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RADIATION-INDUCED SOLUTE SEGREGATION IN A V-15 WT. % Cr ALLOY*

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Measurements of the dose and temperature dependences of radiation-induced segregation in a V-ion irradiated alloy of V-15 Cr are reported. Very rapid migration of Cr atoms toward the external surface occurs during irradiation in the temperature range from -450°C to 700°C .¹⁻³ A maximum in the degree of segregation is found near 650°C for a peak dose rate of $\sim 3 \times 10^3$ dpa s^{-1} .

1. INTRODUCTION

Considerable experimental evidence now exists showing that the spatial distribution of alloying components can be altered during irradiation at elevated temperatures.¹⁻⁷ In particular, the enrichment of undersize substitutional solutes near defect sinks has been demonstrated in several alloy systems. Since many material's properties depend sensitively upon alloy composition, this radiation-induced segregation (RIS) phenomenon will impact directly upon the performance of alloys in a fusion reactor environment.

The interaction of alloying elements with lattice defects can cause the chemical composition of defect fluxes to differ from the composition of the host alloy. Segregation of alloy components will then result during irradiation at elevated temperatures because of defect concentration gradients which exist, for example, near defect sinks. Because of the large defect fluxes which are created during irradiation, RIS can be both extensive and rapid. An order of magnitude increase in the Si concentration was found near defect sinks in a Ni-1 at. % Si alloy after irradiation to only a small fraction of a dpa.⁸ Transport of solute via defect fluxes is limited at low temperatures by defect recombination, and at high temperatures by the decreased effectiveness of solute-defect binding, faster back diffusion, and enhanced recombination due to the higher equilibrium vacancy concentration. The temperature dependence of RIS⁹ is therefore expected to resemble that of void swelling, which also results from the flow of point defects to sinks. A similar temperature dependence has been reported for void swelling and RIS in Ni-Si alloys.^{2,10}

Vanadium-base alloys are candidate materials for fusion reactor applications. We have employed ion-bombardment techniques in combination with postirradiation Auger chemical depth-profiling and transmission-electron-microscopy to investigate the irradiation response of a BCC V-15 wt. % Cr alloy at elevated temperatures. In this paper, we report measurements of the dose and temperature dependences of RIS in V-15 Cr

during irradiation with 3.5 MeV $^{51}\text{V}^+$ ions.

2. EXPERIMENTAL

Inert-gas arc-melting and levitation-melting techniques were used to prepare the V-15 wt. % Cr alloy from high-purity starting materials. A ribbon ($20 \times 0.4 \times 0.02$ cm³) of the cold-rolled alloy was homogenized at 1150°C for 3h in a dynamic vacuum of $< 10^{-6}$ Pa. To ensure a solid-solution microstructure, the ribbon was quenched from 1150°C with liquid nitrogen cooled He gas. Disks (3mm in diameter) were punched from this material and irradiated with 3.5 MeV $^{51}\text{V}^+$ ions in the ANL 4 MeV dual-beam irradiation facility.¹² Deposited energy densities were calculated as a function of depth with Brice Codes RASE3 and DAMG2¹³ and converted to dpa using a threshold energy of 40 eV. For 3.5 MeV V^+ irradiation, the depth of maximum damage was $\sim 1\mu\text{m}$, with a corresponding peak dose rate of $\sim 3 \times 10^{-3}$ dpa s^{-1} . The damage rate in the near-surface region was $\sim 1 \times 10^{-3}$ dpa s^{-1} .

Auger analysis was performed at room temperature using a primary electron beam of 5kV with a diameter of $\sim 10\mu\text{m}$ to excite the transitions. Depth profiling was accomplished by sputtering with 1kV Ar ions in an Ar atmosphere of 6.5×10^{-3} Pa. Measurements of the total sputtered depth in several V-15 Cr samples yielded sputtering rates of 3.0 ± 0.5 nm per minute. A value of 3.0 nm per minute was used to convert the actual measured sputtering times into depths.

The Auger technique measures the derivative with respect to electron energy, E , of the number of electrons, N , which are ejected from a thin (~ 1 nm) surface layer by the primary analysis beam.¹⁴ To a good approximation, the concentration of a particular element is proportional to the peak-to-peak height of this derivative at an appropriate Auger transition energy.¹⁵ V and Cr are adjacent elements in the periodic table and some overlap occurs in their Auger spectra. The presence of O, particularly near the specimen surface, further restricts the portion of the combined

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Fig. 1. Auger spectra after sputtering for ~90s from a) unirradiated and b) irradiated portions of a V-15 Cr specimen which had received a peak dose of 5 dpa at 665°C.

spectrum which can be used to determine the relative concentrations of V and Cr. However, the V transition at 437 eV and that of Cr at 571 eV are relatively free of these complications.¹⁴

An ~0.7 mm thick ring on the outer edge of the specimen is shielded by the specimen holder from the incident ion beam during irradiation. This permits irradiated and unirradiated portions of the same sample to be compared, and provides a very good check for experimental artifacts which might occur as a result of, for example, sample preparation, thermal cycling or preferential sputtering. Some manipulation of the specimen is required however, to move between the irradiated and unirradiated areas. Since the absolute height of any particular Auger peak-to-peak signal is a function of several alignment parameters, changes in absolute magnitude due to variations in these parameters occur when moving between different portions of the sample surface. Changes in the relative magnitudes of the peak-to-peak signals from the two alloy components must therefore be used to monitor changes in alloy composition between different portions of the sample.

