Doctoral thesis
Mechanism of ceramic deposition by aerosol deposition method

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Abstract
Aerosol deposition method (ADM) has recently been attracting attentions as a new method for formation of ceramic films. Dense ceramic films with thickness of 1-100 μm can be formed directly on a substrate by impacting fine ceramic particles with around 1 μm or sub-micrometer in diameter. The most distinguishing feature of this method is that the process temperature can be room temperature. Heating a substrate or starting materials is not required in ADM. From the viewpoint of industrial applications, the low process temperature is the most significant advantage of ADM. However, the mechanism of ceramic deposition has not been understood well. The objective of this study is to clarify the mechanism of ceramic deposition by ADM, more explicitly, to clarify the bonding mechanism between the ceramic film and the metal substrate and between the ceramic particles themselves.

To clarify the bonding mechanism between Al₂O₃ films and Cu substrates, transmission electron microscopy (TEM) observation and electron energy-loss spectroscopy (EELS) analysis were conducted. The EELS spectra near O-K edge obtained at the Al₂O₃/Cu interface had a pre-peak feature at around 528 eV. This suggests interactions between Cu and O in Al₂O₃. It was inferred that not only the anchoring effect but also the ionic bonding and covalent bonding that originates from the Cu-O interactions contribute to the bonding between Al₂O₃ films and Cu substrates.

To clarify the bonding mechanism between ceramic particles themselves, the dependency of the deposition efficiency on various deposition conditions was systematically investigated. As the conditions, the process for producing Al₂O₃ particles, the impact velocity of Al₂O₃ particles, and the substrate temperature during the deposition were focused in this study. As a result, it was inferred that the bonding
between the ceramic particles is based on the formation of clean and activated surface by the deformation of the particles during the impact.

The author has succeeded in clarifying the mechanism of ceramic deposition by ADM through the understanding the bonding mechanism between the ceramic film and the metal substrate and between the ceramic particles themselves. The results obtained in this study will ultimately lead to cost reduction of ADM by increasing the deposition efficiency, which is necessary to use ADM industrially in the near future.
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Chapter 1. Introduction

1.1. Aerosol deposition method

1.1.1. Features

Aerosol Deposition Method (ADM) has recently been attracting attentions as a new method for formation of ceramic films [1, 2]. By ADM, dense ceramic films with thickness range of 1-100 μm can be formed directly on a substrate [3]. ADM is based on shock loading solidification due to the impact of fine ceramic particles with sub-micrometer in diameter, which are accelerated by carrier gas [4]. The most distinguishing feature of this method is that the process temperature can be room temperature. Heating a substrate or starting materials, which is quite important to form high-quality films in conventional method for formation of ceramic films such as thermal spray, physical vapor deposition (PVD), and chemical vapor deposition (CVD), is not required in ADM. It has been reported that a wide variety of ceramic films, such as Al₂O₃ [5-7], Pb(Zr, Ti)O₃ [4, 9-13], AlN [14, 15], Y₂O₃ [16], and MgB₂ [17] can be formed at room temperature. This novel phenomenon is referred to as room temperature impact consolidation (RTIC) [3, 17], and the detail is explained in Section 1.1.2. From the viewpoint of industrial application, the low process temperature is the most significant advantage of ADM. ADM can prevent not only a substrate but also a film from be thermally damaged. The thermal damages, such as oxidation, phase transformation, lattice defects, and segregation, can influence mechanical, physical, and chemical properties of a substrate and a film. For example, in the case of the thermal spray, which is a conventional method for formation of ceramic films, films are porous, and oxidation or phase transformation of films can be caused by heating ceramic particles over the melting point.
In the late 1990s, the early type of ADM was developed as a revised type of gas deposition method (GDM) [18]. GDM has been developed as a technique to form metal thin films using nanoparticles. In GDM, nanoparticles generated by vaporizing metal materials, such as Ag and Au, with induction heating system are transferred by gas flow and ejected onto a substrate. The early type of ADM was named the Jet Molding System (JMS) [19, 20]. The apparatus of JMS can be regarded as a combination between the apparatus of GDM and a new component supplying ceramic fine particles. It was reported that a thick PZT film with a dimension of 5 mm × 3 mm × 21 μm was formed without heating a substrate [19]. Furthermore, it was confirmed that the film had the same crystal structure as the starting particles. It meant that the JMS method was a promising handling technology for the fabrication of functional materials without changing their structures or compositions [19].

It seems that the current apparatus of ADM had been developed based on this knowledge. The current apparatus of ADM was introduced in 1999 [21, 22]. A schematic illustration of the apparatus is shown in Fig. 1.1. This apparatus consists of two chambers: an aerosol chamber and a deposition chamber. The aerosol chamber generates aerosol by vibration that mixes ceramic powder with carrier gas. A substrate is attached to an X-Y stage in the deposition chamber, and the deposition chamber is vacuumed by a mechanical booster pump and an oil rotary vacuum pump. The aerosol is delivered to the deposition chamber as a result of the pressure difference between the deposition chamber and the aerosol chamber. The ceramic particles in the aerosol are accelerated through a nozzle and impacted on the substrate.
1.1.2. Deposition mechanism

The most distinguishing feature of ADM is that the process temperature can be room temperature. Dense ceramic films with thickness range of 1-100 μm can be formed directly on a substrate at room temperature. The mechanism that causes this novel phenomenon has been discussed since ADM was reported in the late 1990s. In this subsection, the deposition mechanisms that have been clarified so far are explained.

Fundamental phenomena that promote bonding between a substrate and ceramic particles and between ceramic particles themselves during the deposition have been inferred by comparing similar methods of ceramic formation. It was assumed that a part of particle’s kinetic energy was converted into local thermal energy that promoted the
bonding, because ADM was based on shock loading solidification due to the impact of fine ceramic particles [4]. Because consolidation features of ceramic material fabricated by ADM were fundamentally similar to those by the shock compaction method [23], the deposition mechanism of ADM was discussed based on the local rising temperature and shock pressure. To estimate these conditions, the actual velocity of particles during the deposition was needed to be measured. Then, a time-of-flight method was developed, in which some part of the particle flow was mechanically cut from the total flow and deposited onto a moving substrate [24]. The deflection of deposited pattern from the center axis, geometrical dimensions and moving speed of substrate provided data to determine impact particle velocity [24]. The merit of this method was that the impact particle velocity was directly measured, whereas the conventional measurement using a high-speed camera could only estimate particle flow velocity [3]. As a result, the particle impact velocities were estimated as varying from 150 up to 500 m/s [7]. This was a very small kinetic energy compared with that in the conventional shock compaction process [23]. Moreover, using this experimental impact velocity, the local rising temperature and shock pressure by the impact of particle with the substrate were simulated by finite-element method (FEM) [7]. As a result, it was found that the maximum local temperature and shock pressure at the impact area during the process were about 500 °C and 3.5 GPa, respectively. This local heating temperature was too low to induce ceramic sintering. Although it seemed that consolidation features of ceramic material fabricated by ADM were fundamentally similar to those by the shock compaction method, these local rising temperature and pressure were less than those of the conventional shock compaction method, in which typical local temperature and pressure were over 1000 °C and 10 GPa, respectively.
Microstructures of films formed by ADM have been observed eagerly to clarify the deposition mechanism of ADM [5, 6, 8]. Although the starting particles were not melted during the deposition as shown in the above FEM simulation, films had dense and void-free structure. In the case of Al₂O₃ films, the transmittance of 1 μm film was over 99% in the optical region of 400 ~ 800 nm [7]. It meant that there were few defects for optical scattering and absorption, and high-density film formation could be achieved. From XRD patterns of films formed by ADM, it was revealed that the films had the same crystal structure as the starting particles and no second phase existed [5, 7, 19]. However, peak broadening in the X-ray diffraction patterns was confirmed. With transmission electron microscopy (TEM) observation and selective area diffraction (SAD) patterns, it was found that the as-deposited film consisted of randomly oriented crystal grains less than 20 nm, which was smaller by an order of magnitude than crystallites of the starting particles [7]. To investigate this reduction of the crystallite size, a mixed aerosol of α-Al₂O₃ and PZT particles was deposited to form the composite film [7]. A laminar structure of the composite film along the substrate plain was observed in the cross-sectional TEM image. Randomly oriented crystal grains less than 20 nm were also observed in the high magnification image. The volume of a PZT part in the laminar structure was close to that of a PZT starting particle. From these results, it was concluded that fracture or plastic deformation of starting particles during the deposition leads to the dense structure and the reduction of crystallite [7]. It seemed that the fracture or plastic deformation of the starting particles could fill up the gaps between the particles. A possibility was also suggested that the deformation of ceramic particles resulted in the formation of new and activated surface which promoted the bonding between the ceramic particles [5]. This explanation for densification of ceramic particles
was completely different from those of conventional methods for formation of ceramic materials. Furthermore, the plastic deformation of fine ceramic particles under certain conditions was thought to be a general phenomenon, because films of a wide variety of ceramic such as oxide, nitride, and boride, were able to be formed by ADM [7].

Deformation behavior of a fine ceramic particle has been investigated to understand the deposition mechanism of ADM, because the deformation behavior of fine ceramic particles is thought to play an important role to form dense ceramic films as described above. A compression test system was developed for measuring the strength of a single particle with a cross-sectional dimension of less than 1 μm [25]. With the system, the mean strength of Al₂O₃ particles with nominal mean diameter of 0.7 μm was estimated to be 2.9 GPa [25]. It was found that the maximum rising impact pressure during the deposition, which was about 3.5 GPa as mentioned above, was almost the same as the experimental fracture toughness of the starting particle. Interestingly, from SEM observation, it was also found that a fine ceramic particle whose diameter was lower than about 1μm could show plastic deformation like a metal particle by the compression test, whereas a ceramic particle whose diameter was over 5 μm showed brittle fracture and broke to pieces [26]. The reason why fine particles with around 1 μm or sub-micrometer in diameter are suitable for ADM is thought to be this difference of the deformation behavior under compression load. The plastic deformation of the starting ceramic particles can fill up the gaps between the particles and resulted in the formation of dense ceramic films.

Although the important characteristics of the bonding between ceramic particles themselves have been clarified as described above, the mechanism of ceramic deposition by ADM has not been understood well. For example, there are still several
questions remained to be answered, what kind of bonding is induced between the ceramic particles and the metal substrate, or whether a hypothesis that clean and activated surface of ceramic particles promotes bonding between the particles is reasonable to account for ceramic deposition by ADM.

1.1.3. Properties of ceramic film formed by aerosol deposition method and its application fields

Ceramic films formed by ADM (AD films) have dense structure composed of tiny crystal grains about 10 ~ 20 nm large, and show high breakdown voltage, high hardness, and high transparency. Various applications of AD films have been proposed as follows.

AD films generally show high breakdown voltage that exceeds that of a sintered bulk material. For example, the breakdown voltage of an \( \alpha \)-Al\(_2\)O\(_3\) film is 150 ~ 200 V/\( \mu \)m [6, 27], and that of a Y\(_2\)O\(_3\) film is about 150 V/\( \mu \)m [16]. These values are higher by an order of magnitude than those of the sintered bulk materials. The micro Vickers hardness of an \( \alpha \)-Al\(_2\)O\(_3\) film ranges from 1000 to 1600 Hv, which indicates that the film exhibit mechanical properties similar to those of the bulk material [27]. The tensile strength of an AD film on a stainless steel or fused silica substrate is estimated to be higher than 50 MPa [27]. The volume resistivity, the dielectric constant, and the dielectric loss of an \( \alpha \)-Al\(_2\)O\(_3\) film are \( 1.5 \times 10^{15} \) \( \Omega \)·cm, 9.8 at 1 kHz, and 0.2%, respectively [28]. These values are almost the same as the sintered bulk material. These electrical and mechanical properties of AD films can be available for various devices such as electrostatic chucks, electrical insulation layers for high power electric devices [3, 29]. Moreover, the possibility of miniaturization of RF modules is proposed using Al\(_2\)O\(_3\) films fabricated by ADM as an integral substrate [5].
Although the breakdown voltage of a PZT film exceeds 50 V/μm [3], which is comparable to that of the bulk material, piezoelectric and ferroelectric properties of as-deposited PZT films are unacceptable for practical applications. This is because the structural defects are introduced in the films and the size of the crystal grain of the films is reduced during the deposition. However, by post-annealing in air at temperatures ranging from 500 to 600 °C, a grain growth of fine crystals and a defect recovery in AD films can be achieved, which dramatically improves the ferroelectric properties. The dielectric constant and the piezoelectric constant ($d_{31}$) of post-annealed PZT films formed at 600 °C are 800 ~ 1200 and -100 pm/V [30], respectively, which is comparable to the values obtained with conventional thin-film formation methods. Even without adding any special additives to the starting particles or using special procedures, ADM permits a 300 ~ 400 °C reduction of the process temperature compared with a conventional screen printing method. The most important characteristic of AD films is that, compared with the properties of films deposited using classic coating methods, the as-deposited film has a more dense and crystallized structure being close to the bulk material [3]. Using these properties of PZT films, various applications have been proposed such as piezoelectric devices [31] and optical devices [32, 33].

