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COMPUTER SIMULATION OF THE EFFECT OF COPPER ON DEFECT PRODUCTION AND DAMAGE EVOLUTION IN FERRITIC STEELS

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ABSTRACT

It has long been noticed that the effect of Cu solute atoms is important for the microstructural evolution of ferritic pressure vessel steels under neutron irradiation conditions. Despite the low concentration of Cu in steel, Cu precipitates form inside the α-Fe surrounding matrix and by impeding free dislocation motion considerably contribute to the hardening of the material. It has been suggested that Cu-rich clusters and combined Cu solute atoms-defect clusters that may act as initiating structures of further precipitates nucleate during annealing of displacement cascades. In order to assess the importance of the different mechanisms taking place during collision events in the formation and later evolution of these structures, a detailed Molecular Dynamics (MD) analysis of displacement cascades in a Fe-1.3% at. Cu binary alloy has been carried out. Cascade energies ranging from 1 to 20 keV have been simulated at temperatures of 100 and 600 K using the MDCASK code, in which the Ackland-Finnis-Sinclair many-body interatomic potential has been implemented. The behaviour of metastable Cu self-interstitial atoms (SIAs) in the form of mixed Fe-Cu features is studied as well as their impact on the resulting defect structures. It is observed that above 300 K generated Cu SIAs undergo recombination with no substantial effect on the after-cascade microstructure while at 100 K Cu SIAs remain sessile and exhibit a considerable binding to interstitial and vacancy clusters. Finally, the effect that the production of vacancies via collision cascades may have on the self-diffusion of Cu solute atoms is quantitatively addressed by means of determining diffusion coefficients for Cu atoms under different microstructural conditions.

INTRODUCTION

As many nuclear power plants approach the end of their licensed operational life, one topic of current concern is the change in the mechanical properties that reactor pressure vessels (RPVs) may suffer after prolonged exposures to neutron irradiation environments. It is well known that pressure vessel steels embrittle under irradiation conditions due to the production of atomic-scale defect aggregates that hinder free dislocation motion resulting in hardening of the material. In addition to hardening caused by radiation produced clusters of defects, there is the contribution of nano-scale features such as Cu and Mn-Ni rich precipitates that form in the core of the material despite the low concentration of these elements in RPV steels [1,2]. Depending on alloy composition, Cu-rich precipitates are the dominant nanofeature in steels containing more than 0.1 at. % Cu [3] and this issue has attracted much research using a variety of techniques [4]. While there has been a number of experimental studies concerning the effect of Cu solute atoms as well as of the precipitates' structure in the microstructural evolution of irradiated steels [5,6,7], computer simulation of the precipitation kinetics has been treated recently [8,9,10,11]. This computational research effort has consisted mainly of lattice and kinetic MonteCarlo simulations of the Cu precipitation during thermal or cascade ageing and

the interaction of these precipitates with cascade debris, particularly vacancies [8,11]. Results of these simulations indicate that both well-formed precipitates and solute atmospheres are formed as a consequence of highly correlated vacancy-solute transport processes and radiation-enhanced diffusion [8,12]. Moreover, there is a general belief that vacancy cluster-Cu solute atoms complexes that may act as precipitate precursors are produced during annealing of displacement collision cascades [12]. Other cascade effects of interest such as Cu SIA production and their interaction with characteristic cascade defect-structures (vacancy and SIA clusters) or more generally, the significance that solute atoms in a dilute substitutional solid solution have in the cascade evolution, are issues that occur in time scales (ps) much shorter than those related with the creation and coalescence of Cu precipitates (seconds). In this paper, a number of high-energy displacement cascades in a diluted Fe-Cu binary alloy at 600 K and 100 K has been carried out in order to investigate the process of in-cascade formation of vacancy-Cu complexes and Cu SIAs. The Cu content in the solution has been chosen to be 1.3% at. to enhance the statistics concerning the Cu atoms and due to the existence of several experimental works where Fe-1.34% Cu type alloys were employed [7,13].

SIMULATION MODEL

Molecular Dynamics

Although, collision events have been thoroughly analyzed with MD in pure metals [14,15,16], except for some specific papers [17], MD simulations in binary alloys have not been sufficiently studied. All the cascade simulations presented in this paper have been performed with the MDCASK code in which the new Fe-Cu potential derived by Ackland [18] from the Finnis-Sinclair many-body formulation [19] has been implemented. Details about the MDCASK code as to potential implementation, integration of the equations of motion, etc. are given elsewhere [20]. The simulations were carried out with periodic boundary conditions at constant volume. The Langevin equation of motion is applied to the atoms of the cell boundaries in order to control the temperature of the crystal.

