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Modeling of radiation-induced segregation at grain boundaries in Fe–Cr–Ni alloys

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Abstract

Modeling of radiation-induced segregation at grain boundaries in Fe–Cr–Ni alloys was carried out for wide ranges of temperatures, point defects generation rates and doses taking into account both the vacancy and interstitial mechanisms of the alloy components diffusion. To explain available data on deterioration of both the radiation-induced segregation and void swelling in austenitic stainless steels doped with oversized substitutional atoms (Ti, Nb, Ta, Zr or Hf) a physical model is proposed. Results of calculating the time of desegregation of components in Fe–Cr–Ni alloys near grain boundary during isothermal post-irradiation annealing are presented.

1. Introduction

Last years data on radiation-induced segregation (RIS) have been obtained in such alloys irradiated at low temperatures with electrons and ions [1,2], and also in the commercial steel CP304 [3] neutron irradiated. Since vacancies are practically immobile at investigated irradiation temperatures of 25–50 °C, these data give evidence about the interstitial mechanism of RIS (under interstitial migration mechanism the migration of atoms as mixed dumbbells is supposed). RIS was modeled under conditions of low-temperature electron irradiation in Ref. [1]. However, an abnormally large (~0.75 eV) binding energy of mixed dumbbells with Ni atom was taken for the calculations. As the components of Fe–Cr–Ni alloys have nearly identical atom radii, such a high value of the binding energy is difficult to justify.

As it has been shown in Refs. [4,5], alloying of austenitic stainless steels with oversized chemical elements such as Ti, Nb, Ta, Zr or Hf results in an essential suppression of both RIS near grain boundaries (GB) and void swelling, the effect increases with increasing the alloying chemical element radius. In [6] the suppression of RIS near GB by impurity atoms is explained by formation of slowly migrating mixed dumbbells of the 'interstitial-oversized impurity atom' type, that leads to an enhancement of the point defects (PD) recombination (i.e. in lowering of concentrations of freely migrating vacancies and interstitials) and, hence, to weakening RIS. In the present paper a model is proposed which allows us to explain both the observable reduction RIS and suppression of void swelling by capture of vacancies by alloying element atoms.

The objectives of the present paper are (1) modeling of RIS near GB in Fe–Cr–Ni alloys under low-temperature electron irradiation to estimate the parameters of the interstitial mechanism of RIS by comparison of calculation results with experimental data; (2) verification of these parameters for motionless and moving GBs; (3) calculation of RIS near motionless GBs for a wide range of temperatures and PD generation rates; (4) investigation of influence of oversized alloying elements on RIS and (5) modeling of desegregation of components of Fe–Cr–Ni alloys near GB in conditions of post-irradiation annealing.

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2. Results and discussion

2.1. Estimation and verification of parameters for the interstitial mechanism of RIS

As it was noted above, the RIS of alloy components near GB of initially homogeneous Fe–16Cr–20Ni alloy is observed under low-temperature electron irradiation [1]. As well as at higher irradiation temperatures, an enrichment at GB of Ni and depletion of Cr and Fe occurs, that cannot be explained only by the vacancy mechanism of diffusion [1]. Following the authors of Ref. [1] it will be supposed below that Ni-atoms are undersized ones relative to Cr and Fe atoms and form mixed dumbbells with Cr and Fe-interstitials.

The system of diffusion equations for alloy components and point defects proposed for modeling of RIS near GB in Ref. [7] for a ternary substitutional alloy was used. The equilibrium segregation was not taken into account because for the present the binding energies of chemical elements with grain boundaries in Fe–Cr–Ni alloys are not available in the literature. For a correct comparison of calculated alloy component profiles near GB with experimental data, it is necessary to take into account the resolution of an experimental method (in the given case, the radius R of the Gaussian electron beam intensity distribution used usually for microanalysis). Therefore, the calculated alloy component profiles were averaged using the formula proposed in Ref. [8], and the best fit of mixed dumbbell binding energy was obtained by comparison of the averaged calculation profiles with experimental data. Most of parameters used for modeling of RIS in the Fe–Cr–Ni alloy were taken from Ref. [1] excepting the vacancy formation energy $E_{\mathrm{v}}^{\mathrm{f}}$ and $E_{\mathrm{i}}^{\mathrm{m}}$ interstitial migration energy which were taken to be equal 1.6 and 0.2 eV, respectively. In addition, it was supposed that the spontaneous PD recombination zone consists of $Z = 100$ lattice sites. The best agreement between the experimental and calculated profiles was achieved at the binding energy of 0.03 eV (see Fig. 1).

