

# Corrosion behaviour of Ti/Al<sub>2</sub>O<sub>3</sub> interfaces produced by an active metal brazing methodology

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Metal/ceramic joints are used in a broad range of applications in biomedicine, such as the encapsulation of implantable telemetric devices, the fabrication of crowns and bridges for dental restoration, or the production of drug delivery systems, biomedical sensors and electrodes. Apart of other characteristics, the corrosion resistance of metal/ceramic interfaces is of prime importance when biomedical applications are considered. Most of metal/ceramic joints are produced by the active metal brazing technique or by diffusion bonding. Both techniques originates a multi-layered interface which should be able of accommodating the abrupt electronic, crystallographic, chemical, mechanical and thermomechanical discontinuity that characterize these metal/ceramic systems. However, galvanic interactions between those chemically distinct layers are likely to occur, affecting the degradation behaviour of the interface. In this work the corrosion behaviour of Ti-Al<sub>2</sub>O<sub>3</sub> interfaces produced by an active metal brazing methodology was studied. SEM analyses evidenced an interface mainly constituted by four different layers. A first layer rich on titanium and copper, located near to the pure titanium, another layer also rich on Ti and Cu, but with a higher Ag content, an intermediate layer rich in silver which contains some little precipitates of Ti-Cu and finally, a reaction layer with a composition profile containing Ti, Cu, Ag, and Al, located near the alumina part. Potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) measurements, carried out in a simulated physiological solution at ambient temperature, revealed a strong influence of the rich silver layer on the passivating behaviour of the interface. On the other hand, the reaction layer appears to be the main responsible for the degradation process of the interface. This degradation is accompanied by a relatively high release of copper. Through EIS data simulation it was possible to obtain an electrochemical equivalent circuit that describes the corrosion process and allowed an estimation of the polarisation resistance of the constitute layers of the interface. The electrochemical interaction between the different constitutive layers was evaluated, and was correlated with the overall degradation behaviour of the Ti-Al<sub>2</sub>O<sub>3</sub> interface.

**Keywords :** EIS, Metal/Ceramic Interfaces, Active Metal Brazing,

## 1. Introduction

The metal/ceramic joining technologies have been subject of intensive research efforts, during the last decades. Despite the big differences between the mechanical, chemical and physical properties of the involved materials, a large interest exists in the establishment of a useful combination of its properties to produce components to be used in a wide range of industrial applications.

In spite of the great variety of existing techniques to produce metal/ceramic (M/C) joints, active metal brazing appears to be the best technique to produce M/C interfaces with the best combination of properties[1,2]. This technique involves a third material, a brazing alloy, which is characterized by its low melting point and is expected to promote wetting between both materials. From the corrosion point of view, one of the drawbacks of this methodology is associated with the formation of a complex interface which is characterized by chemical, mechanical and thermo-mechanical discontinuities, resulting in a critical region of the component, i.e. mechanical and/or corrosion failures can be occurs in the M/C interface of the produced component.

Practical applications of such metal/ceramic joints may be found in a wide variety of areas, being the biomedical applications on of the most important fields. In this area, the M/C interfaces may be found in a wide diversity of devices ranging from external or implantable sensors up to dental implants. In despite of the great amount of efforts that has been realized in last years to understand and to improve the mechanical performance of metal/ceramic systems, little is known on the corrosion behaviour of metal/ceramic interfaces[3-5]. This knowledge is indispensable for components that will work in contact with aggressive environments, and the lack of information regarding this subject may be due to the practical difficulties in studying the interfaces. In fact, a multi-layered M/C interface obtained by an active metal brazing process is constituted by different layers, which have very small dimensions and complex variations in the chemical composition between them. As a consequence, the electrochemical characterisation of the whole interface by standard techniques becomes very difficult, as well as the understanding of the mechanisms leading to its degradation, due to fact that this degradation may be influenced by galvanic interactions between layers, which can be very complex.

