UNIVERSITY POLITEHNICA OF BUCHAREST
FACULTY OF MATERIALS SCIENCE AND ENGINEERING
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PhD THESIS
SUMMARY

THEORETICAL AND EXPERIMENTAL RESEARCHES REGARDING THE OBTAINING OF NEW HIGH ENTROPY ALLOYS WITH BIOCOMPATIBLE PROPERTIES

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PART I: THEORETICAL STUDY REGARDING THE OBTAINING AND PROPERTIES OF BIOCOMPATIBLE MATERIALS

I. THEORETICAL CONSIDERATIONS ON BIOCOMPATIBLE MATERIALS

Biocompatibility is the property of biomaterials through which, after their implantation in a living organism, they do not produce side effects and are accepted by the surrounding tissues [8]. Researchers Wintermatel and Mayer [8] extended the definition of biocompatibility and came to separate it in two categories: intrinsic biocompatibility and extrinsic (functional) biocompatibility.

The biocompatibility of an implant depends on factors as: the patient's general condition, age, tissue permeability, immunological factors and implant characteristics (roughness and porosity of the material, chemical reactions, corrosion properties, toxicity) [9].

Depending on their nature, biomaterials [9] can be:

• Natural biomaterials (biological materials): organic; inorganic.

• Synthetic biomaterials: metals; polymers; ceramics; composites.

I.1 Characteristics of biocompatible materials

Each class of biomaterials has a number of characteristics, depending on the materials from which they are made and the functional requirements of the implant [6]. The properties that an implant should have are:

• Mechanical properties: elasticity modulus; tensile, compressive and shear strength; resistance to bending and fatigue; ductility; hardness [19].

• Surface properties: surface tension and surface energy; surface roughness.

• Biocompatibility properties: biocompatibility covers all aspects related to the function of bio-devices, including the interaction of cells and tissues with implanted biomaterials. Biocompatibility requirements are complex and strict, varying according to specific medical applications [6].

• Corrosion resistance: corrosion resistance involves the resistance of the material to the loss of metal ions on its surface and their release in the environment [23].

• The efficiency of biomaterials: refers to the reliability in use, accessibility in manufacturing, a low price due to accessible raw materials, easy processing and sterilization capacity, aesthetic aspect.

I.2 Applications of biocompatible materials

Depending on the nature of the biomaterials, they can have multiple applications [26], such as:

• Replacement of an injured part: artificial hip joints, artificial kidneys, etc.;

• Healing assistance: sutures, plates or bone screws;

• Improving function: pacemaker, contact lenses, etc .;

• Correction of functional anomalies: Harrinton vertical rod;

• Correction of aesthetic problems: chin enlargement, etc.;

• Help in establishing the diagnosis: wells, drainage tubes, etc.;

• Help in applying the treatments: drainage tubes, cannulas, etc.

II. STATE OF THE ART OF THE RESEARCHES REGARDING THE USAGE OF HIGH ENTROPY ALLOYS IN MEDICAL APPLICATIONS

II.1 Generalities of high entropy alloys. Effects and characteristics

High entropy alloys (HEA) are a new class of metallic materials with a different synthesis strategy. They are different from conventional alloys, which are based on one or two main elements, as they are composed of five or more main elements [33].

It has been reported in the literature [33] that HEA has a multitude of attractive characteristics, such as high hardness, very good wear resistance, fatigue resistance, very good breaking strength at high temperatures, good thermal stability and increased strength to oxidation and corrosion.

Most scientific studies in the literature have focused on investigating the correlation between phase composition, microstructure and mechanical properties [34]. For the elaboration of equiatomic multicomponent alloys, a thorough understanding of the thermodynamic aspects that define these alloys is necessary. In estimating the entropy of forming a metal alloy, Boltzmann's hypothesis states that it is maximum in the case of echiatomic compositions, as follows from the following formula [33]:

$$\Delta S = -k \ln w = -R(\frac{1}{n \ln 1/n} + \frac{1}{n \ln 1/n} + .. + \frac{1}{n \ln 1/n} = -R \ln \frac{1}{n} = R \ln n \qquad \text{(II.1)}$$

R: the universal constant of the ideal gas;

n: the number of elements in the system.

Starting with n = 5, ΔS becomes higher than in the case of most intermetallic compounds, leading to the preferential formation of solid solutions. In the range between n = 5 and n = 13 elements, the alloys have entropies with values between 1.61R and 2.56R and belong to the high entropy range (figure II.1.1).

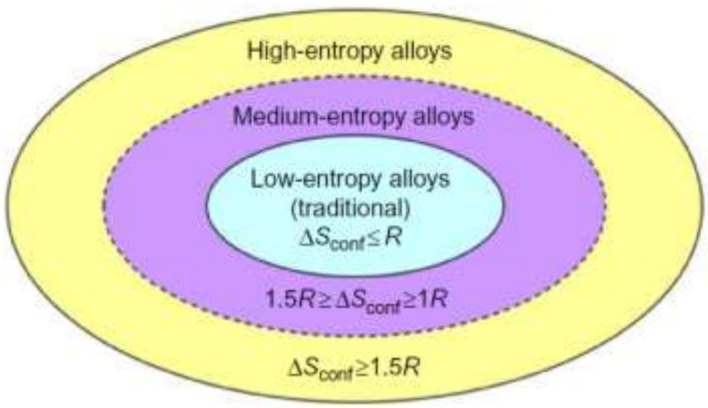


Figure II.1 – Alloy entropy domains (after Murty B. S. et al, [33])

The expected upper limit is thirteen elements and is arbitrary. It has been shown that once this value is exceeded, the benefits obtained by the addition of alloying elements are insignificant [33].

Being different from conventional alloys, the chemical compositions of high entropy alloys differ from those of conventional alloys, with a higher degree of complexity, given by the equimolar concentration of each constituent element [33].

Four main effects that influence and define high entropy alloys have been highlighted in the literature [33], as follows:

- From a thermodynamic point of view: the effect of high entropy;

- From a kinetic point of view: slow diffusion;

- From a structural point of view: severe deformation of the atomic lattice;

- In terms of properties: the cocktail effect.

Researches have shown that high entropy alloys can be developed, processed and analyzed in the same way as conventional alloys. HEA has also been found to have a number of particularly interesting features [39], [40], such as:

1. The tendency to form simple phases composed of solid CFC or CVC solutions, nano-structures or even amorphous structures;

2. Hardness which can vary between 100 and 1100 HV;

3. Microstructure that has a good thermal stability;

4. Deformation through a joining mechanism at nanometer level;

5. Very good resistance to softening on annealing;

6. Hardening by precipitation at high temperatures, between 500 and 1000°C;

7. The mechanical resistance has a high temperature coefficient, which determines a high resistance to high temperatures;

8. Very good resistance to corrosion, oxidation and wear.

II.2 Actual situation of high entropy alloys with biocompatible applications

Metallic materials are key elements for the manufacture of implants, due to the advantages they have, compared to other materials: superior mechanical properties - resistance to breakage and flow, ductility, resistance to fatigue. Currently, Co - Cr - Mo and Ti alloys are used for artificial joint replacement (hip, knee and shoulder prostheses). However, although they have good biocompatibility, titanium alloys (example: Ti6Al4V) cannot be used as contact surfaces between two materials, due to their low wear resistance, associated with low shear strength and repassivation behavior of the oxide layer on the surface [6].

Alloys in the Co - Cr - Mo system (example: Co28Cr6Mo) have a higher wear resistance and can be used as contact surfaces of joint prostheses, but recently it has been observed that in some alloys, the failure rate is increasing [42].

Analysing titanium-rich Ti-Nb-Ta-Zr alloys with a CVC phase, Kambic H. E. [45] considers that they have superior mechanical properties to titanium-based metal biomaterials. The constituents of these alloys are non-toxic and do not cause allergies. The combination of Ti, Nb, Ta and Zr is favorable for the formation of a single solid solution phase in these alloys, based on a suitable compositional design. In these alloys there is the possibility of forming a solid solution in the equiatomic alloy TiNbTaZr and TiNbTaZrX (X can be Cr, V, Mo, W, Fe).

II.3 Main objectives

High entropy alloys with biocompatible properties need to have a modulus of elasticity similar to that of human bone (to ensure a uniform distribution of implant strength and to minimize movement relative to the bone-to-implant interface), high hardness, low thermal conductivity and corrosion resistance. The doctoral thesis has as main purpose the design of high entropy alloy compositions with biocompatible properties, with superior characteristics to the materials traditionally used to obtain implants. In this context, the following objectives were taken into consideration:

- Design of high entropy alloys using a thermodynamic and kinetic model, based on the CALPHAD analysis method and solid state phase transformations;

- Development of high entropy alloys with biocompatible properties from FeTaNbTiZr and FeMnNbTiZr systems, through the process of melting - casting in induction furnace;

- Application of annealing heat treatments to high entropy alloys developed in the induction furnace, in order to eliminate internal stresses and improve the internal structure;

- Structural and microstructural characterization of high entropy alloys with biocompatible properties, by electron microscopy;

- Mechanical characterization of the obtained alloys;

- Determination of corrosion resistance in human physiological simulant environments, such as NaCl infusion solution and Ringer lactate infusion solution;

- Development of a mathematical model, using the ordering technique by similarity with the ideal solution, TOPSIS, which can determine which of the high entropy alloys obtained in the induction furnace has the best properties.

