Electrochemical and corrosion resistance of new Ti-Mo-Fe alloys for biomedical applications

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Abstract

Titanium and its alloys have been used extensively in the last few decades as materials for orthopaedic and dental implants and other medical devices due to their high strength, low modulus and high corrosion resistance in biological media. Besides other important material features, the corrosion parameters and corrosion products are responsible for limiting the biocompatibility of metallic materials and can produce undesirable reactions in implant-adjacent and/or more distant tissues. Electrochemical corrosion behaviour of novel beta titanium alloys, Ti-4.7Mo-4.5Fe, Ti-3Mo-0.5Fe and Ti-2Mo-0.5Fe was investigated in naturally aerated Ringer's solution at room temperature compared with currently used biomedical titanium alloy, Ti-6Al-4V. Very low current densities were obtained from the potentiodynamic polarization curves, indicating a passive behaviour for all the studied alloys. Electrochemical impedance spectroscopic (EIS) studies showed high impedance values for all samples indicating an improvement in corrosion resistance of the spontaneous oxide layer. The fitting data obtained suggest a single passive layer form on the virgin surfaces of the alloys. The EIS results exhibited capacitive behaviour (high corrosion resistance) with phase angles close to -80° and high impedance values at low and medium frequencies, which are indicative of the formation of a highly stable film on these alloys in the test solution. The new alloys are promising metallic biomaterials for the future, owing to their very low elastic modulus and good corrosion resistance capabilities.

Keywords: titanium alloys, corrosion resistance, Ringer's solution.

1 Introduction

More than two thirds of implants are made of metallic biomaterials i.e. stainless steel, cobalt (Co)-chromium (Cr) alloys, and titanium (Ti) and its alloys. Among these metallic biomaterials, Ti alloys exhibit the highest biocompatibility, corrosion resistance and specific strength (ratio of strength to density), compared with the other metallic biomaterials [1]. Recently, researchers paid much attention to developing low rigidity β and near β type titanium alloys composed of non-toxic and non-allergic elements with excellent biocompatibility, superior corrosion resistance, high strength and low elastic modulus (close to that of human bone). The relatively low modulus of β and near- β titanium alloys may also reduce the “stress-shielding” effect [2–6]. Although titanium alloys possess a set of suitable properties for biomedical applications, their corrosion resistance still plays a vital role in such applications, whereas the corrosion products are largely responsible for limiting their biocompatibility and can cause inflammations with the implant-adjunct tissues. Therefore, a corrosion resistance investigation is considered one of the in-vitro evaluation procedures for the acceptance of these alloys as biomaterials. Fortunately, titanium and its alloys show high corrosion resistance due to the spontaneous formation of a protective oxide film of 1–4 nm thickness [7] on its surface at open circuit conditions. In physiological fluids that contain about 1 wt.% NaCl, the chloride present can destroy the oxide film, so it is necessary to investigate the durability and stability of these passive films in simulated body fluids [8].

Ti-4.7Mo-4.5Fe, Ti-3Mo-0.5Fe and Ti-2Mo-0.5Fe are a set of new beta titanium alloys developed to be used as biomaterials. The present work is undertaken to study the corrosion behaviour of the investigated alloys, as well as to compare their performance with that of commercial alloys such as Ti-6Al-4V thus to assess their performance and the possibility of their being used as biomaterials. Although there are many alloys used as biomaterials, they still have high cost, so the candidate materials are presented as low cost biomaterials.

2 Experimental procedure

2.1 Materials preparation

Nominal compositions of Ti-4.7Mo-4.5Fe, Ti-3Mo-0.5Fe and Ti-2Mo-0.5Fe (in atom %) alloys were arc-melted with a tungsten electrode on a water-cooled copper hearth. Titanium blocks were melted to purify the Ar gas atmosphere before the Ar-arc melting. All the ingots of the alloys were melted and inverted six times in order to promote their homogeneities. Specimens were solid-solution-treated (ST) at 1173 K in β phase field for 3.6 ks followed by rapid quenching into ice water. The designed alloys were selected to be investigated and characterized from the point view of corrosion to assess their performance as biomaterials.

