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Photo-catalytic Properties of Titanium Oxide film Deposited by SPPS using Air Plasma
液相前駆体エアプラズマ溶射酸化チタン皮膜の光触媒特性

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Since oxide films can be deposited by atmospheric solution precursor plasma spray (SPPS), this process is hoped to be a high rate and low cost photo-catalytic oxide film deposition process. However, since Ar has been mainly used as working gas conventionally, development of a low running cost SPPS process is desired. In this study, in order to decrease the running cost of SPPS, atmospheric SPPS equipment using air working gas was developed and titanium oxide film deposition using this equipment was carried out. Consequently, photo-catalytic titanium oxide films could be deposited on the conditions of 50 mm in deposition distance in the case of air working gas use.

1. Introduction

Solution precursor plasma spray (SPPS) is a vapor deposition process using liquid precursor as feedstock and utilizing chemical reactivity and thermal energy of thermal plasma. Since the chemical reaction can be conducted under a high temperature environment including ions and radicals in this process, high rate film deposition (over 10μm/min) with controlling film's microstructure and components can be operated [1]. Previously, titanium oxide film deposition on stainless steel substrate by atmospheric SPPS using Ar working gas was carried out [2]. Consequently, it was proved that photo-catalytic titanium oxide film which had enough photo-catalytic properties to decolor the methylene-blue and generate photo-electromotive force as DSC could be deposited even in the case of atmospheric SPPS. However, in the study, since Ar was used as working gas, its running cost was high enough not to be used practically.

In this study, in order to develop a low running cost oxide film deposition process using atmospheric SPPS, as a basic study, titanium oxides film deposition by atmospheric SPPS using air working gas was carried out and the photo-catalytic properties of the deposited titanium oxide film were investigated.

2. Experimental procedure

Atmospheric SPPS equipment used in this study is shown schematically in Fig.1. The SPPS equipment consisted of plasma torch, DC power supplying system, micro tube pump (feedstock supplying system) and working gas supplying system. As the feedstock for titanium oxide film deposition, ethanol diluted titanium tetra iso butoxide (TTIB, $Ti(OC_4H_9)_4$) was used. 15 mm x 15 mm x 1 mm 304 stainless steel plates without grit blasting were used as substrate. The substrate was horizontally set on the substrate holder and the central area of the sample was placed perpendicular to the axial center of the plasma jet. The deposition distance (distance between the nozzle outlet of the plasma torch and the surface of the substrate) was varied from 50 mm to 150 mm. The deposition time was 7 min. The input power for discharge was fixed at 100 V, 10 A. Deposition temperature (substrate temperature during film deposition) was measured by thermometer. After Titanium oxide film deposition, the microstructures of the films were investigated by X-ray diffraction (CuKa, 40 kV, 100 mA). In addition, in order to confirm photo-catalytic property of the film, methylene-blue decoloration test were carried out in the UV room. Table I shows deposition conditions.

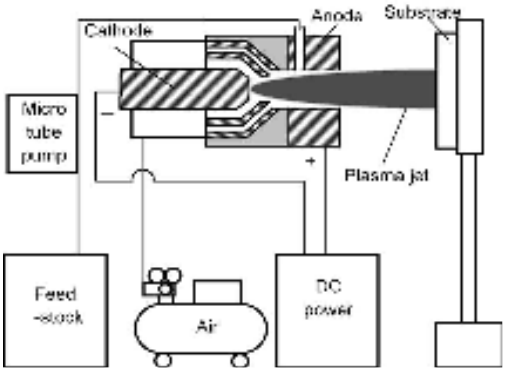


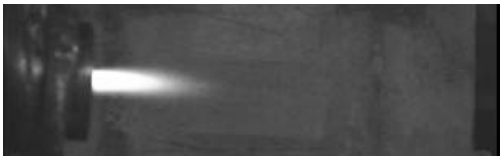
Fig.1.Schematic diagram of atmospheric SPPS equipment.

