Influence of high velocity oxy-fuel parameters on properties of nanostructured TiO$_2$ coatings

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Abstract. A liquid fuel high velocity oxy-fuel (HVOF) thermal spray process has been used to deposit TiO$_2$ nanostructured coatings utilizing a commercially available nanopowder as the feedstock. The coatings were characterized by means of X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and transmission electron microscope (TEM), respectively. Photocatalytic activity was evaluated as a rate constant of decomposition reaction of methylene blue (MB) determined from the changes of relative concentration of MB with UV irradiation time. The results indicate that the sprayed TiO$_2$ coatings were composed of both TiO$_2$ phases viz. anatase and rutile, with different phase contents and crystallite sizes. A high anatase content of 80% by volume was achieved at 0·00015, fuel-to-oxygen ratio with nanostructure coating by grain size smaller than feedstock powder. Photocatalytic activity evaluation results indicated that all the TiO$_2$ coatings are effective to degradation MB under UV radiation and their activities differ in different spray conditions. It is found that fuel flow rate strongly influenced on phase transformation of anatase to rutile and by optimizing the rate which can promote structural transformation and grain coarsening in coating and improving photocatalytic activity.

Keywords. HVOF; TiO$_2$; phase transformation; nanostructure coating.

1. Introduction

In high velocity oxy-fuel (HVOF) thermal spraying, a gaseous or liquid fuel is pre-mixed with oxygen at high pressure and flow rates, before entering an internal combustion chamber. The oxy-fuel mixture is continuously ignited and the combustion products accelerated along the gun barrel nozzle to produce a supersonic flame (~2000 m/s). In liquid-fuelled HVOF, guns are normally designed with a convergent–divergent nozzle, which gives superior acceleration to the gas flow and high momentum output to powder particles (Kamnis and Gu 2006). Powder is normally fed into the hot gas stream at downstream of the nozzle instead of being directly fed into combustion chambers, which effectively reduces overheating to powder particles and contributes to the unique feature of high powder impact velocity without overheating. The combustion of liquid fuel, such as kerosene is very complicated, due to the large variation of composition and fuel quality. Altering the gas flows and mixing ratios, the ratio of fuel to oxygen, will influence both the flame's temperature and velocity (Hearley and Little 2000).

HVOF thermal spray can provide an efficient way for depositing coatings of nanostructured materials because: (i) the powder particles hit the substrate with relatively high speed, which produces coatings with high density and (ii) relatively low gas temperature prevents particles from being superheated during flight and helps to preserve the nano-crystalline structure of powders deposited on the substrate (Kim 2007).

The studies performed in recent years showed that the thermal spray technique could be employed to obtain TiO$_2$ coatings with an effective photocatalytic performance for the decomposition of organic compounds (Kanazawa and Ohmori 2005). TiO$_2$ possesses three crystal polymorphs in nature: brookite, anatase and rutile (Ye and Ohmori 2002). Anatase is a metastable TiO$_2$ polymorph, it tends to transform into the rutile upon heating, resulting in a loss of photocatalytic activity (Grzmil *et al* 2004). In thermal spray processes, the heat induced in the particle during spray can cause transformation of anatase to rutile. Due to this effect, the spray coatings usually contain more rutile with low photocatalytic properties (Yi *et al* 2008). Toma *et al* (2006)

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and Yang *et al* (2007) reported that the coating with 12·6% and 55% by volume and anatase content could be deposited through gas fuel and HVOF spray of anatase TiO_2.

In this paper, the coatings were deposited through a liquid fuel high velocity oxy-fuel spray with different fuel rates using TiO_2 nanopowders as feedstock. The influence of the fuel rate on phase transformation of anatase to rutile, crystal size, morphology and photocatalytic activity of the coatings was investigated accordingly.

2. Materials and experimental

Degussa P25/20 TiO_2 nanopowder was used as feedstock for the coating deposition. Commercially agglomerated and granulated nanopowders were used in this study. The average agglomerated size of the powder was 20 μm. $5 \times 50 \times 50$ mm 316 Stainless steel plates were employed as substrates for the coating deposition. Prior to spraying, the substrate was blasted with silicon carbide grit.

