Influence of Substrate Temperature on the Structure and Cohesive/Adhesive Strength of Fe–Co–Si–B–Nb Metallic Glass Coating Films Produced by Thermal Spraying

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The influence of the substrate temperature on the structure, pore distribution and cohesive/adhesive strength of Fe–Co-based metallic glass coating films has been examined. The metallic glass coating films have been produced by a thermal spraying technique using our developed cylindrical nozzle on SS400 substrates. The splat morphology of the sprayed particles changed from an irregular splash to a disk shape at a transition temperature of about 300°C. When the substrate temperature increased to the transition temperature region (300–323°C), the porosity in the boundaries between the sprayed coating films and the substrates decreased. This can be produced by the strong increase in the wettability of the sprayed particles which is accompanied with a morphological change from splashed to disk-shaped particles. At temperatures ranging from 375 to 400°C, the porosity in both the boundary and inside regions decreased, and the volume fraction of the amorphous phase increased with temperature, resulting in an increase in the cohesive/adhesive strength up to about 27 MPa.

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1. Introduction

In our previous study, the influence of the substrate temperature on the structure, pore distribution and cohesive/adhesive strength of Fe–Cr-based amorphous coating films was examined by a thermal spraying technique using our developed cylindrical nozzle on SS400 substrates.1,3

The volume fraction of amorphous phase in the sprayed coating films was found to strongly dependent on the cooling rate of the sprayed particles. This volume fraction increased at temperatures ranging from 325 to 400°C. In this temperature region, the heat transfer may be substantially increased with substrate temperature because of the lower porosity in the boundary region, resulting in a higher cooling rate of the sprayed particles. Therefore, the optimum substrate temperature providing the maximum cooling rate of the sprayed particles may be determined.

In the present study, the influence of the substrate temperature on the structure, pore distribution and cohesive/adhesive strength of Fe–Co-based metallic glass coating films have been examined with the aim to collect the basic data required for spray-coating soft magnetic materials onto various magnetic sensors.

2. Experimental Procedures

The thermal spraying equipment used in this study was composed of a gas flame spraying gun and a cylindrical nozzle. The thermal spraying material was a gas-atomized Fe36Co36Si4B20Nb4 (Fe–Co, numbers indicate at%) powder (grain size: 63–88 µm) with a melting temperature of 1103°C. SS400 steel plates (120 mm x 120 mm x 6 mm) were used as substrates. The surface finishing of the substrates was done by shot blasting with alumina powders, while the surface roughness was adjusted to about Ra = 4 µm. The micro-vickers hardness of the thermal sprayed coating films on the substrates was measured by using a 0.2 kg load and a loading time of 10 s at the center of the inside region in cross section. Structural analysis of the sprayed coating films was carried out by X-ray diffraction (XRD, Cu–Kα radiation with a graphite monochromator, 40 kV, 200 mA) and scanning electron microscope (SEM, 15 kV, Hitachi SU1500). The volume fraction of the amorphous phase in the sprayed coating films separated from the substrate was estimated by measuring the heat evolution during crystallization in differential scanning calorimetry (DSC, SII 6220) with a heating rate of 40°C/min under a high-purity argon gas atmosphere. The weight of the samples was set to about 20 mg.

Table 1 summarises the thermal spraying conditions used in the present study. In order to prevent the formation of oxides in the sprayed coating films, the flame was kept in a reducing atmosphere by using an acetylene-rich gas fuel mixture while

| Table 1 Thermal spraying condition for Fe–Co–Si–B–Nb metallic glass coating films. |
|---------------------------------|-----------------|
| Acetylene flow rate             | 37.8 dm³/min    |
| Oxygen flow rate               | 28.3 dm³/min    |
| External cooling gas (N2) flow rate | 400 dm³/min |
| Cooling air pressure from the back side | 0–0.1 MPa |
| Gun scan rate                  | 300 mm/s        |
| Spraying pitch                 | 5 mm            |
| Thickness of the sprayed coating | 400 µm         |

Figure 1 shows a schematic illustration of the cylindrical nozzle-type thermal spraying gun and the flat substrate.
introducing nitrogen gas into the cylindrical nozzle. With the aim to control the substrate temperature, the cooling air pressure from the rear side was controlled to be between 0 and 0.1 MPa with an intermittent operation of thermal spraying, as described later in Fig. 5.

Figure 2 shows schematic illustrations of the tensile test specimen used for measuring the cohesive/adhesive strength between the sprayed coating film and the substrate. In particular, Fig. 2(a) shows the tensile test specimen. The substrate was first bonded to an aluminum dolly (effective area: 314 mm², diameter: 20 mm) using the 3M Company adhesive agent AF163-2, and then annealed at 120°C for 2 h to harden the adhesive. Figure 2(b) shows the assembly diagrams of the tensile test jig and the tensile test specimen. The aluminum dolly and the substrate were installed in upper and lower test jigs, respectively. The cross-head speed of the tensile test was set to 1 mm/min.

