MODELING THE EFFECT OF IRRADIATION AND POST-IRRADIATION ANNEALING ON GRAIN BOUNDARY COMPOSITION IN AUSTENITIC Fe-Cr-Ni ALLOYS

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ABSTRACT

Many irradiation effects in Fe-Cr-Ni alloys such as radiation-induced segregation, radiation-enhanced diffusion, and void swelling are known to vary with bulk alloy composition. The development of microstructural and microchemical changes during irradiation and during post-irradiation annealing is determined by the rate of diffusion of point defects and alloying elements. To accurately predict the changes in grain boundary chemistry due to radiation-induced segregation and post-irradiation annealing, the composition dependence of diffusion parameters, such as the migration energy, must be known. A model has been developed which calculates migration energies using pair interaction energies, thereby accounting for the effect of composition on diffusivity. The advantages of this calculational method are that a single set of input parameters can be used for a wide range of bulk alloy compositions, and the effects of local order can easily be incorporated into the calculations. A description of the model is presented, and model calculations are compared to segregation measurements from seven different iron-chromium-nickel alloys, irradiated with protons to doses from 0.1 to 3.0 dpa at temperatures between 200°C and 600°C. Results show that segregation trends can be modeled using a single set of input parameters with the difference between model calculation and measurement being less than 5 at%, but usually less than 2 at%. Additionally, model predictions are compared to grain boundary composition measurements of neutron irradiated 304 stainless steel following annealing. For the limited annealing data available, model calculations correctly predict the magnitude and time scale for recovery of the grain boundary composition.

INTRODUCTION

Radiation-induced segregation (RIS) in austenitic Fe-Cr-Ni alloys is of interest because of its potential link to irradiation assisted stress corrosion cracking [1]. The examination of grain boundary composition changes has provided a greater understanding of the mechanisms of RIS in irradiated Fe-Cr-Ni alloys. Specifically, three major factors affect grain boundary segregation. First, segregation is caused by the preferential interaction of alloying elements with the vacancy flux [2,3]. Additionally, the diffusivities that describe the atom and point defect mobilities are alloy specific [4]. Finally, ordering forces are significant in the segregation process [5]. To better describe RIS in Fe-Cr-Ni alloys, a model (called the modified inverse Kirkendall, or MIK) was developed which calculates migration energies using pair potentials and includes the effect of ordering [6]. The model was tested against RIS measurements from seven different Fe-Cr-Ni alloys, irradiated with protons at 400°C to doses from 0.1 to 3.0 dpa, and at 0.5 dpa at temperatures from 200-600°C. In total, over 1100 grain boundary composition measurements were obtained. The MIK model was found to be superior to other proposed RIS models [7,8], predicting the measured segregation with no error greater than 5 at% but usually less than 2 at%. This improvement is due to the fact that the MIK model calculates atom-vacancy migration energies based on pair potentials, the ordering energy, and the local composition. Further, if the MIK model is an accurate description of atom-point defect interactions in Fe-Cr-Ni alloys, the model should also correctly describe the behavior of the grain boundary composition profiles during annealing. In this work, the MIK model is described briefly, the comparison of the MIK model to

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RIS measurements is reviewed, and model predictions are compared to grain boundary composition measurements from irradiated 304 stainless steel following annealing.

MIK MODEL

The MIK model improves on previous RIS models by calculating the diffusivity for each atom-vacancy exchange based on the local composition. To describe alloy-specific diffusivities, migration energies are calculated as a function of composition. For an atom (Cr migrating in an Fe-Cr-Ni lattice for example) to diffuse, it must jump from its equilibrium position in the lattice (with equilibrium energy E_{eq}^{Cr}) through a position of maximum potential (known as the saddle point, with saddle point energy $ES_{Fe-Cr-Ni}^{Cr}$). The migration energy is the difference between the saddle point energy and the equilibrium energy:

$$E_{vm}^{Cr} = ES_{Fe-Cr-Ni}^{Cr} - E_{eq}^{Cr}. \tag{1}$$

In this simple model, the equilibrium energy can be described as the interaction energy between nearest neighbors. For a Cr atom:

