Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Nuclear Materials 329–333 (2004) 1166–1169

journal of nuclear materials

www.elsevier.com/locate/jnucmat

# A multi-scale approach to radiation-induced segregation at various grain boundaries

N. Sakaguchi [a,*], S. Watanabe [b], H. Takahashi [a], R.G. Faulkner [c]

[a] *Center for Advanced Research of Energy Technology, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo 060-8628, Japan*
[b] *Faculty of Engineering, Department of Materials Science and Engineering, Hokkaido University, Sapporo 060-8628, Japan*
[c] *Institute of Polymer Technology and Materials Engineering, Loughborough University, Leicestershire LE11 3TU, UK*

## Abstract

We investigated the dependence of radiation-induced segregation (RIS) in austenitic stainless steels on grain boundary orientation by numerical calculations. A new rate equation model for RIS that incorporates the grain boundary sink strength for point defects was developed. The sink strength was determined as functions of misorientation angle and $\Sigma$ values using interaction energies of vacancy near grain boundaries as determined by molecular dynamics (MD) and statics (MS). It was shown that the calculated results can reproduce the experimental data obtained by electron and proton irradiation experiments. The good agreement supports the validity of the present model.

## 1. Introduction

Radiation-induced segregation (RIS) near grain boundaries is one of the primary causes of irradiation-assisted stress corrosion cracking (IASCC) in light-water reactor (LWR) component materials such as type 304 austenitic stainless steels [1,2]. The primary source for the solute redistribution is highly supersaturated point defects introduced by the irradiation. Point defect fluxes to the grain boundaries are responsible for the rearrangement of solute elements as a result of preferential interactions between point defects, solute elements, and grain boundaries [3,4]. According to recent reviews, RIS behavior is strongly affected by the nature of grain boundaries, i.e., by the misorientation angle and $\Sigma$ value [5,6]. It is believed that these phenomena are related to the strength of the interaction between excess point defects and grain boundaries. Theoretical investigation is therefore needed to clarify the mechanism of retardation of the RIS behavior at certain grain boundaries.

The main purpose of the present study was to investigate the effect of grain boundary character on RIS for austenitic stainless steels by means of computer simulation. A newly developed rate equation model for intergranular RIS, which was developed previously [5,7] and modified in the present work, was used to evaluate the grain boundary sink efficiency for point defects. Molecular dynamics (MD) and statics (MS) calculations were also performed to estimate the strengths of interactions between certain grain boundaries and vacancy.

## 2. Model and calculation method

Calculations using rate equations were performed to estimate the concentrations of alloying elements and point defects under various irradiation conditions. The approach was based on solving the reaction rate and diffusional equations for vacancies, interstitials and alloying elements. The equations used are described in detail in Refs. [5,7]. In the present study, the most important parameter was sink strength of grain boundaries, which was given previously [5] in terms of the spacing of grain boundary dislocations and can be expressed as

---

[*] Corresponding author. Tel.: +81-11 706 6768/6766; fax: +81-11 706 6768/757 3537.

*E-mail address:* sakagu@ufml.caret.hokudai.ac.jp (N. Sakaguchi).

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.04.268

$$S^{\mathrm{GB}} = A \sin\frac{\theta}{2}, \tag{1}$$

where $A$ is a parameter in units of the inverse square of the length ($\sim 10^{21}$ m$^{-2}$) and $\theta$ is the misorientation angle. Eq. (1) could reproduce the RIS behavior not only for low angle tilt boundaries but also for large angle tilt boundaries and general random boundaries. However, it could not explain the RIS behaviors around boundaries with low $\Sigma$ coincidence [5]. This indicates that a relationship different from that in Eq. (1) is needed to determine the sink strength of low $\Sigma$ boundaries. For this purpose, we performed MD and MS calculations for Ni [0 0 1] symmetric tilt boundaries and investigated the interaction energy between the grain boundaries and point defects. An EAM potential for Ni [8] was employed to describe the atomic interaction. Each MD cell was about $50a_0$ ($X$-coordinate) × $20a_0$ ($Y$-coordinate) × $10a_0$ ($Z$-coordinate) in size and contained two grain boundaries parallel to the $YZ$ plane, and a three-dimensional periodical boundary condition was applied. From the MS results, we obtained new equations for calculating sink strength of grain boundaries.

