



INFLUENCE OF TEMPERATURE ON RESIDUAL STRESS AND DAMAGE IN BCC IRON CONTAINING Cu NANOPARTICLES

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ABSTRACT

The paper is devoted to 3D molecular dynamic simulations in bcc iron containing coherent copper nano-particles and to analysis of thermal effects on residual stress and damage in the Fe-Cu system, which is important topic for older reactor vessels containing copper impurities.

KEYWORDS

Thermal effects, residual stress, Fe-Cu alloys, stability of Cu nano-precipitates

INTRODUCTION

Copper in older reactor ferritic steels creates small particles, which plays a significant role in the embrittlement process [1, 2]. To understand the phenomenon, experiments on model (thermally aged) Fe-Cu alloys [2 - 4] are being performed and theoretical studies as well [2, 5-12].

Experiments show that small Cu particles ($\phi \approx 2$ nm) have a bcc lattice coherent with iron matrix, while larger Cu particles ($\phi \geq 6$ nm) undergo phase transformation to 9R and an fcc structure [2,3], causing incoherence at the Fe-Cu interfaces.

Theoretical studies have consisted of atomistic simulations of the phase transition [2, 11], the relaxation of Cu particles in bcc iron and stress calculations in the Fe-Cu system at zero Kelvin temperature [5, 7], the interaction vacancy vs. Cu precipitate [2, 5, 6], radiation damage and structure evolution in the Fe-Cu system [6, 8] and interaction of dislocations with Cu particles [9, 10]. The study [12], using plane strain (2D) similar to [7], indicates that the residual stress plays an important role for twinning and dislocation pinning at the Fe-Cu interfaces and as well for interfacial crack nucleation, which may contribute to embrittlement observed in post-irradiation experiments [11, 13].

This contribution is devoted to 3D molecular dynamic (MD) simulations in the bcc iron containing the small coherent copper nano-particles and to analysis of thermal effects on residual stress in the Fe-Cu system. Stability of the Cu nano-precipitates against phase transformation and damage in the system under various applied stresses at temperature of 0 K and 600 K have been studied. The topic was not examined in the previous theoretical studies.

Similar to [11, 12], the N-body potentials from [6] are used to describe the Fe-Fe, Fe-Cu and Cu-Cu interactions. According to these potentials, the bcc Cu has larger atomic volume and

elastic constants than bcc iron and so, the level of residual stresses at 0 K is influenced by the misfit and elastic inhomogeneity effects, as discussed already in continuum treatment by Eshelby [14]. At elevated temperatures it can also be influenced by the different thermal expansion [15]. Analysis of thermal effects requires knowledge of the thermal expansion coefficients. These are not known for the potentials from [6]. For that reason, thermal MD simulations have been utilised to determine the linear coefficient of thermal expansion in pure bcc iron. Unlike iron, the bcc Cu from [6] is metastable and motion of arbitrary atom in a pure bcc copper crystal causes its phase transformation. It means, there is no possibility how to determine the thermal expansion coefficient directly from thermal simulations with a pure bcc Cu crystal. Instead, a modified continuum treatment from [14, 15] is used to understand significant changes of the residual (misfit) pressure in the Fe-Cu system at temperature of 600 K.

The interplanar concept (introduced and verified for the N-body potentials in [16, 17]) is used to calculate the stress from the potential energy in the Fe-Cu system. The stress component is denoted as S_{ij} . Another stress component, coming from the kinetic energy at elevated temperature [18], has been calculated as well and it is denoted by T_{ij} .

MD SIMULATIONS

3D crystals are oriented along the basic cubic directions $\langle 100 \rangle$. They are relaxed using viscous damping at the initial temperature of 0 K to avoid the influence of surface relaxation during thermal simulations and to allow relaxation of the bcc Cu particles. Free border conditions are used in all runs.

To evaluate the thermal expansion coefficient in pure bcc iron, a smaller crystal containing 1729 atoms has been utilised. Larger crystal containing 671 509 atoms is used for the Fe-Cu simulations to accommodate the residual stress. Copper nano-precipitate is placed in the middle of the Fe-Cu crystal. The bcc Cu particle considered here has a simple cubic shape of initial size $\approx 2\text{nm}$ and copper atoms occupy in the initial stage (before relaxation) the atomic positions according to bcc iron lattice.