3. RESULTS

Auger spectra taken a few nanometers beneath the surface of unirradiated and irradiated areas of the same V-15 Cr sample after exposure to a peak dose of ~5 dpa at 665°C are presented in Fig. 1. The amplification was adjusted to yield approximately equal peak-to-peak signals for the V 437 eV transition from the irradiated and unirradiated portions of the specimen; the signal obtained above an electron energy of ~540 eV

has been amplified in both spectra by a factor of 10 relative to the signal at lower energies. For approximately equal magnitudes of the V peak-to-peak signals, the height of the Cr transition at 571 eV is ~3 times larger in the spectrum from the irradiated portion of the specimen surface. The much larger Cr signal indicates a significantly higher Cr concentration in the irradiated area.

A quantitative estimate of the degree of Cr segregation can be obtained from the assumption that the peak-to-peak height of the Auger signal, I_x , varies linearly with the atom fraction of the element, C_x . For a binary alloy, AB,

$$\frac{C_A}{C_B} = K \frac{I_A}{I_B} \quad (1)$$

and

$$C_A + C_B = 1. \quad (2)$$

The normalization constant, K, can be found from the spectrum of the unirradiated area of the specimen, which contains 15 wt. % (14.7 at. %) Cr. The relative magnitudes of the V and Cr signals from the unirradiated area in Fig. 1 are the same as those found at large depths in both the irradiated and unirradiated areas of the specimen, which indicates that no significant variation in the near surface alloy concentration occurred because of effects unrelated to the irradiation.

Equations 1 and 2 were used to convert the spectra obtained from the specimen described in Fig. 1 into the composition vs depth profile shown in Fig. 2. Also shown in Fig. 2 is a profile from a control specimen which was held in the same irradiation holder at a temperature of 685°C, but was kept shielded from the ion beam. The spatial redistribution of Cr atoms which results from the irradiation can be seen clearly in Fig. 2. Maximum enrichment is to ~50 wt. % Cr near the bombarded surface, and the Cr enriched layer extends to a depth of approximately 10 nm. A region depleted to ~13 % Cr occurs beneath the enriched layer to a depth of ~120 nm (not shown on figure). Only a slight variation of Cr concentration with depth is evident in the control (0 dpa) specimen.

Composition vs depth profiles measured in three different V-15 Cr specimens after irradiation at approximately the same temperature to peak doses of 5, 15 and 60 dpa are presented in Fig. 3. To ensure a small spread in irradiation temperatures and beam conditions, all three specimens were mounted in the same irradiation holder. Thermal annealing effects were minimized by sequentially exposing the specimens in the following manner. Initially, only the 60 dpa specimens were exposed to the beam of V ions. After they had accumulated a dose of 45 dpa, the 15 dpa specimens were also exposed. After an additional dose of 10 dpa, the 5 dpa specimens were unmasked and all three specimens were irradiated simultaneously for the final 5 dpa.

Fig. 2. Cr concentration as a function of depth below the irradiated surface of a control (0 dpa at 685°C) and an irradiated (5 dpa at 665°C) specimen of V-15 Cr.

Following completion of the irradiation, the specimens were cooled to room temperature by turning off the furnace power. The Cr enrichment found in all three specimens in the near-surface region is remarkably similar. Development of the concentration gradient is complete at these irradiation temperatures after a peak dose of only 5 dpa. No significant change in either the degree or spatial distribution of the Cr segregation is observed between 5 and 60 dpa.

Composition vs depth profiles measured in three V-15 Cr specimens after irradiation to approximately the same dose level (20-24 dpa), but at three different temperatures, are shown in Fig. 4. These specimens were irradiated in separate sample holders. All three profiles exhibit Cr enrichment in the near-surface region and subsequent depletion at intermediate depths. The magnitude of segregation, however, varies with irradiation temperature. The least enrichment is found after irradiation at the lowest temperature, 460°C. Significantly more enrichment of Cr in the near-surface region occurs at 565°C, and a further increase is evident in the sample irradiated at 680°C. An additional sample, not shown in the figure, was irradiated to a dose of 30 dpa at 685°C; it exhibited slightly less enrichment than the 24 dpa sample irradiated at 680°C. Reference to Fig. 3 shows that a maximum in the Cr segre-

gation is found at irradiation temperatures between 650-665°C.

