Biomimetic coatings on Ti-based alloys obtained by powder metallurgy for biomedical applications

E.C.S Rigo[1]; M.C. Bottino[2]; B.D Carraro[3]; E.B. Taddei[4]; V.A.R. Henriques[4]; C.R.M. Silva[4]; A.H.A. Bressiani[2]; J.C. Bressiani[2].

[1]PPG-Engenharia e Ciência dos Materiais, Universidade São Francisco, Rua Alexandre R. Barbosa 45, Itatiba-SP, 13251-900, Brasil.
[2]Instituto de Pesquisas Energéticas e Nucleares - IPEN, São Paulo, SP, Brazil.
[3]Laboratório de Biocerâmicas, Dep. Eng. de Materiais, UFSCar, São Carlos-SP, Brasil.
[4]AMR - Divisão de Materiais - Centro Técnico Aeroespacial (CTA)
eliana.rigo@saofrancisco.edu.br

Abstract: Comparing to hydroxyapatite (HA), which forms a strong chemical bond with the bony tissues, metallic materials are not able to bond with bone. For this reason, a great variety of complex coating methods, such as pulse-laser deposition, ion-beam assisted deposition and plasma-spray has been used to form a HA layer onto metallic surfaces. This study evaluated the performance of the biomimetic technique on apatite-based coating formation on two Ti-alloys. Ti-13Nb-13Zr and Ti-35Nb-7Zr-5Ta were obtained via powder metallurgy. The Ti-based alloys were biomimetically coated using a technique which was modified from the conventional ones using a sodium silicate solution as the nucleant agent. Both alloys presented similar behavior in the evaluated conditions which means the formation of a homogeneous and well defined HA coating. These results show that these new non-toxic Ti-alloys seem to be very promising for biomedical applications.

Introduction

Due to a high strength-to-weight ratio, good corrosion resistance in the physiological environment, fatigue resistance and low elastic modulus, pure titanium and some of its alloys have been extensively used as load-bearing implants for biomedical applications [1,2]. However, some investigations have indicated that there is still an unsolved question concerned to the possible cytotoxic effects of elements such as Al and V [1,3,4]. On that regard, it has been demonstrated that refractory metals such as titanium (Ti), niobium (Nb), zirconium (Zr), and tantalum (Ta) are considered highly biocompatible and also present an excellent corrosion resistance [5,6,7]. In addition, considering that a biomechanical mismatch may lead to an abnormal stress distribution at the bone-implant interface, retarding both bone healing and remodelling [8], Ti-alloys with low elastic modulus, such as Ti-13Nb-13Zr and Ti-35Nb-7Zr-5Ta alloys have been developed and researched [5,7,9].

It is well established that the osseointegration process is affected by surface modifications in terms of chemical and physical properties [10]. Calcium-phosphate (CaP) layers have been indicated to coat metallic surfaces due to their osteoconductive properties, which speed up and

also enhance the bone implant contact and consequently improve the bone-biomaterial interface competence [11]. The problem is that some coatings may suffer catastrophic changes such as microcracking and delamination leading to problems related to implant fixation [12]. Since was reported that Ti-based materials become highly bioactive after being subjected to chemical, alkali and heat treatments [13,14,15,16] the biomimetic approach has been gaining special attention. This procedure enhances the implant stabilization due to a chemical bond achieved between the bioactive titanium surface and bone [12]. On that regard, the purpose of this study was to evaluate the performance of a modified biomimetic technique, using sodium silicate solution as nucleant agent, on apatite-based coating formation on Ti-13Nb-13Zr and Ti-35Nb-7Zr-5Ta alloys obtained via powder metallurgy (P/M).

Experimental procedure

Powder metallurgic process

The blended elemental (BE) technique followed by a sequence of uniaxial and cold isostatic pressing with subsequent densification by sintering was the route chosen for the Ti-13Nb-13Zr (wt%) and the Ti-35Nb-7Zr-5Ta (wt%) alloys preparation. These samples were codified TNZ and TNZT, respectively.

