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Research Article

Development of Photocatalytic Active TiO_2 Surfaces by Thermal Spraying of Nanopowders

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Titanium dioxide is a very useful photocatalyst for the decomposition and diminution of environmental water and air pollutants. In such applications, it can be used as slurry or as immobilized coating obtained by different deposition methods. The studies performed in the last years showed that thermal spraying could be employed to elaborate TiO_2 coatings with high performance for the decomposition of organic compounds. This manuscript presents a comparative study on the microstructure and photocatalytic performance of titania coatings obtained by different thermal spray techniques: atmospheric plasma spraying (APS), suspension plasma spraying (SPS), and high-velocity oxygen fuel spray process (HVOF). Different titania powders and suspensions were used to study the influence of the feedstock materials on the coating characteristics. The deposits were mainly characterised by SEM and X-ray diffraction. The photocatalytic performance was evaluated from the removal of nitrogen oxides. The experimental results showed that a drastic reduction of the pollutant concentration was obtained in presence of coatings elaborated by suspension plasma spraying. TiO_2 coatings resulting from the spraying of agglomerated powder presentd less efficiency. That was mainly explained by the significant phase transformation from anatase to rutile that occurred in the enthalpic source during the spray processes.

1. INTRODUCTION

Titanium dioxide (TiO_2) is an attractive material for numerous technological processes. It finds applications as gas sensors, as pigments in foodstuffs, paints, cosmetics, or pharmacology, as a corrosion resistant coating, in heterogeneous catalysis and photocatalysis, in solar cells for the production of hydrogen and electric energy, in electronic devices, and so on. After the initial work by Fujishima and Honda [1] on the photolysis of water on TiO_2 electrodes, extensive studies on titania photochemical applications have been carried out in the last few decades. As a photocatalyst, titanium dioxide can be used in the degradation of air and water pollutants, in medical sterilization, and even in cancer therapy [2–4]. Among the two TiO_2 crystalline phases, anatase and rutile that can contribute to the photocatalysis, it is generally assumed that the anatase—the metastable phase, which by thermal treatment irreversibly turns into rutile—allows a higher-photocatalytic degradation of the pollutants. However, some anatase powders containing small quantities of rutile present a better efficiency than those of pure anatase [5, 6]. For the photocatalytic applications, titanium dioxide can be used in powder form (slurry) or immobilized in thin film or coating form obtained by different deposition techniques (sol-gel, dip-coating, and physical or chemical vapour deposition, etc.). TiO_2 powders have an outstanding photocatalytic efficiency compared with their coating counterparts due to their higher specific surface area. However, the separation of powder from the liquid state used in water treatments and recycling processes is troublesome, mainly because of the formation of aggregates. On the other hand, it is considered that the aforementioned difficulties concerning films and coatings can be overcome and their applications can also be expanded by employing various materials as substrates.

Thermal spraying is widely used to prepare titania coatings for mechanical and biomedical applications due to their hardness, wear and corrosion resistance, and biocompatibility [7–12]. The studies performed in the last 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 [13–16].

In thermal spraying, the material feedstock (commonly a powder with typical particles size distribution ranging from 10 to 100 μm) is injected in an enthalpic source (thermal plasma or flame obtained by ionization-excitation of inert gases or combustion, resp.). The particles are melted (or partially melted), accelerated by a gas flow, and crushed on the target substrate where rapid solidification and deposit built-up occur. In the last years, a new technique, called liquid thermal spraying, with liquid materials as feedstock precursors was developed [17–24]. The liquid precursors can be (i) organic (ethoxide, butoxide, acetate, etc.) or inorganic (nitrate, chloride, etc.) solutions, and (ii) aqueous or alcoholic suspensions of the material to be sprayed. The suspension allows the feeding of particles with diameters ranging from several nm to 1 μm into the plasma plume. To be used as a precursor in thermal spraying, the slurry (suspension of fine particles in a solvent) has to contain a high-powder load with a low viscosity and a high stability. The deposition depends on different parameters such as the hydrodynamic properties of the liquid which depend on the solid content, droplet diameters, and thermal and kinetics history of the droplets before impinging on the substrate [25].

