ON THE DESIGN OF NEW β-PHASE TITANIUM ALLOYS Ti-Mo-W

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This paper presents preliminary results of research undertaken in order to obtain a β-Ti alloy biocompatible, with mechanical and tribological properties well defined. Designing the alloy (which focuses on the stability of phase β-Ti) has taken into account: the bond order (Bo), the energy level of metal d - orbital (Md), the ratio of valence electrons / atom (e/a), the equivalent of Mo and the influence of the addition of W. The elaboration of the alloy was performed in a vacuum arc remelting equipment (VAR) 900 ABD MRF model using pure metals. The analysis to identify the phase of the alloy obtained (confirmation of the structure of β-Ti) was performed by X-ray diffraction. For the identification of metallic inclusions in the alloy obtained were performed micro-compositional analyses.

Keywords: alloy design, titanium alloys, bond order, d-orbital

1. Introduction

Titanium alloys are widely used as biocompatible materials because of their good mechanical properties and outstanding corrosion resistance.

A number of researchers [1, 2] showed that titanium alloys, containing enough high-Mo, have a very high resistance to corrosion. Nishimura [3] has been

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found that an alloy, Ti-15Mo (wt %), which was developed in the 1950s have a very high resistance to corrosion and is capable of withstanding corrosion in aggressive environments at high temperatures.

Titanium alloys have a unique profile of properties, which are increasingly used in numerous areas ranging from aerospace structures to biomedical applications. Among the newly developed titanium-based alloys, alloys β-Ti appear to have a promising combination of mechanical properties, such as for example a new generation of biocompatible β-Ti alloys with alloying elements such as Ta, Nb, Zr and Mo, which being designed as super elastic alloys (low modulus of elasticity), mainly for orthopaedic and dental applications as osteo-integrated implants [4, 5, 6, 7]. These β-Ti alloys can support multiple deformations reversible or irreversible, depending on the stability of β phase.

The modulus of elasticity of the titanium is reduced by adding elements such as niobium, tantalum and vanadium [8]. In this regard has been made many efforts in order to develop the new titanium alloys. The alloys must have a low modulus of elasticity, and a high level of resistance, in particular for use in implants [9-11].

However, none of these types of alloys are been completely satisfactory. Moreover, there have been several attempts to calculate and predict theoretically the modulus of elasticity of the titanium alloy [12]. This new calculation method can accurately predict the modulus of elasticity by calculating the elastic constants (c11, c12, c44) for binary alloy Ti-X (X = V, Nb, Ta, Mo and W). From the calculation results, it was found [8] that (c11-c12) is correlated with the average of valence electrons, the value of *e/a*.

In the alloy Ti-25% the Nb to which the *e/a* ratio is 4.25, the elastic anisotropy is significant and the modulus of elasticity has a very low value. This coincides with the result that the value (c11-c12) approaches zero when *e/a* ratio is close to 4.24.

The results indicated that the modulus of elasticity for Ti-X polycrystalline binary alloys, which is calculated from the elastic constants of single crystal by the method Voigt-Reuss-Hill reaches a minimum for an *e/a* ratio of about 4.24 [12]. As a result, it can be considered that *e/a* ratio of approximately 4.24 is one of the most important requirements for the design of a titanium alloy with low modulus of elasticity.

2. Alloy design

Phase stability of titanium alloys can be predicted by some parameters such as bond order (Bo), the energy level of metal d-orbital (Md) [13, 14], the ratio of valence electrons / atom (*e/a*) [15, 16] and the equivalent of Mo [3, 12].

Physical stability of Ti-15Mo alloy increases with increasing of Bo and decreasing Md and by increasing the *e/a* ratio and equivalent of Mo.

Meanwhile, Morishita et al. [17] have investigated the effects of alloying element on the corrosion resistance of the titanium alloys with α and β structure in solution of 10% HCl and 10% H_2SO_4, and concluded that the alloy with superior Bo has higher corrosion resistance.