2.2 Electrochemical evolution

Electrochemical experiments were conducted in two standard cells, namely, a polarization cell and a reference cell, connected by a salt-bridge probe. The polarization cell contained the working electrode and a platinum wire as a counter electrode, while the reference cell contained the standard saturated KCl Ag/AgCl reference electrode. Working electrolyte was a naturally aerated aqueous Ringer's physiological solution. The Ringer's solution has an electrolyte composition closer to that of plasma as compared to normal saline; this solution is composed of 0.32 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.3 g KCl, 8.6 g NaCl, and quantum sufficit of water for each 1000 mL of electrolyte; its measured pH was 5.4. Prior to any immersion, the working electrodes were grinded using 2000 grade silicon carbide paper and rinsed with distilled and de-ionized water. All electrochemical measurements were managed by a Princeton Applied Research potentiostat and controlled by a personal computer with dedicated software (VersaSTAT 4). In order to verify the reproducibility of electrochemical results, all experiments were repeated three times measured at the same sample, after a new polish for the surface of the working electrode and good reproducibility was observed.

Measurements of the open-circuit potential (OCP), for each composition were performed on the polished samples, until the potential values became reasonably stable. The corrosion potential was measured as a function of time for about 116 min. with a stability of about 0.005 mV/s.

Potential-dynamic polarization studies were carried out after 7,000 s of immersion in Ringer's solution after almost reaching the steady state. Potential-dynamic polarization measurements were performed in the potential range from -500 mV in the cathodic direction to 1600 mV in the anodic direction from the OCP vs. the Ag/AgCl reference electrode at a scan rate of 0.167 mV/s. The corrosion potential E_{corr} and corrosion current density i_{corr} were determined from the polarization curves using the Tafel extrapolation method.

Electrochemical impedance spectroscopy (EIS) measurements were carried out at open-circuit potential and the impedance spectra were acquired in the frequency range from 100 kHz to 100 mHz. The applied alternating potential signal had an amplitude of 10 mV. EIS plots were obtained after the specimens solution was treated at 900°C. Data acquisition and analysis were performed with a personal computer. The spectra were interpreted using the ZSimpWin software. Impedance data were represented in Bode amplitude and phase angle plots. The charge transfer resistance, R_s , and double-layer capacitance, CPE , values were determined. The Bode representation shows the logarithm of the impedance modulus ($\log Z$) and phase angle as a function of the frequency logarithm ($\log$ frequency).

2.3 Corroded surface

To characterize the anodic oxide films formed on the surface of the specimens, the latter were ultrasonically cleaned with methanol after the potential-dynamic polarization tests and then examined by the optical microscope.

3 Results and discussion

3.1 Open-circuit potential analysis

The OCP is the potential at which the specimen is in equilibrium with the surrounding environment. The open-circuit potential of metals is always measured as a function of time, until it stabilizes at a stationary value after a certain period of immersion. The open-circuit potential is used as a criterion for the corrosion behaviour. This type of measurement is qualitative and still insufficient for a complete electrochemical analysis.

The results obtained from the OCP with immersion time in Ringer's solution are presented in Fig. 1 and Table 1 for the studied alloys and at the different heat treatment conditions. As can be seen from Fig. 1, the potentials increase quickly during the first few minutes and then shift slowly in the more noble direction, until they reach quasi-stationary values. This behaviour is indicative on the spontaneous formation and growth of the oxide film on the surfaces of the samples. Furthermore, the OCP in the noble direction indicates that an oxide film is passivating the metallic surface [9]; this suggests that a protective passive film acts as a barrier against metal dissolution, reducing the corrosion rate. Al-Mobarak [10], in his research, gave another interpretation to the appearance of the initial shift of potential during the first few minutes; he claimed that the first shift is due to the dissolution of the pre-immersion oxide layer that formed in air before immersing the samples in the solution.

Figure 1: Open-circuit potential (OCP) versus time in Ringer's solution of Ti-4.7Mo-4.5Fe (denoted as "1"), Ti-3Mo-0.5Fe (denoted as "2"), Ti-2Mo-0.5Fe (denoted as "3"), and Ti-6Al-4V.

From the OCP profiles, a comparison among the obtained quasi-stationary OCP values for the specimens at different heat treatment conditions can be made. There is clear evidence regarding the effect of the heat treatment process from the variation of OCP values. As a result of the solution treatment process (ST900) after the hot rolling process (HR900), all the OCP values for all studied compositions were towards the noble direction; this result indicates that the

spontaneous oxide film formed on the alloys due to the solution treatment process displays better corrosion protection characteristics than the oxide film formed on hot rolled samples. By comparing the obtained results of the OCP of the studied compositions with the OCP of most widely used titanium alloy in the biomedical applications, Ti-6Al-4V, one can notice that the oxide film on the studied samples formed more rapidly than on Ti-6Al-4V. Nevertheless, they are mostly in agreement regarding the direction towards the noble direction.