Starting Assumptions

As in regular MD cascade simulation procedures, the solid solution was first equilibrated during several (8~10) picoseconds before the introduction into the system of the primary knock-on atom (PKA). The Cu atoms were introduced randomly into the bcc α-Fe matrix up to a proportion of 1.3 at. %. The effect that the Cu solute atoms have on the lattice parameter according to Wriedt *et al.* [21] has also been taken into account in our simulations, i.e. $\Delta a_o = 0.94\times10^{-3}$ Å per at. % Cu gives $\Delta a_o = 0.0012$ Å, which means that $a_o = 2.867$ Å rather than 2.866 Å for the bcc pure α-Fe lattice. Although this consideration is expected to have little or no effect on the results, this minute rigid dilation of the lattice may help ease down the additional strain introduced by Cu solute atoms and Cu SIAs during cascade ageing and yield more reliable results. Once the crystal was stabilized at the desired temperature, the resulting configuration was taken as starting point for all the cascades of a given energy. In order to get a reasonable statistics as to the number and type of defects produced, up to ten cascades were simulated for each PKA energy corresponding to different crystallographic directions. Both Fe and Cu PKAs were essayed for each one of the cascade energies in order to facilitate comparison between the effects of both species on atomic-scale damage production.

RESULTS

Cascade Analysis

The total number of cascades simulated for each energy can be seen in Table I. Simulations at 100 K and 600 K were performed only for 20 keV cascades since it is for high energies that variable conditions are more meaningful to microstructural evolution. The average number of Frenkel pairs produced in each cascade is also shown in Table I for cascades in the Fe-Cu solution and in pure α-Fe. It is noteworthy that the number of defects in pure Fe is consistently higher than in Fe-Cu as if the Cu atoms in the substitutional solution deadened the expansion of the cascade. A preliminary estimation of this effect can be extracted calculating the volume of the cascade applying the criteria used by Gao and Bacon [22] where this cascade volume is defined as the sphere that contains at least 90% of the displaced atoms at its maximum expansion. Following this, the radius of such a sphere for a 10 keV cascade ($45a_o \times 45a_o \times 45a_o$ box) in the Fe-Cu alloy was found to be approximately $12.5a_o$ whereas the volume in a pure Fe block in equivalent conditions was $14.2a_o$. For 5 keV cascades ($30a_o \times 30a_o \times 30a_o$ box), the radius in the Fe-Cu system is $7.6a_o$ while the volume in the equivalent pure Fe block was $\sim 9a_o$. Although a satisfactory explanation for this behavior may involve other physical factors such as threshold displacement energies or linear energy transport along replacement collision sequences (RCSs), this effect seems to be somewhat an artifact of the interatomic potentials employed. The resulting RCSs are shorter in length giving rise to a lesser production of defects.

Table I: Number of cascades and defect production in the analyzed Fe-Cu alloy. Numbers in parentheses in the fourth column are data for comparison from cascades simulated in pure α-Fe at 600 K with the EAM potential [23].

PKA energy (keV)	Number of cascades		Average total number of Frenkel pairs	Average number of Cu SIAs generated
	600 K	100 K		
2	10	—	8 (10)	0
5	10	—	12 (19.5)	0
10	10	—	27 (35)	0.5
20	4	2	53 / 56 (58)	1.8 / 2.1

As reported by some authors [16,17], vacancy clustering in bcc metals is limited. In addition to this intrinsic feature, vacancies are not left to freely rearrange themselves into clusters or collapsed plates due to the effect of Cu solute atoms that, if sufficient annealing is allowed, form shells around the vacancy-rich core. This indeed has to do with the enhanced diffusion that Cu atoms close to the core of the cascade suffer via the vacancy mechanism. Some of the 10 keV cascades at 600 K were granted 1.15 additional ns of relaxation to check if this forced diffusion could affect the redistribution of Cu solute atoms and the vacancy clustering fraction. Results can be observed in Figure 1, where weak clouds of Cu atoms tend to form around the cascade core, as anticipated by Odette *et al.* [13]. A quantitative measure of this effect can be extracted by calculating the moment of inertia, I, of the Cu atoms in figures 1 (a) and 1 (b) ($I = \Sigma(\mathbf{r}_{Cu} - \mathbf{r}_g)^2 / N_{Cu}$, where $\mathbf{r}_g$ is the center of mass of the cascade vacancies and N_{Cu} the total number of Cu atoms). The value for the initial configuration is $I \approx 232a_o^2$ whereas for the final configuration after 1.15 ns, $I \approx 228a_o^2$. With respect to the vacancy clustering fraction, the Ackland-Finnis-Sinclair potential yields a binding energy (e_b) of 0.14 eV for the 1st nearest neighbor (1nn) divacancy in pure Fe, and a value of 0.19 eV for the 2nd nearest neighbor

(2nn) divacancy. Beyond this distance the vacancies are not bound at all (e_b=0) so our criterion for vacancy clustering is that they be within 2nn distances. Following this, for our Fe-Cu 20 keV cascades, we get a value of 0.25 at 600 K and 0.22 at 100 K for the vacancy clustering fraction, while, for instance, Stoller [24], for pure Fe, obtained values of 0.37 and 0.50 respectively, using the 2nn clustering criterion. Nevertheless, there is probably some potential-dependence contribution to this difference. These numbers, however, indicate that, even though vacancies are more strongly bound to each other (e_b=0.14 eV) than to Cu atoms (e_b=0.09 eV), the effect of the solute over the clustering tendency of the vacancies is to hinder it.

