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Diffusion of 3D-migrating self-interstitial clusters in diluted and concentrated Fe–Cr alloys

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ABSTRACT

We show, using atomic-level simulations, that the mobility of small 3D-migrating self-interstitial atom (SIA) clusters produced in displacement cascades is significantly reduced in concentrated Fe–Cr alloys (up to 15%Cr) as compared to Fe. The presence of α' precipitates, on the other hand, is only expected to provide scattering centers for interstitial-type defects, whose formation inside the precipitates is energetically unfavorable. The significant reduction in the mobility of 3D-migrating SIA clusters is expected to have an important impact on the microstructure evolution of high-Cr steels, depending on Cr concentration.

1. Introduction

Fe–Cr binary alloys can be used as model materials to study fundamental processes occurring in reduced activation ferritic/martensitic (RAFM) steels for fusion and to determine their microstructure evolution under irradiation [1]. The latter is known to be strongly affected by the actual Cr content in the range of technological application (<20%Cr). For example, both dislocation loops density [2] and radiation-induced void swelling [2,3] exhibit a non-monotonic dependence on Cr content.

The microstructure evolution under irradiation in metals is known to be largely determined by the migration properties of self-interstitial clusters [4]. A proper understanding of these properties versus Cr concentration is thus expected to help rationalize the experimental observations. For example, there is experimental evidence that the presence of Cr reduces the mobility of visible dislocation loops [5]. The problem of quantitatively assessing this diffusion coefficient reduction has been addressed, using atomistic simulations combined with theoretical considerations, in the case of loops of intermediate size (around the limit of resolution of transmission electron microscopes), finding that the mentioned non-monotonic dependence of swelling on Cr concentration may correlate with the similarly non-monotonic dependence of loop diffusion reduction [6]. There is also evidence, from resistivity recovery experiments, that sufficiently high-Cr concentrations produce a strong reduction of the effective mobility of single self-interstitial atoms (SIA) [7]. This problem was preliminarily addressed some time ago [8], and more recently in a more rigorous and systematic way [9], in atomistic simulation studies, finding results that can, to a certain extent, quantitatively explain the experimental observations. However, no information is available, either from experiments, or from atomic-level studies, on the mobility of small SIA clusters in Fe–Cr, which represent the largest fraction of clusters directly created in displacement cascades [10]. Recently, it has been shown in a molecular dynamics (MD) study that not only single SIAs, but also di- and tri-SIA clusters are three-dimensionally (3D) migrating defects in iron and only clusters containing more than 7-SIAs are strictly limited to one-dimensional (1D) trajectories, whereas clusters of intermediate sizes exhibit mixed 1D–3D motion, from time to time changing glide direction [11]. In this work we extend the approach recently applied to study the single SIA [9], to address the issue of the mobility of small, 3D-migrating SIA clusters in Fe–Cr alloys, using atomistic modeling techniques.

2. Method

In [9] it has been pointed out that the presence of configuration traps for SIAs in Fe–Cr alloys, defined by specific local Cr distributions around the defect, hinders the application of MD simulations to study SIA migration at low temperatures. Because of the limitations of MD in terms of time (tens of ns) and space (few thousands of atoms in long dynamic studies), the effect of these low-density ($\sim10^2$–10^3 ppm) and comparatively strong (up to 0.5–0.6 eV) traps cannot be correctly accounted for in small crystallites, while the usage of large ones requires enormous computation time. A possible solution to the problem, proposed and described in [9], is to compute the set of configuration-dependent relaxed formation energies, E_f, of the

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SIA, using computationally less heavy molecular static techniques, after putting the defect in all the possible configurations that it can find in a large simulation box (the larger, the better the statistical significance). Here we used 128×10^3 atom crystallites, where single SIAs and di- and tri-SIA clusters were introduced and then relaxed by quenching the system down to 0 K. The clusters were initially created as $\langle 110 \rangle$ dumbbells collections and their final configurations were checked again after relaxation. The calculations were performed using a recent, *ab initio* based, two-band model empirical interatomic potential (EIP) [12]. From this set of calculations, for a given Cr concentration, C_{Cr}, the formation energy probability density, $P(E_{\mathrm{f}}) = n(E_{\mathrm{f}})/n_{\mathrm{states}}$ can be deduced ($n(E_{\mathrm{f}})$ is the number of times a certain energy E_{f} is found, n_{states} is the total number of possible states). It can subsequently be used to define trap concentration, C_{trap}, and strength, E_{trap}, for the studied defect, as proposed in [9].

