Elaboration and characterization of environmental properties of TiO_2 plasma sprayed coatings

L. Toma, N. Keller, G. Bertrand, D. Klein, and C. Coddet

LERMPS - UTBM, Site de Sévenans, 90010 Belfort Cedex, France

ABSTRACT. Titanium dioxide (TiO_2) is an attractive material for numerous technological applications such as photocatalytical applications. These materials can in some conditions have the ability to allow the environmental purification of air and water by the decomposition and removal of harmful substances, such as volatile organic compounds (VOC), benzene compounds, NOx, SO_2, etc. Our work was focused on the elaboration and the evaluation of the environmental properties of titanium dioxide coatings by plasma spray techniques. The principle of plasma spraying consists by the injection in an enthalpic source (plasma) of the powder of one material to be sprayed. The molten powder is transported and accelerated by the plasma-producing gas flow and crushed on the target substrate, where the particles of material solidify with high speeds, thus forming the coating. The advantages of thermal spraying consist in the fact that the coating has stability, durability, adherence and cohesion. For this study, the initial powder material was an anatase TiO_2. The photocatalyst coating was realized by a few kinds of thermal spray method: gas flame, APS (atmospheric plasma), VPS (vacuum plasma) and HVOF (high velocity oxygen fuel). The microstructures of the deposits, as a function of the coating process, are analysed by optical microscopy, scanning electronic microscopy, and the X-rays diffraction. To carry out the step of validation of these surfaces for their environmental functionalities, we used a control test process for the photocatalytic effectiveness with respect to nitrogen oxides. For that an original test chamber has been developed. Ultraviolet rays irradiated the coating specimens and the efficiency of NOx elimination has been controlled using a gas analyser. We studied the photocatalytical properties of different obtained coatings as a function of various parameters (porosity, thickness, ratio anatase/rutile).

1. INTRODUCTION

Environmental pollution and destruction on a global scale have drawn attention to the necessity of new, safe and clean chemical technologies and processes. The reduction of pollutants in our environment is one of the most ambitious challenges for the scientific world. Among strong contenders—environmentally friendly are the photocatalysts [1, 2], which can operate at room temperature in a cleaner and safer manner. The most important photocatalyst is the titanium dioxide (TiO_2) [3–5]. It is biologically and chemically inert, photo-stable, non-toxic and un-expensive and allows the decomposition of toxicological organic compounds in the water and the harmful gases in the atmosphere.

Our work focused on the elaboration and the evaluation of the environmental properties of titanium dioxide coatings by thermal spraying technique.

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1.* TiO_2 *powder. The TiO_2 presents three crystalline phases: rutile, the most stable phase, anatase that by annealing at the temperature higher than 625 K changes in rutile structure and brookite phase. The two TiO_2 phases, anatase and rutile take part at photocatalytic reaction, but the anatase provides better photocatalytical properties. Several results [6] obtained in the literature show that the TiO_2 could contain both phases anatase and rutile, but the relationship between the two phases and their photocatalytic effects are not yet well defined.

Our laboratory permits the elaboration of powder by the spray drying processes. One of the main interests of the spray drying process is the possibility to change the architectural features of powder. The anatase TiO_2 powder elaborated in the framework of N. Keller's thesis, presents the spherical particles and characteristics that permitted their use in the thermal spraying process. The size distribution is +10–44 μm. Figure 1 shows the shapes of the anatase powder observed by scanning electron microscopy (SEM). Figure 2 presents the X-ray diffraction pattern of the powder showing the single anatase crystalline structure.

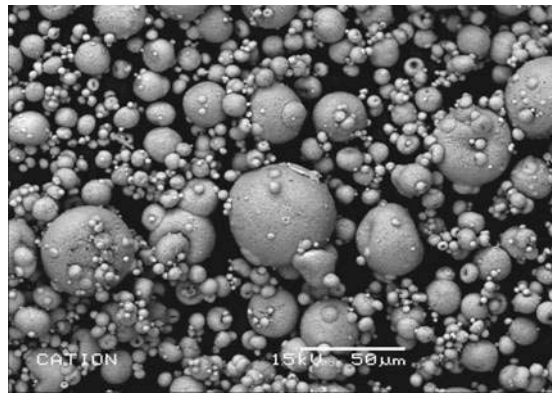


Figure 1. *SEM photography of the* TiO_2 *anatase powder.*

Table 1. *Parameters used for APS spraying of the* TiO_2 *anatase powder.*

Ref.	Flow rate Ar (NL/min)	Flow rate H_2 (NL/min)	Flow rate He (NL/min)	Spray distance (mm)	Cooling
A	40	10	0	110 mm	Air, CO_2
B	40	6	0	110 mm	Air, CO_2
C	40	3	40	110 mm	Air, CO_2

