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SCIENTIFIC REPORT
SCK•CEN-BLG-963

Molecular dynamics simulation of displacement cascades in Fe-Cr alloys for fusion applications

First results

Lorenzo Malerba, Dmitry Terentyev
and Abderrahim Almazouzi

with the contribution of
P. Olsson (U. Uppsala) and J. Wallenius (KTH Stockholm)

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Abstract

An Embedded Atom Method (EAM) empirical potential recently fitted and validated for Fe-Cr systems is used to simulate several displacement cascades initiated by recoils up to 15 keV in Fe and Fe-10%Cr, model alloys for high-Cr ferritic-martensitic steels. The evolution of these cascades up to the stabilisation of the primary damage state is followed and quantitatively analysed by counting produced point defects and point defect clusters, using the Wigner-Seitz cell criterion to identify point defects. Particular attention is devoted to assessing the effect of the presence of Cr atoms on the defect distribution as compared to the outcome of cascades in pure Fe. First results show that the main effect of the presence of Cr in the system is the preferential formation of mixed Fe-Cr dumbbells and mixed interstitial clusters, of expected lower mobility than in pure Fe.

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1. Introduction

The development of models to assess the mechanical stability under intense neutron irradiation of high-Cr reduced-activation ferritic/martensitic (RAFM) steels is an important part of fusion reactor materials research. The starting point for any neutron irradiation damage modelling effort is the study of the primary damage state produced by displacement cascades in the relevant material. Molecular dynamics (MD) is well known to be the simulation tool "par excellence" for the study of displacement cascades, provided that a valid and adequately stiffened many-body interatomic potential is available for the system of interest [1]. In the past, much work has been done on MD simulation of displacement cascades, using pure Fe as model alloy for a steel, described by means of a variety of interatomic potentials [2,3,4,5,6]. However, in order to take a step forward towards real engineering materials in the modelling effort, an assessment of the effect on the primary damage state of the main alloying elements, such as Cr in the case of RAFM steels, is important. In this framework, this paper reports a first set of results on displacement cascades initiated by Fe recoils up to 15 keV in Fe-10%Cr obtained using a recently fitted and thoroughly validated empirical interatomic potential for the Fe-Cr system [7,8]. For comparison, cascades in pure Fe were simulated as well, using the same potential. The objective of the reported work is to show that our interatomic potential produces results in agreement with earlier work for pure Fe. On this basis, the main effects of the presence of Cr in terms of primary defect population are analysed and discussed.

2. Simulation method

The details of the fitting procedure and validation of the Embedded Atom Method (EAM) [9] interatomic potential for Fe-Cr used in this work can be found elsewhere [7,8]. Briefly, the Fe-Fe potential was fitted following the approach described in ref. [10] and stiffened using the same method as in ref. [2]. The Cr-Cr potential was taken from the literature [11]: although it is known that it cannot correctly reproduce the elastic properties of pure Cr, this is assumed to be a minor shortcoming when dealing with sufficiently diluted alloys (≤20%). The Fe-Cr crossed pair contribution was fitted, using the procedure described in [12], to the experimental values of the bulk modulus

(1544 kbar), cohesive energy (-4.262 eV) and lattice parameter (2.866 Å) of the Fe-10%Cr alloy, as well as to the mixing enthalpy for the same alloy (5.16 meV), calculated by *ab initio* methods in order to take into account the effect of ferromagnetism [13]. This potential provides a description of the interaction between Cr atoms and point defects in a ferritic matrix in very reasonable agreement with *ab initio* results obtained with the VASP code [8,14,15]. In particular, the stability of the Fe-Cr and Cr-Cr dumbbells is correctly reproduced, as well as the negligible binding energy of Cr atoms with vacancies [8]. In addition, the description of Cr diffusivity in Fe is also in good agreement with experimental results [16,17]. The validation work, where a comparison with other existing potentials for Fe-Cr alloys was also performed, proved that, within the limits of the EAM description, the potential used is presently the best available for these systems, in the range of compositions where no α'-phase nano-segregation is expected.