In order to explain the mechanisms by which are obtained low modulus of elasticity (Young's modulus), were calculated the elastic constants of the binary alloys systems Ti (1-n) - X (n) (X = V, Nb, Ta, Mo, and W) and Zr 1-x X x (X = Nb and Mo) for x = 0.0, 0.25, 0.5, 0.75, 1.0 by the method USPP - Vanderbilt (Ultra Soft Pseudo-potential method) [18] in the vicinity of the generalized gradient approximated using the density functional theory (DFT).

The modules of elasticity of the polycrystalline metallic materials based on titanium, were calculated from the elastic constants calculated for the single crystal, using the scheme Voigt-Reuss-Hill [19] (*the approximation Voigt-Reuss-Hill - VRH, it is a very useful method whereby the elastic modulus can be approximated using the elastic constants of anisotropic single-crystal converted to an isotropic cubic polycrystalline material*). The calculation results show that elasticity modules for binary alloys Ti-X, have minimum values in the vicinity of x = 0.25. From the results of calculations, it was found that the difference c11 - c12 is correlated with the number of electrons valence of the atom (*e/a*) and this difference becomes almost zero (minimum modulus of elasticity) once the *e/a* ratio is approximately 4.20 - 4.24. The difference c11 - c12 represents also the stability of the cubic structure in these alloys and therefore can highlight the importance of controlling the number of valence electrons per atom to about 4.20 - 4.24 for a material with a low Young's modulus in titanium based alloys with β structure.

Fig. 1 shows the influence of the W addition over Bo and Md values in the alloy Ti-15Mo. The addition of W in alloy Ti-15Mo decreases the value of Md with a visible increase in the value of Bo and addition of iron decreases the value of Md without a significant decrease of the Bo, Fig. 2. On the basis of the Bo - Md map, Figure 3 (the phase stability map) [14, 15], Ti-15Mo alloy is located in the β phase region, and in Table 1, the values of bond order (Bo) and the orbital energy level of d (Md) in β-Ti. The influence of the addition W and Fe over the *e/a* ratio and the equivalent of Mo, Mo_{eq} are shown in Figures 4 and 5.

It is noted that both the addition of W and Fe are growing the values of *e/a* ratio and the Mo_{eq}. Thus, it is expected that phase stability of the alloy Ti-15Mo to increase by the addition of W, which induces a change in the processability by deformation without any degradation of the corrosion resistance and to obtain a biocompatible material with a low modulus of elasticity, under the increase of mechanical strength and high resistance to corrosion.
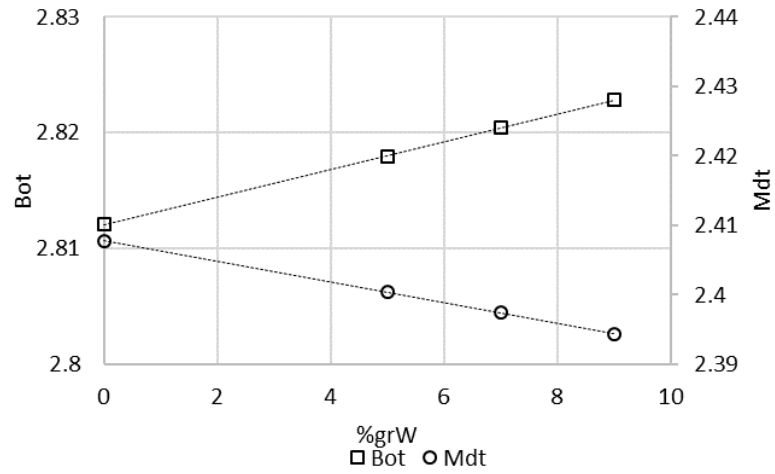
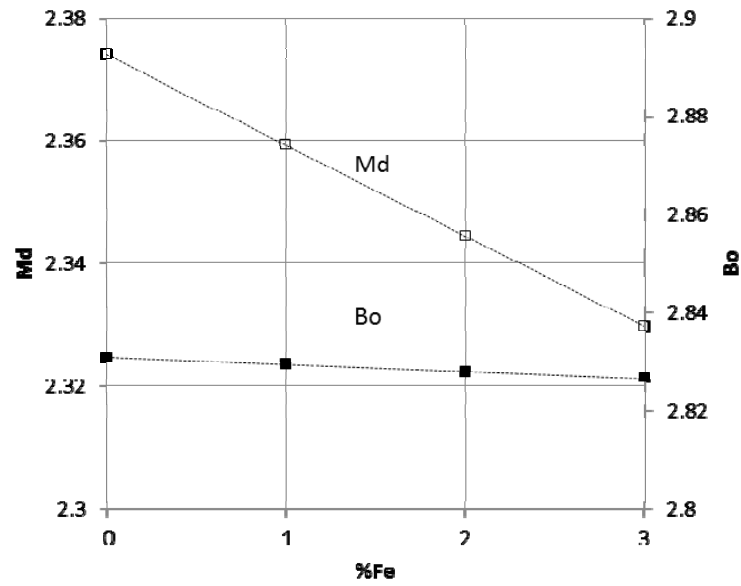Fig.1. The influence of the W addition over Md and Bo in the alloy Ti-15Mo

