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Nanostructured Photocatalytic Titania Coatings Formed by Suspension Plasma Spraying

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This paper describes formation of titanium dioxide coatings designed for photocatalytic applications, obtained by suspension plasma spraying (SPS), an alternative of the atmospheric plasma spraying (APS) technique in which the material feedstock is a suspension of the material to be sprayed. Two different TiO_2 powders were dispersed in distilled water and ethanol and injected in Ar-H_2 or Ar-H_2-He plasma under atmospheric conditions. Scanning electron microscopy (SEM) and x-ray diffraction (XRD) analyses were performed to study the microstructure of the titania coatings. Photocatalytic efficiency of the elaborated samples was evaluated from the conversion ratio of different air pollutants: nitrogen oxides (NOx) and sulfur dioxide (SO_2). The morphology and crystalline structure of the deposits depended mainly on the nature of the solvent (water or alcohol) used in the preparation of the slurries. Dense coatings were obtained starting from aqueous suspensions and porous deposits were elaborated by plasma spraying of a PC105 alcoholic suspension. A significant phase transformation from anatase to rutile occurred when ethanol was used as a solvent. Different photocatalytic performances were observed as a function of the nature of the liquid material feedstock, the spraying parameters, and the nature of the pollutant.

Keywords nitrogen oxides, photocatalysis, sulfur dioxide, suspension plasma spraying, titanium dioxide

1. Introduction

Photocatalysis is a well-known method used to solve the major problems of air and water pollution. Titanium dioxide (TiO_2) is one the most important photocatalyst because of its structural and electronic properties (Ref 1). For photocatalytic applications, titanium dioxide can be used in powder form or immobilized in the form of a coating formed by different deposition techniques.

The thermal spraying technique is widely used to prepare titania coatings for mechanical and biomedical applications due to their hardness, wear and corrosion resistance, and biocompatibility (Ref 2-5). Research performed in recent years has shown that the thermal spray technique could be used to obtain TiO_2 deposits with effective photocatalytic performance for decomposition of organic compounds. In addition, several thermal spraying methods were developed to obtain active photocatalytic coatings (Ref 6-9).

Suspension plasma spraying (SPS) is an alternative method to atmospheric plasma spraying that allows formation of nanostructured thin coatings and consists of injection in the plasma jet of submicron particles or nanopowders dispersed in a liquid solvent. The suspension permits particles to be fed with diameters ranging from several nanometers to 10 μm into the plasma plume.

This paper discusses the formation of titanium dioxide coatings starting from different titania feedstock suspensions injected in Ar-H_2/Ar-H_2-He plasma under atmospheric conditions. The effects of different parameters (solvent nature, plasma gases) on the microstructural characteristics of the deposits were investigated. The photocatalytic activity of the sprayed coatings was evaluated by the conversion rate of nitrogen oxides NOx (NO, NO_2) and sulfur dioxide (SO_2), which are major air pollutants that participate in acid rain formation and can cause serious problems with respect to human health (i.e., affecting the respiratory tract, causing lung edema, and reducing oxygen-carrying capacity by transformation of hemoglobin to methemoglobin).

2. Experimental Procedures

2.1 Materials

Two different titania powders were used in the preparation of liquid suspensions: P25 (Degussa AG, Frankfurt, Germany), generally considered as a reference in the photocatalytic tests, contains 80 vol% anatase (25 nm crystalline size) and 20 vol% rutile phase (50 nm) and has a specific surface area of ~50 $m^2\ g^{-1}$; and PC105 (Millennium Inorganic Chemicals, Rueil Malmaison, France), 100% anatase phase (23 nm) with a specific surface area of 85 $m^2\ g^{-1}$. Powder loading in the slurry was fixed

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at 20 wt.%. Distilled water and ethyl alcohol were used as solvents in the formation of the suspensions, without addition of a dispersing agent. The suspension properties are presented elsewhere (Ref 10).

