Effect of B on the Corrosion Resistance of a Ni-Ti Alloy in Simulated Human Body Solution

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An investigation about the effect of boron contents and heat treatment on the corrosion resistance of a Ni-Ti alloy in simulated human body fluid environments has been carried out using electrochemical techniques. Tested alloys included 55 (wt %) Ni-45Ti with 250, 500 and 1000 ppm B with and without heat treatment at 900°C during 4 h. Electrochemical techniques included potentiodynamic polarization curves and electrochemical impedance spectroscopy. Addition of either 200 or 500 ppm B decreased the corrosion rate, but with the addition of 1000 ppm B or thermal annealing the alloy increased it.

Keywords: NiTi alloy, Hank's solution, electrochemical impedance

1. INTRODUCTION

Corrosion of human body metallic implants is critical because it can adversely affect biocompatibility and mechanical integrity [1]. Corrosion and surface film dissolution are two responsible mechanisms for introducing ions in the body from the implants. Extensive release of metal ions from human body implants can result in adverse biological reactions and even lead to mechanical failure of the device. Most of the used materials for human implants include 316L type stainless steels [2, 3], titanium-base alloys [4-12], or cobalt-base alloys [13-15]. For instance, Shukla [16] studied the effect of surface treatment on electrochemical behavior of Ti, Ti-6Al-4V and Ti-13Nb-13Zr alloys in simulated human body fluid. For untreated alloys, there was a minimal change in the passive film resistance, but when they were treated, there were two additional layers. Li et al. [17] studied the corrosion behavior of $Ti_{44}Ni_{47}Nb_9$ alloys in simulated human body fluids at different pH values, finding that the pH value had different effects on the corrosion resistance of these alloys, but the

addition of Nb improved the corrosion resistance of the TiNi alloy. In a different work, Wong et al. [18] studied the effect of laser oxidation of NiTi for improving its corrosion resistance in Hank's solution, finding that laser oxidized samples did not show pitting type of corrosion up to an applied potential of 1550 mV SCE and the passive current density was one order of magnitude lower than that for the untreated alloy. Oliveira et al. [19] developed Ti-(10-20 wt. %)Mo alloys for biomedical applications and studied their corrosion resistance in Ringer solution. They found that the alloys exhibited good corrosion resistance. However, Ti-based alloys are still the most widely used alloys for their corrosion resistance and the biocompatibility. It has been shown that by adding elements such as B, V, Zr and Ti to memory shape alloys or to Ti-based alloys, helps to refine the grain size [20-22] in such a way that both their mechanical properties and corrosion resistance are affected. Thus, the goal of this work is to investigate the effect of B additions to a Ni-Ti alloy on its corrosion resistance in human body solutions for their potential use as biomaterials

2. EXPERIMENTAL PART

The Ni-Ti alloys were produced by the induction-melting technique under argon atmosphere (99.99% purity) with a constant Ni content of 55 wt. % and Ti 45 wt. %, and various levels of B addition, namely 200, 500 and 1000 ppm. The alloys were drop-casted into water-cooled copper molds to form the cast bars with a diameter of 12.5 mm. Upon casting, the specimens were annealed in a vacuum of 10⁻⁴ Pa during 4 h at 900°C, and then furnace cooled. Metallographic specimens were cut from the cast bars, ground, polished, and then etched with Murakami's reagent during 1-2 s. Analysis of the microstructures was performed in a scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS) analyzer. Testing solution was the Hank's solution, with a chemical composition as given on table 1. Specimens with an exposed area of 1.0 cm² were encapsulated in epoxy resin and polished with diamond paste to a 1.0 µm finish. Electrochemical experiments were performed using an ACM Instruments potentiostat controlled by a personal computer. Potentiodynamic polarization curves were obtained by varying the applied potential from -500 mV with respect to the free corrosion potential, E_{corr} , up to +600 mV at a scan rate of 1 mV/s. Before the experiments, the E_{corr} value was measured during approximately 30 minutes, until it was stable. All potentials were measured using a Saturated Calomel Electrode (SCE) as reference electrode. The counter electrode was a platinum wire. All tests were performed at 37 ± 2 °C. Electrochemical impedance spectroscopy tests, EIS, were carried out at Ecorr by using a signal with amplitude of 10 mV and a frequency interval of 0.1 Hz-30 kHz every 24 hours during 16 days.

