Effects of particle dispersion on the properties of suspension-sprayed coatings

Naoya IWATA and Takamasa MORI*,**,†

Graduate School of Science and Engineering, Hosei University, 3–7–2 Kajino, Koganei, Tokyo 184–8584, Japan
*Department of Chemical Science and Technology, Faculty of Bioscience and Applied Chemistry, Hosei University, 3–7–2 Kajino, Koganei, Tokyo 184–8584, Japan
**Hosei University Research Institute for Slurry Engineering, 3–7–2 Kajino, Koganei, Tokyo 184–8584, Japan

Suspension spraying is a promising surface modification technique, because finer particles can be used in contrast to the case of conventional thermal spraying. However, the optimal conditions for preparing suitable suspensions have not yet been established. Thus, the effects of particle dispersion and flocculation states on the properties of suspension-sprayed coatings were examined in the present study. Y2O3 suspensions were prepared using various quantities of the dispersant. The flow curves and gravitational settling behaviors of the prepared suspensions were investigated. The amounts of the dispersant adsorbed on the particles were also determined. In addition, Y2O3 coatings were fabricated using suspension spraying, and the properties of the obtained coatings were investigated. The addition of the dispersant affected the suspension flow characteristics, because the amount of the dispersant adsorbed increased with increasing dispersant concentration. Furthermore, the coating characteristics improved as the apparent viscosity of the suspension decreased.

Key-words : Suspension, Suspension spraying, Dispersion, Y2O3

1. Introduction

Thermal spraying is a surface modification technology, in which the spray consists of particles that have been melted or softened by heating. This technique has the following advantages: (i) fast film formation, (ii) applicability to various materials and substrates, and (iii) ease of use. Therefore, thermal spraying is widely used in various fields, including semiconductors, liquid crystals, and medical products.1–4

Recently, thermal spraying of suspensions has been developed (Fig. 1) because the suspensions are easier to control than dry powders.5–14 In this technique, the particle dispersion state and flow characteristics, because the amount of the dispersant adsorbed increased with increasing dispersant concentration. Furthermore, the coating characteristics improved as the apparent viscosity of the suspension decreased.

Previously, the effects of particle dispersion and flocculation states on the properties of sprayed coatings have been investigated.15–14 For example, Carpio et al.5,12,14 reported the effects of the suspending distance and speed on the properties of sprayed coatings. Ramon et al.7 researched the effects of the viscosity and surface tension of the suspension medium on suspension-sprayed coatings. Furthermore, He et al.13 attempted to produce high-performance coatings using low-pressure suspension spraying conditions.

In contrast, few reports have focused on the particle dispersion and flocculation states of suspensions for spray coating. Therefore, in the present study, we investigated the effects of particle dispersion and flocculation states on the properties of coatings fabricated using suspension spraying.

2. Experimental procedure

2.1 Suspension preparation

Suspensions were prepared from yttria powder (yttrium oxide, Nippon Yttrium Co., Ltd.) with an average particle size of 3.0 μm, distilled water, and polyacrylic acid ammonium (PCA; D-305, Chukyo Yushi Co., Ltd.) as a dispersant. Polyacrylic ammonium was mixed with distilled water prior to suspension preparation. The yttria powder was mixed with the suspension medium for 1 h by the ball-milling technique, using zirconia balls with a diameter of 4 mm in a polyethylene bottle. Subsequently, the zirconia balls were separated using a sieve, and the resulting suspension was used for experiments. The particle concentration was 23 vol % and 1 kg of zirconia balls was used to process 500 mL of suspension. Suspending with different particle dispersion and flocculation states were obtained by adjusting the PCA additive dosage: 0, 2.0, 3.5, 4.0, and 10.0 mg g−1 Y2O3.

2.2 Suspension characterization

2.2.1 Measurement of PCA adsorbed on yttria

Suspensions prepared following the method described in section 2.1 were centrifuged under the following conditions: the centrifugal acceleration was 3,300 G for 1 h. The concentrations

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Corresponding author: T. Mori; E-mail: tmori@hosei.ac.jp
of non-adsorbed PCA in the resulting supernatants were measured using a total organic carbon analyzer (TOC-V, Shimadzu Corp.). The quantities of PCA adsorbed were calculated using Eq. (1), which demonstrates that the amount of the adsorbed PCA is proportional to the difference between the initial and non-adsorbed concentrations of PCA,

$$W = \frac{(C_0 - C)V}{M}$$  (1)

where $C_0$ is the initial PCA concentration (mg·L$^{-1}$), $C$ is the non-adsorbed PCA concentration (mg·L$^{-1}$), $V$ is the volume of the supernatant (L), and $M$ is the mass of particles (g).

