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ABSTRACT

Radiation-induced segregation (RIS) to grain boundaries in Fe-Ni-Cr-Si stainless alloys has been measured as a function of irradiation temperature and dose. Heavy-ion irradiation was used to produce damage levels from 1 to 20 displacements per atom (dpa) at temperatures from 175 to 550°C. Measured Fe, Ni, and Cr segregation increased sharply with irradiation dose (from 0 to 5 dpa) and temperature (from 175 to about 350°C). However, grain boundary concentrations did not change significantly as dose or temperatures were further increased. Although interfacial compositions were similar, the width of radiation-induced enrichment or depletion profiles increased consistently with increasing dose or temperature. Impurity segregation (Si and P) was also measured, but only Si enrichment appeared to be radiation-induced. Grain boundary Si peaked at levels approaching 10 at% after irradiation doses to 10 dpa at an intermediate temperature of 325°C. No evidence of grain boundary silicide precipitation was detected after irradiation at any temperature. Equilibrium segregation of P was measured in the high-P alloys, but interfacial concentration did not increase with irradiation exposure. Comparisons to reported RIS in neutron-irradiated stainless steels revealed similar grain boundary compositional changes for both major alloying and impurity elements.

INTRODUCTION

Radiation-induced segregation (RIS) is a nonequilibrium process that results from the migration of vacancies and interstitials created by displacement damage to various sinks [1]. The incorporation of these point defects into a sink such as a grain boundary induces a change in the alloy composition at the interface. Significant RIS will occur only during specific irradiation conditions of dose rate and temperature. A competition exists among recombination, segregation and back diffusion, as illustrated in Figure 1 for an austenitic stainless steel (SS). Maximum RIS is expected near the center of the RIS region where a high concentration of vacancies and interstitials are being produced and are able to diffuse relatively long distances. The concentration of mobile point defects is believed to decrease at higher temperatures primarily due to an increase in the thermal equilibrium for vacancies, and to decrease at lower temperatures due to restricted defect mobility and enhanced recombination.

Interactions of individual alloying and impurity elements with the defect flow control RIS and dictate the relative change in sink composition. Most grain boundary RIS measurements have been conducted on austenitic SSs because of their use in nuclear reactor core components [2,3]. Grain boundary depletion of Cr and Fe, and enrichment of Ni have been attributed to inverse-Kirkendall segregation [4]. This redistribution of major alloying elements is consistent with theirrelative diffusion rates; Cr diffuses fastest in SS, followed by Fe and finally Ni. As a result, Cr and Fe are more

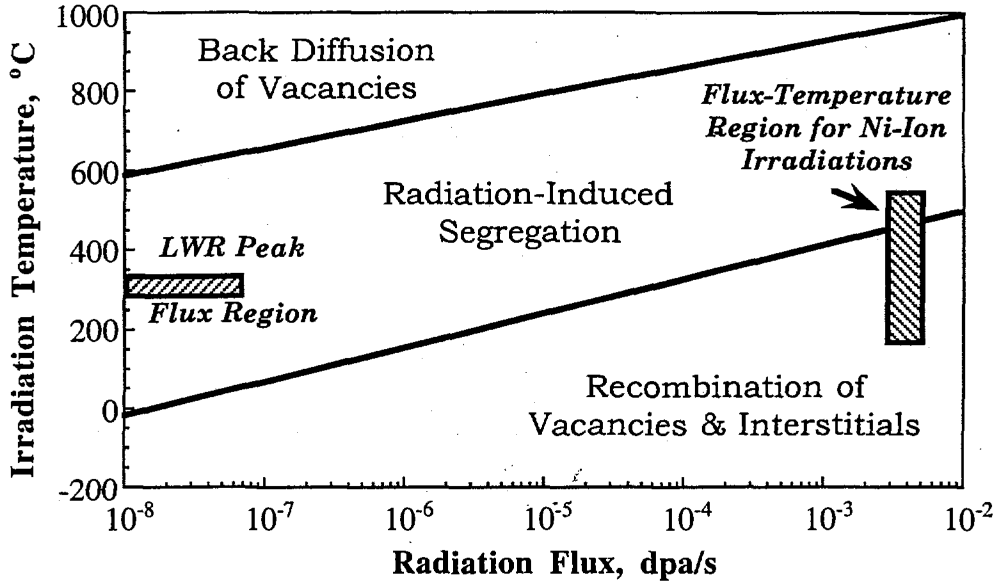


Figure 1. Irradiation Temperature-Flux Diagram for an Austenitic 300-Series SS Illustrating Region Where Radiation-Induced Segregation is Most Pronounced. [1,2]

likely to migrate away from the interface (in response to the incoming vacancy flow), leaving Ni enriched at the boundary. Si and P have been identified to enrich sinks in SSs. These "undersized" solutes are believed to interact preferentially with interstitials and segregate by an interstitial drag mechanism [1,5].

