

## EFFECT OF THE SINTERING ATMOSPHERE ON THE CORROSION RESISTANCE OF TITANIUM FOR APPLICATION AS BIOMATERIAL

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**Abstract:** In this work, the effect of sintering atmosphere on the corrosion resistance of sintered titanium has been evaluated in 0.9 % aqueous NaCl solution to simulate physiological environment. Corrosion tests were performed on titanium porous sintered under vacuum and vacuum plus dynamic argon. The results showed better passive properties associated to the titanium sintered under argon plus vacuum atmosphere than to the vacuum sintered titanium. The better corrosion resistance of the argon plus vacuum sintered titanium was attributed to the formation of a thin passive film on the titanium surface during sintering due the low oxygen content present in this atmosphere.

### INTRODUCTION

Many materials have been used as implants since the sixteenth century. It was not until this century that two classes of metals, namely stainless steels and cobalt-chromium-molybdenum alloys, emerged as preferred materials for orthopedic implants<sup>[1,2]</sup>. Recently, a third class of material, titanium and its alloys are being used in restorative surgery such as dental and orthopedic prostheses, pace-makers and heart valves due to their excellent mechanical properties, good corrosion resistance and biocompatibility in biological fluids. The high corrosion resistance of titanium alloys results from the formation of very stable, continuous, highly adherent, and protective oxide film on metal surface. The physicochemical and electrochemical properties of this film and its long term stability in biological environments play a decisive role for the biocompatibility of titanium implants<sup>[2-7]</sup>.

For application as biomaterial, one of the important properties is osseointegration that occurs through the contact between the implant surface and receiving living tissues<sup>[1,2]</sup>. Besides osseointegration, it is important a strong adhesion of the implant with the bone. Powder Metallurgy (PM) is a favorable fabrication technique for titanium porous systems; with the advantage of producing materials with high mechanical properties and strong adhesion to the substrate<sup>[2,7]</sup>. This is one of the reasons for the use of porous titanium biomaterials. One of the main disadvantages of porous materials, however, is their reduced corrosion resistance. Their inherent porosity leads to increased susceptibility to crevice corrosion, due to differential aeration cells between the inner pore regions and the outside areas of easier access of oxygen. In addition, there is a decrease in corrosion resistance due to larger surface area exposed to the electrolyte compared to non-porous materials.

The corrosion resistance of materials produced by powder metallurgy is affected by the sintering atmosphere. This is due to the effect of the type of sintering atmosphere on the nature, composition, and thickness of protective surface oxides that form on the metallic material.

Blackwood et al.<sup>[8]</sup> investigated the relative stability of various oxide films on porous titanium either air-formed or obtained by anodizing at different oxide growth rates. Their results suggested that the natural air-formed film is less crystalline (or less compact) and consequently less protective than that obtained by slow growth rates.

In the present work, the effect of the sintering atmosphere on the corrosion resistance of porous titanium for application as biomaterial has been evaluated, in a 0.9 wt. % sodium chloride solution. The sintered titanium was prepared using a commercial pure titanium powder obtained by hydrogenation and de-hydrogenation method (HDH). The sintering atmospheres adopted were vacuum and dynamic argon plus vacuum.

