Diffusivity of solute atoms, matrix atoms and interstitial atoms in Fe–Cr alloys: a molecular dynamics study

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Abstract

Three embedded atom method (EAM) empirical potentials recently fitted and validated for Fe–Cr alloys of different Cr concentrations are used to simulate by molecular dynamics (MD) Cr and Fe diffusion in Fe–12%Cr. The results are compared with experimental data. The most adequate potential of the three is then used for a first quantitative evaluation of the slowing down of single interstitial atom diffusion determined by the presence of Cr in ferritic alloys. The results are discussed through comparison with previously published work on self-interstitial atom (SIA) diffusion in Fe.

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1. Introduction

The application of multiscale-modelling approaches for the assessment of the mechanical stability under intense neutron irradiation of high-Cr reduced-activation ferritic/martensitic (RAFM) steels has its starting point in the selection of an adequate many-body interatomic potential for the Fe–Cr model system, of use for atomistic simulations, particularly molecular dynamics (MD). Among other aspects, a good interatomic potential should describe as correctly as possible the diffusion of, on the one hand, matrix and solute atoms and, on the other, point-defects and clusters thereof. The diffusivity of atoms and point-defects at medium-high temperature will partially decide the outcome of the cooling phase of displacement cascades, in terms of damage state [1]. On longer timescales, the mobility of interstitials and interstitial clusters versus vacancies and vacancy clusters is key to the explanation of e.g. radiation induced swelling [2]. Atomic diffusion through vacancies, with a possible contribution under irradiation from intersti-

tials, will determine α'-phase segregation and therefore embrittlement in high-Cr alloys of appropriate concentration [3]. Hence, as a basis for model studies of long term radiation damage evolution in high-Cr alloys, a correct MD assessment of the diffusivity of atoms and point-defects in Fe–Cr alloys, using an adequate interatomic potential, is extremely important.

Recently, three embedded atom method (EAM) interatomic potentials for the description of ferromagnetic Fe–Cr alloys of different concentrations (5%, 10% and 20%) have been produced and validated [4,5]. In this work, their validation is extended by computing, via MD, the diffusivity of Fe and Cr atoms in an Fe–12%Cr alloy. This composition was chosen as the closest Cr concentration to RAFM steels for which experimental data of Cr diffusivity are available [6]. This test allowed us to select the best available potential for our purposes. This potential was subsequently used to give a first assessment of the slowing down of single interstitial diffusion determined by the presence of Cr in ferritic alloys. Ab initio calculations and empirical potential studies show indeed that the formation of interstitial configurations containing Cr atoms is highly favourable [1,5] and it is expected that this fact will influence the mobility of interstitials in Fe–Cr alloys. The results are discussed through comparison with previously published work on self-interstitial atom (SIA) diffusion in Fe.

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2. Calculation procedures

2.1. Interatomic potentials

The details of the fitting procedure and validation of the three EAM [7] potentials for Fe–Cr used in this work can be found elsewhere [4,5]. Briefly, the Fe–Fe potential was fitted following the procedure of Ref. [8], while the Cr–Cr potential was taken from Ref. [9]: although it is known that the latter cannot correctly predict the elastic properties of pure Cr, this is assumed to be a minor shortcoming when dealing with sufficiently diluted alloys. The Fe–Cr crossed pair contribution was fitted, following [10], to the experimental values of bulk modulus, cohesive energy and lattice parameter for, respectively 5%, 10% and 20% Cr ferritic alloys. Moreover, the mixing enthalpies for the same alloys, calculated by ab initio methods to take into account the effect of ferromagnetism [11], were also used as fitting parameters and are the main cause of the difference between the three potentials (−5.91, 5.16 and 41.49 meV for, respectively, 5%, 10% and 20% Cr). The three potentials will be henceforth denoted as FM5, FM10 and FM20. The description of the interaction between Cr atoms and point-defects in Fe that these three potentials provide is different depending on the fitted Cr concentration. FM5 and FM10 turn out to give very similar predictions, in very reasonable agreement with ab initio results obtained with the VASP code [5,12]. In particular, the stability of the Fe–Cr and Cr–Cr dumbbells is correctly reproduced by FM5 and FM10, as well as the negligible binding energy of Cr atoms with vacancies [5]. Conversely, FM20 yields a somewhat higher Cr–V binding energy and does not favour the formation of Fe–Cr and Cr–Cr dumbbells [5]. However, the latter potential was retained as it is the only one capable of predicting some kind of Cr-rich phase segregation [5]. The main shortcoming, common to all three potentials, is that they give the $\langle 1\,1\,1 \rangle$ Fe–Fe dumbbell more stable than the $\langle 1\,1\,0 \rangle$. This feature, which disagrees with experimental observations [13], stems from the choice of a long-range cutoff for the Fe–Fe potential [8] and will be carefully taken into account in the analysis of our results.

