

USPOREDBA MIKROSTRUKTURNIH KARAKTERISTIKA BIOMEDICINSKIH Ti (70,80 AT.%) -Cr-Mo i Ti(70,80 AT.%) -Nb-Zr LEGURA

COMPARISON OF MICROSTRUCTURAL CHARACTERISTICS FOR BIOMEDICAL Ti(70,80 at.%) -Cr-Mo AND Ti(70,80 at.%) -Nb-Zr ALLOYS

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Izvorni znanstveni rad

Sažetak: Ovaj rad prikazuje usporedbu mikrostrukturnih karakteristika Ti-Cr-Mo i Ti-Nb-Zr legura. Svrha rada bila je ispitati mikrostrukturu i tvrdoću navedenih legura za potencijalnu primjenu u medicini. Od svake skupine legura laboratorijski su pripremljena po tri uzorka različitog sastava u lučnoj peći. Njihova mikrostruktura je ispitana svjetlosnim i skenirajućim elektronskim mikroskopom s energijsko-disperzivnim spektrometrom. Tvrdoća je određena Vickersovom metodom. Rezultati pokazuju da su Ti-Cr-Mo legure dvofazne, odnosno da sadrže β i α ili α' fazu, dok su Ti-Nb-Zr legure uglavnom β -jednofazne s ω -fazom u tragovima. EDS analiza je pokazala da α (α') i β faze imaju vrlo sličan kemijski sastav. Tvrdoća prema Vickersu Ti-Cr-Mo legura povećava se s udjelom molibdena u leguri, dok se ona za Ti-Nb-Zr legure povećava s udjelom niobija. Zbog skoro β -jednofazne mikrostrukture i niže tvrdoće u odnosu na Ti-Cr-Mo legure, Ti-Nb-Zr legure imaju veći potencijal za primjenu kao biomedicinski materijali.

Ključne riječi: Ti-Cr-Mo legure, Ti-Nb-Zr legure, biomedicinske legure, mikrostruktura, tvrdoća prema Vickersu

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Abstract: This paper shows comparison of microstructural characteristics of Ti-Cr-Mo and Ti-Nb-Zr alloys. Purpose of this investigation was to examine the microstructure and hardness of these alloys with potential for biomedical use. Three samples of each alloy type with different composition were laboratory prepared by an arc melting method. Their microstructure was examined by light and scanning electron microscope with EDS. Hardness was determined by Vickers method. Results show that Ti-Cr-Mo alloys have two-phases microstructure containing β and α or α' phase, while Ti-Nb-Zr alloys were nearly β single-phase with traces of ω -phase. EDS analysis indicates that α and β have similar chemical composition. Vickers hardness of Ti-Cr-Mo alloys increases with molybdenum content, while those for Ti-Nb-Zr alloys increases with niobium content. According to the closely single-phase microstructure and lower hardness, Ti-Nb-Zr alloys have advantage as potential biomedical materials.

Key words: Ti-Cr-Mo alloys Ti-Nb-Zr alloys, biomedical alloys, microstructure, Vickers hardness

1. INTRODUCTION

In a few last decades development of biomedical titanium alloys without undesirable elements, aluminum and vanadium, has continued to increase. Due to their light weight, excellent mechanical properties and corrosion resistance, titanium alloys are popularly used today in many medical applications. The most widely used titanium biomedical alloy is Ti-6Al-4V. But, since aluminum and vanadium are known to might cause some long-term health problems, alternative Ti-based alloys without toxic elements have been developed.

The goal of this study was to prepare new titanium-based alloys with potential for biomedical use. Chromium is a β -eutectoid element, which stabilizes β -phase of titanium. Besides, it is cheap and decreases Young's modulus in a manner similar to niobium as β -isomorphous element in Ti-Nb alloys. Zirconium

suppresses the athermal ω -phase produced during quenching and as a result decreases Young's modulus to be similar to the cortical bone (4-30 GPa).

2. MATERIALS AND METHODS

In this work two types of titanium alloys were prepared with purpose to examine and compare their microstructure and hardness which would satisfy conditions for biomedical applications.

First, titanium was alloyed with chromium and molybdenum. In second type, niobium and zirconium were added to titanium. Cr and Mo were chosen as β -stabilizers as well as zirconium and niobium, which are not toxic and do not cause allergic reactions in body tissue. Chemical compositions of experimental alloys were selected according to the similar biomedical Ti-based alloys. Their positions in the portion of

isothermal sections of ternary diagrams at the room temperature are presented in Figure 1.

