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STUDY OF THE RESISTANCE TO DEGRADATION OF Al_2O_3/Al_2TiO_5 COMPOSITES FOR POSSIBLE USE AS BONE TISSUE

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Abstract. In this work we studied the response to degradation of Al_2O_3/Al_2TiO_5 composites in a Hanks' solution, which simulates human synovial fluid in contact with bone tissues. Electrochemical impedance study determined that the resistance to polarization of composite rises with increases in the amount of Al_2TiO_5 and with the sintering time.

Keywords: Al_2O_3/Al_2TiO_5 composites, bone substitute, electrochemical impedance, resistance to degradation.

1. Introduction

Recent research has focused on the manufacture of new materials that can be used as implants in living beings, from this research it has been established that the first requirement to be used as such is that the material must be biocompatible. This situation is associated with good resistance to degradation of the materials that are to be considered as possible implants. To determine whether a material can be used as an implant, it is necessary to perform *in vitro* tests to analyze the response of the material in physiological solutions similar to those of human plasma.[1]

Modification techniques are used as an alternative to develop new materials that can be used as biomaterials. Such is the case of metal alloys coated with some ceramic material such as titania,[2] calcium phosphate and hydroxyapatite,[3] alumina[4] or zirconia, where the function of these coatings is to improve resistance to degradation, without sacrificing the mechanical strength of the metal core, and in some cases with a view to increasing its bioactivity, to promote the growth of new bone tissue. Among other metals, the following have been used: magnesium and titanium alloys,[3] nickel-chromium stainless steels[5] and low carbon steels.[6] A disadvantage of this type of coating is that an appropriate surface treatment is required to obtain homogeneous surfaces in order to reduce the level of degradation of this type of material.

The development of new materials for their application as biomaterials has presented a considerable evolution, classifying in several generations ceramics for such application; the first generation is focused on the development of inert ceramics to replace parts of the human body, the second generation is focused on mimicking some functions related to biomineralization, finally the third generation is focused on obtaining materials that function as adequate scaffolding to help bone cells perform their natural processes or as scaffolding to support and allow the administration and release of drugs; all this with the aim of developing new materials capable of replacing biological tissues.[7-8] A viable option for obtaining biomaterials with properties similar to those of bone tissue is the manufacture of ceramic-metal composites, such is the case of tricalcium phosphate-iron composites (α-TCP/Iron), which with the addition of 25 % in volume of iron, can obtain values of the elastic module similar to those of the cortical bone, and compound of which exhibits an optimal resistance to degradation that allows this compound to be considered as a potential alternative for producing implants for the temporary reduction of bone fractures.[9] Other materials with mechanical properties and good biocompatibility are graphene oxide composites with calcium silicate, where the graphene oxide acts as an additive to improve the mechanical properties reflected in an increase in the

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toughness to fracture of the composite.[10] Another option is the ZrO_2 composites with bioglass additions, which at low concentrations of the bioglass reach high values of fracture toughness in the order of 6.3 $MPa \cdot m^{0.5}$, although this research focused only on the improvement of mechanical properties, without considering or evaluating the degradation behavior of these compounds.[11] Also the use of Al_2TiO_5 as a reinforced material of Al_2O_3 has been suggested due to its excellent mechanical properties and good biocompatible characteristics.[12] However, until now there are no papers in which any study of the use of Al_2O_3/Al_2TiO_5 as a biomaterial is reported.

To evaluate the degradation resistance behavior of various materials, many researchers use the electrochemical impedance technique, either for biomedical applications or for any other application.[5,13-17] Electrochemical impedance spectroscopy (EIS) is a powerful technique that utilizes small amplitude, alternating current (AC) signal to probe the impedance characteristics of a cell. The AC signal is scanned over a wide range of frequencies to generate an impedance spectrum for the electrochemical cell under test. EIS is most commonly run in 3-electrode mode. In this configuration there is a working electrode (material sample of study), counter electrode (graphite and platinum are commonly utilized), and an independent reference electrode – silver/silver chloride (Ag/AgCl) is the most common.

