"The Influence of Pre-irradiation Heat Treatments on Thermal Non-Equilibrium and Radiation-induced Segregation Behavior in Model Austenitic Stainless Steel Alloys"

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Abstract: The effect of pre-irradiation heat treatments on thermal non-equilibrium grain boundary segregation (TNES) and subsequent radiation-induced grain boundary segregation (RIS) is studied in a series of model austenitic stainless steels. The alloys used for this study are based on AISI 316 stainless steel and have the following nominal compositions: Fe-16Cr-13Ni-1.25Mn (base 316), Fe-16Cr-13Ni-1.25Mn-2.0Mo (316 + Mo) and Fe-16Cr-13Ni-1.25Mn-2.0Mo-0.07P (316 + Mo + P). Samples were heat treated at temperatures ranging from 1100 to 1300°C and cooled at 4 different rates (salt brine quench, water quench, air cool and furnace cool) to evaluate the effect of annealing temperature and quench rate on TNES. The alloys were than processed with the treatment (temperature and cooling rate) that resulted in the maximum Cr enrichment. Alloys with and without the heat treatment to enrich the grain boundaries with Cr were characterized following irradiation to 1 dpa at 400°C with high-energy protons in order to understand the influence of alloying additions and pre-irradiation grain boundary chemistry on irradiation-induced elemental enrichment and depletion profiles. Various mechanistic models will be examined to explain the observed behavior.

Keywords: radiation-induced segregation, irradiation-assisted stress-corrosion cracking, proton irradiation, austenitic stainless steels

Introduction:

Over the past decade, there have been significant advances in the understanding of degradation mechanisms in austenitic stainless steel reactor internals as summarized in several review papers [*1,2*]. Based substantially on this advance in knowledge, efforts to develop austenitic stainless steel structural materials with enhanced radiation resistance have been undertaken. Many of these efforts have focussed on the mitigation of two of the primary degradation mechanisms, namely dimensional changes caused by void swelling and material failures caused by irradiation assisted stress corrosion cracking (IASCC).

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Table 1 Model alloy compositions (wt%).

Alloy Designation	Fe	Cr	Ni	Mn	Mo	P	C
1638 (base 316) Fe-16Cr-13Ni-1.25Mn	bal.	15.6	12.9	1.2	<0.01	<0.01	0.01
1639 (base 316 + Mo) Fe-16Cr-13Ni-1.25Mn + Mo	bal.	15.4	13.2	1.2	1.85	<0.01	0.01
1640 (base 316 +Mo + P) Fe-16Cr-13Ni-1.25Mn + Mo + P	bal.	15.4	13.0	1.2	1.83	0.05	0.01

IASCC has been linked to both microstructural hardening [*2,3*] and changes in grain boundary composition during irradiation [*4*]. The radiation-induced hardening of the grain interiors can lead to grain boundary stress concentrations and increase the likelihood of cracking along the relatively weak grain boundary. Depletion of Cr at the grain boundaries as a result of RIS sensitizes the boundary and makes it more susceptible to corrosive attack. In both instances, it is evident that boundaries are the weak link and efforts to enhance resistance to IASCC must focus on the grain boundary.

The present study focuses on improving IASCC resistance by modifying grain boundary chemistry. Non-equilibrium grain boundary segregation in alloys has been observed to occur as a result of heat treatments, strain and due to displacement damage caused by irradiation [*5*]. Radiation induced segregation results in Cr depletion at the grain boundaries, on the other hand, enrichment of grain boundary Cr has been observed to occur under certain heat treatment conditions (annealing temperature and cooling rates) [*5-7*]. The overall object of the current study is to develop heat treatments that maximize pre-irradiation enrichment of Cr at grain boundaries in an effort to inhibit Cr depletion during subsequent irradiation and hopefully improve IASCC resistance.

Proton irradiation will be used as a rapid screening tool. The advantage of proton irradiation, along with substantially lower experimental costs, is rapid sample throughput and precisely controlled experimental conditions. In using proton irradiations as a screening tool, alloys with the highest probability of improved resistance to swelling and IASCC can be developed and later tested in the reactor environment to verify property improvements.