Although basic mechanisms have been proposed, little quantitative information has been available to evaluate RIS to grain boundaries. Difficulties in working with irradiated materials and limitations in characterization techniques have produced an existing data base that can only suggest trends in segregation behavior. The current work represents a first step to develop a comprehensive RIS data set mapping irradiation temperature and dose effects on the grain boundary composition of Fe-Ni-Cr stainless alloys. Analytical transmission electron microscopy (TEM) was used to characterize interfacial compositions and composition profiles in alloys irradiated by heavy ions. A wide range of temperatures (175 to 550°C) and dose (1 to 20 displacements per atom, dpa) conditions were examined to establish RIS behavior. Many grain boundaries were interrogated for each condition to document boundary-to-boundary anisotropy and to determine relevant averages for quantitative comparisons. Additional experimental results investigating dose and temperature effects on RIS in proton-irradiated SS [6], as well as RIS comparisons to model predictions [7], are given in companion papers within these proceedings.

EXPERIMENTAL PROCEDURE

Materials

RIS was evaluated in a series of ion-irradiated, Fe-Ni-Cr alloys. Primary alloying and impurity element compositions for these alloys are listed in Table 1. Bulk C and N levels were less than 0.01 at% in all alloys except for the 304L SS which contained 0.07 at% C and 0.31 at% N. The FeNiCr and FeNiCr+Si alloys were sputter deposited as 0.13-mm-thick foil. The higher Ni concentration was necessary to stabilize the austenite phase in the as-sputtered condition. Both deposits were given a 750°C/1-h heat treatment to stabilize a grain size of ~0.5 μm. A detailed description of the

TABLE 1. Compositions of Stainless Alloys Used for RIS Studies, at%

Alloy	Ni	Cr	Mn	Si	P
FeNiCr	20.1	19.0	1.5	1.1	0.08
FeNiCr+Si/P	20.7	19.1	1.5	2.1	0.12
304L SS	8.4	19.7	1.8	0.9	0.04
UHP	8.9	20.7	1.1	0.09	0.01
UHP+Si	8.6	20.4	1.3	0.87	<0.01

production of these fine-grained stainless alloys, and their microstructures, is given elsewhere [8,9]. The 304LSS is a commercial alloy cold rolled and heat-treated at 900°C to stabilize a grain size of ~30 µm, while the UHP and UHP+Si alloys are ultra-high-purity laboratory heats [10] with a grain size of ~10 µm.

Ion Irradiation

To minimize compositional and structural effects of the embedding atoms, 5 MeV Ni^{2+} ions were used for ion bombardment. Prior to irradiation, 3-mm-diameter discs were lightly abraded and given an electrochemical polish (in a solution of 5% perchloric acid in methanol at -35°C). Discs were irradiated under vacuum ($<5 \times 10^{-6}$ Pa) at a dose rate of 3 to 5×10^{-3} dpa/s. Detailed information concerning the accelerator facility and the irradiation procedure has been previously reported [8]. A standard dose of 10 dpa was employed to map irradiation temperature (175 to 550°C) effects on RIS. The flux-temperature range studied is shown in Figure 1 and lies primarily in the region predicted to be recombination-dominated. Dose effects were also examined at selected temperatures ranging from 1 to 20 dpa.

Grain Boundary Composition Measurements

Elemental compositions across grain boundaries were measured in a Vacuum Generators HB501 field-emission-gun, scanning transmission electron microscope (FEG-STEM) with an energy dispersive x-ray spectrometer (EDS). Sample preparation was done by electrochemical jetting and polishing in a 5 vol% perchloric acid-methanol solution cooled to -40°C. STEM-EDS analysis was obtained using a 2-nm incident probe and for foil thicknesses from 50 to 75 nm. This resulted in a through-thickness resolution generally less than 4 nm. To ensure that boundary-to-boundary variability was accounted for and a reasonable average composition was obtained, more than 10 high-angle grain boundaries were examined for each material condition. Multiple analyses were also made along individual grain boundaries to assess the reproducibility of the composition measurement.

RESULTS AND DISCUSSION

FEG-STEM Measurement of RIS

The number of reported measurements of RIS at grain boundaries has increased over the last few years, but still remains limited. Most investigators have used FEG-STEM and EDS techniques to identify Ni, Si, and P enrichment, along with Cr and Fe depletion, in commercial 300-series SSs. Heavy-ion, proton, electron, and neutron irradiations have shown that RIS is very localized (within several nanometers) at grain interfaces. Accurate assessment of RIS characteristics is difficult because very few (~2) grain boundaries are typically examined. The current measurements on the fine-grained stainless alloys enable a large number of grain boundaries to be analyzed and a statistically relevant determination of RIS to be made.

Boundary-to-Boundary RIS Anisotropy

Interfacial composition was discovered to be significantly different among the 10 to 20 high-angle grain boundaries analyzed per irradiation condition. Examples of boundary-to-boundary variability in Cr and Si concentrations are shown in Figures 2 and 3 for the FeNiCr alloy. Clear differences in the measured boundary compositions can be seen in the Figure 2 histograms for 350°C/10-dpa and 400°C/10-dpa specimens. Cr levels range from about 10 to 16 at% and 7 to 14 at% at 350 and 400°C, respectively. Similar variability was observed for Ni, Fe, and Si concentrations in the irradiated specimens. Full Cr and Si profiles for a 400°C/10-dpa specimen plotted in Figure 3 demonstrate that both the interfacial composition and the width of the depleted or enriched region varies among the boundaries. This anisotropy was identified in all irradiated specimens in which significant RIS occurred.