In this work the corrosion behaviour of Ti/Al<sub>2</sub>O<sub>3</sub> interfaces obtained by an active metal brazing methodology is investigated. For this propose, standard electrochemical techniques and electrochemical impedance spectroscopy (EIS) were used. Furthermore, in order to study the galvanic interaction between couples involved in the interface and with the aim of establishing a relation of its individual behaviour with the overall degradation behaviour of the Ti-Al<sub>2</sub>O<sub>3</sub> interface, galvanic corrosion measurements between the individual layers was carried out.

## 2. Materials and Methods

### 2.1. Production of Ti/Al<sub>2</sub>O<sub>3</sub> interfaces

Commercial pure titanium (ASTM grade II) and alumina (*Frialit-Degussit Al23* from *Friatec*, Germany) rods of 13 mm diameter were joined together by means of active metal brazing, in order to produce metal/ceramic interfaces. A brazing alloy, with the following composition in weight: 70.5Ag-26.5Cu-3.0Ti (*CB4* from *Degussa*, Germany) has been selected.

Active metal brazing was carried out in a high vacuum *Termolab* resistance furnace. During the thermal cycle it was applied to the metal/ceramic system a static pressure of  $0.14 \times 10^5$  Pa. Samples were heated up to 300°C at a heating rate of  $5^\circ\text{C}\cdot\text{min}^{-1}$  and kept at that temperature during 30 min. Then, samples were heated up to 900°C at the same heating rate and kept at that temperature during 15 minutes; finally they were cooled down to room temperature ( $2^\circ\text{C}\cdot\text{min}^{-1}$ ).

## 2.2. Chemical and morphological characterization

The chemical composition and morphology of the interface were studied by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analysis. Through EDS analysis it was possible quantitatively to established the composition of constitutive layers of the interface.

Based on the composition of constitutive layers founded at the interface, standard samples simulating the composition of these main layers were fabricated. These samples were produced in an arc-melting furnace, under an argon protective atmosphere.

## 2.3. Electrochemical Characterization

The corrosion behaviour of the Ti/Al<sub>2</sub>O<sub>3</sub> interface and its individual constitutive layers was studied by different electrochemical test. All electrochemical measurements were performed at room temperature in a Hank's Balanced Salt Solution (HBSS), *H-8264* from *Sigma*<sup>®</sup>, with a pH of 7.3.

Previously to corrosion tests the surface of the samples was abraded with SiC paper followed by polishing with diamond paste. Finally, all samples were sonicated in ethanol (15 min) and distilled water (20 min) and dried.

An electrochemical cell constituted by a standard three electrodes arrangement was used for the electrochemical test. The counter electrode was a platinum wire with an area of 1 cm<sup>2</sup> and a saturated calomel electrode (SCE) was used as reference.

A PGP201 potentiostat/galvanostat (Radiometer, Denmark), controlled by the VoltaMaster-1 software, was used in the open circuit potential ( $E_{\text{corr}}$ ) and potentiodynamic polarisation measurements.  $E_{\text{corr}}$  was monitored for 60 min, and following the samples were polarised from -600 mV up to 2000 mV at a scan rate of  $2 \text{ mV}\cdot\text{s}^{-1}$ . A PGZ100 Voltalab potentiostat (Radiometer, Denmark), controlled by the VoltaMaster-4 software, was used in the electrochemical impedance spectroscopy (EIS) experiments. EIS measurements were performed at increasing immersion times (1, 2 and 3 hours, as well as 1 to 10 days) in the frequency range from 100 kHz to 5 mHz, with an AC signal wave amplitude of 10 mV applied at the corrosion potential. The analysis of EIS results was performed through EIS data simulation using the ZView2 software, in order to obtain an equivalent circuit model that describes the corrosion behaviour of the interface.

After potentiodynamic polarisation test of the layers A, B, C and D, an analysis of the Cu and Ag contents present in the electrolyte was realized. For this propose atomic-absorption spectroscopy measurements were carried out in a *GBC 904 AA* spectrophotometer.

