Obtaining and Characterization of the Ti15Mo5W Alloy for Biomedical Applications

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In the paper are presented the experimental researches made in order to obtain a new titanium alloy - Ti15Mo5W used for medical applications with improved mechanical characteristics and modulus of elasticity. In this regard Ti15Mo with addition of W alloy was designed with the intention of obtaining β-Ti phase stability. For this, we studied the influence of: the bond order, energy level of metal d-orbital, ratio of valence electrons/atom and influence of the addition of W. After designing the alloy compositions and setting the parameters, the Ti15Mo5W composition was chosen to run the experiments. The experimental Ti15Mo5W alloy was obtained by vacuum arc remelting technique using Ti, Mo and W high purity metals. The alloy was characterized by SEM, EDS and tested for Vickers hardness and compression. The microstructural characterization of the alloy proved to be homogeneous, and the mechanical characterization highlighted the obtaining of an alloy with a low elasticity modulus of about 30 GPa and an average hardness of 320 HV.

Key words: biocompatible metallic material; Ti15Mo5W alloy; microstructural characterization; mechanical properties.

The biocompatible metallic materials should ideally have a modulus of elasticity similar to bone, excellent fatigue resistance, corrosion and wear resistance and good osseointegration capacity. A metallic material must fulfill certain conditions to be used as implant in the human body [1]: outstanding biocompatibility, better osseointegration (bone in-growth), improved mechanical properties (specific strength, fatigue resistance, ductility and low Young's modulus), good tribological characteristics, long term dimensional stability and machinability. Titanium alloys have been developed for biomedical application because they have good specific strength, corrosion resistance, low modulus of elasticity, no allergic problems and the best biocompatibility in comparison with other metallic biomaterials.

Titanium alloys are classified in three classes: α alloys, α + β alloys and β alloys (at the temperature of 880°C, α phase, with hcp structure, turns in β phase with bcc structure). Alloying elements for Ti alloys can be α-stabilizers (Al, O, N, C), β–stabilizers (V, Nb, Ta, Mo, Fe, W, Cr, Ni, Si, Co, Mn, H) and neutrals (Zr, Sn). The Ti α alloys exhibit superior corrosion resistance but have limited low temperature strength. The Ti α + β alloys exhibit higher strength due to the presence of both α and β phases. Alloys containing primarily β phase tend to exhibit significantly lower modulus value than α and α + β alloys; on the other hand, α-structure shows values between 100 and 120 GPa of Young's modulus and β-structure exhibits about 60-80 GPa of Young's modulus [2].

Ti6Al4V is the most widely used as an implant material (especially for orthopedic applications) because of its good combination of biocompatibility, corrosion resistance and mechanical properties. But the use of this material does not solve several problems [3-7] as: too high Young's modulus compared to the human bone, low shear strength, low wear resistance and bio-toxicity of Al and V for the human body. The new generation β-type Ti alloys have been developed using binary systems (Ti-Nb, Ti-Mo, Ti-Ta, Ti-Zr), ternary systems (Ti-Nb-Mo, Ti-Nb-Zr, Ti-Nb-Sn) or quaternary systems (Ti-Nb-Zr-Sn, Ti-Fe-Ta-Zr, Ti-Mo-Zr-Fe).

Starting with the results obtained by several researchers [8] a theoretical method for alloy design has been developed without any trial-and-error experiments. The design strategy has been developed by combined some parameters as: the bond order (*Bo*); the metal – orbital energy level (*Md*); the electron/atom (*e/a*) ratio, and the Mo equivalency [9, 10].

Ti-Mo alloys have a good combination of tensile properties, corrosion resistance and significantly lower Young's modulus value at ambient temperature. Studying Ti-Mo alloys, a number of researchers [11] highlighted that when Mo contents was 10 wt.% or higher, the retained β phase became the only dominant phase.

Recently, some researchers [12] have reported that for bio-implant alloy, two parameters are close to optimum in *Bo-Md* diagram: *Bo* = 2.87 and *Md* = 2.45. On the other hand, others [13-14] support that C11 - C12 represents the stability of the bcc structure; in this respect, by controlling the valence electron number at around 4.20 - 4.24 it is possible the obtainment of a low Young's modulus material in the Ti binary alloys having bcc structure. Physical stability of Ti-15Mo alloy increases with increasing of *Bo* and decreasing *Md* and by increasing the *e/a* ratio.

