

PAPER • OPEN ACCESS

Obtaining and characterisation of high entropy alloys used for medical applications

To cite this article: V Geantă *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **572** 012023

View the [article online](#) for updates and enhancements.

You may also like

- [Iron and chromium co-doped cobalt phosphide porous nanosheets as robust bifunctional electrocatalyst for efficient water splitting](#)

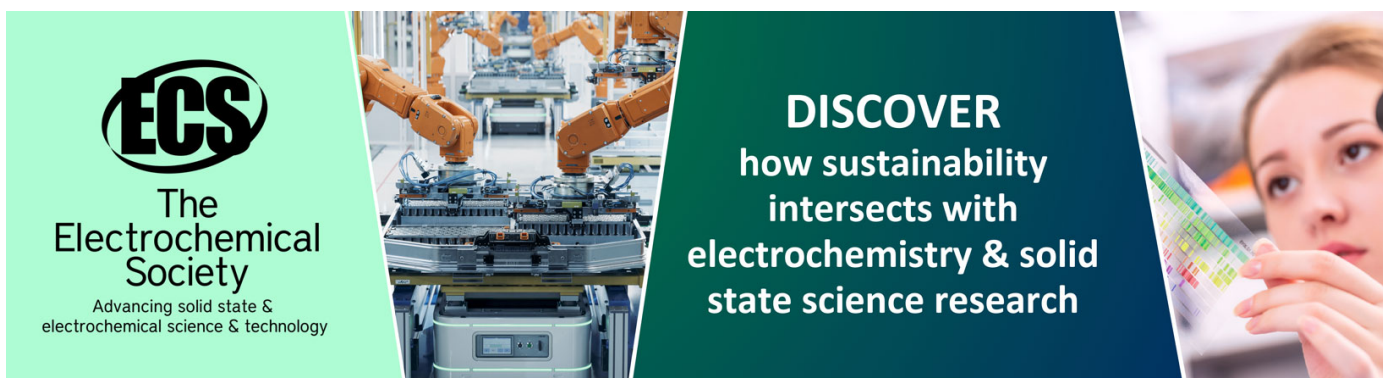
Shichao Sun, Zhihong Wang, Suci Meng et al.

- [Fabrication of Highly Sensitive Electrochemical Sensor Based on Chromium-Doped Ferrite Nanoparticles: Hybrid Graphene Nanosheets for the First Voltammetric Determination of Asenapine Maleate in Formulations and Human Plasma](#)

Mohamed S. Gado, Hanaa S. El-Desoky and Mohamed M. Abdel-Galeil

- [Computational exploration of biomedical HfNbTaTiZr and Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{0.5}Zr refractory high-entropy alloys](#)

Uttam Bhandari, Hamed Ghadimi, Congyan Zhang et al.



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Obtaining and characterisation of high entropy alloys used for medical applications

V Geantă¹, I Voiculescu¹, R Ștefănoiu^{1*}, M Codescu², H Kelemen³, G Pavel⁴,
A Vlădescu⁵ and V A Sandu⁶

¹ POLITEHNICA University of Bucharest, 313 Splaiul Independenței, 060042, Bucharest, Romania

² National Institute for R&D in Electrical Engineering ICPE-CA, 313 Splaiul Unirii, District 3, 030138, Bucharest, Romania

³ University of Medicine, Pharmacy, Science and Technology of Targu Mures, Gheorghe Marinescu 38, 540139, Targu Mures, Romania

⁴ The University of Agricultural Sciences and Veterinary Medicine, Iași, 3, Mihail Sadoveanu Alley, 700490, Iași, Romania

⁵ National Institute for Research and Development in Optoelectronics INOE 2000, 409 Atomiștilor street, 077125, Măgurele, Romania

⁶ Gheorghe Asachi Technical University of Iasi, 67 Dimitrie Mangeron Blvd., 700050, Iasi, Romania

E-mail: victorgeanta@yahoo.com

Abstract. The experimental CrFeMoNbTaTiZr alloys were designed based on the extremely low bio-toxicity of the chemical elements. They are currently used as a basis for alloying of classical alloys used in medical device manufacturing. From this alloying system, were obtained in a Vacuum Arc Remelting (VAR) equipment six alloys: CrFeMoNbTaTi, CrFeMoNbTaZr, CrFeMoTaTiZr, CrFeTaNbTiZr, CrTaNbTiZrMo and FeTaNbTiZrMo. The microstructural analysis of the obtained alloys have been performed by optical and SEM microscopy. The microhardness tests show results in the range of 575 – 1337 HV_{0.2/10}. In order to improve the mechanical properties heat treatment procedures have been applied.