Figure 3 shows the shape of the substrate designed to measure the cohesive/adhesive strengths of the tensile test specimens with an effective area 20 mm in diameter. As a pretest, substrate surface temperatures at the center points of the four central specimens (6, 7, 10, 11) and the center point of the substrate were measured by the spot-welded K-thermocouples, respectively. In the result, the temperature difference of five points changed less than ±5°C. For this reason, the substrate surface temperature was measured at the center point by a spot-welded K-thermocouple as a typical temperature. After the thermal spraying treatment, the substrate was cut along the dotted lines by wire cutting equipment. Finally, four specimens around the K-thermocouple were selected for subsequent cohesive/adhesive strength measurements. After bonding the coated substrate and the aluminum dolly, the remaining sprayed coating film was removed from the effective area by shot blasting. With this purpose, a ring groove with a 2 mm depth around the 20 mm diameter area was used for precise removal.

Figure 4 shows the thermal gradients of the spraying flame, as measured by the thermocouple, along the distance from the cylindrical nozzle head to the substrate. In this diagram, the 0 mm curve indicates the thermal gradient in the center of the flame, while the 5 and 10 mm curves refer to the thermal gradient at the corresponding distances from the
center of the flame. Although the flame hits the substrate at a temperature of approximately 1000°C at its center, this temperature decreased sharply to about 300 and 500°C at 10 and 5 mm, respectively, from this position.

Figure 5 shows the thermal spraying scanning patterns on the SS400 substrates. The spraying gun was mounted on a robot arm and scanned at a feed rate of 300 mm/s. In a first step, the thermal spraying was started at point A, and subsequently scanned back and forth along the solid lines with a 10 mm pitch. Once the spraying reached point B, the spraying gun was returned to point A and held in standby while the substrate temperature decreased to the preset value. In the second step, the scanning pattern was shifted about 5 mm downward. In the third step, the scanning pattern returned to that of the 1st step. After that, these steps were repeated until reaching the preset thickness value of the spraying films.
Figure 6 shows a representative example of the substrate temperature over 50 consecutive steps for a given target temperature of 300°C. The substrate temperature was measured by the spot-welded K-thermocouple at the center point. Figure 7 shows a magnified picture of the dotted circle area represented in Fig. 6. After preheating the substrate above the preset value (305°C), the gun was held in standby at the starting point while the substrate cooled down to 305°C. Once this point was reached, the first spraying step was started. In this case, the bottom temperature of the substrate \( T_{\text{min}} \) was obtained when the thermal spraying was started, while the local maximum temperature \( T_{\text{max}} \) was reached when the gun was scanned over the spot-welded point of the K-thermocouple. After scanning the first step, the gun was held at standby at the starting point while the substrate temperature decreased to the preset value. Once the substrate temperature had decreased below 305°C, the second spraying step was started. In this study, 400-µm-thick films were prepared over 50 steps. Hereafter, the average value of \( T_{\text{min}} \) for all the steps will be referred to substrate temperature \( T_s \). In this case, \( T_s \) was 300°C. The difference between \( T_{\text{max}} \) and \( T_{\text{min}} \) remained within 50°C, and \( T_{\text{min}} \) ranged within ±6°C, as shown in Fig. 8.

3. Results

3.1 Structure of the sprayed coating films

Figure 9 shows cross-sectional SEM micrographs of the Fe–Co-based metallic glass coating films on SS400 substrates. The pores in the cross sections are shown as white spots. A high porosity (≥4.0%) was observed in the boundary region framed by the dotted line for \( T_s ≤ 300°C \) (Figs. 9(a)–9(c)). The porosity in the boundary region decreased to about 3.0% at \( T_s = 323°C \), and a further increase in \( T_s \) to 401°C led to a drop in the porosity to a minimum of about 2.6%. Porosity in the boundary region gradually increased to about 3.4% when \( T_s \) increased to 451°C. In the inside region of the sprayed coating film, framed by the solid line, the observed porosity reached only 1.0% or above at \( T_s \) values ranging from 250 to 323°C, as shown in Figs. 9(a)–9(d). At \( T_s ≥ 350°C \), the porosity in the inside region remained below 1.0%, reaching a minimum value of about 0.2% at 401°C. A further increase in \( T_s \) (451°C) led to a gradual increase in the inside region porosity to a maximum of about 0.6%. Figure 10 shows the porosity of the sprayed coating films as a function of \( T_s \), as summarized in the results of Fig. 9.

