NANO-TIO$_2$ COATINGS OF ALUMINUM SURFACES PRODUCED BY AEROSOL FLAME SYNTHESIS


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Abstract

This work reports the development of a one-step method for the coating of aluminum surfaces with titania nanoparticles. Narrowly sized, ultra-fine TiO$_2$ nanoparticles were synthesized by Flame Aerosol Synthesis and directly deposited by thermophoresis onto cylindrical samples of aluminum alloy AA2024. Submicron coatings of different thickness and porosity were produced by varying the total time of deposition. Two flame synthesis conditions were investigated in order to study the effect of titania particle dimension and phase composition on the characteristics of coatings. Pure anatase nanoparticles of 3.5 nm diameter were produced in fuel-lean synthesis condition, while fuel-rich non-sooting condition was used to synthesize a mixture of rutile and anatase nanoparticle of 22 nm in diameter, rutile being the predominant phase. Confocal Microscopy measurements allowed to calculate coatings thickness. The electrochemical behavior of the coatings was characterized by means of Electrochemical Impedance Spectroscopy by analyzing the impedance phase angle and modulus, which is an index of the capability of the coating to protect the aluminum substrate. The results obtained show an improvement of the electrochemical behavior of the AA2024 substrate when TiO$_2$ nanoparticles are deposited. Specifically, processed samples have a capacitive behavior with a higher impedance modulus in a larger range of frequencies. Substrates processed with rutile phase nanoparticles of 3.5 nm in diameter and with a lower exposition time showed better results with respect to all the other operating parameters.

Introduction

In the last decades aluminum alloys have been widely used in the aeronautic industry for the construction of structural components (such as fuselage panels, frames, etc.) due to their high mechanical properties, in terms of damage tolerance and tensile strength, coupled with the low weight and fabrication simplicity. On the other hand, some aluminum alloys, such as the AA 2024 (one of the most used) are very sensitive to corrosion, in particular in aggressive external environments (such as chlorides). For these reason, superficial treatments, such as anodizing, are
usually required to improve the corrosion resistance of the aluminum components [1]. Moreover, nowadays the need of components with higher mechanical performances and improved corrosion resistance led to the increasing widespread use of carbon fibers reinforced polymer (CFRP). Consequently, titanium and its alloys have found an increasing use in the construction of structural components, due to high specific mechanical properties, corrosion resistance, and compatibility with CFRP [2]. On the other hand, high costs and difficulty in machining pose severe limitations to a widespread use of titanium alloys. For these reasons, the possibility to realize titanium coating layers on aluminum components and structures represents a promising solution to achieve a satisfactory trade-off between the aforementioned features.

In this paper TiO\textsubscript{2} coatings were produced by varying the main process parameters, in order to find out the coating with the best electrochemical properties. The influence of the process parameters on the corrosion behavior was also investigated. The aim of this work was to improve the electrochemical behavior of the aluminum surface with the deposition of uniform coatings TiO\textsubscript{2} nanoparticles through thermophoresis process with a low cost process.

**Experimental**

The aerosol flame synthesis set-up consists of the combination of a Berglund Liu type Vibrating Orifice Aerosol Generator (VOAG, TSI 3450) and a honeycomb burner. The burner was composed by an 18 mm ID stainless steel tube, with 26 mm long Mullite Zirconia Honeycomb (400 CPSI) placed on its top, used to stabilize the flame. The burner had an outside ring (ID 24 mm, OD 34 mm) used to flow sheath Argon (65 Nl/hr) to isolate the flame from the surrounding air. Burner walls were equipped with electrical resistances controlled by a proportional-integrated controller. A 0.3 M solution of titanium tetraisopropoxide (TTIP, Aldrich, 97%) into ethanol was used as precursor. VOAG generated a uniform droplets jet (0.6 cm\textsuperscript{3}/min), which was then dispersed into an air stream and injected directly into the burner. The burner walls were heated to 450 K to ensure complete evaporation of both ethanol and TTIP before reaching the flame front. Ethylene was used as fuel, with air as oxidant to generate a burned stabilized, flat, atmospheric premixed flame. Two different experimental flame conditions were investigated, as reported in Table 1.

On-line measurement of particle size distribution (PSD) was performed using a TapCon 3/150 Wien Type Differential Mobility Analyzer (DMA). The sampling probe was made of a stainless steel tube (8 mm inside diameter and 1 mm wall thickness), with a 0.3 mm side pinhole through which flame gases were sampled and diluted in nitrogen, following a procedure reported elsewhere [3].

Aluminum alloys substrates - diameter of 16 mm and a thickness of 1.5 mm - were first grinded by P320 emery paper and then polished by three different diamond suspensions. Substrates placed on a stainless steel support were inserted in the flame facing down towards the flame at 100 mm HAB for Flame A and 150 mm
HAB for Flame. The substrate support was attached to a mobile extension, controlled by a double-acting pneumatic cylinder and inserted in the flame with different residence times and with varying insertion numbers. Residence times and insertion repetition times were optimized to maintain substrate temperature at low temperature, in order to allow particles produced in the hot flame region to move by thermophoretic forces from the flame towards the cold substrate depositing on the substrate itself upon contact [4].

