Surface conditioning of porous titanium for endosseous implants by chemical and heat treatments

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The aim of this work was to modify the surface chemistry and morphology of porous titanium in order to improve its bioactivity. Porous titanium compacts obtained by the pressing-sintering route were submitted to alkali and acid treatments in order to improve the bioactivity. C.p. Ti powder with grain size of less than 150 μm was employed. The surface morphology and chemical composition was examined by SEM, XRD and XPS analysis. A homogeneous layer of crystalline TiO_2 with traces of TiOH was formed after alkali treatment, while the acid treatment lead to the formation of a non-uniform layer containing titanium sub-oxides TiO and Ti_2O_3.

1. Introduction

Porous titanium structures are essential for orthopaedic applications due to their biological and mechanical compatibilities with the human bone tissue [1]. Although titanium has been used intensively for biomedical applications, its surface is not bioactive [1,2]. When in contact with bone, bioactive materials must form a layer of biologically active apatite on its surface and incorporate themselves to the surrounding tissue with the help of this layer [3]. The titanium's lack of bioactivity problem can be solved by applying different coatings on its surface or submitting this surface to different chemical treatments. Of all these methods, alkaline and acid treatments proved to have a significant effectiveness, which is coupled with the low technological costs, if compared to other techniques. The surface structural changes induced by the chemical treatments lead to the formation of a bioactive titanate layer, which can promote and accelerate the nucleation of bone-like apatite on the titanium surface [4]. In order to improve the stability of titanate layer, these chemical treatments are followed by heat treatments. The goal of the heat treatment is mainly to crystallize and improve the hardness of the amorphous gel layer formed after the chemical treatment. Moreover, the porous surface enhances the focal contacts for cellular adherence and guide cytoskeletal assembly. Osteoblasts, like most tissue cells, are typically several tens of microns in diameter. Furthermore, they have relatively flexible cell membranes and can change their shape depending on their local environment [3]. Therefore, it is assumed that a porous structure with pore size up to 100 μm will enhance cell adhesion capacity and proliferation.

This study presents the effect of alkali-heat treatments and acid-heat treatments on porous titanium samples obtained by a powder metallurgy route.

2. Experimental

Commercially pure titanium powder, <150 μm mesh, was used to fabricate cylindrical shaped samples, 6 mm in diameter and 8 to 10 mm in height. The size distribution analysis was performed using a Fritsch Analysette laser beam analyzer, results being showed in Fig. 1.
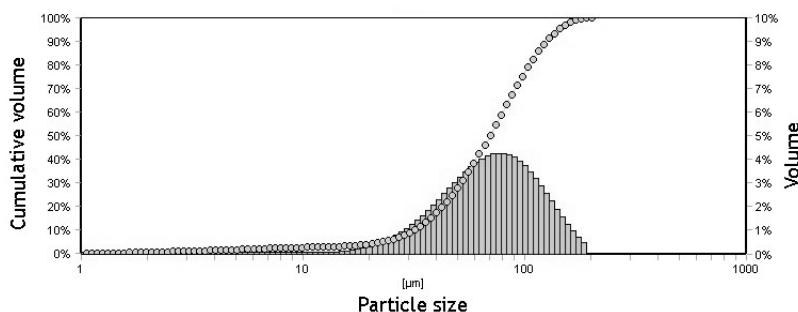

Fig. 1. Particle size distribution of titanium powder.

Fig. 2 shows the shape of titanium powder particles. Samples were fabricated by closed die pressing at 400 MPa followed by vacuum sintering at 1150ºC for 1 hour, 10^{-4} Torr. These sintering parameters were previously established as optimal for adequate mechanical strength coupled with sufficient pore size and porosity.
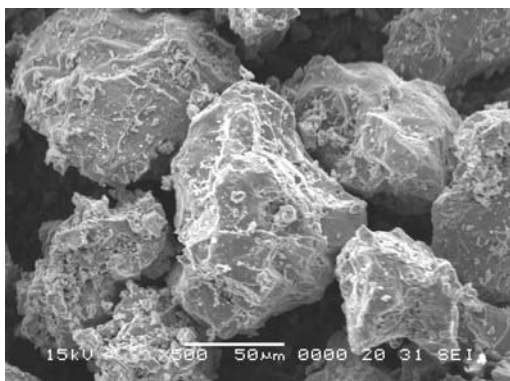

