Functionalization of Suspension Sprayed HVOF TiO₂ Coatings by Direct Laser Interference Patterning

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Abstract For more than one decade, suspension spraying has been gaining interest for the development and manufacture of coatings for wide range of applications such as photocatalysis, thermal barrier coatings, wear resistance, biomaterials or superhydrophobicity. Even though these coatings are already promising, a modification of their surface properties can further improve their functionality and lifetime in order to meet the growing requirements on the coating demands. Direct laser interference patterning (DLIP) is a versatile laser technology which allows fabricating microstructures with high flexibility and therefore designing surface properties on a large diversity of materials, including metals, polymers, ceramics and coatings. In this contribution, DLIP technology was applied to texture the surface of suspension sprayed high velocity oxy-fuel (HVOF) TiO₂ coatings. In particular, a nanosecond-pulsed laser has been used to produce cross-like patterns and the effect of laser parameters on the coating properties was investigated. The coatings were characterized by means of scanning electron microscopy, Raman spectroscopy and UV–Vis–IR measurements, and the influence of the laser treatment on the photocatalytic activity and wettability behavior has been investigated. The results showed that the DLIP technology is suitable for designing and tailoring of the surface properties of the suspension sprayed coatings.

Keywords direct laser interference patterning · suspension spraying · surface functionalization · TiO₂

Introduction

For more than one decade, modified thermal spraying processes using suspensions of fine submicron- and nano-sized powders as feedstock materials have continuously been gaining interest. Suspensions are used as feedstock for both atmospheric plasma spraying (APS) and for high velocity oxy-fuel (HVOF) spraying. Compared with the conventional thermal spray methods, the suspension spraying technique presents some advantages: direct feeding of fine nano- and submicron-scale particles; tailored coating architecture that can be adapted to the given application; less anisotropy and lower surface roughness of the coating; retention of the initial crystalline phases resulting in improved or new coating properties. Moreover, the technique allows thick and thin, finely (nano)-structured coatings to be prepared (Ref 1). Due to these properties, the suspension sprayed coatings find a high interest in applications such as electrical and thermal insulation, air and water purification, wear and corrosion protection, wettability, antibacterial and biomaterials.

A further improvement of the functionality of the suspension sprayed coatings can be achieved by coating surface modification. Laser patterning is a versatile technology allowing functionalization of the surfaces by producing textures with well-controlled feature sizes and geometries. Laser patterning is flexible, precise and reproducible being applicable on a large diversity of materials, including metals, polymers, ceramics and coatings. Additionally, laser-based processes offer attractive perspectives in terms of industrial scalability, processing times and process environment variables. A well-established laser technique to produce periodic structures in the micro- and sub-micrometer range is the direct laser interference patterning (DLIP). The principle consists in the

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splitting of the principal coherent laser beam to obtain two or more laser beams, which are overlapped on the surface of the material, where interference patterns in the micro- and sub-micro range are created (Ref 2–4). In the case of two-beam interference, a line-like periodic pattern is obtained where the spatial period (p) can be controlled by the used laser wavelength (λ) and the half-angle of incidence between impinging laser beams, as shown in Equation (1):

$$p = \frac{\lambda}{2 \cdot \sin\theta} \quad (\text{Eq 1})$$

For a given laser wavelength and number of beams, the pattern period can be easily adjusted by modifying the angle, the polarization and the intensity of the interfering beams (Ref 3).

In this work, we aim to study the influence of laser texturing on the suspension-HVOF sprayed TiO_2 coatings, fabricated under different spraying conditions. In particular, DLIP technology was applied for the first time to pattern TiO_2 sprayed coatings in order to create well-defined and ordered microtextures on top surfaces. Two main properties relevant to the applications of S-HVOF sprayed TiO_2 coatings were studied, namely the photocatalytic activity and the wettability behavior. In order to investigate the laser-induced changes on the coatings surface, the deposits were characterized by scanning electron microscopy, Raman spectroscopy, FTIR spectroscopy and UV–Vis measurements.

Materials and Experimental Procedure

Suspension-HVOF Spraying of TiO_2 Coatings

Commercial available TiO_2 Aeroxide® P25 nano-powder (Degussa Evonik Industries AG, Germany) containing about 80% anatase phase and 20% rutile phase with an average grain size of about 50 nm was used to produce an aqueous suspension with 20 wt.% solid content. The suspension was fed using the industrial suitable three pressurized-vessels suspension feeder developed by Fraunhofer IWS (Ref 1, 5) and internally injected in the modified combustion chamber of a HVOF Top Gun torch (8-mm-diameter and 78-mm-length nozzle, GTV Verschleißschutz GmbH, Germany). Ethene was used as fuel gas. The suspension feed rate was fixed at 25 mL/min. For the coating deposition, the main variable parameters were the gas flow rates, normalized oxygen-to-fuel ratio and spray distance, Table 1. Stainless substrates ($20 \times 30 \text{ mm}^2$) previously cleaned and grit-blasted with corundum were used as substrates. During the spraying, the substrates were cooled using air jets systems. The surface temperature was

monitored using a Testo 830 IR thermometer (Testo SE & Co. KGaA, Germany). Temperatures up to about 300–350 °C were measured on the coating surfaces during spraying processing.

