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Effect of self-interstitial cluster migration on helium diffusion in iron

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Abstract

The influence of self-interstitial cluster migration on defect evolution in irradiated α-Fe is studied using an object kinetic Monte Carlo model with input from *ab initio* and molecular dynamics calculations. Helium implantation and desorption is simulated during isothermal annealing under different conditions of temperature and sample thickness. Results are compared with experimental measurements existing in the literature. In particular, the effect of self-interstitial cluster migration on the fraction of He released during annealing is studied. The results of these calculations point towards a strong effect of traps in the nucleation and growth of He-vacancy clusters.
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1. Introduction

Due to neutron-induced transmutation reactions, high levels of helium can be accumulated in nuclear reactor structural materials. During operation at high temperature He atoms migrate and agglomerate with vacancies, which can severely deteriorate the lifetime of these materials. Consequently, He diffusion in metals has been studied for several decades [1,2]. However, there are still some unresolved issues in modelling He effects, as pointed out recently by Trinkaus and Singh [3].

The migration of self-interstitial clusters is one of the controversial points in modelling damage accumulation in metals. In Fe in particular it is known

from *ab initio* calculations [4,5] that small interstitial clusters are mobile, while the mobility of larger clusters has been studied with empirical potentials by several authors [6–8]. This information has then been used to study damage evolution using rate theory or kinetic Monte Carlo models. For example, Hardouin Duparc et al. [9] have shown that a rate theory model can describe electron irradiation experiments considering only single self-interstitial and single vacancies as mobile species and all clusters immobile. On the other hand Domain et al. [10] have shown that in order to reproduce neutron irradiation experiments it is necessary to introduce the mobility of self-interstitial clusters and the presence of traps for these clusters.

In this paper the effect of self-interstitial cluster migration on the desorption of He during isothermal annealing is addressed. In the first part of the paper the parameters used in the object kinetic

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Monte Carlo model (OKMC) are described. The results of the calculations for different conditions are presented in Section 3. Four different sets of parameters are considered: (a) only single self-interstitials are mobile, (b) small self-interstitial clusters are mobile, (c) all self-interstitial clusters are mobile and finally and (d) all self-interstitial clusters are mobile but traps are included. The results obtained and their consequences are discussed.

2. Kinetic Monte Carlo model

The migration mechanisms for He described by Fu and Willaime [11] have been implemented in an object kinetic Monte Carlo model. According to their calculations He at an interstitial position (He_i) can migrate with a barrier of 0.06 eV. When He is at a substitutional position (He_s) it can migrate through a vacancy mechanism with a barrier of 1.1 eV, or through the dissociative mechanism by which a substitutional He (He_s) moves to an interstitial position (He_i) leaving a vacancy (v) behind, described by the reaction: $He_s \rightarrow He_i + v$, with an activation barrier of 2.36 eV. A substitutional He can also move to an interstitial position through the replacement mechanism, also known as the kick-out mechanism [1,2]. This mechanism occurs in the presence of defects since it involves a self-interstitial atom (i) replacing the position of the He substitutional (He_s): $He_s + i \rightarrow He_i$.

Binding energies (E_b) of small Hev clusters were also calculated by Fu and Willaime [11] and have been included in the model. Values for different clusters are shown in Table 1. The values for larger cluster sizes are obtained from a fit. For the case of the binding energy of a vacancy to a $He_n v_{m-1}$ cluster, where n is the number of He in the cluster and m the number of vacancies in the cluster is:

$$E_b(v - He_n v_{m-1}) = E_f(v) + E_0(v)(m^{2/3} - (m-1)^{2/3}), \tag{1}$$

where, $E_f(v)$ is the formation energy for a single vacancy and $E_0(v)$ is a parameter obtained from fitting this equation to the binding energies of small cluster sizes in Table 1. The same type of relationship is used for the case of the binding of a He interstitial to a $He_{n-1} v_m$ cluster

$$E_b(He_i - He_{n-1} v_m) = E_f(He_i) + E_0(He_i)(n^{2/3} - (n-1)^{2/3}). \tag{2}$$

Regarding pure vacancies and self-interstitials the migration energies and binding energies used are those described in Ref. [4].

Using this input data, the desorption experiments performed by Vassen et al. [12] have been simulated. In these experiments Fe samples of different thickness were homogeneously implanted with He at different concentrations and annealed at constant temperature, monitoring in time the amount of He released.