Figure 11 shows the hardness of the sprayed coating films as a function of \( T_s \). The hardness was found to increase with \( T_s \) (−HV1080 at 300°C) and dropped thereafter (−HV1060 at 325°C). The hardness reached a maximum value of about HV1100 for \( T_s = 450°C \).

Figure 12 shows the XRD patterns of the as-sprayed Fe–Co coating films at various \( T_s \) values. Broad diffraction peaks (2θ = 40–50°) were obtained at \( T_s ≤ 425°C \), indicating that the structure of the sprayed coating films was practically amorphous. When \( T_s \) was increased to 451°C, some sharp peaks attributable to \( α\)-Fe, Fe₂B and Fe₃B phases appeared superimposed on the broad pattern of the amorphous phase, thereby indicating the partial crystallization of the amorphous phase.

Figure 13 shows the DSC curves for the Fe–Co sprayed coating films at various \( T_s \) values. In the case of the rapidly quenched ribbon sample, a large exothermic peak was
observed with a peak temperature of 600°C. For powder (grain size: 38–63 µm), peak temperature shifted to higher value as compared with ribbon sample. This may be attributed to a compositional shift due to the difference in a production method. For sprayed coating films, the peak temperatures did not change with an increase in $T_s$ as compared with powder.

![Cross-sectional SEM micrographs](image)

Fig. 9 Cross-sectional SEM micrographs of the Fe-Co-based metallic glass coating films on SS400 substrates: (a) $T_s = 250°C$; (b) $T_s = 274°C$; (c) $T_s = 300°C$; (d) $T_s = 323°C$; (e) $T_s = 350°C$; (f) $T_s = 376°C$; (g) $T_s = 401°C$; (h) $T_s = 425°C$; (i) $T_s = 451°C$.

![Porosity vs. Substrate Temperature](image)

Fig. 10 Porosity of the sprayed coating films as a function of $T_s$, as summarized the results of Fig. 9.

![Hardness vs. Substrate Temperature](image)

Fig. 11 Hardness of the sprayed coating films as a function of $T_s$.

Figure 14 shows the volume fractions of the amorphous phase for the Fe-Co sprayed coating films as a function of $T_s$. These values were estimated from the sizes of the exothermic peaks based on that of the rapidly quenched ribbon sample. The volume fraction of the amorphous phase decreased with $T_s$ to a minimum value of about 91% at 275°C. This value increased to a maximum value of about 97% at a $T_s$ value of about 400°C, and decreased thereafter.
Fig. 12 XRD patterns of the as-sprayed Fe-Co coating films at various $T_s$ values (Cu-Kα radiation with a graphite monochromator, 40 kV, 20 mA).

Fig. 13 DSC curves for the Fe-Co sprayed coating films at various $T_s$ values.

Fig. 14 Volume fractions of the amorphous phase for the Fe-Co sprayed coating films as a function of $T_s$.

3.2 Tensile tests

Figure 15 shows the fracture surfaces of the four specimens around the K-thermocouple region after tensile tests at each $T_s$ value. Small fractured areas with dark colored cohesive/adhesive agent were observed at $T_s = 350, 401, 425$ and $451^\circ C$, thereby indicating that the fracture was caused by the sprayed coating film peeled from the dolly. However, almost entire fractured area having rough metallic luster surface was created by the fracture inside the sprayed coating film.

Figure 16 shows the average cohesive/adhesive strength of the four specimens around the K-thermocouple region (as previously shown in Fig. 3) as a function of $T_s$. An increase in $T_s$ between 250 and $450^\circ C$ led to increased cohesive/adhesive strengths ($\geq 19$ MPa, minimum value at $300^\circ C$, maximum of $27$ MPa at $400^\circ C$). This maximum can result from the observed decrease in porosity in both the boundary and inside regions, as previously shown in Fig. 10. A further increase in $T_s$ ($\geq 400^\circ C$) led to lower cohesive/adhesive strengths, which may be due to partial crystallization and embrittlement accompanying crystallization of the Fe-based amorphous phase, as previously shown in Fig. 12.\(^3,4\)

4. Discussion

In order to obtain large volume fractions of the amorphous phase and high cohesive/adhesive strengths between the sprayed coating films and the substrates, control over $T_s$ may be an important factor.\(^3,6\)

The splat morphology of the sprayed particles has been reported to be a useful parameter to estimate optimum thermal spraying conditions.\(^5,6\) The splat morphology of the sprayed particles changed from irregular splash to a disk shape at the transition temperature.\(^7\) It is therefore suggested that the cohesive/adhesive strength is strongly influenced by $T_s$.