1.2. Objective

Ceramic films formed by ADM have dense and crystallized structure without thermally damaged. From the viewpoint of industrial applications, ADM has advantages against the conventional ceramic deposition method such as thermal spray, PVD, and CVD. Several important characteristics of the bonding between ceramic particles themselves have been clarified as described in Section 1.1.2. However, the mechanism
of ceramic deposition by ADM has not been understood well. For example, there are still some questions remained to be answered, what kind of bonding is induced between the ceramic particles and the metal substrate, or whether a hypothesis that clean and activated surface of ceramic particles promotes bonding between the particles is reasonable to account for ceramic deposition by ADM. The objective of this study is to clarify the mechanism of ceramic deposition by ADM, more explicitly, to clarify the bonding mechanism between the ceramic film and the metal substrate and between the ceramic particles themselves.

To investigate the bonding between the ceramic film and the metal substrate, TEM observation and electron energy-loss spectroscopy analysis of the interface were conducted in this study. The results and conclusion are described in Chapter 2.

To clarify the bonding mechanism between ceramic particles themselves, the dependency of the deposition efficiency on various deposition conditions was systematically investigated in this study. The deposition efficiency means the ratio of the film weight to the consumed particle weight during the deposition. By systematically investigating the dependency of the deposition efficiency on deposition conditions, factors related to the deposition mechanism between the ceramic particles can be identified and the mechanism can be discussed more precisely. In addition, by investigating the deposition efficiency, general guidelines for increasing the deposition efficiency can be found. Increasing the deposition efficiency ultimately results in cost reduction of ADM by increasing the deposition rate or reducing the weight of the starting particles. These guidelines will be essential to use ADM industrially in the near future. The results and conclusion are described in Chapter 3, 4, and 5.
References


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Chapter 2. Microstructure of ceramic film and interface between ceramic film and metal substrate

2.1. Introduction

ADM has recently been attracting attention as a new method for forming ceramic films [1-3] because it can form dense ceramic films directly on a substrate even at room temperature [4-6]. By impacting solid ceramic particles around 1μm in diameter on a substrate, many kinds of ceramic films, such as Al₂O₃, PZT, AlN, and MgB₂, can be obtained [1]. This novel phenomenon is referred to as room temperature impact consolidation (RTIC) [1]. The most distinguishing feature of this method is that the process temperature can be room temperature. From the viewpoint of industrial applications, the low process temperature is the most significant advantage of ADM. ADM can prevent not only a substrate but also a film from being thermally damaged. In the case of thermal spray, which is a conventional method for forming ceramic films, films are porous, and oxidation or phase transformation of films can be caused by heating ceramic particles above the melting point. By employing ADM as a new method for forming ceramic films, various applications have been proposed, such as piezoelectric devices [7], high-frequency devices [8], optical devices [9, 10], and insulating substrates for electronic devices [11].

To use ADM industrially, clarifying the bonding mechanism between ceramic films and metal substrates has been an important theme in the study of ADM. Previous reports revealed the morphologies and the atomic distribution of the interface between ceramic films and various substrates [1, 4, 12, 13]. In the case of Al₂O₃ films on SiO₂ substrates, the uneven interface about 100 ~ 200 nm thick between the film and the substrate was
observed in the cross-sectional TEM image, and the region was interpreted as the anchoring layer [1, 12]. In the case of Al$_2$O$_3$ films on metallic substrates such as Al, Cu, and stainless steel, the uneven interface was also observed [13]. So far, the bonding between ceramic films and substrates is explained by the anchoring effect [1, 12], or in other words, the mechanical interlock effect [13]. In the case of PZT films on Si substrates, energy dispersive X-ray spectra (EDX) analysis revealed that the Pb/Zr/Ti ratio of the film was almost consistent with that of the bulk sample even at the PZT/Si interface [4]. This result suggests that there was barely any thermal diffusion in the anchoring layer. In addition, FEM computing simulations revealed that the maximal local temperature rise in the impact area during the process was about 500 °C and lasted only several nanoseconds [12]. This local temperature rise is considered too low and too short to induce sintering.

Although the important characteristics of the interface between ceramic films and metal substrates have been obtained as described above, the bonding mechanism has not been understood well. For example, it has not been clarified whether the chemical bonding exists nor whether a bonding mechanism other than the anchoring effect really works.

In this study, to clarify the bonding mechanism between ceramic films and metal substrates, TEM observation and electron energy-loss spectroscopy (EELS) analysis of the interface between ceramic films and metal substrates were conducted.
2.2. Experimental procedure

2.2.1. Deposition apparatus

A schematic illustration of an ADM apparatus is shown in Fig. 1.1. This apparatus consists of two chambers: an aerosol chamber and a deposition chamber. The aerosol chamber generates aerosol by vibration that mixes ceramic powder with carrier gas. A substrate is attached to an X-Y stage in the deposition chamber, and the deposition chamber is vacuumed by a mechanical booster pump and an oil rotary vacuum pump. The aerosol is delivered to the deposition chamber as a result of the pressure difference between the deposition chamber and the aerosol chamber. The ceramic particles in the aerosol are accelerated through a nozzle and impacted on the substrate. The nozzle with a 10 mm × 0.4 mm rectangular exit was used in experiments of Chapter 2.

2.2.2. Materials and deposition condition

In experiments of Chapter 2, commercially available α-Al₂O₃ particles (AKP-20, Sumitomo Chemical Company, Ltd.) were used as starting particles. Fig. 2.1 shows the size distribution of the particles, which was measured by a particle size analyzer (Microtrac MT3000, Nikkiso Co., Ltd.). The size distribution ranged from 0.19 μm to 3.27 μm, and the average size was 0.52 μm. The morphology of the particles is shown in Fig. 2.2.

Before deposition, Al₂O₃ particles were heat-treated at 600 °C for 1 hour in air to eliminate moisture. Tough-pitch copper plates with dimensions of 30 mm × 30 mm × 0.3 mm were used as substrates. The plates were washed by ethanol and dried to eliminate organic impurities on the surface. Roughness (Ra) of the surface was 0.071 μm, which was measured by a surface roughness measuring instrument (Surfcoorder
SE3300, Kosaka Laboratory Ltd.). The nozzle exit and the substrate were 8 mm apart. The carrier gas was N₂, and the gas consumption was 1.8 L/min. Neither the substrates nor the carrier gas were heated. The pressures in the aerosol chamber and the deposition chamber were 12.8 kPa and 0.060 kPa, respectively. The traverse speed of the nozzle motion along the substrate was 1.0 mm/s, and the traverse was repeated 60 times with the traverse distance of 10 mm. The experimental parameters used in this chapter are summarized in Table 2.1.

![Figure 2.1](image1.png)

**Fig. 2.1** Size distribution of Al₂O₃ particles.

![Figure 2.2](image2.png)

**Fig. 2.2** Morphology of Al₂O₃ particles.
Table 2.1 Experimental parameters.

<table>
<thead>
<tr>
<th>Ceramic particle</th>
<th>$\alpha$-Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Cu</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>22 (R.T.)</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>N$_2$</td>
</tr>
<tr>
<td>Gas consumption (L/min)</td>
<td>1.8</td>
</tr>
<tr>
<td>Distance between substrate and nozzle (mm)</td>
<td>8</td>
</tr>
<tr>
<td>Pressure in aerosol chamber (kPa)</td>
<td>12.8</td>
</tr>
<tr>
<td>Pressure in deposition chamber (kPa)</td>
<td>0.060</td>
</tr>
<tr>
<td>Traverse speed (mm/s)</td>
<td>1.0</td>
</tr>
<tr>
<td>Number of traverses (times)</td>
<td>60</td>
</tr>
<tr>
<td>Traverse distance (mm)</td>
<td>10</td>
</tr>
</tbody>
</table>

2.2.3. Evaluation

The properties of Al$_2$O$_3$ films were evaluated as follows.

The crystal structures of the Al$_2$O$_3$ films and the starting Al$_2$O$_3$ particles were confirmed by X-ray diffraction (XRD) (MXP18VAHF, Bruker AXS K.K.) using Cu Kα radiation at 40 kV and 100 mA with a scanning step of 0.0200 deg and scanning speed of 5.00 deg/min. And crystallite sizes were calculated by Scherrer’s equation as described in Eq. 2.1 using the XRD patterns, where $t$ is the crystallite size, $B$ is the width of the Bragg peak, $\lambda$ is the wavelength of the X-ray (0.154 nm), and $\theta_B$ is the Bragg angle.

$$t = \frac{\lambda}{B \cos \theta_B}$$  \hspace{1cm} (Eq. 2.1)
The microstructure of Al₂O₃ films was observed by scanning electron microscopy (SEM) (S-4800, Hitachi High-Technologies Corporation.) operated at 15.0 kV and TEM (H-9000UHR, Hitachi High-Technologies Corporation.) operated at 300 kV. The specimen for TEM observation was fabricated by a focused ion beam (FIB) method (STRARA 400s Omni-probe system, FEI Company) and thinned down to about 65 nm in thickness.

The chemical bonding states of atoms near the interface between the Al₂O₃ film and the Cu substrate were investigated by EELS (GIF Tridiem, GATAN, Inc.) with energy resolution of 1.0 eV (FWHM) attached to TEM (JEM-2100F, JEOL Ltd) at accelerating voltage of 200 kV. The electron beam diameter was 0.7 nm. EELS spectra near the Al-L edge, the Cu-L edge, and the O-K edge were recorded with acquisition time of 0.8 s, 2.5 s, and 2.5 s, respectively.

2.3. Results and discussion
2.3.1. Microstructure

Fig. 2.3 shows a cross-sectional SEM image of the Al₂O₃ film. At this cross section, it is found that the dense and crack-free film was successfully formed on the substrate. The shape of the starting particle could not be recognized in the image. The uneven interface between the film and the substrate, which can be regarded as the anchoring layer in the previous reports [1, 12, 13], was also observed. Fig. 2.4 shows a cross-sectional SEM image of the substrate before deposition. The roughness of the surface, which was defined as the distance between the bottom line and the top line of the surface as shown in Fig. 2.4, was 0.3 μm before deposition. In contrast, the roughness of the interface after deposition was 0.7 μm as shown in Fig. 2.3. This result
indicates that the substrate surface was deformed unevenly by the impact of the particles during the deposition. The deformation of the substrate surface suggests that clear and active surface of Cu could be partially formed at the Al₂O₃/Cu interface, although a natural oxidation film was thought to exist on the substrate surface before the deposition.

Fig. 2.3 Cross-sectional SEM image of Al₂O₃ film.

Fig. 2.4 Cross-sectional SEM image of Cu substrate before deposition.
XRD pattern indicated that the crystal structure of the film was \( \alpha \)-\( \text{Al}_2\text{O}_3 \). The average crystallite size of the film, which was calculated using (012), (104), and (116) XRD peaks of \( \alpha \)-\( \text{Al}_2\text{O}_3 \), was 11.6 nm. In contrast, the average crystallite size of the starting powder was 54.1 nm. The reduction of crystallite size was observed as previously reported [1, 2, 6, 12].

