MICROSTRUCTURE OF Ti - Mo - Zr - Ta - Sn ALLOY PREPARED BY PLASMA MELTING

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Abstract

The β titanium alloys are promising candidates for biocompatible implant applications because of their low Young modulus when compared to (α + β) titanium alloys. In this study three β titanium alloys Ti-12Mo-6Zr, Ti-8Mo-6Zr-2Ta-2Sn and Ti-8Mo-6Zr-2Ta-4Sn (in at%) were prepared by plasma metallurgy method. Melted ingots were submitted to homogenization at 950 ºC for 35 hours by means of vacuum high temperature furnace followed by furnace cooling under argon atmosphere. Subsequent heat treatment consisted of solid solution annealing at 900 °C for 1 hour under flowing argon with following water quenching. The phase analysis of the microstructure was performed using optical and scanning electron microscopies. The analysis was completed by EDX measurement that confirmed the β grains and α precipitates contained in the microstructure. Specimens of all three prepared alloys were subjected to microhardness testing to evaluate the influence of different thermal treatment. It was concluded that the solution treatment and water quenching promoted increase in the microhardness of Ti-12Mo-6Zr alloy whereas for developed Sn doped alloys the microhardness values remained the same.

Keywords: Ti - Mo - Zr - Sn alloy, biocompatible material, microstructure, microhardness, heat treatment

1. INTRODUCTION

Biocompatible materials for applications in traumatology and orthopedics typically require a combination of excellent biocompatibility and convenient mechanical properties. The mechanical characteristics, especially the Young's modulus must be as close as possible to those of bone to avoid or minimize the bone atrophy due to the stress shielding effect [1-3]. It is well known that the Young's modulus of β Ti alloys decreases while controlling the metastability of single-phase state of the β phase. By controlling the concentration of β stabilizing elements, alloys based on metastable β phase with promising mechanical properties can be developed for prospective orthopedic or traumatology implant applications. To date, wide range of new multicomponent β Ti alloys composed of less-toxic elements have been prepared [1-8].

The new generation of low modulus β Ti alloys based on Ti-Mo-Zr-Ta-Sn system which are free of cytotoxic elements can be prepared using theoretical method based on electron-to-atom (e/a) ratio [7,8] being an imperative tool for formulating the stability of β phase at room temperature. Conforming with this theory and considering the alloys biocompatibility, we selected three β stabilizers (that are Ta, Mo, and Zr) as the alloying elements in order to develop new metastable β Ti alloys for metallic implant applications. As it has been widely reported, decreasing metastability of β phase to a critical extent increases the Young's moduli of β Ti alloys which is attributed to α" martensitic and/or ω phase transformations. So, it is widely considered, that the adding of Sn content to metastable β Ti alloys suppresses α" and/or ω phase transformations. Therefore, quaternary Sn additions to our newly designed metastable β Ti alloys were also chosen in order to suppress the formation of the harmful ω phase. In particular to this, all of the four selected alloying elements are on one hand highly biocompatible and on the other hand are non-ferromagnetic metals, which might offer great advantage during post-operative MR imaging.

In this study, three compositions of β Ti alloys: Ti-12Mo-6Zr, Ti-8Mo-2Ta-2Sn alloy and Ti-8Mo-2Ta-4Sn alloy (in at%) were designed aiming for promising combination of low Young's modulus and high mechanical strength. For all three β Ti alloys, the effect of the thermal processing, i.e. homogenization and slow cooling followed by solution treatment and water quenching, on the microstructure and microhardness was examined.

