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Diffusion coefficients and thermal stability of small helium–vacancy clusters in iron

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Abstract

Recent studies of helium clustering kinetics in bcc iron have revealed noticeable mobility of small He–vacancy complexes, which are commonly thought of as immobile. Here, the lifetimes and diffusion coefficients of small He–vacancy clusters were quantified. These kinetic parameters were estimated for clusters of different sizes and compositions by lattice kinetic Monte-Carlo using *ab initio* data for helium and vacancy interactions energies. It is shown that nanosized He–vacancy clusters have high thermal stability. It is also found that the diffusion coefficients of some small clusters are indeed very high, being at 573 K only 1–2 orders of magnitude lower than the diffusion coefficient of a monovacancy. Finally, it is demonstrated how the coupling of Monte-Carlo numeric experiments with the rate theory approach can be used for the estimation of the rate theory parameters, such as the defect and cluster agglomeration rates.

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1. Introduction

Irradiation of ferritic–martensitic steels in fusion and advanced nuclear facilities (such as accelerator-driven system) is accompanied by the production and accumulation of noticeable amounts of helium (up to hundreds or even thousands of appm). At elevated temperatures this results in the formation of He gas bubbles (that is, clusters of vacancies (v) containing a certain amount of He atoms inside), which are known to cause swelling and the degradation of mechanical properties of irradiated steels, bearing a risk of material failure. In order to predict the kinetics of bubble growth in a broad range of time and length scales relevant for the operation of reactor structural components, one usually relies on analytical treatments in the framework on the chemical rate theory [1,2], or on appropriate simulation techniques, such as object kinetic Monte-Carlo (see e.g. [3,4]). In order not to be lost in details, these approaches retain only the most important features of the microstructure kinetic in irradiated materials. Hence, when modelling any particular aspect of defect kinetics, it is important not to lose essential defect reactions and to use reliable input parameters (defect diffusivities, reaction rates, etc.), because otherwise the modelling output risks to have nothing in common with the reality.

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As applied to helium bubble kinetics in irradiated ferritic steels, a recent study [5] indicates that a number of important details of the early stages of helium clustering kinetics is overlooked in the modern rate theory approaches. For example, a common assumption is that the diffusion of He atoms occurs via the vacancy mechanism, while the helium–vacancy clusters formed as a result of He atom collisions are immobile starting from the smallest cluster sizes. The validity of these assumptions is practically impossible to check experimentally, because the clusters smaller than ~1 nm cannot be observed directly (e.g. by transmission electron microscopy) and are revealed only by indirect experimental techniques, e.g. small angle neutron scattering, thermal helium desorption, or positron annihilation. However, it was discovered [5], when modelling the annealing of a solid solution of vacancies and He atoms, that the picture is probably more complicated. In particular, it has been found that the transport of substitutional He occurs most probably in the form of mobile Hev_2 complexes (one helium atom in a divacancy), which move in a bound state via the ring mechanism. Moreover, small He_nv_m clusters (with $m > n$) demonstrated quite high mobility at least up to $m = 4$–5 and gave noticeable contribution to He transport at helium concentrations exceeding 100 appm.

In simulations described above were performed applying a lattice kinetic Monte-Carlo (LKMC) approach [6], which, being an atomic-level simulation technique operates at relatively short time and length scales. In order to better understand the role played by small Hev clusters in the 'long-term' bubble kinetics, it is desirable, in compliance with the modern multiscale modelling approach, to explicitly include the relevant features of small Hev_m cluster behaviour into the rate theory or object KMC description. In order to do that, one must, first of all, quantify the relevant parameters of Hev_m clusters that are used by these techniques. These parameters can be roughly divided into two classes. The first class includes the 'inherent' parameters of clusters, such as diffusion coefficients and thermal lifetimes in particular material. In order to specify the parameters of the other class, such as collision rates of mobile clusters and point defects, one has to consider the properties of the ensemble of simulated defects and clusters.

The observations of cluster mobility in [5] were mostly qualitative. The primary aim of this paper is to give quantitative estimates of diffusion coefficients and thermal lifetimes of small Hev_m complexes in alpha-iron, which is the basic component of ferritic steels. For this purpose LKMC simulations were used based on very reliable interaction energies and diffusion barriers of vacancies and He atoms in iron, predicted by first-principles quantum mechanical calculations. In addition, it was demonstrated on a simple example, how the defect collision rates can be determined from fitting the relevant rate theory parameters to LKMC simulations.

