Comparative Study of Anodic Treatment on New $Ti_{70}Cu_{30}$ Alloy Passivation in 1N H_3PO_4, 1N $HClO_4$ and 1N HNO_3, at 25°C

H. Bouchemel and A. Benchettara

Laboratory of Electrochemistry-Corrosion, Metallurgy and Inorganic Chemistry,
-Faculty of Chemistry-USTHB-BP 32, El Alia-Bab Ezzouar, Algiers 16 111-Algeria
E-mail: bouchemelhassiba@gmail.com
E-mail: bbenchettara@hotmail.com

Abstract. Titanium is used in the medical prostheses but its expensive cost limits its use. A solution to this problem is to alloy it with copper. In this optic, we have elaborated the binary $Ti_{70}Cu_{30}$ and have anodically treated it in three acidic solutions. XRD, chronocoulometry and potentiodynamic polarization techniques are used to study the corrosion behaviour of $Ti_{70}Cu_{30}$ alloy in three acidic solutions. Different effects such as anodic treatment and copper addition on titanium has been examinated. This study revealed that $Ti_{70}Cu_{30}$ alloy resists better to corrosion in phosphoric acid before and after anodic treatment. Addition of 30at. % of copper has lead to a denser material with more noble corrosion potential and a cheap cost than pure titanium.

1. Introduction

Titanium and its alloys are widely employed in several applications (Biomedical, aeronautic and space industries, optical devices ...) [1, 2, 3-5]. In fact, together with their excellent mechanical properties, these materials present a high corrosion resistance [1, 6], even in very aggressive environments [7] as those containing chloride ions or in strongly acid electrolytes. This is due to the spontaneous formation of TiO_2 layer [1, 8-13] which is very stable chemically; its native thickness is in the order of few nm, but it can be increased greatly by anodic oxidation [7]. Anodising titanium and its alloys has been investigated by varying a wide range of parameters [14], including also the contribution of the electrolyte components, e.g. anions, in the formation of anodic films [14]. However, raising temperature accelerates the corrosion reaction and passive film dissolution [10-12] and makes non protective the TiO_2 oxide layer [13].

Titanium and its alloys have been the subject of many investigations in acid mediums, for example, in sulphuric acid environment [11, 15-19] in which the passivation is enhanced by the presence of the sulphate ions; in hydrochloric acid environment [20, 21] in which the phenomenon of pitting predominates

and finally in phosphoric acid [14] where an active-passive behaviour is observed.

The aim of this work is the study of the anodic treatment effect on the passivation of $Ti_{70}Cu_{30}$ alloy in phosphoric, perchloric and nitric acids. The objective of this anodic passivation is to reinforce the passive film spontaneously formed during time immersion of $Ti_{70}Cu_{30}$.

