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Diffusion and conversion of interstitial dumbbells in segregated ternary alloys under irradiation

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Abstract

A radiation-induced segregation model for concentrated alloys based on the inverse Kirkendall effect is successfully used to predict element segregation in model alloys under irradiation conditions. In this model the segregation is the result of preferential atom-vacancy jumps. But under conditions of high irradiation flux or wide temperature range, a description of interstitial migration must be included in the model. In the present work the rate theory was used to simulate radiation-induced segregation near the grain boundary in Fe–Cr–Ni alloys. A model of diffusion and conversion of a mixed interstitial dumbbell was applied to describe the flux of interstitial. Six types of interstitial dumbbells and their conversion by a jump of one of its constituent atoms to a neighbouring site to form a dumbbell of different orientation, were considered. The vacancy flux was described similarly to the Wiedersich–Okamoto–Lam model, considering its migration through position exchange with a lattice atom.
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1. Introduction

Austenitic steel is widely used as reactor and active zone materials at a temperature of 300–500 °C and dose rate of 10^{-8}–10^{-6} dpa/s. Under the conditions of ion irradiation experiments the temperature and dose rate could be higher. Under the above conditions, the material must possess radiation stability to void swelling, irradiation creep, solute segregation, and embrittlement. The segregation leads to a change in the chemical composition near the grain boundary and affect the mechanical properties of the material. It can cause the failure and corrosion.

Segregation occurs in vacancy mobile temperature range and it is caused by the appearance of additional mass transfer mechanisms, which are absent without irradiation. These mass transfer mechanisms arise due to coupling between fluxes of alloying components and fluxes of non-equilibrium point defects to the sinks. In the general case, a preferable coupling of one alloying element with a point defect flux leads to accumulation of this element near the sink. In dilute alloys coupling is realized by mobile defect–impurity complexes [1,2]. In concentrated alloys segregation is the result of preferential atom-vacancy jumps (the inverse Kirkendall effect) [3]. In this model the effect of preferential interstitial mechanisms was ignored. Also excluded from the model was the effect of the migration of bound clusters of atoms and point defects [4,5]. The contribution of interstitial flux to radiation-induced segregation was considered as an interstitial migration. In the interstitial migration, one atom of the dumbbell jumps onto an adjacent lattice site forming a new dumbbell there, and the other atom left behind returns to the lattice site [6,7].

In the first part of this paper we summarize results provided by a random alloy model for segregated ternary alloy under irradiation. We study the dose rate effect and temperature dependence of changes in the composition at the grain boundary under irradiation. In the second part we add an interstitialcy migration mechanism to the random alloy model.

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2. Random alloy model

At a microscopic level, the concentration of the point defects and solute in a crystalline lattice is described by the rate equations:

$$\begin{aligned}\frac{\partial C_k}{\partial t} &= -\nabla J_k,\\ \frac{\partial C_i}{\partial t} &= -\nabla J_i + P - RC_iC_v - Z_d^i D_i C_i \rho_d,\\ \frac{\partial C_v}{\partial t} &= -\nabla J_v + P - RC_iC_v - Z_d^v D_v C_v \rho_d,\end{aligned} \tag{1}$$

where C_k is the concentration of the respective species k (Fe, Ni, Cr), C_i is the concentration of interstitials, C_v is the concentration of vacancies, J is the flux of each species and t is the time. P is the point defects production rate, R is the recombination rate, ρ_d is the dislocation density and Z is the loss rate to the sinks.

The flux of interstitials (J_i), vacancies (J_v) and respective solute atoms (J_k) are:

$$\begin{aligned}J_k &= -D_k \alpha \nabla C_k + C_k(d_{kv}\nabla C_v - d_{ki}\nabla C_i),\\ J_i &= -C_i \sum_k d_{ki}\alpha \nabla C_k - D_i \nabla C_i,\\ J_v &= C_v \sum_k d_{kv}\alpha \nabla C_k - D_v \nabla C_v,\end{aligned} \tag{2}$$

where α is the thermodynamic factor and D is the diffusion coefficient, for solute atoms $D_k = d_{kv}C_v + d_{ki}C_i$, for interstitials $D_i = \sum_k d_{ki}C_i$ and for vacancies $D_v = \sum_k d_{kv}C_v$ where d_{ki} and d_{kv} are partial atomic diffusion coefficients. For detailed descriptions of coefficients, see Ref. [5]. The model parameters are summarized in Table 1.