Keywords: high entropy alloys, biocompatibility, mathematical model, elaboration, characterization, properties.

PART II: EXPERIMENTAL RESEARCHES REGARDING THE OBTAINING AND CHARACTERISATION OF BIOCOMPATIBLE MATERIALS

III. METHODS FOR SELECTION AND MODELLING THE COMPOSITION OF HIGH ENTROPY ALLOYS WITH BIOCOMPATIBLE PROPERTIES

III.1 The influence of alloying elements on high entropy alloys properties

To determine the optimal composition of high entropy alloys, with biocompatible properties, were used various selection methods based on: the influence of alloying elements on the properties of the alloy, structural, thermodynamic and kinetic criteria.

High entropy alloys (HEA) contain mainly elements from transitional groups, as Co, Cr, Fe and Ni. They are most often used in the development of compositions that form stable phase structures [6].

The composition of high entropy alloys is based, in particular, on chemical elements such as Co, Cr, Cu, Fe, Mn, Mo, Ni, Ti, Nb, Zr, V, W, Ta, Mg, Ca, Y, Zn, Hf , Ce, Sn; Co, Cr, Fe and Ni form a group of elements that are present in the most studied alloy systems. The elements from the main groups (eg Al, Si, B, etc.) are added in certain HEA compositions to improve the structural stability, having an important role in the design of alloys with predetermined properties [6].

Considering that the main elements that are used to form the structures of high entropy alloys are Co, Cr, Fe and Ni, the systems that can be formed are: the system with centered faces, the cubic crystalline system, or a combination of them. In present, Ni is known to be a stabilizer of the centered face system, and Cr is a stabilizer of the cubic crystal system; therefore, Ren et al [51] established a mathematical model for identifying the type of structure found in high entropy alloys, similar to stainless steels. The mechanical properties are strongly influenced by the type of structure; therefore, it is known that the alloys in the centered face system are ductile and malleable, while the alloys belonging to the cubic crystalline system are strong and brittle. However, these equations are not sufficient to describe the structural behavior of high entropy alloys, because there are many ways to combine chemical elements, but also due to the influence of additional elements (Al, Si, Ti, Zr, etc.). For example, equimolar addition of aluminum will produce phases in the crystalline cubic system in the case of high entropy alloys [52, 53].

Analyzing the properties of the main chemical elements used to obtain high entropy alloys with biocompatible properties, we selected four elements that are currently used in practice: Ti, Zr, Nb, Ta, which are considered the basis of elaborate alloy systems. They have excellent anticorrosive properties, wear resistance, machinability and biocompatibility. To this group of elements were added Fe and Mn, that have properties of biocompatibility, and the quality of stabilizing structures based mainly on solid solutions in high entropy alloys. These elements are also low priced and can significantly reduce the final cost of the alloy. Based on these chemical elements, two alloy systems were selected: one of them contains Ta, which has a high price and excellent biocompatibility properties (FeTaNbTiZr). The second alloys system contains Mn instead of Ta (FeMnNbTiZr), in order to reduce the obtaining costs, manganese being an element with a low price compared to tantalum and gives the alloy fatigue resistance, a necessary property for implants.

III.2 The modelling of high entropy alloys

MatCalc is a program used in the thermodynamic and kinetic simulation of metal systems, with an easy-to-use graphical interface. Thermodynamic modeling is based on the CALPHAD analysis method (CALculation of PHAse Diagrams), and the kinetic modules are developed based on solid state phase transformations, especially considering the accuracy of the calculations performed and their applicability in case of multicomponent systems.

FeTaNbTiZr alloys system

In figure III.2.1 – a is shown the evolution of the phases, depending of the Zr content, at the temperature of 200^0C. It can be observed that with the increase of Zr content is increasing the CVC – A2 solid solution proportion and is decreasing Laves intermetallic phase. On a percentage of 20%Zr appears A3 compact hexagonal phase, characteristic to the Zr structure. In conclusion, Zr is favorable for the formation of solid solutions, with the mention of introducing it up to a percentage of 20%, when fragile structures can appear. The increase of Nb percentage in the alloy (figure III.2.1 – b) has a similar result with the influence of the Zr increase and also up to 20%, where HCP – A3 begins to form. In this case, up to 15% Nb, is a significant proportion of the HCP-A3 phase, which is then suppressed in the range of 15-20% Nb. Similarly, the proportions of the phases were obtained for the rest of the elements: Fe, Ta, Ti.

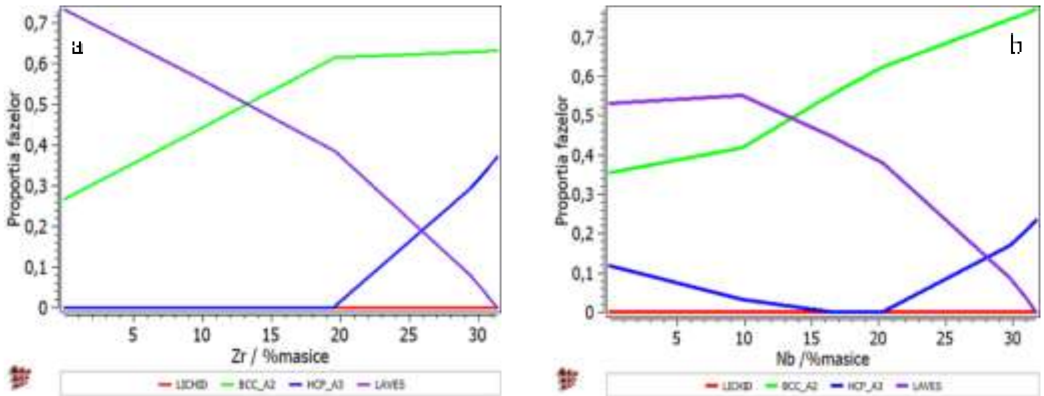


Figure III.2.1 – Phases proportion in the FeTaNbTiZr alloy system, depending on the variation of a: Zr; b: Nb, at a temperature of 200^0C

FeMnNbTiZr alloys system

The influence of the alloying elements on the evolution of the phases in the FeMnNbTiZr alloy system is shown in figure III.2.2. It is observed that with the increase of the percentage of Ti there is a significant increase of the percentage of solid solution CVC-A2 and a significant decrease of the hexagonal phase HCP-A3. Niobium has a high CVC-A2 phase stabilization capacity, superior to Ti and Zr, so at percentages over 27% it can form exclusively solid solutions in alloys. Similarly, the proportions of the phases were obtained for the rest of the elements: Fe, Ta, Mn.

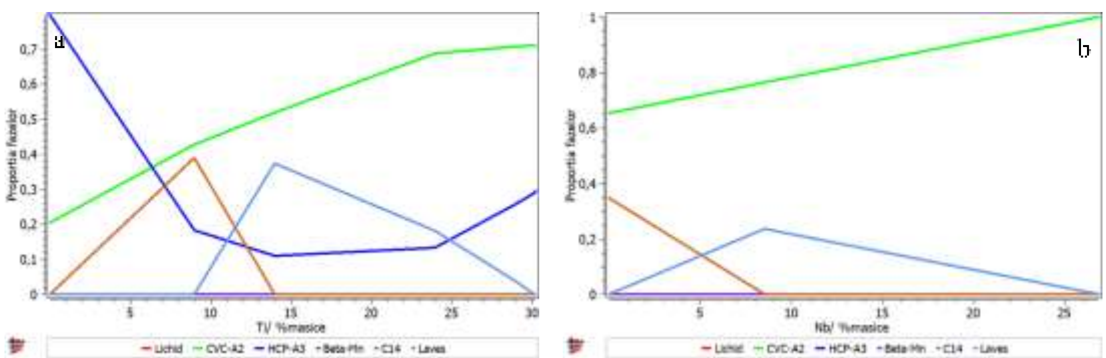


Figure III.2.2 – Phases proportion in the FeMnNbTiZr alloy system, depending on the variation of a: Ti; b: Nb, at a temperature of 200^0C

III.3 The selection of high entropy alloys with biocompatible properties using MatCalc software and specific criteria for high entropy alloys

From the analysis of the MatCalc modeling results for the FeTaNbTiZr alloy system, it is observed that the obtaining of a structure mainly composed of solid solutions is obtained at high percentages of Ta, Nb and Zr. Otherwise, Ti must be kept at relatively low percentages. It is observed that by replacing Ta with Mn, in the FeMnNbTiZr alloy system, the most important influence on the formation of the structure rich in solid solutions has Zr. However, the other elements remain relatively high.