Titanium powders were obtained by hydriding reaction at 500°C in a vertical furnace for 3 hours under a pressure of 10^{-7} Torr. In contrast, temperatures around 800°C was used to obtain Nb, Zr and Ta powders in the same manner as described for titanium [9]. After cooling at room temperature, the brittle materials were milled in a rotative milling with titanium balls under vacuum (10^{-2} Torr). Both Ti-based alloys (TNZ and TNZT) were produced according to the following procedure: starting powders were weighed and dried for one hour in stove and blended for 30 minutes in a rotative ball mill. After blending, the powders were cold uniaxially pressed under 80 MPa, in a metallic rectangular matrix. Subsequently, samples were encapsulated under vacuum in flexible rubber molds and cold isostatically pressed at 300 MPa during 30 s. Green bodies were sintered in high vacuum condition (Thermal Technology Inc. model Astro 1000 equipment) at 1500 °C with heating rates of 20°C/min. After reaching the nominal temperature, samples were hold at the chosen temperature for 2 h and then furnace-cooled to room temperature.

Sintered samples were characterized in respect to density, by the geometrical method, which involves measuring the dimensions of the samples and also the weight. X ray diffraction analyses (XRD, DMAX 2000, Rigaku) were performed in order to identify the crystalline phases present in the titanium alloys. Metallographic preparation was carried out according to conventional techniques and assessed by scanning electron microscopy (SEM, Philips XL 30). Afterwards, samples of both alloys were mirror-like polished and then allocated to the biomimetic coating procedure.

Biomimetic coating

The solutions used were SBF, 1.5 SBF and sodium silicate solution (SS) as an alternative agent [17]. They were prepared by dissolution in distilled and deionized water of the following analytical grade reagents: NaCl, KCl, K_2HPO_4, $CaCl_2.2H_2O$, $MgCl_2.6H_2O$, $NaHCO_3$, Na_2SO_4 and $(Na_2O).SiO_2$. The pH of all solutions was adjusted with HCl 0.1M and tris (hidroxymetil) aminomethane at 7.25 (37 °C). The solutions were kept in closed polyetylene containers.

Titanium alloys substrates were placed in a polyetylene recipient and were immersed in SS. All the substrates in their respective recipient were put in an incubator at 37 °C for 7 days. After this incubation period, the substrates were immersed in distilled and deionized water and finally dried at room temperature.

Each treated substrate was re-immersed in 1.5 SBF and put back in the incubator for more 6 days at 37°C. The 1.5 SBF were renewed every two days. Finally, the substrates were washed again in distilled and deionized water and dried at room temperature.

Titanium alloys coating characterization

The coated specimens were analyzed by diffuse reflectance infrared Fourier transformed (FTIR Nicolet Magna 550 coupled with diffuse reflectance DRIFT Collector[TM]), and by scanning electron microscopy (Philips, XL30-FEG).

Results and Discussion

Titanium alloys characterization

After sintering, the samples presented high densification, arounding 93% for both alloys. The estimated densities of the obtained alloys are for Ti-13Nb-13Zr and Ti-35Nb-7Zr-5Ta alloy 5.01 g/cm^3 and 5.72 g/cm^3, respectively.

X-ray diffraction analysis revealed α and β-phase peaks for TNZ alloy, not identified peaks related to the hydrides, oxide or intermetallics (Fig. 1). On the other hand, the TNZT alloy presented β-phase peaks and also peaks related to Nb and Ta.

In respect to the TNZ it is possible to verify, based on the SEM micrograph, that residual pores still remained, which is a characteristic of the final sintering stage (Fig. 2a). The microstructural findings for TNZT alloy (Fig. 2b) show a good densification, with complete dissolution of alloying elements in the titanium matrix which are coherent to the β-Ti phase. The results show that a β-homogeneous microstructure is obtained in the whole sample extension.
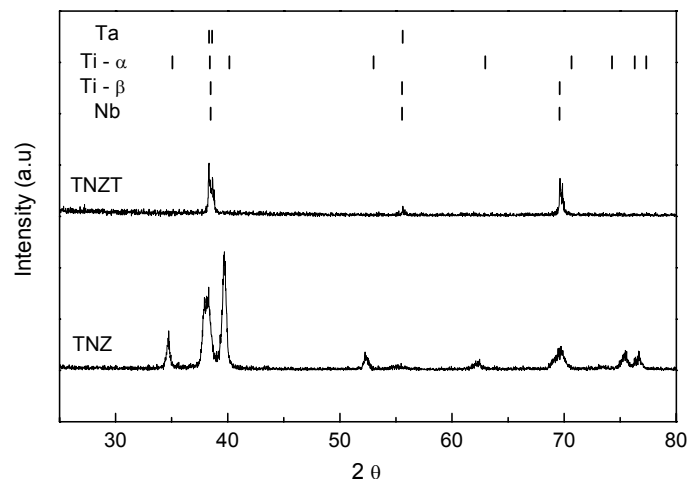