2. Experimental

Electrochemical measurements were made at 25° C using a cell containing aerated 1N orthophosphoric, perchloric or nitric acid. Ti (purity 99.99%, Aldrich) and Cu (Panreac, 8.96 density) were mixed in the appropriate proportions to obtain the $Ti_{70}Cu_{30}$ alloy. The mixture is arc melted in a furnace BUHLER MAMI under argon atmosphere. By preoccupation with a homogenisation of the sample, its fusion was repeated three times. The reference electrode was a saturated calomel electrode (SCE), which all potentials are referred to it. A platinum electrode was used as the counter electrode. The specimen was electrically connected to a copper wire and then imbedded into a dental resin. Before measurements were taken, the working electrode was polished with emery paper, washed thoroughly with distilled water
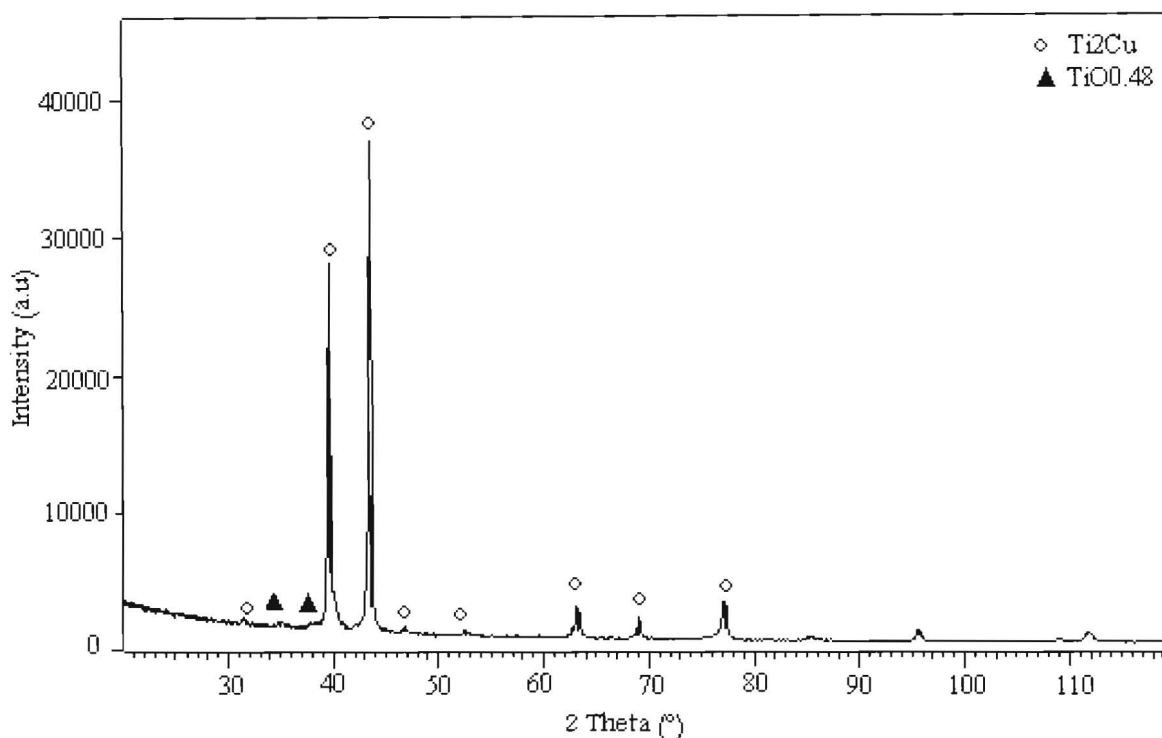
3. Characterization of $Ti_{70}Cu_{30}$ alloy

Fig.1. XRD pattern of $Ti_{70}Cu_{30}$ alloy (•) Ti_2Cu, (▲) $TiO_{0.48}$

Table.1. Crystallographic parameters of $Ti_{70}Cu_{30}$ alloy

	Chemical formula	Crystal system	a(A°)	b(A°)	c(A°)	α=β=γ(°)	Density(g/cm³)
$Ti_{70}Cu_{30}$	Ti_2Cu	Tetragonal	2.9438	2.9438	10.7861	90	5.66

and it was immediately immersed in the test solution. Corrosion measurements were performed with a computer-controlled potentiostat PGP 201, using Volta Master4.0 software. The tests were executed in the following order. First, OCP was monitored for 30min to establish a steady state open circuit potential. Then, without withdrawing the electrode from the corrosive acid solution, a constant potential of 0.4V has been applied to the interface $Ti_{70}Cu_{30}$ /corrosive solution, during 30 min in the same time chronocoulogram has been recorded. When the record of chronocoulogram is achieved the OCP was monitored again for 10 min. Finally, after all these steps. the anodic polarization was monitored at a scan rate of 1mV/s. During This protocol the temperature has been maintained constant at 25 ± 1°C. To be able to compare the alloy passivation after anodic treatment in relation to the one in absence of this treatment, another protocol consisting in the follow up of the free potential during 30min and the anodic polarization, with a potential scan rate of 1mV/s have been applied to the $Ti_{70}Cu_{30}$ / corrosive solution, at 25°C.

4. Results and discussion

4.1. Curves of chronocoulometry (anodic treatment)

Figure 2 shows the chronocoulogram curves of $Ti_{70}Cu_{30}$ immersed in 1N aqueous solutions of H_3PO_4, $HClO_4$ and HNO_3, at 25 ° C.

Figure 2 represents the chronocoulograms of $Ti_{70}Cu_{30}$ alloy. It has be seen from this figure that the current quantity consumes at 0.4V/SCE by this binary are more important in perchloric acid ($263mC/cm^2$) than those in phosphoric acid ($11mC/cm^2$) and nitric acid ($130mC/cm^2$) at 25° C. Therefore, $Ti_{70}Cu_{30}$ alloy is more reactive in perchloric solution. This observation shows clearly that the passive film

formed in perchloric acid is thicker than those formed in phosphoric and nitric acids; for the reason that, the faradic current increases in the same sense that the current quantities with the passive film thickness.
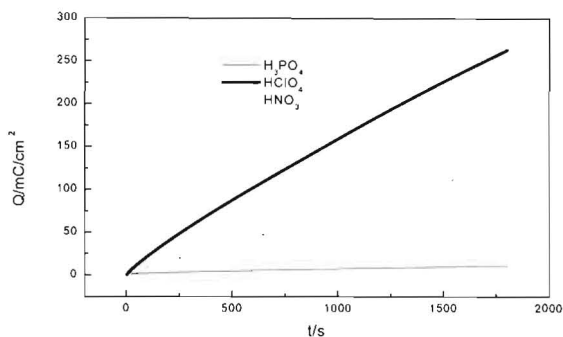

