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U₃Si AT 30°C AND 350°C***

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NEUTRON DIFFRACTION STUDY OF RADIATION DAMAGE IN U_3Si AT 30°C AND 350°C

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ABSTRACT

Neutron diffraction has been used to follow damage evolution in U_3Si produced by neutron irradiation at 30°C and 350°C. Increasing neutron irradiation dose at 30°C results in monotonic expansion of the a-axis and contraction of the c-axis that transforms the crystal structure from tetragonal to cubic. Additional irradiation results in amorphization. Neutron irradiation at 350°C results in little change to the a-axis and expansion of the c-axis. The complete alteration in lattice dilatation during irradiation is interpreted as due to modification of surviving defect configurations at the higher temperature. The high temperature lattice dilations can be explained by defect loop formation in the a-b plane. TEM observations have shown that ion irradiation at temperatures below 280°C results in amorphization while twin boundaries dissolve and new subgrains form at higher temperatures. Confinement of lattice strain to the c-axis during irradiation at 350°C may be the mechanism that prevents the total lattice dilatation from exceeding the critical level required for amorphization.

INTRODUCTION

High-density uranium silicides have potential uses in the nuclear industry for use in high power or low enrichment applications. However, U_3Si exhibits a mechanical instability during reactor irradiation that results in catastrophic swelling [1]. Such behavior would preclude use of these materials as reactor fuels. Transmission electron microscopy studies have found that heavy ion bombardment renders U_3Si amorphous at temperatures below about 280 C [2], and that amorphous U_3Si becomes mechanically unstable suffering rapid growth by plastic flow during irradiation [1,2].

The crystallographic changes preceding U_3Si amorphization by fission fragment damage have been studied by high-resolution neutron diffraction as a function of damage produced by uranium fission at room temperature [3]. Unirradiated U_3Si has a tetragonal crystal structure at room temperature. Damage introduced by room temperature irradiation results in a monotonic expansion of the a-axis and contraction of the c-axis with increasing irradiation dose. The net effect is an expansion of the tetragonal unit cell. The expansion, coupled with a concomitant shift of midplane/midcell uranium atoms to symmetric positions, would result in a new cubic unit cell of the Cu_3Au type. The phase transformation appears to be homogeneous and continuous without indication of coexistence of the initial and final phases. Increases in background scattering reflect damage accumulation that saturates after a dose of 0.02 displacements per atom (dpa). Amorphization begins after a lattice expansion of about 1.2 at.% at 0.05 dpa.

In this work, the changes produced by neutron irradiation at a temperature above the amorphization temperature limit, 350°C, have been investigated by high-resolution neutron diffraction.

EXPERIMENTAL

Powder U_3Si specimens were fabricated from high purity Si and highly depleted Uranium, 0.022 at % ^{235}U . The behavior of this powder has been studied after room temperature neutron irradiation to low doses [3]. The high dose irradiation behaviors of this powder, roll bounded between aluminum plates, has been previously reported [1]. 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 annealing.

Neutron irradiations were performed at IPNS in an irradiation facility located adjacent to the neutron source [4]. Neutrons are produced as the result of 500 MeV protons striking a U target. The neutron spectrum for this facility is characteristic of a reactor neutron spectrum with the addition of neutrons having energies up to 500 MeV. In U_3Si , damage was produced primarily by uranium fission in a manner identical to damage production in nuclear reactor fuel. The nuclear-reaction cross sections for fast and thermal fission were determined by standard activation techniques to give a total fission rate of 5.4×10^{-27} /proton [5]. The number of defects per fission has been calculated to be 7.8×10^4 [6]. At a proton current of 10 μ Amp, the damage rate was 2×10^{-8} dpa/sec. Irradiations were performed in small steps in order to closely follow changes in the crystal structure.

After irradiations to total doses of 0.028 and then 0.039 dpa, with appropriate periods of radioactive decay, neutron diffraction was performed at room temperature with the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS). Data were analyzed using the Rietveld profile refinement technique [7]. Details of data collection and analysis are given in a recent paper [8].