2. Computational methods

The simulation of diffusion coefficients and lifetimes of small He–vacancy clusters was performed using the lattice kinetic Monte-Carlo code CASINO-LKMC described e.g. in [7]. For the purposes of the current study the code was supplemented with a special utility that allowed to trace the diffusion and integrity of individual Hev clusters and to extract cluster lifetimes and diffusion coefficients from the raw simulation output. Simulations were performed on a body-centred cubic (bcc) lattice, as appropriate for alpha-iron. The simulation box had periodic boundary conditions in all directions and included typically about 520 thousands of lattice sites. The binding energies and jump barriers of vacancies and helium atoms were borrowed from the recent first principles calculations [8–10].

The numerical solution of the rate equations has been performed using specially developed flexible environment, the central part of which is a nonlinear differential equation solver, implementing four algorithms (Runge–Kutta, Adams, Gear and Petzold-Gear) suitable for systems of stiff ordinary equations. A set of nonlinear differential equations to be solved at each time step is formed on the fly, using a list of possible reactions between simulated entities (vacancies, interstitials, vacancy complexes, etc.). Therefore any of the allowed reactions can be easily excluded or included in consideration, allowing direct evaluation of contributions from various defect interaction mechanisms and straightforward imitation of KMC numeric experiments.

3. Results

Here clusters consisting of up to five vacancies were considered because such empty sites (but not all) could be filled with helium atoms. It is assumed during calculations that helium is located strictly on

lattice sites. This is not necessarily true for helium in real Hev clusters; for example, in Hev_2 complex the lowest energy of the helium atom is achieved when it is located in a split position between two vacant sites [9]. However, this discrepancy is not so important for the conclusions about cluster mobilities and lifetimes, because at finite temperatures the He atoms can easily move inside the cluster [9] and can be found on any vacant site with the frequency determined by the relative energetic profitability of the site for a He atom. On the other hand, the description of vacancy jumps along the cluster surface and out of the cluster (providing, respectively, cluster movement and dissociation) involves the jump barriers calculated in [9] for Hev clusters and take into account that vacancy jumps can be accompanied by He atom shifts.

3.1. Lifetimes and diffusion coefficients of vacancy clusters and He–vacancy clusters

When the energies of interaction between vacancies and helium atoms constituting a Hev cluster are known (e.g. from *ab initio* calculations), the cluster lifetimes and diffusion coefficients can be, at least in principle, calculated analytically, provided the clusters live sufficiently long to pass many times through various possible cluster configurations. Then the probability to meet a certain cluster configuration is determined by the free energy of this configuration and the calculation of cluster lifetime and mobility is reduced to the detailed bookkeeping of weighted contributions of all possible cluster configurations to elementary events that lead to cluster dissociation or 'centre of mass' shift. Such analytical estimates of lifetimes and diffusion coefficients for several simplest clusters can be found in Table 1. Both here and in LKMC calculations described below the vacancy and helium interaction energies as listed in [5] were used as well as a vacancy migration energy in the bulk E_m^V of 0.67 eV, an atomic vibration frequency v_0 of 10^{13} Hz, an iron lattice parameter of 0.286 nm and a temperature T of 573 K.

Unfortunately, already for clusters containing more than three vacancies the analytical estimates become practically unmanageable without the development of appropriate numerical tools. On the contrary, in lattice kinetic Monte-Carlo simulations the statistical averaging of possible cluster configurations, as required for the determination of cluster lifetime and mobility, occurs automatically and requires no additional simplifying assumptions about the frequencies of individual cluster configurations. In order to estimate the kinetic parameters of a cluster He_nv_m, n He atoms were simply distributed randomly over a compact cluster of m empty lattice sites (with $m > n$) and let the unoccupied vacancies perform diffusion jumps with probabilities determined by Boltzmann factors appropriate for each particular jump. As the employed Monte-Carlo code estimates the average

Table 1
The average cluster lifetimes and diffusion coefficients for different vacancy and He–v clusters at 573 K, as predicted by Monte-Carlo simulations and analytical estimates