The potential was implemented in the classical MD code Dymoka, which is suitable for the simulation of displacement cascades [6]. Dymoka uses the link cell method to generate the neighbour list for the interaction between atoms and allows a variable timestep to be used, depending on the simulated cascade stage (0.1 fs at the beginning of the collisional phase, when some atoms receive high amounts of kinetic energy from the primary recoil, increased with time up to 5 fs at post-collisional stage). Prior to initiating the cascade, a block was equilibrated for 1 ps at 300 K. This atom block was then used as starting point for the cascade simulation and defect detection further on. Following a common, first approximation practice [1,2,3,5,6], no rigorous attempt was made to control the temperature of the system, like was done e.g. in ref. [18], and all presented results were obtained working in the NVE microcanonical ensemble (constant number of particle, N; volume, V; and total energy, E) with periodic boundary conditions, as was frequently done in the past [3,4,6]. Only in the case of high recoil energy (10 and 15 keV) were the boundary atoms damped using the rescaling velocity algorithm, to partially extract heat, thereby limiting the increase of the box temperature that inevitably follows the introduction of the recoil. However, it is well accepted that the simulation temperature scarcely influences the defect population produced in displacement cascades in Fe [18,5]. The cascade was started by imparting a kinetic energy E_{PKA} to the selected primary knock-on atom (PKA), following which the system was allowed to evolve for

typically 10-15 ps. A high-index direction <135> was chosen for the PKA in order to avoid chanelling [2,5]. For each E_{PKA}, a number of cascades were generated to achieve meaningful statistics (5 for the highest energies, 10 or 20 for the lower ones). In total, the results reported in this work correspond to more than 250 cascades. The size of the simulated box was increased with increasing E_{PKA}, so as to ensure that the cascade was retained within the block and no artificial overlap of cascade regions occured. The progress of the cascades was monitored using a visualization tools (Visatom). The final atomic configuration was then analysed to detect and count defects, using the Wigner-Seitz cell method: an empty cell corresponds to a vacancy, two atoms in the same cell correspond to an interstitial configuration. Replacements were also accounted for and the number of displaced atoms was defined as the sum of replaced and interstitial atoms. Clusters were defined using a 3rd nearest neighbour (nn) criterion for interstitials and 2nd nn for vacancies.

3. Results and discussion

3.1 Defect number

During the collisional phase of a cascade, many atoms are temporarily displaced from their initial lattice positions, but most of them finally end up re-occupying vacant sites during the phase that accompanies and follows the thermal spike. Eventually, only a small fraction of the displaced atoms remains in interstitial position, thereby leaving vacancies behind (surviving Frenkel pairs). Traditionally, the NRT formula [19] is used for estimating the number of Frenkel pairs produced per cascade (N_{NRT}), core magnitude for the evaluation of the displacements per atom (dpa) in irradiated metals [20]:

$$N_{NRT} = \frac{0.8 \cdot E_D}{2 \cdot E_d} \qquad (1)$$

where E_d is the average displacement energy for all crystallographic directions and E_D is the damage energy, i.e. the fraction of the recoil energy that goes into displacive damage,

after subtracting the portion dissipated in electronic excitation. In the present work, for the sake of simplicity in the comparison, we used E_d=40 eV [20] for both pure Fe and Fe-10%Cr. Since in MD the interaction between ions and electrons is not included, it is customary to assume that $E_D=E_{PKA}$ [1].

