

## A possible mechanism of copper corrosion in anoxic water

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Recent experiments show that solid Cu reacts with anoxic water. The reaction is observed by measuring the hydrogen release. This release is continuous and stable over a period of months. We have since theoretically found that water adsorbs dissociatively at a copper surface. But this adsorption is not enough to explain the amount of hydrogen released in the experiment. This observation calls for the explanation of the removal of the reaction product from the surface to provide a clean Cu surface where the water dissociation takes place. In this paper we investigate, by first-principles calculations, two possible mechanisms for this removal: first the possibility of Cu–O–H nanoparticulate formation, and second the diffusion of the dissociation products into Cu. We show that while the formation of nanoparticulates is energetically unfavorable, the diffusion of OH along grain boundaries can be substantial. The OH being placed in a grain boundary of the Cu sample quickly dissociates and O and H atoms diffuse independently of each other. Such a diffusion is markedly larger than the diffusion in bulk Cu. Thus, grain boundary diffusion is a viable mechanism for providing a clean Cu surface for the dissociation of water at the Cu surface. An order-of-magnitude estimate of the amount of hydrogen released in this case agrees with experiment. But this mechanism is not enough to explain the result of the experiment. We propose the formation of nanocrystals of copper oxide as a second step. A decisive experiment is proposed.

**Keywords:** copper corrosion; molecular dynamics; *ab initio*; diffusion; clusters; water

### 1. Introduction

It has long been commonly believed that copper is immune to anoxic water [1]. However recent experiments [2] show the evolution of hydrogen gas for copper immersed in anoxic water. This proves that water corrodes copper. Water is dissociatively adsorbed on the surface and CuOH is formed. Taking into account that it is known that Cu is the least noble metal among the metals in the 11th column and that oxygen species are adsorbed on the copper surface as hydroxyl groups [3,4], the findings of Ref. [2] should perhaps not be considered as controversial as they were first thought to be. One basis for simply rejecting the finding was that the

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outcome seems to be in disagreement with thermodynamic calculations [5,6]. However, the thermodynamic databases might not be complete due to, e.g. slow kinetics of the formation of Cu–O–H compounds. Two years later the evolution of hydrogen was independently confirmed [7]. In the meantime we performed *ab initio* calculations for water interaction with the Cu(100) surface [8]. We found dissociative adsorption of H<sub>2</sub>O on the surface, in agreement with what Taylor *et al.* [9] found for the Cu(111) surface. For the Cu(110) surface, see Refs. [10–13]. The hydrogen atoms either form hydrogen gas or diffuse into the Cu metal. The equilibrium pressure for the hydrogen gas was calculated by us to be in the millibar range, in agreement with experiment [2]. That dissociative adsorption of water occurs and that hydrogen is released was very recently confirmed by another calculation [14].

However, there is then the \$64,000 question. In the experiment [2] the evolution of hydrogen continues for months whereas the dissociative adsorption of water on the surface would stop as soon as the copper surface is covered by the adsorbed hydroxyls. Therefore, in order to explain the experiment, the mechanism that continuously provides a free Cu surface for water dissociation has to be understood. In our earlier paper [8] we suggested as one possible mechanism that clusters of Cu atoms form nanoparticulates that are detached from the surface and thus provide the Cu surface necessary for a continued reaction. In this paper we investigate this possibility to increase the surface for adsorption. Another way to increase this surface is to take grain boundary corrosion into account, i.e. diffusion of adsorbed OH into the grain boundaries. Diffusion in bulk Cu is extremely small but may be substantial along grain boundaries [15,16]. If grain boundaries facilitate the removal of OH from the surface, the available surface for OH adsorption is greatly increased, representing essentially the surface of all grains within the sample. Considering that the typical grain size is of order  $10^{-5}$  m, a sample with a characteristic size of  $10^{-1} \times 10^{-1} \times 10^{-3}$  m<sup>3</sup> has an internal surface of 6 m<sup>2</sup>. Such a large surface might account for a considerable amount of emitted hydrogen. These two possible mechanisms, the formation of nanoparticulates and grain boundary corrosion, are investigated in this paper.

