Effect of Plasma Spraying Parameters on the Microstructure and Strength of TiO_2 Coatings

Muhammad Jabir Suleiman, Siti Mariam Mohamad, and Ahmad Nizam Abdullah

***Abstract*—** TiO_2 coatings were prepared on metal substrate by atmospheric plasma spraying (APS) using nano-sized feedstock powder. The coatings were prepared by varying the plasma spray deposition parameters in order to evaluate the mechanical and microstructural properties of the coatings. The microstructure and phase composition of the coatings were characterized using FE-SEM and XRD. Most of the prepared coatings were dominated by rutile phase as major phase and only few coatings revealed anatase as minor phase. The coatings were consisted of melted and partially melted particles. The coatings hardness and adhesion strength were determined using Vickers microhardness and pull-off adhesion test. The adhesion strength of the prepared coatings was between 8 - 16 MPa, while the microhardness measurement was more than 500 Hv. The study revealed that by varying the plasma spraying parameters, the coatings would experience the changes in microstructure and strength.

***Keywords*—** microstructure, microhardness, plasma spraying, titanium oxide.

I. Introduction

TiO_2 nanopowders have extensive application in photocatalyzed field because of characteristics such as innocuity, strong oxidizability, fine stability, high light-transfer characteristic, etc. [1]. As a photocatalyst, it has been utilized to decompose harmful air pollutants and organic contaminants in water [1]. Among all the physical and chemical characteristics of TiO_2 that have an influence on the photocatalytic activity, the crystalline structure appears to be the most important. Despite that some authors have found that the rutile (stable phase) photoactivity may not be negligible regarding the preparation method, TiO_2 in anatase phase (metastable phase) has shown the greater photocatalytic efficiency for the degradation of organic pollutants [1,2].

At present, the preparing methods of TiO_2 are sol-gel route, immersion method, magnetron sputtering method, etc. Plasma spray is a method to prepare wear-resistant coating, in which molten metal powders and high-melting point powder are sprayed on the substrate. As thermal plasma has high temperature, high enthalpy, high thermal gradient, etc., the uniform nanopowders can be prepared when the atomized liquid transfer through plasma torch and react quickly in the plasma [2].

The widely used thermal spray technology offers the possibility to prepare large active coatings, which can exhibit an excellent adhesion to substrates with rather complex shapes. However a consequence of the melting, rapid cooling and solidification of the TiO_2 feedstock powder during plasma spraying is that plasma sprayed TiO_2 coatings consist mainly of the rutile phase with a varying ratio of the anatase phase in whatever the crystalline structure of the initial powder. Therefore, the key problem in plasma sprayed TiO_2 coatings is to retain the pre-existing metastable anatase phase of the powder feedstock and minimize the transformation from anatase to rutile during the spraying [3,4].

To maintain the anatase metastable phase, several spray parameters have to be very carefully adjusted in order to minimize the particle heat input. The main plasma spraying operating parameters that have an influence on this phenomenon are: the plasma arc current, the ratio of primary and secondary gas, the total plasma gas flow rate or the ratio between the plasma power and the argon flow rate. But other parameters such as the solidification speed and temperature, federate, spraying distance or the powder size appear to play a primary role [4,5].

In the present work, a TiO_2 powders were plasma sprayed on a standard stainless steel which were used as substrates. The effects of the plasma parameters, specifically the spraying distance on the anatase phase ratio and of the coatings were investigated. To better qualify the microstructural characteristics of the coatings, microhardness and strength was also studied.

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II. Materials and Methods

A. Feedstock Powders

The TiO_2 powders from Inframat Bond Coat were used as the feedstock for coating deposition. Fig. 1 shows the surface morphologies of the powders which show the anatase powder is in a particle size range from 20 to 45 µm. Fig. 2 displays the XRD patterns of TiO_2 particles composed of anatase, and no rutile phase was observed in the powders.

