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Corrosion Behaviour in Human Stimulation Media of a High Entropy Titan-Based Alloy

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Abstract. The paper presents results on the corrosion behavior of high entropy alloys, commonly called BIOHEA in human physiological simulating media, respectively in the NaCl infusion solution and Ringer's lactate infusion solution. Corrosion tests were performed by potendiodinamic test using AUTOLAB type potentiostat equipped with specialized corrosion software including the PGSTAT302N, BA and SCAN250 modules. Three entropy alloy systems were investigated: FeTa0.5Nb0.5Ti1.5Zr0.5 (BIOHEA 1), FeMnNb0.5TiZr0.5 (BIOHEA 3), FeTa0.5Nb0.5TiZr0.5 (BIOHEA 4), and BIOHEA alloy 2 was obtained by remelting BIOHEA 1. A comparison of the results obtained in the present tests and the data from the literature shows, on the one hand, that the global results can be compared with the different results from the literature, and, on the other hand, the results are new, in the sense that in any work there are no combinations of alloys studied here or human simulating medians used for testing. The conclusion of the experimental investigations in the present paper is the fact that regardless of the simulation test environment, all the alloys experimental alloys have similar behaviors, there is a difference between the chemical composition of the experimental alloy and the displacement of the corrosion potential values at electropositive values, decreasing of corrosion current, and corrosion rates. The experimental results allow the corrosion resistance of the investigated alloys, alloy BIOHEA 2 having the best corrosion behavior in both test media, with very low corrosion rates (respectively 0.067 μm/year in NaCl infusion solution, and 0.021 μm / year in Ringer's lactate infusion solution).

1. Introduction

Mechanical biocompatibility of biomaterials is an important factor for development of new β-titanium alloys, which are advantageous for manufacturing orthopaedic implants.

The β stability can be described by a lot of alloying elements, such as niobium (Nb), tantalum (Ta), zirconium (Zr), molybdenum (Mo), vanadium (V), iron (Fe), etc [1].

Thus, in the last years Nb, Ta and Zr are considered the most favorable non-toxic and non-allergic alloying elements for β-titanium alloys for biomedical applications.

The advantages of the beta titanium alloys consist in the highest strength to weight ratios, lower modulus and very attractive combinations of strength, toughness and fatigue resistance compared to α-type and α+β-type Ti-alloys.
From β-type Ti-based alloys the most reported biomaterials are: Ti-Nb-Ta-Mo, Ti-Nb-Ta-Sn, Ti-Nb-Ta-Zr, Ti-Nb-Sn, Ti-Zr-Cr-Mo, Ti-Mo-Nb, Ti-Mo-Ta, Ti-Ta, Ti-Zr-Mo, Ti-Nb-Zr-Ta, [2÷10]. Many of these alloys contain more or less amounts of Nb, Ta, Zr, Mo, Sn and/or Cr.

These alloys are generally obtained by melting followed by heat treatment or sintering followed by hot-forging and cold rolling.

These alloys have elastic modulus between 42-93 GPa, tensile strength between 597 ÷ 1037 MPa, yield strength 547 - 908 MPa and elongation 13-19% [11, 12].

Recently, a new Ti-based alloy (Ti-Nb-Zr-Ta-Fe) was reported with 2425 MPa yield strength and 52 Young modulus obtained after heat treatment at 960°C, with dual β structure and grain size with average of 200-300nm [13].

Another method for obtaining Ti-based alloys more and more investigated in the last years is powder metallurgy, that use elemental or pre-alloyed powders, and leads to porous titanium parts at much lower temperature, with more precise control of process variables and pore size, as well as physical and chemical characteristics.

The most investigated Ti-based alloy obtained by this method are: Ti-Nb, Ti-Nb-Zr, Ti-Nb-Ta-Zr, Ti-Mo, Ti-Nb-Mo, Ti-Nb-Zr-Sn, Ti-Nb-Ta-Mn, Ti-Nb-Zr-Ta-Si etc [14÷23].

The paper presents study the corrosion behavior of high entropy alloys, commonly called BIOHEA in human physiological simulating media, respectively in the NaCl infusion solution and Ringer's lactate infusion solution.

2. Materials and experimental procedures
Chemical composition of the experimental BIOHEA alloys is given in Table 1.

| Alloy     | Chemical composition of the alloy, %wt |
|-----------|----------------------------------------|
|           | Fe   | Mn   | Nb   | Ta   | Zr   | Ti   |
| BIOBEA 1,2| 49.51 | -    | 41.17| 80.22| 40.42| 63.65|
| BIOHEA 3  | 66.83 | 65.74| 55.58| -    | 54.56| 57.28|
| BIOHEA 4  | 58.52 | -    | 48.67| 94.84| 47.78| 50.16|

The corrosion behavior of the BIOHEA experimental alloys in human physiological simulating media, respectively, in the NaCl infusion solution and Ringer's lactate infusion solution, was performed by potentiotodynamic testing using a potentiostat - galvanostat of type AUTOLAB type equipped with specialized corrosion software including the PGSTAT302N, BA and SCAN250, endowed with the Department of Materials Science and Physical Metallurgy, Polytechnic University of Bucharest.