$$E_{eq}^{Cr} = Z\left[C_{Cr}E_{CrCr} + C_{Ni}E_{NiCr} + C_{Fe}E_{FeCr} + C_{v}E_{Crv}\right], \tag{2}$$

where Z is the number of nearest neighbors, C is the atomic fraction of atom or vacancy nearest neighbors, and E_{xy} is the pair interaction energy between species x and y which can be atoms or vacancies. The interaction energy of like atoms is calculated by dividing the cohesive energy of the pure metal by the number of bond pairs between nearest neighbors:

$$E_{CrCr} = E_{coh}^{Cr} / (Z/2). \tag{3}$$

Because both pure Fe and Cr are BCC, and all alloys in this study are FCC, the energy required to convert Fe and Cr to the FCC structure must be included in calculating E_{CrCr} and E_{FeFe}. Pair interaction energies between unlike neighbors are defined to be a linear average of the like atom pair energies minus any ordering energy. For instance:

$$E_{NiCr} = \frac{E_{NiNi} + E_{CrCr}}{2} - E_{NiCr}^{ord}. \tag{4}$$

The atom/vacancy interaction energy is fitted to the formation energy of the pure metal and is given by:

$$E_{Crv} = \left(\frac{E_{coh}^{Cr} + E_{vf}^{Cr}}{Z}\right). \tag{5}$$

A method for choosing the saddle point energy must be selected. If the saddle point is calculated from the pure element saddle point energies for each segregating species, then the saddle point energy is independent of the lattice and dependent only on the diffusing species. Alternatively, if the saddle point energy is dependent only on the local composition, defined by the average local bulk composition, then the saddle point energy is independent of the diffusing species. The saddle point energy should be a function of both the local composition and the diffusing species. Therefore, the saddle point energy for each element is defined as the average of the pure element saddle point energy and the average lattice saddle point energy. For instance, the saddle point energy for Cr in an Fe-Cr-Ni lattice is:

$$ES^{Cr}_{Fe-Cr-Ni} = \frac{ES^{Cr}_{pure} + ES^{avg}_{Fe-Cr-Ni}}{2}, \quad (6)$$

with the lattice average saddle point energy defined for the local composition. This formulation is the simplest method that ensures the saddle point energy is dependent both on the local composition and the diffusing species. The input parameters used for model calculations and a detailed justification of these input parameters can be found in reference [6].

MODEL RESULTS

The superior predictive capability of the MIK model can be seen by comparing the model predictions from both the MIK model and the Perks model [7] to the complete RIS data base from Fe-Cr-Ni alloys irradiated with protons. The Perks model calculations assume the migration energy is a constant for alloy compositions. Figure 1 plots the measured Cr concentration versus the Cr concentration predicted by the MIK and Perks models for grain boundary concentrations in Fe-16Cr-24Ni, Fe-20Cr-24Ni, Fe-24Cr-24Ni, Fe-24Cr-19Ni [4], Fe-20Cr-9Ni, Ni-18Cr-9Fe, and Ni-18Cr [2], irradiated at 400°C to doses from 0.1 to 3.0 dpa and at 0.5 dpa at temperatures from 200-600°C. If the model perfectly describes the segregation, the predicted segregation would fall on a line of slope equal to one. As shown in figure 1, the predictions of the MIK model are superior to those of the Perks model across all alloys and irradiation conditions.

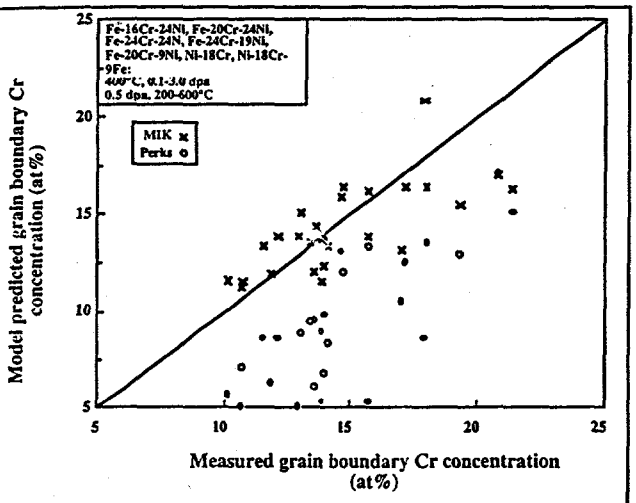

Fig.1 Relationship between model predicted (using the Perks and MIK models) and measured grain boundary Cr concentration for Fe-Cr-Ni alloys irradiated with protons. Modified inverse Kirkendall (MIK) is a better predictor of segregation than is the Perks model across all alloys at all irradiation temperatures and doses.

