Preliminary Tests for Ti-Mo-Zr-Ta Alloys as Potential Biomaterials

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Abstract. Nowadays, there is a continuing concern for the research and development of alloys for medical and biomedical applications. In order to check the biocompatible character of a new Ti-Mo-Zr-Ta alloys, it is necessary to carry out preliminary laboratory tests to follow how a biomaterial surface would interact with the host. The paper presents tests for Ti-Mo-Zr-Ta alloys like contact angle and DSC test to identify biocompatible character. Contact angle measurement is an experimental technique used to assess the hydrophilic or hydrophobic character of surfaces by reference to the 90º contact angle value and to characterize the thermal behavior, for temperature range between 36.5-37.2°C, interval which a biomaterial works inside the healthy human body, was used DSC test.

1. Introduction
Biomaterials play an important role in many aspects of the contemporary medical field through considerable progress over time. These are products of organic or inorganic nature that find various uses: prostheses or implants in biological tissues in humans or animals. In order to obtain these materials used for biological purposes, are used metals, ceramics, organic polymers etc. [1-5].

The common element of all biomaterials is their biocompatibility with human tissue, so that the response to the interaction between the implant and human tissue is positive without causing adverse reactions [1, 6, 7].

Pure titanium and Ti6Al4V alloy were the first titanium-based materials for commercial use, used as biomaterials. Titanium and its alloys have lately become an important alternative in medical applications being considered the safest material for implantation. There has been a growing interest in their application in the medical field taking into account the properties they present (mechanical properties, low density, good biocompatibility, increased corrosion resistance, etc.) [6-9].

As the alloying elements are added to the titanium, there is a modification of temperature at which occurs the phase transformation. Alloying the pure titanium with stabilizing elements α, increases the
temperature range in which there is phase α, respectively the alloy with elements β, leads to an increase of the β phase domain. Other elements such as Zr or Sn have a neutral contribution to the temperature domains in which the two phases exist [1, 6-11].

Studies have shown that β-type alloys, due to molybdenum stabilizing, tantalum and niobium stabilizers, have the advantage of increasing mechanical strength and an elastic modulus close to that of the human bone, important aspects of the use long time of biomaterials in the medical field [6-9].

Ti-Mo alloys with various biocompatible elements such as zirconium and tantalum show superior mechanical properties such as high tensile strength and a much lower modulus of elasticity close to that of human bone compared to other classical biomaterials [1].

This research work is focus on tests for two alloys, Ti15Mo7Zr15Ta and Ti20Mo7Zr15Ta (TMZT), tests like contact angle and DSC test to identify biocompatible character.

Biocompatible materials, such as titanium alloys, have been used and are used in the form of implants that come in contact with tissues. The wettability of biomaterial surfaces is a physico-chemical property of the important surface in the realization / optimization of cell adhesion and proliferation. Thus, the surface properties of the materials are essentially to be analyzed to determine interactions with host tissues.

Differential Calorimetric Analysis (DSC) refers to the quantitative measurement of heat exchange during a thermodynamic process. To characterize the thermal behavior, the temperature range to be watched is between 36.5-37.2ºC, the interval within which a biomaterial works inside the healthy human body.

2. Methodology
The alloys analyzed were obtained with a vacuum arc vacuuming equipment MRF ABJ 900 using as raw materials high purity elements such as Ti-99.8%, Mo-99.7%, Zr-99.2% and 99.5% Ta.

One of the biomaterial requirements is cellular adhesion on the surface of the material, depending on surface energy. Specialty studies have indicated that contact angle measurement is important for the study of cell adhesion to the surface of the studied material [12].

Measurement of the contact angle (Figure 1) is an experimental technique used to assess the hydrophilic or hydrophobic character of the surfaces. If the angle of contact is between 0-90°, the material is hydrophilic and hydrophobic, if the angle of contact is between 90-180° [13].

![Figure 1. Measurement of contact angle for hydrophilic and hydrophobic surfaces [12].](image)

The choice to use distilled water as a control sample in assessing contact angle for experimental TMZT alloys is based on the fact that water represents 70% of the human body.

