NEUTRON IRRADIATED URANIUM SILICIDES STUDIED BY NEUTRON DIFFRACTION AND RIETVELD ANALYSIS*

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INTRODUCTION

Uranium silicides have been considered for use as reactor fuels in both high power and low enrichment applications. However, U_3Si was found to become amorphous under irradiation [1] and to become mechanically unstable to rapid growth by plastic flow [2,3]. U_3Si_2 appears to be stable against amorphization at low displacement rates, but the extent of this stability is uncertain. Although the mechanisms responsible for plastic flow in U_3Si and other amorphous systems are unknown, as is the importance of crystal structure for amorphization, it may not be surprising that these materials amorphize, in light of the fact that many radioactive nuclide - containing minerals are known to metaminctize (lose crystallinity) under irradiation [4]. The present experiment follows the detailed changes in the crystal structures of U_3Si and U_3Si_2 introduced by neutron bombardment and subsequent uranium fission at room temperature. U-Si seems the ideal system for a neutron diffraction investigation since the crystallographic and amorphous forms can be studied simultaneously by combining conventional Rietveld refinement of the crystallographic phases with Fourier-filtering analysis [5] of the non-crystalline scattering component.

EXPERIMENTAL

Powdered U_3Si and U_3Si_2 specimens were fabricated from high purity Si and highly depleted Uranium, 0.022 at % ^{235}U. The high dose irradiation behaviors of these powders, roll bounded between alumium plates, have been previously studied [2]. For this study, each powder was doubly encapsulated in thin wall Vanadium cans that had been evacuated and filled with He gas. The U_3Si specimen also contained precipitates of U_3Si_2 (<15 volume %) and the uranium oxides UO and UO_2 (< 5 volume %) introduced by vacuum annealing.

Neutron irradiations were performed at IPNS in a room temperature facility located adjacent to the neutron source [6]. Neutrons are produced as the result of 500 MeV protons stricking a ^{235}U target. The neutron spectrum for this facility is characteristic of a reactor neutron spectrum with the addition of neutron having energies up to 500 MeV. In these specimens, damage was produced primarily by uranium fission in a manner identical to damage production in operating nuclear reactor fuel. The nuclear-reaction cross sections for fast and thermal fission were determined by standard activation techniques [7]. The irradiations were performed in small steps, ^{235}U burn-up $< 3 \times 10^{-8}$, in order to closely follow changes in the crystal structure. The amount of damage per fission is typically given in terms of displacements per atom, dpa. The number of defects per fission has been calculated to be 7.8×10^4 [8].

After each irradiation and appropriate cool-down, a powder pattern was measured on the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS) and the data were analyzed using the Rietveld profile refinement technique [9]. Details of data collection and analysis are given in a recent paper [10].

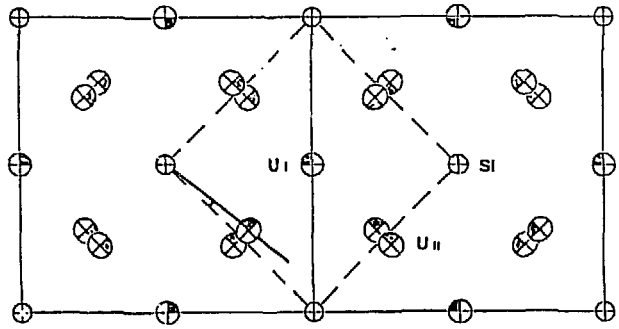

Fig. 1 [001] projection of U_3Si structure showing relationship between tetragonal and cubic Cu_3Au-like cells.

RESULTS

The crystal structure refinements of unirradiated U_3Si and U_3Si_2, including the U_3Si_2 precipitates in U_3Si, agree with those previously obtained from X-ray diffraction [11,12]. The repeated irradiation doses produced structural changes in both alloys which resulted in a broadening and shifting of the Bragg peaks. The behaviors of U_3Si, U_3Si_2 and the U_3Si_2 precipitates in U_3Si will be discussed separately.