Cu Self-Interstitials

As anticipated before, Cu SIAs are metastable defects that appear as final links of RCSs in displacement cascades. When found isolated, Cu interstitials are observed forming mixed Fe-Cu split dumbbells (formation energy, e_f = 6.18 eV). The activation energy for the Cu atom to take the split lattice position (recombine) has been calculated to be approximately 0.16 eV, i.e. forcing the formation of a pure Fe-Fe dumbbell via the interstitialcy mechanism. This means that in the cascades at 600 K, Cu SIAs undergo recombination quickly and have no further significant effect on the crystal lattice. However, at 100 K Fe-Cu dumbbells remain sessile and their average lifetime has been extrapolated to be as long as 0.5 μs.

On the other hand, in some cascades at 600 K Cu interstitials were found in the form of <111> crowdions (e_f = 6.40 eV) forming small dislocation loops with a considerable binding energy (e_b = 1.15 eV). These Cu interstitials, however, did not seem to be any obstacle to the further propagation of the loops.

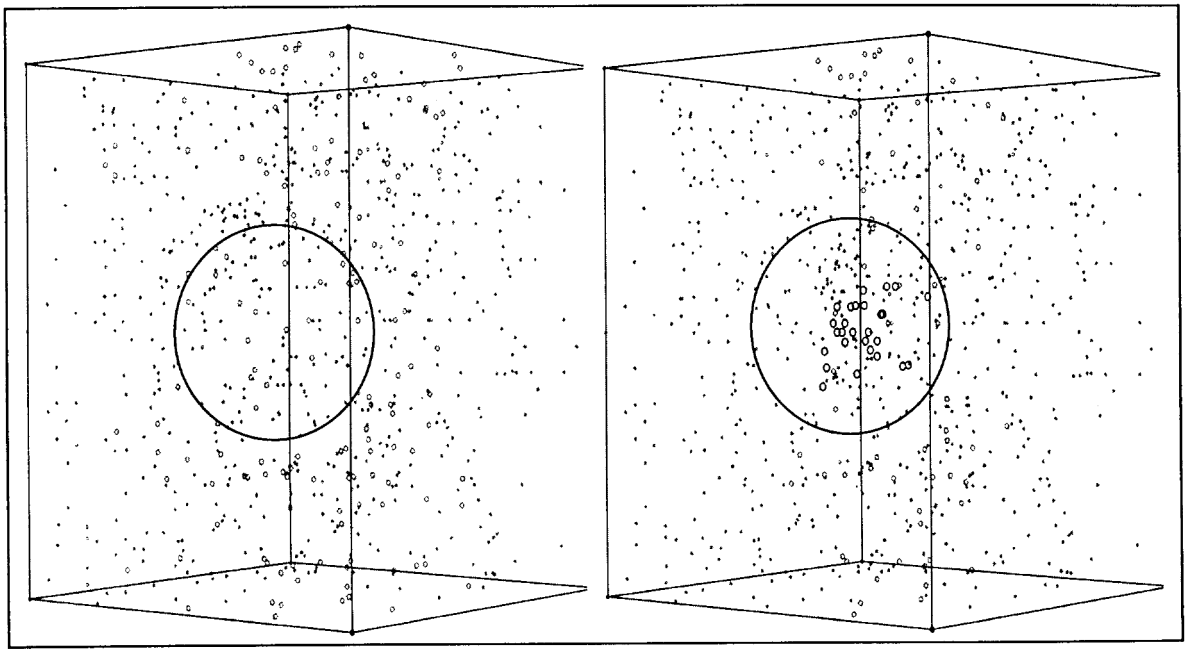

Figure 1. (a) Initial atomic configuration of the computation box. Only Cu solute atoms are shown (gray dots). (b) Final distribution of Cu atoms and vacancies (big circles) 1.15 ns after the 10 keV-PKA event. Note the increased density of solute in the encircled area (cascade core).