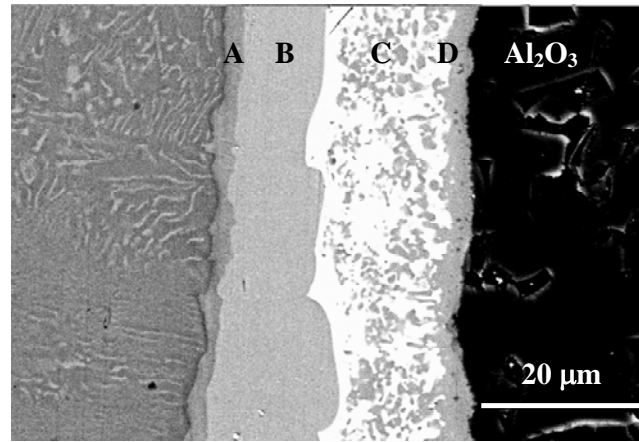
The galvanic corrosion behaviour of the A/B, B/C and C/D couples of layers was evaluated through the determination of Evans diagrams[6] in a *PGZ100 Voltalab* potentiostat. The surface area ratio between samples was kept equal to one. The method is based on the measurement of galvanic current ( $I_{\text{couple}}$ ) and potential ( $E_{\text{couple}}$ ) of the couples. Samples were first kept electrically isolated, immersed in HBSS for 60 min for potential stabilisation. Current steps of  $0.001 \mu\text{A}$  were then imposed during 30 seconds step by step to the system until the curves converged to the  $E_{\text{couple}}$  value.

Before and after corrosion test the interface and the standard samples were also characterized by SEM and EDS analysis.

### 3. Results and discussion

#### 3.1. Chemical and morphological characterisation of Ti/Al<sub>2</sub>O<sub>3</sub> interfaces

The chemical composition of the interface was determined by EDS analysis. Fig. 1, shows a representative SEM micrograph of the interface. As previously described by Paiva[3], the interface is constituted by a reaction layer, near to the Al<sub>2</sub>O<sub>3</sub> side (layer D), which is rich in Ti and Cu and which has low contents of Ag and Al; immediately adjacent there is an intermediate layer rich in Ag (layer C), containing some precipitates of Ti and Cu, finally, near to the Ti diffusion layer, exist two layers (A and B) rich in Ti and Cu, being the more rich in Ti that placed near to Pure Ti (layer A). The results of the EDS analysis are presented in the Table 1.



**Fig. 1.** SEM micrography of Ti/Al<sub>2</sub>O<sub>3</sub> interface obtained by active metal brazing.

In order to study the contribution of each layer for the overall degradation of the interface, four representative standard samples, simulating the composition of the layers present in the interface, were prepared. They were namely A, B, C and D. The chemical composition of each sample is shown in Table 1.

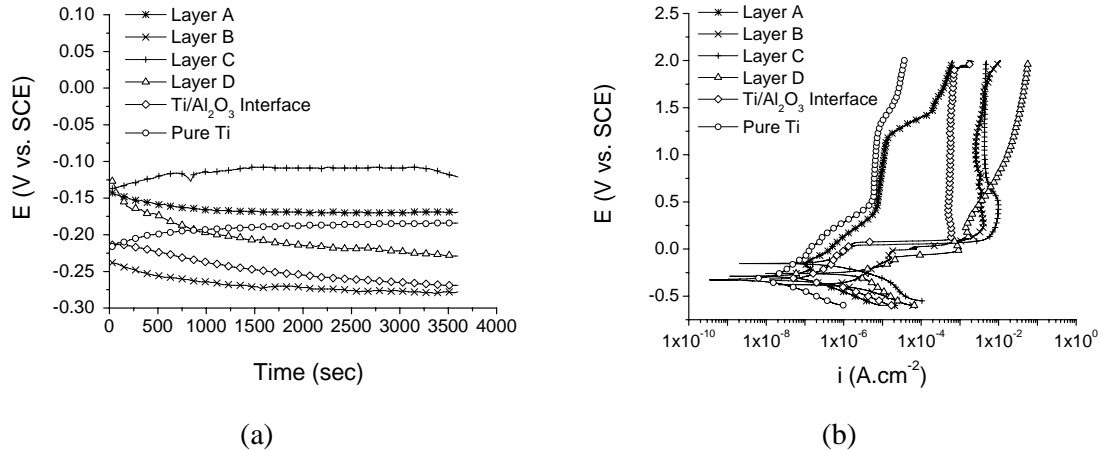
**Table 1.** Chemical composition of layers and individual samples, fabricated to simulate the interfacial layers constitutive of the Ti/Al<sub>2</sub>O<sub>3</sub> interface.

