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STRUCTURAL AND MORPHOLOGICAL CHARACTERISTICS OF PLASMA SPRAYED TiO_2-COATINGS

Dwi Bayuwati
Research Center for Physics, Indonesian Institute of Sciences
Kawasan Puspiptek, Serpong 15314, Tangerang Selatan
e-mail: dwib001@lipi.go.id

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ABSTRACT

STRUCTURAL AND MORPHOLOGICAL CHARACTERISTICS OF PLASMA SPRAYED TiO_2-COATINGS. TiO_2 thin layers have been deposited on glass substrates using Plasma Spray technique. The TiO_2 starting powders are a laboratory grade commercial powders. Before spraying, to check the availability of the basic material for Plasma Spray technique, a series of characterization was conducted. The TiO_2 starting powders were identified its particle size using Particle Size Analyzer (PSA) resulting diameter at 90% was 42.72 μm. X-Ray Diffractometer (XRD) measurement was done to identify the peaks of the basic material elements using Kα radiation at wavelength 1.5406 Å resulted TiO_2 of Anatase structure. Spray dry process was then conducted in order to get circular and free flowing particles for feedstock of plasma spray system. Distribution of particles showed a dominat of 20 μm diameter-free flowing particle. Plasma Spray process of TiO_2 powder furthermore was conducted on slide glass microscope under several parameter conditions such as power, flame-substrate distance and preheating treatment variation. The TiO_2/glass coatings with variation of flame-substrate distance (10 and 12 cm) resulted in 5.806 μm and 4.913 μm layer thickness with grain size in the range of 0.8-2 μm and 1-2.8 μm, respectively. XRD diffractogram results revealed that the TiO_2 layer are dominat in rutile phase but at a little higher of plasma power, low anatase phase existed. The preheated-plasma sprayed TiO_2 coatings were visibly difussed into the glass substrate and resulted in dominat rutile phase (at 2 cycles preheating) but not existed in a longer preheating time (4 cycles preheating treatment).

Keywords: TiO_2/glass, Plasma spray technique

ABSTRAK

KARAKTERISASI STRUKTUR DAN MORFOLOGI LAPISAN TiO_2 *PLASMA SPRAY*. Lapisan TiO_2 telah dilapiskan pada substrat gelas menggunakan teknik Plasma *Spray*. Bahan dasar yang digunakan adalah bubuk komersial TiO_2 standar laboratorium. Untuk mengetahui apakah bubuk TiO_2 sudah memenuhi syarat sebagai bahan dasar dalam proses plasma spray, perlu dilakukan terlebih dahulu proses karakterisasi. Bahan TiO_2 dikarakterisasi menggunakan *Particle Size Analyzer* (*PSA*) menghasilkan diameter butir kisaran 90% sebesar 42,72 μm. Pengukuran spektrum *X-Ray Diffractometer* (*XRD*) dilakukan untuk mengidentifikasi punak-puncak-puncak unsur bubuk TiO_2 yang akan digunakan menggunakan gelombang radiasi sinar-X dengan Kα pada panjang gelombang 1,5406 Å menghasilkan puncak-puncak struktur TiO_2 *anatase*. Proses *spray dry* kemudian dilakukan untuk mendapatkan bentuk yang bulat dan licin agar lancar mengalir dari *feed powder* menuju *flame* plasma. Analisis pengukuran partikel memperlihatkan susunan partikel bulat dengan dominan diameter 20 μm diameter. Proses plasma *spray* bahan TiO_2 selanjutnya dilakukan pada substrat gelas dengan variasi parameter yaitu variasi arus daya plasma, jarak plasma ke substrat dan *treatment* proses pemanasan substrat. Proses pelapisan bahan TiO_2/gelas dengan variasi jarak plasma substrat (10 cm and 12 cm) rmenghasilkan lapisan masing-masing dengan ketebalan 5,806 μm dan 4,913 μm dan ukuran butiran berkisar 0,8 μm hingga 2 μm dan 1 μm hingga 2,8 μm. Pengukuran dengan *XRD* menghasilkan lapisan-lapisan TiO_2 *dominant* dalam fasa *rutile*; tetapi dengan menambah sedikit *power* plasma, puncak-puncak *anatase* yang lemah tetapi pasti terbentuk. Lapisan TiO_2 dengan perlakuan *preheated* jelas terlihat secara *visual* terdifusi ke dalam gelas dan dalam bentuk *rutile dominant* (pada *preheat* 2 *cycles*) tetapi untuk waktu *preheating* yang agak lama (*preheating* 4 *cycles*), hanya muncul puncak fasa *rutile* yang sangat rendah.