Fig. 2. SEM image of initial Ti powder

General porosity was calculated by volumetric and weight measurements, while the pore size was determined by microscopic measurements on five different areas using SEM images of as-sintered samples. All samples were thoroughly cleaned in an ultrasonic bath using distilled water and ethyl alcohol. For the alkali-heat treatment, samples were immersed in a 5M NaOH solution for 24 hours at 60ºC, and then ultrasonically cleaned again in distilled water. Subsequently, samples were subjected to heat treatment at 600ºC for 1 hour. The acid-heat treatment involved immersion in an 8.8M H_2O_2/0.1M HCl solution for 30 minutes at 80ºC, followed by ultrasonic distilled water cleaning. The subsequent heat treatment was performed at 450ºC for 1 hour. Both heat treatments were performed in air. The surface and pore morphology of treated and untreated titanium samples was studied by SEM analysis, using a JEOL 5600 LV microscope with EDX probe. Surface chemical composition was analyzed by XRD and XPS. X-Ray diffraction was performed using a Shimadzu XRD 6000 equipment, with CuKα radiation (λ=1.54 Å). X-Ray photoelectron spectroscopy was performed using a PHI 5600ci Multi Technique system with monochromatised Al Kα radiation from a 250 W X-Ray source (hν=1486.6 eV). Scratch testing were performed using custom made equipment with Vickers diamond indenter and piezo-electric load cell. The load applied on the sample surface was 10 N, while the scratch distance was 3 mm.

3. Results and discussion

The pore size was 30 to 90 μm, while the pores were interconnected, at least at the surface level, as seen in SEM images of samples in as sintered, alkali-heat treatment, and acid-heat treatment conditions, Figure 3.

The average general porosity of as-sintered samples was 27%. A significant difference of surface aspect was observed for treated samples when compared to untreated ones. Alkali-heat treatment has lead to the formation of a continuous micro-porous oxide layer. The oxide layer formed after acid-heat treatment presented superficial micro-cracks. This can be due to a higher thickness of amorphous gel layer formed after H_2O_2/HCl treatment which tends to crack during the heat treatment.

EDX chemical analysis on untreated and treated samples, figure 4, showed the presence of oxygen and sodium for alkali-heat treated samples, while the acid-heat treated samples showed only the presence of oxygen. The detected sodium (8.11 wt. %) on alkali-heat treated samples is probably in the form of sodium titanates $Na_2Ti_yO_{2y+1}$, y=5, 6. Traces of chloride were detected, but in a relative small quantity, this being considered as an impurity. Acid-heat treated samples showed significantly lower oxygen content (28 wt. %) compared to alkali-heat treated samples (49 wt. %).
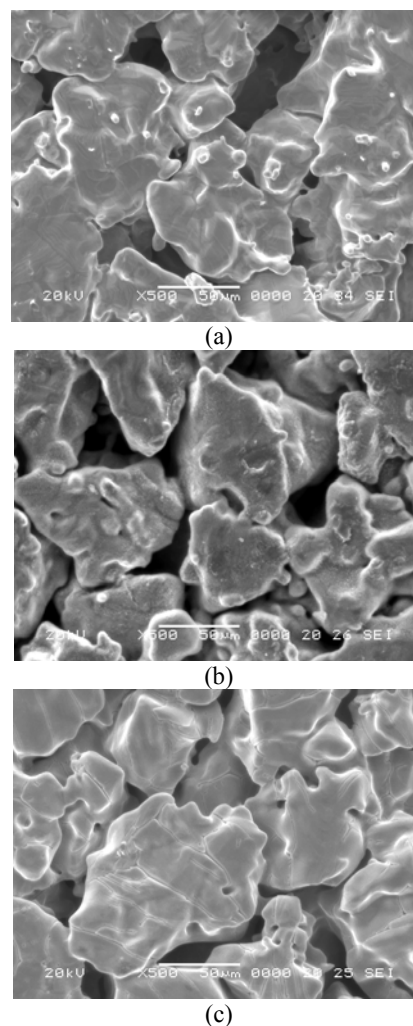

(a)

(b)

(c)