Table 1. Chemical composition of the Hank's solution.

	NaCl	CaCl ₂	KCl	Glucose	NaHCO ₃	MgCl ₂ .6H ₂ O	Na ₂ HPO _{4.} 2H ₂ O	KH ₂ PO ₄	MgSO ₄ 7H ₂ O
g/l	8	0.14	0.4	1	0.35	1	0.06	0.06	0.06



Figure 1. Microstructure of the samples with a) 0, b) 200, c) 500, and d) 1000 ppm B in the annealed condition.



Figure 2. Effect of B addition on the polarization curves for the as-received NiTi alloy in the Hank's solution



Figure 3. Effect of B addition on the polarization curves for the annealed NiTi alloy in the Hank's solution

3. RESULTS AND DISCUSSION

Fig. 1 shows the microstructures of the Ni-Ti alloys with the different boron additions in the annealing condition. For alloy with no boron additions (which was present at higher magnifications), Fig 1a, it can be seen in that the matrix consisted mainly of the NiTi phase, while the secondary phase was Ni₃Ti, as expected from the binary alloys phase diagram, where a eutectic reaction was produced at this Ni content. In this figure, highly aligned phases array with some preferential symmetry could be observed on the alloys surface. For alloys with 200 or 500 ppm B, Fig. 1 b and c, no remarkable difference could be observed, assuming that, at these levels of boron additions, there were not any visible changes in the microstructure, however, the phases homogeneity along the surface samples could be seen. On the other hand, a coarse microstructure was observed on the sample with 1000 ppm B, perhaps this boron levels produced a distortion on the lattice, generating the development of defects observed on the surface sample.

The effect of B addition and heat treatment on the polarization curves for NiTi alloy in the Hank's solution is shown on Figs. 2 and 3 respectively. Fig. 2 shows that the unalloyed NiTi alloy showed an active-passive behavior with an E_{corr} value of -466 mV_{SCE} and a corrosion current density value, I_{corr} close to 6.8 10⁻⁵ mA/cm². As soon as either 200 or 500 ppm B were added, the E_{corr} became nobler, -354 and -251 mV_{SCE} respectively, but with the addition of 1000 ppm B the E_{corr} value, -425 mV_{SCE}, was very close to the obtained for the unalloyed NiTi alloy. The I_{corr} value was increased with either addition of B, obtaining the highest value with 500 ppm B. The passive current density value was decreased also by adding B, increasing this up to $4.1X10^{-4}$ mA/cm². When the alloys with B were annealed, Fig. 3, all the I_{corr} values increased, the E_{corr} values practically did not change, remaining

very close respect to the alloys without this heat treatment, but the alloys did not show an activepassive behavior, except the alloy containing 1000 ppm B, which exhibited a passive region with an I_{pass} value of 1.7 10^{-2} mA/cm², very similar to that for unalloyed NiTi intermetallic alloy. Table 2 summarizes the electrochemical parameters obtained from polarization curves for all specimens. Thus, by adding B or heat treating the alloy, the corrosion rate always increased for the NiTi alloy.

Alloy	$E_{\rm corr}$	$I_{\rm corr} ({\rm mA/cm}^2)$	b_a (mV/dec)	$b_c (mV/dec)$	$I_{\rm pass}~({\rm mA/cm}^2)$	
	(mV _{SCE})					
NiTi	-466	6.8 10 ⁻⁵			1.9 10 ⁻²	
NiTi+200 ppm B	-354	$2.5 \ 10^{-4}$	111.28	337.91	3.8 10 ⁻³	
Annealed 200 ppm B	-353	5.5 10-4	90.97	68.47		
NiTi+500 ppm B	-251	4.1 10 ⁻⁴	152.24	114.56	2.5 10-3	
Annealed 500 ppm B	-402	6.6 10 ⁻⁴	115.35	91.5		
NiTi+1000 ppm B	-425	$2.1 \ 10^{-4}$	88.59	73.71	1.2 10 ⁻³	
Annealed 1000 ppm B	-405	9.3 10-3	108.31	171.72	1.7 10 ⁻²	

 Table 2. Electrochemical parameters obtained from polarization curves



Figure 4. Nyquist diagrams for the NiTi+200 ppm B alloy in the Hank's solution.

