Molecular Dynamics Analysis of Elementary Process of Coating by a High-Temperature, High-Speed Droplet
(Flattening Process and Atomic Behavior of a Droplet)

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Three-dimensional molecular dynamics simulation was conducted to clarify at an atomic level the flattening process of a high-temperature droplet impacting a substrate at high speed. The droplet and the substrate were assumed to consist of pure aluminum, and the Morse potential was postulated between a pair of aluminum atoms. By visualizing the analytical results, the processes of melting and solidification, temperature distribution, deformation velocity, and potential energy of atoms of the droplet were clarified. The following conclusions were obtained: (1) Transfer of the droplet atoms to the horizontal direction in the flattening process increases in proportion to the horizontal distance from the central axis of the droplet. (2) The increase of the flattening ratio of the droplet ends as soon as solidification of the droplet starts from the outside edge of the droplet. This behavior indicates the end of flattening.

Key Words: Coating, Droplet, Flattening, Solidification, Substrate, Thermal Spraying, Pulsed Laser Deposition, Molecular Dynamics, Computer Simulation

1. Introduction

Deposition with high-temperature, high-speed droplets such as by thermal spraying is widely utilized(1). In particular, it is often applied to the coating of functional materials that are difficult to machine because a comparatively thick coating can be obtained in a relatively short time(2)–(5). On the other hand, the pulsed laser deposition (PLD) technique is employed to form fine thin films using high-temperature, high-speed droplets with a diameter of nanometer or hundred-nanometer order(6), (7). In this case, the use of finer droplets and denser organization of the thin film increases the strength of the thin film, making it advantageous for application to ultra-precise electronic, magnetic, or optical devices.

It is important to understand the flattening behavior of a droplet as the elementary process involved, in order to clarify the adhesion state, residual stress, and the other physical properties. Many researchers have been studying the flattening behavior of droplets(8)–(17). Some mechanical models with different assumptions have been proposed, and thermohydrodynamic calculations and experiments have been reported for a limited range of materials and conditions. However, the results do not always agree with each other, and a theory that can satisfactorily estimate the flattening behavior of a droplet has not yet been developed. One reason for this is the difficulty of theoretically analyzing the impact and flattening processes of a droplet, since its change of shape is so drastic. It is also difficult to experimentally verify the behavior of a droplet, because the processes take place in a time span of microseconds for a small droplet of micrometer order.

Rather than conducting conventional continuum modeling, we considered an atomistic model that can be
optimized to flexibly deal with drastic physical change. The atomistic model also has some limitations, such as the number of atoms that can be treated, and there is a problem in that the interatomic potential between different atoms has not always been clarified. Nevertheless, we tried to elucidate the targeted phenomenon using an atomistic model because such an approach has not yet been made. As the first step, this paper reports the results of molecular dynamics analysis of the impact of a globular high-temperature, high-speed aluminum (Al) droplet on a flat Al substrate and its flattening process. Al atoms were used because their interatomic potential has been clarified.

2. Analysis Model

The proposed model for three-dimensional molecular dynamics analysis is shown in Fig. 1. The substrate surface is Al(001) and is assumed to have a well-defined surface. By taking the mass of atom \(i\) to be \(m\), its position vector at the time step \(t\) to be \(r_i(t)\), and the resultant force vector of all forces acting from other atoms to be \(F_i(t)\), the following equation of motion is obtained:

\[
m \frac{d^2 r_i(t)}{dt^2} = F_i(t)
\]

(1)

\(F_i(t)\) is calculated using the following equation:

\[
F_i(t) = - \sum_{j \neq i} \text{grad} \phi_{ij}
\]

(2)

where \(\phi\) is the interatomic potential depending on the distance between atoms, and the index \(j\) indicates atoms except for atom \(i\). The numerical integration of Eq. (1) is carried out using the leapfrog method with a time step of 3 fs.

