Atomistic Simulation of the Aerosol Deposition Method with Zirconia Nanoparticles

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Impacts of nanometer sized ceramic particles to the substrate with different incident angles were simulated by molecular dynamics to investigate the mechanism of aerosol deposition method. Comparing with the normal incident case, obliquely incident particles to the substrate show different characteristics of fragmentation including particle rolling on the substrate and a tail structure of depositing atoms. Structural modification and its incident angle dependence were also observed in the substrate. Elevations of temperatures in nanoparticle and substrate show different dependencies on the incident angle.  

Keywords: aerosol deposition method, molecular dynamics, impact, incident angle, zirconia, nanoparticle

1. Introduction

The aerosol deposition (AD) method is a new process developed by Akedo et al. 1–3) for manufacturing ceramic thin films by spraying nanoparticles at high velocity. It possesses several merits comparing with the existing methods: large growth rate and possibility for patterning for example. Typical temperature of the AD process is low, almost the room temperature, since it does not include a thermal sintering process. Hence the AD method is expected for generating new materials which cannot be created by traditional methods.

Mechanism of the AD process is considered to be fragmentation and deposition of incident particles on the substrate. Observation by transmission electron microscopy2) showed that the grains in the as-grown film were fragmented into 10 nm scales which was considerably small compared with raw particles in 100 nm order. Detailed mechanisms of fragmentation and deposition, however, are not fully understood because the difficulty of in-situ observation of growth process.

The present author investigated the mechanism of the AD process by molecular dynamics (MD) simulation, and showed that the fragmentation is associated with the dislocation migration and slips.4,5) In the simulation, ceramic nanoparticles collide with higher speed than 750 m/s were divided into a few grains and deposited to the substrate. The detailed structures of fragmented grains, however, were dependent on not only the incident speed5) but also other conditions such as crystal orientation of the incident particle.5) Hence a systematic simulation covering wide variety of incident conditions is desirable.

In this study, incident angle of aerosol particle to the substrate is focused as one of such conditions. In the real AD process, obliquely incident settings were used as trials to improve film properties.5) The objective of this study is to investigate the difference in the AD processes with various incident angles by MD simulation.

2. MD Simulation

Figure 1 shows the schematic diagram of the simulation model. It includes a incident nanoparticle and a substrate in a rectangular MD cell of about 14 × 14 × 30 nm³. The particle has a spherical shape of 10 nm in diameter which is composed of a single crystal of monoclinic zirconia. Three initial orientations of incident particle, E, Rx, and Ry, were assumed.5) Orientation E denotes the angular configuration that the crystal axes b and c are parallel to y and z axes in the model coordinates, respectively. Orientations Rx and Ry
correspond to the configurations of 90° rotation to E about x and y axes, respectively. The substrate is assumed to be also a zirconia single crystal with two-dimensional periodicities on xy plane. It has \{111\} surfaces with [10\bar{1}] axis toward x. The atoms at the bottom of the substrate (hatched in the figure) are loosely fixed to reference coordinates by a harmonic potential in order to keep the substrate position against the collision. The numbers of atoms in the present model is about 50000 and 90000 for particle and substrate, respectively.

The translational velocities of incident particles were assumed to be \((-v_0 \sin \theta, 0, -v_0 \cos \theta)\) where \(v_0 = 1000 \text{ m/s}\) and \(\theta = 0\) (normal to the substrate), 22.5, 45 and 67.5°. Any initial rotation (spin) of the particle was not assumed. Initial temperatures of particle and substrate are adjusted to 300 K except for the translational velocity of incident particle. Interatomic potentials by Dwivedi and Cormack\(^7\) were adopted which were developed so as to describe the energy difference in zirconia polymorphs. MD simulation was carried out by constant NVE algorithm, and the long ranged Coulombic forces were calculated by Ewald summation. Since no temperature control was used throughout the simulation, temperature of the system should increase after the impact.

3. Results

In order to observe the variation inside the particle and the substrate, the MD cell was divided into many small voxels, and physical properties in each voxel were calculated. Figure 2 shows the two-dimensional distributions of temperature (a), Mises equivalent stress (b), crystallinity (c) and rotation angle from the initial state (d) in the xz cross section at 30 ps after the contact. Incident angles to the substrate are 0, 22.5, 45 and 67.5° from top to bottom. The initial particle orientation is E in all cases.