2. EXPERIMENTAL

Three alloys of the composition (in at%): Ti-12Mo-6Zr, Ti-8Mo-6Zr-2Ta-2Sn and Ti-8Mo-6Zr-2Ta-4Sn, were prepared by plasma metallurgy method. Melted ingots were submitted to homogenization at 950 ºC for 35 hours by means of vacuum high temperature furnace followed by furnace cooling under vacuum. Subsequent heat treatment consisted of solid solution annealing at 900 °C for 1 hour under flowing argon with following water quenching. Specimens of all three prepared alloys were metallographically prepared by grinding on SiC papers, polishing in alumina suspension of 3 and 1 µm and etching in Kroll's reagent solution. Microstructure was observed by means of an OLYMPUS GX51 optical microscope equipped with OLYMPUS DP12 digital camera. Phase analysis was performed using a scanning electron microscope SEM JEOL JSM-6490LV type equipped with INCA x-act analyzer (EDX). The Vickers microhardness HV0.1 was measured by FUTURE-TECH FM-100 automatic microhardness tester with FM-ARS900 control unit and evaluated on the base of 10 indents across the specimens.

3. RESULTS AND DISCUSSION

The composition of all three prepared alloys after the homogenization process at 950 ºC is compared with the nominal one in **Table 1**. As indicated in the table, some inhomogeneity has to be considered in Ti-8Mo-6Zr-2Ta-2Sn alloy due to wrong solution of Mo and Ta during plasma melting even the melting process was repeated three times and homogenization treatment was kept for 35 hours. Thus, the Sn content seems to be higher than it was demanded. However, the Ta concentration was measured to be lower too for both quaternary alloyed alloys.

Table 1 The nominal composition, calculated density and analyzed composition of the prepared Ti alloys

Alloy (at%)	**Calculated density** (g/cm^3)	**Measured composition** (at%)
Ti-12Mo-6Zr	6.38	Ti-11.1Mo-6.1Zr
Ti-8Mo-6Zr-2Ta-2Sn	5.87	Ti-5.6Mo-3.8Zr-0.9Ta-4.1Sn
Ti-8Mo-6Zr-2Ta-4Sn	6.31	Ti-8.4Mo-4.8Zr-1.1Ta-3.5Sn

The microstructure of all three alloys after homogenization treatment was formed of prior β grains and needles of α phase that precipitated at grain boundaries as well as in grain volumes, as seen in **Figure 1**. The solution treated and water quenched alloys contained finer α needles in β grains (**Figure 2**). The compositions of α and β phases in different thermal treatment conditions are summarized in **Table 2** and **3**.

As Mo is β stabilizer, its content in α phase was lower for all three Ti alloys and both thermal conditions. Unlike higher Zr concentration in α precipitates of the alloys in homogenized condition, the solution treated samples showed very low differences in its content for both α and β phases because Zr is rather neutral alloying element. The β stabilizing Ta was more contained in β phase in both heat treated conditions and the amount of Sn as neutral stabilizer was very close in both thermal conditions for both Sn doped alloys. The Ti-12Mo-6Zr alloy displayed the lowest microhardness in homogenized condition (**Figure 3**) but the solution annealing and water quenching increased significantly its values. The microhardness increase can be related with more intense precipitation of α particles, as seen in **Figure 2a** and **2b**, as well as it can indirectly prove that ω phase transformation proceed more easily in the alloys without Sn. Besides α and β phases the intermetallic particles of Ti34Zr36Sn28Mo1 and Ti71Zr12Sn16 (in at%) were found in both solutions treated Sn and Ta doped alloys.

Despite the intermetallic phases presence, the microhardness remained conserved the same after solution annealing and water quenching. In any case, the microhardness of three alloys studied exceeded the value of 294HV measured for Ti6Al4V with (α + β) bimodal microstructure.