DLIP Patterning of S-HVOF TiO_2 Sprayed Coatings

The DLIP laser experiments were carried out under ambient environment conditions. The surfaces of TiO_2 coatings were laser-treated using an infrared ($\lambda = 1053 \text{ nm}$) Q-switched diode pumped solid-state TECH-1053 Basic laser (Laser-export Co. Ltd., Moscow, Russia) with pulse duration of 15 ns and a repetition rate of 1 kHz. Line-like interference patterns with a spatial period of 8.5 μm and an interference area (pixel) of $\sim 90 \mu\text{m}$ were generated using a DLIP two-beam optical module developed by Fraunhofer IWS, as shown in Fig. 1 (Ref 3).

To cover larger areas, the substrate was translated using an Aerotech PRO155-05 motorized linear stages (Aerotech, Inc., Pittsburg, PA, USA) in x and y directions, and a specific distance between the pixels was defined. The pulses overlap was fixed at 5 pulses/pixel and 45 pulses/pixel, corresponding to a pulse to pulse distance p of 18 μm and 2 μm , respectively. The hatch distance h was kept constant at 42.5 μm , and the laser fluence was of about 4.1 J/cm². To produce cross-like patterns, the samples were first laser-processed using the line-like pattern approach; after that, they were rotated 90° in the x-y plane and the laser interference patterning was performed once again.

Characterization Methods

The coating microstructures were examined by optical microscopy and scanning electron microscopy (SEM) on metallographic mirror-polished cross sections. The topographies of the as-sprayed and laser-patterned surfaces were characterized by scanning electron microscope (Philips ESEM). The pattern heights were measured using confocal microscopy (Leica DCM 3D) employing a 50× magnification objective with a nominal lateral and vertical resolutions of 340 nm and 4 nm, respectively.

Raman analysis of the anatase and rutile phases on the top surface of the as-sprayed and laser-treated coatings was performed using a Renishaw InVia Raman spectrometer (Renishaw GmbH, Pliezhausen, Germany) with a laser wavelength of 514 nm; the scanning was performed from 100 to 1100 cm^{−1} wavenumber shift. The localization of the analysis spot of the laser was performed using an optical microscope with an objective with a magnification of 50×.

Adsorbed species on the surfaces of the as-sprayed and laser-treated coatings were detected with total reflectance infrared spectroscopy at wavelengths between 2 and 15 μm

Table 1 Main S-HVOF spraying parameters

TiO ₂ coating	C ₂ H ₄ , l/min	O ₂ , l/min	O/F ratio*	Spray distance, mm	Passes
A	60	180	1.0	80	8
B	75	180	0.8	80	8
C	50	180	1.2	80	8
D	75	180	0.8	70	8

O/F ratio*—normalized oxygen-to-fuel ratio determined with the formula

$$O/F \text{ ratio} = \frac{\text{FlowrateO}_2}{3 \times \text{FlowrateC}_2\text{H}_4}$$

Fig. 1 Two-beam DLIP optical module (a) that forms the line-like shaped irradiation area containing a two beam interference pattern (b); scanning strategy to cover larger areas (c)

at room temperature and under atmospheric conditions using a FTIR spectrometer Perkin Elmer FrontierTM (PerkinElmer Inc., Massachusetts, USA). Varian Cary 5000 UV–Vis–NIR spectrometer ((Agilent Technologies Inc., Santa Clara, USA) with integrating sphere was used to record the UV–Vis–NIR total reflectance spectra of the coatings at wavelengths from 0.3 to 2 μm .

The photocatalytic activity of TiO₂ coatings was evaluated by the degradation of an aqueous solution of methylene blue (MB) according to the German standard DIN 52980 as previously described (Ref 6). The TiO₂ samples, prior cleaned by irradiation (using an UV lamp emitting the wavelength of $\lambda = 254 \text{ nm}$), were immersed in a 10 μM aqueous solution of MB. After the adsorption equilibrium between MB and TiO₂ was reached, the system was irradiated with UV-lamp with wavelength of $\lambda = 366 \text{ nm}$ and density of radiation power of 10 W/m^2 . The degree of MB degradation was determined by absorbance measurements at $\lambda = 664 \text{ nm}$ using a UV–NIS–NIR spectrometer Varian Cary 500 every 20 min for 3 h. From the measured absorbance values, the concentration of the MB

can determined following the Beer–Lambert law. The specific photocatalytic activity (P_{MB} in $\text{mol}/\text{m}^2 \cdot \text{h}$) was calculated using the following equation:

$$P_{\text{MB}} = R_{\text{dark}} - R_{\text{irr}} \quad (\text{Eq } 2)$$

where R_{dark} and R_{irr} are expressed by the general formula

$$R = \frac{\Delta A \cdot V}{\Delta t \cdot \varepsilon \cdot d \cdot S} \quad (\text{Eq } 3)$$