The adsorption ratio was calculated from the initial concentration and the adsorbed amount of PCA [Eq. (2)],

$$R = \frac{W}{10^3 C_0 V/M} \times 100$$  (2)

where $W$ is the quantity of PCA adsorbed (mg g$^{-1}$).

### 2.2.2 Sedimentation test

Suspensions prepared as per the method described in section 2.1 were placed in acrylic test tubes (inner diameter: 20 mm) and left to settle. The packing fraction was calculated by introducing the measured height of the sediment, and the initial suspension height and concentration into the following mass balance equation [Eq. (3)]

$$\Phi_\infty = \frac{h_0}{H_\infty} \phi_0$$  (3)

where $h_0$ is the initial suspension height (m), $H_\infty$ is the sediment height (m), and $\phi_0$ is the initial solid volumetric concentration. The initial height of the suspension was 160 mm.

### 2.2.3 Flow curve measurement

The flow curves of the suspensions prepared by the method described in section 2.1 were measured using a coaxial double-cylinder rotation viscometer (RheoLab QC, Anton Paar). The shear stress was measured while changing the shear rate from 0 to 1000 s$^{-1}$ and from 1000 to 0 s$^{-1}$. The total measurement time was 360 s.

### 2.2.4 Hydrostatic pressure measurement

The suspensions prepared were transferred into acrylic test tubes. The hydrostatic pressure at the bottom of the tubes was measured over time using a HYSTAP-3 instrument (JHGS, Japan). The particle dispersion and flocculation states were estimated from the rate of hydrostatic pressure decrease, which is proportional to the particle settling velocity. The maximum ($P_{\text{max}}$) and minimum ($P_{\text{min}}$) hydrostatic pressures (Pa) were calculated using the following equations:

$$P_{\text{max}} = \rho_s g(h_0 - \rho_p H_{\infty} - 0.05)$$  (4)

$$P_{\text{min}} = \rho_s g(h_{\infty} - 0.05)$$  (5)

where $\rho_s$ is the medium density (kg·m$^{-3}$), $\rho_p$ is the particle density (kg·m$^{-3}$), $g$ is the gravitational acceleration (m·s$^{-2}$), and $H$ is the suspension height (m). The initial suspension height was 150 mm.

### 2.3 Suspension spraying and coating characterization

The suspensions prepared were sprayed using high-speed frame spraying. First, an aluminum alloy substrate (50 × 50 × 5 mm) was blasted to roughen its surface. The substrate was fixed with the blasted side facing upwards, and the suspension was deposited from above using a scanning spray gun. All the spraying processes were conducted under the same conditions: suspension feed rate: 240 g·min$^{-1}$; oxygen feed rate: 1200 scfh; and spraying distance: 100 mm.

Cross-sections of the suspension-sprayed coatings were observed using scanning electron microscopy (SEM), and their porosities were calculated from binarized SEM images. The Vickers hardness and surface roughness of each coating were measured using a hardness tester (MMT-X, Matsuzawa Co., Ltd.) and a surface roughness tester (SURFCOM1400D, Tokyo Seimitsu Co., Ltd.), respectively.

### 3. Results and discussion

#### 3.1 Suspension characterization

Figure 2 shows the adsorbed amount and adsorption ratio of PCA on the yttria particles. The bars in these figures indicate the maximum and minimum values obtained from the repeat measurements. From this figure, it can be seen that the amount of PCA adsorbed increased with increasing PCA concentration; the maximum amount of PCA adsorbed was 2.4 mg·g$^{-1}$. Conversely, the PCA adsorption ratio decreased with increasing PCA concentration. The PCA adsorption behavior was similar to that described by the Langmuir isotherm, which suggests that a single layer of PCA was absorbed on the yttria particles.