Metjet III Metallization high velocity oxy-fuel (HVOF) system was used with kerosene as its fuel liquid. Powder was deposited using four sets of spray parameters which differed only in the flow rate of fuel and oxygen into the HVOF gun. The powder feed rate was 8 g/min and carried by N_2 at a flow rate of 4 L/min. Stand-off distance was maintained at 336 mm and the nozzle diameter was 11 mm. Oxygen flow rate was fixed at 800 l/min. Different fuel flow rates were employed as shown in table 1. The morphology of the surface and cross-section of coatings was examined using S360 Cambridge Scanning Electron Microscope (SEM). TEM images were obtained using the LEO 912 transmission electron microscope that employed a tungsten electron gun in the voltage range of 120 kV with an optical point to point resolution of 1 nm. Samples were softly scraped-off from the substrate and examined by TEM. X-ray diffraction (XRD) patterns were recorded on a Philips PW3710 diffractometer using CuKα radiation. After thermal spray, the percentages of anatase and rutile were calculated from X-ray diffraction intensities. The content of anatase TiO_2 in the coatings was calculated by the following equation (Spurr and Myers 1957):

$$A = 1/(1 + 1 \cdot 265(IR/IA)) \times 100, \tag{1}$$

where IA is the highest peak intensity of anatase phase ((101)), IR the highest peak intensity of rutile phase ((110)) and A the content of anatase in the coatings. The crystallite size was evaluated from the X-ray diffraction patterns based

on the Scherrer formula as shown in the following equation (Spurr and Myers 1957):

$$t = (0 \cdot 9\lambda)/(B \cos \theta), \tag{2}$$

where B is peak width at half maximum intensity, λ the X-ray wavelength and θ the Bragg diffraction angle.

The photocatalytic performance of the coatings was determined by the degradation of methylene blue (MB) dye solution. The coated steel (5×5 cm) was immersed into 35 ml aqueous MB solution with a concentration of 10^{-5} mol/l in a reaction cell. The cell was located in the photo-reactor ready for UV-irradiation having 5×8 watt black UV lamps, inducing the photochemical reaction to proceed. The coating/dye solution was irradiated in the horizontal direction and the distance between the UV lamp and the coating was kept within 20 cm. The change of MB concentration in accordance with irradiation time was measured by UV-VIS spectrophotometer under UV irradiation. The photocatalytic degradation generally follows a Langmuir–Hinshelwood mechanism (Yu *et al* 2002).

$$Ln(C0/C) = t/\tau, \tag{3}$$

where C is the concentration of the reactant (ppm), $C0$ the initial concentration of the reactant (ppm), t the irradiation time (h), and τ a constant of photocatalytic activity. According to (3), the smaller value of τ, the better the photocatalytic activity of the coatings. Therefore, τ can be used as the characteristic decomposition time to evaluate the effectiveness of the sprayed coating in decomposing the pollutants.

3. Results and discussion

The crystalline structure of each of the coated test samples was studied by XRD analysis. It is generally assumed that the anatase metastable phase causes a higher photocatalytic degradation of the pollutants (Daniel *et al* 2008). Figure 1 shows the XRD patterns of TiO_2 sprayed coatings and feedstock powder. The results have been summarized in table 1. These results demonstrate that fuel flow rate influences the deposition characteristics such as the anatase content and anatase/ rutile average crystallite size. The peak belonging to Fe is due to the effect from the substrate. The thickness of the applied coatings was about 5 μm so due to substrate peak

Table 1. Anatase content and anatase/rutile average crystallite size in different sprayed coatings.