To ensure that measured compositional differences were due to differences among individual boundaries, multiple measurements along individual interfaces were recorded, as illustrated in Figure 4. Detectable (±1.5 at%) changes in elemental compositions were measured with position along a grain boundary, but these were much less than that identified among different boundaries. Care was taken to avoid any significant analysis-technique changes known to affect measurement resolution, such as foil thickness and boundary tilt. Current results indicate that RIS depends on individual boundary characteristics, as does equilibrium segregation. Lower RIS was observed at incoherent twin boundaries, and very little segregation was seen at coherent twins.

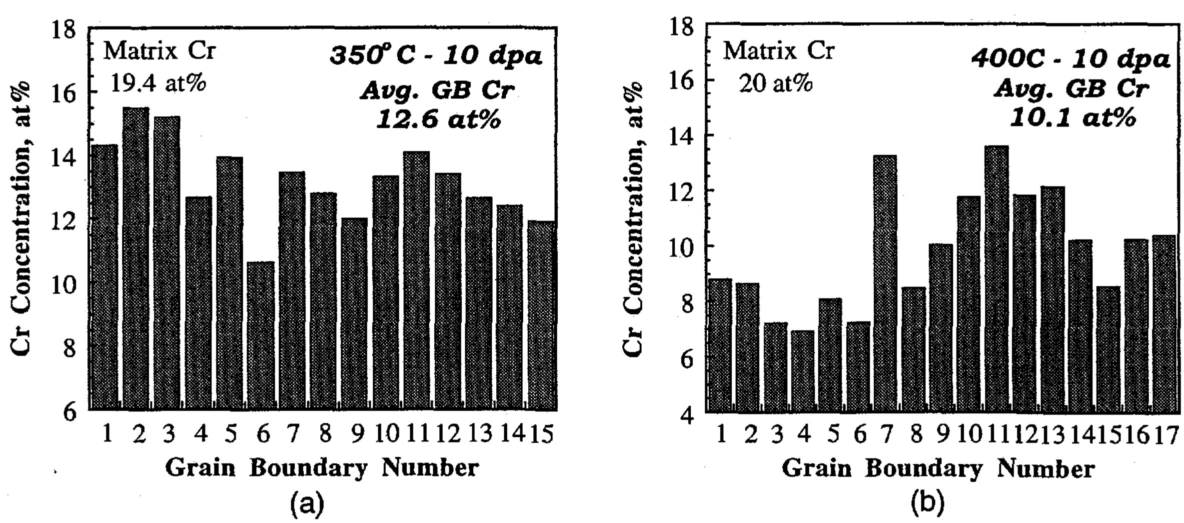


Figure 2. Grain Boundary Cr Composition Histograms for 350° (a) and 400°C (b) Irradiations Showing Boundary-to-Boundary Differences Measured in the Ni-Ion Irradiated FeNiCr Alloy.

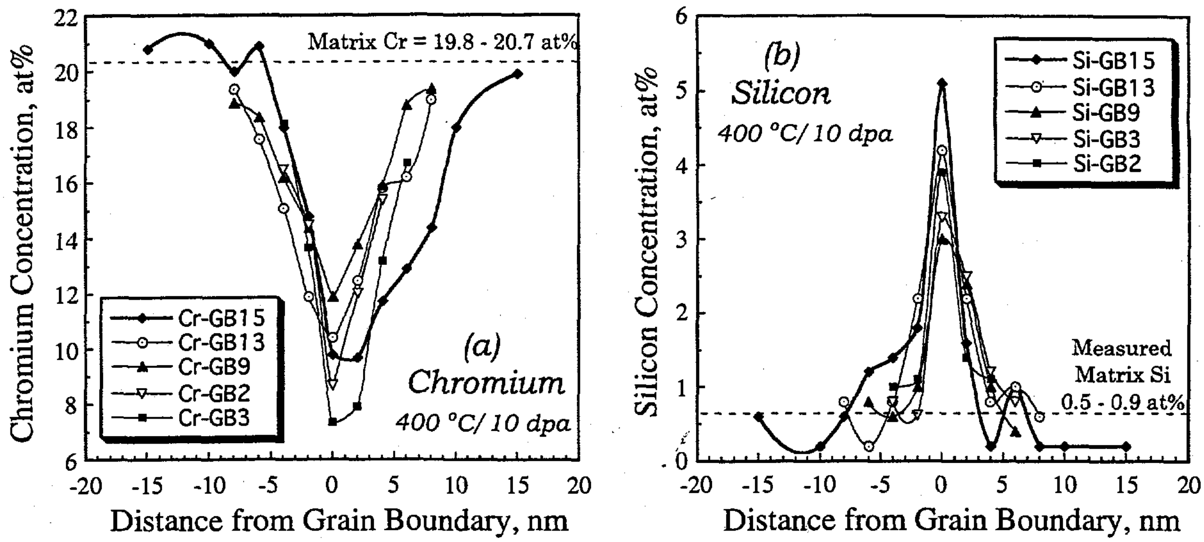


Figure 3. STEM-EDS Measured Composition Profiles for Cr (a) and Si (b) Across Various High-Angle Grain Boundaries in the Ion-Irradiated FeNiCr Alloy.