Cluster	Thermal lifetime (s)	Diffusion coefficient ($nm^2\ s^{-1}$)	Thermal lifetime (s)	Diffusion coefficient ($nm^2\ s^{-1}$)	Thermal lifetime (s)	Diffusion coefficient ($nm^2\ s^{-1}$)
	No barrier correction		With barrier correction			
	Kinetic Monte-Carlo results				Analytical evaluation	
v	–	1.04×10^{6}	–	1.04×10^{6}	–	1.03×10^{6}
v_2	2×10^{-6}	7.5×10^{4}	2×10^{-6}	9.0×10^{5}	2.0×10^{-6}	8.61×10^{5}
v_3	4×10^{-6}	8.5×10^{4}	5×10^{-7}	2.6×10^{7}	5.1×10^{-7}	2.41×10^{7}
v_4	8×10^{-5}	8.5×10^{3}	1.5×10^{-6}	4.9×10^{6}	–	–
v_5	–	–	1.8×10^{-6}	1.7×10^{6}	–	–
Hev_2	1.5×10^{-2}	7.8×10^{3}	7.9×10^{-4}	8.5×10^{4}	8.2×10^{-4}	1.00×10^{5}
Hev_3	>2.5	4.5×10^{3}	1.4×10^{-2}	1.1×10^{5}	–	–
Hev_4	0.15	3.6×10^{3}	1.3×10^{-2}	1.2×10^{5}	–	–
Hev_5	0.3	0.8×10^{3}	$>5.6\times10^{-2}$	1.1×10^{4}	–	–
He_2v_3	>0.25	1.6×10^{4}	>1.1	2.3×10^{4}	–	–
He_2v_4	0.26	0.7×10^{3}	>1.5	7.8×10^{3}	–	–
He_2v_5	>1	2.5×10^{2}	>6.5	1.3×10^{2}	–	–
He_3v_4	>0.1	0.06	>1.3	0.3	–	–
He_3v_5	–	–	>112	1.2	–	–
He_4v_5	–	–	>73	0.3	–	–

time for each performed jump and evaluates a position of the cluster centre, the trajectory of each cluster can be traced jump by jump until a predefined limit of vacancy jumps (typically 50–100 millions) is reached or until the cluster dissociates. Having in mind that according to *ab initio* calculations helium atoms and vacancies are bound to each other up to the second nearest neighbour (NN) separations, a cluster dissociation is assumed to occur when at least one vacancy or He atom is found at a larger than 2NN separation from any other vacancy/He atom that belonged to the initial cluster.

In practical calculations the dissociation of a cluster could occur before a predefined limit of jumps was reached. In this case the original cluster configuration was automatically restored and a new diffusion campaign was started without stopping the run, until the predefined limit of steps was reached. After each run, histograms of the occurrence frequencies of the ratio $\langle r^2\rangle/t$ (where $\langle r^2\rangle$ is the random mean square shift of the cluster centre during time interval t) were generated using the data accumulated in all diffusion campaigns within the same run. The histograms were fitted by an appropriate Gaussian distribution that included the cluster diffusion coefficient D_{cl} as the only fitting parameter.

Table 1 summarizes the values obtained for diffusion coefficients of several small vacancy and He–vacancy clusters at 573 K. As demonstrated in [10], the jumps of matrix atoms at the surface of the cluster, which result in cluster shape change and movement, can have noticeably lower activation barriers than the vacancy migration energy in the bulk. In order to clarify the effect of the 'in-cluster' jump barrier decrease, two series of KMC runs were performed, either assuming the same barriers for vacancy jumps within the cluster and in the bulk, or taking into account the reduction of the barrier for atomic jumps into 'in-cluster' vacancies by 0.16 eV per each vacant site in the lens of nearest neighbour lattice sites around the saddle point of the jump (the value was taken as a best fit to the results of [10]).

It should be noted that due to the limited number of campaigns used for the estimation of cluster lifetime, the variance of the lifetime distribution could be quite large. Indeed, even for the 'short-living' vacancy clusters, where the lifetime statistics is sufficiently rich (several thousands of diffusion campaigns per KMC run), the variance in the lifetimes was quite broad and some clusters managed to dwell an order of magnitude longer than the average value. In case of relatively stable He–v clusters, where only several campaigns within KMC run occurred, the lifetimes cited in Table 1 give at best order of magnitude estimates. Some clusters did not dissociate at all and for them only the duration of the corresponding KMC run as a lower bound of the lifetime is given (in this case a value in Table 1 is preceded with '>' sign).

