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Microstructure and Property of Zr-Based Metallic Glass Coating Formed by Gas Tunnel Type Plasma Spraying

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Metallic glass has excellent functions such as high strength and high corrosion resistance. Therefore, it is one of the most attractive materials, and various developmental research works have been conducted by many researchers. However, the metallic glass material is expensive to use, and a composite material is preferred for the industrial application. Thermal spraying method is one of potential candidates to produce such metallic glass composites. The gas tunnel type plasma system, which has high energy density and efficiency, is useful for smart plasma processing to obtain high quality ceramic coatings such as Al_2O_3 and ZrO_2 coatings. In this study, the Zr-based metallic glass (Zr60Cu15Al15Ni7.5Co2.5) coatings were produced by the gas tunnel type plasma spraying, and their microstructure and mechanical properties were investigated. The Zr-based metallic glass coatings of 50 μm in thickness were formed densely with Vickers hardness of *Hv*=600-700.

Keywords: Zr-based metallic glass, Sprayed coating, Gas tunnel type plasma spraying, Microstructure, XRD, Vickers hardness.

1. Introduction

Metallic glass has excellent physical and chemical functions such as high strength and high corrosion resistance [1-4]. Therefore, as one of the most attractive advanced materials, many researchers have conducted many attractive researches and development works. Metallic glass is expected to be used as functional materials. However, as the metallic glass material is expensive, the application for small size parts has been carried out only in some 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 [5] and laser-assisted methods [6], it is difficult to form a thick coating due to their low deposition rate. Thermal spraying method is one of potential candidates to produce metallic glass composites. Because of the cost-effectiveness method compared to other conventional ones, metallic glass coatings can be applied to the longer parts and therefore widen the application field.

The gas tunnel plasma spraying is one of the most important technologies for depositing high quality ceramic coating [7,8] and synthesizing functional materials [9], because the plasma jet has high speed and high energy density under various operating conditions [10]. The performances of gas tunnel type plasma jets were clarified in previous studies [11,12]. Because it is superior characteristics to other conventional plasma jets [13], this plasma has great possibilities for various applications in thermal processing. As to the formation of high performance materials, high quality ceramic coatings were fabricated by the gas tunnel type plasma spraying method [14-16].

In this study, the Zr based metallic glass coating was deposited on the stainless-steel substrate by gas tunnel plasma spraying, using Zr based metallic glass powder as starting material. The microstructure and the morphology of the cross section of as sprayed metallic glass coatings were examined. Also the structure of the metallic glass coatings was analyzed by XRD method. The Vickers hardness was measured on the cross section of the coating.

2. Experimental Procedure

2.1 Gas tunnel type plasma spraying

By a gas tunnel type plasma spraying torch which is shown schematically in **Fig.1**, the powder was atmospherically plasma-sprayed (APS) on a flat 304 stainless steel substrate. Zr-based metallic glass powder

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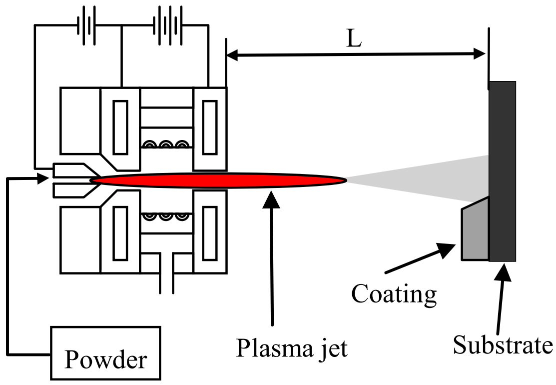

Fig. 1 Gas tunnel type plasma spraying used in this study (L=spraying distance).

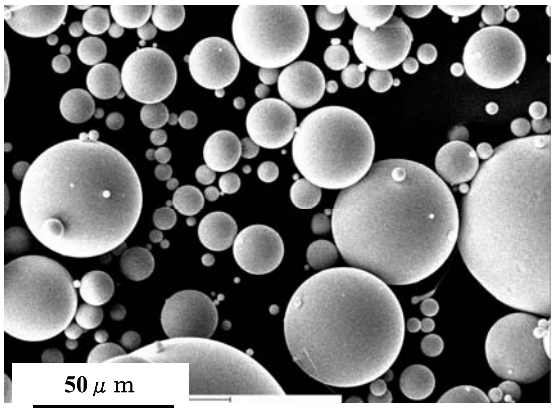

Fig.2 SEM micrograph of this Zr-based metallic glass powder.

Table 1 Spraying conditions.

Arc current	300A
Voltage	40-50V
Spraying distance	45 mm
Working gas flow rate (Ar)	170 l/min
Powder feed gas flow rate(Ar)	10 l/min
Powder feed rate	24 g/min
Traverse number	4 times
Spraying time	10 s

Table 2 Zr-based metallic glass composition. (Zr-Cu-Al-Ni-Co)

Element	Content (at %)	Size (μm)
Zr	60	5-50
Cu	15	
Al	15	
Ni	7.5	
Co	2.5	

was axially fed inside the plasma flame to melt the metallic glass powder effectively.