Figure 3 shows a photograph of the sediments three days after the start of the sedimentation tests; no subsequent changes were observed in the sediment heights. The interface of the 0 mg·g$^{-1}$ PCA suspension is indicated by an arrow in Fig. 3(a). A proportion of the particles remained in the supernatant; heat weight

![Fig. 2.](image)

*Fig. 2. Effect of PCA additive dosage on adsorbed amount of PCA and adsorption ratio.*

![Fig. 3.](image)

*Fig. 3. Photographs of settling Y$_2$O$_3$ suspensions containing (a) 0, (b) 2.0, (c) 3.5, (d) 4.0, and (e) 10.0 mg·g$^{-1}$ PCA.*
and 4.0 mg·g
densely packed. In addition, PCA additive dosages of 2.0, 3.5, with a PCA concentration of 10.0 mg·g
behaved di
with di
dosage of 0 mg·g
Figure 3 and Table 1 show that the sediment with a PCA additive packing fractions calculated using Eq. (3) are listed in Table 1. Final packing fractions and apparent viscosities for suspensions with different additive dosages

<table>
<thead>
<tr>
<th>Additive dosage (mg·g⁻¹)</th>
<th>0</th>
<th>2.0</th>
<th>3.5</th>
<th>4.0</th>
<th>10.0</th>
</tr>
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<tr>
<td>Packing fraction (–)</td>
<td>0.37</td>
<td>0.24</td>
<td>0.25</td>
<td>0.24</td>
<td>0.36</td>
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<tr>
<td>Apparent viscosity @ 200 s⁻¹ (mPa·s)</td>
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<td>5.3</td>
<td>5.1</td>
<td>5.2</td>
<td>5.9</td>
</tr>
<tr>
<td>Apparent viscosity @ 1000 s⁻¹ (mPa·s)</td>
<td>14.8</td>
<td>9.0</td>
<td>7.4</td>
<td>7.2</td>
<td>6.7</td>
</tr>
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</table>

Fig. 4. Flow curves for Y₂O₃ suspensions.

Fig. 5. Apparent viscosities of Y₂O₃ suspensions.

analysis confirmed that these particles amount were negligibly small, and did not have an effect on the sediment height. The other samples exhibited clear supernatant; thus, the sediment heights were determined from the liquid-solid interface. The final packing fractions calculated using Eq. (3) are listed in Table 1. Figure 3 and Table 1 show that the sediment with a PCA additive dosage of 0 mg·g⁻¹ was the densest, and the suspension prepared with a PCA concentration of 10.0 mg·g⁻¹ was the second-most densely packed. In addition, PCA additive dosages of 2.0, 3.5, and 4.0 mg·g⁻¹ produced suspensions with sparse sediments; that is, the particles in these suspensions were considered to be flocculated.

Figures 4 and 5 show the flow curves and changes in the apparent viscosities (section 2.2.3) of the suspensions, respectively. From these figures, it can be seen that the apparent viscosities of all of the suspensions increased with increasing shear rate; thus, these yttria suspensions were categorized as dilatant fluids. In Fig. 4, all of the suspensions show the same behavior until around 400 s⁻¹; however, at higher shear rates, the suspensions behaved differently. Hence, although the yttria particles were well dispersed at shear rates of 0–400 s⁻¹, the particles began to flocculate above 400 s⁻¹. Furthermore, the degree of flocculation was greater with lower PCA concentrations. The results shown in Fig. 5 indicate that the dilatancy characteristics were weakened by the addition of PCA, and the behavior of the suspensions approached that of a Newtonian fluid.

The amount of adsorbed PCA increased with increasing PCA concentration (Fig. 2). Hence, repulsion increased between yttria particles, resulting in well dispersion at any shear rate. Table 1 shows the average of two apparent viscosity measurements at shear rates of 200 and 1000 s⁻¹. Because the suspension without PCA had strong dilatancy characteristics, it exhibited relatively high viscosity at both shear rates. For the suspensions containing PCA, differences in the viscosity were not evident at a shear rate of 200 s⁻¹. At a shear rate of 1000 s⁻¹, the viscosity decreased with increasing PCA concentration. Thus, the suspension containing 10.0 mg·g⁻¹ of PCA exhibited the lowest apparent viscosity; the particles in this suspension were considered to be well dispersed.

