Deposition behavior of glass thick film formation on substrates with different hardness by aerosol deposition

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ABSTRACT
Films fabricated by aerosol deposition (AD) can be coated through interactions between the particles and substrate. Accelerated particles collide with the substrate, generating impact energy at the contact point. These interactions depend on the hardness of the substrate. This study examined the effects of the hardness of the substrate on the deposition behavior of thick glass films by AD. Substrates with different hardness, Al₂O₃ glass, and STS304, were used, and the film formation behavior was observed. The coating thickness of the initial layer was inversely proportional to the hardness of the substrate. The STS304 substrate exhibited a phase transition after the coating process that was induced by the strong impact energy. The film formation mechanism depending on the substrate hardness was proposed based on the microstructure of the interface between the film and substrate.

1. Introduction
Glass coating layers are used widely across many fields, such as the semiconductor and display industries, using high-density plasma and biomaterials for dental implants and bones. The thickness of the coating layer ranges from 2 μm to 250 μm depending on the application [1–6]. On the other hand, the coating process has been limited to certain substrates due to mismatch of the thermal expansion coefficients between the substrates and materials. Therefore, new technologies are needed to facilitate simpler manufacturing and a wider application of glass coating layers.

Aerosol deposition (AD), which enables the manufacture of thick ceramic films at room temperature, is a technique that sprays an aerosol formed from raw material powder onto a substrate through a nozzle to obtain a dense, thick film [7,8]. This method can theoretically form thick films of various materials on any substrate at room temperature without additional heat treatments [2,4,5,9,10]. AD film formation is less affected by the difference in the coefficient of thermal expansion between the film and the substrate because of room temperature processing.

AD films can be coated by an interaction between particles and the substrate. Previous studies reported that when particles accelerated by a carrier gas collide with the substrate, the kinetic energy is converted to impact energy [8,11,12]. At this time, the particles are crushed by the impact energy, which instantaneously generates thermal energy at the contact point of the crushed particles, anchoring them to the substrate [13,14]. Therefore, the initial coating layer state is affected by the hardness of the substrate. Once this initial layer is formed, the coating layer was thickened further via the impact of subsequent particles [5,12]. From the second layer, coating layer conditions, such as the microstructure and thickness, are affected by the coating process [7,9]. On the other hand, little research has been done on the AD layer formation process and key factors. Therefore, it is necessary to study the factors affecting the fabrication of AD coating layers.

To examine the substrate effect on the AD coating behavior of glass, a glass frit with a composition of SiO₂-Al₂O₃-Y₂O₃ was prepared, and a coating layer was formed on Al₂O₃ glass, and metal STS304 substrates with different hardness using the AD method. The coating layers were formed on various substrates by increasing the number of scans. The intersectional observation of the coating layer and substrates confirmed the effect of the substrate hardness on the formation of the initial layers. To analyze the effects of the substrate hardness on the coating process after the initial layer, the thickness of the coating layer according to the number of scans, and the size and amount of fine grains remaining on the surface after coating were observed.

2. Experimental procedure
55SiO₂-28Al₂O₃-17Y₂O₃ mol% (SAY) composition (99.9%, Sigma-Aldrich, USA) was mixed for one hour

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and added to a platinum crucible. This was then placed within a super Kanthal furnace at a heating rate of 10°C/min to a final temperature of 1600°C for two hours. Once melted, the mixture was quenched at room temperature to obtain a glass cullet. The resulting glass cullet was first coarsely ground in an alumina mortar and added to zirconia jars with zirconia balls using a planetary mono mill (Pulverisette-7, Fritsch, Germany). The particle size of the prepared frit was measured to a powder size of $d_{50} = 17.3 \mu m$ using a particle size analyzer (PSA, Mastersizer 2000, Malvern Instruments, UK) (Figure 1(a)). Owing to the low density ($3.42 \text{ g/cm}^3$) of the glass frit, the glass powder size was larger than typical ceramic particles for the AD process (Figure 1(b)). Figure 1(c) presents XRD patterns of the fabricated powders with a typical amorphous phase. The measured glass transition temperature ($T_g$) was 903.4°C in Figure 1(d). The substrate hardness was measured using a nanoindenter (G200, KLA, USA). $\mathrm{Al}_2\mathrm{O}_3$, glass, and STS304 exhibited values of 11.4, 6.5, and 4.5 GPa, respectively. AD was used to coat the $\mathrm{Al}_2\mathrm{O}_3$, glass, and STS304 substrates.