The paper is organized as follows. First, we describe the methods we use to calculate energies and forces in the Cu–O–H system. The application of this method to cluster calculations and the results are provided next. Then we explain the model and method for computing diffusion of O and H in grain boundaries. Then we discuss whether the energies of cluster formation and diffusion of O and H facilitate the hydrogen production observed in experiments. In the conclusion we summarize our results and suggest an experiment that would resolve the ongoing debate.

## 2. Methods and results

### 2.1. Energy and forces calculations

The calculations of the total energies and forces were done by the projector augmented-wave (PAW) method as implemented in the Vienna *Ab initio* Software Package (VASP) [17–19]) based on density functional theory (DFT). We used the PBE (Perdew–Burke–Ernzerhof) exchange-correlation functional [20] as implemented in VASP. This functional is reliable in describing the hydrogen bonds and

bulk properties of water as well as surface properties [11]. The energy cut-off was set to 400 eV. The  $2 \times 2 \times 2$  Monkhorst–Pack  $k$ -point mesh [21] is used for the supercell with 108 Cu atoms. The finite temperatures for the electronic structure and force calculations were implemented within the Fermi–Dirac smearing approach [22].

## 2.2. Energy of $\text{Cu}_N$ clusters for $2 < N < 55$

Metal clusters have been an object of extensive experimental and theoretical investigations due to their unique physical and chemical properties determined by their restricted size. Of particular interest are the so-called magic number clusters that possess closed electronic and/or geometric shells, which makes them unusually stable. Such clusters have been found to consist of 13, 38, 55, 75, ... atoms. Cu clusters have been studied assuming the embedded-atom model (EAM), see e.g. [23], in the size range from 2 to 150 atoms [24]. It was noted that the cluster energy varies depending on the particular EAM chosen. By using the EAM much larger systems can be studied than by first-principles methods, of course at the expense of losing rigor. First-principles methods have accordingly been applied to smaller clusters [25–27]. The accuracy of density functional approximations has been studied for metallic clusters, in particular for  $\text{Cu}_{13}$  [28]. By a comparison to a diffusion quantum Monte Carlo method it was concluded that DFT provides adequate accuracy for cluster calculations. To the best of our knowledge, first-principles studies have not been performed systematically in such a wide range as in this paper. The aim of our calculations is to find out how much energy is needed to transfer atoms from bulk Cu to create a cluster of a particular size and whether this energy can be compensated by the gain caused by a presumably higher energy bonding of OH to the cluster than to the metal surface [9,29]. The energy of clusters was calculated by placing Cu atoms in the center of a cubic box with an edge of 15 Å. After that, the configuration was relaxed. The energy of the clusters was calculated by two different methods. In the first method we started with two atoms placed at a distance that corresponds to the closest neighbor distance in bulk Cu. After this configuration of two atoms was relaxed, the next configuration was chosen by adding one more atom. All larger clusters up to the size of 55 atoms were obtained in this way, which we call the up-method. In the second method we started with the 55 atom cluster. This cluster is a so-called magic cluster where the central atom is surrounded by a 12 atom icosahedron and this, in turn, is surrounded by a 42 atom icosahedron. After relaxation, the 54 atom cluster was formed by removing one atom from the external icosahedron and relaxing again. This procedure was repeated until only two atoms were left. This method is called the down-method. Neither of the methods guarantees a global minimum of cluster energy, yet they give a most reasonable estimate of the energy variation. The relaxed  $\text{Cu}_{55}$  cluster is shown in Figure 1. The energies calculated in these two ways are shown in Figure 2 as the energy per atom and compared to the energy per Cu atom in the face-centered bulk crystal at ambient pressure. One can see that the energy cost to transfer atoms from the bulk Cu to a cluster decreases with increasing size of the cluster, yet this energy is substantial even for the largest cluster ( $N = 55$ ) considered.