TABLE I
PLASMA SPRAYING PARAMETERS FOR NANOSIZED TiO_2 POWDERS

Parameters	P4	P5	P6	P7	P8
Current (A)	200	200	200	200	200
Voltage (V)	32.0	34.0	33.0	35.5	33.5
Primary gas, Ar. (psi)	80	80	40	80	40
Secondary gas, He. (psi)	0	30	30	30	30
Carrier gas, Ar. (psi)	30	30	30	30	30
Feedrate (rpm)	4	4	4	4	4
Spraying Distance (cm)	8	8	8	6.5	6.5
Robot Speed (mm/s)	250	250	250	250	250

B. Plasma Spraying

TiO_2 coatings were deposited with atmospheric plasma spraying (APS) (3710 Plasma Control, PRAXAIR Surface Technology, USA) on stainless steel substrates (SS304). Argon was used as powder carrier gas. Spraying distance was varies between 6.5 and 8 cm. The spray gun was manipulated by a robot (721-68 Vasteras, ABB Automation Technologies, Sweden) and traversed at a relative speed of 250 mm/s over the substrate. The main spraying parameters are given in Table 1. Stainless steel plate was employed as a substrate for coating deposition. Prior to spraying, the substrate was blasted with alumina grits.

C. Characterization

The phases of the crystalline structure of TiO_2 coating were determined and recorded using an XRD (Bruker D8 Advance, Germany) at ambient temperature using Ni-filtered Cu-Kα radiation (λ = 0.15406 nm). The data collected was in the range of 20°–80° (2θ), with a step of 0.05° and a scanning rate of 1.2° per minute. Then, the anatase content in TiO2 coating was estimated based on the relative peak area of anatase (101) and rutile (110) peaks in XRD pattern.

The topographic morphology of the coatings was examined by scanning electron microscopy (SEM) (LEO 1525, LEO, Germany). Prior to this examination, the substrates were coated with Gold using a sputter coater. Coating porosity was also observed by image analysis from micrographs.

The hardness of coatings was determined using an indentation technique. A conventional diamond pyramid indenter (Vickers) was fit to the piece of equipment (HM-200, Mitutoyo, Japan) and a load of 3 N was applied on this powder for 10 s according to the standard specification ASTM E92-72.

The adhesion tests were performed according to ASTM D4541 using an Automatic Adhesion Tester (PosiTest, AT-A, DeFelsko, USA). A 10 mm diameter dolly was attached to the coating surface with a curable epoxy adhesive for 8 h. After that, the dolly was vertically pulled off (with a 5.0 MPa/s rate) while measuring the necessary force. The results are the average of 3 repeated tests done on each sample.

III. RESULTS AND DISCUSSION

A. Coating Microstructure

Coating microstructure was observed by SEM (Fig. 3) where it shows the granules morphology and polished cross section of this powder after their passage in the plasma. It is clear evidence that this powder was partially melted and all these coatings were dense and the porosity measurable by optical or electronic microscopy was negligible. Indeed, on the outer surface, localized fully melted zones appear whereas in the inner part the particles are very similar to the initial ones.

So generally the powder core is strengthened but the TiO2 particles are not sintered and the surface shows more or less extended molten area. By observing the various granules cross section, only powders with certain size are fully melted. In general, the coatings microstructure is inhomogeneity which consisted of a bimodal microstructure characterized by the presence of completely fused regions and of non-molten regions consisting of agglomerated nanoparticles based on Fig. 3 (a), (d) and Fig. 4 (a), respectively.

Such microstructures, characterized by a distribution of non-melted and melted regions, have been previously reported in suspension plasma sprayed coatings obtained from titania and other materials such as alumina [5].