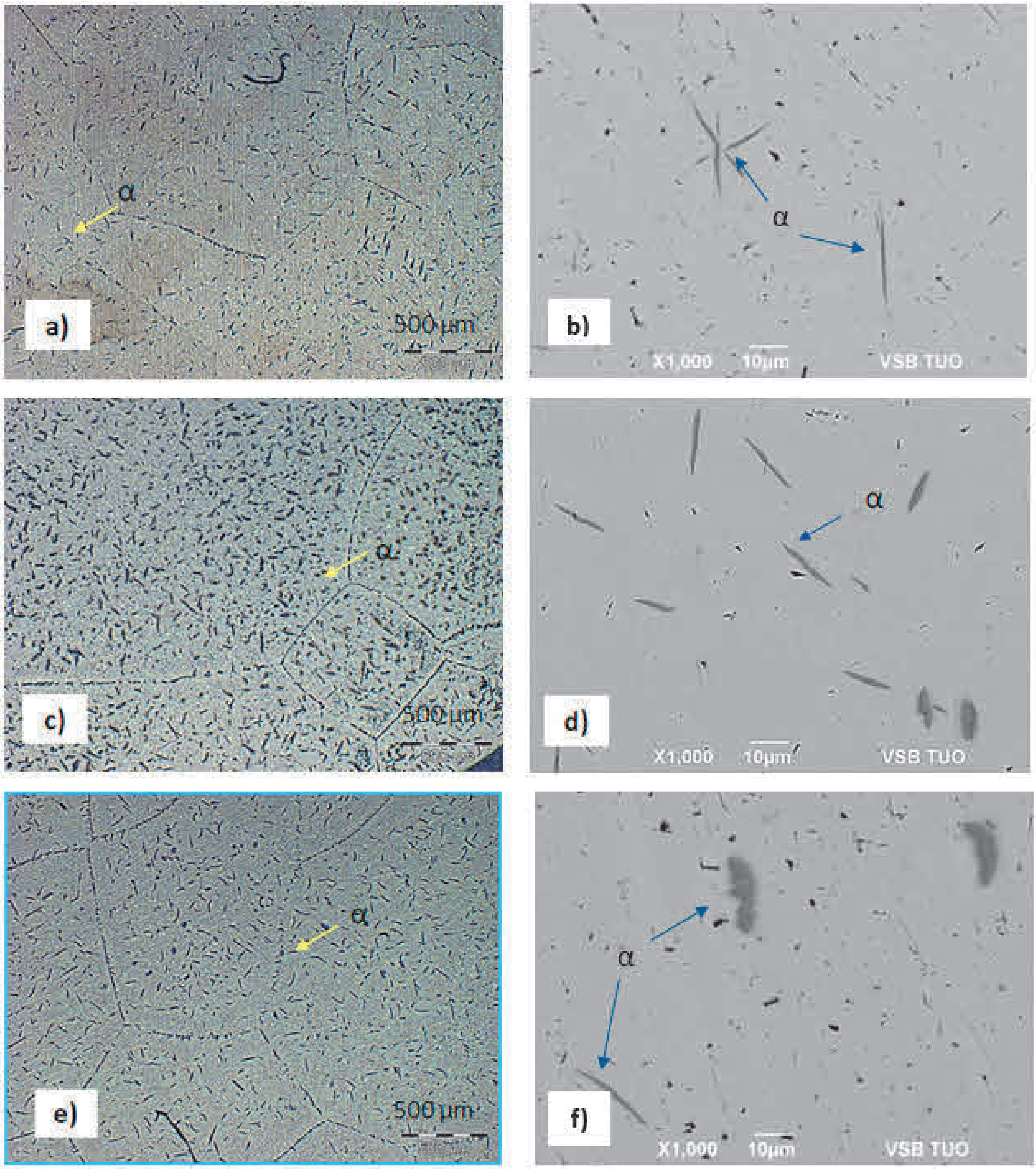

Figure 1 Microstructure of β Ti alloys homogenized at 950 °C for 35 hours under vacuum and slowly furnace cooled: α needles in β phase for a) and b) Ti-12Mo-6Zr; c) and d) Ti-8Mo-6Zr-2Ta-2Sn; e) and f) Ti-8Mo-6Zr-2Ta-4Sn