In order to handle as many atoms as possible, the following Morse potential \((18)\), which requires a comparatively short calculation time, is applied as the interatomic potential:

\[
\phi(r) = D \left[ \exp(-2\alpha(r-r_0)) - 2 \exp(-\alpha(r-r_0)) \right]
\]

(3)

where \(r\) is the atomic distance between a pair of atoms, \(D\) is the dissociation energy, \(\alpha\) is the potential coefficient, and \(r_0\) is the equilibrium distance. Here, the parameters for aluminum described in Ref. (18) are applied as follows: \(D = 0.2703 \text{ eV}, \alpha = 1.1646 \text{ Å}^{-1}, r_0 = 3.253 \text{ Å}\).

The dimensions of the substrate analysis area in the \(x, y,\) and \(z\) directions are \(100\alpha \times 100\alpha \times 5\alpha\), respectively, where, \(\alpha\) is the lattice constant of aluminum and equals 0.4 nm. The thickness of the substrate is relatively small at only \(5\alpha\). However, the results of several simulations with \(V_D < 2500 \text{ m/s}\) have shown that the flattening ratios and magnitudes of plastic deformations increased in proportion to \(V_D^{(19)}\). Therefore, the validity of the simulation in the region of these impact velocities can be considered to have been ensured. Still, the flattening ratios increased in proportion to the Reynolds number in the low Reynolds number region, which corresponds to a low impact velocity in a study conducted with continuum modeling \((20)\).

The uppermost part of the analysis area of the substrate is assumed to be a free surface. Outside the analysis area except for the free surface, atoms are arrayed in a lattice of constant length as the temperature control layer. Energy can dissipate from this layer when mechanical energy is generated inside the analysis area. The area outside the temperature control layer is assumed to be a perfect rigid body. The present simulation was conducted in a vacuum without considering the ambient pressure.

Considering the principle of minimum potential energy, atomic arrays of Al were obtained at absolute zero temperature, then atomic arrays at 1 500 K and 300 K for the droplet and substrate, respectively, were arranged considering thermal expansion, and mean-velocity vectors at corresponding temperatures were randomly assigned to all atoms. Next, Newton’s motion-equations were solved and scaling velocity was implemented sequentially until the system became stable. As a result, an atomic array model with a surface was constructed. It was also confirmed that the velocity of the atoms had corresponding Maxwell distributions \((20)\). These results confirmed the validity of the initial array models constructed respectively for the substrate and the droplet.

3. Analysis Results and Discussion

The parameters of the molecular dynamics simulation discussed in this paper are listed in Table 1. Here, we examine the impact and deformation processes of a droplet with a temperature of 1 500 K (which is about 550 K

<table>
<thead>
<tr>
<th>Simulation parameters</th>
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<tbody>
<tr>
<td>Aluminum (Al)</td>
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<tr>
<td>Substrate</td>
</tr>
<tr>
<td>Aluminum (Al, (a = 0.4 \text{ nm}))</td>
</tr>
<tr>
<td>Analyzed area of substrate</td>
</tr>
<tr>
<td>100(a \times 100\alpha \times 5\alpha)</td>
</tr>
<tr>
<td>(40 \text{ nm} \times 40 \text{ nm} \times 2 \text{ nm})</td>
</tr>
<tr>
<td>Inter-atomic potential</td>
</tr>
<tr>
<td>Morse</td>
</tr>
<tr>
<td>Initial temperature (T)</td>
</tr>
<tr>
<td>(T_D = 1500 \text{ K (Droplet)})</td>
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<tr>
<td>(T_S = 300 \text{ K (Substrate)})</td>
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<tr>
<td>Diameter of droplet (d)</td>
</tr>
<tr>
<td>12.4 \text{ nm (55505 atoms)}</td>
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<tr>
<td>Droplet velocity (V_D)</td>
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<tr>
<td>2500 \text{ m/s}</td>
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Table 1
higher than the melting point of aluminum), a diameter of 12.4 nm (55,505 atoms), and a velocity of 2,500 m/s. The flattening ratio is defined as $\xi = D/d$, where $D$ is the maximum diameter of the droplet during or after flattening. According to studies of $\xi$ at different values of $V_D$, $\xi$ became 2.36 at $V_D = 2,500$ m/s, and the flattening process is considered to have been sufficiently completed as shown concretely in the following figures. Therefore, the result when $V_D = 2,500$ m/s is examined here. The flattening process was examined by visualizing the atomic arrangement, traveling distance, deformation speed, temperature, and potential energy of the droplet and substrate, respectively.

