

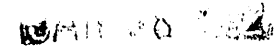
**STABILITY OF URANIUM SILICIDES DURING  
HIGH ENERGY ION IRRADIATION**

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# STABILITY OF URANIUM SILICIDES DURING HIGH ENERGY ION IRRADIATION

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## ABSTRACT

Changes induced by 1.5 MeV Kr ion irradiation of both  $U_3Si$  and  $U_3Si_2$  have been followed by in situ transmission electron microscopy. When irradiated at sufficiently low temperatures, both alloys transform from the crystalline to the amorphous state. When irradiated at temperatures above the temperature limit for ion-beam amorphization, both compounds disorder, with the Martensite twin structure in  $U_3Si$  disappearing from view in TEM. Prolonged irradiation of the disordered crystalline phases results in nucleation of small crystallites within the initially large crystal grains. The new crystallites increase in number during continued irradiation until a fine grain structure is formed. Electron diffraction yields a powder-like diffraction pattern that indicates a random alignment of the small crystallites. During a second irradiation at lower temperatures, the small crystallites retard amorphization. After 2 dpa at high temperatures, the amorphization dose is increased by over twenty times compared to that of initially unirradiated material.

## INTRODUCTION

The history of irradiation effects is replete with examples of unexpected new behaviors that alter apparently reasonable expectations for the response of materials to an irradiation environment. Such examples include void swelling and irradiation induced segregation. A recent example has arisen from the desire to use intermetallics Uranium silicides as reactor fuel. Uranium silicides are being considered for use as reactor fuels in both high power and low enrichment applications because they have the advantages of high Uranium density and good thermal properties. However,  $U_3Si$  and  $U_3Si_2$  were found to become amorphous under irradiation [1]. In general, during irradiation amorphous materials become mechanically unstable to rapid swelling by plastic flow [2]. Prolonged reactor or ion irradiation of the amorphous  $U_3Si$  results in gross mechanical deformation and swelling due to plastic flow [1,3]. The mechanisms responsible for plastic flow of irradiated amorphous systems are unknown.

A second anomaly in this chemical system comes from reactor irradiations of  $U_3Si_2$  which have yielded a strong nonlinear swelling behavior. This behavior has been modelled on the basis of a irradiation-induced reduction in the grain size [4]. The importance of the grain structure lies in its acting as a rapid path for fission gas diffusion and providing sites for gas precipitation and bubble growth. This rapid swelling behavior in  $U_3Si_2$  began at a Uranium burn-up of about 10% or about 8000 dpa. Although this dose is not achievable by ion beam techniques, it is possible to investigate the preliminary stages at lower doses. The present experiment follows the changes in the crystals and microstructures of  $U_3Si$  and  $U_3Si_2$  produced by high energy ion irradiation at temperatures above the temperature limit for amorphization.

## EXPERIMENTAL

Alloys of depleted uranium and Silicon were arc melted and heat treated at 1075 K for 72 hours. For  $U_3Si$  this treatment produced Martensite phase material containing dispersed small  $U_3Si_2$  precipitates. The  $U_3Si_2$  alloy was single phase. The starting ingots were sliced into 400  $\mu m$  thick wafers, and disks 3 mm in diameter were core-drilled from the wafers. TEM specimens were produced by jet polishing to create a perforation [5].

Irradiations were performed with 1.5 MeV  $Kr^+$  ions at fluxes less than  $2 \times 10^{12}$   $Kr\ cm^{-2}\ sec^{-1}$ . The average projected range of the Kr ions in both  $U_3Si$  and  $U_3Si_2$  is estimated from TRIM [6] calculations to be about 200 nm. Based on TRIM calculations, a fluence of  $1 \times 10^{16}$   $Kr/cm$  produces about 25 dpa for a displacement threshold of 20 eV. Less than 1% of the Kr

would stop in the TEM transparent areas of the specimens. Specimens were irradiated in situ in the High Voltage Electron Microscopy-Tandem Accelerator User Facility at Argonne National Laboratory [7] in a Gatan double-tilt heating stage. This facility permits simultaneous ion irradiation and TEM observation over a wide range of temperature. The HVEM was operated at 300 kV, below the threshold for production of visible damage by electrons (approximately 600 kV). The specimen normal was tilted 25 degrees away from the electron beam so that the ion beam was incident about 5 degrees from the specimen normal. Images of the specimen were recorded with the Kr beam interrupted but without moving the specimen. Amorphization was defined as disappearance of all spots in the electron diffraction pattern.

