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GAUGE TO QUANTIFY FUNDAMENTAL DEFECT PARAMETERS**

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RADIATION-INDUCED SEGREGATION: A MICROCHEMICAL GAUGE TO QUANTIFY FUNDAMENTAL DEFECT PARAMETERS

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ABSTRACT

Defect kinetic parameters are evaluated for austenitic stainless alloys by comparing model predictions to measured responses for radiation-induced grain boundary segregation. Heavy-ions, neutrons and proton irradiations having substantial statistical bases are examined. The combined modeling and measurement approach is shown to be useful for quantifying fundamental defect parameters. The mechanism evaluation indicates vacancy migration energies of 1.15 eV or less and a vacancy formation energy at grain boundaries of 1.5 eV. Damage efficiencies of about 0.03 were established for heavy-ions and for light-water reactor neutrons. Inferred proton damage efficiencies were about 0.15. Segregation measured in an advanced gas-cooled reactor component was much greater than expected using the above parameters.

INTRODUCTION

Radiation-induced segregation (RIS) results from the discriminating interaction of solute with defect flow toward grain boundaries [1]. Relative solute diffusivity as well as solute-defect binding energy dictate the degree of enrichment or depletion of solute at grain boundaries. Significant depletion of Cr and enrichment of Ni at grain boundaries after irradiation of austenitic stainless alloys have been documented using field-emission-gun, scanning-transmission-electron microscopy (FEG-STEM) and Auger electron spectroscopy (AES). This segregation, shown to be inverse-Kirkendall segregation, occurs because of differential diffusion rates of major alloying elements in stainless steel [3,4]. Slow diffusing Ni enriches and fast diffusing Cr depletes at grain boundaries.

The proportion of Cr depletion relative to Ni enrichment is uniquely dictated by the relative diffusion rates of Fe, Cr and Ni. The absolute magnitude of composition change, on the other hand, is controlled by the kinetics of irradiation. Models for inverse-Kirkendall kinetics are in reasonable accord with measured segregation [3,4]. Relative diffusion rates for Fe, Cr, and Ni have been determined from a comparison of the Cr depletion dependence on Ni enrichment. The relative diffusion rates indicated by the inverse-Kirkendall model have been shown to be consistent with measured rates determined during thermal annealing experiments [3].

Irradiation kinetics dictate the absolute change in the solute concentrations. The kinetics are primarily influenced by processes that control long range migration of vacancies. These processes include the damage efficiency, defect sink densities, vacancy migration energy, and vacancy formation energy at grain boundaries. The relative importance of defect loss mechanisms depends on the damage rate and temperature of irradiation. For Ni⁺⁺ ion irradiation at temperatures less than 400°C, the vacancy migration energy dominates control of mutual recombination. For neutron irradiation at temperatures greater than 400°C, vacancy formation energies can control loss rates of vacancies at grain boundaries. At temperatures near 400°C, proton irradiation is controlled by a combination of vacancy migration, loss to defect sinks, and vacancy emission from grain boundaries. Inverse-Kirkendall modeling and microchemical characterization can be used as a tool for quantitative evaluation of these competitive defect processes. RIS is a function of the vacancy arrival rate at grain boundaries and grain boundary interactions with the incoming defects.

In this paper, the inverse-Kirkendall model for major alloying elements is used to quantify fundamental defect parameters. The temperature and dose dependencies of segregation measured using FEG-STEM or AES is used to establish expected defect characteristics. Heavy-ion, proton and neutron irradiations are evaluated using a consistent set of assumed defect parameters and observations based on a large number of measurements. The parameters of principal interest in the

present study are the vacancy migration energy, the vacancy formation energy at grain boundaries and the damage efficiency of irradiation particles.

MECHANISM ANALYSIS

Rate equations for solute and defect species are solved to predict the influence of defect flows on solute redistribution at and near grain boundaries. Finite difference numerical methods [5] and the GEAR numerical subroutines [6] have been used to solve the rate equations. Material constants were selected to be consistent with those assumed by Perk's et al. except when noted. Alloy compositions and irradiation temperatures, dose rates and doses were selected to represent conditions for experimentally measured segregation responses. Model predictions for grain boundary concentrations have been convoluted to account for the spatial intensity distribution of FEG-STEM and AES probes [2].

