Characterization of Pure Aluminum and Zinc Sprayed Coatings Produced by Flame Spraying*1

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We investigate flame spraying of pure aluminum and pure zinc powders on various different substrates and study shrinkage properties and thermal analysis curves of sprayed coatings during the forming process. We also examined effects of the spray distance on the porosity, tensile strength and hardness of sprayed coatings, and obtained the following results. With an increase in spray distance, shrinkage of the sprayed coating and the maximum temperature in the thermal analysis curve decrease. When the cooling ability of the substrate is higher, the shrinkage ratio and the maximum temperature become decrease. The porosity and the hardness of a sprayed coating increase with an increase in spray distance. This occurs because with the increase in the spray distance, the temperature of the sprayed particles decreases, the amount of air taken in the spray increases and, as a result, the cooling rate of the coating increases. The tensile strength of a pure aluminum coating decreases with an increase in spray distance due to the introduction of pores. On the contrary, the tensile strength of a pure zinc coating increases with an increase in spray distance. This occurs because when the spray distance is short, coating temperature is high and, as a result, a large quantity of zinc oxide is formed.

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1. Introduction

Spray coating is widely used as a means of reforming the surface of a substrates and it is essential to establish strong adhesion between the substrate surface and the sprayed coating. However, in spray forming situations where structures such as metal molds are made of a sprayed coating, the above-mentioned adhesion is not required, although shrinkage of the sprayed coating, which affects the dimensional accuracy of formed structures, should be considered. Accordingly, it is important to gain an understanding of the physical and mechanical properties of the coating formed during spray processing. To manufacture various types of metal molds, housings and others with high dimensional accuracy by spray forming, it is most important to understanding shrinkage properties of all the physical properties of a coating.

In this study, we investigate changes in temperature and shrinkage of coatings on various types of substrates as a function of time after spraying under the condition that pure aluminum and pure zinc coatings do not adhere closely to the substrate surface in an unrestrained state. Furthermore, we study relationships between the spray distance and the porosity, surface roughness, tensile strength, and the hardness of formed spray coatings.

2. Experimental Procedure

2.1 Spray material, substrate and spraying conditions

A powder flame spraying apparatus using oxygen and acetylene (Terodyne System 2000) was used. The spray powders used were pure aluminum and pure zinc, and the particle size of the powders used was 5-150 μm. Steel plates, shell molds for casting, mullite wool boards, and plaster molds for casting were used as substrates each with dimension of 110 mm × 100 mm × 10 mm. Table 1 gives the spraying conditions for the powder flame spraying in this study. For the purpose of this study, a sprayed coating formed on the surface of a substrate should not adhere to the surface but solidify and shrink freely. To meet this requirement, the surfaces of the steel plates and plaster molds were lined with a fine powder of boron nitride as parting powder. After spraying, the sprayed coatings were removed from the substrate surfaces and their physical and mechanical properties were examined.

| Table 1 Spraying conditions for powder flame spraying. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Powder | Gas pressure, $P_{CO2}$/kPa | Gas flow rate, $FR$/m$^3$.h$^{-1}$ | Carrier gas pressure, $P_{GAS}$/kPa | Coating rate, $CR$/kg.h$^{-1}$ |
| Al | 78 | 343 | 1.0 | 1.8 | 27 | 3.6 |
| Zn | 78 | 343 | 0.6 | 1.8 | 137 | 9.0 |

2.2 Method for measuring shrinkage of sprayed coatings

To manufacture metal molds with high dimensional accuracy by sprayed coatings and to use them practically, it is necessary to gain clear understanding of the shrinkage behavior of sprayed coatings. The effects of spray distance and type of substrate on the shrinkage of sprayed coatings
were investigated. Figure 1 shows the apparatus for measuring the shrinkage of sprayed coatings. Two hooks, separated by about 30 mm, made of silica tubing are set on the surface of the substrate: the left-side hook in the figure is fixed, while the right-side hook is connected to a gauge sensor. To prevent interference by spraying on the gauge sensor, an insulating cover is used. The region between the two hooks is sprayed for 10 s. Shrinkage length is measured continuously after finishing spraying until the temperature of sprayed coatings cooled to 323 K, and a K (JIS standard) thermocouple is inserted at the center of the coating layer. The shrinkage ratio (known hereafter as “shrinkage”), \( r_s \), is the value in which the shrinkage is divided by the distance between the two hooks.