Experimental

Model 316 stainless steel alloys were fabricated at GE's Corporate R&D center. A list of the alloys is provided in Table 1 including the compositions as determined by chemical analysis. The initial cast ingots of material were cold-rolled to ~30% reduction. The ingots were then solution annealed at 1100°C for one hour and rolled a further 66%. Two millimeter wide bars for transmission electron microscopy (TEM) samples were then electric discharge machined (EDM) from the cold-worked plates.

The TEM bars were then further processed depending on which experimental path they were to be used for. The alloys without the heat treatment to enrich grain boundaries underwent a recrystallization anneal to produce a grain size on the order of 20 μm. Table 2 lists the recrystallization anneal parameters for each of the model alloys. The grain boundary Cr enrichment treatment was first developed for the 316 + Mo + P

Table 2 Heat treatment to achieve ~20μm diameter grain size.

Alloy Designation	Heat Treatment
1638 (base 316) Fe-16Cr-13Ni-1.25Mn	850°C, 2 hrs, water quench
1639 (base 316 + Mo) Fe-16Cr-13Ni-1.25Mn + Mo	950°C, 2 hrs, water quench
1640 (base 316 +Mo + P) Fe-16Cr-13Ni-1.25Mn + Mo + P	900°C, 2 hrs, water quench

alloy then later applied to the base 316 and 316 + Mo alloys. Samples of the 316 + Mo + P alloy were first heat treated at 1200°C for 1 hour then cooled using 4 separate paths: salt brine quench, water quench, air cool and furnace cool. Subsequently, samples with the greatest grain boundary Cr enrichment were heat treated at 1100°C and 1300°C for 15 minutes and then cooled using the best cooling media determined at 1200°C.

Proton irradiations were carried out at the University of Michigan. The irradiations were performed at a proton beam current of about 1 $\mu A/cm^2$ for a dose rate of 7×10^{-6} dpa/s. The beam energy was 3.2 MeV. The irradiation was conducted with a sample temperature of 400°C to a dose of 1.0 dpa.

TEM thin foils of the alloys were prepared in a solution of 5% $HClO_4$ / 95% methanol at a temperatures between -30 and -40°C. Grain boundary segregation measurements were performed using a Phillips CM200 field emission gun scanning transmission electron microscope (FEG/STEM) located at the SHaRE user facility at Oak Ridge National Laboratory. Grain boundaries which could be aligned parallel to the electron beam were selected for analysis. Typically 2 to 3 boundaries in each sample could be aligned parallel, and on each boundary generally 3 profiles were taken. Grain boundary chemistry profiles were measured along a linear distance of 20 nm with spectra taken at a spacing of 2 nm. The electron probe was approximately 1 nm in diameter. Composition measurements were also made in the bulk (away from the boundary) and with the beam positioned directly on the grain boundary. For each of the alloys examined, compositional differences between the grain boundary and the bulk were

calculated.

Results

Heat Treatment Development to Cr Enrich Grain Boundaries

This experimental path involves efforts to produced grain boundaries with pre-irradiation enrichment of Cr in order to inhibit Cr grain boundary depletion during irradiation. For the first series of studies to optimize enrichment, a single alloy, base 316 + Mo + P, was selected.

Quench Rate – In order to examine the effect of quench rate, samples of the base 316 + Mo + P alloy were heat treated at 1200°C for 1 hour and quenched or slowly cooled in several media to achieve different cooling rates. The four media chosen were: ice brine, room temperature water, air cooling, and furnace cooling. The grains in the alloys were rather large, and typically only one to three grain boundaries could be observed in the thin regions of the TEM foil. Grain boundary chemistry profiles were measured for samples exposed to each of the four cooling rates. For each of the alloys examined, compositional differences between the grain boundary and the bulk were calculated. Grain boundaries showing the maximum segregation in each alloy were compared and these are listed in Table 3. The maximum was used as opposed to the average because of the limited number of grain boundaries available for analysis and the observation that some of the boundaries that were analyzed showed no segregation. The absence of segregation in some boundaries may be an indication that these boundaries were twin boundaries which typically do not exhibit segregation. The results indicate that Cr, Mo and P are enriched at the grain boundaries, while Fe and Ni are depleted. A graphical representation of the Cr and Mo enrichment as a function of quench rate in the 316 + Mo + P alloy is provided in Figure 1. Both the furnace cooled and air cooled samples had similar amounts of Cr enrichment, so both alloys were selected for the next phase of the study.

