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Suppression of interstitial cluster diffusion by oversized solute atoms

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Abstract

We study the diffusion of self-interstitial atom (SIA) clusters in metals with oversized substitutional impurities. Kinetic Monte Carlo (kMC) simulations are performed which include elastic interactions between defects. We show that the SIA clusters can become confined in a 1-D segment between impurity atoms due to repulsion from these stress centres. Rare rotation of the easy direction of motion of the clusters allows them to escape to new confined segments. This suppressed diffusion is examined by both kMC simulations and an analytic theory, which are shown to agree well. We suggest some of the possible applications of these findings to radiation damage resistance in structural materials for fusion devices.

1. Introduction

The history of our understanding of self-interstitial atom (SIA) clustering and transport has shown the importance of this behaviour to the microstructural evolution of pure materials irradiated at high energies. 3-D diffusing single SIAs were assumed in standard rate theory (SRT) [1,2] which describes the effects of electron irradiation well. When the production bias model (PBM) [3] was introduced it showed the importance of SIA clustering within the cascade region of high-energy radiation damage. Molecular dynamics (MD) simulations then suggested the possibility that these clusters can themselves be glissile along their glide prism, in both FCC [4] and BCC [5–7] materials. Glissile clusters have also been observed experimentally [8,9]. This allowed the refinement of the PBM to incorporate 1-D transport, explaining mesoscale structure observed in many situations [10]. Further generalisation of this transport model [11–13] has incorporated the importance of the slight non-one-dimensionality of the transport, for example the infrequent rotations of the glide direction onto other close packed axes [5,14,15], or conservative climb of clusters diffusing slowly in the plane perpendicular to the direction of their fast glide [16]. Recent kinetic Monte Carlo (kMC) simulations incorporating elastic interactions have indicated drastic decreases in long range SIA cluster transport due to 'focusing' in the stress field of a dislocation. In the case of a concentrated system of SIA clusters the focusing is achieved by mutual elastic interactions with other SIA clusters [17].

There has long been experimental evidence that other stress centres such as solute atoms and impurity atoms (in this paper we shall use the terms 'solute' and 'impurity' interchangeably) can influence the evolution of irradiated materials. Examples include the stark differences in irradiated microstructure in nickel alloyed with 2 at.% of variously sized substitutional solutes [18], and MD simulations of SIA clusters interacting with single vacancies [19] and with oversized copper impurities in α-iron [20]. The latter study found a decrease in the diffusion prefactor of the cluster, and for small clusters there was an increased frequency of rotations of the Burgers vector (BV). One of the most common methods of describing the effects of impurities, or modelling them in kMC simulations of radiation

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damage is to consider them as temporary traps for SIA clusters, forming sessile complexes. The complexes may subsequently spontaneously break apart, releasing single interstitials, or the cluster, back into a mobile state. This may be appropriate for some types of solute or impurity atoms, but it does not cover the whole range of possibilities.

In this paper we describe another transport regime where 1-D confinement of these SIA clusters occurs through repulsive interactions with oversized solute atoms. When the repulsive interaction is strong enough, the clusters can escape from these confined segments only by changing their direction of motion. The 1-D confinement during the period between direction changes can dramatically reduce the effective diffusion coefficient of the SIA cluster. If the confinement distance is small compared to the characteristic microstructural distances in the system, confinement causes a transition to behaviour more like the 3-D transport of SRT, even when changes to the direction of motion of the cluster are infrequent. This is a possible origin for the 1-D to 3-D transition assumed in recent explanations of void swelling profiles near grain boundaries, formally similar to SRT [21].

2. Simulation methodology

We used the kMC program 'bigmac' [22], to which we have added elastic interactions between all defects [23], to simulate the motion of SIA clusters in a random distribution of solute atoms in α-iron.

The interaction between interstitial clusters and oversized impurities was calculated by linear elasticity theory. The interstitial cluster was modelled by a circular perfect dislocation loop with its BV in a close packed ⟨1 1 1⟩ direction perpendicular to the plane of the loop. The direction of easy motion for these clusters is parallel to the BV of the loop. The energy of interaction between a dislocation loop and an impurity atom, modelled as a centre of dilatation with relaxation volume ΔV, is then $E = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})\Delta V$, where $(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$ is the hydrostatic stress generated by the loop at the centre of the point defect.