Table 1: Open-circuit potentials at the steady state conditions for Ti-4.7Mo-4.5Fe (denoted as “1”), Ti-3Mo-0.5Fe (denoted as “2”), Ti-2Mo-0.5Fe (denoted as “3”), and Ti-6Al-4V in Ringer’s solution.

Heat treatment process ST900	
Samples	[OCP/mv vs. Ag/AgCl]
(1) Ti-4.7Mo-4.5Fe	-129±7
(2) Ti-3Mo-0.5Fe	-139±13
(3) Ti-2Mo-0.5Fe	-223±17
*Ti-6Al-4V	-233±15
<i>*Ti-6Al-4V used only for comparison and not subjected to any heat treatment process (used as received).</i>	

It is clear from the above OCP results that the heat treatment process is a strong factor in the electrochemical performance of the metals. These values of the OCP can be interpreted in the light of the present microstructures due to the heat treatment process. The type of the present crystal structure, i.e. hcp (α -phase), bcc (β -phase), orthorhombic α'' ...etc. influences the number of dislocations leading to differences in the mechanical properties of the alloys. These differences, i.e. in ductility, strength and so on, due to the heat treatment, will of course have an effect on the electrochemical properties such as OCP. The formed β -phase as a result of the solution treatment process affected the OCP values of the alloys and directed them towards the noble direction. Therefore, the denser the phase present is, the greater the reduction in the corrosion rate.

3.2 Potentio-dynamic polarization studies

Fig. 2 shows the potentio-dynamic polarization curves for the studied alloys compared with that for Ti-6Al-4V as tested in Ringer’s solution at 25°C. Potentio-dynamic polarization studies were conducted in the potential range of -500 mV to +1600 mV with respect to OCP vs. Ag/AgCl for all alloys. From these curves, the corrosion parameters, i.e. the corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) were obtained from the Tafel region, then the corrosion current density was used to determine the corrosion rate for all alloys. The corrosion current density is representative for the degradation degree of the alloy. A distinctive passivation region was observed on the anodic polarization curves for all the studied alloys. This region of passive film formation

was studied through the passivation current density (i_{pass}) which is obtained around the middle of the passive range. It was observed from Fig. 2 that the shape of the polarization curves is quite similar, while different corrosion parameters were determined for all alloys after heat treatment; see Table 2. This qualitative analysis of the polarization curves shows that the studied alloys have good potential to be used as biomaterials. The corrosion behaviour of the present new alloys shifts towards nobility, i.e. the corrosion potentials, (E_{corr}) shift towards positive values and the corrosion currents (i_{corr}) decrease compared to those of Ti-6Al-4V. The new alloys exhibit very high resistance to corrosion compared with one of the most commonly used biomaterial, Ti-6Al-4V. The corrosion parameters of the present new alloys are about ten times better than those of Ti-6Al-4V and this clearly indicates that these alloys have excellent pitting and crevice corrosion resistance.

Figure 2: Potentio-dynamic polarization curves for Ti-4.7Mo-4.5Fe (denoted as “1”), Ti-3Mo-0.5Fe (denoted as “2”) and Ti-2Mo-0.5Fe (denoted as “3”) after the heat treatment compared with Ti-6Al-4V (as received) in Ringer’s solution at room temperature.

The corrosion rates were obtained from the corrosion current densities using the following equation (ASTM Standard G102-89 [11]):

$$\text{Corrosion rate (in } \mu\text{m/year)} = 3.27 (i_{corr}/\rho) EW \quad (1)$$

where, i_{corr} is the corrosion current density in $\mu\text{A}/\text{cm}^2$, ρ the density ($4.51 \text{ g}/\text{cm}^3$) and the EW is the equivalent weight for titanium alloys:

$$EW = [\text{atomic weight (47.9)}] / [\text{the valence (4)}].$$

The calculated corrosion rates for the new present alloys at various heat treatments are tabulated in Table 2. The value of the corrosion rate is a significant parameter that gives valuable information about the real behaviour of the corrosion. The corrosion rate is directly proportional to the corrosion current density so they have the same trend. In conclusion, the present new alloys are more resistant to corrosion compared with the most widely used biomaterial, Ti-6Al-4V.