The model is based on the following assumptions: (i) the concentration of traps is low enough to say that the mobile defect interacts only with one trap a time; (ii) the traps are localized, so defect jumps are affected only in their immediate vicinity; (iii) when not trapped, a defect executes a d-dimensional ($d = 1,2,3$) random walk with a constant migration energy and jump frequency, assumed to be equal to those in Fe. The third assumption is the strongest one, as recent density functional theory (DFT) calculations show that the migration barrier for a translation-rotation jump of the Fe–Cr dumbbell is slightly lower than that for the Fe–Fe dumbbell [9,13]; the difference is, however, negligible, particularly compared with the typical trapping energy in both dilute and concentrated alloys, as will be shown in Section 3. With these assumptions, the defect diffusivity reduction can be estimated as follows. For a given distance R covered by the migrating defect and larger than the characteristic correlation length in the system ($\sim C_{\mathrm{trap}}^{-1/3}$), D is:

$$D = \frac{R^2}{2\mathrm{d}\langle t \rangle} \tag{1}$$

Here the brackets denote averaging over all possible trajectories connecting two points separated by distance R; t is the time required to travel along a particular trajectory. In addition, $t \propto \sum_{j=1,N} \exp(E_B^j / k_B T)$, where N is the number of sites (on a particular trajectory) visited by the diffusing defect and E_B^j is the binding energy of a defect at site j (k_{B} is the Boltzmann constant, T is the absolute temperature). The binding energy is the same at each site in the pure metal and different in an alloy, due to the presence of traps. The ratio of the diffusion coefficients in the pure metal (D_{M}) and in an alloy (D_{A}) can thus be estimated as the reciprocal of the ratio of the corresponding mean times. Hence, if M is the number of sites on all possible trajectories and n_{t} is the number of traps, the ratio of the diffusion coefficients is equal to:

$$\begin{aligned} D_{\mathrm{M}}/D_{\mathrm{A}} &= \frac{(M - n_{\mathrm{t}}) + n_{\mathrm{t}} \exp(-E_{\mathrm{trap}}/k_{\mathrm{B}}T)}{M} \\ &= 1 + C_{\mathrm{trap}}[\exp(-E_{\mathrm{trap}}/k_{\mathrm{B}}T) - 1] \end{aligned} \tag{2}$$

It is assumed in this equation that all traps in the system have the same energy, E_{trap}. For a spectrum of trap energy E^i_{trap}, each with concentration C^i_{trap}, the ratio of the diffusion coefficients is:

$$D_{\mathrm{M}}/D_{\mathrm{A}} = 1 + \sum_i \{C^i_{\mathrm{trap}}[\exp(-E^i_{\mathrm{trap}}/k_{\mathrm{B}}T) - 1]\} \tag{3}$$

According to this equation, data on the distribution $C_i(E_i)$ are sufficient to estimate the reduction of the diffusion coefficient in the alloy.

3. Results, discussion, conclusions

The formation energy probability density, $P(E_{\mathrm{f}})$, for single, di- and tri-SIA in Fe–Cr alloys of different concentrations is plotted in Fig. 1. The formation energies of the same defects, in their lowest energy configurations in pure Fe [11], are shown as vertical lines. Already in a dilute alloy (Fe–1%Cr), $P(E_{\mathrm{f}})$ broadens, showing that the defect formation energy can both increase or decrease, because of the interaction with surrounding Cr atoms. All configurations were found to be sets of $\langle 110 \rangle$ dumbbells after relaxation. With increasing Cr content $P(E_{\mathrm{f}})$ broadens further and low-energy states with probability $\sim 10^{-3}$ and lower appear. In Fe–5 and Fe–10%Cr more than 95% of the clusters relaxed into parallel $\langle 110 \rangle$ dumbbells configurations, while in Fe–15%Cr about 15% of them took a parallel $\langle 111 \rangle$ crowdion configuration. This suggests that, although the studied clusters may take $\langle 111 \rangle$ glissile configurations, their frequency is low. Thus, it is reasonable to assume that clusters spend most time in $\langle 110 \rangle$ configurations, thereby migrating along 3D paths. The strength and density of the strongest traps can then be identified for each SIA defect in each alloy [9]. The results are summarized in Table 1: E_{trap} varies from 0.2 to 0.8 eV, depending on SIA defect size, generally increasing with C_{Cr}. These values are broadly consistent with *ab initio* calculations in concentrated Fe–Cr alloys [14]. C_{trap} is higher in Fe–1%Cr than in the other alloys and roughly proportional to the mean distance between Cr atoms, $\sim C_{\mathrm{Cr}}^{1/3}$.