In this paper, a comparative study on the microstructure and photocatalytic performance of the nanostructured TiO_2 coatings obtained by different thermal spray techniques: atmospheric plasma spraying (APS), suspension plasma spraying (SPS), and high-velocity oxygen fuel (HVOF) spray process is proposed. The coating microstructure was mainly characterized by scanning electron microscopy and X-ray diffraction. The photocatalytic behavior of sprayed coatings was evaluated by a degradation of gaseous nitrogen oxide pollutants (NO, NOx), major air pollutants that cause serious problems on the environment and human health.

2. EXPERIMENTAL PROCEDURE

2.1. Material feedstock

Three commercial TiO_2 powders were used in this study: a pure anatase nanopowder, with 7 nm crystalline size, namely, TiO_2-ST01 (Ishihra Sangyo, Japan) agglomerated by spray-drying in order to prepare spherical microsized anatase particles (with a size distribution ranging from 10 to 50 μm); a 23 nm anatase nanopowder TiO_2-PC105 (Millennium Inorganic Chemicals, France) and TiO_2-P25 powder (Degussa AG, Germany) generally considered as a reference in the photocatalytic applications, containing 80 vol.% anatase (25 nm) and 20 vol.% rutile (50 nm).

Distilled water and ethylic alcohol were used as solvents in the preparation of suspensions, in which the powder load was set to 20–25 wt%. No dispersing agent was added in the composition of the suspensions.

2.2. Thermal spraying

Different thermal spray techniques were used to elaborate nanostructured coatings. Moreover, the spray conditions had been adjusted in order to minimize the particle heat input and to maintain the original anatase phase in the elaborated coating.

Atmospheric plasma spraying (APS) was carried out with a Sulzer-Metco PTF4 plasma gun (6 mm nozzle torch). Ar at 40 $L\cdot min^{-1}$ was used as primary plasma gas; H_2 (3 $L\cdot min^{-1}$) and He (20 $L\cdot min^{-1}$) were added as secondary plasma gases. The arc intensity was about 400 A. Stainless steel substrates ($60\times70\times2$ mm^3) previously sand-blasted were set to 80 and 100 mm from the exit of the nozzle torch. The powder rate was 14 $g\cdot min^{-1}$ and carried by Ar at 3 $L\cdot min^{-1}$.

A special device was designed for the injection of liquid in the plasma [26]. The suspensions were introduced by a peristaltic pump, at a feed rate of about 20–25 $mL\cdot min^{-1}$, in the system that ensured the atomization of the liquid and radial injection of the resulting drops in the plasma jet (Figure 1). Argon at a flow rate of 3–5 $L\cdot min^{-1}$ allowed the atomization of the liquid before entering in the plasma.

High-velocity oxygen flame spraying (HVOF spraying) was performed with a Sulzer-Metco CDS 100 gun (with a 3-inche nozzle) using natural methane, as fuel gas. The flame was obtained by the combustion of 100 $L\cdot min^{-1}$ CH_4 with 400 $L\cdot min^{-1}$ O_2. N_2 at a flow rate of 50 $L\cdot min^{-1}$ was also added to the gas mixture to decrease the flame temperature. The powder feed rate was 20 $g\cdot min^{-1}$ and was carried by N_2 at a flow rate of 9.5 $L\cdot min^{-1}$. The spray distance was set to 150 mm.

2.3. Characterisation

The coatings morphology was examined using a JEOL JSM-5800 LV scanning electron microscopy. X-ray diffraction (X'Pert MPD Philips diffractometer) with Cu Kα radiation was used to assess the anatase to rutile ratio. Scan step was 0.02° s^{-1} with a step time of 0.5 second in the 20–90° 2θ range. The volume percentage of anatase was determined according to the relation developed by Berger-Keller et al. [27]. $C_A = 8I_A/(8I_A + 13I_R)$, where I_A and I_R are the X-ray intensities of the anatase (1 0 1) and rutile (1 1 0) peaks, respectively. The crystallite size was evaluated from the X-ray diffraction based on the Scherrer formula.