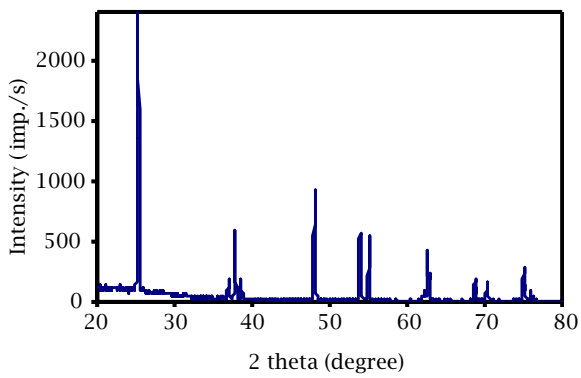


Figure 2. *XRD of the* TiO_2 *anatase powder.*

2.2. Thermal spraying. The principle of thermal spraying consists in injecting in an enthalpic source (plasma or flame) the material feedstock (powder or wire). The molten material is carried and accelerated by a gas flow and crushed on the target substrate where the particles of melt material solidify with high speeds, thus forming the coating. Two spraying processes were used to elaborate the TiO_2 coatings: atmospheric plasma spraying (APS) and flame spraying.

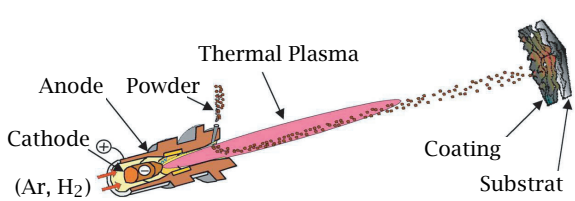


Figure 3. *Atmospheric Plasma Spraying (APS).*

In the plasma spraying (Figure 3), an inert gas (generally argon, nitrogen) enters a direct-current arc between a tungsten cathode and a cooper anode that makes up the nozzle and becomes thermal plasma (by ionisation and heat). The temperature of the plasma just outside the nozzle exit is about 10000 K. The powder suspended in a caring gas is injected into the plasma and as result it is melted and accelerated with a velocity that can reach 300 m/s. A small amount of a secondary gas such as hydrogen or helium is mixed with the primary plasma gas to increase the thermal energy or the conductivity of the plasma.

In the flame spraying (Figure 4), a combustion reaction between air or oxygen and a variety of fuel (e.g. acetylene, propane, hydrogen) allows to melt and accelerate the molten particles. The flame temperature is lower than the plasma temperature, around 3000 K and the velocity of particles reaches 100 m/s.

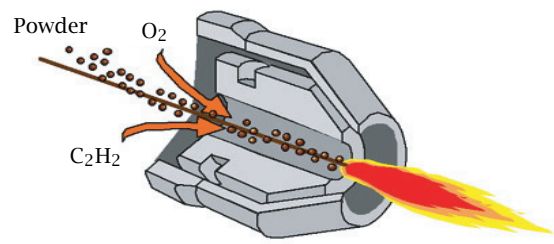


Figure 4. *Flame spraying.*

The deposit is built-up by successive pilings up of individual flattened particles or splats and resulting in a lamellar structure (Figure 5). The sprayed coatings show some surfaces particularities as porosity, interlamellar joints, cracks, oxides and un-melted particles. The advantages of thermal spraying are cleaning, stability, durability, adherence and cohesion of the sprayed coatings.