Table 1 shows the spraying conditions under those experiments carried out. The plasma torch was operated at power levels up to 20kW and the arc current was fixed at I = 300 A. The Ar plasma jet was generated with an argon gas flow of 170 l/m. The torch was maintained at a spray distance of 45 mm from the substrate surface. The powder feed rate was 24 g/min. The stainless steel substrate was fixed for 16 s (0 traverse), or was traversed 4 times during the spraying time of 10 s. The substrate of dimension of 50 x50 x2 mm^3 was grit-blasted with alumina grit on one side.

The morphology of this Zr-based metallic glass powder is shown in **Fig.2**. It is clear from SEM micrographs that the particle is a spherical type and the size of the powder ranging from 5 μm to 50 μm. The compositions of this Zr-based metallic glass (Zr-Cu-Al-Ni-Co) powder used in the experiment are shown in **Table 2**: The Zr content was 60%, and Cu and Al was 15% respectively, with some addition of Ni and Co. **Fig. 3** shows the XRD pattern of this Zr-based metallic glass powder. This XRD pattern of metallic glass powder showed that the broad peak at about 38 degree corresponds to the amorphous phase of metallic glass. Also, it contains some crystalline peaks.

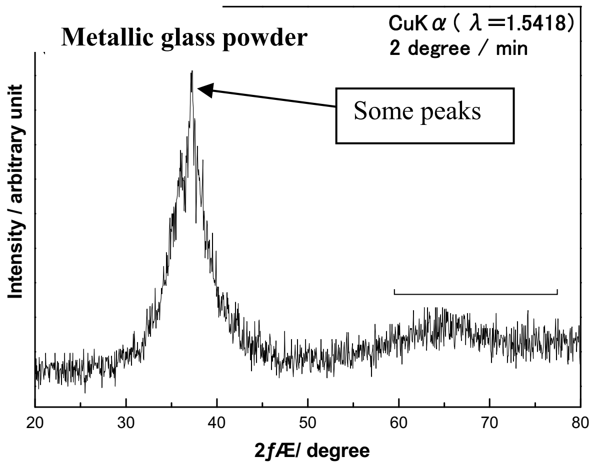

Fig.3 XRD pattern of this Zr-based metallic glass powder.

The thermal property of the Zr-based metallic glass powder was analyzed by the Differential Scanning Calorimetry (DSC). Glass Translation Temperature (Tg), Crystallization Temperature (Tx) of the metallic glass powder was about 700K, 760K. Super Cooled Liquid Region Temperature (ΔTx) was a little lower as compared to the ribbon material produced by the liquid rapid cooling method.

2.2 Analysis of sprayed coatings

Microscopic observation of the coatings was performed using an optical microscopy and the average thickness of the sprayed coatings was determined through the cross section of the coating. The surface morphology of the feedstock powders and cross-sectional microstructure of the metallic glass coating was examined by an ERA8800FE scanning electron microscope. The samples mounted in epoxy resin were polished by using Grinder-polisher, and buffed with alumina paste (1.0, 0.3, and 0.05 μm, respectively). All samples were coated with a thin film of gold using gold ion sputtering system.

Phase constituents of metallic glass coating were identified by using a JEOL JDX- 3530M X-ray diffractmeter 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 on each material. Indentation parameters were set as calculated 20s loading time. Average thickness was derived from five measurements at different position in the same test piece.

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 current of 300 A.

In the Zr-based metallic glass coating sprayed by 4 times scanning of the substrate, there are some pores on the cross section of as sprayed coatings, but still low porosity of 5% or less. And the coating was a little thin: the coating thickness was 50 μm. The bonding between the coating and the substrate was good.

The XRD pattern from the surface of the coating shown in Fig.4 is shown in **Fig.5**. In this case, there were also some crystalline peaks corresponding to Zr, Cu, Al, Ni, etc in the XRD pattern of the coating. And a broad amorphous phase with a peak maximum at about 38 degree was observed in the pattern which is shown in Fig. 3. But many crystalline peeks were observed at the same time (circle marks in Fig.5).

When the metallic glass powder is injected into the plasma jet, particles in the high temperature region are heated up to fully melted or partially melted states and may be simultaneously decomposed. So, there is the possibility of the crystalline peaks of any other composite oxidized materials, but there were no peaks from Cu or Al detected in the XRD spectra. **Fig.6** shows the comparison of XRD patterns between as sprayed coating and Zr based metallic glass foil after the heat treatment (734K, 3.6ks). There are similarly

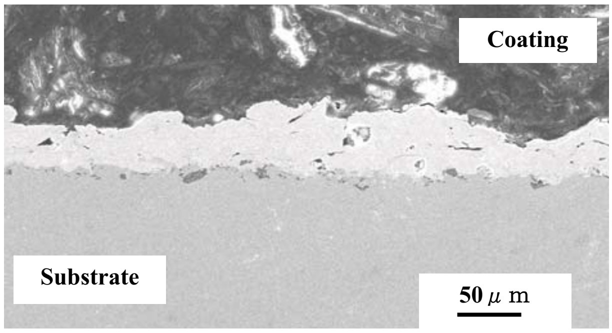

Fig.4 SEM micrographs of the cross-section of the metallic glass sprayed at 300A, on the traversed substrate.