2.2. Atomic diffusivity

Standard MD simulations in the microcanonical statistical ensemble, with periodic boundary conditions, were used for these calculations. The diffusivity D_{A}^{*} of an atomic species A in a virtual specimen of alloy can be computed using Einstein's random-walk law [14]:

$$D_{\mathrm{A}}^{*}(T) = \frac{\langle R^2(t) \rangle(T)}{6t}, \qquad (1)$$

where t is the simulation time and $\langle R^2(t) \rangle(T)$ is the time-increasing mean square displacement (MSD) of diffusing

A atoms, calculated from the MD simulation after a long enough run at a certain temperature T. The vacancy concentration used in the simulation, C_{V}^{*}, is inevitably much higher than the equilibrium concentration at T, $C_{\mathrm{V}}^{\mathrm{eq}}(T)$. Hence, to obtain a coefficient diffusion $D_{\mathrm{A}}(T)$ comparable with experimental data, $D_{\mathrm{A}}^{*}(T)$ has to be corrected by a factor $C_{\mathrm{V}}^{\mathrm{eq}}(T)/C_{\mathrm{V}}^{*}$. Here, $C_{\mathrm{V}}^{\mathrm{eq}}(T) = \exp[-(H_{\mathrm{f}}^{\mathrm{V}} - TS_{\mathrm{f}}^{\mathrm{V}})/k_{\mathrm{B}}T]$, where k_{B} is the Boltzmann constant and $H_{\mathrm{f}}^{\mathrm{V}}$ and $S_{\mathrm{f}}^{\mathrm{V}}$ are, respectively the vacancy formation enthalpy and entropy. In the present work, we took for these magnitudes the values provided by the Fe–Fe potential: 1.54 eV [5] and 2.7 k_{B} [15], respectively. By repeating the calculation embodied by Eq. (1) at different temperatures (to which the atom block was previously equilibrated) and applying the correction factor, the Arrhenius plot of the diffusion coefficient is obtained and, by interpolating with the usual expression [16]

$$D_{\mathrm{A}}(T) = D_0 \cdot e^{-\frac{E_{\mathrm{a}}}{kT}}, \qquad (2)$$

both prefactor D_0 and activation energy E_{a} as predicted by the potential can be derived and compared with experimental data. A block of 8192 lattice sites was used for all simulations, conducted in a range of temperatures from 1200 to 1700 K, the MSD being traced up to 1 ns. Additional information about the procedure can be found in [17].

2.3. Interstitial diffusivity

The interstitial diffusion coefficient was evaluated using Eq. (1), by means of a technique first proposed by Guinan et al. [18] to assess the MSD of interstitial atoms and widely used by other authors in Refs. [19,20], where more details about the methodology can be found. Broadly, one long simulation is run and the simulated time is divided into shorter intervals of equal length. The distance covered by the only interstitial introduced in the block is calculated at each time-interval and the average value (MSD) is calculated from the different time-intervals. In other words, instead of introducing simultaneously n interstitials and calculating their MSD by tracking the path of each of them, which is impossible because they have no individuality, the average of the n displacements of the same interstitial was taken as MSD. The t to be used in Eq. (1) is then the time-interval length, and not the total simulated time. Of course, the result may be sensitive to the choice of the time-interval length. In this work we used 1 ps, the total simulated time being 500 ps. In the simulation temperature range considered here (300–900 K, at 100 K intervals), this choice fulfills the 'residence requirement time' criterion discussed by Ostesky [20], which ensures that real jumps and not just vibrations around a constant position are taken by the interstitial, while allowing enough jumps to

be seen and possible boundary-crossings to be taken correctly into account. The simulations were run in a 54 000 atom block.