Grain Boundary Segregation in Ion-Irradiated Stainless Alloys

Average compositions at high-angle grain boundaries have been determined and used to investigate dose and temperature effects on RIS. Enrichment of Ni and Si and depletion of Cr and Fe was detected in each alloy after irradiation. Comprehensive experiments were performed on fine-grained FeNiCr alloys to examine a wide range of irradiation doses (1 to 20 dpa) and temperatures (175 to 550°C). RIS was found to increase with dose and reach maximum interfacial enrichment or depletion at intermediate temperatures. Selected irradiations were also performed on commercial and high-purity 304 SSs to compare to the higher Ni stainless alloys.

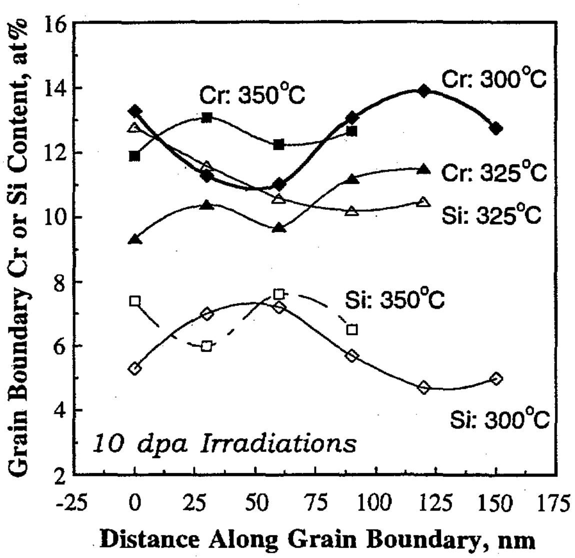


Figure 4. Measured Variations in Cr and Si Concentration Along High-Angle Grain Boundaries in the FeNiCr Alloy.

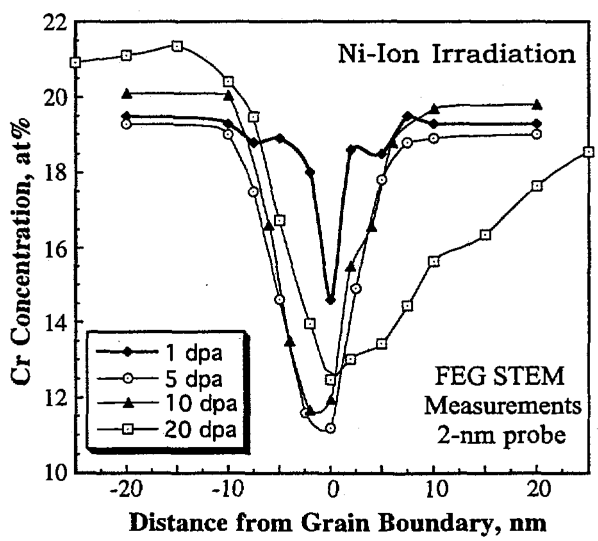


Figure 5. Typical Cr Composition Profiles after Ion Irradiation at 500°C to Doses from 1 to 20 dpa.

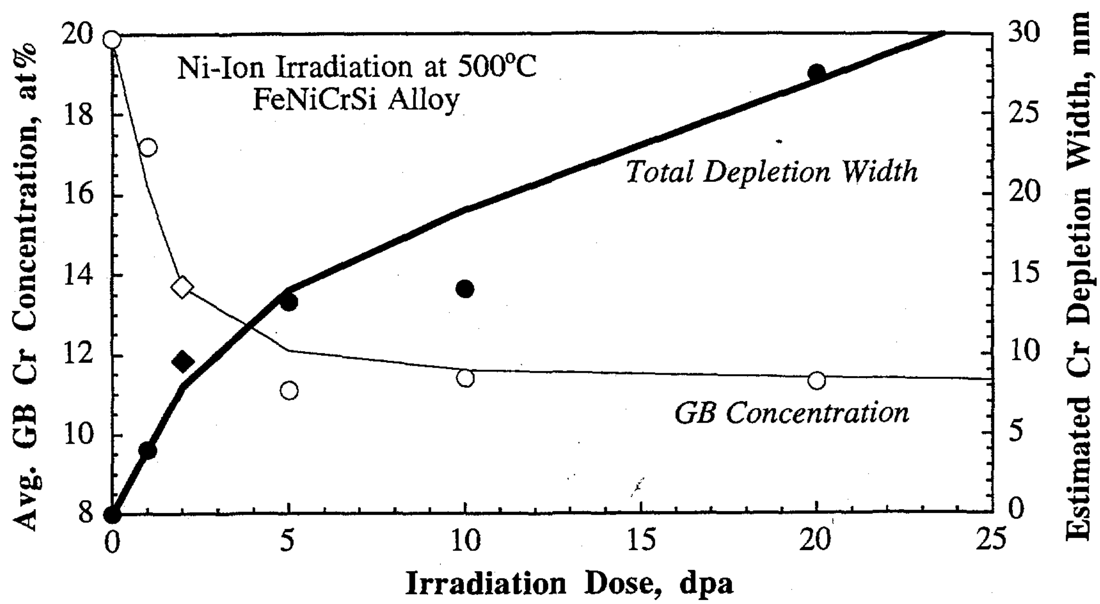


Figure 6. Dose Effects on the Average Grain Boundary Cr Depletion.

