Properties of Fe-base Metal Glass Coatings Produced by Gas Tunnel Type Plasma Spraying†

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Abstract

Metal glass has excellent functions such as high toughness and corrosion resistance. Therefore it is one of the most attractive materials, and many researchers have conducted various developmental research works. However, the metal glass material is expensive and a composite material is preferred for the industrial application. Thermal spraying method is one of potential candidates to produce metal 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 alumina (Al_2O_3) and zirconia (ZrO_2) coatings. Also, the gas tunnel type plasma spraying can produce metal glass coatings. In this study, the Fe-base metal glass coatings were produced by gas tunnel type plasma spraying, and the microstructure and mechanical properties were investigated. The Fe-base metal glass coatings of about 200μm in thickness were dense with a Vickers hardness of about Hv =1100 at plasma current of 300A. The abrasive wear resistance of Fe-base metal glass coating was higher than the SUS substrate.

KEY WORDS: (Metal Glass), (Gas Tunnel Type Plasma Spraying), (Fe Based Materials), (Microstructure), (XRD), (Hardness).

1. Introduction

Metal 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, and many researchers have conducted various developmental research works. For example, metal glass is expected to be used as a functional material at high temperature. However, as the metal 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 metal glass with the conventional deposition techniques such as plasma sputtering and laser-assisted methods, there is a problem of the difficulty of forming thick coatings due to their low deposition rate. Thermal spraying method is one of the potential candidates to produce metal glass composites. Because of the cheaper method compared to other conventional ones, metal 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 high quality ceramic coating and synthesizing functional materials, because the gas tunnel type plasma jet has high speed and high energy density under various operating conditions. Also, it operates at a high voltage and with easy control of power. The performances of gas tunnel type plasma jets were clarified in previous studies[4-6]. For example, a gas tunnel type plasma jet, of the 200 kW class, has a high temperature of more than 20,000K and high energy density. Also, the thermal efficiency of the gas tunnel plasma jet is about 80 %, which is much higher than that of a conventional type of plasma jet (≈ 50 %).

The property is superior to the properties of other conventional type plasma jets[7]. Therefore this plasma has great possibilities for various applications in thermal processing[8]. As to the formation of high performance materials, high quality ceramic coatings were obtained by the gas tunnel type plasma spraying method[9,10]; for example, typical alumina coatings produced had a high Vickers hardness of *Hv* =1200-1600[11]. Also, it is possible to produce sprayed coatings of refractory materials[12] such as tungsten (W). In another application, the gas tunnel type plasma jet was applied for the surface

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Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

nitridation of titanium. This experiment also investigated the possibility of the speedy formation of a high functionally thick TiN coating [13,14]

Also, Fe-base metal glass coatings were produced by the gas tunnel type plasma spraying, which was used as the smart plasma spraying method, and the fundamental characteristics (the structure and the hardness) were investigated. The Fe-base metal glass coatings of 100μm in thickness were formed to be dense with Vickers hardness of Hv =1000 at plasma current of 300A[15].

In this study, the Fe-base metal glass coating was formed on a stainless-steel substrate by the gas tunnel plasma spraying using Fe based metal glass powder as the spraying material. The formation process and some mechanical properties of the metal glass coating were investigated. The microstructure and surface morphology of the metal glass coatings were examined. The porosity and the crystallinity were examined. For the mechanical properties the Vickers hardness was measured on the cross section of the coating. The abrasive wear test was also measured and the value was compared to that of the SUS substrate.

2. Experimental

2.1 Preparation of metal glass coatings

The metal glass powder was atmospherically plasma sprayed (APS) on a flat 304 stainless-steel substrate by using a gas tunnel type plasma spraying torch which is shown in **Fig. 1**. Fe-based metallic glass powder was internally fed inside the plasma flame stream to obtain a maximum temperature because metal glass has high melting point ≈ 2000 °C.