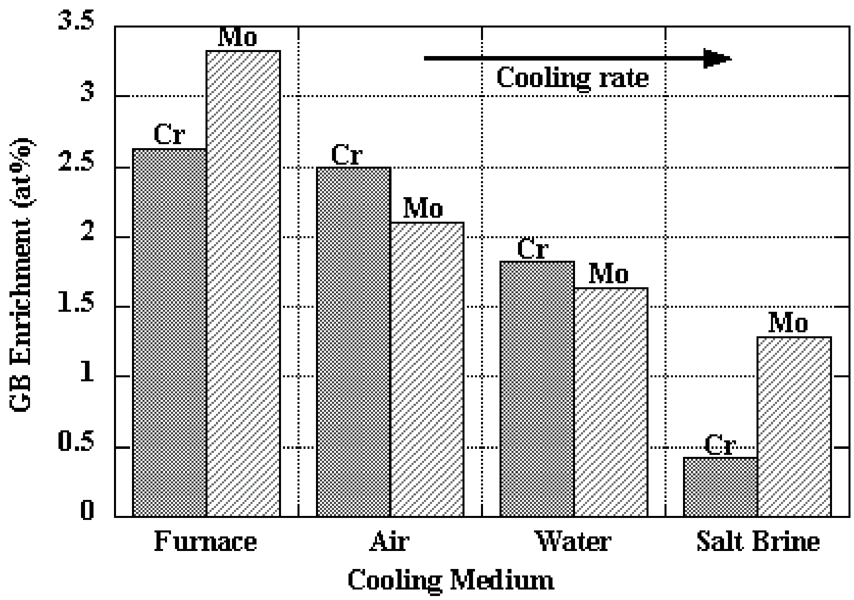

Figure 1 Effect of cooling medium on extent of grain boundary elemental enrichment in Fe-16Cr-13Ni + Mo + P annealed at 1200°C for 1 hour.

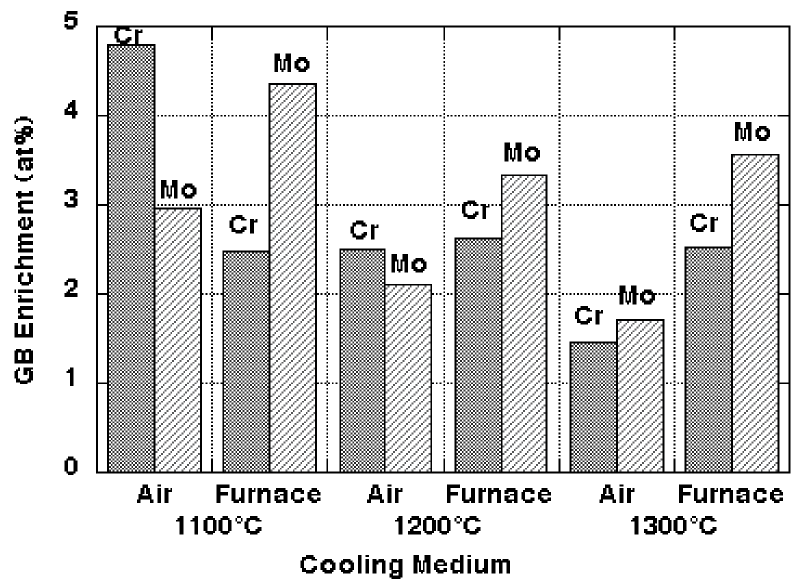

Figure 2 Grain boundary Cr and Mo enrichment as a function of annealing temperature.

Annealing Temperature Studies- To examine the effects of annealing temperature on grain boundary segregation, the base 316 + Mo + P alloy was annealed at 1100°C and 1300°C for 15 minutes prior to furnace and air cools. TEM samples were then examined as before using the FEG/STEM. The measured bulk versus grain boundary compositional differences are listed in Table 4. From the data, it is evident that the optimum treatment conditions are an 1100°C anneal for 15 minutes followed by air cooling. On average these parameters produced the greatest amount of Cr segregation to the grain boundary. It should also be noted that the furnace cooled sample showed more grain boundary Mo segregation. A graphical representation of the Cr and Mo enrichment as a function of annealing temperature in the 316 + Mo + P alloy is provided in Figure 2.