1. Introduction

High entropy alloys featuring different compositional characteristics provided by the presence and quantity of various chemical elements in their composition impart extremely interesting properties. The development of refractory high entropy alloys composed of a single BCC phase in the W-Nb-Mo-Ta and W-Nb-Mo-Ta-V alloy systems has driven the production of BCC HEAs based on transition metals of the Nb-Mo-Ta-W, V-Nb-Mo-Ta-W, Ta-Nb-Hf-Zr-Ti, Hf-Nb-Ti-Mo-Ta-Ti-Zr type and the Hf-Mo-Nb-Ta-Zr equiatomic alloys. In terms of biocompatibility, it is interesting to note that most of these elements are biocompatible, except vanadium. Based on these concepts, there was initiated the production of biocompatible HEAs from the previously listed systems, to be potentially used for orthopaedic implants. There are known high entropy alloys in the TiNbTaZrMo, TiNbTaZrFe, TiNbTaZrW, TiNbTaZrCr, TiNbTaZrHf system, featuring higher deformability and biocompatibility characteristics than pure titanium, which is considered the least cytotoxic metal [1-5].



The high entropy alloys in the CrCoFeMoMnNiNb system, microalloyed with Ta, Ti or Zr, have outstanding mechanical characteristics (compressive strength above 2000 MPa, good deformation capacity in heavy duty conditions and good dynamic impact behaviour, chemical stability of the passivating film (corrosion potential in simulated biological environment) and reduced cytotoxicity (determined via the MTT test, ISO 10993). Compared to classical alloys employed for widely used medical devices (CoCr or CoCrMo alloys), with side effects (tissue necrosis and release of metal ions in the body over acceptable limits), the CrCoFeMoMnNiNbTaTi Zr alloys appear to be significantly superior.

2. Materials and methods

High entropy alloys for medical applications can be obtained in optimum conditions in vacuum arc remelting - VAR - furnaces and in high-purity argon (Ar 5.3) controlled environment. The CrFeMoNbTaTiZr system alloys presented in this paper were based on the selection of chemical elements exhibiting extremely low bio-toxicity and which are currently used in the manufacture of medical devices.

In order to obtain high entropy alloys from the CrFeMoNbTaTiZr system in the VAR MRF ABJ 900 vacuum arc remelting furnace in the laboratory ERAMET - Materials Science and Engineering Faculty from POLITEHNICA University of Bucharest, there were chosen the following 7 classes of alloys in which the chemical composition was varied but the equiatomic proportion was preserved in each of them as follows: HEA 1 – CrFeMoNbTaTiZr; HEA 2 – CrFeMoNbTaTi; HEA 3 – CrFeMoNbTaZr; HEA 4 – CrFeMoTaTiZr; HEA 5 – CrFeTaNbTiZr; HEA 6 – CrTaNbTiZrMo; HEA 7 – FeTaNbTiZrMo [6]. The raw materials used were chemical elements of purity greater than 99.5% which were machined for placement into the VAR furnace, then weighed and dosed in equiatomic ratios, with quasi-constant weights of about 30 g. The composition of the load is shown in Table 1.

Table 1. Composition of HEA biocompatible load.

Alloy	Element, g							Total weight, g	Efficiency, g
	Cr	Fe	Mo	Nb	Ta	Ti	Zr		
HEA 1 – CrFeMoNbTaTiZr	2.55	2.73	4.66	4.54	8.77	2.37	4.38	30.02	29.85
HEA 2 – CrFeMoNbTaTi	2.97	3.19	5.47	5.30	10.32	2.74	-	29.99	29.91
HEA 3 – CrFeMoNbTaZr	2.74	2.95	5.06	4.9	9.54	-	4.8	29.99	29.42
HEA 4 – CrFeMoTaTiZr	2.98	3.2	5.5	-	10.36	2.75	5.21	30	29.69
HEA 5 – CrFeTaNbTiZr	3	3.22	-	5.36	10.42	2.76	5.24	30	29.72
HEA 6 – CrTaNbTiZrMo	2.78	-	5.13	4.98	9.68	2.56	4.87	30	29.94
HEA 7 – FeTaNbTiZrMo	-	2.97	5.1	4.94	9.61	2.55	4.83	30	29.95

On the copper plate of the VAR furnace, in specific crucibles, the load materials were introduced in an order which ensures the formation of a metal bath under the action of the electric arc. The installation was connected to the cooling system and then the process continued with the introduction of argon and successive suctions until a pressure of 5×10^{-3} mbar was obtained in the working chamber [7-11]. The actual melting was carried out with about 8 to 10 homogenisation passes to ensure a uniform distribution of the elements in the prepared alloys. The high number of remelting operations

was required by the fact that the load contains elements melting at high temperatures, as follows: Fe - 1538 °C; Ti - 1668 °C; Zr - 1855 °C; Cr - 1907°C; Nb - 2477 °C; Mo - 2623 °C; Ta - 3017°C. Images from the technological processes for obtaining biocompatible HEAs in the VAR furnace are shown in Figures 1 and 2.