U_3Si Unirradiated U_3Si (projection shown in Fig. 1) is tetragonal, space group I4/mcm, with $a_0 = 6.0358(1)$, $c_0 = 8.6925(1)$ Å, $c/a = 1.440$ and 16 atoms per unit cell. There are: 4 U_I at $0,1/2,1/4$; 8 U_{II} at $x, x+1/2,0$ with $x=0.2251(1)$ and 4 Si at $0,0,1/4$. The base layer ($z=0$) contains U atoms only, the next layer ($z=1/4$) is $1/2$ U and $1/2$ Si, and the sequence repeats. The layer at $z = 1/2$ (U only) is rotated slightly

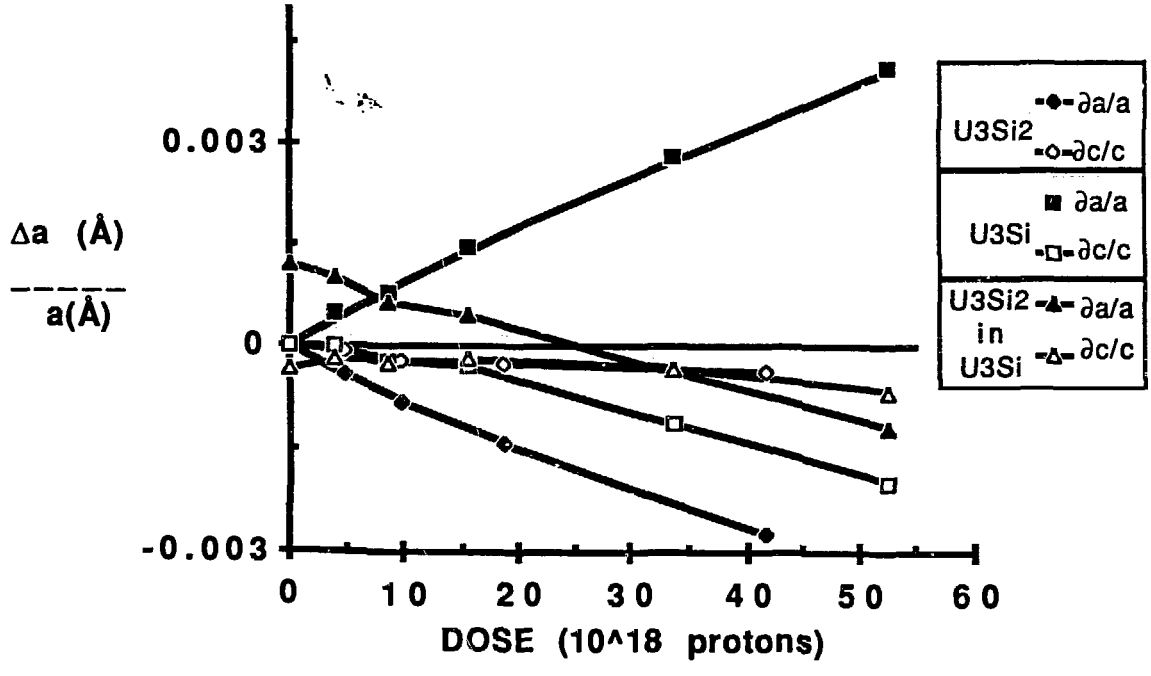

Fig 2. Fractional lattice parameter changes for U_3Si and U_3Si_2.

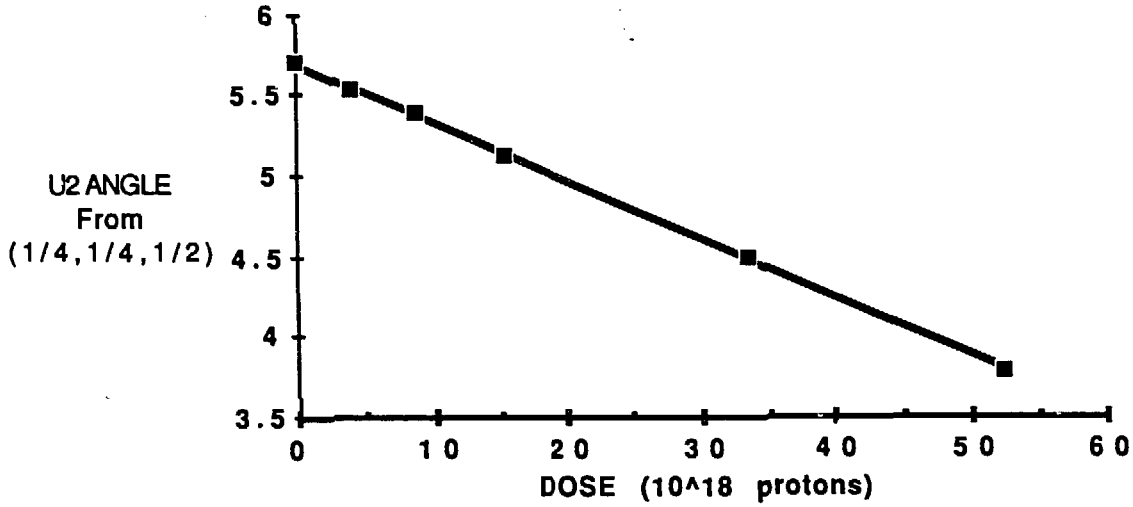

Fig 3. Variation of angle defined in Fig. 1 with irradiation dose.