The photocatalytic performance of TiO_2 was evaluated by the decrease of nitrogen oxides (NO, NOx) concentration in a purpose-built test chamber described elsewhere [28]. A 15-W daylight lamp with a fraction of 30% UVA and 4% UVB ensured the irradiation of the TiO_2. The NO and NOx concentrations were measured continuously using an AC-30M NOx dual chamber analyzer (environmental SA, France) and recorded with a data acquisition system.

The photocatalytic tests were performed over the sprayed coatings and the initial powders. The photocatalytic performances were evaluated as the ratio of the photocatalytic

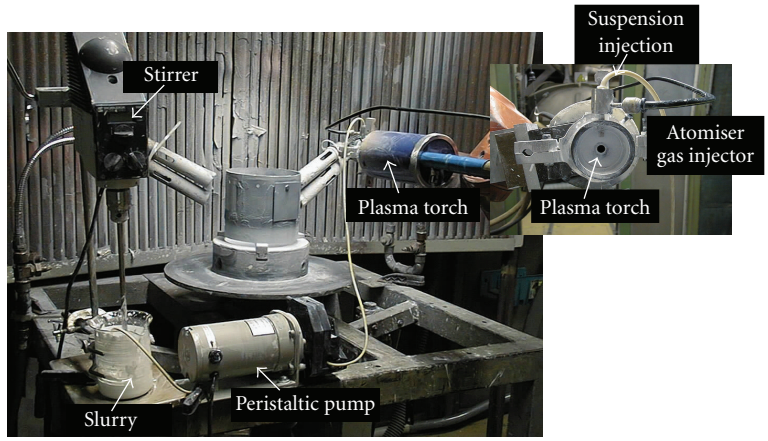


Figure 1: Suspension plasma spraying setup.

conversion of nitrogen oxides and determined by the following relations:

$$\text{NO conversion } (\%) = \frac{[\text{NO}]_{\text{initial}} - [\text{NO}]_{\text{UV}}}{[\text{NO}]_{\text{initial}}} \times 100,$$
$$\text{NOx conversion } (\%) = \frac{[\text{NOx}]_{\text{initial}} - [\text{NOx}]_{\text{UV}}}{[\text{NOx}]_{\text{initial}}} \times 100, \quad (1)$$

where NO conversion (%) and NOx conversion (%) were the photocatalytic removal of NO and NOx concentrations in the presence of the catalyst and UV irradiation; $[\text{NO}]_{\text{initial}}$ and $[\text{NOx}]_{\text{initial}}$ represented the values of the NO and NOx concentrations without UV irradiation; $[\text{NO}]_{\text{UV}}$ and $[\text{NOx}]_{\text{UV}}$ were the values of the NO and NOx concentrations under UV irradiation.

3. RESULTS AND DISCUSSION

3.1. Coating microstructure

3.1.1. Plasma spraying

The morphology of the sprayed coating was mainly dependent on the thermal spray technique. The deposits obtained by the plasma spraying of the agglomerated TiO_2-ST01 nanopowder were characterized by a bimodal microstructure (Figure 2): on the one hand, a thin lamellar morphology commonly observed with sprayed coatings that contained fully melted particles, and on the other hand, a structure of densely agglomerated grains that contained partially melted particles.

When the agglomerated ST01 nanopowder was dispersed in distilled water (25 wt% powder loading) and injected in the plasma jet as a suspension, the microstructure of the resulting coatings did not present the lamellar structure, which is a characteristic of the thermal sprayed coatings. The TiO_2-ST01 suspension-sprayed coatings were relatively porous and constituted of partially melted or unmelted fine particles as depicted in Figure 3. The different microstructure

