Molecular Dynamics Simulation on the Single Particle Impacts in the Aerosol Deposition Process

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Single nano-particle impacts in the aerosol deposition (AD) method were simulated by the molecular dynamics calculation. By changing the incident speed, angle, and the crystal orientation of the aerosol particle, structural variation in the particle and the substrate was examined. It was found that the structural changes of the particle by the impact are classified into three cases. The particle maintains the original structure when the incident speed is low. If the incident speed is intermediate and if the particle is properly oriented, the particle was divided into a few grains. If the speed is high enough, the atomic structure of the particle is composed of a disordered phase and small crystal regions.

1. Introduction

The aerosol deposition (AD) method possesses several attractive features as a manufacturing process of high quality ceramic thin films. This method was developed based on the gas deposition method and attained higher growth rate than former methods. It was striking to be revealed that the high temperature process is unnecessary to produce high density ceramics; the typical temperature in the AD method is about 800 K. Such low process temperature is expected to be useful to generate a new material property which cannot be obtained by traditional methods.

By the experimental measurement, it was found that the grain size in the resulted texture by the AD method is in the order of 10 nm which is considerably smaller than that of raw particles, usually 100 to 300 nm. Hence, the fundamental mechanism of the AD process is expected to be the fragmentation of raw particles into smaller grains due to the high-speed impact. However, details of the mechanism have not been fully understood because direct observation of the growth process in the AD method is very difficult.

Computer simulation is helpful to understand what happens in the AD process. Molecular dynamics (MD) method has been applied to several studies on cluster impacts to the substrate. For example, Moseler calculated on Cu2000 cluster impact by the MD method. Webb et al. simulated the C60 impact on graphite substrate, and Hu et al. dealt with C60 impact on diamond substrate. In the case of ceramic systems, Sayle analyzed the SrO, CaO and MgO clusters on BaO substrate. Chagurov simulated the mechanical polishing of the substrate by a moving SiO2 tip. However, these studies assumed quite different conditions on the cluster size, incident speed, and composition in comparison with those in the AD method.

In the present study, the author carried out the MD simulation on the particle impacts in the AD process by using much larger particle size than the former studies on cluster impacts. The objective of this work is to understand the structural variation of the incident ceramic particle due to the high-speed impact to the substrate.

2. MD Simulation

There are several experimental conditions in the AD process such as the particle size, incident speed and angle to the substrate, temperature of the substrate, etc. In order to perform the MD simulation, we must consider other atomistic conditions such as the crystal orientation of particles and the substrate. In the actual AD process, aerosol particles are considered to collide against the substrate with randomly distributed crystal orientation. In the present study, MD simulations were carried out on single particle impacts to the substrate by assuming several selected conditions of incident speed, incident angle, and crystal orientation. Pure zirconia (ZrO2) was selected as the composition of the particle and the substrate. The interatomic potentials proposed by Dwivedi and Cormack were adopted. Their potential parameters were adjusted to reproduce the polymorphs of zirconia: monoclinic, tetragonal and cubic phases. Since the crystal phase of zirconia at the temperature of the AD method is monoclinic, initial atomic configurations were prepared as the monoclinic phase. The aerosol particle was assumed to have a spherical shape of which radius is 5 nm. The substrate was assumed to be also zirconia and was modeled by the rectangular shape of 14×14×5.5 nm3 with (111) surface. The numbers of atoms in the model particle and substrate are about 60000 and 90000, respectively.

Schematic diagram of the model structure is given in Fig. 1. A rectangular MD cell and three-dimensional periodic boundary conditions were assumed. The horizontal (x–y) dimensions of the MD cell are the same to those of the substrate, and the vertical (z) dimension is assumed to be 25 nm. The vertical periodicity is necessary for the Ewald summations. In order to fix the vertical position of the substrate against the particle impact, z-coordinates of cations in several atomic layers at the bottom were restricted by connecting to fixed z values with one-dimensional harmonic potential. The force constant of the harmonic potential was assumed to be equal to that of the Zr–O potential at the bottom surface, and linearly decreases to zero at the top of the restricted region.