The Ti15Mo5W alloy design

In order to obtain a biocompatible titanium alloy for medical applications, especially articular prostheses, we started from a known biocompatible binary alloy - Ti-15Mo, and as alloying elements that show no toxicity to the body, tungsten and molybdenum were selected. We have chosen tungsten with the intent of obtaining a high-strength and

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corrosion-resistant biocompatible alloy with a low modulus of elasticity. This metal has 6 valence electrons and therefore we can obtain a high electron density (*e/a*) alloy to influence the modulus of elasticity in the direction of decreasing it. In this regard we proposed the preparation of Ti15Mo(5-11)W type compositions to obtain a stable β-phase (body-centered cubic structure) with low modulus of elasticity and good mechanical and corrosion characteristics. In the paper are in detail presented the obtaining and characterization of the Ti15Mo5W type alloy.

The theory can predict the alloy features by employing first two electronic parameters: *Bo* (characterization of covalent bond strength between Ti and alloying elements) and *Md* (characterization of d-orbital energy, relating to radius and electro-negativity of elements) [15-17]. It is found that the elastic modulus of the alloys decreased with increasing the values of *Bo* and *Md* in the region of β titanium alloy. In *Bo-Md* diagram (fig. 1), the single β-phase region is clearly separated from the β + ω phase region. The formation of the thermal β phase in titanium alloys has been reported to be predictable by the *e/a* ratio [18]. The formation of the thermal ω phase attained maximum at the *e/a* ratio 4.13 and minimum at 4.3. When the *e/a* ratio is larger than 4.3, the β phase becomes the dominant phase.

In the production of β titanium alloys, there are many β phase stabilizing elements to be added. The stabilizing degree of β phase depends on the respective selected elements. Mo is the most important β phase stabilizing element. The equivalent of Mo (Mo_{eq}) indexes the stability of β phase [19] and it can be computed using the equation (1):

$$Mo_{eq} = Mo_{mass} + 0.67V_{mass} + 0.44W_{mass} + 0.28Nb_{mass} + 0.22Ta_{mass} + 2.9Fe_{mass} + 1.6Cr_{mass} + 0.77Cu_{mass} \quad (1)$$

where the Mo_{mass}, V_{mass}, W_{mass}, Nb_{mass}, Ta_{mass}, Fe_{mass}, Cr_{mass}, Cu_{mass} are expressed in mass percentages (wt%).

Figure 1 presents the *Bo-Md* diagram for Ti-Mo type alloys with the β / β+ ω phase boundary; the value of the Young's modulus (GPa) is given in parentheses for typical alloys [20].

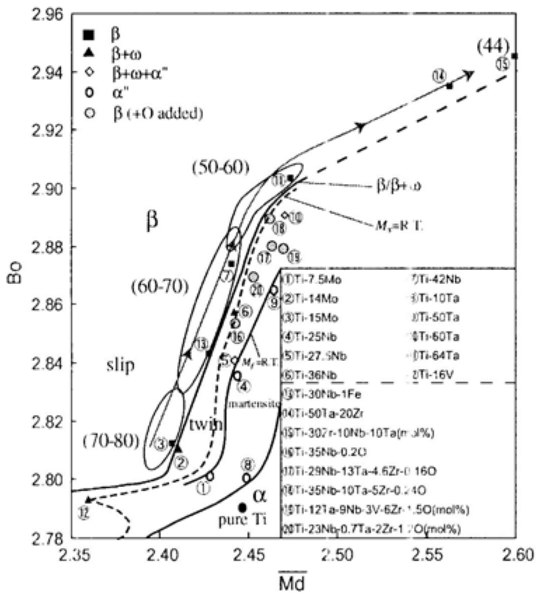


Fig. 1. The *Bo-Md* diagram for Ti-Mo type alloys

It is intended that the obtained alloy to be in the β-Ti domain. Points 1, 2 and 3, corresponding to concentrations of 7.5% Mo, 14% Mo and 15% Mo respectively, show displacement to β domain. According to the calculations and experimental data obtained, the addition of W in the alloy leads to a more pronounced shift within the β-Ti domain.