Review of the literature indicates uncertainty in the selection of defect parameters for austenitic stainless steels. A goal of the present research is to examine the compatibility of quantitative assumptions of defect parameters with observed RIS responses at grain boundaries. Reported values for vacancy migration energy range from 0.92 eV [7] to 1.33 eV [8]. Early RIS analysis [1] were based on a value of 1.28 eV consistent with measurements in Ni, whereas later analyses for stainless steel have indicated a value of about 1.17 eV [9]. Similarly, assumed values of vacancy formation energy have ranged from 1.39 eV [10] to 1.9 eV [5]. These discrepancies arise because of differences in irradiation, analysis and modeling techniques used to infer the defect parameter values.

Two additional defect parameters required for applying the inverse-Kirkendall model include the damage efficiency and the defect sink strength, i.e., the radiation-induced dislocation density. Damage efficiency refers to the fraction of total dpa that are available as freely migrating defects. The freely migrating defects are those that can influence long-term development of microchemistry and microstructure. Estimated damage efficiencies for a wide range of irradiation conditions [11] are from 0.01 to 0.1. Estimates for specific irradiations [12] include 0.0375 for 3 MeV Ni⁺⁺ and 0.19 for 2 MeV H⁺. Dislocation densities are sometimes but not always reported. Densities in the range of $1 \times 10^{14} \text{ cm}^{-2}$ to $6 \times 10^{14} \text{ cm}^{-2}$ are typical [3]. The parameters established as reference values in the present paper are 1.15 eV for vacancy migration energy, 1.5 eV for vacancy formation energy, $1 \times 10^{14} \text{ cm}^{-2}$ for dislocation density, and a damage efficiency of 0.03 for heavy ions and neutrons but 0.15 for protons.

Grain boundary compositions have been reported for irradiation of austenitic alloys containing Fe, Cr and Ni. The experiments utilize FEG-STEM analysis of grain boundaries irradiated using either 5 MeV Ni⁺⁺ ions or neutrons from power reactors [13]. Proton irradiated austenitic alloys have been evaluated using AES [14]. The temperature and dose dependencies of RIS in heavy-ion and proton irradiated alloys having about 20 at% Cr and 20 at% Ni have been measured. For neutrons, controlled experiments to measure the temperature and dose dependence of RIS have not been performed. The dose dependence of BWR irradiated austenitic stainless steels can be extracted from various independent experiments [13]. One study [3] of advanced gas-cooled reactor (AGR) neutron irradiation as a function of temperature has been reported.

Evaluation of Relative Solute Diffusivities

The measured Cr concentration as a function of measured Ni concentration has been evaluated for heavy-ion, proton and neutron-irradiated austenitic alloys having the same approximate bulk compositions of Fe, Cr and Ni. The plot of measured Cr and Ni concentrations is shown in Figure 1 and includes a total of 468 data points. The RIS-induced Cr concentration is seen to follow the same dependence on the RIS-induced Ni concentration for all three types of particle irradiation.

Figure 1. Comparison of the Cr-Ni relationship is made for three types of irradiation particles, ion (small open symbol), protons [14] (plus symbol) and neutrons [3] (large open symbol). The ion and neutron measurements were made using FEG-STEM analysis and the proton measurements were made using AES.

Furthermore, the ion data includes measurements at and away from grain boundaries. The remarkable similarity in the data trends strongly suggests that the same inverse-Kirkendall mechanism is causing the RIS responses for each of the three types of irradiation. Model calculations compared to measured composition changes caused by ions and protons indicated that an assumed Fe to Ni diffusivity ratio near to 2.0 provided a reasonable description of the measured response for Fe-Cr-Ni alloys having about 20 at% Cr and 20 at% Ni. The ratio compares favorably with the measured value of 1.8 reported by Rothman et al. [15] for higher temperature thermal annealing.

