Electrical properties of plasma-sprayed TiO$_2$ coatings

N. Branland$^1$, F. Gitzhofer$^1$, M. Boulos$^1$, E. Meillot$^2$, A. Vardelle$^3$ and P. Fauchais$^3$

$^1$CRTP, Université de Sherbrooke, 2500 Boul. Université, J1K 2R1, Sherbrooke, Canada
$^2$C.E.A. Le Ripault, B.P. 16, 37260 Monts, France
$^3$SPCTS, Université de Limoges, 123 av. A. Thomas, 87000 Limoges, France

ABSTRACT

Titania coatings were deposited on stainless steel substrates by induction plasma spraying technology. The electrical properties of the coatings were characterized using impedance spectroscopy in the frequency range 1 Hz to 10$^6$ Hz. The measurements show that the electrical resistivity is dependent on the coating microstructure and its stoichiometry. Through the heat treatment of the coating in an oxygen flow, its stoichiometry could be modified resulting in an increase of its specific resistivity. The result indicates that mobile charge carriers originated predominantly from the non-stoichiometric crystal structure. The effect of coating densification on resistivity values was also studied by means of thermal treatments in argon atmosphere.

INTRODUCTION

In plasma spraying, coatings are formed from the piling up of molten or semi-molten particles that strike the prepared substrate$^1$, where they are flattened and quenched within a very short time. Through this technique, reliable coatings of metals, alloys and ceramics, also monolithic and near-net shape metallic and ceramic parts can be produced. The industrial applications in the chemical, automotive, aeronautic, electronic fields have greatly increased over the last decades.

Titanium dioxide in the form of plasma-sprayed coatings has been the subject of numerous investigations because of its interesting electrical properties and in particular for its activity in photo-electric or photo-chemical energy applications$^{2,3,4}$. Some previous studies$^{5,6}$ have dealt with the relationships between the coatings electrical properties and spraying conditions. It has been shown that the plasma spraying of TiO$_2$ coatings results in large variations in stoichiometric composition that affect the electrical properties of the sprayed materials. Stoichiometric rutile (the most stable phase of titania) is an insulator but becomes a n-type semiconductor with the color changing from white to grey-black when its oxygen content is lowered compared to that of rutile stoichiometry$^7$.

This paper presents an attempt to understand the roles of the microstructure and composition stoichiometry on the electrical resistivity of inductively plasma-sprayed TiO$_2$. In order to correlate the coating oxygen loss with the resultant electrical resistivity, the coatings were heat-treated at different temperatures in an oxygen flow. The electrical properties of the coatings have been measured by impedance spectroscopy. This method is an effective technique for the characterization of the electrical nature of heterogeneous composite systems$^8$. 
2. **Experimental**

The TiO₂ materials used in this investigation were commercially available titanium dioxide powders: H.C. Starck - Amperit 742. The particle size distribution ranged between 22 to 45 μm. In order to eliminate the magneli structure (Ti₅O₂₉₋ with n = 4-10) present in the as-received powders, the powder was heat-treated in air for a period of three hours at 1000°C. After this treatment, the structure of the powder became that of pure rutile phase. Stainless steel substrates (X13M), 25 mm in diameter and 5 mm in thickness, were prepared by gritblasting and degreasing before spraying.

An inductive plasma torch (Model PL35 by Tekna Plasma Systems Inc, Sherbrooke, Canada) with a ceramic plasma confinement tube of 35 mm in internal diameter, was used to produce the titania coatings. The torch sheath gas was oxygen while the central and powder carrier gases were pure argon. The torch operating conditions are summarized in Table 1. The exit tip of the central powder injection probe was located at 40 mm upstream of the exit plane of the torch nozzle.

<table>
<thead>
<tr>
<th>Operating conditions for titanium dioxide deposition.</th>
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<tr>
<td>Carrier gas</td>
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<tr>
<td>Central gas</td>
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<tr>
<td>Sheath gas</td>
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<tr>
<td>Plate power</td>
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<tr>
<td>Chamber pressure</td>
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<tr>
<td>Particle size distribution</td>
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<tr>
<td>Spray distance</td>
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<tr>
<td>Probe position</td>
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<tr>
<td>Powder feed rate</td>
</tr>
<tr>
<td>4 slm (Ar)</td>
</tr>
<tr>
<td>40 slm (Ar)</td>
</tr>
<tr>
<td>70 slm (O₂)</td>
</tr>
<tr>
<td>40 kW or 50 kW</td>
</tr>
<tr>
<td>33,3 kPa or 53,3 kPa</td>
</tr>
<tr>
<td>22-45 μm</td>
</tr>
<tr>
<td>150 mm</td>
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<tr>
<td>40 mm</td>
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<td>11 g/min</td>
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The electrical impedance of the coating was measured by means of a two-contact electrode system. A gold electrode was sputter-coated onto the titania coating to provide for good electrical contact. The diameter of this electrode was smaller than that of the sprayed coating in order to minimize the effects of surface current leakage. Copper wires were attached to either side of the sample with the aid of a conductive silver paint to serve as electrical measurement leads. Impedance spectroscopy was performed with a Solartron 1287 coupled to an impedance analyzer Solartron 1260 (Schlumberger Technologies), scanning over the frequency range from 1 to 10⁶ Hz, in air. The measured data are known as the values of the complex impedance $Z^*$ with $Z^* = Z' + iZ''$.