In figure 1a the number of surviving Frenkel pairs at the end of the cascade (N_{FP}) in both pure Fe and Fe-10%Cr resulting from the MD simulations is plotted as a function of the energy of the PKA. The points have been interpolated using the empirical power law proposed by Bacon and co-workers, $N_{FP}=A\cdot E_{PKA}^{\ m}$ [1], whose validity, though unexplained, has been determined to cover the range from about 1 to 20 keV [5]. The prefactors and exponents that we obtained in a least-square fit were, for Fe, A_{Fe}=5.23 and m_{Fe}=0.81; for Fe-10%Cr, A_{Fe10Cr}=4.53 and m_{Fe10Cr}=0.85. The first pair of parameters is in close agreement with the values obtained by Bacon and co-workers for pure Fe, using a different interatomic potential, from simulations with an initial temperature of 100 K (respectively, A=5.67 and m=0.78 [1]), our exponent being in even closer agreement with a later assessement proposed by Stoller, m=0.795 [5]. Despite the somewhat lower prefactor, the higher exponent in the case of Fe-10%Cr points to a tendency to slightly higher defect production when Cr is present. The same conclusion about the effect of Cr can be drawn from figure 1b, where the ratio of surviving Frenkel pairs in pure Fe and Fe-10%Cr to the number of NRT displacements (equation 1) is shown. As is by now well known, once again this figure clearly demonstrates that the defect production efficiency, compared to the NRT prediction, decreases with recoil energy down to a more or less asymptotic value of about 0.3 in the case of pure Fe [1,5,6]. In the case of Fe-10%Cr, at low energies the fraction of defects is significantly higher, the difference with pure Fe becoming negligible at higher energies. A study of the threshold displacement energies of a Cr atom in a ferritic matrix along the three main crystallographic directions showed that in one direction, ⟨110⟩, the threshold is 5 eV lower than for Fe atoms, indepedently of the Cr concentration [21]. It is possible that this lower threshold energy for Cr atoms explains the slightly higher defect production efficiency in Fe-10%Cr.

The main difference between the outcome of cascades in Fe and Fe-10%Cr is not the number of defects, but their nature. In agreement with *ab initio* calculations [8], the

potential we use predicts a positive binding energy for Fe-Cr and Cr-Cr dumbbells (larger than 0.3 eV). This feature leads to the formation, at the end of the cascade, of a number of mixed dumbells that is remarkably higher than the number of Fe-Fe dumbells, as is shown in figure 2a. Independently of the recoil energy, 67% (±6% of standard deviation) of the dumbbells contain Cr atoms, despite the 10% Cr concentration of the alloy. Figure 2b shows clearly, in the case of 5 keV cascades, that the formation of mixed dumbbells is a post-collisional-phase phenomenon. Initially, as is to be expected, more Fe atoms than Cr atoms are displaced and counted as interstitials. However, during the cooling stage most of these Fe-Fe dumbbells, possibly assisted by the still high temperature, glide till they become trapped at the closest Cr atoms, thereby determining a cross-over of the curves of the number of mixed and self-interstitial dumbbells versus time in figure 2b. The same process has been seen to occur for cascades of all energies.

In summary: Cr atoms do not appear to significantly affect the collisional stage of the cascade, as may be expected, considering the negligible difference in mass between Fe and Cr atoms, but they do determine a redistribution of dumbbell species during the post-collisional stage, where most of the dumbbells end up containing Cr atoms, in percentage far higher than the concentration in the alloy.

3.2 Cluster formation

All previous papers on displacement cascades in Fe coincide on the fact that very little in-cascade vacancy clustering occurs in this material, while sizeable interstitial clusters are seen to form [1,2,5,6]. This is what we find, too, as is shown in figures 3a and 3b, where the fraction of, respectively, surviving vacancies and interstitials that are found in clusters (containing at least two elements) is plotted versus recoil energy for both Fe and Fe-10%Cr. We find that the average fraction of clustered vacancies is never bigger than 30% in Fe, except for a high point at 15 keV, which may be a partial outlier and require more statistics. the mean cluster size being at any rate rather small (2-3 vacancies). Conversely, up to 50% of the interstitials are found in clusters, of sizes (so far!) up to 11. These results, allowing for the large scatter which is typical of these magnitudes [5,6], are