A*lloying Effects*- Following development of the optimum heat treatment (1100°C for 15 minutes followed by air cooling) to Cr enrich the boundaries, the treatment was performed the base 316 and base 316 + Mo alloys. Typical segregation profile plots,

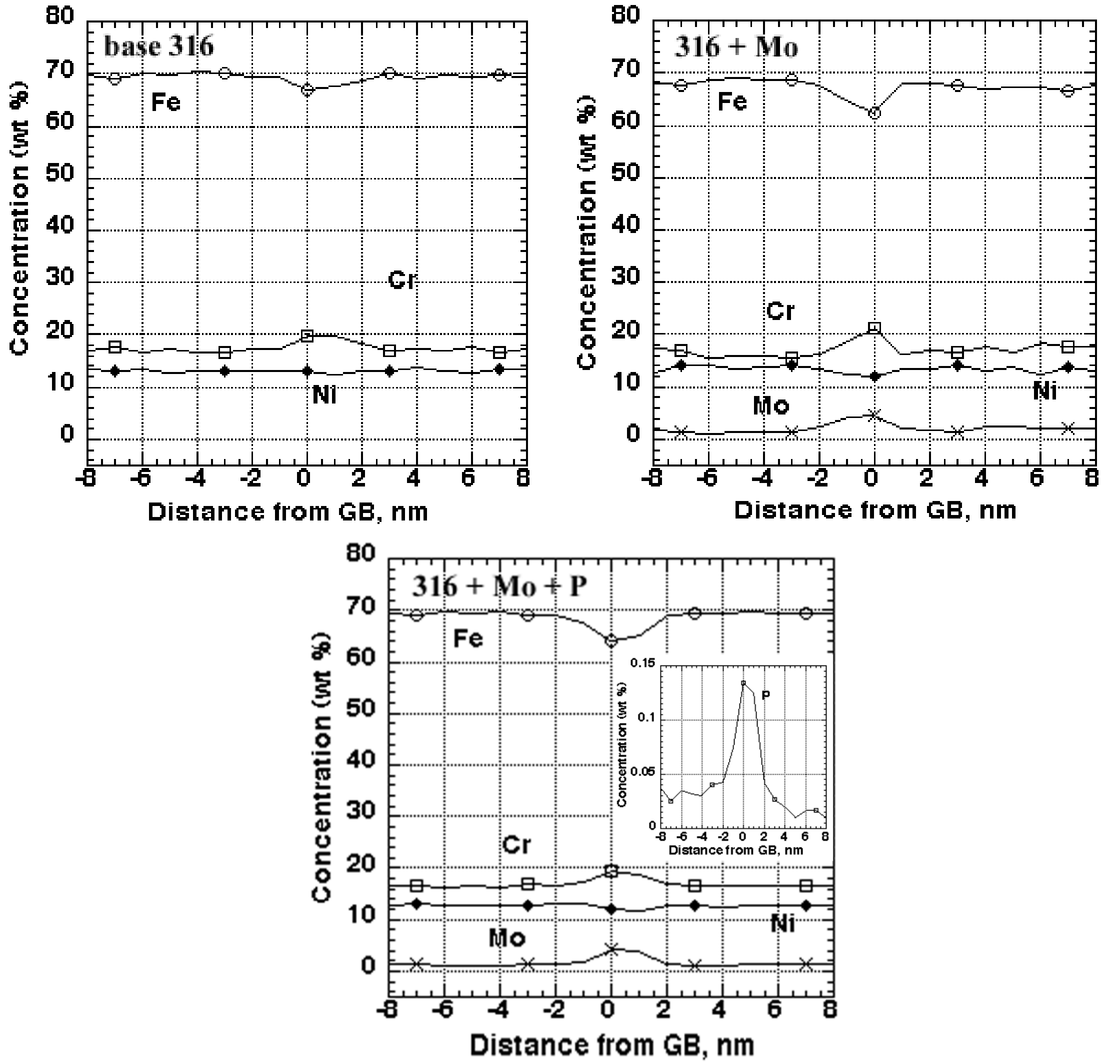

Figure 3 Segregation profiles for the 316 series of alloys following heat treatments to Cr enrich the grain boundaries. Inset in 316 + Mo + P plot shows P enrichment.

measured using FEG-STEM, from the base 316, base 316 + Mo and base 316 + Mo + P with enriched grain boundaries are shown in Figure 3. The plots illustrate that Cr enrichment can occur in the simplest alloy (base 316) to a comparable extent as alloys containing alloying additions such as Mo and P. The extent of Fe depletion and Ni enrichment in the base 316 alloy was less than the other two alloys. As with the base 316 + Mo + P, substantial enrichment of Mo also occurs in the base 316 + Mo.