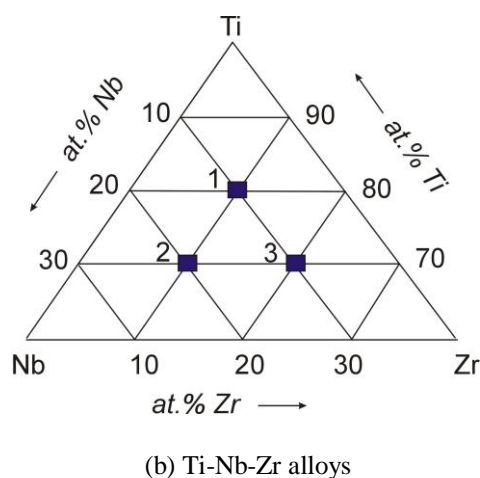
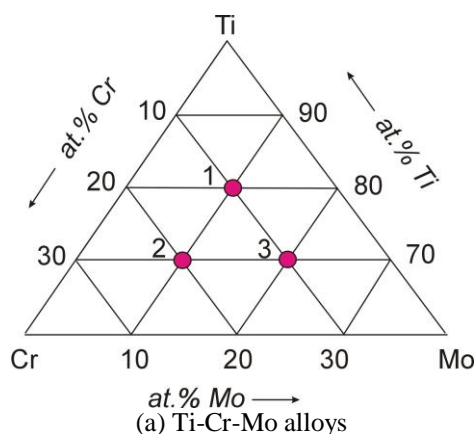


Figure 1. Chemical compositions of investigated alloys

Alloys were prepared by melting pure elements (with purity better than 99.9%) in vacuum arc-furnace under argon atmosphere. Because of large difference in melting temperature of elements in Ti-Cr-Mo system, first chromium and molybdenum were melted into a „button-shape“. These buttons were remelted for a three times, and then titanium was added. Such samples were remelted for another four times to ensure their homogeneity. In the similar way Ti-Nb-Zr alloys were prepared. Namely, niobium and zirconium were remelted for three times, and then titanium was added.

Alloys in forms of buttons of approximately 7g were casted in the same equipment by means of specially constructed water-cooled copper anode, which served as a casting mould. In this way, as-cast cylindrical specimens with dimensions 8 mm x 25 mm were produced and they were sectioned using a Buehler Isomet low-speed diamond saw. After embedding in conductive resin Conductomet, specimens were metallographically prepared by grinding and polishing. The microstructure of two Ti-Cr-Mo alloys ($Ti_{70}Cr_{20}Mo_{10}$, $Ti_{70}Cr_{10}Mo_{20}$) was remarked easily, but there was a need for etching other samples. Microstructural analysis was performed by using a light microscope Leitz Ortholux and scanning electron microscope (SEM) Tescan Vega TS 5136 MM with Bruker energy-dispersive spectrometer (EDS).

Point analysis by EDS was performed in 5 points for each phase and average value was calculated. Hardness of as-cast experimental alloys was determined by Vickers method with load 19.60N for 10 s.

3. RESULTS AND DISCUSSION

Microstructure and hardness of $Ti_{80}Cr_{10}Mo_{10}$, $Ti_{70}Cr_{20}Mo_{10}$, $Ti_{70}Cr_{10}Mo_{20}$ and $Ti_{80}Nb_{10}Zr_{10}$, $Ti_{70}Nb_{20}Zr_{10}$, $Ti_{70}Nb_{10}Zr_{20}$ respectively were examined. Observation of microstructure by light microscope at 280x magnification showed that all investigated Ti-Cr-Mo alloys have two-phases microstructure (Figs. 2 a-c). In $Ti_{80}Cr_{10}Mo_{10}$ alloy it reveals a dark phase in light matrix with large primary grains, while in microstructure of $Ti_{70}Cr_{20}Mo_{10}$ and $Ti_{70}Cr_{10}Mo_{20}$ alloys dark dendrites and matrix-phase are present.

