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# IRRADIATION MIXING OF Al INTO U<sub>3</sub>Si

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## ABSTRACT

Thermal and irradiation induced intermixing of uranium silicide reactor fuels with the aluminum cladding is an important consideration in understanding their fission gas and fuel swelling behavior. We have used Rutherford backscattering to follow the behavior of an Al thin film on U<sub>3</sub>Si and U<sub>3</sub>Si<sub>2</sub> during 1.5 MeV Kr ion irradiation at temperatures of 30 and 350°C. After an initial dose during which no intermixing occurs, the Al mixes quickly into U<sub>3</sub>Si. The threshold dose is believed to be associated with an oxide layer between the Al and the uranium silicide. At 300°C and doses greater than threshold, rates of mixing and aluminide phase growth are extracted.

## INTRODUCTION

Ion beam mixing plays an important role in the behavior of many nuclear reactor fuels during their use. High density reactor fuels are required for either high power density or low uranium enrichment applications. In such applications, particles of the fuel, U<sub>3</sub>Si, and the cladding, Al, are mixed together and roll-bonded together between Al plates. During irradiation of the fuel plates, the uranium fissions into several fission fragments that produce tracks of damage that may penetrate the interface between the fuel particles and their Al cladding. Examination [1] after irradiation reveals an intermixed layer of Al and the fuel around the periphery of each fuel particle. This layer appears to be single phase and its thickness varies as the square root of the irradiation dose [2].

The mixed layer is important in the fuel plate swelling behavior [1]. No visible fission gas bubbles are observed in the mixed layer, while very large bubbles are found on the interior of the fuel particles. At high fuel particle density, fuel failure can occur when the Al is locally consumed by a fuel particle. A complicating factor is that U<sub>3</sub>Si is amorphized by neutrons or 1.5 MeV Kr ions after an irradiation dose of 0.3 dpa at temperatures below 280°C [3]. Amorphous materials under irradiation undergo plastic flow. In this situation the amorphous U<sub>3</sub>Si has little or no strength and catastrophic swelling will occur [1,4].

In this work, we have used Rutherford backscattering to follow the behavior of an Al thin film on U<sub>3</sub>Si during 1.5 MeV Kr ion irradiation at temperatures of 30°C, when the alloy becomes amorphous, and 300°C, when the alloy remains crystalline. After irradiation the surface of the specimens have been examined by scanning electron microscopy equipped with x-ray detectors for high resolution elementary mapping.

## EXPERIMENTAL

Specimens were produced from an alloy of depleted uranium and silicon that were arc melted and heat treated at 1075 K for 72 hours. The melt was made Si rich to avoid the presence of free uranium. The starting ingots were sliced into wafers that

were then polished flat with 0.5  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  grit. The polished wafers were mounted on copper blocks using Sauereisen and then coated with 1800  $\text{\AA}$  of Al by electron beam evaporation in ultrahigh vacuum. Because of the exposure to air before Al coating, the specimens initially had an oxide layer between the Al and the  $\text{U}_3\text{Si}$ .

In-situ ion irradiations were performed at the 2 MV tandem National Electrostatics ion accelerator facility at Argonne National Laboratory. Irradiations were performed with 1.5 MeV Kr ions at dose rates of approximately  $6 \times 10^{11}$  Kr/cm<sup>2</sup>sec. TRIM95 damage calculations [5] using a 20 eV threshold energy yield 18 dpa /  $10^{16}$  Kr/cm<sup>2</sup> at the interface between the Al and the  $\text{U}_3\text{Si}$ . Average damage rate at the interface was  $1 \times 10^{-3}$  dpa/s. RBS with 1.5 MeV He with a detector angle of 45° and a sample angle of 20°. The spectra were deconvoluted by standard curve fitting techniques [6].

## RESULTS

A series of RBS spectra taken from one wafer of Al coated  $\text{U}_3\text{Si}$  before and after increasing doses of 1.5 MeV Kr ion irradiation at 30°C and 300°C are shown in figures 1 and 2. Fitting of the RBS spectra indicate that the Al/ $\text{U}_3\text{Si}$  interface initially had an oxide layer which SEM shows consists of a combination of small  $\text{UO}_2$  precipitates and an overall oxide layer on the  $\text{U}_3\text{Si}$ . When the  $\text{U}_3\text{Si}$  is amorphized at 30°C, the Al mixing proceeds at a slow rate. However, it is clear from a cursory observation that at 300°C when the  $\text{U}_3\text{Si}$  remains crystalline, Al mixing and diffusion is quite rapid after a threshold dose of approximately  $1.0 \times 10^{16}$  Kr/cm<sup>2</sup> and a new phase forms.