Kata kunci: TiO_2/gelas, Teknik *spray* plasma

INTRODUCTION

Titanium dioxide (TiO_2) films and coatings have been widely studied because of its interesting physical, chemical and electrical properties which are suited for several aplications such as in paintings [1], optics (optical waveguides, photonic crystals) [2,3], energy devices (solar cells) [4] and biomedical devices [5].

TiO_2 has three forms, the stable phase, rutile and two metastable polymorph phases, brookite (orthorhombic) and anatase (tetragonal). Both metastable phases become rutile (stable) when submitting the material at temperatures above 700 °C [6]. New techniques for depositing good crystalline and flat surface properties of TiO_2 films for various application in research and industry are still explored. TiO_2 films have been deposited using several techniques such as rf sputtering, sol-gel, Chemical Vapor Deposition (CVD) [7-8]. TiO_2 has been studied its structural and morphological properties using Spray Pyrolysis (SP) deposition technique [9] reported the appearance of rutile phase at 620 °C. Deposition of TiO_2 using Chemical Vapor Deposition (CVD) technique was reported in 2001 by Asahi R. and Taga Y. [10]. TiO_2 has also been studied on its in vivo corrosion behavior as a chemical barrier against release of metal ions from biomedical implants [11].

The purpose of this work is to study the growth of TiO_2 material on glass microscope slide using plasma spray technique. Plasma spraying technique is a economical and versatile fabrication process for production large suface coatings with almost unlimited types of materials. Several works on plasma spray process has been described [12,13], but the study here in stressed on the existence of anatase and rutile phase and its related parameter process and olso the coating performance of the deposited TiO_2/glass layer. The plasma spray experiment consists of basic or raw material identification, powder and substrate preparation, coatings process using plasma spray system followed by characterization process. Particle Size Analysis (PSA), X-Ray Diffractometer (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectrometry (SEM-EDS) were used to characterize the starting powders and the coatings, respectively.

EXPERIMENTAL METHOD

All experiments were conducted at AMREC-SIRIM (Advanced Materials Research Centre, Standards and Industrial Research Institute of Malaysia) Berhard, Penang Malaysia. The schematic diagram of the plasma spray experiment is shown in Figure 1.

Raw Material Identification

The TiO_2 material were analytical grade of commercial powders from Merck, Germany. Before

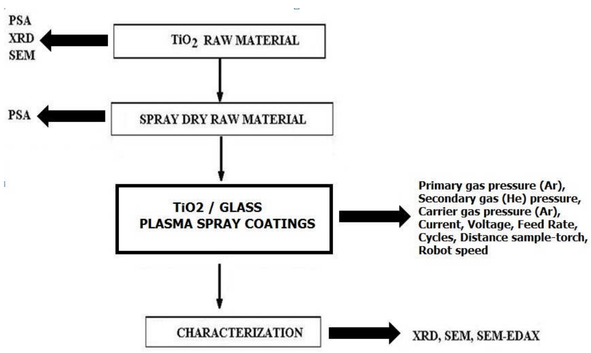

Figure 1. Schematic diagram of the plasma spray of TiO_2/glass coatings.

feedstock formation, the TiO_2 starting powders were identified its particle size using Particle Size Analyzer (PSA), CILAS 1190 DRY to see the availability of the grain for plasma spray process. The crystal structure was examined using X-Ray Diffractometer (XRD), Bruker Germany using CuKα radiation at wavelength 1.5418 μm. The analyzes of XRD curves use the database of International Centre of Diffraction Data JCPDS-ICDD.

Powder and Substrate Preparation

Aqueous suspensions consists of 70 g of TiO_2 powders, 35 g distilled water and 10% wt% of Carboxymethyl Cellulose (CMC) binder were prepared for spraying. Firstly, the mixture of TiO_2 powders and distilled water were dispersed using ultrasonic cleaner for 2 hours. Then, 10% wt% CMC binder was added and the liquid was stirred for about 5 hours to homogenize the liquid. Furthermore, it was ballmilled for 8 hours using zirconia balls, followed by spray dry process to get final powders for feedstock in the TiO_2 plasma spray process. The spray dry process has been reported in the earlier paper [14]. Basically, it is a drying process which is capable of producing microsized, free flowing and round powders from a liquid or slurry by using a hot gas [15]. Lastly, the spray dried TiO_2 powders were sieved at 20 μm size ready for plasma process.