Fig.2. The influence of the Fe addition over Md and Bo in the alloy Ti-15Mo
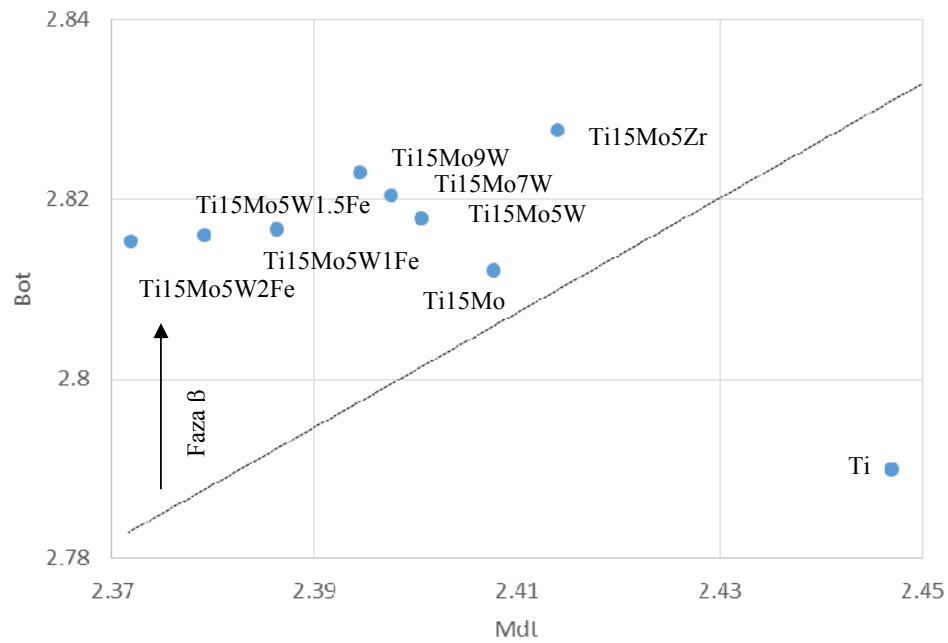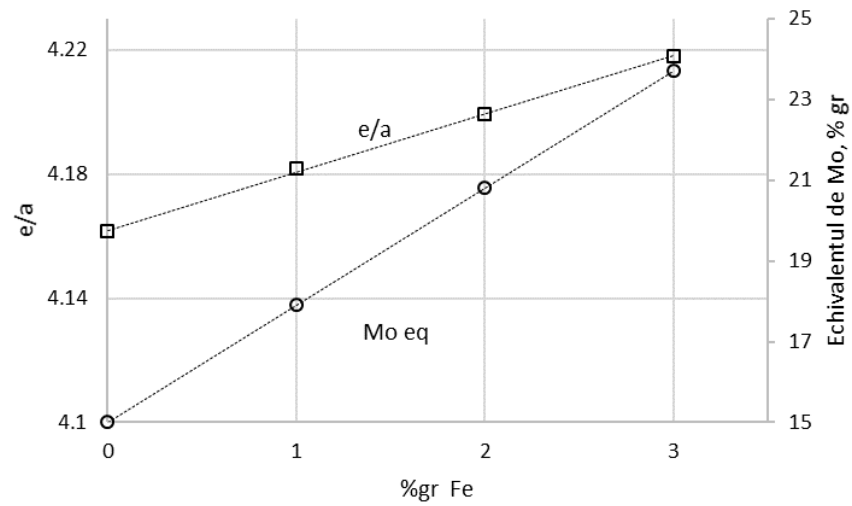
Fig.3. Md-Bo map