## 3. Results and discussions

Fig. 1 shows the calculated formation energy changes of vacancies around (a) low angle, (b) large angle and (c) $\Sigma 5$ boundaries. At a low angle tilt grain boundary, remarkable decreases in energy occurred only in regions close to the core regions of grain boundary dislocations. This indicates that the dislocation core acts as a preferential sink site for excess point defects. We also found similar structures at large angle tilt grain boundaries, although grain boundaries of this type can not be represented by grain boundary dislocation models. The disordered regions on the grain boundary also act as point defect sinks. However, the formation energy changes were quite different around a $\Sigma 5$ coincidence boundary as shown in Fig. 1(c). Significant formation energy changes occurred only at and near the boundary interfacial plane, and the magnitude of decreases was less that at other grain boundaries. This indicates that the coincidence boundaries act more as trapping sites for vacancies rather than as sink sites, and a different approach is therefore needed to estimate the sink strength for low $\Sigma$ boundaries.

The mean spacings of dislocation cores or disordered regions for low angle and large angle tilt boundaries are shown as a function of tilt angle in Fig. 2. It can be seen that the mean spacing decreases with increase in tilt angle for both (1 0 0)||(1 0 0) and (1 1 0)||(1 1 0) boundaries. We also show the theoretical values of boundary dislocation spacing calculated from

$$h = h_0 / \sin\frac{\theta}{2}, \tag{2}$$

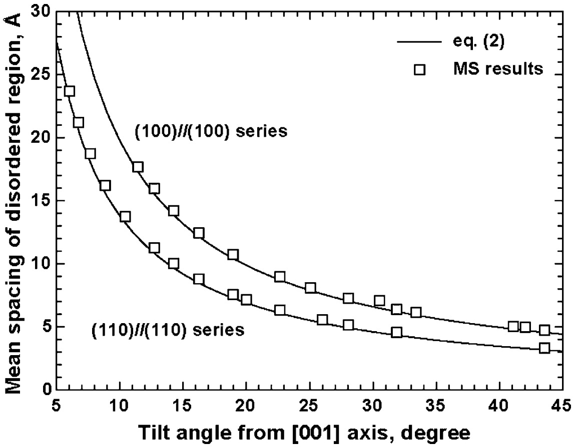

Fig. 2. Relationship between mean spacing of disordered region and tilt angle.

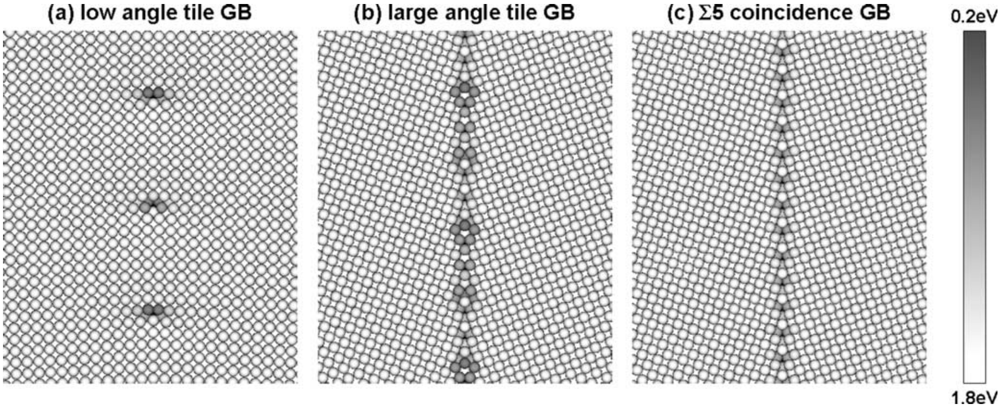

Fig. 1. Vacancy formation energy changes around Ni [0 0 1] tilt grain boundaries.