Analyzing the influence of the alloying elements on the characteristics required for biocompatible alloys and the tendency to form solid solutions for each alloy system, three high entropy alloys were proposed:

- $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$
- $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$
- $FeMnNb_{0.5}TiZr_{0.5}$

As it can be observed, two alloys from the FeTaNbTiZr system were chosen to determine the influence of the Ti percentage in the alloy. In this case, Ti will replace part of Ta to considerably reduce the density and the price of the alloy. Ta, Nb, and Zr were maintained at an equal percentage to induce the typical structure of high entropy alloys. The numbers from the alloy formula represent modified molar fractions according to the symbolism of high entropy alloys, where the molar fraction is equal to one when the element is at equimolar concentration.

In table III.3.1 are presented the calculated results of high entropy alloys criteria, for the selected alloys:

Table III.3.1 – Thermodynamic criteria of forming the optimal high entropy alloys with biocompatible properties

Alloy	**ΔS_{conf}, J/molK**	**ΔH_{mix}, kJ/mol**	**δ, %**	**VEC, %**	**Δ_{mix}, % Allen**	**T_m**	**Ω**	**ΔH_{im}**	**k1cr**	**ρ**
$FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$	12,42	-15,56	8,02	5,25	12,78	2201,78	1,76	-15,56	1,31	7,61
$FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$	12,89	-16,41	8,52	5,43	13,28	2239,01	1,76	-16,41	1,31	8,06
$FeMnNb_{0.5}TiZr_{0.5}$	12,97	-15,38	8,23	5,88	12,92	1927,40	1,63	-15,38	1,33	6,65

IV. ELABORATION PROCESS OF HIGH ENTROPY ALLOYS WITH BIOCOMPATIBLE PROPERTIES

High entropy alloys with biocompatible properties can be obtained as solid materials by melting – casting process [77]. The elaboration of high entropy alloys ($FeMnNb_{0.5}TiZr_{0.5}$, $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$, $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$) was carried out in an induction furnace Linn MFG - 30 type, with inert argon atmosphere (figure IV.1). Pure metals were used as raw materials for the charges. The molten alloy was poured into the furnace in a cylindrical copper shell (Ø5x20cm). Subsequently (in the case of $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy), the metallic material was remelted in the same working conditions, in order to obtain a more homogeneous chemical composition.

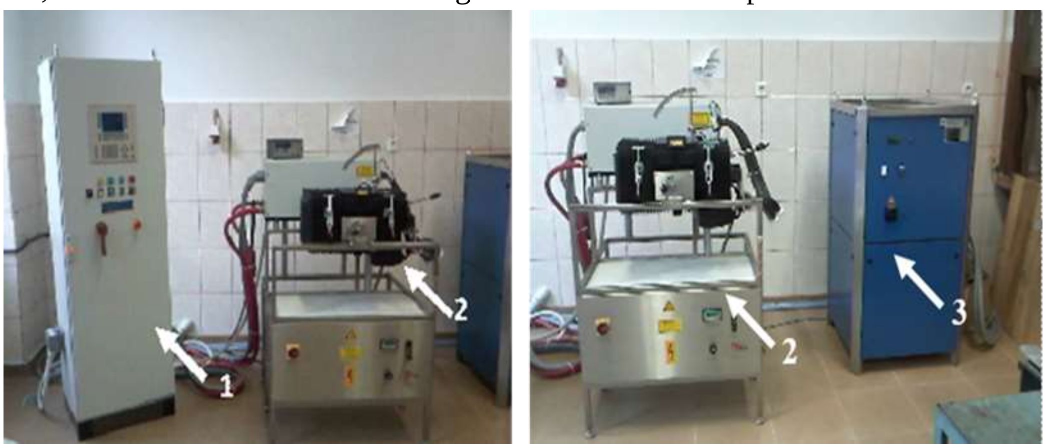


Figura IV.1 – The induction furnace Linn MFG – 30: 1 – voltage generator; 2 – melting room; 3 – cooling water recirculator

The technological process of casting the high entropy alloys is presented in figure IV.2.

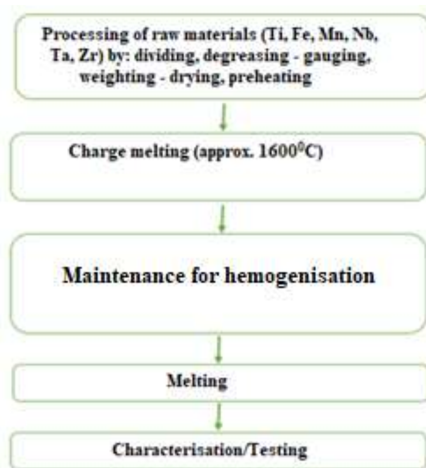


Figure IV.2 – The technological process of high entropy alloys elaboration

V. METHODS FOR IMPROVING THE PROPERTIES OF HIGH ENTROPY ALLOYS WITH BIOCOMPATIBLE PROPERTIES

Improving the structure of high entropy alloys is achieved by applying annealing heat treatments, in order to to eliminate the internal stresses and improve the structure obtained from melting / casting processes [87].

The annealing heat treatment aims to direct, by heating and cooling, the transformations in solid state, in the sense of bringing the alloy closer to the energetic and structural balance, of the chemical homogenization or of obtaining constituents with a certain degree of fineness, dimensional uniformity and distribution in structure [88].

The applied heat treatment restores the plasticity to high entropy alloys with biocompatible properties and eliminates the internal stresses and ensures a balanced structure, neccesary conditions for high resistance to corrosion and to high temperatures resistance. [88].

In the case of high entropy alloys with biocompatible properties, obtained using the melting – casting method in the induction furnace, there were applied annealing heat treatments, in order to homogenize the structure (fig. V.1). It was used a Nabertherm (fig. V.2) heat treatment furnace, located in the National Research and Development Institute for Non-Ferrous and Rare Metals (INCDMNR – IMNR). Figure V.3 shows the alloy samples after the application of the heat treatment.

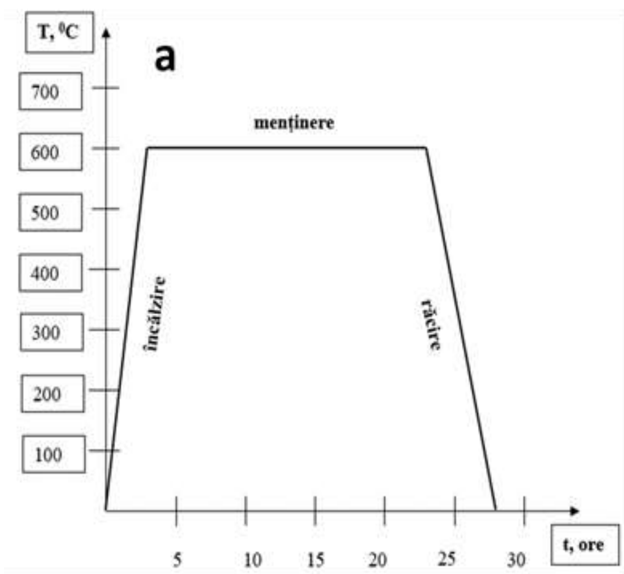


Figure V.1 - a. Heat transfer diagram of high entropy alloys with biocompatible properties; b. Nabertherm heat treatment furnace

Figure V.3 – High entropy alloys with biocompatible properties samples after the application of homogenization annealing heat treatment

It can be observed that the high entropy alloy with biocompatible properties based on Mn ($FeMnNb_{0,5}TiZr_{0,5}$) has been affected by the oxidant atmosphere during the heat treatment. The three ingots of high entropy alloys with biocompatible properties based on Ta ($FeTa_{0,5}Nb_{0,5}Ti_{1,5}Zr_{0,5}$; $FeTa_{0,5}Nb_{0,5}TiZr_{0,5}$; $FeTa_{0,5}Nb_{0,5}Ti_{1,5}Zr_{0,5}$ remelted) resisted very well to the high temperature heat treatment.

VI. CHARACTERISATION OF HIGH ENTROPY ALLOYS OBTAINED IN THE INDUCTION FURNACE

VI.1 Chemical characterization

High entropy alloys obtained in the induction furnace have been chemically analyzed, in order to establish the percentage of chemical elements. The data obtained are presented in table VI.1.1

In table VI.1.1 is presented the nominal chemical composition and that determined by chemical analysis of the elaborated alloys.