In the above equations, R_{dark} is the specific degradation of MB in the dark (before UV radiation ($\text{mol}/\text{m}^2 \cdot \text{h}$); R_{irr} is the specific degradation of MB during UV-irradiation ($\text{mol}/\text{m}^2 \cdot \text{h}$); ΔA is the variation of the absorbance of MB in the time Δt ; S is the surface of titania coatings; d is the length of cell for spectroscopic measurements ($d = 10 \text{ mm}$); V is the volume of the solution ($V = 35 \text{ mL}$); and ε is the molar extinction coefficient of MB at 664 nm ($\varepsilon = 7402.8 \text{ m}^2/\text{mol}$).

The wetting behavior of the as-sprayed and laser-treated TiO₂ surfaces was characterized via static contact angle measurements using an OCA20 system (DataPhysics

Instruments GmbH, Filderstadt, Germany). A drop of de-ionized water with a volume of 4 μL was put on the cleaned surfaces with a cannula of 0.25 mm diameter. The analysis was done with SCA 20-contact angle software module (OCA, DataPhysics Instruments GmbH, Germany) and the “tangent leaning” method.

Results

Microstructure of As-Sprayed TiO_2 S-HVOF Coatings

Suspension-HVOF sprayed TiO_2 coatings with thicknesses between 20 to 30 μm were deposited onto steel substrates. Dense bimodal structures with light-gray regions containing well-melted particles homogeneously mixed with dark-gray regions of non-melted nanoparticles or already solidified grains were observed in the polished cross sections, Fig. 2. The light gray corresponds mostly to rutile phase, whereas the anatase phase was mainly found in the dark-gray zones (Ref 7–9). The bimodal structure was mostly influenced by the normalized oxygen-to-fuel ratio. When the suspension was injected into a fuel-rich HVOF flame with oxygen-to-fuel ratio of 0.8, which corresponds to the highest flame temperature, a major phase transformation from anatase to rutile took place and the fine particles could reach the substrate in a well-molten state. This observation is supported by the higher amount of light-gray area in the micrographs. By injection of the suspension in an oxygen-rich HVOF flame with an oxygen-to-fuel ratio of 1.2 corresponding to low energy and low flame temperature, less heat transfer from the HVOF flame to the particles occurred; a higher amount of the particles impacted on the substrate in a partially molten or non-molten state retaining mainly their initial phase composition.

Surface Topography of As-Sprayed and DLIP-Treated TiO_2 S-HVOF Coatings

The top-surface morphologies of suspension sprayed coatings before and after laser patterning are shown exemplary for the TiO_2 B coating in the SEM micrographs of Fig. 3. The topography of the as-sprayed coating was slightly inhomogeneous (average roughness of about 2–3 μm) and the presence of some “bumps” of finely submicron- and nano-sized particles was observed, which is mostly typical for suspension sprayed coatings starting from agglomerated nano-powders.

By using a laser patterning with 5 pulses/pixel, periodic surface patterns with heights of about 5 μm were obtained. Tiny loose particles resulting from the vaporization and

condensation of the material during the patterning, as well as the formation of microcracks were observed on the treated surface. During DLIP with 45 pulses/pixel, columnar-like surface patterns with heights of up to 11 μm were produced. The presence of some locally distributed overmelted “humps” because of near-surface melt (Ref 3, 10) could be identified, too.