The glass microscope slides substrates were cut into (25 mm x 25 mm x 1 mm) size and ultrasonically cleaned in methanol and then dried. All working solution were prepared using analytical grade chemical and distilled water.

Plasma Spray Process

The plasma spray system used here is a machine for depositing layers using coating precursor in the form of powders; which is heated by plasma until melted or semimolten; and sprayed onto the substrates. Actually, this machine can produce layers with thickness range from several micrometers to several mm on any substrates such as metals, alloys, ceramics, plastics and composites [12,13,16].

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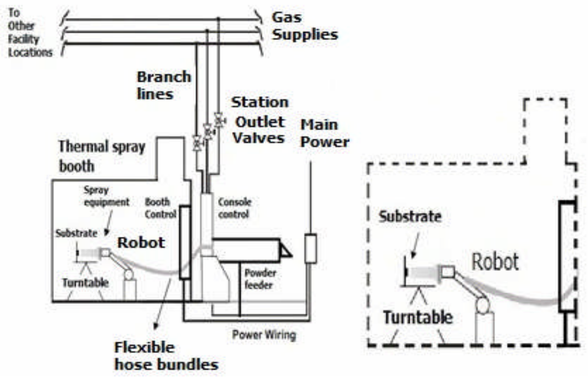

Figure 2. Plasma spray system [16].

The plasma spray system consists of a spray gun (for performing the melting and acceleration of the particles to be deposited), feeder (for supplying the powder to the torch), supply media (argon gas for generation of the plasma jet), gases (argon; for carrying the powder), robot (for manipulating the torch), substrate stand and cooling system, power supply, and control system (Figure 2) [11,16].

There are many process parameters which affect the quality of the deposited layers such as feedstock type, plasma gas composition and flow rate, energy input, torch offset distance and substrate cooling [16]. Plasma spray process was conducted here under various condition of spray, namely, power variation (400 A and 500 A), plasma flame substrate distance variation (10 cm and 12 cm) and preheating time variation (0, 2, and 4 cycles).

Coatings Characterization

The surface morphologies, cross-sectional microstructures, and composition of the TiO_2/glass coatings were examined by scanning electron microscope and Energy Dispersive X-Ray Spectrometry (EDS), Bruker AXS, Germany. XRD evaluations were carried out using the Bruker X-Ray Diffractometer with CuK_α radiation at wavelength 1.5406 Å.

RESULTS AND DISCUSSION

Raw Material Identification

The particle size measurement before and after spray dry process is presented in Table 1. As described

Table 1. Particle size distribution of TiO_2 before and after spray dry process.

		Diameter (μm)
Before spray-dry	Diameter at 10%	1.22
	Diameter at 50%	7.33
	Diameter at 90%	42.72
After spray-dry	Diameter at 10%	3.35
	Diameter at 50%	10.77
	Diameter at 90%:	26.40

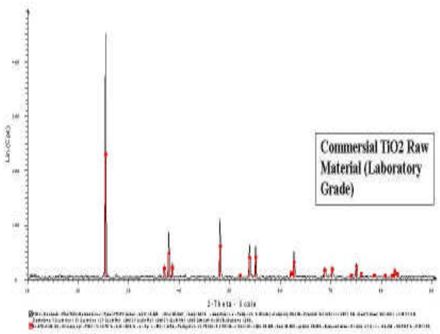

Figure 3. XRD measurement of the TiO_2 raw material

before, PSA measurements commonly define the population distribution (the TiO_2 grain diameter ditribution, in this case) in 3 state; 10,50 and 90 percent distribution. So it can be explained here, for example, from Table 1, in before spray-dry, 10% of the TiO_2 grain lies below diameter 1.22 μm or 50% of TiO_2 grain lies below diameter 7.33 μm or 90% of TiO_2 grain lies below diameter 42.72 μm. Roughly, the range of grain diamater before spray dry is about 1.22-42.72 μm. Similar explanation can be stated for after spray dry condition.

For deposition with plasma spray technique, the TiO2-spray dried powder was used as feedstock of plasma spray coatings of TiO_2/glass (grain size about 3.35-26.40 um). XRD measurement of the raw material elements using K radiation at wavelength 1.5406 Å resulted TiO_2 of anatase structure (see Figure 3).