If the MIK model is an accurate description of diffusion in Fe-Cr-Ni alloys, it should also correctly predict diffusion coefficients. For three of the alloys studied, the ratios of calculated diffusion coefficients at 1200°C, a temperature appropriate to high temperature diffusion experiments, are listed in Table I. The ratios of the *calculated* diffusion coefficients for Fe-20Cr-24Ni are within the uncertainty of Rothman's [10] *measurements* for Fe-15Cr-20Ni ($D_{Cr}/D_{Ni} = 2.55 \pm 0.57$, $D_{Fe}/D_{Ni} = 1.67 \pm 0.31$). For Ni-18Cr-9Fe, the ratios of the *calculated* diffusion coefficients ($D_{Cr}/D_{Fe} = 1.21$) are close to those *measured* by Million et al. [16] for Ni-20Cr-16.5Fe ($D_{Cr}/D_{Fe} = 1.20$). The ratio of the *calculated* diffusion coefficients for Ni-18Cr ($D_{Cr}/D_{Ni} = 1.95$) is about 20% larger than the *measurements* of Ruzickova et al. [17] ($D_{Cr}/D_{Ni} = 1.65$). For both of the Ni-base alloys, neither author provided error bars for the

ratios of measured diffusion coefficients. Using error bars similar to Rothman as an estimate (±20%), the calculated ratio of the diffusion coefficients for Cr and Ni in Ni-18Cr are within the experimental uncertainty of Ruzickova's data.

The predictions of the MIK model are also consistent with RIS measurements in alloys irradiated with Ni ions. Simonen et al.[18] compared Perks model calculations with RIS measurements from an Fe-20Cr-20Ni alloy irradiated with 5MeV Ni ions. The diffusivity ratios d^{Cr}/d^{Ni} and d^{Fe}/d^{Ni} were adjusted until the model predictions best fit the experimental data. The Cr-Fe diffusivity ratio which gave best agreement between model calculations and RIS data was $d_{Cr}/d_{Fe} = 1.25$ A *calculation* of the diffusivity ratio gives $d_{Cr}/d_{Fe} = 1.30$ which agrees well with the calculations of Simonen.

Table I Diffusion coefficients using MIK calculated migration energies

Alloy	D_{Cr}/D_{Ni} (1200° C)	D_{Fe}/D_{Ni} (1200° C)	D_{Cr}/D_{Fe} (1200° C)
Fe-20Cr-24Ni	2.06	1.49	1.38
Ni-18Cr-9Fe	1.97	1.63	1.21
Ni-18Cr	1.95	-----	-----

Since the MIK model predicts both RIS and high temperature diffusion coefficient ratios correctly, it should also correctly predict the annealing of grain boundary composition profiles. The only published work on annealing of grain boundary segregation comes from the work of Jacobs and Dumbill [19]. Grain boundary segregation as a function of annealing time measured by Jacobs can be compared to the predictions for annealing of RIS from the MIK model.

Figures 2 and 3 plot the percent of remaining grain boundary Cr segregation as a function of annealing time for annealing temperatures of 500°C and 475°C respectively. Jacobs reported his data as the maximum segregation and average segregation and both are plotted in figures 2 and 3. The maximum segregation is the difference between the *minimum Cr concentration* in the profile and the average concentration at the 10, 15, and 20 nm (from the boundary) points in the profile (defined as the average matrix concentration). The average segregation is the difference between the *average grain boundary concentration* and the average matrix concentration. Because most of the profiles in Jacob's work are asymmetric or "W" shaped (Cr enrichment on the boundary with depletion in the regions near the boundary), the average grain boundary concentration can underestimate the chromium depletion in the profile. Therefore, the maximum segregation is a more accurate description of the Cr segregation. For the annealing times used by Jacobs, the reduction of grain boundary segregation (increase in grain boundary Cr concentration) is small. The MIK model reasonably predicts the magnitude and time scale of the recovery for the 500°C anneals and slightly underpredicts the recovery in the 475°C anneals (using the maximum segregation). As the profiles in Jacob's work are not fully developed (still retaining Cr enrichment on the boundary) and because only a small number of measurements were reported, a more detailed study of grain boundary segregation annealing is required to fully test the annealing predictions of the MIK model.