3. Results and discussions
Results concerning corrosion resistance of the experimental BIOHEA alloys are given in Figure 1, Figure 2 and Figure 3.
Figure 1. Tafel slope construction of the BIOHEA experimental alloys after testing in the NaCl infusion solution: a-alloy BIOHEA 3, b-alloy BIOHEA 4, alloy BIOHEA 1, alloy BIOHEA 2.
Figure 2. Tafel slope construction of BIOHEA experimental alloys after testing in Ringer's solution: a-alloy BIOHEA 3, b-alloy BIOHEA 4, c-alloy BIOHEA 1, alloy BIOHEA 2.
Analysis of comparative results by type of test environment led to the following observations:

3.1. NaCl solution environment for infusion (with 9 g NaCl per 1000 ml solution for infusion)
The comparative analysis of the experimental alloys in NaCl infusion solution is given in Table 2. For the experimental alloys, it is observed that the corrosion potential moves to more electropositive values depending on the type of experimental alloy, respectively from -187 mV (BIOHEA 3 alloy), at -177 mV (BIOHEA 4 alloy), then at -70 mV (BIOHEA 1 alloy), reaching to a positive value of +79 mV (for BIOHEA 2 alloy). Similarly, the values of corrosion currents, namely 1.9x10⁻³ μA / cm² (for BIOHEA 3 alloy), 1.1x10⁻³ μA / cm² (for BIOHEA 4 alloy), 5.89x10⁻⁵ μA / cm² (for BIOHEA alloy 1), having the lowest value on the reheated alloy, respectively 3.16 x 10⁻⁶ μA / cm² (at BIOHEA 2 alloy). Also, the corrosion rate, which is related to the corrosion current density, decreases in the same manner from 40.36 μm / year (at BIOHEA 3 alloy) to 22.9 μm / year (at BIOHEA 4 alloy), 11.93 μm / year (at BIOHEA 1 alloy) and reaching 0.067 μm / year (at BIOHEA 2 alloy).

It can thus be concluded that in this test environment, all the experimental alloys have similar behaviors, there being a differentiation given by the chemical composition of the experimental alloy, respectively the displacement of the corrosion potential values at electropositive values, decreases the density of the corrosion current, and the decrease of the velocity of corrosion to a very low value, 0.067μm / year, as shown in Figure 4.

3.2. Lactate medium, Ringer’s solution
Analysis of the comparative results in the Ringer Solution Test Medium of the experimental alloys is shown in Table 1. For the experimental alloys, it is observed the displacement of the corrosion potential from -188 mV (at BIOHEA 3 alloy) to -177 mV (at BIOHEA 4 alloy), -90 mV (at BIOHEA 1 alloy) reaching -80 mV (on BIOHEA alloy 2). Also, corrosion density values drop from 1.16. 10⁻³ μA / cm² (at BIOHEA alloy 3) at 2.01-10⁻⁴ μA/cm² (at BIOHEA 4 alloy), 8.24.10⁻³ μA/cm² (at
BIOHEA 1 alloy) and $3.71.105 \mu A / cm^2$ (to BIOHEA alloy 2). In the same way, corrosion rate values also drop from $23.45 \mu m / year$ (at BIOHEA 3 alloy) to $4.063 \mu m / year$ (at BIOHEA 4 alloy), at $1.66 \mu m / year$ (on BIOHEA 1 alloy) up to at $0.75 \mu m / year$ (at BIOHEA 2 alloy). Regarding the behavior of alloys in NaCl solution, the Ringer Solution Corrosion Parameters can be estimated to be approximately similar except for BIOHEA 2 alloy with a positive corrosion potential and a low corrosion rate relative to other alloys in the same state.

### Table 2. Corrosion parameters and Tafel slope construction results for the experimental alloys after corrosion testing in human simulant solutions.

| Alloy   | E_corr [mV] | i_corr, [µA] | Rp [Ohm] | I_corr [µA/cm²] | Corrosion rate [µm/an] | bc [V/dec] | ba [V/dec] | character |
|---------|-------------|--------------|----------|-----------------|------------------------|------------|-----------|-----------|
| **Corrosion test in NaCl solution** |             |              |          |                 |                        |            |           |           |
| BIOHEA 3 | -187        | 5.58.10^4    | 40034    | 1.99.10^-3     | 40,36                  | 0,010      | 0,016     | Chatodic  |
| BIOHEA 4 | -177        | 3.18.10^4    | 93189    | 1.13.10^-3     | 22,90                  | 0,016      | 0,014     | anodic    |
| BIOHEA 1 | -70         | 1.65.10^4    | 119440   | 5.89.10^-4     | 11,93                  | 0,013      | 0,014     | Chatodic  |
| BIOHEA 2 | +79         | 1.27.10^-6   | 1780900  | 3.16.10^-6     | 0,067                  | 0,010      | 0,010     | mixt      |
| **Corrosion test in Ringer's solution** |             |              |          |                 |                        |            |           |           |
| BIOHEA 3 | -188        | 5.61.10^-5   | 62118    | 1.16.10^-3     | 23,45                  | 0,017      | 0,015     | anodic    |
| BIOHEA 4 | -177        | 3.24.10^-4   | 98339    | 2.01.10^-4     | 4,063                  | 0,014      | 0,017     | Chatodic  |
| BIOHEA 1 | -90         | 2.34.10^-5   | 212540   | 8.24.10^-5     | 1,660                  | 0,021      | 0,024     | Chatodic  |
| BIOHEA 2 | -80         | 1.04.10^-5   | 440390   | 3.71.10^-5     | 0,75                   | 0,020      | 0,021     | Chatodic  |