Table VI.1.1 – The nominal chemical composition and that determined by chemical analysis of the elaborated alloys

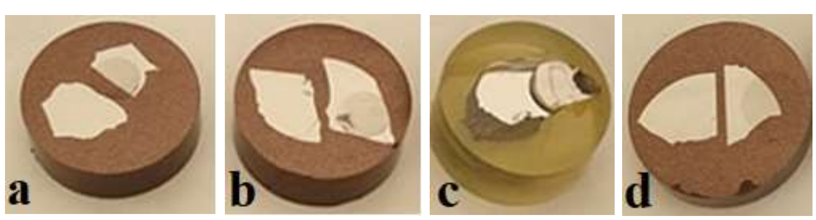
	%. gr					
	Ti	**Fe**	**Mn**	**Nb**	**Ta**	**Zr**
$FeTa_{0,5}Nb_{0,5}Ti_{1,5}Zr_{0,5}$ – ρ = 7,61 g/ cm^3						
Nominal	23,14	18,02	-	14,97	29,17	14,7
Analysis	22,0	22,0	-	16,1	18,0	13,0
$FeMnNb_{0,5}TiZr_{0,5}$ – ρ = 6,65 g/ cm^3						
Nominal	19,09	22,28	21,92	18,53	-	18,18

Analysis	16,8	20,4	21,0	20,7	-	15,0
$FeTa_{0,5}Nb_{0,5}TiZr_{0,5}$ – ρ = 8,06 g/ cm^3						
Nominal	16,73	19,51	-	16,22	31,62	15,92
Analysis	17,0	22,1	-	14,7	23,0	13,5
$FeTa_{0,5}Nb_{0,5}Ti_{1,5}Zr_{0,5}$ remelted – ρ = 7,61 g/ cm3						
Nominal	23,14	18,02	-	14,97	29,17	14,7
Analysis	19,2	18,42	-	15,8	25,0	12,4
$FeTa_{0,5}Nb_{0,5}Ti_{1,5}Zr_{0,5}$ heat treated						
Analysis	24,0	19,0	-	16,9	15,8	15,5
$FeTa_{0,5}Nb_{0,5}TiZr_{0,5}$ heat treated						
Analysis	16,4	18,7	-	11,2	30,0	14,0
$FeMnNb_{0,5}TiZr_{0,5}$ heat treated						
Analysis	20,0	16,0	-	16,1	25,0	13,0

VI.2 Optical microscopy characterization

Characterization by optical microscopy was performed using an Axio Scope A1m Imager microscope (figure VI.2.1) produced by Zeiss, which offers light field, dark field and polarization functions and is equipped with EC Epiplan 10 X contrast lenses/50 X/100X. The microscope is equipped with a Canon Pomer Shot A 640 digital camera with 10X digital zoom for high-performance image capture and AxioVision Release 4.6.3 software for the analysis and processing of specialized images.

In figure VI.2.1 are shown samples of high entropy alloys, with biocompatible properties, elaborated in the induction furnace and included in epoxy resin, for optical characterization.



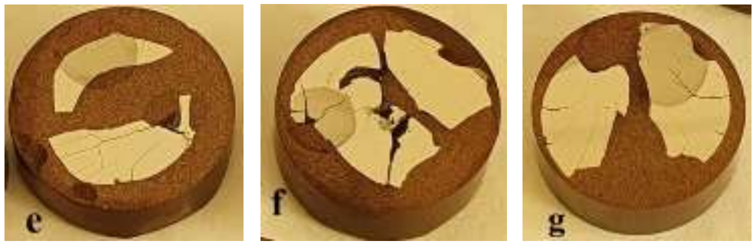


Figure VI.2.1 – High entropy alloys with biocompatible properties, included in epoxy resin, for optical microscopy (a- $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$; b – $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$; c – $FeMnNb_{0.5}TiZr_{0.5}$; d - $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ remelted; e - $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ thermal treated; f – $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ thermal treated; g - $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ remelted and thermal treated)

In figures VI.2.2 and VI.2.3 are presented the micrographies of the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ and $FeMnNb_{0.5}TiZr_{0.5}$ high entropy alloys.

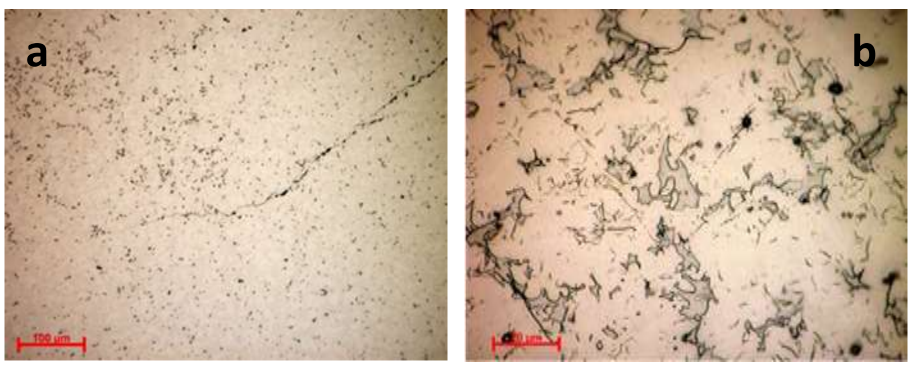


Figure VI.2.2 – $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy micrographies (a – unattacked sample, 200x; b – attacked sample, immersed in cedar oil, 900x)

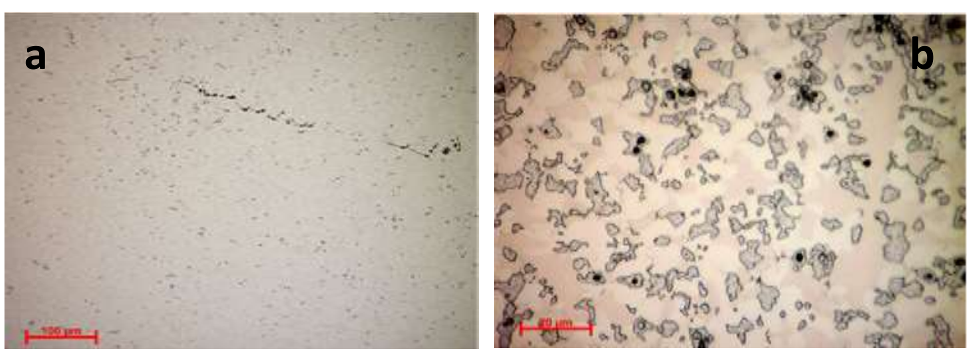


Figure VI.2.3 – $FeMnNb_{0.5}TiZr_{0.5}$ alloy micrographies (a – unattacked sample, 200x; b – attacked sample, immersed in cedar oil, 900x)

In order to be able to analyze the behavior of high entropy alloys with biocompatible properties, the Vickers microhardness was determined [97 - 98], by performing three indentations, following which an average was calculated and noted in table VI.2.1.

Table VI.2.1 – Vickers microhardness values for high entropy alloys

Aliaj	**Microduritate Vickers**
$FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$	802,8 HV
$FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$	898,2 HV
$FeMnNb_{0.5}TiZr_{0.5}$	802,9 HV
$FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ remelted	699,0 HV
$FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ heat treated	910,4 HV
$FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ heat treated	782,2 HV
$FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ remelted, heat treated	729,4 HV

VI.3 XRD characterisation

XRD detection was performed using a Bruker D8 diffractometer, which has an X-ray focusing tube on the Cu wavelength and a SOL X detector in Bragg-Brentano geometry, with a primary and secondary radius of 250 mm.

In figures VI.3.1 - VI.3.2 are presented the diffractograms of the samples of high entropy alloys with biocompatible properties $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ remelted and $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ heat treated and the qualitative analyzes of the identified phases.

In tables VI.3.1 - VI.3.2 are presented the legends of the qualitative phase analyzes for high entropy alloys with biocompatible properties: $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ remelted and $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ heat treated. Were used the notations: BCC - body centered cubic; HC - compact hexagonal structure; CC - cubic complex structure.