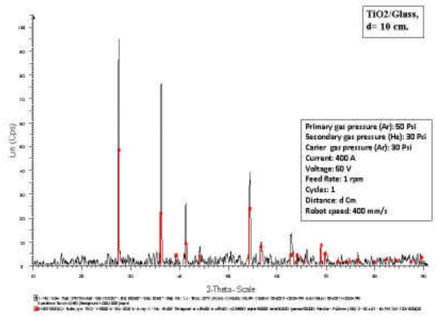

Figure 4. XRD pattern of TiO_2/glass coating at d = 10 cm and current 400 A.

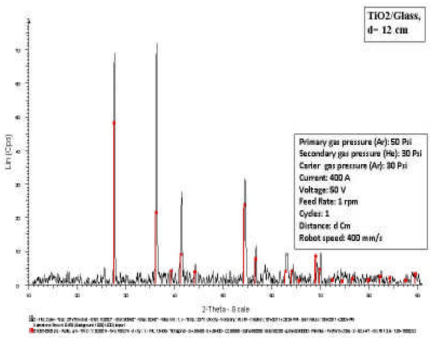

Figure 5. XRD pattern of TiO_2/glass coating at d = 12 cm and current 400 A.

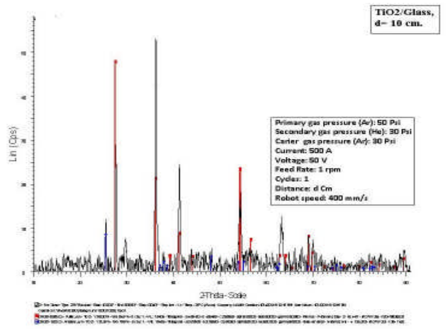

Figure 6. XRD pattern of TiO_2/glass coating at d = 10 cm and current 500 A

Table 2. Summary results of XRD measurements for TiO_2/glass coatings.

	Plasma – substrate distance (cm) and current power (Ampere)	TiO_2 existed peaks
Figure 3	TiO_2 RAW MATERIAL	Anatase
Figure 4	d= 10 cm, current 400 A	Rutile
Figure 5	d= 12 cm, current 400 A	Rutile
Figure 6	d= 10 cm, current 500 A	Rutile dominant, Anatase

Plasma Spray Characterization Results

XRD Measurements

XRD measurements were conducted for the TiO2/ glass with various parameter process and the resulted spectra patterns are presented in Figures 4, 5 and 6. The summary results for XRD measurements are presented in Table 2; compared with result in Figure 3 for XRD of raw material.

Other process parameters which used at this stage here are fixed: primary gas pressure 50 psi, secondary gas pressure 30 psi, carrier gas pressure 30 psi, voltage 50 Volt, feed rate 1 rpm and robot speed 400 mm/s. All parameters were chosen based on the best results experiment obtained before using this plasma spray system.

From the experiment, it can be seen that the rutile phases appeared in all TiO_2/glass plasma spray process (at 400 and 500 A current power). This has been predicted theoretically that the anatase phase of TiO_2 raw material changed into rutile phase at temperature > 8000C in general plasma spray process [16]; as stated earlier. But, here, it is still unclear that anatase peak existed only at 500 A (at higher current power or higher temperature), not in 400 A current power, see Figure 6.

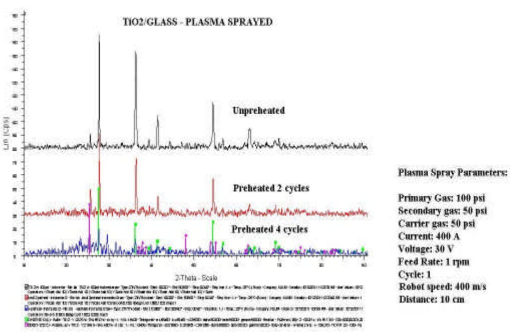

Figure 7. XRD pattern of TiO_2/glass coating at d = 10 cm and current 500 A

Further experiments were then conducted to study the effect of preheating treatment on substrates. This stage was done because some layers did not stick well on the substrate. With substrate preheating, TiO2 layers stick quite well in glass samples. First glass sampel was TiO2 plasma sprayed without preheating and two others were preheated for 2 and 4 cycles each before TiO2 plasma spray process. The XRD patterns of all the three samples are presented in Figure 7 with mention of all parameters used in plasma process.

XRD pattern of plasma sprayed TiO2/glass coating without preheating process is shown in upper part of Figure 7 which shows rutile dominant and small anatase peaks of the TiO2 coating. Different with earlier result in Figure 4 (at the same current power, 400 A), anatase phase appeared here. But, the later experiment here using different composition of gas pressure (see details in Figure 7). This might explain the question why anatase did not exist in the first 400 A plasma spray process. More experiments with many variation of process parameters should be conducted next to have complete conclusion.

