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NEUTRON-INDUCED COLLISION CASCADE MIXING IN Nb/V SUPERLATTICES*

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ABSTRACT

High-angle X-ray diffraction was used to determine cascade mixing efficiencies, Dt/dpa , in Nb/V superlattices irradiated to small doses (≤ 0.26 dpa). Samples were neutron irradiated in the core of the High Flux Beam Reactor at Brookhaven National Laboratory and ion irradiated with 1.5 MeV Ne. No significant differences were observed in cascade mixing efficiencies between the two types of irradiation. Values of Dt/dpa were observed to vary with the modulation wavelength of the superlattice, with thicker wavelength samples yielding values approaching that determined from ion mixing thick Nb/V bilayers ($Dt/dpa \approx 110 \text{ \AA}^2/dpa$). The decrease in mixing efficiency observed at lower wavelengths may be related to an observed structural transition in which the interfaces of the superlattice become coherent.

1. Introduction

Irradiation with ions and neutrons can enhance mass transport in metals and alloys [1]. This enhancement may lead to significant alterations in the microstructure of materials, an understanding of which is critical in evaluating and predicting the integrity of components used in high radiation environments such as the core of a nuclear reactor.

The enhancement in transport during irradiation occurs primarily in two ways depending on the irradiation temperature [1]. At low temperatures ballistic relocation mechanisms dominate which are essentially temperature-independent. At sufficiently high primary recoil energies energetically dense collision cascades may be produced. Thermally-stimulated atomic mixing occurs within the core of the cascades (cascade mixing). At elevated irradiation temperatures, below which thermal equilibrium point defect concentrations are significant, in addition to cascade mixing irradiation produces freely migrating defects that enhance atomic diffusivity.

Ion beam mixing experiments have been extensively used to study cascade mixing in metals. Quantitative values of cascade mixing efficiencies have been determined for a variety of elemental and binary alloys [2,3]. Despite their technological importance, similar measurements for neutron irradiations are not available. Although similarities exist between neutron and ion irradiation, significant differences remain in damage production rates and in primary recoil energy spectra and these differences can impact mass transport processes during irradiation. Due to the low damage rate of neutron irradiations, long times are required to produce mass transport detectable using conventional analysis techniques such as Rutherford backscattering spectrometry (RBS) or secondary ion mass spectrometry (SIMS). Neutron sources, typically reactors, invariably undergo changes in power level during such extended irradiation periods which alter neutron flux and temperature making control of important experimental parameters prohibitively difficult. Additionally, long neutron exposures often produce highly radioactive samples which are difficult to handle.

These difficulties are minimized by using X-ray diffraction from superlattices to measure irradiation-induced mass transport. Originally employed to study thermal interdiffusion [4], this technique has also been successfully applied to low dose ion beam mixing [5,6]. X-ray diffraction is highly sensitive to interfacial structure thus making it well-suited for measuring small amounts of mixing. This is particularly convenient for neutron irradiations because it significantly reduces irradiation times required to obtain measurable results. High-angle X-ray diffraction from Nb/V superlattices was used in this work to obtain quantitative measurements of neutron-induced cascade mixing efficiencies. It is believed that these are the first such measurements of their kind. Parallel experiments using ions were also performed for comparison.

2. Experimental

Superlattices were grown by sputtering alternate layers of 99.9 at.% pure Nb and V layers onto ambient temperature sapphire substrates. These materials were chosen to minimize neutron-induced activation and because they are completely miscible at all compositions below 1860°C [7] thus simplifying interdiffusion analysis. In addition previous work [8] had demonstrated the ability to form good quality superlattices via sputtering in this system. Samples were fabricated with equal layer thicknesses over a wide range of modulation wavelengths ($\Lambda=11-285$ Å). The number of layers were adjusted to keep the total film thickness constant at about 4000 Å. The superlattices were (110) textured with a mosaic spread of $\approx 10^\circ$ and polycrystalline in the plane of the superlattice.