Raman Spectroscopy

Raman spectroscopy is a suitable tool to study the chemical composition from small laser-irradiated area. This technique is very sensitive to perturbations in chemical bonding caused by localized distortions or induced phase transformations (Ref 11). Figure 4 shows the Raman spectra taken from the as-sprayed and DLIP-treated suspension sprayed coatings. The typical Raman active phonon modes for both anatase and rutile could be identified in the TiO_2 coatings. The very strong intensity peak at 144 cm^{-1} (*Eg*), the medium intensity bands at 397 cm^{-1} (*B1g*), 516 cm^{-1} (combination of *A1g* and *B1g*) and 639 cm^{-1} (*Eg*) in addition to weak peak at 198 cm^{-1} (*Eg*) corresponded to active Raman vibrational modes of the anatase (Ref 12, 13). For anatase, the very strong *Eg* Raman mode depends of the stoichiometric ratio O/Ti. The frequencies of Raman-active modes for the rutile phase were given by strong peaks at 449 cm^{-1} (*Eg*) and 610 cm^{-1} (*A1g*), weak peaks at 143 cm^{-1} (*B1g*) and broader low-intensity Raman modes at 320 and 832 cm^{-1} (*B2g*). For rutile, the strong phonon mode *Eg* attributed to in-plane bands of O–O bonds (Ref 13) is sensitive to the presence of oxygen vacancies in TiO_2 . The broad Raman band of rutile at 235 cm^{-1} is of complex nature and does not coincide with any theoretical calculations for the fundamental modes allowed by symmetry in this phase. The nature of this Raman band was suggested that it might be either second-order or disorder-induced scattering effects (Ref 14).

The anatase phase was predominantly found in the coatings produced with a stoichiometric and an oxygen-rich HVOF flame (spraying conditions A and C). Spraying with a sub-stoichiometric HVOF flame and short spray distance (spraying conditions D) resulted in a significant phase transformation, where the rutile was the main phase. The results were in agreement with the SEM microstructure analysis and with those presented in our previous work (Ref 7).

High intensities of the peaks were recorded for samples laser-treated with DLIP 5 pulses, mostly because of their smoother surface, involving a low scattering effect of the laser during the Raman measurements. Changes in the phase compositions were identified in the laser patterned coatings. With exception of the TiO_2 C coating, enhanced anatase content was identified on the coating surfaces

Fig. 2 Cross-sectional SEM micrographs of as-sprayed TiO₂ S-HVOF coatings

DLIP-treated at low pulses/pixel. With increase in the DLIP pulses/pixel, the phase transformation from anatase to rutile is favorable and the rutile was the principal phase on the coating surface irradiated with DLIP 45 pulses/pixel.

FTIR Spectroscopy

Figure 5 presents the IR results of the as-sprayed TiO₂ coatings. The IR spectra of the as-sprayed coatings are almost similar, showing a broad band in the 3800–2700 cm⁻¹ region (with peak around 3350 cm⁻¹), a band between 1800 and 1580 cm⁻¹ with peak at 1630 cm⁻¹, and a band in the 1000 and 700 cm⁻¹ region centered at 880 cm⁻¹. The broad band between 3600 and 3200 cm⁻¹ is attributed to the OH stretching of water

molecules (physisorbed molecular water), whereas the band centered at about 1630 cm⁻¹ was assigned to their OH bending modes (Ref 9). The peaks located in the range 2460–2200 cm⁻¹ could be associated with CO₂ from air. The bands in the range 1580–1450 cm⁻¹ are generally assigned to adsorbed carbonate species. Absorption in the range 1100–700 cm⁻¹ (with peak at about 890 cm⁻¹) was attributed to the stretching and surface vibrations of Ti–O groups, i.e., Ti–O–Ti and Ti–OH, respectively.

The IR spectra of laser-treated coatings were different from those of the as-sprayed coatings (Fig. 6). The band located at 3600–3200 cm⁻¹ and the peak at 1630 cm⁻¹ that could be attributed to OH stretching and bending modes of water molecules, respectively, were less intense for DLIP 5 pulses. The intensities of the peaks associated with

Fig. 3 Top surface SEM micrographs of as-sprayed and laser-treated TiO_2 B coatings after DLIP 5 pulses and DLIP 45 pulses

carbonated species were reduced with increase in the laser pulses. Moreover, a strong displacement of the bands associated with the vibrations of the Ti-O bonds in the region $1000\text{--}660\text{ cm}^{-1}$ with peak at 780 cm^{-1} was observed on the samples treated with low pulses overlap. For the coatings treated with DLIP 45 pulses, the vibrations modes of Ti-OH were less evident, probably due the increase in the Ti-O-Ti bonds.

UV-Vis Spectroscopy

The UV-Vis diffuse reflectance spectra of TiO_2 coatings in as-sprayed state and after laser patterning are given in Fig. 7. For the coatings produced with a stoichiometric and an oxygen-rich HVOF flame (spraying conditions A and C), the UV-light absorption was measured in the range $350\text{--}360\text{ nm}$ which corresponds to a bandgap of $3.44\text{--}3.54\text{ eV}$ (Fig. 7a). Spraying with a sub-stoichiometric HVOF flame (spraying conditions B and D) where the rutile was the main phase, the UV-light absorption was in the range $370\text{--}380\text{ nm}$ (bandgap of $3.26\text{--}3.35\text{ eV}$). For the laser treated coating surfaces, the reflectance decreased strongly in intensity and the UV-light absorption was red-shifted. This can be explained by the significant light scattering in

the patterns. For samples treated at low pulses, the maximal light absorption was between 390 and 400 nm (Fig. 7b). Noteworthy was the very low reflectance level of the samples treated at high pulses where the light signal was almost kept constant in the entire UV-Vis domain (Fig. 7c). This result shows the possibility to produce laser patterned suspension sprayed coatings for the fabrication of light trapping layers.

