Influence of Silicon and Phosphorus on Radiation-Induced Segregation of Chromium and Nickel in Austenitic Model Alloys

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The influence of undersized solute additions on radiation-induced segregation (RIS) at grain boundaries was examined for austenitic model alloys. High-purity Fe-15Cr-20Ni alloys, doped with either 0.5 mass% silicon or 0.025 mass% phosphorus, were exposed to electron irradiation at several temperatures in a high-voltage electron microscope. The grain boundary depletion of chromium and segregation of nickel were significantly suppressed by the addition of silicon and phosphorus, and the addition of phosphorus significantly reduced the RIS at a grain boundary. It was shown by numerical simulation that the present results stem from the strong interaction between the additives and interstitial atoms produced by the electron irradiation.

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1. Introduction

Solute redistribution in a concentrated alloy under irradiation occurs due to the preferential interaction between the solute atoms and excess point defects migrating toward sinks, such as surface or grain boundaries. In the austenitic stainless steel type 304, which is used as a light-water reactor component, radiation-induced segregation (RIS) near the grain boundary significantly degrades its mechanical and chemical properties.1,2) The seriousness of this problem has been considered as irradiation-assisted stress corrosion cracking (IASCC) induced by the RIS3,4) because of the depletion of chromium atoms near grain boundaries. Transmission electron microscopic (TEM) in-situ observation coupled with computer calculation is one of the most powerful methods for clarifying the mechanism of irradiation-induced solute redistribution near grain boundaries.5–7)

Results of several experimental studies showing desirable effect of oversized solute additives on RIS in austenitic stainless steels have been reported,8–10) but there are few reports on the effect of undersized solute additives. In this study, therefore, undersized solutes, silicon and phosphorus, were added to the high-purity Fe-15Cr-20Ni based alloy and the influence of them on RIS at grain boundaries was investigated. Electron irradiation experiments at several different temperatures were performed using a high-voltage electron microscope (HVEM), and the results were compared with the results of computational simulation based on rate theory.

2. Experimental Procedure

Three high-purity austenitic Fe-Cr-Ni based alloys containing 20.1 mass% nickel, 15.2 mass% chromium and, as impurities, 0.003 mass% carbon and 0.0011 mass% nitrogen were used. Two alloys with the same composition as that stated above were doped with 0.5 mass% silicon or 0.025 mass% phosphorus. A specimen was solution-annealed at 1323 K for 1 hour and was thinned by electrochemical polishing. The foil specimen (about 400 nm in thickness) was irradiated with 1.25 MeV electrons at several different temperatures using an HVEM (JEOL JEM-ARM-1300) of Hokkaido University HVEM Center. The incident electron beam was adjusted to be parallel to the [110] axis. High-angle grain boundaries except for low Σ value boundaries were irradiated, avoiding the effect of misorientation angle on RIS.11–13) The mean displacement rate of the irradiation was $1 \times 10^{-3}$ dpa/s. The irradiation temperatures were in the range of 473 to 773 K. The dose was less than 1.8 dpa. After the irradiation, the specimen surface was removed from both sides by ion-milling a few hundred nanometers in thickness, and then chemical compositions were measured by using an energy dispersive X-ray spectroscope (EDX) of a field-emission type transmission electron microscope (JEOL JEM-2010F).

3. Calculation Method

Considering the flux of both vacancies and interstitial atoms toward the grain boundary and the interaction of solution atoms with these point defects, the rate equation was solved to obtain solute redistribution near the grain boundary. Since the additives, silicon and phosphorus, are undersized solute in an austenitic stainless steel, they are thought to interact with interstitial atoms and form mixed dumbbells. Migration of the mixed dumbbell was assumed to occur. Therefore, the equations differed from those based on the model for oversized solute addition previously proposed.9)

The approach is to solve the couple diffusion equations for vacancies, interstitial atoms and solute atoms including additional elements to obtain the terms coupling the defect and solute fluxes. The continuity equations are as follows.

$$\frac{\partial C_v}{\partial t} = \frac{\partial}{\partial x} \left[ D_v \frac{\partial C_v}{\partial x} - C_v \sum_k d_k \frac{\partial C_k}{\partial x} \right] + G_{dpa} - R_{v_i} D_i C_i C_v - \rho Z_{v_i} D_{v_i} (C_v - C_{eq}^v). \quad (1)$$