## RESULTS AND DISCUSSION

The microstructure of our unirradiated  $U_3Si$  consisted of large grains tens of  $\mu\text{m}$ s in size and showed a rib Martensite structure, Figure 1. The crystal structure was tetragonal [8]. Extensive studies have been made of the stability of  $U_3Si$  against amorphization by 1.5 MeV Kr ions [1] and Uranium fission [8]. The upper temperature limit for amorphization is about  $250^\circ\text{C}$ . At lower temperatures, a Kr dose of less than  $10^{14}$  ions/ $\text{cm}^2$ , or 0.2 dpa, was sufficient to fully amorphize  $U_3Si$ . During low temperature ion irradiation, the  $U_3Si$  chemically disordered, as seen by the loss of super lattice reflection in electron diffraction, and the Martensite structure disappeared from the TEM images. A detail neutron diffraction study was made of the crystallographic changes preceding amorphization induced by Uranium fission produced by neutron bombardment at room temperature [8]. Amorphization was preceded by a transformation from the tetragonal Martensite phase to the high temperature cubic phase. In spite of the localized nature of the cascade damage, this transformation was homogeneous through the material.

The response of  $U_3Si$  to 1.5 MeV Kr ion irradiation at temperatures above the temperature limit for amorphization is shown by TEM images and electron diffraction patterns in Figures. 1 and 2. The atomically ordered Martensite crystal grains are visible as parallel platelets, and the diffraction shows the ordered tetragonal crystal structure.

