



Inconsistencies in modelling interstitials in FeCr with empirical potentials



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ABSTRACT

We present empirical potential and Density Functional Theory results of interstitials in FeCr and pure Cr. Results show that potentials for the original and revised two-band model, a recently introduced third two-band model, and for the revised concentration-dependent model produce errors of up to multiple eV in formation and binding energies for Fe-containing interstitials in pure Cr. Fe-interstitial binding in Cr is much stronger than Cr-interstitial binding in Fe according to Density Functional Theory, but all four potentials still strongly overestimate the binding strength. At the Fe-rich end errors in empirical potentials are smaller and most of the errors are not a linear extrapolation in concentration of the larger errors in pure Cr. Interstitial formation energies in Fe-rich FeCr are underestimated by all four empirical potentials, but much less so than in pure Cr. In Fe-rich FeCr the revised concentration-dependent model produces Cr-interstitial binding energies quite similar to Density Functional Theory values, while all three two-band models show almost no binding or repulsion.

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1. Introduction

FeCr is an alloy that has good properties for application as a structural material in nuclear environments. Since operating conditions like MeV neutron bombardment coming from fusion plasma can only be studied in special facilities, the alloy has been the subject of extensive atomistic modelling for over a decade. Much of the atomistic simulation work has come in the form of molecular dynamics or atomistic Monte Carlo simulations employing empirical potentials. Several FeCr potentials have been constructed explicitly in the context of radiation damage, including reproducing the change of sign in the heat of formation in Fe-rich FeCr, i.e. the original [1,2] and revised [3] versions of the two-band model (2BM) and the revised [4] version of the concentration dependent model (CDM). These potentials represent the established state of the art for atomistic radiation damage modelling of FeCr systems too large to be handled by electronic structure

methods, like Density Functional Theory (DFT). Recently, Eich *et al.* [5] published a third 2BM potential, focussing on an accurate thermodynamic description at both low and high temperature. During the construction of the original and revised 2BM and CDM, attention was focussed mostly on the Fe-rich end of the concentration range, since structural FeCr alloys consist mostly of Fe. Fitting data included Cr atoms interacting with or becoming part of self-interstitials, the archetypal point defect found in metals only after exposure to radiation. By contrast, the 3rd 2BM by Eich *et al.* did not include point defect data in the fitting.

Despite the application of the original and revised 2BM potentials and the CDM potential in many studies (on topics including phase diagram prediction e.g. [6,7], phase separation, e.g. [8], homogeneous e.g. [9] and heterogeneous e.g. [10] precipitation, short e.g. [11,12] and long range order e.g. [13], impact cascades e.g. [14–16], microstructure e.g. [17–19], Cr-interstitial interaction e.g. [20,21], Cr-dislocation interaction e.g. [22–24], dislocation-precipitate interaction e.g. [25], grain boundary segregation e.g. [26,27], radiation-induced segregation e.g. [28], point defect annealing e.g. [29], effect of Cr concentration on vacancy stability e.g. [4], vacancy cluster stability e.g. [30], bubble formation e.g. [31]) and their detailed benchmarking [7, 32–34] to assess their

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strengths and weaknesses, it is still not fully known which situations they manage or fail to describe accurately. The 3rd 2BM by Eich *et al.* has not been as extensively tested yet since its publication in 2015. Recently, we calculated interstitial formation energies with the revised CDM in FeCr alloys with 1–17 at.% Cr and found an unlikely formation energy trend that decreased with increasing Cr concentration, see below. This prompted us to investigate how accurate FeCr interstitial formation energies are reproduced at the Cr-rich end and if the energies might be ‘extrapolating towards the wrong end value’ in pure Cr. Having established, by comparing empirical potential and DFT results, that this is indeed the case, we determined how much of the large errors present in pure Cr are still present at concentrations in the Fe-rich end.

The build-up of this paper is as follows. In the next section a description of the computational methodology is presented. In Section 3.1 CDM results are presented for interstitials in 1–17 at.% Cr, showing the aforementioned questionable formation energy trend in that concentration range. In Section 3.2 we compare revised CDM and original, revised, and 3rd 2BM results for FeFe and FeCr interstitials (and Fe solutes next to vacancies) in pure Cr to DFT, showing that all four of these empirical potentials produce big errors for Fe-containing interstitials in pure Cr. Then in Section 3.3 we show how much of the errors for pure Cr are still present at two Cr concentrations (8% and 16%) in the Fe-rich end. Finally, in latter part of the summary and conclusions section we briefly discuss how to improve the empirical potentials.

2. Computational details

Empirical potential calculations were performed with four different potentials obtained following two different extensions to the EAM formalism: a CDM model [35], modified to better describe the relative energy of the mixed interstitials [4]; the original [1,2] 2BM model; the revised 2BM [3], modified to better describe the asymmetric heat of formation of FeCr; and the 3rd 2BM, constructed to give an accurate thermodynamic description at low and high temperatures.