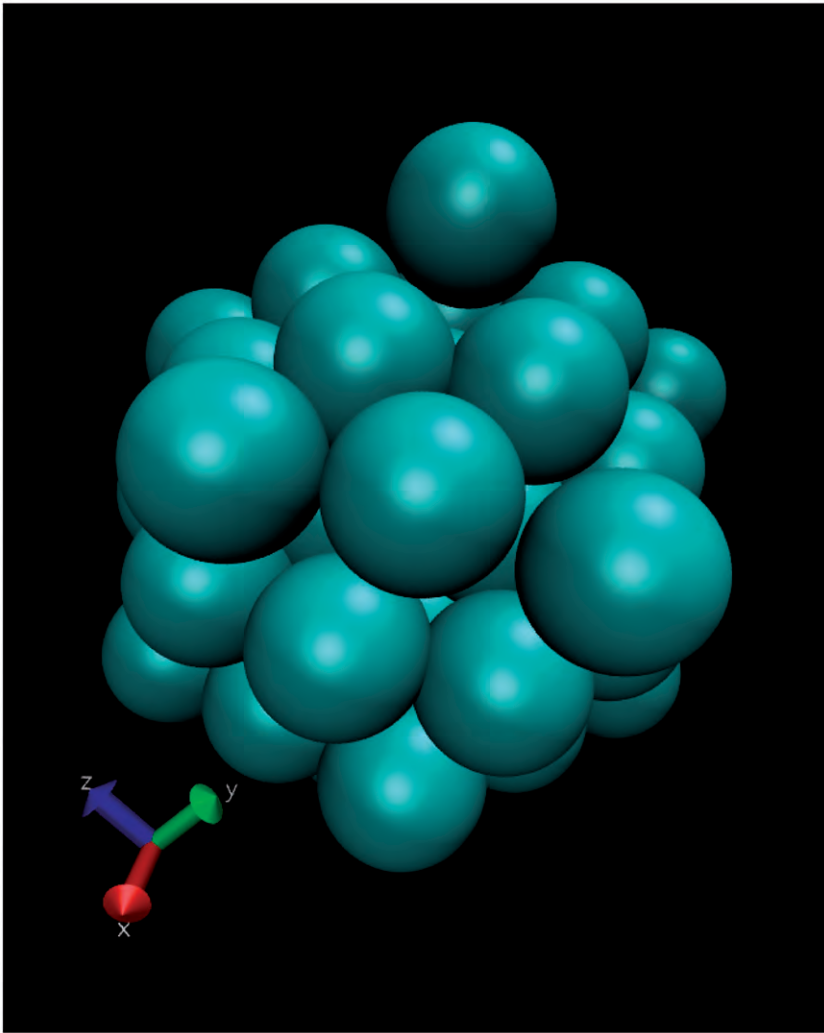


Figure 1. The Cu cluster of 55 atoms. The cluster consists of one atom in the center, 12 atoms in the middle layer and 42 atoms in the outer layer.

### 2.3. OH binding to Cu cluster

The binding energy of OH to clusters varies with cluster size and the number of hydroxyls bonded to the cluster. The general trend is that the first OH binds stronger than the next one. This can be understood as the Cu atoms can comparably freely adjust to get a larger binding energy. The energy of OH binding to the Cu(001) surface is  $-2.61$  eV [8]. This energy of OH binding is smaller than that to a reasonably large cluster. We checked whether the energy gain due to OH binding to a cluster is capable of compensating the energy loss due to transfer of Cu atoms from the bulk to the cluster. We placed hydroxyls with the oxygen next to each of the 42