In thermal simulations, Maxwell distribution of atomic velocities is prescribed to heat the relaxed crystal up to an initial temperature T_0 . After the initial heating, Newtonian equations of motion are solved using a time integration step $h = 1 \times 10^{-15}$ s. After some relaxation time t , the system reaches a steady state, where the average kinetic energy $E_{\text{KIN}}(t)$ in the system corresponds to an average temperature $\bar{T} = \frac{1}{2} T_0$. Here, $\bar{T}$ is given by the Boltzmann relation for three degree of freedom $\frac{3}{2} N k_B \bar{T} = E_{\text{KIN}}(t)$, N represents the number of atoms in the system and k_B is the Boltzmann's constant. Heating causes also an increase of the potential energy in the system since the atoms deviate from their initial equilibrium positions and the lattice undergo thermal expansion. In a steady state, the average change of the potential energy should be $EPOT(t, 0) = EPOT(t) - EPOT(0) = E_{\text{KIN}}(t)$ according to the equipartition theorem.

The energy balance and the total number of existing interactions in the system are monitored each time step to check the conservation of energy. Also, interatomic distances of interior atoms and crystal dimensions are monitored each time step to evaluate their time averaged values and to estimate thermal expansion in the system. As well, the stress components S_{11} , S_{22} , S_{33} and T_{11} , T_{22} , T_{33} are calculated in each time step along the $x_1 = [100]$ axis in the

middle of the crystal to evaluate their time averaged values in the steady state. Besides the mentioned thermal simulations free of external forces, also various quasistatic external loads have been applied at external borders of the crystal in steady state to examine the critical stresses and influence of temperature on damage processes in the Fe-Cu system.

RESULTS AND DISCUSSION

Thermal simulations with the pure bcc iron crystal for temperatures $\bar{T} = 300$ and 600 K have been shown [19, 20] that the linear coefficient of thermal expansion in MD corresponds to $11.30 - 12.25 \times 10^{-6} \text{ K}^{-1}$. The coefficient of thermal expansion with the used N-body potential from [6] agrees well with the experimental data $11.76 - 12 \times 10^{-6} \text{ K}^{-1}$ for bcc iron published in [21, 22]. The time averaged stresses T_{11} , T_{22} and T_{33} , coming from the kinetic energy, corresponds well to a simple thermodynamic estimate $k_B T / v_0$, where v_0 is the volume per one atom. It is also in agreement with a more general formulation by Nielsen and Martin in [23]. The time averaged stress components S_{11} , S_{22} and S_{33} , coming from the potential energy change, are numerically zero after the heating, since free thermal expansion is possible in the homogeneous bcc iron crystal. A full description of the heated system is possible via so called virial stress [18], that is given by the superposition $T_{ij} + S_{ij}$. In pure bcc iron the time averaged virial stress is given just by the thermal pressure $k_B T / v_0$.

In simulations with the larger Fe-Cu crystal, the copper atoms were initially placed on the bcc iron lattice. During the initial relaxation at temperature of 0 K, the Cu nano-particle expands and the internal stresses become smaller. The radial component S_{11} of the residual stresses in the Fe-Cu crystal after relaxation is shown in Fig. 1. The copper region in Fig.1 lies at the positions $x_1 / d_{100} = 63 - 77$. It may be seen that the misfit pressure exists inside the copper nano-particle and as well in iron matrix near by the Fe-Cu interfaces. The peak stress corresponds well to an elastic estimate -8.03 GPa, based on the elastic constants for bcc Cu from [6] and on the monitored misfit strain $\epsilon = -0.01206$ in MD. These values agree well with those presented in [2], where the Fe-Cu bonds at the interfaces were not included. The value of the residual stress at the Fe-Cu interface can be estimated using Eshelby continuum treatment [14] for a spherical, elastically inhomogeneous, inclusion (placed into our cubic Cu precipitate). Stress continuity at the interface matrix - inclusion requires [14, 15] to obey the condition

$$\sigma_1(\text{in}) = 3 B_{\text{Fe}} (\epsilon_1^C - \epsilon_1^T) = 3 B_{\text{Cu}} (\epsilon_1^C - \epsilon^*), \quad \text{where} \quad \epsilon_1^C = 1/3 [(1+\nu) / (1-\nu)] \epsilon_1^T.$$