2.2 Suspension Plasma Spraying

Titanium dioxide suspensions were sprayed using a 6 mm nozzle PTF4 plasma torch (Sulzer-Metco, Wohlen, Switzerland). Argon at flow rate of ~40 slpm was used as primary plasma gas. Hydrogen (3 slpm flow rate) and helium (20 slpm flow rate) were added to increase the conductivity and viscosity of the plasma. The arc current intensity was fixed at 400 A, and the arc voltage was ~50-56 V. A home-made experimental set-up allowed injection of the liquid feedstock in the plasma jet (Ref 10). The suspension, mechanically stirred, was introduced with a peristaltic pump in the system that ensured atomization of the slurry and radial injection of the droplets in the plasma plume. Argon at 3 slpm permitted atomization of the liquid in the enthalpic source. Stainless steel plates ($60 \times 70 \times 2$ mm^3), previously sand-blasted with alumina grit to ensure particle adhesion, were used as substrates and fixed at 80 mm from the plasma torch.

2.3 Characterization

The coating morphologies were examined using a JEOL JSM-5800 LV scanning electron microscope. X-ray diffraction (XRD) (X'Pert MPD Philips diffractometer, Eindhoven, The Netherlands) with Cu Kα radiation was used to assess the ratio of anatase to rutile and the crystalline size. Photocatalytic efficiencies of the coatings were evaluated versus degradation of nitrogen oxides and sulfur dioxide in a home-made set-up presented elsewhere (Ref 11). The catalysts were up-side irradiated by a light from a 15 W daylight lamp with 30% UVA and 4% UVB. Photocatalytic performance was evaluated after the first 30 min of UV irradiation, as the ratio of the concentration of removed pollutants to the concentration of pollutants.

3. Results and Discussion

3.1 Microstructural Characterization

The processes that occur during the SPS can be described through three main stages. The slurry is first disintegrated in liquid drops in the injector-atomizer by the atomizing gas. The suspension drops are then introduced into the plasma jet, where they are fragmented into smaller drops. A more efficient and faster breaking up of liquid droplets was observed when ethanol was used as the suspension solvent. Finally, the droplet solvent is evaporated during the plasma flight time, and the resulting particles are heated, melted, or partially melted and accelerated to the substrate, thus forming the coating.

The morphology of the deposits was affected by the nature of the slurry injected in the enthalpic source. The coatings formed from an aqueous suspension of TiO_2 particles, are dense and characterized by a wave-like structure (Fig. 1). The coating seems to result from impinging partially melted particles as well as nonmelted ones (overspray particles), which can maintain an almost spherical morphology (Fig. 2). Moreover, the microstructure of the coatings produced using aqueous suspensions with P25 or PC105 materials was almost similar.

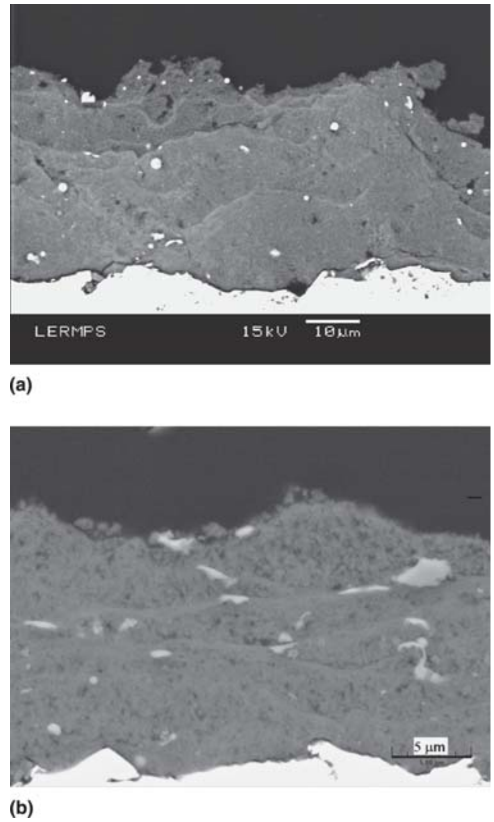

Fig. 1 SEM micrographs of sprayed coatings resulted from injection of aqueous suspensions of TiO_2 powders: (a) P25; (b) PC105 (Ar-H_2 plasma)

