THE EFFECT OF HEAT TREATMENT ON THE CORROSION RESISTANCE OF Ti AND Ti-Nb ALLOYS IN FLUORIDE SOLUTION

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Introduction
Titanium alloys are usually used in dental applications as materials for implants and orthodontic wires fabrication due to their biocompatibility and high corrosion resistance [1,2]. However, fluoride ions form complexes with titanium [2] resulting in corrosion resistance degradation. Acidulated phosphate-fluoride (APF) is used in dentifrices to help fighting caries. It allows the contact of fluorides with dental metallic parts leading to corrosion of the metallic materials and metal ions liberation in the organism and might result in adverse physiological effects such as cytotoxicity and allergic reactions [2,3]. The fabrication of Ti alloys with biocompatible elements, such as Nb, has been investigated in search for new materials with improved corrosion and mechanical properties. The aim of the present study is to investigate the corrosion resistance of commercially pure Ti and two Ti-Nb alloys, specifically, Ti-5%Nb and Ti-10%Nb. These materials were prepared by arc furnace melting and then hot forging. Part of the material was heat treated at 1000 °C for 24 hours for homogenization. The corrosion resistance of Ti and Ti alloys, either hot forged or heat treated, was investigated in the present study. The electrolyte consisted of an acidulated phosphate-fluoride solution (APF) with 0.3% F (1357 ppm F) which was prepared with NaF and H₃PO₄. The pH of this solution was 3.5. The corrosion resistance of the various types of materials was investigated by electrochemical techniques, specifically open circuit potential measurements, electrochemical impedance spectroscopy and polarization curves.

Experimental
Ti-Nb alloys with 5 and 10 wt. (%) of niobium were produced by arc furnace melting at the UNESP/Bauru using an arc-melting furnace with a nonconsumable tungsten electrode and water-cooled copper crucible in an argon-controlled atmosphere. The materials used as precursors were commercially pure titanium (99.7% purity) and niobium (99.8% purity), both supplied by Aldrich Inc. After melting, two ingots (Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb alloys) with 80 g each one. Following melting, the obtained ingots were subjected to swaging, yielding samples 4.0 mm in diameter and 40.0 mm in length. The alloys were then subjected to quantitative chemical analysis using the Spectra Spectrora Xx model (Molecular Devices, USA). Homogenization heat treatment was carried out to improve the homogeneity of the alloys and remove internal stresses arising from the swaging. The heating rate used was 10 °C/min to 1000 °C. This temperature was maintained for 24 hours, and then, cooling down was carried out slowly after the shutdown of the furnace. The produced material was analyzed using density measurements and X-ray powder diffraction.

The test solution used as electrolyte consisted of acidulated phosphate-fluoride solution with 0.3% F (1357 ppm F). This was prepared with NaF and H₃PO₄. The pH of this solution was 3.5. The corrosion resistance was investigated by electrochemical techniques, specifically electrochemical impedance spectroscopy (EIS) and polarization curves.

Results and Discussion
Nyquist and Bode phase angle diagrams for the various tested materials, either with or without heat treatment, after 12 hours of immersion in the electrolyte (0.3% APF) are shown in Figures 1 to 3.
Figure 1 – Nyquist and Bode phase angle diagrams for Ti cp, heat treated (TT) or without heat treatment, after 12 hours of immersion in APF solution.

Figure 2 – Nyquist and Bode phase angle diagrams for Ti 5 wt.% Nb, heat treated (TT) or without heat treatment, after 12 hours of immersion in APF solution.

Figure 3 – Nyquist and Bode phase angle diagrams for Ti 10 wt.% Nb, heat treated (TT) or without heat treatment, after 12 hours of immersion in APF solution.

The EIS results show much higher impedances associated to the heat treated (TT) samples, comparatively to the untreated ones, Figures 1 to 3. This is clearly related to the effect of the heat treatment carried out on the Ti and Ti alloys microstructure homogenization, as it can be seen in Figure 4. Despite of the large increase in impedance due to the heat treatment, the mechanism involved in the corrosive attack of both Ti-Nb alloys, either heat treated or without heat treatment, was similar, showing a time constant associated to charge transfer processes related to the dissolution of Ti in the fluoride containing test medium. The results
do not indicate the formation of a highly protective passive film, typical of Ti alloys in neutral solutions without fluoride. The formation of complexes of titanium with fluoride ions [2] explains this behavior.

Figure 4. Ti-cp and Ti-5Nb, Ti-10Nb alloys, prior to (samples on the right) or after (samples on the left) heat treatment showing homogenization of the materials microstructure.

Conclusions
The heat treatment used in this study largely increased the corrosion resistance of the Ti-cp and Ti-Nb alloys due to microstructure homogenization.

References