Major Alloying Element Segregation

Dose effects on the grain boundary Cr concentration and the width-of-depletion profile is shown in Figures 5 and 6 for an irradiation temperature of 500°C. Measured Cr levels dropped sharply over the first few dpa and then changed very little at doses exceeding 5 dpa. Depletion width, on the other hand, increased with dose over the full range examined. Similar changes in boundary concentrations and near-boundary gradients were established for Ni and Fe. Interfacial Ni nearly doubled with irradiation from ~22 to 40 at%, while Fe decreased from ~53 to 42 at%. As for Cr, the most significant change after increasing dose from 5 to 20 dpa was in the width of the RIS profile. Limited variable dose exposures at 300 and 400°C reveal dose-dependent RIS in agreement with that documented at 500°C.

A strong influence of irradiation temperature on RIS was discovered. Little change in grain boundary concentrations was detected in specimens irradiated to a dose level of 10 dpa at temperatures below 200°C. RIS increased rapidly with temperature up to ~300°C, as illustrated for Cr and Ni in Figure 7. Grain boundary Cr dropped sharply from 18 at% at 175°C to 13 at% at 300°C, while Ni rose from 22 to 40 at%. Surprisingly, Cr did not continue to significantly decrease, or Ni levels increase, at higher temperatures. Interfacial Cr and Ni concentrations showed some scatter at temperatures from 300 to 550°C, but remained at ~12 and ~39 at%, respectively. Although boundary concentrations were comparable, profile widths increased over the entire range of temperatures examined. For example, Cr depletion widths nearly doubled between 275 and 400°C, and then doubled again between 400 and 550°C. RIS characterizations on the lower-Ni 304 SSs after irradiations at 250 and 500°C also indicated this strong effect of temperature and showed slightly less RIS (Figure 7).

Impurity Segregation

Si was consistently observed to enrich grain boundaries due to irradiation. Average Si interfacial composition in the FeNiCr alloy increased with irradiation dose at 500°C, reaching ~7 at% at high dose levels, as shown in Figure 8. The width of the measured enrichment profile also increased with dose, but remained somewhat narrower than for

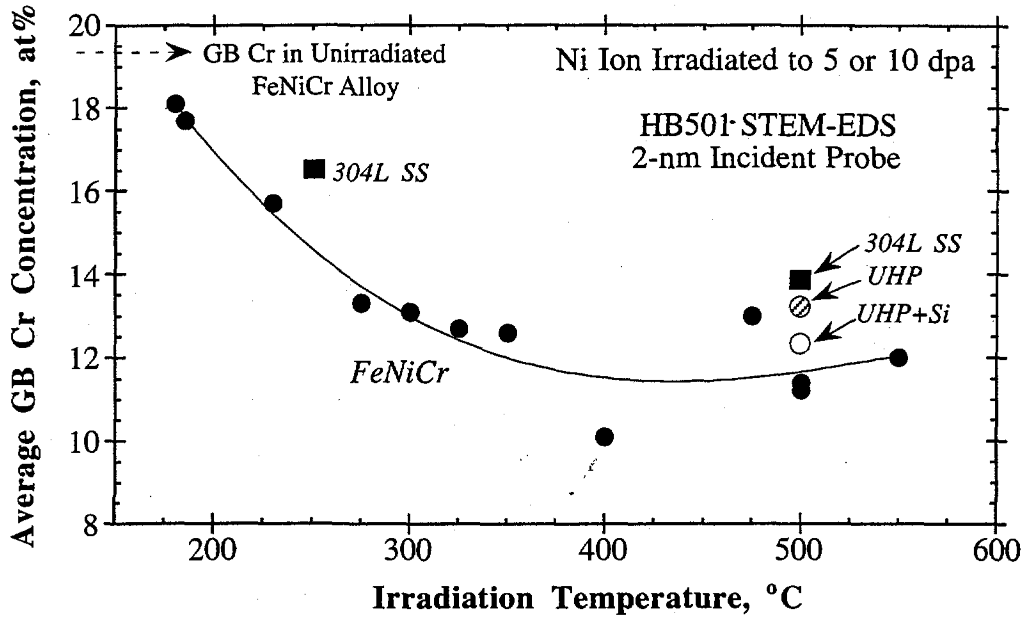


Figure 7. Irradiation Temperature Effects on the Grain Boundary Cr Concentration. Most Irradiations at to a Dose of 10 dpa Except for Several Points at 500°C.