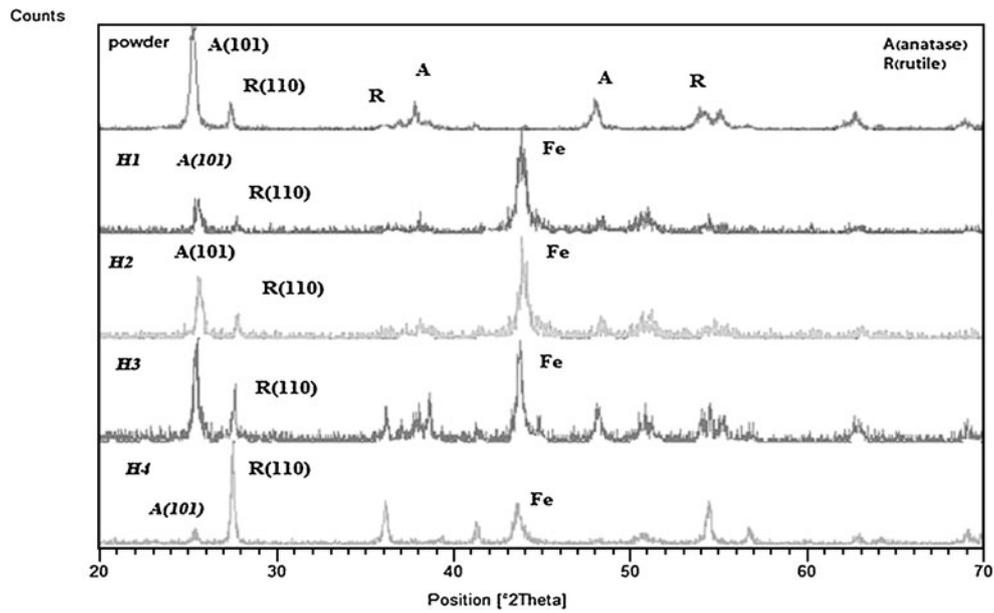| Samples	Fuel flow rate (mL/min)	Fuel-to-oxygen ratio	Anatase % by volume	Anatase crystallite size (nm)	Rutile crystallite size (nm)
Feedstock powder	–		75·0	25·9	41·7
H1	120	0·00015	80·0	20·7	17·3
H2	160	0·0002	78·0	25·9	17·3
H3	200	0·00025	65·8	25·9	34·6
H4	240	0·0003	8·00	25·9	41·7

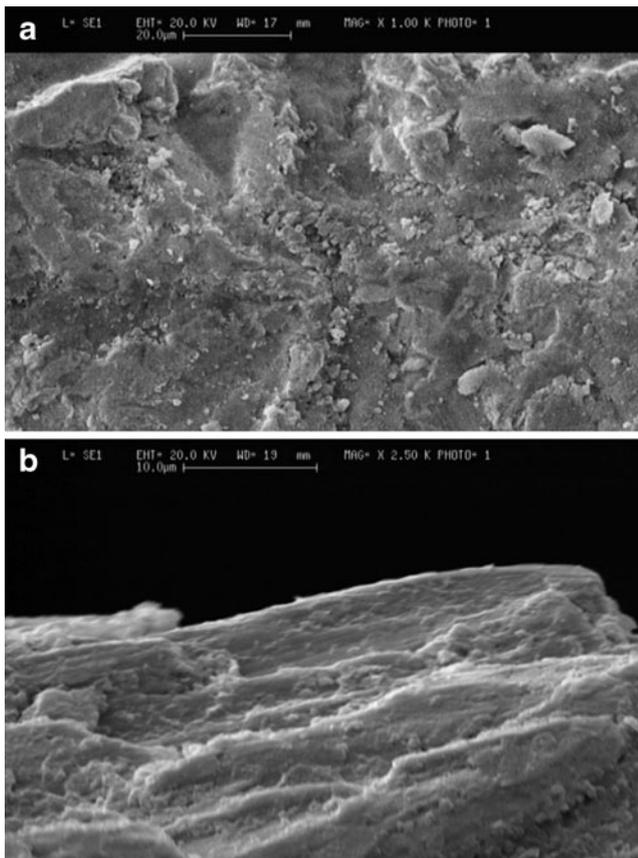**Figure 1.** XRD pattern of feedstock powder and HVOF sprayed TiO₂ coatings.