Evaluation of the Specific Photocatalytic Activity

The tendencies in the degradation of the methylene blue solution in presence of suspension sprayed titanium oxide coatings during tests are shown in graphs of Fig. 8. A low degradation of the MB (below 4%) was recorded while the tests were performed in the dark, i.e., without external UV-light irradiation. In the presence of the UV-irradiation, the concentration of MB decreased continuously with the time, and after three hours of tests, up to about 15% of the dye solution could be degraded. The photocatalytic degradation of the MB follows the Langmuir-Hinshelwood pseudo-first-order kinetics (Ref 6) described by the equation:

Fig. 4 Raman spectra of as-sprayed and laser-treated TiO_2 coatings: (a) A coating, (b) B coating, (c) C coating and (d) D coating

Fig. 5 IR-spectra of as-sprayed TiO_2 coatings

$$-\frac{dC}{dt} = k' C \quad (\text{Eq 4})$$

where C is the concentration C of the methylene blue, t is the time, and k' is the apparent rate constant of the photocatalytic activity.

From equations (2) and (3), the specific photocatalytic activities (P_{MB}) of the as-sprayed and laser-treated TiO_2 samples after 3 h of UV-irradiation were determined, Fig. 9. For the as-sprayed coatings, the highest specific photocatalytic activity was recorded for TiO_2 C coating, which correlated well with the presence of a majority anatase phase on the coating surfaces. When the rutile was the main phase, the photocatalytic activity of the as-sprayed TiO_2 D was reduced.

In the case of the laser-treated coatings, the photocatalytic responses were different. Excepted for the laser-treated TiO_2 C coating, the samples irradiated at higher pulses overlap showed comparable specific photocatalytic activities, with values even better than the as-sprayed coatings, despite the presence of the main rutile phase on the surfaces of the irradiated coatings.

Wettability Behavior

The wettability behavior of the suspension sprayed coatings was characterized by static water contact angle (WCA) measurements performed on as-sprayed, polished and laser-treated surfaces, Fig.10.

Fig. 6 IR-spectra of laser-treated TiO_2 coatings: (a) A coating, (b) B coating, (c) C coating and (d) D coating. The IR-spectra of as-sprayed coatings are given for comparison purposes

The as-sprayed TiO_2 coatings have a hydrophilic behavior, with WCA values up to 25.6° . Laser patterning of the coatings at low pulses involved a significant decrease of the static WCA below 10° , most probably because of formation of a smoother coating surface when compared to the as-sprayed ones. On the surface treated at higher pulses/pixel, the WCA values slightly increased up to 10° , but these values are in the most of cases lower than those measured on the as-sprayed coatings. The enhancement of hydrophilicity of surfaces is mainly explained by modification of the surface chemistry (Ref 15). Very low contact angle near 0° corresponding to superhydrophilic surfaces was measured on polished laser-patterned coatings. Li et al. (Ref 16) correlated the superhydrophilicity of TiO_2 by significantly increase the surface energy of TiO_2 films due

to an increase in the Ti-O-Ti bonds. A superhydrophilic surface disposes a self-cleaning behavior which is favorable for ease removal of surface contaminants.

In order to further modify the surface tension of the coatings, selected laser-treated samples were treated with the hydrophobic agent Mecasurf® perfluoropolyether compound (Surfactis, Angers, France). The hydrophobized laser-treated samples presented a water-repellent superhydrophobic behavior, the WCA values being recorded between 158° and 163° . The superhydrophobicity was mainly due to the formation of the covalent bonds between the $-\text{CF}_3$ groups of perfluoropolyether and Ti-O bonds of TiO_2 resulting in lowering of the surface energy of the material. Moreover, the fine refinement of the surface texture with micro- and nano-hierarchical structures plays a

Fig. 7 UV–Vis spectra of as-sprayed (a) and laser-treated TiO₂ coatings at DLIP 5 pulses (b) and DLIP 45 pulses (c), respectively

primordial role in the designing and fabrication of the superhydrophobicity (Ref 17, 18). Superhydrophobic surfaces are interesting for self-cleaning, anti-corrosive coatings, anti-icing, bio-inspired surfaces or antibacterial applications (Ref 19, 20).

Discussions on the Influence of the Laser Patterning on the Coatings Properties

Surface Topography

At low pulses overlap, the laser patterning process was driven mainly by local melting and smoothing of the coating surface. With increase in pulses overlap, the patterning occurred by local melting, vaporization and

ablation of the coating material. Additionally, the intrinsic surface roughness has a significant influence on the optical absorption of the laser radiation. On a rough topography, multi-reflections of the laser can occur, which result in accumulation of a higher amount of energy in the coating material.

