TiO_2 NANOSTRUCTURED COATING OBTAINED VIA TERMOPHORETICAL DEPOSITION OF FLAME SYNTHETIZED NANOPARTICLES

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Abstract
A one-step method to produce coatings of TiO_2 nanoparticles on metallic substrates is presented. TiO_2 nanoparticles have been synthesized by Aerosol Flame Synthesis (AFS) and deposited through the mechanism of thermophoresis onto aluminum alloy substrates. The deposition system is constituted by a rotating disc, in order to increase the heat exchange and to promote a uniform distribution of the nanoparticles on the substrates. A fuel-lean flame is used as flame reactor. The average dimension of the nanoparticles is about 5 nm. Three different coatings have been obtained by varying the time of exposure of the substrates into the flame. A full experimental campaign, including SEM observation, thickness detection obtained via confocal microscopy and Electrochemical Impedance Spectroscopy (EIS) has been conducted, in order to characterize the surface and the electrochemical behavior of the coatings. Results show an improvement of the electrochemical behavior, since the deposition is uniform and the coating does not present agglomerates on the aluminum alloy substrates.

Introduction
In the last decades, aluminum alloys played an increasing role in many manufacturing contexts due to their peculiar properties. More specifically, high mechanical properties like tensile strength and damage tolerance, combined with low specific weight, make these alloys very suitable as structural materials, representing still today an almost primary choice in the aeronautic and automotive fields [1, 2]. On the other hand, one of the most relevant problems to deal with, when using aluminum alloys, is corrosion. So, the protection of aluminum alloys offered by coatings remains a key aspect in the designing process of structural components.
It is well known that the most common coating procedures for anticorrosive applications, like chromium-based treatments, are strongly toxic [3]. A considerable leap forward in this field has been done thanks to the introduction of

nanomaterials, which possesses particular properties that significantly differ from their respective massive materials. In particular, TiO_2 nanoparticles are currently the most attractive due to their excellent chemical stability and high compatibility with aluminum alloys and Carbon Fiber Reinforced Plastics (CFRP).
A promising solution to realize nanocoatings is given by the possibility to produce well defined nanoparticles from the chemical conversion of precursors in flames, a method known as Flame Synthesis [4]. Focusing on this technology, the aim of this work is to illustrate a cheap coating procedure of aluminum substrates for anticorrosive applications based on flame synthetized TiO_2 nanoparticles, obtained from the conversion of Titanium TetraIsoPropoxide (TTIP) in a laminar premixed ethylene-air flame, directly deposited on the substrates through termophoretical forces [5]. Following similar experiments reported elsewhere [6], a Flame Stagnation Rotating Surface System (FSRS) is employed, allowing to perform multiple coatings and to retain the thermal treatments of the aluminum alloys, as well as to keep constant the necessary thermal gradient that allows the thermophoretical deposition, thanks to the convection cooling of the rotating surface itself. Through scanning electron microscopy (SEM) and confocal microscopy, the coating morphology and thickness are investigated, while using Electrochemical Impedance Spectroscopy (EIS) the electrochemical behavior is tested.

Materials and Methods

Nanoparticle Production System

TiO_2 nanoparticles are produced in an AFS system, constituted by a Berglund Liu type Vibrating Orifice Aerosol Generator (VOAG, TSI 3450) and a honeycomb burner. Details on the AFS system are reported elsewhere [7]. The flame reactor is constituted by a laminar premixed flame of ethylene and air (flow rates: C_2H_4= 36 Nl/h; air = 700 Nl/h, with a resulting cold gas velocity of 100 cm/s, Φ=0.83). The characterization of titania nanoparticles produced in this flame reactor has been the object of a previous work [8].
In order to increase the heat convection, and to obtain more uniform coatings avoiding agglomeration, a FSRS on which the aluminum alloy substrates are mounted has been developed. The latter consists of an aluminum disc of 3.5 mm thickness and of 300 mm diameter mounted on a stainless steel tube whose diameter is of 20 mm and whose length is of 100 mm. The disc is kept in rotation by a brushless c.c. geared motor (Crouzet 80035508). On the disc, six couples of slots are obtained by milling. Fig. 1 reports a picture of the system herein described. The temperature of the disc is a function of rotational speed. It is demonstrated in some experiments that for angular speed of the disc greater or equal to 300 rpm, the air convection represents the predominant refrigeration mechanism by which any external cooling jets do not affect in any way the thermophoretical deposition [6].
The FSRS allows the installation of six substrates, specifically created with

rectangular (10 x 30 x 1.5 mm) and circular (Ø16 x 3 mm) geometry.

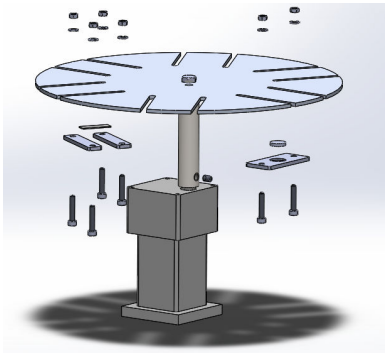

Figure 1. Graphical representation of the FSRS.