Studies [8,9] of the U Si Al alloy system indicate at equilibrium the formation of  $\text{U}(\text{SiAl})_3$ . In our experiments, the averaged mixed phase contains approximately 33 at.% U corresponding to  $\text{U}(\text{Si}_x\text{Al}_{1-x})_2$ . The mixing of Al into U also resulted in the formation of  $\text{UAl}_2$  at elevated temperatures [7]. Growth of the  $\text{U}(\text{Si}_x\text{Al}_{1-x})_2$  layer at 300°C is shown in Figure 3. The growth occurs with a square of dose dependence typical of phase formation under ion irradiation. There is evidence of the same phase forming in the RBS spectra after the 30°C irradiations, fig. 1. During neutron irradiation and uranium burn up, mixing of Al into  $\text{U}_3\text{Si}_2$  has been reported to occur with a square root of dose dependence and to form a phase of  $\text{U}(\text{Si},\text{Al})_3$  [2] that is similar in structure to  $\text{UAl}_3$ . The similarity of ion beam mixing of Al into U and  $\text{U}_3\text{Si}$  may indicate that the mixing is controlled by phase formation and the diffusion of Al through the phase.

The amount of Al diffusion, extract by fitting the Al and U edges of the RBS spectra, is shown in figure 4 for both irradiation temperatures. At 300°C after a dose of  $2 \times 10^{16}$  Kr/cm<sup>2</sup>, signal from the discrete Al layer has disappeared as the new phase formed. The rate of mixing,  $\partial(4Dt)/\partial\phi$ , of Al into  $\text{U}_3\text{Si}$  is 0.05 nm<sup>2</sup>/dpa at 30°C. Due to the rapid mixing and phase formation, we can only estimate a lower limit of at least 2.07 nm<sup>2</sup>/dpa at 300°C. These values can be compared to mixing of Al into pure U by 400 keV Ar ions [7] which occurs at a rate of 0.14 nm<sup>2</sup>/dpa at 30°C and at a rate of about 6.1 nm<sup>2</sup>/dpa at 300°C. The rates of Al mixing appear to be three times higher than for Al mixing into  $\text{U}_3\text{Si}$ .

Details of the surface morphology after irradiation have been observed by scanning electron microscopy (SEM). An SEM image of the specimen surface after 300°C irradiation is shown in figure 5 along with elementary maps made from characteristic X-rays. The brighter areas in the X-ray images indicate higher concentration of the detected element. Apparent in figure 5 are precipitates of a silicon

rich phase,  $U_3Si_2$  and oxide particles formed during melting of the alloy. The  $U_3Si_2$  phase arises because the alloy was intentionally made with excess Si to avoid the presence of unreacted uranium. Detailed elementary analysis shows that  $UO_2$  precipitates do not contain either Si or Al except for small Al islands remaining on their surfaces. Al is found with equal concentration within the  $U_3Si$  and the  $U_3Si_2$  phases, however, Al is depleted in the areas surrounding oxide precipitates.

## SUMMARY

The mixing of Al into  $U_3Si$  is controlled by the formation of a  $U(Si,Al)$  phase with 33% U. The mixing rates of Al into  $U_3Si$  are similar to those of Al mixing into pure uranium at the same temperatures and thus likely do not depend on the  $U_3Si$  being crystalline or amorphous. Once the phase has been formed, the Al surface layer is rapidly consumed as the phase grows. At 300°C, the phase thickens as the square root of ion dose after a threshold dose. An oxide barrier may be responsible for the threshold dose since no Al was detected in oxide precipitates.

## ACKNOWLEDGEMENT

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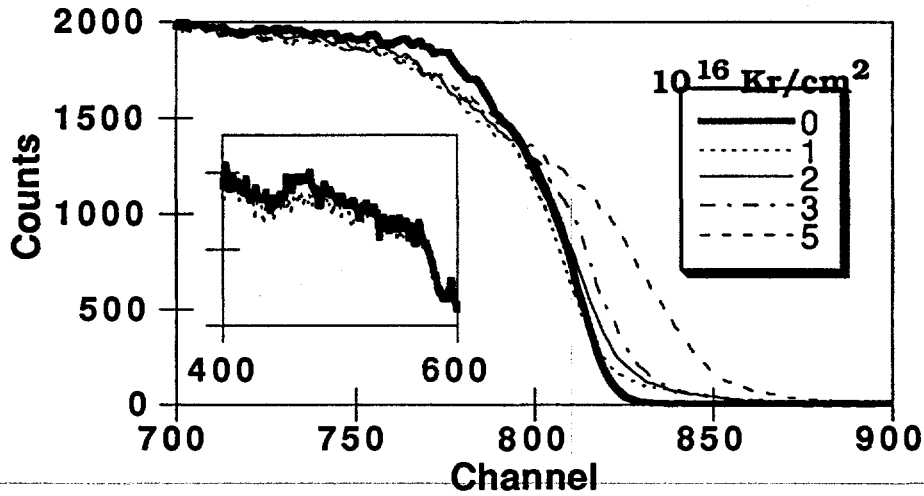


Fig. 1. RBS spectra of  $U_3Si$  coated with Al and irradiated with 1.5 MeV Kr ions at 30°C. Ion doses are: 0.0, 1.0, 2.0, 3.0, and 5.0  $10^{16}$  Kr/cm<sup>2</sup>. The insert shows the Al signal before and after 5.0  $10^{16}$  Kr/cm<sup>2</sup>.

