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Modelling of the diffusion of self-interstitial atom clusters in Fe-Cr alloys

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The results of molecular dynamics simulations of the diffusion of clusters of self-interstitial atoms in Fe-Cr alloys of different Cr content are presented. It is shown that with increasing Cr concentration the cluster diffusivity first decreases and then increases, in accordance with the predictions of a model developed recently, based on molecular static calculations. The minimum diffusivity is found at about 10 at.%Cr for small clusters and it shifts towards lower concentration with increasing cluster size. The migration energy of SIA clusters is found to lie in between the binding energy of a Cr atom with a crowdion and half of it. This indicates that the mechanism of ~~a~~ cluster migration is via the movement of individual crowdions from one Cr atom to another. The values obtained statically are much higher and are argued to be more reliable due to better sampling of different configurations in a bigger simulation box.

Key words: Iron alloys; Chromium; Interstitial clusters; Diffusion; Molecular dynamics

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1. Introduction

The experimental evidence and modern theory emphasizes the role clusters of self-interstitial atoms (SIAs) play in the microstructure evolution in metals and alloys under neutron irradiation in nuclear reactors [1-3]. According to molecular dynamics (MD) studies, in pure bcc-iron about 60% of SIAs are produced in displacement cascades as ½⟨111⟩ clusters [4,5], which migrate along ⟨111⟩ close-packed directions with a very low activation energy (a few tens of meV) [6]. It is known that SIA

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cluster diffusivity can be reduced significantly by interactions with various lattice imperfections, as has been shown using elasticity theory for different substitutional solute atoms [7] and by MD for vacancies [8] and Cu atoms [9] in α-iron. This may affect strongly the rates of the cluster annihilation at dislocations and grain boundaries, as well as of the dislocation loop forests formation. As a result of an increased sink strength of the clusters for freely migrating vacancies, there will be a decrease in the void swelling rate. This was proposed in [10] as an explanation for swelling variation with Cr content observed in binary Fe-Cr alloys [11,12].

The effect of Cr on the SIA cluster mobility was demonstrated in [10] in the framework of a static model, namely where the configuration energy was calculated at 0K. According to the model, independently of cluster size, the minimum diffusivity is realized at Cr concentration ~11 at.%, when all crowdions constituting the cluster interact with Cr atoms but the interaction fields of different Cr atoms do not overlap. In this work we continue these studies and perform MD (including those at 0K, i.e. static) simulations of the SIA cluster migration in Fe-Cr alloys containing up to 20at.%Cr. We use a two-band Fe-Cr potential developed recently [13], where the Fe-Cr interaction was fitted to *ab initio* data on the heat of mixing and the binding energy of various SIA-Cr complexes.

The paper is organized in a conventional order. The calculation method is described in section 2 and the results in section 3. The results are discussed in section 4 and the conclusions are drawn in section 5.

2. Method

Simulation box of rectangular shape with axes along the [111], $[11\bar{2}]$ and $[1\bar{1}0]$ directions and periodic boundary conditions was used. The box dimensions were $12\sqrt{6}a_0$ along the $[11\bar{2}]$ and $12\sqrt{2}a_0$ along the $[1\bar{1}0]$ directions, where a_0 is the lattice parameter of bcc Fe, which is equal to 0.28553 nm at T=0 K for the potential set used. Along the orthogonal [111] dir ection it varied from 50b to 70b depending on the size of the SIA cluster (here $b = \sqrt{3}a_0 / 2$ is the length of the Burgers vector of a ½⟨111⟩ loop). The corresponding number of bcc lattice sites ranged from 43,200 to 60,480. Calculations were carried out for clusters of he xagonal shape consisting of 7, 37 and 91 SIAs in the temperature range 300 to 1200 K and for Cr concentrations, C_{Cr}, up to 20 at.%. Cr atoms were distributed randomly.

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The EAM-type potential of Ackland *et al.* [14] was used for the description of Fe-Fe interaction. It reproduces the elastic properties of α-Fe and the *ab initio* data on the relative stability of different SIA configurations obtained in [15]. The Fe-Cr interaction has been described using a two-band model potential developed recently in [13]. It has been fitted to *ab initio* data on the heat of mixing and reproduces experimental results on short-range order parameter versus Cr concentration in Fe-Cr. It also reproduces *ab initio* data on the binding energy of various SIA-Cr complexes calculated in [16]. In particular, it gives 0.42 eV for the binding energy of a Cr atom with a crowdion and 4*b* for the interaction range in the [111] direction of the crowdion axis.