![Fig. 2 Two-dimensional distribution of temperature (a), Mises equivalent stress (b), crystallinity (c) and rotation angle from the initial state (d) in the xz cross section at 30 ps after the contact. Incident angles to the substrate are 0, 22.5, 45 and 67.5° from top to bottom. The initial particle orientation is E in all cases.](image-url)
fragmented grains and amorphous-like, low crystallinity region. In the case of normal incidence, two small grains can be recognized as white areas in (b) and (c). The crystal orientations of these grains are known by (d) to be different from the initial orientation E. Kinetic energy of incident particle was firstly converted to the potential energy of such modified structures, and then released as heat during the relaxation process. Distribution in (a) denotes that temperature distribution in the system is fairly homogeneous at 30 ps after the contact. Temperature of the particle increases to about 700 K from the initial value 300 K. Details of the temperature variation will be discussed later.

Incident angle dependence of structural variation is also recognized. Structurally modified region reduces as the incident angle increases. Small fragmented grains found in the normal incident case become unclear in 22.5 and 45° cases, and disappears in 67.5° case. Alternatively, a tail structure of depositing atoms at upstream side of incident particle is generated in 45 and 67.5° cases. Nanoparticles show forward rollings of 20 to 50° except for the normal incident case as shown in (d).

Atomistic structure in the substrate was modified by slips on {100} planes. Slips were also observed in obliquely incident cases, but the activated slip system seems to converge on one direction in 67.5° case. Temperature of the substrate is almost equal to the particle but slightly higher in 67.5° case. Figure 3 shows the time variation and incident angle dependency of averaged temperatures in particle and substrate. Temperature variations in two regions denote different features. In the particle region, a sharp increment was observed toward the peak at about 10 ps followed by gradual decrease. Elevation of the temperature at the peak is about 420 K in the case of normal incidence, and decreases as the incident angle increases. In the case of the substrate, on the other hand, the time variation shows slow and monotonic increase. In 0, 22.5 and 45° cases, averaged temperatures of the substrate are always lower than those of the particle. In the 67.5° case, however, temperature of the substrate increases at almost the same rate to the particle and turn to be higher than the particle at 12 ps after the contact. The difference between the particle and substrate temperatures is about 80 K at 30 ps.

These results are understood as follows. The heat was generated from the structurally modified region. In the first stage, the heat propagates mainly in the particle in normal incident case, hence the temperature increment is larger in the particle. In the high incident angle case, on the other hand, structurally modified region distributes as a tail contacting both the particle and the substrate, and the heat flows toward both sides.

Variation with the incident angle is also recognized in the total pressure values. Figure 4 shows the incident angle and particle orientation dependencies of the observed maximum pressures after the contact in the whole MD system. The dashed line denote a curve if the maximum pressure is proportional to the cosine of incident angle.

4. Discussion

In the previous studies, mechanism of AD process was expected to be the fragmentation of incident aerosol particles...
and deposition to the substrate by the collision impact. In this study, similar mechanism was reproduced again for obliquely incident cases. Several differences, however, were found between the normal and obliquely incident cases: rolling motion of the particle after the contact, the tail structure, and the activated slip planes in the substrate.

These variations, however, possibly depend on the simulation conditions such as the particle size. In order to confirm the particle size effect, simulation using a smaller particle was carried out on the same condition. Figure 5 shows the results same to Fig. 2 but using a smaller particle of 6 nm in diameter for normal incidence. The number of atoms in this case is about one forth of that in Fig. 2. Results in both figures have several points of similarity: (i) temperature of the particle is slightly higher than the substrate, (ii) area of the structurally modified region is almost at the same rate, about one third of the particle, and (iii) two small fragmented grains were found in the structurally modified region.

Such similarities are understood if the kinetic energy of the incident particle is homogeneously redistributed in the particle, because both the kinetic and converted potential energies are proportional to the number of atoms. At the present stage, it is difficult to evaluate the system size effect of AD process. The incident angle dependence found in this study is, however, considered to be effective for, at least, to the cases with the particle diameter smaller than 10 nm.

5. Conclusion

Mechanisms of the fragmentation and deposition and their dependencies on the incident angle were investigated by molecular dynamics simulation. If the particle diameter is less than 10 nm, obliquely incidence of aerosol particle results different structural variations from the normal incident case: particle rolling, a tail structure depositing on the substrate, and difference in the activated slip planes in the substrate. Structure in the grown film by actual AD process is possibly affected by these factors. The present result is, however, derived for limited cases, and further studies covering wide ranges of conditions are expected for understanding and improving the AD process.

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REFERENCES