To investigate the microstructure of the anchoring layer closely, TEM observation was conducted. Fig. 2.5 shows a bright-field image of the interface between the \( \text{Al}_2\text{O}_3 \) film and the Cu substrate. The film was directly adhered to the substrate without any void or crack. The film was composed of tiny crystal grains about 10 ~ 20 nm large, as indicated by contrast in the film shown in Fig. 2.5. The crystal grain size agrees well with the crystallite size calculated by the XRD pattern of the film. Figure 2.6 shows a bright-field image of the \( \text{Al}_2\text{O}_3 \) film at a point about 1.5 \( \mu \text{m} \) far from the \( \text{Al}_2\text{O}_3 / \text{Cu} \) interface. The crystal size was about 10 ~ 20 nm, and the same as that at the \( \text{Al}_2\text{O}_3 / \text{Cu} \) interface.
Fig. 2.5 Bright-field image of interface between Al₂O₃ film and Cu substrate.

Fig. 2.6 Bright-field image of Al₂O₃ film at point about 1.5μm far from Al₂O₃/Cu interface.
To confirm the crystal structure of the Al$_2$O$_3$ film at the Al$_2$O$_3$/Cu interface, a SAD pattern was obtained in the area indicated by the circle in Fig. 2.5. Fig. 2.7 shows the SAD pattern. The diffraction spots existed concentrically and the spot spacing corresponded to the lattice spacing of $\alpha$-Al$_2$O$_3$. It indicates that the crystal structure was $\alpha$-Al$_2$O$_3$ and not amorphous, and the crystal grains were randomly oriented. This structure agrees well with the XRD pattern in this study and those of previously reported AD films [1, 11, 12].

![SAD pattern of Al$_2$O$_3$ film in area indicated by a circle in Fig. 2.5.](image)

Fig. 2.7 SAD pattern of Al$_2$O$_3$ film in area indicated by a circle in Fig. 2.5.
In the case of cold spray, which is a technology to form dense metal films such as Cu, Al, and Ni, by impacting solid metal particles on a substrate, a thin interfacial layer with nanometer order thickness (for example, an amorphous and oxygen-rich layer) could sometimes be found at the interface between impacted solid particles and a substrate [14, 15]. These interfacial layers seem to play an important role in the bonding between the impacted particles and the substrate. This might suggest the possibility that there was an interfacial layer at the Al₂O₃/Cu interface in this study as well, because cold spray and ADM are common in impacting solid particles on a substrate. To clarify if the interfacial layer exists at the Al₂O₃/Cu interface, the microstructure was observed at higher magnification. Fig. 2.8-(a) shows a high resolution TEM image of the Al₂O₃/Cu interface. Randomly oriented lattice fringes were observed in the Al₂O₃ film. This indicates the film had a randomly oriented crystal structure, which is consistent with the SAD pattern shown in Fig. 2.7. Fig. 2.8-(b) shows the enlarged image of the interfacial region indicated by the rectangle in Fig. 2.8-(a). The lattice fringes of the Al₂O₃ film were recognized at the interface with the Cu substrate, and no interfacial layer with nanometer order thickness could be found at the Al₂O₃/Cu interface in this study. It is inferred that the Al₂O₃ film retained α-Al₂O₃ crystal structure at the interface with the Cu substrate, and there was some direct interaction among Al, O, and Cu at the atomic scale such as chemical bonding among these elements.
Fig. 2.8 High-resolution TEM image. (a) Al$_2$O$_3$/Cu interface.

(b) Enlarged image of interfacial region indicated by a rectangle in Fig. 2.8-(a).
2.3.2. Chemical bonding states

To reveal the chemical bonding states of the interface, the electronic structures were investigated by EELS. Fig. 2.9 shows a cross-sectional high angle annular dark field (HAADF)-Scanning TEM (STEM) image of the interface. EELS spectra were obtained at six points as indicated by the circles in Fig. 2.9.

Fig. 2.9 Cross-sectional HAADF-STEM image of Al$_2$O$_3$/Cu interface.

Fig. 2.10 shows the EELS spectra near the Al-$L$ edge and the Cu-$M$ edge. Spectra at positions 2 through 5 reflected electron-energy-loss near-edge structure (ELNES) at the Al-$L$ edge (73 eV), whereas spectra at positions 0 and 1 reflected ELNES at the Cu-$M$ edge (74 eV). The shapes of spectra at positions 2, 3, and 4 were almost consistent with that at position 5, where the SAD pattern of $\alpha$-Al$_2$O$_3$ was obtained as shown in Fig. 2.7. This means that the electronic structures of Al atoms at the interface, i.e., positions 2, 3, and 4, were consistent with that of Al atoms consisting of $\alpha$-Al$_2$O$_3$. Fig. 2.11 shows the EELS spectra near the Cu-$L$ edge. The shapes of spectra at positions 0 through 4 were
almost the same, and no distinctive sharp peaks were observed, although the intensity was lower at the interface, i.e., positions 2, 3, and 4, than that at the Cu substrate, i.e., positions 0. This means that the electronic structures of Cu atoms at the interface were consistent with that of Cu atoms consisting of metallic Cu. In the case of CuO and Cu$_2$O, it is known that sharp L$_3$ peak appears around 930 eV [18]. On the conditions of the EELS analysis in this study, it can be said that the Al$_2$O$_3$ film was directly adhered to the Cu substrate without copper oxides. The quantity of a natural oxidation film on the Cu substrate surface that still remained at the Al$_2$O$_3$/Cu interface after deposition was, if any, too small to be detected by EELS. At positions 2, 3, and 4, the existence of both Al in $\alpha$-Al$_2$O$_3$ and Cu in metallic Cu was confirmed. This is because the specimen was about 65 nm in thickness and the Al$_2$O$_3$/Cu interface had an uneven structure along the direction of the electron transmission as well. It is concluded that neither Al nor Cu diffused over the Al$_2$O$_3$/Cu interface during the film formation, because the spectra indicating Cu in Al$_2$O$_3$ or Al in metallic Cu could not be detected.

![EELS spectra](attachment:image.png)

Fig. 2.10 EELS spectra near Al-$L$ edge and Cu-$M$ edge.
Fig. 2.12 shows the EELS spectra near O-K edge. In addition to the main peaks observed at around 537 eV at positions 1 through 5, there was also the pre-peak at 528 eV at position 4. This indicates that the electronic structure at position 4 was slightly different from those at positions 1, 2, 3, and 5. Regarding the pre-peak feature, the electronic structure has been revealed by experiments and theoretical calculations [17, 18]. It has been reported that the pre-peak in the O-K ELNES of Al₂O₃/Cu interface prepared by a pulsed-laser deposition is attributed to an interaction between Cu and O in Al₂O₃ across the interface [17]. Furthermore, it has been revealed that the pre-peak feature originates from interactions between Cu and O in Al₂O₃ using a first principles orthogonalized linear combination of atomic orbital methods [18]. Considering the EELS spectra at position 4 shown in Fig. 2.12 and the above literature, it can be concluded that there were the Cu-O interactions at the Al₂O₃/Cu interface in this study. This conclusion
suggests that the O-terminated interface was formed at the edge of the $\text{Al}_2\text{O}_3$ film. In the case of the O-terminated interface, it has been shown that both the ionic bonding and the covalent bonding can be formed at the $\text{Al}_2\text{O}_3$/Cu interface [18]. It is inferred that not only the anchoring effect but also the ionic bonding and covalent bonding that originates from the Cu-O interactions contribute to the bonding between $\text{Al}_2\text{O}_3$ films and Cu substrates.

![Fig. 2.12 EELS spectra near O-K edge.](image)

So far, some in-plane orientation relationships of the interface were observed in experiments, e.g., Cu[110]/$\text{Al}_2\text{O}_3$[1100] at Cu(111)/$\text{Al}_2\text{O}_3$(0001) interface and Cu[110]/$\text{Al}_2\text{O}_3$(0001) at Cu(001)/$\text{Al}_2\text{O}_3$(1120) interface [17]. Considering that both the ionic and covalent bonding strongly depend on the atomic configuration, the specific in-plane orientation relationship may possibly be found at the interface between the $\text{Al}_2\text{O}_3$ film formed by ADM and the Cu substrate. Closer analysis of the orientation relationship at
the Al₂O₃/Cu interface may provide important information about the interface.

2.4. Summary

To clarify the bonding mechanism between ceramic films formed by ADM and metal substrates, TEM observation and EELS analysis of the interface between Al₂O₃ films and Cu substrates were conducted. The results and discussion are summarized as follows.

1. The Al₂O₃ film was directly adhered to the Cu substrate without any void or crack. The film was composed of randomly oriented α-Al₂O₃ crystal grains about 10 ~ 20 nm large. At the Al₂O₃/Cu interface, the lattice fringes of the film were recognized and no interfacial layer with nanometer order thickness could be found.

2. The EELS spectra near the Al-L and Cu-L edges obtained at the Al₂O₃/Cu interface indicate that the electronic structures of Al atoms were consistent with that of Al atoms consisting of α-Al₂O₃ and that the electronic structures of Cu atoms were consistent with that of metallic Cu.

3. The EELS spectra near O-K edge obtained at the Al₂O₃/Cu interface had a pre-peak feature at around 528 eV. According to previously reported experiments and theoretical calculations, this suggests interactions between Cu and O in Al₂O₃ at the interface. It is inferred that not only the anchoring effect but also the ionic bonding and covalent bonding that originates from the Cu-O interactions contribute to the bonding between Al₂O₃ films and Cu substrates.
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Chapter 3. Relationship between process for producing ceramic particles and deposition efficiency

3.1. Introduction

ADM has recently been attracting attention as a new method for formation of ceramic films [1-4] because it can form dense ceramic films (AD films) directly on a substrate even at room temperature [5-9]. The most distinguishing feature of this method is that the process temperature can be room temperature. From the viewpoint of industrial application, the low process temperature is the most significant advantage of ADM.

To use ADM industrially, the bonding mechanism between ceramic particles themselves has to be clarified. Regarding the bonding mechanism, the following fact could provide valuable information. In the case of forming dense ZrO$_2$ films by the ADM, it has been reported that dry-milled particles were superior to chemically prepared wet-type ones [10]. When dry-milled ZrO$_2$ particles were used, the film was successfully formed with a wide range of particle sizes ranging from 0.73 to 10.2 μm [10]. In contrast, when wet-type ZrO$_2$ particles were used, the film could be formed only with a narrow range of particle sizes ranging from 2.1 to 3.5 μm [11]. This result regarding the difference in the starting particles suggests that the bonding mechanism depends on the properties of the particles that reflect the process for producing them. Moreover, other previous reports also revealed several important characteristics of the ADM regarding the bonding mechanism. The laminar structure of an AD film composed of a mixture of Al$_2$O$_3$ and PZT was observed along the substrate in the cross-sectional TEM image [8]. The structure indicated that the bonding between ceramic particles was caused by the deformation of the particles during the deposition.
A possibility was also suggested that the deformation of ceramic particles resulted in the formation of new and activated surface which promoted the bonding between the ceramic particles [7]. The author presumes that promoting the deformation of ceramic particles could favorably affect the deposition efficiency and parameters related to the deformation behavior of ceramic particles could be important to understand the bonding mechanism between ceramic particles themselves.

In Chapter 3, the effect of the process for producing Al₂O₃ particles on the deposition efficiency was investigated. And the difference in the deposition efficiency was discussed in terms of the deformation behavior of the Al₂O₃ particle.