By inserting the data from Table 1 in Eq. (3), we can find $D_{\mathrm{Fe-Cr}}/D_{\mathrm{Fe}}$ for each defect at any temperature. For example, the results at 600 K for single, di- and tri-SIAs are plotted in Fig. 2 versus Cr concentration. For comparison, data from [6] for a 1D migrating 7-SIA cluster are also shown. The mobility of a single and di-SIA can be reduced by a factor of 2–3 in Fe-10%Cr, but for the tri-SIA cluster

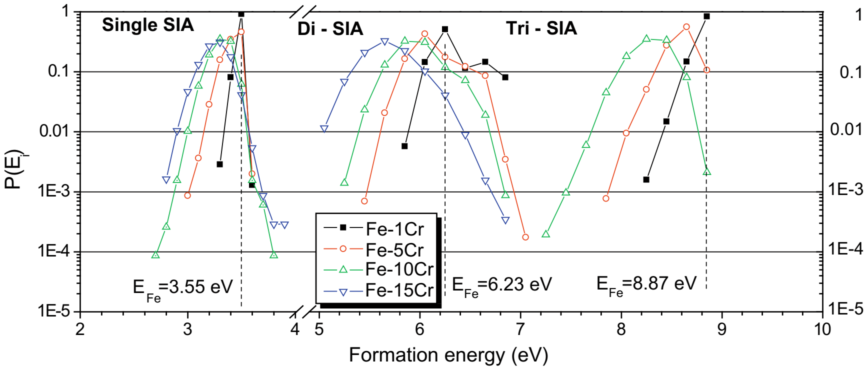

Fig. 1. Formation energy probability density, $P(E_{\mathrm{f}})$, for a single, di- and tri-SIA clusters in Fe–Cr alloys with random distributions of Cr, obtained by performing static calculations.

Table 1
Trap concentrations (atomic fraction) and energies (eV) for 3D-migrating SIA defects in Fe–Cr alloys.

Defect	Quantity	Fe–1%Cr	Fe–5%Cr	Fe–10%Cr	Fe–15%Cr
Single SIA	C_{trap}	2.8×10^{-3}	8.6×10^{-4}	8.6×10^{-5}	1.6×10^{-3}
	E_{trap}	0.2	0.3	0.5	0.3
Di-SIA	C_{trap}	5.7×10^{-3}	6.9×10^{-4}	1.3×10^{-3}	1.1×10^{-2}
	E_{trap}	0.2	0.4	0.4	0.4
Tri-SIA	C_{trap}	1.5×10^{-3}	7.7×10^{-4}	1.9×10^{-4}	6.25×10^{-4}
	E_{trap}	0.4	0.6	0.8	0.8

Table 2
Formation energies (eV) of SIA defects in pure Cr for ⟨110⟩ and ⟨111⟩ configurations.

Method	EIP calculations		*Ab initio* calculations [13]	
Defect	⟨110⟩ config.	⟨111⟩ config.	⟨110⟩ config.	⟨111⟩ config.
E_f (SIA)	5.59	5.62	5.69	5.76
E_f (di-SIA)	10.31	9.55	10.30	10.10
E_f (tri-SIA)	14.78	13.91	14.80	14.00

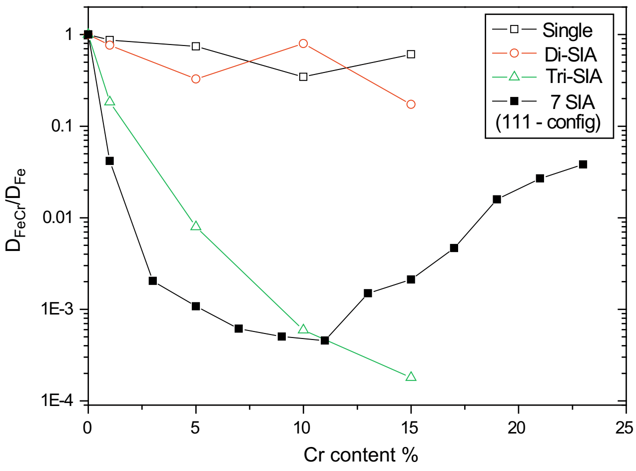

Fig. 2. D_{Fe-Cr}/D_{Fe} ratio at 600 K estimated using Eq. (3) for single, di- and tri-SIA clusters. For comparison, the data for the 1D migrating ⟨111⟩ 7-SIA cluster from [6] are also given.

the reduction can be as large as three orders of magnitude, or more. Hence, these defects migrate in Fe–Cr with the same diffusivity as single vacancies (note that the weak interaction between vacancies and Cr atoms in Fe [9,15] suggests a comparatively weak influence of the Cr content on vacancy diffusivity, consistently with experimental measurements [16]). This should result in enhanced SIA-vacancy recombination, leading to a decrease in the steady-state vacancy concentration under neutron irradiation, thereby delaying the onset of void swelling, as is known to occur in Fe–Cr alloys [3].