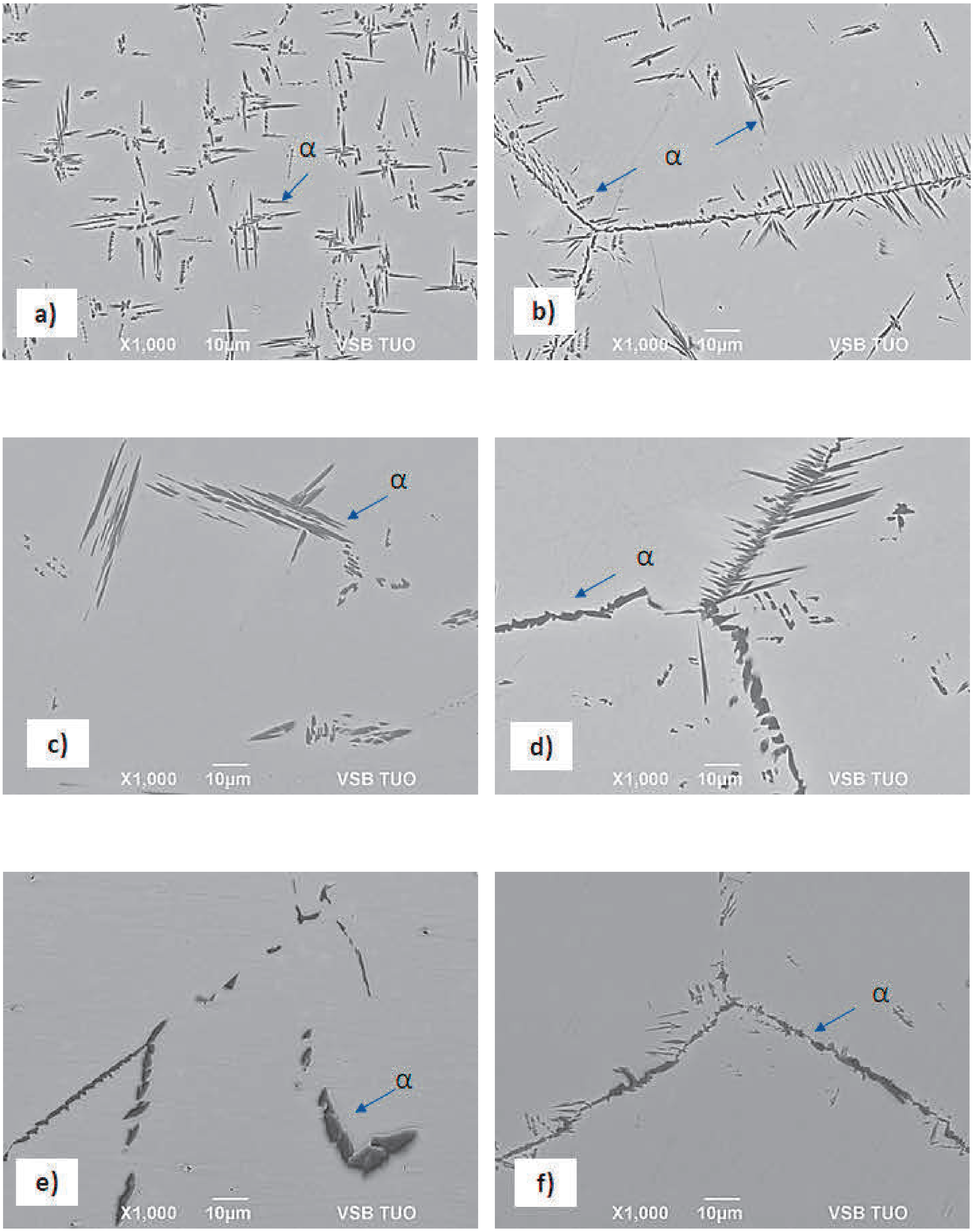

Figure 2 Microstructure of β Ti alloys after subsequent solution treatment at 900 °C for 1 hour under flowing Ar and water quenching: α needles in β phase for a) and b) Ti-12Mo-6Zr; c) and d) Ti-8Mo-6Zr-2Ta-2Sn; e) and f) Ti-8Mo-6Zr-2Ta-4Sn

Table 2 Results of EDX analysis of homogenized Ti alloys (at%)

Alloy	Analyzed phase	Ti	Mo	Zr	Ta	Sn
Ti-12Mo-6Zr-0Sn	α	85.4	6.2	8.4		
	β	82.8	11.1	6.1		
Ti-8Mo-6Zr-2Ta-2Sn	α	87.8	2.6	5.1	1,0	3.6
	β	85.6	5.5	3.7	1.1	4.1
Ti-8Mo-6Zr-2Ta-4Sn	α	85.9	3.8	6.6	0.9	2.8
	β	82.3	8.3	4.7	1.1	3.5