3.2. Experimental procedure

3.2.1. Materials and deposition condition

In experiments of Chapter 3, two types of commercially available α-Al₂O₃ particles were used, and the processes for producing the particles were different. One was composed of α-Al₂O₃ particles produced by sintering Al(OH)₃ (sintered particles). The other type was composed of α-Al₂O₃ particles produced by chemical vapor deposition (CVD) (CVD particles). Furthermore, to separate the effect of size distribution of particles on the deposition efficiency from that of the process for producing them, 3 kinds of powder with different size distributions were prepared in both sintered particles and CVD ones. AL-160SG-3 (Showa Denko K.K.), AES-23 (Sumitomo Chemical Company, Ltd.), and AMS-5020F (Sumitomo Chemical Company, Ltd.), which are marked as S1, S2, and S3, respectively, were used as sintered particles. Fig. 3.1 shows the size distributions of S1, S2, and S3, which were measured by a particle size analyzer (Microtrac MT3000, Nikkiso Co., Ltd.). The size distributions of S1 and S3 had peaks
at 0.58 μm and 3.57 μm, respectively. The size distribution of S2 had two peaks at 0.49 μm and 3.15 μm. AA-05 (Sumitomo Chemical Company, Ltd.), AA-1.5 (Sumitomo Chemical Company, Ltd.), and AA-3 (Sumitomo Chemical Company, Ltd.), which are marked as C1, C2, and C3, respectively, were used as CVD particles [14]. Each CVD particle was composed of a single crystal [14]. Fig. 3.2 shows the size distributions of C1, C2, and C3, which had peaks at 0.66 μm, 1.78 μm, and 3.57 μm, respectively. The size distributions of S1 and C1 were almost same (D10, D50, and D90 of S1 were 0.37 μm, 0.65 μm, and 1.58 μm, respectively. D10, D50, and D90 of C1 were 0.40 μm, 0.70 μm, and 1.42 μm, respectively.). The size distributions of C2 and C3 were narrower than those of the sintered particles. The morphologies of the α-Al₂O₃ particles used in this study are shown in Fig. 3.3.
Fig. 3.1 Size distributions of sintered particles.

Fig. 3.2 Size distributions of CVD particles.
Fig. 3.3. Morphologies of $\alpha$-Al$_2$O$_3$ particles with different production processes and size distributions. (a) S1 (AL-160SG-3). (b) C1 (AA-05). (c) S2 (AES-23). (d) C2 (AA-1.5). (e) S3 (AMS-5020F). (f) C3 (AA-3).
In preparation of starting particles, the author paid attention to pretreatment of particles. It has been reported that the agglomeration of particles interfered with the film formation because it could serve as a cushion for absorbing the kinetic energy [7, 15]. So, it was necessary to reduce the agglomeration of particles to investigate the effect of the process for producing Al₂O₃ particles. Therefore, in this study, the Al₂O₃ particles were heat-treated at 600 °C for 1 hour to eliminate moisture before deposition, because it has been indicated that eliminating moisture contents contained in particles by heat-treatment was effective to reducing agglomeration of particles [15].

Other experimental parameters are as follows. Tough-pitch copper plates with dimensions of 50 mm × 40 mm × 3 mm were used as substrates. The plates were washed by ethanol and dried to eliminate organic impurities on the surface. The distance from the nozzle exit to the substrate was 8 mm. The carrier gas was N₂, and the gas consumption was 1.8 L/min. Neither the substrates nor the carrier gas were heated. The pressures in the aerosol chamber and the deposition chamber were 12.8 kPa and 0.060 kPa, respectively. The traverse speed of the nozzle motion along the substrate was 1.0 mm/s, and the traverse was repeated 60 times with the traverse distance of 10 mm. The used ADM apparatus was the same as the one described in Section 2.2.1. The experimental parameters used in Chapter 3 are summarized in Table 3.1.

Fig. 3.4 shows the size distributions of the starting particles (S3) and the particles ejected from the nozzle, which were captured by plastic bags set at the X-Y stage. Although the fraction of the particles with diameters of over 4 μm slightly decreased, it was found that the size distribution as a whole was retained after ejected from the nozzle under the experimental condition shown in Table 3.1. Therefore, considering the size distribution of the starting particles is thought to be reasonable to discuss the
deposition efficiency in the following sections.

Table 3.1 Experimental parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic particle</td>
<td>$\alpha$-$\text{Al}_2\text{O}_3$</td>
</tr>
<tr>
<td>Substrate</td>
<td>Cu</td>
</tr>
<tr>
<td>Substrate temperature ($^\circ\text{C}$)</td>
<td>22 (R.T.)</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>$\text{N}_2$</td>
</tr>
<tr>
<td>Gas consumption (L/min)</td>
<td>1.8</td>
</tr>
<tr>
<td>Distance between substrate and nozzle (mm)</td>
<td>8</td>
</tr>
<tr>
<td>Pressure in aerosol chamber (kPa)</td>
<td>12.8</td>
</tr>
<tr>
<td>Pressure in deposition chamber (kPa)</td>
<td>0.060</td>
</tr>
<tr>
<td>Traverse speed (mm/s)</td>
<td>1.0</td>
</tr>
<tr>
<td>Number of traverse (times)</td>
<td>60</td>
</tr>
<tr>
<td>Traverse distance (mm)</td>
<td>10</td>
</tr>
</tbody>
</table>

Fig. 3.4 Size distributions of starting particles and particles ejected from nozzle.
3.2.2. Evaluation

The properties of the starting \( \text{Al}_2\text{O}_3 \) particles and the \( \text{Al}_2\text{O}_3 \) AD films were evaluated as follows.

The microstructures of the starting particles and the films were observed with SEM (S-4800, Hitachi High-Technologies Corporation). The thicknesses of the AD films were measured with a surface roughness measuring instrument (Surfcorder SE3300, Kosaka Laboratory Ltd.).

The crystal structures of the films and the particles were measured with XRD (MXP18VAHF, Bruker AXS K.K.) using Cu K\( \alpha \) radiation at 40 kV and 100 mA with a scanning step of 0.0200 deg and scanning speed of 5.00 deg/min. And the crystallite size was calculated by Scherrer’s equation as described in Section 2.2.3.

To evaluate the deformation behavior of the starting particles, the author focused on the fracture energy of the particles. The fracture energy of a particle was estimated using a force-displacement curve derived from a compression test of a particle (MCT-W500, Shimadzu Corporation). Fig. 3.5 schematically illustrates the compression test apparatus. A particle on the lower plate was compressed by the upper plate, which had a flat surface and was 20 \( \mu \text{m} \) in diameter. The test procedure was as follows. First, the particles were dispersed in acetone solvent, and this mixture was dropped on the lower plate. After the solvent evaporated, the particle to be evaluated was chosen with an optical microscope equipped with the system, and the lower plate was moved horizontally so that the particle was set under the upper plate. In this system, it was difficult to properly compress a particle of less than 2 \( \mu \text{m} \) in diameter because the flat surface of the upper plate was much larger than the particle and could touch the lower plate directly. Therefore, particles of more than 2 \( \mu \text{m} \) in diameter were chosen to be
evaluated. Next, a compressive force was loaded on such a particle. The force rate was 3.87 mN/sec, and the data was taken every 0.2 seconds. Finally, a force-displacement curve was derived from the compression test, and the fracture strength and the fracture energy of the particle were estimated using this force-displacement curve.

![Compression Test Apparatus](image)

**Fig. 3.5** Schematic illustration of compression test apparatus.

The deposition efficiency ($\eta$) was measured as follows. Before deposition, the weight of $\text{Al}_2\text{O}_3$ particles in the aerosol chamber ($W_{p0}$) was measured. After deposition, the weight of $\text{Al}_2\text{O}_3$ particles in the aerosol chamber ($W_{p1}$) was measured. The weight of $\text{Al}_2\text{O}_3$ AD film ($W_f$) was calculated from the thickness, deposition area, and density. The density used in this calculation was $3.7 \, \text{g/cm}^3$, which was 95% of the density of the bulk $\text{Al}_2\text{O}_3$ [5]. Then, the deposition efficiency was determined by Eq. 3.1.

$$
\eta = \frac{W_f}{W_{p0} - W_{p1}} \times 100
$$

*(Eq. 3.1)*

In this measurement of the deposition efficiency, the weight of the particles that remained in the apparatus, such as the inside of the tube connecting the aerosol chamber to the deposition chamber or the inside of the nozzle, is not taken into account.
evaluate the deposition efficiency. To evaluate the accuracy of this measurement, the weight of the particles that remained in the apparatus was measured by removing the tube and the nozzle and comparing the weight before and after deposition. As a result, it was confirmed that the weight was less than 0.5% of the weight change of the aerosol chamber after deposition. It meant that the more than 99.5% of the particles were successfully ejected from the nozzle to substrates. It was concluded that the deposition efficiency determined by this measurement included error by only 0.5% at most.

3.3. Results and discussion

3.3.1. Effect of ceramic particle type on deposition efficiency

Fig. 3.6 shows the deposition efficiency of sintered particles (S1, S2, and S3) and CVD ones (C1, C2, and C3). The error bars show the maximum and minimum values obtained by 3 experiments conducted under the same experimental condition. The average deposition efficiency of the sintered particles ranged from 0.067 to 0.088% and was much higher than that of the CVD particles, which ranged from 0.005 to 0.012%. Since the size distributions of S1 and C1 were almost same as shown in Fig. 3.1 and Fig. 3.2, it is thought that the difference in the deposition efficiency between S1 and C1 was mainly caused by the difference in particle properties, which can be ascribed to the process for producing particles. Furthermore, Fig. 3.6 shows that the deposition efficiency of the sintered particles was superior to that of the CVD particles even when the size distribution of the starting particles was changed. These results clearly suggest that the process for producing particles can affect the deposition efficiency more significantly than the size distribution of the starting particles and the difference in the deposition efficiency between the sintered particles and the CVD ones is mainly caused
by the process for producing them.

Fig. 3.6 Deposition efficiency of sintered particles (S1, S2, and S3) and CVD ones (C1, C2, and C3).

Fig. 3.7 shows the cross-sectional SEM image of the AD film using the sintered particles of S3. A dense and crack-free film with a thickness of about 30 μm was observed. The shape of the starting particle could not be seen in the microstructure. The deposition rate was 2.8 μm/min for a deposition area of 10 mm × 10 mm. This microstructure and deposition rate agreed well with those of Al₂O₃ AD films previously reported [8]. Fig. 3.8 shows a cross-sectional SEM image of the AD film using the CVD particles of C3. In contrast to when the sintered particles were used, the AD film did not grow over several μm, and the impacted particles seemed to be just implanted into the substrate.
Fig. 3.7 Cross-sectional SEM image of AD film using sintered particles of S3.

Fig. 3.8 Cross-sectional SEM image of AD film using CVD particles of C3.

The morphologies of the AD films were compared at higher magnification. Fig. 3.9 shows the cross-sectional SEM image of the interface between the AD film and the substrate. The roughness of the interface, which was defined as the distance between the bottom line and the top line of the interface as shown in Fig. 3.9, was 0.7 μm when the sintered particles were used. And, when the CVD particles were used, the roughness of the interface was 1.5 μm. Because the particle sizes of both S3 and C3 were around 3.57 μm, the morphologies suggest that deformed volume of the sintered particles was larger.
than that of the CVD particles. It is inferred from the morphologies that the difference in the process for producing particles resulted in that in the deformation behavior of the particles.

![AD film and substrate morphology](image)

Fig. 3.9 Morphology of interface between AD film and substrate.

(a) Sintered particle of S3. (b) CVD particle of C3.

To closely investigate the deformation of the particles, the crystallite sizes of starting particles, AD films, and scattered particles in the deposition chamber after the impact into a substrate were compared. The XRD patterns of them confirmed that the crystal structure of $\alpha$-$\text{Al}_2\text{O}_3$ was retained in the AD films and the scattered particles. The crystallite sizes in the followings were the average of crystallite sizes calculated using (012), (104), and (116) peaks of $\alpha$-$\text{Al}_2\text{O}_3$. In the case of the sintered particles of S3, the crystallite size of starting particles was 48 nm, and that of AD film was 13 nm. The reduction of crystallite size was observed as previously reported [1, 2, 7, 8]. This result indicates that the deposited sintered particles did deform during the impact and the deformation corresponded to 73% reduction of the crystallite size. In contrast, the crystallite size of the scattered particles was 40 nm. The crystallite size was reduced
about 17%, but much larger than that of the AD film. It suggests that the deformation of particles corresponding to 17% reduction of the crystallite size was insufficient to form dense AD films.

3.3.2. Fracture energy of ceramic particles

Because the author presumed that the difference in the deposition efficiency and the morphologies of AD films between sintered particles and CVD ones had something to do with the deformation behavior of the particles, the compression test of the particle was conducted to evaluate the fracture energy. Fig. 3.10 and Fig. 3.11 show the typical force-displacement curves of a sintered particle of S3 and a CVD particle of C3, respectively. When the force was lower than the critical value ($F_c$), the displacement increased nearly linearly as the force increased, indicating that the deformation was elastic. When the force reached $F_c$, the displacement abruptly increased, indicating that the particle was destroyed. The fracture strength and the fracture energy of the particle were estimated using these force-displacement curves.