qualitatively in agreement with most previous work [1,2,4,5,6], and also quantitatively, provided that the same criterion is used for the definition of clusters (2^{nd} nn for vacancies, 3^{rd} nn for interstitials). In Fe-10%Cr there seem to be a trend to a somewhat smaller fraction of clustered vacancies and also, to a much lesser extent, interstitials, visible at higher energies. However, caution is necessary when interpreting largely scattered data such as these, particularly considering that for higher recoil energy we have less statistics than for lower energy. The size distribution of the clusters (not shown) seems anyhow comparable in both materials. Nonetheless, the nature of the clusters is significantly different, since a large part of the interstitials atoms – as mentioned - is made of Cr atoms, in a concentration far above the average Cr concentration in the alloy. Although further inverstigation is required, it is to be expected that these largely mixed clusters, which are somehow stabilised by the presence of Cr interstitial atoms, will be significantly less mobile than their equivalent in pure Fe, with an a priori large impact on the subsequent evolution of radiation damage. A first study of single interstitial diffusivity in Fe and Fe-Cr showed that, while the migration energy is comparable, the prefactor of the interstitial diffusion coefficient can drop by about one order of magnitude due to the presence of Cr atoms [16]. It should be noted that experimentally Okada *et al.* observed that the addition of even small percentages (0.1%) of Cr to ultra-pure Fe induces more frequent nucleation of small loops of interstitial nature than in ultra-pure Fe, since the early stage of the irradiation, both using neutrons and electrons, in a range of irradiation temperatures between 200°C and 500°C [22]. These findings seem to be correctly reflected by the results of our simulations. For the moment, no detailed analysis was conducted in order to detect a possible association of vacancies and vacancy clusters to Cr atoms, above what should be expected in a random alloy. Although this may explain the slightly lower fraction of clustered vacancies, due to the very low Cr-V binding energy this is not likely to be a large effect.

Summary and Conclusions

More than 250 displacement cascades, up to 15 keV recoil energy, were simulated by molecular dynamics in Fe and Fe-10%Cr, using a recently fitted and validated many-body potential which, at the moment, seems to be the best available for the Fe-Cr system, within the limits of the EAM approach. The different phases of the cascades where monitored and analysed using *ad hoc* post-processing tools. In this work, the results concerning the number of surviving defects and their distribution in clusters have been reported. In the case of pure Fe, our results are in line with previous ones. The presence of 10% Cr atoms does not seem to affect the collisional stage of the cascade, as expected, because of the negligible difference in mass between Fe and Cr atoms, but it does determine a redistribution of dumbbell species during the post-collisional stage, where most of the interstitial atoms become Cr atoms, in percentage far higher than the concentration in the alloy. No substantial difference is detected between Fe and Fe-10%Cr in the fraction of clustered defects. However, interstitial clusters contain a large percentage of Cr atoms which somewhat stabilise them. This feature may drastically reduce the mobility of interstitial loops in Fe-Cr compared to pure Fe, with significant impact on the subsequent evolution of radiation induced defects. Experimental evidence in support of this view has also been reported.