Experiments were carried out under the spraying conditions as shown in **Table 1**. The plasma torch was operated at power levels up to 20kW and the arc current was chosen I =200, 300 and 400 A, respectively. The plasma jet was generated with the aid of argon gas, which was supplied at 170 l/min. The torch was maintained at a spray distance of 50 mm from the substrate surface. The powder injection was internal to the torch and directed parallel to the plasma flow and parallel to the torch trajectory. The powder feed rate was about 32 g/min.

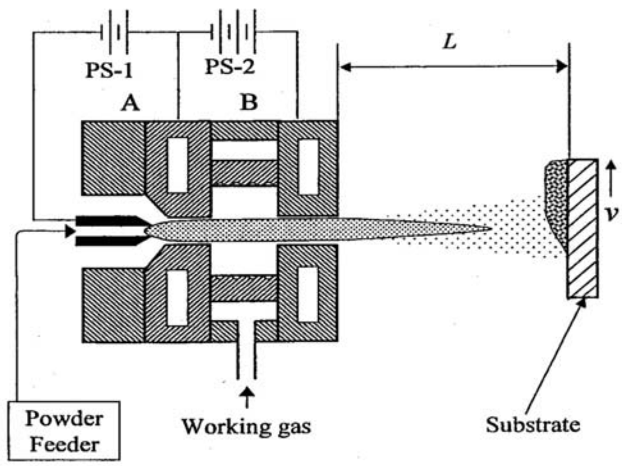

Fig. 1 Schematic diagram of gas tunnel type plasma spraying torch. L: spraying distance.

Table 1 Spraying condition.

Arc current	200, 300, 400 A
Voltage	40-50 V
Spraying distance	50 mm
Working gas Ar flow rate	120 l/min
Feed gas flow rate	8 l/min
Powder feed rate	32 g/min
Traverse number	16 times
Spraying time	30 s

The spray configuration was a combination of a rotating sample holder and fixed torch uniformly. The defined substrate was traversed 16 times, and the spraying time was 30s. To avoid adhesion problems due to different thermal expansion coefficients between the coating and the substrate and to limit the stress level, cooling gas of nitrogen was applied to the spraying configuration to lower the coating temperature during deposition.

As a metal glass powder, Fe-based metallic glass powder (Fe-B-Si-Cr-Mo) was used in this study. The components of this Fe-based metallic glass powder used in the experiment are shown in **Table 2**. The Fe content was 50 at% or more and there were 20 at% Mo, and some B content.

The SEM micrograph of this Fe-based metallic glass powder is shown in **Fig. 2**. It is clear from the SEM micrographs that the particles are of a spherical type. The particle size of the powder was 30-60 μm. As for the properties of the Fe-based metallic glass: the density is similar to Fe. Yield strength is 700 MPa. Stable crystallinity is at 560°C. Elastic modulus was 6000 MPa. Hardness was Hv_{50} =990.

The grit blasted substrates were used for plasma spraying of metal glass. The substrates of dimension 50 x50 x2 mm^3 were grit-blasted with alumina grit on one side to clean and roughen the surface (5-7 μm), followed by ultrasonic cleaning using acetone to remove any grease and other contaminations.

Table 2 Fe-based metallic glass composition. (Fe-Si-B-Cr-Mo)

component	Content (at %)	Size (μm)
Fe	50.26	30-60
Si	2.41	
B	2.62	
Cr	23.86	
Mo	20.85	

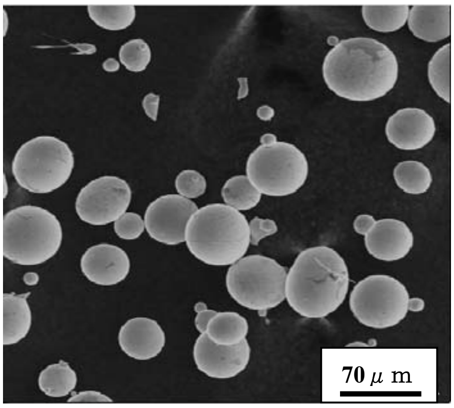

Fig. 2 SEM micrographs of metal glass feedstock powder. Spherical shape “30-50 μm”.