The expression from linear elasticity theory [24] for the stress tensor of circular dislocation loops, like those we use to model our SIA clusters, has singularities at the circumference of the loop, corresponding to the core of the dislocation. To model the situation where the edge of an interstitial cluster approaches very close to an impurity, we have smoothed out the field near the core of the dislocation. Fig. 1 shows how the smoothed hydrostatic stress behaves along a cross-section of a loop consisting of 10 SIAs, with a radius of 0.22 nm. In the direction parallel to the axis of the loop, there is recent evidence from atomistic models that elasticity theory

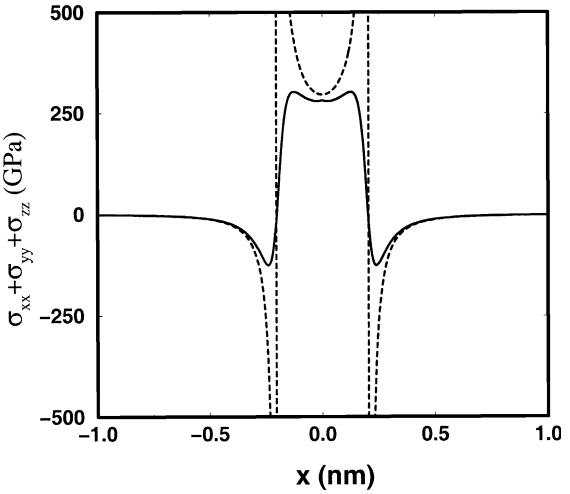

Fig. 1. Total hydrostatic stress on a cross-section through a 10 interstitial loop. Dashed line: according to linear elasticity theory [24]. Full line: with smoothing terms included to remove singularities.

underestimates the 'length' of the cluster, in that it has an extended cluster-of-crowdions shape [25]. Although this will slightly affect the range at which our interactions become strongly repulsive, it is unlikely to affect our results significantly, because the path lengths we consider between solute atoms are far greater than the length of the extended crowdion cluster.

For a SIA cluster placed in a randomly distributed field of impurities, Fig. 2 shows a sample potential energy landscape. We see numerous potential wells, with small potential barriers to entry, where the cluster passes close to an impurity. There are rarer occasions where

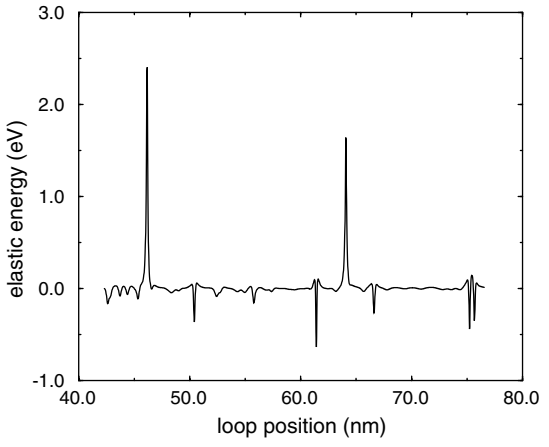

Fig. 2. Sample energy landscape for a cluster of 10 self-interstitial atoms in a random field of oversized impurities (formation volume +1.2% of the host atomic volume) at a concentration of 4.0×10^{20} cm^{-3} (corresponding to 0.47 at.%).

there is a very large potential barrier, when the loop attempts to go past an impurity located within its glide cylinder. These energy barriers are higher than the depth of the deepest energy wells. This is because all segments of the dislocation loop contribute constructively to the compression within the loop. Outside the loop only nearby segments will contribute tensile stresses, other segments will tend to contribute compressive stresses. The difference between the peak height and the maximum well depth indicates that there is a range of temperature at which loops will be able to pass over all energy wells, but will be able to surmount the energy barriers only very rarely. In this way they may become trapped between pairs of impurities over which effectively they cannot pass.

3. kMC results

This section describes our simulations of the characteristic motion of the interstitial cluster in a random field of solute atoms, the effective diffusion coefficient as a function of solute concentration, and the rate of reaction with a third, immobile species.