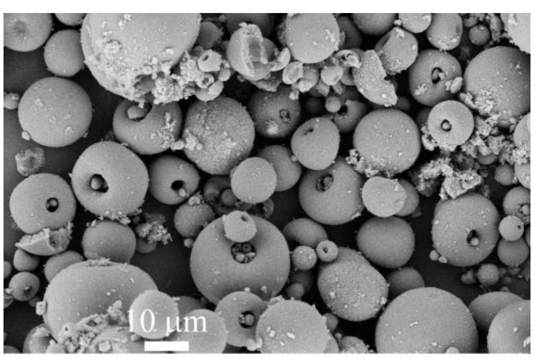


Fig. 1 SEM micrograph of TiO_2 powder

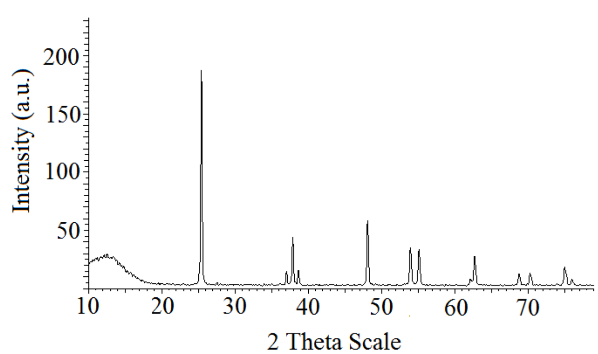
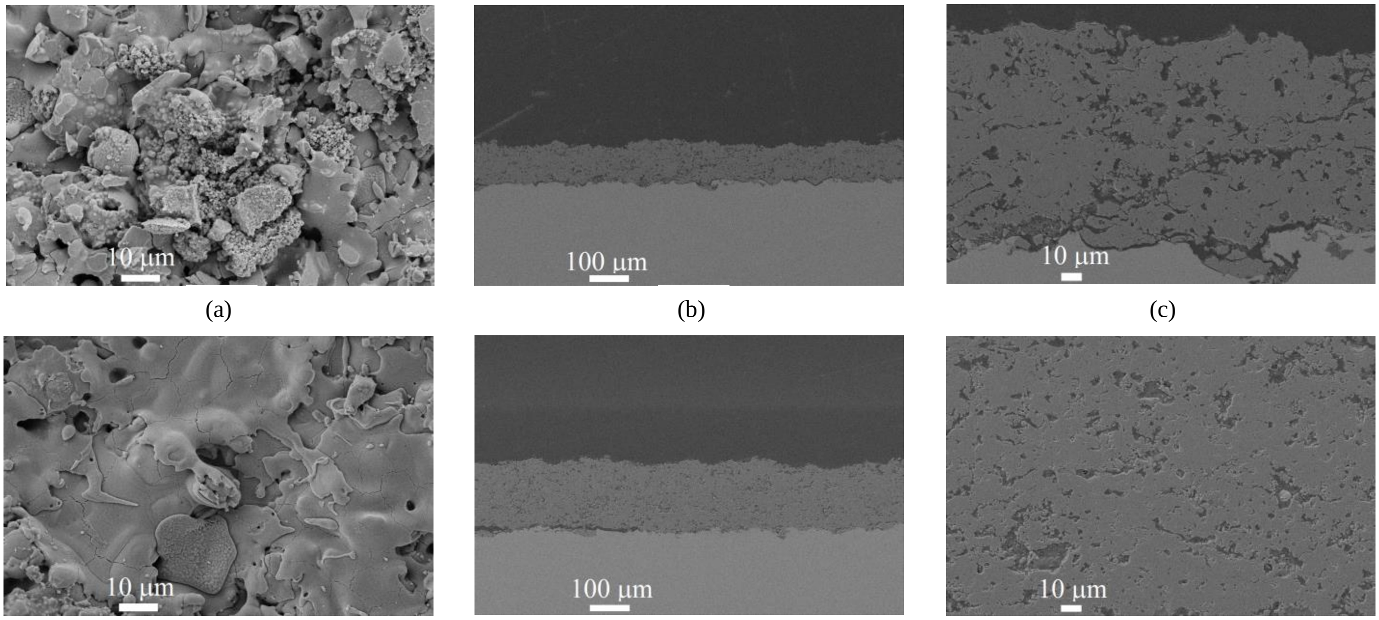


Fig. 2 XRD pattern of TiO_2 powder



(a) (b) (c)

(d) (e) (f)