Furthermore, the XRD pattern of the unheated TiO2/glass sample in Figure 7 was compared to other 2 preheated TiO2/glass samples. The 2 cycles preheating sample shows some peaks of rutile dominant and anatase TiO2 which is lower than that of the unheated sample. Meanwhile, almost no peaks of TiO2/glass at 4 cycles preheating, only several very low rutile peaks appeared. This might be caused by the over melting of the TiO2 feedstock materials that stick on this substrate, resulting only very low rutile phase formed

SEM Analysis of TiO_2/Glass Coatings

SEM Analysis of TiO_2/Glass with Preheating Variations 0,2 and 4 cycles

The surface morphology of the TiO2 /glass plasma sprayed coatings with variation of preheating conditions is shown in Figure 8. At 4(four) cycles preheating, most TiO_2 grains were agglomerated and molten (see Figure 8). Otherwise, in normal heating without preheating, in left side of Figure 8, several TiO_2 grains remained separate and were not molten. In the middle, at 2 cycles preheating, some TiO_2 grains werre partially molten.

SEM Analysis of TiO_2/Glass Coatings with Plasma-Substrate Distance Variation 10 and 12 cm

The cross section morphology of the TiO_2/glass plasma sprayed coatings with variation of plasma-substrate distance (d) is shown in Figure 9. For higher d

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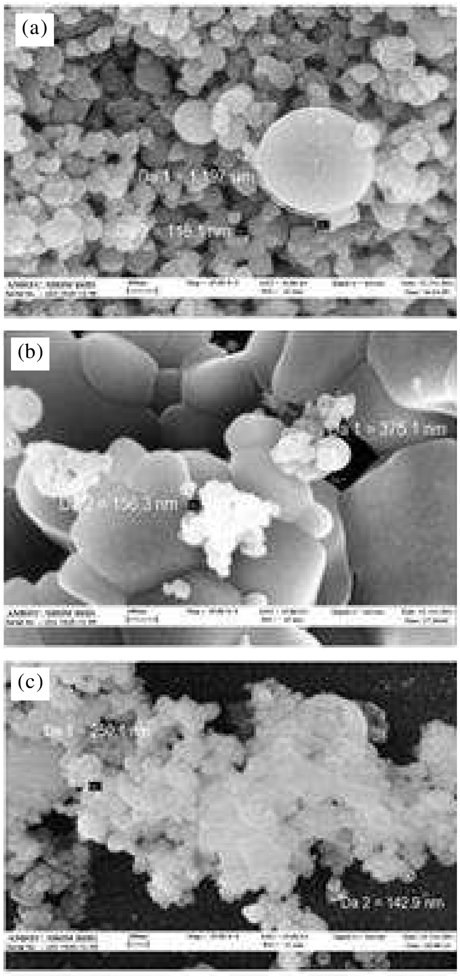


Figure 8. SEM analysis of TiO_2/glass coatings with preheating variation (a). 0 cycles, (b). 2 cycles and (c). 4 cycles (left, middle and right).

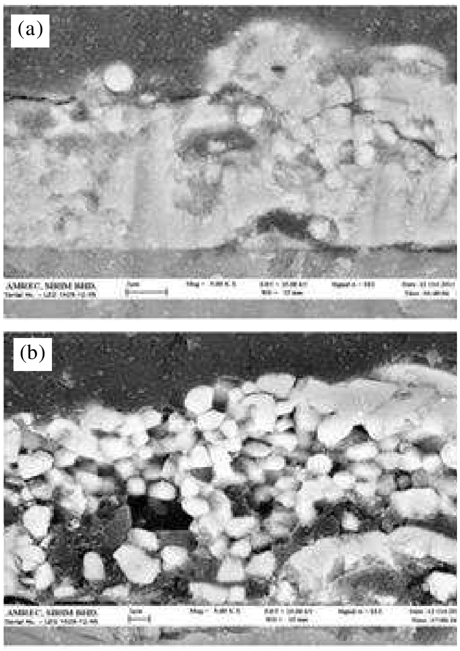
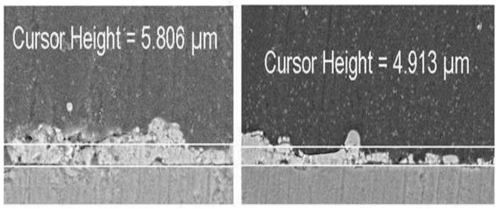


Figure 9. SEM Analysis of TiO_2/glass coatings with plasma substrate distance variation (a). d =10, left and (b). d = 12 cm, right.



