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<td>Kobayashi, Akira; Kuroda, Toshio; Kimura, Hisamichi; Inoue, Akihisa</td>
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Influence of Spraying Conditions on Properties of Zr-Based
Metallic Glass Coating by Gas Tunnel Type Plasma Spraying†

KOBAYASHI Akira *, KURODA Toshio *, KIMURA Hisamichi ** and
INOUE Akihisa **

Abstract

Metallic glass has excellent functions such as high strength and high corrosion resistance. However, as metallic glass is an expensive material, a composite material is preferred for the cost performance. The gas tunnel type plasma spraying is useful for obtaining high quality metallic glass coatings. In this study, Zr-based metallic glass (Zr55Cu30Al10Ni5) coatings were produced by gas tunnel type plasma spraying, and the influence of spraying conditions on the properties of Zr-based metallic glass coatings were investigated. The Zr-based metallic glass coatings of about 200 μm in thickness were dense with a Vickers hardness of about Hv = 500-600 at a plasma current of about 250A. The amorphous phase of this metallic glass coatings seem to be maintained in good condition.

KEY WORDS: (Zr-based metallic glass), (Sprayed condition), (Fusion materials), (Gas tunnel type plasma spraying), (Microstructure) (Vickers Hardness), (XRD)

1. Introduction

Among various functional materials, metallic glass has excellent physical and chemical functions such as high toughness and corrosion resistance [1-3]. Therefore it is one of the most attractive advanced materials on which many researchers have conducted various developmental research studies. However, as metallic glass material is expensive material, the application for small size parts has been carried out only in limited industrial fields. In order to widen the industrial application fields, a composite material is preferred for the cost performance.

In the coating processes of metallic glass with the conventional deposition techniques such as plasma sputtering, there is a problem of the difficulty in forming thick coatings due to their low deposition rate. Thermal spraying method is one of potential candidates to produce metallic glass coatings on a large scale at low cost, and therefore can widen the application fields.

The gas tunnel plasma spraying is one of the most effective technologies for depositing high quality ceramic coatings [4,5] and synthesizing functional materials [6], because the plasma jet has high speed and high energy density under various operating conditions [7]. The performances of gas tunnel type plasma jets were clarified in previous studies [8,9]. Because of its superior advantages compared with other conventional plasma jets [10], this plasma has great possibilities for various applications in thermal processing [7]. High quality ceramic coatings were fabricated by the gas tunnel type plasma spraying method [11]. For example, typical alumina coatings produced had a high Vickers hardness of Hv = 1200-1600 [12]. Also, it is possible to produce sprayed coatings of refractory materials such as W [13]. In another application, the gas tunnel type plasma jet was applied for the surface nitridation of titanium. This experiment also investigated the possibility of the speedy formation of a high functionally thick TiN coating [14, 15]

Regarding the metallic glass coatings, Fe-based metallic glass thick coatings were easily produced by gas tunnel type plasma spraying16). The characteristics of the metallic glass coatings were investigated in the previous study, and new results by plasma spraying method were obtained. The amorphous phase of this
Influence of Spraying Conditions on Properties of Zr-Based Metallic Glass Coating

The Fe-base metal glass coatings of about 200 μm in thickness were dense with a Vickers hardness of about Hv =1100 at a plasma current of 300 A.

In this study, Zr based metallic glass coating was deposited on a stainless-steel substrate by gas tunnel plasma spraying, using Zr based metallic glass powder (Zr55-Cu30-Al10-Ni5) as starting material. The influence of spraying conditions on the properties of the Zr-based metallic glass coating was investigated. The plasma torch was operated at a power level of 10-25 kW and the arc current was changed from I = 200 A to 400 A. The spraying distance of 40-45 mm was used.

The microstructure and the morphology of the cross section of as-sprayed metallic glass coatings were examined. The structure of the metallic glass coatings was analyzed by XRD method. The Vickers hardness was measured on the cross section of the coating. (The Zr-based metallic glass powder was externally fed from the torch exit into the plasma flame in order to melt the metallic glass powder effectively.)

2. Experimental Procedure

2.1 Preparation of metal glass coatings

The gas tunnel type plasma spraying torch is shown schematically in Fig.1. The powder was atmospherically plasma-sprayed (APS) onto a flat 304 stainless steel substrate, and the metallic glass coating was formed. Zr-based metallic glass powder can be axially fed into the plasma flame through a hole on the center axis of the cathode, but, the powder was provided from the outside of the gas divertor nozzle (20mm in diameter) of the torch in this study. In this case also, Zr-based metallic glass powder was fed inside the plasma flame and melted effectively.