Fig.4. The influence of the Fe addition on the ratio *e/a* in the alloy Ti-15Mo
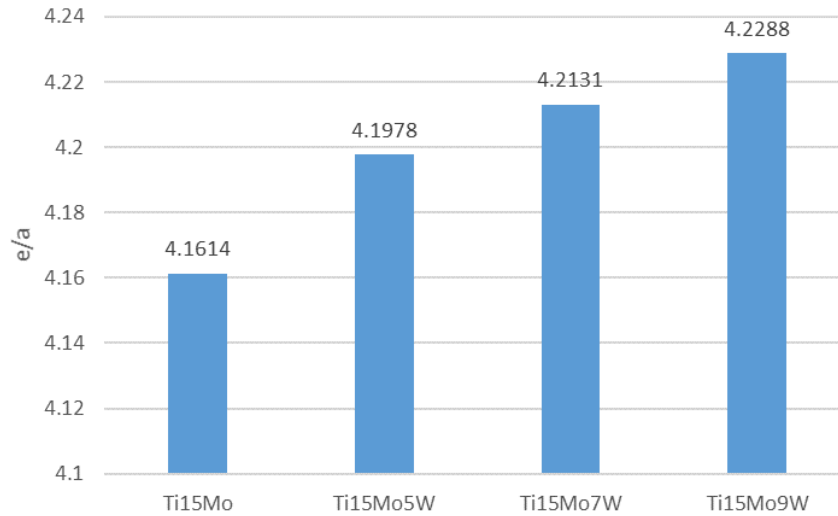
Fig.5. The influence of the W addition on the ratio *e/a* in the alloy Ti-15Mo

Table 1

Values of bond order (Bo) and energy level of d orbital (Md) in β-Ti

No.	*Element*	*Electronic layer*	*Bond order Bo*	*Energy level of orbital d, Md*
1	Ti		2.790	2.447
2	V		2.805	1.872
3	Cr		2.779	1.478
4	Mn	3d	2.723	1.194
5	Fe		2.651	0.969
6	Co		2.529	0.807
7	Ni		2.412	0.724
8	Cu		2.114	0.567
9	Zr		3.086	2.934
10	Nb	4d	3.099	2.424
11	Mo		3.063	1.961
12	Hf		3.110	2.957
13	Ta	5d	3.114	2.531
14	W		3.125	2.072
15	Al	others	2.426	2.200
16	Si		2.283	2.100

Next, we experimentally investigated the influence of the addition of W on the properties of the alloy Ti-15Mo, an element that enhances the mechanical strength of the alloy without increasing the modulus of elasticity, by changing the combination of the three electronic numbers, order bond (Bo) and the energy level metal d-orbital (Md) while maintaining an *e/a* value of 4.20 - 4.24.

It is proposed a combination of all three electronic numbers of the form: an e/a ratio around 4.24 value (to obtain a low modulus of elasticity), Md of about 2.39 - 2.40 and Bo approximately of 2.80 (for a sufficient stability of β phase and a good resistance to corrosion). The unique properties such as a low modulus of elasticity, good cold workability, and good resistance to corrosion occur only when all three of these numbers are simultaneously satisfied.

Composition of the new alloy taken into account, is based on the classic Ti15Mo alloy composition with the addition of 5-11% W for obtaining a stable β phase, 1.2% Fe to improve the processability and can be added as well as 5-9% Zr or Hf for the adjustment of Md and Bo values.