The integration of equations of motion was performed in the NVE ensemble at zero pressure conditions using Gear's predictor-corrector algorithm for the velocity [17] with a constant time step of 0.5 fs and for a simulation time, t_S, up to 30 ns. During simulations, the cluster position was recorded every 10 fs. The simulated trajectory was then subdivided into segments of a fixed length Δ, and the diffusion coefficient, *D*, estimated as

$$D = \frac{\Delta^2}{2\langle t \rangle}, \qquad (1)$$

where $\langle t \rangle$ is the mean time the cluster spent in a segment. The standard error of the diffusion coefficient (similarly for other characteristics) was calculated using the standard procedure of uncertainty propagation: $\sigma_D = D\sigma_t / \langle t \rangle$, where the standard error of the mean time $\sigma_t = \sqrt{[\langle t^2 \rangle - \langle t \rangle^2]/(N-1)}$, where *N* is the total number of segments. Since equation (1) requires the trajectories to be long enough to include all correlations [18], in the following we varied Δ, to obtain independence of its choice.

3. Results

Figure 1 shows two examples of a general procedure applied here to estimate the diffusion coefficient, which is based on the analysis of the dependence of the estimate of diffusion coefficient on the trajectory length Δ. The examples presented are for a seven SIA cluster in pure Fe and Fe-5at.%Cr at 640K. As can be seen, the cluster diffusivity has tendency to saturation at some Δ, while the standard error keeps increasing due to decreasing statistics of trajectory segments. The best

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estimate of the diffusion coefficient in each calculation was chosen for a value of Δ that provides convergence while giving the smallest statistical error. Generally, Δ corresponding to the best choice ranged from 4*b* to 7*b*. For the examples shown in figure 1, the best choices are for Δ=6*b* in pure Fe and for Δ=7*b* in Fe-5at.%Cr alloy. No clear correlation of the best choice Δ with Cr concentration or cluster size was established. Finally we note that, for the data presented in figure 1, we verified that a more conventional method of estimating diffusion coefficient, which uses trajectories of constant time, gives the same results. The comparison between the two methods was performed for the trajectory time equal to the trajectory length squared divided by twice the diffusion coefficient, i.e. for the same number of segments *N*.

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'[Insert figure 1 about here]'

The Cr concentration dependence of the ratio of diffusion coefficients in Fe-Cr and pure Fe at 640K, D^{FeCr}/D^{Fe}, is shown in figure 2. For pure Fe, the reference values used are (in $m^2\ s^{-1}$): $D_7^{Fe} = 1.05\times10^{-7}$, $D_{37}^{Fe} = 3.02\times10^{-8}$, $D_{91}^{Fe} = 1.40\times10^{-8}$ as obtained in the present calculations. The right-hand side axis of figure 2 shows the change in the SIA cluster free energy, ΔF^{MD}, as defined in [10]:

$$\Delta F_n^{MD} = k_B T \ln(D_n^{FeCr} / D_n^{Fe}) . \qquad (2)$$

As seen, the effect of Cr atoms on the diffusivity is strong. So, the diffusion coefficient of a seven SIA cluster reaches minimum at 10%Cr, when it is ~100 times smaller than in pure Fe. Another observation in figure 2 is that, with increasing cluster size, the minimum diffusivity shifts towards smaller Cr concentration, e.g. 2at.% for a 91 SIA cluster. This is an effect originating from finite diffusion length, when a cluster encounters not all energy states possible. Bigger clusters have less chances of encountering higher energy states on the same diffusion length, especially at high Cr concentrations, when the probability of a high-energy state is small. In other words, local fluctuations of Cr concentration and spatial arrangement near a bigger SIA cluster have lesser effect on its energy. For example, let us consider a cluster of n SIAs in the highest possible energy state, when it does not interact with any Cr atom within the interaction range $n_1 b$ (=9*b*) along the [111] direction of the cluster axis. In a random solid solution, the fraction of these states is $p = (1 - C_{Cr})^{nn_1}$ and decreases strongly with increasing cluster size. So, for C_{Cr}=0.1, $p \sim 10^{-3}$ for n=7 and $p \sim 10^{-8}$ for n=19, i.e. changes by five orders of magnitude. The reciprocal of this

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fraction is proportional to the mean trajectory length containing one such a state. In other words, short trajectories have smaller probability of containing a high-energy state, while, for a given trajectory length, the highest energy state must be smaller for a bigger cluster, which explains why the depth of the minimum decreases with increasing cluster size (see figure 2).

'[Insert figure 2 about here]'

Figure 3 shows the temperature dependence of the diffusivity of a seven SIA cluster in Fe-Cr alloys with 5 and 10 at.%Cr and compared with that in pure Fe. As seen from the best fit lines, the temperature dependence is well described by the Arrhenius relationship with an activation energy of 0.26±0.06 eV in Fe-5at.%Cr and 0.33±0.06 eV in Fe-10at.%Cr. These values lie in between the binding energy of a Cr atom with a single crowdion, 0.42 eV for this potential, and half of this value. (The migration barrier and its half value represent the low and the high-temperature limits for the effective free energy in the situation, when only one barrier type is present [10].) This indicates that the mechanism of a cluster migration must be via movement of individual crowdions from one Cr atom to another, similarly to the model of independent crowdions in pure iron developed in [19]. In pure Fe, the migration energy is very small (0.04 eV with this potential) resulting in the diffusion coefficient practically independent on the temperature.