Fig. 1 - X ray diffraction patterns of Ti-13Nb-13Zr (TNZ) and Ti-35Nb-7Zr-5Ta (TNZT) alloys after sintering at 1500 ^{o}C/2h.
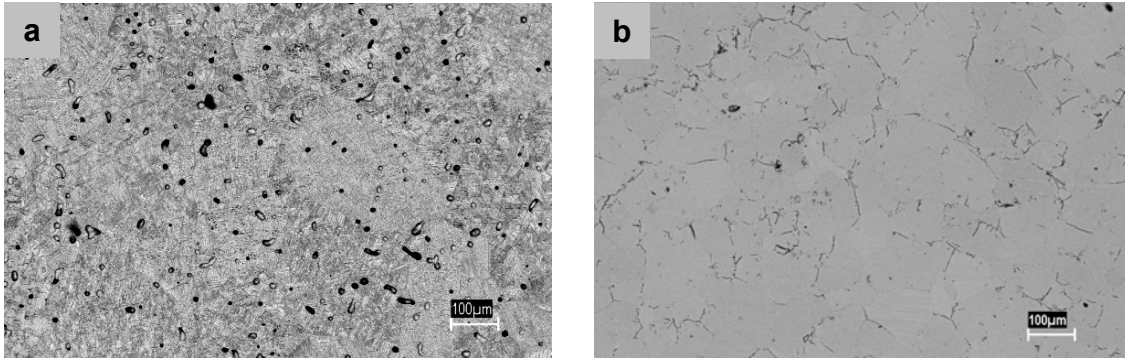
Fig. 2 - SEM micrographs of the powder metallurgic processed Ti-based alloys. a) Ti-13Nb-13Zr alloy - general aspect, note the residual pores and (b) Ti-35Nb-7Zr-5Ta alloy showing a good densification, with complete dissolution of alloying elements in the titanium matrix.

Titanium alloys coating characterization

The substrates treated for 7 days in SS, re-immersed in 1.5 SBF were observed by IR absorption (Fig. 3a and 3b). The presence of well defined wide bands of 600 cm^{-1} and 1050 cm^{-1} can be observed, all of them characteristic of the PO_4^{3-} ion vibration; of 870, 1410 and 1490 cm^{-1}, characteristic of the CO_3^{2-} ions; of 1650cm^{-1}, characteristic of the H_2O; and a very wide band in the 3000-3600 cm^{-1} region, characteristic of the OH$^-$ [14,18,19].
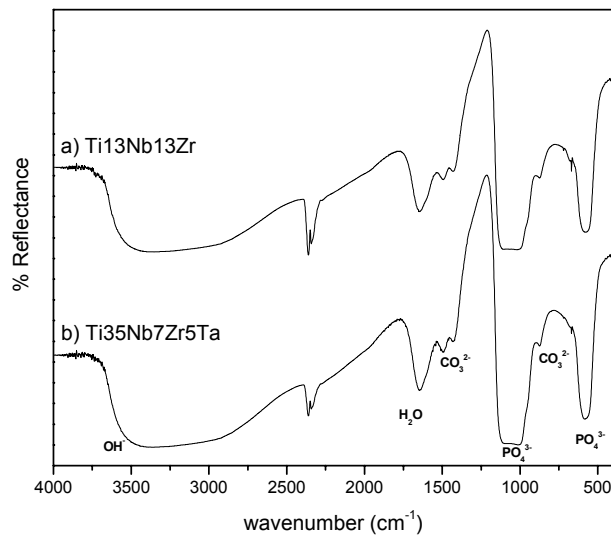

Fig. 3 - Diffuse reflectance infrared (DRIFT) of the recovered titanium alloys by biomimetic method, using as nucleating agent sodium silicate solution (SS) and re-immersion in 1.5 SBF; a) Ti-13Nb-13Zr and b) Ti-35Nb-7Zr-5Ta.

The mechanism of the apatite layer formation by the traditional biomimetic method, which uses bioactive glass is the following: (1) silicate ions dissolved from the glass are adsorbed

on the substrate, (2) apatite nucleation occurs on the adsorbed silicate ions from the Ca^{2+} and PO_4^{3-} ions present in the SBF, (3) apatite nuclei grow directly on the substrate by a reaction with the solution which is supersaturated to apatite. The silicate ions adsorbed on the surface of the substrate produce silanol groups (Si-OH), which are accepted to be the responsible for the apatite nucleation action [20].