Figure 2. SEM images of **a**. surface and **b**. cross-section of H1 coating with 120 ml/min fuel flow rate.
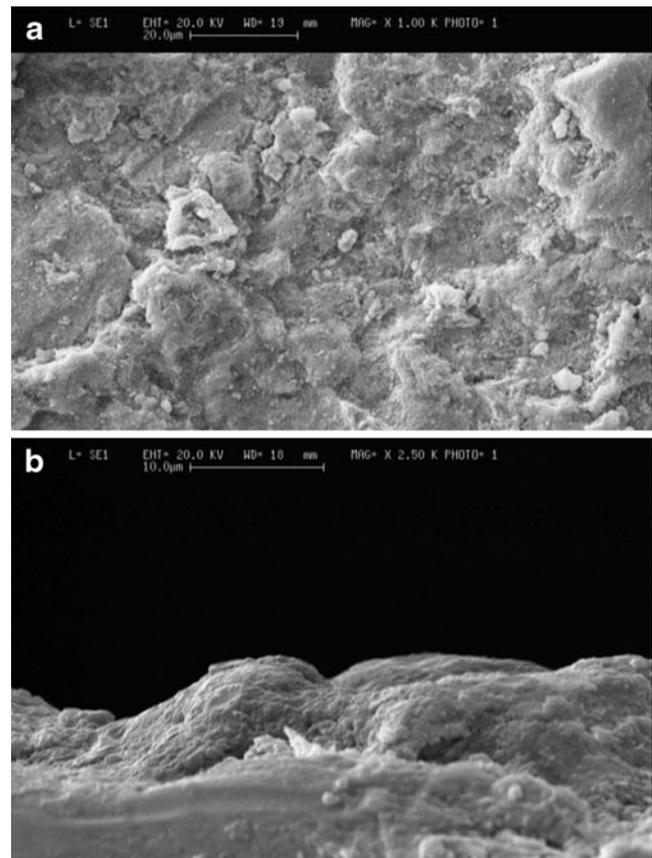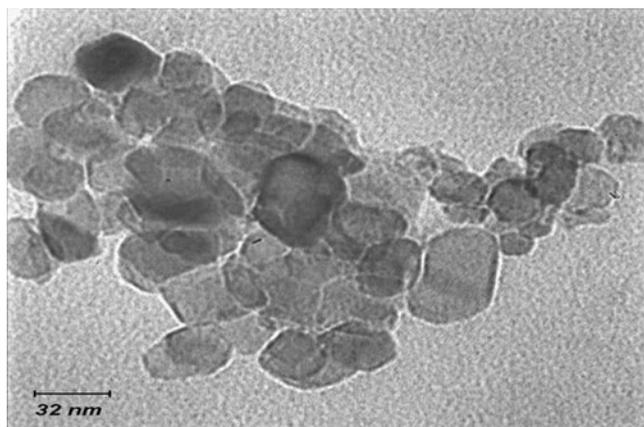

Figure 3. SEM images of **a**. surface and **b**. cross-section of H4 coating with 240 ml/min fuel flow rate.

the height of TiO₂ peaks became low. It is assumed that the temperature and velocity of the powder particle prior to impact on the substrate or component surface and cooling rate of impacted droplets on substrate, will control the coating characteristics.

Figures 2 and 3 present the SEM images of (a) surface and (b) cross-section of TiO₂ spray coatings. It can be seen that there are two kinds of structures in the coating. One is the continuous molten phase and the other is a porous microstructure, which resulted from the existence of the
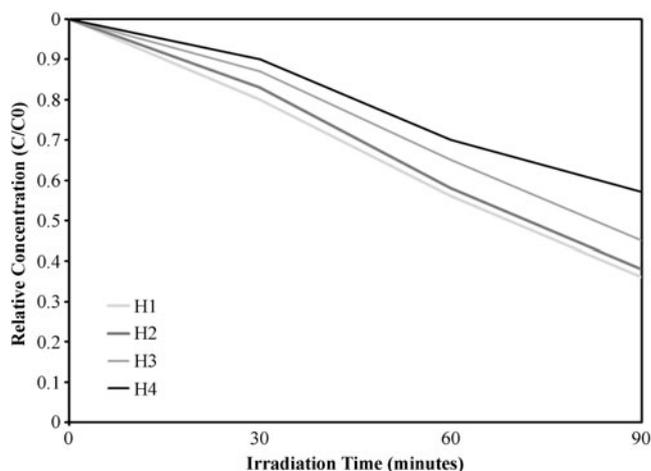
Figure 4. TEM image of H1 coating with 120 ml/min fuel flow rate.