Figure 6 shows the hydrostatic pressures of the suspensions, as measured by the HYSTAP-3 instrument. In this figure, the slopes of the decrease in hydrostatic pressure indicate the settling velocities of the yttria particles. The particles in the suspensions with PCA additive dosages of 0 and 10.0 mg·g⁻¹ settled slowly. Thus, the particles in these suspensions may be regarded as dispersed. However, the hydrostatic pressures of the suspensions with PCA additive concentrations of 2.0, 3.5, and 4.0 mg·g⁻¹ also slowly decreased after the initial measurements; the corresponding slopes increased around 4 h later. These results suggest that these suspensions were initially well-dispersed, and that flocculation occurred after approximately 4 h.

The flow curves of the suspensions just after the preparation indicate that these tended to disperse with increasing PCA concentration. In the sedimentation tests, suspensions with PCA additive dosages of 0 and 10.0 mg·g⁻¹ were characterized as dispersion systems, and suspensions with PCA dosages of 2.0, 3.5, and 4.0 mg·g⁻¹ as flocculation systems. All of the suspensions were well dispersed immediately after preparation; however, suspensions with PCA additive concentrations of 2.0, 3.5, and 4.0 mg·g⁻¹ changed to flocculation state during gravitational settling (Fig. 6). Therefore, the sediments were re-dispersed, and flow curve measurements were conducted to confirm the dependence of the viscosity changes on the dispersion and flocculation states. Table 2 shows the apparent viscosity ratios at a shear rate of 1000 s⁻¹. These ratios were calculated using the following equation: viscosity ratio = (viscosity after sedimentation) / (viscosity immediately after preparation). The suspensions
with PCA dosages of 3.5 and 4.0 mg·g⁻¹, which exhibited low viscosities immediately after preparation, were found to have high viscosities after sedimentation, compared with the suspension containing 10.0 mg·g⁻¹ PCA. Hence, temporal changes in the particle dispersion and flocculation state were confirmed. However, we hypothesized that PCA adsorption alone was insufficient to account for these changes. In the 10.0 mg·g⁻¹ suspension, 2.4 mg·g⁻¹ of adsorbed PCA was sufficient to suppress the temporal changes in the dispersion state. The amount of PCA adsorption observed in the 3.5 and 4.0 mg·g⁻¹ suspensions was 70% of that observed in the 10.0 mg·g⁻¹ suspension. Therefore, we assumed that the yttria particles in the 3.5 and 4.0 mg·g⁻¹ suspensions were flocculated owing to collisions during the sedimentation process.

Although the suspension without PCA had a higher apparent viscosity, even at low shear rates, it was characterized as a dispersion state based on hydrostatic pressure measurements. This contradiction occurs because of the difference in the applied shear field; the shear applied to the particles during sedimentation was considerably smaller than the detection limit of the viscometer; as a result, the differences in the particle dispersion state during sedimentation were not measurable as a viscosity change.

### 3.2 Coating characterization

Cross-sectional SEM images of coatings formed using yttria suspension spraying are shown in Fig. 7. The thermal spraying experiment using the suspension without PCA could not be completed because the equipment became clogged with the suspension. This suspension exhibited significant dilatancy (Figs. 4 and 5); therefore, the clogging was attributed to agglomeration of the particles because of the relatively large shear rate applied to the suspension in the pipe. The coatings obtained from the suspensions containing 0 and 2.0 mg·g⁻¹ PCA exhibited greater porosity (3.7%) than the other suspensions. Figures 8–10 show the porosity, Vickers hardness, and surface roughness, respectively, of each coating. The porosity and surface analyses were conducted five times, and the Vickers hardness measurements were conducted ten times. The bars in these figures indicate the maximum and minimum measurements. The porosity tended to decrease with increasing PCA concentration. The Vickers hardness initially increased with increasing PCA dosage, from 0 to 3.5 mg·g⁻¹, and then remained almost constant at higher additive concentrations. Figures 8 and 9 indicate that the coatings fabricated from suspensions containing 0 and 2.0 mg·g⁻¹ of PCA were relatively weak, because of their comparatively large pore volumes. The surface roughness was similar for all of the coatings (~1.6 μm). Therefore, a PCA additive concentration of 4.0 mg·g⁻¹ was considered to be sufficient to obtain acceptably hard and dense coatings.

