Journal of Nuclear Materials 386–388 (2009) 86–89

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Ab initio study of interstitial migration in Fe–Cr alloys

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A B S T R A C T

The migration barriers for self-interstitial defects in Fe in the presence of solute Cr has been investigated using density functional theory calculations. It is seen that the dumbbell migration barrier is lower for a mixed interstitial than for a pure Fe one, in agreement with experiments. As a consequence, single self-interstitials in dilute Fe–Cr alloys will associate themselves to solute Cr atoms, and under irradiation conditions, the Cr can diffuse via both interstitial and vacancy mechanisms. Furthermore, the stability of self-interstitial defects and defect clusters in pure Cr have been calculated, showing that they should be significantly less stable in Cr rich precipitates than in the matrix. The most stable self-interstitial in Cr is shown to be a low-symmetry $\langle 221 \rangle$ configuration.

1. Introduction

Reduced activation ferritic/martensitic steels are candidate structural materials for future fusion reactors as well as for Gen IV fission reactors. These steels can to a first approximation be modelled by considering the behaviour of binary Fe–Cr alloys. It has been shown that a significant amount of Cr, in the range of 6–14 at.%, is necessary to provide good radiation and corrosion resistance as well as to improve the mechanical properties. The microstructure evolution induced by neutron irradiation is known to depend on the Cr content [1], the void swelling dependence on the Cr concentration being an excellent example of this feature [2]. The microstructure evolution depends heavily on the diffusion of point defects and point defect clusters. Resistivity recovery experiments on Fe and dilute Fe–Cr alloys [3] have shown that the migration of mixed dumbbells should be slightly faster than that of the dumbbell in pure Fe and that the mixed dumbbell is stable; the latter having also been previously verified by *ab initio* calculations [4]. The migration barriers of self-interstitial defects in pure Fe [5] as well as in reactor pressure vessel model alloys containing Cu, Mn, Si and Ni [6] has been previously calculated *ab initio*. For Fe–Cr alloys, the experimental evidence suggests that Cr can diffuse via an interstitial mechanism. Thus, under irradiation conditions, the precipitation of the Cr rich α' phase can be accelerated [7]. From resistivity recovery experiments on concentrated Fe–Cr alloys, it has been shown that the effective mobility of the interstitials can be reduced [8]. This effect is due to the strong binding of self-interstitials by solute Cr in concentrated alloys, as confirmed by recent *ab initio* calculations [9]. Several atomistic studies using molecular dynamics and classical interatomic potentials [10] have been performed on Fe–Cr alloys, investigating the effect on the resistivity recovery [11], the interaction of self-interstitial loops with precipitates [12] and the reduction of mobility of single- and clustered defect configurations in concentrated Fe–Cr alloys [11–14]. We have here performed an *ab initio* investigation of the migration barriers of self-interstitials in dilute Fe–Cr alloys. Furthermore, we have calculated the formation energies of small self-interstitial clusters in Cr in order to confirm previously made conclusions [4] on the interactions between diffusing defect- and defect clusters with α' precipitates, also discussed by Terentyev et al. [15].

2. Method

The calculations were performed in the framework of density functional theory (DFT) using pseudopotentials generated within the projector augmented wave (PAW) approach [16] implemented in the Vienna *ab initio* simulation package (VASP) [17]. The calculations were spin-polarized and the exchange-correlation functional used was the generalized gradient approximation (GGA) of Perdew et al. [18] with the Vosko–Wilk–Nusair interpolation of the correlation potential [19]. The supercell approach with periodic boundary conditions was used for all calculations. Brillouin zone sampling was performed using the Monkhorst and Pack scheme [20]. The electronic configurations of Fe and Cr are Ar$3d^7 4s^1$ and Ar$3d^5 4s^1$, respectively. The defect calculations were performed at constant volume, relaxing the atomic positions using either the conjugate gradient algorithm for far from equilibrium starting positions or a quasi-Newton algorithm for close to equilibrium starting positions. The theoretical equilibrium lattice parameter for ferromagnetic bcc Fe (2.831 Å) or respectively, anti-ferromagnetic (2.850 Å) or non-magnetic (2.836 Å) bcc Cr has been used. The calculated migration energies were converged with 27 *k*-points with 128-atom supercells, following the convergence