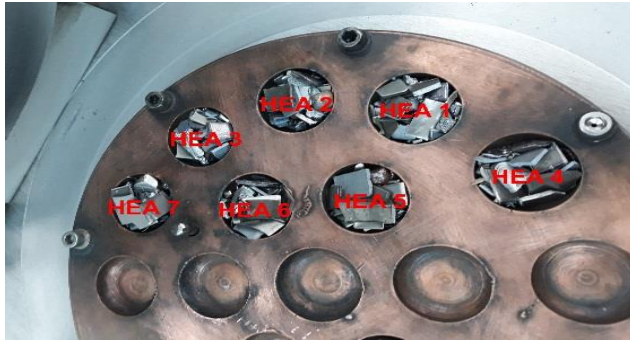


Figure 1. HEA 1 - HEA 7 batch load composition on the copper plate of the VAR furnace.



Figure 2. Buttons made of HEA 1 - HEA 7 alloys after preparation.

After melting and homogenising, the batches were cooled on the copper plate in argon atmosphere. The biocompatible HEA buttons produced (Figure 2) were weighed to determine the efficiency of the process (removal of material), which proves to be very close to the amount of material introduced. The efficiency of the production process ranged from 98.96 to 99.83%. The buttons of biocompatible high entropy alloys thus obtained are prepared for microhardness tests and metallographic analysis.

3. Microstructural characterization of biocompatible high entropy alloy in raw cast state

The microstructural characterization of biocompatible high entropy alloys was performed for the following classes, consisting of 6 chemical elements, as follows: HEA 2 - CrFeMoNbTaTi, HEA 3 - CrFeMoNbTaZr, HEA 4 - CrFeMoTaTiZr, HEA 5 - CrFeTaNbTiZr, HEA 6 - CrTaNbTiZrMo, HEA - 7 FeTaNbTiZrMo (Figures 3 - 8).

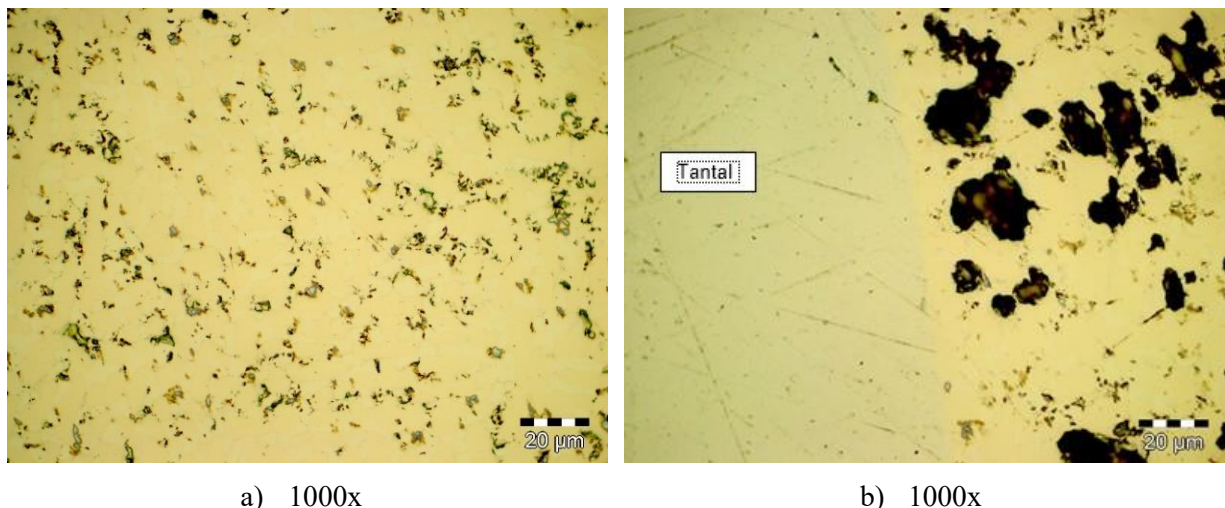


Figure 3. HEA 2 - CrFeMoNbTaTi, without chemical attack (LAMET Laboratory - PUB).

Figure 3 shows that many of the elements that formed the matrix of the HEA 2 - CrFeMoNbTaTi alloy are dissolved and they formed a solid homogeneous solution. There can be noticed as well a number compounds of hard-to-melt elements (Mo, Nb), relatively uniformly dispersed in the base

metal matrix (Figure 3, a). The raw materials melting at high temperatures, such as Ta and Mo, did not melt entirely and they are embedded in the molten metal matrix of the other elements (Figure 3, b).