The value of contact angle of water in contact with TMZT alloys was determined by the Sessile Drop [13]. Method (Sessile Drop Method), determining the hydrophilic or hydrophobic character of investigated experimental alloys. The principle of measuring the angle of contact is by placing a drop of water with a microsurge, with the drop volume of 4 microlitres. Drop lighting is made from behind and recorded from the opposite side with a digital camera. The image obtained is further analyzed by the Famas software, an integrated software for KYOWA goniometers [13, 14].

In order to measure the contact angle of TMZT alloys, 10 mm x 10 mm x 5 mm samples were used.
The DSC allows to obtain information on the processing temperatures associated with the alloying processes. The results of the calorimetric measurements are represented by a curve called a thermogram, conventionally denominated in the DSC curve [15, 18].

Both the sample crucible and the standard (which is an empty crucible) are placed inside the DSC system cell. The temperature difference between the sample and the reference is measured and recorded as a heat flux.

The temperature is measured with three thermocouples, one indicating the sample temperature, the second reference temperature, and the final temperature of the furnace. The output signal from DSC is taken over by a computer that performs data analysis with a suitable software (NETZSCH PROTEUS Thermal Analysis). DSC analysis equipment also includes a cylinder with inert gas (argon) and one with coolant (liquid nitrogen).

In view of the thermal analysis by differential calorimetric analysis of TMZT alloys, samples were prepared at sizes corresponding to the mass up to 50 mg, the dimensions being imposed by the dimensions of the crucibles where the samples were tested. From the measurements made after the sampling, it was found that the actual mass is in a range of 42-49 mg.

3. Results and discussion

The water drop on the sample surface was recorded using a digital camera. The images obtained were then analyzed through the Famas program. Figure 2 shows the water droplet image on the surface of the TMZT alloys. These differ depending on the contact angle the water forms on the surface of the sample.

Research in the field, affirm that materials with moderately hydrophilic surfaces improve adhesion, cell growth and ultimately biocompatibility, and a hydrophobic surface can lead to decreased adhesion and loss of biocompatibility [16-19].

10 measurements of the contact angle (θ) for each experimental alloy were performed and the value presented is the average of the measured measurements with the maximum error of ± 1º. The mean value of contact angle for each alloy is shown in Table 1.

| Table 1. Values of contact angle with water at the surface of TMZT alloys. |
|------------------|------------------|------------------|
| Alloy            | Ti15Mo7Zr15Ta    | Ti20Mo7Zr15Ta    |
| Liquid used      | water            | water            |
| Contact angle (degrees) | 57,93            | 56,11            |

Figure 2. Images of water droplet on the surface of TMZT alloys: (a) Ti15Mo7Zr15Ta, (b) Ti20Mo7Zr15Ta.
The two investigated alloys have a contact angle of less than 90° (Figure 2), thus exhibiting a hydrophilic character, which means high cell adhesion to the surface of the alloys. From the data obtained for the surfaces of the two TMZT alloys analyzed, the highest arithmetic mean value is recorded at the water contact angle on the Ti15Mo7Zr15Ta alloy surface and the lowest at the Ti20Mo7Zr15Ta alloy, this alloy having a more pronounced hydrophilic character.

From the results obtained it was observed that the alloy with a percentage of 20% Mo, shows the best value. The values of TMZT alloys obtained from the surface moisture analysis are certified to be that titanium alloys have a good interaction with tissues host. Thus, we have the certainty of good cellular adhesion, which could allow for the "in vitro" analysis of the determination of good biocompatibility for the use of alloys developed in the human body.

Thermograms recorded following the DSC analysis performed with PROTEUS are shown in Figure 3. The thermal regime to which the analyzed samples were subjected was:

- a. heating from room temperature to 40ºC at a rate of 10ºC / min;
- b. cooling at 10ºC / min to room temperature.

The thermograms of the investigated TMZT alloys did not record phase transformations in the 30-40ºC temperature range. As a result of the thermal analysis, the investigated alloys show stable values for the analyzed interval, interval which a biomaterial works in a human body.