In contrast to lifetimes, the database for the determination of cluster diffusion coefficients is abundant and the main uncertainty in the estimation of D_{cl} comes from the fitting procedure itself. At present, the fitting error is mostly within 1–2%, except for the slowest clusters, where it could reach 10%.

As can be judged from Table 1, without the barrier redaction for the internal vacancy jumps the purely vacancy complexes move at 573 K at a rate, which is only 2–3 orders of magnitude lower than that of monovacancy. When the internal barrier decrease is taken into account, the vacancy clusters are as fast as or even faster than a monovacancy, just as it has been predicted in [10]. However, the low stability against thermal dissociation at the considered temperature makes the contribution of purely vacancy clusters to self-diffusion rather ethereal.

The addition of helium efficiently stabilizes vacancy clusters with respect to thermal dissociation. On the other hand, the cluster mobility remains quite high, though lower than that of a vacancy cluster with the same number of vacancies, because the vacancies occupied by He atoms are not allowed to jump. These results quantify earlier observations [5] that small He–v clusters are mobile at 573 K.

3.2. Agglomeration rates for small vacancy clusters

As discussed in the introduction, the rate theory parameters that describe interaction of various defects (e.g. the rates of collisions of vacancies and various He–vacancy clusters) cannot be calculated by LKMC directly, as carried out in Section 3.1. However, it is possible to determine these parameters, combining rate equation theory and LKMC simulations. The advantage of this approach is the possibility to perform numerical experiments that are specially 'tailored' for the determination of the relevant encounter rates, which is impossible in the real life experiments. Below such coupling of two

methods is demonstrated for a simple case, when dealing with vacancy clustering only.

Let consider a system that initially contains a certain concentration C_0 of mobile mono-vacancies. During the annealing of the system, moving vacancies collide with each other and can form bigger clusters. Strictly speaking, the variety of possible reactions is broad, but in order to make the description of the system analytically tractable, introduction of a condition (clusters with the sizes above a certain limiting value are removed from the system immediately as they are formed) may be required. For example, assuming that all clusters containing more than three vacancies are eliminated from the system, the set of allowed defect reactions is reduced to that shown in Fig. 1 (in order to additionally simplify matters, no thermal decomposition of clusters is permitted). In terms of the rate theory, the annealing of such vacancy system can be described by the following set of rate equations:

$$\frac{dC_1}{dt} = -2k_1C_1^2 - k_2C_1C_2 - k_3C_1C_3 - 3k_5C_1^3, \quad (1)$$

$$\frac{dC_2}{dt} = k_1C_1^2 - k_2C_1C_2 - 2k_4C_2^2 - k_6C_2C_3, \quad (2)$$

$$\frac{dC_3}{dt} = k_5C_1^3 + k_2C_1C_2 - k_3C_1C_3 - k_6C_2C_3 - 2k_7C_3^2, \quad (3)$$

where C_m is the concentration of clusters containing m vacancies ($m = 1$–3) and k_i is the agglomeration rate for the ith reaction (according to the nomenclature of Fig. 1). Supplementing equation set (1)–(3) with the initial conditions of $C_1(t = 0) = C_0$ and vanishing C_2 and C_3, an example of the rate theory description of a vacancy annealing experiment can be obtained, which can be realized in a specially tailored LKMC simulation (see below).

Evidently, the kinetics of vacancies and vacancy cluster concentration depend on the selected values of agglomeration rates, which are determined in the literature mostly analytically and expressed either in terms of diffusion coefficients and capture radii (see e.g. [11]), or in terms of geometry factors and jump frequencies [12]. However, analytical estimates from geometrical considerations inevitably imply that at least two additional assumptions are fulfilled, namely: (i) there are no correlations between the positions of colliding species and (ii) vacancy jumps leading to the shape change of clusters are much more frequent than either cluster thermal decomposition events, or vacancy–cluster and cluster–cluster collisions. Assumption (ii) guarantees that the cluster size does not change for sufficiently long time in order to permit the estimation of the probability of different cluster configurations in terms of the relative energy proficiency of these configurations.

1. $V + V \Leftrightarrow V_2$
2. $V + V_2 \Leftrightarrow V_3$
3. $V + V_2 \Rightarrow \varnothing$
4. $V_2 + V_2 \Rightarrow \varnothing$
5. $V + V + V \Leftrightarrow V_3$
6. $V_2 + V_3 \Rightarrow \varnothing$
7. $V_3 + V_3 \Rightarrow \varnothing$

Fig. 1. Reactions between vacancies and vacancy clusters (up to trivacancies). Symbol $\varnothing$ indicates that the resulting cluster is removed from the system.