3. Results and discussion

3.1. Atomic diffusion via vacancy mechanism

In Fig. 1 the diffusivities of Fe (a) and Cr (b) atoms in Fe–12%Cr versus temperature, obtained using FM5, FM10 and FM20 potentials, are compared with experimental curves [6]. The experimental Cr diffusivity curve is traced using the actual prefactor (1.1177 cm²/s) and activation energy (2.39 eV) measured by Wolfe and Paxton in Fe–12%Cr, as reported in [6]. The prefactor (2.117 cm²/s) and activation energy (2.54 eV) for the Fe diffusivity curve were interpolated for Fe–12%Cr from experimental curves provided in [6]. The three potentials predict an activation energy for diffusion (slope of the Arrhenius plot) reasonably close to the experimental value (2.11 eV for Cr atoms and 2.19 eV for Fe atoms according to FM5 and FM10; respectively 2.14 and 2.21 eV for FM20), but slightly underestimate the prefactor. Considering the uncertainty in the actual vacancy for-
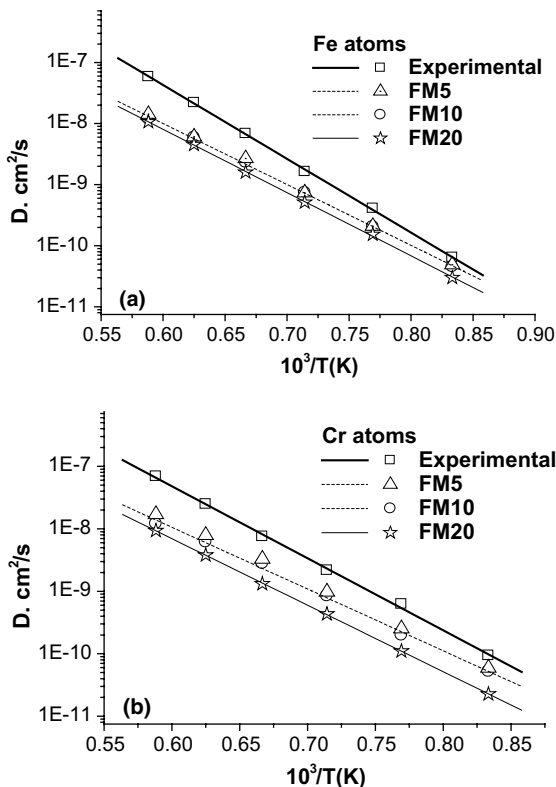
mation enthalpy and entropy to determine the correction factor described in Section 2.2, these results can anyhow be regarded as being in excellent agreement with the experimental measurements. Moreover, FM5 and FM10 yield a D_{Cr}/D_{Fe} ratio in Fe–12%Cr (respectively, 1.24 and 1.08) in close agreement with the experimental findings (1.28), Cr being a fast diffuser. Conversely, FM20 predicts slow-diffusing Cr atoms (D_{Cr}/D_{Fe} = 0.81), most likely as a consequence of the higher Cr–V binding energy predicted by this potential. For this and other reasons [5], the latter potential cannot be considered satisfactory. Among FM5 and FM10, which seem to be equally good, the latter is used for the following studies because it was fitted more specifically to the properties of Fe–Cr alloys in the range of composition considered in this work.