Figure 5. Degradation of MB by TiO_2 coatings at different spray parameters as indicated in table 1.

Figure 6. τ value of TiO_2 coatings at different spray parameters as indicated in table 1.

non-molten or semi-molten starting powders. In H4 coating with 240 ml/min fuel flow rate, the porous structure increased as a result of higher fuel rate.

Figure 4 shows the typical TEM morphologies of the sprayed H1 coating with 120 ml/min fuel flow rate. The size of most grains in the H1 coating is <30 nm. The average grain size is about 20 nm which coincides with the grain size in the as-sprayed coatings measured by XRD.

In H1 and H2 coating with 0·00015 and 0·0002 fuel-to-oxygen ratios, respectively the content of anatase reached 80% and 78% by volume, slightly more than the original feedstock powder content of 75% by volume. In the HVOF process, velocity of the torch is too high (about 1200 m/s) and its temperature is too low (about 2400°C), respectively. Thus this high speed causes very little heat to flow into the in-flight particles, therefore, the degree of melting of particles becomes too low. Consequently, semi-molten (molten surface and non-molten cores) particles contain higher amounts of anatase than the fully molten particles (Yang *et al* 2004). As the particles impinge on the substrate the liquid fraction of droplet spreads to form a splat and solidified under a high cooling rate of about $10^7 - 10^8$ °K/s. Under such splat cooling conditions, metastable phases such as γ-Al_2O_3 in HVOF alumina, is easily formed in the coating (Mcpherson 1973). In agreement with the mentioned conclusions, the semi-molten TiO_2 droplets can be solidified in an anatase form. The XRD results clearly indicated that the anatase phase was readily formed in the TiO_2 deposited coating.

As the fuel flow rate into the gun increases whilst the oxygen flow rate remains constant in the sprayed coatings, the anatase content reached 80% by volume, 78% by volume, 65% by volume and 8% by volume, respectively. Thus the % anatase content had reduced as the fuel-to-oxygen ratio in the combustion chamber had increased, which causes a more significant explosion and resulting in higher torch temperatures. This higher explosion causes the torch velocity to increase due to a constant nozzle diameter, so by increasing the fuel-to-oxygen ratio, both the temperature and torch velocity will be increased (Dolatabadi *et al* 2003).
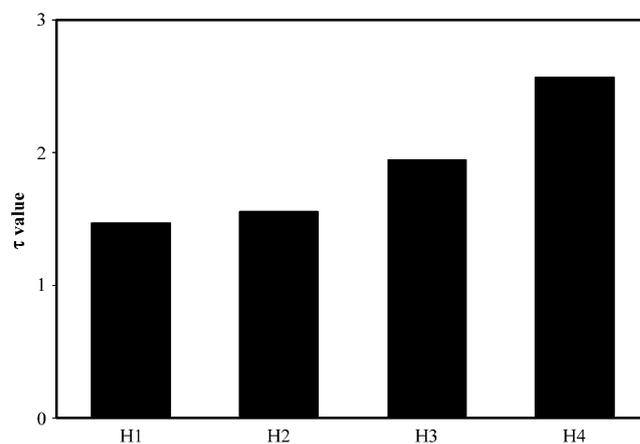
By increasing the fuel-to-oxygen ratio, the gas velocity at the exit of the nozzle changed very little compared to the change in the gas temperature (Li and Christodes 2003) which on the one hand, created more semi-molten particles and on the other hand, caused a lower solidification rate of particle droplet on the substrate, consequently the rutile phase content in the coating increased. In coating with 240 ml/min fuel flow rate the anatase content drastically decreased compared with 200 ml/min fuel flow rate coating. As mentioned later, by increasing fuel flow rate the temperature and velocity of torch increased. This phenomenon has two effects, one, it causes higher degree of molten particles and, two, it also provides lower cooling rate of droplet on substrate. Probably in 240 ml/min fuel flow rate coating compared with 200 ml/min, the degree of molten particles are too high, so high amount of anatase transforms to rutile during spray and also the cooling rate is too low to form anatase on substrate.