2.2 Characterization techniques

Microscopic observation of the coatings was performed using an optical microscope. Each specimen was mounted in conductive resin, ground with SiC paper and finally polished with 0.05 micron alumina slurry. The average thickness of the sprayed coatings was observed by optical microscope. Also the porosity on the cross section of the metal glass coating was measured for the different arc currents.

The surface morphology of the feedstock powder and the metal glass coating cross-section was examined by an ERA8800FE scanning electron microscope. The examined cross-section samples were mounted in epoxy resin using (HMP-Molding hand press, Wingo Seiki Co., Ltd. Osaka, Japan), polished by using (Buehler Metaser V Grinder-polisher) and buffed with alumina paste (1.0, 0.3, and 0.05 μm, respectively) to obtain a mirror finished surface. All examined samples were coated with a thin film of gold using a gold ion sputtering system (Thermo VG Scientific Polaron Sc7620 Sputter Coater) to make them electrically conductive before SEM observation.

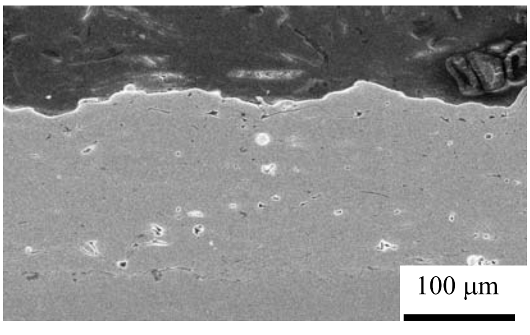

Fig. 3 SEM micrographs of the cross-section of the metal glass sprayed at: plasma current of 300 A. Carrier gas of Ar flow rate: 8 l/min, Ar plasma gas flow rate: 120 l/min, spray distance: 50 mm, and spray time: 30 sec.

Phase constituents of feedstock powder and metal glass coating were identified by using a JEOL JDX-3530M X- ray diffractmeter system with CuKα radiation source at voltage of 40 kV and current of 40 mA.

Micro Vickers hardness measurements were made on polished sample surfaces using a load of 50 g on each material. Indentation parameters were set as 20 s loading time and average thickness was derived from five measurements.

The abrasive wear test was carried out using SUGA Abrasion Tester, which follows the ISO standard. The size of sample was50x50 mm^2, and the load on the wheel covered with SiC emery paper was 29.42N. The abrasive wear test was done at different loading times for both the metal glass coating and SUS substrate.

3. Results

3.1 Microstructure of plasma-sprayed metal glass coating

Figure 3 shows a SEM micrograph of the cross-section of a plasma-sprayed Fe-Si-B-Cr-Mo metal glass coating sprayed at plasma current of 300 A. In this case, the spraying distance was L =50 mm. The primary plasma gas (Ar) flow rate was 120 l/min, and the powder feed rate was 32 g/min (feed gas flow rate 8 l/min) during the spraying time of 30 sec.

The coating thickness is 180 μm and very dense at 300 A. A thick coating with low porosity was obtained at large plasma power. It was revealed that the Fe-based metal glass coating was compact, smooth, dense, free from pores, adhering well, and with no cracking. The absence of pores from metal glass coating indicated that the metal glass particles did not undergo decomposition during plasma spraying.

The surface morphology of the metal glass coating was by examined the SEM. **Figure 4** shows the result of the same coating as in Fig.3. Many powders uniformly deposited on the surface of the stainless steel substrate and formed metal glass coating shown in Fig. 4.

