XI Naučno/stručni simpozij sa međunarodnim učešćem „METALNI I NEMETALNI MATERIJALI“ Zenica, BiH, 21-22. april 2016.

THE EVALUATION OF THE STRUCTURE AND HARDNESS OF DENTAL Ti-Zr ALLOYS

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Key words: Ti-Zr alloys, microstructure, hardness, dental alloys

ABSTRACT
Many types of alloys are available as dental implants, but titanium and its alloys have been widely used due to their outstanding properties. In this research titanium alloys with different Zr contents were prepared by arc-melting. Phase identification was performed by XRD analysis. Microstructure was observed by light microscope after etching in two solutions. Detailed microstructural observations were realized by SEM and EDS. Vickers hardness measurements were performed as well. Alloy with higher Zr content shows nearly beta-phase structure and more adequate hardness values for dental implants than alloy with lower Zr content.

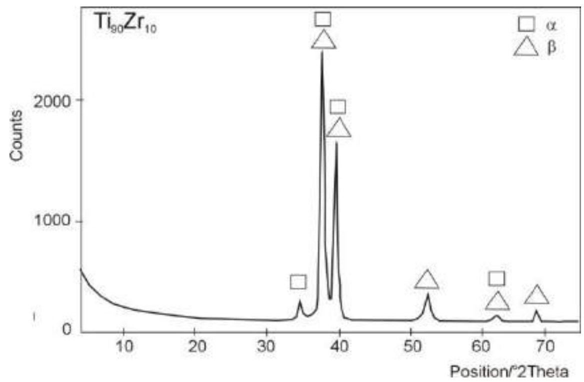
1. INTRODUCTION
The development of new biomaterials is becoming more interesting, both in the commercial as well as in the scientific sense. In the last few decades the application of titanium and its alloys in dental medicine is growing due to their excellent properties such as outstanding biocompatibility and light weight. However, titanium shows some disadvantages to be used as dental implant: difficult casting and high hardness value (830-3240 HVN). For comparison, Vickers hardness of titanium human tooth, both in enamel and dentin, are in the range from 270 to 360 VHN for enamel and 50 to 60 VHN for dentin. In order to improve these and some other properties, titanium is alloyed. These alloying elements could stabilize α or β phase of titanium. The temperature of phase transformation α/β is 863 °C. Zirconium is neutral element which slightly decreases α/β transformation temperature and increases it when is added in higher concentrations [1-3]. It improves a resistance to corrosion of titanium and its mechanical properties [4]. Besides, zirconium and titanium form solid solutions in the entire range of concentrations [5]. Purpose of this work is to develop a new titanium alloy with adequate properties for use in dental medicine.

2. MATERIALS AND METHODS
In this research Ti alloys with 10 and 17 at.% Zr were investigated. Samples of alloys were prepared by melting the pure elements in a laboratory arc-melting furnace under argon atmosphere in the water cooled copper mould. Melting was repeated for four times to ensure a chemical homogeneity. Obtained samples were casted in the same conditions into cylindrical shape. Phase analysis by X-ray diffraction (XRD) was performed on Philips PW3710 diffractometer using CuK_{α} radiation. Lattice parameters were calculated using the computer program Celref. For microstructural analysis alloys were metalographically

prepared by grinding, polishing and etching in two different solutions recommended by [6] for five seconds at room temperature. The composition of the first etching solution (solution 1) is: 5 cm^3 HF, 5 cm^3 HNO_3, 10 cm^3 glycerin, and of the second (solution 2) is: 1 cm^3 HF, 3 cm^3 HNO_3, 16 cm^3 H_2O. Microstructure of etched alloys was observed by light microscope Olympus GX 51 and taken with digital camera. Detailed microstructural analysis was perfomed by scanning electron microscope (SEM) Tescan Vega TS 5136 MM equipped with Bruker energy-dispersive spectrometer (EDS). Vickers hardness of polished experimental alloys was determined by Vickers method at loads of 1,98 N (HV0.2) during 10 s at microscope magnification of 500x.

3. RESULTS AND DISCUSSION

XRD patterns of investigated alloys with 10 and 17 at.% are shown in Figure 1. Identification of phases was done using the JCPDS-ICDD files [6]. It can be seen that in both alloys two phases are present. In diffractograms for $Ti_{90}Zr_{10}$ alloy the obtained peaks match the diffraction angles for α and β phases, while in $Ti_{83}Zr_{17}$ diffraction angles for β and α'' phases are identified. Although zirconium slightly affects the temperature of α/β transformation, depending on its addition to titanium [5], it is obvious that 10 at.% is not enough to achieve the single beta phase of titanium. Further, these XRD results indicate that 17 at.% of zirconium, along with fast water cooling of alloy through a cooper mould during its preparation, is sufficient to obtain and retain the β, however not single phase but together with martensitic α'' phase. The martensite transformation involves the cooperative movements of atoms by a shear process resulting in a microscopically homogenous transformation of body-centered cubic into the hexagonal crystal lattice over a given volume. This hexagonal structure of the martensite (α') with the increasing solute content becomes distorted, and from the crystallographic point of view, crystal structure losses its hexagonal symmetry and must be described as orthorhombic. This orthorhombic martensite is designated as α'' [1]. Though, all of these phases show diffraction peaks at similar values of 2Theta angles. Therefore it is needed to analyze the micrographs in order to clarify and confirm these results.