4. DISCUSSION

A comparison of the composition vs depth profiles for the irradiated and control specimens clearly demonstrates that the irradiation causes a net migration of Cr atoms from the interior of the sample toward the surface. Conservation of solute is observed within the accuracy of the measurements. Cr is undersize in V and produces a fractional change in lattice parameter per atom fraction of solute equal to -6 %.¹⁶ The observed enrichment of Cr at the specimen surface, which serves as a sink for both interstitial- and vacancy-type defects, and its depletion at intermediate depths is consistent with the RIS mechanism proposed by Okamoto and Wiedersich.¹ These authors have suggested that since undersize atoms can be accommodated more readily into interstitial sites, undersize solute atoms will preferentially migrate via interstitial fluxes at elevated temperatures. Hence, interstitial fluxes will sweep undersize solute atoms toward defect sinks during irradiation.

Enrichment of undersize substitutional solute atoms at an irradiated surface was first observed in an 18Cr-8Ni-1Si stainless steel,¹ and subsequently in Ni-Si²⁻⁴ and Ni-Be⁷ binary alloys. All three materials possess the FCC lattice

Fig. 3. Measured dose dependence of RIS in the V-15 Cr alloy near 650°C.

Fig. 4. Measured temperature dependence of RIS in the V-15 Cr alloy.

structure. The present series of measurements on V-15 Cr¹¹ has provided the first direct experimental evidence for RIS of substitutional atoms in a BCC material. More recently, surface enrichment of the undersize solute Al has been reported after irradiation of an HCP Ti-Al alloy.⁷

Cr enrichment near the specimen surface occurs quite rapidly during irradiation near 650°C. Back diffusion of Cr down the induced concentration gradient apparently balances the migration of Cr toward the surface via the defect fluxes at doses greater than 5 dpa. A more detailed study⁸ of the dose-dependence of RIS in a Ni-1 at. % Si alloy in approximately the same temperature range also showed large concentration changes near the irradiated surface at quite low damage levels; the amount of Si enrichment near the external surface appeared to approach saturation in the dose range from 1-10 dpa. The rapidity with which RIS occurs reflects the existence of an extremely efficient segregation process.

The peak swelling temperature of unalloyed V occurs near 700°C¹⁸ for a displacement rate approximately equal to that of the present investigation. The maximum amount of segregation in the V-15 Cr alloy occurs at an irradiation temperature of 665°C. Maximum segregation has been found to occur in Ni-Si alloys approximately 50°C below the peak swelling temperature of Ni irradiated under similar conditions.^{2,10} The Johnson-Lam model of RIS

predicts that maximum segregation should appear at a temperature slightly below that of the void swelling peak.⁹ The decrease of Cr segregation observed at higher and lower temperatures, and the fact that RIS occurs in approximately the same temperature range as void swelling, are readily explained in terms of preferential transport of solute via defect fluxes. Long range defect fluxes are responsible for RIS and void swelling. The magnitudes of these fluxes at different temperatures therefore determine the temperature dependence of both phenomena.

Enrichment of Cr occurs near the irradiated surface because the surface is a sink for defects. Analogous segregation effects can be expected to occur in the vicinity of internal sinks. The dose dependence of RIS near internal sinks will differ somewhat from that observed near the sample surface, since the formation of many internal sinks, e.g., voids and dislocation loops, is in itself dose dependent.

Figure 5 shows the measured dose-dependence of void swelling in unalloyed V¹⁹, and in V-15 wt. % Cr. Although they were irradiated under essentially identical conditions, the dose dependence of swelling is quite different for the two materials. In the unalloyed V, total swelling increases with dose to a maximum value of 0.4 % at ~14 dpa. Above 14 dpa, swelling decreases as the dose increases. The reduction in swelling at higher doses coincides with the appearance in the microscope of irradiation-induced, coherent {012}-type precipitates. Identification of the precipitates is difficult, but they are believed to be associated with the presence of interstitial impurities (C, O and N).¹⁹ In the V-15 Cr alloy, total swelling increases monotonically with dose and no precipitates appear. A large increase in void size, not number density, is responsible for the strong increase in total swelling.

The differences in swelling of V and V-15 Cr could be attributed to any of several factors, some of which are directly related to the observed RIS of Cr toward defect sinks. The precipitates in V, which are not found in V-15 Cr, may suppress swelling by providing a large number of recombination sites. The addition of Cr prevents the formation of these precipitates, presumably by altering the mobility and/or chemical activity of interstitial impurities during irradiation. In particular, the Cr enriched layer formed near the sample surface may act as a barrier to retard the pick-up of additional interstitial impurities during the irradiation. RIS of Cr toward internal sinks also might be responsible for the change in void swelling behavior. The elastic constants of Cr are larger than those of V.²⁰ Strong segregation of Cr in the alloy will cause the voids to be surrounded by a shell of material with larger elastic constants than those of the matrix. According to recent

Fig. 5. Dose dependence of swelling in unalloyed V and V-15 wt. % Cr under essentially identical irradiation conditions. The irradiation temperature was -650°C , which lies near the peak RIS temperature.

calculations by Mansur and Wolfer,²¹ this should increase the capture efficiency of voids for vacancies, and therefore increase the total swelling.

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