Radiation-Induced Segregation Behavior

An earlier study [*8*] highlighted results from experiments on the proton irradiation response of the model austenitic stainless steels without heat treatment to Cr enrich the grain boundaries. A brief summary of these results will be given here. In the study, the alloys were irradiated to 0.5 dpa at a temperature of 400°C. This earlier study was also

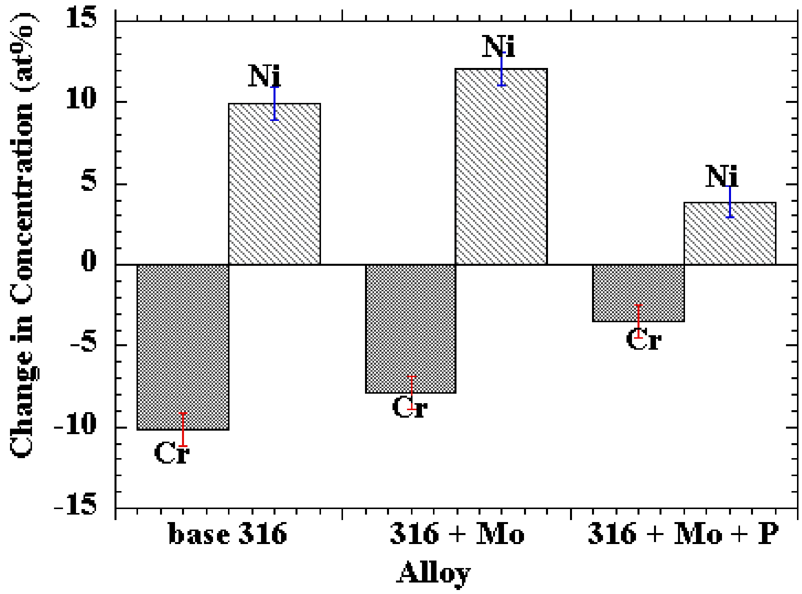

Figure 4 Plot showing change in Cr and Ni concentration for the 316 series of model alloys without heat treatment to Cr enrich the grain boundaries. Alloys were irradiated to 0.5 dpa at 400°C,

performed to investigate the influence of alloying content on void swelling. Results revealed that molybdenum additions did not have a significant impact on the swelling and RIS behavior of the 316 series model alloys, but the addition of phosphorus led to a substantial refinement of the dislocation microstructure, suppression of void formation, and a reduction in the extent of Cr depletion at grain boundaries. A plot of grain boundary Cr depletion and Ni enrichment as a function of composition in the model 316 SS alloys is shown if Figure 4. P enrichment in the proton irradiated samples was at a similar level to the sample heat treated to Cr enrich the grain boundary, indicating that grain boundary P levels do not significantly change as a result of RIS.

Currently, only one of the alloys (base 316 + Mo) with Cr enriched boundaries has been characterized following proton irradiation. Figure 5 shows a comparison of segregation profiles in the proton irradiated base 316 + Mo with and without the heat treatment designed to Cr enrich the grain boundaries. It should be noted that even though the dose for the sample without Cr enriched boundaries was half the dose of the sample with the enriched boundaries, the extent of grain boundary Cr depletion was actually greater. In the enriched sample, a W shaped profile forms and Cr depletion at the grain boundary is reduced compared to the unenriched boundary. In addition, the Fe and Ni show evident W profiles. However, Mo profile is less conclusive, and it appears the rate at which the Mo is depleting is substantially greater than the Cr. However, because of the limited number of boundaries that could be examined, this may just be a statistical anomaly.