Layer	Ti (Atomic %)		Cu (Atomic %)		Ag (Atomic %)		Al (Atomic %)	
	EDS	EDS	EDS	EDS	EDS	EDS	EDS	EDS
	Interface	Standard sample	Interface	Standard sample	Interface	Standard sample	Interface	Standard sample
A	69.3	68.9	29.0	29.1	1.7	1.9	-	-
B	48.9	49.4	46.8	47.1	4.3	3.6	-	-
C	1.6	1.5	4.2	4.0	94.3	94.5	-	-
D	53.3	53.6	40.0	37.8	5.1	5.8	1.5	2.7

### 3.2. Electrochemical Characterization

Fig. 2 a, shows the variation of  $E_{\text{corr}}$  with the time for the Ti/Al<sub>2</sub>O<sub>3</sub> interface and for its individual constitutive layers. For comparison, the behaviour of pure Ti is also shown. As it can be seen, after 60 min all samples reach a stable  $E_{\text{corr}}$  value. Also, layer C is the layer presenting a nobler potential, while layer B appears to be the most active sample in terms of  $E_{\text{corr}}$ . The nobler potential exhibited by layer C reflects the formation of a passive film, which seems to be thermodynamically more stable than that present in the other samples. For the Ti/Al<sub>2</sub>O<sub>3</sub> interface and for layers B, D, and A, a slight decrease of  $E_{\text{corr}}$  with time is observed, indicating an eventual degradation of the protective characteristics of the passive film.

Results of the anodic polarization tests are shown in Fig. 2 b. As it can be observed, on all samples a clearly defined passive region may be observed. It is important to refer that pure Ti and layer A are the samples exhibiting lower passive current densities. In contrast, the high passive current density of the layer D, show the poor corrosion behaviour of this layer in the interface. Finally, it should be referred that the Ti/Al<sub>2</sub>O<sub>3</sub> interface shows a passive plateau presenting a current density ca. one decade higher than that found for Ti and layer A, but lower than that found for the other samples.



**Fig. 2.-** Evolution of the open circuit potential with the time (a), and potentiodynamic polarization curves (b) obtained to Ti/Al<sub>2</sub>O<sub>3</sub> interface and its constitutive layers. Pure Ti is also shown.

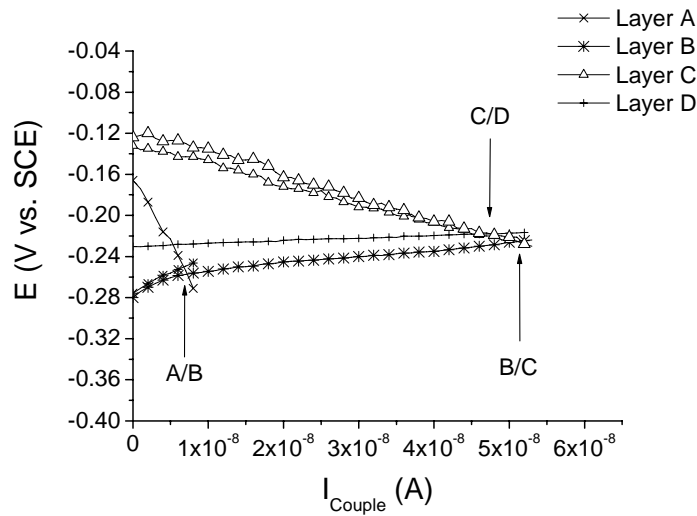
Table 2, shows the corrosion parameters obtained in the potentiodynamic polarisation test. As it can be seen layer D reveals a corrosion current density two times higher than layer C, three times higher than the Ti/Al<sub>2</sub>O<sub>3</sub> interface and approximately thirteen times higher than the layer A. Also,  $i_{\text{corr}}$  of the Ti/Al<sub>2</sub>O<sub>3</sub> interface is relatively lower when compared with layers B, C and D. Thus, it can be concluded that some layers can be acting in the sense of providing protection to the whole interface, counterbalancing the negative effects of layer D, i.e. galvanic effects between the individual layers might be dictating the degradation behaviour of the whole interface.