Fig. 3. SEM images of Ti samples (a) as sintered, (b) alkali-heat treated, (c) acid-heat treated
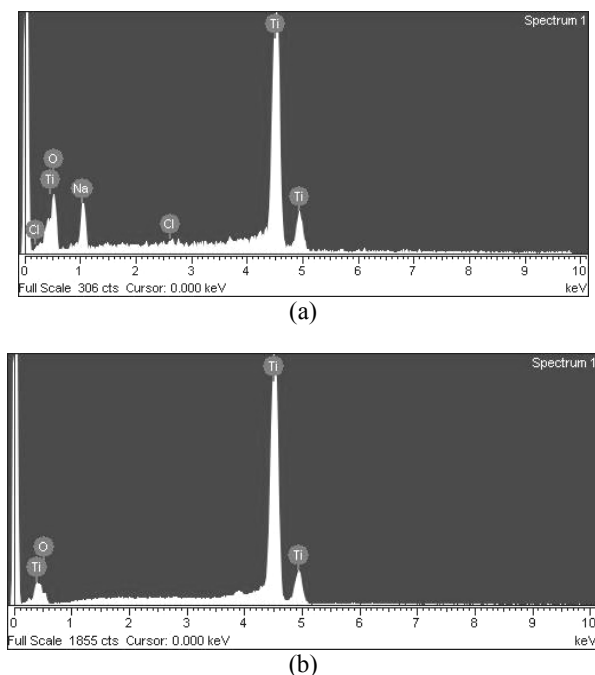
Fig. 4. EDX results for (a) alkali-heat treatment,
(b) acid-heat treatment.

X-ray diffraction patterns are shown in Fig. 5. As a general observation, titanium fluoresces under CuKα radiation that increases the background intensity in diffraction patterns obtained using this radiation. One consequence of this peculiarity is the possibility of masking low intensity peaks [5].
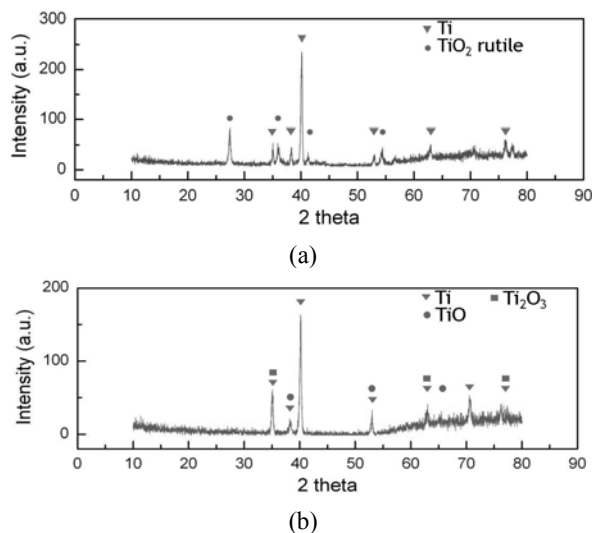

Fig. 5. XRD diagrams for (a) alkali-heat treatment, (b) acid-heat treatment

The chemical nature of the surface layer can favour the growth of hydroxyapatite by surface charging and ion release [8].

The presence of TiO_2 was clearly detected in the case of alkali-heat treated samples. TiO_2 is known to have three natural polymorphs: rutile, anatase, and brookite. Rutile, as the stable form of TiO_2 at ambient conditions, possesses unique semiconducting characteristics [5]. According to Bokhimi [6], in most cases of TiO_2 synthesis, anatase is the main phase and brookite occurs as a minority phase, depending on synthesis conditions. The rutile phase is obtained by annealing anatase and brookite at temperatures higher than 500°C [5].

With regard to the chemical properties, anatase is an important phase since it is more reactive and thus more effective in forming bone-like apatite [5]. Despite this, rutile also has a positive effect on improving the bioactivity of titanium surface.

In the case of acid-heat treated samples, titanium dioxide was not present. However, two different titanium oxides were detected with lower oxidation states, TiO and Ti_2O_3 with Ti^{2+} and Ti^{3+} oxidation states. The lack of TiO_2 is probably due to the fact that H_2O_2 hinders anatase formation owing to the formation of a passivating gel consisting of titanium oxides with lower oxidation states [5].

For further examination of the surface oxide layer of treated samples, XPS analysis was employed. Figure 6a shows the XPS Ti 2p core-level spectra, while figure 6b shows the XPS O 1s spectra.

In the Ti 2p spectra, two peaks, one Ti $2p_{3/2}$ located at binding energy of 458.0 ±0.3 eV, and one Ti $2p_{1/2}$ located at 464.0 ±0.3 eV, respectively, have been fitted. The first one (458.0 ±0.3 eV) was assigned to Ti^{2+} and Ti^{3+}, which corresponds to TiO and Ti_2O_3 respectively, while the second one (464.0 ±0.3 eV) corresponds to Ti^{4+} (TiO_2) [7].

The O 1s spectrum shows a significant difference between the two surface conditions. The spectrum for alkali-heat treated samples shows a peak centred at 530.0 eV which corresponds to O 1s in TiO_2, and possibly Ti_2O_3, since the peak position of O 1s in the TiO_2 is the same as that on Ti_2O_3. The spectrum for acid-heat treated samples is asymmetric. It is decomposed into two peaks centred at 530.0 eV and 532.0 eV. The lower binding energy component corresponds to O 1s in TiO_2 and Ti_2O_3. The higher BE component 532.0 eV in the O 1s XPS spectrum was attributed to the defective oxides 531.5 ±0.5 eV (TiO) or hydroxyl groups [7].