Fig. 2. Chronocoulogram curves of Ti$_{70}$Cu$_{30}$ immersed in 1N aqueous solutions of H$_3$PO$_4$, HClO$_4$ and HNO$_3$, at 25 °C.
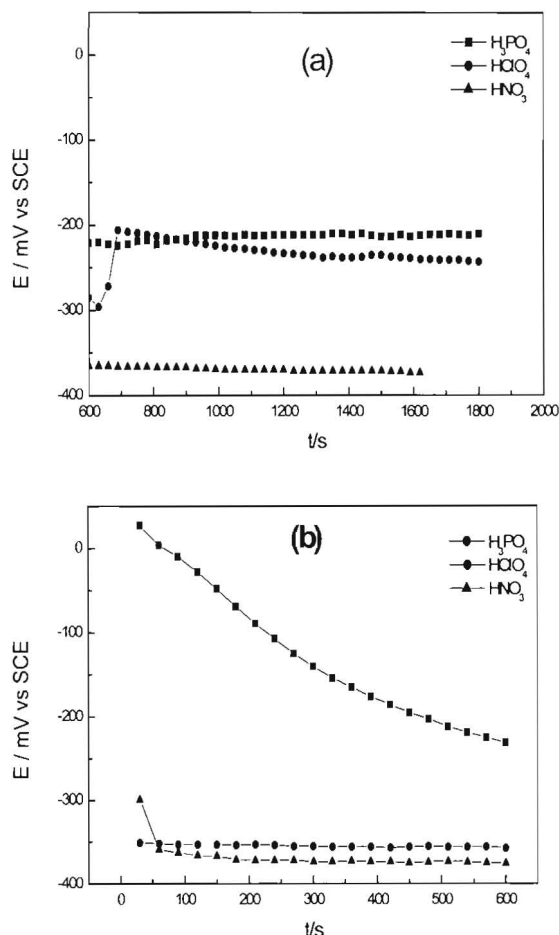

Fig. 3. Curves of free potentials of Ti$_{70}$Cu$_{30}$/corrosive solution interface at 25°C, (a): before anodic treatment, (b): after anodic treatment.

4.2 Effect of anodic treatment on Ti$_{70}$Cu$_{30}$ alloy free potential

Figure (3) shows the variation of OCP with time of Ti$_{70}$Cu$_{30}$ immersed in 1N aqueous solutions of H$_3$PO$_4$, HClO$_4$ and HNO$_3$, before and after anodic treatment.

In all studied acids, the OCP of Ti$_{70}$Cu$_{30}$ alloy is steady before anodic treatment. It stabilizes after 1800 s in phosphoric acid at -0.21V (SCE), in perchloric acid at -0.24 V (SCE) and in nitric acid at –0.37 V (SCE) (Fig.3a). Fig.3b shows that anodic treatment has no effect on free potential of Ti$_{70}$Cu$_{30}$ alloy in nitric acid; but it has displaced the free potential of binary in more cathodic value in perchloric acid. In phosphoric acid, the free potential of Ti$_{70}$Cu$_{30}$ alloy decreases continuously attesting that the passive film is unsteady. In phosphoric acid, the treatment has led to a passive film more anodic than those obtained in nitric and perchloric acids. But, this film at open circuit becomes less anodic, and its OCP shifts slowly towards less positive value. Despite this displacement of the potential remains more anodic than those formed in nitric and perchloric acids. In conclusion, in closed circuit, the phosphoric acid is more adequate to the passivation of Ti$_{70}$Cu$_{30}$.

