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Microstructural evolution under high flux irradiation of dilute Fe–CuNiMnSi alloys studied by an atomic kinetic Monte Carlo model accounting for both vacancies and self interstitials

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ABSTRACT

Under neutron irradiation, a large amount of point defects (vacancies and interstitials) are created. In the irradiated pressure vessel steels, weakly alloyed, these point defects are responsible for the diffusion of the solute atoms, leading to the formation of solute rich precipitates within the matrix. Ab initio calculations based on the density functional theory have been performed to determine the interactions of point defects with solute atoms in dilute FeX alloys (X = Cu, Mn, Ni or Si). For Mn, the results of these calculations lead to think that solute transport in α-Fe can very likely take place through an interstitial mechanism as well as via vacancies while the other solutes (Cu, Ni and Si) which establish strong bonds with vacancies diffuse more likely via vacancies only. The database thus created has been used to parameterize an atomic kinetic Monte Carlo model taking into account both vacancies and interstitials. Some results of irradiation damage in dilute Fe–CuNiMnSi alloys obtained with this model will be presented.

1. Introduction

The formation of solute rich precipitates or clusters in reactor pressure vessel steels under neutron irradiation is a very intriguing phenomenon. It is now well accepted that during irradiation, a large amount of point defects (vacancies and interstitials) are created within displacement cascades. In the irradiated pressure vessel steels, weakly alloyed, these point defects are very probably responsible for the diffusion of solute atoms, leading to the formation of clusters enriched in Cu, Ni, Mn and Si [1,2]. Light can be shed on the cluster formation with the help of numerical simulations at the atomistic level, as they can help understanding the elementary mechanisms which lead to the changes observed. Among the different techniques available, Atomic kinetic Monte Carlo (AKMC) based on the diffusion of point defects is a powerful tool to simulate the microstructural kinetic evolution under irradiation. We have thus used ab initio calculations compared to experimental data to parameterize an atomic kinetic Monte Carlo model whose aim is to simulate the medium term formation of Cu–Ni–Mn–Si enriched clusters under irradiation. The energetic properties used in the fitting procedure were the solute mixing energies in Fe, different binding energies of solute (Cu, Ni, Mn, Si)-point defect complexes, migration energies and interface energies. The model was in a first step parameterized on thermal ageing experiments of alloys of growing complexity [3–5]. This first step insured that the interactions between vacancies and solute atoms were correctly modeled. In a second step, we introduced interstitials in the model. This paper describes the method used as well as some results obtained for the simulation of 'neutron' or electron irradiations of model alloys.

2. Methodology

2.1. Ab initio calculations

Our calculations have been done using the Vienna Ab initio Simulation Package VASP [6,7]. They were performed in a plane-wave basis. Exchange and correlation were described by the Perdew–Zunger functional, adding a non-local correction in the form of the generalised gradient approximation (GGA) of Perdew and Wang. All the calculations were done in the spin polarised GGA using the supercell approach with periodic boundary conditions. The ultrasoft pseudopotentials used in this work come from the VASP library. Brillouin zone (BZ) sampling was performed using the Monkhorst–Pack scheme. The defect calculations were done at constant volume, relaxing only the atomic positions in a supercell dimensioned with the equilibrium lattice parameter for Fe (2.8544 Å). The plane wave cut-off energy was 240 eV. The results were obtained using 128-atom supercells with a BZ sampling of

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27 k points. More details on the method can be found in a previous work [8].

After a thorough comparison [5] of the data obtained using the Projector Augmented Wave (PAW) and the UltraSoft PseudoPotential (USPP) formalisms, USPP was chosen. The PAW method should theoretically give better results than the USPP one for 3d-transition metals as it gives a better description of the core electrons. This method gives indeed better results as far as the magnetic moments are concerned but appears to be less appropriate for the energies needed to parameterize our model.