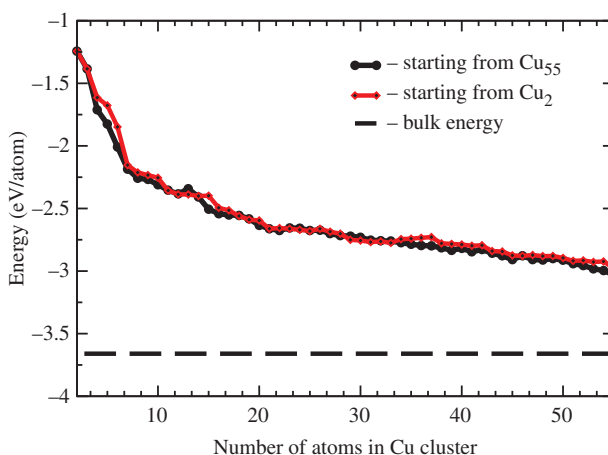


Figure 2. Average energy of a Cu atom in the cluster depending on its size. The clusters were formed by adding atoms one by one starting from two atoms (up) or taking away the atoms one by one from the 55 atom cluster (down). At each size the positions of Cu atoms have been optimized to minimize the cluster energy. The bulk energy was computed by the same method for the bulk copper.

Cu atoms in the external icosahedron with the OH bond on the line connecting the central Cu atom and the O. This structure was then relaxed. The resulting configuration is shown in Figure 3. The energy of Cu<sub>55</sub> is equal to  $-166.63$  eV. The energy of Cu<sub>55</sub>(OH)<sub>42</sub> is equal to  $-620.07$  eV. The energy of the isolated hydroxyls is equal to  $-318.78$  eV. This gives us an energy of OH binding to the Cu<sub>55</sub> cluster equal to  $-3.21$  eV. Therefore, transfer of 55 Cu atoms from the bulk and 42 OH atoms from the surface will cost us 9.89 eV (the bulk Cu energy, i.e. the calculated cohesive energy, 3.66 eV, is provided in Figure 2). From this, and similar reasoning for the other cluster sizes, we conclude that the formation of nanoparticulates requires considerable energy and, therefore, their equilibrium concentration will be very low. However, it should be kept in mind that the comparison of OH binding to clusters and to the Cu surface has been performed without taking the effect of surrounding water molecules into account. To a first approximation the effect would be to shift these binding energies to the same extent.

#### 2.4. Diffusivity of O and H in disordered Cu

The diffusion of O in bulk Cu is negligible [30]. Therefore, the removal of OH adsorbed on the surface of Cu to the inside of the Cu specimen is possible via grain boundaries only. Grain boundaries are regions of atomic mismatch and less dense atomic packing. Lower density implies that atoms can more easily diffuse in grain boundaries. Thus grain boundaries will oxidize or corrode more rapidly. This phenomenon is usually referred to as grain-boundary penetration or intergranular attack. At high temperature a grain boundary might be approximated by a liquid structure [15] due to premelting. We decided to model the grain boundary in Cu in a