![Thermograms obtained for experimental alloys: (a) Ti15Mo7Zr15Ta, (b) Ti20Mo7Zr15Ta.](image)

Figure 3. Thermograms obtained for experimental alloys: (a) Ti15Mo7Zr15Ta, (b) Ti20Mo7Zr15Ta.

Following thermal analysis by DSC, TMZT alloys showed thermal stability at the temperature of the human body, showing good interaction with the cellular host for use as medical implants.

4. Conclusions

Biocompatible materials, such as titanium alloys, have been used and are used in the form of implants that come into contact with living tissues, thus the surface properties of these materials are essentially to be analyzed to determine interactions with host tissues.

This research work is focus on tests for two alloys, Ti15Mo7Zr15Ta and Ti20Mo7Zr15Ta, tests like contact angle and DSC test to identify biocompatible character.

The values determined for the contact angle of the TMZT alloys are hydrophilic, which means a high adhesion of the cells to the surface of the alloys, the Ti15Mo7Zr15Ta alloy have a pronounced hydrophilic character, the alloy of a less pronounced hydrophilic character is Ti20Mo7Zr15Ta.

Thermal analysis by differential scanning calorimetry revealed that TMZT alloys did not show phase transformations in the range of 30-40ºC, being stable at the temperature of the human body.
5. References

[1] Bălţatu M S, Vizureanu P, Ţierean M H, Minciună M G and Achiţei D C 2015 Advanced Materials Research 1128 105-111

[2] Geetha M, Singh A K, Asokamani R and Gogia A K 2009 Mater. Sci. 54 397-425

[3] Minciună M G, Vizureanu P, Achiţei D C, Ghiban N, Sandu A V and Forna N C 2014 REV. CHIM. (Bucharest) 3 335-338

[4] Istrate B, Munteanu C, Matei M, Oprisan B, Chicet D and Earar K 2016 IOP Conference Series: Materials Science and Engineering 133 12010

[5] Istrate B, Mareci D, Munteanu C, Stanciu S, Luca D, Crimu C I and Kamel E 2015 Journal of Optoelectronics and Advanced Materials 17(7-8) 1186-1192

[6] Niinomi M 1998 Mater. Sci. Eng. 243 231-236

[7] Elias C N, Lima J H C, Valiev R and Meyers M A 2008 Biological Materials Science 46- 49

[8] Bombac D M, Brojan M, Fajfar P, Kosel F and Turk R 2007 Materials and Geoenvironment 54 (4) 471-499

[9] Elias C N, Lima J H C, Valiev R and Meyers M A 2008 Biological Materials Science 46- 49

[10] Minciună M G, Vizureanu P, Achiței D C, Sandu A V, Berbecaru A and Sandu I G 2016 Journal of optoelectronics and advanced materials 18(1-2) 174-178

[11] Minciună M G, Vizureanu P, Geanta V, Voiculescu I, Sandu A V, Achiței D C and Vitalariu A M 2015 Revista de chimie 66(6) 891-894

[12] Vogler E A 1998 Adv. Colloid Interface Sci. 74 69-117

[13] Baier R E 2006 Journal of material science: Materials in medicine 17(11) 1057-1062

[14] ***http://www.ramehart.com/contactangle.htm

[15] Rusu I 2011 Tehnici de analiza in ingineria materialelor Ed. PIM, Iași

[16] Kwork D Y, Lam C N C, Li A, Leung A, Wu R, Mok E and Neumann A W 1998 Colloids and surfaces A. 142 219-235

[17] Minciună M G, Vizureanu P, Achiței D C, Sandu A V, Berbecaru A and Sandu I G 2016 Journal of Optoelectronics and Advanced Materials 18(1-2)

[18] Ștefănoiu R, Geantă V, Voiculescu I, Csakin I and Ghiban N 2014 Revista de Chimie 65(7 819-821

[19] Geantă V, Voiculescu I and Stanciu E M 2016 International Conference on Innovative Research, Iop Conf Series: Materials Science And Engineering 133 1-8

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