It is possible to verify the obtained binding energy by comparing the RIS near motionless and moving GB in Fe–Cr–Ni alloys at higher irradiation temperatures, when both interstitial and vacancy mechanisms of diffusion contribute to the alloy component segregation. The averaged calculation profiles of components and experimental data of the Ni and Cr concentrations near a motionless GB in Fe–14.5Cr–20.8Ni alloy irradiated with electrons at the temperature of 723 K and dose rate of 2×10^{-3} dpa/s to the dose of 3 dpa, $R = 1$ nm [9] are shown in Fig. 2.

Fig. 3 shows the experimental (irradiation temperature $T_{\mathrm{irr}} = 573$ K, dose rate of 1×10^{-3} dpa/s, dose of 3 dpa [10]) and calculated and averaged profiles of components in Fe–15Cr–20Ni alloy near moving GB. The

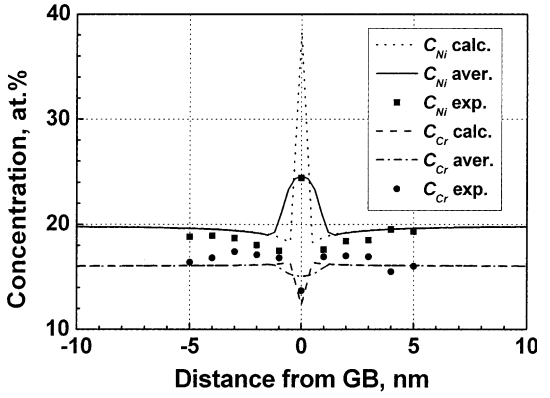

Fig. 1. Experimental (from Ref. [1]) and calculated profiles of Ni and Cr concentration near GB at dose of 7.2 dpa, dose rate of 2×10^{-3} dps/s, and $T_{\mathrm{irr}} = 323$ K.

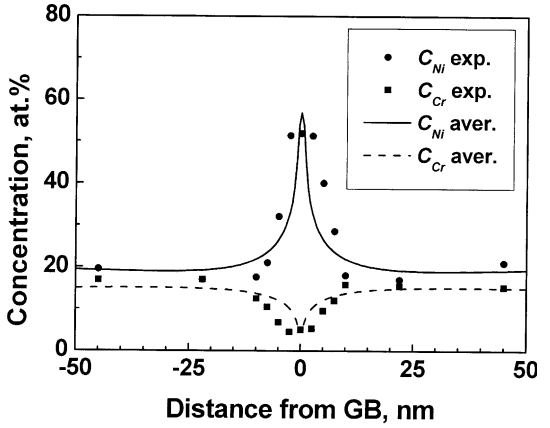

Fig. 2. Experiment [9] and calculated profiles of Ni and Cr concentrations near a motionless GB at the dose of 3 dpa, dose rate of 2×10^{-3} dps/s, and $T_{\mathrm{irr}} = 723$ K.

displacement of the GB from its initial location was equal to ~4 nm. The experimental data were obtained using electron microscopes of various resolution: HF-2000 ($R = 1$ nm), JOEL-2000FX ($R = 10$ nm) [10]. Fig. 4 shows the experimental and calculated profiles of Ni, Cr and Fe in Fe–15.2Cr–20.1Ni alloy near moving GB ($T_{\mathrm{irr}} = 623$ K, dose rate of 4×10^{-3} dpa/s, dose of 14.4 dpa [11]). According to Ref. [11] during irradiation GB has displaced on distance ~20 run from the initial location.

As a whole, the calculations and experiments are in a satisfactory agreement in the temperature range of 573–723 K. This gives evidence that the proposed RIS model is rather correct and that the value of binding energy obtained on the basis of low-temperature irradiation results is reasonable.

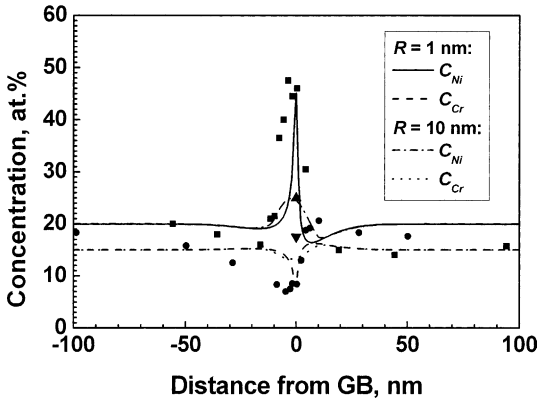

Fig. 3. Experiment [10] (■ – C_{Ni}, ● – C_{Cr}, $R = 1$ nm; ▲ – C_{Ni}, ▼ – C_{Cr}, $R = 1$ nm) and calculated profiles of Ni and Cr concentrations near a motionless GB at the dose of 3 dpa, dose rate of 1×10^{-3} dps/s, and $T_{irr} = 573$ K.