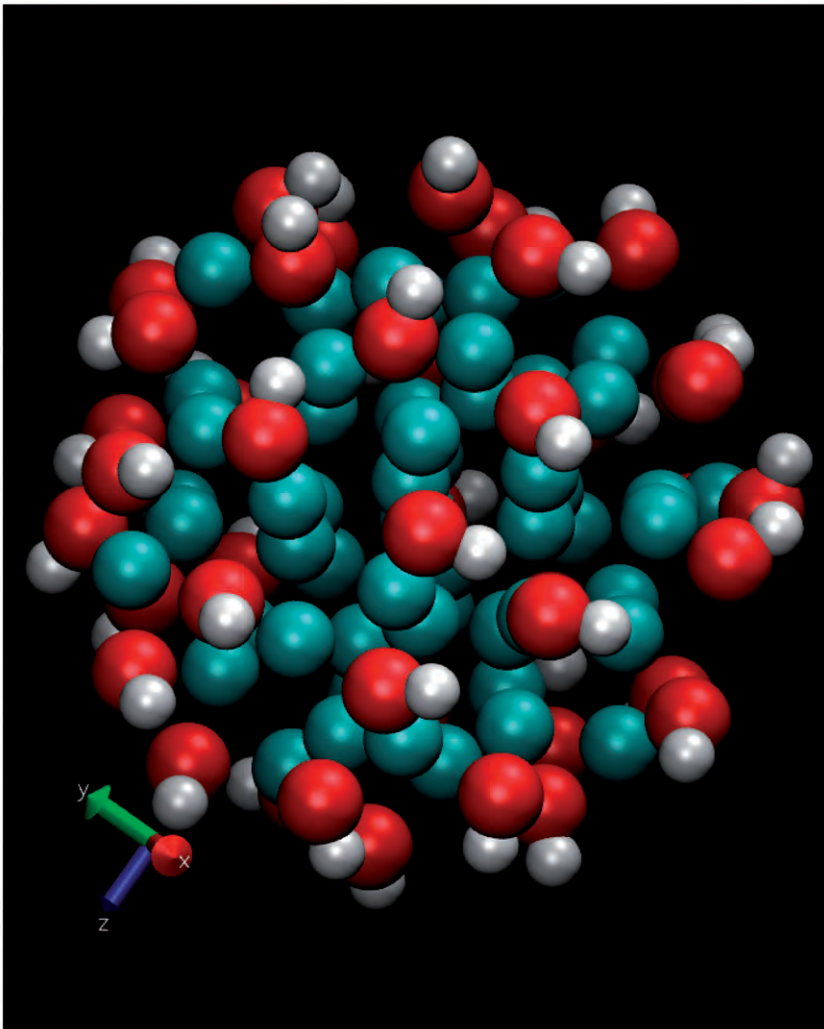


Figure 3. The Cu cluster of 55 atoms (grey) and 42 OH hydroxyls (red and white). The hydroxyls bind to individual Cu atoms with the OH axis bent towards the cluster.

similar yet different way. First, we heated solid Cu to a temperature of 4000 K to make sure it is liquid. To do this, we run *ab initio* molecular dynamics for 6000 time-steps and with a time-step of 2 femtoseconds on 108 atoms starting from the face-centered cubic Cu lattice. After that, the liquid Cu structure was annealed for 4000 time-steps at temperatures of 300 K, 1200 K, and 2200 K. At the 300 K and 1200 K simulations Cu became solid (no self-diffusion), however the radial distribution function remained distinctly non-solid (Figure 4). This is obvious from the comparison of radial distribution functions. One can also see the formation of quasi-crystalline planes characteristic of the fcc lattice (Figure 5a and 5b). At the temperature of 2200 K the structure is liquid-like and the quasi-crystalline

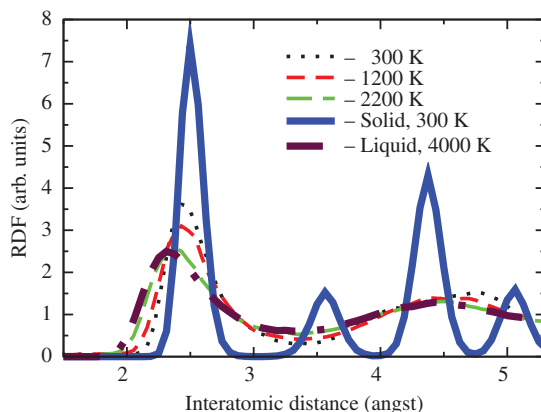


Figure 4. Radial distribution functions for solid Cu, liquid Cu, and the Cu–O–H system according to the legend. The structure of the Cu–O–H system is neither solid nor liquid but rather a disordered Cu possibly representing the grain boundary structural environment.

planes vanish. The OH was then embedded in the Cu structure in the following way. Two adjacent Cu atoms were removed from the center of the computational cell. One of these empty positions was filled with an O atom and the other one with an H atom. After that, the O and H atoms were shifted towards each other to form the OH bond. This served as the initial configuration in our *ab initio* MD simulations of OH diffusion. We accumulated configurations for more than 10,000 time-steps. The diffusion was computed as the average of the mean square displacements of particles from the origin of time. We also averaged over time origins. The origins were distributed evenly over the configurations (the number of time origins was chosen to be 75% of the total number of configurations to get good statistics; this explains the comparably short trajectories of about 2.5 picosecond durations). In Figure 5 it is shown that the O and H atoms quickly separate and diffuse independently of each other at all temperatures. The diffusion is high as compared to the diffusion in solid Cu [30]. A comparison of the data in Figure 6 to the data for diffusion in liquid Cu at 1800 K suggests that the diffusion at 2200 K in our simulation is lower than in experiments, likely due to the larger density in our simulation. We obtain the diffusion constant  $D$  to be  $2.25 \times 10^{-8}$  (2200 K),  $1.04 \times 10^{-8}$  (1200 K), and  $2.08 \times 10^{-9}$  (300 K)  $\text{m}^2/\text{s}$ . This is significantly larger than the diffusivity in solid Cu but smaller than the diffusivity in liquid Cu.