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left[ D_i \frac{\partial C_i}{\partial x} + C_i \sum_k d_k \frac{\partial \beta_k C_k}{\partial x} \right]$$

where $D_v$ and $D_i$ are the self-diffusion coefficients of vacancies and interstitials, $d_k$ is the solute flux, $C_v$ and $C_i$ are the concentrations of vacancies and interstitials, $C_k$ is the concentration of the $k$th solute, $\beta_k$ is the interaction coefficient between the $k$th solute and interstitials, and $G_{dpa}$ and $R_{v_i}$ are the generation rate of vacancies by displacement and recombination rate of vacancies, respectively.
+ \frac{G_{\text{dis}} - R_{\text{re}}}{\rho Z_{\text{c}} D_{\text{c}, i}} C_{\text{c}, i} = \rho Z_{\text{c}} D_{\text{c}, i} C_{\text{c}, i}, \quad (2)

\frac{\partial C_k}{\partial t} = \frac{\partial}{\partial x} \left[ D_k \frac{\partial C_k}{\partial x} - C_k \left( d_k \frac{\partial C_{\text{c}, v}}{\partial x} - d_k \frac{\partial \beta_k C_{\text{c}, v}}{\partial x} \right) \right]. \quad (3)

The set of six equations, two for point defects and four for solutes and additional elements, are solved numerically for concentrations as a function of time and distance from a grain boundary. Solute species (iron, chromium, nickel, silicon and phosphorus) are identified by the index \( k \), and vacancies and interstitial atoms are represented by \( v \) and \( i \), respectively. The important parameters here are the coupling parameter between interstitial and solute atoms described by

\[ \beta_k = C_k \exp \left( E_{(v \rightarrow i)/kT} \right) \sum_m C_m \exp \left( E_{(m \rightarrow v)/kT} \right), \quad (4) \]

where \( E_{(v \rightarrow i)/kT} \) is the binding energy between an interstitial atom and solute atom. This parameter provides the fraction of each solute element forming the mixed dumbbell in all of the mixed dumbbells, and the magnitude of \( \beta_k \) becomes large with increase in binding energy. Undersized-solute elements such as silicon and phosphorus, which are expected to easily form a mixed dumbbell, are thought to have larger \( \beta \) than those of the other solute elements. Therefore, in this calculation, the binding energies were selected to be positive values for silicon and phosphorus and zero for the other alloying elements.

The partial diffusion coefficients of solutes by vacancies or interstitial mechanism were determined by

\[ d_k^i = v_k^i a_k^i \exp \left( - E_{(v \rightarrow i)/kT} \right), \quad (5) \]

where \( v_k^i \) is the jump frequency of the vacancy (\( y = v \)) and interstitial atom (\( y = i \)) via the \( k \)-atom, \( a_k \) is the lattice constant, and \( E_{(v \rightarrow i)/kT} \) is the migration energy of the vacancy or interstitial atom. The diffusivities of point defects and the radiation-enhanced diffusivities of solutes are then given by

\[ D_v = \sum_k d_k^v C_k, \quad (6) \]

\[ D_i = d_k^i \beta_k C_k, \quad (7) \]

\[ D_k = d_k^i C_k + d_k^v \beta_k C_k. \quad (8) \]

Other parameters shown are the displacement rate, \( G_{\text{dis}} \), the mutual recombination rate, \( R_{\text{re}} \), the dislocation density, \( \rho \), and bias factors for each of the point defects, \( Z_v \) and \( Z_i \). The boundary conditions for the solutes are zero flux at the grain boundary and at the center of a grain. Similarly, the defect flux is assumed to be zero at the center of a grain, but the grain boundary concentrations are fixed at the equilibrium concentration for vacancies and zero for interstitial atoms described by

\[ C_v |_{\text{GB}} = \exp \left( \frac{S^v}{k} \right) \exp \left( - \frac{E_v^v}{kT} \right), \quad (9) \]

\[ C_i |_{\text{GB}} = 0, \quad (10) \]

where \( S^v \) and \( E_v^v \) are the formation entropy and energy of a vacancy. In the present calculations, we assumed that the vacancy equilibrium concentration at the grain boundary was same as that in bulk, although the formation entropy and energy of the vacancy should change around general grain boundaries.

Most of the material constants used in this study are consistent with those assumed by Sakaguchi et al.\textsuperscript{14} The most important unknown parameters are the binding energies between an interstitial atom and silicon or phosphorus and the migration energies of the mixed dumbbell. The former parameters greatly influence the segregation behavior of major alloying elements such as chromium and nickel, whereas the latter ones only influence the segregation of themselves. In addition, it is generally known that the migration energy of a mixed dumbbell is much greater than that of a dumbbell, and the values used in the present calculations are not contradictory to this fact. These parameters were fixed to fit to the experimental results on RIS at grain boundaries and are listed in Table 1. The binding energy between phosphorus and interstitial atom was assumed to be greater than that of the value obtained by measurements on temperature dependence of the loop density.\textsuperscript{15}