**Table 1. Summary of flame conditions and particle properties.**

<table>
<thead>
<tr>
<th>Flame</th>
<th>TTIP (%) mol</th>
<th>Velocity (cm/s)</th>
<th>PSDF &lt;D_p&gt; (nm)</th>
<th>Anatase %wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.107</td>
<td>1.52</td>
<td>22</td>
<td>15</td>
</tr>
<tr>
<td>B</td>
<td>0.028</td>
<td>0.83</td>
<td>3.5</td>
<td>100</td>
</tr>
</tbody>
</table>

Coating layers were analyzed to have information on the morphology, the microgeometry and the chemical and electrochemical characteristics. XRD spectra were recorded on a Bruker D2 Phaser X-Ray Powder Diffractometer operated with a Cu(Kα) radiation. Layer thickness was measured using a Confocal Leica DCM3D microscope.

Electrochemical characterization was performed by means of EIS measurement, using a Biologic SP150 potentiostat in a three electrode conventional cell: an Ag/AgCl 3 M KCl was used as reference electrode and a platinum disk as counter electrode. The test was conducted after immersion in a deaerated 0.5 M Na2SO4 solution at room temperature and neutral pH for 90 min. A signal of 10mV of amplitude was applied in the frequency range from 50,000 Hz to 0.01 Hz with 10 points per decade. Impedance spectra were reported in Bode plot format in which the logarithm of the impedance modulus |Z| and the phase angle ϕ are plotted vs the logarithm of the frequency f of the applied signal.

**Results and Discussion**

Particles were collected from flame by a suction probe and analyzed on line by a DMA to obtain the size distribution of particles (PSDFs) suspended in the gas. The PSDFs were fitted by a lognormal distribution function. Figure 1 reports the distributions of the particle equivalent diameters for the two flame conditions, together with their best fit from Equation 2. Mean particle diameters were calculated to be 22 nm for Flame A and 3.5 nm for Flame B, with a geometric standard deviation of 1.59 and 1.47, respectively. These values are close to a typical standard deviation of a self-preserving distribution function [5].
The different particle number concentration, given by the different TTIP concentrations in the unburned mixture, and the different residence times in the flame allowed to synthesize titania nanoparticles with various dimensions, differing one from the other by about one order of magnitude, by just varying the progress of the coagulation process in the flame.

XRD spectroscopy was used to characterized the phase composition of flame-produced nanoparticles.

XRD spectra were measured for nanoparticles produced in Flame A and Flame B conditions, and they are reported in Fig. 2. In the spectrum relative to the Flame A condition, only XRD peaks relative to the anatase phase are present, while in the spectrum of particles from Flame B the peaks corresponding to both phases are present. So, particles synthesized in Flame B condition are composed by a mixture of rutile and anatase, rutile being the predominant phase. The variation in particle phase composition is caused by the different equivalent ratio that result in an oxygen-lean environment for Flame A and an oxygen-rich environment for Flame B.
B. From the XRD peaks of Flame A spectrum, the weight fraction of the rutile phase has been calculated to be equal to 85% [6].

Different titania nanoparticles coatings were produced and characterized for both flame conditions by varying the deposition time and the number of insertions of the substrate into the flames. Four different samples were produced from each flame conditions as reported in Table 2. The nomenclature of the samples is of the type SZ_X,Y, where: Z refers to the flame condition, X to the number of insertions and Y to the exposure time to the flame of each insertion.

Thickness of the sample has been determined through confocal microscopy by measuring the step between the aluminum substrate and the layer of nanoparticles and elaborating through the Gauss filter at 0.08 mm [7]. Measured values range from 180 nm and 230 nm for sample SB_1,30 and SA_1,30 respectively, up to 500 nm and 650 nm for sample SB_10,30 and SA_10,30 respectively.

EIS measurements have been carried out to understand the electrochemical behavior of the coating and to characterize it with respect to the original surface.

![Figure 3. Bode diagram relative to all the samples compared between them.](image)

The Bode diagram reports the phase angle and the modulus of the impedance in function of the frequency. Typical capacitive behavior is showed when the phase angle is about -90°, while at 0° the material has a typical resistive behavior. The Bode diagram for all the samples and for the bare aluminum is reported in Fig. 3. Flame B gives results better than flame A. Indeed, focusing the attention especially on the phase angle, it can be observed that the capacitive behavior is extended for a larger range of frequency for flame B condition.
This behavior indicates an improvement of the surface characteristics with respect to the bare aluminum. Moreover, the higher modulus of impedance in the “B” samples indicates also a higher resistance of the coating. In particular, the best treatment for both the flames is experienced from S(A,B)₁,₃₀ and S(A,B)₁,₁₀. The advantage with respect to the bare aluminum is offered by SB₁,₃₀ with an increase of impedance in all the range analyzed.

Conclusions
The aim of this study was to find the best procedure to obtain nanosized-thick, cheap and protective coatings on the aluminum surfaces based on the direct deposition, driven by thermophoresis, of TiO₂ nanoparticles produced at high temperature by flame aerosol synthesis. Flame synthesis conditions which produce nanoparticles with size lower than 10 nm (Flame B) give a more regular coating on aluminum surfaces. Moreover, EIS analysis demonstrates that the aluminum substrates processed in Flame B conditions are characterized by a larger range of frequencies in which the samples posses a capacitive behavior. It has been demonstrated also that the modulus of the resistance is higher with respect to the bare aluminum. In conclusion it can be noted that the coated aluminum substrates showed a significant improvement of the electrochemical properties, especially for the samples that experienced just one immersion in flame with respect to the bare aluminum.

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References

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