![Force-displacement curve](image)

**Fig. 3.10** Force-displacement curve of sintered particle with diameter of 2.65 μm.
Fig. 3.11 Force-displacement curve of CVD particle with diameter of 3.39 μm.

The fracture strength ($S_t$) of the particle was estimated by applying the Hiramatsu method [16] as described in Eq. 3.2, where $F_c$ is the critical force mentioned above and $d$ is the particle diameter that was measured with an optical microscope before each compression test.

$$S_t = 2.8 \frac{F_c}{\pi d^2}$$  \hspace{1cm} (Eq. 3.2)

The specific fracture energy of the particle ($E_d$) was estimated using the accumulated elastic energy until the destruction of the particle as described in Eq. 3.3, where $F$ is the applied force, $x$ is the displacement, $x_c$ is the displacement when the critical force is applied, and $V$ is the particle volume. In this study, to take into account the effect of the particle size on the accumulated elastic energy, the elastic energy was normalized by the particle volume, which was approximated to that of a sphere as described in Eq. 3.4.
This compression test was conducted to a static particle, so the fracture energy of the particle determined by this test is not exactly coincident with the fracture energy under the actual deposition condition, in which particles move toward a substrate at 150 ~ 300 m/s [8]. However, the stress propagates in a particle at the sound velocity, which is over 9000 m/s in the case of Al₂O₃ [17], and it is much higher than the particle velocity. Therefore, the author thinks that considering the fracture energy of the particles determined by the compression test is reasonable to discuss the deposition mechanism.

Fig. 3.12 shows the fracture strength of the sintered particles of S3 and CVD particles of C3. The error bars show the maximum and minimum values among the data of 7 particles. The average fracture strength of the sintered particles was 752 MPa, and that of the CVD particles was 1935 MPa. The fracture strength of the sintered particles was about 39% of that of the CVD particles. Fig. 3.13 shows the specific fracture energy of the particles, which was derived from the same force-displacement curve. The error bars show the maximum and minimum values among the data of 7 particles. The average fracture energy of the sintered particles was $7.3 \times 10^7$ J/m³, which was about 32% of that of the CVD particle ($2.3 \times 10^8$ J/m³). These results show that both the fracture strength and the fracture energy of the particle depend on the process for producing the particle.
Fig. 3.12 Fracture strength of sintered particles of S3 and CVD particles of C3.

Fig. 3.13 Specific fracture energy of sintered particles of S3 and CVD particles of C3.
When a particle impacts on a substrate in the ADM, the fracture energy of the particle can be supplied by the kinetic energy of the particle. Assuming that the size, density, and impact velocity of these particles were the same, the kinetic energy of the particle after being ejected from the nozzle was also the same. The typical particle velocity of the ADM was reported to be $150 \sim 300 \text{ m/s}$ [8]. The specific kinetic energy of the particle was estimated by Eq. 3.5, where $E_k$ is the specific kinetic energy, $m$ is the mass, $v$ is the velocity, $V$ is the volume, and $\rho$ is the density.

$$E_k = \frac{mv^2}{2V} = \frac{\rho v^2}{2}$$

(Eq. 3.5)

The estimated specific kinetic energy of the particle ranged from $4.4 \times 10^7$ to $1.8 \times 10^8$ J/m$^3$. Comparing the specific fracture energy with this kinetic energy, it can be said that the fracture energy of the sintered particles was low enough to be sufficiently supplied by the kinetic energy and the particles could deform during impact. In contrast, in the case of the CVD particles, the fracture energy was higher than the kinetic energy, so the particle could not deform during the process.

It is thought that the deformation of the particle results in the formation of clean and activated surface around it. Generally, clean and activated surface has higher energy than stable surface and readily forms bonding between the activated surfaces. For example, it is known that activating surface by removing contaminates on surface using a fast atom beam in vacuum condition can be applied to bonding of metals, and semiconductors at room temperature [18, 19]. Furthermore, in the case of the ultrasonic welding between ceramics and metals, it has been suggested that clean surface appears by deformation during the process and plays an important role to the bonding between
ceramics and metals [20]. In the case of the ADM, there is a possibility that the sintered particles showed higher deposition efficiency because they could deform by their kinetic energy and readily form activated surface around them promoting the bonding between the ceramic particles. In contrast, the CVD particles couldn’t deform by their kinetic energy and the activated surface hardly appeared. As a result, the particles were just implanted into the substrate, and the film growth did not occur. Fig. 3.14 shows the difference in the deposition mechanism between the sintered particles and the CVD ones inferred from the results obtained in this study.

It is inferred that the fracture energy of the particle has something to do with the defects that could work as starting points of a fracture, such as cracks [21]. In the case of the sintered particles, it is assumed that these defects could be induced near the grain boundaries during the sintering process because of the anisotropy of the thermal expansion coefficient. It has been also reported that when Al₂O₃ specimens showed elastic deformation during shock loading, the failure was along the grain boundaries [22]. In contrast, the CVD particle was produced as a single crystal, so it is assumed that its microstructure was hardly affected by the anisotropy of the thermal expansion coefficient during the production process. As a result, the CVD process resulted in fewer defects inside the particle.

It was found that the fracture energy of the particle could be the crucial property to improve the deposition deficiency. This will be useful to establish the guidelines for designing ceramic particles for the ADM. However, the deposition efficiency using the sintered particles was about 0.10% at most. In the compression test of this study, the force was loaded until the particle was completely destroyed. However, this ideal loading condition might hardly ever occur in the actual impact of the particle in the
ADM because the gas flow or other surrounding particles interfere with the impact of the particle. There is a possibility that this interference limits the deposition efficiency to only 0.10%.

Fig. 3.14 Schematic illustration of difference in deposition mechanism.

(a) Sintered particles. (b) CVD particles.
3.4. Summary

To clarify the bonding mechanism between ceramic particles themselves, the effect of the process for producing Al2O3 particles on the deposition efficiency was investigated. The results and discussion are summarized as follows.

1. The average deposition efficiency of the sintered particles ranged from 0.067 to 0.088% and was much higher than that of the CVD particles, which ranged from 0.005 to 0.012%. The deposition efficiency of the sintered particles was superior to that of the CVD particles.

2. When the sintered particles were used, the AD films grew about 30 μm. In contrast, when the CVD particles were used, the AD films didn’t grow over several μm. The morphologies of the AD films suggested that the deformed volume of the sintered particles was larger than that of the CVD particles.

3. The average specific fracture energy of the sintered particles was $7.3 \times 10^7$ J/m$^3$, which was about 32% of that of the CVD particles ($2.3 \times 10^8$ J/m$^3$).

4. The typical kinetic energy of the particle was estimated to range from $4.4 \times 10^7$ to $1.8 \times 10^8$ J/m$^3$. Comparing the specific fracture energy with the kinetic energy, there is a possibility that the sintered particles showed higher deposition efficiency because they could deform by their kinetic energy and readily form activated surface around them promoting the bonding between the ceramic particles. In contrast, the CVD particles couldn’t deform by their kinetic energy and the activated surface hardly appeared. It is concluded that the specific fracture energy of the particle depends on the process for producing it and could be the crucial property to focus on to improve the deposition deficiency.
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Chapter 4. Relationship between impact velocity of ceramic particles and deposition efficiency

4.1. Introduction

ADM has recently been attracting attention as a new method for formation of ceramic films [1-3] because it can form dense ceramic films (AD films) directly on a substrate even at room temperature [4-6]. The most distinguishing feature of this method is that the process temperature can be room temperature. From the viewpoint of industrial application, the low process temperature is the most significant advantage of ADM.

To use ADM industrially, the bonding mechanism between ceramic particles themselves has to be clarified. Previous reports revealed some important characteristics regarding the bonding mechanism. A laminar structure of an AD film composed of mixture of Al$_2$O$_3$ and PZT was observed along the substrate in the cross-sectional TEM image, and the bonding was indicated to be caused by plastic deformation of ceramic particles during the process [7]. When using Al$_2$O$_3$ particles more than 1 μm in diameter, Al$_2$O$_3$ thick films were not grown and substrates were eroded [6]. It is inferred that the ability of a ceramic particle to deform plastically has something to do with its size as described in Section 1.1.2. Despite these efforts, the bonding mechanism between ceramic particles themselves has not been well understood, and not all the factors influencing the deposition efficiency have been clarified.

As a technology to form dense films by impacting solid particles on a substrate, cold spray has also been developed. Some metals (for example Cu, Al, and Ni) have been effectively formed by the process with the high deposition efficiency, which can reach over 70% [8, 9]. Furthermore, increasing the particle velocity effectively improves the
deposition efficiency in cold spray [10]. This might suggest the possibility that particle velocity significantly affect the bonding between particles themselves and the deposition efficiency in ADM as well, because both processes are common in impacting solid particles on a substrate. The critical particle velocity, which means the minimum particle velocity for deposition, exists in ADM and is estimated to be about 150 m/s [7]. However, the effect of the particle velocity exceeding the critical velocity on the deposition efficiency and the bonding between the particles in ADM has not been reported yet. The author presumed that increasing particle velocity could promote plastic deformation of the particles and result in improved deposition efficiency. Therefore, in this study, the relationship between the impact velocity of ceramic particles and the deposition efficiency was investigated.
4.2. Experimental procedure

4.2.1. Nozzle design

The used apparatus was the same as the one described in Chapter 2 and 3 except the nozzle. In experiments of Chapter 4, to increase the impact particle velocity, two different nozzles were compared as follows.

Eq. 4.1 shows acceleration of a particle in flow, where $U_p$ is particle velocity, $U_g$ is gas velocity, $\rho_p$ is particle density, $d_p$ is particle diameter, $\rho_g$ is gas density, and $C_D$ is drag coefficient of a particle [11]. Assuming that $C_D$, $d_p$, and $\rho_p$ are constant, gas density $\rho_g$ and gas velocity $U_g$ can affect the acceleration of particle. Gas density and gas velocity can be increased by increasing gas consumption and redesigning the nozzle, respectively.

$$
\frac{dU_p}{dt} = \frac{3\rho_g}{4\rho_p d_p} C_D |U_g - U_p| \left(U_g - U_p\right)
$$

(Eq. 4.1)

In this study, gas consumption ranged from 1.8 to 15 L/min. A converging nozzle and a Laval nozzle, which was fabricated to meet the deposition conditions of ADM, were prepared. Fig. 4.1 shows the difference in the nozzle shape between the converging nozzle and the Laval nozzle. The converging nozzle has a rectangle exit with dimensions of 10 mm $\times$ 0.4 mm, and its cross-sectional area gradually decreases and reaches a constant value as it proceeds to the nozzle exit. The reachable gas velocity is the velocity of sound because of choking. On the other hand, the Laval nozzle has a round throat with 3.7 mm in diameter and a round exit with 8.1 mm in diameter. Carrier gas can be accelerated over the velocity of sound after the throat. The Mach number at the exit is designed to be 3.1.
Fig. 4.1 Cross-sectional area of nozzle. (a) Converging nozzle. (b) Laval nozzle.
4.2.2. Materials and deposition condition

Commercially available \( \alpha \)-\( \text{Al}_2\text{O}_3 \) particles (AMS-5020F, Sumitomo Chemical Company, Ltd.) were used as starting particles. This type of \( \text{Al}_2\text{O}_3 \) particles showed the highest deposition efficiency in this study as described in Chapter 3. Fig. 4.2 and Fig. 4.3 show the morphology and the particle size distribution, respectively. D10, D50, and D90 were 0.73 \( \mu \text{m} \), 2.83 \( \mu \text{m} \), and 5.36 \( \mu \text{m} \), respectively. Before deposition, \( \text{Al}_2\text{O}_3 \) particles were heat-treated at 600 °C for 1 hour in air to eliminate moisture. Tough-pitch copper plates with dimensions of 50 mm \( \times \) 40 mm \( \times \) 3 mm were used as substrates. The plates were washed by ethanol and dried to eliminate organic impurities on the surface. Roughness (Ra) of substrates was 0.070 \( \mu \text{m} \). Carrier gas was \( \text{N}_2 \). Neither substrates nor carrier gas were heated.