The aim of this research is to produce a biomaterial that exhibits mechanical properties and resistance to degradation similar to those of bone tissue. The resistance to degradation shall be assessed using the electrochemical impedance technique of the compound immersed in a physiological solution with a chemical composition similar to that of biological body fluids.

2. Experimental

Alumina-aluminum titanate composites were manufactured using titanium metal powders (Aldrich, purity 99.99 %, 5–10 μm) and alumina (Aldrich, purity 99.99 %, 5–10 μm). During the sintering stage, reactions 1 and 2 will occur *in situ* to form Al_2TiO_5, from the initial metallic Ti. This as a variant of the RBAO process, which is used to obtain nanometric Al_2O_3 particles from the oxidation of metallic Al and thus the advantages of the oxide formation from the metal oxidation are obtained.[18] In order to determine the effect of Ti on the amount of Al_2TiO_5 formed, and in turn, on the physical and chemical properties in the manufactured composite, titanium was added to the alumina matrix in the proportions of 0, 0.5, 1, 2, and 3 wt %. Each mixture of different composition was subjected to a high-energy milling process (Fritsch, Pulviressete 6), using isopropyl alcohol as a control agent, ZrO_2 spherical grinding media of 13 and 10 mm, keeping a grinding ratio of 20:1, during 3 h at 300 rpm. With the powders resulting from the grinding, using a press (Porter-30T), cylindrical tablets (2 cm in diameter and 0.3 cm thickness) were formed by uniaxial compaction at 350 MPa, which were then subjected to sintering treatments for 1, 2 and 3 h at 1673 K in an electric furnace. To determine the crystalline phases, present in the compound formed, an X-ray diffraction study was carried out (Philips X´Pert). For the identification of the diffraction peaks, the obtained diffractograms were compared with the charts available in the PCPDFWIN database. Fracture toughness was obtained by the indentation fracture technique using the Evans' equation.[19] The microstructure was analyzed by scanning electron microscopy (JOEL, JSM6400). The response to degradation of Al_2O_3/Al_2TiO_5 composites and of compact bovine bone was determined by electrochemical impedance spectroscopy (EIS) in a potenciostat-galvanostat (VersaSTAT-4) using a conventional three-electrode electrochemical cell with a capacity of 30 mL, a graphite bar was used as a counter electrode (CE), Ag/AgCl was used as a reference electrode and the different Al_2O_3/Al_2TiO_5 composites were used as working electrodes, previously to the electrochemical impedance study, composites were kept in immersion for 24 h in the solution of the study; the study was performed at room temperature in a Hanks' physiological solution, that is a sterile 0.9 % (w/v) sodium chloride solution in water (solution that simulates the organic fluid inside the human body).

$$Ti + O_2 \rightarrow TiO_2 \quad (1)$$

$$\Delta G = -765.7 \text{ kJ}^{20}$$

$$TiO_2 + Al_2O_3 \rightarrow Al_2TiO_5 \quad (2)$$

$$\Delta G = -2806.2 \text{ kJ/mol}^{21}$$

3. Results and Discussion

3.1. X-ray Diffraction

Fig. 1 presents the XRD patterns of the samples that were sintered at 1673 K for 2 h, for all wt% Ti contents in the composite. In the figure, the lower diffraction pattern corresponds to pure Al_2O_3. In this spectrum the presence of a single compound which corresponds to alumina (identified with a green circle) is observed; the diffraction patterns found in the upper part of the figure correspond to the samples with the different additions of Ti, in these spectra we observe in addition to the phase of Al_2O_3, the presence of the phase corresponding to Al_2TiO_5 (identified with a purple inverted triangle), in these spectra no peak corresponding

to metallic Ti is observed, so the presence of Al_2TiO_5 indicates that reactions 1 and 2 indeed occurred *in situ* during the sintering of the samples. Accordingly, the final amount of Al_2TiO_5 present in each composition is 1.93, 3.87, 7.75, and 11.6 % for the samples with 0.5, 1, 2 and 3 wt % of initial titanium, respectively.

