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CORROSION BEHAVIOUR OF TI-NB-AG POWDER METALLURGICAL ALLOYS AND THEIR POTENTIAL APPLICATION AS BIOMATERIALS

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Abstract: One of the most important characteristics of medical devices are materials and their properties. Specially, the corrosion resistance, which is considered very relevant. Furthermore, several alloys have been developed by powder metallurgic processes to control the composition. Accordingly, the propose of this work is to study the influence in Ti-35Nb alloys of the addition of silver (X=0, 2, 4 and 6 wt%) respect to the mechanical properties and the corrosion performance, in solutions similar to human body fluids. Corrosion resistance has been analyzed by ion release as well as polarization in artificial saliva Fusayama [1] and Hartmann solution as electrolytes. Likewise, the microstructural characteristics and mechanical properties have been studied. The results obtained demonstrate the viability of these Ti35NbXAg alloys for their possible use as biomedical implants.
Keywords: Powder metallurgy, titanium alloys, TiNbAg, , microstructure, corrosion behavior, ion release.

INTRODUCCIÓN

Titanium and its alloys are the most widely used materials to make bone replacement prostheses [2]. In particular, the new titanium β alloys that incorporate elements such as niobium, zirconium and tantalum are the most promising for the manufacture of biomedical implants [3]. Although β alloys with low elastic modulus, high corrosion resistance and great biocompatibility have been obtained, there is still a high rate of inflammation and infection when implanting these materials in the human body [2-3]. Silver is an element recognized by its high bactericidal properties and it has been used in the field of medicine to avoid infections [4]. The release of silver ions greatly increases the potential bactericidal properties of these alloys and its presence in the metal is quite sufficient to prevent the formation of bacterial biofilms on the materials.

The alloys were successfully produced by conventional powder metallurgy. As composition can be modified by this method, this works studied the influence on mechanical and corrosion properties of TiNb alloy with three different percentage of Ag.

EXPERIMENTAL PROCEDURE

Ti35Nb alloys with different Ag weight percentages (0, 2, 4 and 6 wt%) were obtained via conventional powder metallurgical process from commercial Ti, Nb, and Ag powders. These samples designation is PM. Elemental powders in appropriate proportions were mixed homogeneously, compacted under pressure of 700 MPa and sintered in HVT 15-75-450 Carbolite vacuum furnace under 5·10-4 mbar at a temperature of 825ºC and 1300ºC for 3h at each. All samples were metallographically prepared wet-ground with 220, 500, and 1000 grit SiC papers, polished until mirror-like finishing with diamond suspension (3 μm) and colloidal silica and cleaned in ethanol-acetone mixture ultrasonically for 10 min.

The microstructure was observed under a SEM Zeiss AURIGA. A microanalysis was carried out by EDS Oxford Instr. Phase identification was confirmed by X-ray diffraction patterns with a Bruker D2 Phaser diffractometer. Three-point bending tests were carried out by Autograph AG-100 kN Xplus Shimadzu. HV microhardness tests were run by Shimadzu, the impulse excitation – by Sonelastic.

Corrosion tests [5] were performed by potentiostat AUTOLAB PGSTAT204 with a typical three-electrode cell configuration (Ag/AgCl electrode, platinum wire and the investigated alloy) at 37ºC. The Fusayama artificial saliva (NaCl 0.4 g/L, KCl 0.4 g/L, $CaCl_2$*$2H_2O$ 0.795 g/L, Na_2S*$9H_2O$ 0.005 g/L, NaH_2PO_4*$2H_2O$ 0.69 g/L, Urea1 g/L) and

Hartmann solution (NaCl 5.97 g/L, KCl 0.37 g/L, CaCl2 0.22 g/L, Na lactate 3.25 g/L, pH 6.5) were used as the electrolytes [4]. For ion release tests samples were submerged in both solutions at 37ºC for 730 hours.

RESULTS AND DISCUSSION

The 85% of β-phase Ti was found in the alloy samples characterized as quite homogeneous materials, through XRD analysis as shown if Figure 1.