It is also found in testing the Ringer’s solution that the corrosion potential moves to more electropositive values, the corrosion current and the corrosion rates decrease in the same way depending on the chemical composition of the alloy. The same observation can be made for both the current density values, from $3.43.10^-4 \mu A / cm^2$ (for BIOHEA 3 alloy), $9.89.10^-5 \mu A / cm^2$ (for BIOHEA 4 alloy), $2.36.10^-5\mu A / cm^2$ (for BIOHEA 1 alloy) and $1.23.10^-6 \mu A / cm^2$ (for BIOHEA 2 alloy) and for corrosion rate values, which are in the range of $6.9\mu m / year\div 0.026\mu m / year$. Corrosion potential decomposed from $-188mV$ (at BIOHEA 3 alloy), $-70mV$ (at BIOHEA 4 alloy), $-40mV$ (at BIOHEA 1 alloy), reaching $-20mV$ (at BIOHEA 2 alloy). There is also a decrease in the value of the current ranges, from $4,67.10^-3 \mu A / cm^2$, to $1.26.10^-3 \mu A / cm^2$, to $1.13.10^-3 \mu A / cm^2$ and $9.83.10^-3 \mu A / cm^2$, and corrosion rates from $99.7\mu m / year$ to $22.5\mu m / year$, $22.9\mu m / year$ and reaching $0.021\mu m / year$ for BIOHEA 2 alloy.

A comparison of the results obtained in the present tests and the data from the literature allow us to make some interesting observations. On the one hand, the overall results can be compared to the different results from the literature, on the other hand the results are new, meaning that in any paper there are no combinations of alloys studied here or the simulating human environments used for testing. Thus, Ho [24÷26] indicates corrosion potential values between $-400 \div -200mV$, but on Ti-7,5Mo alloys compared to the classical Ti6Al4V alloy, the tests here are in physiological simulant liquid, different from the two solutions treatment in this paper. Oliviera [27-30] studying the electrochemical behavior of a set of Ti-Mo alloys, obtain curves on another, that of the open stream of Na₂SO₄ and Ringer's solution.
Figure 4. Comparative results concerning corrosion rates of the BIOHEA experimental alloys after testing in human simulating environments.

Comparable results also offer More [31], but on Ti-29Nb-13Ta-4.6Zr alloys, which compares with the Ti-12.5Mo alloy, resulting in 900mV (more electronegative potential than in our). Kumar [32÷35] studies the behavior of pure titanium in Ringer's solution to create maps of the occurrence of simultaneous corrosion-friction-wear phenomena. Gonzales [36] studying the corrosion behavior of titanium and titanium alloys as a biomaterial for dental applications concludes that molybdenum increases the stability of the passive phase, widening the passive alloy domain, by forming chlorides in molybdenum-soluble. All Kumar [32÷35] in other works obtains for Ti-15Mo alloys, with different concentrations of NaCl, the corrosion potential in the range -275 ÷ -457 mV, with corrosion currents of 0.31 ÷ 2.3 μA/cm² which increase with the concentration of floral ions in the solution. Mayouf [37] compares the Ti₆Al₄V to pure titanium and Ti₃O₁₀Ag in different flora-containing media, yielding low potency values ~ -500mv. These authors mark the presence of corrosion located on the surface of the materials. Chapel [38] studies the repeatability of the corrosion parameters of Ti-Mo alloys in 0.9% NaCl solution, demonstrating the beneficial effect of molybdenum by lowering the corrosion susceptibility of Ti-Mo alloys in human simulating aggressive media containing 0.9% NaCl. Karthega [39] studies the electrochemical behavior of β-Ti alloys, but in the Hanck’s solution. They show the high corrosion resistance of Ti-Mo alloys by forming compact layers on the surface of the metal.

4. Conclusions
The corrosion tests carried out in this paper confirm the possibility of obtaining HEA biocompatible alloys with superior characteristics and confer the judicious selection of selected chemical elements.

Alloys containing Nb and Ta have superior corrosion resistance characteristics, which confirm the beneficial effect of these elements on corrosion resistance;

The reheated alloy (BIOHEA 2) exhibits the best corrosion resistance due to the improvement of the alloy microstructure and the increase of the homogeneity of the chemical composition in its volume.

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