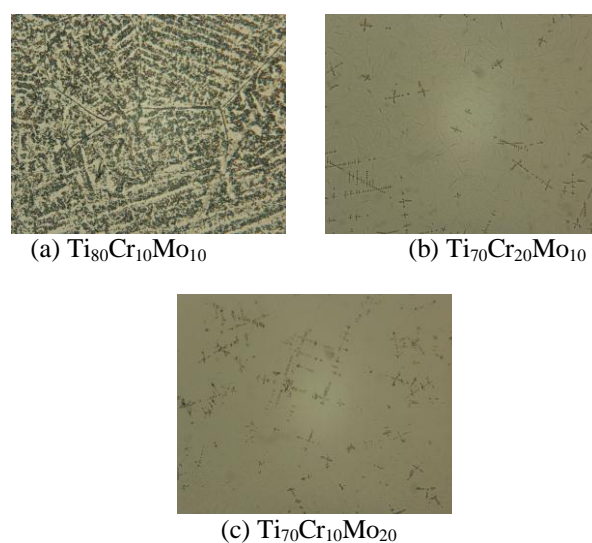


Figure 2. Light micrographs of investigated Ti-Cr-Mo alloys, 280x

The microstructure of Ti-Nb-Zr alloys consists of one single phase with uniformly size of grains (Figs. 3 a-c).

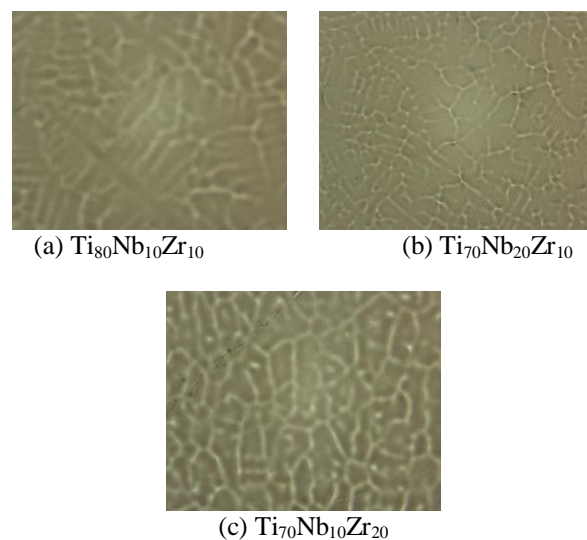


Figure 3. Light micrographs of investigated Ti-Nb-Zr alloys, 280x

Detailed investigation of microstructure by SEM analysis confirmed that all of three Ti–Cr–Mo alloys have two-phases microstructure (Figs. 4 a–c). Alloy Ti₈₀Cr₁₀Mo₁₀ with highest titanium content revealed a white needles of α'' -phase in a matrix of β -phase. Other two alloys showed dark dendrites of α -phase in a matrix of β -phase.

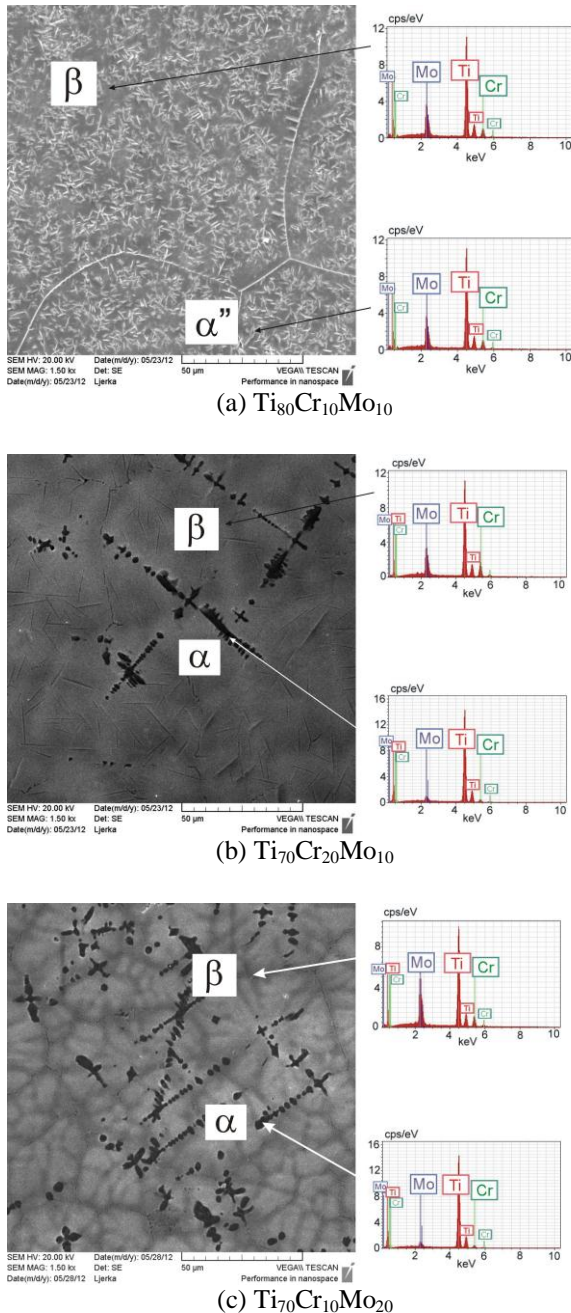


Figure 4. SEM micrographs of investigated Ti–Cr–Mo alloys with EDS spectrum of phases

SEM micrographs of Ti–Nb–Zr alloys (Figs. 5 a–c) show β -matrix and probably the presence of ω -phase according to the reference [1].