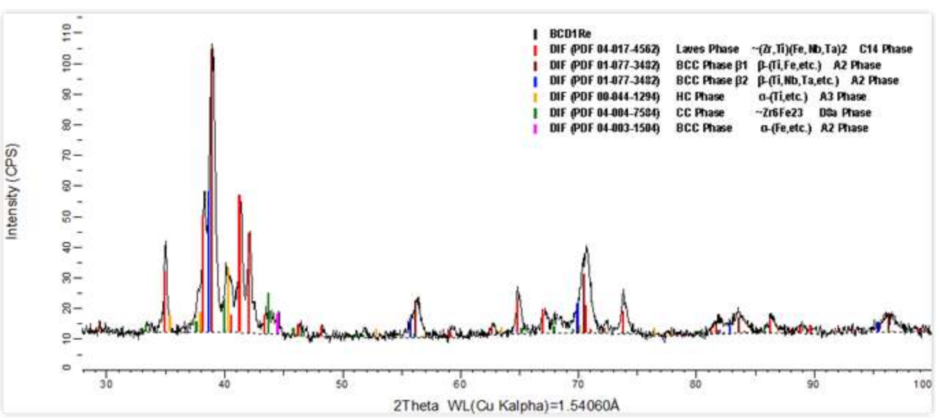


Figure VI.3.1 – Reprezentative qualitative phase analysis for remelted $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy sample

Table VI.3.1 – Qualitative phase analysis legend for the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ remelted alloy

Legend	Compound name	Phase proportion	Legend	Compound name	Phase proportion
Red	Laves phase; type C14; (Zr,Ti)(Fe,Nb,Ta)$_2$	32	Orange	HC phase; type A3 α-(Ti, etc.)	11
Maroon	Phase BCC- β1; type A2 β-(Ti, Fe, etc.)	31	Green	CC Phase; type $D8_a$~Zr_6Fe_{23}	9
Blue	Phase BCC β2; type A2 β-(Ti, Nb, Ta, etc.)	15	Magenta	BCC Phase; type A2 α-(Fe, etc.)	2

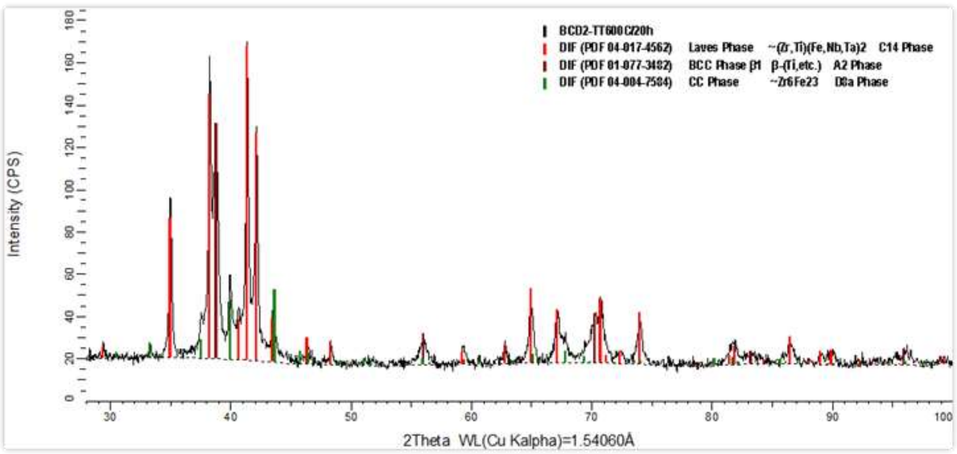


Figure VI.3.2 – Reprezentative qualitative phase analysis for heat treated $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy sample

Table VI.3.2 – Qualitative phase analysis legend for the $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ heat treated alloy

Legend	Compound name	Phase proportion	Legend	Compound name	Phase proportion
Red	Laves phase; type C14; (Zr,Ti)(Fe,Nb,Ta)$_2$	63	Green	CC phase; type $D8_a$~Zr_6Fe_{23}	14
Maroon	BCC- β1; type A2 β-(Ti, Fe, etc.)	23			

The phases identified in high entropy alloys with biocompatible properties are substitution solid solutions. It can also be seen that the variation of phases proportion is more sensitive to remelting than to heat treatment (TT): The Laves phase remains practically constant after the application of heat treatment, but decreases in the remelted alloy. On the other hand, the amount of BCC: β1 + β2 phases tends to increase by remelting.

VI.4 Scanning electron microscopy characterisation

The SEM-EDAX characterization was performed with a high resolution scanning electron microscope, FEI Inspect F50 (Field Emission Gun) and EDAX type X-ray spectrometry, with the evaluation of chemical composition gradients, identification and quantitative evaluation of the chemical elements in the sample or structural elements: phases, precipitates, inclusions, etc. [103 - 105]. Representative SEM-EDAX images for $FeMnNb_{0.5}TiZr_{0.5}$ and heat-treated $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ alloy samples resulting from the manufacturing process are shown in figures VI.4.1 and VI.4.2.

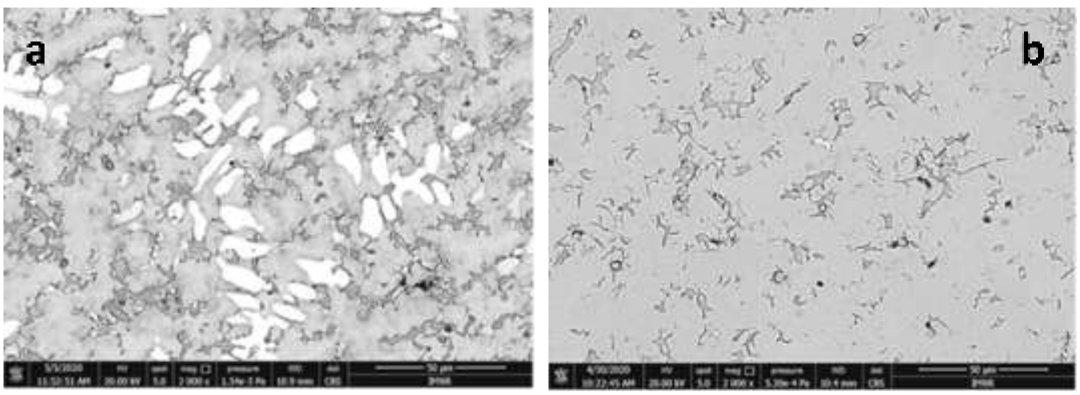


Figure VI.4.1 - SEM images of the alloy samples a: $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ heat treated and b: $FeMnNb_{0.5}TiZr_{0.5}$

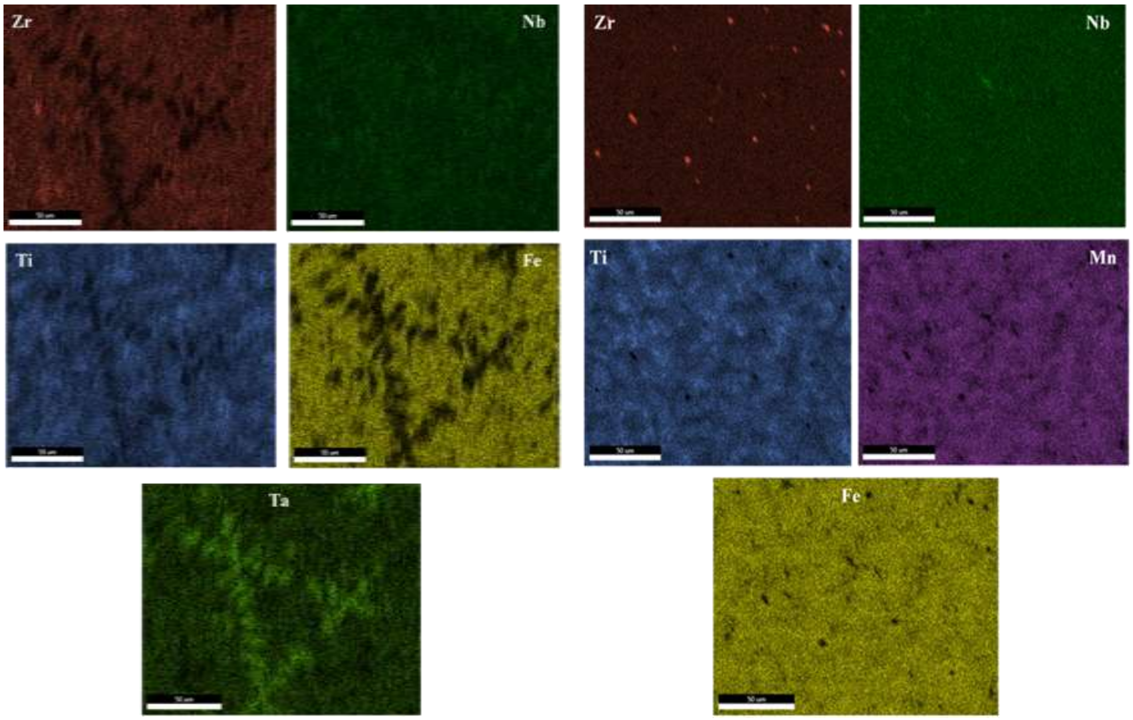


Figure VI.4.2 – EDS/Map analysis results of the alloy samples a: $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ heat treated and b: $FeMnNb_{0.5}TiZr_{0.5}$

VI.5 Mechanical characterisation

The mechanical properties of the alloys determine the behavior under external forces, in case of different mechanical stresses [106 - 109]. High entropy alloys $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ and $FeMnNb_{0.5}TiZr_{0.5}$ were chosen for the mechanical characterization. They were obtained by melting-casting processes in induction furnace. These two alloys were chosen because three of the four developed alloys were selected from the FeTaNbTiZr system, the difference between them being the proportion of constituent elements. Also, the $FeTa_{0,5}Nb_{0,5}Ti_{1,5}Zr_{0,5}$ alloy was remelted, in order to homogenize the internal structure. The fourth high entropy alloy with biocompatible properties developed was selected from the FeMnNbTiZr system, so a comparison of the behavior of $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ and $FeMnNb_{0.5}TiZr_{0.5}$ alloys, when applying different external forces, is extremely useful.