The influence of W addition on *Md*, *Bo*, *e/a* and Mo equivalency (Mo_{eq}) is obtained by using the values from the table 1, computed with the equations 2-5:

$$Md = \sum Md_i x_i \quad (2)$$

$$Bo = \sum Bo_i x_i \quad (3)$$

$$\frac{e}{a} = \sum e_i x_i \quad (4)$$

$$Mo_{eq} = Mo_{mass} + 0.44W_{mass} \quad (5)$$

where:

x_i = at% for 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;* Mo_{mass}, W_{mass}, are expressed in mass percent.

In figures 2 and 3 are presented the variation of average values of *Bo* and *Mo* in the Ti-15Mo alloy vs. W content. The W addition in the Ti-15Mo alloy decreases insignificant the *Md* with a visible increase in the *Bo*. Based on *Bo-Md* map (fig. 1 – phase stability map [20]), the Ti-15Mo alloy is located in the β phase region, and addition of W lead to better positioned the alloy inβ phase region. The stability of Ti-15Mo alloy can be increased by increasing the value of *Bo* and decreasing the value of *Md*.

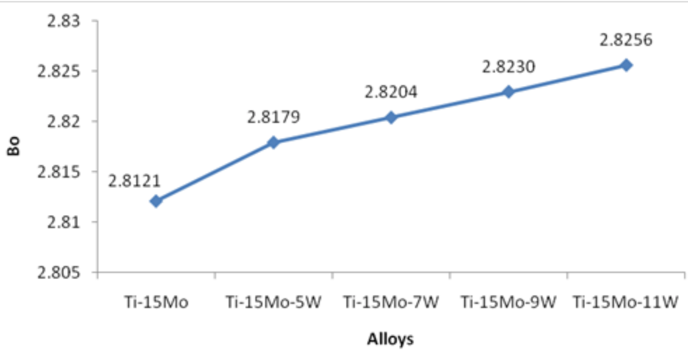


Fig. 2. The influence of the W addition over *Bo* in the alloy Ti-15Mo (nominal values)

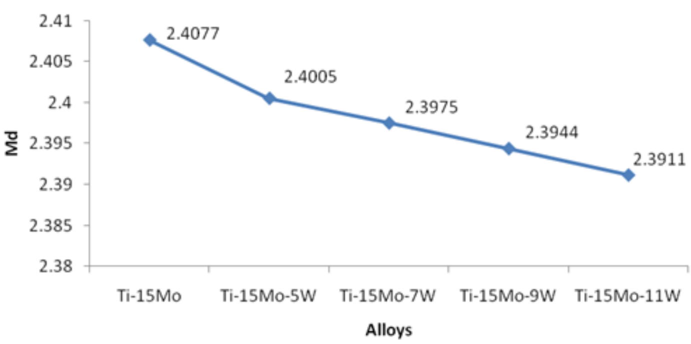


Fig. 3. The influence of the W addition over *Md* in the alloy Ti-15Mo (nominal values)

Table 1
VALUES OF THE *Bo* AND *Md* FOR Mo AND W ALLOYING ELEMENTS IN bcc Ti [20]

3d	*Bo*	*Md* (eV)	4d	*Bo*	*Md* (eV)	5d	*Bo*	*Md* (eV)
Ti	2.790	2.447						
			Mo	3.063	1.961			
						W	3.125	2.072

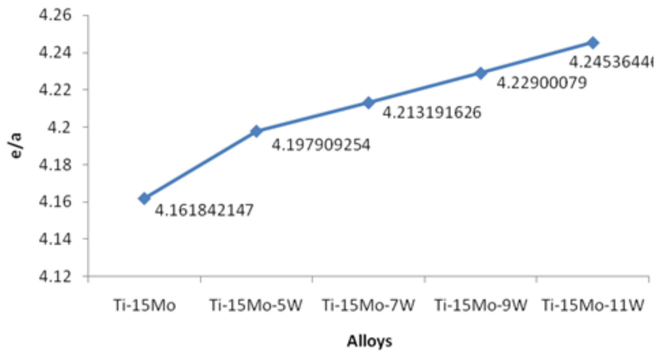


Fig. 4. The influence of the W addition over *e/a* in the alloy Ti-15Mo (nominal values)