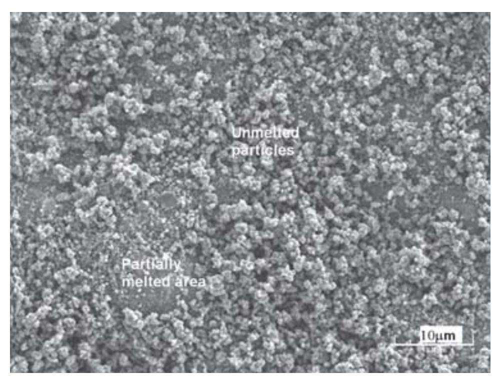

Fig. 2 Surface SEM micrograph of coating resulting from injection of PC105 aqueous suspension in Ar-H_2 plasma

Different morphologies were observed in the case of the deposits formed from alcoholic suspensions of the two titania powders. A scanning electron microscopy (SEM) image of the P25 alcohol-sprayed coating is given in Fig. 3, where melted and nonmelted particles are seen. The presence of melted zones is explained by the fact that the enthalpy of evaporation of ethanol is lower (0.8×10^6 J/Kg) than that of water (2.3×10^6 J/Kg).

It was also affirmed that injection of an alcoholic suspension into the plasma plume was assumed to increase the jet temperature as well as the gas speed (Ref 12). In this case, thermal trans-

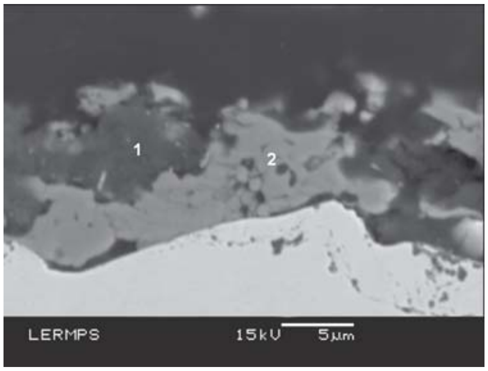

Fig. 3 Morphology of sprayed coating obtained from P25 alcoholic suspension: (1) nonmelted particles; (2) melted region (Ar-H_2 plasma)

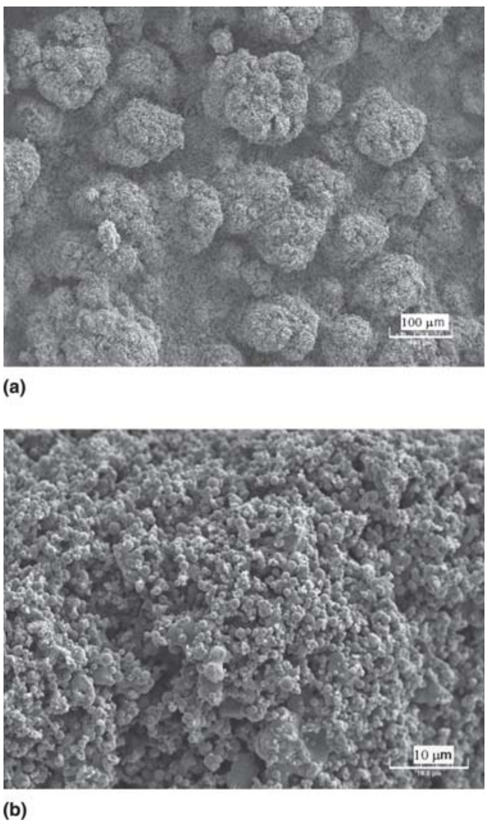

Fig. 4 Surface SEM micrographs of the PC105 alcoholic SPS coating

fer between the plasma and the particles is more important, so the particles are easily heated and then melted. Thus the molten particles have enough momentum to impinge upon the substrate and spread out in the form of splats, as is usually achieved in thermal spraying processes.

The coatings produced from an alcoholic suspension of PC105 particles are very porous; the surface is characterized by a significant roughness (cauliflower structure) compared with that obtained from an aqueous suspension (Fig. 4). Different microstructural features can be distinguished on the cross section of the coating: fully melted zones, nonmelted regions, and spherical particles with sizes ranging from 0.5 to 2 µm (Fig. 5).