A comparison of the elasticity modulus of high entropy alloys $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ and $FeMnNb_{0.5}TiZr_{0.5}$ is presented in figure VI.5.1, and a comparison of the rigidity modulus of these alloys is made in figure VI.5.2.

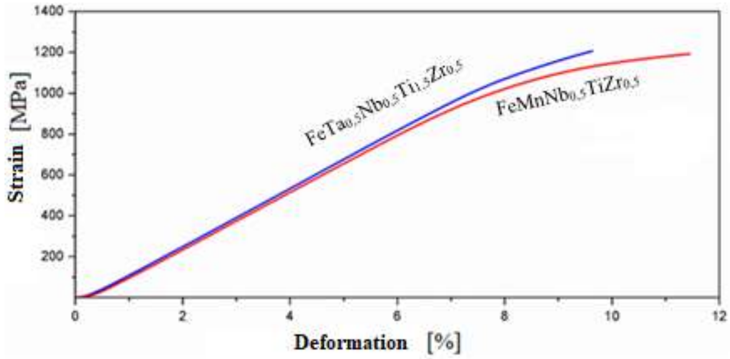


Figure VI.5.1 – Elasticity modulus comparison of $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ and $FeMnNb_{0.5}TiZr_{0.5}$ high entropy alloys

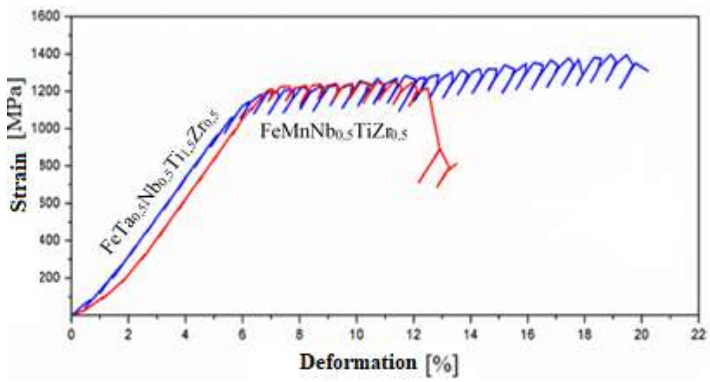


Figure VI.5.2 – Rigidity modulus comparison of $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ and $FeMnNb_{0.5}TiZr_{0.5}$ high entropy alloys

The modulus of elasticity was obtained for the two high entropy alloy samples. It is observed that the flow resistances of the two alloys are higher than 1200 MPa, and the modulus of elasticity for the two samples are 35.49 GPa, respectively 34.47 GPa.

The rigidity modulus for the two alloy samples is 13.34 GPa and 12.96 GPa, respectively.

The compression tests showed high values for the relative deformation, comparable to that of Ti-based alloys, at a much higher strength. The $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy sample (1255.89 GPa and a tensile strength of 13.481%) has superior compressive properties compared to the $FeMnNb_{0.5}TiZr_{0.5}$ alloy sample (strength of 1398.45 GPa and tensile strength of 20.21).

VI.6 Studies regarding the corrosion resistance of high entropy alloys with biocompatible properties

The corrosion behavior of high entropy alloys with biocompatible properties, experimentally obtained, was investigated in human physiological simulant environments, respectively in the environment of NaCl infusion solution and Ringer lactate infusion solution. The experiments were performed by potentio - dynamic testing using an AUTOLAB equipment with specialized corrosion software, including PGSTAT302N, BA and SCAN250 modules, located in the Faculty of Materials Science and Engineering, University Politehnica of Bucharest. The corrosion behavior results are presented in figures VI.6.1 - VI.6.2.

Environment of NaCl infusion solution

For experimental alloys, it is observed that the corrosion potential is tending to more electropositive values, depending on the type of experimental alloy, respectively from -187mV (for $FeMnNb_{0.5}TiZr_{0.5}$ alloy), to -65mV (for $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ alloy), then at -70mV (for the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy), reaching a positive value of +79 mV (for the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy). Corrosion current values also decrease, respectively 1,99.10-^{3}μA/cm^{2} (for $FeMnNb_{0.5}TiZr_{0.5}$ alloy), 1.13.10-3μA/cm^{2} (for $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ alloy), 5.89.10 $^{-5}$μA/cm^{2} (for the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy), having the lowest value for the remelted alloy, respectively 3.16. 10^{-6}μA/cm^{2} (for $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy). Also, the corrosion rate, which is related to the density of the corrosion current, decreases in the same way from 40.36μm/year (for $FeMnNb_{0.5}TiZr_{0.5}$ alloy), to 22.9 μm/year (for $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$), 11.93 μm/year (for $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy) and reaching 0.067 μm/year (for $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy). It can be concluded that in this testing environment, all alloys developed by melting - casting have similar behaviors, there is a differentiation given by the chemical composition of the experimental alloy, respectively the tendence of the values of corrosion potential to more electropositive values, which causes a decrease in corrosion current density and decreasing the corrosion rate to a very small value of 0.067μm/year.

Environment of Ringer lactate solution

For the experimental alloys it is observed the displacement of the corrosion potential from -188mV (to the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy), to -65mV (to the $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ alloy), -90mV (to the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$) reaching values of -80mV (for the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy melted in the induction furnace). Also, the corrosion density values decrease from 1.16. 10^{-3}μA/cm^{2} (for the $FeMnNb_{0.5}TiZr_{0.5}$ alloy), for 2.01 .10^{-4}μA/cm^{2} (for the $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ alloy), 8.24.10^{-3}μA/cm^{2} (for the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$) and respectively 3,71.105μA/cm^{2} (for the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy melted in the induction furnace). In the same way, the corrosion rate values decrease, from 23.45 23m/year (for the $FeMnNb_{0.5}TiZr_{0.5}$ alloy), to 4.063μm/year (for the $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ alloy), to 1.66μm/year (for $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy), up to 0.75μm/year (for $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy melted in induction furnace).

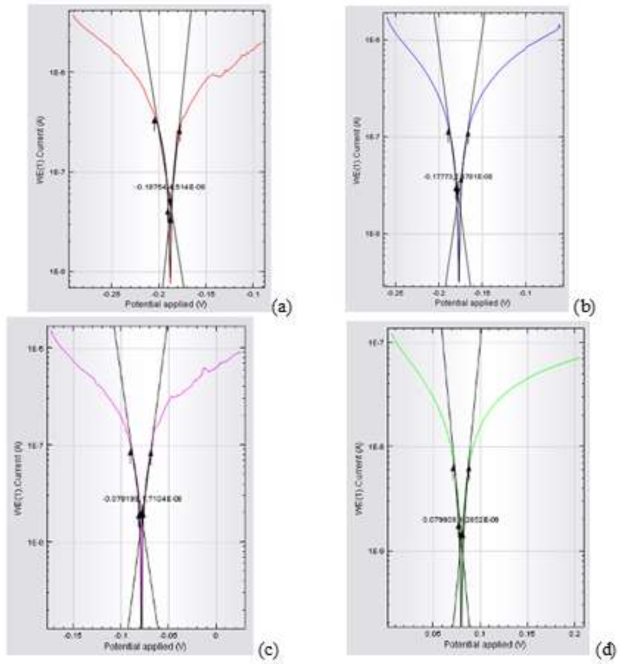


Figure VI.6.1 – Tafel slope of high entropy alloys, experimentally obtained, after testing in NaCl solution: a - FeMnNb$_{0.5}$TiZr$_{0.5}$ alloy; b - FeTa$_{0,5}$Nb$_{0,5}$TiZr$_{0,5}$ alloy; c - FeTa$_{0,5}$Nb$_{0,5}$Ti$_{1,5}$Zr$_{0,5}$ alloy; FeTa$_{0,5}$Nb$_{0,5}$Ti$_{1,5}$Zr$_{0,5}$ remelted alloy