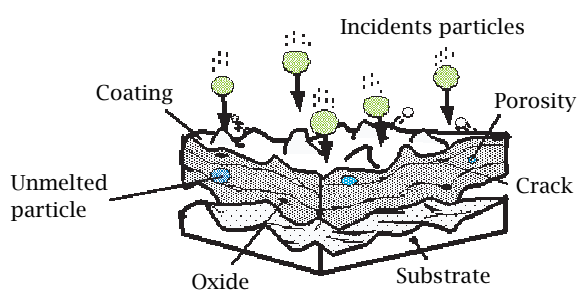
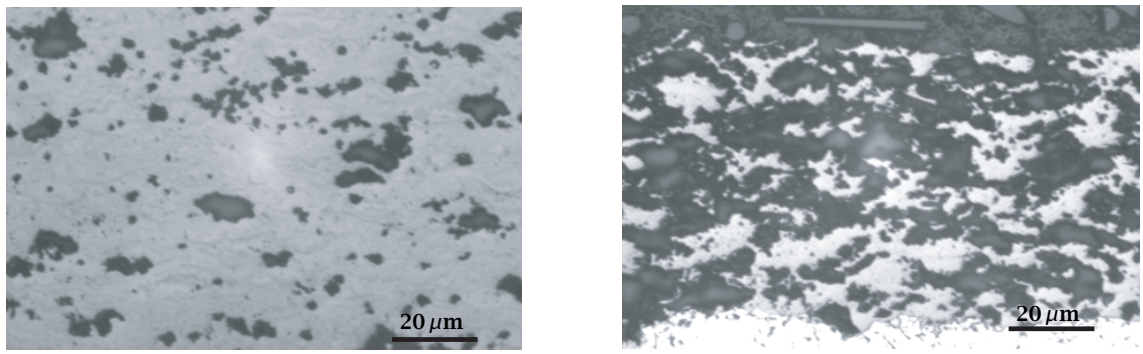


Figure 5. *Lamellar structure of the sprayed coating.*

2.3. Experimental parameters. In the APS, the spray powder is injected by an argon stream inside different mixtures of plasma gas based on the Ar, H_2, He system. Table 1 presents the different experimental parameters used.

Using the hydrogen in the plasma jets allows obtaining very energetic plasmas; thermal exchange between the plasma plume and particles is very high, so the particles can be easily molten and thus a higher spraying efficiency is obtained. When helium is added to the plasma gas the particle velocity is higher but thermal exchange is reduced. During the spraying, the specimens were cooled with compressed air and CO_2.



B (APS Ar: 40 – H_2: 6) C (APS Ar: 40 – H_2: 3 – He: 40)