Samples were encapsulated in 10 mm diameter quartz tubes that were evacuated and backfilled with about 0.5 atm of He gas. The encapsulated samples were irradiated in the core (thimble location V-15) of the High Flux Beam Reactor (HFBR) at Brookhaven National Laboratory (BNL) for a total of 15 days at 30 MW power. Previous dosimetry at this position in the core indicated a fast neutron ($E>0.11$ MeV) flux of $4.2 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ and a thermal neutron ($E<5.5 \times 10^{-7}$ MeV) flux of $1.3 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$. Using this dosimetry as input, SPECTER [9] calculations (assuming a threshold displacement energy, E_d , of 40 eV) determined the total damage in Nb for the duration of the irradiation to be 0.26 displacement per atom (dpa). Gamma heating rates (6 W/g in aluminum) were minimal therefore sample temperature during irradiation was believed to be maintained near the 40°C ambient temperature of the cooling water in the thimble.

Ion irradiation experiments were performed on the superlattices grown during the same deposition as those used for neutron irradiation. 1.5 MeV Ne was chosen to reproduce the median damage primary recoil energy of the fast neutrons in HFBR ($T_{1/2} \approx 16$ keV). TRIM calculations [10] were used to evaluate damage in a homogeneous VNb target with $E_d=40$ eV. Damage production varied linearly across the target increasing by 75% from front to back with the average being 8.6×10^{-17} dpa per ion cm^{-2} . Samples were irradiated at room temperature to $3 \times 10^{15} \text{ cm}^{-2}$ to produce the same damage (~ 0.26 dpa) as in the neutron irradiation. Two samples ($\Lambda=28$ Å and $\Lambda=72$ Å) were irradiated sequentially to 0.09, 0.17 and 0.26 dpa in order to study mixing as a function of ion dose.

High angle X-ray diffraction scans were performed in $\theta-2\theta$ geometry about the (110) Bragg reflection of the samples using Cu K_α radiation. Superlattice diffraction peaks were observed for all modulation wavelengths indicating that the crystalline coherence length was larger than Λ . To determine the interface structure of the superlattice, the diffraction spectra were fitted to a general structural model using the SUPREX refinement code [11]. The fitting parameters included: the average Nb and V layer thicknesses and discrete fluctuations about the

average thickness, Nb and V (110) lattice spacings, continuous interface roughness, and a linear compositional gradient of width Δ in monolayers (ML) at each interface. The lattice spacings at the interface are assumed to follow the compositional profile via Vergard's law [12]. The spectra from the unirradiated and irradiated samples were fit in a self-consistent manner to avoid significant fluctuations in fitting parameters which should be independent of irradiation (i.e. average layers thicknesses). By fitting the spectra from different starting parameters to avoid local minima and determining the sensitivity of Δ to fluctuations in the other fitting parameters, we determined the uncertainty in Δ to be on the order of 1 ML. Diffraction results on the unirradiated samples including assymmetric diffraction scans are discussed elsewhere [13].

3. Results and Discussion

Pronounced changes in the X-ray diffraction spectra were observed even after small increments of irradiation. Fig. 1 shows changes in the x-ray spectra sample $\Lambda=28 \text{ \AA}$ sample when irradiated to only 0.26 dpa with either neutrons or ions. Decay of higher order satellite peaks after irradiation is readily apparent. Computer refinement of these spectra determined the width Δ of intermixing at the interfaces in the superlattices. Irradiation increased this width from 2.4 ML before irradiation to 6.6 ML after neutron irradiation and to 6.3 ML after ion irradiation. This monolayer sensitivity of superlattice diffraction is unparalleled by more conventional methods of measuring interdiffusion such as RBS and SIMS.

In order to convert the fitted Δ values to the conventional diffusion quantity Dt (D is diffusivity, t is time), the linear composition gradient was approximated by a complementary error function profile. Equating the integral of the two composition profile functions (i.e. equating total numbers of atoms diffused across the interface), the value of Δ is related to a net Dt due to irradiation according to,

$$Dt \approx \frac{\bar{d}^2}{5} \left[\left(\frac{\Delta_i}{2} \right)^2 - \left(\frac{\Delta_c}{2} \right)^2 \right], \quad (1)$$

where $\bar{d}$ is the average (110) interplanar spacing of V and Nb and Δ_i and Δ_0 are the diffused widths of interfaces in monolayers of the irradiated and unirradiated samples, respectively.