In the H1 coating, the average anatase/rutile crystallite size was 20·7/17·3 nm which is smaller than the feedstock powder which was 25·9/41·7 nm, respectively. It is assumed that a lower torch temperature, a lower degree of melting

and a higher solidification rate creates the anatase in the particle cores and also forms anatase in coating during solidification on the substrate. The rutile present in the coating is probably due to the higher degree of melted particles and lower rate of solidification. The high solidification rate and high velocity impact of the particles on to the substrate would tend to break up the size of the anatase and rutile crystallites. In addition, significant rutile size reduction could also be the result of the rapid solidification of the particle droplets. In sprayed coatings with higher torch temperature, anatase/rutile crystallite sizes have been increased. Probably increasing torch temperature and decreasing solidification rate causes increase in the size of crystallites.

The HVOF TiO₂ coatings were tested in the photocatalysis to evaluate their effectiveness for the degradation of MB. The decomposition characteristics of MB is illustrated in figure 5, as it is indicated in all the sprayed coatings that MB was decomposed. According to (3), the τ values of the sprayed TiO₂ coatings under different spraying parameters were calculated, and then summarized in figure 6. Lower τ values indicate a higher photocatalytic activity, so the τ value of the coatings with lower fuel flow rate, which is lower than the τ value of the coatings by higher fuel flow rate demonstrated a higher photocatalytic activity.

TiO₂ absorbs ultraviolet rays and forms electron (e^-) and positive hole (h^+). Hydroxyl radical (OH°) is created from the positive hole and adsorption water. Some researchers have stated that some pollutants were decomposed by the hydroxyl radical (Sayilkan *et al* 2008). On the other hand, anatase TiO₂ shows more efficient photocatalytic activity than rutile, so a lower anatase content ratio causes a lower photocatalytic performance. The photocatalytic activity of each of the sprayed coatings was different, which shows a behaviour dependent on the spray parameters. The different spray conditions cause different phase transformation of anatase to rutile and anatase content, respectively. The different photocatalytic performances in the degradation of the pollutants correlated mainly with the crystalline structure of the titanium coatings.

4. Conclusions

This paper proposed a study on the crystal structure, size, morphology and photocatalytic activity of TiO₂ coatings obtained by high-velocity oxygen fuel spray methods with different fuel rates, using liquid fuel and agglomerated TiO₂ nano-powder as feedstock material.

The coating obtained by the HVOF technique was characterized by the crystal structure, size, morphology and photocatalytic activity that was obtained by XRD, SEM, TEM and degradation of MB under UV irradiation. The as-sprayed TiO₂ coating was composed of different contents of anatase and rutile phases obtained by different fuel ratios. HVOF spraying parameters were found to influence the coating quality. A lower fuel-to-oxygen ratio equivalent to 0·00015 is the preferred coating parameter to provide a high anatase content of 80% by volume. This coating has higher photocatalytic activity. This high anatase content in the coating is attributed to the retention of the anatase in the starting powder and also from forming anatase from the molten particles due to its rapid solidification. Furthermore, the preferred HVOF sprayed coatings presented a smaller crystallite size than the corresponding original powders. It can be concluded that the HVOF spraying with kerosene fuel and an optimum fuel-to-oxygen ratio is an appropriate technique to create photocatalytic TiO₂ surfaces with a high anatase ratio and nanostructure morphology.

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