The values of Md, Bo and e/a ratio were calculated by equations (1), (2) and (3):

$$Md = \sum Md_i x_i \tag{1}$$

$$Bo = \sum Bo_i x_i \tag{2}$$

$$\frac{e}{a} = \sum e_i x_i \tag{3}$$

Were:

x_i = at% element i;
Md_i = energy level metal d-orbital of the element i;
Bo_i = bond order for i;
e_i = valence electrons of element i;

3. Experimental results and discussion

For selecting an alloy for medical applications has to be taken into account criteria such as biocompatibility, mechanical and tribological properties, corrosion resistance. The β type titanium alloys meet simultaneously the best properties to fulfil the criteria mentioned. In order to obtain new Ti based biomaterials, was started with the design of the new material using the electronic numbers Bo (bond order), Md (energy level metal d-orbital), the ratio of valence electrons / atom (e/a) and molybdenum equivalent. To fulfil the requirements proposed (stable β phase, corrosion resistance, low modulus of elasticity) it is necessary that these three numbers to be simultaneously satisfied.

To obtain a biocompatible material was started from an elastic Ti15Mo alloy with a very good corrosion resistance, to which was added W for raising the e/a ratio's to the value of 4.24 because W has six valence electrons and can

increase this ratio with relatively low additions. In order to adjust the values of Md and Bo can be used additions of Zr or Hf, and to improve processability may be added 1 to 3 wt%. Fe.

The obtaining process was performed in a vacuum arc remelting equipment (VAR) 900 ABD MRF model using pure metals. Initially it was introduced to melting materials to obtain, first, a Ti15Mo5W alloy. After the initial melting was not achieved a homogeneous material, being highlighted metallic inclusions of W and / or Mo - undissolved metal, Fig. 6-7.

The alloy obtained in a VAR equipment was characterized by electronic microscopy, observing that the material is homogenous both compositionally and phasic. Characterization in terms of mechanical properties will be achieved in a forthcoming paper.

For better homogenization the material has been remelted, thus achieving a homogeneous material, as shown in Figure 8, the alloying elements being uniformly distributed in the alloy. Table 2 shows the chemical composition of the alloy.

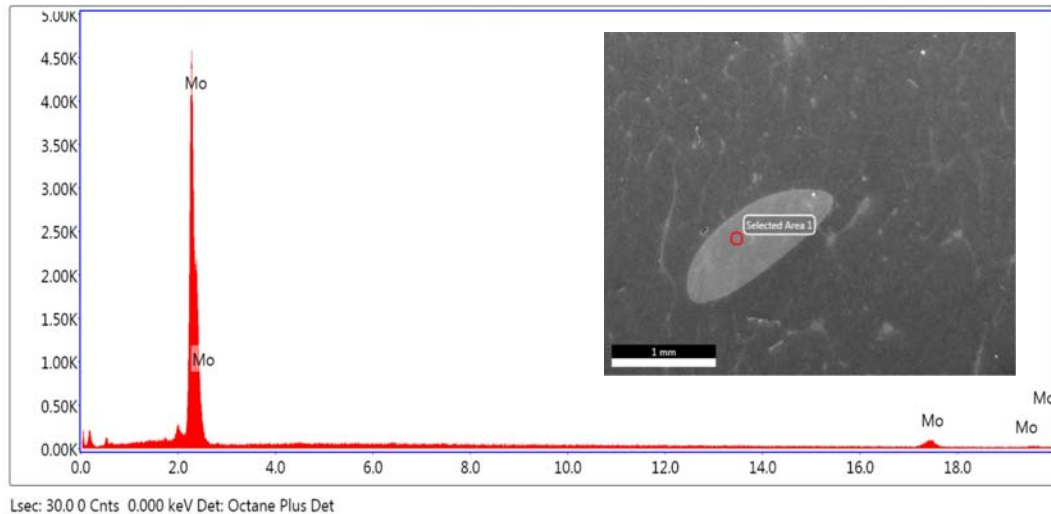Lsec: 30.0 0 Cnts 0.000 keV Det: Octane Plus Det

Fig.6. Metallic inclusions of Mo - undissolved metal

For the characterization of the obtained alloy were performed micro - compositional analyzes (Figures 6 to 9) to identify the metallic inclusions, using the scanning electron microscope type FEI QUANTA qualitative EGF 450. The structural analysis was carried out using an X-ray diffractometer PANalytical X'Pert PRO MRD model with the wave length of lCu = 1.544, as seen in Fig. 10.