Parameters used in experiments of Chapter 4 are summarized in Table 4.1. The distance from the nozzle exit to the substrate was 8 mm. The pressure in the aerosol chamber and the deposition chamber depended on the nozzle type and increased in proportion to the gas consumption. The traverse speed of the nozzle motion along the substrate was 1.0 mm/s, and the traverse was repeated 60 times with the traverse distance of 10 mm.
Fig. 4.2 Morphology of Al$_2$O$_3$ particles.

Fig. 4.3 Size distribution of Al$_2$O$_3$ particles.
Table 4.1 Experimental parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic powder</td>
<td>$\alpha$-Al$_2$O$_3$</td>
</tr>
<tr>
<td>Substrate</td>
<td>Cu</td>
</tr>
<tr>
<td>Substrate temperature ($^\circ$C)</td>
<td>22 (R.T.)</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>$N_2$</td>
</tr>
<tr>
<td>Gas consumption (L/min)</td>
<td>1.8 ~ 15.0</td>
</tr>
<tr>
<td>Nozzle type</td>
<td>Converging/Laval</td>
</tr>
<tr>
<td>Distance between substrate and nozzle (mm)</td>
<td>8</td>
</tr>
<tr>
<td>Pressure in aerosol chamber (kPa)</td>
<td>12.8 ~ 74.8 (Converging)</td>
</tr>
<tr>
<td></td>
<td>1.2 ~ 10.4 (Laval)</td>
</tr>
<tr>
<td>Pressure in deposition chamber (kPa)</td>
<td>0.060 ~ 0.360 (Converging)</td>
</tr>
<tr>
<td></td>
<td>0.044 ~ 0.210 (Laval)</td>
</tr>
<tr>
<td>Traverse speed (mm/s)</td>
<td>1.0</td>
</tr>
<tr>
<td>Number of traverse (times)</td>
<td>60</td>
</tr>
<tr>
<td>Traverse distance (mm)</td>
<td>10</td>
</tr>
</tbody>
</table>
4.2.3. Evaluation

The deposition efficiency was measured with the same way as the one described in Chapter 3. Before deposition, the weight of Al₂O₃ particles in the aerosol chamber was measured. After deposition, the weight of Al₂O₃ particles in the aerosol chamber was measured and the weight of Al₂O₃ AD film was calculated from the thickness, deposition area, and density. Then, the deposition efficiency was determined by Eq. 3.1.

The microstructure of AD films was observed by SEM (S-4800, Hitachi High-Technologies Corporation).

The thickness and hardness of AD film were measured by a surface roughness measuring instrument (Surfcorder SE3300, Kosaka Laboratory Ltd.) and a nano-indentation system (FisherscopeH100V, Fisher Instruments K.K.), respectively.

The impact particle velocity was evaluated as follows. In the case of cold spray, the measurement of the particle velocity is often conducted by particle imaging velocimetry (PIV) [10]. Although this method can directly measure the particle flow velocity, there is a possibility that the particle flow velocity can be different from the actual impact particle velocity due to bow shock near a substrate, which was mentioned to affect the impact particle velocity in the case of cold spray [8]. Therefore, in this study, the author employed another simple method that could evaluate impact particle velocity relatively using the shape of the substrate surface, which reflected the actually impacted particles. Fig. 4.4 shows cross-sectional SEM images of substrates before and after deposition. Before deposition, the substrate surface is almost flat. On the other hand, after deposition, the AD film is formed on the substrate and the substrate surface becomes rough because of the impact of the particles. In the cavitation erosion field, the increment percentage of the surface area (ΔS) damaged by cavitation, which is
measured from the surface profile data, is a good index for the intensity of the cavitation impact [13]. In the case of ADM, $\Delta S$, which means the increment percentage of the substrate surface after deposition, is assumed to reflect the intensity of the particle impact and increases as the impact particle velocity increases. In this study, relative difference in impact particle velocity was evaluated by $\Delta S$.

Fig. 4.4 Typical cross-sectional SEM images of substrate surface.

(a) Before deposition. (b) After deposition.
$\Delta S$ was determined as follows. Fig. 4.5 schematically illustrates the interface between an AD film and a Cu substrate. It was divided vertically at 0.7 $\mu$m pitch (indicated by dash lines in Fig. 4.5), and every intersection of the dash lines and the Cu surface was connected (indicated by solid lines in Fig. 4.5). The total length of the solid lines was measured and defined as $L_1$. In the same way, the length of the Cu surface before deposition was measured and defined as $L_0$. Then, $\Delta S$ was determined by Eq. 4.2.

$$
\Delta S = \frac{L_1^2 - L_0^2}{L_0^2} \times 100
$$

(Eq. 4.2)

Fig. 4.5 Schematic illustration of interface between AD film and substrate.
4.3. Results and discussion

4.3.1. Effect of nozzle type on impact particle velocity

Fig. 4.6 shows the cross-sectional SEM images under the condition of gas consumption ranging from 1.8 to 15 L/min. The interface between the AD film and the substrate became rougher as the gas consumption increased. Fig. 4.7 shows the effect of the gas consumption on $\Delta S$. $\Delta S$ increased as the gas consumption increased. It is thought that the impact particle velocity increased as the gas consumption increased regardless of the nozzle type. $\Delta S$ were measured at 3 points per specimen, and the maximum and minimum values are shown as error bars in Fig. 4.7. Since the acceleration of the particle also depends on the particle size as described in Eq. 4.1, it is inferred that the error bars of $\Delta S$ reflect the distribution of the impact particle velocity ascribed to that of the particle size.

Fig. 4.8 shows the SEM images of the substrate surface before deposition and after 1 traverse using the converging nozzle with the gas consumption of 1.8 L/min and the particle consumption of 0.18 g. It is clear that the AD film could be formed by only 1 traverse. This result indicates that there was no incubation time for film formation, which was reported to exist to eliminate inactive native oxide film on a substrate in low-pressure cold-spray deposition [14], under this experimental condition of ADM. Even when increasing the traverse speed to 5 mm/s (the maximum value of the apparatus), no incubation time was observed. It indicates that $\Delta S$ was determined by the impact of the particles during a few initial traverses. Fig. 4.9 shows the cross-sectional SEM image of the film after 3 traverses using the converging nozzle with the gas consumption of 1.8 L/min. $\Delta S$ was 6.58 and this value agrees well with 5.20 ~ 8.51, which was the $\Delta S$ values after 60 traverses as shown in Fig. 4.7.
Fig. 4.6 Cross-sectional SEM images of interface between AD film and substrate.

(a) Converting nozzle, gas consumption: 1.8 L/min. (b) Converting nozzle, 5.0 L/min.
(c) Converting nozzle, 10.0 L/min. (d) Converting nozzle, 15.0 L/min.
(e) Laval nozzle, 2.0 L/min. (f) Laval nozzle, 4.0 L/min.
(g) Laval nozzle, 8.0 L/min. (h) Laval nozzle, 13.0 L/min.

Fig. 4.7 Relationship between gas consumption and $\Delta S$.

---

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Fig. 4.8 SEM images of substrate surface. (a) Before deposition. (b) After 1 traverse using the converging nozzle with gas consumption of 1.8 L/min.

Fig. 4.9 Cross-sectional SEM image of AD film after 3 traverses using the converging nozzle with gas consumption of 1.8 L/min.
Fig. 4.7 shows that \( \Delta S \) when using the converging nozzle was larger than that when using the Laval nozzle. However, it is difficult to be concluded that the actual impact particle velocity are equivalent simply when the \( \Delta S \) values of both nozzles are equivalent. More evidences are needed, such as direct measurement of particle velocity or gas dynamics calculation, to find if the Laval nozzle is effective to increase the particle velocity in ADM or not. In the following section, the dependence of the deposition efficiency on the impact particle velocity is discussed using \( \Delta S \).

4.3.2. Effect of impact particle velocity on deposition efficiency

Fig. 4.10 shows the relationship between the deposition efficiency and \( \Delta S \). In all \( \Delta S \) ranges, the AD films were formed on the substrates. This means that the particle velocity under all conditions in this experiment exceeded the critical velocity, 150 m/s. Remarkably, the deposition efficiency showed different trends depending on \( \Delta S \).

When \( \Delta S \) was lower than 10\%, the deposition efficiency increased from 0.082 to 0.104\% as \( \Delta S \) increased from 3.46 to 9.25\%. This result indicates that increasing impact particle velocity can promote the bonding between the particles themselves to some extent unless \( \Delta S \) does not exceed 10\%. However, the deposition efficiency was 0.104\% at most and still much lower than that of cold spray [10]. Fig. 4.11 shows the cross-sectional SEM image of the AD film deposited under the condition of \( \Delta S = 6.98\% \) using the converging nozzle. The weight change of the aerosol chamber and the weight of the film were 10.70 g and \( 1.05 \times 10^{-2} \) g, respectively. The dense and crack-free film was observed. The hardness of this film was 890 Hv. The deposition rate was 2.8 \( \mu \)m/min for a deposition area of 10 mm \( \times \) 10 mm. These properties of the \( \text{Al}_2\text{O}_3 \) AD film and the deposition rate agreed well with those of \( \text{Al}_2\text{O}_3 \) AD films previously reported [7,
On the other hand, when $\Delta S$ was higher than 10%, the deposition efficiency decreased to about 0.02% as $\Delta S$ increased to about 40%. In this region, the erosion of the film was observed. Fig. 4.12 shows the cross-sectional SEM image of the AD film deposited under the condition of $\Delta S = 30.6\%$ using the Laval nozzle. The weight change of the aerosol chamber and the weight of the film were 4.46 g and $2.17 \times 10^{-3}$ g, respectively. The AD film was eroded, and cracks parallel to the film surface were propagated. These cracks seemed to cause the removal of some parts of the film. This result indicates that the particles with excessive impact velocity contribute to the erosion of the AD film rather than the bonding between the particles themselves. Fig. 4.10 also shows that the deposition efficiency of the Laval nozzle was higher than that of the converging nozzle when $\Delta S$ was higher than 10%. It means that the nozzle type did influence the impact particle velocity and the deposition behavior. It is inferred that the effect of the nozzle type on the particle velocity will be prominent if direct measurement of the particle velocity or gas dynamics calculation is conducted in this $\Delta S$ region.

![Fig. 4.10 Relationship between $\Delta S$ and deposition efficiency.](image-url)
In the case of forming Al₂O₃ films by ADM, increasing impact velocity of Al₂O₃ particles was found to promote the bonding between the particles themselves unless ΔS was lower than 10%. On the other hand, when ΔS was higher than 10%, increasing impact velocity of Al₂O₃ particles resulted in the film erosion and the deposition efficiency decreased. There is a possibility that this tendency of the deposition efficiency toward the impact particle velocity is common among the methods for forming ceramic films by impacting solid ceramic particles. For example, in the case of
forming ceramic films by Powder Jet Deposition (PJD) [16], which is a technique to form ceramic films by impacting solid ceramic particles on a substrate at the atmospheric pressure, it was reported that the excessive particle velocity decreased the deposited thickness of films and lower particle velocity was better for the deposition [17]. There seems to be the erosion velocity of particle, which means the minimum particle velocity that causes the erosion of films or substrates [9], in the case of forming ceramic films by impacting solid ceramic particles as well. Moreover, the erosion velocity of ADM seems to be much lower than that of forming metal films by cold spray. Fig. 4.13 shows the relationship between the gas consumption and the particle flow velocity using the converging nozzle at the 8 mm distance from the nozzle exit. The particle flow velocities were measured by PIV (PIV System, Seika Corporation). As the gas consumption increased, the particle flow velocity increased. When the gas consumption was 5.0 L/min, the particle flow velocity was 200.3 m/s. Under the same condition, ∆S was 19.7% as shown in Fig. 4.7 and the erosion of the film occurred. It shows that the erosion velocity was approximately 200 m/s. These results suggest that the process window for forming ceramic films by impacting solid ceramic particles such as ADM and PJD is quite narrow in comparison with that for forming metal films by cold spray, in which metal films can be successfully formed in the wide range of the particle flow velocity ranging about 300 to over 800 m/s [8, 10].