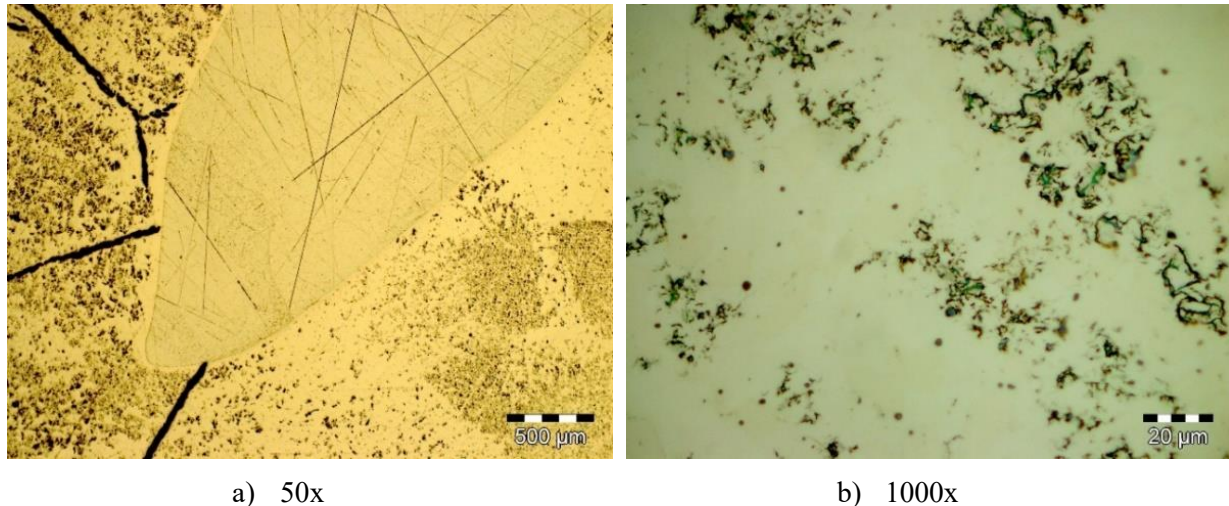


Figure 4. HEA 3 - CrFeMoNbTaZr, without chemical attack (LAMET Laboratory - PUB).

As in the case of the HEA 3-CrFeMoNbTaZr alloy, the complete melting of Ta was not possible within the designed metal volume of the batch. The high difference between the melting temperatures of the chemical constituents of the alloy, coupled with the rapid cooling on the water-cooled copper plate, also generated cracking effects in the metal matrix surrounding the Ta or Mo grains (Figure 4, a). Elements like Cr, Zr, Fe, Nb formed a common solid solution in which intermetallic compounds precipitated (Figure 4, b).

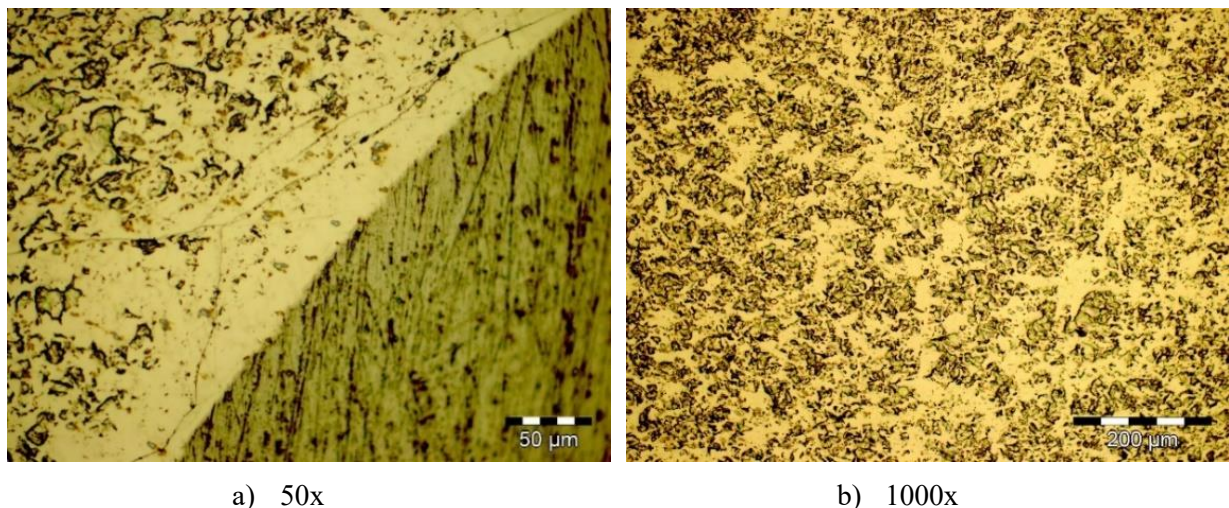
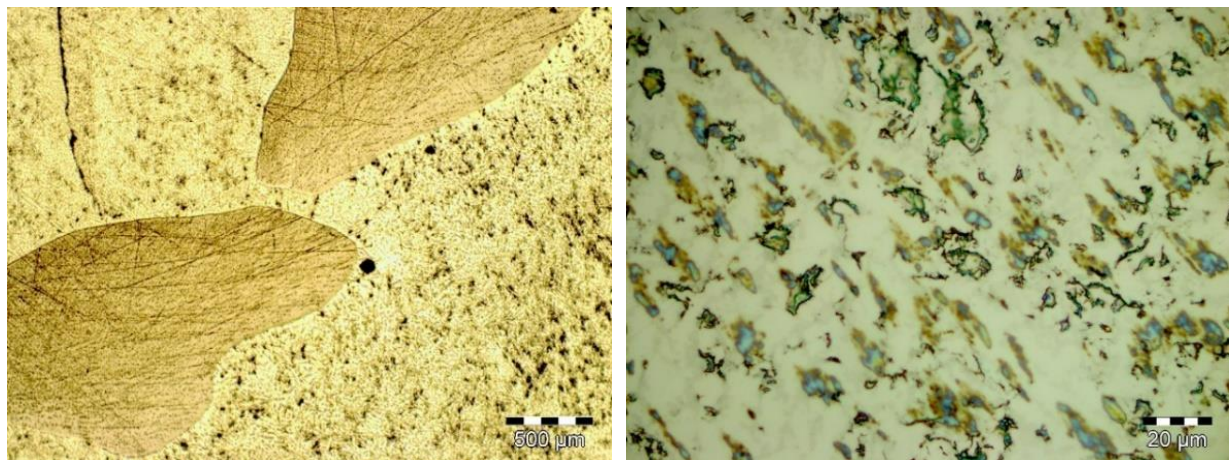