In order to identify the phases, in Figure 10 is shown the diffraction pattern of the alloy obtained, for the diffraction angle in the range of $2\theta = 30\text{-}75$ degrees. X-ray diffraction pattern analysis shows that the only present phase is the

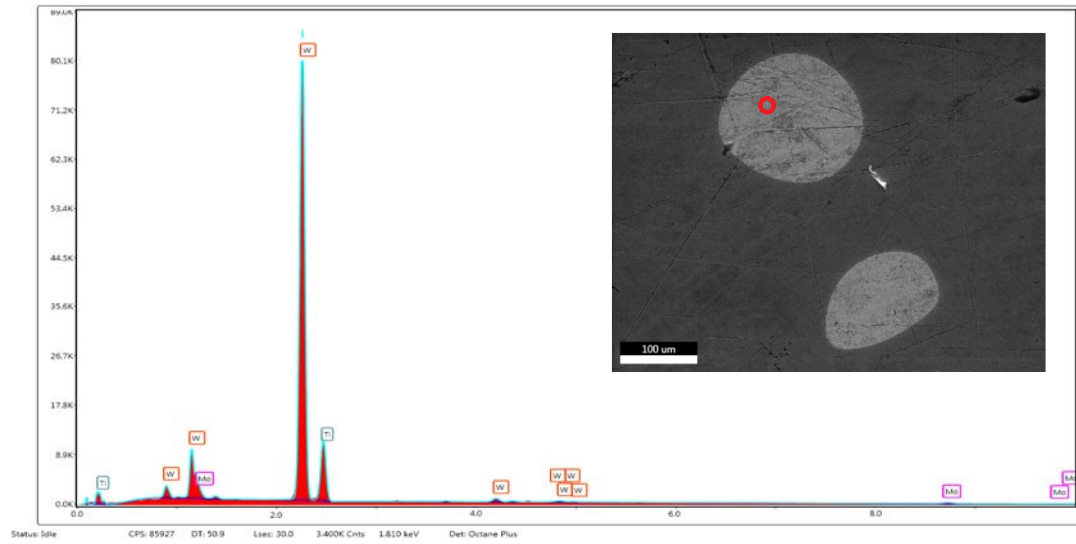β phase corresponding to planes (110), (211) and (200), so the alloy is part of β-monophasic alloys.
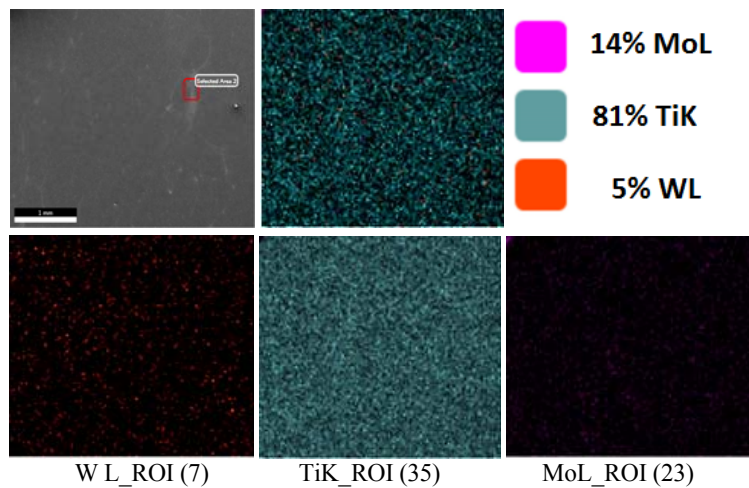