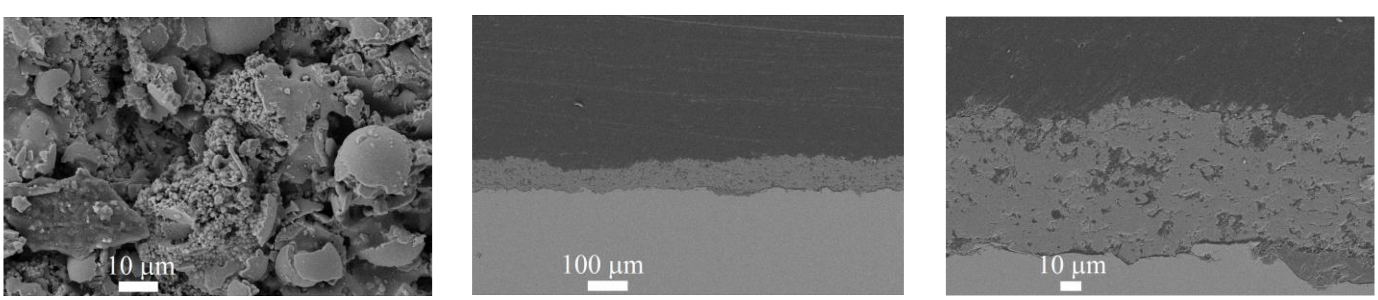
Fig. 3 SEM micrograph of surface (a) and cross section (b), (c) of P6; and surface (d) and cross section (e), (f) of P8

Fig. 3(a), Fig. 3 (d) and Fig. 4(a) also shows that the thermal sprayed coatings are characterized as a layered microstructure consisted of many individual molten droplets impacting on the substrate flatten to form "splats" which consecutively pile on top of other deposits. And the coatings are mainly constructed from mixtures of full-molten and partial-molten droplets, and the selective deposition of intended particles is impossible. As shown in Fig. 3(d), TiO_2 coatings from parameter P8 are sprayed with closer distance of 6.5 cm as compared to TiO_2 coatings from parameter P6 with distance of 8 cm. The coated P8 display more pronounced disk-shaped splat morphology than the coating which contains embedded partial-molten or non-molten particles [4,6].

This is likely related to the increased fraction of molten particles resulting from increased heat when the TiO_2 are sprayed from a closer distance. The significant differences were also noted in coating thickness (Table 3) whereas P8 shows higher thickness of 209.4 μm as compared to P4 and P6 with 79.8 μm and 110.0 μm, respectively. The difference of thickness for these samples can be observed from the cross section of SEM micrograph in Fig. 3(b) for sample P6, Fig. 3(e) for samples P8 and Fig. 4(b) for sample P4. As it can be seen, the lowest thickness was obtained with the spraying distance of 8 cm. In particular, on steel substrate the coating thickness increased when the spraying distance decreased and this is probably owing to higher spraying efficiency.

Fig. 3(f) displays denser microstructure as it is mainly formed by fully molten areas, as a consequence of the sintering grade and very low porosity of the initial granules. And also, the decrease of fine debris probably arising from the splashing and poor contact between the impacting particles and underlying deposits was observed in Fig. 3(c) for sample P6 and Fig. 4(c) [6,7].

The XRD patterns of the coatings are shown in Fig. 5. It can be seen that from the phases observed in this work that it display a slightly higher amount of rutile phases as compared to anatase phase. Anatase phase is expected to occur mostly in the non-molten areas. However, part of the anatase may have crystallised from liquid droplets and may, therefore, belong to the molten areas. The anatase phase, which is stable at temperatures below approximately 900 °C would transform to a stable rutile phase during the thermal spraying process.



(a) (b) (c)