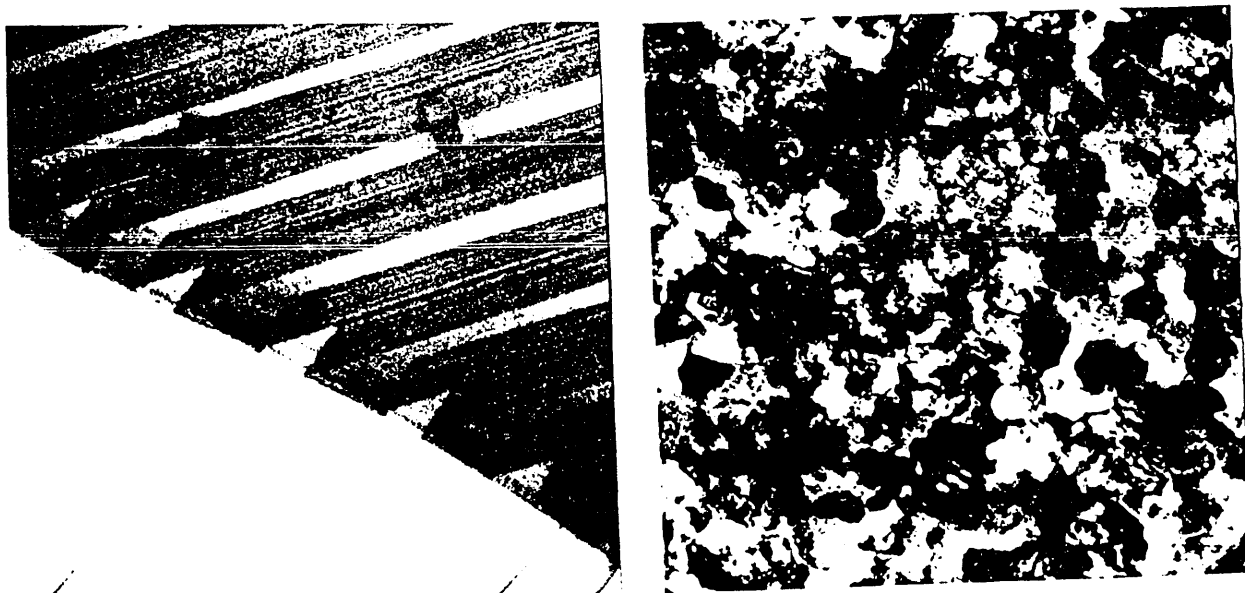


Figure 1. TEM images of  $U_3Si$  before and after irradiation with 1.5 MeV Kr ions to a dose of  $8 \cdot 10^{15}$  ions/ $\text{cm}^2$  at  $350^\circ\text{C}$ .

During irradiation at  $350^\circ\text{C}$ , the Martensite structure disordered to the point that it disappeared from the TEM image after a dose of  $5 \cdot 10^{13}$  ions/ $\text{cm}^2$ . The disordered structure was replaced by small crystal grains having sizes on the order of 100 to  $200 \text{ \AA}$  at doses greater than  $10^{15}$  ions/ $\text{cm}^2$ .

During the course of irradiation the small grains increased in number and appear to increase very slowly in size. Due to the complex overlapping microstructure this last point remains uncertain. The crystallographic transformation is illustrated in Figure 2 by a series of diffraction patterns taken at different doses during interruptions of the Kr irradiation.

