OXIDATION DYNAMICS OF NANOPHASE ALUMINUM CLUSTERS: A MOLECULAR DYNAMICS STUDY

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ABSTRACT

Oxidation of an aluminum nanocluster (252,158 atoms) of radius 100Å placed in gaseous oxygen (530,727 atoms) is investigated by performing molecular-dynamics simulations on parallel computers. The simulation takes into account the effect of charge transfer between Al and O based on the electronegativity equalization principles. We find that the oxidation starts at the surface of the cluster and the oxide layer grows to a thickness of ~28Å. Evolutions of local temperature and densities of Al and O are investigated. The surface oxide melts because of the high temperature resulting from the release of energy associated with Al-O bondings. Amorphous surface-oxides are obtained by quenching the cluster. Vibrational density-of-states for the surface oxide is analyzed through comparisons with those for crystalline Al, Al nanocluster, and α -Al₂O₃.

INTRODUCTION

Various kinds of solid materials including metals and certain semiconductors oxidize easily, resulting in alteration of their physical and mechanical properties [1]. The nanophase materials, produced by consolidating nanometer-sized clusters, have recently drawn much interest because of their novel properties. Aluminum nanoclusters of radii 70-200Å are known to form amorphous-alumina (i.e., Al_xO_y) layers limited to thickness of 20-30Å when they are exposed to an oxygen environment at room temperatures [2,3]. Alumina is one of the most widely used ceramics famous for its high hardness, high melting temperature, and high electric resistance. Passivated nanophase-Al [4-6], a consolidation of those passivated Al-nanoclusters, may retain such useful properties as well as high oxidation resistance.

In this paper we report on the first molecular-dynamics simulations for the oxidation of an Al-nanocluster (radius 100Å). The simulation takes into account the process of dynamic charge transfer between O and Al on the basis of the electronegativity equalization principles [7,8]. We find that the oxidation starts from the surface of the cluster accompanied by substantial charge transfer between the atoms. The local temperature in the surface region rises owing to substantial release of Al-O bond-formation energies. In the initial stage of the oxidation process ($t=0$ -25ps), the thickness of the surface oxide increases linearly with time. The surface temperature rises linearly with time to a value 2,300K at $t=24$ ps, which corresponds to the melting temperature of alumina. For $t>25$ ps, the oxide layer saturates to ~28Å at $t=30$ ps. Continuation of the oxidation simulation results in thermal emission of fragmented oxides of various sizes. By quenching the melted surface-oxides at $t=35$ ps, we obtain amorphous oxides covering the Al core. We calculate vibrational spectra of atoms in various radial shells of the

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oxidized cluster. We thereby find that the spectra for the surface oxides have the characteristics of both crystalline Al and α -Al₂O₃.

PARALLEL MOLECULAR DYNAMICS OF Al AND O SYSTEMS

The principal difficulty in simulating large-scale MD of materials composed of Al and O stems from ionic nature of Al and O. Substantial charge transfer takes place between these atoms due to their difference in electronegativity [9], which depends sensitively on the atomic configuration in the material [10]. Realization of MD simulations for such systems requires efficient ways of determining local atomic-charges [7,8] and the resulting long-range Coulomb interactions.

In the present simulations, we adopt the empirical interatomic potentials developed by Streitz and Mintmire [7] for aluminum and alumina systems (referred to ES+). In the ES+ model, local atomic-charges vary with the environment in accordance with the electronegativity equalization principles. With those potentials, we can reproduce cohesive energies [7], elastic constants [7], and phonon spectra [11]. Furthermore the surface energies [7] for low-index faces of α -Al₂O₃ predicted by the model agree well with those obtained by the first-principles calculations [10]. The Coulomb interaction is computed efficiently with the fast-multipole method (FMM) [12,13] with a useful extension for the local stress calculations [14]. The FMM enables us to calculate the Coulomb interactions in O(*N*) operations; multipoles upto the quadrupole are taken in the FMM.

Present MD code is highly parallelized; the parallel efficiency is close to unity. All the simulations are performed on 40-node DEC-Alpha 4/175 cluster interconnected by two Gigaswitches and on 8-node DEC-Alpha 5/500 cluster interconnected by Fast Ethernet in the Concurrent Computing Laboratory for Materials Simulations at Louisiana State University.

Fig 1: The x-y projection maps of a slice ($x=0-160\text{\AA}$, $y=0-160\text{\AA}$, $z=0-8\text{\AA}$) at various times. The larger spheres correspond to O; the smaller to Al.