where $h_0$ is Burgers vector of the boundary dislocations. The theoretical values calculated from Eq. (2) are in good agreement with the MS results, whereas the large angle grain boundaries are not represented well by the grain boundary dislocation model. Thus, it is reasonable to use Eq. (1) to estimate sink strength for general grain boundaries excluding coincidence boundaries. For coincidence boundaries, the practical solution is to calculate the dynamics of trapping behavior for point defects using rate equations and to fit the sink strength to the RIS data obtained from several coincidence boundaries. The fitted values are listed in Table 1. We used the following interpolation equation to obtain sink strength for grain boundaries with deviation angles:

$$S_c^{\mathrm{GB}}(\theta_{\mathrm{dev}}) = S^{\mathrm{GB}}(\theta_\Sigma + \theta_{\mathrm{dev}}) \sin\frac{|\theta_{\mathrm{dev}}|}{\theta_{\mathrm{dev}}^{\mathrm{Max}}} + S_\Sigma^{\mathrm{GB}}\left[1 - \sin\frac{|\theta_{\mathrm{dev}}|}{\theta_{\mathrm{dev}}^{\mathrm{Max}}}\right], \qquad (3)$$

where $S_\Sigma^{\mathrm{GB}}$ is the sink strength of a coincidence boundary with the $\Sigma$ value, $\theta_{\mathrm{dev}}$ is the deviation angle, $\theta_\Sigma$ is the misorientation angle for the exact coincidence relationship, and $\theta_{\mathrm{dev}}^{\mathrm{Max}}$ is the maximum deviation angle from coincidence [9,10] as determined by

$$\theta_{\mathrm{dev}}^{\mathrm{Max}} = 15°/\sqrt{\Sigma}. \qquad (4)$$

For the case of $\theta_{\mathrm{dev}} > \theta_{\mathrm{dev}}^{\mathrm{Max}}$, we calculated the grain boundary sink strength using Eq. (1).

The calculated tilt angle dependence on RIS for ⟨1 1 0⟩ tilt grain boundary series in high purity Fe–15Cr–20Ni ternary alloys after electron irradiation is shown in Fig. 3 together with experimental data obtained by EDX measurements using FEG-TEM [5]. The experimental data show that the magnitude of RIS at grain boundaries increases with increase in tilt angle but suddenly drops at angles close to low $\Sigma$ boundaries such as $\Sigma 3$ and $\Sigma 9$. The calculated values also reproduce the RIS behavior not only around low angle tilt grain boundaries but also at large angle and coincidence boundaries. Fig. 4 shows the amount of Cr depletion at ⟨2 1 0⟩ misorientation angles in proton-irradiated type 304L stainless steels obtained by FEG-TEM EDX analysis [6]. The solid line in the figure shows calculated results using the present model. Both the experimental and calculated results show that the magnitude of Cr depletion increases with increase in the $\Sigma$ value and that the RIS increases with increases in deviation angles from exact coincidence. The good agreement between the experimental and theoretical results around low $\Sigma$ coincidence boundaries supports the validity of the present model for RIS prediction.

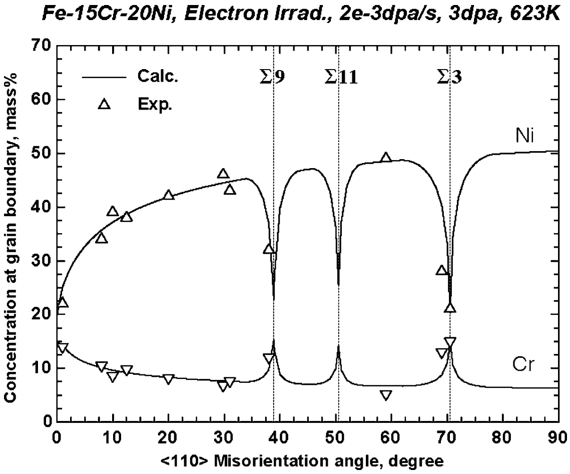

Fig. 3. ⟨1 1 0⟩ Tilt angle dependence of RIS at grain boundaries in electron-irradiated Fe–15Cr–20Ni alloys [5]. The solid lines are calculated dependence.