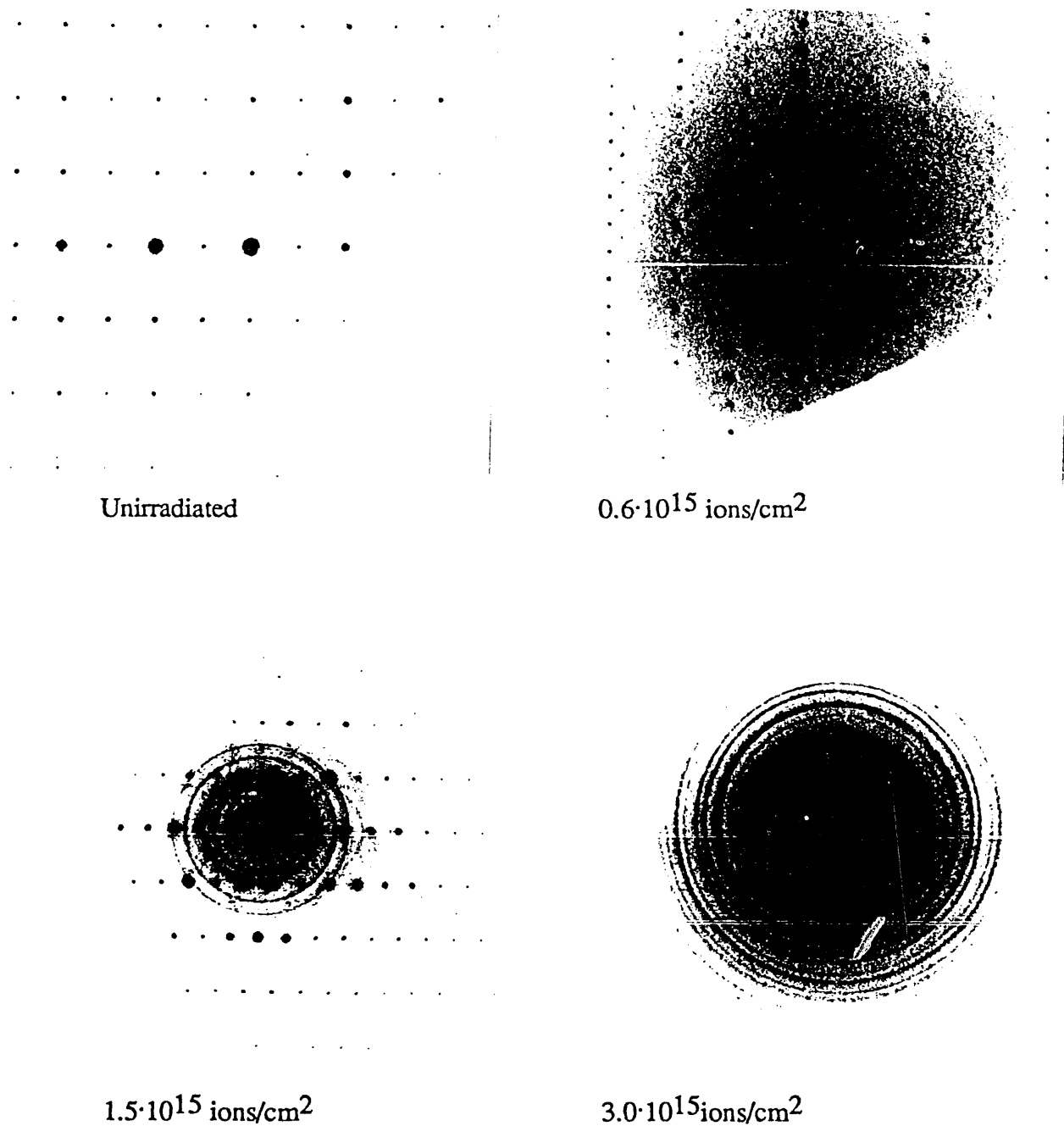


Figure 2. Electron diffraction from  $U_3Si$  irradiated with 1.5 MeV Kr ion to dose of 0; 0.6; 1.5 and  $3.0 \cdot 10^{15}$  ions/cm<sup>2</sup>

Deterioration of the initial crystalline diffraction was concurrent with the polynanochotomization. Complete removal of the initial crystal structure occurs by a dose of  $3 \cdot 10^{15}$  ions/cm<sup>2</sup> or about 3.5 dpa, and the resultant diffraction pattern corresponds to that of powder cubic  $U_3Si$  which is the high temperature parent phase. This crystallographic transformation sequence differs in several fundamental ways from the changes preceding amorphization found during room temperature neutron irradiation of  $U_3Si$ . Fission fragment damage at room temperature homogeneously

distorted the  $U_3Si$  crystal structure from the tetragonal phase toward the cubic phase without the coexistence of the initial and final crystalline phases. After transformation, the defected cubic phase was unstable and amorphized. During high-temperature ion irradiation the localized damage events transformed finite size volumes of material, and the two phases coexisted together. Because of limited microscope resolution, it has not been possible to determine whether a single ion tract is capable of directly converting a small volume of either the tetragonal or disordered crystal to the cubic phase. While amorphization requires a fraction of a dpa, high temperature grain refinement is complete after  $3 \cdot 10^{15}$  ions/cm<sup>2</sup> or 7.5 dpa. This is likely due to thermal annealing of the damage during the irradiation.