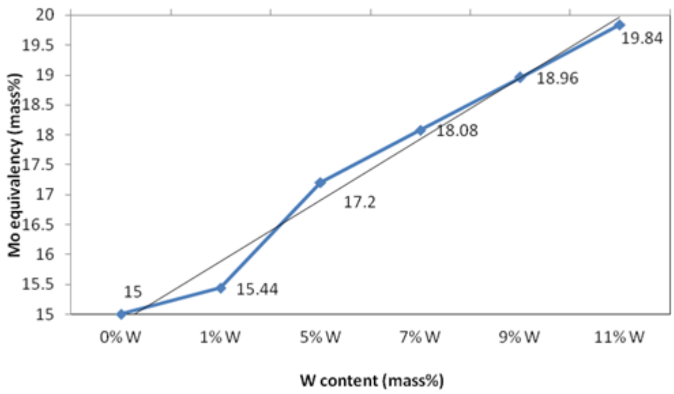


Fig. 5. Changes in Mo equivalency (Mo_{eq}) with W content in the Ti-15Mo alloy (nominal values)

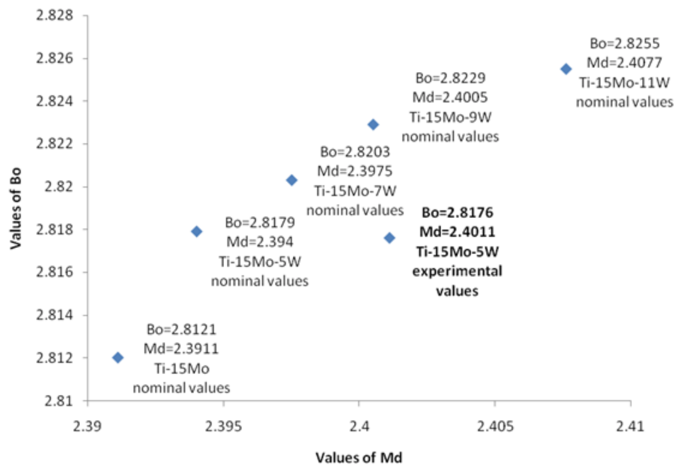


Fig. 6. Values of *Bo* and *Md* calculated by nominal and analyzed chemical composition in the Ti15Mo5W alloy

Some researchers [13] investigated the relationship between the *e/a* ratio and the deformation mode in the β titanium alloys, and concluded that *e/a* must be in the range of 4.1 - 4.24. A Ti15Mo5W alloy satisfies this condition. Figure 4 shows the changes in the *e/a* ratio in the Ti-15Mo alloy with the W content.

From figure 4 it is observed that the addition of tungsten in the Ti-15Mo alloy leads to an increase of the *e/a* ratio from 4.1618 for the Ti15Mo alloy to 4.2454 for the T15Mo11W alloy.

Figure 5 shows the changes in the equivalent of Mo in the Ti-15Mo alloy with the W content; a content of 5 wt% W increase Mo_{eq} from 15% to 17.2%.

Values of *Bo* and *Md* calculated by nominal and analyzed chemical composition in the alloys are presented in figur e 6; the nominal values of *Bo* and *Md* for Ti15Mo5W alloy were calculated to be 2.8203 and 2.4005 and the experimental ones are 2.8176 for *Bo* and 2.4011 for *Md*.

Experimental part

Choosing tungsten as alloying element was made with the intent of obtaining a high-strength and corrosion-resistant biocompatible alloy with a low modulus of elasticity. We started from a known biocompatible binary alloy, Ti-15Mo with additions of up to 11 wt.% W. The obtaining process was developed in a vacuum arc remelting equipment (VAR) model MRF ABD 900 using high purity Ti, Mo and W metals. The obtained ternary alloys are intended for use in the manufacture of medical prostheses with low elasticity, improved corrosion resistance and good mechanical strength. For better homogenization the alloy has been remelted for five times, thus achieving a homogeneous material.

The samples of Ti-Mo-W having the diameter of 15 mm and the height of 20 mm were prepared and analysed by scanning electron microscopy using a Quanta Inspect F50, with a field emission gun (FEG) with 1.2 nm resolution and an Energy Dispersive X-ray Spectrometer (EDXS) having 133 eV resolution at MnK_{α}.