### 3. Discussion

The quantity of the emitted hydrogen in the ongoing experiment [2] was measured as  $3 \times 10^{-6} \text{ g/cm}^2$ . A typical grain size in the Cu foil used was  $10^{-5} \text{ m}$ . In order to make an order-of-magnitude estimate of how much hydrogen can be emitted if hydroxyls diffuse into the grain boundaries, we approximate the grains, which are irregular polyhedra, with fcc cubes with an edge of  $10^{-5} \text{ m}$ . Assuming that all surfaces of the grains have adsorbed OH in the same manner as the Cu surface, and noting that a



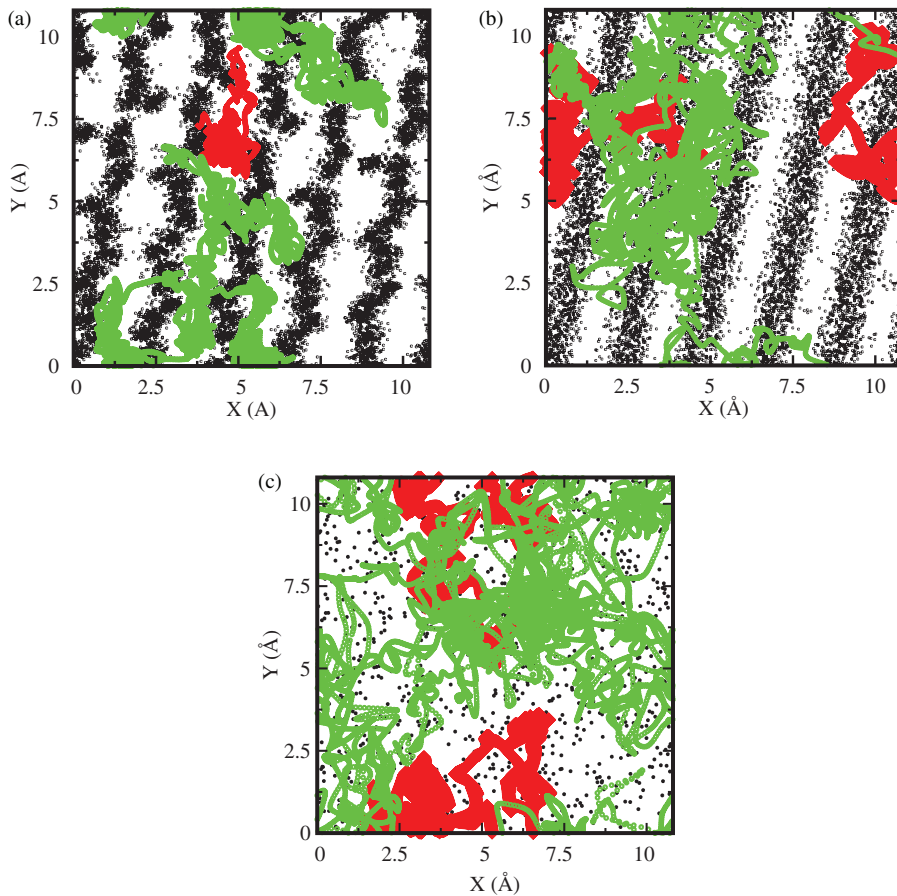


Figure 5. Atom trajectories of Cu (black dots – every 80th position is shown), O (red diamonds), H (green circles) at  $V = 11.664 \text{ \AA}^3/\text{atom}$  and temperatures (a) 300 K, (b) 1200 K and (c) 2200 K. The trajectories were obtained by *ab initio* molecular dynamics simulations for about 10000 time-steps.