Here the index C and T denote the constraint and transformation strain and ϵ^* is the misfit strain. The unknown transformation strain is given by the relation :

$$\epsilon^* = \epsilon_1^T \{ 1/3 [(1+\nu) / (1-\nu)] (1 - B_{\text{Fe}} / B_{\text{Cu}}) + B_{\text{Fe}} / B_{\text{Cu}} \}$$

where B is the bulk modulus and ν is Poisson ratio in the matrix. The elastic constants for the bcc Cu and bcc Fe from [6] lead to $B_{\text{Fe}} = 1.78 \cdot 10^{11} \text{ N/m}^2$, $B_{\text{Cu}} = 2.22 \cdot 10^{11} \text{ N/m}^2$ and $\nu = 0.3737$. The corresponding lattice parameters from [6] are $a_{\text{Cu}} = 2.9607 \text{ \AA}$ and $a_{\text{Fe}} = 2.8665 \text{ \AA}$, which gives the initial misfit $\epsilon^* = 0.03286$ at temperature of 0 K. It leads [20] to $\epsilon_1^T = 0.03664$ and $\epsilon_1^C = 0.02537$. The misfit stress at the interface matrix - inclusion at zero temperature is

$$\sigma_1(\text{in}, 0 \text{ K}) = -4.86 \text{ GPa}$$

in a good agreement with MD results in Fig. 1.

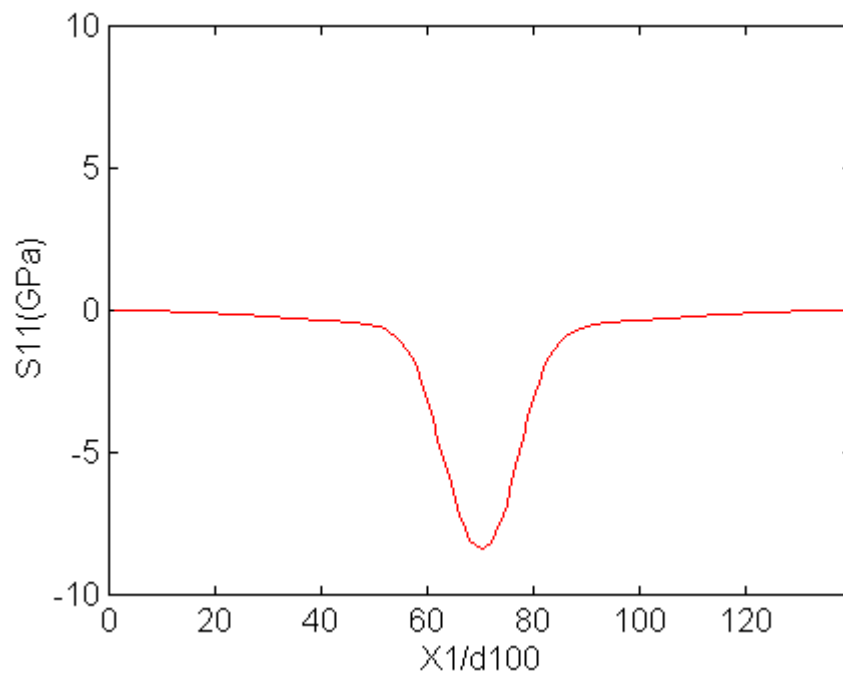


Fig.1 The radial component of the residual stress in the Fe-Cu crystal at temperature of 0 K