3.2. Interstitial diffusivity

In Fig. 2 the result of our D^*_{SIA} calculation in pure Fe is compared with analogous results obtained with different many-body interatomic potentials by Soneda [19] and Osetsky [20] and respective co-workers. Our calculations give a lower migration energy (E_m = 0.063 eV) and a generally higher diffusivity (with prefactor D_0 = 3.03×10^{-4} cm²/s). This was expected and is the main consequence of the fact that our potential, differently from the Johnson-Oh and Ackland ones, and contrary to experimental evidence [13], predicts the ⟨1 1 1⟩ Fe–Fe dumbbell to be more stable than the ⟨1 1 0⟩. When the most stable configuration is ⟨1 1 0⟩, the SIA needs, before jumping, to re-orient itself to the ⟨1 1 1⟩, where it can glide, with an additional expense of time and energy hindering migration [20]. In our case no rotation between different orientations takes place between jumps, thereby enabling a faster diffusion. Strictly, therefore, our potential should probably not be used to study
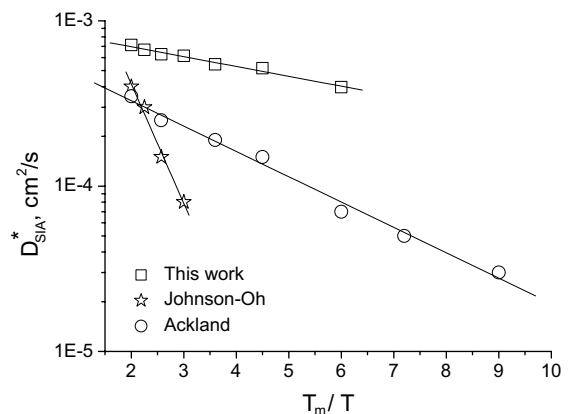

Fig. 1. Diffusion coefficient of iron (a) and chromium (b) in an Fe–12%Cr alloy: experimental and calculated data.

Fig. 2. Interstitial diffusivity in pure Fe: our result (FM10), compared with results obtained by other authors using Johnson-Oh [19] and Ackland [20] potentials.

single SIA migration in pure Fe. However, we are here mostly interested in assessing the difference in interstitial diffusivity between Fe and Fe–Cr and for this purpose the FM10 potential is currently the only and best choice possible [5]. On the other hand, the migration energy and prefactor found by Soneda ($E_m = 0.16$ eV and $D_0 = 20.9 \times 10^4$ cm^2/s) are not much closer to Osetsky's ($E_m = 0.078$ eV and $D_0 = 3.6 \times 10^{-4}$ cm^2/s) than ours. Soneda's results were obtained in the 600–900 K temperature region. It is known that two different regimes of interstitial migration are found at low and high temperature according to Osetsky [20] and Soneda's result reflect only the high temperature regime [19]. The fact that our migration energy and prefactor are finally rather close to Osetsky's calculations makes us believe that, for the purpose of the Fe–Cr versus Fe assessment, the FM10 potential can be rather safely used. To this regard, it is useful to notice that currently no many-body empirical potential can predict the experimental 0.3 eV SIA migration energy in Fe [13].

