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# Stability and mobility of small vacancy and copper-vacancy clusters in bcc-Fe: An atomistic kinetic Monte Carlo study

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**Abstract**

The mobility and the stability of small vacancy (V) and copper-vacancy (Cu-V) clusters play a key role in the microstructural evolution of Fe–Cu alloys under irradiation, but these are largely unknown parameters that cannot be experimentally measured. These parameters have therefore been determined using atomistic kinetic Monte Carlo (AKMC) simulations, where the vacancy jump activation energies as functions of the local atomic environment had been previously calculated using a molecular dynamics (MD) code and tabulated for use in the AKMC code. This method allowed relaxation effects to be implicitly included in the model and possible differences between the predictions of different interatomic potentials to be evaluated. In this work the mobility, lifetime and mean free path of clusters containing up to six vacancies and Cu-V complexes containing up to four components has been studied. In the case of the VV and Cu-V pairs, the results obtained with different many-body potentials are compared with ab initio results. All results are briefly discussed in terms of their impact on the microstructure evolution in irradiated FeCu alloys.


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*Keywords:* Mobility; Diffusivity; Small vacancy clusters; Copper-vacancy clusters; Kinetic Monte Carlo; Iron–copper alloy

## 1. Introduction

Reactor pressure vessel (RPV) steel embrittlement in existing nuclear power plants is driven by the formation of matrix damage and copper precipitation under irradiation [1]. The mobility and stability of small vacancy (V) and copper-vacancy (Cu-V) clusters in bcc-Fe, in terms of jump frequency, diffusion coefficient, lifetime and mean free path, are therefore key parameters for the simulation of the microstructural evolution under irradiation of RPV steels using e.g. object kinetic Monte Carlo (OKMC) methods [2,3]. These parameters cannot be experimentally deduced, but can be obtained from atomistic simulations. Ideally, the most reliable method to obtain information on the stability and mobility of defects are molecular dynamics (MD) simulations with suitable interatomic potentials [4]. The timeframe for V migration, however, largely exceeds that encompassed by MD. We therefore used atomistic kinetic Monte Carlo (AKMC) simulations, where atoms and vacancies are distributed on a rigid lattice and the system evolves via stochastically chosen diffusion jumps [3,5,6], in which the vacancies exchange position with neighbouring atoms. The input for the method are the activation energies for all possible jumps. These energies have been therefore calculated and tabulated as functions of the local atomic environment using MD, with different interatomic potentials. In some simple cases, it was also possible to calculate all the relevant barriers using density functional theory (DFT) methods [7].

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## 2. Computational model

KMC methods determine the evolution of a system based on the classical transition state theory expression for the frequency of thermally activated phenomena:

$$\Gamma = v\exp(-E_a/k_BT) \quad (1)$$

where $k_B$ is Boltzmann's constant, $T$ the absolute temperature, $v$ an attempt frequency that can be considered constant (in the present work we chose $6\times10^{12}\,s^{-1}$ [3,5]), and $E_a$ is the activation energy. The associated time is estimated using a residence time algorithm [8]:

$$dt = \frac{-\ln(rand)}{\sum_{i=1}^{N}\Gamma_i} \quad (2)$$

where $\Gamma_i$ are the frequencies whereby the possible events happen (Eq. (1)) and *rand* is a random number between 0 and 1. In our case, $E_a$ corresponds to the energy barrier for the exchange of a V with a neighbouring atom, hearafter denoted as $E_m$ (migration energy), and is an *a priori* unknown function of the atomic configuration around the exchanged atom-V pair. In the past, this function has been heuristically taken to be a linear function of the total energy variation after the transition [5,6], such as

$$E_m = E_0 + \frac{E_f - E_i}{2} \quad (3)$$

where $E_i$ and $E_f$ are the total energies before and after the vacancy jump, respectively, and $E_0$ is a constant barrier that may depend on the chemical nature of the jumping atom. Alternatively, saddle point energy estimates based on pair interaction models (broken bond method) have been used [9]. As shown in [10], however, neither of these methods can actually grasp the complexity of the expected dependence of $E_m$ on the local atomic environment. In addition, neither method includes the effect of relaxation in the calculation of $E_m$. For this reason, in the present work the energy barriers corresponding to transitions occurring in all the possible local configurations that a vacancy may encounter in the simulation have been previously calculated using a MD code and tabulated once and for all for use by the AKMC code. This approach is supposed to provide a description of the evolution of the system that is as close as possible to what would be found in a fully MD study, without actually doing MD, as it would require a totally prohibitive amount of computing time. The method we use in the present work is a generalization of the method already used in [11,12].

The local atomic configurations have been identified for convenience by vectors of integer numbers indicating the type of atomic species (0 for a V, 1 for an Fe atom, 2 for a Cu atom). Each position in the vector corresponds to a precise lattice site around the V and the jumping atom. Lattice sites up to the third nearest neighbour (3nn) shell have been included to define the local configuration, corresponding to vectors of 38 integer numbers in the body-centred-cubic structure. These vectors represent in the current framework simply an easy way to define the local configuration and to find it in the table, so as to retrieve the corresponding barrier. In [10] these vectors were also used as input for a more sophisticated regression calculation, based on the use of artificial intelligence.

The energy barriers were calculated using the MD code DYMOKA [13] in the following way: the "jumping" atom was displaced by discrete steps from the initial to the final position (i.e. along the straight line to the first nearest neighbour, 1nn, lattice position where the vacancy is initially located). At each step the system was relaxed by MD via a quasi-dynamic quench to zero Kelvin, with the atom constrained in a plane normal to the segment joining initial and final positions, so as to avoid that it either regains its initial position or falls into the final one. In this way, the total energy profile corresponding to the atomic jump is traced. The total energy difference between the maximum value encountered along the path and the initial value defines the energy barrier. This simple method has been found to be accurate and fast enough for our purposes. Alternative methods, such as nudged elastic bands [14] or the dimer method [15], could in principle be used too and would provide the same result, but they have not been considered in this work.

In the case of the simplest cluster that we have studied, i.e. the di-vacancy, tables containing all the required barriers were built using results available from DFT [7], as well as using five different many-body interatomic potentials for Fe, namely: Ackland–Bacon, AB [16], Ackland–Mendelev, AM [17], Chakarova–Wallenius, CW [18], Dudarev–Derlet, DD (potential 2) [19] and Simonelli–Pasianot (potential A), SP [20]. The reason for using a number of many-body interatomic potentials was twofold: on the one hand, we wanted to verify up to what extent the results depend on the used potential, both quantitatively and qualitatively, and whether common trends can be devised; on the other hand, we wanted to identify the potential providing the closest result to DFT, and use only that potential for the study of larger clusters, for which the calculation of all possible barriers by DFT becomes prohibitive. The best agreement in the di-vacancy case has been found with the AM potential [17]; hence, for all the other V clusters only results obtained with this potential are reported.

In the case of mixed Cu-V clusters, all reported results were obtained using tables built with a recent FeCu potential by Pasianot and Malerba (PM), which is based on AM for the Fe–Fe part and was fitted not only to the thermodynamic behaviour of the alloy, but also to a few DFT-calculated energy barriers for vacancy migration in Fe–Cu [21]. In the case of the study of the CuV pair, complete tables of energy barriers calculated using DFT methods were available from [7] and were therefore used for the validation of the results from the interatomic potential. Calculations using other existing Fe–Cu potentials, such as AB [16] or Ludwig–Farkas (LF) [22] were attempted, but the results were discarded precisely because, according to these potentials, CuV pairs are either unbound and dissociate immedi-