Figure 5. HEA 4 - CrFeMoTaTiZr, without chemical attack (LAMET Laboratory - PUB).

The CrFeMoTaTiZr alloy shown in Figure 5 contains only 2 hard-to-melt elements (Mo and Ta); however, these grains could not melt completely either. In addition, at the interface between the grain of the hard-to-melt metal - Ta - and the embedding metal matrix, parallel cracks formed due to the solidification stresses (or rather, due to the inability of the high-strength metal matrix to disperse the stresses generated by the ultra-fast cooling).

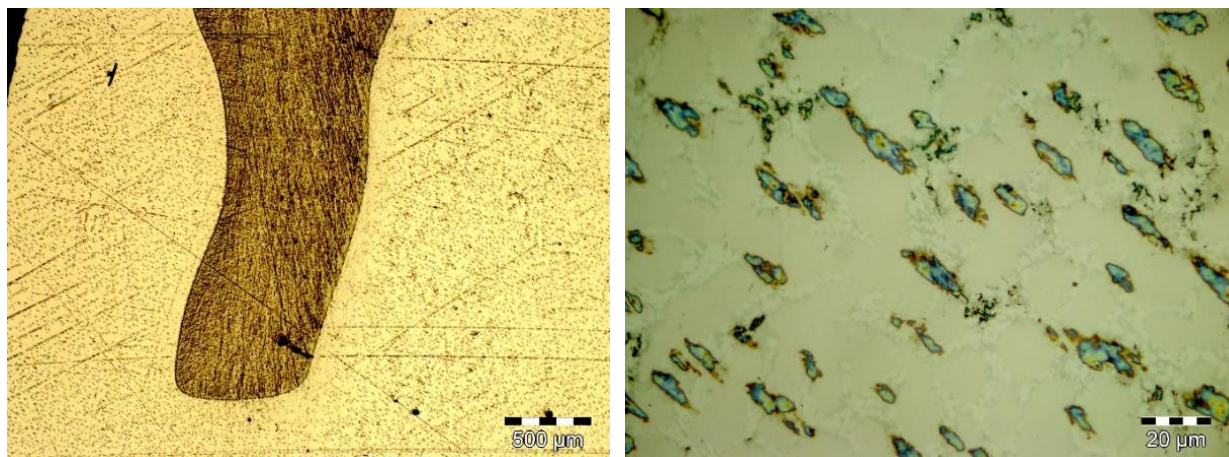


a) 50x

b) 1000x

Figure 6. HEA 5 - CrFeTaNbTiZr, without chemical attack (LAMET Laboratory - PUB).