To relax the configurations, different MD codes were used. The CDM calculations were performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) classical molecular dynamics code [36]. For the original and revised 2BM calculations an in-house standard code was used. For the 3rd 2BM calculations, static energy minimization was performed using another standard MD code.

Calculations have been carried out at constant volume, relaxing the atomic positions by using the conjugate gradient algorithm [37]. Periodic boundary conditions were set for all the calculations. For the CDM, concentrations investigated are 1–17 at.% Cr and pure Cr. It should be mentioned that, although the solid solution is thermodynamically unstable for concentrations above ~10%, these static calculations do not allow for precipitation to occur. The equilibrium lattice parameter employed in the calculations was changed as a function of Cr concentration, ranging from 2.855 Å for pure Fe to 2.878 Å for pure Cr. Different cell sizes have been used in the calculations depending on the afforded problem. Systems of 2000 + 1 atoms were used for the calculation of interstitial formation energies as a function of Cr concentration with the CDM. Smaller (250 + 1 atoms) systems were used for the interstitial formation energies at 8% and 16% Cr with empirical potentials and DFT. Systems of 250 ± 1 atoms were used for point defects in pure Cr with empirical potentials and DFT. The point defects in pure Cr were also calculated in 2000 ± 1 atom systems with the empirical potentials. Point defect formation energy differences between 250 ± 1 and 2000 ± 1 atom systems were less than 0.02 eV for vacancies and less than 0.06 eV for interstitials. In the calculation

of binding energies the differences were mostly systematic and cancelled out. Therefore, system size effects can be disregarded for our purposes.

As the formation energy not only depends on the quantity of Cr atoms in the sample but also on the local position of these Cr atoms with respect to each other and to the defect, several calculations for each concentration and interstitial type were performed in the case of the study of the Cr concentration effect and also in the calculations for the 8% and 16% Cr and the mean value of the formation energy is reported.

Spin-polarised Density Functional Theory calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) [38,39]. VASP is a plane-wave DFT code that implements the Projector Augmented Wave method [40]. We used standard PAW potentials with Perdew–Wang 91 parameterisation in the Generalized Gradient Approximation, that are distributed with VASP [41], with Vosko–Wilk–Nusair interpolation [42]. Fe and Cr potentials with eight and six valence electrons, respectively, were used. The plane wave energy cutoff was set to 300 eV, which is sufficient for convergence of energy differences between our systems. Brillouin zone sampling was done using 3 × 3 × 3 meshes in the Monkhorst–Pack scheme [43]. We used first order ($N = 1$) Methfessel–Paxton smearing [44] with a smearing width of 0.3 eV.

The formation energy E_f of a system of atoms with composition Fe_nCr_m and total energy $E(\text{Fe}_n\text{Cr}_m)$ is calculated using

$$E_f = E(\text{Fe}_n\text{Cr}_m) - nE(\text{Fe}) - mE(\text{Cr}) \quad (1)$$

where $E(\text{Fe})$ and $E(\text{Cr})$ are the energies per atom of Fe and Cr in their pure equilibrium states.

The binding energy E_b between objects (e.g., the binding energy that is released when a solute atom and a self-interstitial merge to become a mixed dumbbell) is defined as the formation energy difference between a system in which the objects are close together and a system in which the objects are far apart. Within the limited size of our systems it is not possible to separate objects over large distances. Therefore the formation energy of the situation where the objects are separated is usually calculated by calculating each object individually in a supercell. The binding energy then becomes

$$E_b = -[E_f(\text{combined}) - E_f(\text{object1}) - E_f(\text{object2}) - \dots] \quad (2)$$

in which a positive binding energy means attraction between the objects and a negative binding energy means repulsion.

3. Results

3.1. Revised CDM interstitial formation energies in Fe-rich FeCr as a function of Cr content

Single interstitials of different types were inserted in random FeCr alloys with Cr concentrations ranging from 1 to 17 at.% in 1% increments. Interstitials were created by deleting one by one each of the atoms in the cell and replacing them by a single interstitial (FeFe or FeCr), so that the interstitial is created in each of the possible positions in the cell. Only a given number of stable configurations are taken into account in the calculation of the medium formation energy. First, we have observed that in some cases the geometry of the final configuration does not coincide with the starting one. Second, the number of Cr atoms changes depending on the type of atom deleted (Fe or Cr) and the interstitial created (FeFe or FeCr). Only those configurations with the same initial and final geometries and a constant number of Cr atoms are used to calculate the mean formation energy for each concentration. An interstitial was deemed to have relaxed to another orientation if the angle between the original and relaxed axes of the atoms

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