The XRD pattern from the surface of the coating at plasma current of 300 A is shown in **Fig. 5** (a), also, the

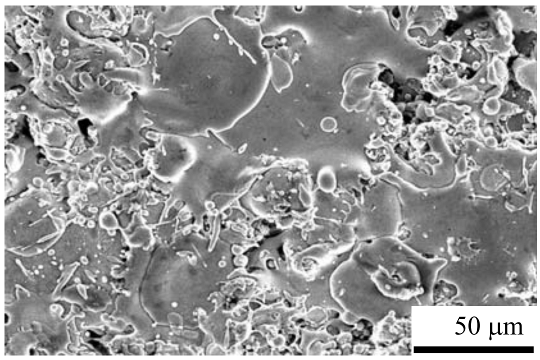

Fig. 4 SEM micrographs of the surface of the metal glass sprayed coating at plasma current of 300 A. The same coating as shown in Fig. 3.

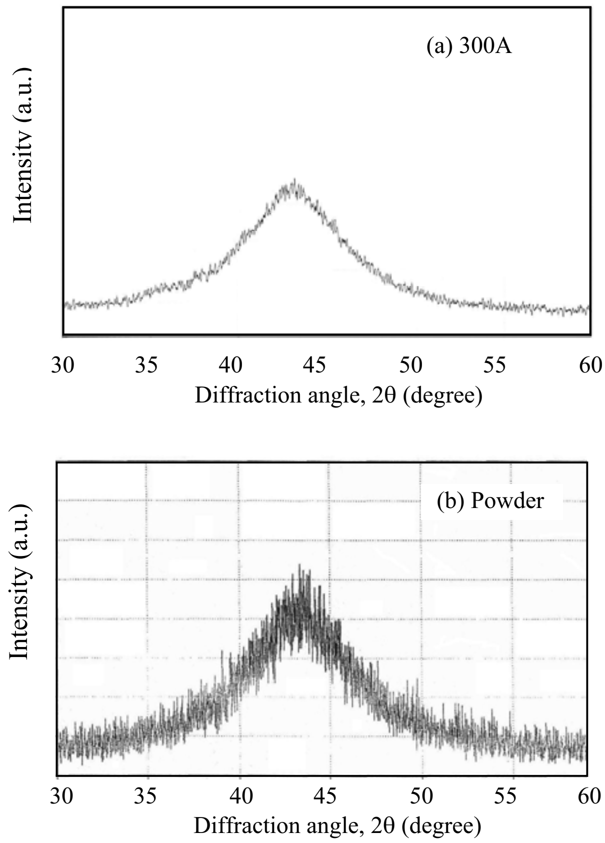

Fig. 5 XRD pattern of Fe-based metal glass coating.
(a): coating deposited at 300 A, (b): powder used in this study.

result of that for metal glass powder is shown in Fig. 5 (b). These results revealed that the broad peaks corresponding to the amorphous phase of the sprayed coatings. There were no crystalline peaks in the XRD pattern of the coating in Fig. 5 (a). And the broad amorphous phase (Phase center is about 43 degree) was observed clearly in the pattern. This pattern of Fig. 5 (a) is similar to the of the metal glass powder shown in Fig. 5 (b). Also, other peaks corresponding to the stainless-steel substrate, and any other oxidized materials were not detected.

3.2 Vickers hardness of plasma-sprayed metal glass coating

Figure 6 shows the distribution of Vickers hardness on the cross section of metal glass coatings formed by gas tunnel type plasma spraying. In this case, the plasma current was 300 A. The spraying distance was L =50mm, and the traverse number was 16. The coating thickness was 180 μm.