For the full range of the spraying parameters used in this investigation, grey colored coatings were invariably obtained, the coloration indicating that the coatings were oxygen deficient. So, the electrical properties of the titania coatings were largely modified as the TiO₂ rutile was converted into non-stoichiometric TiO₂ₓ becoming a semiconductor. To study the influence of re-oxidation, the coatings were annealed for 2½h in an oxygen flow at various temperatures, namely 505°C, 640°C and 705°C. To follow the re-oxidation, coating color measurements were carried out in the CIELAB colorimetry system with a Diano Match Scan II spectrophotometer. A parameter of particular interest was the lightness value L which can vary from 0 (absence of color, i.e. black) to 100 (i.e. pure white).

The thickness and porosity of the coatings were determined by SEM analysis of sample cross sections.
3. Results and Discussion

3.1. Influence of plasma spraying conditions

As already mentioned, all the titania coatings prepared by plasma deposition had a grey color, indicating the presence of oxygen deficiency even if the plasma flow had a partial pressure of oxygen above 60 vol.% The grey color is due to oxygen loss during spraying. This is accommodated by the production of structural defects that are most readily formed in the TiO₂ particles at high temperatures (titania melting point Tm = 1830°C) and subsequently retained within the rapidly quenched splats (splat cooling rate ~ 10⁶-10⁷ °C/s). The defects are normally found in the form of planar crystallographic shear planes.

The electrical resistivity measured by impedance spectroscopy, is deduced from the Nyquist diagram in which the imaginary component of the impedance is plotted against its real component.

![Nyquist diagram](image)

Figure 1 - Nyquist diagram for as-sprayed titania coating (33,3 kPa - 40 kW) and associated R-C equivalent circuit.

The single relaxation such as the semicircular arc in the Z* plane represents the total resistance of the coatings. A R-C model can be used to fit the results as illustrated in Figure 1 where, Rc represents the electrical contact resistance, C the capacitance and R the resistance of the coating.

The heat treatment received by the particles in the plasma affects appreciably the porosity and stoichiometry of the sprayed coatings and, consequently, the lightness values as shown in Table 2.

<table>
<thead>
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<th>Table 2 - Electrical resistivity ρ, porosity and lightness of as-sprayed coatings.</th>
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<tr>
<td>Conditions</td>
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<td>----------------</td>
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<tr>
<td>40 kW - 53,3 kPa</td>
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<td>50 kW - 53,3 kPa</td>
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<td>40 kW - 33,3 kPa</td>
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Decreasing the chamber pressure and plate power leads to a lowering of the heat transfer between plasma flow and particles. Consequently, the particles are not completely
melted and do not flatten evenly on the substrate surface. There is some formation of porosity and interlamellar contacts of poor quality which act as barriers for the charge carriers involved in the electrical current flow. Indeed, the way the particles impinge on the substrate, or on the previously deposited layers strongly influences the bonding between the resultant lamellae and, thus, the physical properties of the coatings.

Lower plasma temperatures result in a decrease of the rates of heat transfer to the in-flight particles, therefore, their temperature is lowered and oxygen loss reduced. Consequently, the coating lightness value for the condition 40kW – 33.3 kPa is higher than that of the other deposits.

The effect of the various plasma spray conditions on coatings electrical resistivity is not easy to discern because of the combined effects of two different parameters: the coating porosity and titania deposit stoichiometry.

3.2. Heat treatment under oxygen

During the thermal treatment of the coatings in oxygen at different temperatures, the non-stoichiometric titania picks up oxygen and tries to recreate the stoichiometric structure. Figure 2 shows the evolution of the lightness difference $\Delta L$ ($\Delta L = L$ after heat treatment – $L$ before heat treatment) against the re-oxidation temperature. It can be seen that for all the samples examined, $\Delta L$ increases with temperature. However, this evolution is not identical for all the plasma spray conditions investigated in this study, suggesting that the diffusion of oxygen might be different.

![Figure 2](image-url)  
**Figure 2** – Evolution of the lightness difference with the oxidation temperature for the various spray conditions of this study.