The effect of heat accumulation is further promoted by multi-shot laser ablations (Ref 3), which in combination with an increase of pulses overlap result in a significant increase in the structure heights. The presence of microcracks on the coating surfaces treated at low pulses overlap could be observed in high magnification SEM micrographs (Fig. 3). These microcracks could be explained by the presence of thermal stresses coming from the local heating and melting of the material during laser treatment. Moreover, the presence of microcracks in laser treated samples

Fig. 8 Degradation of methylene blue in the presence of suspension sprayed coatings during tests without (dark) and with UV-irradiation: (a) A coating, (b) B coating, (c) C coating and (d) D coating

could also be related to a density change in the coating because of the crystalline phase transformation from anatase (stable phase at room temperature) to rutile (stable phase at high temperature).

The presence of overmelted “humps,” locally distributed on the surface of laser patterned coatings, could be explained as a result of near-surface melt, which increases with the heat accumulation. A generally accepted theory for near-surface melt dynamics during laser processes is provided by Marangoni convection. Lang et al. (Ref 3) proposed a possible mechanism applying the Marangoni convection model (Ref 10) for the DLIP using multiple pulses. The molten material merges with the material being released from the neighboring interference maxima

positions (hot areas) to the interference minima positions (to colder peripheral areas) due to surface tension gradients induced by the temperature differences. The application of a high pulses overlap resulted in additional melt leading to patterns with higher aspect ratios. While the structure height can be significantly boosted especially for the larger spatial periods due to stacking of molten material, an increase of the pulses overlap can result in a reduction of the structure height for smaller periods due to material overmelting. The overmelting leads to a local collapse of the structures resulting in emergence of overhang structures. This is in accordance with known phenomena in the wake of Marangoni convection, such as the humping phenomenon in laser welding (Ref 10, 21). In fact, overhang

Fig. 9 Specific photocatalytic activity P_{MB} of as-sprayed and laser-treated suspension sprayed coatings, after first 3 h of UV-irradiation.

Fig. 10 Static WCA results determined on as-sprayed and laser-treated TiO₂ coatings

structures can be seen as an advantage compared to simple structures. For instance, microtextures with overhang structures can enable to obtain superhydrophobic surfaces, even in materials which are intrinsically hydrophilic (Ref 19).

Raman Spectroscopy

The anatase to rutile phase transformation from melt/vapors is dependent from one side on the in-flight history of the particles and forms other side on the solidification rate

of splats at impact, with shorter spray distances and /or faster cooling rates resulting in retain of the metastable anatase phase (Ref 6, 7, 22). The anatase could also originates either from non-molten anatase feedstock particles or from small and/or undercooled particles, which nucleate as anatase, thus is explained why some anatase is found even when the feedstock is purely rutile (Ref 23). After impingement onto the substrate, the anatase to rutile transformation is promoted by the reheating of previously deposited layers by successive passes of the torch (Ref 9).

Two possible mechanisms could explain the presence of a higher content of the anatase phase on low-irradiated coating surfaces: (1) ablation of irradiated thin overlayer and release of the underlying anatase-rutile layer; (2) melting of the irradiated thin overlayer followed by the rapid condensation and nucleation/crystallization of the anatase phase, due to the lower interfacial energy between anatase and liquid compared with the interfacial energy between rutile and liquid (Ref 24). When the surface is irradiated under high pulses overlap, the heat accumulates and the cooling rate decreases; thus, the phase transformation is thermodynamically more favorable and the rutile solidification can occur (Ref 25).

Li and Ishigaki (Ref 24) studied by thermodynamic calculation the nucleation of rutile and anatase from TiO₂ melt using estimated values of the interfacial energy between the condensed phases and the liquid phase in the pure TiO₂ system. Under a high cooling rate, anatase nucleates directly from the melt below 2057 K, while stable rutile solidifies at a temperature close to the melting point of TiO₂. The authors showed that anatase is formed in

a rapid cooling process, while rutile is formed under near-equilibrium solidification conditions.

The laser irradiation parameters such as laser scanning step, pulses energy or number of pulses affect strongly the phase transformation. Low scanning step or high pulses energy induce besides the ablation/vaporization of the material but also the thermal annealing of the irradiated surfaces resulting in slow solidification (Ref 27, 28). The long period of molted state in the film promotes finally the phase transformation in addition to vaporization and the rutile crystallizes as main phase. Yang et al. (Ref 27) proposed that during transformation of anatase to rutile, the rutile grains first nucleate on the surfaces of the anatase nanoparticles and then growth of rutile followed by the formation of a shell of rutile phase covering the anatase core.