relative to the base layer. This structure can be viewed as pseudo-cubic, in that if the U_{II} are shifted such that $x = {}^1/_4$ and simultaneously the axial ratio ($^c/_a$) is reduced to $\sqrt{2}$, U_3Si would have the cubic Cu_3Au type structure ($a_c = {}^{a_T}/_{\sqrt{2}} = {}^{c_T}/_2$) shown by the dashed lines in Fig. 1. This transformation is known to occur upon heating to 1038K [13].

Changes produced by neutron irradiation are shown in Figs 2 and 3. After 5 irradiation cycles (52.4 x 10^{18} protons or 0.02 dispacements per atom), the a-axis increased by 0.5% and the c-axis decreased by 0.1% (Fig. 2), resulting in a net unit cell volume increase of 0.1%. A number of other important changes occur during the irradiation. U_{II} is approaching its idealized Cu_3Au position ${}^1/_4,{}^3/_4,0$ (the deviation from this can be expressed as the angle of rotation (shown in Fig. 3) about the c-axis away from this position). Fig. 4 illustrates some additional features: the the $(220)_T$ and $(004)_T$ reflections are gradually converging to become the cubic $(200)_C$, all diffraction peaks broaden, and the diffuse background is significantly increased (possible evidence for amorphous phase formation). Finally, the Debye-Waller factors for all atoms increase with each irradiation and the rms values for the Si atom are somewhat less than for the U atoms. This may be indicative of deviations - static or dynamic - of the uraniums from their ideal locations. Thus, it would appear that irradiation is producing, on a defect cascade scale, a thermal spike event which is driving the tetragonal crystal structure to the reported high temperature cubic form and/or to an amorphous form.

U_3Si_2 Unirradiated U_3Si_2 is tetragonal, space group P4/mbm, with a_0 = 7.3299 Å, c_0 = 3.9004 Å, $^c/_a$ = 0.532 and 10 atoms per unit cell. As shown in Fig. 5, there are: 2 U_I at 0,0,0; 4 U_{II} at x, x+${}^1/_2$,${}^1/_2$ with x=0.1820(1) and 4 Si at x', x'+${}^1/_2$,0 with x'=0.3841(2). Lattice parameter changes as a function of dose are shown in Fig. 2. The unit cell volume decreases for U_3Si_2 , in contrast to the increase observed in U_3Si. The most striking feature resulting from the Rietveld refinements is the large out-of-plane displacement parameter for U_I in all forms of the U_3Si_2: both unirradiated and irradiated, pure phase and second phase in U_3Si (Fig. 5). This could be an indication that the space group is not correct, and that the correct structure includes ordered displacements of the U_I atoms from the origin, either within the plane or between planes. It is conceivable, on the other hand, that the huge thermal displacement parameter represents a random distribution of static