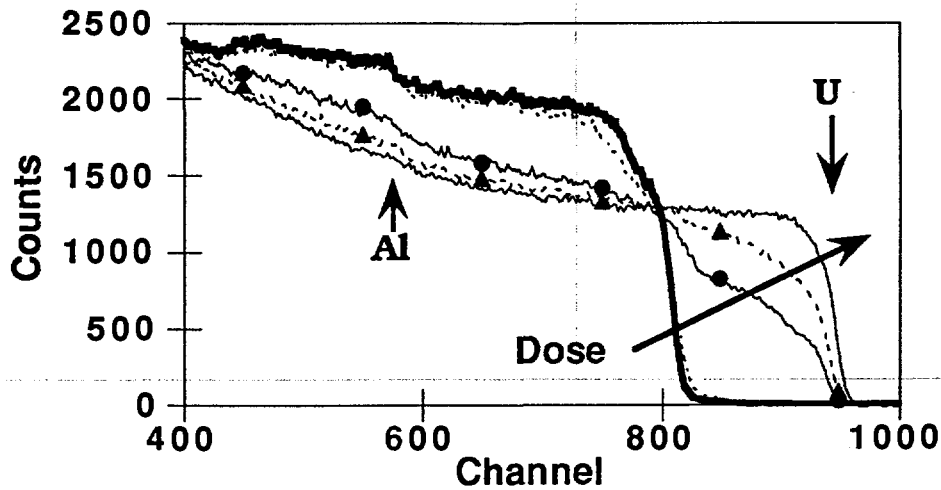


Fig. 2. RBS spectra of  $U_3Si$  coated with Al and irradiated with 1.5 MeV Kr ions at 300°C. Ion doses are: 0.0, 0.5, 1.0, 1.5, and 4.0  $10^{16}$  Kr/cm<sup>2</sup>. The positions of the Al and U edges are indicated.

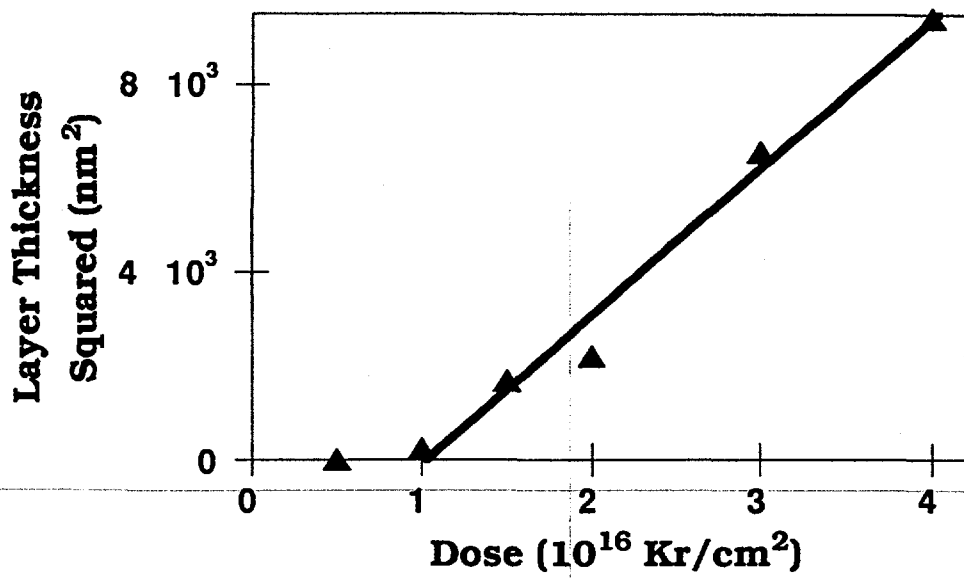


Fig. 3 Square of the  $U(Si_xAl_{1-x})$  layer thickness as a function of the Kr ion dose,  $\Phi$ , at 300°C.