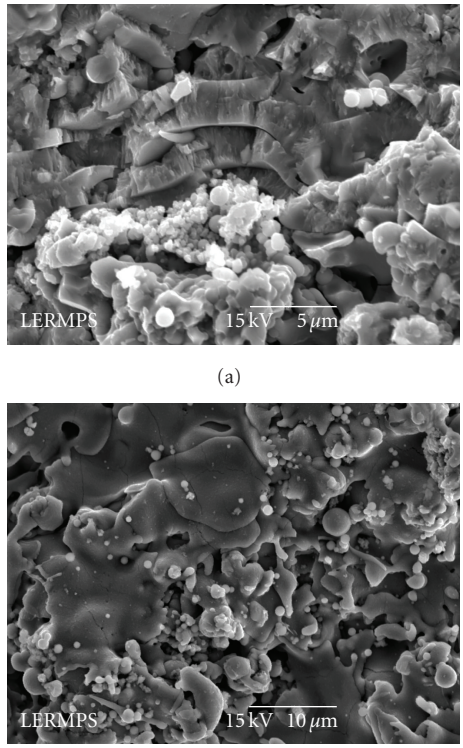


Figure 2: SEM-microstructures of nanostructured TiO_2-ST01 coating prepared by APS technique: (a) fracture; (b) surface.

of the ST01 coatings elaborated by suspension plasma spraying compared with their counterparts obtained from conventional APS was explained by the fact that the thermal transfer between the plasma jet and the material was less important when the suspension was used as feedstock material. In this case, a part of the plasma energy was used to evaporate the solvent of the suspension droplets; the flying time of the resulting particles (free of liquid) was not enough to ensure a complete melting of the particles before impact on substrate.

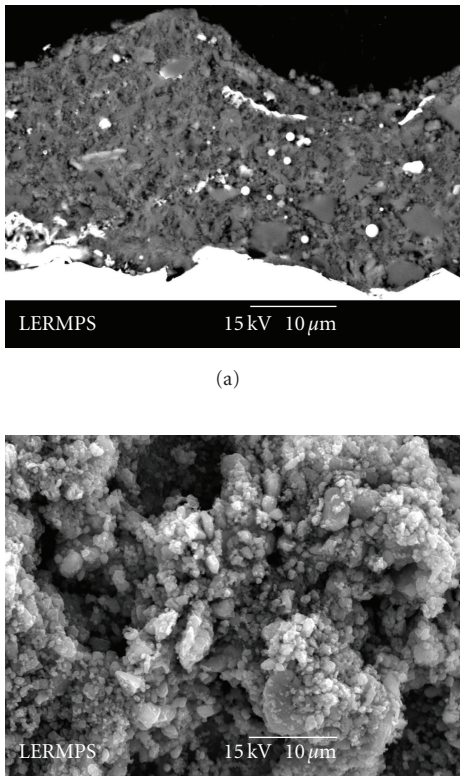


Figure 3: SEM-microstructures of TiO_2-ST01 coating prepared by suspension plasma technique: (a) cross-section; (b) surface.

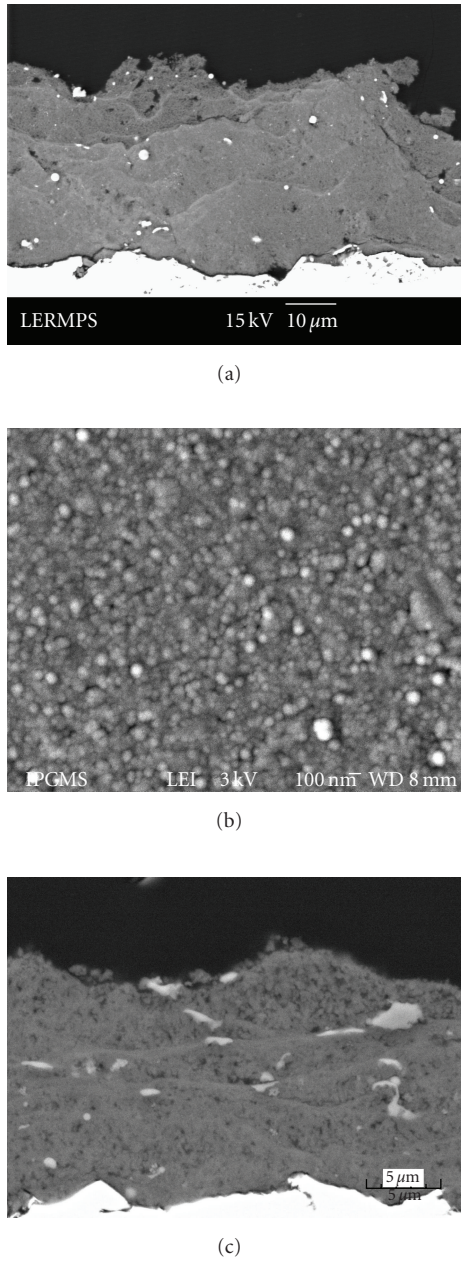
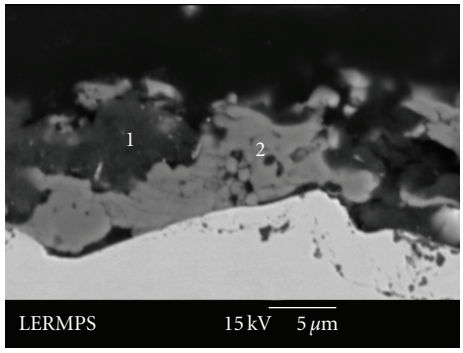