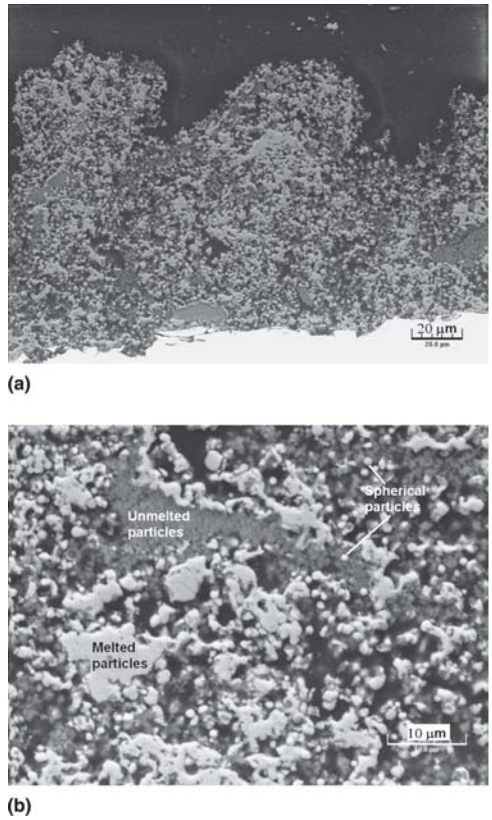

Fig. 5 SEM images (cross section) of the PC105 alcoholic SPS coating

These features can be explained by the large distribution of the liquid droplets injected in the plasma as well as the different thermal history of the particles in the enthalpic source before impinging on the substrate.

It is interesting to note the very different microstructures of these coatings compared with that resulting from the P25 alcoholic suspension. This singular structure could be first due to the different physical properties of the suspensions, such as density, viscosity, surface tension, and stability because of interaction of ethanol with the surface of the titania particles (presence of hydrogen bonds). On the other hand, the porous microstructure of the PC105 alcoholic coating could be attributed to an inhomogeneous atomization of the suspension, into a large droplet size distribution that creates disturbances in the plasma jet. In this case, some fine droplets are not able to enter into the plasma core or reach the desired melting temperature.

3.2 Crystalline Structure of the TiO_2 Coatings

It is generally assumed that, for the photocatalytic applications, the plasma power must be high enough to ensure evaporation of the liquid but low enough to maintain the crystalline structure of the titanium dioxide, thus avoiding phase transformations from anatase to rutile. XRD was performed to study the crystalline structure of the suspension-sprayed coatings. The analysis showed that the anatase phase content depended mainly on the nature of the solvent used in the formation of the liquid suspension.

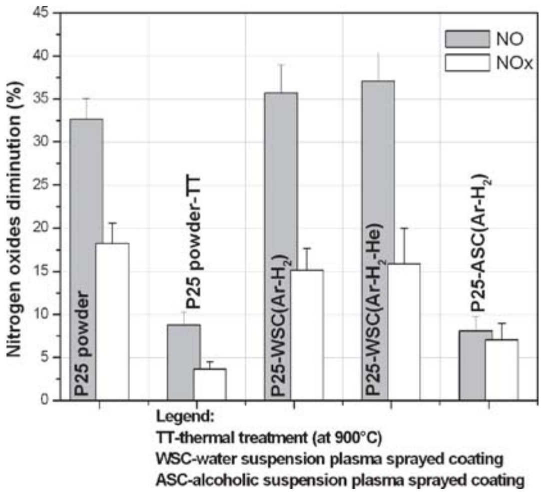

Fig. 6 Photocatalytic removal of nitrogen oxides in presence of TiO_2 P25 in powder and SPS coatings (after first 30 min of ultraviolet irradiation)

The plasma spraying of an aqueous slurry led to coatings where the anatase content and the average crystallite size were almost the same as were identified in the initial powders, ~78-80 vol% for the P25 coating and ~91-95 vol% for the PC105 coating. On the other hand, injection of the alcoholic suspensions involved the structural transformation from anatase to rutile (~23 vol% for P25-coating and 36 vol% for PC105-coating) as well as the increase of the crystallites' size of the anatase from 23-25 nm to 120-150 nm. In this case, phase transformation was attributed to easier fragmentation of the alcoholic slurry (thanks to a lower surface tension of the ethanol), followed by a rapid vaporization of the ethanol. Thus, the flight time of the resulting particles had to be long enough to ensure structural transformation from anatase to rutile.