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doi:10.1016/j.jnucmat.2008.12.065

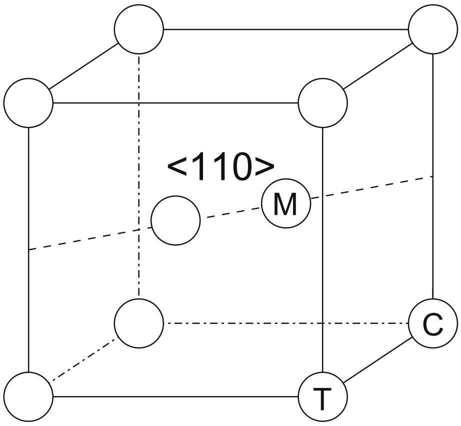

Fig. 1. A solute atom in or in close proximity to a $\langle 1\,1\,0\rangle$ self-interstitial defect in the mixed (M) position, the compression (C) zone or the tensile (T) zone.

tests explained in previous works [4,21]. The plane wave cutoff energy was 300 eV. The formation energies of the self-interstitial clusters in Cr were calculated using simulation boxes containing 128 and 250 atoms with the same number of *k*-points and energy cutoff as for the migration energy calculations. The first nearest neighbour positions around a self-interstitial defect in a bcc matrix are either in a compression zone or a tensile zone, see Fig. 1. The migration barriers were calculated using the nudged elastic band method [22] with seven images along the migration path. The atomic configurations and migration pathways here studied were chosen after considering the previously reported formation and binding energies of defects in dilute Fe–Cr alloys [4]. The formation energies are defined as the total energy difference between the simulation box containing the defect and the reference state, normalised to compare the same number of atoms. The migration energy is here defined as the difference between the equilibrium energy and the highest energy along the migration path.

3. Results

The lowest energy state for a dumbbell in proximity to a Cr atom is the mixed dumbbell (position M in Fig. 1), with a formation energy of 3.83 eV, compared to 4.02 eV for a pure Fe self-interstitial [4]. Almost as low is the state where the Cr atom is in the compression zone (position C in Fig. 1) close to the dumbbell (3.86 eV). These two states are the dynamical minima in which the dumbbell will be most likely to stay. The mixed dumbbell itself can migrate either via the translation–rotation process (Fig. 2(a)) so that the Cr atom is contained in the defect or by weakly disassociating from the Cr atom, that ends up in the compression zone (Fig. 2(b)). It may migrate via a temporary rotation to the $\langle 1\,1\,1\rangle$ configuration