Figure 17 shows the morphological changes of a Fe-Co thermal spray droplet on a flat SS400 substrate (90 mm × 90 mm × 6 mm) at various $T_s$ values. In this case, the thermal spraying gun was scanned only one time. Figure 18 shows schematic descriptions of the shapes and cross-sectional optical micrographs of the thermal spray droplets represented in Fig. 17. The droplet splashed irregularly at $T_s \leq 249^\circ C$, as shown in Figs. 17(a) and 17(b). The splat morphology changed to a disk shape at $T_s = 300^\circ C$, the transition point. At this temperature, the disk-shaped droplets showed very smooth surfaces with metallic luster, with some small spots that may be small crystallites (indicated by arrows in Figs. 17(c) and 17(d)). At $T_s = 400^\circ C$, the droplet was also disk-shaped, although many small branches were observed, as shown in Fig. 17(e). It has been reported that these branches can be formed when the relative wettability between the droplet and the substrate increases.\(^7\) Small spots on the surface of the droplet were rarely observed at $T_s = 400^\circ C$. This temperature yielded the maximum volume fraction of the amorphous phase, as previously shown in Fig. 14. When $T_s$ was increased to $450^\circ C$, some spots were observed on the surface of the droplet and many long branches which shrank by the surface tension effect were observed around it, as shown in Fig. 17(f). This may be attributed to the decrease of
the relative wettability between the droplet and the substrate by oxide generation on the surface of the SS400 substrate and the sprayed particles, resulting in partial crystallization and embrittlement accompanying crystallization of the Fe-based amorphous phase. In this temperature region, the adhesion failure by this droplet may be occurred in the sprayed coating film, this resulting in the gradual increase in the porosity. On the basis of the results shown in Figs. 14 and 17, it can be concluded that 300°C is the transition temperature for the morphological change of the sprayed droplet, while the optimum temperature leading to a maximum volume fraction of the amorphous phase is about 400°C.

Figure 19 shows the relationships between the porosity (in both the boundary and inside regions), cohesive/adhesive strength, and volume fraction of the amorphous phase in the Fe–Co sprayed coating films as a function of $T_s$.

At $T_s \leq 300°C$, the volume fractions of the amorphous phase in the sprayed coating films were high ($\geq 90\%$). However, a high porosity ($>4.3\%$) in the boundary region between the sprayed coating film and the substrate was observed. This may be the result of the low wettability of the sprayed particles showing irregular splash shape.$^{5,6}$ In this temperature region, both the volume fraction of the amorphous phase and the cohesive/adhesive strength decreased with increasing $T_s$.

At $T_s$ values ranging from 300 to 375°C, the porosity in the boundary region decreased to about 3%, and this can be attributed to the increase in the wettability of the sprayed coating film. This resulted in the gradual increase in the porosity.
particles as a result of the morphological change from splash to disk shape.\(^5\),\(^6\)

At \(T_s\) values ranging from 375 to 400°C, the porosity in both the boundary and inside regions dropped with decrease in viscosity of the sprayed particles, whereas the volume fraction of the amorphous phase increased with \(T_s\), this resulting in an enhancement of the cohesive/adhesive strength up to 27 MPa. In general, the volume fraction of the amorphous phase was found to be strongly dependent on the cooling rate of the sprayed particles; when \(T_s\) is increased, the cooling rate of the sprayed particles should decrease. In this temperature region, the amount of heat transfer may be substantially increased because of the lower porosity in both the boundary and inside regions, resulting in an improved
cooling rate of the sprayed particles. Therefore, the optimum $T_s$ value leading to a maximum cooling rate of the sprayed particles was determined to be about 400°C.

At $T_s \geq 400°C$, the increase in the porosity was accompanied with a drop in the volume fraction of the amorphous phase with $T_s$, resulting in a decrease in the cohesive/adhesive strength to about 20 MPa. In this temperature region, the heat transfer may be negatively affected by a lower wettability as a result of oxide generation on the surface of the SS400 substrate and the sprayed particles, this resulting in a partial crystallization and embrittlement accompanying crystallization of the Fe-based amorphous phase.

5. Summary

Control of $T_s$ is the most important point to achieve Fe$_{30}$Co$_{36}$Si$_{14}$B$_{20}$Nb$_4$ metallic glass coating films with superior properties such as high hardness, high corrosion resistance, and soft magnetic properties.

The volume fraction of the amorphous phase of the sprayed coating films was found to be strongly dependent on the cooling rate of the sprayed particles. The volume fraction of the amorphous phase was found to increase for $T_s$ ranging from 375 to 400°C. In this temperature region, the heat transfer may be substantially improved with $T_s$ as a result of the lower porosity in both the boundary and inside regions, resulting in a faster cooling of the sprayed particles. Therefore, the optimum $T_s$ leading to a maximum cooling rate of the sprayed particles was determined to be around 400°C at which cohesive/adhesive strength was also maximum.

REFERENCES