

Electrochemical Behavior of Ti/Al₂O₃ Interfaces Produced by Diffusion Bonding

Luis Augusto Rocha^{a,b}, Edith Ariza^{a*}, Angela Maria Costa^a,
Filipe José Oliveira^c, Rui Ferreira Silva^{c,d}

^aCIICS - Centro de Investigação em Interfaces e Comportamento de Superfícies
Universidade do Minho, Campus de Azurém
P-4800-058 Guimarães, Portugal

^bDEM - Departamento de Engenharia Mecânica, Universidade do Minho

^cCICECO - Centro de Investigação em Materiais Cerâmicos e Compósitos

^dDECV - Departamento de Engenharia Cerâmica e do Vidro, Universidade de Aveiro

Received: January 27, 2003; Revised: July 1, 2003

In the field of biomedical applications a special interest exists regarding the study of the physicochemical and mechanical behaviour of materials, with special focus on the electrochemical degradation of metal/ceramic interfaces. In fact, metal/ceramic interfaces may be present in several biomedical devices, ranging from external or implantable sensors, to dental implants. Diffusion bonding represents an important technique since, in opposition to other production technologies, such as active metal brazing, avoid the possible liberation of certain chemical components harmful to health. The aim of this work is to study the electrochemical degradation of the interface formed between commercially pure Ti and Al₂O₃ produced by diffusion bonding, in contact with a physiological solution. The present approach included the evaluation of the contribution of individual and pairs of interfacial layers on the global degradation processes. For this propose d.c. electrochemical techniques were used to monitor the open-circuit potential, and to perform potentiodynamic polarization and galvanic corrosion evaluation. Also, electrochemical impedance spectroscopy was used as a complementary technique of the corrosion behaviour of the interface. Chemical composition and morphology of samples and corrosion products were evaluated by SEM and EDS analysis. According to experimental results, two principal reaction layers were formed in the interface: TiAl and Ti₃Al. The TiAl layer appears to be the responsible for the strong increase in corrosion rate of the interface.

Keywords: *degradation, interfaces, metal/ceramic joining, galvanic corrosion, EIS*

1. Introduction

Metal/ceramic joining technologies play an important role in the fabrication of a large number of components requiring a combination of physicochemical, and/or mechanical characteristics of both metallic and ceramic materials. Diffusion bonding is considered as an advantageous technique for producing that type of joint since high-temperature mechanical resistance and defect-free interfaces can be achieved. The main drawback of this technique is the high magnitude of thermal stresses across the interface, typical of this kind of joints, resulting from the high temperatures used to produce the joint and the difference in thermal

expansion coefficients of the components¹. However, when compared to other joint technologies, as active metal brazing, diffusion bonding does not involve the introduction of foreign chemical elements in the interface, which is built by the reaction/diffusion/dissolution of the elements constituting the components to be joined. This can be advantageous from the point of view of corrosion resistance of the joint because no unfamiliar chemical elements are brought to the system.

It should be stressed that when bearing in mind biomedical applications, practical applications of such metal/ceramic interfaces may be found in a wide variety of devices rang-

*e-mail: edith@dem.uminho.pt

Trabalho apresentado no XV CBECIMAT, Natal - RN, Novembro de 2002.

ing from external or implantable sensors to dental implants. For these applications, corrosion resistance becomes a particularly important characteristic to be considered.

However, it should be referred that, apart elemental chemical composition, the nature and structure of the interface severely affect the properties of metal/ceramic joints. In most cases the interface is the critical region of the component where mechanical and/or corrosion failures occurs^{1,2}. In fact, in general, metal/ceramic interfaces presents different layers, which have very small dimensions and complex variations in chemical compositions 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 degradation. In fact, the corrosion behaviour of the interface may be governed by complex microscopic galvanic interactions between layers, and the contribution of each individual layer to the entire corrosion process is, in most cases, difficult to evaluate.

In this work the corrosion behaviour of the Ti/Al₂O₃ interfaces obtained by diffusion bonding is investigated. For this propose both the interface and samples fabricated to simulate the chemical composition of the layers found at the interface were studied by standard electrochemical techniques and by electrochemical impedance spectroscopy (EIS). Also, the galvanic interaction between couples involved in the interface was studied.