A specimen measuring 10 mm \( \times \) 20 mm was taken out from the center of each sprayed coating after measuring its shrinkage length. The specimen was used for measurement of porosity, microstructure observation, measurement of roughness on the contact surface with the substrate, and hardness measurement (Hv, 0.49 N). Tensile specimens were taken from sprayed coatings obtained by spraying onto plaster molds under the same spraying conditions.

### 2.3 Measuring method for the porosity, surface roughness and tensile strength of sprayed coatings

Vaseline was applied thinly to the surfaces of specimens (10 mm \( \times \) 20 mm) for measuring porosity, and porosity was measured with the buoyancy method. \(^1\) The porosity was calculated according to the following equation:

\[
rp(\%) = \frac{1 - (M_c / \rho_c \cdot \rho_w)/(M - M' - M_m/\rho_m \cdot \rho_w) - M_c/\rho_c \cdot \rho_w)}{100}
\]  

(1)

The temperature was 297 K (24°C) during measurement. The parameters used are defined as follows:

- \( \rho_c \): density of coating (g cm\(^{-3}\))
- \( \rho_w \): density of pure water (g cm\(^{-3}\))
- \( \rho_m \): density of specific gravity pan (g cm\(^{-3}\))
- \( \rho_v \): density of Vaseline (g cm\(^{-3}\))
- \( M_c \): Weight of coating in air (g)
- \( M \): Total weight of coating, specific gravity pan and Vaseline in air (g)
- \( M' \): Total weight of coating, specific gravity pan and Vaseline in pure water (g)
- \( M_m \): Weight of specific gravity pan in pure water (g)
- \( M_v \): weight of Vaseline applied to coating (g)

After porosity was measured the specimens were washed with petroleum benzine to remove the vaseline from the surface and cut through the center for microscopic observation. Using a surface roughness tester (Surftest 201), the centerline average roughness (\( R_m \)) was measured for the surface of the cut specimens that had been in contact with the substrate.

Tensile test specimens with dimensions of 20 \( \times \) 90 \( \times \) (0.6 ~ 1.03) mm were taken from sprayed coatings sprayed on the shell mold, and smaller size specimens with dimensions of 20 mm \( \times \) 20 mm were also taken from the same sprayed coatings and attached to both grips of the tensile specimens with an adhesive agent to reinforce the gripping strength. To obtain uniform thickness of the sprayed coatings, the thermal spraying torch was slightly agitated relative to the specimen position. The relationship between spray distance and thickness of the sprayed coating is shown in Fig. 2. The spray time was constant at 10 s, and it is clear that the thickness of the sprayed coating decreases with increasing spray distance. The thicknesses of tensile test specimens were 0.75-0.60 mm for pure aluminum and 1.03-0.73 mm for pure zinc. Tensile strength was measured using a tensile testing machine (Instron type, Shimazu Autograph DCS-2000). The crosshead speed was fixed to 1.67 \( \times \) 10\(^{-2}\) mm s\(^{-1}\).

### 3. Experimental Results and Discussion

#### 3.1 Shrinkage and thermal analysis curves for the sprayed coatings of pure aluminum and pure zinc

Figure 3 shows some examples of shrinkage curves and thermal analysis curves for the sprayed coatings obtained by spraying pure aluminum and pure zinc powders onto the surfaces of plaster molds. The temperature of the sprayed coatings rises dramatically with the start of spraying. During this initial period, minute fluctuations in temperature repeatedly occur repeated. This phenomenon is caused by intermittent adhesion of spray particles to the sprayed coating and intermittent exfoliation of sprayed coating from the substrate. After spraying for 10 s, the coating temperature begins to drop, and as can be seen in the figure, the maximum temperature of the sprayed coatings is higher when the spray distance is shorter.

