

Surface roughness of the strained polycrystalline copper during the early stage oxidation



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ABSTRACT

Using the reactive molecular dynamic simulation, the surface roughness and oxide layer morphology are studied during the early oxidation of polycrystalline copper under applied tensile strains at 900 K. We find that the surface roughness of oxide layer increases with the formation and growth of oxide islands. The transformation of oxide wetting layer to the island structure occurs as a result of atom diffusion triggered by the oxidation-induced growth stress. Such a transformation process is enhanced by promoting the free energy of copper atoms, especially along the grain boundary when the external tensile strain is applied. This new insight provides a fundamental interpretation of the instability of oxide layer and the origin of surface defects under applied tensile loadings.

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1. Introduction

Oxidation reaction can cause the great chemical damage on the surface of metal in the aggressive oxidizing environment. It would directly affect the performance and lifetime of metallic devices by altering the material property (e.g. mechanical properties [1], conductivity [2]). Thus, oxidation of metal has attracted a great attention over the last decades. It is a common phenomenon that oxidation of metal can lead to the formation and growth of a continuous oxide film [3–5]. This kind of oxide layer plays an important role in the protective barrier and thus slows down the growth rate of oxidation. Recently, vast experimental studies have shown that, under the external tensile loadings, fatigue loadings, etc., the oxide thickness tends to increase and hence leads to the decrease of the effectiveness of barrier protection [6–8]. There are mainly two aspects of interpretation for the influence of mechanical stresses, especially tensile stresses on the chemical attack.

On one hand, oxidation of metal is a complicated process. It includes oxygen adsorption, dissociation and diffusion. Their thermodynamics and kinetics properties may be changed when the metal substrate is subjected to mechanical stresses. It has been recognized that external tensile stresses can enhance the driving force for adsorption and dissociation in the CO(O)/Ru, H₂O/SiO₂ system by using the first-principle calculation [9,10]. In addition, experimental

results indicate that external tensile stresses can promote the dynamics of dissociative chemisorption of O₂ on Cu(001) [11]. As for the diffusion behavior, the applied tensile stress can alter the diffusion potential and accelerate the ions diffusion in the oxide layer, and then promote the growth kinetics during the oxidation or nitridation of TiAl [12]. On the other hand, the performance of oxidation resistance is also greatly dependent on the integrity of oxide layer [13,14]. If spalling or cracking occur on the oxide surface, the fresh metal will be directly exposed to the oxidizing media. This will accelerate the internal oxidation reaction.

A great deal of work has been carried out to investigate the damage of oxide layer under mechanical loadings [15–18]. Schütze [15] has shown that there exists a critical strain value for the initiation of crack in the oxide layer of steels under the tensile stress. Then, a similar conclusion has been proposed by Gaillet et al. [16] in the pure nickel under creep loading using acoustic emission. After that, Zhou et al. [17] have found that the tensile loading can accelerate the brittle failure of oxide scales by enhancing the compaction of oxide–metal interface due to the vacancy flux injection into the substrate. However, almost all the work is done at the macroscale and the related theoretical studies are mainly based on the fracture mechanics [18]. The origin of those defects is still not known although they always appear at the presence of mechanical stresses. During the early stage of oxidation, oxygen molecules can be adsorbed and dissociated into oxygen atoms, then incorporated into the substrate. In this process, dissociated oxygen will interact with substrate atoms and induce the pronounced surface roughness [19], which may induce the initiation of cracks [20]. To the

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best of our knowledge, however, there is few study about the influence of applied strains on the surface roughness of oxide layer and the origin of surface defects at the early stage of oxidation.

Oxygen reaction on the Cu surface is considered to be an appropriate model system for the oxidation of metal and has been studied extensively [21,22]. In order to gain an atomic scale insight into the oxidation process, in this work, we simulate the oxidation of polycrystalline copper under applied tensile strains by using the molecular dynamics simulation. The main attention is focused on the effect of mechanical stress on the surface roughness and stability of oxide layer during the oxidation of copper substrate.

2. Computational details

An initial simulation box of polycrystalline copper was constructed with the domain size of $59.32 \times 63.72 \times 50$ Å. The thickness of copper substrate was 10 Å, with two 20 Å vacuum slab on each side of the substrate. The polycrystalline copper structure shown in Fig. 1 was generated using the Voronoi tessellation which had been widely used in the computational model construction [23]. The grain boundary was marked with a blue color. All the simulations were conducted using the reactive force field (ReaxFF) developed by van Duin et al. [24]. The ReaxFF was integrated into LAMMPS code to describe the chemical reaction. The feasibility has been certified in the molecular dynamics simulation of the initial oxidation in the interaction systems such as Cu/O [25], Ni/H₂O [26], Fe/O₂ [27].