2. Materials and Methods

Alumina (Al₂O₃) and ASTM grade II commercially pure titanium rods with a diameter of 5 mm were used to obtain, by diffusion bonding, the interfaces involved in the present study. Diffusion bonding experiments were performed in a vertical vacuum furnace at a temperature of 800 °C, a static applied pressure of 5 MPa and a processing time of 1.5 h. The vacuum level inside of the chamber was of ca. 5×10^{-5} mbar at the maximum temperature of the cycle.

The morphology and chemical composition of Ti/Al₂O₃ interface were evaluated by SEM and EDS analysis. Representative samples of the chemical composition of individual layers found at the Ti/Al₂O₃ interface (TiAl and Ti₃Al) were fabricated in an arc-melting furnace, under an argon protective atmosphere. The morphology and chemical composition of these samples were also confirmed by SEM and EDS.

The electrochemical tests were carried out in a Hank's Balanced Salt Solution (HBSS), H-8264 from Sigma®, with a pH of 7.3. The chemical composition of the HBSS is indicated in Table 1. 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.

A PGP201 potentiostat/galvanostat (Radiometer, Denmark), controlled by the *VoltaMaster* software, was used in the open-circuit potential (E_{corr}) and potentiodynamic tests. E_{corr} was monitored for 60 min, and in the potentiodynamic tests samples were polarised from -600 mV up to 2000 mV at a scan rate of 2 mV/s. 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 in the frequency range from 100 KHz to 100 mHz, with an ac sine wave amplitude of 10 mV applied to the sample at its corrosion potential.

The galvanic corrosion behaviour of Ti/TiAl, Ti/Ti₃Al and TiAl/Ti₃Al couples was evaluated through the determination of Evans diagrams in a PGZ100 *VoltaLab* potentiostat³. The surface area ratio between samples was kept equal to one. The method is based on the measurement of galvanic current (I_{couple}) and potential (E_{couple}) of the couples. Samples were first kept electrically isolated, immersed in HBSS for 60 min for potential stabilisation. Current steps of 0.001 μ A were then imposed for 1 s to the system until curves converged to the E_{couple} value.

In all experiments a saturated calomel electrode (SCE) was used as reference electrode and a platinum electrode, with an exposed area of 1 cm², was employed as counter electrode.

3. Results and Discussion

3.1. Morphology and chemical composition of Ti/Al₂O₃ Interface

In Fig. 1 a SEM micrograph representative of the cross-section of the Ti/Al₂O₃ interface is presented. As it can be observed, the interface is constituted essentially by two layers. Results obtained by EDS suggest that those layers are mainly constituted TiAl and Ti₃Al. In Ti/Al₂O₃ couples the

Table 1. Chemical composition of physiological solution used in corrosion tests.

Component	g/l	Component	g/l	Component	g/l
CaCl ₂ .2H ₂ O	0.185	KCl	0.40	MgSO ₄ (Anhyd.)	0.09767
KH ₂ PO ₄ (Anhyd.)	0.06	NaCl	8.00	NaHCO ₃	0.35
Na ₂ HPO ₄ (Anhyd.)	0.04788	D-Glucose	1.00		

nature of the reaction products depends on the local oxygen activity and temperature⁴⁻⁷. When the bonding process is carried out under vacuum aluminium oxide is reduced and dissolution of both oxygen and Al takes place^{4,7}. Also, as it can be observed in Fig. 2, the formation of Ti-Al intermetallics is, likely to occur. As reported in several works⁴⁻⁷, TiAl and/or Ti₃Al, are usually found as reaction products in this system.

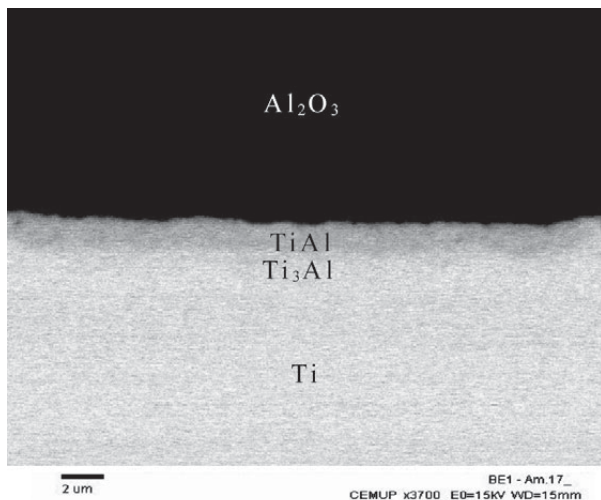


Figure 1. SEM micrograph of the Ti/Al₂O₃ Interface.

