# Molecular dynamics study on the particle fragmentation in the aerosol deposition method

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Fragmentation of the impacted particle in the aerosol deposition (AD) method was studied by the molecular dynamics method. Structural variation inside the particle after the impact was estimated for a spherical zirconia particle of which diameter is 10 nm by changing the incident velocity. Fragmentation of the particle was simulated when the incident speed is higher than 500 m/s. When the speed is higher than 1500 m/s, the crystal structure of the particle was disordered except a few small crystal regions. Such structural variation of the particle was found to be dependent on the crystal orientation of the particle to the substrate.

Keywords: aerosol deposition method, particle fragmentaion, zirconia, molecular dynamics, impact

## 1. INTRODUCTION

The aerosol deposition (AD) method 1) is promising technique for manufacturing new ceramics. The most important feature of this method is the low temperature process: the representative temperature is about 800 K and is much lower than the traditional methods. Hence a new material property which cannot be obtained by traditional methods is expected.

Experimental revealed that the grain size in the ceramics film created by the AD method is in the order of 10 nm 2) which is much smaller than that of raw particles, usually 100 to 300 nm. Hence, the fundamental mechanism of the AD process is considered to be the fragmentation of the particles into smaller grains due to the impact. However, due to the high speed and the microsopic scales, it is difficult to observe what happens in the AD process experimentally.

Molecular dynamics (MD) simulation is useful for understanding the mechanism of the AD process. Several studies were carried out for the fullerens 3,4), metal 5), and oxides. 6,7) However, these studies assumed different conditions comparing with the AD process especially on the particle size and the incident speed. In this paper, the MD calculation was carried out to simulate the single particle impact to the substrate. The objective of the simulation is to know the fundamental mechanism taking place in the AD method.

## 2. MD SIMULATION

The MD model is composed of a particle and the substrate in a rectangular MD cell. Zirconia (ZrO2) was selected as the composition of the particle and the substrate. The aerosol particle was assumed to have a spherical shape of which radius is 5.1 nm. The substrate was modeled by the rectangular of 18 x 18 x 4 nm3. The numbers of atoms in the model particle and substrate are about 60000 and 90000, respectively. The interatomic potentials proposed by Dwivedi and Cormack 8) 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 in monoclinic phases.

Three-dimensional periodic boundary conditions were assumed. The vertical (z) dimension of the MD cell is assumed to be 30 nm. The vertical periodicity is necessary for the Ewald summations. In order to fix the vertical position of the substrate against the particle impact, zcoordinates of the cations in several atomic layers at the bottom were restricted near the fixed positions by connecting with a harmonic potential. The force constant of the harmonic potential was adjusted to that at the minimum of the Zr-O potential.

Simulations were carried out by assuming several values on the incident speed from 250 to 2000 m/s and the incident angle from 0 ° (perpendicular to the substrate) to 45 °. We must also set the microscopic conditions on the model structure. Crystal orientation of the particle is not fixed but is randomly distributed in the actual AD process. In this study, three crystal orientation of the particle were used in the simulation: E, Rx, and Ry which denote the cases of the same axes for both crystal and MD coordinates, 90° rotation about x axis of E, and 90° rotation about y axis of E. The orientation of the substrate was assumed to be the (111) surface.

The initial temperatures of the particle and the substrate were adjusted to 300 K. MD simulation

was carried out at constant-NV condition without temperature control for 40 ps from just before the contact.

## 3. RESULTS AND DISCUSSION

Three-dimensional views of the simulated particle and substrate at 20 ps after the contacts are shown in Fig. 1 for incident velocity of 500, 1000 and 1500 m/s. The particle maintains a spherical shape at the lower velocity, but is deformed in the lower half at higher velocities than 1000 m/s. The atomic arrangement in the substrate is also modified with slip planes at higher velocities.

The impact between the incident particle and the substrate causes the temperature increase due to the release of the kinetic energy. The temperature of the system at 20 ps after the impact increases up to 480, 730 and 890 K for the incident speeds of 500, 1000 and 1500 m/s, respectively. The impact also causes large compression near the contact point. The maximum value of the local pressure was observed at 3 to 5 ps after the impact. Figure 2 shows the velocity dependence of the maximum value of the total pressure at the contact point. The relation between the maximum value and the velocity is almost linear, and seems to be not sensitive to the crystal orientation of the particle. At peak value of the pressure reaches to 16 GPa at the incident velocity of 1000 m/s.

Such high pressure causes a large deformation of the particle. Figure 3 shows the variation of the aspect ratio of the particle shape as a function of the incident velocity. It decreases as the velocity increases, and is dependent on the crystal orientation of the particle. In the case of the crystal orientation E, the aspect ratio gradually reduces from 0.99 to 0.86 as the velocity increases from 250 to 1500 m/s.





In the case of Rx, however, it suddenly reduces at 650 to 750 m/s and reached to 0.65 at 1500 m/s. Such difference on the crystal orientation is considered to be caused by the change of the slip plane geometry.

The impact causes not only the variation of the particle shape but also the atomistic structure inside the particle. Figure 4 shows the cross section distributions of the crystal rotation in the impacted particle for three cases. They show the fragmentation



Fig. 1 Three-dimensional views of the simulated models at 20 ps after the impact in the cases of 500 (left), 1000 (middle) and 1500 (right) m/s. Assumed values of incident angle and crystal orientation are 0° and E, respectively.

of the particle into a few grains. Such fragmentation was generally observed when the incident speed is larger than 500 m/s. If the velocity is larger than 1500 m/s, not only the fragmented grains but also a disordered phase was found in the impacted grain.

By these results, the mechanism of the AD process was considered to be the fragmentation of the particles due to the large pressure caused by the impact. In the present simulation, the assumed diameter of the particle is about 10 nm which is almost one order smaller than the representative size used in the real AD processes. Variation of the impacted particle as shown above may changes if the particle size is larger than 10 nm, but the main difference is considered to be the dependency on the incident velocity: the larger particle causes the same effect as the higher velocity.

## 5. SUMMARY

The MD simulation of the particle impact to the substrate was carried out to observe the structural change inside the particle. It shows that the mechanism of the AD method is the fragmentation of the particles into a few grains. Such fragmentation takes place if the incident velocity is larger than 500 m/s for the particle of which size is 10 nm, and is also dependent on the crystal orientation. If the particle is larger than 10 nm, the structural variation may take place at lower velocities.



Fig. 3 Aspect ratio of the simulated particle after the impact as a function of the incident velocity. Incident angles are 0°.

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Fig. 4 Variations of the crystal orientation in the simulated particle at 20 ps after the impact. Figures are drawn by the rotation angle from the initial crystal orientation of the particle. Assumed values of incident speeds, incident angles, and crystal orientations are 1000 m/s, 0°, E (left); 1000 m/s, 22.5°, Rx (left); and 1500 m/s, 0°, Rx (left), respectively.

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