3.1 Atomic behavior in flattening process of droplet

The horizontal traveling distance and the behavior of the atoms in the droplet and substrate are shown in Fig. 2.

![Fig. 2 Deformation process of droplet and traveling distance of atoms in horizontal direction](image)

The gray scale displays the horizontal traveling distance of the droplet atom. The time when the droplet contacts the substrate surface is set at $t = 0$. The snapshots in Fig. 2 display the cross section including the center line of the droplet.

In Fig. 2(a), the droplet and substrate exhibit significant plastic deformation at the impact interface. It can also be seen that the deformation of the droplet is concentrated at the impact interface and that the width (maximum diameter) of the droplet has not yet increased. In Fig. 2(b) to Fig. 2(d), the droplet is flattened and the substrate surface atoms are plastically deformed and removed by the frictional force caused by the horizontal movement of the droplet atoms at the impact interface. The width (maximum diameter) of the droplet is unchanged in Fig. 2(e) and (f), although its height is slightly lower in Fig. 2(e). This fact indicates that the flattening process has already ended at the stage shown in Fig. 2(e). From Fig. 2(g), which shows the condition 60 ps after that in Fig. 2(f), it can be confirmed that almost all of the atoms are regularly lined up. This indicates the final conclusion of flattening as well as solidification.

Our molecular dynamics analysis clarifies for the first time the phenomenon whereby the flattening of a droplet causes frictional force from the horizontal movement of the droplet atoms, which induces removal of the substrate surface atoms and creates a piled-up formation at the outside edge of the droplet after flattening. This phenomenon is not explained in the conventional continuum modeling.

In order to clarify the transfer or flow of the atoms in the droplet, the atomic trajectories in representative positions in the droplet are shown in Fig. 3. Figure 4 shows the relationship between the initial atomic arrays and the horizontal atomic traveling distance. These results demonstrate that the transfer of atoms in the droplet to the horizontal direction increases in proportion to the horizon-
Fig. 4 Relationship between initial position of atoms and their traveling distance in horizontal direction

Fig. 5 Change of deformation ratio with time

The initial position of atoms was related to their traveling distance from the central axis of the droplet, and that atoms located a small distance below the horizontal center line of the droplet travel the longest distance.

Figure 5 shows the variation with time of the deformation ratio of the height and width to the initial diameter of the droplet, $H/d$ and $D/d$, respectively. The flattening of the droplet starts at time 1.5 ps, and the flattening ratio increases along a logarithmic curve until about 10 ps. The flattening can be regarded to have ended at that time. Meanwhile, the vertical deformation ratio monotonously decreases until 4.5 ps and gently decreases after that, finally reaching its minimum value after 12 ps. From this fact, it can be understood that the solidification and contraction of the droplet in the height direction advances even after flattening (increase of the flattening ratio) has ended, because the end of deformation in the height direction is slightly later (2 ps) compared with that in the horizontal direction.

3.2 Variations of traveling velocity and mechanical energy of atoms

Figure 6 shows the horizontal and vertical traveling velocities ($v_x, v_z$) of the atoms in the form of a gray scale. The results clearly show the conversion of the vertical velocity component of the droplet into the horizontal component due to the impact. The horizontal and vertical directions are almost the same, and it is understood that the flattening of the droplet has already ended.

The instantaneous potential energy of each atom is examined next to clarify whether the material is molten or solidified in the flattening process and to investigate the stress state after flattening. Figure 7 shows the potential energy of each atom at each time. The potential energy is assumed to be zero when the inside of the material is in thermal equilibrium at 300 K. In Fig. 7, the regions are divided by a solid line according to the arrangement and potential energy of the atoms, so that it can be roughly grasped whether or not recrystallization has occurred yet. Here, the right side of the droplet from the center axis has been enlarged in order to clearly observe the crystal arrays, on the assumption that the deformation process occurs axisymmetrically.