Fig.7. Metallic inclusions of W, Mo - undissolved metal

W L_ROI (7)   TiK_ROI (35)   MoL_ROI (23)
Fig. 8. SEM images with the distribution in the matrix of the constituent elements
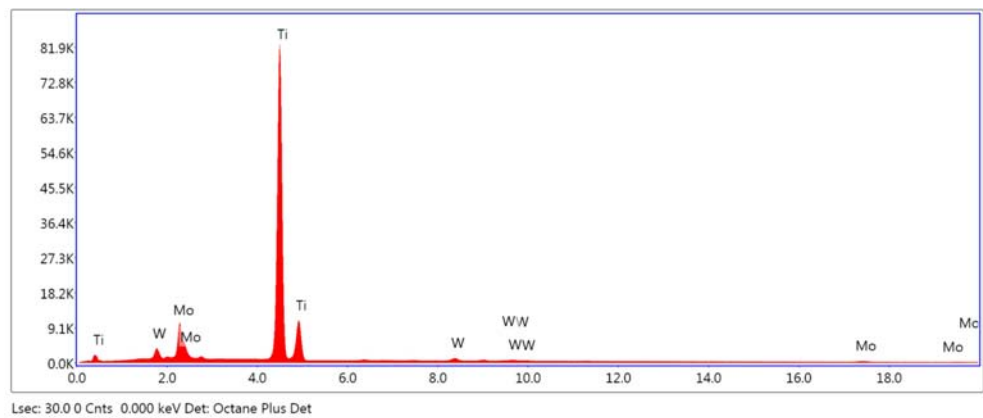
Fig. 9. EDAX image for the area marked in Fig 7

Table 2

The chemical composition of the alloy

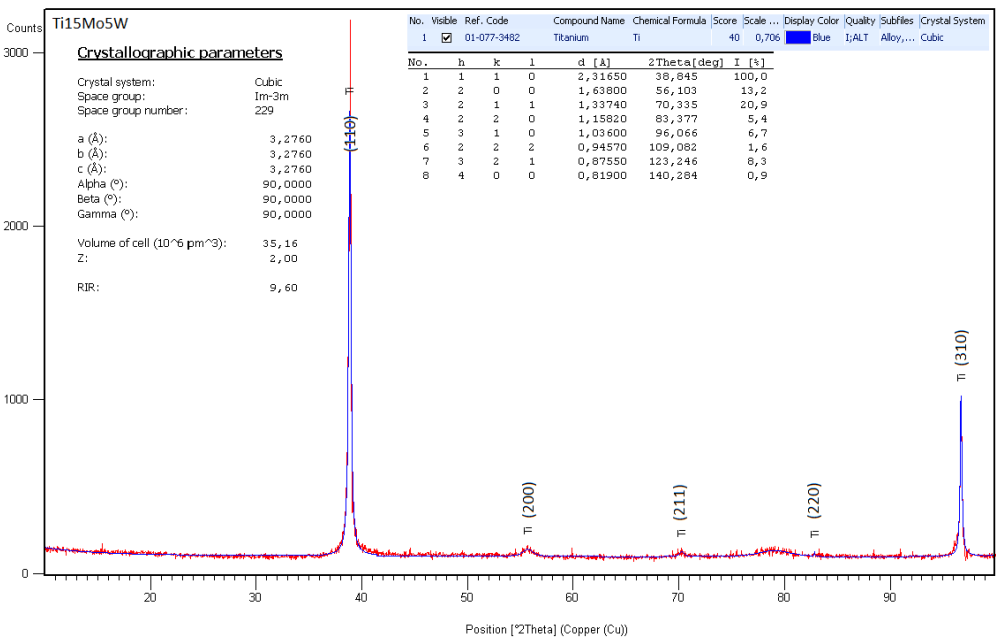| Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
MoL	14.73	8.27	2765.82	2.91	0.1024	0.9262	1.1192	0.9109	1.0343
TiK	80.08	90.21	34411.05	1.71	0.8026	1.0219	0.9805	0.9194	1.0159
W L	5.19	1.52	385.36	7.99	0.0374	0.7955	1.2237	1.0017	1.1217

Fig.10. Diffraction pattern of the obtained Ti15Mo5W alloy (Fig.8)

4. Conclusions

1. Starting from the calculated elastic constants of single crystal, converted to a polycrystalline cubic isotropic material (by using the scheme Voigt-Reuss-Hill) was able to design a titanium based alloy with β structure and low Young's modulus.

2. By adding of W, the phase stability of the alloy Ti-15Mo increased.

3. The elaboration of the alloy was performed in a vacuum arc remelting equipment (VAR) 900 ABD MRF model using pure metals; to homogenize the material was required remelting.

4. After the second melting, in the homogeneous material, the alloying elements were uniformly distributed in the alloy.

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