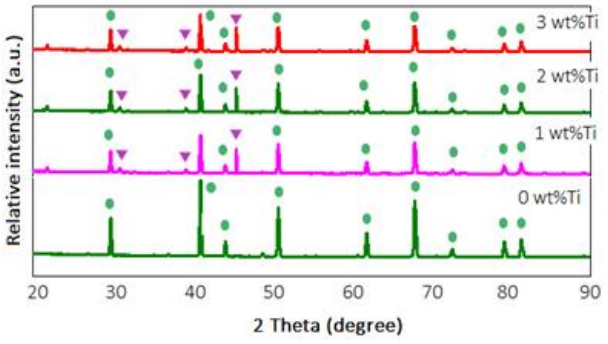

Fig. 1. X-ray diffraction patterns of the sintered compounds at 1673 K for 2 h: Al_2O_3 ● and Al_2TiO_5 ▼

3.2. Hardness

Fig. 2 shows the hardness results for the sintered composites at 1673 K for 1, 2, and 3 h, for each studied composition. The samples, the composition of which is 100 % alumina, have the lowest hardness, which is very similar to that of bone (horizontal line dotted at the bottom of the figure). However, when 0.5 wt% of titanium is added to the alumina matrix, the hardness increases significantly for all time values, mainly the hardness of the sample sintered for 1 h, which had an increase of more than 200 % in this property. As the original titanium content in the sample increases, the hardness decreases considerably; this behavior may be associated with the formation of a higher amount of Al_2TiO_5. However, despite this drastic drop in the hardness of the composite, it is still much higher than that of bone for the different study compositions and the different sintering temperatures.

3.3. Fracture Toughness

Fig. 3 shows the results of fracture toughness (K_{IC}) measurements for Al_2O_3/Al_2TiO_5 composites sintered at 1673 K during different times (1, 2, and 3 h) as a function of the initial amount of Ti. The figure shows an upward trend in K_{IC} as the amount of Al_2TiO_5 increases. Regarding the sintering time, there is also a positive effect on the increase of the K_{IC} with the increase of the sintering time which is more significant at 3 h of treatment. The same figure shows a horizontal line at 4.3 $mPa{\cdot}m^{-0.5}$, which is the K_{IC} value of bone. The sample sintered for 3 h, even with low amounts of Al_2TiO_5, improves considerably the fracture toughness of the composite. From this, it can be concluded that the sintering time together with the initial Ti additions, which when oxidized form *in situ* Al_2TiO_5 in the presence of Al_2O_3, have an important combined effect in obtaining bodies with high values of fracture toughness, where the highest K_{IC} values are achieved by combining high sintering times with high Al_2TiO_5 amounts, in part this can be explained by the fact that Al_2TiO_5 has a lower melting point (2133 K) than Al_2O_3 (2345 K), which favors the sintering of the composite when this compound is present in the sample.

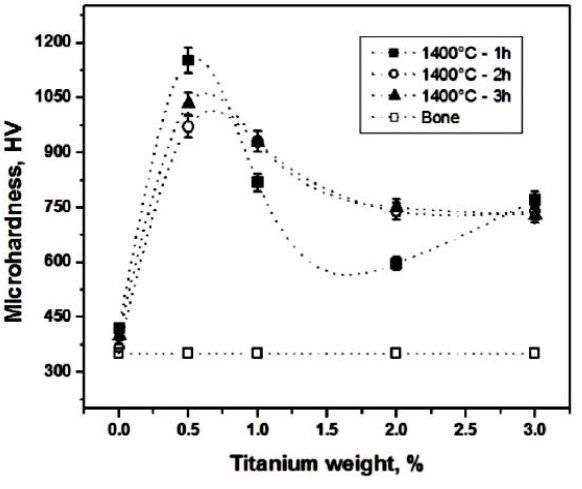

Fig. 2. Hardness values of sintered compounds at 1673 K as a function of sintering time