Computer refinement interdiffusion results for all the samples (with the exception of the two extreme modulation wavelengths) along with the derived values of cascade mixing efficiency, Dt/dpa , are listed in Table I. Complete homogenization was observed in the $\Lambda=11 \text{ \AA}$ sample after 0.26 dpa (ions or neutrons) indicating that the amount of interdiffusion was, at a minimum, on a scale comparable with this sample's modulation wavelength. At the other

extreme, $\Lambda = 284 \text{ \AA}$, it was not possible to accurately fit the spectra due to the small intensity and poor resolution of the satellite peaks. Superlattice samples ($\Lambda = 28 \text{ \AA}$ and $\Lambda = 72 \text{ \AA}$) were irradiated to sequential increments of ion dose and demonstrated a linear dependence of Dt with dose. The slopes of linear fits to this data were used to determine the mixing efficiency values listed in Table I for these samples.

As observed in Table I, no significant differences were detected in measured cascade mixing efficiencies between neutron and ion irradiation. Unlike the neutron irradiation, about 10% of the displacement damage from ion irradiation is produced by PKA's with energies greater than 200 keV. Molecular dynamics simulations cascades indicate that mixing efficiency increases with PKA energy [14]. This would imply that the higher energy cascades produced by ion irradiation should result in increased mixing efficiency relative to the neutrons. Such a difference could not be discerned by the present measurements thus suggesting that the high energy ion-induced PKA's are initiating multiple lower energy subcascades rather than forming single high energy cascades.

The most striking effect observed in these experiments was the dependence of cascade mixing efficiency on Λ as evidenced by the results in Table I. The dependence is displayed in Fig. 2 along with the average Dt/dpa determined by RBS from ion mixing a $1000 \text{ \AA}$ Nb/ $1000 \text{ \AA}$ V bilayer sample with 1.5 MeV Ne to about 20 dpa. For $\Lambda < 30 \text{ \AA}$ the cascade mixing efficiency was about $35 \text{ \AA}^2/dpa$. Above $\Lambda = 70 \text{ \AA}$, in the limit of thick samples, the mixing efficiency correlated well with that observed from conventional RBS analysis of the mixed bilayer ($Dt/dpa \approx 110 \text{ \AA}^2/dpa$). This modulation wavelength dependence was not observed in previous superlattice ion mixing experiments [5,6,15,16]. Those experiments typically examined a few thicker modulation wavelengths as opposed to a systematic variation in Λ over a large range as performed in this work.

Previous work studying thermal interdiffusion in multilayers/superlattices identified additional driving forces (gradient energy and strain) that are operative in small modulation wavelength samples [4,17,18] and result in a Λ dependence on interdiffusion. A gradient energy effect [17] was identified due to the presence of steep concentration gradients. Diffusion was enhanced or inhibited depending on the heat of mixing of the sample. This effect is insignificant for Nb/V which has a negligible calculated heat of mixing ($\Delta H_{\text{mix}} = -0.02 \text{ eV/atom}$ for equiatomic compositions [19]) and therefore does not contribute to the Λ dependence observed in the irradiation experiments. Strain was also previously observed to affect thermal interdiffusion in small Λ superlattices [18]. Below a certain critical modulation wavelength, Λ_c , superlattice interfaces become coherent. Below Λ_c the interface mismatch is accommodated by strain in the constituent layers whereas above Λ_c the mismatch is accommodated by the introduction of misfit

dislocations. Strains resulting from this coherence can affect thermal interdiffusion at the interface.