For dose rate effect, the solution of this differential equations system shows that long-term irradiation at the low dose rate has caused big changes in the composition. Respectively, large depletion of Cr at the grain boundary in Fe–20Cr–25Ni is connected with high concentration and segregation of Ni (Fig. 1). For temperature effect, also, highest changes in composition have been reached at the low dose rate. Decrease in the segregation level at high temperature has been caused by thermal diffusion, which becomes important at the low dose rate (Fig. 2).

This model includes both interstitial and vacancy induced segregation mechanisms. But parameters for migration of each component as an interstitial were set equal. This means that interstitial-induced segregation was neglected. The chromium-vacancy exchange rate was higher than the nickel-vacancy exchange rate. Therefore, chromium was depleted and nickel was enriched at the grain boundary by the vacancy-induced segregation mechanism.

Table 1
The model parameters used in random alloy model

Quantity	Value
Vacancy formation entropy	1.0 k
Vacancy formation energy	1.9 eV
Interstitial formation energy	4.0 eV
Vacancy migration energy	1.2 eV
Interstitial migration energy	1.1 eV
Vacancy jump frequency	1.5×10^{13} s^{-1}
Interstitial jump frequency	1.5×10^{12} s^{-1}
Fe-vacancy relative jump rate	1.86
Cr-vacancy relative jump rate	3.32
Ni-vacancy relative jump rate	1.0
Interstitial relative jump rate	1.0
Fe-vacancy correlation factor	0.785
Cr-vacancy correlation factor	0.668
Ni-vacancy correlation factor	0.872
Interstitial correlation factor	0.44
Damage efficiency	0.1
Recombination volume	12
Vacancy annihilation rate constant	1.0
Interstitial annihilation rate constant	1.4
Dislocation density	10^{14} m^{-2}
Thermodynamic factor	1.0
Unit cell size	3.5×10^{-10}

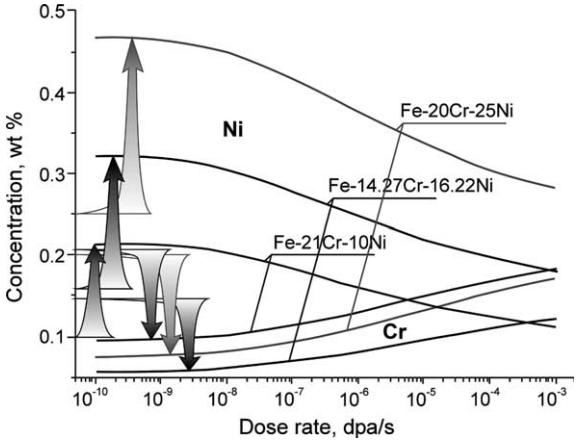

Fig. 1. Dose dependence of Ni and Cr segregation at the grain boundary after irradiation to 1 dpa at 560 K.

The simulation model of segregation needs a description of solute atoms and defects in more detail. In the middle temperature range especially at high irradiation dose rate interstitial flux must be considered. It becomes very important for connection of high dose rate irradiation experiments with low dose rate irradiation environment. Ni–Ni coupling together with Ni–Fe bonding might be responsible for the difference in migration mechanisms experimentally observed in low and high-dose rate irradiation experiments.

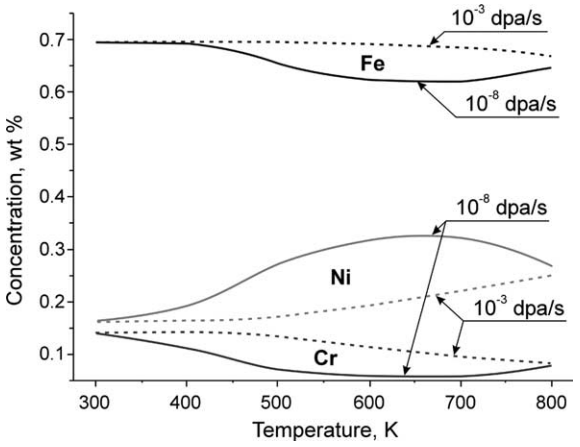

Fig. 2. Temperature dependence of Ni and Cr segregation at the grain boundary after irradiation to 1 dpa for Fe–14.27Cr–16.22Ni alloy.