EIS data in the Nyquist diagram format for the unalloyed NiTi intermetallic alloy is shown on Fig. 4, which shows that the data display a capacitive-like semicircle with its center in the real axis at high frequency values, and a second semicircle at lower frequencies. The first semicircle has been related to the charge transfer reaction from the alloy to the electrolyte through the double electrochemical layer, whereas the second, the low frequency semicircle has been related to the

formation of a passive layer, probably TiO_2 and some NiO oxide layer. The charge transfer resistance, R_{ct} , was obtained by extrapolation of the charge transfer semicircle corresponding to the diameter of the semicircle. A similar process can be done to obtain the corrosion products or surface film resistance, R_f . The diameter of the first, high frequency semicircle does not a have a constant behavior as time elapses, since sometimes it increases and some other times it decreases, reaching the maximum value after seven days of exposure to the corrosive environment. This erratic behavior of the R_{ct} value probably means that the passive layer increases in thickness, but after some time, this layer is detached from the alloy surface, decreasing the film layer.



Figure 5. Nyquist diagrams for the annealed NiTi+200 ppm B alloy in the Hank's solution.

When 200 ppm B were added to the NiTi alloy, Fig. 5, the data displayed a depressed, capacitive-like semicircle at high frequency values with its center in the real axis, indicating that the corrosion process is under charge transfer control from the alloy to the electrolyte through the double electrochemical layer, but at low frequency values the data described a straight line, indicating that now the corrosion process is under charge transfer and diffusion control, diffusion of the reactants through the passive layer. This type of diffusion is called Warburg type of diffusion. The diameter of the semicircle, the charge transfer resistance or R_{ct} , showed the highest value around 2 or 3 days, and after that, it had an erratic behavior, but it had a tendency to decrease towards the end of the test. For the rest of the alloys, regardless of the B contents or heat treatment, the EIS data described a depressed semicircle at high frequency values. The diameter of the high frequency semicircle reached a maximum value during the early stages of the process and then decreased towards the end of the test, as can be seen, as example, on Figs. 6 and 7.



Figure 6. Nyquist diagrams for the NiTi+1000 ppm B alloy in the Hank's solution.



Figure 7. Effect of B and heat treatment on the Bode diagrams for NiTi alloy after 1 day in the Hank's solution.

Fig. 8 shows the Bode diagrams after one day of exposure to the Hank's solution for the different alloys, where it can be seen that the modulus of the impedance for alloy containing 500 ppm of B was higher than that for NiTi alloy, whereas the lowest impedance modulus was shown by alloys containing 1000 ppm of B with or without thermal annealing. On the other hand, Bode-phase diagrams for the different alloys after one day of exposure to the Hank's solution is shown on Fig. 9. The large

phase angle peak could be indicative of the interaction of at least two time constants; a highly capacitive behavior, typical of passive materials, is indicated from medium to low frequencies by phase angles approaching -90°, suggesting that a very stable film is formed on all tested alloys in the used electrolyte, which is consistent with the very low corrosion rates obtained from polarization tests.



Figure 8. Effect of B and heat treatment on the Bode-phase diagrams for NiTi alloy after 1 day in the Hank's solution.



Figure 9. Electric circuits used to simulate the EIS data for a) NiTi and b) NiTi+B alloys.

Equivalent electric circuits to simulate the EIS data for the different alloys are shown on Fig. 10. On these circuits R_s represents the solution or electrolyte resistance, R_{ct} is the charge transfer resistance associated to the double electrochemical layer and C_{dl} its capacitance, R_f is the resistance of the barrier layer associated to the participation of adsorbed intermediates and C_f its capacitance. When a non-ideal frequency response is present, it is commonly accepted to employ distributed circuit elements in an equivalent circuit. The most widely used is constant phase element (*CPE*), which has a

non-integer power dependence on the frequency. The impedance of a CPE is described by the expression:

$$Z_{\rm CPE} = Y^1 (j\omega)^{-n} \tag{1}$$

where *Y* is a proportional factor, j is $\sqrt{-1}$, ω is the frequency and -1 < n < 1 has the meaning of a phase shift. Often a *CPE* is used in a model in place of a capacitor to compensate for non-homogeneity in the system. To describe the behavior of impedance spectra at low frequencies an exponent α is introduced in the expression for the Warburg impedance. Several models and expressions are used to describe this characteristic behavior, but the finite–element Warburg impedance is expressed by:

$$Z_{w} = R_{w}(j\omega)^{\alpha}$$
⁽²⁾

were R_w is the modulus of the Warburg or diffusion resistance and α is the Warburg coefficient. Calculated parameters to simulate the EIS data for different alloys are shown on table 3. It can be seen that the lowest R_{ct} value, and thus, the highest corrosion rate, was for the two alloys containing 1000 ppm B, especially the thermally annealed, whereas the highest R_{ct} value was for the alloys containing 500 ppm B regardless the heat treatment. These data are in agreement with the data obtained from polarization curves shown on table 2 and with those shown by Bode data shown on Fig. 8.



Figure 10. Effect of B and heat treatment on the change of R_{ct} with time for NiTi alloy in the Hank's solution.

By using electric circuits shown on Fig. 9, the change of the R_{ct} value with time for the different alloys can be calculated as given on Fig. 10. This figure shows high R_{ct} values, which

represent very low corrosion rates, and justify the use of these alloys in this environment, and that only the alloys with the addition of either 200 or 500 ppm B showed a higher R_{ct} and, thus, a lower corrosion rate than that for unalloyed NiTi alloy, but only during the first days. After a few days of exposure to the corrosive solution, the R_{ct} value for all the alloys doped with B, heat treated or not, decreased, showing practically similar values among them, always lower than that for unalloyed NiTi alloy, which showed the highest corrosion resistance at the late stage of the test.

	C		W ₀		R	Re
	(Farads/cm ²)	$C_{\rm dl}$ (Farads/cm ²)	R_w (Ohms cm ²)	α	(Ohms cm^2)	(Ohms cm^2)
0 ppm B	2.9 X10 ⁻⁵	5.6 X 10 ⁻⁵			3.6 X 10 ⁶	45
200 ppm B		7.9 x 10 ⁻⁶	1.14 X 10 ⁵	0.9	8.5 x 10 ⁵	
Annealed		7.1 x 10 ⁻⁶	5.5 X 10 ⁶	2.9	$1.2 \text{ X } 10^{6}$	
200 ppm B						
500 ppm B		8.3 x 10 ⁻⁶	1.3 X 10 ⁶	2.6	1.7 X 10 ⁶	
Annealed		1.3 x 10 ⁻⁵	5.4 X 10 ⁵	0.9	1.1 X 10 ⁶	
500 ppm B						
1000 ppm		1.2 x 10 ⁻⁵	3.2×10^3	1.1	5.6 X 10 ⁵	
В						
Annealed		2.4 X 10 ⁻⁵	2.4×10^{6}	0.9	1.3×10^5	
1000 ppm						
В						

Table 3. Fitting parameters to simulate the EIS data.

A micrograph of the corroded surface of the NiTi-base alloy is shown on Fig. 11, whereas that for the NiTi+200 ppm B alloy is shown on Fig. 12. Both figures show the presence of a layer of compact, adherent, insoluble corrosion products, which are responsible of the high corrosion rates exhibited by this type of alloys. The presence of some spherical particles, which look like microorganisms was evident in both cases, which is an evidence of the biocompatibility of the alloys.

The difference in corrosion protection by the addition of B has to be considered as an effect on the anchoring of any protective film by the addition of B and thermal annealing. It was observed that boron additions up to 500 ppm improved the corrosion resistance, which can be explained in terms of film formation on the surface sample which is generated by the boron presence on the matrix metal and specially (as it is well known) along the grain boundaries, generating a strong cohesion of the grains, fulfilling the groves between the grains, allowing a better anchoring of the formed passive film. Beyond this boron concentration, the corrosion resistance decreased, perhaps due to an over saturation of grain boundaries by boron, which produces a depletion of the corrosion passive products. It is very highly that the corrosion resistance decreased in the heat treated samples due to the boron volatilization during the heating process, where the rate of volatilization increases dramatically with increasing partial pressure of oxygen in the atmosphere surrounding the alloy at constant temperature [16]. When boron is removed from the surface, the surface activation is enhanced, leaving it exposed to the electrolytic solution.