Thus, in Fig. 3(a) we show the Arrhenius plots of the interstitial diffusion coefficients in Fe–12%Cr and pure Fe, in the 300–900 K range of temperatures. The interstitial diffusivity is visibly lower in Fe–Cr than in pure Fe. This view is also supported by the graph in Fig. 3(b), where the actual number of 'useful' (i.e. producing atomic replacement) interstitial jumps per unit time is displayed. However, the $D_{I,Fe}^*/D_{I,Fe-Cr}^*$ ratio changes with temperature: it is higher below 600 K and increasingly lower above. Indeed, although we fitted single exponential functions to both data point sets, shown as straight lines in Fig. 3(a) ($E_m = 0.078$ eV and $D_0 = 3.2 \times 10^4$ cm^2/s in the Fe–Cr alloy), two different pre-exponential factors and migration energies (slopes) could be obtained for low (<600 K) and high (>600 K) temperatures. This is true also for pure Fe and has already been observed [20], but is remarkably more evident in the case of Fe–Cr. For the moment, we can only provide a tentative explanation for this change of interstitial diffusion regime in Fe–Cr. At low temperature, the combination of the existence of a significant binding energy for Cr atoms in interstitial position [1,5] with the irregular and changing modifications of the strain field around the interstitial atom produced by the presence of other Cr atoms, creates a sort of trap for the interstitial. An inspection of the paths followed by the interstitial during the simulation (not shown here) reveals that the interstitial remains bound in his diffusion to a relatively small region, while at the same temperature in pure Fe the interstitial is seen to cover large stretches, keeping mostly a unidirectional motion. However, the actual migration energy required for most jumps is not significantly different from the migration energy in pure Fe, thus it is the prefactor that is mostly affected by this trapping effect. At higher temperatures, the trapping effect becomes increasingly less effective and
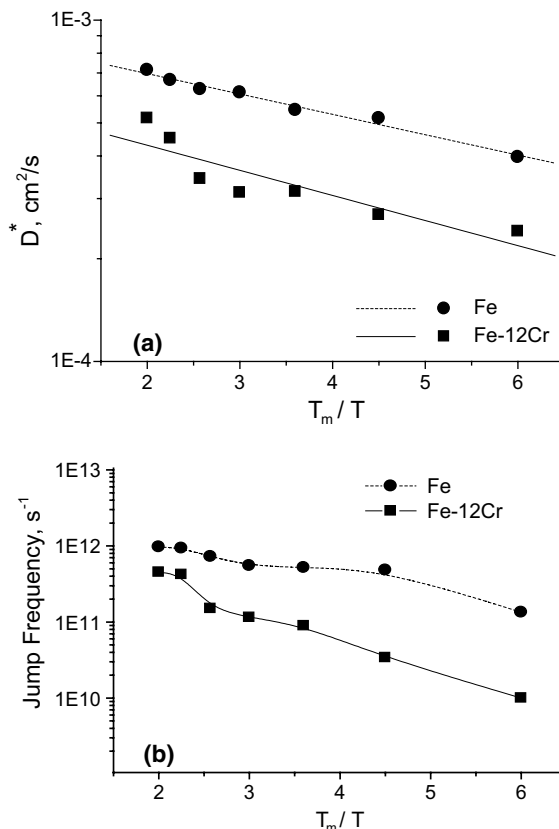

Fig. 3. (a) Interstitial diffusivity in pure Fe compared to Fe–12%Cr according to FM10. (b) Same type of comparison, using the number of jumps per unit time.

the moving interstitial grows free to cover larger distances, like in pure Fe. However, the presence of Cr atoms induces more frequent changes of direction than in pure Fe, thereby explaining a higher effective migration energy. Longer simulations at low temperature, in order to increase the statistics in the actual number of jumps, and additional data points at higher temperatures, together with a more detailed analysis of interstitial paths and direction changes, are needed in order to clarify the actual mechanisms.

4. Conclusions

The EAM potentials for the Fe–Cr system denoted as FM5 and FM10, fitted specifically for a concentration of Cr around, respectively, 5% and 10%, reproduce satisfactorily experimentally measured high temperature diffusion coefficients of Fe and Cr atoms in Fe–12%Cr, as well as other properties of the Fe–Cr system, particularly the favourable formation of Cr interstitials, in agreement with ab initio results and available experimental evidence [5].

The main problem of these potentials is the description of the most stable interstitial configuration in pure Fe: the $\langle 1\,1\,1 \rangle$ dumbbell is considered more stable than the $\langle 1\,1\,0 \rangle$. This feature has been seen to influence the predicted diffusivity of SIA in pure Fe, giving a slightly lower migration energy and a generally higher diffusion coefficient than interatomic potentials predicting the correct interstitial configuration. However, the difference has been shown not to be large, so that this potential can be used for a first assessment of the slowing down of interstitial atom diffusion determined by the presence of Cr in ferritic alloys. Such a study has revealed that the number of interstitial diffusion jumps per unit time at low temperature (300 K) in Fe–12%Cr can be almost two orders of magnitude lower than in pure Fe, although this difference decreases significantly at high temperature (900 K). In addition, two regimes of interstitial migration, above and below 600 K, characterised by different migration energies and prefactors, have been identified. While the presence of Cr is clearly the reason of the existence of these two regimes, further investigation is required to understand better the actual mechanisms behind them.

Acknowledgements

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