Coating production and characterization

A rotating speed of 500 rpm is used, corresponding to an insertion time relative to a single substrate of about 3.6 ms for each rotation. Three different times of total flame exposure of the substrates were selected, i.e. 10 s, 20 s, and 30 s. The samples obtained will be named as: "S_Actual time spent in flame by the substrates", thus: S_10, S_20, S_30. Aluminum substrates - diameter of 16 mm and a thickness of 1.5 mm - were first grinded and polished until a final surface roughness of about 1 μm is obtained. The coatings were analyzed in order to detect the morphology, the microgeometry and the chemical and electrochemical characteristics. In particular, the coating thickness was measured using a Confocal Leica DCM3D microscope. The samples used for this analysis are aluminum stripes covered by a copper tape on half of the surface. The chemical microanalyses were conducted by the SEM Hitachi TM3000, in order to evaluate the TiO_2 distribution on the surface and its morphology. EIS tests of the samples, in comparison with the bare aluminum substrates, were performed using a Biologic SP150 potentiostat in a three electrode conventional cell: the Ag/AgCl (3M KCl), used as reference electrod, the platinum electrode used as counter electrode and the coated samples used as working electrode. Tests were conducted after immersion in a de-aerated 0.05M Na_2SO_4 solution at room temperature and neutral pH for 90 min. A signal of 10 mV of amplitude was applied in the frequency range from 50,000 Hz to 0.01 Hz with 10 points per decade. Impedance spectrum are reported in Bode plot format in which the logarithm of the impedance modulus and the phase angle are plotted vs. the frequency logarithm of the applied signal.

Experimental Results

The SEM images for sample S_10, shown in Fig. 2, reveal the presence of a uniform coverage for all the samples analyzed. However, it is also possible to observe the presence of some agglomerates of nanoparticles upon the surface. These agglomerates represent a relative risk factor of exposure of the substrate to the external aggressive environment, since they tend to detach from the surface, leaving some unprotected areas that would represent the anodes in the corrosion process [8]. For S_10 a low presence of agglomerated particles was observed, which have almost a spherical shape and dimensions not exceeding 15 µm.

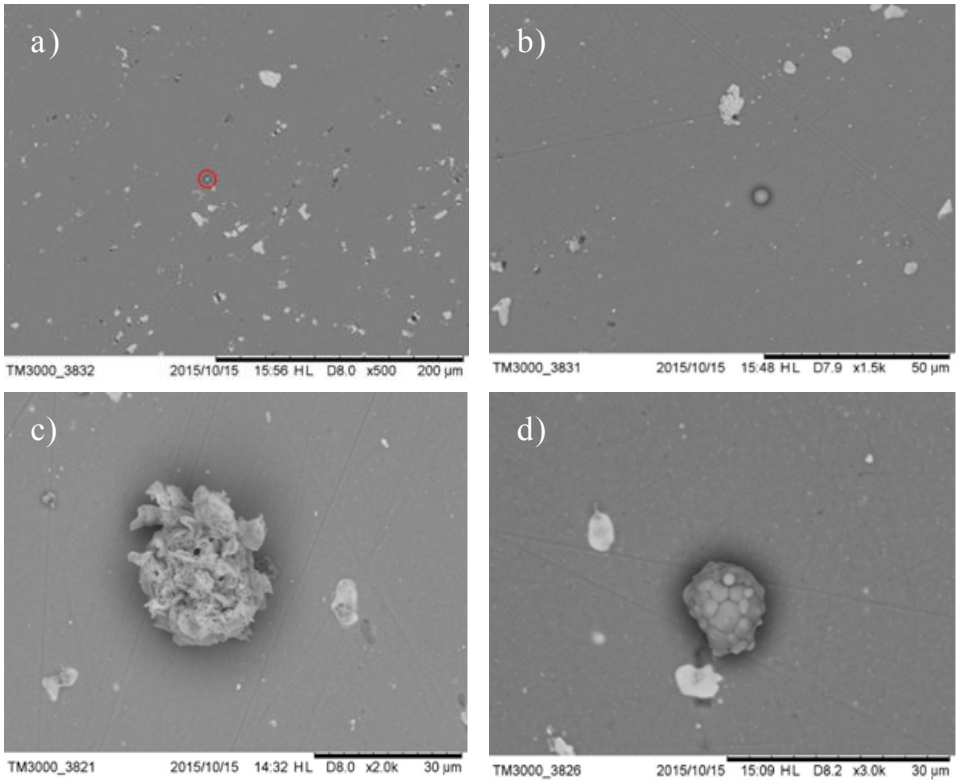

Figure 2. Images at different magnification of the sample S_10. (a) 500 X; (b) 1500 X and focus on the amorphous agglomerates found on the sample S_30. (c) 2000 X; (d) 3000 X.