The galvanic corrosion behaviour of the couples formed between the constitutive layers is showed in Fig. 3. A summary of the results obtained in these measurements is also presented in Table 3. As it can be seen in Fig. 3 and in Table 3, the B/C and C/D pairs reveal the highest galvanic currents, 7-8 times higher than that measured in the A/B couple. In contrast, little galvanic effect between the A/B pair is observed.

The high  $I_{\text{couple}}$  values observed for the B/C and C/D couples, confirms the detrimental influence of the layers B and D on the corrosion resistance of the interface, in agreement with the results of the potentiodynamic tests above referred. In fact, layers B and D, having the lower  $E_{\text{corr}}$  (see Fig. 2 a), appear to have a strong galvanic effect over the layer C (the one presenting an higher  $E_{\text{corr}}$ ). Moreover, the  $E_{\text{couple}}$  and  $I_{\text{couple}}$  values obtained in the pairs B/C and C/D, are in the same order of magnitude of the  $E_{\text{corr}}$  and  $I_{\text{corr}}$  values observed in the Ti/Al<sub>2</sub>O<sub>3</sub> interface (see Table 2), again suggesting the large influence of the layers B and C in the corrosion behaviour of the whole interface.

**Table 2.** Summary of results obtained from electrochemical tests

Sample	Open Circuit potential $E_{\text{corr}}$ (mV)	$i_{\text{corr}}$ (nA/cm <sup>2</sup> )
Pure Ti	-184	7.42
Layer A	-169	75
Layer B	-278	754
Layer C	-121	480
Layer D	-229	983
Ti/Al <sub>2</sub> O <sub>3</sub> interface	-269	301



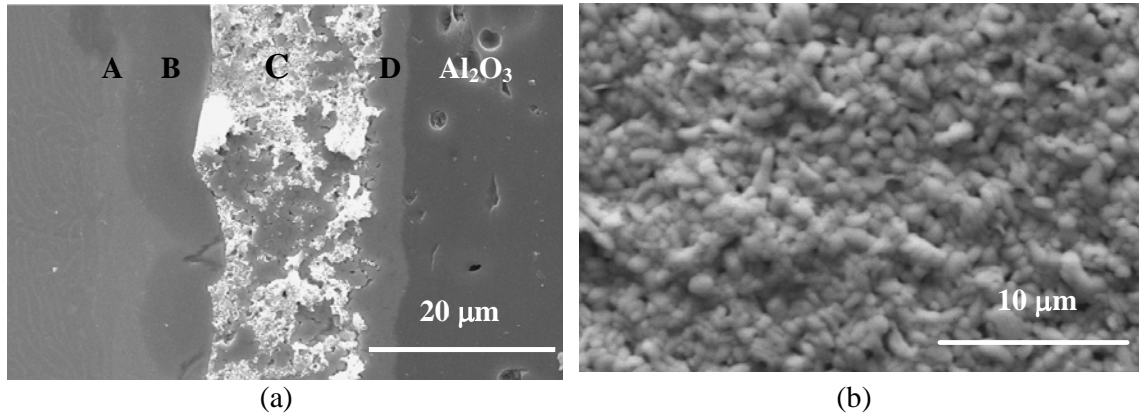
**Fig. 3** – Evans diagram expressing the galvanic corrosion behaviour of the A/B, B/C and C/D couples.