The CrFeTaNbTiZr alloy (Figure 6) has a similar evolution to the other alloys shown above. In this case, the dissolution of the Ta particles is not possible entirely. It is quite possible that the lack of dissolution of the Ta granules can be attributed to their too high volume (10.42 g) within the total batch volume (about 29.22 g).



a) 50x

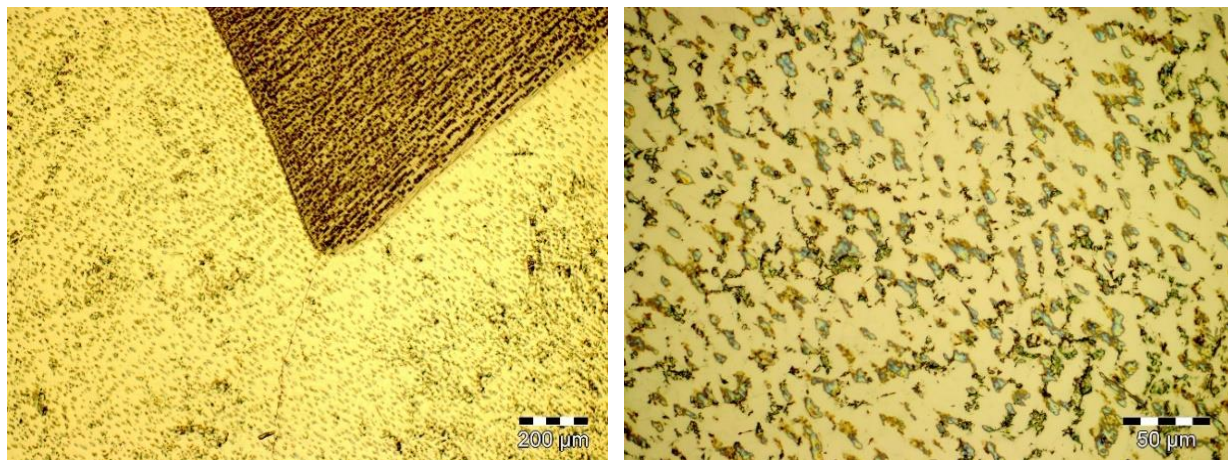
b) 1000x

Figure 7. HEA 6 - CrTaNbTiZrMo, without chemical attack (LAMET Laboratory - PUB).

In the case of the CrTaNbTiZrMo alloy, the problem of dissolving the particles of hard-to-melt metals (Ta, Mo) remains unsolved (Figure 7, a). In the solid solution base matrix, consisting of Cr, Ti, Zr, Nb, the dendritic nature of the alloy is configured more clearly (Figure 7, b), with the separation of the evenly distributed intermetallic compounds.

The FeTaNbTiZrMo alloy (Figure 8) preserves features similar to those previously described. The Ta particle did not melt entirely, and a fissure developed in the metal matrix from its interface with the base matrix (Figure 8, a).

The rest of the elements formed a fairly homogeneous, dendritic solid solution in which a number of intermetallic compounds are dispersed and distributed evenly (Figure 8, b).



a) 200x

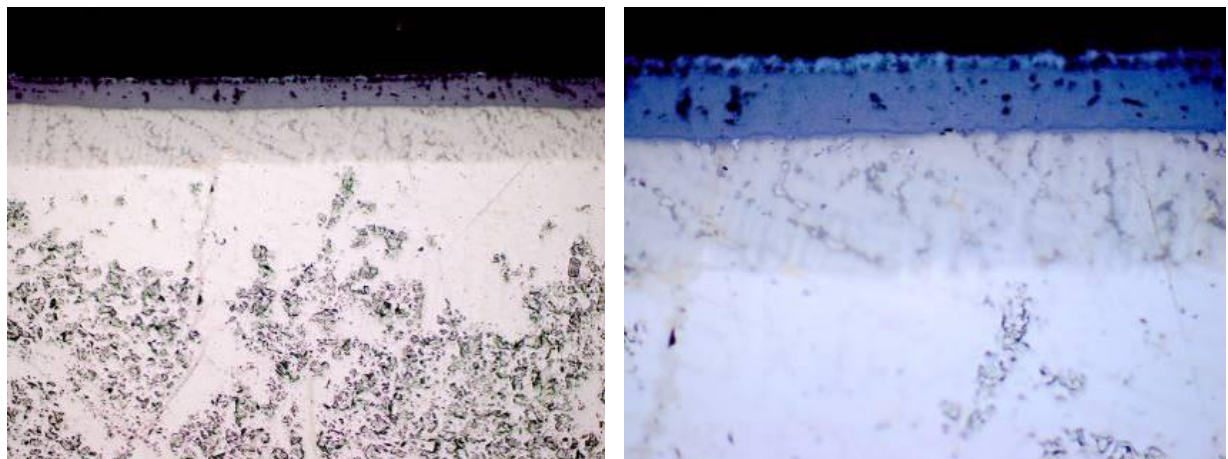
b) 500x

Figure 8. HEA 7 - FeTaNbTiZrMo, without chemical attack (LAMET Laboratory - PUB).

4. Heat treatments aimed at improving the properties of the biocompatible high entropy alloys

The heat treatments applied to the experimental alloys consisted of heating to 800 °C and holding for 24 hours, followed by slow cooling in the oven. The heating speed of about 0.25 °C/hour was obtained using the electronic control of the furnace Nabertherm LT 15/12/P320 used for heat treatments, fitted with a temperature regulator. The application of this treatment was aimed at the microstructural homogenisation and the improvement of the elastic properties of the metal matrix. The development of the HEA microstructure was highlighted by optical and electronic microscopy.