OXIDATION DYNAMICS OF NANOPHASE ALUMINUM CLUSTERS

A fcc-crystalline Al-nanosphere of radius 100Å composed of 252,158 atoms is placed at the center ($x=y=z=0\text{\AA}$) of the MD box (800Å x 800Å x 800Å). The Al nanocluster is equilibrated at 300K. The cluster is surrounded by 530,727 oxygen atoms distributed randomly in an annulus with radii $r=110\text{-}400\text{\AA}$ from the center of the MD box. A spherical hard wall of radius 400Å is used to confine the system. Density of O is about 41 times that of O₂ gas in the standard state (i.e., 1atm and 300K). Starting with the initial velocities of O atoms corresponding to 300K, we integrate the Newton's equation of motion using the velocity-Verlet algorithm [15]. To accelerate computations, we adopt multiple-time steps [15] of 1fs for short-range forces ($< 6\text{\AA}$) and 20fs for long-range forces.

Figures 1 display x - y projection maps of a slice ($x=0\text{-}160\text{\AA}$, $y=0\text{-}160\text{\AA}$, $z=0\text{-}8\text{\AA}$) at $t=8$, 16, 24, 32, 40, and 48ps; the left bottom corner in each map corresponds to the center ($x=y=z=0\text{\AA}$). Larger spheres in Fig. 1 correspond to O, smaller spheres to Al. Figure 2 depicts (top) spherically averaged temperatures, (middle) radial densities of O, and (bottom) radial densities of Al in every 10Å-shell at $t=8$, 24, and 40ps.

Fig 2: (top) Spherically averaged temperatures in every 10Å-shell at $t=8$, 24, and 40ps. (middle) Same as (top) but for densities of O. (bottom) Same as (top) but for densities of Al.

Oxygen atoms located closer than $\sim 4\text{\AA}$ from the surface of the Al cluster are strongly attracted by the cluster. In the early stage of oxidation ($t=0\text{-}25\text{ps}$), we find that the thickness of the surface oxides increases linearly with time. Owing to the release of the bond-formation

energy between O and Al, the surface temperature rises linearly with time until it reaches $\sim 2,300\text{K}$ at $t=24\text{ps}$ as seen in Fig. 2 (top). This is close to the melting temperature of alumina (i.e., $2,327\text{K}$). Significant diffusions of Al and O along the tangential direction to the surface are observed in the melted surface-oxides: for O atoms in the range $r=90\text{-}100\text{\AA}$ at $t=24\text{ps}$, $\Delta r_t^2/\Delta t \sim 14 \times 10^{-4} \text{ cm}^2/\text{s}$ for tangential and $\Delta r_r^2/\Delta t \sim 7 \times 10^{-4} \text{ cm}^2/\text{s}$ for radial motions. Radial diffusion toward the center is suppressed because of lower temperatures at smaller radii. Uniformity in the oxidation thickness at various polar angles observed in Figs. 1 results from such enhanced surface-diffusion.

For $t=25\text{-}35\text{ps}$, the surface oxides reach a thickness $\sim 28\text{\AA}$. One of the reasons for the saturation of the oxide thickness is that O atoms are depleted near the surface of the cluster ($r \sim 120\text{\AA}$) as shown in Fig. 2 (middle). It is known that suboxides such as AlO are stable in the gaseous state at temperatures higher than $\sim 1,900\text{K}$ [16]. In the present simulation, the temperatures at $r \sim 120\text{\AA}$ are in fact higher than $1,900\text{K}$ for $t > 24\text{ps}$ as shown in Fig. 2 (top). Therefore, a possible reason for such a depletion of O near the surface is that further increase in n_{O} is hindered since $n_{\text{O}}/n_{\text{Al}} \sim 1$ near the surface of the cluster at $t \sim 24\text{ps}$. Disorder of the crystalline structure is observed to develop from the surface, which extends to $r \sim 50\text{\AA}$ at $t=32\text{ps}$ (see, Fig. 1). It is because crystalline Al melts at temperatures higher than $\sim 1,000\text{K}$.

For $t > 40\text{ps}$, we observe in Fig. 1 thermal emission of fragmented oxides of various sizes. The surface temperature is higher than $3,000\text{K}$ for $t > 40\text{ps}$ as depicted in Fig. 2 (top). The entire cluster melts at $t \sim 55\text{ps}$.

VIBRATIONAL PROPERTIES OF OXIDIZED ALUMINUM CLUSTERS

Laboratory experiments [2,3] show that Al nanoclusters form amorphous- Al_xO_y surface layers of thickness $20\text{-}30\text{\AA}$ in the environmental oxygen gas at room temperatures. Therefore, we quench the melted surface-oxides to form solid oxides in the surface region of the cluster. Subsequently, we calculate vibrational density-of-states (DOS) in various radial shells of the cluster. These are compared with vibrational spectra for crystalline Al, Al cluster, and $\alpha\text{-Al}_2\text{O}_3$.