Cr. Consistent with the measured major alloying element segregation, Si RIS was found to be a strong function of temperature (Figure 9). Grain boundary Si levels peaked at ~8 at% at 325°C for the 10-dpa exposures, and dropped to 7 at% or less at 400 to 550°C. The maximum Si composition measured at any grain boundary was ~13 at% in the 325°C/10-dpa sample. TEM characterization of this and other segregated boundaries revealed no evidence of second-phase (i.e., Ni_3Si) precipitation in any of the stainless alloys. High-dose (10-dpa) irradiations on the FeNiCr+Si/P alloy (Si about 2x higher) showed interfacial Si enrichments similar to the FeNiCr alloy, as did the UHP+Si alloy irradiated at 500°C.

P segregation was not consistently observed at boundaries in the irradiated FeNiCr alloy, even though it was present at high levels (~0.08 at%) in the bulk. Maximum

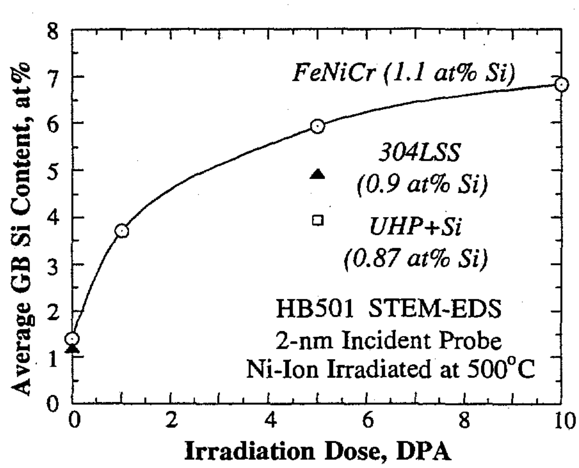


Figure 8. Influence of Irradiation Dose on the Grain Boundary Silicon Concentration.

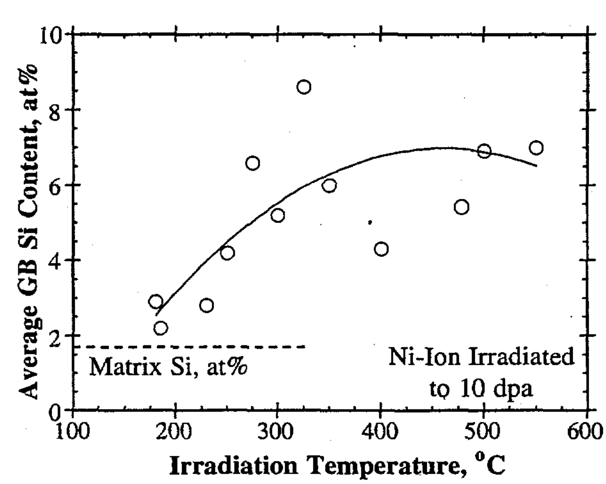


Figure 9. Irradiation Temperature Effects on the Grain Boundary Silicon Content.

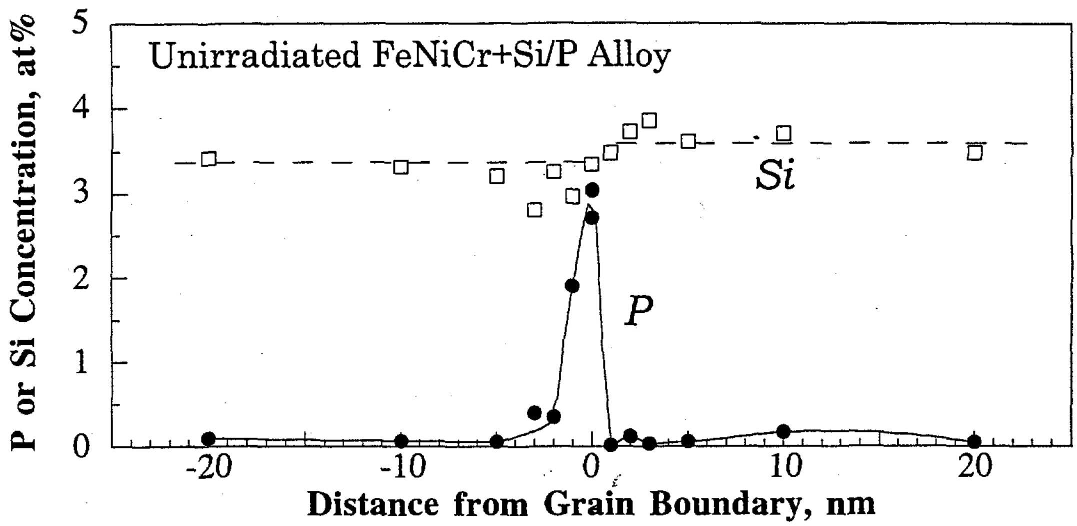


Figure 10. Measured P and Si Concentration Profiles Across Grain Boundaries in Unirradiated FeNiCr+Si/P Alloy Heat Treated at 750°C for 1 h.

concentrations were less than 0.7 at% at any boundary regardless of irradiation dose or temperature. Most boundaries showed levels near the EDS resolution limit (~0.4 at%) for P. No consistent differences in P were observed as a function of dose or temperature. However, equilibrium segregation of P was detected by FEG-STEM in the unirradiated FeNiCr+Si/P alloy, as illustrated in Figure 10. A maximum concentration of 3 at% and an average concentration of 1.7 at% were identified, while no Si segregation was discovered. Irradiations to 10 dpa at temperatures where significant RIS was documented for Si, Ni, Cr, and Fe have not shown any enhanced P enrichment. In all cases, measured P composition profiles were extremely narrow ($\leq$3 nm), consistent with FEG-STEM resolution for equilibrium monolayer segregation.