Besides changes in the phase composition, color modification from light gray (as-sprayed coating) to dark gray (DLIP 5 pulses) and velvet black (DLIP 45 pulses) occurred when the coating surfaces were exposed to laser-treatment (Fig. 11). Robert et al. (Ref 28) discussed the color changes induced by an excimer laser irradiation of TiO₂ anatase pellets. The authors endorsed these modifications to an oxygen deficiency and/or the phonon confinement effect related to the nano-size of the particles. An intensification of the color was attributed to the melting state of the surface layer. The melting of the surface plays a crucial role in the competition between the non-equilibrium regime of reduction and the pseudo-thermodynamic regime of re-oxidation by atmospheric oxygen, which should appear at sufficiently high laser fluence (Ref 28). Melting promotes surface reactions, because convection and diffusion processes within the melt allow fast transport of any induced non-stoichiometry from the surface to the liquid–solid interface. Which of the two regimes will be mostly favored depends on the reactivity of the reduced phase toward oxygen and the melting temperature itself. In our experiments, the presence of sub-stoichiometric titanium oxides was not obvious; mainly the presence of the

stoichiometric oxides on the overlayer of the irradiated surfaces could be identified. Instead, the presence of defects like microcracks, micropores and networks formed during the laser irradiation may also trap light and therefore contribute to the darkening effect (Ref 26).

Photocatalytic Response

The consensus among the scientific community is that anatase is more favorable to the photocatalytic activity (Ref 6, 7). This affirmation is in good agreement with the Raman spectroscopy of the as-sprayed coatings and the laser-treated TiO₂ C coatings. In the others cases, TiO₂ coatings containing higher content of rutile phase were more photocatalytic active. Moreover using appropriate laser parameters, the photocatalytic response of coatings was significantly increased. Excepted for the laser-treated TiO₂ C coating, the samples irradiated at higher pulses overlap were more active than samples irradiated at low pulses overlap and even better than the as-sprayed coatings.

In our previous works, it was shown that various surface properties such as the presence of hydroxyl species, phonon absorption, surface topography and developed surface area, layer thickness are important factors in the improvement of the photocatalytic activity of the titania coatings (Ref 7–9).

A laser patterning with low pulses resulted mainly in coatings with a smoother surface topography (Fig. 3), with lower developed surface area when compared with the surface of the as-sprayed coatings. Moreover, the DLIP 5 pulses/pixel resulted probably in a decrease of the surface ability to adsorb the water via the stretching OH bonds (see IR-spectra of Fig. 5) which are important for photocatalytic process. Laser patterning with 45 pulses/pixel allowed formation of refined micron-sized surface patterns with depths up to 11 µm, which resulted in a higher developed surface area. Although mainly rutile phase was identified in Raman spectroscopy (Fig. 4), in the IR-spectroscopy the bands corresponding of stretching OH bonds were stronger

Fig. 11 Modification of the coating color with laser treatment: from light gray (as-sprayed coating) to dark gray (DLIP 5 pulses) and velvet black (DLIP 45 pulses)

than observed in coating treated at DLIP 5 pulses (Fig. 6). Moreover, surface of these coatings seemed to be “laser cleaned,” where the peaks coming from the adsorption of carbonated species were less evident in the IR-spectra when compared to those of as-sprayed coatings (Fig. 5).

For the as-sprayed coatings, TiO₂ C coating was the most efficient for the photocatalytic degradation of the MB solution, thanks to its higher content of anatase and the presence of fine “nanoparticles” on the top surface. Contrary, the specific photocatalytic activity of the laser-treated TiO₂ C samples decreased with increase in the laser pulses. For coating C, the laser treatment involved a strongly phase transformation from anatase to rutile as shown in the Raman spectroscopy (Fig. 4c). Besides the rutile nucleation, the growth of the rutile grains could occur. An increase in the crystallites sizes will induce a reduction of the photocatalytic activity as previously shown by Toma et al. (Ref 29, 30). Furthermore, with increase in the laser treatment, the light absorption of the laser treated TiO₂ C samples was red-shifted to higher light wavelength as depicted in the UV–Vis spectra depicted in Fig. 7. Moreover, deeper investigation of the surface properties, e.g., stoichiometry in the crystal lattice, oxygen vacancies and presence of defects using X-ray photon spectroscopy (XPS), as well as the examination of the electronic properties and energetic states by means of photoluminescence is needed.

Wettability Behavior

In this work, the as-sprayed S-HVOF TiO₂ coatings have mainly a strong hydrophilic behavior, showing static water contact angles (WCA) between 2.6° and 25.6°, as shown in Fig. 10.

