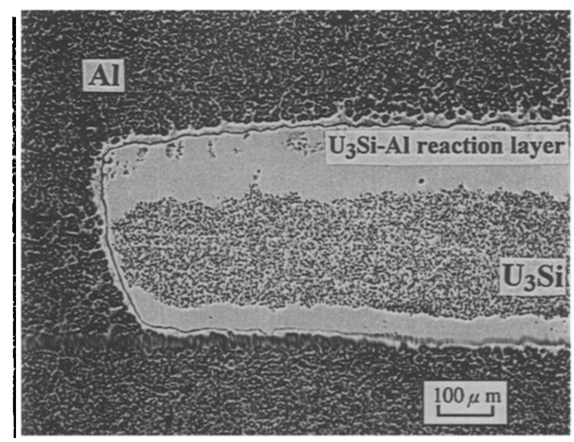

Fig. 3. As-polished cross-section of disk-type U_3Si irradiated to 60% at 270°C for 216 days with the cladding restraint (no splitting). Thickness of the U_3Si–Al reaction layer is smaller on the lower side (surface-oxidized) than on the upper side (non-oxidized) of U_3Si.

Table 1
Approximate maximum sizes of fission-product gas bubbles in U_3Si-based alloys irradiated for 216 days

Alloy	Fuel type	Burnup (% ^{235}U)	Irrad. temp. (°C)	Cladding [a] restraint	Max. bubble size (μm)
U_3Si-a	disk	60	270	yes	4
U_3Si-b	disk	62	280	no	110
U_3Si-c	disk	36	250	no	6
$U_3Si + U_3Si_2$	disk	59	250	yes	2
U_3SG [b]	plate	57	190	yes	2

[a] 'Yes' indicates the intact Al cladding (i.e., no splitting); 'No' means that metallurgical bonding of the Al cladding was lost completely or partly during irradiation due to the splitting at the original interface of Al plates.
[b] $U_3SG = U_3(Si_{0.8}Ge_{0.2})$.
Fission density: U_3Si-a = 3.7, U_3Si-b = 3.9, U_3Si-c = 2.2 (irradiated for 108 days), $U_3SG = 3.5 \times 10^{21}$ fissions/cm^3.

Table 2
Approximate layer thickness of the reaction of U_3Si-based alloys with aluminum after irradiation for 216 days

Alloy	Fuel type	Burnup (% ^{235}U)	Irrad. Temp. (°C)	Thickness (μm)
U_3Si	disk	60	270	140
U_3Si (with oxide film)	disk	60	270	50
$U_3Si + U_3Si_2$ (with oxide film)	disk	59	250	30
U_3SG	plate	57	190	25

effective compressive stress will become weaker than in the central part, thus forming very large gas-bubbles near the chip. Furthermore, even if unrestrained, bubble size was observed to remain relatively small when burnup was low. This is seen from the data of 36%-burnup U_3Si (Table 1); in this case, the outflow of U_3Si into the gap was not observed. Consequently, gas-bubble size and hence gas-bubble-driven swelling are verified to depend also on a degree of fuel burnup. It is concluded that the cladding restraint and material self-restraint will contribute to reduce gas-bubble swelling; the larger the mechanical restraint, the smaller the volume increase in irradiated amorphous U_3Si.

The effect of restraint on the U_3Si swelling described here is in qualitative agreement with that calculated for a fuel temperature of 100°C in the different configurations of the fuel elements: U_3Si–Al dispersion plate and rod with hoop [13]. The lower fuel swelling in the rod-type element is due to stronger restraint generated by the hoop stress state in a solid-clad rod.

3.3. Fuel-aluminum reaction

Table 2 lists mean thickness of the layer formed by reactions between U_3Si-based alloys and aluminum after irradiation for 216 days. Ex-reactor experiments demonstrated that the U_3Si–Al reaction takes place according to

$$U_3Si + 8Al \rightarrow 3U(Al_{8/9}Si_{1/9})_3,$$

which is in consistent with the equilibrium phase diagram of the U–Si–Al system shown for 400°C [14]. The reaction accompanies a theoretical volume increase of approximately 6%, estimating from the lower density (~7.1 g/cm^3) of the product compared to 15.6 g/cm^3 for U_3Si. In the U_3Si disk irradiated to 36% at 250°C for 108 days, silicon was not produced as a discrete phase. But the solid solution $U(Al, Si)_3$ was formed by its dissolution into UAl_3 at the periphery of the fuel according to the above reaction.

The new finding in this area of study is that the reaction layer thickness of surface-oxidized U_3Si can be reduced to 30–40% of that of non-oxidized U_3Si at 270°C (Fig. 3 and Table 2). This reduction in the reaction layer thickness is attributed to the thin (5–10 μm) protective film of UO_2 that has been formed at the surface of U_3Si by its oxidation pretreatment. The uranium dioxide acting as a barrier, cannot be corroded by Al owing to the thermodynamically unfavorable reaction. Any pore or void formed by, for example, Kirkendall effect was not observed at the interfaces of the U_3Si–Al reactions in this study.

Acknowledgements

The authors gratefully thank Dr T. Aruga for discussion on the damage in U_3Si due to ion and neutron irradiations.

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