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Kinetic properties of small He–vacancy clusters in iron

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ABSTRACT

The paper deals with the lattice kinetic Monte-Carlo simulation of the mobility of small vacancy and vacancy–helium clusters in iron in the temperature range of 200–500 C. The input parameters characterizing vacancy and helium binding and mobility were taken from recently published *ab initio* calculations. The temperature dependence of diffusion coefficients and lifetimes of small clusters have been numerically estimated.

1. Introduction

Irradiation of ferritic–martensitic steels in fusion and advanced nuclear facilities (such as accelerator-driven system) is accompanied with accumulation of noticeable amounts of both point defects and helium atoms. At fusion reactor operation temperatures this results in the formation of helium bubble arrays, which are largely responsible for swelling and embrittlement degrading material mechanical properties. For reliable predictions of bubble kinetics one should understand the physical mechanisms of He bubble formation. Especially important is the kinetics of sub-nanometer helium–vacancy (He–V) clusters which act as helium bubble nuclei. Such clusters are too small to be observed in transmission electron microscope and atomistic simulations are often used to clarify the kinetics of the early stages of He bubble nucleation [1–4].

Helium is known to be poorly soluble in iron, while its mobility in interstitial position is very high (the *ab initio* estimate for the migration barrier of interstitial He in alpha-iron is ~0.06 eV [5]). Hence, even when a helium projectile with the energy in MeV range stops in interstitial position, it can be nearly immediately captured by a vacancy in a vacancy-rich core of a displacement cascade, inevitably created at the projectile end-of-range. Moreover, an interstitial He atoms escaping the cascade vacancies can quickly finds either a vacancy (in fusion environment up to 10^4 vacancies are created per one He atom implanted in steel, even taking into account possible direct in-cascade recombination of primary damage) or another sink (bubble, dislocation, grain boundary, etc). The dissociation of substitutional He requires ~2.4 eV [5], making the dissociative mechanism of He diffusion (as proposed e.g. in [6]) virtually impossible [7]. Hence, one can expect that a large share of He transport, as needed for the growth of small He–vacancy clusters, is due to substitutional He and is promoted by vacancies.

Our previous lattice kinetic Monte-Carlo (LKMC) simulation of He clustering [4] has demonstrated that the diffusion of substitutional He atoms involves the formation of mobile HeV_2-complexes (that is – substitutional He plus a free vacancy). Moreover, small He_nV_m clusters (with $m = 4$–5 and $n < m$) were shown to be quite mobile at 300 °C [3]. However, neither the cluster migration energies, nor their dissociation energies have been estimated up to now.

Here we report the diffusion coefficients and lifetimes of small vacancy and He–V clusters in iron in the temperature range of 200–500 °C, calculated using LKMC, which is a technique particularly suited for the simulation of cluster mobility.

2. Simulation details

The simulations have been performed using the code CASINO-LKMC [4,8], which is based on the 'pair bond' approximation for the total crystal energy. Correspondingly, the necessary input parameters for the code are the pairwise binding energies of individual atomic species, that is – the vacancies and substitutional helium atoms at separations up to the second nearest neighbour (NN). The account of interactions at the 2NN separation is necessary for the correct description of He–V cluster diffusion, which involves noticeable contribution from the so-called 'ring mechanism' [3]. Here we have used the binding energies predicted by *ab initio* calculations for small vacancy [9–11] and vacancy–helium [5] clusters in bcc iron. A summary of input parameters can be found in Table 1 of our earlier paper [4].

Among the relevant code features are the tracking of 'real' time of diffusion kinetics (through the use of 'continuos time' algorithm [12]) and an explicit account for the vacancy migration barrier decrease in the neighbourhood of another vacancy [10]. The latter

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effect is important for the correct description of the 'in-cluster' jumps of vacancies [3].

In order to study the diffusion of He–vacancy clusters, we used a special utility implemented in CASINO-LKMC. In order to create He_nV_m cluster, n helium atoms are distributed over the lattice sites of a compact cluster of m vacancies ($m > n$) and then the unoccupied vacancies are allowed to perform diffusion jumps on bcc iron lattice with probabilities determined by Boltzmann factors appropriate for each particular jump. The trajectory of each cluster is traced jump by jump until the required limit of vacancy jumps (from 10 to 20 millions for short-living clusters and 100–300 millions for sufficiently stable ones) are reached. In case of cluster dissociation within the KMC run duration, the original cluster configuration is restored and a new diffusion campaign is automatically started. The cluster dissociation is assumed to happen, when at least one vacancy or He atom is found at larger than 2NN separation from any other vacancy/He atom that belonged to the initial cluster.