Table 2: Corrosion potential (E_{corr}), current density (i_{corr}) and passivation current density (i_{pass}) determined from the polarization curves for Ti-4.7Mo-4.5Fe (denoted as “1”), Ti-3Mo-0.5Fe (denoted as “2”) and Ti-2Mo-0.5Fe (denoted as “3”), after the heat treatment process, compared with those of Ti-6Al-4V (as-received) in Ringer’s solution at room temperature.

Potentio-dynamic characterization					
Compositions	Heat treatment	E_{corr} [mv vs. Ag/AgCl]	i_{corr} [nA/cm ²]	i_{pass} [μA/cm ²]	Corrosion rate [μm/year]
1	ST900 ^a	-110	6.876	2.804	0.060
2	ST900	-64	3.338	0.3915	0.029
3	ST900	-138	5.838	0.3449	0.051
Ti-6Al-4V	As-received	-319	661.8	6.561	5.746

Impedance (EIS) results of studied alloys were represented through the Bode plots as shown in Fig. 3. All specimens exhibit no significant change in their behaviour. This result could be due to a complete coverage of the surface of newly formed spontaneous oxide layer. In this paper, a satisfactory fit of all data could be obtained using simple equivalent circuit $R_s (Q R_p)$, see Fig. 4, where R_s and R_p are the solution and the oxide film resistances, respectively, while, Q is the constant phase element (CPE), indicating the capacitive behaviour of the film. It can be seen in Table 3 that all compositions have very small capacitance values and the values of n are near to 1, so Q presents an almost pure capacitive behaviour. For the oxide film resistance, R_p (Table 3) is of the same order of magnitude, $10^5 \Omega \cdot \text{cm}^2$, and these high values demonstrated that the spontaneous formed oxide layer on the alloys is a highly stable and resistive layer.

Table 3: Values of the equivalent circuit parameters derived from the fitting of the impedance data measured for the passive film grown spontaneously on the studied alloys, using the equivalent electric circuit $R_s (Q R_p)$, from Fig. 4.

Compositions	$R_s (\Omega \cdot \text{cm}^2)$	$Q (\text{S cm}^{-2} \text{s}^n)$	n	$R_p, (\Omega \cdot \text{cm}^2)$
1	24.45	7.13×10^{-5}	0.844	1.54×10^5
2	22.22	4.10×10^{-5}	0.825	7.53×10^5
3	29.63	3.92×10^{-5}	0.835	4.06×10^5

Figure 3: Bode diagrams of the studied alloys after solution treatment process at 900°C: (1) Ti-4.7Mo-4.5Fe, (2) Ti-3Mo-0.5Fe and (3) Ti-2Mo-0.5Fe.

Figure 4: Equivalent circuit, used for fitting the experimental data.

3.3 Corroded surfaces evaluation

Error! Reference source not found.5 shows the optical microscope (OM) micrographs of the passive oxide films formed on the surfaces of the designed alloys. The OM micrographs are in agreement with the above anodic curves whereas the morphologies of anodic films critically depend on the behaviour of the oxide layer growth. The oxide layer formed on the surfaces of the specimens after solution treatment depends on the composition of the specimen. For all studied compositions, passivation occurred and the very small corrosion rates give a good indication on the promise of the candidate alloys as biomaterials.

Figure 5: Optical microscope micrographs of oxide films on the surfaces of the studied alloys after anodic test: (a) Ti-4.7Mo-4.5Fe, (b) Ti-3Mo-0.5Fe and (c) Ti-2Mo-0.5Fe.

4 Conclusions

In this study, new titanium-iron based alloys were developed using a low-cost alloying element, iron, to reduce the total cost of the product. Two beta stabilizer elements were used in our alloys, Mo and Fe; the electrochemical properties of these alloys were studied. The main results are summarized as follows:

- The open circuit potentials (OCP) of the designed alloys in the Ringer's solution directed towards the positive direction and reached almost steady state condition within 30 min. The short time which has taken to

reach the steady state is good evidence of the stability of the formed oxide layer.

- The potentiodynamic tests after the solution treatment show very low corrosion rates for the present alloys.
- High impedance values were obtained for all studied alloys; the obtained fit suggests a single passive film present on the metals' surface.

All these electrochemical results are connected and suggest that Ti-Mo-Fe alloys are promising materials for biomedical applications because of their electrochemical stability.

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