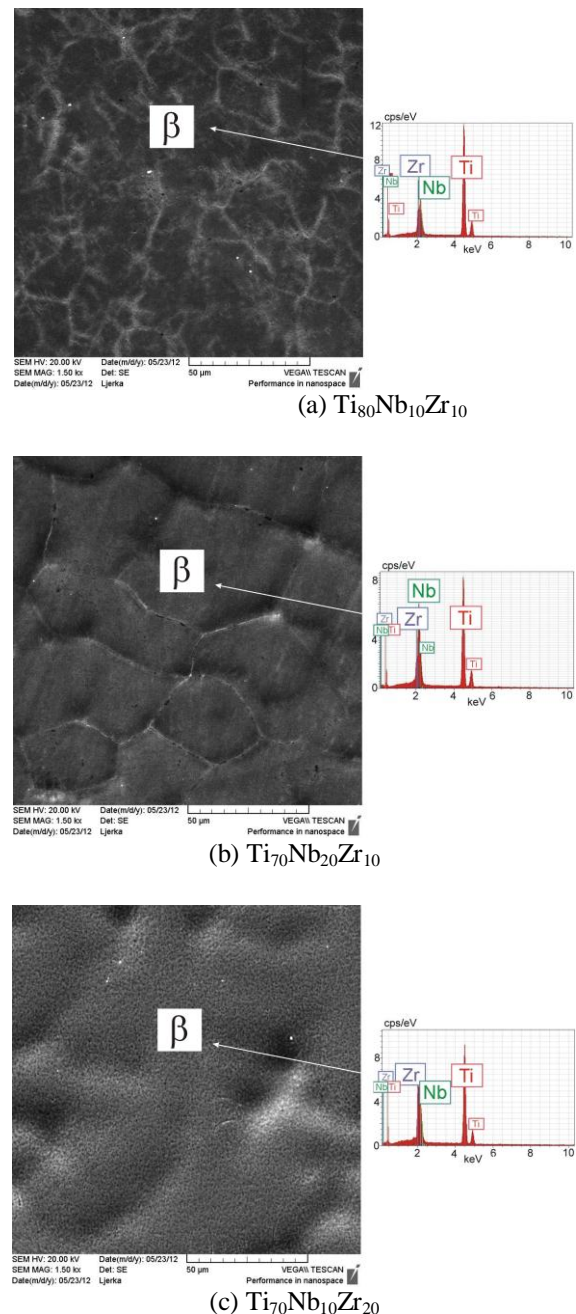


Figure 5. SEM micrographs of investigated Ti–Nb–Zr alloys with EDS spectrum of phases

Chemical compositions of all phases in investigated alloys were determined by EDS point analysis (Table 1). These results revealed very similar data for composition of β -phase which mainly corresponds to the alloy composition. The composition of β and α'' -phases are equal for Ti₈₀Cr₁₀Mo₁₀ alloy. This suggests that during an alloys casting with the fast cooling rate the phase transformation occurred, without change in composition, as the evidence of martensitic transformation $\beta \leftrightarrow \alpha''$. SEM and EDS analysis of Ti–Nb–Zr alloys showed that all of them have homogenous structure of β -phase (Fig. 5). Chemical composition determined in all points revealed the same data, which corresponds to alloy composition (Table 1).

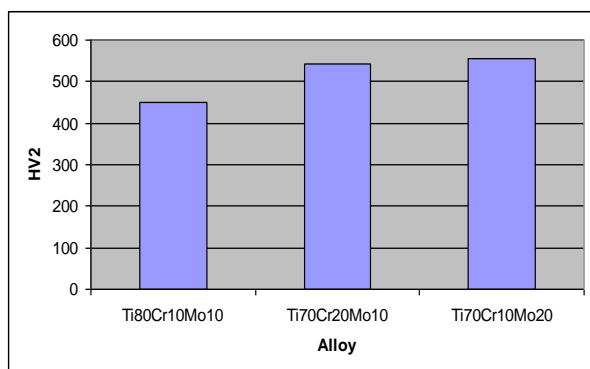
Table 1. EDS results obtained by point analysis