Table 1
Binding energies for different He-v clusters from [11]

Reaction	Binding energy (eV)	Reaction	Binding energy (eV)
Hev → He + v	2.30		
Hev_2 → Hev + v	0.78	Hev_2 → v_2 + He	2.85
Hev_3 → Hev_2 + v	0.83	Hev_3 → v_3 + He	3.30
Hev_4 → Hev_3 + v	1.16	Hev_4 → v_4 + He	3.84
		He_2 → He + He	0.46
He_2v → He_2 + v	3.71	He_2v → Hev + He	1.84
He_2v_2 → He_2v + v	1.61	He_2v_2 → Hev_2 + He	2.75
He_2v_3 → He_2v_2 + v	1.04	He_2v_3 → Hev_3 + He	2.96
He_2v_4 → He_2v_3 + v	1.32	He_2v_4 → Hev_4 + He	3.12
		He_3 → He_2 + He	0.81
He_3v → He_3 + v	4.59	He_3v → He_2v + He	1.83
He_3v_2 → He_3v + v	1.85	He_3v_2 → He_2v_2 + He	2.07
He_3v_3 → He_3v_2 + v	1.80	He_3v_3 → He_2v_3 + He	2.91
He_3v_4 → He_3v_3 + v	1.57	He_3v_4 → He_2v_4 + He	3.16
		He_4 → He_3 + He	0.84
He_4v → He_4 + v	5.52	He_4v → He_3v + He	1.91
He_4v_2 → He_4v + v	2.30	He_4v_2 → He_3v_2 + He	2.36
He_4v_3 → He_4v_2 + v	2.03	He_4v_3 → He_3v_3 + He	2.57
He_4v_4 → He_4v_3 + v	1.97	He_4v_4 → He_3v_4 + He	3.05

The simulations start with a homogeneous distribution of He at interstitial sites, vacancies and self-interstitials. TRIM [13] calculations show that for the energies used in these experiments a total of approximately 200 Frenkel-pairs per implanted He is expected, for a threshold displacement energy of 40 eV. Assuming this initial condition, the evolution of these defects is simulated at room temperature until steady state is reached. After the room temperature simulation, He desorption during isothermal annealing is simulated for the temperature conditions of the experiments in Ref. [12].

Despite the fact that our knowledge of defect energetics in the Fe–He system is quite large, there are still some uncertainties. In particular the behavior of self-interstitial clusters in Fe is not complete, as mentioned above. Calculations using empirical potentials were the first ones to predict that self-interstitial clusters in Fe are mobile [6–8]. *Ab initio* calculations [4,14] show that small clusters of size up to 4 are of $\langle 110 \rangle$ type and move with migration barriers similar to that of single self-interstitials, on the order of 0.3–0.4 eV. For larger self-interstitial clusters the $\langle 111 \rangle$ type is considered to be more stable, and according to calculations based on embedded atom potentials, they migrate with a barrier that is lower than for $\langle 110 \rangle$ type of clusters, on the order of a 0.1 eV [6–8].

Previous OKMC calculations [10,15] have shown that in order to reproduce experimental measurements of irradiated Fe using kinetic models, it is necessary to introduce some type of trapping for these mobile self-interstitial clusters, although the origin of this trapping is still not fully understood. There are several possible mechanisms that could explain this effect. On one hand, the presence of impurities such as carbon could be responsible for this phenomenon. However, *ab initio* calculations [16] point towards a repulsive interaction between self-interstitials and carbon atoms. On the other hand loops of type $\langle 100 \rangle$ are observed under TEM in irradiated Fe [17]. The mechanism to form these clusters is still being debated, although some molecular dynamics simulations point to a reaction between $\langle 111 \rangle$ loops to form these $\langle 100 \rangle$ loops [18], which have a very low mobility. This could be another possible mechanism of trapping of mobile self-interstitials clusters. Finally, OKMC calculations including elastic interactions between mobile self-interstitials and spherical impurities also show an effective trapping for these defects [19]. Since this issue is still not resolved, the OKMC model has

been used to explore the effect that self-interstitial cluster migration could have on He diffusion.