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Figure 1

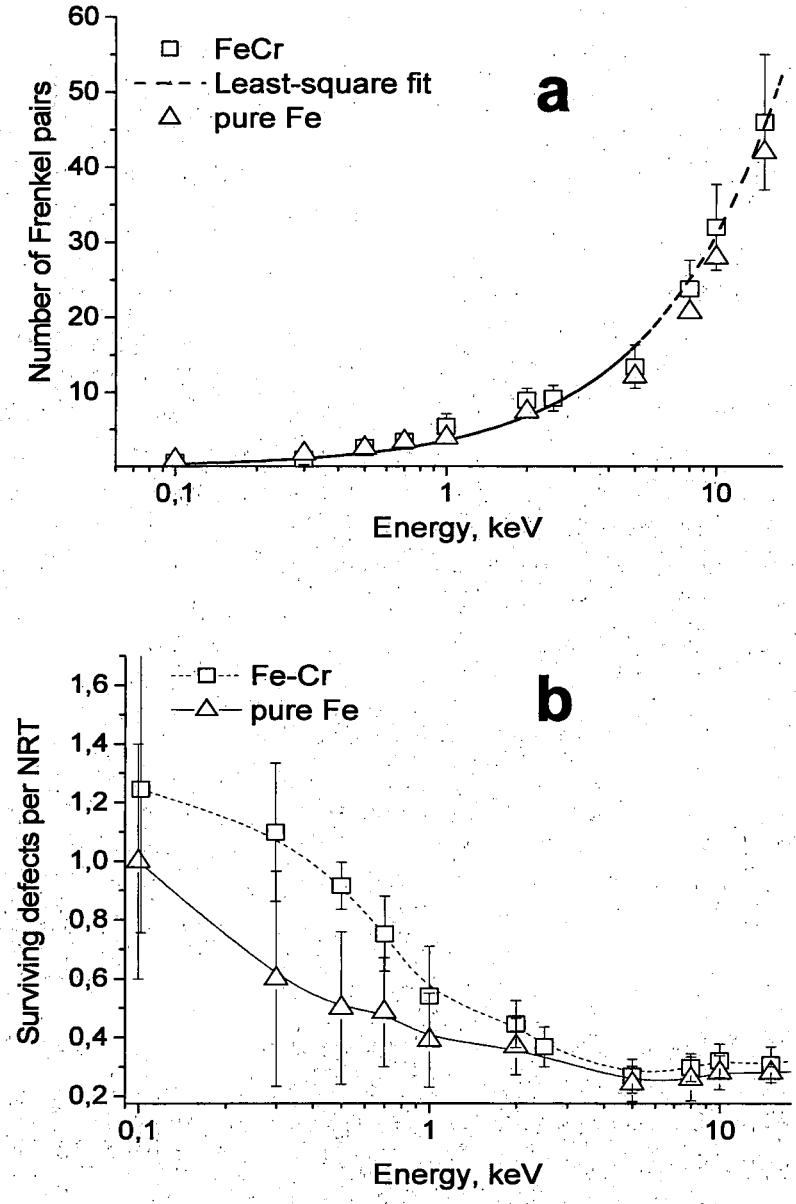

Figure 1 – Number of surviving Frenkel pairs at the end of the displacement cascade versus recoil energy, in both Fe and Fe-10%Cr. (a) absolute values, interpolated using the power law proposed by Bacon et al. [1]. (b) Fraction of corresponding NRT value (equation 1): the lines are simply guides for the eye.