'[Insert figure 3 about here]'

This low migration energy in Fe (as well as in some other pure metals) is lower than the thermal energy ($k_B T$) at temperatures of technological importance. This , undermines the basis for consideration of SIA cluster migration as a thermally activated process [20]. Indeed, a rather non-Arrhenius dependence of a crowdion diffusivity in vanadium has been found at high temperatures [20]. Namely, the diffusion coefficient increases linearly with temperature and is describable in terms of Brownian motion, governed by the velocity-dependent friction force. This description is consistent with that given by Dudarev in the framework of a multistring Frenkel-Kontorova model [21]. This non-Arrhenius behaviour is not expected to occur in Fe-Cr alloys, however, because of high Cr-crowdion binding energy.

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4. Discussion

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The reduction in the mobility of SIA clusters due to Cr atoms obtained here is in accordance with the predictions of the static calculations reported in [10,16]. The change in the free energy for clusters of different size at different Cr concentrations at 640 K, estimated statically for the box of 1000*b* in the direction of the SIA cluster axis is shown in figure 4. (In these simulations, the clusters were relaxed fully; hence, only nearest minimum-energy states were accounted for in the calculations of the cluster free energy *via* equation 1 in [10].) As can be seen, the presence of a minimum and its shift towards smaller Cr concentration with increasing cluster size is similar to the MD results plotted in figure 2. Some higher free energy obtained in static simulations is due to the fact that a larger box allows a better sampling of atomic configurations near the cluster. So, high energy configurations, where the SIA cluster interacts with the least number (e.g. none) of Cr atoms may occur in a larger box, while may not be encountered in a smaller box. This increases the free energy difference and decreases the $D_n^{\mathrm{FeCr}} / D_n^{\mathrm{Fe}}$ ratio.

'[Insert figure 4 about here]'

There is, however, a significant difference in the effective migration energy obtained in MD from that calculated statically. The former value, ~0.3 eV, lies in between the binding energy of a Cr atom with a single crowdion, 0.42 eV with the potential used, and half of this value. As already stated above, this is because the cluster migration is via movement of individual crowdions from one Cr atom to another. The latter (static) value has its maximum of ~1.5 eV in a Fe-10at.%Cr (at 600 K for a seven SIA cluster) [10]. It is much higher than the dynamic value because of a better sampling of the local Cr arrangements in the bigger, ~1000*b*, box used in [10]. Actually, even this value might be an underestimate due to some additional constraints in configuration sampling in [10]: the positions of individual crowdions in the cluster were fixed. Its maximum can be estimated following its physical significance, that is the energy to move the cluster from the lowest possible energy state, when each crowdion interacts with one Cr atom, to the highest possible energy state, with no Cr atoms within the interaction range. The interaction energy of a cluster with Cr atoms is almost exactly the sum of the interaction energy of individual crowdions constituting the cluster with Cr atoms on corresponding axis [10]. Thus, the value under discussion (i.e. for a seven SIA cluster) may be approximated as seven times the maximum binding energy of a crowdion with a Cr atom, i.e. 7x0.4eV=2.8 eV. This is almost twice that estimated statically in [10].

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It is interesting to note that the shift of the minimum diffusivity with increasing size of SIA clusters to smaller concentrations, shown in figures 3 and 4, complies with the shift in the experimentally observed swelling in Fe-Cr alloys with irradiation temperature and irradiation dose. So, according to [11], for the same irradiation dose at 380°C and 460°C the minima of swelling were observed at 10at.%Cr and 5at.%Cr, respectively. At a higher irradiation dose of 140 dpa at 420°C [22], the minimum of swelling was observed at 3at.%Cr. It is tempting to link these observations with the possible increase of the average size of SIA clusters with increasing temperature or dose. In [22] a further decrease of swelling at C_{Cr} >12at.% was observed, but it was accompanied by, and most probably connected with, the formation of α'-phase. It has been shown by MD that small Cr-rich precipitates are repulsive barriers for moving SIA clusters [16]. Therefore, a high density 10^{21}-10^{24} m^{-3} of fine dispersed nanometre size α'-particles [23,24] must suppress SIA cluster migration, leading to an enhanced recombination rate with vacancies and decreasing swelling, as observed.