3. Results

Fig. 1 shows the fraction of He released as a function of time obtained for a 2.6 μm thickness sample annealed at 667 K for an initial He atomic concentration in parts per million (ppm) of 0.109. The curves shown are the result of three different assumptions for self-interstitial cluster migration: (a) only single self-interstitial is mobile, (b) single self-interstitial (i), self-interstitial clusters of size two (i_2) and of size three (i_3) are mobile and (c) self-interstitial clusters of all sizes are mobile. The first case represents the assumption used by Hardouin Duparc et al. [9] in their rate theory model to reproduce electron irradiation experiments. The second case is an effective way of considering that, either all $\langle 111 \rangle$ loops react to form $\langle 100 \rangle$ immobile loops, or that they interact with impurities such as carbon that trap these loops. The last case is equivalent to not including any form of trapping for self-interstitials of any size or type. For this last case the mobilities used are the *ab initio* values of [4] for sizes 1, 2 and 3, and the values obtained by Soneda [8] for clusters larger than 3.

It is clear from this figure that the mobility of self-interstitial clusters plays a very significant role in He desorption. Helium is released at very short times when all self-interstitial clusters are considered immobile. Including mobile self-interstitial clusters delays the release of He by orders of magnitude.
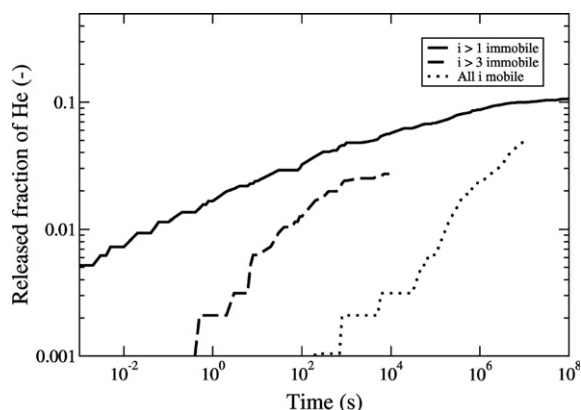

Fig. 1. Influence of self-interstitial cluster migration on He desorption profile. Calculations for annealing temperature 667 K, sample depth of 2.6 μm and He atomic concentration in ppm of 0.109.

Fig. 2 shows the released fraction of He obtained from the OKMC calculations with all self-interstitial clusters mobile (dashed line) together with the experimental data obtained by Vassen et al. for annealing temperature of 667 K. Clearly the simulations with these conditions fail to reproduce the experimental observations. The time scale for He release is too long as compared to the experiment, and the total fraction is also much lower. The results from the simulations when all self-interstitial clusters are immobile (also shown in Fig. 2) are in better agreement with the experiments, although it still underestimates the fraction of He released.

In order to understand the mechanisms involved in He migration during the annealing, the total number of He jumps has been followed in time. Fig. 3 shows the number of He jumps for cases (a), when only single self-interstitials are mobile, and (c), when all self-interstitial clusters are mobile. At the beginning of the high temperature anneal both cases have the same concentration of He at substitutional sites, and there is no He at interstitial sites, since during the room temperature anneal all He moves to vacant sites produced by the irradiation. Therefore the migration of He can be only through the replacement mechanism, the vacancy mechanism or the dissociative mechanism. When all self-interstitial clusters are considered mobile, these clusters migrate and annihilate at the surface at room temperature and almost no self-interstitials are present at the beginning of the 667 K isothermal anneal. Fig. 3 shows that when self-interstitial clus-
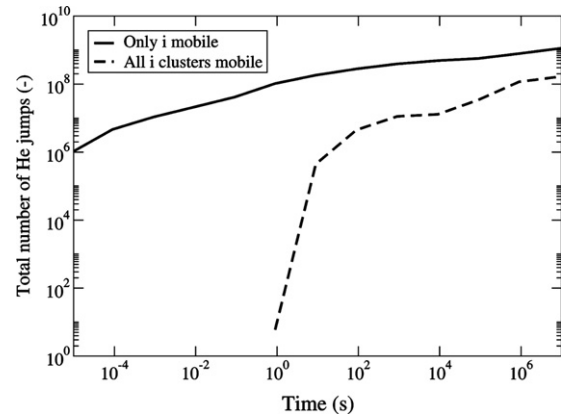
Fig. 3. Total number of He jumps when all interstitials are mobile (dashed line) and when only single interstitials are mobile (solid line).

ters are mobile, He does not start to move until times of about 1 s, while in the case when only single self-interstitials are considered mobile He starts moving at very short times, lower that 10^{-5} s. This clearly evidences the role of self-interstitials during He desorption and strongly suggests that the replacement mechanism is responsible for He migration at the early stages of annealing when clusters are immobile. Indeed, since self-interstitials are highly mobile, at this time scale the only possible mechanism that can be active is the replacement. This mechanism however, is not active when all self-interstitial clusters are mobile, since they recombine at the surface at room temperature. In this case He does not start to move until later times, when the dissociative mechanism can occur. This behaviour is also observed at different conditions of temperature and He concentration.