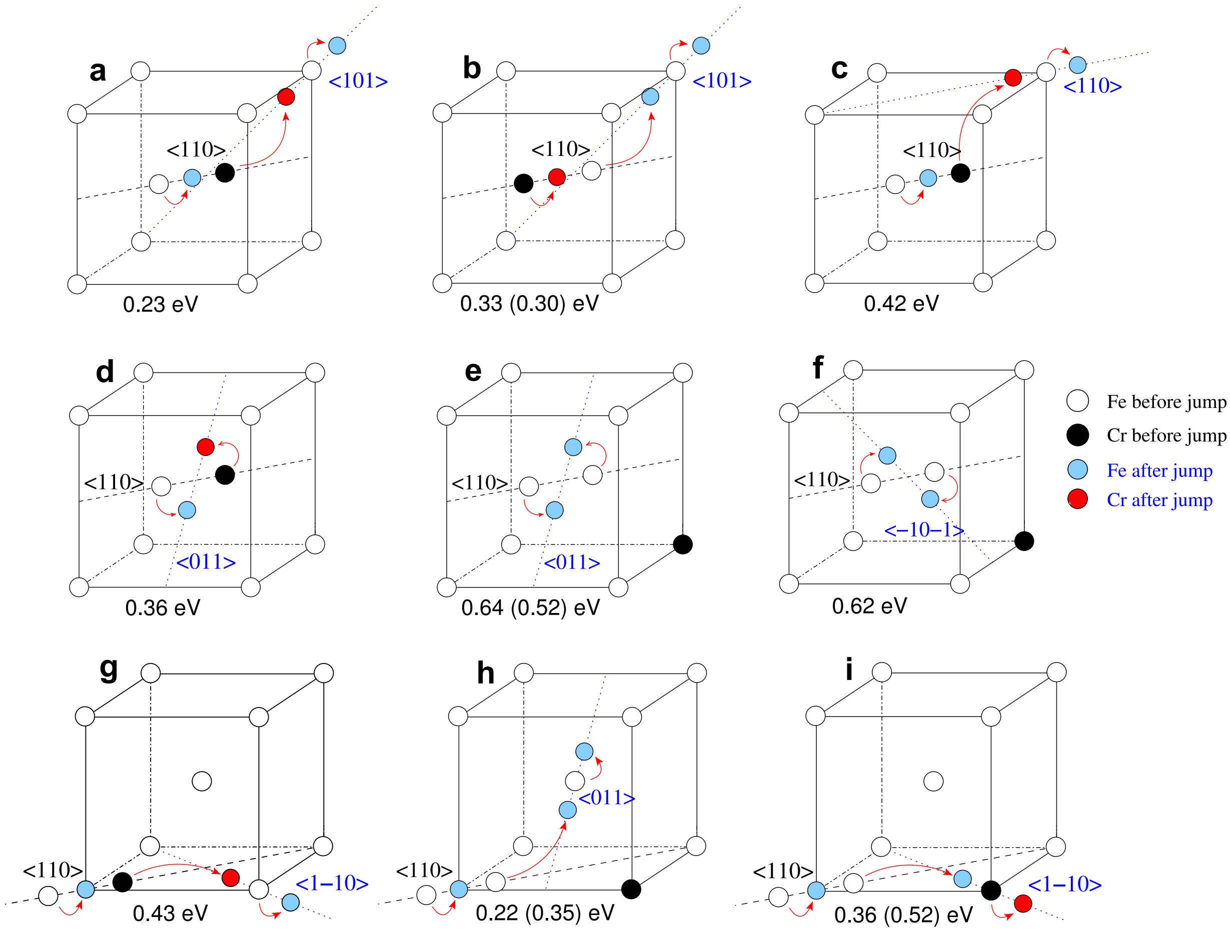

Fig. 2. The mixed interstitial migration pathways. The white circles are Fe atom positions before the jump and the black circle represents the Cr atom. The shaded (blue) circles are the Fe atoms after the jump and the dark shaded red circle is the Cr position after the jump. The migration energy for each jump is given under the figures and in the non-symmetric cases the migration energy of the inverse transition is given in parenthesis. (a) The translation–rotation jump. (b) The weakly disassociating translation–rotation jump. (c) The translation jump via $\langle 1\,1\,1\rangle$. (d) The on-site 60° rotation. (e) The compression-to-tensile on-site 60° rotation. (f) The compression conserving on-site 60° rotation. (g) The 2nn jump. (h) The weak association jump from 2nn. (i) The strongly associating 2nn jump. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