The Vickers hardness of metal glass coatings is around Hv_{50}= 900-1150, wherever measured in the cross section of the coating. This hardness was similar to that of the original powder. The average Vickers hardness on the cross section of metal glass coating slightly increased

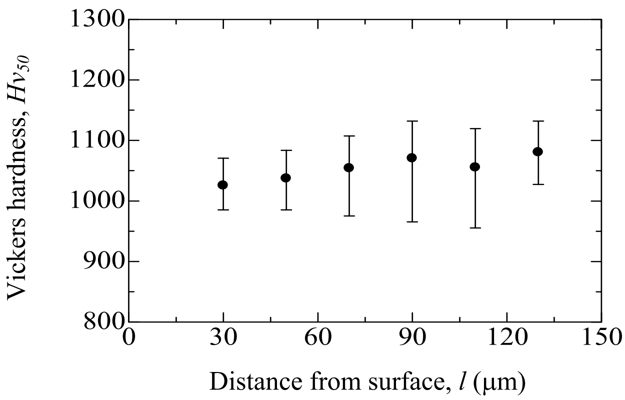

Fig. 6 Distributions of Vickers hardness of Fe-based metal glass coating, deposited at plasma current of 300 A.

with an increase in the distance from the surface. (Hv_{50}= 1020 to 1080) This is thought to result from the thermal condition affecting the amorphous phase of the coating for the different coating conditions, such as the sprayed particle temperature, cooling rate of the coating near the substrate, and so on.

3.3 Effect of plasma current on vickers hardness and porosity of metal glass coating

Figure 7 shows the dependence of Vickers hardness and porosity on the cross section of metal glass coatings on the arc current. The Vickers hardness of metal glass coatings was decided from the average value of the cross section of the coating.

At higher current of 400 A, a high hardness coating was obtained as shown in **Fig. 7** (Hv_{50}= 1050 to 1080). The coating would be thick (about 200 μm) and of high density due to high temperature effect. The plasma current affects the cooling rate of the coating when the particle is deposited on the substrate. In the case of higher current, large power gives higher cooling rate of the deposit metal glass powder. The highest value of Hv_{50} = 1150 (average 1080) was obtained at 400 A.

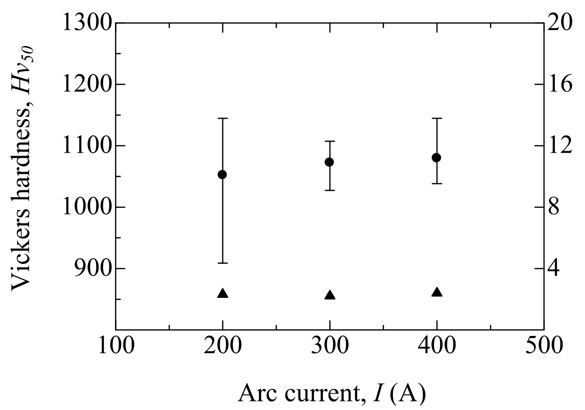

Fig. 7 Dependence of Vickers hardness and porosity of metal glass coatings on the arc current.

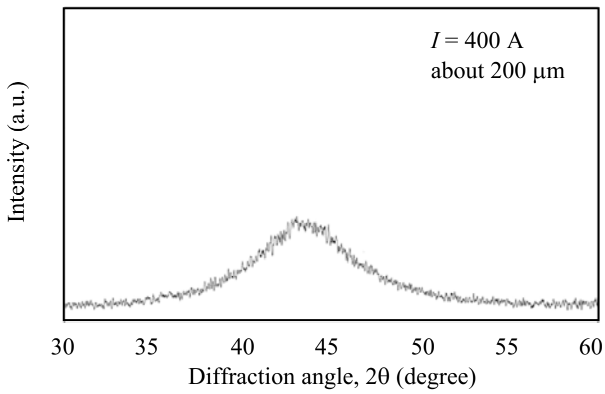

Fig. 8 XRD pattern of the metal glass sprayed at plasma current 400 A.