Likewise, the compaction and sintering cycle conditions have led to a good diffusion of Nb in the alloy and also have prevented a sublimation of Ag, which has been demonstrated by electron microscopy EDS analysis (Figure 2).-

From SEM images high porosity in the sintered alloys was observed, this characteristic plays a role in the mechanical properties as seen in Table 1. Porosity percentage and phase content of the alloys are presented as well, in Table 1.

The average of the elastic modulus of the alloys is on average is 69 GPa for Ti35NbXAg alloys. These values are halfway between the Ti6Al4V alloy (115 GPa) and commercial β alloys such as Ti35Nb7Zr5Ta (55 GPa) [1, 2, 6]. The maximum flexural strength, around 400 MPa, and the hardness, over 130 HV, are values that are well below those of the Ti6Al4V alloy, with a maximum resistance of 1500 MPa and a hardness of 300 HV [2, 6]. Even so, the mechanical characteristics of the alloys are sufficient to be used as bone substitutes [2, 6]. The addition of Ag decreases the elastic modulus, which is beneficial in reducing the stress shielding phenomenon, although it also decreases the breaking stress but no significantly if they are compared to Ti35Nb. The TiNbxAg alloys have lowest range of porosity comparing to Ti35Nb alloy, which means that addition of Ag of alloying element decrease the pores' formation.

The results shown in table 2 of the ion release test indicate that there is a much higher unit release of Ti and Nb (more than 10 times higher) than of Ag from the alloys. No significant Ag release has been obtained in Ti35NbXAg alloys, which would result in non-existent antibacterial activity.

Likewise, the difference between the corrosion resistance of Ti35NbXAg respect to the performance of other Ti alloys evaluated in similar electrolytes is unsignificant [1, 4, 7, 8].

Polarization curves show that Ti35NbXAg are passivated according to the evolution of the current in a wide potential range. As shown in Table 3, OCP values and corrosion potential are not significant different for the three Ag percentages.

Corrosion currents are lightly higher in Hartmann-Ringer solution, however the addition of Ag shows a decrement in the current respect to the Ti35Nb. In fact, a quite stable behavior is obtained along the cathodic and anodic regions as observed in Figure 3a and Figure 3b.

Moreover, the aggressivity of the Fusayama artificial saliva compared to Hartmann Ringer solutions seems to be the responsible on the ions release was noticed between samples results, which is attributed to the chloride content. It also, can explain the small variations on the OCP values and corrosion potentials. Even though, corrosion currents are in the same order of magnitudes for all the evaluated alloys.

CONCLUSIONS

The presence of chlorides ions in the Hartmann Ringer solutions leads to higher ions release and corrosion currents of Ti alloys where additions of Ag are done.

The addition of silver modifies the mechanical properties, an improvement on the strength and hardness was reported

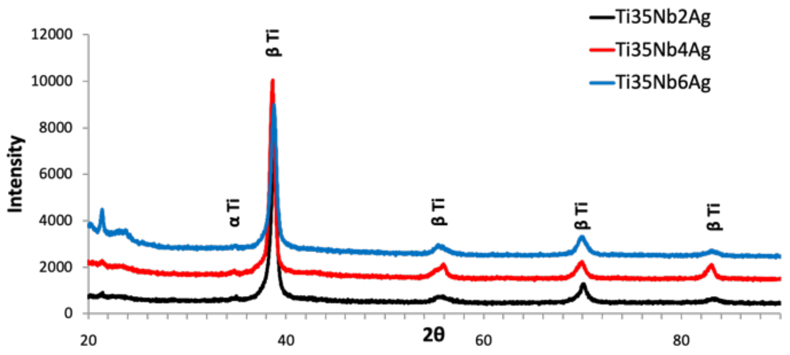

Figure 1. DRX analysis of Ti35NbXAg.