**Table 3** - Summary of the electrochemical parameters  $E_{\text{couple}}$  and  $I_{\text{couple}}$  obtained from galvanic tests

Galvanic couple	$E_{\text{couple}}$ (mV)	$I_{\text{couple}}$ (nA/cm <sup>2</sup> )
A/B	-249.3	38.8
B/C	-227.0	297.9
C/D	-217.9	273.8

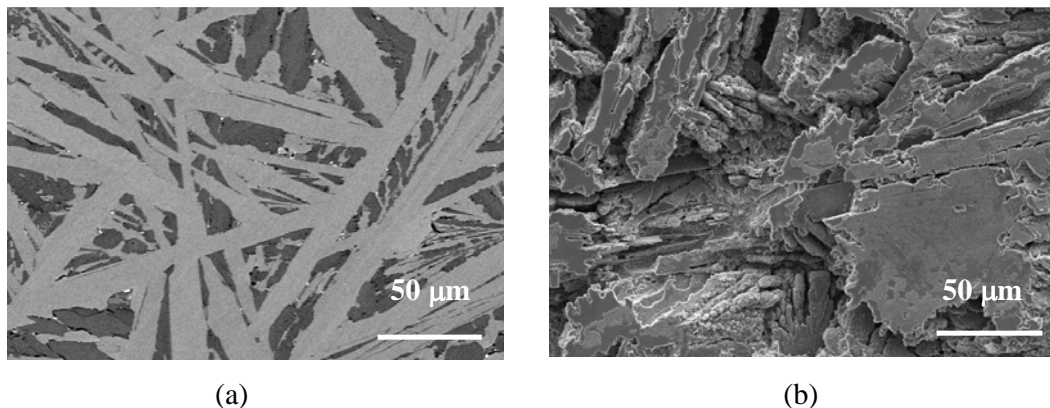
### 3.3. Microstructural characterisation before and after potentiodynamic polarisation test

After the potentiodynamic polarisation tests, the Ti/Al<sub>2</sub>O<sub>3</sub> interface and its constitutive layers were analysed by SEM analysis. As it can be observed in Fig. 4 a, the Ti/Al<sub>2</sub>O<sub>3</sub> interface reveals a surface partially covered by a film, which was identified as AgCl by EDS analysis. An identical film was founded on the surface of sample C, such as it is showed in Fig. 4 b. The formation of this passive film results in a beneficial effect on the corrosion behaviour of the interface, as demonstrated in previous works [3,5].



**Fig. 4.** SEM micrographies of Ti/Al<sub>2</sub>O<sub>3</sub> interface (a) and corrosion product founded in layer C (b), after potentiodynamic polarisation test.

On the other hand, the behaviour of the layers B and D, both containing a high Cu content, is entirely different. As it can be seen in Fig. 5 b), after the potentiodynamic polarisation tests, layer D reveals a strong degradation of the microstructure. As verified by EDS, the high loss of material after corrosion test corresponds to the copper richer zones. The same behaviour, but at a minor scale, was founded in the layer B. This phenomena was already observed in this kind of interfaces by Paiva[3], who explains that in a microstructure constituted by well defined chemical areas, i.e. one of them based in copper and the others rich in silver, the Ag rich areas will reflect a cathodic behaviour, whereas the Cu rich areas will show a anodic behaviour, originating a selective dissolution of the later.