In all these simulations we have used an interstitial cluster of 10 SIAs, the size of some of the larger clusters formed in MD simulations of 40 keV cascades in α-iron [5], modelled by a circular dislocation loop with radius 0.22 nm, and oversized solute atoms with a relaxation volume of +1.2% of the host atomic volume, and a temperature of 1000 K. Under these conditions we expect the confinement between pairs of impurities as described in the previous section. Diffusion is governed by an Arrhenius law $D = \omega_0 a^2 \exp(-E_a/kT)$ with an exponential prefactor of $\omega_0 a^2 = 5.0 \times 10^{-4}$ cm^2 s^{-1}, and an activation energy of $E_a = 0.05$ eV, where ω_0 is the attempt frequency, and a is the diffusive hop length. Rotation to other close packed glide directions is also governed by an Arrhenius law, with an example attempt frequency of 0.75×10^{13} s^{-1}, and an example activation energy of 0.875 eV. Actual values for these reorientation rates are as yet unknown for such large clusters because the timescale involved is too large for MD studies to date. Consequently we restrict ourselves to describing the phenomena qualitatively. The possible dependence of the activation energy of rotation of clusters on the local impurity concentration [20] is not included in this study, but would further enhance the 3-D nature of the SIA cluster transport in an impurity field.

The trajectory of an interstitial cluster through the field of impurities, shows that in some cases, the cluster is confined between two points until a rotation occurs, although it is free to diffuse within that segment. In other cases, if impurities on its trajectory are so far away that it does not explore to this distance by the time it rotates, its 1-D diffusion is unconfined.

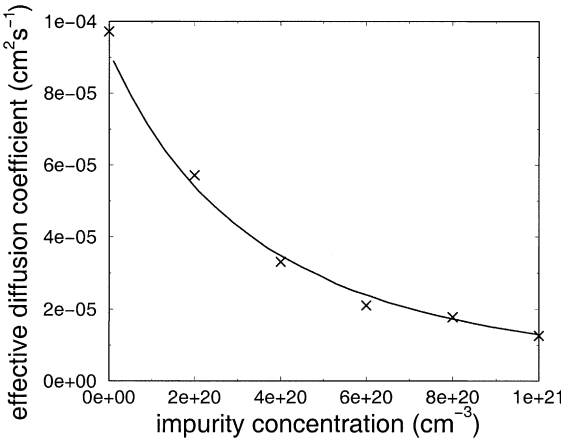

Fig. 3. Effective diffusion coefficient for a 10 SIA cluster of radius 0.22 nm in a field of oversized impurities (formation volume +1.2% of the host atomic volume) at a temperature of 1000 K as a function of impurity concentration. Crosses: kMC results. Line: as predicted by Eq. (9).

To measure the effect of this confinement by impurities on the overall transport, we simulated motion of SIA clusters to obtain numerous trajectories, each over a time of 2×10^{-8} s, from which mean squared displacements could be obtained, and since this is a sufficiently long time to allow a number of rotations on average, effective diffusion coefficients could be extracted. These effective diffusion coefficients are plotted as a function of impurity concentration in Fig. 3. They are compared to results of an analytical model, Eq. (9), which will be described below. Both show an initial insensitivity to impurities, when the concentration of impurities is so low that collisions with them are infrequent. At larger concentrations where confinement can occur within the typical distance between BV rotations, a drastic decrease in the diffusion coefficient occurs with increasing concentration.

4. Theoretical analysis

In this section we present an analytic model system that enables us to generalize the results of the kMC simulations. Consider a temperature where loops are freely able to pass over the energy wells arising from attractive interactions to impurities nearby, but where loops are unable to overcome the large energy barriers provided by direct traversals of an impurity atom. Until the BV of the loop rotates, we treat the transport as 1-D Brownian motion except that it is limited by the fact that it is always reflected when it encounters an impurity within its glide cylinder.

We now focus on estimating the effective diffusion coefficient in the presence of confinement, as a function

of the diffusion coefficient of the SIA cluster in a pure material, the solute concentration, and the frequency of rotations of the BV.

Assuming the impurities in the material are distributed at random, there will be a distribution of lengths of confinement given by

$$P(L) = \frac{4L \exp\left(-\dfrac{L}{L_0/2}\right)}{L_0^2}, \tag{1}$$

where $L_0 = 2/(\pi r_1^2 N)$ is the mean distance between impurities, r_1 is the radius of the loop, N is the concentration of impurities. Furthermore the initial position of the cluster within the confinement length L is selected from a uniform distribution.