Similar results are obtained also for the sample S_20, except for a slight increase in the number of agglomerated particles, whose sizes are comparable with the previous case (for the sake of brevity, images relative to this case are not reported). For the S_30 sample some amorphous agglomerates were also evident, where some

were also cracked. The amorphous nature and the presence of cracks upon the agglomerates may be due to the fact that at the beginning of the exposure to the flame the small spherical agglomerates are created, for longer exposures these small agglomerates tend to coalesce, and finally with the increase of the heat some fractures are created. In order to evaluate the repeatability of the results, the investigations were conducted on three samples for each deposition time considered. Fig. 3 reports one thickness profile detected for the sample S_30. The thicknesses obtained are about 0.7 µm for S_10, 1.5 µm for S_20 and 3 µm for S_30. The convection cooling of the substrates allows to limit nanoparticles agglomeration and to obtain uniform coating.

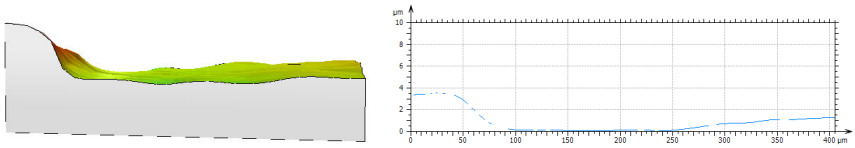

Figure 3. Profile representation, detected with the confocal microscope, of the sample S_30.

Impedance spectrum relative to the EIS tests results are reported in Fig. 4. Firstly, it is possible to highlight the behavior showed by the bare aluminum. Concerning the impedance modulus, a measured value of about 10^5 Ω*cm^2 within the frequency range from 1 Hz to 10^2 Hz can be observed. Moreover, it is possible to observe that the bare aluminum shows a phase angle of about -75° in a very narrow frequency range, i.e., from 3 to 30 Hz. This behavior suggests a not perfect capacitive behavior of the aluminum.

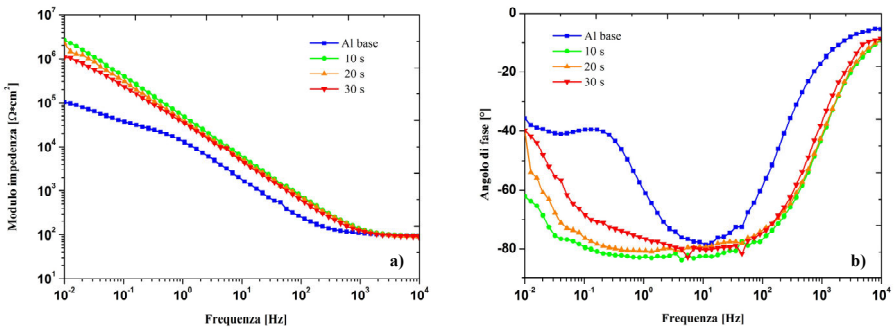

Figure 4. Impedance modulus (a) and Phase angles (b) of the coated samples (S_10, S_20, S_30) compared to the one of the bare aluminum.

For the coated substrates, in general, it is possible to notice an improvement with respect to the electrochemical characteristics of the bare aluminum, both in terms

of impedance modulus and in terms of the phase angle. For values of the phase angle close to 0°, the behavior of the coating is purely resistive, while for values of the angle tending to -90° the behavior is the almost capacitive, giving dielectric properties to the coating. Results show that the sample S_10 has the best electrochemical behavior, as it presents a capacitive behavior in a wide range of frequencies, with respect to S_20 and S_30. For what regards the impedances modulus, the three samples S_10, S_20 and S_30 present almost the same value and there is in general a great improvement with respect to the bare aluminum, in fact, in the coated substrates a value of the impedance modulus from $1*10^6$ to $3*10^6$ $\Omega*cm^2$ is measured.

Conclusions

The aim of this study was to develop a cheap procedure for the production of anticorrosive TiO_2 nanocoatings on aluminum surfaces based on the direct deposition, driven by thermophoresis, of TiO_2 nanoparticles produced at high temperature by Aerosol Flame Synthesis. Homogeneous, nanometric-thick TiO_2 coatings can be easily produced by Aerosol Flame Synthesis; the homogeneity and compactness of the coating are controlled by flame conditions and the number of insertions of the substrate into the flame. Flame produced TiO_2 coating improves significantly the electrochemical properties of aluminum surfaces. The improvement is most evident for the sample S_10 since the reduced number of agglomerates and their smaller dimension, ensure a more homogeneous, uniform and compact coating. From the thicknesses profile detection, performed using confocal microscopy, this result is also evident for the S_20, S_30 samples. Moreover, EIS analysis confirmed the increase of the electrochemical properties of the analyzed coatings, expressed by a capacitive behavior found in a wide range of frequencies and by an overall increase of the values of the impedance modulus.

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doi: 10.4405/39proci2016.III6