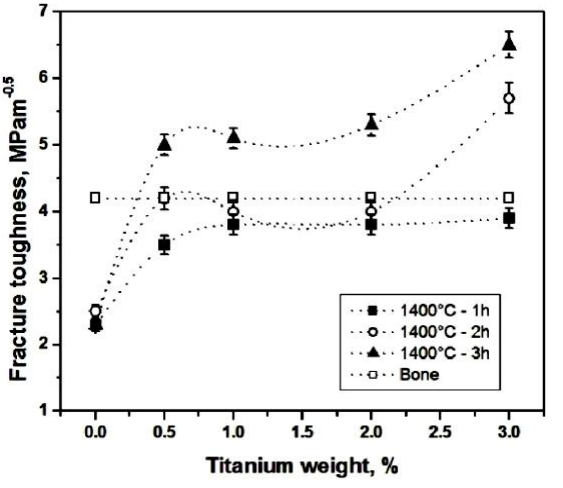

Fig. 3. Fracture toughness values of sintered compounds at 1673 K as a function of sintering time

3.4. Microstructure

Fig. 4 shows the micrographs obtained by SEM, which correspond to the samples sintered at 1673 K during 1, 2, and 3 h for the compounds Al_2O_3-0 wt % Ti, Al_2O_3-0.5 wt % Ti and Al_2O_3-3 wt % Ti. In the microstructures of the Al_2O_3-0 wt % Ti samples sintered at 1, 2, and 3 h, a homogeneous microstructure is observed. The microstructure has irregularly shaped grains with sizes ranging from 1 to 10 µm. The resulting microstructures of the samples, where titanium was added in different proportions, show a homogeneous microstructure, which is made up of two phases.

From the energy dispersive spectroscopy analysis (EDS) it is deduced that the small and bright phase corresponds to the aluminum-titanate (Al_2TiO_5) because these grains indicate the presence of Ti and the opaque grey phase corresponds to the Al_2O_3 (Fig. 5). Al_2TiO_5 phase is mainly located in intergranular positions of the Al_2O_3 matrix and has a size of approximately 1 µm. When comparing the microstructures of Al_2O_3 and Al_2O_3/Al_2TiO_5 composites, it can be seen that the titanium content has a significant effect on the microstructure, since in composites with added titanium it is possible to observe areas where the conglomeration corresponding to sintered areas has started. On the other hand, in the micrographs of the Al_2O_3-3 wt % Ti samples, it can be seen that the formation of conglomeration corresponding to better sintered zones begins after 1 h; these zones grow when the sintering time is longer. This situation is logical because long sintering times allow a greater diffusion of atoms between grains.

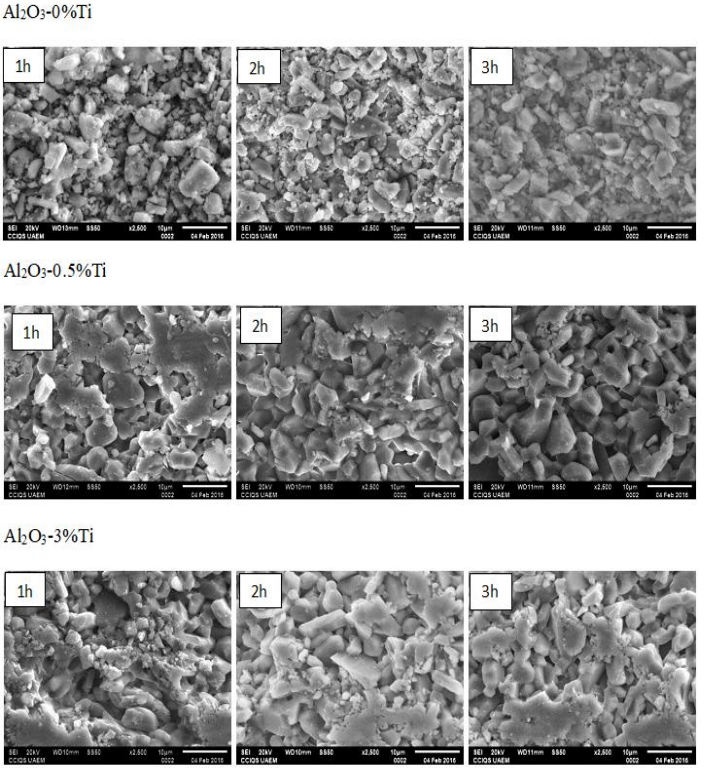

Fig. 4. Typical microstructures obtained by SEM from Al_2O_3/Al_2TiO_5 composites

