Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Suspension high velocity oxy-fuel spraying of a rutile TiO_2 feedstock: Microstructure, phase evolution and photocatalytic behaviour

M. Bai, R. Khammas, L. Guan, J.W. Murray, T. Hussain*

Faculty of Engineering, University of Nottingham, NG7 2RD, UK

ARTICLE INFO

Keywords:
SHVOF
Rutile
Anatase
Microstructure
Phase evolution
Photocatalytic

ABSTRACT

Nano-structured TiO_2 coatings were produced by suspension high velocity oxy fuel (SHVOF) thermal spraying using water-based suspensions containing 30 wt% of submicron rutile powders (~180 nm). By changing the flame heat powers from 40 kW to 101 kW, TiO_2 coatings were obtained with distinctive microstructures, phases and photocatalytic behaviour. Spraying with low power (40 kW) resulted in a more porous microstructure with the presence of un-melted nano-particles and a lower content of the anatase phase; meanwhile, high powers (72/101 kW) resulted in denser coatings and rougher surfaces with distinctive humps but not necessarily with a higher content of anatase. Linear sweep voltammetry (LSV) was used to evaluate the photocatalytic performance. Surprisingly, coatings with the lowest anatase content (~20%) using 40 kW showed the best photocatalytic behaviour with the highest photo-conversion efficiency. It was suggested that this was partially owing to the increased specific surface area of the un-melted nano-particles. More importantly, the structural arrangement of the similarly sized TiO_2 nano-crystallites between rutile and antase phases also created catalytic "hot spots" at the rutile–anatase interface and greatly improved the photo-activity.

1. Introduction

TiO_2 exhibits good photo-catalytic properties for a wide range of applications, such as sensor devices, dye-sensitized solar cells, hydrogen evolution, solar energy harvesting and health care [1,2]. It is also generally believed that as a photo-catalyst, TiO_2 is more effective in the form of nano-particles, given their higher surface area [3,4]. By employing sub-micron or nano-particles, a number of methods have been used for the production of nano-structured TiO_2 coatings, such as electrophoretic deposition (EPD) [5–7], sol–gel [8,9], thermal spray [10,11], and plasma spray [12,13], etc. Among them, suspension high velocity oxy fuel (SHVOF) thermal spray is an emerging technology for producing dense and nano-structured ceramic coatings with a significant improvement in density, strength and durability over conventional thermally sprayed coatings [14,15]. For SHVOF, modifications on conventional HVOF guns were carried out by replacing the ordinary powder injection system with a suspension injection device with a stirrer [16]. Direct injection of suspensions into the combustion chamber also leads to significant improvement of the heat transfer between the HVOF flame and the fine particles, and results in a more uniform microstructure [17]. Nevertheless, the flame heat power needs to be well-controlled as it would strongly affect the phase stability of nano-TiO_2, which is the key to its photocatalytic properties [18]. TiO_2 generally exists in nature in three polymorphic phases: anatase, rutile, and brookite [19–21]. Anatase phase is less stable than rutile, which irreversibly transfers to rutile at high temperatures (728 °C) [22].

In our previous work [23], a range of nano-structured TiO_2 coatings were prepared by SHVOF from a water-based suspension of pure anatase powders using flame heat powers ranging from 40 kW to 101 kW. It was demonstrated that the heat powers had a significant effect on the phase compositions of the TiO_2 coatings as a mixture of rutile and anatase phases. The rutile content increased exponentially with heat powers, which was believed to be undesirable as previous studies suggested that a higher content of anatase was preferred owing to better photo-activity [24]. Nevertheless, it has also been reported that mixed-phase TiO_2 exhibited even better photocatalytic properties than pure anatase or high anatase content [25,26]. To explain these disagreements, it is essential to look into other factors (e.g. microstructure, crystallite size, etc.) that may also contribute to the distinctive photocatalytic behaviour apart from the phase effect. With this question in mind, in this study, we carried on our previous investigations on the nano-structured TiO_2 coatings sprayed by the SHVOF technique using rutile suspensions. The resulting coating microstructure, mechanical properties, and topography were investigated by scanning electron microscopy (SEM), micro-indentation and surface profilometry. Phase content was analysed using X-ray diffraction

* Corresponding author.
E-mail address: tanvir.hussain@nottingham.ac.uk (T. Hussain).

http://dx.doi.org/10.1016/j.ceramint.2017.08.068
Received 27 June 2017; Received in revised form 8 August 2017; Accepted 9 August 2017

(XRD) in combination with Rietveld Refinement. The mechanisms for phase evolution during the SHVOF process with both suspensions of anatase and rutile powders were discussed. Linear sweep voltammetry test (LSV) was used to evaluate the coatings' photocatalytic performance. The correlation between the photocatalytic behaviour of TiO_2 coatings and other coatings' properties was also discussed (e.g. microstructure, phase content, and crystallite size, etc.). We aimed to obtain nano-structured TiO_2 coatings with desirable properties and the most sensitive photo-activity by optimising parameters for suspension HVOF thermal spray.

2. Experimental procedure

2.1. Materials

A commercial water-based rutile suspension (MilliDyne, Finland) with a solid content of 30 wt% was used in this study. The suspension was sprayed onto AISI 304 stainless steels (Fe-19.0Cr-9.3Ni-0.05C in wt%) with dimensions of 60 × 25 × 1.5 mm.