The initial temperatures of the particle and the substrate were 300 K. The incident speeds of the aerosol particle, v,  
were chosen to be 250, 500, 750, 1000, 1500, and 2000 m/s. Incident speeds larger than 1000 m/s are unrealistic in the actual AD process but were adopted in order to simulate high-energy impact cases corresponding to large particle sizes. The incident angle, $\theta$, was assumed to be $0^\circ$ (perpendicular to the substrate surface) or $22.5^\circ$ toward x direction. Hence the initial velocity of the particle is $(-v \sin \theta, 0, -v \cos \theta)$. Three typical crystal orientation of the particle were used in the simulation and are expressed as $E$, $R_x$, and $R_y$ in this paper. The orientation $E$ denotes the case that the crystal axes $b$ and $c$ are parallel to $y$- and $z$-axes in the MD coordinates, respectively. The orientations $R_x$ and $R_y$ correspond to the cases of 90$^\circ$ rotation about $x$- and $y$-axes of $E$, respectively. By using a notation analogous to the ideal orientation in crystal textures, $(ijk)_{\alpha \beta \gamma}$, these orientations are expressed as $(100)_{\alpha \circ \gamma}$, $(010)_{\alpha \circ \gamma}$, and $(100)_{\alpha \circ \gamma}$, respectively, where $\alpha$ and $\beta$ denote the reference surface and direction in the MD coordinate. The crystal orientation of the substrate is expressed as $(111)_{\alpha \circ \gamma}$, in the same manner. The particles were assumed to move without any rotational motion before contacting with the substrate. MD simulation was carried out at constant-NV condition without temperature control.

3. Results

Figure 2 shows the three-dimensional views of the incident particles and the substrates for normal incident by 500 (a), 1000 (b) and 1500 (c) m/s at 20 ps after the contact. The assumed incident angle and crystal orientation of the particle are $0^\circ$ and $E$, respectively. The arrows in (b) denote the planner defects in the substrate.

Figure 3 shows the distributions of temperature (a), total
pressure (b), and Mises stress (c) in the cross section of $x-z$ plane at 2.7 ps after the contact. In the calculation of these values, translational components of the atomic velocity were extracted by evaluating as regional and time averages. The temperature near the contact point started to increase and reached to about 1900 K at 3 ps. It gradually decreases to about 1100 K at 20 ps by thermal diffusion to the whole system. The maximum value of the total pressure was found to be 12.5 GPa at 1.5 ps after the contact. Distributions of the temperature and pressure in the incident particle were asymmetric because the atomic configuration in the particle is horizontally asymmetric.

In the case of the Mises stress (c), high values due to the surface tension were observed at the particle surface. After the contact, anomalously high values were observed in the middle part of the particle and make a clear contrast against the lower part of the particle as denoted by A in the figure. The boundary between these two regions was parallel to (001) plane. The primary slip system in cubic zirconia is known to be $\{001\} \{110\}$\textsuperscript{10}. By the similarity between the atomic arrangements in cubic and monoclinic zirconia, it is expected that $\{001\}$ planes in the monoclinic phase possibly behave as slip planes. This assumption is realized in the MD simulation and was observed as the motion of dislocations. Figure 4 shows an example of dislocation dynamics in the particle observed in the present simulation. This figure is a time series of total pressure distribution in the $x-z$ cross-section, and dislocations can be recognized as pairs of small regions with positive (in this case, upper) and negative (lower) pressures as denoted by A, A’ and B. Both A and B dislocations moved toward upper-left direction along (001) plane and disappeared at the particle surface. It may be worth noting that the trace of these dislocations is recognized as a thin layer with negative pressure as denoted by C in the last snapshot. This result means that some sort of structural modification was induced near the slip plane. The lower part of the particle below the slip plane was deformed due to the impact as shown in Figs. 2 and 3, hence some collective motion of atoms is considered to take place in this region.