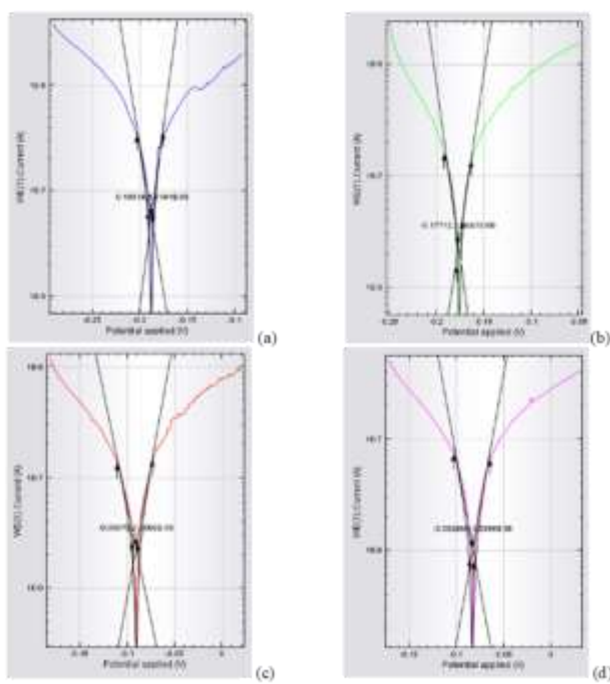


Figure VI.6.2 – Tafel slope of high entropy alloys, experimentally obtained, after testing in Ringer solution: a - FeMnNb$_{0.5}$TiZr$_{0.5}$ alloy; b - FeTa$_{0,5}$Nb$_{0,5}$TiZr$_{0,5}$ alloy; c - FeTa$_{0,5}$Nb$_{0,5}$Ti$_{1,5}$Zr$_{0,5}$ alloy; FeTa$_{0,5}$Nb$_{0,5}$Ti$_{1,5}$Zr$_{0,5}$ remelted alloy

Compared to the behavior of alloys in NaCl solution, the values of the corrosion parameters in Ringer's solution can be considered approximately similar, except for the alloy $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ melted in the induction furnace, with a positive value of the corrosion potential and a very low corrosion current compared to other alloys, in the same condition.

It is also found for testing in Ringer's solution that the corrosion potential is moving to more electropositive values, the corrosion current and corrosion rates decrease in the same way, depending on the chemical composition of the alloy. The same observation can be made both for the values of current densities, from $3.43.10^{-4}\mu A/cm^2$ (for $FeMnNb_{0.5}TiZr_{0.5}$ alloy), to $9.89.10^{-5}\mu A/cm^2$ (for $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ alloy), at $2,36.10^{-5}\mu A/cm^2$ (for the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy) and $1,23.10^{-6}\mu A/cm^2$ (for the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy melted in an induction furnace), as well as for the values of corrosion rates, which are in a range between 6.9µm/year÷0.026µm/year. Corrosion potential ranging from -188mV (for $FeMnNb_{0.5}TiZr_{0.5}$ alloy), -70mV (for $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$ alloy), -40mV (for $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy), reaching -20mV (for the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy melted in an induction furnace). There is also a decrease in both the values of current densities, 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 $9,83.10^{-7}\mu A/cm^2$, as well as corrosion rates from 99.7µm/year, to 22.5µm/year, 22.9µm/year and reaching 0.021µm/year to the $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy melted in induction furnace.

In figure VI.6.3 are presented the comparative results of the corrosion rates of the alloys obtained experimentally after testing in human simulant environments.

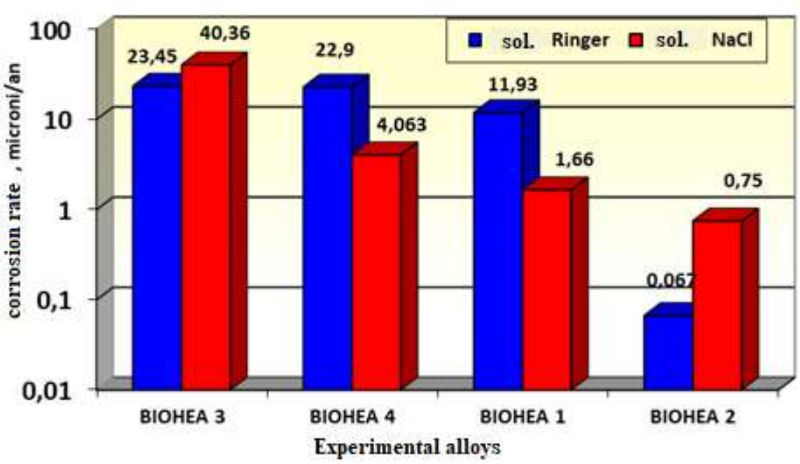


Figure VI.6.3 – Comparative results of the corrosion rates of the experimentally obtained alloys, after testing in human physiological simulant environments (BIOHEA 1: $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$; BIOHEA 2: $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$; BIOHEA 3: $FeMnNb_{0.5}TiZr_{0.5}$; BIOHEA 4: $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$)

VI.7 Selection of the alloy with the best properties, using TOPSIS method

TOPSIS method was developed by Hwang and Youn and presents a sorting technique by similarity to the ideal solution.

In the PhD thesis, this method was used to determine the alloy that is the most suitable to be used for implants. Choosing the alloy that is at the smallest distance from the ideal solution, were selected four criteria: density, microhardness, corrosion rate in NaCl and corrosion rate in Ringer's solution.

It was calculated the standardized consequences matrix (table VI.7.1).

Table VI.7.1 – Standardized consequences matrix

Alloy	Density, g/cm^3	Microhardness, HV	Corrosion rate, NaCl,µm/yr	Corrosion rate, Ringer,µm/yr
$FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$	0.5073	0.4994	0.2490	0.0695
$FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$	0.5373	0.5587	0.4779	0.1702
$FeMnNb_{0.5}Ti_{1.5}Zr_{0.5}$	0.4433	0.4994	0.8424	0.9824
$FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ remelted	0.5073	0.4348	0.0014	0.0314

The normalized decision matrix was calculated in table VI.7.2.

Table VI.7.2 – Normalized decision matrix

Alloy	Density, g/cm^3	Microhardness, HV	Corrosion rate, NaCl, µm/yr	Corrosion rate, Ringer, µm/yr
$FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$	0.1015	0.0999	0.0498	0.0139
$FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$	0.1075	0.1117	0.0956	0.0340

$FeMnNb_{0.5}Ti_{1.5}Zr_{0.5}$	0.0887	0.0999	0.1685	0.1965
$FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ remelted	0.1015	0.0870	0.0003	0.0063

It was calculated the positive ideal solution, V^+ and the negative ideal solution, V^- (table VI.7.3).

Table VI.7.3 – Positive and negative ideal solutions for analyzed criteria

Positive and negative ideal solution	Density, g/cm^3	Microhardness, HV	Corrosion rate, NaCl, µm/yr	Corrosion rate, Ringer, µm/yr
V^+	0.0887	0.1117	0.0003	0.0063
V^-	0.1075	0.0870	0.1685	0.1965

The ideal distance from any alternative to the positive ideal solution or the negative ideal solution was determined in table VI.7.4. It was also calculated a performance score, R_i.

Table VI.7.4 – The ideal distance from any alternative to the positive and negative ideal solution and the performance score

Alloy	d_i^+	d_i^-	R_i
$FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$	0.06	0.22	0.79
$FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$	0.11	0.18	0.61
$FeMnNb_{0.5}Ti_{1.5}Zr_{0.5}$	0.27	0.02	0.08
$FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ remelted	0.03	0.27	0.91

Analyzing the obtained results, it can be observed that the highest value has the alloy $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ remelted, followed by $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$. Also, the lowest value of the performance score has the alloy $FeMnNb_{0.5}Ti_{1.5}Zr_{0.5}$ (figure VI.7.1).

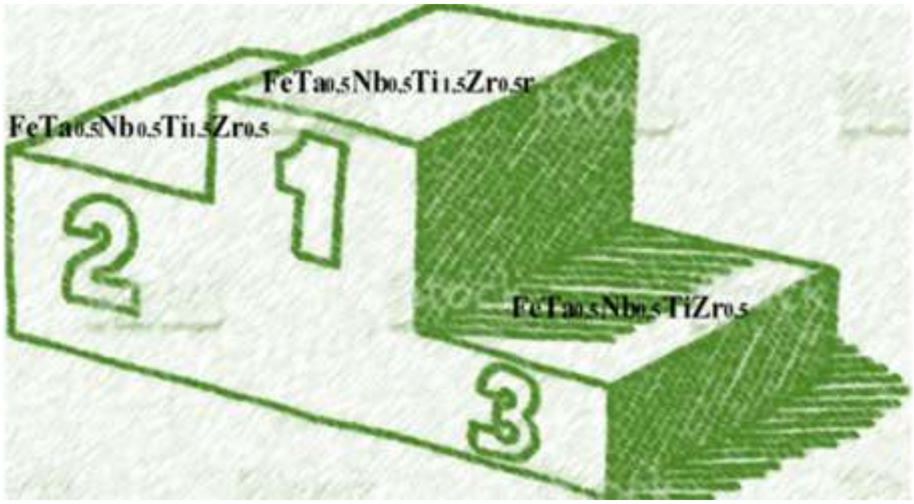


Figure VI.7.1 – The ranking of the performance score obtained by high entropy alloys with biocompatible properties elaborated in the induction furnace

CONCLUSIONS

C1. General conclusions

- From the beginning, people have been concerned of restoring parts of the body that have been damaged or lost due to accidents or illness.
- Although the civilizational journey began with the discovery of native metals and their use, the discovery of the first alloys and techniques for obtaining them brought better properties and new uses.
- Biocompatibility is the property of materials due to no side effects occur in the body and are accepted by the surrounding tissues.
- Each class of biomaterials has a number of characteristics, depending on the materials they are made from and the functional requirements of the implant. The properties that an implant must have are: mechanical properties (modulus of elasticity, tensile strength, compression, shear, ductility, hardness) properties of surfaces (surface tension and energy, roughness), biocompatibility properties, corrosion resistance, efficiency of biomaterials.
- Biomaterials can have multiple applications, such as: replacing an injured part (artificial hip joints, artificial kidneys, etc.), healing assistance (sutures, plaques or bone screws), improving function (pacemaker, contact lenses, etc.), correction of functional anomalies (Harrinton vertical rod), correction of aesthetic problems (chin augmentation, etc.), help in

establishing the diagnosis (probes, drainage tubes, etc.), help in applying treatments (drainage tubes, cannulas, etc.).