Table 3 Results of EDX analysis of solution treated Ti alloys (at%)

Alloy	Analyzed phase	Ti	Mo	Zr	Ta	Sn
Ti-12Mo-6Zr-0Sn	α	89.4	5.5	5.1		
	β	82.8	11.1	6.1		
Ti-8Mo-6Zr-2Ta-2Sn	α	91.5	0.8	3.2	0.7	3.8
	β	85.8	5.1	3.9	1.7	3.5
Ti-8Mo-6Zr-2Ta-4Sn	α	88.3	1.4	6.0	0.6	3.7
	β	81.5	8.7	4.9	1.1	3.8

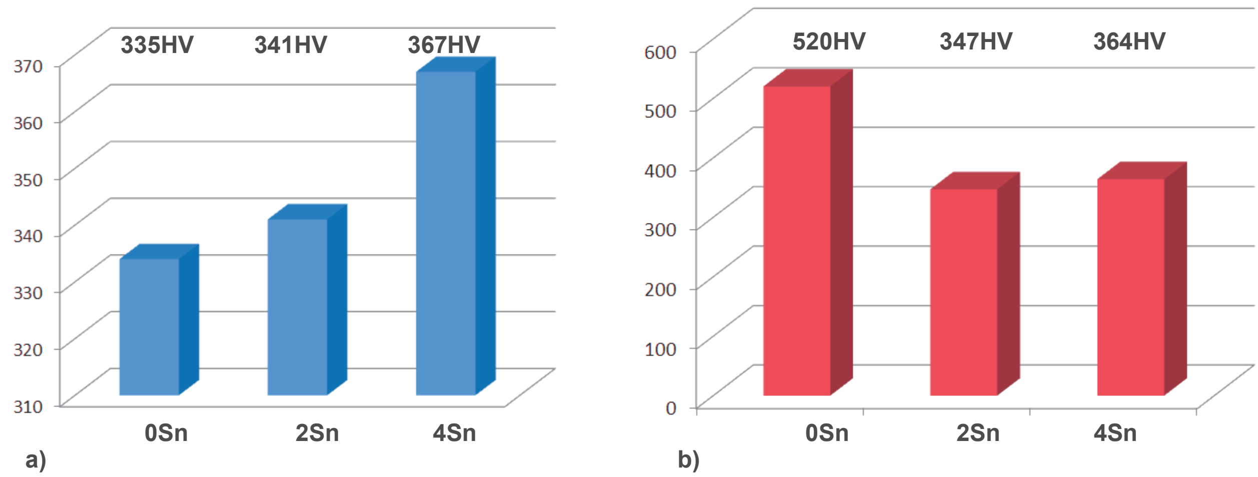

Figure 3 Average values of HV0.1 microhardness measurement for a) homogenized and b) solution treated conditions for the alloys: 0Sn - Ti-12Mo-6Zr (335/520HV); 2Sn - Ti-8Mo-6Zr-2Ta-2Sn (341/347HV); 4Sn - Ti-8Mo-6Zr-2Ta-4Sn (367/364HV)

4. CONCLUSION

Three β titanium alloys for biomedical applications, Ti-12Mo-6Zr, Ti-8Mo-6Zr-2Ta-2Sn and Ti 8Mo-6Zr-2Ta-4Sn, prepared by plasma melting method underwent thermal treatment to optimize microstructural properties. The alloys were subjected to the phase analysis and microhardness testing in order to determine the effects of the heat treatment on the α phase precipitation. The microstructure of the samples in homogenized condition mainly consisted of β grains and α precipitates. It was concluded that the solution annealing and water quenching promoted increasing microhardness of Ti-12Mo-6Zr alloy due to precipitation of finer α phase particles. The microhardness of both Sn doped alloys in solution treated condition remained the same.

Anyhow, the newly prepared alloys showed higher microhardness than it was found for conventionally used biocompatible Ti6Al4V alloy.

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