3. Interstitialcy migration mechanism

3.1. Dumbbell migration and conversions

At high irradiation dose rate especially in fcc alloys interstitials form dumbbells, two atoms occupying a single lattice site. These atoms can migrate through an interstitialcy mechanism [8]. In the interstitialcy migration, one atom of the dumbbell jumps onto an adjacent lattice site forming a new dumbbell there, and the other atom left behind returns to the lattice site. Modified model of segregated ternary alloy describes the evolution of atom and point defect distribution in time and space, considering the interstitial movement via the interstitialcy mechanism.

We consider fcc ternary alloy containing three types of atoms (A, B and C). They can form six types of dumbbells (AA, AB, AC, BB, BC and CC). In the model we describe all possible conversions of these dumbbells. The dumbbell has three different types of jumps, cage motion, rotation and dissociation [8]. Only cage motion associated with rotation can lead to long distance migration. Such movement is characterized by migration energy E_i^{m}. Dissociation of dumbbell leads to conversion of dumbbell type and it is characterized by conversion energy E_i^{c}.

3.2. Flux equations

A random alloy is assumed, and the occupation probability of a lattice site by A- or B- or C-atom is assumed simply to be equal to their concentrations. The fluxes of interstitial dumbbells are given as follows:

$$\begin{aligned} J_{i\mathrm{AA}} = &-D_{i\mathrm{AA}}(C_{\mathrm{A}}\nabla C_{\mathrm{AA}} - C_{\mathrm{AA}}\nabla C_{\mathrm{A}}) \\ &- D(\mathrm{AA}\rightarrow\mathrm{AB})(C_{\mathrm{B}}\nabla C_{\mathrm{AA}} - C_{\mathrm{AA}}\nabla C_{\mathrm{B}})/2 \\ &- D(\mathrm{AA}\rightarrow\mathrm{AC})(C_{\mathrm{C}}\nabla C_{\mathrm{AA}} - C_{\mathrm{AA}}\nabla C_{\mathrm{C}})/2 \\ &- D(\mathrm{AB}\rightarrow\mathrm{AA})(C_{\mathrm{A}}\nabla C_{\mathrm{AB}} - C_{\mathrm{AB}}\nabla C_{\mathrm{A}})/2 \\ &- D(\mathrm{AC}\rightarrow\mathrm{AA})(C_{\mathrm{A}}\nabla C_{\mathrm{AC}} - C_{\mathrm{AC}}\nabla C_{\mathrm{A}})/2. \end{aligned} \tag{3}$$

The first term of right-hand side of this equation is the flux cased by the diffusion of AA-dumbbells. The next terms describe all possible conversion of AA-dumbbell [6,7]. The term 1/2 is necessary because migration of interstitial dumbbell is realized by jump of the one atom of the dumbbell onto an adjacent lattice site. Expressions for $J_{i\mathrm{BB}}$ and $J_{i\mathrm{CC}}$ can be obtained similarly.

$$\begin{aligned} J_{i\mathrm{AB}} &= J_{i\mathrm{ABA}} + J_{i\mathrm{ABB}} + J_{i\mathrm{ABC}}, \\ J_{i\mathrm{AC}} &= J_{i\mathrm{ACA}} + J_{i\mathrm{ACB}} + J_{i\mathrm{ACC}}, \\ J_{i\mathrm{BC}} &= J_{i\mathrm{BCA}} + J_{i\mathrm{BCB}} + J_{i\mathrm{BCC}}, \end{aligned} \tag{4}$$

$$\begin{aligned} J_{i\mathrm{ABA}} = &-D_{i\mathrm{AB}}(C_{\mathrm{A}}\nabla C_{\mathrm{AB}} - C_{\mathrm{AB}}\nabla C_{\mathrm{A}}) \\ &- D(\mathrm{AB}\rightarrow\mathrm{BB})(C_{\mathrm{B}}\nabla C_{\mathrm{AB}} - C_{\mathrm{AB}}\nabla C_{\mathrm{B}})/2 \\ &- D(\mathrm{BB}\rightarrow\mathrm{AB})(C_{\mathrm{A}}\nabla C_{\mathrm{BB}} - C_{\mathrm{BB}}\nabla C_{\mathrm{A}})/2. \end{aligned} \tag{5}$$

Expressions for $J_{i\mathrm{ABB}}$, $J_{i\mathrm{ABC}}$, $J_{i\mathrm{ACA}}$, $J_{i\mathrm{ACB}}$, $J_{i\mathrm{ACC}}$, $J_{i\mathrm{BCA}}$, $J_{i\mathrm{BCB}}$ and $J_{i\mathrm{BCC}}$ can be obtained similarly.

