



Research paper

Effect of ionization on the oxidation kinetics of aluminum nanoparticles

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ABSTRACT

Molecular dynamics simulation (MD) of the observed stepwise oxidation of core-shell structured Al/Al₂O₃ nanoparticles is presented. Different from the metal ion hopping process in the Cabrera-Mott model, which is assumed to occur only at a certain distance from the oxide layer, the MD simulation shows that Al atoms jump over various interfacial gaps directly under the thermal driving force. The energy barrier for Al ionization is found to be increased along with the enlargement of interfacial gap. A mechanism of competition between thermal driving force and ionization potential barrier is proposed in the interpretation of stepwise oxidation behavior.

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1. Introduction

As a solid fuel additive, aluminum powders are commonly used in rocket propellant due to its high combustion enthalpy [1,2]. But the combustion efficiency is always limited by the formation of thick oxide layer [3,4]. The situation can be improved by employing nano-sized Al powder [5–7]. Ever since, the oxidation kinetics and mechanism of Al nanopowders have attracted great attention. Interestingly, the oxidation proceeds in a stepwise manner along with the increase of temperature [4,8–11]. The oxidation behavior is seemingly ascribed to polymorphic transitions which alter the ionic diffusion in the alumina layer [4,8–11]. In most studies, the crystallization of amorphous Al₂O₃ is supposed to promote oxidation reaction by enhancing the ionic diffusion [4,8–11]. However, those conclusions are contrary to prior findings obtained by Reichel et al. [12,13], which show that the energy barrier for cation transport increases during the amorphous-to-crystalline transition in the aluminum oxidation [13]. This contradiction indicates that the diffusion-controlled mechanism is still under debate at nano scale.

Different from the above-mentioned viewpoint of diffusion-based mechanism, in the well-known Cabrera-Mott (CM) model, oxidation of metals is limited by the field-assisted evaporation of atoms on metal surface into the oxide layer [14–16]. Based on this assumption, recent developed oxidation models can be used to describe the oxidation kinetics of metal nanoparticles and nanowire [15], even to predict the overall oxidation time in microseconds for the rapid reaction of Al nanoparticles [16]. But the

theoretical models still cannot explain well the stepwise oxidation of Al nanopowders.

Actually, the formation of hollow oxide structure is a common phenomenon during the oxidation of metal nanoparticles, such as Ni, Fe, Cu and Al [17–19]. It is a result of vacancy aggregation in the oxidation processes through Kirkendall effect [20]. As vacancy clusters coalesce at the metal-oxide interface, a nano-leveled interfacial gap would appear. Such gap is not considered in the CM model which assumes that ion hopping occurs at a certain distance between metal and oxide layer, e.g. 0.4 nm for Al [16]. Under this hypothesis, the ionization potential is treated as a constant. However, this treatment may not be accurate as ions jump over the interfacial gap directly, which is expanded along with the oxidation reaction.

In this letter, reactive molecular dynamics (MD) simulation is performed to investigate the effect of interfacial gaps on the oxidation of Al nanoparticle. The present work shows that the oxidation kinetics can be compared with experimental data and the ionization potential barrier varies on the size of gaps. A mechanism of competition between thermal driving force and ionization potential barrier is proposed in the interpretation of stepwise oxidation behavior. In this work, we focus on the ionization process of Al atoms which is seldom considered before in the study of Al combustion. It could provide us useful information for promoting the combustion efficiency of metal fuels.

2. Computational details

MD simulation of Al nanoparticle oxidation is carried out using reactive force field (REAXFF) integrated in large-scale atomic/

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molecular massively parallel simulator (LAMMPS). The REAXFF is developed by Van Duin et al. [21] and has been validated to be available for the Al-O system [22]. In ReaxFF, breaking and creation of bonds can be achieved through the bond-order terms during the simulation. In our simulation, 10-nm core-shell structured Al/Al₂O₃ nanoparticles are constructed. Here, we focus on the effect of Al ionization on the oxidation kinetics of aluminum nanoparticles. Therefore the pure Al nanoparticles are not used. An intermediate state was chosen, at which the oxide thickness is set to be 1 nm. The dimensions of oxide layer can be compared with those samples or models used in existing researches (1–2 nm) [19,23]. The size of Al core is adjusted to generate specific gaps of 0.4, 0.6, 0.8, 1.0, 1.2 nm at the metal/oxide interface. Thus the ionization process can be simulated as the interfacial gap is about 1–3 atomic layers. This model based on the complete separation between the oxide skin and the metal core can also be named as yolk-shell structure. The yolk-shell structure has been observed in the oxidation of Fe [18], Zn [24], and in many other systems [25]. During the oxidation simulation, the initial configuration would undergo a self-adjusting process and change to a configuration with supervacancies locating at the oxide-metal interface, which is similar to the experimental observation in the oxidation of nanosized Al [26]. The whole system is relaxed at 300 K for 50 ps with O₂ molecules filled in the simulation box. The temperature is increased at a rate of 35 K/ps before Al atom evaporation. Then, a slower heating rate of 5 K/ps is required so that the oxidation reaction can proceed adequately. Periodic boundary conditions are used in the x, y, z directions. The velocity and position are updated with a timestep of 0.1 fs.