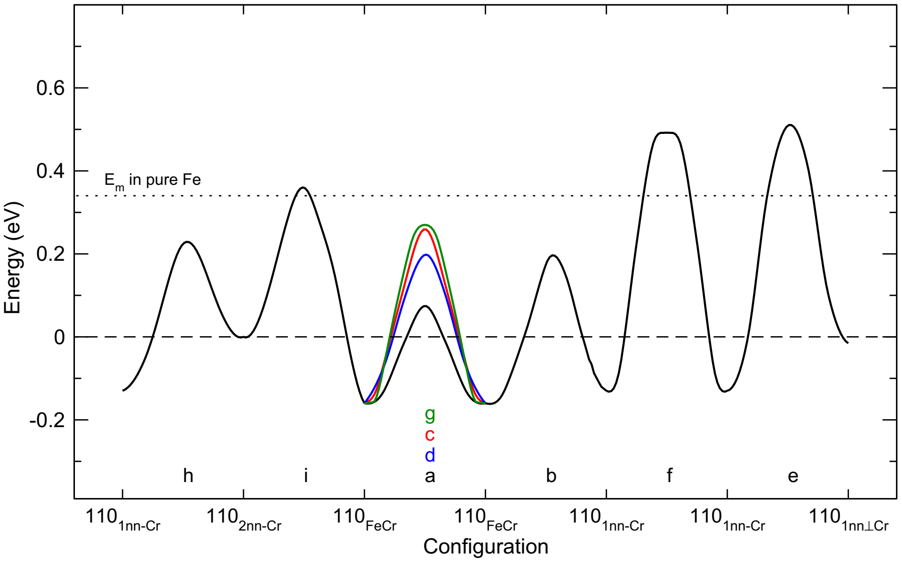

Fig. 3. The energy landscape of self-interstitial migration. The reference state is the ⟨1 1 0⟩ dumbbell with a Cr atom in 2nn position. The pathways are denominated a to i and refer to the corresponding transitions in Fig. 2. The abscissa denominates the start and end states of each pathway. As a point of reference, the migration energy of a self-interstitial in pure Fe is represented by a dotted line.

and subsequent first nearest neighbour (1nn) glide (Fig. 2(c)). It can make an on-site 60° rotation (Fig. 2(d)); an on-site 60° rotation that effectively moves the Cr atom from the compression to the tension zone (Fig. 2(e)) or an on-site 60° rotation that keeps the Cr atom in the compression zone (Fig. 2(f)). Furthermore, it may make a second nearest neighbour (2nn) jump (Fig. 2(g)) or associate or disassociate with the solute Cr either from second nearest neighbour position to the compression zone (Fig 1(h)) or from the second nearest neighbour position into a mixed dumbbell (Fig. 2(i)).

The energy landscape resulting from the above transitions is shown in Fig. 3. The lowest energy state is the mixed dumbbell and the lowest migration barrier is that of an association jump (Fig. 2(h)), followed by the migration barrier of the mixed dumbbell (Fig. 2(a)). The migration energy of a dumbbell in pure Fe using the PAW method is 0.34 eV, in good agreement with experiments [23] and previous calculations [5,6]. Several migration barriers for the mixed dumbbell are lower or equal to the one in pure Fe. All of the examined migration barriers are single humped. The on-site rotations (Fig. 1(e) and (f)) have high migration barriers since their saddle point configurations are close in character to the Fe ⟨1 1 1⟩ self-interstitial, which is 0.7 eV higher in energy than the ⟨1 1 0⟩ configuration [4,5,21]. In contrast, the on-site rotation of the mixed dumbbell (Fig. 1(d)) has a lower migration energy since the saddle point configuration in this case is close to a mixed ⟨1 1 1⟩ interstitial, which is only 0.4 eV higher in energy than the ⟨1 1 0⟩ mixed dumbbell [4].

Table 1
Formation energies of self-interstitials and self-interstitial clusters in anti-ferromagnetic (AF) and non-magnetic (NM) bcc Cr as well as ferromagnetic (FM) Fe [24].

Formation energy (eV)	AF Cr 128 atoms	AF Cr 250 atoms	NM Cr 128 atoms	NM Cr 250 atoms	FM Fe [24]
⟨1 1 0⟩	5.69	5.68	5.46	5.28	3.75
⟨1 1 1⟩	5.76	5.76	5.47	5.29	4.45
⟨2 2 1⟩	5.55	5.53	5.28	5.10	*
2 ⟨1 1 0⟩	10.31	10.24	10.16	9.80	6.68
2 ⟨1 1 1⟩	10.09	10.11	9.87	9.54	7.43
2 ⟨2 2 1⟩	9.94	10.08	9.72	9.42	*
3 ⟨1 1 0⟩	14.79	14.72	14.89	13.53	9.49
3 ⟨1 1 1⟩	13.98	14.08	14.05	13.50	10.01
3 ⟨2 2 1⟩	13.99	14.12	14.09	13.53	*