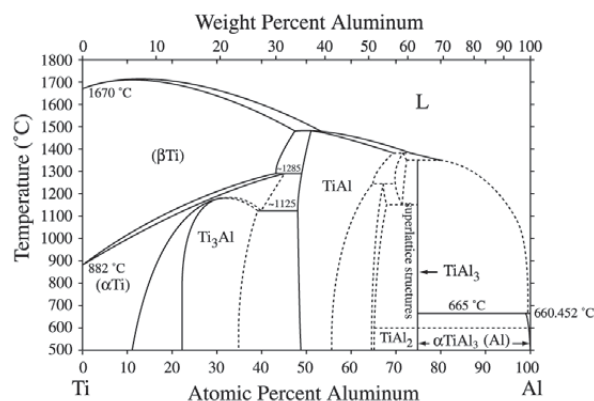


Figure 2. Ti-Al phase diagram.

Table 2. Chemical composition of individual samples fabricated to simulate interfacial layers.

Layer	Ti at %		Al at %	
	Real	EDS	Real	EDS
TiAl	50	43.5	50	56.5
Ti ₃ Al	75	72.6	25	27.4

In Table 2, the chemical composition of standard samples produced to simulate the interfacial layers is presented. For comparison, in Table 2 the chemical composition of the stoichiometric pure components is also presented.

3.2. Electrochemical tests

In Fig. 3 an overlap of open-circuit potential (E_{corr}) measurements obtained in both the Ti/Al₂O₃ interface and in the samples simulating the interfacial layers (TiAl and Ti₃Al) is presented. The behaviour of pure Ti is also shown in the figure.

As it can be observed in Fig. 3, for all samples the E_{corr} value increases monotonically with time. In general, an increase of the open-circuit potential with time is attributed to the formation and/or thickening of a passive layer⁸. Also, common to all samples, the E_{corr} value seems to reach a steady-state value after one hour immersion.

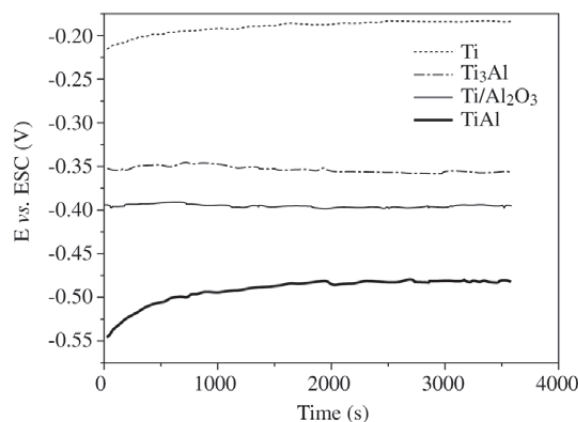


Figure 3. Open-circuit potential for pure titanium, Ti₃Al, Ti/Al₂O₃ interface and TiAl.

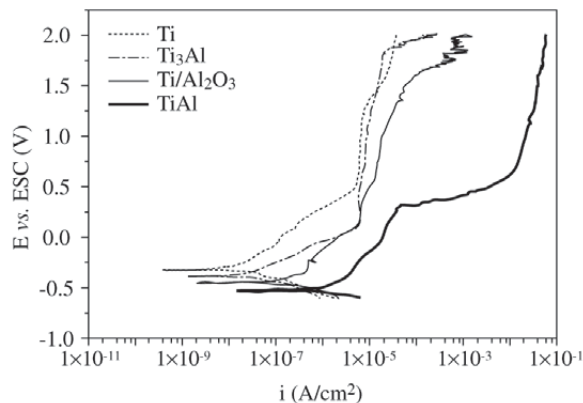


Figure 4. Potentiodynamic polarization curves for pure titanium, Ti₃Al, Ti/Al₂O₃ interface and TiAl.

The passivating behaviour of the samples is confirmed by the results of the potentiodynamic polarisation shown in Fig. 4. In fact, all samples show a passive plateau which, however, varies in extension and in the mean value of the passive current density.