Since it is thought that the plastic deformation of ceramic particles plays an important role for film formation in ADM [7], the author think that investigating how the deformation behavior of the ceramic particle changes depending on loading conditions, impact particle velocity in other words, will provide important information to consider the common mechanism among ADM and PJD. Judging from the data in this study, the
deformation behavior of the ceramic particles might change at the loading condition that corresponds to $\Delta S = 10\%$. If this phenomenon is observed, the meaning of $\Delta S = 10\%$ will be clear.

Fig. 4.13 Relationship between the gas consumption and the particle flow velocity using the converging nozzle.
4.4. Summary

To clarify the bonding mechanism between ceramic particles themselves, the effect of the impact velocity of Al$_2$O$_3$ particles on the deposition efficiency was investigated. In this study, the relative difference in the impact particle velocity was evaluated by the increment percentage of the substrate surface area after deposition ($\Delta S$). It is thought that the increase of $\Delta S$ means the increase of the impact particle velocity. The results and discussion are summarized as follows.

1. $\Delta S$ increased as the gas consumption increased. It is thought that the impact particle velocity increased as the gas consumption increased. There was no incubation time for film formation, and $\Delta S$ was determined by the impact of the particles during a few initial traverses.

2. When $\Delta S$ was lower than 10%, the deposition efficiency increased from 0.082 to 0.104% as $\Delta S$ increased from 3.46 to 9.25%. This result indicates that increasing impact particle velocity can promote the bonding between the particles themselves. When $\Delta S$ was higher than 10%, the erosion of the film was observed and the deposition efficiency decreased to about 0.02% as $\Delta S$ increased to about 40%. SEM observation revealed that cracks parallel to the film surface were propagated. This result indicates that the particles with excessive impact velocity contribute to the erosion of the AD film rather than the bonding between the particles themselves.

3. There is a possibility that this tendency of the deposition efficiency toward the impact particle velocity is common among the methods for forming ceramic films by impacting solid ceramic particles such as ADM and PJD.
References


[8] K. Sakaki, Overview of cold spray technology and cold sprayed light metals coatings,


Chapter 5. Relationship between substrate temperature and deposition efficiency

5.1. Introduction

Principal characteristics of ADM are particle diameter of starting powder, which is around 1 μm or sub-micrometer, and the low process temperature. These characteristics are completely different from those of thermal spray, which is utilized as ceramic deposition method in a wide variety of industry. In the case of thermal spray, particle diameter of starting powder is around several 10 μm and starting particles are heated over the melting point during the process.

The reason why fine particles are suitable for ADM is thought to be the deformation behavior of fine particles as described in Section 1.1.2. Interestingly, it was reported that a fine ceramic particle whose diameter was lower than about 1 μm could show plastic deformation like a metal particle during fracture process [1, 2]. The deformation behavior corresponds to the laminar structure of an AD film composed of a mixture of Al₂O₃ and PZT [3]. And the deformation of ceramic particles during the impact seems to be greatly important in ADM, because it is thought that the deformation results in the formation of clean and activated surface which promotes the bonding between the ceramic particles as shown in Chapter 3. Fine particles suitable for ADM can readily change their surface properties by preparation conditions. And the surface properties can influence the deposition results. For example, it is known that pre-process such as dry-milling or heat treatment of starting particles can influence the density, the deposition rate, and the electrical properties of ceramic films formed by ADM [1, 4]. In addition, the process for producing particles and the impact particle velocity can affect
the deposition results as discussed in Chapter 3 and 4.

In this chapter, the other principal characteristic of ADM, the process temperature, especially the substrate temperature is featured. Previously, it was reported that the hardness and the density of Al₂O₃ films decreased with increasing substrate temperature [5]. This result suggests that the substrate temperature can affect the deposition behavior. However, the effect of heating the substrate on the deposition efficiency has not been investigated, and the deposition mechanism has not been discussed in terms of the process temperature. It is important to investigate the relationship between the substrate temperature and the deposition efficiency in order to clarify the deposition mechanism of ADM.

5.2. Experimental procedure
5.2.1. Materials and deposition condition

Commercially available α-Al₂O₃ particles (AMS-5020F, Sumitomo Chemical Company, Ltd.) was used as starting particles. This Al₂O₃ particles showed the highest deposition efficiency in this study as described in Chapter 3. The morphology of the particles and the size distribution have already been shown in Fig. 4.2 and Fig. 4.3 in Chapter 4, respectively. The purity of the Al₂O₃ particles was 99.6%. Before deposition, Al₂O₃ powder was heat-treated at 600 °C for 1 hour in air to eliminate moisture. Tough-pitch copper plates with dimensions of 50 mm × 40 mm × 3 mm were used as substrates. The plates were washed by ethanol and dried to eliminate organic impurities on the surface. The used ADM apparatus was the same as the one described in Chapter 2, 3, and 4. The nozzle had a 10 mm × 0.4 mm rectangular exit. To control substrate temperature, a heater embedded in the X-Y stage was used. Substrate temperature was
measured with a thermocouple set on a substrate surface. The parameters used in the experiments of the chapter 5 are summarized in Table 5.1.

Table 5.1 Experimental parameters.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td>Ceramic particle</td>
<td>( \alpha-\text{Al}_2\text{O}_3 )</td>
</tr>
<tr>
<td>Substrate</td>
<td>Cu</td>
</tr>
<tr>
<td>Substrate temperature ( (^\circ\text{C}) )</td>
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<tr>
<td>Carrier gas</td>
<td>( \text{N}_2 )</td>
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<td>Gas consumption (L/min)</td>
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<td>Pressure in aerosol chamber (kPa)</td>
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<td>Pressure in deposition chamber (kPa)</td>
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<td>Traverse speed (mm/min)</td>
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<td>Traverse distance (mm)</td>
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</table>

5.2.2. Evaluation

The deposition efficiency was measured with the same way as the one described in Chapter 3 and 4. Before deposition, the weight of Al\(_2\)O\(_3\) particles in the aerosol chamber was measured. After deposition, the weight of Al\(_2\)O\(_3\) particles in the aerosol chamber was measured and the weight of Al\(_2\)O\(_3\) AD film was calculated from the thickness, deposition area, and density. Then, the deposition efficiency was determined by Eq. 3.1.

The crystal structures of the AD films and the starting particles were confirmed by XRD (MXP18VAHF, Bruker AXS K.K.) using Cu K\(\alpha\) radiation at 40 kV and 100 mA with a scanning step of 0.0200 deg and scanning speed of 5.00 deg/min.

The elements contained in Al\(_2\)O\(_3\) AD films were analyzed with secondary ion mass
Cs ions were used as primary ions, and the accelerated voltage was set to 5.0 kV. Before analysis, the film surface was etched about 500 nm in depth with an area of $39 \, \mu m \times 39 \, \mu m$ by ion sputtering to avoid noise from impurities adsorbed on the film. The analysis was conducted along the depth direction of about 3 $\mu m$. To evaluate H amount in Al$_2$O$_3$ AD films quantitatively, the relative sensitivity coefficient of H was calculated by analyzing both the Al$_2$O$_3$ film and a standard Al$_2$O$_3$ sample at the same day under the same condition. The accuracy of this analysis was estimated to be $\pm 40\%$.

The volume resistivity of Al$_2$O$_3$ AD films was measured with the digital ultra-high resistance/micro current meter (R8340A, ADVANTEST CORPORATION). Before measurement, a circular electrode of 15 mm in a diameter was formed on a film surface by applying Ag paste. To calculate the volume resistivity, leak current was measured after applying DC 100 V for 1 minute between the electrode and a substrate.

The desorbed gas of starting Al$_2$O$_3$ particles was analyzed with thermal desorption spectroscopy (TDS) (WA1000S, ESCO). The sample was heated from 60 to 500 $^\circ$C at a rate of 20 $^\circ$C/min during the analysis.
5.3. Results and discussion

5.3.1. Effect of substrate temperature on deposition efficiency

Fig. 5.1 shows the relationship between the deposition efficiency and the substrate temperature during the deposition ($T_S$). The deposition efficiency nearly doubled from 0.05 to 0.11% as $T_S$ increased from 22 to 78 °C. In contrast, the deposition efficiency did not increase significantly when $T_S$ was over 90 °C, and the film partially pealed when $T_S$ was over 160 °C. In the previous report, the partial peal of Al$_2$O$_3$ films was observed as the substrate temperature increased [5]. Fig. 5.2 shows the cross-sectional SEM images of the Al$_2$O$_3$ films with the different $T_S$ ($T_S$=22, 142 °C). In the both cases, the dense and void-free structure was observed. It was found that heating the substrate during the deposition had no effect on the film density.

![Graph showing relationship between deposition efficiency and substrate temperature](image)

Fig. 5.1 Relationship between deposition efficiency and substrate temperature ($T_S$).
To consider the reason why the deposition efficiency nearly doubled as $T_S$ increased from 22 to 78 °C and did not increase significantly when $T_S$ was over about 90 °C, it is necessary to take the thermophoresis effect [6] caused by the temperature difference between the substrate and the carrier gas into account. When this effect works strongly, it is expected that the impact particle velocity perpendicular to the substrate surface deceases and the change of the impact particle velocity influences the deposition efficiency. According to the previous report [5], when $T_S$ was 25 °C, 100 °C and 300 °C,
the crystallite size of the film was 11.1 nm, 12.4 nm and 37.0 nm, respectively. The crystallite size when $T_S$ was 100 °C was nearly one-third of that when $T_S$ was 300 °C, and almost equivalent to that when was 25 °C. Considering that dense films were able to be formed when $T_S$ was 100 °C, it is suggested that the impact particle velocity when $T_S$ was 100 °C was also equivalent to that when $T_S$ was 25 °C and high enough to deform particles during the impact and promote strong bonding between the particles. Although experimental conditions of this study were different from those of the previous report [5] in the carrier gas (N$_2$ in this study, He in the previous report) and the distance between a substrate and a nozzle (8 mm in this study, 10 mm in the previous report), the result of this study that dense films were obtained when $T_S$ was around 100 °C was consistent with that of the previous report. Therefore, it is thought that when $T_S$ was around 100 °C the thermophoresis effect was negligibly small and could not influence the deposition efficiency.

As a result of the above discussion, the author assumed the reason why the deposition efficiency nearly doubled as $T_S$ increased from 22 to 78 °C and did not increase significantly when $T_S$ was over about 90 °C as follows. The effective $T_S$ for improving the deposition efficiency was too low to activate atomic diffusion or chemical reactions. A possibility was suggested that the deformation of starting ceramic particles results in the formation of new and activated surface which promotes the bonding between the ceramic particles in the previous report [7]. Therefore, the author presumed that impurities such as organic matter and H$_2$O remained on the starting particles or substrates could deactivate the clean surface generated by the deformation of the particles and hinder the deposition. Removing the impurities by heating substrates might help to promote the deposition and improve the deposition efficiency. To verify
this hypothesis, the following experiments were conducted.

5.3.2. Impurities contained in ceramic films

To confirm whether Al₂O₃ films formed by ADM contained impurities such as organic matter and H₂O, H content of films was measured with SIMS. To compare the H content of films with that of Al₂O₃ formed by another method, an Al₂O₃ sintered body (AO943, KYOCERA Corporation) was also analyzed under the same conditions. Fig. 5.3 shows the H contents of Al₂O₃ films formed with different Ts and the Al₂O₃ sintered body. The H contents of Al₂O₃ films formed by ADM ranged from 4.5×10²¹ to 7.0×10²¹ atoms/cm³. The contents were larger by 2 orders of magnitude than that of the Al₂O₃ sintered body, which was only 7.0×10¹⁹ atoms/cm³. Furthermore, the H content of the Al₂O₃ film tended to decrease by heating the substrate during the deposition. These results suggest that films formed by ADM could be contaminated by impurities that contained H and the contents of them could be reduced by heating substrates during the deposition.

![Fig. 5.3 H content of Al₂O₃ films with different Ts and Al₂O₃ sintered body.](image-url)
Fig. 5.4 shows the relationship between the H content and the depth from the film surface with different $T_S$. It was found that the H content was almost constant along the depth direction. It suggests that impurities constantly contaminated the films during the deposition. Considering the constant supplied materials during the deposition, the carrier gas and the starting particles were thought to be principal sources of impurities.