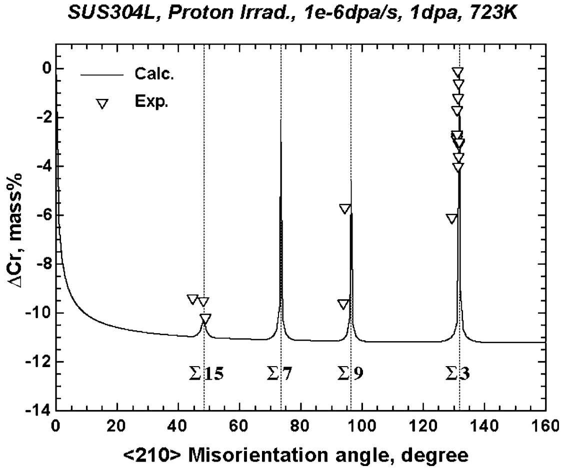

Fig. 4. ⟨2 1 0⟩ Tilt angle dependence of Cr segregation at grain boundaries in proton-irradiated SUS 304L stainless steels [6]. The solid lines are calculated dependence.

Table 1
Sink strength at various coincidence grain boundaries

| $\Sigma$ value | 3 | 7 | 9 | 11 | 15 |
|---|---|---|---|---|---|
| Strength, $\mathrm{m}^{-2}$ | $1\times10^{16}$ | $1\times10^{17}$ | $4\times10^{17}$ | $1\times10^{18}$ | $1\times10^{19}$ |

## 4. Conclusions

We investigated the orientation dependence of RIS on grain boundary orientation in austenitic stainless steels by means of numerical calculations. From basic MD and MS results, a new rate equation model for RIS that incorporates the grain boundary sink strength for point defects was obtained. The main results are as follows:

1. The MD and MS results show that the formation energies of vacancy change around the disordered regions in low and large angle tilt grain boundaries, whereas only slight formation energy changes were induced at and near coincidence boundaries.
2. The sink strength of grain boundaries, excluding low $\Sigma$ coincidence boundaries, can simply be described as a function of misorientation angle.
3. For coincidence boundaries, we fitted the sink strength to the RIS data and considered the effect of deviation angles from the exact coincidence relationship.
4. The calculated RIS behaviors around several tilt grain boundaries accurately reproduced the RIS data obtained from electron and proton irradiation experiments.

## References

[1] G.S. Was, P.L. Andresen, J. Metals 44 (4) (1992) 8.
[2] E.P. Simonen, S.M. Bruemmer, J. Nucl. Mater. 239 (1996) 185.
[3] R.A. Johnson, N.Q. Lam, Phys. Rev. B 13 (1976) 4346.
[4] P.R. Okamoto, L.E. Rehn, J. Nucl. Mater. 83 (1979) 2.
[5] S. Watanabe, Y. Takamatsu, N. Sakaguchi, H. Takahashi, J. Nucl. Mater. 283–287 (2000) 152.
[6] T.S. Duh, J.J. Kai, F.R. Chen, J. Nucl. Mater. 283–287 (2000) 198.
[7] S. Watanabe, N. Sakaguchi, N. Hashimoto, H. Takahashi, J. Nucl. Mater. 224 (1995) 158.
[8] Y. Mishin, D. Farkas, M.J. Mehl, D.A. Papaconstantopoulos, Phys. Rev. B 59 (1999) 3393.
[9] D.G. Brandon, Acta Metall. 14 (1966) 1479.
[10] Y. Ishida, M. McLean, Philos. Mag. 17 (1973) 1125.