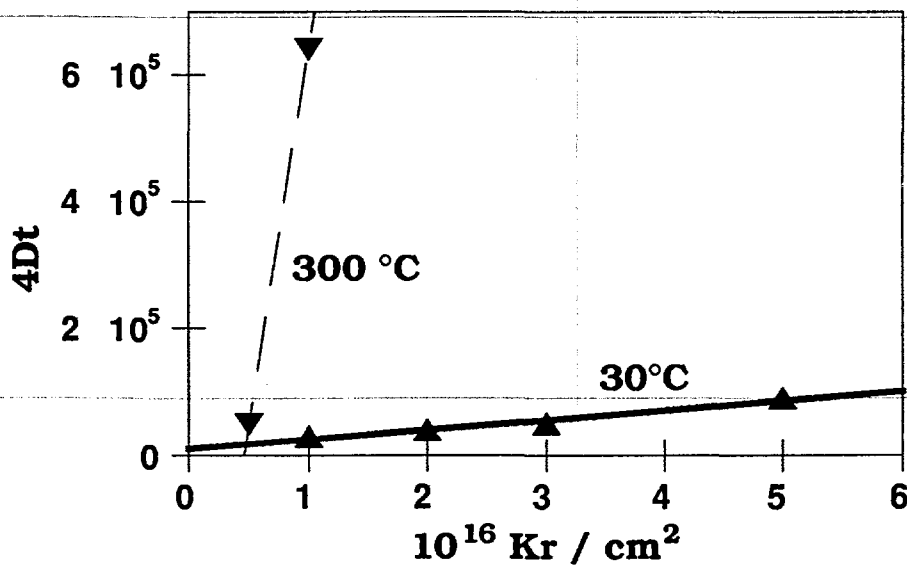
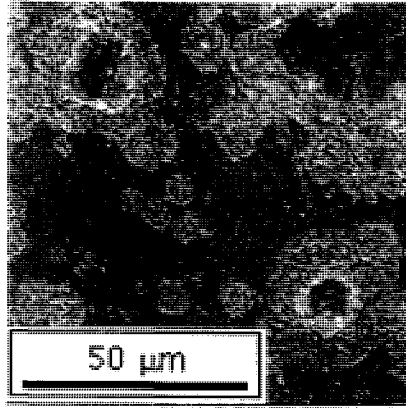
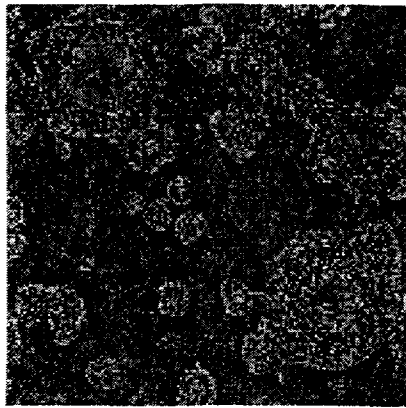


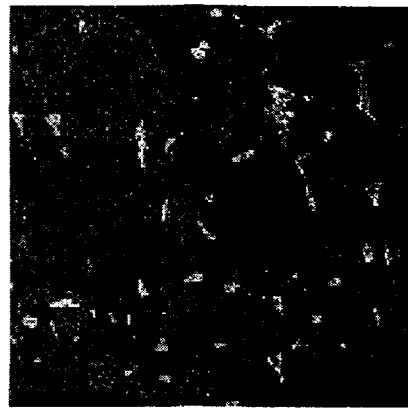
Fig. 4 Variation of the amount of Al mixing, (4Dt), as a function of the Kr ion dose,  $\Phi$ , at 30°C and 300°C.



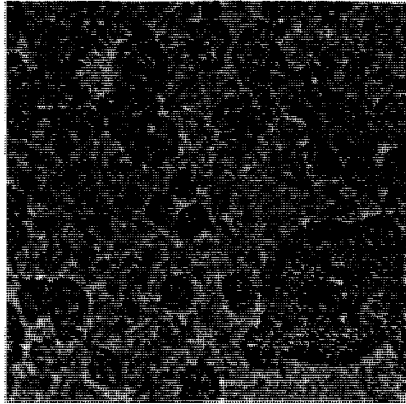
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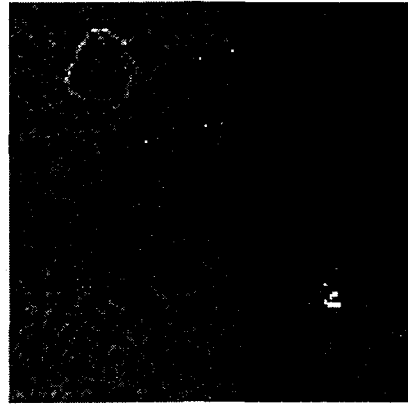
U



Si



Al



O

Figure 5 SEM image and X-ray composition map of the near surface region of the  $U_3Si$  specimen after ion irradiation. White in the X-ray images indicates the presence of the element listed under the picture. The Si X-ray image indicates the presence of a small amount out a second phase of  $U_3Si_2$ . After the final ion irradiation, the original Al coating has completely dissolved into the uranium silicide without regard for the silicide phase.