In vitro corrosion behavior of Ti-Mo-W alloys in artificial saliva

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Abstract. Titanium and its alloys are preferred materials used for medical devices manufacturing due to their specific properties. The corrosion behavior in artificial saliva of the newly developed Ti-Mo-W alloys, with elastic modulus closer to the human bone value was studied by means of linear polarization technique in the following steps: i) measurement/monitoring of open circuit potential (E_{OC}) over 6 hours; ii) tracing linear polarization curves from ±200 mV (vs. OCP) - Tafel plots, with a scan rate of 0.167 mV/s. Electrochemical tests were performed according to ASTM G59-97 (2014) using a Potentiostat/Galvanostat which a low current interface (LCI) was coupled. The tests were performed in Fusayama Meyer artificial saliva with a pH of 5.2 at the human body temperature (37±0.5°C) which mimic the oral environment. The results indicate that the alloys Ti15Mo7W and Ti15Mo11W have better corrosion behavior than Ti6Al4V.

1. Introduction
The discovery of relatively inert metallic and alloy biomaterials has led to their use in the field of biomedical applications (orthopedics, dentistry) [1].

Pure titanium or titanium alloys has enjoyed great interest as one of the most important discoveries in this field. These materials are highly reactive and when exposed to aqueous media or air, they naturally develop a layer of titanium dioxide (TiO₂) through passivation process [2]. The TiO₂ layer is very protective and does not allow any further oxidation when implanted in the human body [3], being very resistant to the corrosive attack.

The corrosion phenomenon is the deterioration of the metal or alloy due to the electrochemical attack of the environment and can lead to the release of undesired and potentially toxic ions in the biological environment. Due to the microstructure of α + β, the Ti-6Al-4V alloy has excellent mechanical properties (high strength of 800-900 MPa and a modulus near 100 GPa) [4-6].

Unfortunately, the passive oxide films of additives (Al₂O₃ and VO₂) that form on the surface of the alloy are less stable than TiO₂, which can lead to corrosion of the alloy. Vanadium in the form of V₂O₅ is cytotoxic and induces adverse tissue reactions [7]. Aluminum plays a role in neurodegenerative disease [8-11]. However, Ti6Al4V is the most commonly used titanium alloy for implants [12-14]. Recently, new titanium alloys with comparable mechanical properties (with higher beta phase and low elasticity), but in which Vanadium has been replaced with Ta, Nb, Mo, Zr(Ti25Nb10Zr, Ti-6Al-7Nb, Ti-5Al-2.5Fe, Ti-5Al-3Mo-4Zr)are investigated [15-17].
The Ti-Mo-W alloys experimentally obtained and presented in this study is a novelty [18-21] and can be considered as a possible candidate for use in medical applications.

2. Materials and methods

2.1 The elaboration of the alloys

To obtain a biocompatible material, as a starting material was chosen the well-known Ti15Mo alloy due to its good corrosion resistance, to which was added a quantity of 7 wt. % wolfram (W) as an alloying element which does not show toxicity to the body and also enhances the elasticity modulus, bringing it closer to the value of human bone (raising the e/a ratio’s to the value of 4.24) as we reported in previous works [20].

The elaboration process of the Ti15Mo7W alloy was performed in vacuum arc remelting (VAR) equipment in a copper crucible cooled with water (VAR model 900 ABD MRF) using commercial high purity metals. Multiple melting’s were used due to the significant difference in density and melting temperature between titanium and molybdenum. The ABD MRF 900 furnace ensures the possibility of melting the metallic samples under the protective atmosphere by means of a mobile non-consumable tungsten electrode. The elaboration method of Ti15Mo7W alloy was made in vacuum, which ensured good homogeneity (advanced finesse of the structure) due to intense agitation and a short cooling time (cold-cooled copper crucible with water), and elimination of impurities by evaporation due to the high vacuum (10^-6 bar) [18-21].

In addition to VAR, we used the method of levitating melting for the Ti15Mo7W sample. The purpose of developing this Ti15Mo7W alloy on this experimental installation was to increase the homogeneity of the sample.

Table 1. Chemical composition of alloys subjected to corrosion test.

| Code | Alloy type     | W   | Mo   | Al   | V    | Ti   |
|------|----------------|-----|------|------|------|------|
| 1    | Ti15Mo11W      | 11.08 | 13.78 | -    | -    | 75.14|
| 2    | Ti15Mo9W       | 9.21  | 15.15 | -    | -    | 75.64|
| 3    | Ti15Mo7W       | 7.29  | 14.97 | -    | -    | 77.74|
| 4    | Ti15Mo7W       | 7.17  | 14.74 | -    | -    | 78.09|
| 5    | Ti6Al4V alloy  | -    | -    | 5.92 | 4.27 | 89.81|

2.2 In vitro corrosion behavior

The corrosion resistance of the experimental samples was carried out with a Potentiostat/Galvanostat (PARSTAT 4000 model, Princeton Applied Research, USA) to which a low current interface was coupled (VersaSTAT LC, Princeton Applied Research) (Figure 1), and potentiodynamic (Tafel) curves were acquired using the Versa Studio software.

The corrosion resistance was determined by linear polarization technique as follows:

- measurement/monitoring of open circuit potential (E_{OC}) over 6 hours;
- tracing linear polarization curves from ± 200 mV (vs. OCP) - Tafel plots, with a scan rate of 0.167 mV/s.