4.3. Effect of anodic treatment on potentiodynamic polarization curves of Ti$_{70}$Cu$_{30}$

In fact most studies found in the literature are based on Ti, with the exception of few investigations such as potentiostatic investigations of the electrochemical behavior in sulphuric media of Ti-Cu alloys (Cu < 20 wt.%) have been carried out. With increasing copper content in the alloys, Tafel slopes decrease and potentials are shifted in the noble direction. The simultaneous dissolution of copper and titanium in the alloy Ti-20% Cu was observed by maintenance the potential at -0.6 V/SCE [22]. Lafargue et al. [22] showed that electrochemical study of Ti-Cu (2%) alloy has been performed in H$_2$SO$_4$ 2.5M showed that the shape of the polarization curves was closer to that of the pure titanium until the passivation peak was reached. Differences occurred in the passive domain where a new hump appeared at -10mV/SCE, and was essentially attributed to dissolution of surface copper. Khadiri et al. [1] showed that Ti-Cu (2%) in phosphoric acid can resists to corrosion in a wide temperature range and that its dissolution / passivation is governed by the Calandra-Müller model which states that the passivation of the metal is based on the formation of an insoluble film on the metal surface. The film formed is porous, as

predicted by Calandra-Müller model, and allow metal dissolution through the pore of the oxide layer [23]. Hodgson et al. [24] show that phosphate ions react with the oxide surface to form Ti-phosphates. Khadiri and Krasicka-Cydzik [1, 14] have been revealed that pure titanium resists to corrosion in phosphoric acid. Fig.4 shows that Ti70Cu30 alloy is more resistant to corrosion in 1N H3PO4 acid, at 25° C. The anodic treatment returned this alloy quasi passive in perchloric acid, and revealed an inflection point on the stage of passivation in phosphoric acid. We attribute this new oxidation to the formation of copper effect on the properties of titanium but it has a positive one because potential is shifted in the anodic direction and less cost. $Ti_{70}Cu_{30}$ alloy is denser ($5.66 g/cm^3$) than pure titanium ($4.50 g/cm^3$).

Table 2 reports the electrochemical parameters of the studied alloy, deduced from Tafel method. As reported in the first column (Before anodic treatment), the E_{cor} in perchloric acid is the noblest.

However, after anodic treatment, a cathodic shift of -97mV in $HClO_4$ and -56 mV in HNO_3 are observed; so, the corrosion potential varied with the anodic treatment. In all studied acids, the anodic treatment is very significant because it lowers the corrosion current densities values; especially in 1N H_3PO_4 where it decreases from 5.95 $\mu A/cm^2$ to 1.49 $\mu A/cm^2$.

Conclusion

In this work it has been shown that $Ti_{70}Cu_{30}$ alloy resists better to corrosion in phosphoric acid such as pure titanium, this is can be explained if we consider the properties of the phosphate film which cover the oxide surface and inhibits its dissolution. PO_4^{3-} ions interact with the surface of TiO_2 to form Ti-phosphates. However, the alloy develops a thicker film in perchloric acid than those formed in phosphoric and nitric acids (significant current quantities consumed). It seems that this film is
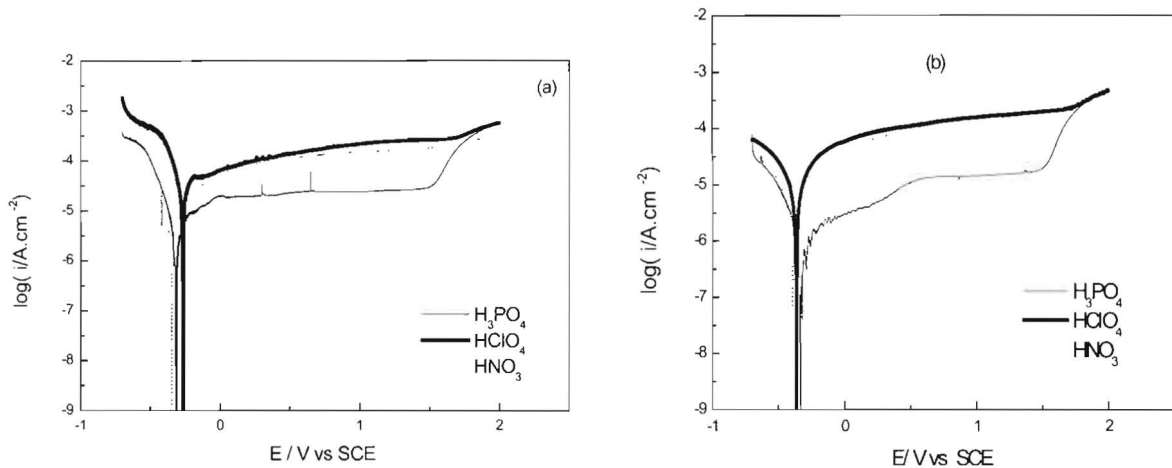

Fig. 4. Potentiodynamic polarization curves of $Ti_{70}Cu_{30}$ / corrosive solution interface at 25° C, (a): before anodic treatment (b):after anodic treatment.