2.2. Monte Carlo model

The Monte Carlo code, LAKIMOCA, developed at Electricité de France (EDF) [9], has been improved to treat complex alloys (Fe–CuNiMnSi) as well as interstitials which play a non negligible role in the embrittlement of RPV steels under irradiation. The motive for introducing interstitials in the vacancy AKMC was two fold. First of all, interstitials move very quickly and can recombine with vacancies, decreasing the amount of vacancies available for diffusion. Second of all, our ab initio results indicate that Mn is very likely to be able to diffuse via some mechanisms involving interstitials [10] as well as vacancies, while the other solutes (Cu, Ni and Si) which establish strong bonds with vacancies are more likely to diffuse via vacancies only [11].

The model is based on the residence time algorithm [12]. Both vacancy and interstitial diffusions are determined by the calculation of the probabilities to jump to a first nearest neighbour site. This probability is obtained as follows:

$$\Gamma_{X,V} = \nu_X \exp\left(-\frac{E_a}{kT}\right), \tag{1}$$

where ν_X is the attempt frequency, equal to $6 \times 10^{12}\ s^{-1}$, and E_a is the activation energy of the jump.

The activation energy E_a is obtained using an environment-dependent model, which satisfies the detailed balance rule:

$$E_a = E_{a_0} + \frac{E_f - E_i}{2} \tag{2}$$

where E_i and E_f are the system energies, respectively, before and after the jump of the vacancy or of the interstitial. Recombination between an interstitial and a vacancy takes place as soon as they become second nearest neighbors.

For vacancy jumps E_i and E_f are determined using pair interactions, according to the following equation:

$$E = \sum_{i=1,2} \sum_{j<k} \varepsilon^{(i)}(S_j - S_k) \tag{3}$$

where i equals 1 or 2 and corresponds respectively to first or second nearest neighbor interaction, j and k to the lattice site and S_j (resp. S_k) is the species occupying site j (resp. k): S_j in {Fe, V, X} where X = Cu, Ni, Mn or Si. In the calculation of the activation energy for a vacancy jump, the interactions due to interstitials are not taken into account. For interstitial jumps, E_i and E_f are determined using (3) and adding to it the contribution of the dumbbells.

2.2.1. Activation energy in the case of a vacancy jump

The reference activation energy E_{a_0} in Eq. (2) depends only on the type of the migrating atom: it is the ab initio vacancy migration energy in pure Fe when the vacancy jumps towards an Fe atom and the ab initio solute migration energy in pure Fe when the vacancy jumps towards a solute atom. The pair interactions, necessary to determine E_i and E_f, have been obtained from the following set of equations:

$$E_{coh}(X) = 4\varepsilon^{(1)}_{(X-X)} + 3\varepsilon^{(2)}_{(X-X)} \tag{4}$$

$$E_{mix}(X \to Fe) = -4\varepsilon^{(1)}_{(Fe-Fe)} - 3\varepsilon^{(2)}_{(Fe-Fe)} + 8\varepsilon^{(1)}_{(Fe-X)} + 6\varepsilon^{(2)}_{(Fe-X)} - 4\varepsilon^{(1)}_{(X-X)} - 3\varepsilon^{(2)}_{(X-X)} \tag{5}$$

$$E_{int(100)}(Fe/X) = -2\varepsilon^{(1)}_{(Fe-Fe)} - \varepsilon^{(2)}_{(Fe-Fe)} + 4\varepsilon^{(1)}_{(Fe-X)} + 2\varepsilon^{(2)}_{(Fe-X)} - 2\varepsilon^{(1)}_{(X-X)} - \varepsilon^{(2)}_{(X-X)} \tag{6}$$

$$E_b^{(1)}(V - X) = \varepsilon^{(1)}_{(Fe-X)} + \varepsilon^{(1)}_{(Fe-V)} - \varepsilon^{(1)}_{(Fe-Fe)} - \varepsilon^{(1)}_{(V-X)} \tag{7}$$

$$E_{for}(V^X) = 8\varepsilon^{(1)}_{(X-V)} + 6\varepsilon^{(2)}_{(X-V)} - 4\varepsilon^{(1)}_{(X-X)} - 3\varepsilon^{(2)}_{(X-X)} \tag{8}$$

$$E_b^{(i)}(V - V) = 2\varepsilon^{(i)}_{(Fe-V)} - \varepsilon^{(i)}_{(Fe-Fe)} - \varepsilon^{(i)}_{(V-V)} \tag{9}$$