For one-dimensional diffusion of a loop along the x-axis, confined to a 'box' between $x = 0$ and $x = L$, and starting at position x_0 within the box, the probability distribution for the location of the loop after time t is given by

$$p(x,t) = \frac{1}{L} + \frac{2}{L}\sum_{n=1}^{\infty} \cos\left(\frac{n\pi x_0}{L}\right)\cos\left(\frac{n\pi x}{L}\right)\exp\left(-\frac{n^2\pi^2 Dt}{L^2}\right). \tag{2}$$

To obtain an effective diffusion coefficient, the first quantity required is the mean squared displacement as a function of time while the loop remains confined in this box, averaged over all possible starting positions, x_0. We denote this mean squared displacement $g(L,t)$:

$$g(L,t) = \frac{1}{L^2}\int_0^L \int_0^L p(x,t)(x-x_0)^2 \,\mathrm{d}x\,\mathrm{d}x_0 = \frac{L^2}{6} - \frac{16L^2}{\pi^4}\sum_{n=0}^{\infty}\frac{\exp\left(-\dfrac{(2n+1)^2\pi^2 Dt}{L^2}\right)}{(2n+1)^4}. \tag{3}$$

It follows from Eqs. (3) and (1) that the mean squared displacement for a 1-D diffusing cluster positioned at random in this impurity field is

$$\bar{g}(t) = \frac{4}{L_0^2}\int_0^{\infty} g(L,t) L \exp\left(-\frac{2L}{L_0}\right)\mathrm{d}L. \tag{4}$$

This function has an initial gradient that is equivalent to that of diffusion in a pure medium, but saturates due to the confinement of all clusters in the field.

Now we examine the case where random infrequent rotations are introduced. Because they are not correlated, the probability $R_n(\tau)$ of having undergone rotations of the BV exactly n times after the system has evolved for time τ is given by the Poisson distribution:

$$R_n(\tau) = \frac{\tau^n \exp\left(-\dfrac{\tau}{t^*}\right)}{n!(t^*)^n}, \tag{5}$$

where t^* is the average time between rotations.

We can find the fraction $j_{n+1}(t,\tau)$ of all the particles, which have made $n+1$ rotations after time τ and have lived in that $n+1$ state for a time t. Clearly $j_{n+1}(t,\tau) = 0$ for $t > \tau$, so the interesting distribution is for $t < \tau$. Also, $j_0(t,\tau)$ is special because a loop that has never rotated must have been in that same state as long as the system has been evolving. Thus we have:

$$j_0(t,\tau) = R_0(\tau)\delta(\tau - t),$$
$$j_{n+1}(t,\tau) = R_n(\tau - t)\frac{1}{t^*}\exp\left(-\frac{t}{t^*}\right) \quad \text{for } t < \tau, \tag{6}$$

which is the fraction R_n that were able to convert to state $n+1$ at time $\tau - t$, multiplied by the rate of conversion $1/t^*$, multiplied by the probability of survival in this state for time t, $\exp(-t/t^*)$.

Each time a rotation occurs, a new pair of impurity endpoints is chosen, which we assume has never been sampled before, i.e. the cluster never returns to a confinement segment it occupied earlier. In that case, the mean squared displacement it undergoes from its new starting point along the new confined segment can simply be added to the total mean squared displacement for its entire journey.

We define $h(\tau)$ as the mean squared displacement after a time τ from the initial position of a loop randomly inserted in the impure crystal.

$$\frac{\mathrm{d}h(\tau)}{\mathrm{d}\tau} = \sum_{n=0}^{\infty}\int_0^{\tau} j_n(t,\tau)\frac{\mathrm{d}\bar{g}(t)}{\mathrm{d}t}\,\mathrm{d}t. \tag{7}$$

This general form for the rate of increase of the mean squared displacement may be explained as follows. For a given number of rotations we multiply the probability distribution function for the SIA cluster being confined for a time t in its current confinement segment, given that the total elapsed time is τ, by the rate of increase of mean squared displacement we would expect after being confined for this time t. We integrate this product over all confinement times and sum over all numbers of rotations.