Figure 6. *Microstructure observed by optical microscopy.*

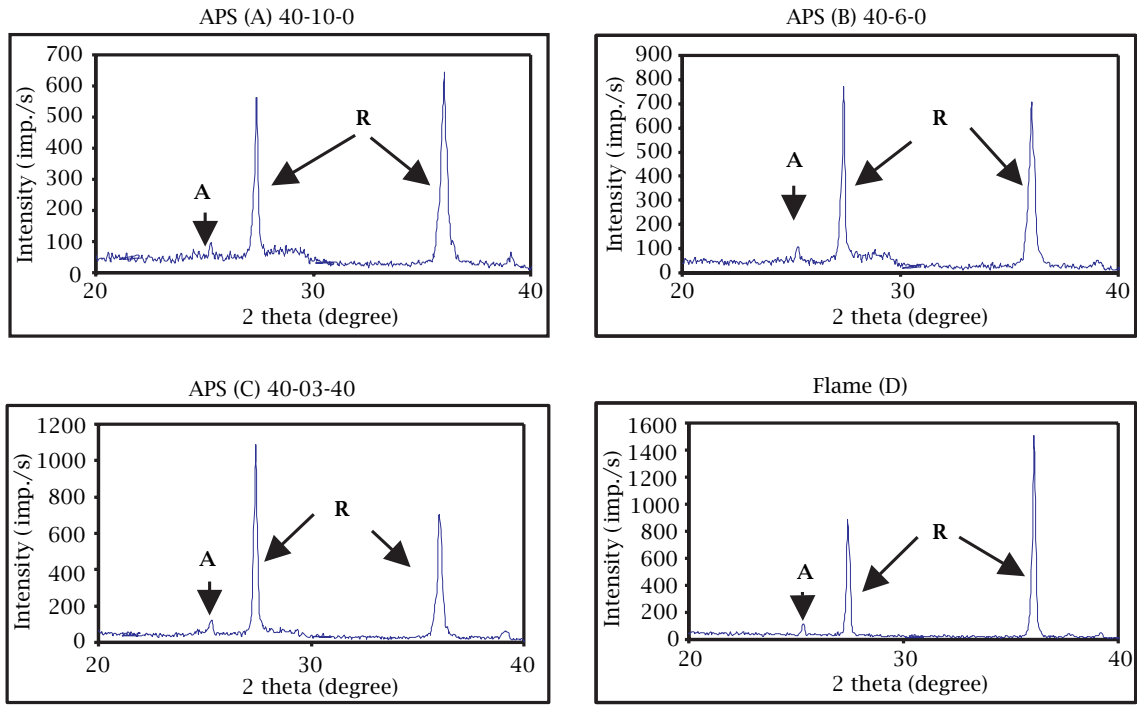


Figure 7. *X-ray diffraction patterns of* TiO_2 *coatings sprayed by APS and flame processes.*

In the flame spraying, the combustion reaction was performed between the O_2 (50 NL/min), air (60 NL/min) and acetylene (20 NL/min). The spray distance was fixed at 150 mm and the coating was cooled with compressed air.

In all cases, the stainless steel plates (70 × 25 × 2 mm) were used as substrate material.

2.4. Coating characterization. The morphology of the sprayed coatings was observed by optical microscopy. Figure 6 shows the microstructure of the coatings for the B and C conditions.

The density of titanium dioxide coatings exhibits a strong dependency on the spraying conditions. The coating C (APS Ar: 40 – H_2: 3 – He: 40) provides a higher porosity (62%), while for the other coatings the porosity is around 15%.

By X-ray diffraction (XRD) the crystalline structure of the coatings was determined. The main XRD patterns (Figure 7) show that all coatings consist of a mixture of rutile and anatase structure.

The concentration of anatase depends on the experimental parameters. In the case of the APS process, the rate in anatase is about 20–25%. The higher concentration in anatase is obtained for the C coating where a low flow rate of hydrogen and a high flow rate of helium were used. The amount in anatase phase for flame coating is less than for the plasma coating (15%).

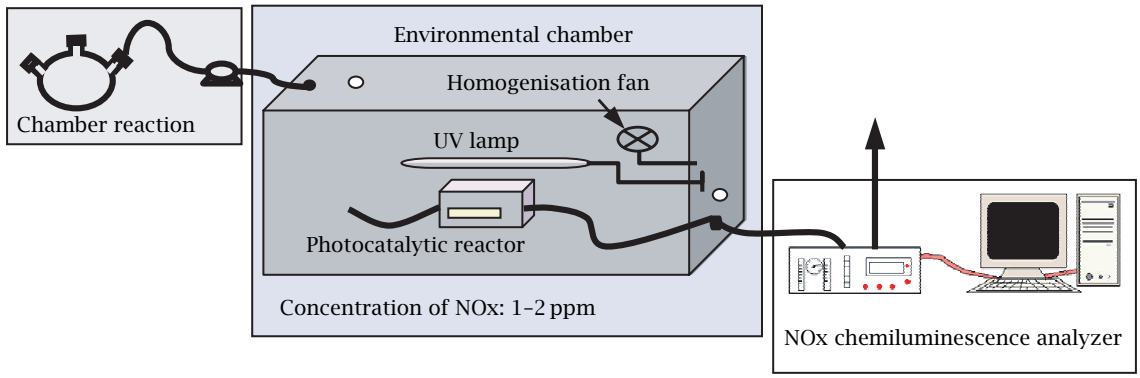


Figure 8. *Photocatalytical test chamber.*

3. PHOTOCATALYTICAL CHARACTERIZATION

3.1. Photocatalytical test for* NOx *removal. In the frame of L. Toma's thesis to verify the efficiency of coatings for NOx removal, we have developed a test chamber. The experimental test can be divided in three parts: chamber reaction, environmental chamber and instrumentation (Figure 8).

In a chamber reaction we have prepared the NOx (NO and NO_2) by the chemical reaction between cooper powder (size distribution 30–55 μm) and a dilute solution of nitric acid. The NOx are sent using a peristaltic pump into the environmental chamber, which allows at constant temperature and pressure to obtain a volumic concentration of NOx between 1–2 ppm (1 ppm NO $\approx$ 1,24 mg/m^3, 1 ppm NO_2 $\approx$ 2 mg/m^3). A homogenisation fan ensures an equivalent repartition of NOx in the environmental chamber. Inside the chamber is placed the photocatalytic reactor (a polycarbonate box, $10 \times 10 \times 5$ cm), on which a Plexiglas window is fixed to allow the light passage from a daylight lamp with UV fraction through 30% UVA and 4% UVB in the spectrum. After the passage through the photoreactor, the NOx are sent towards a NOx chemiluminescence analyser.