Prior to the start of simulation, the thermal controlled layer shown in Fig. 1 was relaxed with 1 picoseconds at 300 K and 1.7 picoseconds at 900 K. The position of atoms in the bottom layer about 2 Å in thickness was fixed to coincide with those of bulk polycrystalline Cu. In our calculation, a series of uniaxial tensile strain (ϵ) were applied: 0%, 5%, and 10%, which was similar with the report of Wang et al. [28]. We performed MD simulations of oxidation behavior on the copper surface with an oxygen exposure time about 80 ps at 900 K. In the whole simulation process, the number of oxygen atoms was kept as a constant (15 atoms in the upper vacuum slab) to prevent the high pressure in the vacuum layer. All the simulations were carried out using Canonical (NVT) ensemble, with Nose–Hoover thermostat technique employed for the temperature control. The velocity and position were updated with a time step of 0.1 fs. Periodic boundary conditions were used in x , y directions and the fixed boundary condition was imposed

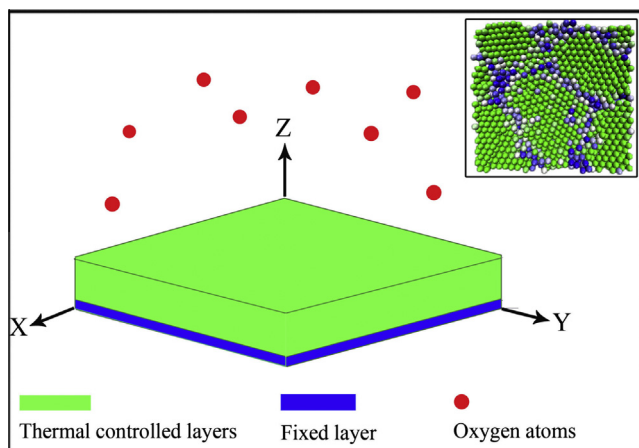


Fig. 1. The simulation model of oxidation on polycrystalline copper. The insert shows the grain boundary marked with a blue color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

along z direction. In addition, the reflecting boundary condition was added to avoid losing atoms in the upper limit of simulation boxes. The initial velocity of the system was set by a Maxwell–Boltzmann distribution at 300 K.

The overall energy of ReaxFF system contains the energy contribution series which is described by Eq. (1) [29]. The first term describes the bonding energy between bonded atoms; E_{val} stands for the energy from the valence angle; E_{tors} ensures the proper dependence of the energy on the torsion angle when a bond order approaches to trivial or exceeds 1; E_{vdW} is the van der Waals interaction energy; E_{Coulomb} comes from the Coulomb interaction between atoms.

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{vdW}} + E_{\text{Coulomb}} \quad (1)$$

The surface roughness varies on different surface morphologies. It can be quantitatively evaluated by employing the definition of root-mean-square roughness [30]:

$$R_s = \sqrt{\frac{\sum_{i=1}^n (Z_i - \bar{Z})^2}{n}} \quad (2)$$

where Z_i represents the height of exposed atoms on the oxide surface, \bar{Z} represents the mean height of all the exposed surface atoms, and n is the total number of exposed surface atoms. The growth stress induced by the oxidation reaction can be evaluated by averaging the atomic stress in the oxide layer. The stress tensors in the x (σ_{xx}), y (σ_{yy}) and z (σ_{zz}) direction are calculated by summing the per-atom stress respectively. Then, the hydrostatic stress is obtained in terms of $(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$. In the simulation, atoms always change their positions and velocities after each time step. As a result, the atomic stress would change accordingly. Thus, the stress tensors fluctuate frequently during the oxidation process [31]. To diminish the effect of pressure fluctuation in the simulation, we get all the stress data in a calculation period of about 0.8 ps and compute an average value.

3. Results and discussion

3.1. Surface morphology and roughness

In our molecular simulations, we mainly focus on the surface morphology and roughness of oxide layer during the oxidation reaction. Fig. 2 displays the evolution of surface morphology as a function of time for the oxidation on an unstrained substrate. In the oxidation process, hill-and-valley structures or 3D islands are generated on an oxide wetting layer. The thickness of wetting layer formed on the substrate surface is about 1 nm. This surface structure has been experimentally observed in the initial stage of oxidation on the bare copper [32,33]. The growth of those 3D islands is supposed to be driven by the Cu–Cu₂O interfacial strain energy [33]. Owing to the existence of those surface structures, the oxide surface turns out to be roughened. With the time increasing, more oxide islands appear and their height increases from 3–4 Å to 8–10 Å. It is worth noting that, during the initial stage of oxidation, the atomic motion mainly occurs on the surface. Owing to the continual migration of atoms on the oxide surface, the surface morphology changes accordingly. As a result, there is no stationary state for the surface roughness during the whole simulation. The surface roughness increases gradually along with the evolution of oxide surface as more and more oxygen atoms are incorporated into the copper substrate. The analysis results based on the final state of oxide film after oxidation in three different strain states are shown in Fig. 3. It can be seen that, when a uniaxial tensile strain is applied to the substrate, the surface morphology changes during the oxidation process. Fig. 3(a) and (b) shows that the surface undulation is enhanced with the increase of applied strains. In

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