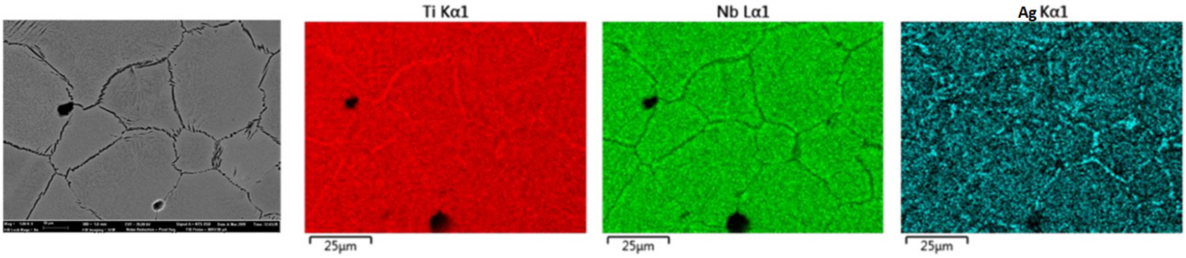

Figure 2. Electron microscopy EDS analysis.

Alloy	Porosity, %	Elastic Modulus, GPa	Strenth, MPa	Hardness, HV
Ti-35Nb	9,1	71	454	126
Ti35Nb-2Ag	5,5	71	403	123
Ti35Nb-4Ag	6,5	68	394	122
Ti35Nb-6Ag	7,1	65	373	121

Table 1. Mechanical properties of alloys.

Artificial saliva Fusayama, µg/L·cm²·h			Alloy	Hartmann-Ringer solution, µg/L·cm²·h		
Ti	Nb	Ag		Ti	Nb	Ag
0.61	0.39	-	**Ti35Nb**	0.008	0.019	-
0.24	0.17	0.004	**Ti35Nb-2Ag**	0.043	0.030	0.001
0.28	0.20	0.005	**Ti35Nb-4Ag**	0.023	0.019	0.019
0.48	0.37	0.012	**Ti35Nb-6Ag**	0.015	0.023	0.001

Table 2. Results of the ion release artificial saliva Fusayama and Hartmann-Ringer solution

Artificial saliva Fusayama			Alloy	Hartmann-Ringer solution		
E_{OCP} (V)	E_{corr} (V)	I_{corr} (A/cm^2) x 10^{-9}		E_{OCP} (V)	E_{corr} (V)	I_{corr} (A/cm^2) x 10^{-9}
-0,28	-0,19	11	**Ti35Nb**	-0,41	-0,43	160
-0,20	-0,29	59	**Ti35Nb-2Ag**	-0,27	-0,36	74
-0,22	-0,27	24	**Ti35Nb-4Ag**	-0,32	-0,38	150
-0,22	-0,38	16	**Ti35Nb-6Ag**	-0,35	-0,42	100

Table 3. The summary of the corrosion test data in and.

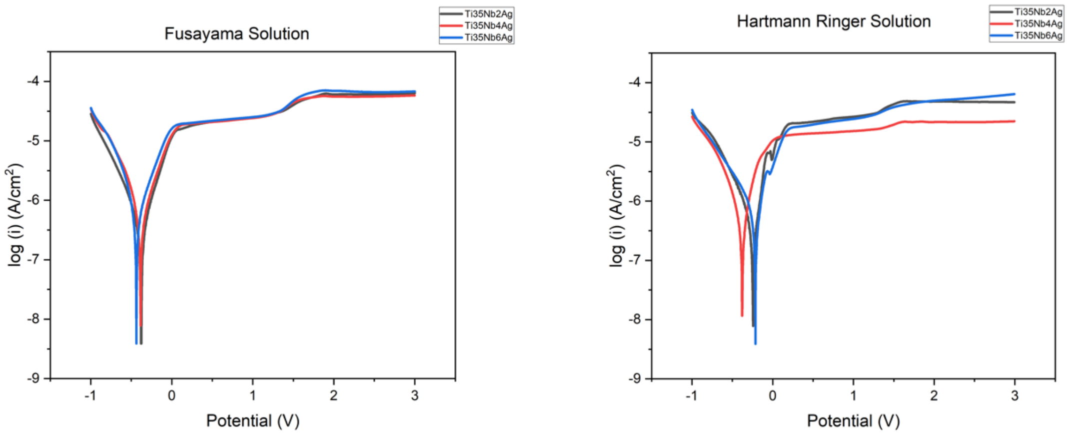

Figure 3. Polarization curves of Ti35NbXAg in a) artificial saliva Fusayama and b) Hartmann – Ringer solution.

respect to the Ti35Nb alloys.

Regarding the mechanical and electrochemical properties, all the alloys can be used as biomaterials for implants.

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