Evaluation of Irradiation Kinetics

Irradiation kinetics do not dictate the composition path shown by the trend lines in Figure 1, but rather irradiation kinetics dictate the degree of travel down a given path for a constant irradiation dose. Data found in the upper left corner of Figure 1 represent weak irradiation kinetics, whereas data found in the lower right corner of the figure represent strong irradiation kinetics. Temperature and dose are the primary irradiation variables that can be experimentally controlled.

Mechanistically, the vacancy migration kinetics dominate influences at low temperature and high damage rates. Vacancy formation energies dominate influences at high temperatures and low damage rates. At intermediate temperatures and damage rates, defect sink efficiencies compete with the vacancy migration and vacancy formation for control of RIS kinetics. These regimes of control are evaluated using the variable dose rate and temperature conditions among heavy ion, proton and neutron irradiations.

Ion irradiation at 5×10^{-3} dpa/s was used to induce RIS at temperatures from 180°C to 550°C [13]. The measured grain boundary Cr concentrations are shown in Figure 2a as a function of temperature at 10 dpa and in Figure 2b as a function of dose at 500°C. At temperatures below 400°C, the level of RIS is dominated by the vacancy migration kinetics. Model predictions for three choices of vacancy migration energy are shown. Migration energies of 1.15 eV or lower are needed to match the measured Cr depletion. Predicted concentrations indicate a minimum grain boundary Cr concentration at temperatures equal to or greater than 500°C, while the data reaches minimum values at 400°C. The predicted dose dependence shows a trend toward saturation that is less severe than indicated by the data.

(a)

(b)

Figure 2. Temperature dependence (a) at 10 dpa and dose dependence (b) at 500°C of an ion irradiated stainless alloy [13]. The effect of the assumed value for vacancy migration energy is shown for 1.0 eV, 1.15 eV and 1.28 eV. The assumed dislocation density is constant at 10^{14} cm^{-2} and the assumed vacancy formation energy is 1.5 eV.

The neutron irradiation data at temperatures greater than 350°C and at low dose rates is complicated by dose and defect sink densities that depend on temperature. Norris et al.[3] examined RIS in a Nb-stabilized stainless steel used in the AGR. The examined component experienced a range of temperatures that allowed evaluation of the temperature dependence of RIS. The component segments also had doses and defect sink densities that varied as a function of reactor position and temperature. Four temperatures were evaluated with measurements at 354°C, 418°C, 455°C and 481°C. At 354°C, the dose and dislocation density was 1.0 dpa and $6 \times 10^{14} \text{ m}^{-2}$. Similarly, doses and densities were 2.16 dpa and $4 \times 10^{14} \text{ m}^{-2}$ at 418°C, 2.8 dpa and $4.5 \times 10^{14} \text{ m}^{-2}$ at 455°C and 3.0 dpa and $1 \times 10^{14} \text{ m}^{-2}$ at 481°C. Using these temperature dependent doses and dislocation densities, the predicted grain boundary Cr concentrations at the four temperatures are shown in Figure 3. The calculated concentrations are connected by a trend line to guide the eye. The dislocation density was assumed to increase from 10^{12} m^{-2} to the final density with a dependence on dose to the one-half power as described by Norris et al. The assumed vacancy formation energy was 1.9 eV, in contrast to the reference value of 1.5 eV.

The lower temperature kinetics were underpredicted and the measured decreasing RIS effect with increasing temperature was not evident in the model calculations. The discrepancy in temperature dependence was accounted for by assuming a lower vacancy formation energy of 1.5 eV and by assuming a higher damage efficiency for producing freely migrating defects. With these model assumptions, the predictions and measurements were more reasonably described as shown in Figure 3. Vacancy formation energies greater than 1.5 eV are inconsistent with the observed RIS temperature dependence.