$$E_b^{(i)}(X - Y) = \varepsilon^{(i)}_{(Fe-X)} + \varepsilon^{(i)}_{(Fe-Y)} - \varepsilon^{(i)}_{(Fe-Fe)} - \varepsilon^{(i)}_{(X-Y)} \tag{10}$$

$$\varepsilon^{(2)}_{(Fe-Fe)} = \alpha\varepsilon^{(1)}_{(Fe-Fe)} \tag{11}$$

$$\varepsilon^{(2)}_{(Fe-V)} = \beta\varepsilon^{(1)}_{(Fe-V)} \tag{12}$$

$$\varepsilon^{(2)}_{(X-X)} = \lambda_X\varepsilon^{(2)}_{(Fe-Fe)} \tag{13}$$

where $E_{coh}(X)$ is the cohesive energy of solute X in the body centered cubic (bcc) structure, E_{mix} ($X \to$ Fe) the mixing energy, $E_{int(100)}$ (Fe/X) the interface energy along the (1 0 0) plane and E_b binding energies. Moreover, i equals 1 or 2 and stands for first or second nearest neighbor respectively; α and β are constants, λ_X is a solute depending constant and X, Y are solute atoms. The energies used in the set of equations have been determined using ab initio calculations [4,10,11,13]. Ab initio calculations do have limitations and uncertainties; thus the ab initio values were examined with a critical eye. The energies calculated have been compared to experiments or thermodynamical data, when that was possible, and sometimes readjusted accordingly. This adjustment was made by simulating age hardening of binaries, then ternaries then more complicated alloys and comparing the results obtained with experimental results. A detailed description of the parameterization of the FeCu system can be found in [14]. During this procedure some of the values obtained ab initio used in Eqs. (4)–(10) had to be slightly modified so as to obtain a set of values more in agreement with experiments and phase diagrams as well as with other ab initio data. The energy difference between the original ab initio data and the adjusted data is less than 0.1 eV which corresponds to the ab initio uncertainty. Two examples of the kind of changes done follow. First, Mn–Cu binding energies were increased in order to better reproduce precipitation in a Fe–CuMnSi alloy aged at 550 °C [15]. With the ab initio values ($E_b^{(1)}$ (Cu–Mn) = 0.02 eV; $E_b^{(2)}$ (Cu–Mn) = –0.07 eV), the precipitates formed were composed of less than 1 at.% of Mn atoms instead of 8.1 at.% as measured experimentally. After some energy adjustments ($E_b^{(1)}$ (Cu–Mn) = 0.05 eV; $E_b^{(2)}$ (Cu–Mn) = 0.03 eV), the Cu precipitates contained 10 at.% of Mn atoms. Second, the Fe/Mn interface energy along the (100) plane was slightly increased, keeping its negative sign. This change was done in order to agree more with the experimental fact that FeMn is an ideal solution. Indeed, using the AKMC model with the ab initio value ($E_{int(100)}$ (Fe/Mn) = –177 mJ m^{-2}), when, for instance, 1.5 at.% Mn atoms were randomly introduced in a simulation box of α-Fe, a great part (around 75%) of the Mn atoms, which were bound to

Table 1
Properties chosen to parameterize each binary system FeX (X = Cu, Mn, Ni et Si)

Property	FeCu	FeMn	FeNi	FeSi
E_{coh} (X) (eV)	–3.49	–2.92	–4.34	–4.03
E_{sol} (X → Fe) (eV)	0.50	–0.16	–0.17	–1.09
$E_{int(100)}$ (Fe/X) (mJ m^{-2})	407	–116	–194	–969
E_{for} (V^X) (eV)	1.6	1.4	1.48	–0.21
$E_b^{(1)}$ (V–X) (eV)	0.07	0.04	0.01	0.11

Cohesive energies of the pure solute: $E_{coh.}$, solution energies of the solute in Fe: $E_{sol.}$, interface energies between Fe and the solute along (100): $E_{int(100)}$, vacancy formation energies in the solute: E_{for} and binding energies between the solute atom and a vacancy in an Fe matrix: E_b.