Figure 4: SEM-morphology of coatings starting from aqueous suspensions of (a) TiO_2-P25; (b) TiO_2-P25 at high-microscopic scale; (c) TiO_2-PC105 [29].

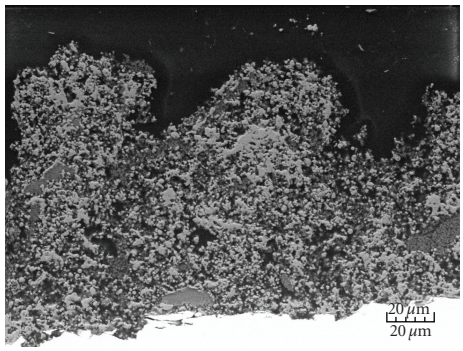
A nonlamellar microstructure was also observed in the coatings obtained by the plasma spraying of the suspensions (20 wt% powder loading) of nonagglomerated titania powders P25 and PC105. The coatings formed from aqueous suspensions exhibited relatively dense structures (see Figure 4). Moreover, it seemed, at high-microscopic scale, that the coatings were built up by the dense stacking up of fine spherical nanoparticles [29].

Different morphologies were observed in the case of the deposits elaborated from alcoholic suspensions of the two titania nonagglomerated powders. TiO_2-P25 alcoholic suspension-sprayed coating contained melted and nonmelted particles as shown in Figure 5(a). The presence of the melted zones was explained by the fact that the enthalpy of the evaporation of ethanol was lower ($0.8 \cdot 10^6$ J/kg) than that of water ($2.3 \cdot 10^6$ J/kg). Moreover, it was claimed that the injection of an alcoholic suspension in the plasma plume was assumed to increase the jet temperature as well as the gas speed [25]. In this case, the thermal transfer between the plasma and the particles was more important so the particles were easily heated and then melted. Thus, the molten particles had enough momentum to impinge on the substrate and spread out in splat forms like usually achieved in thermal spray process.

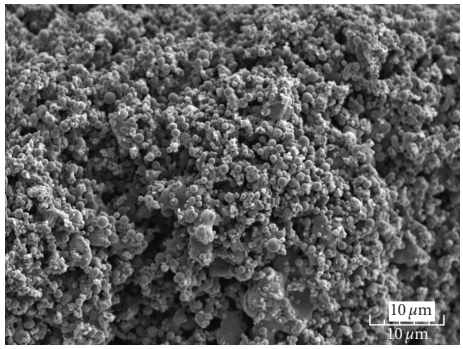
The coatings produced from an alcoholic suspension of PC105 particles were porous; different microstructural features were distinguished on the cross-section of the coating: fully melted zones, nonmelted regions, and spherical particles (Figures 5(b), 5(c)). These features were explained by the large 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 was interesting to notice the very different microstructures of these coatings compared to that resulting from the P25 alcoholic suspension. This structure was probably due to the different physical properties of the suspensions such as viscosity or surface tension.