Table 1 Spraying conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Arc current</td>
<td>150-400 A</td>
</tr>
<tr>
<td>Voltage</td>
<td>40-50 V</td>
</tr>
<tr>
<td>Spraying distance</td>
<td>40, 45 mm</td>
</tr>
<tr>
<td>Working gas flow rate (Ar)</td>
<td>200 l/min</td>
</tr>
<tr>
<td>Powder feed gas flow rate</td>
<td>10 l/min</td>
</tr>
<tr>
<td>Powder feed rate</td>
<td>12 g/min</td>
</tr>
<tr>
<td>Traverse number</td>
<td>16 times</td>
</tr>
<tr>
<td>Spraying time</td>
<td>24 s</td>
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2.2 Zr-based metallic glass powder

Zr-based metallic glass powder (Zr55-Cu30-Al10-Ni5) was used in this investigation. The morphology of the Zr-based metallic glass powder is shown in Fig.2. This was taken with a scanning electron microscope (SEM). The element composition of the Zr-based metallic glass powder is shown in Table 2.

![Fig.1 Gas tunnel type plasma spraying used in this study (L=spraying distance).](image1)

![Table 2 Zr-based metallic glass composition. (Zr-Cu-Al-Ni)](image2)

<table>
<thead>
<tr>
<th>Element</th>
<th>Content (at %)</th>
<th>Size (μm)</th>
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<tbody>
<tr>
<td>Zr</td>
<td>55</td>
<td>40-60</td>
</tr>
<tr>
<td>Cu</td>
<td>30</td>
<td>(18)</td>
</tr>
<tr>
<td>Al</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>5</td>
<td></td>
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</tbody>
</table>

![Fig.2 SEM micrographs of Zr-based metallic glass powder.](image3)
electron microscope (SEM). The particles are a spherical type with sizes ranging from 10 μm to 25 μm. The composition of this Zr-based metallic glass powder is shown in Table 2: Fig. 3 shows the XRD pattern of this Zr-based metallic glass powder. This XRD pattern of metallic glass powder showed a broad peak at about 38 degree corresponding to the amorphous phase, although it contained some small crystalline peaks indicated by arrows.

The thermal property of the Zr-based metallic glass powder was analyzed by the Differential Scanning Calorimetry (DSC). Glass translation temperature (Tg) and crystallization temperature (Tx) of the metallic glass powder were about 700K and 760K, respectively. The temperature difference ΔTx (super cooled liquid region temperature) between Tg and Tx was a little lower than the ribbon material produced by the liquid rapid cooling method.

2.3 Characterization of Zr-based metallic glass coatings

Microscopic observation of the coatings was performed using an optical microscope (OM) and an ERA8800FE scanning electron microscope (SEM). The average thickness of the sprayed coatings was determined through the cross section of the coating. The samples embedded in epoxy resin were polished on metallographic papers, and polished with alumina paste (1.0, 0.3, and 0.05 μm, respectively). All samples were coated with a thin film of gold using an Au ion sputtering system.

Phase constituents of metallic glass coating were identified by using a JEOL JDX-3530M X-ray diffracto-meter with CuKα radiation source at a voltage of 40 kV and a current of 40 mA. Vickers microhardness measurement was made on polished sample surfaces with a load of 50g. Indentation parameter was set at 20s loading time. Average hardness was derived from five measurements.

3. Results and Discussion
3.1 Microstructure of Zr-based metallic glass coatings

Fig.4 shows the SEM micrographs of the cross-section of Zr-based metallic glass coatings sprayed at spraying distance of L=45mm, for the plasma currents of 150 A and 200A respectively. As shown in Fig.4 (a), the coating thickness was about
Influence of Spraying Conditions on Properties of Zr-Based Metallic Glass Coating

3.2 Effect of plasma current on Zr-based metallic glass coating.

At a shorter spraying distance, thicker coatings were obtained. Zr-based metallic glass coatings were formed at the spraying distance of L=40mm, and the effect of plasma current on the coating quality was examined.

Fig.7 shows the SEM micrographs of the cross-section of Zr-based metallic glass coatings sprayed at a distance of L=40mm, for the plasma currents of 200 A, 250A, 300A and 350A respectively. As shown in Fig.7 (a)-(d), the coating thickness was increased from 200 µm to 300 µm with an increase in the plasma current (200 A-350A). Thus, the increase in plasma current enhanced the deposition rate of the Zr-based metallic glass coating.