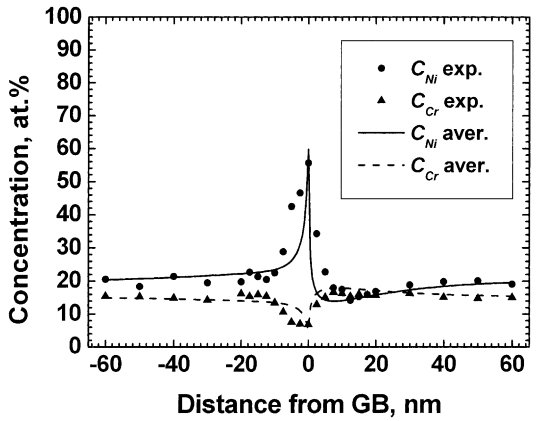

Fig. 4. Experiment [11] and calculated profiles of Ni and Cr concentrations near a moving GB at the dose of 14.4 dpa, dose rate of 4×10^{-3}, $T_{irr} = 623$ K.

2.2. Radiation-induced segregation on motionless grain boundaries

Using the set of parameters chosen it is of interest to carry out model calculations of the RIS near GB in Fe–15Cr–20Ni alloy for a wide range of temperatures, doses and dose rates. In Fig. 5 the calculated temperature dependence of the Ni content on a motionless GB is shown at 100 dpa and three dose rates: 1×10^{-9} dpa/s (such a dose rate is relevant to some PWR internals), 1×10^{-6} dpa/s (irradiation of structural materials in fast reactor cores), 1×10^{-3} dpa/s (such order of value are typical for ion and electron irradiation experiments). It should be noted that the temperature dependence is similar for all dose rates and the profiles shift by approximately on 100 °C along the temperature scale

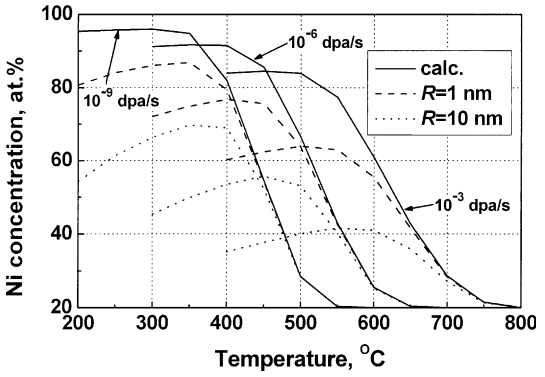

Fig. 5. The temperature dependence of calculated and averaged Ni concentrations on GB in Fe–15Cr–20Ni alloy at 100 dpa and different dose rates.

with increasing the dose rate by three orders of magnitude. The averaged results for different radii of X-ray beams used in microanalysis are shown in Fig. 5, and it can be seen that the calculated and averaged results are considerably different.

2.3. Influence of oversized alloying elements on the RIS of components in Fe–Cr–Ni alloy near grain boundaries

Consider a disordered substitutional alloy with an oversized impurity atom concentration which is low as compared with major component concentrations of the alloy.

The low mobility of impurity atoms allows as a first approximation to consider them as immobile. In contrast to Ref. [6] it will be assumed that the oversized atoms play a role of immobile vacancy traps due to the essential difference between sizes of impurity atoms and major components [12]. The account for such traps results in a simple renormalization of the point defect recombination coefficient in PD diffusion equations [12]:

$$R_{\text{eff}} = R_0 \cdot \left[1 + C_p \cdot \left(2C_{\text{v}} + \exp\left(-\frac{E_{\text{v}}^{\text{b}}}{kT}\right)\right)^{-1}\right], \qquad (1)$$

where R_{eff} is the effective PD recombination coefficient, R_0 is the PD recombination coefficient in the absence of impurities [8], C_{v} is the mean vacancy concentration, C_p is the concentration of oversized atoms, E_{v}^{b} is the vacancy-oversized atom binding energy. In the present model the oversized impurity atoms do not change equations for diffusion fluxes of both alloy components and point defects [7].

Fig. 6 shows the profiles of Ni concentration near GB in the Fe–15Cr–20Ni alloy containing the impurity atom concentration of 1 at.% for a number of binding energies E_{v}^{b} at the $T_{irr} = 500$ °C and the dose rate of 1×10^{-3} dpa/s. It can be seen, that with increase of E_{v}^{b} not only the Ni

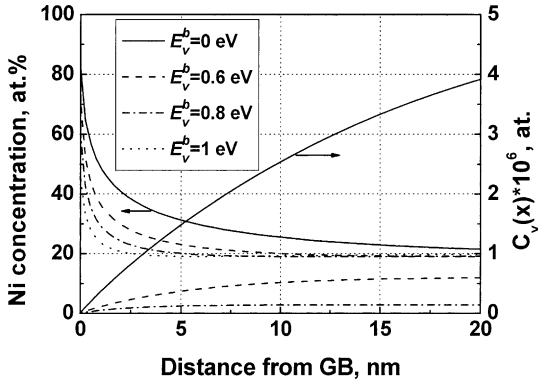

Fig. 6. Near-grain boundary profiles of Ni and vacancy concentrations calculated for various 'vacancy-impurity atom' binding energies at the dose rate of 10 dpa and $T_{irr} = 500$ °C.

concentration on GB decreases but also the segregation zone of Ni near this GB. As a whole, it results in a significant lowering of the averaged Ni concentration on the GB with the increase of E_v^b. It is seen from Fig. 6, that the suppression of RIS occurs only at sufficiently high values of 'vacancy-oversized impurity atom' binding energy.