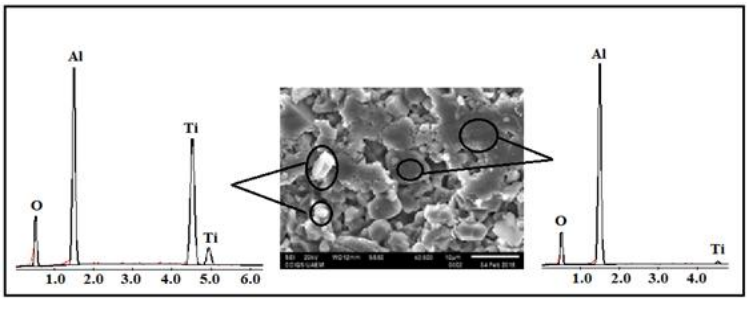

Fig. 5. EDS analysis performed in a spot manner
to identify the composition of the grains in the microstructure

3.5. Response to Degradation

Fig. 6 show the Nyquist diagrams of the Al_2O_3/Al_2TiO_5 composites. In Fig. 6a the impedance curves of the Al_2O_3/Al_2TiO_5 samples (sintered at 1673 K for 1 h) show incomplete distorted semicircles, the diameters associated with these semicircles are dependent on the sintering time, as well as the amount of Ti added and determine the value of the polarization resistance (*Rp*). Using the circuit (Fig. 7) and the ZView 3.1c program, the *Rp* value was obtained for each case (the results are shown in the Table).

The Table shows that the *Rp* value increases with the increase in Ti amount, the *Rp* also increases as the sintering time increases. It is impossible to associate any modification in the structure with the behavior of the *Rp* in the XRD patterns and corresponding micrographs (Figs. 1 and 4). However, electrochemical impedance spectroscopy (EIS) is a technique that is highly sensitive to the characteristics of the interface, so it makes it possible to differentiate this type of behavior. On the other hand, the behavior of the Al_2O_3/Al_2TiO_5 samples (sintered at 1673 K for 3 h, Fig. 7b) is completely similar to the one already presented. Additionally, the impedance curve of a bone sample is included in both figures, the *Rp* value of the bone sample is 356±12.7 kΩ, indicating that the bone has a higher resistance to being degraded in the Hanks' solution compared to the rest of the samples. The compound closest to the *Rp* value of the bone is the one prepared with 3 wt % Ti and sintered at 1673 K for 3 h. In general, the formation of Al_2TiO_5 occurred during sintering due to reactions 1 and 2 favors the resistance to degradation of the alumina in the Hanks' solution. Fig. 6 and Table show that with higher initial Ti content, the resistance to degradation of the final composite is better, indicating that Al_2TiO_5 has good resistance to degradation. Another important observation is that with longer sintering times the resistance to degradation is greater. This is explained by the fact that longer sintering times are associated with more densified bodies, so the longer the sintering time, the less porosity in the composites, and therefore the smaller the surface area of reaction for degradation, which increases the resistance to degradation of the composite.