- A new category of metallic biomaterials can be considered high entropy alloys. They represent a new class of metallic materials with a distinct synthesis strategy and are different from conventional alloys, which are based on one or two main elements, because they are composed of five or more main elements. The expected upper limit is thirteen elements and is arbitrary. It has been shown that once this value is exceeded, the benefits obtained by the addition of alloying elements are insignificant.
- High entropy alloys have a multitude of good characteristics, such as high hardness, very good wear resistance, fatigue resistance, very good breaking strength at high temperatures, good thermal stability and increased resistance to oxidation and corrosion.
- Analyzing the properties of the main chemical elements used to obtain high entropy alloys with biocompatible properties, we selected four elements that are currently used in practice: Ti, Zr, Nb, Ta, which are considered the basis of elaborated alloy systems. They have excellent anticorrosive properties, wear resistance, machinability and biocompatibility. Fe and Mn were added to this group of elements which, although they are not part of the group of elements with high biocompatibility, have the quality of stabilizing structures based mainly on solid solutions in high entropy alloys. These elements are also low priced and can significantly reduce the final cost of the alloy. Based on these chemical elements, two alloys systems were selected: FeTaNbTiZr and FeMnNbTiZr.
- The MatCalc calculation program was used to investigate the redistribution process of solid solutions during the solidification process. The analysis tools consisted in obtaining equilibrium and Scheill-Gulliver diagrams, which provide information on the slow diffusion process, characteristic of high entropy alloys and the theoretical estimation of the solidification limit.
- In order to be able to design the optimal compositions of high entropy alloys with biocompatible properties, for the alloys systems, FeTaNbTiZr and FeMnNbTiZr, calculations of thermodynamic criteria were performed, varying the proportion of each element.
- From the analysis results of the MatCalc modelling for FeTaNbTiZr alloy system, it noted that the obtaining of a structure mainly composed of solid solutions is achieved at high percentages of Ta, Nb and Zr. Otherwise Ti must be kept at relatively low percentages. By replacing Ta with Mn, in the FeMnNbTiZr alloy system, the most important influence on the formation of the structure rich in solid solutions has Zr.
- From the criteria analysis of high entropy alloys, used to determine the structure, it was observed that increasing or decreasing the proportion of an element can have positive or negative effects on the formation of solid solutions.
- The main factor in defining the final alloy compositions are the characteristics required by their field of application. Among these we specify: biocompatibility, moderate modulus of elasticity, low density and cost of the alloy. Biocompatibility is majorly influenced by the

content of Ti, Ta, Nb, Zr. The modulus of elasticity is improved by reducing the content of intermetallic compounds, and the density by increasing the content of Ti and Mn and decreasing the content of Ta. The cost of the material is considerably improved by the addition of a high content of Fe and Mn.

- Following the analysis of the alloying elements influence on the characteristics required for biocompatible alloys and the tendency to form solid solutions for each alloy system, were proposed three high entropy alloys: $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$; $FeTa_{0.5}Nb_{0.5}TiZr_{0.5}$; $FeMnNb_{0.5}TiZr_{0.5}$.
- The proposed alloys were developed by the melting-casting method in the Linn MFG-30 induction furnace with an inert argon atmosphere. It offers special advantages, allowing to obtain a compositional homogeneity when melting alloys with contents of elements with melting points far apart in value, provided the solid-state miscibility.
- Improving the structure of high entropy alloys is achieved by applying annealing heat treatments (maintaining for 20 hours at a temperature of 600^0C), to eliminate internal stresses and improve the structure obtained from melting / casting processes.
- After applying heat treatments, high entropy alloys with biocompatible properties were mechanically, structurally and physico-chemically analyzed. Their corrosion resistance in simulated physiological environments was also evaluated.
- The alloys obtained by the melting / casting process in the induction furnace were characterized by chemical, optical, X-ray diffraction, SEM - EDAX, mechanical analysis and were determined the microhardness and corrosion resistances.
- Optical microscopy and SEM / EDS diffraction analyzes indicate the presence of non-metallic inclusions, both spheroidal aspect and rhombic symmetry, which are mainly in the interdendritic area.
- The obtained alloys were also mechanically characterized; alloys were chosen from the FeTaNbTiZr and FeMnNbTiZr systems, for which the modulus of elasticity and rigidity and the deformation break were determined. It has been observed that Ta-based alloys have superior mechanical properties to Mn-based alloys.
- Studies have been performed on the corrosion resistance of high entropy alloys in the FeTaNbTiZr and FeMnNbTiZr systems, in human physiologic simulant environments, respectively in the medium of NaCl infusion solution and Ringer lactate infusion solution. The best results on corrosion resistance were obtained from $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy.
- In order to determine which of the high entropy alloys developed in the induction furnace has the best properties, the TOPSIS method was used. In the mathematical model, characteristics such as density, microhardness, or corrosion rate were considered, both in NaCl infusion solution medium and Ringer's solution. Following the calculations, it was noted that the remelted $FeTa_{0.5}Nb_{0.5}Ti_{1.5}Zr_{0.5}$ alloy is best suited for use in biocompatible applications.

C2. Original contributions

The original contributions resulted from the research accomplished in the PhD thesis, derived from the approach of some as yet uninvestigated fields at national and international level, and they led to the obtaining of high entropy alloys with biocompatible properties:

- An updated documentary study was carried out on the manufacturing processes and the use of biocompatible materials in the manufacture of implants;
- A thermodynamic and kinetic model was developed based on the CALPHAD analysis method and on the solid state phase transformations, which determines the proportions of the phases that appear in the FeTaNbTiZr and FeMnNbTiZr alloys systems, depending on constituent elements variations. In this sense, thermodynamic equilibrium calculations, precipitation kinetics and microstructure simulations were performed, based on three theoretical models: multicomponent analysis of nuclear theory; modeling the growth of precipitated phases in a complex multicomponent system; modeling the energies formed at the interface between the precipitate and the matrix;
- The specific thermodynamic criteria for the formation of simple solid solutions in high entropy alloys were determined. In this case, the phase formation criteria were associated with the Hume - Rothery rule. Depending on the obtained results, the concentrations of each element were varied, in order to analyze their influence on the tendency to form solid solutions;
- To determine the optimized concentrations, the influence of the alloying elements on the structure based on solid solutions was studied;
- New materials with biocompatible properties were obtained;
- The selected compositions following the CALPHAD analysis and the calculations of the thermodynamic criteria were elaborated by the melting - casting process in the induction furnace;
- Annealing heat treatments of high entropy alloys elaborated in the induction furnace were applied, in order to eliminate internal stresses and improve the internal structure. Therefore, samples of high entropy alloys with heat-treated biocompatible properties were obtained;
- Specific methods for chemical and structural characterization of obtained alloys samples by optical microscopy, X-ray diffraction, SEM, EDX, as well as microhardness, mechanical strength and corrosion resistance analyses of high entropy alloys with biocompatible properties have been established;
- The alloy with the best properties was selected, using the order technique of preference by similarity to ideal solution, called TOPSIS.

C3. Future development

- Development of optimal synthesis and processes to obtain finished products with the required structure and dimensions. Testing techniques in powder metallurgy or multilayer thin film deposition;
- Continuation of biocompatibility tests of selected alloys, through in vitro research;
- Extension of the study of high entropy alloys with biocompatible properties using chemical elements such as yttrium or cerium and determination of physical, chemical, structural and mechanical properties;
- Development of a multi-scale program for modelling the biocompatible materials based on high entropy alloys;
- Submission of future projects for the transfer of the accumulated knowledge to the economic agents in the field.

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