Table I. A sample table

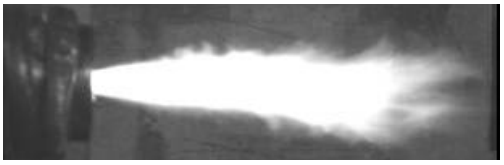
Working gas flow rate	50 l/min.
Discharge power	10A/ 100V
Deposition distance	50,100, 150 mm
Deposition time	7 min
Feedstock material	C_2H_5OH diluted TTIB
Feedstock feed rate	200 ml /h
Substrate	304 stainless steel

3. Experimental results

Figure 2 shows the appearances of the air plasma jet and feedstock injected air plasma jet. Although light purple flame was generated in the previous study using Ar working gas [15], 20 mm long light brown flame was generated in this study using air working gas. On the other hand, by injection of the feedstock, the flame color was changed into light yellow and the length was elongated to over 100 mm. From the result that there was no liquid feedstock droplet in the plasma jet and the color was changed on the condition of the feedstock was injected, the feedstock seemed to be fully vaporized and partially activated and ionized.



a) Air plasma jet



b) Feedstock injected

Fig.2. Appearances of the air plasma jets.

In this experiment, deposition temperatures on the conditions of 50 mm, 100 mm, 150 mm in deposition distance were 823 K, 773 K and 673 K, respectively. In the case of the spray pyrolysis, deposition temperature of over 873 K was required because film deposition was conducted by only thermo chemical reaction. On the other hand, in the case of SPPS, since film deposition was conducted by plasma chemical reaction as well as thermo chemical reaction, oxide film could be deposited on the condition of below 773 K. Figure 3 shows the XRD patterns of the titanium oxide film coated samples on the conditions of 50 mm, 100 mm, 150 mm in deposition distance. As for the crystal structure, rutile dominant titanium oxide film slightly including anatase was deposited in the case of 50 mm and anatase and rutile mixture film was deposited on the condition of 100 mm. However, though anatase and rutile mixture film film could be obtained also on the condition of 150 mm, the degree of crystallinity was drastically deteriorated.

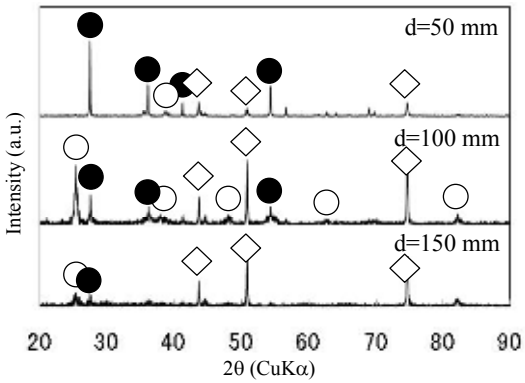
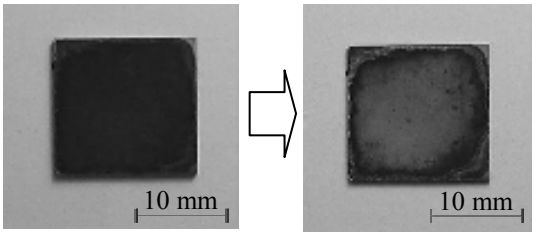


Fig.3. XRD patterns of the titanium oxide films. (◯: Anatase,●: Rutile,◇: Fe (Substrate))

Figure 4 shows the result of the methylene-blue decoloration test in the case of the titanium oxide films deposited on the conditions of 50 mm in deposition distance. This film indicated hydrophilic and decolor methlene-blue droplets at the center of the substrates perfectly after 24 hour UV irradiation.



Before UV irradiation 24 hr UV irradiation

Fig.4. Appearance of the titanium film deposited on the condition of 50mm in deposition distance during methylene-blue decoloration test.

4. Conclusion

In order to develop a low running cost photo-catalysis oxide film deposition process, titanium film deposition by atmospheric SPPS using air plasma jet was carried out. Consequently, in the case of air working gas, titanium oxide film which has enough photo-catalytic properties to indicate hydrophilic and decolor methylene-blue could be deposited on the condition of 50mm in deposition distance.

References

[1] H. Murakami, T. Yoshida, K. Akashi: Advanced Ceramic Materials, 3, 4 (1988) 423.

[2] Y. Ando, S. Tobe, H. Tahara: J IEEE Trans. on Plasma Sci., 34, 4 (2006) 1229.