Discussion

Thermal Non-Equilibrium Segregation

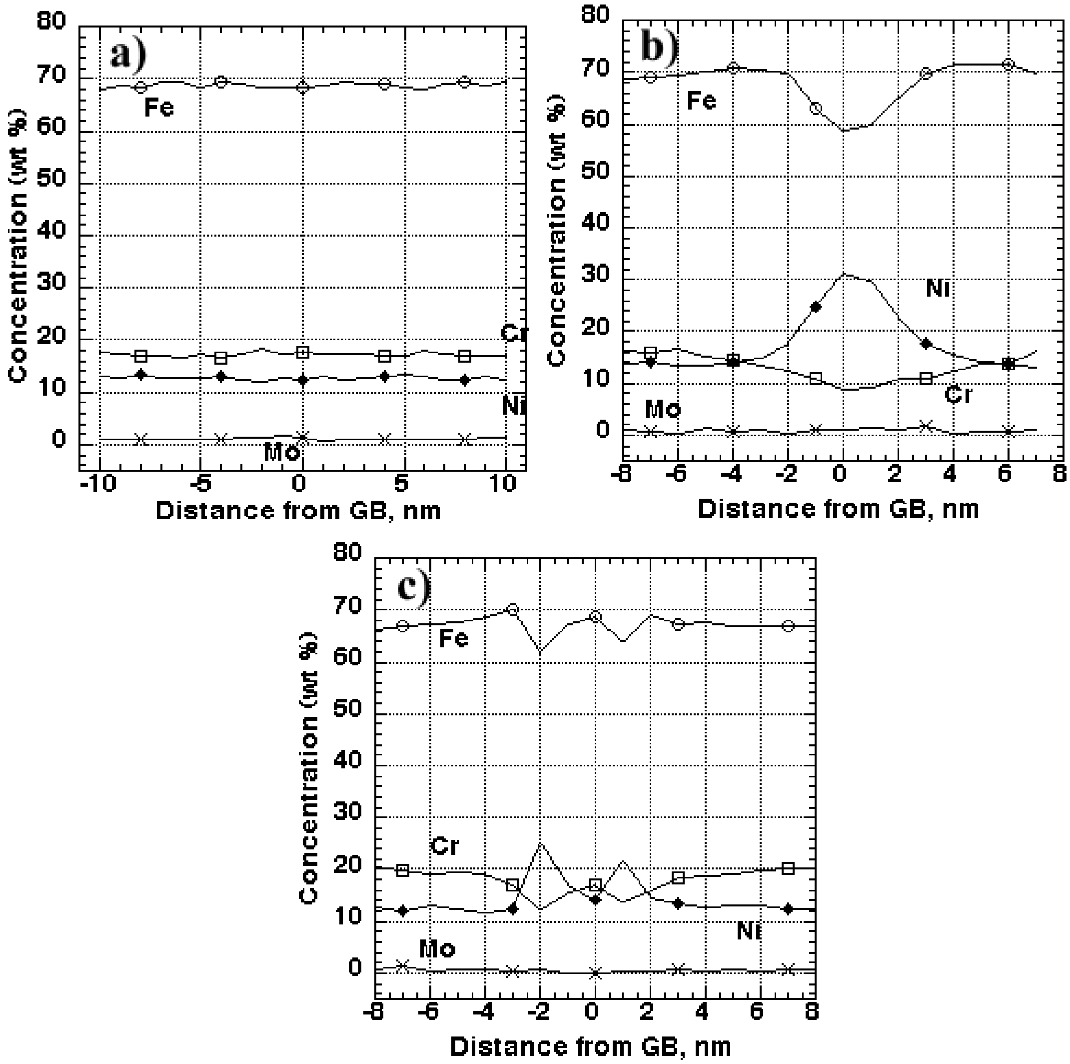

Figure 5 Segregation profiles for the 316 + Mo alloy a) without heat treatment, unirradiated, b) without heat treatment, proton irradiated to 0.5 dpa at 400°C c) with heat treatment, proton irradiated to 1 dpa at 400°C.