In these expressions D is the diffusion coefficient and C is the concentration. $J_{i\mathrm{ABA}}$ corresponds to the C_{AB} change caused by either the dumbbell movement in which the B-atom in the AB dumbbell jumps, leaving the A-atom behind, to the neighbor site, or the movement in which the B-atom in a dumbbell jumps to the lattice site occupied by an A-atom to form AB-dumbbell.

A vacancy migrates by exchangin its position with a lattice atom similarly with random alloy model:

$$\begin{aligned} J_v = &-(D_{v\mathrm{A}}C_{\mathrm{A}} + D_{v\mathrm{B}}C_{\mathrm{B}} + D_{v\mathrm{C}}C_{\mathrm{C}})\nabla C_v \\ &+ D_{v\mathrm{A}}C_v\nabla C_{\mathrm{A}} + D_{v\mathrm{B}}C_v\nabla C_{\mathrm{B}} + D_{v\mathrm{C}}C_v\nabla C_{\mathrm{C}}. \end{aligned} \tag{6}$$

Additional fluxes must be added to solute atom fluxes by vacancy mechanism (Eq. (2)) to account for the C_{A} change caused by AA-dumbbell movement and all possible conversions of dumbbells in which A type of atom is released and similarly for C_{B} and C_{C} changes cased by dumbbell migration and conversion:

$$\begin{aligned} J_{\mathrm{A}} &= -D_{v\mathrm{A}}C_v\nabla C_{\mathrm{A}} + D_{v\mathrm{A}}C_{\mathrm{A}}\nabla C_v - J_{i\mathrm{AA}} - J_{i\mathrm{ABA}} - J_{i\mathrm{ACA}}, \\ J_{\mathrm{B}} &= -D_{v\mathrm{B}}C_v\nabla C_{\mathrm{B}} + D_{v\mathrm{B}}C_{\mathrm{B}}\nabla C_v - J_{i\mathrm{BB}} - J_{i\mathrm{ABB}} - J_{i\mathrm{BCB}}, \\ J_{\mathrm{C}} &= -D_{v\mathrm{C}}C_v\nabla C_{\mathrm{C}} + D_{v\mathrm{C}}C_{\mathrm{C}}\nabla C_v - J_{i\mathrm{CC}} - J_{i\mathrm{ACC}} - J_{i\mathrm{BCC}}. \end{aligned} \tag{7}$$

3.3. Concentration equations

By combining the above fluxes with point defect production, mutual recombination of an interstitial

dumbbell and a vacancy, and conversion between interstitial dumbbells, the following set of equations is obtained:

$$\begin{aligned}\frac{\partial C_{i\mathrm{AA}}}{\partial t} = &-\nabla J_{i\mathrm{AA}} + C_{\mathrm{A}}^2 P - R_{\mathrm{AA}} \\ &- K_2(\mathrm{AA}\rightarrow\mathrm{AB})C_{\mathrm{B}}C_{i\mathrm{AA}} \\ &+ K_2(\mathrm{AB}\rightarrow\mathrm{AA})C_{\mathrm{A}}C_{i\mathrm{AB}} \\ &- K_2(\mathrm{AA}\rightarrow\mathrm{AC})C_{\mathrm{C}}C_{i\mathrm{AA}} \\ &+ K_2(\mathrm{AC}\rightarrow\mathrm{AA})C_{\mathrm{A}}C_{i\mathrm{AC}}. \end{aligned} \tag{8}$$

Expressions for $\frac{\partial C_{i\mathrm{BB}}}{\partial t}$, $\frac{\partial C_{i\mathrm{CC}}}{\partial t}$, $\frac{\partial C_{i\mathrm{AB}}}{\partial t}$, $\frac{\partial C_{i\mathrm{BC}}}{\partial t}$ and $\frac{\partial C_{i\mathrm{AC}}}{\partial t}$ can be obtained similarly.

$$\begin{aligned}\frac{\partial C_v}{\partial t} = &-\nabla J_v + (C_{\mathrm{A}} + C_{\mathrm{B}} + C_{\mathrm{C}})^2 P - R_{\mathrm{AA}} - R_{\mathrm{BB}} \\ &- R_{\mathrm{CC}} - R_{\mathrm{AB}} - R_{\mathrm{AC}} - R_{\mathrm{BC}}. \end{aligned} \tag{9}$$