(a)



(b)

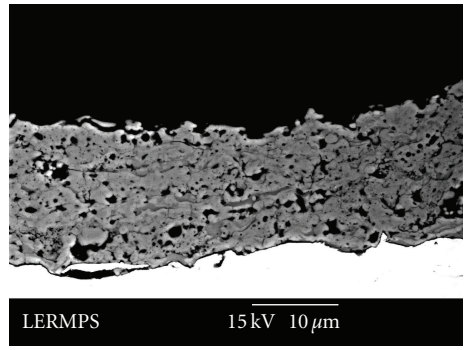


(c)

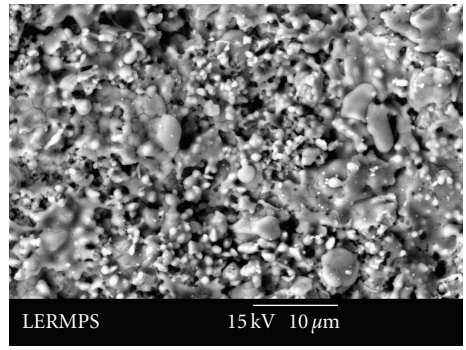
Figure 5: SEM-morphology of coatings starting from alcoholic suspensions of (a) TiO_2-P25, cross-section (1: unmelted regions; 2: melted zones); (b) TiO_2-PC105, cross-section; (c) TiO_2-PC105, surface.

3.1.2. HVOF spraying

The TiO_2 deposits elaborated by the HVOF spraying of agglomerated TiO_2-ST01 nanopowder were porous and characterized by a layered structure (Figure 6). The coatings were mainly built up by the melted nanoparticles impacting on the substrate that flatten to form splats which are consecutively piled on top of the others. Some partially molten particles embedded in the coating structure were also observed. The surface analysis showed the presence of fine particles which conserved the initial features of the agglomerated TiO_2-ST01 nanopowder.



(a)



(b)

Figure 6: SEM-microstructures of TiO_2-ST01 coating prepared by HVOF technique: (a) cross-section; (b) surface.

3.2. Coating crystalline structure

X-ray diffraction was performed to assess the anatase to rutile ratio. The analysis showed that the passage of the feedstock material (as particles or liquid suspension) in the enthalpic source (plasma or flame) involved the modifications of the chemical state of titanium dioxide compared to that of the initial powders. These structural transformations depended on the thermal spray method used in the elaboration of TiO_2 coatings.

Table 1 resumes the crystalline phases and the crystalline size of the particles determined in different sprayed coatings. The coating elaborated by the plasma spraying of agglomerated ST01 powder contained the rutile structure as a major phase; the anatase content was estimated between 10.9 and 12.2 vol.%. Some traces of TiOx or Magnéli phases were also identified. The crystallite sizes of the anatase increased from 7 nm to 34 nm. An important phase transformation from anatase to rutile was also observed in the coating obtained by HVOF process. In contrast, when the agglomerated ST01 powder was injected in the plasma in form of aqueous suspension, the content of anatase phase was higher than 96 vol.%; furthermore, the crystalline size of anatase was preserved (7.0–7.3 nm), practically identical to that of the original powder.

The crystalline structure of the coating was relative to the melting degree of the particles during spraying. It is generally accepted that the rutile phase corresponds to the fully melted

Table 1: Phases and crystallites size in the thermal sprayed coatings.

Ref. TiO_2 coating	Anatase (vol.%)	Anatase crystallites average size (nm)	Rutile crystallites average size (nm)	Observations (other phases)
ST01-APS	10.9–12.2	19.2–34.8	67.0–78.6	Traces of Magnéli phases (Ti_3O_5; Ti_6O_{11})
ST01-WSC*	>96.0	7.0–7.3	0–25.1	—
ST01-HVOF	12.6	80.0	90.0	—
P25-WSC	77.6–81.4	27.1–29.2	51.7–60.5	—
P25-ASC**	23.0	46.0	120.0	—
PC105-WSC	91.9–95.1	34.9–38.7	140.9–194.9	—
PC105-ASC	36.2	151.1	99.2	—

*WSC-coating resulted from plasma spraying of aqueous suspension.
** ASC-coating resulted from plasma spraying of alcoholic suspension.

particles, whereas the anatase structure was mostly presented in the partially and nonmelted particles [13].