5. Conclusions

The MD simulation results on the diffusion of SIA clusters in Fe-Cr alloys, obtained with the potential set fitted to reproduce *ab initio* data on Cr-SIA interaction, show that

1) With increasing Cr concentration, the SIA cluster diffusivity first decreases and then increases, which agrees with the predictions of static calculations presented in [10, 16]. The reduced cluster diffusivity should enhance the recombination rate with vacancies, thereby reducing swelling rate as observed in irradiated ferritic alloys containing between 1 and 12at.%Cr, when compared to pure Fe.
2) For small clusters consisting of ~7 SIAs, which are produced directly in displacement cascades and, hence, are particularly important for the microstructural evolution, the minimum diffusivity appears at ~10 at.% Cr, thus correlating with the minimum of swelling observed in binary Fe-Cr alloys irradiated to 30 dpa by fast neutrons at 380°C [11].
3) With increasing cluster size, the minimum diffusivity shifts towards lower concentration and remains in the range from 1 to 10 at.% Cr for the SIA clusters studied, and the depth of the minimum decreases. This effect may explain the shift of minimum swelling from ~10%Cr to lower Cr concentrations of 5 and 3%Cr, observed at higher temperature [11] and much higher dose [19].

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4) The temperature dependence of 7-SIA cluster migration is well described by the Arrhenius relationship, with an activation energy of 0.26±0.06 eV in Fe-5at.%Cr and 0.33±0.06 eV in Fe-10at.%Cr. These values lie in between the binding energy of a Cr atom with a single crowdion and half of this value, which indicates that the mechanism of cluster migration is governed by hopes of individual crowdions from one Cr atom to another. It should be noted, however, that the small box size used in the simulations restricted sampling of spatial distribution of Cr atoms. So, the higher effective migration energy obtained in [10] statically is more reliable in this sense.

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Acknowledgements

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Figure captions

Figure 1. Dependence of the estimate of the diffusion coefficient of a 7 SIA cluster in pure Fe and Fe-5at.%Cr alloy at 640 K on the trajectory segment length.

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Figure 2. The ratio of the diffusion coefficients $D_n^{\mathrm{FeCr}} / D_n^{\mathrm{Fe}}$ in Fe-Cr alloys versus Cr concentration calculated by MD for SIA clusters of different size. The lines are guides for the eyes.

Figure 3. MD results on the temperature dependence of the diffusivity of a seven SIA cluster in pure Fe and Fe-Cr alloys with 5 and 10 at.%Cr.

Figure 4. Change in the free energy of SIA clusters of different size for different Cr concentrations at 640 K calculated using static simulations in a simulation box of 1000*b* in the direction of the cluster axis [16].

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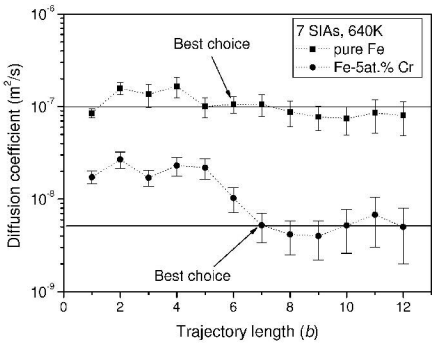

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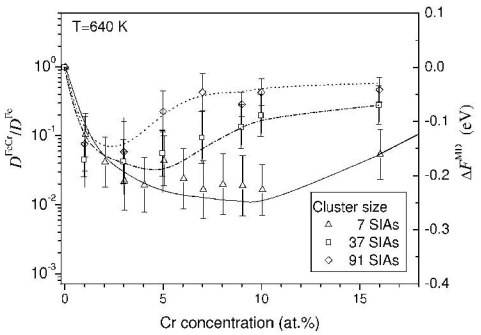

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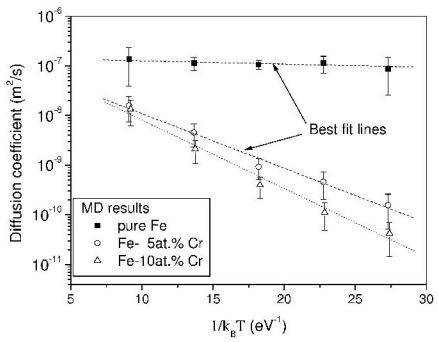

Figure 3. MD results on the temperature dependence of the diffusivity of a seven SIA cluster in pure Fe and in Fe-Cr alloys with 5 and 10 at.%Cr.

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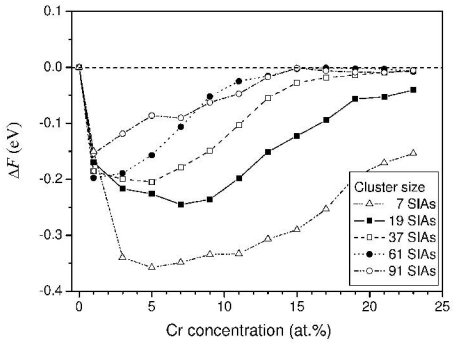

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