Regarding the pores in the coating, for a small current of 200 A, and large current of 350A, some pores were observed in the cross section of the as sprayed coatings. But for 250A and 300A, there were few pores and dense coatings were obtained, and represent a proper conditions for obtaining a good quality coating. Also the bonding between the coating and the substrate was good at the interface in these photographs.

Fig.8 shows the XRD patterns from the surface of the coating shown in Fig.7. The amorphous phase was appeared at the broad peak with maximum at about 38 degree at the current, 200 A, 250A and 300A, but the shape was destroyed at 350A. And many crystalline peaks were observed at the same time (similar to Fig.5). some crystalline oxides of Zr or intermetallic compounds were formed during the plasma spraying.

The XRD pattern at 250A shows a broad peak with a maximum at about 38 degree. There also appears the oxidation peak of ZrO$_2$ at about 30 degree (red circle marks in Fig.8), this means that oxidation occurred during plasma spraying process. It seems to be at a minimum intensity at 250A.

These results show that coating at 250A will be best for good coating, although the intensities of these crystalline peaks were a little lower. This suggests that the coating quality was improved by increasing the plasma current.
Fig. 7 SEM micrographs of the cross-section of Zr-based metallic glass coatings sprayed at spraying distance of L=40mm, for the plasma currents of 200 A, 250A, 300A and 350A respectively.

Fig. 8 XRD patterns from the surface of the coating as shown in Fig. 7....

Fig. 9 shows the dependence of the oxidation ratio to amorphous phase on the current of the power input to the plasma spraying torch. Here the dependence of the oxidation ratio to amorphous phase was determined from the ratio of the intensity of ZrO2 diffraction peak at 30 degree (see Figs. 5 and 6) to that of the amorphous phase of about 38 degree. The oxidation ratio decreased with the plasma current from 1.2 to 0.8. This suggests that the oxidation was suppressed by the proper plasma energy, but too much plasma power would decompose the Zr based metallic glass and would form an oxide of metal Zr.

Fig. 9 Dependence of the oxidation ratio to amorphous phase and thickness of the coating on the plasma current.
Influence of Spraying Conditions on Properties of Zr-Based Metallic Glass Coating

3.3 Vickers hardness of the Zr based metallic glass coating

The Vickers hardness of metallic glass coatings formed by gas tunnel type plasma spraying are shown in Fig.10. The Vickers hardness was rather lower than that of the bulk materials of Zr based metallic glass because of the pores. The bulk materials of this kind of Zr based metallic glass showed the Vickers hardness of around Hv = 550-600, while the Vickers hardness of metallic glass coatings was estimated approximately Hv = 500-550, (wherever measured in the cross section of the coating.) This means the sprayed particle was melted and heated more than the melting point and some parts of the particle were decomposed, and many pores were formed, which will also occur during the re-crystallization or the oxidation after spraying.

Thus, Zr based metallic glass coatings more than 200 µm in thickness were formed by gas tunnel type plasma spraying. Greater amount of amorphous phases could be retained at spraying current of 200A than at higher currents. If we use much more uniform size powder, it will increase the possibility of forming high quality metallic glass coatings with less crystalline content, which is expected to be useful for various industrial applications.

4. Conclusions

Zr-based metallic glass coatings were sprayed by gas tunnel type plasma spraying and the influence of spraying conditions on the properties of the coatings were clarified; the results are as follows:

(1) A Zr based metallic glass sprayed coating of in thickness of about 200 µm was obtained at 200A, which depending on the spraying parameters. At higher plasma current, more than 200 µm in thickness was achieved. This coating has some pores, but the porosity is low, 5% or less. From the XRD pattern of the coating, a broad amorphous peak at about 38 degree was observed, the same as the powder in the XRD pattern.

(2) XRD analyses showed that Zr based metallic glass particles had some decomposition or oxidation during deposition, in spite of the presence of amorphous phases in the sprayed coatings.

(3) The Vickers hardness of the metallic glass coating was around Hv=500-600, which is lower than that of the bulk metallic glass materials. But, Vickers hardness at high plasma current, was increased up to about Hv=700 under a different condition.

(4) Metal glass coating formed on a stainless-steel substrate was of dense morphology with low porosity at plasma current of 200-400A in about 200 µm thickness.

(5) The Vickers hardness of metal glass coating was Hv0.2=1000-1100, in the cross section of all coating regions at plasma current of 300 A. This hardness was similar to that of the original powder.

Acknowledgements

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References

12) A.Kobayashi, Property of an Alumina “Coating