Enhanced Diffusion Kinetics

The combination of excess vacancies and excited Cu solute atoms hastens the process of solute clustering and gives rise to atomic configurations like that shown in Fig. 1 (b). A way to quantify this enhanced Cu solute atom-migration is calculating the self-diffusion coefficient, D, via MD simulations. In principle, a coarse estimation of D (vacancy mechanism) can be obtained through the following expression:

$$D = C \cdot \omega \cdot N_v \cdot a_o^2 \quad (1)$$

where C is a constant that includes the nature of the 1nn jumps in the bcc lattice, ω is the jump frequency, a_o the lattice parameter and N_v is the probability to find a vacancy in a given lattice position, i.e. the percentage of vacancies in the crystal. As to ω, it is ordinarily taken as $\omega = \nu \cdot \exp(-E_m / KT)$, where E_m is the energy required to move an atom to the saddle point position, K the Boltzmann's constant, T the absolute temperature of the crystal and ν is a typical vibration frequency of the material ($\sim 10^{13}$ Hz). We have calculated the Cu-vacancy interchange energy by a static relaxation calculation and computed a value of 0.739 eV, similar to the number employed by Soisson *et al.* (0.69 eV) [9], but quite different to the one obtained by Ackland *et al.* (0.60 eV) [19]. In a system at equilibrium conditions N_v is usually taken as $N_v = N_o \cdot \exp(-E_f / KT)$, E_f being the vacancy formation energy. Hence, in the 1000-1500 K temperature interval, N_v ranges between 2×10^{-9} and 2×10^{-6}, having taken E_f =1.7 eV. However, during cascade ageing highly non-equilibrium conditions are found and the increased local strain due to the excess vacancies tends to be counterbalanced by the diffusion of energetic Cu atoms. Under these extreme conditions, it is not exaggerated to consider $N_v \approx 0.01$ in a domain around the vacancy-rich core of the cascade. We have calculated the temperature dependence of D assuming an Arrhenius behaviour:

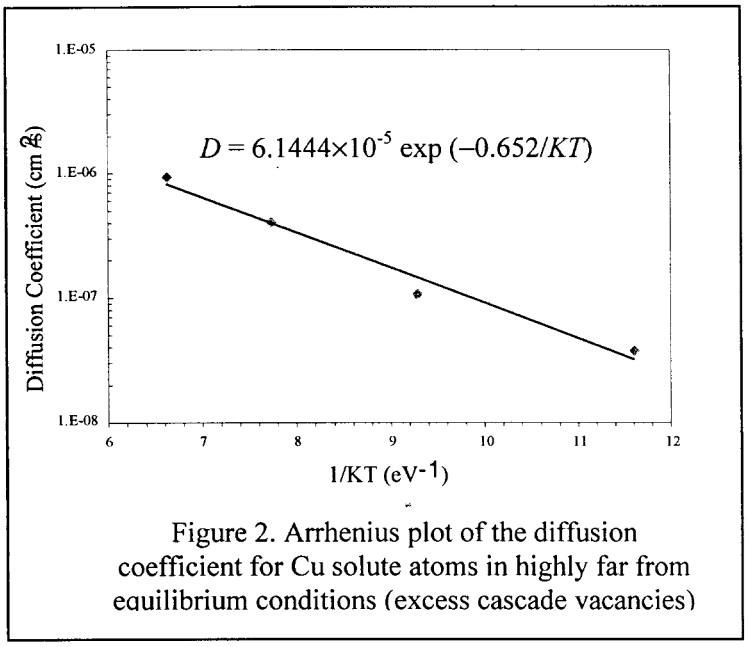

Figure 2. Arrhenius plot of the diffusion coefficient for Cu solute atoms in highly far from equilibrium conditions (excess cascade vacancies)

$$D = D_o \cdot \exp(-E_m / KT) \quad (2)$$

where D has been calculated for four different temperatures ($0.55T_m$, $0.70T_m$, $0.85T_m$ and $0.95T_m$) in a Fe-1.3% at. Cu solution with 1% concentration of vacancies (figure 2). Atoms were allowed to evolve during 0.75 ns and then D_{Cu} was estimated using:

$$D_{Cu} = \frac{1}{6}\frac{d}{dt}\left\langle R_{Cu}^2(t)\right\rangle \quad (3)$$

From (2) and (3) we obtained: $D_{Cu} = 6.144\times10^{-5}\cdot\exp(-0.652/KT)$ ($cm^2\cdot s^{-1}$). This means that, for $T = 1500$ K, $D_{Cu} \sim 3.96\times10^{-7}$ $cm^2\cdot s^{-1}$ which is reasonably close to the value deduced from (1) at 1500 K and $N_v = 0.01$ (4.80×10^{-7} $cm^2\cdot s^{-1}$).

CONCLUSIONS

Preliminary results of the effects of Cu solute atoms at low concentration in Fe in displacement cascades have been presented. The development of the thermal spike is restrained by the containment effect of Cu solute atoms. The formation of precursor Cu solute atom-clouds as well as of Cu-vacancy clusters has been demonstrated as a consequence of cascade enhanced diffusion kinetics. Further work in order to improve the statistics as to cascade defects and diffusion parameters determination is under progress.

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