$$\begin{aligned}\frac{\partial C_{\mathrm{A}}}{\partial t} = &-\nabla J_{\mathrm{A}} - (2C_{\mathrm{A}}^2 + 2C_{\mathrm{A}}C_{\mathrm{B}} + 2C_{\mathrm{A}}C_{\mathrm{C}})P \\ &+ 2R_{\mathrm{AA}} + R_{\mathrm{AB}} + R_{\mathrm{AC}} + K_2(\mathrm{AA}\rightarrow\mathrm{AB})C_{\mathrm{B}}C_{i\mathrm{AA}} \\ &- K_2(\mathrm{AB}\rightarrow\mathrm{AA})C_{\mathrm{A}}C_{i\mathrm{AB}} + K_2(\mathrm{AB}\rightarrow\mathrm{BB})C_{\mathrm{B}}C_{i\mathrm{AB}} \\ &- K_2(\mathrm{BB}\rightarrow\mathrm{AB})C_{A}C_{i\mathrm{BB}} + K_2(\mathrm{AA}\rightarrow\mathrm{AC})C_{\mathrm{C}}C_{i\mathrm{AA}} \\ &- K_2(\mathrm{AC}\rightarrow\mathrm{AA})C_{\mathrm{A}}C_{i\mathrm{AC}} + K_2(\mathrm{AB}\rightarrow\mathrm{BC})C_{\mathrm{C}}C_{i\mathrm{AB}} \\ &- K_2(\mathrm{BC}\rightarrow\mathrm{AB})C_{\mathrm{A}}C_{i\mathrm{BC}} + K_2(\mathrm{AC}\rightarrow\mathrm{BC})C_{\mathrm{B}}C_{i\mathrm{AC}} \\ &- K_2(\mathrm{BC}\rightarrow\mathrm{AC})C_{\mathrm{A}}C_{i\mathrm{BC}} + K_2(\mathrm{AC}\rightarrow\mathrm{CC})C_{\mathrm{C}}C_{i\mathrm{AC}} \\ &- K_2(\mathrm{CC}\rightarrow\mathrm{AC})C_{\mathrm{A}}C_{i\mathrm{CC}}. \end{aligned} \tag{10}$$

Expressions for $\frac{\partial C_{i\mathrm{B}}}{\partial t}$ and $\frac{\partial C_{i\mathrm{C}}}{\partial t}$ can be obtained similarly.

$$\begin{aligned}R_{\mathrm{AA}} = &[K_{1\mathrm{AA}}C_{\mathrm{A}} + K_1(\mathrm{AA}\rightarrow\mathrm{AB})C_{\mathrm{B}} + K_{1v\mathrm{A}}C_{\mathrm{A}} \\ &+ K_{1v\mathrm{B}}C_{\mathrm{B}} + K_1(\mathrm{AA}\rightarrow\mathrm{AC})C_{\mathrm{C}} + K_{1v\mathrm{C}}C_{\mathrm{C}}]C_{i\mathrm{AA}}C_{\mathrm{V}}. \end{aligned} \tag{11}$$

Expressions for R_{BB}, R_{CC}, R_{AB}, R_{AC} and R_{BC} can be obtained similarly.

Here P is the defect production rate, K_1 is the rate constant of recombination, K_2 is the rate constant of dumbbell conversion, and R is recombination rate of dumbbell with a vacancy.

Diffusion coefficients and rate constant are described by the equations [7]:

$$\begin{aligned}&D_n = \alpha_n \nu_n \exp\left(-E_n^{\mathrm{m}}/kT\right), \\ &D_n(\mathrm{conv.}) = \alpha_n \nu_n \exp\left(-E_n^{\mathrm{c}}/kT\right), \\ &K_n = \alpha_n \nu_n \exp\left(-E_n^{\mathrm{c}}/kT\right), \\ &K_n(\mathrm{conv.}) = \alpha_n \nu_n \exp\left(-E_n^{\mathrm{c}}/kT\right), \end{aligned} \tag{12}$$

where α is the corresponding geometrical factor, ν is the jump frequency, E^{m} is the migration energy, E^{c} is energy of dumbbell conversion. Where index n corresponds to each type of migration or conversion of dumbbell.

4. Summary

Contribution of interstitial migration to radiation-induced segregation was investigated in fcc ternary alloys. The model includes three six types of interstitial dumbbells and it describes the evolution of atom and point defect profiles by considering the dumbbell movement, vacancy migration and dumbbell recombination.

Most of the parameters, which determine the migration of the dumbbell interstitials, are unknown. It is impossible to experimentally determine atomic quantities such as the migration or conversion energies of a dumbbell interstitials. Ab initio calculations can be used in order to obtain these parameters.

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