Analysis of the graphs of Figs. 3 and 4 suggests that Ti is the material showing the best behaviour. On the contrary, TiAl appears to be the most reactive sample tested, because it shows the most active E_{corr} value and, at the same time, the extension of its passive plateau is somewhat limited. For TiAl a transpassive region is observed in the potentiodynamic curve, with the pitting potential (E_{pit}) located at ca. 308 mV. For the tested conditions, large pits formed at the surface of the material, with a morphology suggesting that they result from the coalescence of small diameter pits (Fig. 5).

Table 3 shows a summary of the corrosion parameters obtained from the experiments. The analyses of the corrosion parameters presented in Table 3 corroborate the above referred comparative behaviour. In fact, as it can be observed, pure Ti present the most noble value of E_{corr} , and also the lowest current density, suggesting that it possesses a supe-

rior corrosion resistance, while TiAl shows an opposite behaviour.

Considering the i_{corr} value obtained at the Ti/ Al_2O_3 interface, it is ca. 7 times higher than that calculated for pure titanium, meaning that, from the corrosion point of view, this is the critical region of the component. However, results obtained in the samples simulating the interface (TiAl and Ti_3Al) shows that TiAl appears to have a strong detrimental influence on the behaviour of the metal/ceramic interface. In fact, TiAl and Ti_3Al present quite different corrosion behaviour when in contact with physiological solutions, the i_{corr} for TiAl being ca. 37 times higher than that of Ti_3Al .

It should be remarked that Ti_3Al presents an i_{corr} value slightly higher than that of Ti, while, as expected, the Ti/ Al_2O_3 interface has an intermediate behaviour between TiAl and Ti_3Al .

Table 3. Summary of results obtained from electrochemical tests.

Sample	Open Circuit potential E_{corr} (mV)	$E(i=0)$ (mV)	i_{corr} (nA/cm ²)
Pure Ti	-184	-328.8	7.4
Ti_3Al	-358	-383.7	11.7
Ti/ Al_2O_3 interface	-395	-456.6	51.3
TiAl	-482	-529.6	429.2

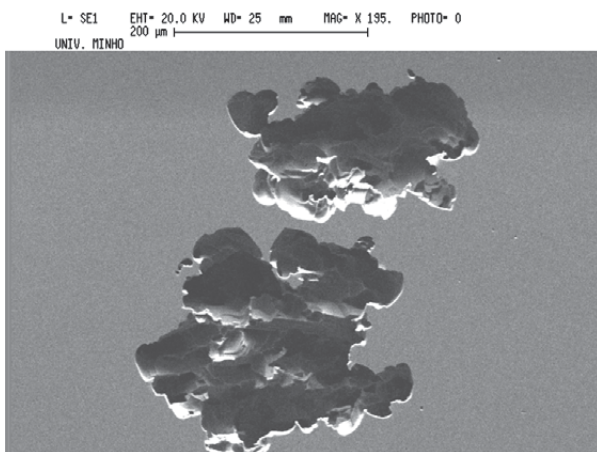


Figure 5. SEM micrograph of the TiAl sample after potentiodynamic tests.

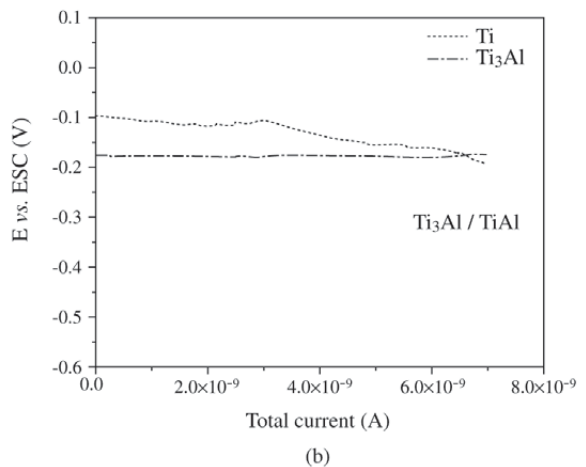
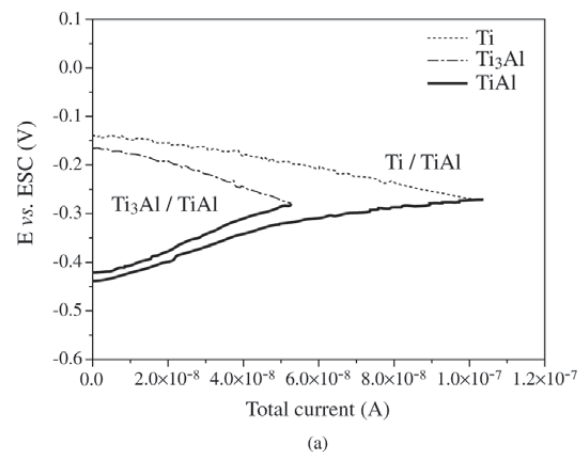