Figure 2

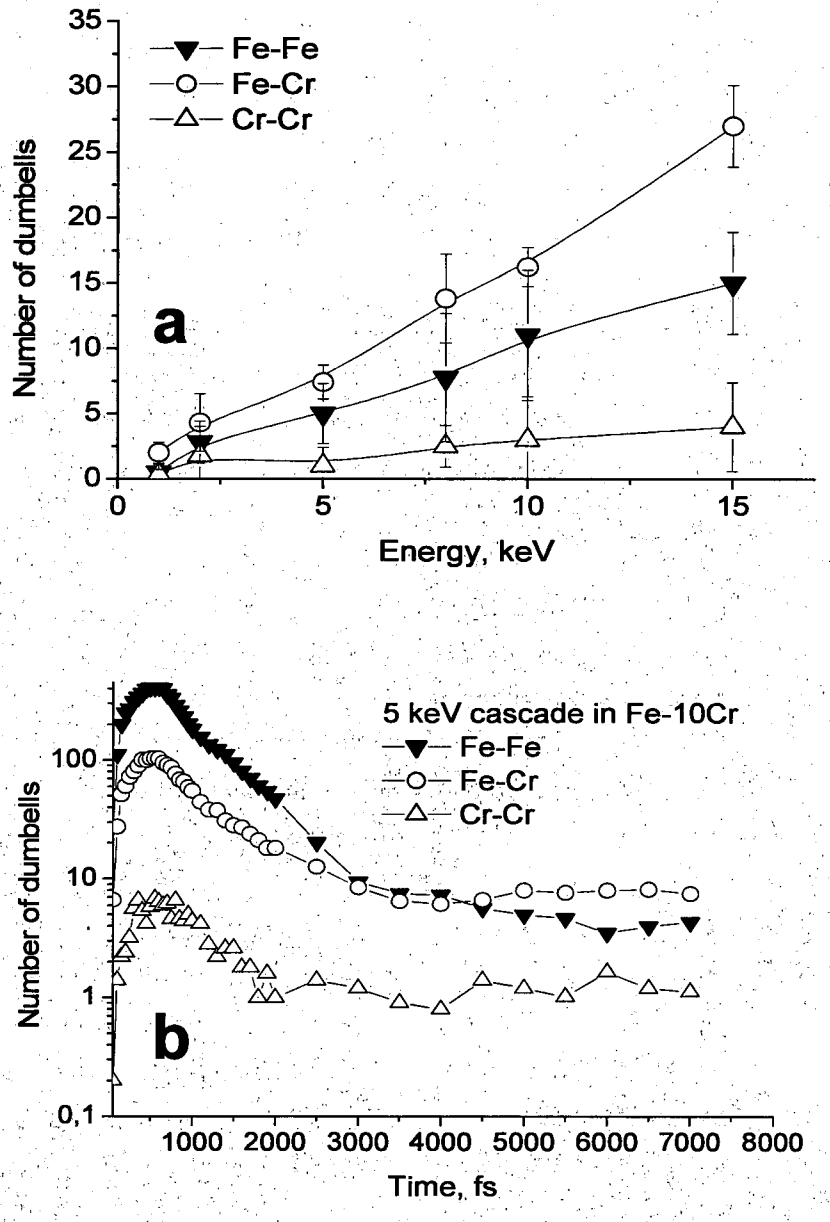

Figure 2 – Number of Fe-Fe, Fe-Cr and Cr-Cr dumbbells in Fe-10%Cr cascades. (a) versus recoil energy. (b) versus time in a 5 keV cascade. The lines are only guides for the eye.

Figure 3

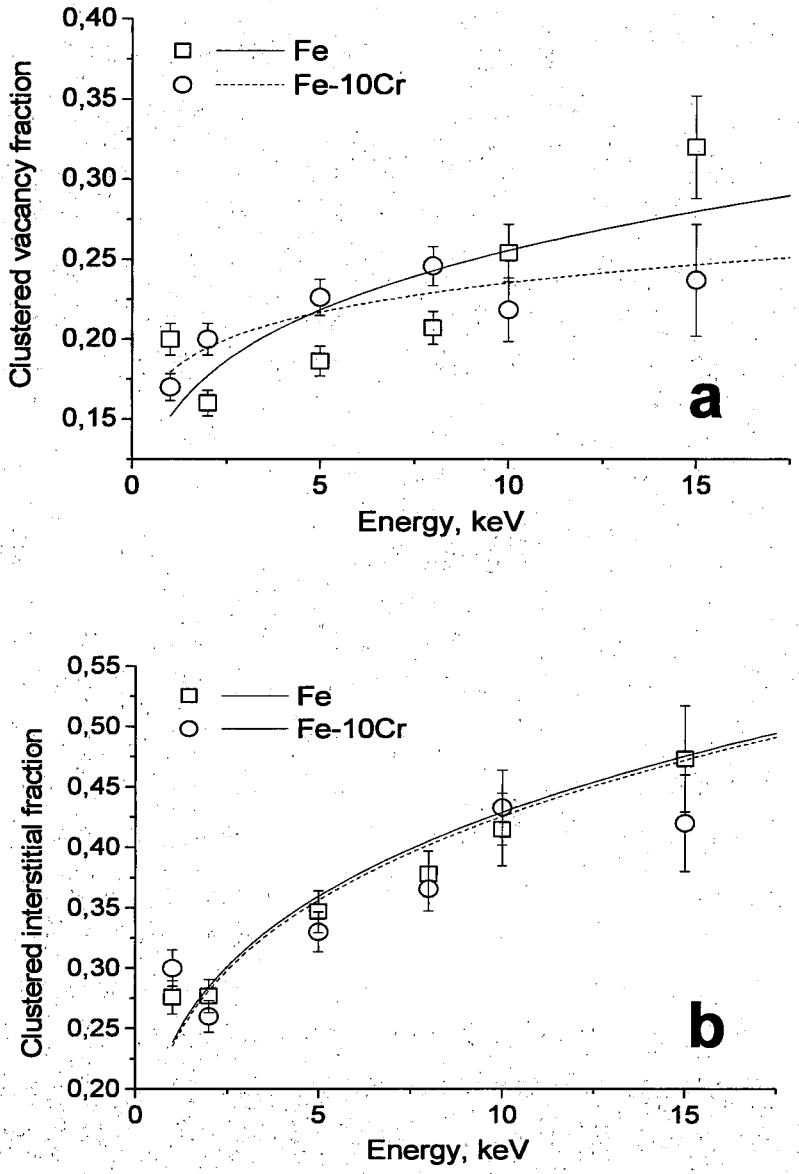

Figure 3 – Fraction of surviving defects in cluster at the end of the cascade, in both Fe and Fe-10%Cr, versus recoil energy. (a) vacancies. (b) interstitials. The lines represent trend power laws.