Thermal non-equilibrium segregation is different from RIS in two significant ways. TNES occurs at higher temperatures and involves only vacancies, while RIS involves both vacancies and self –interstitial atoms. In addition, vacancy concentrations for TNES are much lower than point defect concentrations generated during RIS. Formation of vacancy concentrations during higher temperature annealing and their subsequent migration to sinks during cooling is believed to be the primary process leading to TNES [*5*]. As the material cools a vacancy concentration gradient develops between the grain boundaries, which act as sinks, and the matrix which has a supersaturation of vacancies. During cooldown, both free vacancies and vacancy-solute complexes (both will diffuse to the grain boundaries thus enriching the boundaries with the complexed element. Concentration gradients that form as a result of enrichment at the grain boundaries results in back diffusion of free solute at elevated temperature. Figure 6 is a schematic

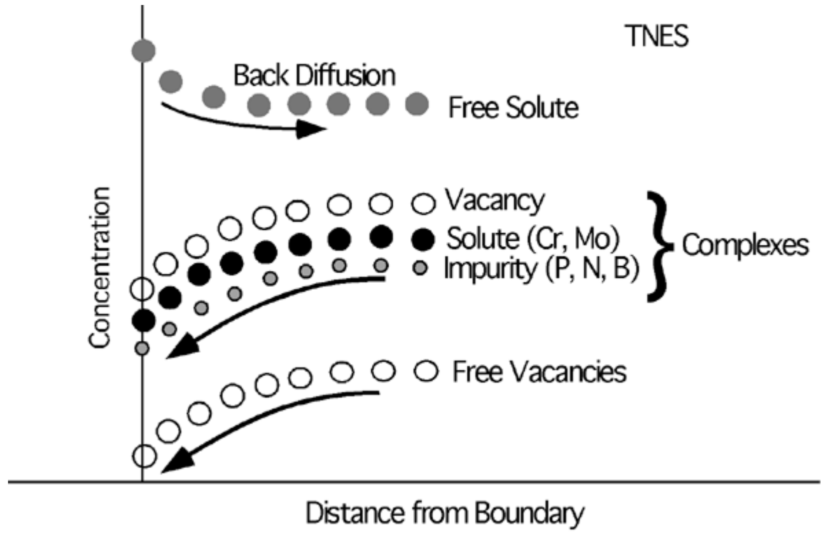

Figure 6 Schematic of TNES process

illustrating the diffusion of species and concentration profiles that result of TNES. If the material is quenched too fast, the supersaturated vacancies are frozen in the matrix and do not have an opportunity to diffuse to the boundary and produce TNES. On the contrary, if the sample is cooled too slow, back diffusion of the free solute will eliminate the enrichment. Only at intermediate cooling rates is the enrichment optimized, as observed with the Cr enrichment during air cooling in the current study. Interestingly, optimized Mo enrichment occurred at the slower furnace cooling rate. It may be that Mo back diffusion is inhibited by a strong interaction with other impurity atoms such as P [*9*]. Slower cooling rates should enhance forward diffusion of vacancy-solute complexes to the grain boundary, but if Mo is bound by impurity atoms, back diffusion will be inhibited.

It is apparent that in order for grain boundary elemental enrichment to occur, a binding between vacancies and the solute atoms must occur. The strength of this binding should dictate the extent of enrichment. However, Simonen et al. [*7*] have pointed out that in order to achieve the amount Cr enrichment observed in austenitic stainless steels, the binding energy between the Cr atoms and vacancies would have to be much higher than can reasonably be expected. The suggestion is that impurity elements such as P, N, B, and C may play a role in enhancing the TNES. However, in this study with relatively high purity alloys, even the base 316 alloy showed a small amount of Cr enrichment. Both P and C were measured in this allow and concentrations were below 0.01 at%. Boron and Nitrogen were not measured, however, it has been suggested that even B impurity levels in the ppm range, can result in significant B enrichment at the grain boundary [*10*]. This is an indication of a strong B and vacancy interaction, and if Cr co-segregates with B, it may be responsible for the Cr enrichment observed in the simple high-purity base 316 alloys examined in this study.