Fig. 6 illustrates the sensitivity of vacancy concentration profiles near GB to the value of E_v^b. The decrease of vacancy concentration with increasing E_v^b should result in lowering of void growth rates. Besides, it was shown in Ref. [12] that void nucleation rates are extremely sensitive to vacancy concentration and sharply fall with decrease of the latter in framework of the theory of homogeneous nucleation. Thus, the decrease of swelling is caused by lowering of both the void growth and void nucleation rate.

2.4. Desegregation of Fe–Cr–Ni alloy components near grain boundaries

To estimate the thermal stability of alloy composition heterogeneity near GB caused by RIS, the kinetics of desegregation of components in the Fe–15Cr–20Ni alloy near motionless GB during post-irradiation annealing at temperatures in the range of 750–1000 K was calculated. Calculated profiles of alloy components arisen due to RIS near GB after irradiation with 100 dpa at 773 K and the dose rate of 1×10^{-3} dpa/s were taken as starting profiles. For an estimation of desegregation time t_d for each alloy component calculations were stopped when the following inequality is valid:

$$(C_m(0,t_d) - C_{m0})/C_{m0} \leqslant \varepsilon, \quad m = Fe, Cr, Ni, \tag{2}$$

where $C_m(0,t)$ are the components concentration on GB at the time t, and C_{m0} is the alloy m-component concentration in the matrix. From calculations it follows

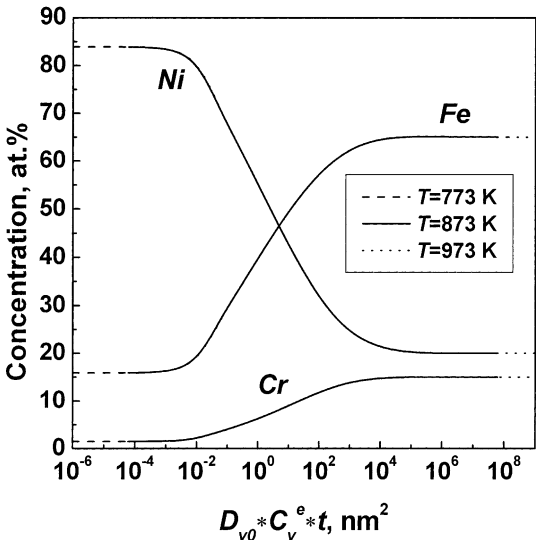

Fig. 7. Kinetics of alloy component desegregation in Fe–15Cr–20Ni alloy near GB at several annealing temperatures.

that $t_d = t_{d0}\exp(2.8\text{eV}/\text{kT})$ with t_{d0} depending on ε. At $\varepsilon = 0.1$, $t_{d0} = 6.12\times10^{-12}$ s for nickel.

Fig. 7 shows the kinetics of desegregation of the Fe–15Cr–20Ni alloy components on GB at various annealing temperatures. As it seen, the alloy component concentrations on GB as a function of squared diffusion length $D_{v0}C_v^e t$ (where D_{v0} is the vacancy diffusion coefficient in a homogeneous alloy, C_{ve} is the vacancy thermal equilibrium concentration, t is the time of annealing) do not depend on the annealing temperature in the range 773–973 K. The desegregation conies to an end when the diffusion length $l = \sqrt{D_{v0}C_v^e t}$ reaches a constant value of 100 nm. It allows to estimate the characteristic time t_d of alloy component desegregation as follows: $t_d = l^2/D_{v0}C_v^e$.

3. Summary

Modeling of RIS of components was carried out in Fe–Cr–Ni alloys near motionless and moving GBs by comparing the calculation results with experimental data. The contribution of the interstitial mechanism to such a segregation was estimated at low irradiation temperatures. It is shown that the simultaneous suppression of the RIS and void swelling observed in austenitic steels doped with oversized chemical elements can be related to capture of vacancies by atoms of these elements and to enhancement of the point defect mutual recombination. Modeling of desegregation in Fe–Cr–Ni alloys near GBs during post-irradiation isothermal annealing was carried out and an analytical estimation of characteristic time of desegregation was obtained.

Acknowledgements

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