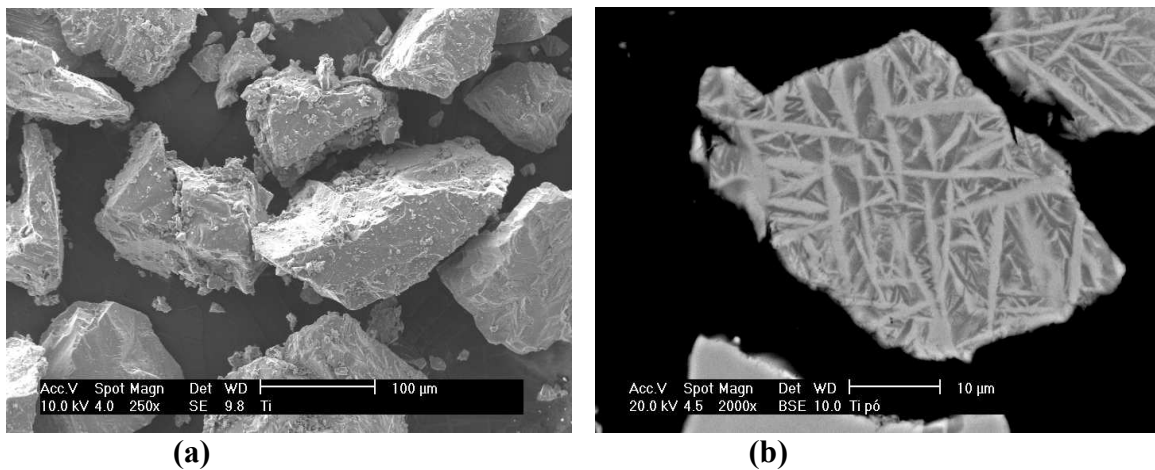
## MATERIALS AND METHODS

The titanium powder used was a commercially pure (cp) grade 2 obtained by hydriding, milling and dehydriding (HDH) methods. The chemical composition was determined by X-ray fluorescence spectrometry and the results are presented in Table 1. The particle size distribution was measured by CILAS 1064. The average size of the particles used is 120  $\mu\text{m}$ . The particle morphology and microstructure were examined by scanning electron microscopy (SEM). The powder was uniaxially pressed at 250 MPa in a cylindrical 10 mm diameter die, and the samples were sintered at 1050  $^{\circ}\text{C}$  for 1 h, either under vacuum  $10^{-6}$  mbar or under vacuum and dynamic argon.

Electrochemical tests were carried out with a potentiostat Gamry Instruments at room temperature ( $22\pm 1^{\circ}\text{C}$ ). A conventional three-electrode cell was used: a saturated calomel reference electrode, a platinum wire as counter electrode and the sintered titanium as working electrode. The corrosion resistance of the titanium sintered in the two types of atmospheres was evaluated in a 0.9 % NaCl solution by polarization measurements at various periods of immersion, using a scan rate of  $1 \text{ mV s}^{-1}$ .

## RESULTS AND DISCUSSION

The morphology of the starting powder is shown in Figure 1 (a) and its microstructure in Figure 1 (b). The chemical composition of the titanium powder is given in Table 1.



**Fig. 1** - SEM micrographs showing: (a) the starting powder and (b) the starting powder microstructure.

**Table 1** - Chemical composition of the titanium powder used.

Element	wt. %
Ti	Balance
O	0.41
H	0.40
Fe	0.08
N	0.04
C	0.02

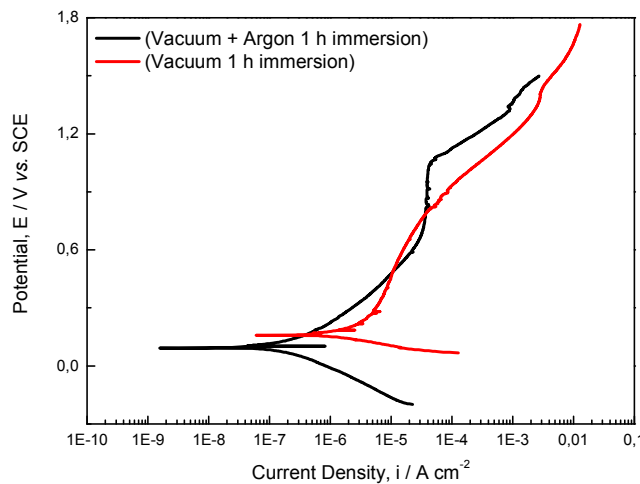
The microstructure of the powders shown in Figure 1(b) is typical of  $\alpha$ -Titanium grains<sup>[9,10]</sup>. In the sintering process, the powder morphology is important to form a continuous structure that leads to proper corrosion and mechanical properties. The properties of the final microstructure depend strongly upon the morphology of the starting powder particles. The particle morphology, for example, determines the packing efficiency of the particles, and, hence, the density and porosity of the final microstructure.