As reported in several works, flat TiO₂ coatings tend to be moderately hydrophobic, which according to Zheng et al. (Ref 31), could be explained either considering a fully oxidized TiO₂ surface that hinders the creation of hydrogen bonds with water molecules or because of the presence of organic molecules from the atmosphere absorbed on the TiO₂ surface. However, the same authors pointed out that an annealed TiO₂ flat sample shows instead a remarked hydrophilic behavior, thanks to the presence of Ti⁺³ ions and formation of the oxygen vacancies on the surface.

Therefore, a heat-induced hydrophilic surface state can be assumed in the case of the suspension sprayed TiO₂ coatings produced in this work. FTIR spectroscopy confirmed the presence of the hydrophilic groups on the TiO₂ surfaces, i.e., hydroxyl groups, physisorbed water molecules (see Fig. 5). Moreover, according to the Wenzel wetting model (Ref 32), commonly known for the contact surface wetting, for the same chemical composition a hydrophilic rough surface tends to increase its hydrophilic

behavior in comparison to a smooth one. Therefore, the low contact angles measured for the as-sprayed TiO₂ coatings could be also due because of the creation of an intrinsically nano/micro-scaled roughness on the as-sprayed coating topography (Fig. 3).

On the other hand, the laser patterning of the coatings at low pulses induced a significant decrease of the static WCA, both for polished and as-sprayed coatings. This could be attributed to the fact that the microtextures resulting after DLIP convey a higher roughness to the coating and, according to the early mentioned Wenzel wetting model, this results in lowering of the static contact angles. It is important to mention that, although the microstructures created by DLIP are ordered and well defined, the nano-scaled roughness visible on the as sprayed TiO₂ coating was significantly decreased mainly due the local melting of the coating during the laser microtexturing, induced by the use of nanosecond laser pulses (Ref 33). Furthermore, very a low contact angle near 0° corresponding to superhydrophilic surfaces was measured on the polished laser-patterned coatings. Li et al. (Ref 16) correlated the superhydrophilicity of TiO₂ by significantly increase the surface energy of TiO₂ films due to an increase in the Ti-O-Ti bonds. In comparison with the non-polished samples, this behavior can be ascribed to a different chemical composition of the inner layers of the coating (richer in Ti-O-Ti bonds) which is brought to the surface thanks to the polishing.

Although the effect of the laser texturing on the properties of suspension sprayed TiO₂ coatings still need further investigation, this work reveals new possibilities in the functionalization of thermally suspension sprayed coatings using the direct laser interference processing.

Conclusions

In this contribution, direct laser interference patterning (DLIP) technology was applied for the first time for the surface treatment and functionalization of thermally sprayed TiO₂ coatings produced by suspension HVOF spraying. The effect of the laser parameters on the coating properties, i.e., microstructure, topography, coating surface properties (Raman phases, UV–Vis–IR properties), photocatalytic activity and wettability behavior, was investigated.

The results showed the possibility to achieve well-defined surface morphologies on TiO₂ surfaces with regularly ordered cross-like patterns. Depending on the process parameters, structure depths of up to 11 μm were achievable for 45 pulses/pixel using nanosecond laser pulses and a period of 8.5 μm. Significant phase modification from anatase (stable at room temperature) to rutile (stable at high

temperature) occurred during laser patterning at high pulses.

The specific photocatalytic activities of the suspension sprayed TiO₂ coatings could be significantly improved when the surface coatings were previously laser-structured. Excepted for the laser-treated TiO₂ C coating, the samples treated at DLIP 45 pulses were more active during the photocatalytic discoloration of the methylene blue solution than samples irradiated at low pulses overlap and even better than the as-sprayed coatings. A significant color modification from (light) gray (as-sprayed coating) to dark gray (DLIP 5 pulses) and velvet black (DLIP 45 pulses) occurred when the coating surfaces were exposed to laser treatment which opens up interesting opportunities for development of matting, light trapping or anti-reflective coatings. The wettability behavior of the TiO₂ coatings from superhydrophilicity to superhydrophobicity could be easily tuned by designing of appropriate surface patterning.

Further works consisting in the investigation of the effect of size of spatial periods and the change in the pattern geometries (e.g., line-like or dot-like) on the surface properties of suspension sprayed coatings are envisaged. Moreover, in comparison with other laser based micro-texturing techniques, DLIP offers the possibility to treat a wide range of materials at process rates up to 0.9 m²/min, making the DLIP a valuable post-treatment technique for suspension spraying coating in industrial environments.

The combination of the suspension spraying as coating technology with the direct laser interference patterning as post-treatment coating technology provides new opportunities to develop functional coatings for applications in the fields of self-cleaning, antibacterial and antiviral surfaces, superhydrophobic surfaces, anti-icing, optical properties, solar cells, sensing, nature-inspired biomimetics or smart coatings.

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