Measurements of RIS in austenitic steels after boiling-water reactor (BWR) irradiation have been compiled to indicate a trend for dose dependence[13]. The experimental response is shown in Figure 4 for a variety of 300-series stainless steels irradiated to doses up to about 10 dpa, where a dose of 1 dpa is equivalent to a neutron fluence of about $0.7 \times 10^{21} \text{ n/cm}^2$ ($E > 1 \text{ MeV}$). Also shown in Figure 4 is the model prediction of fluence dependence for an Fe-18Cr-8Ni alloy with an assumed damage efficiency of 0.03. Both the measurements and the model indicate a strong grain boundary Cr dependence on fluence at low fluence which converts to a weak dependence at high fluence.

Figure 3 The temperature dependence for grain boundary Cr and Ni concentration established from examination of an AGR component at about 1 dpa [3]. Closed symbols are data and open symbols are predictions for the indicated damage efficiency and vacancy formation energies.

Figure 4 Measured and predicted dose dependence of grain boundary chromium concentration in austenitic steels irradiated in a boiling water reactors at 288°C. The experimental values are taken from Bruemmer et al [13]. The cross hatched bands refer to 316SS irradiations and measurements of Jacobs.

The temperature and dose dependencies of Cr and Ni concentration for proton irradiation are shown in Figure 5a and 5b, respectively. A damage efficiency of 0.15 was assumed in contrast to a damage efficiency of 0.03 for heavy ions and BWR neutrons. The measurements suggest a peak RIS near 500°C, whereas the model calculations suggest a peak RIS near 450°C. The dose dependencies for the measured and calculated grain boundary concentrations are similar, but the measurements indicate a stronger trend toward saturation than do the calculated values. In this intermediate temperature regime, the defect sink density is an important controlling parameter but was assumed to be independent of temperature for the calculated behavior.

(a)

(b)

Figure 5 Temperature dependence (a) at 0.5 dpa and dose dependence (b) at 400°C for grain boundary Cr and Ni concentration measured using AES after proton irradiation [14]. Constant dislocation density, 10^{14} cm^{-2} , and vacancy formation energy, 1.5 eV, are assumed.

DISCUSSION/CONCLUSIONS

The inverse-Kirkendall model has been used to interpret the temperature and dose dependence of RIS established for heavy-ions, neutrons and protons. Input parameters for the model were based on independent estimates as well as the quality of fit with the measured RIS values. Heavy-ion irradiation at temperatures below 600°C indicate a vacancy migration energy of 1.15 eV or lower. The agreement between model calculations and measured behavior improves for decreasing assumed values of vacancy migration energy. Both the degree of RIS at temperatures below 400°C and the weak temperature dependence at temperatures above 400°C indicate vacancy migration energies at or below 1.15 eV.

Vacancy formation energies were interpreted from neutron irradiation induced RIS at temperatures greater than 300°C. Model predictions indicated that the extreme degree of measured RIS was inconsistent with the assumed reference damage efficiency of 0.03. The magnitude of measured RIS was consistent with a damage efficiency of 0.3 or ten times the expected value. In this study, the damage efficiency was used as a convenient adjustable parameter to reconcile conflicts between measurement and model calculation. The burden of adjustment could be distributed among other kinetic uncertainties in the model. The dpa estimate is based on approximate conversions of fuel burn up to cladding displacement damage. The spectra of the AGR neutrons may also be such that it is more efficient in producing freely migrating defects. In addition, the measured dislocation densities are subject to error. A factor of two uncertainty in each of these three factors results in an order of magnitude difference in the calculated kinetic opportunity for RIS. It is unlikely that the uncertainty of any single factor could be as large as an order of magnitude. It is more likely that the collective uncertainties may account for the measured high kinetic opportunity for RIS compared to the low calculated opportunity for RIS based on the reference assumptions. The decrease in measured RIS magnitudes was only accounted for by using a vacancy formation energy of 1.5 eV. Larger assumed activation energies did not result in calculated temperature dependencies that were consistent with the measured behavior.