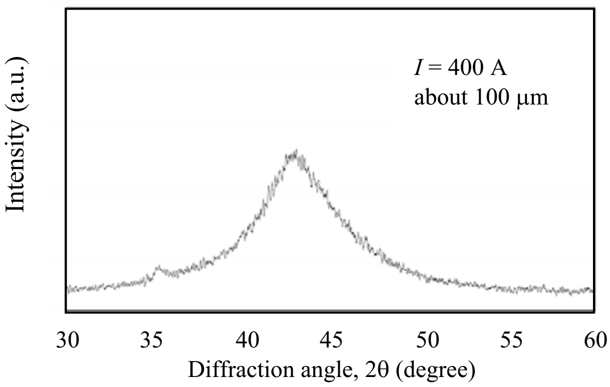

Fig. 9 XRD pattern of the metal glass sprayed at plasma current 400 A, in the case of thin coating.

In this case, however, the porosity in the cross section of the coating was almost constant at any arc current as shown in Fig.7. The porosity is a lower value of about 3% even at 400 A. Another reason of higher hardness is due to the decomposition of metal glass phase by higher plasma power. Then there is a possibility of the formation of some kinds of intermetallic compound such as Fe_xB_{1-X}, Mo_xB_{1-X}, Cr_xB_{1-X}, etc. When intermetallic compound was formed, the hardness should be increased.

The XRD pattern from the surface of the coating at plasma current of 400 A is shown in **Fig. 8**. Figure 8 shows that the broad amorphous phase whose center is at about 43 degree was observed, but there are no crystalline peaks in this case of thick coating. On the other hand, the XRD pattern shown in **Fig. 9**, which was the case of thin coating less than 100μm has the similar amorphous phase, but one peak was confirmed near 35 degree, which seems to be the intermetallic compound.

Thus, Fe based metal glass coating was formed effectively by the gas tunnel type plasma spraying. This allows the development of thick and high functional metal glass coatings, which will be useful for various industrial applications.

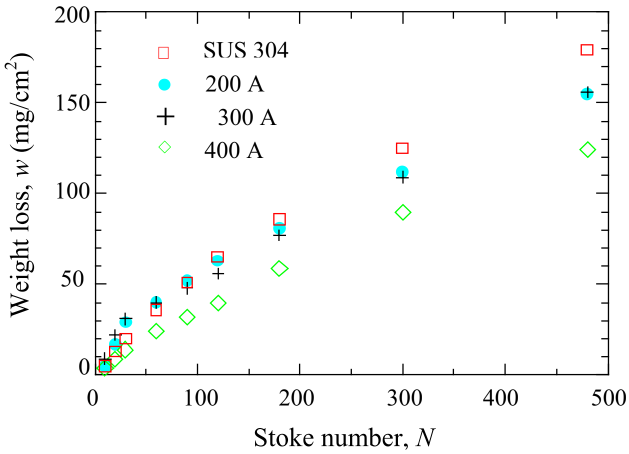

Fig. 10 Abrasive wear weight of Fe-based metal glass coating, deposited at various plasma current.

3.4 Abrasive wear of metal glass coating

Figure 10 shows the results of the abrasive wear test of the metal glass coatings obtained. For comparison, the abrasive wear behavior of the stainless steel is shown in the same figure. The abrasive wear resistance of the metal glass coating was improved at high power current. When the stroke number was 300, the abrasive wear weight loss was 112,110,90 mg/cm^2/min for the coating at 200A, 300A, 400A, respectively.

This result corresponds to the result of the Vickers hardness test. The abrasive wear resistance was increased as the Vickers hardness is increased. As an other reason of increasing for the wear resistance, the effect of the pore might be large. Also, it was found that the abrasive wear resistance of the metal glass coating was higher than that of SUS substrate.

4.Conclusions

The Fe-based metal glass coatings sprayed by gas tunnel type plasma spraying were investigated and the following results were obtained.