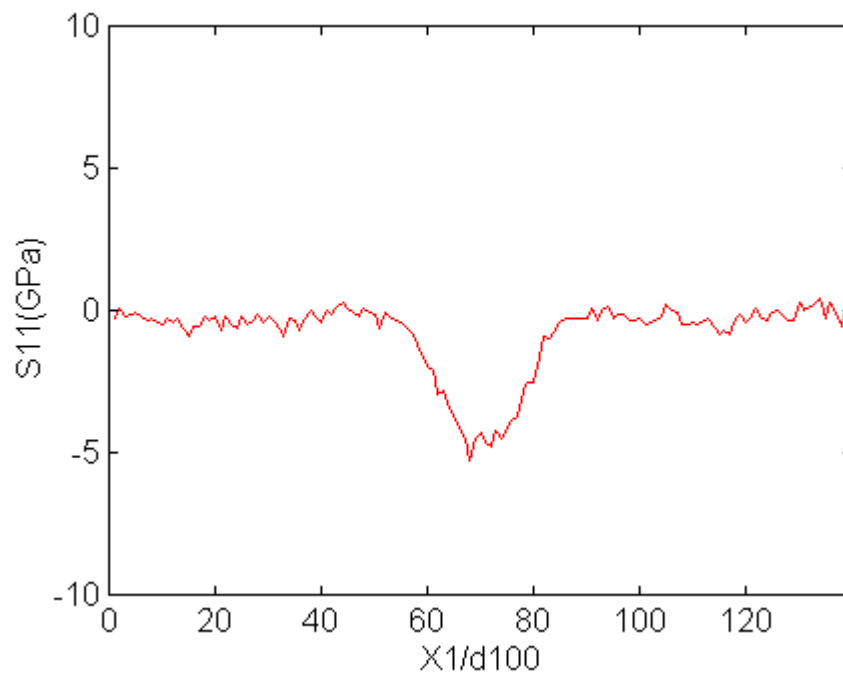


Fig. 2 The radial component of the residual stress in the Fe-Cu crystal at temperature of 600 K

After heating of the Fe-Cu crystal, the average temperature in steady state corresponded to 600 K. Time averaged stress component S_{11} after 5000 time steps is shown in Fig.2. It illustrates that the residual stress (coming from the potential energy) is smaller significantly at temperature of 600 K than at 0 K. The average stresses T_{11} , T_{22} , and T_{33} (coming from the

kinetic energy) agree well with the thermodynamic estimate $k_B \bar{T} / v_0 = 0.7$ GPa for $\bar{T} = 600$ K. The small Cu nano-precipitate survives in bcc structure at temperature of 600 K (Fig.3), which is in a qualitative agreement with experimental observations [2, 3] on thermally aged Fe-Cu alloys.

During thermal simulations at 600 K, smaller dimensions of the Cu particle have been monitored than at 0 K. Using again the continuum treatment by Eshelby, one can show that our MD results at elevated temperature can be understood if the thermal expansion coefficient α in the bcc Cu is positive and smaller than the coefficient for bcc Fe. At elevated temperature the misfit strain is described as

$$\varepsilon^*(T) = [(1 + \alpha_{Cu} \Delta T) a_{Cu}] / [(1 + \alpha_{Fe} \Delta T) a_{Fe}] - 1.$$

Assuming that $\alpha_{Cu} = 5 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{Fe} = 12 \times 10^{-6} \text{ K}^{-1}$ we obtain $\varepsilon^*(T) = 0.02855$, which is less than at 0K. Taking the same elastic constants as for 0 K and the new value $\varepsilon^*(T)$, we obtain in the same way as above $\varepsilon_1^T(T) = 0.03015$ and $\varepsilon_1^C(T) = 0.022049$. The component $\varepsilon_1^C(T) = [R(T) - R_0] / R_0$ determines new equilibrium dimension $R(T)$ of the inclusion with respect to the equilibrium dimension R_0 in pure matrix at 0 K, i.e. the smaller ε_1^C , the smaller R . It illustrates that at elevated temperature and for positive values $\alpha_{Cu} < \alpha_{Fe}$, one should observe smaller dimensions of the Cu particle and smaller lattice parameter at interior atoms in the bcc Cu. Such behavior was really observed in our simulations at $T = 600$ K. Using the new values at elevated temperature in equation for $\sigma_1(\text{in})$, we obtain a smaller misfit pressure at the Fe-Cu interfaces for $T = 600$ K

$$\sigma_1(\text{in}, T) = -4.3 \text{ GPa},$$

which is in qualitative agreement with our results in Fig.2. A more significant decrease of the misfit pressure can be obtained by the Eshelby treatment taking into account the smaller elastic constants at elevated temperature.