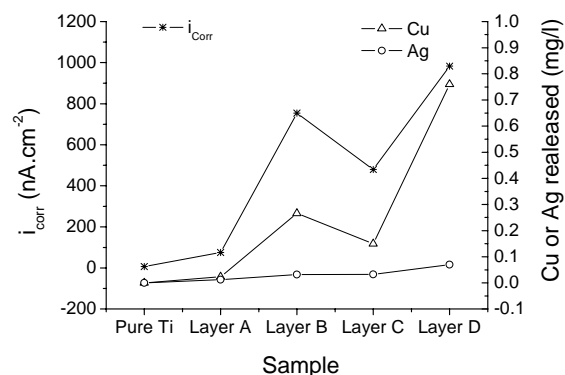


**Fig. 5.** SEM micrographes of layer D before (a) and after (b) potentiodynamic polarisation test.

The referred formation of AgCl film in the layer C, and the higher copper release in layer D, is a characteristic behaviour of Cu and Ag rich materials in chloride-containing solutions[7]. In effect, silver has a noble behaviour in chloride-containing electrolytes and the

AgCl is the product most probably formed in these mediums. Moreover, copper has a natural tendency to form solute compounds with the chloride, resulting in a strong degradation.

In Fig. 6 results from the chemical analysis, referring to the Ag and Cu contents of the solutions, which were determined by atomic-absorption spectroscopy, after the potentiodynamic tests, are presented. In the same Fig. the  $i_{corr}$  values calculated from the potentiodynamic tests are also plotted. As it can be observed, for most layers the amount of Ag released to the solution is relatively low. However, a considerable high release of Cu was observed essentially in layers B and D. Also, as expressed in Fig. 6, a strong correlation between  $i_{corr}$  and the release of Cu is evidenced by the graph.



**Fig. 6.** Relation between the Cu and Ag released in the electrolyte and  $i_{corr}$  for the constitutive layers of the Ti/Al<sub>2</sub>O<sub>3</sub> interface after potentiodynamic polarisation test.

This last results, led to think that the chemical composition of all constitutive layers (A, B, C and D) have an important roll in the corrosion behaviour of Ti/Al<sub>2</sub>O<sub>3</sub> interface. While the layers B and D, rich in copper, releases a high quantity of this element, strongly degrading the interface, the protective layer of AgCl produced over the surface of the layer C and the passive film present in the layer A, rich in Ti, effectively protect the interface and diminish the adverse effects of the Cu rich layers that will conduce to a strong degradation of the interface.

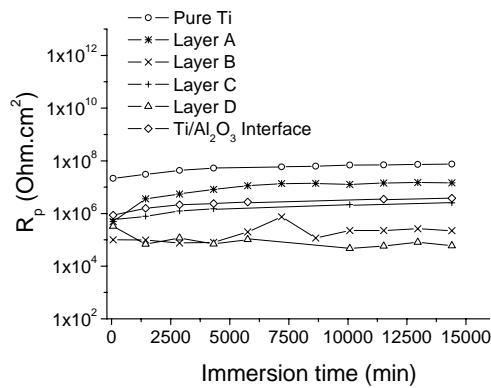
### 3.4. Electrochemical impedance spectroscopy test

Based on the impedance spectra, the corrosion behaviour of the Ti/Al<sub>2</sub>O<sub>3</sub> interface and its constitutive layers was modelled by an electrochemical equivalent circuit that describes its corrosion behaviour. It is generally assumed that the electric elements of an equivalent circuit are well correlated with the corrosion properties of the system. In this work, as described by Gonzales [8], a simple equivalent circuit, composed by the electrolyte resistance ( $R_e$ ) in series with a pair of elements in parallel (resistance and capacitance) was proposed for the pure Ti and for layer A, which is typically associated to the existence of a compact passive film. On the other hand, for the rest of layers (B, C and D) and for the Ti/Al<sub>2</sub>O<sub>3</sub> interface, a similar equivalent circuit, but now containing a second pair of elements, was proposed. In both models, the first pair is composed by the capacitance of the passive film ( $C_f$ ) and by the resistance of the passive film ( $R_{pf}$ ). The second pair, added to indicate the presence of defects in the passive film, for instance, porosity; is related with the charge transfer processes at the passive film, and is composed by the same electric elements: the double layer capacitance ( $C_{dl}$ ) and the charge transfer resistance of the same ( $R_{ct}$ ). It should be referred that a good agreement between the fitted and the experimental data was obtained.