During the period from the start of spraying to the formation of a sprayed coating, the sprayed coating exhibits...
complicated shrinkage behavior. Due to the repeated adhesion of spray particles to the coating and partial exfoliation of the sprayed coating from the substrate, sprayed coatings repeat cycles of expansion and shrinkage. This phenomenon is caused by the fact that the sprayed coating does not behave as a solid until about 60% of the sprayed coating is solidified.2–4)

3.2 Effect of spray distance on the shrinkage and maximum temperature of pure aluminum and pure zinc coatings

Figure 4 shows the relationship between the spray distance and the maximum temperature of pure aluminum and zinc sprayed coatings. With an increase in spray distance, the maximum temperature of the sprayed coatings decreases, and when the spray distance is increased, the flight time of the spray particles increases and the temperature of the molten particles drops. As a result, the maximum temperature of the sprayed coatings decreases. At a spray distance of 250 mm, both the pure aluminum and pure zinc sprayed coatings show their maximum temperatures, which are high above or near the melting point of each respective metal. As for the effect of each type of substrates, the maximum temperature was the lowest when sprayed on the steel plate. In contrast, it was highest when sprayed on the mullite wool board, which is highly porous and is a highly effective insulator. The shell mold and plaster mold have almost the same apparent thermal diffusivity, which is a measure of the cooling ability of the mold.5) Consequently, the maximum temperatures for both are almost the same in this study.

Figure 5 shows the effect of the spray distance on the shrinkage of pure aluminum and pure zinc sprayed coatings; with an increase in spray distance, the shrinkage decreases. This is supposedly because with the increase in spray distance, the number of molten particles that arrive and adhere to the sprayed coating decreases and the ratio of solid...
to liquid particles increases. When sprayed on the steel plate with high cooling ability, molten particles rapidly solidified immediately after they adhere to the substrate, thus the shrinkage of the sprayed coating is small. In contrast, when sprayed on the poorly conducting mullite wool board, the molten particles solidified slowly and the shrinkage of the sprayed coating was much more pronounced. Since the results of the shrinkage shown in Fig. 5 also include shrinkage by solidification, the values are fairly large compared with the absolute values of the coefficients of linear thermal expansion for solid aluminum and solid zinc.6–9)

3.3 Microstructure, porosity and surface roughness of sprayed coatings

Figure 6 shows the relationship between the spray distance and the microstructures on the cross sections of coatings sprayed onto the shell mold. The microstructures of aluminum and zinc sprayed coatings are sedimentary structures, in which grain boundaries can be observed. The black parts in the structures are pores. The images of the pure aluminum sprayed coatings indicate that with an increase in spray distance, the number of pores increases. Figure 7 shows microstructures of the cross-sections of pure aluminum and zinc coatings sprayed onto various substrates. In the cases of aluminum and zinc coatings sprayed onto the mullite wool board, which has the lowest cooling ability, many pores are observed in the microstructure. This is considered to be caused by gas generation from the mullite wool board. In the case of the steel plate, which has the highest cooling ability, many pores are also observed, and the effect can be explained as follows: The cooling rate of the coating on the steel plate is
high and, consequently, when molten particles crash against the steel plate, they are immediately solidified before being flattened completely. Moreover, there is insufficient mutual fusion between particles, resulting many pores being generated.

Figure 8 shows the relationship between the spray distance and the porosity ratio of pure aluminum and zinc sprayed coatings. The figure shows that with an increase in spray distance, the porosity tends to increase. It has been reported that when zinc is sprayed with various types of flame spraying methods, porosity increases with an increase in spray distance,\(^1\) which is consistent with our results.

Porosity depends upon the type of substrate. For the mullite wool board, which has the lowest cooling ability, the porosity is high. Mullite wool board includes an organic binding agent to bond mullite fibers together, but the binding agent is thermally decomposed by molten particles, and decomposition gas is generated. It is supposed that the decomposition gas is trapped in the coating, leading to an increase in porosity. For the case of the steel plate, which has the highest cooling ability, it is supposed that when the spray distance is increased, some of the flying molten particles start solidifying and mutual fusion between particles becomes insufficient. As a result, the porosity is increased. The porosity of both the aluminum and zinc coatings sprayed onto the plaster molds was the lowest in this experiment.