Fig. 4 SEM micrograph of surface (a) and cross section (b), (c) of P4

TABLE II
THICKNESS OF TiO_2 COATING

Parameters	P4	P5	P6	P7	P8
Thickness (μm)	79.8	60.9	110.0	216.1	209.4

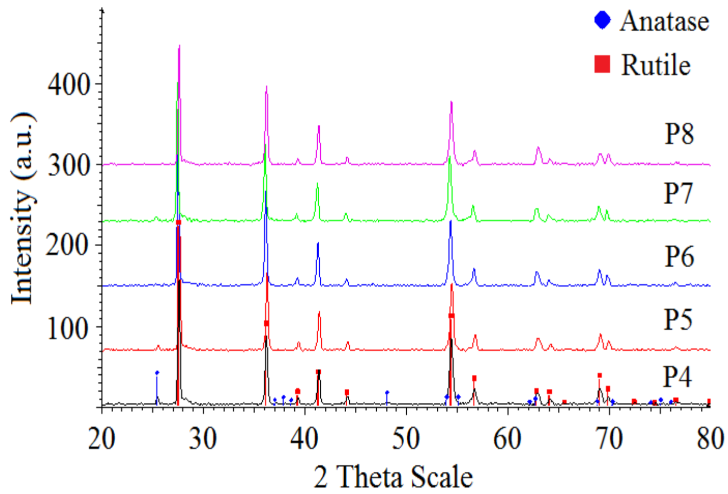


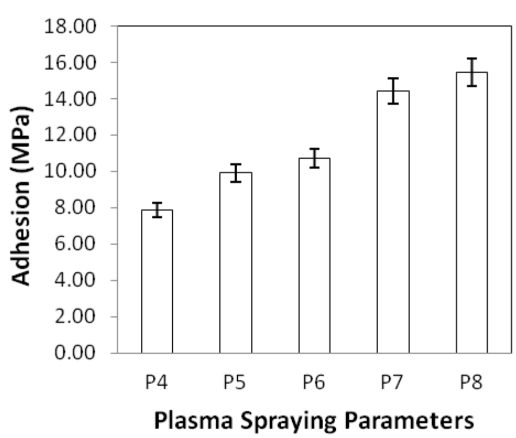
Fig. 5 XRD pattern of TiO_2 powder coating based on various parameters

Coating mechanical properties (adhesion strength and microvickers hardness) for the 5 spray-dried feedstocks are shown in Fig. 6 in terms of bar diagrams. Fig. 6(b) shows the microhardness value of various coatings and it can be seen that the utilization of higher plasma power and by lowering the spraying distances, it slightly increase the microhardness value of coatings. The graph shows increasing trends from parameter P4 until parameter P8.

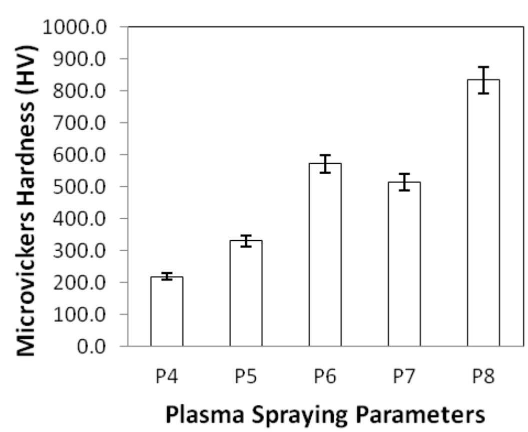
Thermal sprayed coatings are consisted of molten and partial/non-molten particles. Therefore the microhardness is supposed to be high in regions where there exists a higher amount of molten particles, and the hardness is predicted to be low in regions where there exists a notable concentration of loosely bound partial or non-molten particles. The fraction of molten and partial/non-molten particles is one of the major factors determining the microhardness of coatings [6,7].

More interestingly, significant trends were observed for both graph; adhesion strength and microvickers hardness. It can be observed that when then microhardness increases, the adhesion strength is improved. The sample of parameter P8 shows the highest microhardness value and it correspond with the adhesion strength value which also stated the highest as compared to other samples. The reasons showed in the literature for explaining this behavior are because of more homogenous TiO_2 distribution inside the splats leading to a higher splat bonding strength [7].

As referred to Fig. 3(F), the dense microstructure of sample P8 has improved the microvickers hardness value, thus resulting in a significant effect on the adhesion strength value. This is due to difference on the spraying distance whereas sample P4, P5 and P6 stated lower value for both microvickers hardness and adhesion strength properties.



(a)



(b)

Fig. 6 The mechanical properties values of various coatings sprayed with different plasma spraying parameters; (a) adhesion strength and (b) microvickers hardness

IV. Conclusion

The aim of this study was to produce titanium dioxide coatings with an important ratio of anatase phase to provide coatings with interesting structures for photocatalytic applications. The TiO_2 powders were plasma sprayed and it is shown that the powder are partially melted when sprayed but the particles core remain unchanged whereas the outer shell may be locally melted. The splats produced with these powders either are composed of non-molten particles surrounded by molten particles that acts as a binder or a disk shape spread with microcracks. In general, the coatings obtained from a closer distance; 6.5 cm led to better mechanical properties than those of the coating obtained from 8 cm of spraying distance. Although the findings obtained are very promising, further research is still necessary so as to connect feedstock characteristics, coating microstructure and properties, and to improve on the anatase phase.

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