The small self-interstitial clusters here examined in pure Cr contained up to three self-interstitials and were relaxed from ideal parallel ⟨1 1 0⟩ and ⟨1 1 1⟩ configurations, as has previously been done in pure Fe [24]. Due to the previously reported small difference between the ⟨1 1 0⟩ and ⟨1 1 1⟩ single self-interstitial configurations in Cr [4,25], also intermediate ⟨2 2 1⟩ configurations were considered. We show here that this low-symmetry state is the ground state for single self-interstitials in Cr, being 0.15 eV more stable than the previously considered ground state configuration. Also for the di-interstitial defects we find a slightly perturbed ⟨2 2 1⟩ configuration as the most stable state. First for a cluster of three interstitials does the ⟨1 1 1⟩ oriented configuration become the most stable one. It is seen in Table 1 that the formation energies are significantly higher for defects and defect clusters in Cr than in Fe.

4. Discussion and Conclusions

We have shown that the migration of self-interstitial defects is faster in dilute Fe–Cr alloys than in pure Fe, in agreement with resistivity recovery experiments. The interstitials can migrate faster than in pure Fe and can thus affect the long range diffusion of Cr. It has been shown that the lowest barrier of migration is that of an associative jump and the second lowest is the jump of the mixed interstitial but also that the weak association/disassociation jumps are comparable to the migration barrier in pure Fe. Also the low barrier for the mixed dumbbell rotation opens up a diffusion path via on-site rotation, that has a much higher barrier for the pure Fe dumbbell. When in close proximity to Cr atoms, the self-interstitials will preferentially associate themselves with the solute atoms. The strength of this tendency is enforced by the fact that the barrier for a second nearest neighbour associative jump to bind with a Cr atom is of the same height as the migration energy for self-interstitials in pure Fe. Thus, Cr in irradiated Fe–Cr alloys can diffuse via both the interstitial and the vacancy mechanisms. In order to determine which is preferential, further dynamical studies under varying conditions are necessary. The large difference between the rotation energy for a mixed dumbbell and that of the dumbbells with a neighbouring Cr atom is explained by the fact that the saddle points for the latter cases are very close to a pure Fe ⟨1 1 1⟩ self-interstitial and thus notably higher in energy than the mixed ⟨1 1 1⟩ interstitial. As has been shown previously [4,9], the binding energies of Cr atoms with self-interstitials in concentrated alloys are significantly higher than those in dilute alloys. The migration barriers from these strongly bound states containing many Cr atoms in the close proximity of the defect should be higher than those reported here due to the effective lowering of the initial and final states while, *a priori*, the intermediate states should retain their high energies. Thus, for concentrated alloys we can expect the Cr in the matrix to act as traps for self-interstitial defects.

The results on defects and defect clusters in pure Cr show that Cr precipitates in Fe–Cr alloys should act as scattering centres for defect clusters since the formation energies are so much higher in Cr than in the matrix. Molecular dynamics simulations confirm this conclusion [15]. Even for loops, which are not explicitly considered here, we expect the interaction with a precipitate to be strongly repulsive since the basic component of a loop are ⟨1 1 1⟩ interstitial defects and these have much higher formation energy in Cr than in Fe. For large loops that move one-dimensionally we therefore expect the precipitates, or rather pairs of precipitates along a glide line, to act as effective traps since the energy of rotation for the loops should be large. We here predict that the self-interstitial ground state in pure Cr is a low-symmetry configuration close to ⟨2 2 1⟩. This result is coherent with the experimental evidence that the activation temperature for the long range migration of self-interstitials in Cr is larger than for the remaining 6B and 5B bcc metals [25–27]. A new assessment of the resistivity recovery in bcc Cr should be made based on the energy of migration that can be deduced from the ⟨2 2 1⟩ to ⟨1 1 1⟩ transition.

Acknowledgements

The author acknowledges fruitful discussions with C. Domain, L. Malerba, P. Klaver and D. Terentyev. This work has been partially supported by the European Commission within the FP7 project GETMAT (Grant agreement number 212175) and FP6 project PERFECT (FI6O-2003-508840). Most of the calculations have been performed using the supercomputers at Centre de Calcul Recherche et Technologie (CCRT) in the framework of an EDF-CEA contract.

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