In Fig. 7 (a), showing the initial stage, we can see that the collision interface has high potential energy exceeding 0.5 eV and is molten or highly strained. The potential energy increases particularly at places where plastic deformation has been generated due to the friction mentioned above. A comparison of Figs. 7 (a) and 2 (b) reveals that the boundary between the recrystallized region and original crystalline region differs from the interface of the droplet atoms and substrate atoms, because many substrate surface atoms are removed and piled up by the frictional force caused by flattening of the droplet as mentioned above. In other words, not only droplet atoms but also substrate surface atoms removed by this frictional force are included in the recrystallized region. Such a phenomenon can also be said to have been clarified for the first time by the present molecular dynamics analysis. In Fig. 7 (b), it can be observed that the atoms at the collision interface and in the droplet have high potential energy exceeding 0.5 eV.

On the contrary, in Fig. 7 (c) we see that recrystallization, that is, resolidification, has already taken place at the outside edge of the droplet, which also indicates the end of flattening of the droplet. In Fig. 7 (d), the region except for the upper part of the droplet has solidified, and it can also be seen that the portion plastically deformed by the friction in the flattening process of the droplet solidifies last. In Fig. 7 (e), the whole region has been solidified, the atoms are arrayed almost completely in the same orientation as the substrate in the initial state, and little residual strain is seen, although a residual dislocation can be observed.

Figure 8 shows the atomic temperature distribution at each time. In general, although the temperature should
be evaluated in terms of the temporal and/or spatial average, individual atomic temperatures were specially obtained and displayed in order to roughly grasp the temperature changes of the droplet and substrate during the deformation process. The atomic temperature was calculated by deducting the translation motion component. In Fig. 8, the regions where recrystallization has occurred are also divided by the same solid lines as in Fig. 7.

Figure 8 (a) and (b) clarifies the dissemination of the high-temperature region in the substrate; that is, the thermal diffusion process accompanying the increase in the area of contact between the droplet and the substrate. In particular, the temperature of atoms where plastic deformation has been generated by friction inside the substrate becomes higher. On the other hand, it can also be recognized in Fig. 8 (c) that recrystallization, that is, solidification, has already taken place at the outside edge of the droplet from the standpoint of temperature, because the temperature in that region is much lower than the melting point. In Fig. 7 (d) and (e), the solidification process can be clearly observed.

In conventional continuum modeling of the flattening phenomenon of a droplet, a simple assumption has been established that the substrate is a rigid body. However, our study has clarified that the behavior of the crystalline-noncrystalline boundary is complex and greatly differs from such a simple assumption, as shown in Figs. 7 and 8. A more realistic treatment of the solid-fluid interface in continuum modeling needs to be established as a future research subject.

4. Conclusions

Several three-dimensional molecular dynamics simulations were conducted to clarify at an atomic level the flattening process of a high-temperature aluminum droplet impacting an aluminum substrate at high speed. In this study, we examined the impact on a substrate of a droplet of 12.4 nm in diameter, with an initial temperature approximately 550 K higher than the melting point, traveling at a velocity of 2 500 m/s. By visualizing the analytical results, the processes of melting and solidification, temperature distribution, deformation velocity, and shape of the droplet were clarified.

The following conclusions were obtained from this study:

1. The flattening ratio \( \xi = D/d \) reached a final value of 2.3.
2. In the flattening process, the transfer of atoms in
the droplet to the horizontal direction increases in proportion to the horizontal distance from the central axis of the droplet, and the final cross-sectional shape of the droplet after flattening becomes concave.

(3) The force caused by flattening at the contiguous interface between the substrate and droplet becomes frictional force. This removes many substrate surface atoms and creates a piled-up formation at the outside edge of the droplet after flattening.

(4) The increase of the flattening ratio of the droplet ends as soon as solidification of the droplet starts from the outside edge of the droplet. This behavior indicates the end of flattening.

(5) The droplet after flattening recrystallized following the crystal arrays of the substrate, and little strain remains.

(6) After impact, the solid-liquid phase boundary at the contiguous interface between the droplet and substrate shows complex behavior, unlike that assumed in the conventional continuum modeling approach.

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References