3.2 Photocatalytic Activity

Photocatalytic tests were performed to study the activity of the coatings elaborated by SPS, and the results were compared with the those of the initial TiO_2 powders with respect to degradation of different air pollutants: nitrogen oxides and sulfur dioxide. In photocatalysis, the initial powder (0.2 g) was uniformly exposed by mechanical sieving to ensure a homogeneous distribution of the catalyst over the entire geometric surface of a Petri dish with 54 cm^2 surface area. Different behaviors of the photocatalytic performances were noticed depending on the nature of the liquid material feedstock, the spraying parameters, and the pollutant nature.

Photocatalytic Removal of Nitrogen Oxides. The TiO_2 coating performed by plasma spraying of a P25 aqueous suspension permitted to remove 36-38% NO and ~15% NOx; when the alcoholic suspension is sprayed, the coating ensured a degradation of nitrogen oxides of ~8% (Fig. 6). The different photocatalytic performance in the pollutants degradation was principally correlated with the crystalline structure of the coating. As previously described (Ref 13, 14), the anatase phase is a key parameter in the photocatalytic activity and a higher anatase content allows a better decomposition of nitrogen oxides. Moreover, injection of the aqueous suspension in various plasma conditions

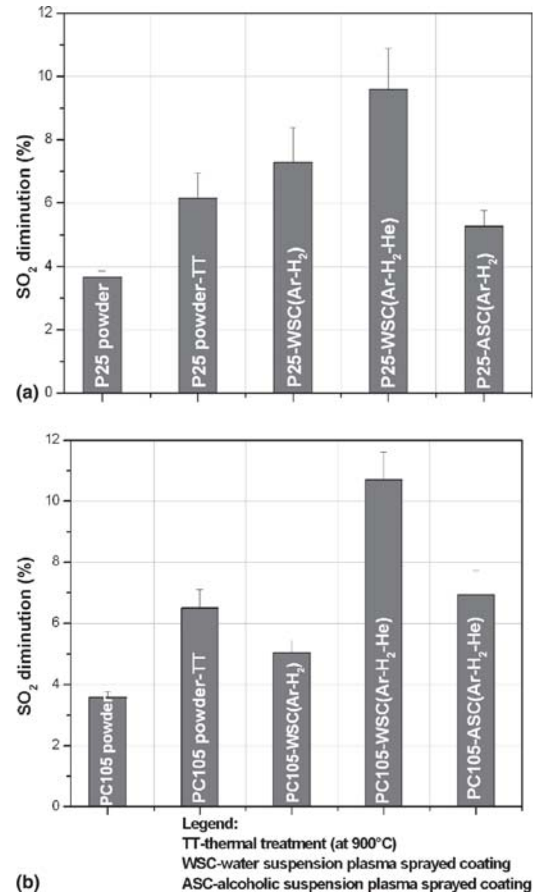

Fig. 7 Photocatalytic removal of sulfur dioxide in presence of TiO_2 in powder and SPS coatings (after first 30 min of ultraviolet irradiation): (a) P25; (b) PC105

(Ar-H_2 or Ar-H_2-He gas mixtures) involved few differences in the photocatalytic performance of the obtained coatings. A slightly better decrease of nitrogen oxides with coatings obtained from a P25 powder aqueous suspension was noticed compared with the result of the raw powder. In this case, the enhanced photocatalytic performance cannot be explained considering only the anatase content. It was assumed that removal of impurities coming from the raw powder preparation and a cleaning up of the free-water particles when crossing the plasma could explain such behavior. Different surface investigation techniques (IR spectroscopy and x-ray photoelectron spectroscopy) performed on the coating surfaces (Ref 15) showed higher hydroxylation compared with that of the powder. The hydroxyl groups played a beneficial role and enhanced the photocatalytic activity of titania, as reported previously (Ref 16, 17).

Photocatalytic Removal of Sulfur Dioxide. To our knowledge, only a few tests have been performed to evaluate the decrease of sulfur oxides by the photocatalysis process (Ref 18, 19), when no SO_2 photodegradation was found using only TiO_2 powder without any substrate.