Reasonable agreement between calculated and measured proton irradiation responses resulted from the reference assumptions of defect parameters. The assumed proton damage efficiency was 0.15 compared to the assumed damage efficiency of 0.03 for heavy-ions and BWR neutrons. Inclusion of a temperature dependent dislocation density is expected to improve the correlation between calculated and measured RIS responses. At low temperatures, higher dislocation densities are expected and therefore lesser segregation would be calculated at 300°C. Conversely at high temperatures, lesser dislocation densities are expected and greater segregation would be calculated at 500°C.

In conclusion, RIS in austenitic stainless alloys has been examined using statistically established data and using multiple irradiation particle types. The data was compared to the inverse-Kirkendall model for a reference set of model parameters. The comparison of measured and calculated RIS responses indicated values for vacancy migration energy equal to or less than 1.15 eV, vacancy formation energies equal to 1.5 eV and damage efficiencies of approximately 0.03 for heavy-ion and neutron irradiation and approximately 0.15 for proton irradiation. The above assumptions were consistent with heavy-ion irradiation, BWR neutron irradiation and proton irradiation. AGR neutron irradiation was anomalous in that it exhibited a much greater kinetic opportunity for RIS than expected. Resolution of the discrepancy would likely require adjustment in several factors of kinetic importance such as estimates of dpa and freely migrating defects for the AGR spectra, and considerations of evolution of dislocation density at relatively high temperatures. The temperature dependence of RIS suggested that an activation energy of 1.5 eV for vacancy formation is most realistic.

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REFERENCES

1. Workshop on Solute Segregation and Phase Stability During Irradiation, edited by J. O. Stiegler, *J. Nucl. Mater.*, **83** (1979).
2. R. D. Carter, D. L. Damcott, M. Atzmon, G. S. Was, S. M. Bruemmer and E. A. Kenik, *J. Nucl. Mater.*, **211**, 70 (1994).
3. D. I. R. Norris, C. Baker, and J. M. Titchmarsh, in Proceedings of Symposium on Radiation-Induced Sensitization of Stainless Steels, INIS-GB-90, ed. by D. I. R. Norris, Berkeley, Gloucestershire, GL13 9PB, Berkeley Nuclear Laboratories, 1981, p. 86.
4. E. P. Simonen and S. M. Bruemmer, in Corrosion '93 paper no. 615, National Association of Corrosion Engineers, Houston, TX., 1993.
5. J. M. Perks, A. D. Marwick and C. A. English, "A Computer Code to Calculate Radiation-Induced Segregation in Concentrated Ternary Alloys," AERE R 12121, Oxfordshire OX11 0RA, Harwell Laboratory, June 1986.
6. A. C. Hindmarsh, GEAR: Ordinary Differential Equation System Solver, Report UCID-30001, Rev. 3, Lawrence Livermore Laboratory, Livermore, CA, 1974.
7. J. Dryzek, C. Wesseling, E. Dryzek and B. Cleff, *Mat. Let.* **21**, 209 (1994).
8. C. Dimitrov and O. Dimitrov, *J. Phys. F: Met. Phys.*, **14**, 783 (1984).
9. O. Dimitrov and C. Dimitrov, *J. Nucl. Mat.* **105**, 39 (1982).
10. A. D. Marwick, R. C. Piller and M. E. Horton, AERE R 10895, Oxfordshire OX11 0RA, Harwell Laboratory, 1983.
11. L. E. Rehn and P. R. Okamoto, *Mat. Sci. Forum* **15-18**, 985 (1987).
12. V. Naundorf, *J. Nucl. Mater.*, **182**, 254 (1991).
13. S. M. Bruemmer, L. A. Charlot and E. P. Simonen, "Radiation-Induced Grain Boundary Segregation in Stainless Alloys, this proceedings.
14. D. L. Damcott, G. S. Was and S. M. Bruemmer, "Proton Irradiation Induced Grain Boundary Segregation in Austenitic Stainless Steels," this proceedings.
15. S. J. Rothman, L.J. Norwicki and G. E. Murch, *J. Phys. F. Metal Phys.*, **10**, 383 (1980).