![Figure 3](image-url)  
**Figure 3** – Impedance diagram for a 40kW – 53.3 kPa coating heat-treated at 640°C in $O_2$.

The impedance data indicate an anomalous frequency dispersion in the overall impedance behaviour, evidenced by the presence of a finite depression angle (Figure 3) which lies between the real impedance component axis and the arc axis. This non-zero depression angle $^8$ could be due to non-uniformity in the defects distribution or to the presence of a second phase. The oxygen diffusion within the coating may also be non-uniform, resulting in two different TiO$_2$ phases (stoichiometric and non-stoichiometric).
As the temperature of thermal treatment rises, the TiO₂ color intensifies and electrical resistivity values increase as shown in Figure 4. It may be noted that the evolution of electrical resistivity is very similar to that of ΔL, shown in Figure 2. The bulk conductivity of non-stoichiometric TiO₂ had been proposed as being caused by the presence of titanium interstitials (Ti³⁺ and Ti⁴⁺) and oxygen vacancies. The increased electrical resistivity can thus be explained by a decreasing presence of oxygen vacancies because of a saturation of titanium free bonds.

![Figure 4 - Evolution of the electrical resistivity ρ with the temperature of re-oxidation.](image)

However, the different evolutions for the electrical resistivity confirm that the oxygen diffusion in coatings does not always follow the same path, depending on parameters such as the thickness and microstructure of the coating. The following experiments were performed to check this hypothesis.

Two coated samples were prepared under the same plasma conditions but with different thickness; they were heat-treated at 640°C, for 2½ h. The resistivity value for the thicker sample was about 10⁴ times greater than that of the thin sample. Even if the thermal expansion coefficient of the substrate (~ 10,7*10⁻⁶°C⁻¹ between 20°C and 100°C) is not too different from that of titania (~ 8,8*10⁻⁶°C⁻¹ between 20°C and 100°C), the difference between these coefficients may generate thermal stresses resulting in the formation of microcracks, which are promoting the diffusion of O₂ into the coating.

To check if the titania coating was stoichiometric after 2½ h of thermal treatment, the time of the latter was increased up to 7 h. After 7 hours, ΔL was greater for all conditions, indicating that the coatings continued to take up oxygen and become more stoichiometric. Subsequent electrical measurements performed on these samples showed a capacitive behaviour with resistance values ≥ 10⁸ Ω, indicating that the heat-treated coatings had become dielectric again.

### 3.3. Heat treatment under argon

The electrical properties of titania coatings are related not only to their stoichiometry but also to their microstructure. In order to evaluate the role of the microstructure i.e. interlamellar contacts, pores ... on the electrical resistivity, the coatings were heat-treated under argon, at the same temperatures and for the same periods as the coatings treated in oxygen. The effects of densification by heat treatment imply that the results could be
obtained only for the coatings sprayed at 40 kW with a pressure of 53.3 kPa, and heat-treated at 505°C. In fact, for the other specimens, the resistance values of the coatings were close to the lower limit for the impedance analyzer operating range. Consequently, this impedance value could not be measured.

The microstructure of the investigated samples is presented in Figure 5. The first point to notice is that the coating lacks internal cohesion, leading to the numerous pull-outs during the operations of grinding and polishing. The porosity of the as-sprayed coating presented in this part is 4.8% whereas for the after heat-treatment specimen it is only 2.5%. The evolution of the interlamellar contacts structures is not clearly shown on these microstructures. Mercury porosimetry measurements are now in progress to quantify this feature of the plasma sprayed titania coatings.

![Figure 5 - SEM microstructure of plasma-sprayed coatings: 40 kW - 53.3 kPa](image)

(a) As-sprayed coating  
(b) After heat treatment at 505°C during 2h30

4. CONCLUSION

The influence of three operating conditions for the production of plasma-sprayed titania coatings on their electrical resistivity was studied. In all cases, non-stoichiometric titania coatings were obtained. Their electrical resistivity varied with porosity and stoichiometry.

Heat treatments conducted under oxygen involve the evolution of stoichiometry and thus changes in the electrical resistivity. In fact, the observed variation is probably attributable to the elimination of oxygen vacancies in the TiO₂ lattice. The impedance data reveal that the diffusion of oxygen may not be homogenous as evidenced by the non-zero depression angle. Moreover, the diffusion of O₂ may also be dependent on the structure of coatings as shown by the varying evolution of the electrical resistivity depending on the sample.

Heat treatments conducted in argon show that the densification of the coatings results in a decrease in electrical resistivity. This behaviour can be explained by a decrease in the interlamellar contacts, which, therefore cannot longer act as barriers to the mobile charge carriers.

REFERENCES