Figure 11. Micrograph of NiTi exposed during 16 days alloy to the Hank's solution.



Figure 12. Micrograph of NiTi +200 ppm B exposed during 16 days alloy to the Hank's solution.

4. CONCLUSIONS

A study on the effect of B contents on the corrosion behavior of a NiTi alloy in the Hank's solution has been carried out. The main results have shown that by adding either 200 or 500 ppm B the corrosion rate of NiTi alloy decreased, but with the addition of 1000 ppm B it increased. When the alloys with B were thermally annealed at 900°C during 4 h, the corrosion rates were increased. In all cases, the passive current density was decreased with the addition of B regardless the heat treatment. For long time tests, regardless the heat treatment, additions of B increased the corrosion rate of NiTi alloy after a few hours of testing. The corrosion process was under charge transfer control for NiTi alloy, whereas it was under a mixed charge transfer and diffusion control for alloys with B. Results were discussed in terms of the stability and anchoring of the protective formed passive film on the different alloys.

References

- 1. N. Hallab, K. Merritt, J.J. Jacobs, J Bone and Joint Surgery 83 (2001) 428.
- 2. A. Choubey, B. Basu, R. Balasubramaniam, Trends Biomater: Artif Organs 18 (2005) 64.
- 3. T.M. Sridhar, U.K. Mudali, M. Subbaiyan, Corros. Sc. 45 (2003) 237.
- 4. Y.L. Zhou, M. Niinomi, T. Akahori, H. Fukui, H. Toda, Mat. Sci. Eng. 398A (2005) 28.
- 5. R.W.Y. Poon, J.P.Y. Ho, X. Liu, C.Y. Chung, Mat. Sci. Eng. 390A (2005) 444.
- 6. F.T. Cheng, K.H. Lo, H.C. Man, J Alloys Compounds 437 (2007) 322.
- 7. Y.F. Zheng, B.L. Wang, J.G. Wang, C. Li, L.C. Zhao, Mat. Sci. Eng. 438A (2006) 891.
- 8. Y.H. Li, G.B. Rao, L.J. Rong, Y.Y. Li, W. Ke, Mat. Sci. Eng. 363A (2003) 356.
- 9. W.Y. Guo, J. Surr, J.S. Wu, Mat. Chem. Phys. 113 (2008) 616.
- 10. J.H. Chern, K.S. Chen, C.P. Ju, Mat. Chem. Phys. 41 (1995) 282.
- 11. J. Mendoza-Canales, J. Marín-Cruz, Int. J. Electrochem. Sci., 3(2008) 346.
- 12. M. Jayalakshmi, Woo-Young Kim, Kwang-Deog Jung, Oh-Shim Joo, *Int. J. Electrochem. Sci.*, 3(2008) 908.
- 13. M. Metikos-Hukovic, R. Babic, Corros. Sci. 49 (2007) 3570.
- 14. M. Metikos-Hukovic, R. Babic, Corros. Sci. 51 (2009) 70.
- M. Clesic, W. Reczyski, A.M. Janus, K. Engvall, R.P. Socha, A. Kotarba, *Corros. Sci.* 51 (2009) 1157.
- 16. A.K. Shukla, R. Balasubramaniam, Corros. Sci. 48 (2006) 1696.
- 17. C.Li, Y.F. Zheng, L.C. Zhao, Mat. Sci. Eng. 438 A (2005) 504.
- 18. M.H. Wong, F.T. Cheng, H.C. Man, Materials Letters 61 (2007) 3391.
- 19. N.T.C. Oliveira, G. Aleixo, R. Caram, A.C. Guastaldi, Mat. Sci. Eng. 452A (2007) 727.
- 20. J.S. Lee, CM. Wayman, Trans. JIM 27, (1986) 584.
- 21. J.S. Lee, CM. Wayman, Proc. Int. Conf. on Martensite Trans. (ICOMAT-86), Japan Inst. Met., Sendai, 920 (1987).
- 22. M.J. Snyder, M.G. Mesko, J.E. Shelby, J Non-Crystalline Solids, 352 (2006) 669.

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