![Graph showing H content vs depth for different $T_S$.]

Fig. 5.4 Relationship between H content and depth from film surface with different $T_S$.

5.3.3. Change of film property by impurities

It is thought that the H content can influence the properties of the films. Fig. 5.5 shows the temperature dependence of the volume resistivity of Al$_2$O$_3$ films formed with different $T_S$. Throughout the entire temperature range, the volume resistivity increased by heating the substrate during the deposition. It means that conductive impurities were reduced by heating the substrate during the deposition. Therefore, H$_2$O was thought to be a principal impurity that contained H discussed in the section 5.3.2.
The volume resistivity measured in this study was $10^9 \, \Omega \cdot m$ at 30 °C. In contrast, in the previous report, the volume resistivity of the Al$_2$O$_3$ films formed by ADM was $10^{13} \, \Omega \cdot m$ [1]. The reason of this difference in the volume resistivity is discussed as follows.

The Al$_2$O$_3$ films formed in this study had the crystal structure of $\alpha$-Al$_2$O$_3$ as shown in Fig. 5.6. In addition, they were dense, and void-free as shown in Fig. 5.2. These characteristics were consistent with those reported previously [8]. Then, the author assumed that the purity of the starting Al$_2$O$_3$ particles caused the difference in the volume resistivity. The purity of the starting particles in this study was 99.6% and they contained Na and others as impurities. On the other hand, the purity of the starting particles in the previous report was 99.98% [8]. It is known that the volume resistivity of Al$_2$O$_3$ decreases by 3 or 4 orders of magnitude by adding Na lower than 1 wt% as an impurity [9]. To clarify the effect of the purity of the starting particles on the deposition, the effect of heating substrates during the deposition on the deposition efficiency and the volume resistivity was again investigated using $\alpha$-Al$_2$O$_3$ particles with the purity of
99.9% (AL-160SG-3, Showa Denko K.K.). The average particle diameter was 0.52 μm. Fig. 5.7 shows the relationship between the deposition efficiency and $T_s$. Fig. 5.8 shows the temperature dependence of volume resistivity of Al₂O₃ films with different $T_s$. The phenomenon that the deposition efficiency and the volume resistivity were able to be increased by heating substrates during the deposition was observed regardless of the purity of the starting particles. However, the volume resistivity at 30 °C was $10^{10} \, \Omega \cdot m$, which was still lower than that in the previous report [1]. Consequently, it is inferred that one of the reasons that caused the difference in the volume resistivity was the difference in the measurement conditions or the oxygen deficit quantity of the films [10].

Fig. 5.6 X-ray diffraction pattern of Al₂O₃ film formed on Cu substrate ($T_s = 22$ °C).
Fig. 5.7 Relationship between deposition efficiency and $T_S$ using Al$_2$O$_3$ particles with purity of over 99.9%.

Fig. 5.8 Temperature dependence of volume resistivity of Al$_2$O$_3$ film with different $T_S$ using Al$_2$O$_3$ particles with purity of over 99.9%.
5.3.4. Impurities in carrier gas

There is a possibility that H$_2$O in Al$_2$O$_3$ films was supplied from the carrier gas or the starting particles during the deposition. In this subsection, the H$_2$O content in the carrier gas was estimated and compared with that in Al$_2$O$_3$ films.

The carrier gas used in this study was supplied from a cold evaporator, and the dew point of the gas was thought to be about -77 ºC. For example, the saturated steam pressure at -70 ºC can be estimated to be 4.92 $\times$ 10$^{-3}$ mb, 0.492 Pa i.e., using the experimentally improved Goff Gratch’s equation [11]. The H$_2$O content can be converted to 2.92 $\times$ 10$^{-4}$ mol/m$^3$ using the ideal gas law. The deposition time and the gas consumption under the condition shown in Table 5.1 were 10.67 min and 4.0 L/min, respectively. It means that the total amount of the consumed gas was 4.3 $\times$ 10$^{-4}$ m$^3$. The H$_2$O amount that the carrier gas carried during the deposition can be calculated as 1.3 $\times$ 10$^7$ ($= 2.92 \times 10^{-4} \times 4.3 \times 10^{-4}$) mol. Meanwhile, the standard particle consumption under the condition shown in Table 5.1 was 35 g. Weight of a film that formed using 35 g particles was 3.5 $\times$ 10$^{-2}$ g, assuming that the deposition efficiency was 0.10% as shown in Fig. 5.1. And the volume was 9.5$\times$10$^{-3}$ cm$^3$, assuming that the film density was 3.7 $\times$ 10$^3$ kg/m$^3$. As a result, the number of H atoms contained in a film can be estimated to be 1.6 $\times$ 10$^{19}$ ($= 1.3 \times 10^{-7} \times 6.02 \times 10^{23} \times 2/(9.5 \times 10^{-3}$), where 6.02 $\times$ 10$^{23}$ is the Avogadro’s number) atoms/cm$^3$, assuming that a film contained all H$_2$O supplied from the carrier gas. This H content is lower by 2 orders of magnitude than that measured with SIMS. Therefore, it is not quantitatively reasonable to explain that the H$_2$O in the film was ascribed to the H$_2$O in the carrier gas only.
5.3.5. Impurities on ceramic particle surface

As a result of the discussion in the section 5.3.4, there is a possibility that H₂O in Al₂O₃ films was mainly supplied from the starting particles during the deposition. In this subsection, to judge whether the amount of H₂O remained on the starting particles was quantitatively reasonable, desorbed gas of the starting particles was analyzed with TDS.

Fig. 5.9 shows the TDS profiles of the starting Al₂O₃ particles, which had been heat-treated at 600 °C for 1 hour as described in the section 5.2.2 before the analysis. The gas with the molecular weight of 18 (H₂O) was detected at around 100 °C. On the other hand, the gas with the molecular weight of 44 (CO₂), which was expected to be generated by combustion of the organic matter, was not detected. These results indicate that H₂O remained on the surface of the starting Al₂O₃ particles. H₂O could desorb at temperature lower than 100 °C as shown in Fig. 5.9, because TDS was conducted at vacuum atmosphere. Likewise, the boiling point of H₂O in the deposition chamber, which was vacuumed by a rotary pump and a mechanical booster pump during the deposition, was thought to be lower than 100 °C. The fact that the effective Tₛ for improving the deposition efficiency was around 80 °C had something to do with the pressure in the deposition chamber.
The H$_2$O amount desorbed from the starting particles was compared with the H$_2$O content in Al$_2$O$_3$ films. The TDS analysis revealed that the desorbed H$_2$O weight was $1.4 \times 10^{-2}$% of the particle weight. It means that the number of H atoms contained in 1.0 g particles was $9.4 \times 10^{18}$ ($= 1.4 \times 10^4 \times 2 \times 6.02 \times 10^{23}/18$, where $6.02 \times 10^{23}$ is the Avogadro's number, and 18 is the molecular weight of H$_2$O) atoms. Weight of a film that formed from 1.0 g particles was $1.0 \times 10^{-3}$ g, assuming that the deposition efficiency was 0.10% as shown in Fig. 5.1. And the volume was $2.7 \times 10^{-4}$ cm$^3$, assuming that the film density was $3.7 \times 10^3$ kg/m$^3$. As a result, the number of H atoms contained in a film can be estimated at $3.5 \times 10^{22}$ ($= 9.4 \times 10^{18}/(2.7 \times 10^{-4})$) atoms/cm$^3$, assuming that a film contained all H$_2$O supplied from the starting particles. This H content is the same order of magnitude as that measured with SIMS. Therefore, it is quantitatively reasonable to explain that the H$_2$O in the film was ascribed to the H$_2$O remained on the starting particles.
Starting particles suitable for ADM is thought to be fine enough to readily absorb moisture during the preparation for the deposition. Considering that the heat-treatment was conducted in the air and the conveyance of the heat-treated starting particles to the aerosol chamber was also conducted in the air, there is a possibility that H₂O was re-absorbed on the starting particles after the heat-treatment of the particles.

Considering the experimental results and the discussion in this section, it can be concluded that H₂O on the starting particles deteriorated the deposition efficiency and contaminate the film during the deposition. Although the most significant advantage of ADM is the low process temperature, it has been found that much attention has to be paid regarding the H₂O contamination. However, this suggests that developing a novel process which can prevent H₂O from contaminating the films can improve the deposition efficiency of the ADM.
5.4. Summary

To clarify the bonding mechanism between ceramic particles themselves, the relationship between the substrate temperature and the deposition efficiency was investigated. The results and discussion are summarized as follows.

1. The deposition efficiency nearly doubled from 0.05 to 0.11% as the substrate temperature during the deposition increased from 22 to 78 °C. In contrast, the deposition efficiency did not increase significantly when $T_S$ was over 90 °C.

2. The H content of the Al$_2$O$_3$ film formed by ADM was larger by 2 orders of magnitude than that of an Al$_2$O$_3$ sintered body. By heating the substrate during the deposition, the H content of the Al$_2$O$_3$ film tended to decrease, and the volume resistivity of the Al$_2$O$_3$ film increased. These results indicate that Al$_2$O$_3$ films formed by ADM contained H$_2$O as an impurity.

3. In ADM, H$_2$O on the starting particles could deteriorate the deposition efficiency and contaminate the film during the deposition. This suggests that developing a novel process which can prevent H$_2$O from contaminating the films can improve the deposition efficiency of the ADM.
References


Chapter 6. Conclusion

The objective of this study is to clarify the mechanism of ceramic deposition by ADM, more explicitly, to clarify the bonding mechanism between the ceramic film and the metal substrate and between the ceramic particles themselves.

To clarify the bonding mechanism between the ceramic films and the metal substrates, TEM observation and EELS analysis of the interface between Al₂O₃ films and Cu substrates were conducted. TEM observation revealed that the Al₂O₃ film was directly adhered to the Cu substrate without any void or crack. Moreover, it was found that the Al₂O₃ film retained α-Al₂O₃ crystal structure at the Al₂O₃/Cu interface without any interfacial layer. The EELS spectra near O-K edge obtained at the Al₂O₃/Cu interface had a pre-peak feature at around 528 eV suggesting interactions between Cu and O. The Cu-O interactions mean that the O-terminated interface was formed at the edge of the Al₂O₃ film. In the case of the O-terminated interface, it is known that both the ionic bonding and the covalent bonding can be formed at the Al₂O₃/Cu interface. It is inferred that not only the anchoring effect but also the ionic bonding and covalent bonding that originates from the Cu-O interactions contribute to the bonding between Al₂O₃ films and Cu substrates.

To clarify the bonding mechanism between ceramic particles themselves, the dependency of the deposition efficiency on various deposition conditions was systematically investigated. As the deposition conditions, the process for producing Al₂O₃ particles, the impact velocity of Al₂O₃ particles, and the substrate temperature during the deposition were focused in this study. By comparing the sintered Al₂O₃ particles with the CVD Al₂O₃ particles, it was found that the specific fracture energy of the particle depended on the process for producing it. When the specific fracture energy
was lower than the kinetic energy of the particle, the particle readily deformed and the ceramic film successfully grew. Furthermore, it was found that the deposition efficiency improved as the impact particle velocity increased, although the excessive particle velocity could cause the erosion of the film. These results suggest that the bonding between the ceramic particles is based on the formation of clean and activated surface by the deformation of the particles during the impact. The surface generally has higher energy than stable surface and readily forms bonding between the activated surfaces. The fact that increasing the substrate temperature during the deposition improved the deposition efficiency and reduced the H$_2$O content of the film also supports the bonding mechanism, because it is thought that impurities such as H$_2$O could deactivate the clean surface generated by the deformation of the particles and hinder the deposition.

The author has succeeded in clarifying the mechanism of ceramic deposition by ADM through the investigation of the bonding between the ceramic film and the metal substrate and the understanding of the effect of various deposition conditions on the bonding between the ceramic particles themselves. The results obtained in this study will ultimately lead to cost reduction of ADM by increasing the deposition efficiency, which is necessary to use ADM industrially in the near future.
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List of publications