Synchrotron studies [13] of the same Nb/V samples used in this work determined that Λ_c 35 Å which is near the Λ for the transition in mixing efficiency observed in Fig. 2. The manner in which a coherent, strained superlattice might inhibit irradiation mixing is presently unclear. However, the validity of this correlation should be verified by studying another superlattice system with a significantly larger Λ_c (i.e. smaller lattice mismatch) to determine whether the transition in mixing efficiency is correspondingly shifted to larger Λ .

One possible consequence of coherence on mixing arises from the reduction in crystal defects (i.e. misfit dislocations, grain boundaries, etc.) in the superlattice. Recent ion mixing experiments in Au/Cu bilayers [20] have demonstrated that laterally inhomogeneous interdiffusion arises due to diffusion-induced grain boundary migration (DIGM). Grain boundaries must be present in order for DIGM to occur. The reduction in grain boundary area in a coherent superlattice will lead to a corresponding reduction in DIGM and a decreased amount of interdiffusion.

4. Conclusions

Computer refinement of high-angle X-ray diffraction spectra was used to analyze cascade mixing in neutron irradiated Nb/V superlattices. This is believed to be the first time quantitative measurements of this kind have been obtained for neutron irradiation. The interfacial sensitivity of the diffraction technique minimizes the time required to obtain measurable amounts of interdiffusion thus avoiding the many difficulties associated with extended period neutron irradiations.

Cascade mixing efficiencies varied between 35 Å²/dpa for $\Lambda < 30$ Å and 110 Å²/dpa $\Lambda > 70$ Å for samples irradiated in the core of HFBR at BNL at about 40 C. These values are the same as those obtained from samples irradiated with 1.5 MeV Ne at room temperature. The efficiencies measured in the larger Λ superlattices correlate well with that determined from ion mixing experiments in thick Nb/V bilayers analyzed using the conventional RBS technique. The similarity in mixing observed for the neutron and ion irradiations, both with the same median PKA energy, indicates that the higher energy PKA's present in the ion irradiation do not contribute significantly to an enhancement in mixing efficiency. The decrease in Dt/dpa observed at shorter modulation wavelengths may be related to a structural transition in which the superlattice becomes coherent.

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Table I. Interdiffusion results for Nb/V superlattices neutron irradiated in HFBR and ion irradiated with 1.5 MeV Ne. Width of interdiffused interface, Δ , in monolayers (ML) and $\text{\AA}$ determined from computer refinement of X-ray diffraction spectra. Δ_i for samples irradiated to 0.26 dpa.

Λ ($\text{\AA}$)	Δ_0 in ML ($\text{\AA}$)	Δ_i in ML ($\text{\AA}$)		Dt/dpa ($\text{\AA}^2/\text{dpa}$)	
	unirradiated	neutron	ion	neutron	ion
18	1.5 (3 $\text{\AA}$)	6.0 (14 $\text{\AA}$)	6.3 (14 $\text{\AA}$)	33	37
28	2.4 (5 $\text{\AA}$)	6.6 (15 $\text{\AA}$)	6.3 (14 $\text{\AA}$)	37	32
44	2.4 (5 $\text{\AA}$)	7.1 (16 $\text{\AA}$)	8.1 (18 $\text{\AA}$)	45	59
72	4.1 (9 $\text{\AA}$)	10.6 (24 $\text{\AA}$)	11.2 (25 $\text{\AA}$)	95	103
120	9.1 (21 $\text{\AA}$)	14.9 (33 $\text{\AA}$)	14.0 (31 $\text{\AA}$)	125	100

Fig. 1 Experimental X-ray diffraction spectra (points) and SUPREX fits (solid lines) for $\Lambda=28$ Å superlattice (a) unirradiated, (b) after neutron irradiation in HFBR to 0.26 dpa, and (c) after 1.5 MeV Ne irradiation to 0.26 dpa. Interdiffusion results are given in Table I.

Fig. 2 Variation in cascade mixing efficiency with modulation wavelength in Nb/V superlattices. Dashed line indicates efficiency determined for a 1000 Å Nb/1000 Å V bilayer mixed with 1.5 MeV Ne.

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