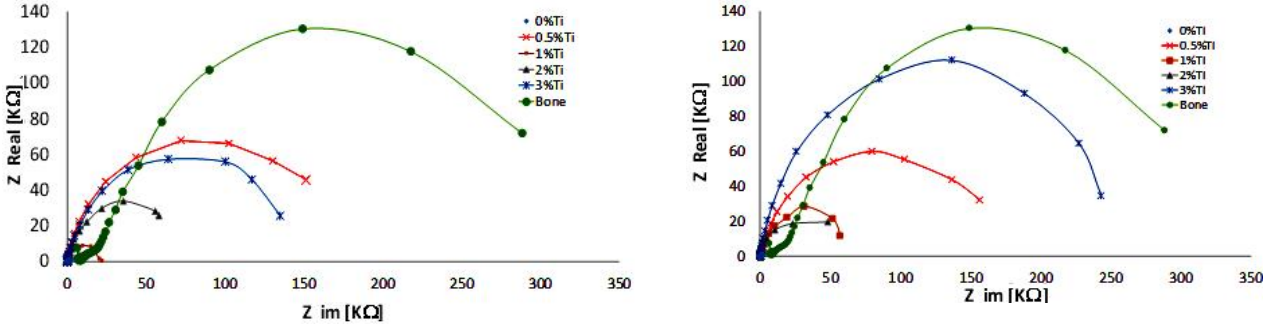

Fig. 6. Set of Nyquist graphs corresponding to the behavior of Al_2O_3/Al_2TiO_5 composites sintered at 1673 K for 1 h (a) and 3 h (b)

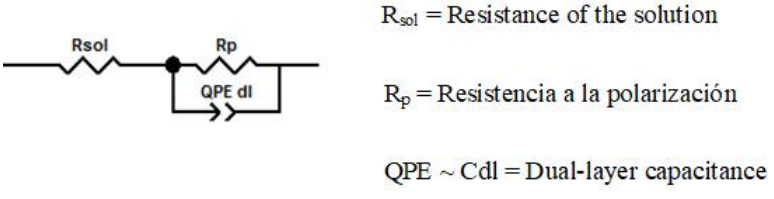

Fig. 7. Schematic representation of the equivalent circuit for EIS studies

Table. *Rp* values of Al_2O_3/Al_2TiO_5 composites at different sintering times and amount of titanium

Sintering time	Response to degradation *Rp*, kΩ				
	0% Ti	0.5% Ti	1% Ti	2% Ti	3% Ti
1 h	8.6 ± 3.5	169.4 ± 7.4	27.6 ± 4.3	82.1 ± 8.6	143.1 ± 5.7
2 h	10.9 ± 2.8	171.5 ± 9.3	42.4 ± 6.8	142.5 ± 10.4	173.1 ± 7.6
3 h	11.7 ± 3.2	159.4 ± 8.7	81.6 ± 5.9	154.2 ± 9.5	330.4 ± 6.6
Bone 356 ± 12.7					

4. Conclusions

From impedance measurements the values of the resistance to polarization (*Rp*) of different composites prepared at 1673 K, with sintering times of 1, 2, and 3 h and with initial additions of 0, 0.5, 1, 2, and 3 wt % Ti were obtained. It was determined that the *Rp* value increases with increases in the initial Ti content (higher amount of Al_2TiO_5 after sintering) and with sintering time. The compound closest to the *Rp* value of the bone is the sample prepared with 3 wt % Ti and sintered at 1673 K for 3 h. With regard to fracture toughness, a behavior similar to that of *Rp* was found, where with increases in the initial Ti content and sintering time the greater values of fracture toughness were obtained for the composites compared with those of bone.

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ДОСЛІДЖЕННЯ СТІЙКОСТІ ДО ДЕГРАДАЦІЇ КОМПОЗИТІВ Al_2O_3/Al_2TiO_5 ДЛЯ МОЖЛИВОГО ВИКОРИСТАННЯ ЯК КІСТКОВОЇ ТКАНИНИ

Анотація. *Вивчено стійкість до деградації композитів Al_2O_3/Al_2TiO_5 у розчині Хенкса, який імітує синовіальну рідину людини, при контакті з кістковими тканинами. За допомогою електрохімічного імпедансу встановлено, що опір поляризації композиту збільшується з підвищенням кількості Al_2TiO_5 та часу спікання.*

Ключові слова: *композит Al_2O_3/Al_2TiO_5, замісник кістки, електрохімічний імпеданс, стійкість до деградації.*