According to Kokubo [21], the surface of metallic Ti is covered with a passive layer of titanium oxide, which reacts with alkaline saline solutions, forming $HTiO_3^- \cdot nH_2O$. These are negatively charged, thus incorporate positively charged ions. As a result, a layer of alkaline titanate hydrogel is formed onto the metallic Ti. The apatite layer is formed on the surface of the hydrogel layer according to the following mechanism: the alkaline ions of the surface layer are substituted by H_3O^+ present in the liquid to form Ti-OH groups on the metallic Ti surface, increasing the product of apatite ionic activity in the fluid due to an increase in the OH^- concentration.

Similar mechanisms occur for bioactive glasses. According to Hench [22], an ionic exchange between Na^+ and K^+ in the glass surface and H^+ or H_3O^+ in the liquid takes place, causing the loss of soluble silica into solution in the $Si(OH)_4$ form. This is the result of Si-O-Si breaking to form SiOH groups (silanols), followed by condensation and re-polymerisation of the silica rich layer. Ca^{2+} and PO_4^{3-} ions migrate to the surface of silica rich layer forming a thin film containing $CaO-P_2O_5$. Further growth of the CaP ($CaO - P_2O_5$) amorphous layer takes place by the incorporation of Ca and P. The final stage of crystallization of the Ca-P layer occurs by the incorporation of OH^-, CO_3^{2-} or F^- from the solution to form hydroxycarbonate or fluoroapatite.

Scanning electron micrographs reveal no differences in layers obtained with the distinct titanium alloys (Fig. 4). The observed cracks are associated to the drying step. The layers originated by nucleation in SS are only formed by small and homogeneous crystals as a result of the number of nucleation sites. This occurred because, in exclusive contact with SS, the silanols groups were greatly adsorbed on created titanates groups. The morphology of substrate surfaces appears to be similar, regardless of the titanium alloys. After re-immersion in 1.5 SBF for 6 days the formation of HA globules is detected (Fig. 4a and 4b). Moreover, these results showed that the sodium silicate solution (SS) could be used to effectively replace the bioactive glass as source of silanols groups.
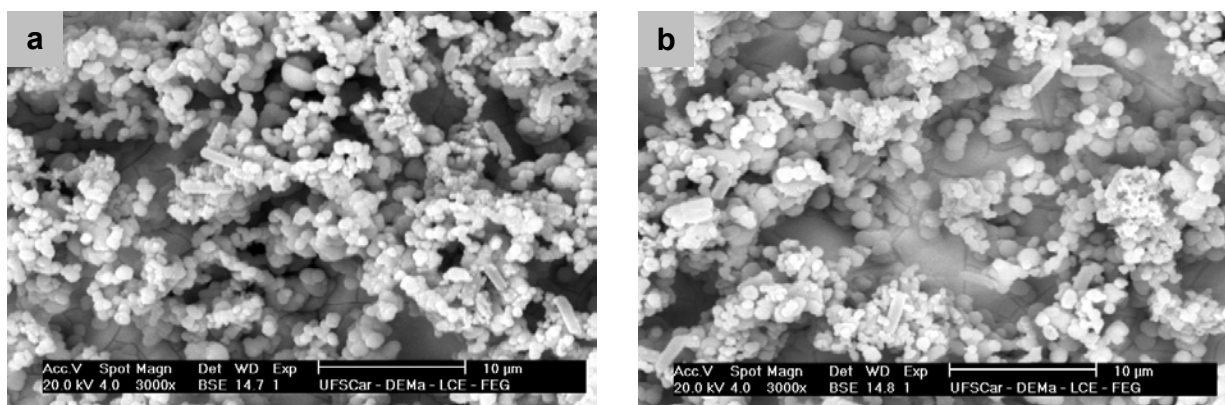

Fig. 4 - SEM micrographs of the recovered titanium alloys by biomimetic method, using as nucleating agent sodium silicate solution (SS) and re-immersion in 1.5 SBF; a) Ti-13Nb-13Zr and b) Ti-35Nb-7Zr-5Ta.

Conclusion

It was concluded that the sodium silicate solution (SS) demonstrated to be effective for the HA layer formation over both titanium alloys. Further, it can be pointed out that the formed layers were homogenous and well characterized by small crystals formation.

Acknowledgements

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