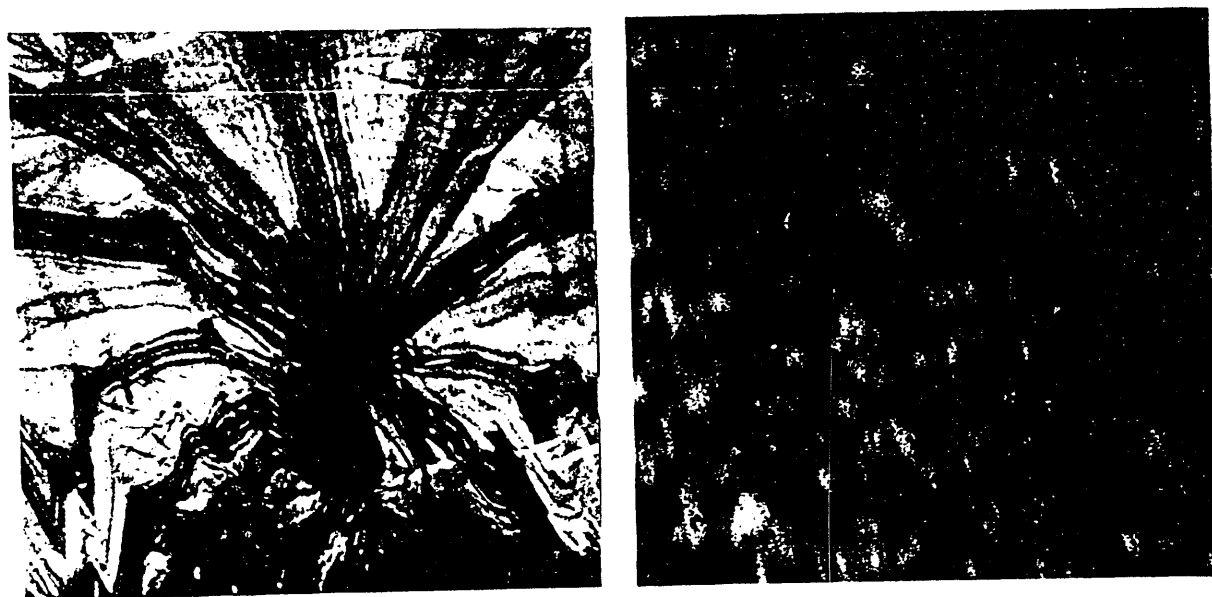


Figure 3. TEM images of  $U_3Si_2$  before and after irradiation with 1.5 MeV Kr ions to a dose of  $4 \cdot 10^{15}$  ions/cm<sup>2</sup> at 350°C.

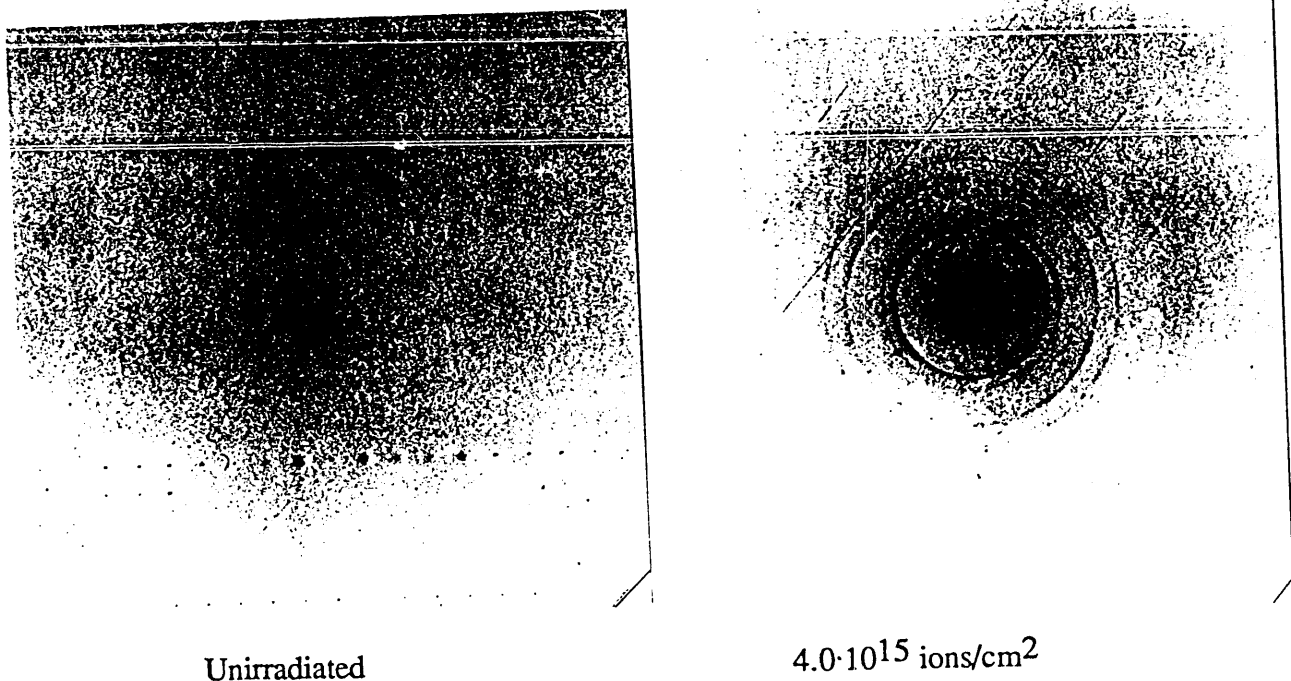


Figure 4. Electron diffraction from  $U_3Si_2$  irradiated with 1.5 MeV Kr ion to dose of 0; 1.0; 2.0 and  $4.0 \cdot 10^{15}$  ions/cm<sup>2</sup>