<table>
<thead>
<tr>
<th>Additive dosage (mg·g⁻¹)</th>
<th>0</th>
<th>2.0</th>
<th>3.5</th>
<th>4.0</th>
<th>10.0</th>
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<tbody>
<tr>
<td>Apparent viscosity ratio</td>
<td>0.4</td>
<td>5.7</td>
<td>8.7</td>
<td>10.8</td>
<td>5.1</td>
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</table>

Fig. 7. Cross-sectional SEM images of coatings formed from aqueous Y₂O₃ suspensions containing (a) 0, (b) 2.0, (c) 3.5, (d) 4.0, and (e) 10.0 mg·g⁻¹ PCA.

Fig. 8. Effect of PCA additive dosage on porosity of sprayed coatings.

Fig. 9. Effect of PCA additive dosage on Vickers hardness of sprayed coatings.
Figures 11–13 show the relationships between the characterization results for the suspensions and sprayed coatings. The bars in these figures indicate the maximum and minimum measurements. These results indicate that the porosity of the coatings correlates with the apparent viscosities of the suspension at a shear rate of 1000 s\(^{-1}\). However, there is no correlation between the porosities and the sediment packing fractions or the apparent viscosities at 200 s\(^{-1}\). The suspension spraying processes were conducted immediately after suspension preparation. Hence, the evaluation of suspensions using sedimentation testing may not be appropriate for suspension-sprayed coating, because the dispersion states appear to change during the one to two days necessary for the suspensions to complete the settling process. Additionally, the flow curve measurements revealed that the apparent viscosities at low shear rates did not correspond with coating characteristics, because the suspensions exhibited significant dilatancy. In the suspension spraying process, the dispersion and flocculation states at high shear rates significantly affected the characteristics of the sprayed coatings.

4. Conclusions

The particle dispersion and flocculation states of yttria suspensions were controlled by adding PCA. The prepared suspensions were evaluated by measuring the adsorbed PCA, sedimentation, flow curves, and hydrostatic pressure changes. Additionally, thermal spraying was conducted using the prepared yttria suspensions. The resultant coatings were also evaluated.

The suspension without PCA was unsuitable for spray coating, because the suspension agglomerated during spraying, resulting in the clogging of the spraying apparatus. The dispersion of the suspended particles increased with increasing PCA concentration, and the apparent viscosity decreased. Moreover, the hardness and density of the sprayed coating increased with increasing PCA concentration. These coating characteristics correlated with the apparent viscosity of the corresponding suspension at a shear rate of 1000 s\(^{-1}\). A PCA additive concentration of around 4.0 mg·g\(^{-1}\) was sufficient to obtain coatings with acceptable hardness and density; however, it is necessary to consider changes in the dispersion state over time, if spray coating for long periods. The evaluation of the apparent viscosity at low shear rates is not suitable for predicting the properties of the sprayed coatings, because the particle dispersion and flocculation state must be evaluated at a shear rate corresponding to that experienced by the suspension in the coating process.

Fig. 10. Effect of PCA additive dosage on surface roughness of sprayed coatings.

Fig. 11. Relationship between the porosity of Y\(_2\)O\(_3\) coatings and sediment packing fraction.

Fig. 12. Relationship between the porosity of Y\(_2\)O\(_3\) coatings and apparent viscosity at 200 s\(^{-1}\).

Fig. 13. Relationship between the porosity of Y\(_2\)O\(_3\) coatings and apparent viscosity at 1000 s\(^{-1}\).

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### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>W</td>
<td>adsorbed amount (mg·g(^{-1}))</td>
</tr>
<tr>
<td>C(_0)</td>
<td>initial dispersant concentration (g·L(^{-1}))</td>
</tr>
<tr>
<td>C</td>
<td>non-adsorbed dispersant concentration (g·L(^{-1}))</td>
</tr>
<tr>
<td>V</td>
<td>volume of dispersant solution (L)</td>
</tr>
<tr>
<td>M</td>
<td>mass of particles (g)</td>
</tr>
<tr>
<td>R</td>
<td>adsorption ratio (%)</td>
</tr>
<tr>
<td>(\phi_s)</td>
<td>packing fraction of the sediment</td>
</tr>
<tr>
<td>(\phi_c)</td>
<td>initial solid volumetric concentration (—)</td>
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<tr>
<td>(H_c)</td>
<td>sediment height (m)</td>
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References