The cluster diffusion coefficient D_c is determined as the proportionality factor between the mean squared shift $\langle r^2 \rangle$ of the cluster 'center of mass' during the time span Δt and the time Δt itself,

$$\langle r^2 \rangle = 6 D_c \, \Delta t. \tag{1}$$

After the end of each calculation run the code processed the cluster positions that had been periodically saved during the run and estimated the average shift $\sqrt{\langle r^2 \rangle}$ for different time spans. A typical output is shown in Fig. 1. As can be seen, the shift follows the square root of time dependence only at time spans <10–20% of the average cluster lifetime, while at bigger Δt the fluctuations strongly distort the shape of the curve, because the number of available points for estimating $\langle r^2 \rangle$ decreases too much. If we present D_c as

$$D_c = a^2 \nu_V \, d_c, \tag{2}$$

where a it the iron lattice parameter, ν_V – the mono-vacancy jump frequency, and d_c – the factor characterising cluster mobility, the lowest mobility limit detectable by the code is $d_c \sim 10^{-8}$.

Cluster lifetime t_c has been estimated as the average over all campaigns at each temperature, which terminated with cluster dissociation. In case of long living clusters the number of such campaigns was very limited (1 to 3) and hence the statistics for such clusters is poor. The cluster lifetimes t_c reported here are in real time (seconds) and were converted from the internal time τ of the program (as used e.g. in Fig. 1) using the relation

$$t_c = \tau_c / \nu_V \; = (\tau_c / \nu_0 \;) \exp(E_V^m / k_B T), \tag{3}$$

where ν_0 is the atomic vibration frequency, E_V^m – the vacancy migration energy and $k_B T$ has its usual meaning. For the estimates below we used $\nu_0 = 10^{13}$ Hz and $E_V^m = 0.67$ eV.

3. Results and discussion

The calculated temperature dependence of the cluster mobility factors and cluster lifetimes are shown in Figs. 2 and 3, respectively. For all considered clusters it has the Arrhenian form,

$$d_c = d_{c0} \exp(-\Delta E_c^m / k_B T) \tag{4}$$

and

$$t_c = t_{c0} \exp(E_c^d / k_B T). \tag{5}$$

The values of prefactors, d_{c0} and t_{c0}, the migration energy corrections, ΔE_c^m and the cluster dissociation energies E_c^d, as obtained by fitting the calculated points, are summarized in Table 1. Note that according to Eqs. (2) and (3) the full activation energy for cluster diffusion is given by the sum $E_V^m + \Delta E_c^m$. Also included in Table 1 are the apparent cluster binding energies, $E_c^b = E_c^d - E_V^m$. These clus-

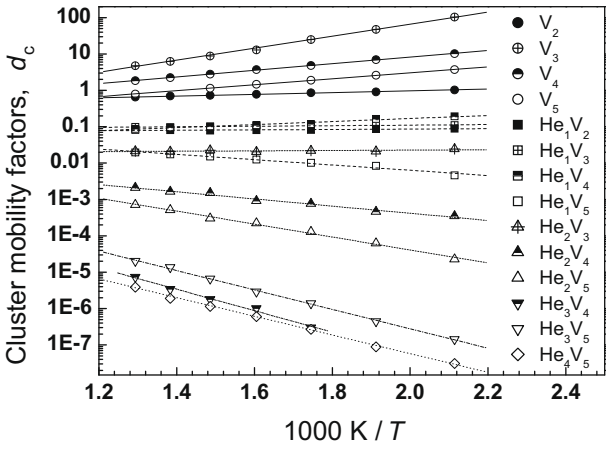

Fig. 2. The temperature dependence of the cluster mobility factors. Straight lines are linear fits to the calculation points. Symbol meanings are explained in the legend.

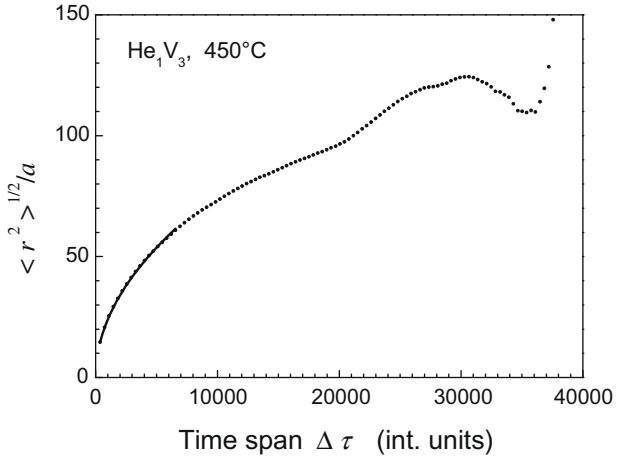

Fig. 1. An example of the dependence of cluster shift (normalized to lattice parameter) on the time span $\Delta\tau$ (measured here in the internal program units). The dot curve is the calculated values for the diffusion of cluster He_1V_3 at 450 °C, while solid line is a square root fit.