Starting with the atomic configuration at $t=35\text{ps}$, we quench by scaling the velocities 0.99 at intervals of 20fs . After 20ps , we isolate the cluster region ($r < 120\text{\AA}$) from the total system and apply the steepest descent method to obtain the final local-equilibrium configuration. We find amorphous surface-oxides of thickness $20\text{-}25\text{\AA}$ covering the Al core. Averaged densities in the midst of the oxides ($r=90\text{-}100\text{\AA}$) are $n_{\text{Al}}=4.37 \times 10^{-2} \text{\AA}^{-3}$ for Al and $n_{\text{O}}=1.56 \times 10^{-2} \text{\AA}^{-3}$ for O. Hence the averaged mass density is 2.4g/cm^3 , which is smaller than 4.0g/cm^3 for $\alpha\text{-Al}_2\text{O}_3$ and 2.7g/cm^3 for crystalline Al.

Normalized vibrational-frequency DOS for the oxidized cluster is calculated by Fourier transforming the velocity auto-correlation functions at 100K . Figure 3 (left) compares the DOS's calculated in various radial shells: $r=70\text{-}80$, $80\text{-}90$, $90\text{-}100$, and $100\text{-}110\text{\AA}$. In the shell $70\text{-}80\text{\AA}$ where $n_{\text{O}}/n_{\text{Al}}=0.01$, prominent peaks are observed at $\hbar\omega \sim 17$ and 35meV . In the shell $80\text{-}90\text{\AA}$, a broad spectrum ranging from $\hbar\omega=50\text{-}120\text{meV}$ emerges while the widths of the two peaks ($\hbar\omega \sim 17$ and 35meV) observed in the shell $70\text{-}80\text{\AA}$ increase. Such a broad spectrum further extends to the range $\hbar\omega=50\text{-}170\text{meV}$ in the shells $90\text{-}100$ and $100\text{-}110\text{\AA}$.

To understand these features in the DOS's, we compare in Fig. 3 (right) the DOS for the surface oxides ($r=80\text{-}110\text{\AA}$) with those for crystalline Al and $\alpha\text{-Al}_2\text{O}_3$. For crystalline Al, we have performed MD simulations of 864-atom fcc crystal using the embedded-atom interatomic potentials [7] and obtained the DOS from the velocity auto-correlation functions. The DOS for crystalline Al has two sharp peaks at $\hbar\omega \sim 17$ and 32meV as shown in Fig. 3 (right). We have also calculated the DOS for Al nanocluster of radius $100\text{\AA}$ and we find that it is indiscernible from that for crystalline Al. The DOS for $\alpha\text{-Al}_2\text{O}_3$ in Fig. 3 (right) is taken from ref. [11]. It was

calculated by diagonalizing the dynamical matrix in which the ES+ interatomic potentials were adopted. There is reasonable agreement between such theoretical prediction and experimental data obtained by the neutron scattering technique [11].

We find through comparisons of the DOS's in Fig. 3 (right) that the two peaks at $\hbar\omega \sim 17$ and 35 meV observed for the oxidized cluster correspond to those for crystalline Al. The broad spectra ($\hbar\omega = 50$ -120 meV) observed in the shell 80-90 Å of the oxidized cluster resembles the DOS for α -Al₂O₃. The high frequencies ($\hbar\omega = 110$ -180 meV) observed for the shells 90-100 and 100-110 Å of the oxidized cluster have no correspondence in the DOS's for either crystalline Al or α -Al₂O₃.

Fig 3: (left) Vibrational DOS in various radial shells for the oxidized Al cluster.

(right) Comparisons of DOS's for the oxidized Al cluster, crystalline Al, and α -Al₂O₃.

CONCLUSIONS

We have performed large-scale MD simulations for the oxidation of an Al nanocluster of radius 100 Å on parallel computers. The simulations take into account the effect of charge transfer between Al and O based on the electronegativity equalization principles. We have found that the oxidation starts at the surface of the cluster and the oxide layer grows until it saturates to a thickness of ~ 28 Å at 35 ps. Local temperature in the surface region due to the release of energy when Al-O bonds form, melts the surface oxide. Amorphous surface-oxides have been obtained by quenching the cluster. Vibrational DOS's for the amorphous oxides have characteristic features of both crystalline Al and α -Al₂O₃.

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