Scratch resistance results emphasized the chemical analysis results obtained so far. The final values for the force on the samples surface are presented in Table 1.
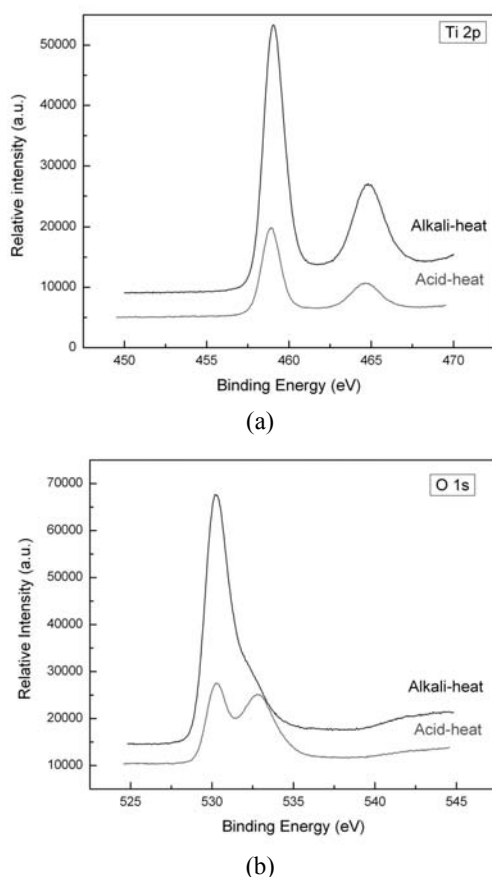
(a)

(b)

*Fig. 6. XPS spectra of treated samples (a) Ti 2p spectra,
(b) O 1s spectra*

Table 1. Scratch test results.

Condition	Initial load, (N)	Final load, (N)
Non-treated	10	10
Alkali-heat	10	11.55
Acid-heat	10	13.15

It can be seen that the scratch resistance changes with surface condition. The value obtained for non-treated samples shows that the surface layer is hard and very brittle, thus it does not hinder the indenter advance. The higher values obtained for alkali-heat and acid-heat treated samples are caused by the altering of the surface layer, leading to a tougher metal-oxide interface, which is consistent with the XPS and XRD tests.

4. Conclusions

Appropriate titania layers for bone implants were produced on commercially pure titanium porous surfaces by alkali-heat treatment. The also studied acid-heat treatment has lead to the formation of an oxide layer consisting mainly of titanium suboxides with lower oxidation degrees, TiO and Ti_2O_3 which are not as efficient in improving titanium bioactivity. The scratch testing results were consistent with the findings from chemical analysis.

Chemical, structural and mechanical analysis results lead to the conclusion that the alkali-heat treated porous titanium structures are best suited for endosseous implants.

References

[1] J. G. Lina, Y. C. Li, C. S.Wong, P. D. Hodgson, C. E. Wen, J. of Alloys and Compounds **485**, 316 (2009).
[2] S. C. P. Cachinho, R. N. Correia, J. Mater. Sci: Mater. Med., **19,** 451 (2008).
[3] Yong Wu, Joseph P. Zitelli, Kevor S. TenHuisen, Xiaojun Yu, Matthew R. Libera, Biomaterials **32**, 951 (2011).
[4] M. Ravelingien, A.S. Hervent, S. Mullens, J. Luyten, C. Vervaet, J. P. Remon, Appl. Surf. Sci. **256,** 3693 (2010).
[5] G. Lütjering, J. C.Williams, Titanium. 2nd edition. Engineering Materials and Processing, Springer, 2007
[6] X. Bokhimi, A. Morales, M. Aguilar, J. A. Toledo-Antonio, F. Pedraza, "Local Order in Titania Polymorphs", Intern. of Hydrogen Energy, **26**, 1279 (2001).
[7] Jianke Yao, Jianda Shao, Hongbo He, Zhengxiu Fan, Vacuum **81,** 1023 (2007).
[8] G. B. de Souza, G. G. de Lima, N. K. Kuromoto, P. Soares, C. M. Lepienski, C. E. Foerster, A. Mikowski, J. of the Mech. Behaviour of Biom. Mater. (2010), doi:10.1016/j.jmbbm. 2010.09.012

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