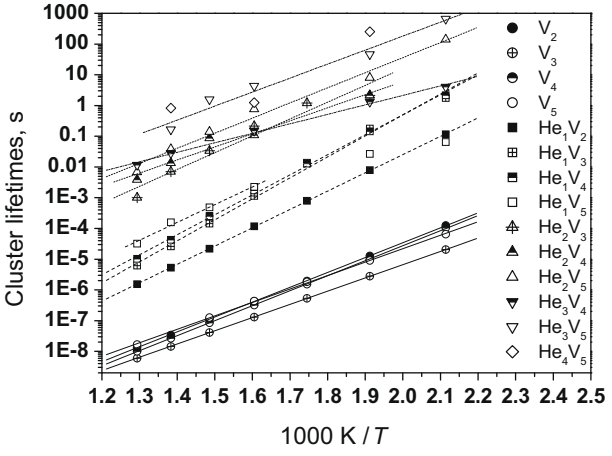

Fig. 3. The temperature dependence of cluster lifetimes. Straight lines are linear fits to the calculation points. Symbol meanings are explained in the legend.

Table 1
Fitted parameter values for cluster mobility factors and cluster lifetimes.

Cluster	d_{c0}	ΔE_c^m, eV	t_{c0}, s	E_c^d, eV	E_c^b, eV
V_2	0.32	−0.05	7.3×10^{-15}	0.96	0.29
V_3	0.033	−0.33	1.6×10^{-14}	0.85	0.18
V_4	0.12	−0.18	4.7×10^{-15}	0.97	0.30
V_5	0.069	−0.16	3.9×10^{-14}	0.87	0.20
HeV_2	0.067	−0.01	3.1×10^{-14}	1.18	0.51
HeV_3	0.078	−0.015	1.1×10^{-14}	1.35	0.68
HeV_4	0.025	−0.083	4.9×10^{-14}	1.29	0.62
HeV_5	0.18	0.14	1.2×10^{-12}	1.15	0.48
He_2V_3	0.018	−0.015	1.8×10^{-10}	1.08	0.41
He_2V_4	0.039	0.19	1.9×10^{-8}	0.84	0.17
He_2V_5	0.15	0.35	5.3×10^{-9}	0.97	0.30
He_3V_4	0.046	0.58	1.4×10^{-6}	0.61	−0.06
He_3V_5	0.053	0.53	7.4×10^{-7}	0.83	0.16
He_4V_5	0.0079	0.51	–	–	–

ter binding energies cannot be, as a rule, straightforwardly associated with input energy parameters used for the numerical experiments.

As can be seen in Fig. 2, among the purely vacancy clusters only divacancy moves slightly slower than monovacancy, whereas tri- and tetra-vacancies move faster than monovacancy in the whole studied temperature range. Pentavacancy is also somewhat faster than monovacancy at temperatures below 250 °C. The mobility acceleration of small vacancy complexes is the result of the above-mentioned barrier decrease for the in-cluster vacancy jumps. Indeed, the obtained effective migration barrier of 0.34 eV for a tri-vacancy, which is able to move exclusively by such jumps, practically coincides with the *ab initio* value for in-cluster vacancy migration barrier [10]. The predicted lifetimes of small vacancy clusters are, however, very short and the average cluster shifts during the lifetime are also quite small, varying from 3 to 10 nm at 200 °C down to 0.5–1 nm at 500 °C.

He atoms efficiently stabilise vacancy clusters. As can be seen in Fig. 3, each He atom captured by a cluster of the fixed size (=number of vacancies) pronouncedly increases cluster lifetime, especially at lower temperatures. For the most stable cluster He_4V_5 it was hard to estimate the lifetime within LKMC runs of reasonable length and several points in Fig. 3 for this cluster give rather a feeling for the relevant lifetimes than a reliable guide for the determination of dissociation barrier. For the other long-living clusters, such as He_2V_5 and He_3V_5, the points are reasonably well aligned, but the scatter is more pronounced than for shorter living clusters.

Two groups of clusters can be separated regarding He effect on cluster mobility. The first group (HeV_2 to HeV_4, He_2V_3) has practically the same migration barrier as individual vacancies and only the diffusion coefficient pre-exponents are decreased due to geometrical restrictions. The migration barriers for the remaining clusters are higher than for monovacancy, correlating to the number of 'free' vacancies in the cluster rather than to cluster size. For the biggest clusters with only 1–2 free vacancies (He_3V_4, He_3V_5, He_4V_5) the migration energy is nearly twice as high as E_V^m. As a result, the average shift of these clusters during the lifetime is only several nanometers, regardless of the pronounced lifetime. The biggest shifts (~30–40 nm at 300 °C) are typical for clusters of intermediate size, the most far-going being He_2V_3 (>100 nm at 300 °C).

Acknowledgments

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