In the environmental chamber, the NOx concentration decreases according to kinetics, which was observed. Then, when the concentration is stable, the photoreactor with the TiO_2 photocatalyst (powder or coating) is placed in the chamber and crossed by the NOx flow (the flow rate is 1.8 NL/min); then the gas is analysed by the NOx chemiluminescence analyser. The concentration is followed continuously and after 10 to 20 minutes the light lamp is turned on. Immediately the photocatalysis begins and the variation of NOx concentration is measured.

3.2. Photocatalytic properties—preliminary results. We present only preliminary results occurring the photocatalytic properties for the thermal sprayed coatings. Some experimental observations can be noted.

When we have turned on the lamp we have observed that the NO concentration has decreased rapidly for a few minutes; then, the NO diminution has become slower in time (Figure 9). When we switched the lamp off, the NO concentration increased. After the exposition of the photocatalysis (when we have turned the lamp off), we have been observed that the concentration of NO is less than the concentration who is giving by the kinetic decrease of NOx without the photocatalysis. This observation argues the activity of TiO_2 as photocatalyst.

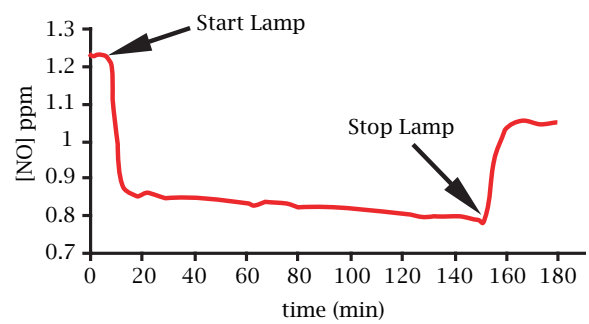


Figure 9. *Photocatalytic decrease in* NO *concentration.*

During the photocatalysis, a weak increase in the NO_2 concentration was observed which could be explained by the oxidation of NO at NO_2 on the TiO_2 surface.

The photocatalytical tests were realised under the anatase powder and the deposited coatings (Figure 10). For the test, 0.4 g anatase powder with a specific surface around 10 m^2/g has been used. The anatase powder provides better photocatalytical activity than the sprayed coatings. Indeed, this effect can be explained considering that the coatings present a weaker reactive surface and the amount in anatase is more reduced than in the powder. Moreover, the coating with a higher rate of porosity is better for NOx removal.

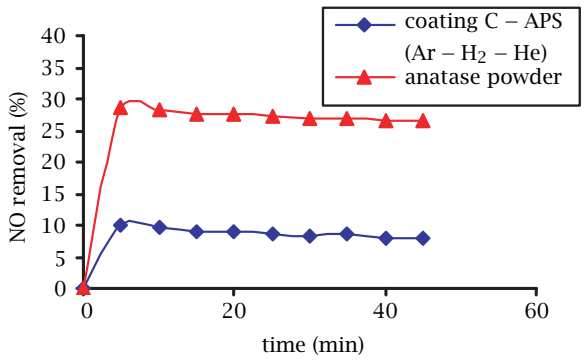


Figure 10. NO *reduction on anatase and coating.*

4. CONCLUSIONS AND FUTURE

According to the preliminary results that we have obtained, some conclusions can be reported. The crystalline structure of the coatings is an important parameter in the photocatalysis. Varying the thermal spray conditions we can obtain anatase-rich TiO_2 coatings for environmental applications. The porosity of the coating is also considered to be a key parameter in the photocatalytic decomposition.

One thing remains: to optimise the technique of the deposit to obtain better structural characteristics (more significant rate in anatase and in porosity) to increase the reactive surfaces and the photocatalysis efficiency.

Modifications in the TiO_2 matrix will be realized by doping with different oxides, as Fe_2O_3, in order to modify the levels of photocatalytic sensitivity by bringing them closer towards visible light.

Once the deposits optimised for the NOx removal, we will try to evaluate their effectiveness for other pollutants, in particular the decomposition of volatile organic compounds (VOC).

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