Even when the assumptions above hold true, the analytical calculations of agglomeration rates are complicated for the collisions of defects bigger than mono-vacancies, but in the simplest case where two vacancies agglomerate into a divacancy the agglomeration probability can be estimated simply as

$$k_1 = Jv_0 \exp(-E_m^V/k_BT),$$

where J is the number of vacancy jumps that result in the transformation of two separate vacancies into a divacancy, E_m^V is the activation barrier for these 'last jumps', which can be assumed equal to the vacancy migration energy in the bulk, and k_B is the Boltzmann factor. As already mentioned above, two vacancies form a bound pair (divacancy) at both 1NN and 2NN separations. A straightforward estimate of the number of jumps in bcc lattice converting two separated vacancies into either of these divacancy configurations gives $J = 56$. Using the other relevant values as cited above, $2k_1 \approx 1.4 \times 10^9\ s^{-1}$ was obtained.

An alternative way to estimate the defect agglomeration rate is the use of numerical LKMC experiment, where no *ad hoc* assumptions concerning the defect stability or positional correlations are required, while the restrictions on the number of permitted defect reactions can be implemented algorithmically. Here, several LKMC simulations of the annealing of monovacancy solid solution with initial concentration of vacancies $C_0 = 10^{-3}$ have been performed. The annealing temperature of 573 K was used. In order to comply with the described analytical scheme, all clusters formed during the annealing by vacancy–vacancy reactions were removed immediately as they were formed (a possibility of such

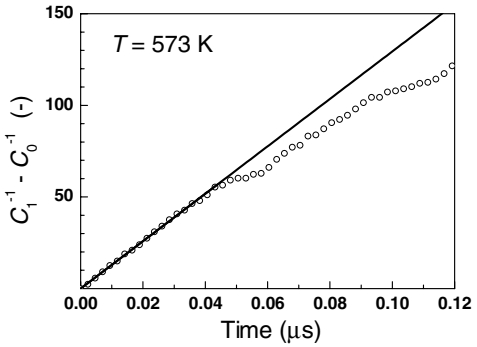

Fig. 2. Monovacancy annealing kinetics governed by monomer collisions. Scatter points represent KMC simulations, solid line shows a linear fit with $k_1 = 0.7 \times 10^9\ s^{-1}$.

artificial removal of defect clusters is implemented in CASINO-LKMC).

The obtained vacancy annealing curve, Fig. 2, was fitted using the exact solution of Eq. (1),

$$C_1^{-1} = C_0^{-1} + 2k_1 t,$$

obtained under assumption that all agglomeration rates except k_1 vanish. The value obtained by the fitting, $2k_1 \approx 1.3 \times 10^9\ s^{-1}$, nicely matches the analytical estimate. It is interesting to mention that during LKMC simulations triple collisions (reaction 5) were observed persistently, but at much lower rate (approximately by two orders of magnitude) than pair collisions, so they were not taken into account during fitting.

4. Conclusions

In this paper the lifetimes and diffusion coefficients of small He–vacancy clusters were estimated with the help of the lattice kinetic Monte-Carlo technique that used *ab initio* data for helium and vacancy interactions energies as an input. A simple example of how the rate of various agglomeration reactions between point defects and their clusters was estimated by coupling LKMC and the rate theory approaches. Based on the results obtained, the following conclusions can be drawn:

1. Small purely vacancy clusters in iron (up to at least a pentavacancy) have diffusion coefficients comparable to or higher than that of monovacancies. However, at the reactor relevant temperature of 573 K these clusters are very unstable with respect to thermal dissociation and cannot give noticeable contribution to self-diffusion.
2. The addition of helium to small vacancy complexes efficiently stabilizes these complexes, fully in compliance with the modern notion concerning the effects of He. However, in contrast to the current notion, small He–v clusters are mobile at 573 K, their diffusion coefficients being only 1–2 orders of magnitude lower than that of mono-vacancies.
3. A combination of lattice KMC and rate theory approaches can be used as an efficient method for numerical estimation of agglomeration rates of mobile point defects and defect clusters.

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