With an aqueous suspension of the agglomerated ST01 nanopowder, the phase transformation was avoided because a part of the plasma energy was used to vaporize the water contained in the liquid droplets. So, the flight time in the plasma jet was not long enough so that the anatase to rutile structural transformation occurred before the particle impact on the substrate.

In the case of suspension spraying of nonagglomerated TiO_2 nanopowders, the XRD analysis showed that the anatase ratio depended on the nature of the solvent (water or alcohol) used in the suspension preparation. The plasma spraying of an aqueous slurry led to coatings where the anatase content and the average crystallite size were almost the same as those identified in the raw powders. On the other hand, the injection of alcoholic suspensions involved the structural transformation from anatase to rutile (about 23 vol.% for P25-coatings and 36 vol.% for PC105 coatings), as well as the increase of the crystallite size of the anatase from 23–25 nm to 150 nm. In this case, the phase transformation was attributed to an easier fragmentation of the alcoholic slurry (due 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 the partial structural transformation from anatase to rutile.

3.3. Photocatalytic performance for the degradation of nitrogen oxides

The photocatalytic properties of the sprayed coatings were evaluated by the diminution of gaseous nitrogen oxides and compared with those obtained in the presence of the corresponding powders. 0.4 g of each powder was uniformly distributed over the entire geometric surface of a Petri dish with 54 cm^2 surface area.

The photocatalytic activities of TiO_2 coatings are represented in Figure 7. Different behaviors in the photocatalytic performances were noticed depending on the spraying parameters and nature of the material feedstock.

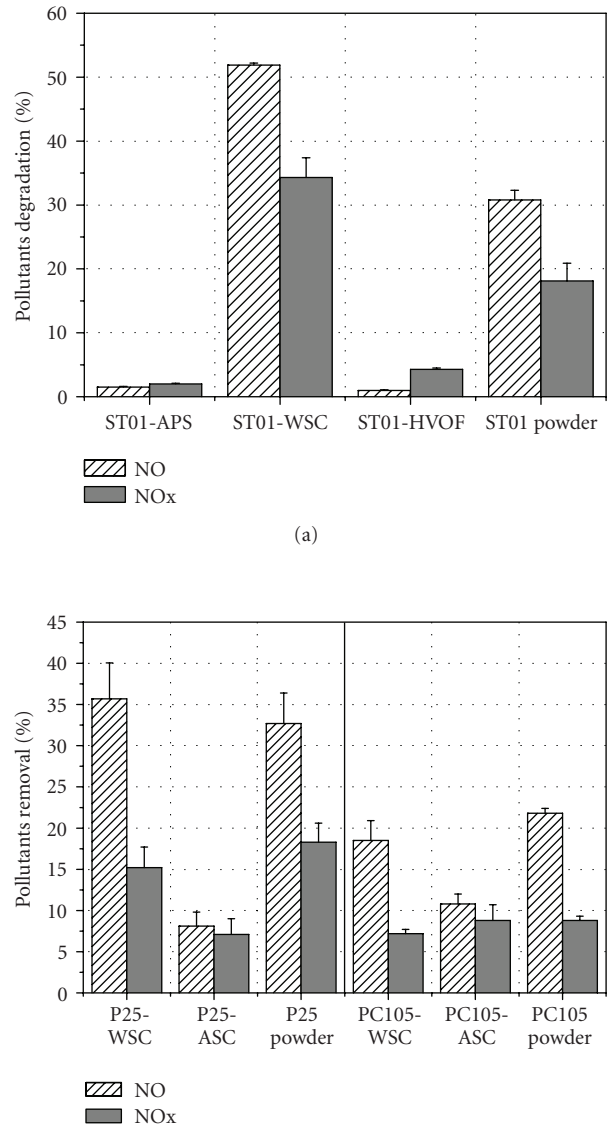


Figure 7: Photocatalytic degradation of nitrogen oxides in presence of coatings elaborated from (a) agglomerated ST01 nanopowder; (b) nonagglomerated P25 and PC105 nanopowders.