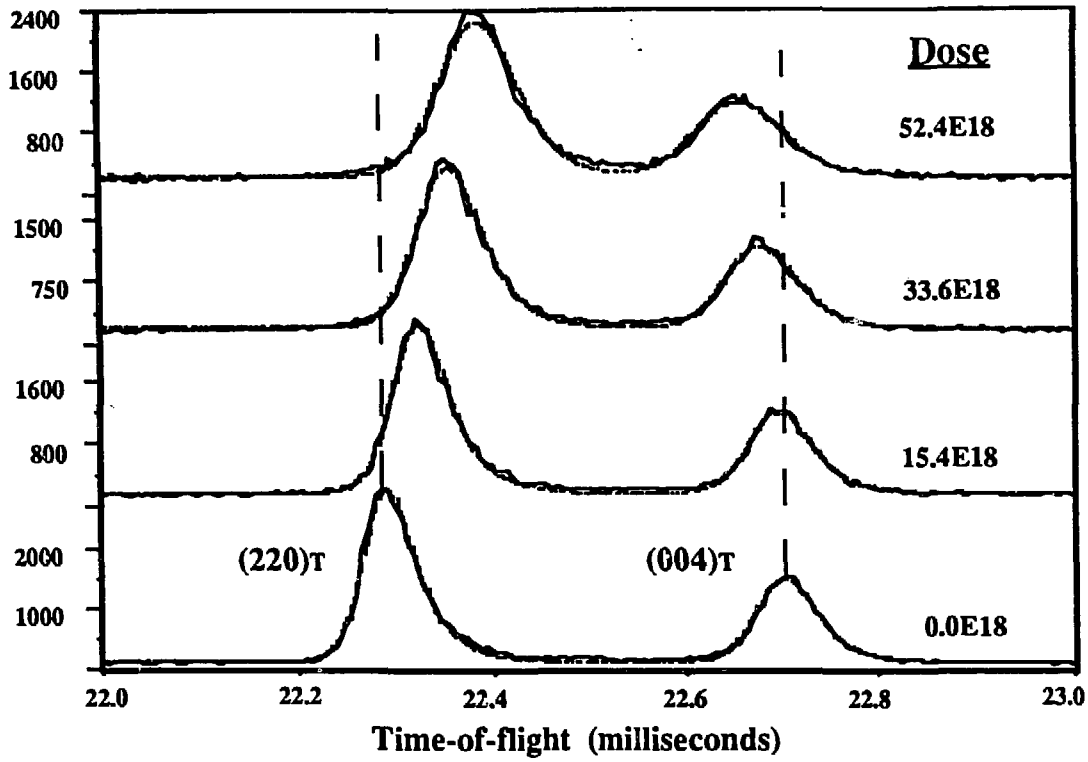

Fig 4. Multiplet peak fitting for the $(220)_T$ and $(004)_T$ reflections of U_3Si. Note the gradual evolution toward cubic, broadening of both peaks, and increasing background between peaks with increasing dose.

displacements along the [001] direction. With increased irradiation, U_{II} moves away from $^1/_4,^1/_4,^1/_2$ toward $^1/_4,0,^1/_2$. Completion of this process would require removal of a similar U_{II} site from the adjacent unit cell.

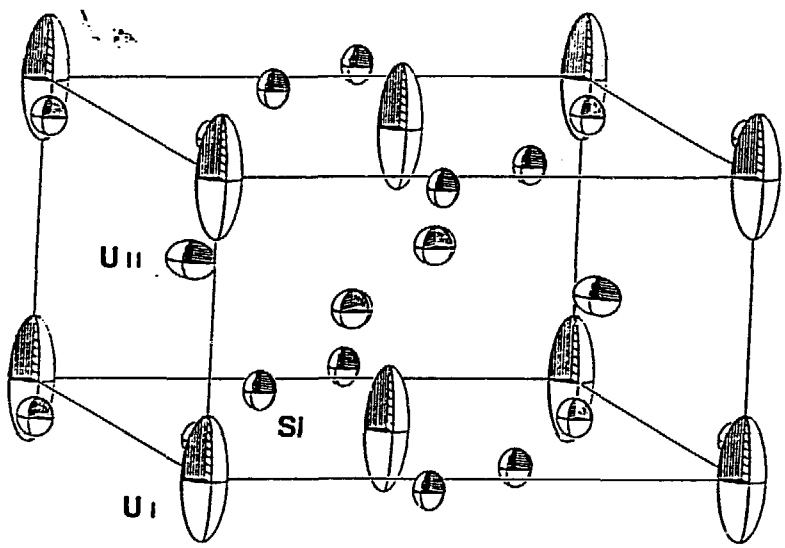

Fig 5. ORTEP drawing of U_3Si_2 structure showing dramatic out-of-plane displacements on U_I.

U_3Si_2 In U_3Si The initial structure of the U_3Si_2 precipitates in U_3Si was the same as the pure U_3Si_2 specimen, however the unirradiated precipitates were expanded 0.012% in the a-direction and contracted 0.04% in the c-direction producing an increase of 2.3×10^{-4} % in the unirradiated unit cell volume. Changes produced by neutron irradiation are also shown in Fig. 2. Both the a-axis and the c-axis contract leading to a decrease in the unit cell volume as in the pure U_3Si_2 specimen. The decrease occurs at about the same rate as for pure U_3Si_2.

SUMMARY

Since this is merely a progress report, we expect further developments with additional irradiations. U_3Si - we expect the complete transformation from tetragonal → cubic (Cu_3Au-type) → cubic (disordered)→ amorphous as seen with electron diffraction (the use of Fourier-filtering should assist in sorting out the amorphous component). U_3Si_2 - we will consider in more detail the implications of the large out-of-plane displacements; is there a space group change or ar these simply uncorrelated static displacements. U_3Si_2 in U_3Si - further investigations will be concerned with the role of strain in promoting crystallographic changes and indeed whether U_3Si_2 becomes amorphous under either or both of the above conditions.

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