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Letter to the Editors

On the mechanism of radiation-induced segregation

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1. Introduction

Radiation-induced segregation (RIS) has been known as one of the radiation induced phenomena closely related to the point defects introduced by irradiation. Notable experimental and theoretical studies on RIS started in the early 1970s Johnson and Lam [1], Okamoto and Wiedersich [2,3], and, independently later, Marwick [4] and Perks et al. [5] extensively studied RIS near alloy surfaces. Recently, RIS in the vicinity of the grain boundary has been of interest [6–9], because of the problem of the irradiation-assisted stress corrosion cracking (IASCC), which promotes the cracking susceptibility in irradiated stainless steels.

There are, however, two candidate mechanisms [10] both of which may explain Ni enrichment and Cr depletion at a grain boundary in a stainless steel. The interstitial mechanism favors Ni enrichment because it is an undersized atom, while the vacancy mechanism favors Cr depletion because it is a oversized atom. In reality, both interstitials and vacancies can influence both Ni enrichment and Cr depletion. The two mechanisms have not clearly been isolated since both can promote the same segregation effect. Others [4,5,8] have emphasized the diffusivity factor without the interstitial dumbbell mechanism [1] to successfully explain observed radiation-induced segregation in stainless steels.

The present study focuses on the size factor of Ni as well as that of Cr to explain the observed radiation-induced grain boundary segregation. Solute segregation under irradiation is then induced by the inverse Kirkendall effect, which is attributed to excess point defect migration, interacting with solutes in the alloys. The undersized solute flows in the same direction in which the interstitial atom diffuses due to the dumbbell mechanism, while the oversized one migrates in the inverse direction to vacancy flow due to the exchange migration mechanism.

To reveal the correctness of the candidate mechanism in RIS in the Fe–Cr–Ni alloy system, we would like to propose, in this letter, two kinds of test.

2. Test 1. measurement of the diffusion coefficients of Ni and Cr as a function of irradiation temperature

Fig. 1 shows diffusivities of solutes under irradiation in an Arrhenius plot. The broken lines represent the total diffusivities based on the vacancy mechanism only [5]; while the thick solid lines correspond to total diffusivities from both the vacancy mechanism and interstitial dumbbell mechanism [6]. Parameters used in the calculation are listed in Table 1. Here, the effective (total) diffusivity of solute A is given by the summation form of partial diffusivity multiplied by each point defect concentrations

$$D_A^{\mathrm{irr}} = d_{\mathrm{Av}} C_{\mathrm{v}} + d_{\mathrm{Ai}} C_{\mathrm{i}}, \tag{1}$$

while the thermal diffusivity is given by

$$D_A^{\mathrm{th}} = d_{\mathrm{Av}} C_{\mathrm{v}}^0 + d_{\mathrm{Ai}} C_{\mathrm{i}}^0, \tag{2}$$

where $C^0 = \exp(S_{\mathrm{f}}/k)\exp(-E_{\mathrm{f}}/kT)$ under the usual definitions.

For the diffusivity on account of the vacancy plus interstitial mechanism [7], the Ni diffusivity is higher than Cr diffusivity at low temperature, while Cr diffusivity at high temperature is greater than Ni one. This reversal in the diffusivities is because of the preferential interaction between the solute Ni and the interstitial atom through the dumbbell effect we have assumed in the present calculation. We have not observed the reversal of diffusivity at low temperature unless we assume the interstitial mecha-

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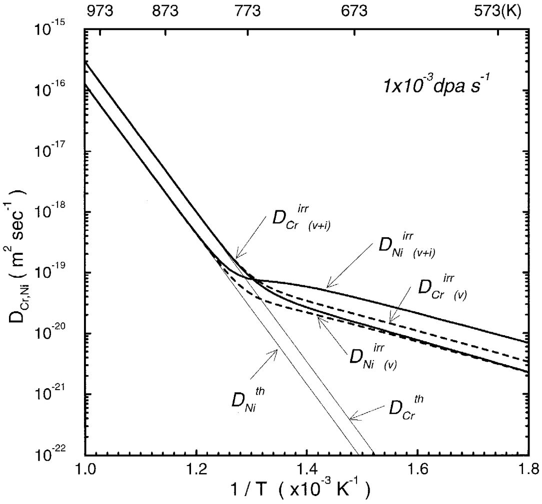

Fig. 1. Effect of temperature on solute diffusivities in an Fe–15Cr–20Ni alloy: D^{irr}, under irradiation at a damage rate of 1×10^{-3} dpa/s at 1 dpa, and D^{th}, thermal. Subscript (v) and (v+i) represent vacancy and vacancy+interstitial mechanisms, respectively.