The response of  $U_3Si_2$  to 1.5 MeV Kr ion irradiation at temperatures above the temperature limit for amorphization is shown by TEM images and electron diffraction patterns in Figures. 3 and 4. Initially the  $U_3Si_2$  consisted of atomically ordered crystalline grains with tetragonal crystal structure, and the TEM image showed only bend contours. During irradiation at 350°C, the crystal structure disordered to the point that bend contours disappeared from the TEM image. The crystalline transformation is illustrated in Figure 5 by a series of diffraction patterns taken during interruptions of the Kr irradiation. Deterioration of the initial crystal structure was concurrent with formation of small grains, Figure 4b. These grains have sizes on the order of 100 to 200Å as was found for  $U_3Si_2$ . During irradiation, the small grains increased in number until they filled the specimen. Complete removal of the initial structure occurred by a dose of  $4 \cdot 10^{15}$  ions/cm<sup>2</sup>.

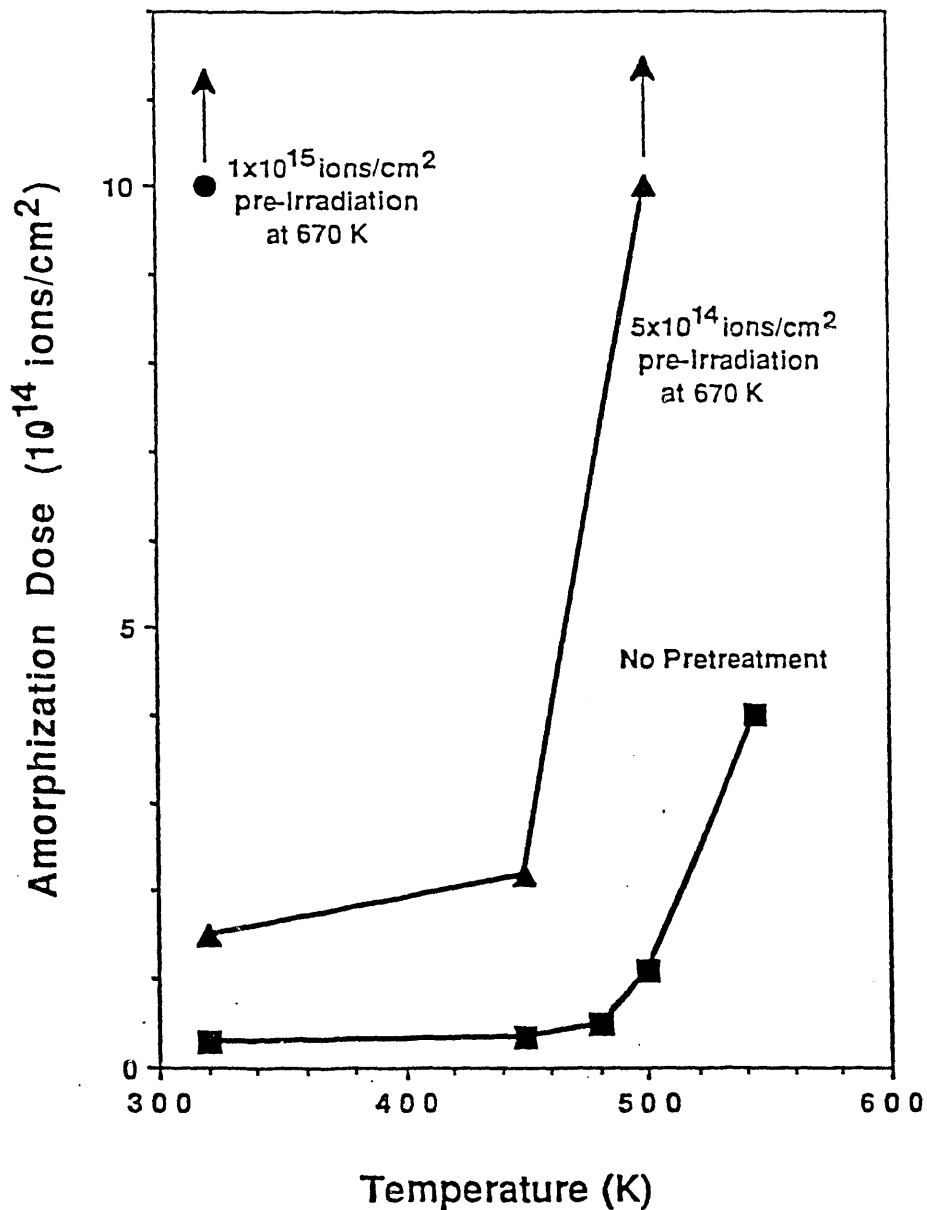


Figure 5. Temperature dependence of the dose of 1.5 MeV Kr ions required to amorphize  $U_3Si_2$  with or without high-temperature irradiation treatments.

Grain refinement has a strong effect on ion-beam amorphization. When grain refined  $U_3Si$  or  $U_3Si_2$  are irradiated at temperatures below the amorphization temperature limit, the ion dose required for amorphization is greatly increased. This effect is illustrated in Figure 5 for  $U_3Si$ . The degree of increase in amorphization dose depends on the irradiation dose at high temperature or the amount of grain refinement. After a dose of  $1 \cdot 10^{15}$  ions/cm<sup>2</sup> at 350°C, complete amorphization was not observed during room temperature irradiation to a dose of  $1 \cdot 10^{15}$  ions/cm<sup>2</sup> or 20 times the normal amorphization dose.

There are several possible explanations for this observation. High density grain boundaries are expected to act as an effective defect sink, and enhanced defect annihilation may be responsible for retarding amorphization at room temperature. A second possible explanation involves the dynamic interaction of the defect cascade with grains on the order of