(1) Metal glass coating formed on the stainless- steel substrate was of dense morphology with low porosity at plasma current of 200-400A in 200 μm thickness.
(2) The Vickers hardness of metal glass coating was Hv_{50} =1000-1100, in the cross section of all coating regions at different plasma currents. This hardness was similar to that of the original powder.
(3) Vickers hardness near the substrate became a little higher. Vickers hardness was increased up to about Hv_{50} =1100 at a higher plasma current. Also, a high hardness coating was obtained at higher currents.
(4) The abrasive wear resistance of the metal glass coating was improved for high power current, and the abrasive wear rate was 90 mg/cm^2/min for the coating at 400A, when the stroke number was 300. The abrasive wear resistance was higher than the SUS substrate.

Acknowledgements

The author would like to thank Dr. J-L. Zhang, Dr. G. Shanmugavelalyutham and other coworkers for their valuable and helpful discussions.

References

1) A.Inoue, A.Takeuchi and B.Shen, Formation and Functional Properties of Fe-Based Bulk Glassy Alloys, *Mater. Trans.,* Vol **42** 2001, p970-978
2) A.Inoue, B.L.Shen and H.M.Kimura, Fundamental Properties and Applications of Fe-Based Bulk Glassy Alloys, *J. Metastable Nanocrys. Mater*. **20-21** 2004, p3-12
3) A.Inoue, and B.L.Shen, A New Fe-based Bulk Glassy Alloy with Outstanding Mechanical Properties, *Adv. Mater*., Vol **16** 2004, p2189-2192
4) Y.Arata and A.Kobayashi, Development of Gas Tunnel Type High Power Plasma Jet (in Japanese), *J.High Temp.Soc*., Vol **11**, (No.3), 1985, p124-131
5) Y.Arata and A.Kobayashi, Application of gas tunnel to high-energy-density plasma beams, *J.Appl.Phys*. Vol.**59**, (No.9), 1986, p3038-3044
6) Y.Arata, A.Kobayashi, and Y.Habara, Basic Characteristics of Gas Tunnel Type Plasma Jet Torch, *Jpn.J.Appl.Phys*., Vol **25**, (No.11), 1986, p1697-1701
7) M.Okada and Y.Arata, Plasma Engineering, *Pub. Nikkan Kogyo Shinbun-sha*, Tokyo, 1965 (in Japanese)
8) A.Kobayashi, New Applied Technology of Plasma Heat Source, *Weld.International*, Vol **4**, (No.4), 1990, p276-282
9) Y.Arata, A.Kobayashi, and Y.Habara, Ceramic coatings produced by means of a gas tunnel type plasma jet, *J.Appl.Phys.*, Vol **62**, (No.12),1987, p4884-4889
10) A.Kobayashi, Y.Habara, and Y.Arata, Effects of Spraying Conditions in Gas Tunnel Type Plasma Spraying, *J.High Temp.Soc*., Vol **18**, (No.2), 1992, p25-32 (in Japanese)
11) A.Kobayashi, Property of an Alumina Coating Sprayed with a Gas Tunnel Plasma Spraying, *Proc.of ITSC*., 1992, p57-62
12) A.Kobayashi, Shahram Sharafat, and Nasr M. Ghoniem, Formation of Tungsten Coatings by Gas Tunnel Type Plasma Spraying, *Surface & Coating Technology* 2006, p4630-4635
13) A.Kobayashi, Surface Nitridation of Titanium Alloy by Means of Gas Tunnel Type Plasma Jet, *Applied Plasma Science*, Vol.**3**, Dec., 1995, p25-32 (in Japanese)
14) A.Kobayashi, Surface Nitridation of Titanium Metals by Means of Gas Tunnel Type Plasma Jet, *J.Mater.Eng.& Performance*, Vol.**5**, (No.3), 1996, p373-380
15) Akira Kobayashi, Shoji Yano, Hisamichi Kimura and Akihisa Inoue, Formation of Fe-base Metal Glass Coating Produced by Gas Tunnel Type Plasma Spraying, *Trans. of JWRI*, Vol **35**-1 (2006) p23-27