Above 10%Cr α/α' phase demixing occurs [17]. We therefore studied the interaction of SIA defects with Cr-rich coherent precipitates. The formation energies of single SIA and di- and tri-SIAs in pure Cr, in the two possible configurations (⟨110⟩ and ⟨111⟩), as calculated with the EIP, are indicated in Table 2, where they are compared to the corresponding *ab initio* values (see [13] for calculation details). The values for the ⟨110⟩ configurations are in excellent agreement; for the ⟨111⟩ configurations the EIP slightly underestimates the formation energies, but the relative stability is correctly predicted. Comparing these numbers with the corresponding energies in pure Fe and Fe–Cr alloys (Fig. 2), it becomes clear that the presence of SIA-type defects in Cr-rich precipitates is energetically unfavorable. Consistently, it was observed in MD simulations that defects located inside the precipitate rapidly (within a few tens of ps at $T = 600$ K) escaped from them to the matrix. Doing this, di- and tri-SIAs were observed to move via 1D glide, in a ⟨111⟩ configuration, which is favoured in Cr-rich environments, re-orienting back to the ⟨110⟩ configuration as soon as they reached the matrix, where they continued to move in a 3D manner. It is therefore expected that Cr-rich precipitates will act as 'scattering' centers for 3D-migrating self-interstitial-type defects. This behavior, predicted by the EIP, is totally consistent with the picture from *ab initio* data (Table 2).

In summary, we have shown that both in dilute and concentrated Fe–Cr alloys the specific arrangement of Cr atoms near small SIA clusters creates effective traps. By assessing the density and strength of these traps, based on molecular statics calculations, we find that the trapping energy increases with Cr content (from 1% to 15%) from ~0.2 to ~0.8 eV, although the density does not necessarily increase. We have proposed a simple method to estimate the corresponding diffusivity reduction, which can be as large as three orders of magnitude in alloys of technological interest. The presence of Cr-rich precipitates, on the other hand, is not expected to alter the mobility of 3D-migrating SIA defects, since the formation of these clusters inside or near them is energetically unfavorable.

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References

[1] L. Malerba, D.A. Terentyev, G. Bonny, A.V. Barashev, C. Bjorkas, N. Juslin, K. Nordlund, C. Domain, P. Olsson, N. Sandberg, J. Wallenius, J. ASTM Intl. 4 (2007) JAI100692.
[2] Y. Katoh, A. Kohyama, D.S. Gelles, J. Nucl. Mater. 225 (1995) 154.
[3] E.A. Little, D.A. Stow, J. Nucl. Mater. 87 (1979) 25.
[4] H. Trinkaus, B.N. Singh, S.I. Golubov, J. Nucl. Mater. 283–287 (2000) 89.
[5] K. Arakawa, M. Hatanaka, H. Mori, K. Ono, J. Nucl. Mater. 329–333 (2004) 1194.
[6] (a) D.A. Terentyev, L. Malerba, A.V. Barashev, Phil. Mag. Lett. 85 (2005) 587;
(b) D. Terentyev, P. Olsson, L. Malerba, A.V. Barashev, J. Nucl. Mater. 362 (2007) 167;
(c) D. Terentyev, A.V. Barashev, L. Malerba, Phil. Mag. 88 (2008) 21.
[7] (a) A.L. Nikolaev, V.L. Arbuzov, A.E. Davletshin, J. Phys.: Condens. Matter 9 (1997) 4385;
(b) A.L. Nikolaev, J. Phys.: Condens. Matter 11 (1999) 8633.
[8] D. Terentyev, L. Malerba, J. Nucl. Mater. 329–333 (2004) 1161.
[9] D. Terentyev, P. Olsson, T.P.C. Klaver, L. Malerba, Comp. Mater. Sci. 43 (2008) 1183.
[10] D. Terentyev, C. Lagerstedt, P. Olsson, K. Nordlund, J. Wallenius, C.S. Becquart, L. Malerba, J. Nucl. Mater. 351 (2006) 65;
C. Björkas, K. Nordlund, L. Malerba, D. Terentyev, P. Olsson, J. Nucl. Mater. 372 (2008) 312.
[11] D.A. Terentyev, L. Malerba, M. Hou, Phys. Rev. B 75 (2007) 104108.
[12] P. Olsson, J. Wallenius, C. Domain, K. Nordlund, L. Malerba, Phys. Rev. B 72 (2005) 214119.
[13] P. Olsson, J. Nucl. Mater. 386–388 (2009) 86.
[14] T.P.C. Klaver, P. Olsson, M. Finnis, Phys. Rev. B 76 (2007) 214110.
[15] P. Olsson, C. Domain, J. Wallenius, Phys. Rev. B 75 (2007) 014110.
[16] (a) A.M. Huntz, P. Guiraldenq, M. Aucouturier, P. Lacombe, Mém. Sci. Rev. Métall. LXVI (1969) 86;
(b) R. Braun, M. Feller-Kniepmeier, Phys. Stat. Sol. (a) 90 (1985) 553.
[17] P. Dubuisson, D. Gilbon, J.L. Séran, J. Nucl. Mater. 205 (1993) 178.