cascade sizes. When a cascade forms, a volume of material is melted and quenched. It may be that with boundaries in close proximity on all side that the crystalline phase regrows and the amorphous phase does not form. A third possibility is that a crystal stiffening prevents the decrease in elastic modulus observed to precede amorphization [9].

## CONCLUSIONS

Grain refinement has been observed for  $U_3Si$  and  $U_3Si_2$  irradiated at temperatures above their amorphization temperature limits. Their behaviors are quite similar to that observed for  $Zr_3Al$  [9].  $U_3Si_2$  was converted to fine grain polycrystal material at a dose 1/3 greater than that required for  $U_3Si$ . The dose required to amorphize  $U_3Si_2$  is also 1/3 greater than that for  $U_3Si$ . The fact that these ion doses have the same ratio likely indicate that the same displacement processes are involved in the two materials and only the threshold energies differ. The conversion of tetragonal  $U_3Si$  to the high temperature cubic phase by irradiation defects has a parallel to the high temperature phase transformation driven by the thermal vacancy concentration.

Grain refinement during irradiation has several important impacts on irradiation behavior. The first is the suppression of amorphization displayed in Figure 5. Because of plastic flow during irradiation of amorphous materials, any phenomenon that stabilizes a crystalline phase is important. In addition, understanding this effect should help elucidate the mechanism(s) for irradiation induced amorphization. It is not clear at this time if the suppression is due to enhanced defect annihilation at the additional grain boundaries or due to a crystal stiffening that prevents the decrease in elastic modulus observed to precede amorphization [9].

A second major impact is enhanced reactor-fuel swelling expected when fission gas is able to migrate to grain boundaries before being trapped. This more efficient gas collection may increase the swelling rate by a factor of ten [4]. Such grain refinement has been observed for  $UO_2$  and is suspected to play a major role in the swelling behavior of other reactor fuels.

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