RESULTS and CONCLUSIONS

Figure 1 shows a part of the neutron diffraction spectrum from U_3Si as a function of neutron irradiation dose at 30°C. The diffraction arises from the $\langle 220 \rangle$ and $\langle 004 \rangle$ reflections. As the irradiation progresses the two reflections converge. The $\langle 220 \rangle$ and $\langle 004 \rangle$ directions become equivalent, and their corresponding reflections represents the $\langle 200 \rangle$ reflection in the high temperature cubic phase of U_3Si . In addition, the diffraction peaks broaden, and the diffuse background scattering increases significantly. The increase in experimental scatter in figure 1 is due to the increasing background from diffuse scattering relative to the peak heights. Note that the cubic phase is not directly formed at low irradiation doses and that the transformation is continuous and homogeneous. Additional irradiation results in amorphization [3].

Figure 1. Neutron diffraction [$\langle 220 \rangle$ and $\langle 004 \rangle$ peaks] from U_3Si after increasing irradiation dose at room temperature.

The changes in the lattice parameters of U_3Si are shown in figure 2 for irradiations at both 30°C and 350°C . At the lower temperature the a -axis expands while the c -axis contracts. At the same time as lattice is expanding and the $\langle 220 \rangle$ and $\langle 004 \rangle$ directions are becoming equivalent, there are shifts of atomic positions within the unit cell. The Debye-Waller factors for all atomic sites increase with irradiation although the RMS values for Si atoms are somewhat less than for the U atoms. These are indications of deviations, static and dynamic, of atoms from their ideal lattice locations. In total these changes in atomic positions result in a transformation towards a defected $\text{L}_{12} \text{Cu}_3\text{Au}$ structure which is also the structure of U_3Si at temperatures above 765°C [9]. The continuous peak shifts in figure 1 indicate the accumulation of a homogeneous lattice strain but without direct formation of the cubic phase within the small volumes damaged by the fission fragments as would be indicated by the growth of a third peak representing the $\langle 002 \rangle$ cubic reflection. Changes in the crystal structure approach a saturation concomitantly with formation of the amorphous phase. The maximum unit cell volume expansion is 1.4 % due to the a -axis increasing by about 1% and the c -axis decreasing by 0.5%. With increasing irradiation doses an increasingly larger fraction of the specimen transforms into the amorphous phase.

Figure 2. Changes in lattice of U_3Si after neutron irradiation at room temperature [open symbols] or 350°C [filled symbols].

Figure 3. Neutron diffraction [$\langle 220 \rangle$ and $\langle 004 \rangle$ peaks] from U_3Si irradiated at 350°C [thin line] and unirradiated [thick line]. The peaks are normalized to the same integral intensity.

The irradiation behavior of U_3Si lattice parameters at a temperature above the limit for amorphization, $350^\circ C$, is completely different from that at temperatures below the limit. Figure 3 shows the normalized $\langle 220 \rangle$ and $\langle 004 \rangle$ diffraction peaks before and after $350^\circ C$ neutron irradiation. Instead of converging, the $\langle 220 \rangle$ peak is nearly unchanged while the $\langle 004 \rangle$ peak shifts to larger d spacing, and the two peaks move apart. As at $30^\circ C$, the peaks also broaden and decrease in intensity because of diffuse scattering from the defects. As shown in figure 2, after irradiation at $350^\circ C$ there is little change in the a-axis while the c-axis expands.

Above the temperature limit for amorphization, defects are highly mobile, and mobile defects will annihilate and agglomerate. The neutron scattering results suggest that the defects have clustered into configurations with strain fields only along the c-axis. One possible defect configuration is loops in the a-b plane. The net effect of the defect arrangement is to lower the total lattice strain, figure 2. The driving force for amorphization is believed to be an increase in static atomic displacements to a critical level at which the crystal structure become unstable [10]. In many materials this level corresponds to a volume change greater than 1% as observed during $30^\circ C$ irradiation of U_3Si . Since the defects remaining after irradiation at $350^\circ C$ are in a lower strain configuration, the critical strain can not be achieved and the material does not become amorphous.

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