In the present paper, a study of SO_2 photocatalytic removal was also proposed, and, as depicted in Fig. 7, the raw powders (P25 and PC105) present very low activity versus sulfur dioxide

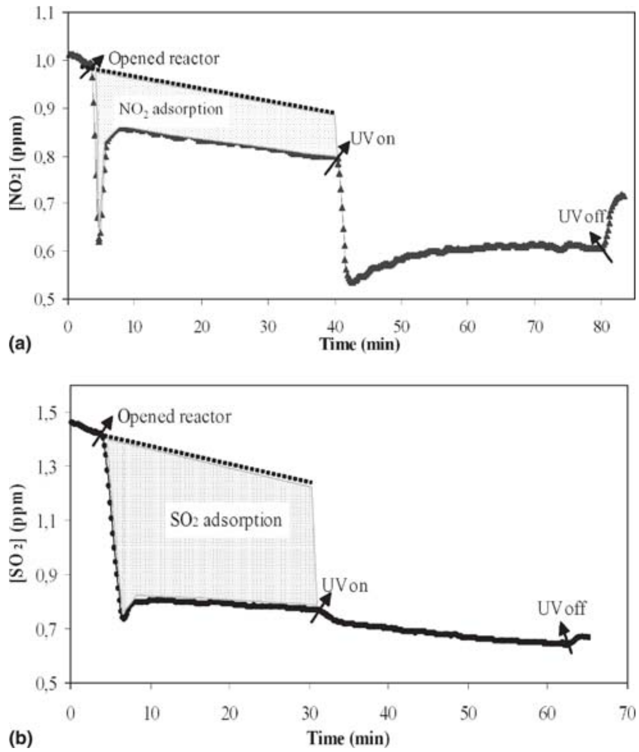

Fig. 8 Photocatalytic tests of the pollutants over a TiO_2 coating, case of P25 aqueous suspension coating (Ar-H_2-He plasma): (a) NO_2; (b) SO_2

photodegradation. The photocatalytic diminution was only ~4% after 30 min of ultraviolet irradiation. A slightly higher removal of ~6-7% was observed with thermally treated powders (at 900 °C during 24 h in an air thermal furnace) when only the rutile phase was identified by XRD analysis. As in the case of nitrogen oxides, a better photocatalytic diminution of SO_2 was observed with coatings formed by aqueous suspension plasma spraying. Moreover, the suspensions injected in an Ar-H_2-He plasma mixture permitted removal of ~10-11% of SO_2.

The low ratios of SO_2 removal over TiO_2 in the form of powder or coating could be explained by strong chemical interactions of sulfur dioxide molecules with metallic oxide surfaces (an SO_2 adsorption ~5 times higher compared with that of nitrogen oxides, as depicted in Fig. 8), and thus the TiO_2 was no longer activated by ultraviolet irradiation. Mahzoul et al. (Ref 20, 21) showed that the amount of SO_2 stored was 1.6 times higher than the amount of NOx that was stored by the same material at the same temperature. Interactions of SO_2 with metallic oxides were believed to lead to sulfite (SO_3^{2-}). In the same conditions, formation of sulfate (SO_4^{2-}) has also been reported (Ref 22-24).

As a consequence, additional analyses must be performed to investigate interactions of the sulfur dioxide with TiO_2 surfaces (powder and coating) during the photocatalytic process.

4. Conclusions

Titanium dioxide coatings were elaborated by a modified method of plasma spraying using different liquid suspensions of two titania powders (P25, PC105) as feedstocks. The coating morphologies and crystalline structures depended mainly on the nature of the solvent (water or alcohol) used in the preparation of the slurries. Dense coatings were obtained starting from aqueous suspensions, and porous deposits were formed by plasma spraying of the PC105 alcoholic suspension. Using a water-based suspension permitted the anatase phase to remain in the coating, whereas a significant phase transformation occurred when ethanol was the suspension solvent. The photocatalytic efficiency of the samples so formed was evaluated from the conversion ratio of different air pollutants: NOx and SO_2. Different photocatalytic performances were observed as a function of the nature of the material feedstock, the spray parameters, and the pollutant type.

The results showed that SPS allowed production of active surfaces for removal of air pollutants that, under similar operating conditions, had higher photocatalytic activity than did the initial raw powders.

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