![Figure 1](image-url)

**Figure 1.** (a) Particle size distribution, (b) SEM image, (c) XRD pattern, and (d) DSC result of the SAY glass frit.
Table 1. Conditions of the AD method using glass frit for the coating layer.

| Parameter             | Conditions |
|-----------------------|------------|
| Carrier gas           | N₂        |
| Distance between nozzle and substrate | 5 mm |
| Gas flow              | 10 s⁻¹    |
| Scanning cycle        | 1–4       |
| Scanning length       | 10 mm     |
| Stage speed           | 1 mm/s    |

(thickness = 1 mm) with a frit using nitrogen as the carrier gas. The substrate to nozzle distance (slit size: 1 x 5 mm²) was 5 mm and the scan speed was 0.1 mm/s. Table 1 lists the AD process conditions. The thickness of the formed coating layer was measured using a surface profiler (Surfcorder, ET3000, Kosaka Laboratory Ltd., Japan). A reliable film thickness value was obtained by calculating the average value and the standard deviation form 2 mm in the center of the coated part. The crystal structure of the coating layer formed on each substrate was analyzed by X-ray diffraction (XRD, DMAX-2500, Rigaku, Japan), while the surface microstructure of the coating layer was observed by field emission scanning electron microscopy (FE-SEM). The cross-section of the interface between the substrate and the coating layer was analyzed by scanning transmission electron microscopy (STEM) after focused ion beam milling (JIB-4601 F, JEOL Japan).

3. Results and discussion

Figure 2 presents XRD patterns of the SAY film on (a) Al₂O₃, (b) glass, and (c) STS304 substrates, each as raw substrates and from one to four scanning cycles. The XRD patterns of the films prepared on the Al₂O₃ and glass substrates using the SAY glass frit were the same as the uncoated substrate because of the low crystallinity of raw SAY. (Figure 1(c)) In the case of the STS304 substrate, the XRD patterns of the film were not detected. On the other hand, a change in the XRD pattern of the STS304 substrate was observed, as shown in Figure 2(c). An uncoated substrate and a one scanning number sample were selected to compare the XRD results of the STS304 substrate in detail (Figure 3). STS304 is an austenitic stainless steel with an XRD peak of the γ (111) plane at 43.5° 2θ, which was stronger than that of the martensite (α (110)) plane at 44.4° 2θ (Figure 3(a)). On the other hand, after one scan of the AD process, the intensity of the XRD pattern of the γ (111) plane at 43.5° 2θ and the 74.6° 2θ γ (220) plane became weak. Furthermore, the peak for the α (110) plane of 44.4° 2θ became stronger, and a peak for the α (200) plane was observed at 64.5° 2θ (Figure 3(b)). The accelerated particles induced plastic deformation and a phase transformation of the STS304 substrate [15].

A cross section of the interface between the substrate and the film was studied by TEM to observe the coating layer state according to the substrate (Figure 4). The microstructure of each interface had different shapes depending on the type of substrate. The interface between the Al₂O₃ substrate and the SAY film was smoother than in the other two substrates (Figure 4(a)) because the particles were not physically well anchored to the substrate. In other words, as the kinetic energy of the accelerated particles was converted to the impact energy with the substrate, the particles were crushed without damaging the Al₂O₃ substrate. The interface between the glass substrate and SAY film with high roughness was observed (Figure 4(b)). This suggests that the SAY particle broke with the partially damaged substrate immediately after impact. Subsequently, broken SAY particles were anchored in the glass substrate due to the generated thermal energy [13]. The interface of STS304 was observed as a film surrounding the substrate surface (Figure 4(c)), unlike the case of the Al₂O₃ and glass substrates. When the particles collide with the STS304 substrate, the soft substrate surface deformed plastically and expanded. The surface was subject to residual compressive stress to maintain the tensioned surface in its previous state.