Table 2. Electrochemical parameters of $Ti_{70}Cu_{30}$ alloy in various acid media 1N

Mediums	Before anodic treatment at 25° C					After anodic treatment at 25° C				
	E_{cor}/mV/ SCE	i_{cor}/μA /cm^2	R_p /kΩ.cm^2	β_a/ mV/dec	β_c / mV/dec	E_{cor}/ mV/ SCE	i_{cor}/μA /cm^2	R_p/ kΩ.cm^2	β_a/ mV/dec	β_c/ mV/dec
H_3PO_4	-315	5.95	18.33	490	-148	-337	1.49	5.76	315	-205
$HClO_4$	-267	33.66	1.13	940	-141	-364	16.84	9.34	585	-540
HNO_3	-348	13.51	5.49	567	-355	-404	6.15	9.39	307	-353

porous and allows metal dissolution through the pore of the oxide layer but the film formed in the phosphoric acid is more compact. Anodic treatment lowers the cathodic branches, decreases the passivation and corrosion current densities and shifts the corrosion potential towards more negative values. The addition of 30% Cu to pure titanium shifts the potential in the anodic direction. $Ti_{70}Cu_{30}$ alloy is denser than pure titanium.

References

[1] M. Khadiri, A.Benyaïch, A.Outzourhit, E-L.Ameziane, Ann.Chim.Sci.Mat 25 (2000) 447.

[2] C.E.B.Marino, L. H. Mascaro, Journal of Electroanalytical Chemistry 568 (2004) 115.

[3] F. Guillemot, J. Debuigne, D. Ansel, C .R. Acad. Sci. Paris, Chimie / Chemistry 4 (2001) 381.

[4] Mardare, G.I. Rusu, F. Iacomi, M. Girtan, I. Vida-Simiti, Materials Science and Engineering B 118 (2005) 187.

[5] Conforto, B.-O. Aronsson, A. Salito, C. Crestou, D. Caillard, Materials Science and Engineering C 24 (2004) 611.

[6] H.H. Uhlig, in: Wiley (Ed.), The Corrosion Handbook, New York, (1948).

[7] N.T.C. Oliveira, S.R. Biaggio, S. Piazza, C. Sunseri, F. Di Quarto, Electrochimica Acta 49 (2004) 4563.

[8] L. L .Shreir, Corrosion IMetal/ Environment Reactions, 2nd ed., 1976.

[9] M.F.Lopez, A. Gutierrez, J.A.Jimenez, Surface Science 482 (2001) 300.

[10] C. Kuphasuk, Y.Oshida, C.J.Andres, S.T.Hovijitra, M.T. Barco, T. Brown, The Journal of Prothestic Dentistry, 85 (2001) 195.

[11] L.Young, in: Academic Press (Ed.), Anodic Oxide Films, New York, 1962.

[12] Metikos-Hukovic, J. Bozicevic, S. Brinic, Electrochemical Society, 149 9 (2002) B450.

[13] Gurappa, Materials Science and Engineering A356 (2003) 372.

[14] E. Krasicka-Cydzik, Corrosion Science 46 (2004) 2487.

[15] L. Riggs.Jr, Corrosion N.A.C.E, 31 (1975) 11.

[16] T. Szauer, A.Brandt, Electrochimica Acta, 26 (1981) 1219.

[17] D. P. Schweinsberg, G. A. George, Corrosion Science 28 (1988) 33.

[18] Radu, S. Dumitru, Rev.Roum Chim, 34 (1989) 35.

[19] J. M. Macak, K.Sirotna, P.Schmuki, Electrochimica Acta 50 (2005) 3679.

[20] G.Wranglav, in: N.A.C.E (Ed.), Localised Corrosion, Houston, 1974.

[21] G.S.Ercund, Jer Kont Ann 154 (1970) 321.

[22] Lafargue, J. A. Petit et F. Dabosi, Journal of the Less-Common Metals, 56 (1977) 233.

[23] A.J.Calandra, W.J.Müller, Transient Techniques in Electrochemistry. Plenum Press (1977) 295.

[24] W.E Hodgson, Y. Mueller, D. Forster, S. Virtanen, Electrochimica Acta 47 (2002) 1913.