Figure 6. Evans diagram expressing the galvanic corrosion behaviour of the Ti/TiAl, $\text{Ti}_3\text{Al}/\text{TiAl}$ (a), and Ti/ Ti_3Al couples (b). Please observe the difference in scale of the total current between graphs.

The galvanic behaviour of couples formed between layers is expressed in the graphs presented in Fig. 6. For clarity results concerning the Ti/Ti₃Al couple are presented in separate in Fig. 6b), because its current value is much lower than that obtained in the other galvanic pairs. In Table 4 the electrochemical parameters obtained in these experiments (E_{couple} and I_{couple}) are presented.

As it can be seen the Ti/Ti₃Al pair reveals a galvanic current (22.3 nA/cm²) characterised by being 8 to 16 times lower than other couples. In agreement with the results of the potentiodynamic tests, the higher I_{couple} value is also observed for the Ti/TiAl couple, confirming the detrimental influence of this layer on the corrosion resistance of the interface.

The results obtained from the EIS experiments are shown in Figs. 7 and 8. In Fig. 7 an overlap of the Nyquist plots obtained for the pure Ti, Ti/Al₂O₃ (after 60 min and 3 days

Table 4. Summary of the electrochemical parameters E_{couple} and I_{couple} obtained from galvanic tests.

Galvanic couple	E_{couple} (mV)	I_{couple} (nA/cm ²)
Ti/Ti ₃ Al	-176.6	22.3
TiAl/Ti ₃ Al	-281.1	186.0
Ti/TiAl	-271.6	364.0

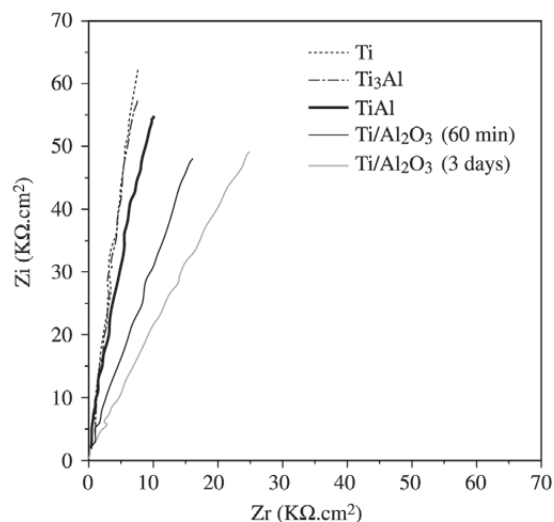


Figure 7. Nyquist plot of the EIS results obtained in Ti, Ti₃Al, TiAl and Ti/Al₂O₃ interface. The influence of immersion time (60 min and 3 days) on the Ti/Al₂O₃ interface passivating characteristics was also evaluated. Fig. 8 plots the Bode curves for the same samples.

of immersion), Ti₃Al and TiAl is plotted. Figure 8, shows the Bode curves for the same samples.

As seen in Fig. 7, pure Ti together with Ti₃Al presents the best corrosion behaviour. These materials show a pure capacitive response, as demonstrated by the -1 slope in the Z curve and by the occurrence of a phase angle close to -90° over a wide frequency range (Fig. 8). This behaviour indicates the presence of a compact passive film at the surface of the materials, i.e. they point to a superior corrosion resistance of the materials⁹.

In opposition, EIS results reveal that TiAl has a poorer corrosion resistance when compared with Ti and Ti₃Al. The oscillation of the phase angle observed in the frequency range of 4 to 10⁻¹ Hz in Fig. 8, may be an indication of passive film instability or, perhaps, of pit initiation.