The Vickers hardness measurements were measured using a HV0.2 Vickers tester with a load of 1.961 N and 15 s. Determination of Vickers hardness on the Ti15Mo5W alloy sample was carried out by performing a number of 10 tests, starting from the centre of the sample to the outside thereof, and achieving an average of these values.

Results and discussions

In figure 7(a) the non-uniform dendrite structure of the as-cast alloy is observed. The Vickers indentation after hardness testing (with an average value of 320 HV) is presented in figure 7(b).

Figure 8 shows the results of EDS elemental analysis for the obtained alloy; it can be observed that the alloying elements are uniformly distributed in the alloy. Table 2 shows the chemical composition of the alloy.

The results obtained from tests of Vickers micro-hardness are shown in figure 9. It can be observed that the Vickers micro-hardness measured values for different samples are in the range of 300-350 HV.

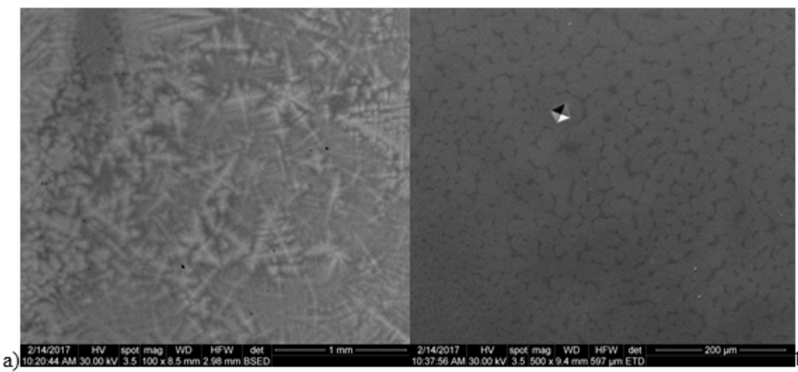
a)

b)

Fig. 7. (a) BSED image of the as-cast Ti15Mo5W alloy structure; (b) the Vickers micro-hardness indentation

Table 2
COMPOSITION OF THE Ti15Mo5W ALLOY

Element	*Weight, %*	*Atomic, %*	*Net Int.*	*Error, %*	*K, ratio*	*Z*	*R*	*A*	*F*
Mo	14.73	8.27	2765.82	2.91	0.1024	0.9262	1.1192	0.9109	1.0343
Ti	80.08	90.21	34411.05	1.71	0.8026	1.0219	0.9805	0.9194	1.0159
W	5.19	1.52	385.36	7.99	0.0374	0.7955	1.2237	1.0017	1.1217

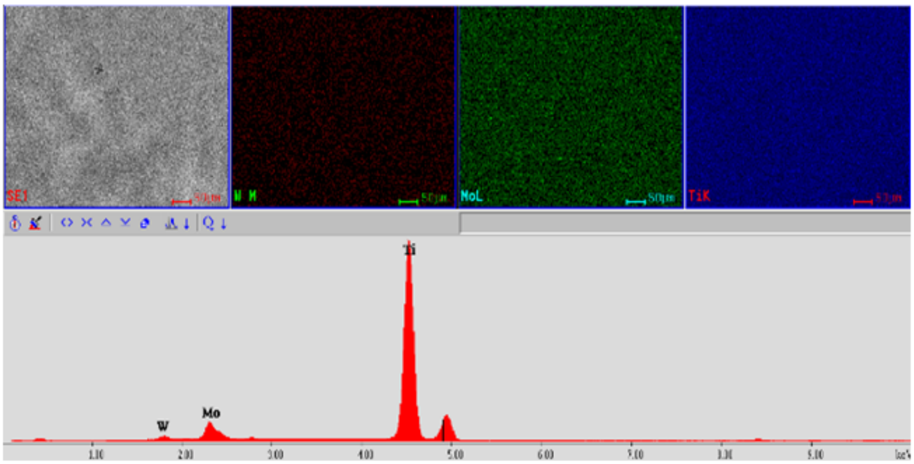


Fig. 8. SEM image, EDS analysis maps with the distribution in the matrix of the constituent elements, and EDS spectrum for Ti15Mo5W alloy