2.2. Spray Process

Substrates were grit blasted with F100 brown alumina particles (0.125–0.149 mm) under 2 bar pressure, and cleaned by an ultrasonic acetone bath to remove any embedded alumina particles. The samples were then mounted onto a carousel rotating at 73 rpm with a vertical axis of rotation. The suspension was mixed for 90 min using mechanical stirrer at a speed of 940 rpm to achieve homogeneous suspension. A modified UTP/Miller Thermal HVOF system with a direct injection at the centre of the gas mixing block was used to spray the suspension. The suspension injector had a diameter of 0.3 mm to inject the suspension into the centre of the combustion chamber. A 22 mm long combustion chamber with 110 mm long barrel nozzle was used in this study. The suspension was fed using a pressurised 2 L vessel equipped with a mechanical stirrer to ensure uniform dispersion of the nanoparticles in solution and consistent flow onto the substrate without clogging of the nozzle. The pressure of the feeding system was fixed at 3 bar during the spray with a flow rate of 80 mL/min. The gun was mounted on a z-axis traverse unit in front of the rotating carousel and it was set to a stand-off distance from the surface of the substrate of 85 mm. The gun was scanned vertically up and down at 5 mm/s to build up a coating of the required thickness. The substrates were cooled by compressed air jets during and after the spray. The flow rates were set using a volume control system for fuel gas and oxygen as shown in Table 1. Hydrogen was used as combustion fuel to achieve a cleaner flame and also to reduce any hydrocarbon combustion products in the resulting coating, as any contamination might affect the photocatalytic behaviour. The theoretical flame heat power for each spray was calculated using standard combustion formulae and the samples are labelled by the flame heat powers throughout the paper.

2.3. Characterisation

A scanning electron microscope (SEM, JEOL JSM-6490LV, USA) operated at 20 kV was used to examine the suspension feedstock powder and the coating microstructure under secondary electron (SE) and back-scattered electron (BSE) modes. Coating thickness and porosity were analysed by Image-pro plus software (Media Cybernetics, USA) using the BSE images from 3 different locations with a total area of 600 × 600 μm^2. The coating roughness was measured by Talysurf CLI 1000 tester (Taylor Hobson, UK). Six profiles (2 mm in length) for each sample were conducted, three along the length, and three along the width of the sample surface area. Micro-hardness testing was carried out on polished cross-sections near the central area of coatings using a Vickers tester (BUEHLER, UK). A loading of 25 gf was applied for 30 s in 10 different regions for each sample. An X-ray diffractometer (XRD, D500 Siemens) was used to analyse the feedstock suspension powder and the as-sprayed coating. The anatase content in the TiO_2 coating is usually quantified by an equation developed by Keller et al. [27] using the intensities of anatase (101) and rutile (110) peaks as follows:

$$C_A = \frac{8I^{A(101)}}{8I^{A(101)}+13I^{R(110)}}\times 100\% \quad (1)$$

When the crystallite size is smaller than 300 nm, XRD peaks are broadened so the use of relative height of XRD peaks in XRD patterns can result in errors. Alternatively, the peak area was used to calculate the anatase content in the TiO_2 coating by the following equation:

$$C_A = \frac{A^{A(101)}}{A^{A(101)}+1.265A^{R(110)}}\times 100\% \quad (2)$$

where C_A is the anatase content in the coating, $A^{R(110)}$ and $A^{A(101)}$ the areas of the rutile (110) peak and the anatase (101) peak respectively [28]. Quantitative Rietveld refinement (TOPAS V5, Bruker) was also employed to analyse the phase composition in coatings, and principles of whole powder pattern modelling (WPPM) were used for crystallite size and micro-strain calculations [29]. The Lotgering factor F(*hkl*) was computed for the three theoretically most intensive rutile reflections of (110), (101) and (211). The Lotgering factor represents a simple qualitative measure to assess whether any preferred orientation in the irradiated volume is present by comparing peak or integral intensities of the measured XRD pattern and those of a randomly oriented powder sample [23]. The comparison is made for the intensity of selected (*hkl*) (I^{hkl}) and the intensities I in a chosen 2θ range in the following manner:

$$F(hkl) = \frac{\frac{I^{hkl}}{\Sigma_{2\theta\ range} I} - \frac{I_0^{hkl}}{\Sigma_{2\theta\ range} I_0}}{1 - \frac{I_0^{hkl}}{\Sigma_{2\theta\ range} I_0}} \quad (3)$$

Lotgering factor of 0 corresponds to a completely random distribution while the value of 1 would indicate a complete orientation of the chosen (*hkl*) planes in the sample. Due to overlap of anatase and rutile reflections in measured XRD patterns, Lotgering factor was computed using peak intensity values after background level subtraction of the measured data and I_0 were taken from rutile powder diffraction PDF 21–1276. The considered rutile reflections in the chosen 2θ range were (110), (101), (200), (111), (210), (211), (220) and (310).

2.4. Photo-activity test

Electrochemical characterisations were carried out using Autolab PGSTAT30 (EcoChemie, Netherlands) in a two-electrode cell with the sample as photo-anode and a platinum wire with a 0.5 mm diameter as counter-electrode. The photocurrent was recorded under the linear sweep voltammetry (LSV) scan starting from the open circuit potential to 1.2 V at a scan rate of 10 V/s. A sacrificial electrolyte (0.28 M Na_2S/ 0.32M Na_2SO_3, Sigma-Aldrich) was used in order to prohibit the backward reactions and the rapid recombination of e^-/h^+ pairs [2]. Experiments were conducted under both light and dark conditions to determine the photocatalytic properties of the prepared samples. A xenon lamp-based Oriel 96000 150 W solar simulator (AM 1.5 G,

Table 1
Gas flow rate and flame heat power.

Coating	H_2 flow rate (L/min)	O_2 flow rate (L/min)	Total flow rate (L/min)	Flame heat power kW
R40	244	122	367	40
R72	438	219	657	72
R101	611	306	917	101