grain boundary has a thickness of 2–10 atomic distances, we obtain  $10^{-6} \text{ g/cm}^2$  for the amount of emitted hydrogen. This is of the same order as the measured quantity. By this order-of-magnitude agreement we do not claim that we have explained all the release of hydrogen. If the hydrogen gas is evacuated, the release of hydrogen gas will continue. Further some hydrogen in our estimate will stay in the copper and not all is released. But our calculations further show that O and H quickly, almost immediately, dissociate and diffuse independently. This dissociation is due to the formation of a strong bond between O and surrounding Cu atoms. The hydrogen is quickly carried away by thermal motion. This means that even more hydrogen will be produced. But, more important, copper oxide will be formed inside the crystal, probably as nanocrystals. This oxidation will lead to a lattice expansion process [31]. This might give rise to cracks and even more copper surface will be made available for adsorption.



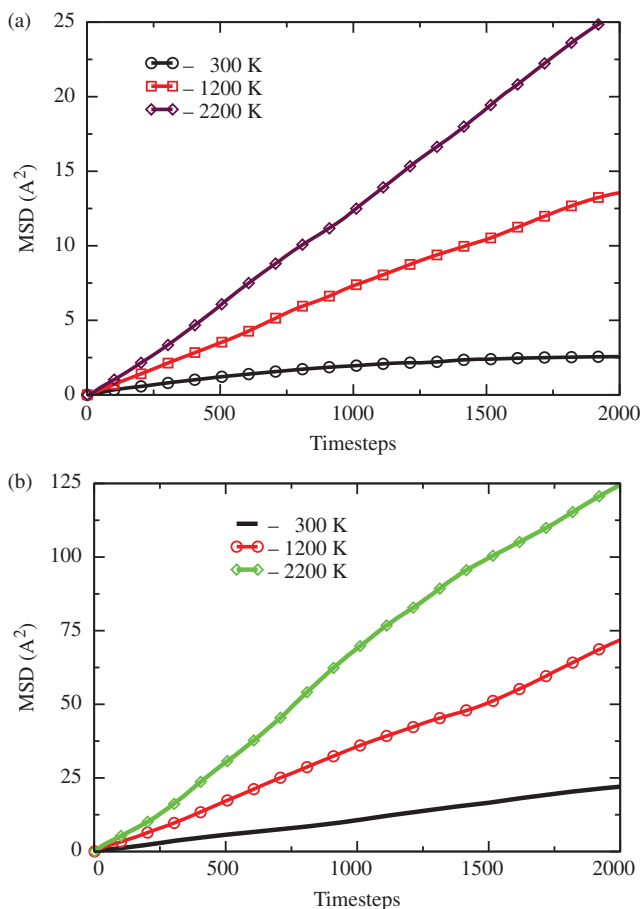


Figure 6. (Color online) Diffusion of O (a) and H (b) at 300 K, 1200 K, and 2200 K. The slope of the curves is the diffusivity.

#### 4. Conclusions

We have investigated two possible mechanisms of OH removal from the Cu surface, namely, by formation of Cu clusters with OH adsorbed on their surface and diffusion of OH in grain boundaries. While the first one does not seem to be important, diffusion is capable of removing OH from the surface. An order-of-magnitude estimate shows that if grain boundaries can accommodate the OH removed from the surface to the same extent as the surface itself, the amount of hydrogen emitted during the experiment can be explained. However, this agreement is superficial. If the experiment were to be continued, more hydrogen would be released, whereas the mechanism with adsorption in the grain boundaries would be exhausted. We have pointed to the consecutive possible formation of nanocrystals of copper oxide inside the bulk and its consequences, such as formation of cracks. Of course the mechanism proposed here has to be verified by experiments. A repetition of the experiment in Ref. [2] but with a single crystal of copper would be most enlightening.

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