From the results shown in Fig. 2 it seems that a better agreement with the experiment is obtained when self-interstitial clusters are considered immobile. This assumption has been used successfully by Hardouin Duparc et al. [9] to simulate electron irradiation of Fe within a rate theory model. In contrast, Domain et al. [10] have shown that it is necessary to include the mobility of self-interstitial clusters and the presence of traps for these clusters to be able to reproduce neutron irradiation experiments on Fe. Using the same approach, traps for self-interstitial clusters with a binding energy of 1.0 eV have been included in our model of the Fe–He system. Calculations were performed for two different conditions, annealing at 667 K of an irradiated sample of 2.6 μm depth and a He atomic
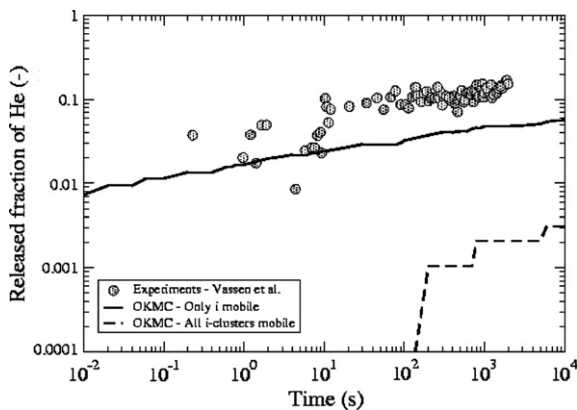

Fig. 2. Released fraction of He for annealing temperature of 667 K, sample depth of 2.6 μm and He atomic concentration in ppm of 0.109. Comparison between experimental data from Vassen et al. [12], and calculations from OKMC with only single self-interstitial mobile (solid line) and with all self-interstitial clusters mobile (dashed line).
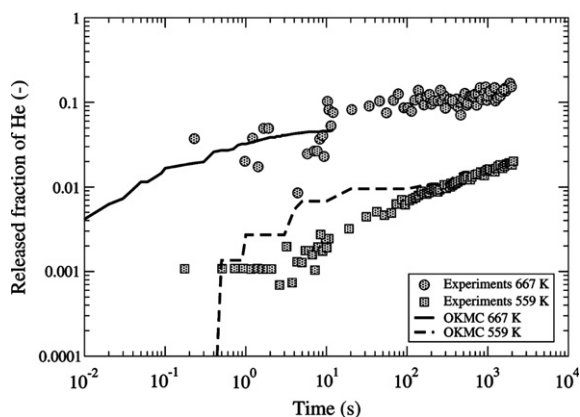
Fig. 4. Released fraction of He for annealing at 667 and 559 K. Comparison between experiments (symbols) and simulations (lines) considering all self-interstitial mobiles and the presence of traps (atomic concentration of traps in ppm of 12).

concentration in ppm of 0.109, and for a case of annealing at lower temperature, 559 K. For this last case the sample depth was 2.5 μm and the initial He atomic concentration in ppm is 1.39. The simulations were performed with an atomic concentration of traps in ppm of 12. Fig. 4 shows the results of the simulations under these conditions (lines) compared with the experimental measurements (circles). Clearly a much better agreement with the experimental observations is now obtained.

4. Conclusions

The desorption of He from Fe has been studied under different conditions of temperature and He concentration using object kinetic Monte Carlo. In particular, the effect of self-interstitial cluster migration on the release of He has been studied. The calculations show a strong effect, with a delayed release of He when self-interstitial clusters of all sizes are considered mobile. The replacement mechanism, by which a He substitutional is moved to a He interstitial position with the aid of a self-interstitial atom, is responsible for a fast He release at early times in the annealing. Experimental results obtained by Vassen et al. show He released at short times (around 0.2 s for the case of 559 K), which could be explained by this mechanism. Results from calculations are closer to experimental measurements when all clusters are considered immobile, however, the calculations still underestimate the released fraction. Introducing traps for self-interstitial cluster migration provides a better fit to the experimental observations, in agreement with the

OKMC model developed by Domain et al. [10]. Our results indicate that the role of traps for self-interstitial clusters in crucial not only for the evolution of these types of defects, but also for the migration and nucleation of He and He-v clusters.

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