After the calculations, spatial resolution in EDX analysis was determined by convoluting the calculated profiles to the beam intensity distribution function. We assumed a normalized two-dimensional Gaussian profile with full width at a half-maximum of 3 nm, which is necessary for simulating the experimental profile data obtained by TEM-EDX analysis.\textsuperscript{16}

4. Results and Discussion

The effects of additive silicon and phosphorus are summarized in Fig. 1 and Fig. 2, which show typical theoretical and experimental results regarding the segregation phenomena of the major alloying elements near the grain boundary after electron irradiation of 1.8 dpa at 573 K and at 673 K. After the irradiation, remarkable nickel enrichment and iron/chromium depletions occurred at grain boundaries due to RIS in all samples. However, several important points became apparent by careful evaluation of the concentration profiles near the grain boundaries in each sample. First, the magnitude of...
segregation at the grain boundaries was significantly decreased by the addition of undersized solute elements, compared with that of the base alloy. The addition of phosphorus particularly was effective in reducing RIS at grain boundaries. Second, the segregated region near the grain boundaries tended to become narrow when undersized solutes were added. These tendencies were not changed by change in irradiation temperature (Fig. 1, Fig. 2). The calculated concentration profiles predicted a similar tendency, even though a strong interaction between phosphorus and interstitial atoms was assumed to occur. This result implies that the strong interaction of undersized solute atoms with interstitial atoms effectively reduces the segregation of major alloying elements at the grain boundaries as oversized solute atoms do. However, the mechanism of the RIS suppression by undersized solute atoms is different from that in the case of oversized solute.
of oversized solute atoms as follows. Newly introduced interstitial atoms by the irradiation immediately interact with undersized solute atoms and form mixed dumbbells, which do not easily migrate. It is thought that the formation of mixed dumbbells reduces the diffusivity of the atoms because the excess vacancies produced by the irradiation are absorbed by the mixed dumbbells, as is seen in eq. (8). At high temperatures, the suppressive effect on RIS by undersized solute atoms could be small because of dissolution of the mixed dumbbells.

Segregation of solutes at grain boundaries was effectively reduced by the addition of undersized solutes, such as silicon and phosphorous, at lower temperatures (Fig. 3), although the experimental data were limited to below 773 K. However, an apparent discrepancy between the results of calculation and the experimental results is seen at the temperature of 773 K in the alloys doped with phosphorus (Fig. 3(c)). This discrepancy suggested that RIS is reduced by phosphorus addition by a mechanism other than mixed dumbbell formation. Phosphide formed under the irradiation\(^{17}\) may absorb vacancies, which could retard the solute diffusion, but not so many phosphides were observed by TEM.

Simonen and Bruemmer showed by a computer simulation study that the migration and formation energies of vacancy strongly influence the temperature dependence of the RIS\(^{18}\), indicating that the peak temperature of the RIS shifts to a higher temperature with increase in migration energy and/or formation energy.

Since the present experimental data are in good agreement with calculated RIS behavior below the temperatures of 673 K, only the formation energy of vacancy at the grain boundary was adjusted.

Figure 4 shows the re-calculated temperature dependence on concentration of major alloying elements at a grain boundary with the experimental data of the alloys doped with phosphorus. By reducing the formation energy of vacancy \((E_v^{f})\) from 1.6 to 1.4 eV, a quantitative coincidence with experiment results was obtained not only in the low temperature region but also at 773 K. This good agreement with experimental data indicates that the vacancy formation energy at the grain boundary is reduced by phosphorus addition. Generally, phosphorus is an element that is easily segregated at grain boundaries in steels, and it is therefore expected that the segregation of phosphorus atoms is one of the causes of the reduction of vacancy formation energy at grain boundaries. Further investigation is needed for quantitative discussion.

**Fig. 3** Temperature dependencies of concentration of major alloying elements at grain boundaries after electron irradiation to 1.8 dpa in (a) Fe-15Cr-20Ni, (b) Fe-15Cr-20Ni doped with 0.5 mass% Si and (c) Fe-15Cr-20Ni doped with 0.025 mass% P alloys.

**Fig. 4** Temperature dependence of concentration of major alloying elements at grain boundaries after electron irradiation to 1.8 dpa in phosphorus 0.025 mass% doped alloys.
5. Summary

We investigated the influence of addition of undersized solutes such as silicon and phosphorus on radiation-induced segregation (RIS) at grain boundaries. It was shown that grain boundary depletion of chromium and segregation of nickel were significantly suppressed by the addition of silicon and phosphorus. Phosphorus suppressed the RIS more effectively. The suppression of RIS was more remarkable at a lower temperature. Numerical simulations showed that the experimentally observed RIS suppression is attributable to the strong interaction of undersized elements with interstitial atoms.

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