Thus, before the heat treatments were applied, it was noticed that the hard-to-melt elements (Ta, Nb, Mo) had not completely dissolved in the metal melt, there being only their diffusion within the boundaries of separation, on short distances (Figures 3-8). After applying the heat treatment, there was found an enhanced oxidation tendency of the elements located in the superficial layer of the samples and the formation of a homogenised alloy strip immediately below the complex oxide layer (Figure 9) No chemical attack was performed on the metallographically prepared samples.



a) 200x

b) 500x

Figure 9. CrFeNbTiZr alloy after the heat treatment at 800 °C/24 hours/slow cooling.

The effects of heat treatment were also highlighted using the EDS analysis with AMETEC Z2e analyser on the microzones located both in the centre of the samples and at the edge, in order to

quantify the oxidation and diffusion effects. An image on the boundary between an undissolved/unmelt Ta particle with the embedding metal matrix is shown in Figure 10.

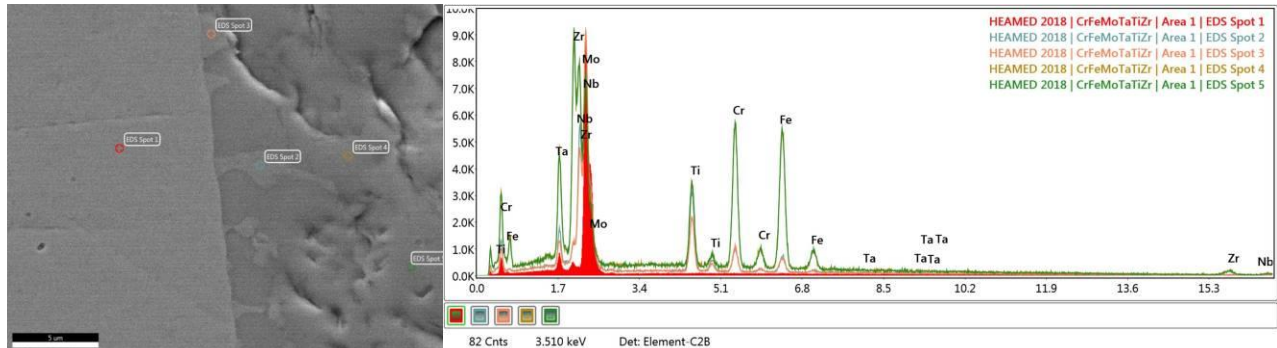


Figure 10. Elemental distribution on a microzone of HEA 4 - CrFeMoTaTiZr.

5. The microhardness of biocompatible high entropy alloys

The mechanical characteristics of the biocompatible high entropy alloys in raw cast state and after heat treatments are highlighted by the different microhardness values determined using the Shimadzu HMV 2T microhardness tester and they are shown in Table 2.

The analysis of the microhardness values obtained by applying the homogenisation treatment reveals that the hardness increases in the highly alloyed metal matrix up to the average value of 1290 HV_{0.2} in case of the alloy CrFeMoTaTiZr. The diffusion of the chemical elements during the heat treatment caused lower hardness in the marginal area adjacent to the surface (located at a distance of about 200 μm), where the average hardness was 882 HV_{0.2}, i.e. about 66 HRC, as well as the formation of a homogenisation strip of about 45 μm , in which the hardness increased to 1337 HV_{0.2}. The microstructural aspects are consistent with the microhardness values (Figure 11).

Table 2. Microhardness values for biocompatible HEA samples.

Alloy	Spot microhardness values HV _{0.2/10}	Value average, HV _{0.2}	Standard deviation	Variation coefficient
HEA 1 - CrFeMoNbTaTiZr	749, 739, 700, 743, 747	736	20.27	2.76
HEA 2 - CrFeMoNbTaTi	750, 732, 747, 804, 736	754	29.04	3.85
HEA 3 - CrFeMoNbTaZr	775, 748, 719, 725, 803	754	35.16	4.66
HEA 4 - CrFeMoTaTiZr	697, 764, 795, 790, 712	752	44.89	5.97
HEA 5 - CrFeMTaNbTiZr	749, 700, 748, 736, 705	728	23.54	3.24
HEA 6 - CrTaNbTiZrMo	581, 567, 591, 590, 544	575	19.63	3.42
HEA 7 - FeTaNbTiZrMo	626, 686, 655, 657, 651	655	21.34	3.26
CrFeMoNbTiZr				
Central zone	791, 832, 817, 775, 772	797	26.31	3.30
Marginal zone	801, 809, 822, 798, 815	809	9.87	1.22
HEA 4 - Heat treated CrFeMoTaTiZr				
Central zone	974, 1349, 1406, 1286, 1434	1290	185.44	14.38
Marginal zone	906, 876, 893, 893, 840	882	25.45	2.88
		(66HRC)		
Homogenisation layer	1296, 1429, 1305, 1339, 1316	1337	53.88	4.03