Figure 5 shows the process of depositing a particle onto Al₂O₃, glass, and STS304 substrates and forming an initial layer. When accelerated particles hit the substrate, the kinetic energy is converted to thermal energy, and the particle fractures [11,12]. In the case of the film on the Al₂O₃ substrate with high hardness, most of the particles did not anchor to the substrate but rebounded [7]. This means that the coating layer was formed by molten glass due to thermal energy rather than the anchoring process. Therefore, small SAY particles with insufficient kinetic energy to form a layer were scattered when they impacted the substrate. SAY particles with sufficient kinetic energy were broken and changed to a molten glass state to form a thin 1st layer. In the case of the film on a glass substrate with lower hardness than Al₂O₃, most of the SAY particles were fractured by the AD process, and the fractured SAY particles were anchored to the glass substrate. As a result, the interface between the anchoring layer and substrate showed sharp edges. Unlike other substrates, the STS304 substrate had ductility, and SAY particles with high kinetic energy were anchored to the substrate by deforming the metal substrate. Therefore, the interface layer can have an entangled shape.
Figure 6 (a), (b), and (c) show the surface profiler results of a layer in each cycle according to the substrate (Al₂O₃, glass, and STS304, respectively). In the case of Al₂O₃ substrates, there was little change in the coating layer thickness depending on the number of scans. The coating layer on the glass substrates became thicker in proportion to the number of scans. Little change in the coating layer thickness was observed on the STS304 substrate since the first scan. The layer thickness was difficult to measure using the surface profiler results. The mean and standard deviations of the data in Figure 6 (a), (b), and (c) were calculated to solve these problems, as shown in Figure 6(d). In the case of the 1st layer, the film thicknesses on Al₂O₃, glass, and STS304 were 0.85, 4.61, and 7.53 µm, respectively. After coating four times, however, the film thicknesses on Al₂O₃, glass, and STS304 were 2.43, 14.54, and 9.53 µm, respectively. STS304 showed different coating behavior in the first and subsequent layers, unlike the other two substrates. The layer stacking mechanism after the 1st layer according to the substrate was analyzed by calculating the layer thickness per cycle on various substrates, as shown in Figure 7. The film thickness on
Figure 3. XRD results of (a) 40–55° 2θ and (b) 60–77° 2θ range on STS304 substrates.

Figure 4. Cross-section TEM images of interface between the coating layer and substrate on various substrates: (a) Al₂O₃, (b) glass, and (c) STS304.
Al$_2$O$_3$ and glass showed little change with the number of coating cycles. In contrast to the Al$_2$O$_3$ and glass substrates, the film thickness on STS304 decreased exponentially with increasing coating number of scans.
cycles. These phenomena were attributed to the ductility of STS304. The ductility of STS304 played a buffer role. The energy generated by the impact between the SAY particles and the STS304 substrate was reduced because of this buffer layer. Most SAY particles did not form a coating layer and bounced off after hitting the substrate. As a result, film growth on STS304 decreased exponentially.

Figure 8 presents the surface microstructure of the coating layer; the Al₂O₃ substrates are shown in (a) and (b), glass in (c) and (d), and STS304 in (e) and (f). Figure 8(a), (c), and (e) depict one scanning cycle, while Figure 8(b), (d), and (f) depict the microstructures of the surfaces coated with four scanning cycles. A clear difference was observed according to the number of scanning cycles. In the case of the Al₂O₃ substrate with high hardness, the shape of the crater was difficult to observe because of the low deposition rate, but the crater shape was observed in the film on the glass and STS304 substrates as it progressed from one to four scanning cycles. Partially deposited particles, less than 5 µm in size, were observed in the film on the STS304 substrate (Figure 8(f)). The size of partially deposited particles depended on the substrate hardness [14]. The size of partially deposited particles on the glass substrate was smaller than on the STS304 substrate. The number of partially deposited particles on a glass substrate was less than on the STS304 substrate. An analysis of the surface microstructure showed that the hardness of the substrate affected the film deposition behavior (craters and partially deposited particles).

4. Conclusion

The AD film formation mechanism of glass particles was examined according to the substrate type. A SAY frit was prepared and coated on Al₂O₃, glass, and STS304 substrates by AD, and various measurements were conducted. Different deposition behavior was observed depending on the substrate hardness. The film fabrication process of AD was divided into initial layer formation and stacking layers after the initial layer. In the initial layer formation, the thickest film was formed on the STS304 substrate with the lowest hardness. On the other hand, as the number of coatings increased up to four scanning cycles, the glass substrate, which has a similar hardness to the glass frit, showed the thickest film. The ductility of STS304 decreased the impact energy of the SAY particles, so they did not have sufficient energy for the crushing particles and forming layers. The microstructural image at the interface between the glass film and substrate showed a smooth interface at the high hardness substrate and a rough interface at the low hardness substrate. A higher substrate hardness means less damage to the substrate during impact. The parti-
cles that impacted the $\text{Al}_2\text{O}_3$ substrate were crushed the most and formed a smooth interface and the thinnest film. The particles that impacted the glass substrate were crushed slightly and anchored to the medium-thick layer with a rough interface.

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