3. Results and discussion

Fig. 1 shows the critical temperature for Al evaporation under different interfacial gap sizes. It increases from 310.4 K to 853.5 K as the gap is enlarged from 0.4 nm to 1.2 nm. At the cases of small gap size ($d \leq 1$ nm), the dissociation of Al atoms on metal surface from Al core occurs below the melting point. Thus, the lattice almost remains intact as shown in the inset a in Fig. 1. However, as the gap increases to 1.2 nm, Al atoms will not dissolve into the oxide layer until Al core starts to melt when the temperature reaches 853.5 K. In this case, Al core tends to transform from a crystalline to an amorphous state as shown in the inset b in Fig. 1, which indicates that the evaporation of Al atoms into the

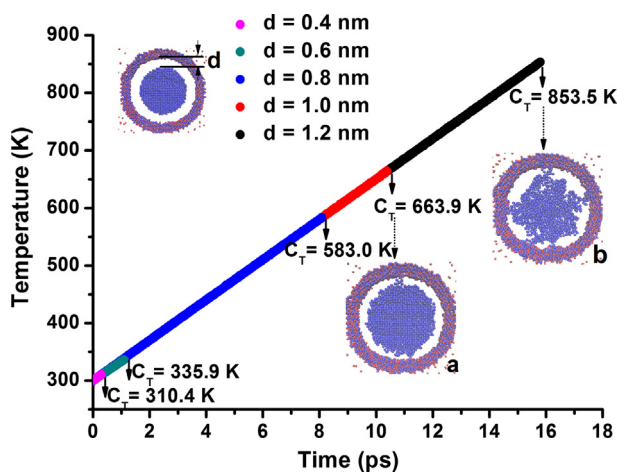


Fig. 1. Critical temperature for the occurrence of Al atom hopping across different interfacial gaps (0.4, 0.6, 0.8, 1.0, 1.2 nm), with cross section morphologies in the inset a and b.

oxide layer is thermally activated and it is greatly dependent on the interfacial gap size.

Typically, the oxidation process of core-shell structured Al/Al₂O₃ nanoparticle ($d = 1$ nm) is investigated as a function of

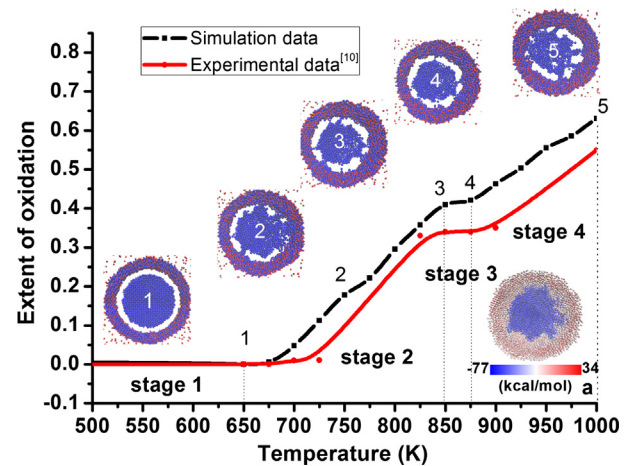


Fig. 2. Stepwise oxidation process with the increase of temperature, with corresponding cross-section morphologies in the inset 1, 2, 3, 4, 5 at different stages. Al atoms colored by atomic potential energy in the inset a.

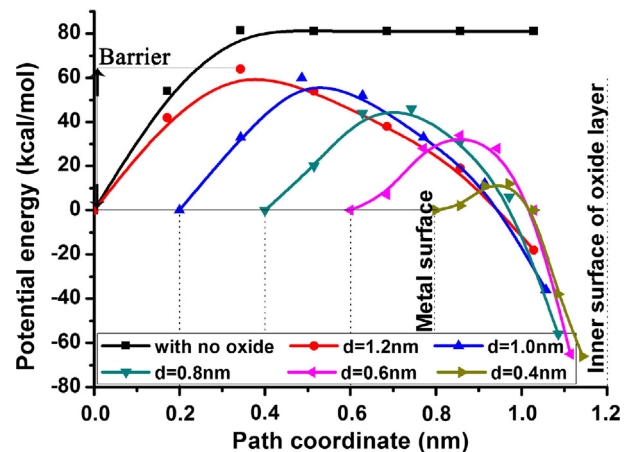


Fig. 3. Potential barriers for Al atoms ionization under different interfacial gap sizes of 0.4, 0.6, 0.8, 1.0, 1.2 nm and Al evaporation into the vacuum.

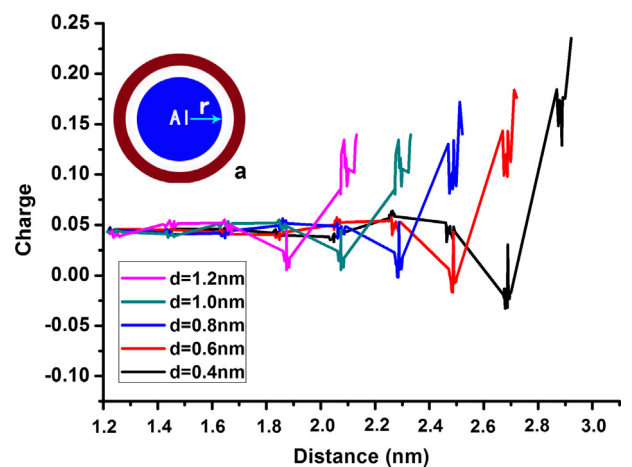


Fig. 4. Radial charge distribution of Al core induced by the electric field at the metal oxide interface for $d = 0.4, 0.6, 0.8, 1.0, 1.2$ nm. The horizontal axis represents the distance between Al atoms and the center of Al core.

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