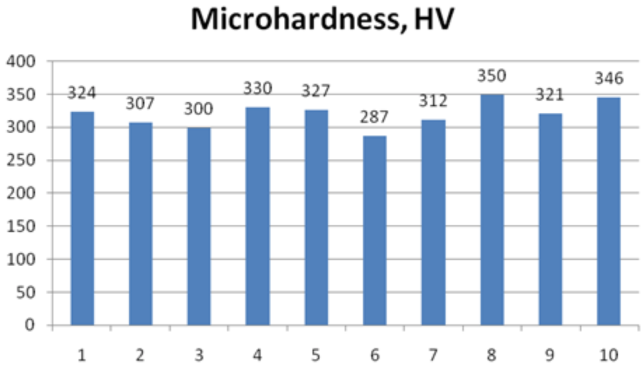


Fig. 9. Variation of Vickers micro-hardness of the Ti-15Mo5W alloy

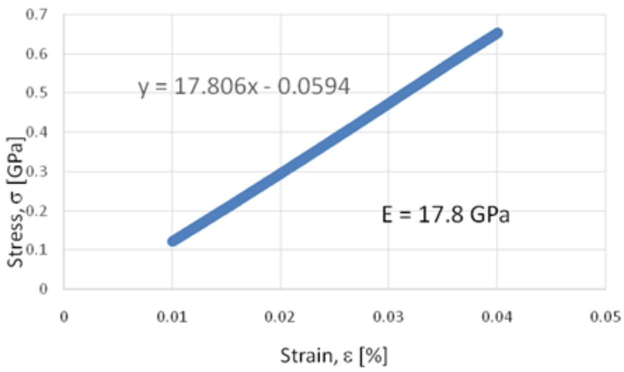


Fig. 11. The elastic modulus of the Ti15Mo5W deformed sample at a deformation degree of 54%

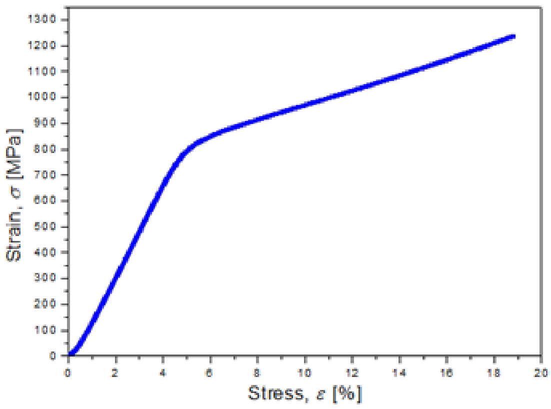


Fig. 10. Tension-strain curve after compression test of Ti15Mo5W cast alloy

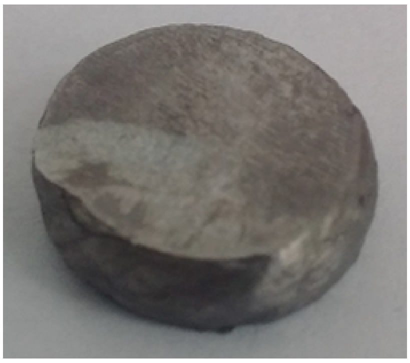


Fig. 12. Ti15Mo5W alloy sample after application of a force of 40 tf

Figures 10-12 show the results of the compression tests at a stress of 40 tf. The examination of the samples shows that no cracks exist after the compression. The modulus of elasticity was determined for the deformed material, resulting in fairly low values (29.5 Gpa).

Conclusions

A new titanium based metallic material was obtained by choosing the alloying elements so that the bond order, energy level of metal d-orbital, electron density and the equivalent of Mo parameters to have certain values that can predict the range in the phase equilibrium diagram - or rather, where the alloy is positioned from the point of view of phase stability and mechanical properties. The new alloy was obtained by adding 5 wt.% W to the Ti-15Mo alloy. The microstructural characterization of the alloy demonstrated the obtaining after remelting of a homogeneous material with a monophasic β structure, and with the alloying elements being uniformly distributed in the alloy structure. The mechanical characterization highlighted the obtaining of a metallic material with average value for hardness of 320 HV and a low elastic modulus, around 29.5 GPa. Also, the Ti15Mo5W samples are not showing cracks after the compression tests.

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