Alloy	Element	Elements content in	
		β -phase, at. %	α -phase, at. %
Ti ₈₀ Cr ₁₀ Mo ₁₀	Ti	80	80 (α'')
	Cr	9	9 (α'')
	Mo	11	11 (α'')
Ti ₇₀ Cr ₂₀ Mo ₁₀	Ti	72	89
	Cr	16	7
	Mo	12	4
Ti ₇₀ Cr ₁₀ Mo ₂₀	Ti	70	92
	Cr	10	3
	Mo	20	5
Ti ₈₀ Nb ₁₀ Zr ₁₀	Ti	81	-
	Nb	9	-
	Zr	10	-
Ti ₇₀ Nb ₂₀ Zr ₁₀	Ti	72	-
	Nb	19	-
	Zr	9	-
Ti ₇₀ Nb ₁₀ Zr ₂₀	Ti	70	-
	Nb	7	-
	Zr	23	-

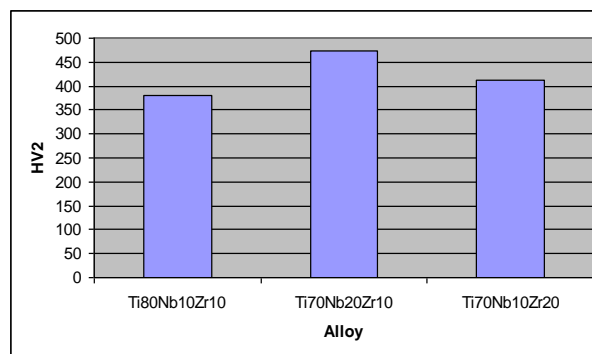
The Vickers hardness measurements (Table 2) show the strong effect of chemical composition and microstructure on hardness values. Obtained data for Ti-Cr-Mo alloys were in the range of 449 to 555 HV2 and they were increased with increasing molybdenum content (Fig. 6). So, the highest value of 555 HV2 has alloy Ti₇₀Cr₁₀Mo₂₀.

Table 2. Vickers hardness of experimental alloys

Alloy composition, at. %	HV2
Ti ₈₀ Cr ₁₀ Mo ₁₀	449
Ti ₇₀ Cr ₂₀ Mo ₁₀	542
Ti ₇₀ Cr ₁₀ Mo ₂₀	555
Ti ₈₀ Nb ₁₀ Zr ₁₀	379
Ti ₇₀ Nb ₂₀ Zr ₁₀	474
Ti ₇₀ Nb ₁₀ Zr ₂₀	411

**Figure 6.** HV dependance on Ti-Cr-Mo alloys composition

Hardness of Ti-Nb-Zr alloys depends on niobium content (Fig. 7). So, alloy with the highest content of this element has the highest value of Vickers hardness. Ti-Nb-Zr alloys have lower hardness values (379 – 474 HV2) when compared with Ti-Cr-Mo alloys. This could be explained by fact that β -phase has lower hardness than α -phase. Measured values are similar to that of other titanium β -type biomedical alloys.

**Figure 7.** HV dependance on Ti-Nb-Zr alloys composition

4. CONCLUSIONS

In this paper two types of titanium-based alloys for biomedical application were studied. Light microscopy showed two-phases microstructure of Ti₈₀Cr₁₀Mo₁₀, Ti₇₀Cr₂₀Mo₁₀ and Ti₇₀Cr₁₀Mo₂₀ alloys, which consists of β and α or α'' phases. As-cast alloys Ti₈₀Nb₁₀Zr₁₀, Ti₇₀Nb₂₀Zr₁₀ and Ti₇₀Nb₁₀Zr₂₀ were single β -phases. That was confirmed by SEM analysis. EDS indicated that chemical composition of β and α'' phases are equal for Ti₈₀Cr₁₀Mo₁₀ alloy. This is the evidence that martensitic transformation $\beta \leftrightarrow \alpha''$ takes place. Vickers hardness of Ti-Cr-Mo alloys depends on molybdenum content, and that of Ti-Nb-Zr alloys depends on niobium content. Hardness of Ti-Nb-Zr alloys was lower than that for Ti-Cr-Mo alloys because the β -alloys has lower hardness than β/α alloys.

According to the results showing single-phase microstructure and lower hardness, Ti-Nb-Zr alloys have advantage in front of Ti-Cr-Mo alloys as potential biomedical materials.

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