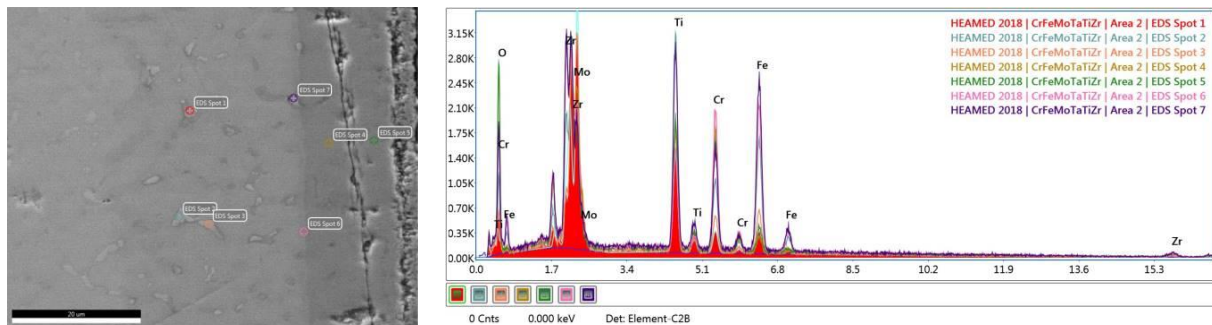


Figure 11. Elemental distribution on a microzone of heat-treated HEA 4 - CrFeMoTaTiZr.

6. Conclusions

High entropy alloys in the CrFeMoNbTaTiZr alloying systems can be obtained in the VAR furnace subject to the following conditions:

- the batch volume must be sufficiently large to allow for the dissolution of the hard-to-melt elements and the holding time in liquid state must be longer in order to achieve the complete dissolution of the particles from the hard-to-melt elements;
- the chemical elements of the alloy component must be introduced as particles of much smaller grain size so as to favour the diffusion dissolution phenomena in the common molten metal bath.

The heat treatments applied to the experimental alloys consisted of heating to 800 °C and holding for 24 hours, and the aim was the microstructural homogenisation and the improvement of the elastic properties of the metal matrix. After applying the heat treatment, there was found an enhanced oxidation tendency of the elements located in the superficial layer of the samples and the formation of a homogenised alloy strip immediately below the complex oxide layer.

The analysis of the microhardness values obtained by applying the homogenisation treatment reveals that the hardness increases in the highly alloyed metal matrix up to the average value of 1290 HV_{0.2} in case of the alloy CrFeMoTaTiZr. The diffusion of the chemical elements during the heat treatment caused lower hardness in the marginal area adjacent to the surface (located at a distance of about 200 μm), where the average hardness was 882 HV_{0.2}, i.e. about 66 HRC, as well as the formation of a homogenisation strip of about 45 μm, in which the hardness increased to 1337 HV_{0.2}.

7. References

- [1] Yeh J W 2006 *Annales De Chimie – Science des Materiaux* **31** 633
- [2] Yeh J W, Chen S K, Lin S J, Gan J W, Chin T S, Shun T T, Tsau C H and Chang S Y 2004 *Adv. Eng. Mat* **6** 299
- [3] Li C, Li J C, Zhao M and Jiang Q 2009 *J. Alloys Compd* **475** 752
- [4] Santos G A 2017 *Advances in Tissue Engineering and Regenerative Medicine* **3** 300
- [5] Breme H J, Biehl V and Helsen J A *Metals and implants. Metals as Biomaterials*, (England: John Wiley and Sons Ltd, Baffins Lane, Chichester, West Sussex PO19 1UD) ISBN 0471-969354
- [6] Geantă V and Voiculescu I 2018 *Tratat de obținere a materialelor metalice biocompatibile* (Bucharest Romania: Printech) ISBN 978-606-23-0845-2
- [7] Geantă V, Voiculescu I, Miloșan I, Istrate B and Mateș I M 2018 *Rev. Chim. Bucharest* **69** 798
- [8] Geantă V, Voiculescu I, Istrate B, Vrâncănu D, Ciocoiu R and Cotruț C 2018 *Transtech International Journal of Engineering Research in Africa* **37** 23
- [9] Ștefănoiu R, Geantă V, Voiculescu I, Csaki I and Ghiban N 2014 *Rev. Chim. Bucharest* **65** 819
- [10] Geantă V, Voiculescu I, Ștefănoiu R, Savastru D, Csaki I, Patroi D and Leonat L 2013 *Optoelectron Adv. Mat.* **7** 874
- [11] Voiculescu I, Geantă V, Ștefănoiu R, Patroi D and Binciciu H 2013 *Rev. Chim. Bucharest* **64** 1441