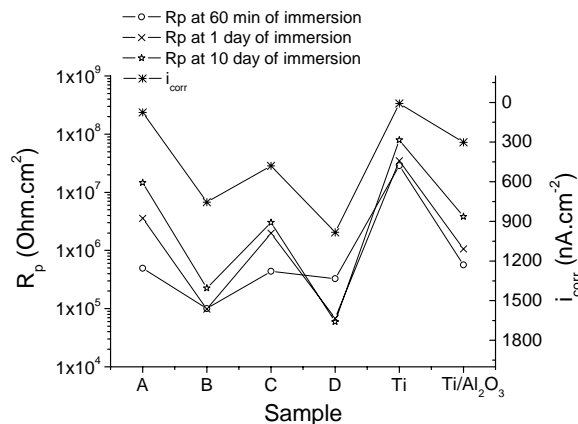
Fig. 7 shows the evolution of the polarization resistance ( $R_p$ ) with the immersion time, for all samples. The polarisation resistance ( $R_p$ ) is an electrochemical parameter, which is inversely proportional to the corrosion rate; this parameter was calculated by the sum of  $R_{pf}$  and  $R_{ct}$ , and deduced from the EIS data simulation.

As it can be seen in Fig. 7, pure Ti and layer A, show the better corrosion resistance, as deduced from the higher polarization resistance values which are slightly improve with the time. Also, in accordance with the potentiodynamic polarisation results, layers B and D reveal the poorer corrosion resistance. For layer D a decrease of  $R_p$  with the immersion time is observed, indicating an increase of the corrosion rate caused by the contact with the solution. Also, layer B presents a low  $R_p$ , which is ca. one decade lower than that found for the other layers. This behaviour shows the thermodynamic instability of the film formed over the layers B and D, and the good protector character of the passive films formed in the other samples. As it can be observed in Fig. 7, the  $R_p$  of the Ti/ $Al_2O_3$  interface shows intermediate values between the layer A and the other constitutive layers. This behaviour can be attributed to a mixed effect of the individual microstructures and chemical compositions of the individual layers constitutive of the interface.



**Fig.7.** Evolution of polarisation resistance with the immersion time, in the Ti/ $Al_2O_3$  interface and its constitutive layers. Pure Ti behaviour is also presented.

Moreover, it is important to note, that the EIS results are in total accordance with the potentiodynamic polarisation results, such as it is demonstrated in Fig. 8. In effect, as it can be deduced from this figure a good correlation between the  $i_{corr}$  and  $R_p$  can be observed.



**Fig.8.** Relation between  $i_{corr}$  and  $R_p$  at different immersion times for the Ti/ $Al_2O_3$  interface and its constitutive layers. Pure Ti behaviour is also presented.

#### 4. Conclusions

The corrosion behaviour of Ti/Al<sub>2</sub>O<sub>3</sub> interfaces immersed in simulated physiological solutions was studied by d.c and a.c electrochemical techniques.

It was demonstrated that the EIS technique combined with the electrochemical standard test are powerful methods to characterize the influence of the different constitutive layers on the corrosion behaviour of the Ti/Al<sub>2</sub>O<sub>3</sub> interfaces.

It was also observed that galvanic interactions between chemically distinct layers of the Ti/Al<sub>2</sub>O<sub>3</sub> interface are governing the whole degradation behaviour of the interface. In general terms, the chemical composition of individual constitutive layers (A, B, C and D) shows an important roll in the corrosion behaviour of the Ti/Al<sub>2</sub>O<sub>3</sub> interface. While the layers B and D, rich in copper, releases a high quantity of this element, strongly degrading the interface, the protective layer formed in the surface of layer C, which is Ag-rich, effectively protects the interface and diminishes the adverse effect of the Cu release from the layers rich in this last element.

Results obtained in the potentiodynamic polarisation tests, galvanic corrosion studies and electrochemical impedance spectroscopy indicates that copper has a strong detrimental influence on the corrosion resistance of the interface. It means that great efforts should be realized in order to develop Cu-free brazing alloys.

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