Table 2 shows the concentration of hydrogen and oxygen after sintering obtained by combustion with the titanium sintered under the two types of atmospheres adopted. As expected, for the titanium sintered under argon atmosphere, the oxygen content increased and hydrogen content did not change. However, for the vacuum sintered titanium, hydrogen and oxygen contents decreased.

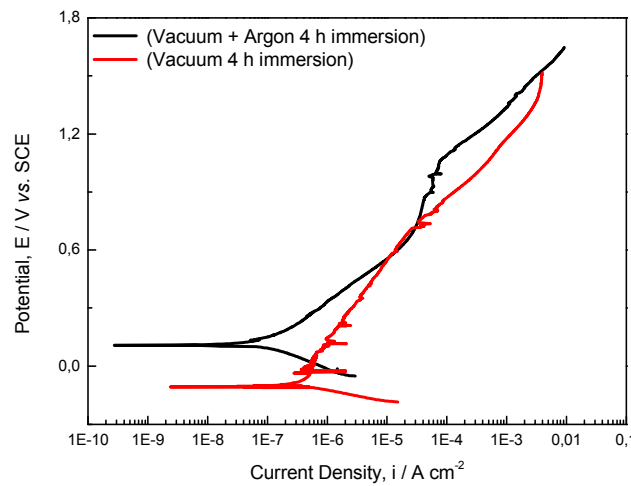
**Table 2 - Oxygen and hydrogen content after sintering.**

Atmosphere	Hydrogen %	Oxygen %
Vacuum+Argon	0.45	0.89
Vacuum	0.22	0.05

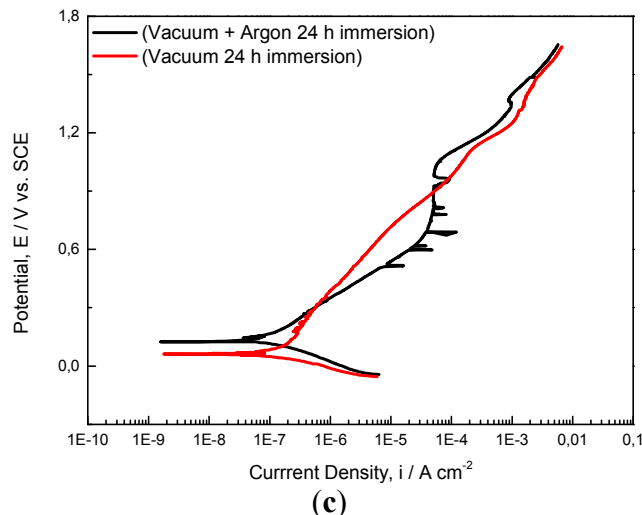
The results of polarization tests, in different immersion times, for the titanium sintered under vacuum plus argon atmosphere are compared with those sintered under vacuum in Figure 2 (a), (b) e (c).



(a)



(b)



**Fig. 2** - Potentiodynamic polarization curves for titanium sintered under Vacuum + Argon or Vacuum for different immersion times in 0.9% NaCl solution: (a) 1h (b) 4h, and (c) 24h immersion.

The polarization results show that the current densities at the corrosion potential for the samples sintered under vacuum atmosphere decreased with immersion time likely due to thickening of the oxide film on the titanium surface from 1h to 24h. The potential also decreased between 1h and 4h suggesting polarization of the cathodic reaction. The cathodic polarization curves suggest that this reaction is activation controlled in the cathodic polarization range tested. The anodic polarization results for the vacuum sintered samples also showed the increase in current oscillations with immersion time showing increased susceptibility to pitting as the passive film thickens. For the vacuum sintered titanium samples the corrosion process is anodically controlled and this shows that the increase in corrosion potential between 4h and 24h is due to polarization of the anodic reaction probably caused by thickening of the passive oxide layer during this period. The polarization curves of the titanium sintered under vacuum plus argon atmosphere showed increasing pitting susceptibility with immersion time in the chloride solution indicated by the enhanced current oscillations with time. Despite of the current oscillations, a breakdown potential was not associated to any of the two types of titanium samples obtained showing a very high resistance to pitting corrosion.