A very low degradation of nitrogen oxide pollutants (<5%) was obtained in presence of the TiO_2 surfaces produced by APS and HVOF sprayings of agglomerated ST01 nanopowder. Other authors reported good photocatalytic responses of APS- or HVOF-sprayed TiO_2 coatings in the decomposition of different organic compounds such as phenol, acetaldehyde, or methylene blue [13–16]. Moreover, the photocatalytic properties of sprayed coatings were improved by the doping of TiO_2 with Pt [30], metallic oxides such as Al_2O_3, Fe_3O_4, ZnO, SnO_2 [31–33], or hydroxyapatite [34]. In our case, the lower-photocatalytic efficiency of APS- and HVOF-sprayed coatings was also correlated with the chemistry and reactivity of nitrogen oxides that are more complex than that of other molecules [35].

When the ST01 powder was injected in aqueous suspension form, the sprayed coating ensured a substantial removal of the nitrogen oxides (around 52% for NO and 34% for NOx), much higher than that of the powder (31% for NO and 18% for NOx). High rates of degradation of gaseous pollutants were also recorded in the presence of aqueous suspension plasma sprayed coatings of nonagglomerated nanopowders P25 (around 36% for NO and 15% for NOx) and PC105 (around 18% for NO and 8% for NOx), comparable with that measured in the presence of the powders. Meanwhile, a lower degradation of pollutants (8–10%) was obtained for the coating resulting from the plasma spraying of alcoholic suspensions.

The different photocatalytic performances were principally correlated with the crystalline structures of the sprayed coating. Anatase phase was a key parameter in the photocatalytic activity and a higher-anatase ratio with reduced crystallite size allowed a better degradation of nitrogen oxides. Besides, the titania deposits elaborated by the spraying of aqueous ST01 and P25 suspensions provided a higher performance than that of the raw powders. In these cases, the enhanced photocatalytic performance could not be explained considering only the anatase ratio. It was assumed that the removal of the impurities coming from the raw powder elaboration and a cleaning up of the free-water particles when crossing the plasma could explain such behavior. Different techniques of surface investigations (infrared spectroscopy and X-ray photoelectrons spectroscopy) performed on the surface of P25 aqueous suspension sprayed coating [29] showed the presence of a higher hydroxylation compared to that on the raw powder surface. The hydroxyl groups played a beneficial role and enhanced the photocatalytic activity of titania as already reported in the literature [36, 37].

4. CONCLUSION

This paper proposed a comparative study on the microstructure and photocatalytic properties of titanium dioxide coatings obtained by different thermal spray methods: atmospheric plasma spraying, suspension plasma spraying, and high-velocity oxygen fuel process using agglomerated and nonagglomerated TiO_2 nanopowders as feedstock materials. The coatings elaborated by APS and HVOF techniques were characterized by the common lamellar microstructure observed in all thermal sprayed deposits. Besides, the use of agglomerated nanoparticles as feedstock materials involved an important phase transformation from anatase to rutile. The photocatalytic ability for nitrogen oxides was lower than 5% and was correlated principally with the reduced anatase content.

The coatings elaborated by suspension plasma spraying presented a specific structure that depended on the nature of the solvent used in the preparation of the suspensions. The anatase crystalline structure and the crystallite size were preserved in the coatings resulting from an aqueous suspension, whereas a significant phase transformation occurred with alcoholic suspensions. Furthermore, the aqueous suspension sprayed coatings presented a remarkable photocatalytic efficiency that in some conditions was higher than that of the corresponding powder.

It can be concluded that the suspension plasma spraying is an appropriate technique to elaborate active titania surfaces for the photocatalytic reduction of reactive gaseous pollutants such as nitrogen oxides.

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