A classical three electrode cell (Figure 2) consisting of a calomel saturated electrode (SCE) - a reference electrode (RE), a platinum electrode - as counter electrode (CE) and a working electrode (WE) consisting of the experimental samples investigated (Figure 3) was used. The electrochemical tests were conducted in a Faraday cage to eliminate electromagnetic field interference.
Figure 1. Potentiostat/Galvanostat PARSTAT 4000 and low current module VersaSTAT LC.

Figure 2. The electrochemical cell configuration used in electrochemical tests.

Figure 3. Aspect of samples used in corrosion tests.

The tests were performed at the human body temperature (37 ± 0.5°C) which was kept constant by using a heating and recirculation bath model CW-05G produced by Jeio Tech.

The electrolyte used for corrosion tests was artificial saliva (AS) Fusayama Meyer (composition: 0.4 g·l\(^{-1}\) NaCl, 0.9 g·l\(^{-1}\) KCl, 1 g·l\(^{-1}\) urea, 0.69 g·l\(^{-1}\) NaH\(_2\)PO\(_4\), 0.795 g·l\(^{-1}\) CaCl\(_2\)·2H\(_2\)O) at pH = 5.2.

The polarization resistance was calculated according to ASTM G59-97 (2014) [22] using the equation:

\[
R_p = \frac{1}{2.3} \left( \frac{\beta_a |\beta_c|}{\beta_a + |\beta_c| i_{corr}} \right) \quad (1)
\]

Where:
- \(\beta_a\) – anodic Tafel slope,
- \(\beta_c\) – cathodic Tafel slope,
- \(i_{corr}\) – corrosion current density.

The corrosion rate was calculated according to ASTM G102-89 (2015)[23] using the formula:

\[
CR = K_i \frac{i_{corr}}{\rho} EW \quad (2)
\]
Where:

- CR – corrosion rate,
- $K_i$ – constant which defines the units of corrosion rate ($3.27 \times 10^{-3}$),
- $\rho$ – density,
- $i_{corr}$ – corrosion current density,
- EW – equivalent weight.

3. Results and discussions

In Figure 4-8 are presented the Tafel curves, based on which the main electrochemical parameters were extracted.

**Figure 4.** Tafel plot of the Ti15Mo11W sample.

**Figure 5.** Tafel plot of the Ti15Mo9W sample.
Figure 6. Tafel plot of the Ti15Mo7W sample.

Figure 7. Tafel plot of the Ti15Mo7W sample (elaborated in a levitating furnace).

Figure 8. Tafel plot of the Ti6Al4V sample.
For a better results comparison, they were overlapped in a graph (Figure 9).

![Figure 9. Tafel plots of the investigated samples.](image)

In Table 2 are presented the values of the main electrochemical parameters of the investigated samples.

| Sample code | $E_{\text{corr}}$ (mV) | $i_{\text{corr}}$ (nA/cm$^2$) | $\beta_c$ (mV) | $\beta_a$ (mV) | $R_p$ (kΩ·cm$^2$) | CR (µm/year) |
|-------------|------------------------|-------------------------------|----------------|---------------|-----------------|--------------|
| 1           | -204.6                 | 24.155                        | 100.6          | 218.2         | 1239.55         | 0.247        |
| 2           | 107.7                  | 66.577                        | 234.6          | 335.8         | 902.17          | 0.688        |
| 3           | -269.5                 | 15.364                        | 52.2           | 135.4         | 1067.65         | 0.150        |
| 4           | -163.4                 | 39.923                        | 78.4           | 357.5         | 700.47          | 0.409        |
| 5           | 33.92                  | 42.693                        | 130.94         | 163.88        | 932.78          | 0.390        |

4. Conclusions
If we take into account the value of the corrosion potential ($E_{\text{corr}}$), it is considered that a more electropositive corrosion potential $E_{\text{corr}}$ values indicates a better corrosion behavior. Based on this criterion we noticed that sample 2 showed the most electropositive value (107.7 mV) and from this point of view a better corrosion behavior in the electrolyte used.

It is known that a low corrosion current density ($i_{\text{corr}}$) indicates good corrosion resistance. Thus, if we consider this criterion, it can be observed that sample 3 recorded the lowest value (15.364 nA/cm$^2$) of all and a lower value than Ti6Al4V sample (42.693 nA/cm$^2$) demonstrating that it exhibits better corrosion resistance. At a small difference of approximately 9 nA/cm$^2$, sample 1 with a corrosion current density value of 24.155 nA/cm$^2$ can be found. It is noticed that the coded alloys 1, 3 and 4 record smaller values compared to Ti6Al4V alloy (sample 5).

It is known that a high polarization resistance ($R_p$) highlights a good corrosion behavior of a material, while a lower value of this parameter indicates a poor corrosion behavior. Thus, it was observed that the highest value compared to Ti6Al4V, were noted for sample 1 (1239.55 kΩ·cm$^2$) followed by sample 3 (1067.65 kΩ·cm$^2$).
According to the corrosion rate (CR) of the investigated alloys, it was observed that the lowest value was registered for sample 3 (0.15 μm/year), followed by sample 1 (0.247 μm/year). Thus, samples 1 and 3 have a lower corrosion rate than Ti6Al4V alloy. Also, sample 4 has a value of CR very close to that of the Ti6Al4V alloy.

By comparing the values of the main electrochemical parameters corresponding to the investigated alloys it can be concluded that the experimental samples demonstrate good corrosion resistance in the artificial saliva, except sample 2 which have indicated the poorest corrosion resistance of all samples. Due to their remarkable corrosion behavior, sample 3 which had the lowest corrosion current density and corrosion rate and sample 1 with the highest passivation resistance can be considered as potential candidates for medical applications.

5. References
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