Concerning the Ti/Al₂O₃ interface the influence of the immersion time (60 min and 3 days) on the characteristics of the passive film was investigated. Even after 3 days of immersion the passive film is still present, as shown by the capacitive response of the interface. However results also suggest some loss of the resistive characteristics of the film after 3 days of immersion, which may be attributed to the local instability of the passive film, i.e. to a decrease of corrosion resistance.

4. Conclusions

In this work the corrosion resistance of Ti/Al₂O₃ interfaces obtained by diffusion bonding was investigated by electrochemical techniques. Results allow the following conclusions to be drawn:

- Diffusion bonding can be successfully used to produce defect-free joints between Ti and Al₂O₃.

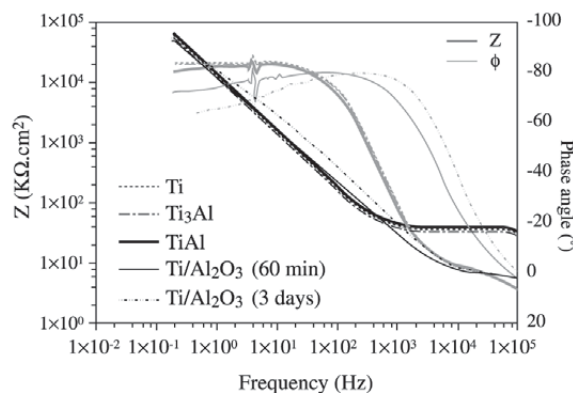


Figure 8. Bode plot of the EIS results obtained in Ti, Ti₃Al, TiAl and Ti/Al₂O₃ interface. The influence of immersion time (60 min and 3 days) on the Ti/Al₂O₃ interface passivating characteristics was also evaluated.

- As a result of the processing parameters used in this work, the interface is constituted by two main layers; Ti_3Al and $TiAl$.
- Results obtained in the potentiodynamic tests, galvanic corrosion studies and electrochemical impedance spectroscopy indicates that the chemical degradation of the interface when in contact with a physiological solution is dictated by the presence of $TiAl$ in the interface. This compound has a strong detrimental influence on the corrosion resistance of the interface.
- Results from the galvanic corrosion tests indicate that Ti_3Al may be considered as electrochemical compatible with Ti . It means that the diffusion bonding processing parameters should be adapted in order to obtain $TiAl$ -free interfaces.

Acknowledgements

The authors acknowledge the financial support provided by Fundação para a Ciência e a Tecnologia (FCT), Portugal (projects POCTI/CTM/33384/2000 and SFRH/BPD/5518/2001).

References

1. Breme, H.J.; Barbosa, M.A.; Rocha, L.A. Adhesion to Ceramics, in "Metals as Biomaterials", Jef A. Helsen and H. Jürgen Breme (Edts), Biomaterials Science and Engineering Series, John Wiley & Sons Ltd., England, Chapter 8, p. 219-264, 1998.
2. Paiva, O.C. *Ligação Metal/Cerâmico: Tecnologia e Caracterização*, PhD's Thesis, Universidade do Porto, Portugal, 2000.
3. Hack, H.P. *Galvanic corrosion Test Methods*, NACE International Huston Texas, Syrett, B.C., Series Editor, 1993.
4. Kliauga, A.M.; Ferrante, M. Interface compounds formed during the diffusion bonding of Al_2O_3 to Ti , *J. Materials Science*, n. 35, p. 4243-4249, 2000.
5. Gubbels, G.H.M.; Heikinheimo, L.S.K.; Klomp, J.T. A comparison between titanium-alumina diffusion bonding and titanium active brazing, *Z. Metallkunde*, n. 85, p. 828-832, 1994.
6. Lee, B.J. Prediction of Ti/Al_2O_3 interface reaction products by diffusion simulation, *Acta Materialia*, n. 45, p. 3993-3999, 1997.
7. S. Kang, J.H. Selverian, Interactions between Ti and alumina-based ceramics, *J. Materials Science*, n. 27, p. 4536-4544, 1992.
8. Williams, D.F. *Titanium and titanium alloys*, in "Biocompatibility of Clinical Implant Materials", vol. 1, D.F. Williams (Edt.), CRC Press, 1981.
9. González, J.E.G.; Mirza-Rosca, J.C. *Study of the corrosion behavior of titanium and some of its alloys for biomedical and dental implant applications*. *Journal of Electroanalytical Chemistry*, n. 471, p. 109-115, 1999.