In summary, Si has been shown to enrich grain boundaries as a function of dose and temperature. P, on the other hand, did not exhibit significant RIS. It was present in irradiated SSs, but appeared to result primarily from thermal segregation. Measured grain boundary compositions of Si in irradiated SSs were consistently greater than P. FEG-STEM measurements indicated the extent of segregation in the boundary region, but actual interfacial compositions were somewhat greater due to the narrow enrichment profiles in comparison to the technique's through-thickness resolution. This was particularly true for monolayer-type profiles for P, in which actual interfacial compositions were estimated to be ~5 times greater than the FEG-STEM values [10].

Grain Boundary Segregation in Neutron-Irradiated Stainless Steels

Major Alloying Elements

Radiation-induced Cr depletion has been the focus of many IASCC studies because of its well-documented effects in promoting IGSCC in sensitized SSs. Grain boundary Cr concentrations measured in neutron-irradiated 304, 316 and 348 SSs have been compiled [3] and minimum concentrations plotted as a function of fluence in Figure 11. The most detailed characterization of neutron fluence effects on grain boundary RIS has been reported by Jacobs [11] on 304 SSs. A consistent decrease in interfacial Cr was detected with increasing fluence up to ~2×10^{21} n/cm^2, i.e. about 3 dpa. Samples irradiated to slightly higher fluences did not show a continued decrease in the grain

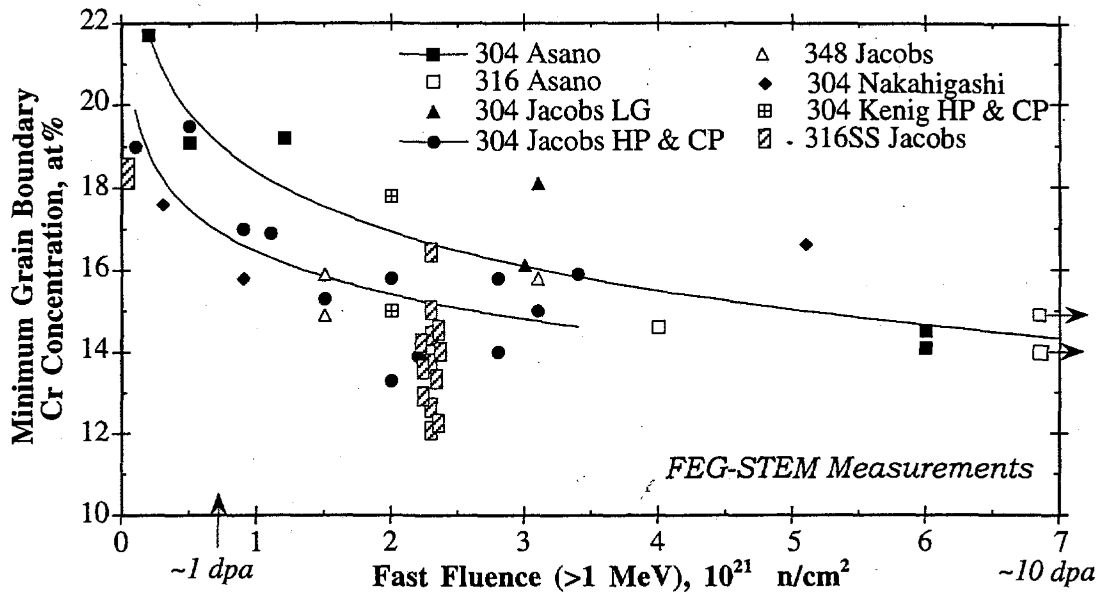


Figure 11. FEG-STEM Measurements of Cr Grain Boundary Concentrations as a Function of Fluence in Neutron-Irradiated Stainless Steels.