In order to discuss the details of the structural changes, it is necessary to evaluate the crystal structure in the particle. Figure 5 was drawn by the coefficient of three-dimensional Fourier transformation of atomic coordinates to show the distribution of crystallinity in the particle. The dark part in the figure denotes the crystal region, and the white denotes...
the disordered phase. Typical four examples at 20 ps after the contact were shown for different conditions. Figures (a) and (b) shows the cases of 1000 m/s, 0°/C14 with crystal orientations $E$ and $R_y$, respectively. In both cases, about one third of the particle from the bottom was structurally modified. Boundaries between the upper and the modified parts were not flat but stepwise along (001) and (100) planes. In comparison between Figs. 3(c) and 5(a), it is known that the stepwise structure was formed by structural relaxation after the initial formation of the boundary. In the case of (b), the crystallinity below the slip plane is lower than the case (a), and the resulted structure of the boundary is more complicated.

Figures (c) and (d) show the results of the crystal orientation $R_x$ by 1000 m/s, 22.5°, 1500 m/s, 0° incidents, respectively. In both cases, incident particles were divided into a few crystal regions as denoted by C, D, E and F, G, H, respectively. The disordered phase like in (b) is not dominant in (c) but extends to both the particle and the substrate in (d). Such mixed structures of grains and disordered regions were commonly observed in the 1500 and 2000 m/s cases. Planner defects in the substrate are recognizable in each case in Fig. 5. The arrows A and B in (a) show such structurally modified layers in the substrate, and are found to be parallel to (100) and (001) planes, respectively.

4. Discussion

The main mechanism of the AD process has been expected to be the fragmentation of aerosol particles by the impact. Such assumption was successfully reproduced in the present MD simulation as shown above. In the case of lower speed less than 500 m/s, crystal structure and its initial orientation was conserved in almost whole part of the particle except near the contact point. In the middle range of the incident speed higher than 500 m/s, the particle was divided into a few grains by the slip mechanism. At higher speed than 1500 m/s, a mixed structure composed of a few grains and disordered phase was observed, and the disordered regions was extended to the substrate.

In the present simulation, the assumed diameter of the particle is about 10 nm and is almost one order smaller than the typical size in real AD processes. It means that the kinetic energy of the incident particle in this study is much smaller than that in the real process. If the kinetic energy of the incident particle is converted to heat and potential energy in whole part of the particle, the simulation is comparable to the real AD process with the same aerosol size. However, it may be more natural to consider that the converted kinetic energy is heterogeneously distributed to some limited area: for example, vicinity of the contact point or a thin layer near the
slip plane. In such a case, the present simulation corresponds to a case of larger particle with lower incident speed. Hence the result of the MD simulation is considered to represent more or less the real process in the AD method using relatively small particles.

Expected mechanism of the AD process is as follows. When the particle speed exceeds a threshold value of about 500 m/s, which may depend on the particle radius, one or more slip planes inside the particle are activated. The anisotropic stress due to the impact and slips may cause modification of the crystal orientation or the crystal structure, and hence the particle are divided into several grains. This mechanism is enhanced as the particle speed increases. If the particle speed is high enough to destroy the crystal structure, the disordered phase may appear in the particle and the underlying substrate. Grain growths in the disordered phase may occur if the temperature is high enough, but it is difficult to trace such phenomena within a limited time scale of MD simulation.

5. Conclusion

Fundamental mechanism in the AD process was successfully reproduced by the MD simulation of single particle impacts to the substrate. When the particle of 10 nm diameter collides to a substrate, the particle was divided into a few grains in the medium range of the particle speed from 500 to 1500 m/s. If the speed is higher than 1500 m/s, a mixed structure of disordered phase and a few small crystals was generated. These variations of the atomistic structure of the particle were found to depend on not only the particle speed but also the crystal orientation. The atomistic structure of the substrate was modified to include planner defects and disordered phases at medium and high speeds, respectively.

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