Radiation Induced Segregation

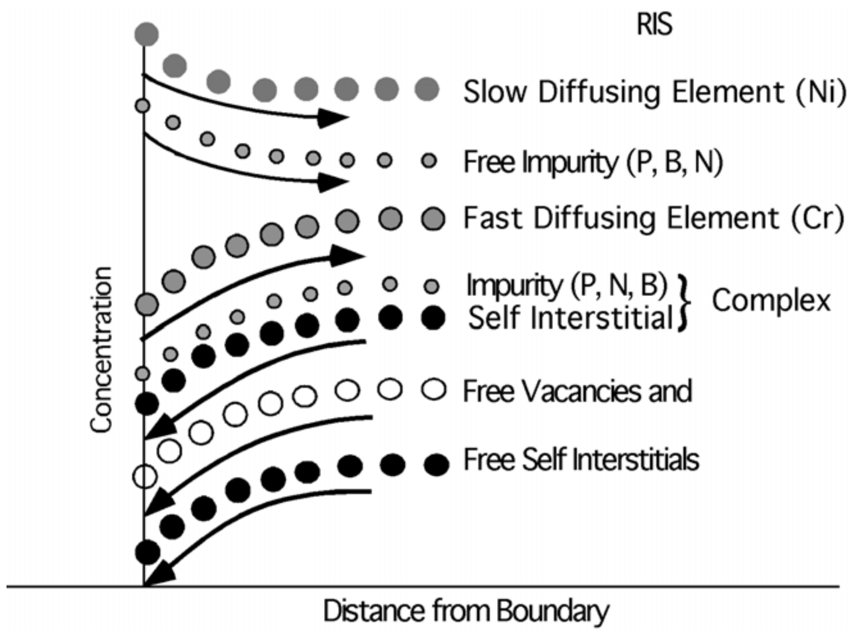

Figure 7 Schematic of RIS process.

The development of RIS profiles in austenitic stainless steels has been studied extensively [*2,11,12*]. Point defects (vacancies and self-interstitials) generated as a result of displacement damage migrate to the grain boundary. As a result of interactions with vacancies, faster diffusing elements such Cr tend to deplete at the boundary, while a slow diffusing element such as Ni tends to enrich. In addition, it is thought that interstitial-impurity complexes diffusing to the grain boundary may be responsible for radiation-induced enrichment of some impurity atoms at the grain boundary. A schematic depiction of these processes is provided in Figure 7.

Busby et al. [*6*] have shown the rate at which Cr depletion occurs due to RIS in samples with Cr pre-enriched grain boundaries is significantly lower than that predicted by inverse-Kirkendall models. Simulations suggest that the Cr enrichment should be completely eliminated by 0.01 dpa. The simulations also completely fail to predict the formation of a W profile observed in their experiments. An explanation for this behavior is indicated which involves, as discussed earlier, the binding of elements at the grain boundary by impurity atoms such as C, N, B, and P. Subsequent RIS is inhibited by this binding, and Cr depletion is delayed to a greater extent than can be predicted by inverse-Kirkendall. Binding of elements at the grain boundary would also tend to explain the formation of a W shaped segregation profile. While the Cr at the boundary is strongly held by the impurity atoms, Cr adjacent to the boundary can freely diffuse, thus resulting in near boundary depletion and a consequent W profile.

The current results suggest that if impurity atoms are responsible for the observed behavior, the concentrations necessary to achieve a delay in RIS are extremely small, and below the detection limits of FEG/STEM analysis. Kenik et al. [*10*] did in fact detect substantial B grain boundary enrichment and a strong interaction between N and Mo using the technique of atom probe field ion microscopy (APFIM) . However, the alloys used in Kenik study were commercial purity. APFIM of high purity alloys, such as those used in the current study, may provide a key piece of data on whether grain boundary impurity enrichment can explain TNES and the subsequent delay in RIS. It is apparent that the current models developed for predicting RIS behavior can not be directly adapted to explain the processes that occur during TNES and subsequent RIS. Modifications accounting for impurity enrichment and binding of atoms at the boundaries by these impurities may be necessary.

Conclusions

Results of a study on TNES and RIS behavior in model 316 series of stainless steels were described. Studies on the effect of cooling rate and annealing temperature revealed that faster cooling rates provided by water and salt-brine quenching resulted in minimal non-equilibrium segregation. However, slower cooling rates provided by both air and furnace cooling led to grain boundary enrichment of Cr, Mo and depletion of Ni, and Fe. Lower annealing temperatures also tended to enhance the degree of non-equilibrium segregation. Grain boundary Cr enrichment occurred in all three alloys examined, base 316, base 316 + Mo and Base 316 + Mo + P. The current study also reveals that heat treatments to Cr enrich grain boundaries of a 316 + Mo model alloy prior to irradiation delays the onset of grain boundary Cr depletion caused by RIS and results in the formation of a W shaped segregation profile. The results suggest that impurity elements such as B, C, P, N are either not necessary for TNES or are at such low levels as to not be detectable by FEG-STEM.

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