Regarding the surface roughness of the substrates used in this study, the shell mold featured the roughest surface with a roughness value of 26-34 µm \((R_a)\). On the other hand, the steel plate had the smoothest surface, with a roughness value of was 2-3 µm \((R_a)\). Figure 9 shows roughness profiles of the surfaces of a shell mold and pure aluminum and zinc sprayed coatings in contact with the shell mold surface. The surface roughness of the aluminum and zinc sprayed coatings is smoother than that of the shell mold, implying that the molten particles in flame spraying do not perfectly trace the contour of the mold surface. Figure 10 shows the relationship
between the spray distance and the surface roughness of pure aluminum and zinc sprayed coatings for various substrates. The figure shows that the surface roughness of the sprayed coatings tends to increase with an increase in spray distance. This increased roughness is thought to result from the insufficient adhesion between molten particles and substrate, which is caused by the increase in spray distance. The surface roughness of sprayed coatings also depends upon the substrate surface. For the steel substrate, however, the surface of the sprayed coatings is rougher than that of the steel substrate due to insufficient mutual fusion between adhered particles. Furthermore, the surface of the sprayed coating on the steel substrate is rougher than that on the plaster substrate.

3.4 Tensile strength and hardness of sprayed coatings

Figure 11(a) shows the relationship between the spray distance and the tensile strength of sprayed coatings. Figure 12 shows the tensile test specimens after testing and the microstructures of the longitudinal sections in the fracture surface vicinity. Figure 12(a) shows that the fracture positions are almost all in center of the specimens. The aluminum sprayed coatings showed a decrease in tensile strength with an increase in spray distance. The microstructures of the longitudinal sections show that when the spray distance is increased up to 350 mm, fracture occurs at the boundaries between sprayed particles, implying that with an increase in spray distance, tensile strength decreases because of the insufficient fusion between particles. On the contrary, the tensile strength of zinc sprayed coatings increases with an increase in spray distance. The microstructures of the longitudinal sections show that when the spray distance is short, many oxides exist between the sprayed particles. This implies that with a decrease in spray distance, the temperature of the sprayed coatings increases and, as a result, many oxides are formed. Furthermore, the microstructure is similar to that of cast material because when the spray distance is short, the coating exists in a liquid state on the substrate surface for a long time. Thus, tensile strength may be affected by the oxide formation and the microstructural evolution. It has been reported that the tensile strength of a zinc alloy sprayed coating deposited by electric arc spraying is as low as about 6 MPa.10)

Figures 11(b) and (c) show the effects of the spray distance on the Vickers hardness of pure aluminum and zinc sprayed coatings. With an increase in spray distance, the hardness of pure aluminum and zinc sprayed coatings increases. This can be explained as follows: When the spray distance is increased, molten particles cool rapidly during flight, and the strain due to rapid cooling in the coating is increased, resulting in the increased hardness. This explanation is consistent with the fact that the increase in hardness is more remarkable for substrates having a higher cooling ability.

Fig. 12 Appearance of tensile test pieces after testing and microstructure of longitudinal sections at the fracture zone.

![Figure 11 Effects of spray distance on tensile strength and hardness of pure aluminum and zinc sprayed coating.](image-url)
4. Conclusion

Flame spraying of pure aluminum and pure zinc powders on various substrates was conducted, and the shrinkage properties, porosity, microstructure, surface roughness and mechanical properties of the sprayed coatings were investigated. The following results were obtained.

(1) The shrinkage ratio and maximum temperature of the coatings decrease with an increase in the spray distance. When the cooling ability of the substrate is high, the shrinkage ratio and maximum temperature of the coatings decrease.

(2) The microstructures of sprayed coatings are sedimentary structures. With an increase in the spray distance, the number of pores tends to increase. When the cooling ability of the substrate is low, the microstructure of the sprayed coating becomes similar to a cast microstructure and the porosity increases.

(3) The surface roughness of sprayed coatings generally reflects the substrate surface. However, for the steel plate, which has a higher cooling ability, the surface becomes rougher due to insufficient fusion between molten particles.

(4) The tensile strength of the aluminum sprayed coating tends to decrease with an increase in spray distance due to the insufficient fusion between sprayed particles. The tensile strength of the zinc sprayed coating decreases with increase in spray distance because many oxides form in the coating with a cast microstructure. An increase in the spray distance leads to increased hardness of the coating due to rapid cooling of the coating.

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REFERENCES