The corrosion potential and corrosion current densities for the titanium samples sintered under vacuum plus argon atmosphere were fairly constant along the immersion period showing that the oxide film formed on this type of samples is more stable. This could be explained by the higher oxygen content in the vacuum plus argon atmosphere leading to a thicker oxide surface film prior to immersion comparatively to the vacuum atmosphere.

The sintering process under vacuum plus dynamic argon is produced under mechanical vacuum (approximately  $10^{-2}$  mbar), and the oxygen content in this atmosphere is much larger when compared with that expected for the vacuum ( $10^{-6}$  mbar) one. Despite of this, the polarization curves obtained after 24 h of immersion in the electrolyte show similar behavior for the samples sintered in both atmospheres used, although a slightly higher pitting susceptibility was associated to the samples sintered under vacuum plus argon. These results suggest that for longer exposures periods there are no significant differences in the corrosion resistance of the titanium obtained in the two types of sintering atmospheres tested.

The literature reports<sup>[11,12]</sup> that electrochemical grown films on titanium present amorphous hydrated structures. It is proposed that this hydrated film also forms on the titanium sintered on both types of atmospheres under immersion conditions used in this study. This could lead to the similar corrosion resistance found for longer immersion periods on the titanium samples.

The results also showed low current densities (order of  $10^{-7}$  A cm<sup>-2</sup>) at the corrosion potential and typical of passive metals due to the very thin and passive oxide film formed at atmospheres of low oxygen concentrations<sup>[8,13]</sup>. This film resists to chloride ions attack, which are present in the body fluids.

## CONCLUSIONS

The results of the present work showed that for short periods of immersion (1 h to 4 h) the corrosion resistance of titanium sintered samples under vacuum atmosphere ( $10^{-6}$  mbar) was inferior to that of samples sintered under vacuum plus argon atmosphere ( $10^{-2}$  mbar). This was credited to the higher oxygen content found in the samples sintered in the last type of atmosphere favoring the formation of a thicker oxide. For longer periods of immersion (24 h) however, the corrosion resistance of both types of samples were similar showing that the two sintering atmospheres tested had analogous effects on the corrosion resistance of the titanium samples.

## REFERENCES

- [1] K.H.W. Seah, R. Thampuran, X. Chen and S.H. Teoh: *Corr. Sci.* Vol. 37 (1995), p. 1333.
- [2] H. Arslan, H. Çelikkán, N. Örnek, O. Ozan, A.E. Ersoy and M. L. Aksu: *J. Appl. Electrochem.* Vol. 38 (2008), p. 853.
- [3] C. Chu, X. Xue, J. Zhu and Z. Yin: *Mater. Sci. Eng. A* Vol. 429 (2006), p. 18.
- [4] M.V. Oliveira, L.C. Pereira and C.A.A. Cairo: *Materials Research* Vol. 5 (3) (2002), p. 269.
- [5] L. Barbosa, L. Salgado, N. Karsokas F<sup>o</sup>, M. K. Nagamine: *Mater. Sci. Forum* Vols. 660-661 (2010), p. 188.
- [6] D.J. Blackwood, A.W.C. Chua, K.H.W. Seah, R. Thampuran and S.H. Teoh: *Corrosion Science* Vol. 42 (2000), p. 481.
- [7] S.H. Teoh, R. Thampuran, W.K.H. Seah and J.C.H. Goh: *Biomaterials* Vol. 14 (6) (1993), p. 407.
- [8] D.J. Blackwood and S.K.M. Chooi: *Corrosion Science* Vol. 44 (2002), p. 395.
- [9] V.M. Anokhin, O.M. Ivasishin and A.N. Petrunko: *Mater. Sci. Eng. A* Vol. 243 (1998), p. 269.
- [10] K. Wang: *Mater. Sci. Eng. A* Vol. 213 (1996), p. 134.
- [11] L.C. Covington and R.W. Shultz: *Corrosion* Vol.81, 7.
- [12] L. Holland: *Vacuum Deposition of Thin Films*, Chapman and Hall, London, 1963, p.122.
- [13] K.H.W. Seah, R. Thampuran and S.H. Teoh: *Corrosion Science* Vol. 40 (1998), p. 547.

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