As to damage processes at temperature of 0 K, ductile behavior has been monitored in the Fe-Cu system under applied axial tension stress for the studied $\langle 100 \rangle$ crystal orientation. Under tri-axial tension stress, the Fe-Cu crystal was resistant against interfacial crack nucleation up to very high stress of 25 GPa, when iron corners of the loaded sample became unstable. The lowest (critical) loading for this crystal orientation seems to be a combination of tension and pressure stress, when phase transformation in the bcc Cu and bond breakage (incoherence) at the Fe-Cu interfaces occurs. Onset of phase transformation to 9R in the bcc Cu particle at temperature of 600 K (Fig.4) in our Fe-Cu crystal has been detected under an external quasistatic tri-axial load $\sigma_1 = \sigma_2 = +4$ GPa and $\sigma_3 = -4$ GPa. Under an equivalent loading applied at 0 K, the process requires larger external load of 6.87 GPa, since there is no thermal activation. Similar behavior has been observed in MD also for $\sigma_3 = 0$, but it was under larger applied load. It illustrates that due to different level of internal stresses at elevated and low temperature, one may expect also different behavior in the Fe-Cu system after loading. Note that the tri-axial stress agrees qualitatively with loading of volume elements in reactor wall, but the stress level in serving reactors is substantially (by one order) smaller than the critical stresses presented above. Phase transformation in a larger bcc Cu crystal with $\langle 100 \rangle$ orientation to deformed fcc structure has been reported in [2] by applying pressure of 12.5 GPa. The 9R structure reported here and in [11] is an intermediate structure before transformation to fcc [3, 11].

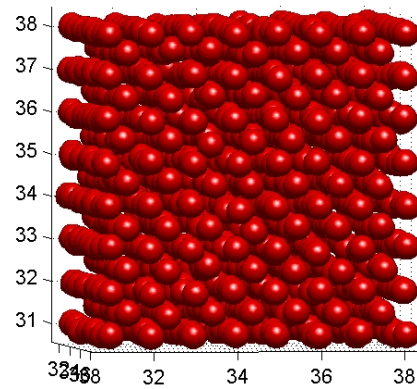


Fig. 3 bcc structure of the Cu nano-precipitate at temperature of 600 K, time step 5000

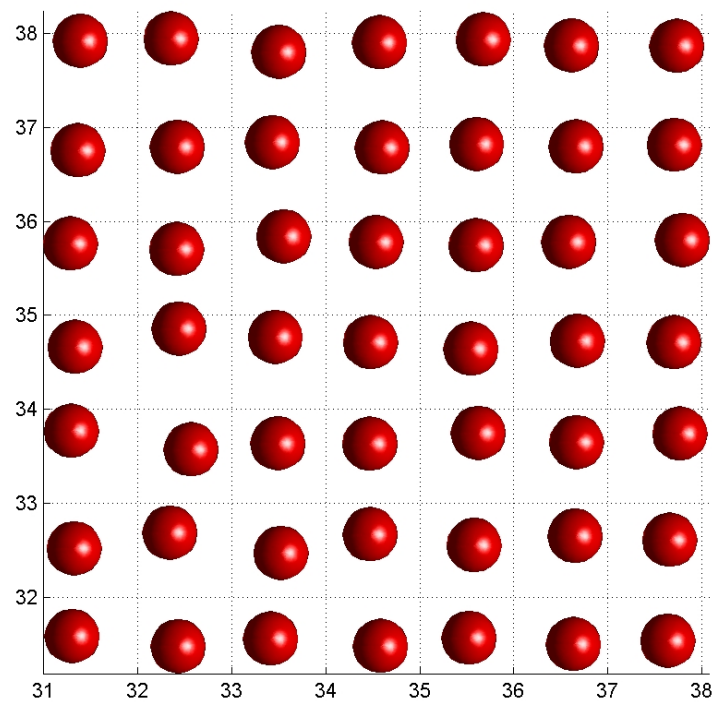


Fig. 4 Onset of phase transformation to 9R structure at the left lower corner of a central (001) plane in the bcc Cu nano-precipitate after external loading at temperature of 600 K. Further simulations in 3D should be oriented to studies of brittle-ductile behavior in bcc iron containing copper nano-precipitates having crystal orientation according to experiment [3].

CONCLUSIONS

MD simulations show that residual stress in bcc iron containing coherent bcc Cu nano-precipitate decreases significantly at elevated temperature of 600 K. Smaller resistance of Cu-nano-precipitate against phase transformation has been monitored after loading at temperature of 600 K than at 0 K.

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