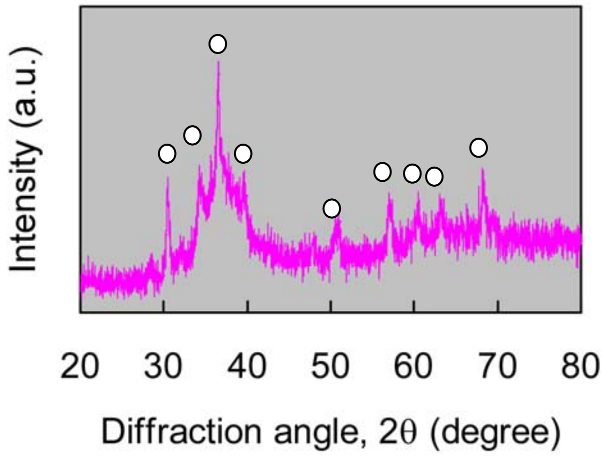

Fig.5 XRD patterns of the metallic glass coating sprayed on stainless-steel substrate.

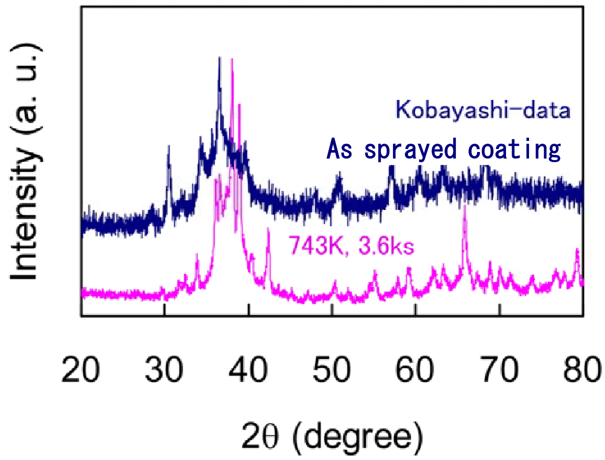

Fig.6 Comparison of XRD patterns between as sprayed coating and Zr based metallic glass foil after the heat treatment (734K, 3.6ks).

The occurrence of the decomposition attributes to the recrystallization by the formation of the alloy and/or composite from the amorphous phases in the deposit formation on the substrate. These results will lead to the increase in the Vickers hardness of metallic glass coatings.

3.2 Vickers hardness of the metallic glass coating

Fig.7 shows the Vickers hardness of metallic glass coatings formed by the gas tunnel type plasma spraying. In the case of the bulk materials of this kinds of Zr based metallic glass, Vickers hardness is around Hv= 600. This hardness value was similar to that of the original powder: (a).

The Vickers hardness of the metallic glass coating (b) was rather higher compared to the as received powder. The Vickers hardness of metallic glass coatings is approximately Hv= 700, 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 part of the particle was decomposed, and there will be occurred the recrystallization or the oxidization after spraying.

Thus, Zr based metallic glass coatings were formed by the gas tunnel type plasma spraying. More amorphous phases would be realized by choosing the optimized spraying conditions, through control of relative motion of substrate with the torch. The results indicate the possibility to form high quality metallic glass coatings, which is expected to be useful for various industrial applications.

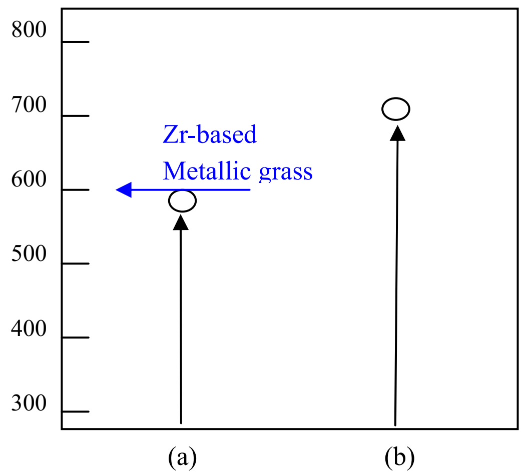

Fig.7 Comparison of Vickers hardness between Zr-based metallic glass material (a) and the Zr-based metallic glass coating on the 4 times traversed substrate (b).

4. Conclusions

The Zr-based metallic glass coatings were produced by gas tunnel type plasma spraying and the following results were obtained.

(1) The Zr base metallic glass sprayed coating in thickness of about 50μm, which depending on the spraying parameters.

(2) XRD analysis confirms the presence of amorphous phases in the sprayed coatings and Zr base metallic glass particles had some decomposition of oxidation during deposition.

(3) The Vickers hardness of metallic glass coating was approximately Hv_{50} = 700, in the cross section of all coating regions. , which is higher than that of the powder.

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