TiO2/glass, plasma - substrate distance=10cm   TiO2/glass, plasma - substrate distance=12 cm

NO.	TIO2/GLASS - PLASMA SPRAYED	GRAIN DIAMETER (µm)	THICKNESS (µm)
1.	Flame-Substrate distance = 10 cm	0.8 – 2.5	5.806
2.	Flame-Substrate distance = 12 cm	1.0 – 2.8	4.913

Plasma Spray Parameter:

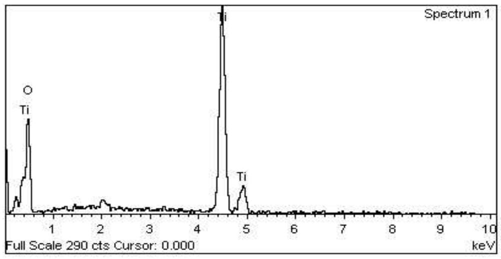
Primary gas: 50 psi
Secondary gas: 30 Psi
Carrier gas: 30 psi
Current: 400A
Voltage: 30V
Feed rate: 1 rpm
Cycle: 1
Robot speed: 400 m/s

Figure 10. SEM evaluation for grain and thickness analyzes of TiO_2/glass coatings.

Processing option : All elements analyzed (Normalised)
Number of iterations = 3

Standard :
O SiO2 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	46.83	72.51
Ti K	53.17	27.49
Totals	100.00	



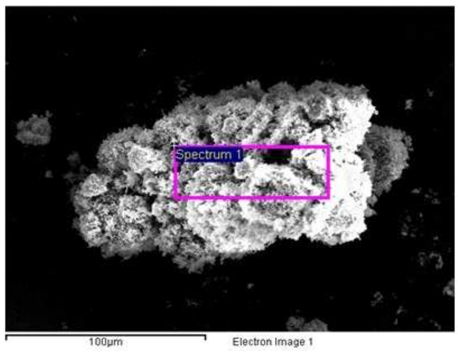


Figure 11. A typical SEM-EDX measurement results of TiO_2/glass coatings.

value (d=12 cm) it is clear that the TiO_2 plasma which adhered or sticked in the substrate is slightly cooled because of longer distance so the coatings were not so molten compared with another (d=10 cm).

Figure 10 summarizes the grain and thickness evaluation of 2 (two) condition of TiO2/glass plasma coatings. As can be seen, the longer plasma-substrate distance resulted bigger grain diameter and thinner of TiO2 layer.

At shorter distance (d=10 cm), plasma spray process still involved more quantity and higher temperature of TiO2 plasma arrived in the substrate so it resulted thicker layer and smaller grain size of TiO2. For longer distance, there was a slightly cooling and evaporation process in the additional air gap between plasma gun and substrate, resulted less material stick on the substrate with bigger grain.

As explained before, in plasma spray process, the TiO2 is heated until melted or semi molten and then sprayed onto the substrate and formed a layer later in the substrate. So, the grain diameter of the TiO2 layer (0.8 - 2.8 um) will be thinner than the TiO2 feedstock grain (3.35-26.40 um) because of the melting process during plasma spray deposition.

Lastly, Figure 11 presents a typical SEM-EDX measurement result which shows the existence of Ti and O in TiO2/glass coatings with compositions of 72.51 and 27.49%, respectively, which proved that TiO2 is really deposited in glass substrate.

CONCLUSION

Plasma spray system was used to deposit TiO2 on glass substrates under various process parameters (current-power, plasma-substrate distance and substrate preheating). The effects of different spraying conditions on microstructure, crystal structure and surface features were investigated. Experiment results show that the existed phase and the grain size highly depend on the current power and composition of gas pressure. The TiO2/glass coating with variation current power of 400 and 500 A resulted of dominant rutile phase and a very small amount of anatase phase. The TiO2/glass coatings with variation of flame-substrate distance (10 and 12 cm) resulted in 5.806 m and 4.913 m layer thickness, with grain size in the range of 0.8-2 m and 1 -2.8 m, respectively. Preheat treatment on substrate can result in a more conform and adhere deposited material in the substrate but also degrades the peak intensity, so a compromise of all process parameter process is important. The typical composition of the Ti and O in the layer is about 72.51 and 27.49%, respectively

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