Combining Eqs. (5)–(7), we get:

$$\frac{\mathrm{d}h(\tau)}{\mathrm{d}\tau} = \exp\left(-\frac{\tau}{t^*}\right)\frac{\mathrm{d}\bar{g}(\tau)}{\mathrm{d}\tau} + \frac{1}{t^*}\int_0^{\tau}\exp\left(-\frac{t}{t^*}\right)\frac{\mathrm{d}\bar{g}(t)}{\mathrm{d}t}\,\mathrm{d}t. \tag{8}$$

Integration of this equation predicts a range of possible behaviour. The limit in a pure material ($L_0 \to \infty$), corresponds to free diffusion, and the mean squared displacement is simply proportional to the elapsed time. The limit where no rotations are allowed ($t^* \to \infty$), in a

randomly distributed field of solute atoms, gives a saturation of mean squared displacement, indicative of the complete confinement. Other cases have an initial period of exploration where the mean squared displacement increases rapidly, until confinement sets in, when they reach a steady gradient, the clusters being dependent on rotations of the BV to explore further. To obtain effective diffusion coefficients at long times, corresponding to linear parts of these intermediate curves, we take the limit $\tau \to \infty$ and recalling that $\bar{g}(0) = 0$, we get:

$$\left.\frac{\mathrm{d}h(\tau)}{\mathrm{d}\tau}\right|_{\tau=\infty} = \frac{1}{t^{*2}} \int_0^\infty \exp\left(-\frac{t}{t^*}\right)\bar{g}(t)\,\mathrm{d}t. \tag{9}$$

When the lengths of paths between rotations are small compared to the mean distance between impurities, Eq. (9) reduces to the same diffusive behaviour as the loop would undergo in a pure crystal

$$D_{\mathrm{eff}} = \frac{1}{6}\left.\frac{\mathrm{d}h(\tau)}{\mathrm{d}\tau}\right|_{\tau=\infty} \approx \frac{D}{3}. \tag{10}$$

The factor of 3 comes from the fact that we have 'bent' 1-D motion into three-dimensions. The opposite limit where rotations are rare and the impurity concentrations are significant, results in an effective diffusion coefficient:

$$D_{\mathrm{eff}} = \frac{1}{6}\left.\frac{\mathrm{d}h(\tau)}{\mathrm{d}\tau}\right|_{\tau=\infty} \approx \frac{L_0^2}{24t^*} = \frac{1}{6(\pi r_1^2 N)^2 t^*}. \tag{11}$$

5. Implications and conclusions

We have argued that under certain conditions of temperature, frequency of rotation of SIA clusters, and concentration of solute atoms, the diffusivity of these clusters, and their ability to reach and react with other defects, may be severely curtailed by oversized solute atoms confining their one-dimensional excursions. Undersized impurities or oversized impurities at low temperatures may attract and trap SIA clusters. At higher temperatures we expect confinement by repulsion from oversized impurities at either end of a 1-D segment along which there is otherwise free diffusion. We have observed this confinement in the kinetic Monte Carlo simulations. Rotation of the BV eventually allows the SIA clusters to migrate over greater distances, but the effective diffusion coefficient can be much lower than that of a cluster diffusing in a pure material. The analytic model presented here successfully accounts for the reduction in effective diffusion coefficient found in the kMC simulations. The confinement to short segments accompanied by rotations of the BV destroys the long ballistic motion characteristic of typical 1-D transport of these interstitial clusters, making the diffusion effectively 3-D on a smaller spatial scale. This is possible even for clusters which rotate only very infrequently and would in a pure material be considered to have near 1-D transport. Near 3-D motion of the clusters in such alloys may prevent larger-scale microstructural features that rely on near 1-D transport.

The partially confined motion of SIA clusters able to undergo BV rotations presents further questions about how the impurity interaction affects the evolution of a high-energy radiation cascade in alloys. Because the SIA clusters will remain in the vicinity of where they were created for longer, near the vacancies and vacancy clusters, and because they will explore more three-dimensionally in that region, we expect higher levels of recombination within the cascade after the thermal spike. More generally, it should be possible to tailor the solute composition in reactor materials to take advantage of their reduction of the transport of SIA clusters, to design alloys resistant to high-energy radiation damage, for example enhancing recombination and thereby reducing swelling.

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