CONCLUSIONS

The MIK model has been developed to describe changes in grain boundary composition in irradiated Fe-Cr-Ni alloys more accurately. The model calculates composition-specific migration energies using pair interaction energies and short range order. The model more accurately

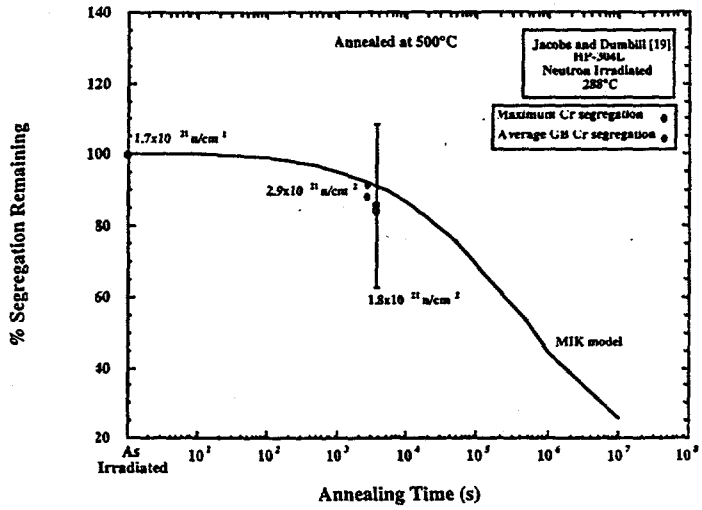

Fig.2 Comparison of measurement and the MIK model prediction for the removal of grain boundary Cr segregation during a 500°C anneal. Maximum segregation is the difference between the minimum Cr concentration in the profile and the average of the 10, 15, and 20 nm points in the profile. Average segregation is the difference between the average grain boundary concentration and the average matrix concentration. Uncertainty bars are for the maximum segregation.

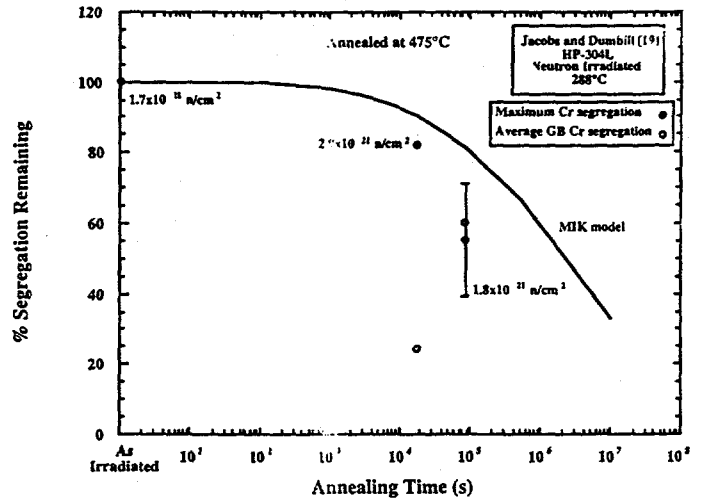

Fig.3 Comparison of measurement and the MIK model prediction for the removal of grain boundary Cr segregation during a 475°C anneal. Maximum segregation is the difference between the minimum Cr concentration in the profile and the average of the 10, 15, and 20 nm points in the profile. Average segregation is the difference between the average grain boundary concentration and the average matrix concentration. Uncertainty bars are on the maximum concentrations.

calculates radiation-induced changes in grain boundary composition than any previously proposed model. For the limited data available on grain boundary composition of irradiated and annealed 304 stainless steel, the MIK model reasonably tracks the recovery in grain boundary composition. The agreement of the model predictions with measurements of grain boundary composition for post-irradiation annealed alloys is further evidence that the MIK model correctly describes kinetics in Fe-Cr-Ni alloys.

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