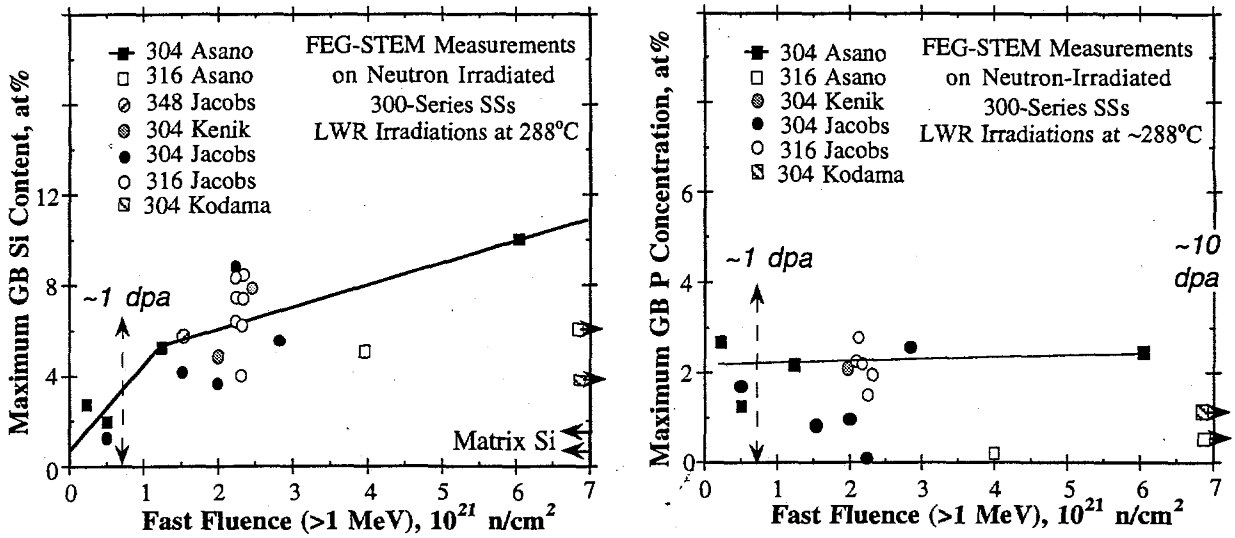
boundary Cr level. This change in the rate of segregation agrees with the ion-irradiation dose dependence. Cr enrichment has been reported at low fluence levels, as indicated by the data of Asano, et al. [12] This initial enrichment shifted the fluence dependence curve to higher Cr concentrations and may require an increased fluence to achieve comparable grain boundary depletion. Considering the wide range of materials and starting conditions, most data showed a consistent exponential decrease in interfacial Cr content with increasing fluence out to several dpa.

Impurity Segregation

Bruemmer, et al. [13] recently reviewed measurements of Si and P enrichment at grain boundaries in neutron-irradiated SSs. Si observations are more common because of its high bulk content (0.7 to 2.0 at%) compared to P (0.01 to 0.08 at%). Measured grain boundary concentrations for Si appear to increase with fluence (Figure 12a) and reach levels of about 6-8 at% at a moderate dose of ~2.2×10^{21} n/cm^2; i.e., ~3 dpa. Very few FEG-STEM measurements are available at higher doses to determine if segregation levels continue to increase. However, Ni-silicide precipitation has often been observed at dislocation loops and boundaries in SSs irradiated at higher temperatures (>380°C) and to higher doses (>20 dpa).

The few measurements of grain boundary P in neutron-irradiated SSs do not show any clear indication of RIS. Interfacial compositions range from not detectable (<0.4 at%) to ~3 at% regardless of dose, as shown in Figure 12(b). Such variability may result from differences in P segregation before irradiation. P strongly segregates to grain boundaries in both Fe- and Ni-base stainless alloys during thermal treatments approaching levels of several at% in the solution-annealed condition. Unfortunately, unirradiated archive materials are rarely characterized and compared to results on neutron-irradiated samples.

Measurements of RIS in neutron-irradiated SSs are in qualitative agreement with the heavy-ion results for both major alloying elements and impurities. Cr and Si



(a) (b)

Figure 12. FEG-STEM Measurements of Si (a) and P (b) RIS as a Function of Neutron Fluence in Neutron-Irradiated Stainless Steels.

segregation increases with dose at 288°C for neutrons (Figures 11 and 12a), comparable to that at 500°C for Ni ions (Figures 6 and 8). Radiation-induced grain boundary compositions change rapidly with dose and reach similar levels at a moderate dose; e.g., Cr drops to ~13 at% and Si reaches ~6 at%. Part of this sharp change in measured interfacial composition with dose at low dpa may result from the narrow width of the RIS profile. The measured boundary composition may be significantly different than the actual composition at low dose because the profile width is smaller than the FEG-STEM resolution. Ion irradiations demonstrate that the width of the segregation profile increases with dose. Results in Figures 6 and 11 indicate that interfacial Cr compositions do not change as rapidly with dose above 3 dpa. The other major alloying elements, Ni and Fe, follow this same behavior as apparently does Si. The strong RIS observed at temperatures below 300°C in the heavy-ion irradiated alloys (Figure 7) suggests that significant RIS is likely at temperatures below 100°C in neutron-irradiated stainless steels.

CONCLUSIONS

Radiation-induced segregation to grain boundaries in Fe-Ni-Cr-Si stainless alloys was found to increase sharply with irradiation dose (from 0 to 5 dpa) and temperature (from 175 to about 350°C). However, grain boundary concentrations of major alloying elements stabilized at approximately 12 at% Cr and 38 at% Ni for higher dose or higher temperature irradiations. Although interfacial compositions were similar, the width of radiation-induced enrichment or depletion profiles increased with increasing dose or temperature. Grain boundary Si and P segregation was also measured, but only Si enrichment appeared to be radiation induced. Si reached a maximum content of nearly 10 at% at an intermediate temperature of 325°C. Interfacial P levels were comparable in both irradiated and unirradiated materials. Stainless steels neutron irradiated at 288°C reveal similar effects of dose on grain boundary compositions of major alloying elements (Cr, Ni, and Fe) and impurity elements (Si and P).

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