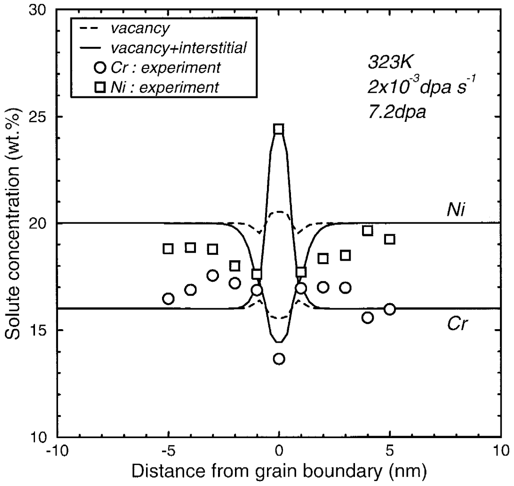

Fig. 2. Solute concentration profiles in Fe–16Cr–20Ni alloy after electron irradiation to 7.2 dpa with damage rate of 2.0×10^{-3} dpa/s at 323 K (————) theoretical results for vacancy and interstitial mechanisms, (– – –) vacancy mechanism only.

nism, as in the broken lines in Fig. 1. In the present study we have used 0.75 eV as Ni-interstitial binding energy [6]. Although the exact value of Ni-interstitial binding energy is not certain, we believe the present value is reasonable to explain the low temperature RIS data.

3. Test 2. Low temperature radiation-induced test: Radiation-induced segregation at low temperature such as 50°C

In the model which considers both vacancy with interstitial mechanisms, the interstitial mechanism is dominant in RIS at a lower temperature. Hence, a low temperature irradiation reveals, indirectly, the interstitial mechanism. Fig. 2 shows the comparison of 50°C electron irradiation data of RIS in Fe–Cr–Ni alloy with simulation. The experiment was conducted in a high-voltage electron microscope at a damage rate of 2×10^{-3} dpa/s to 7.2 dpa. By comparison of simulations of the two mechanisms, the interstitial dumbbell mechanism must be considered as the candidate mechanism at low temperature. The vacancy mechanism alone can not explain the low temperature irradiation data in Fig. 2 unless one assumes an extremely low migration energy such as 0.85 eV, which is inconsistent with the existing literature. On the other hand, RIS with dumbbell mechanism can explain the data as shown in Fig. 2. However, in order to confirm the correctness of the mechanism one needs to investigate the temperature dependence of diffusivities as indicated in Fig. 1.

In conclusion, the present authors propose to carry out direct measurement of diffusivity under irradiation and check the validity of Fig. 1. This test will reveal the mechanism of RIS and remove the confusion over the RIS mechanism.

Table 1
Parameters used in the comparison. Values are referred to vacancy plus interstitial mechanism [6,11] and vacancy only [4,8]

Parameter	Notation	Vacancy + interstitial	Vacancy
Vacancy jump frequency via Fe	$\nu_{\mathrm{Fe\text{-}v}}$	2.5×10^{13} s^{-1}	2.5×10^{13} s^{-1}
Vacancy jump frequency via Cr	$\nu_{\mathrm{Cr\text{-}v}}$	3.5×10^{13} s^{-1}	3.5×10^{13} s^{-1}
Vacancy jump frequency via Ni	$\nu_{\mathrm{Ni\text{-}v}}$	1.5×10^{13} s^{-1}	1.5×10^{13} s^{-1}
Interstitial jump frequency	ν_{i}	5.0×10^{12} s^{-1}	5.0×10^{12} s^{-1}
Vacancy migration energy	E_{ν}^{m}	1.05 eV	1.2 eV
Interstitial migration energy via Fe	$E_{\mathrm{Fe\text{-}i}}^{\mathrm{m}}$	0.3 eV	0.9 eV
Interstitial migration energy via Cr	$E_{\mathrm{Cr\text{-}i}}^{\mathrm{m}}$	0.3 eV	0.9 eV
Interstitial migration energy via Ni	$E_{\mathrm{Ni\text{-}i}}^{\mathrm{m}}$	0.9 eV	0.9 eV
Ni-interstitial binding energy	$E_{\mathrm{Ni\text{-}i}}^{\mathrm{b}}$	0.75 eV	N.A.
Formation energy of vacancy	E_{ν}^{f}	1.4 eV	1.4 eV

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