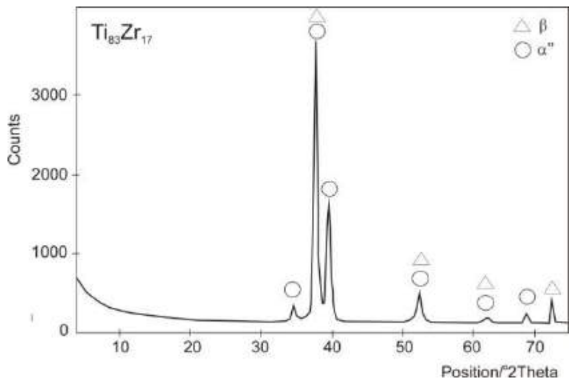


Figure 1. XRD analysis of Ti90Zr_{10} and $Ti_{83}Zr_{17}$

For microstructural observations samples of both alloys were etched in the solution 1 and corresponding micrographs are displayed in Figure 2. These revealed microstructures were not satisfactory for interpretation; therefore etching in the solution 2 was applied.

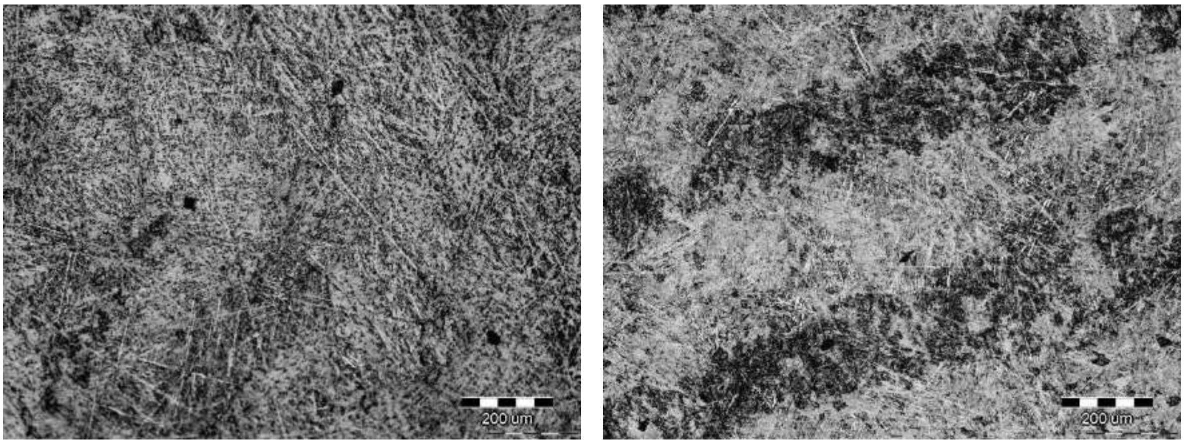


Figure 2. Microstructures of $Ti_{90}Zr_{10}$ and $Ti_{83}Zr_{17}$ (solution 1) at magnification 100x

Microstructures of investigated alloys etched in solution 2 are presented in Figure 3. It is obvious the two-phase microstructure of alloy with lower zirconium content. In the microstructure of alloy with higher zirconium content coarse grains of β phase is visible. Due to a small magnification (100x) and probably small quantity a martensitic α'' phase is not evident in the micrograph of $Ti_{83}Zr_{17}$ alloy.

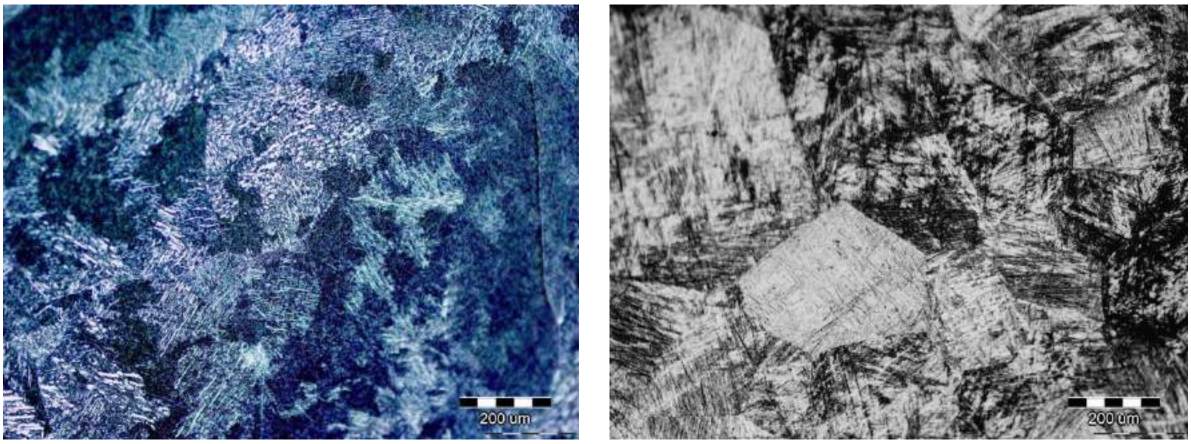


Figure 3. Microstructures of $Ti_{90}Zr_{10}$ and $Ti_{83}Zr_{17}$ (solution 2) at magnification 100x

Microstructures were analyzed in detail using the scanning electron microscope and larger magnification (Figure 4). SEM micrographs confirm the XRD results. Namely, in the microstructure of alloy with 10 at.% of zirconium two phases are present. This characteristic appearance of lamellar structure is so called „basket weave“ or Widmanstätten structure. It occurs when titanium alloy is cooled at higher rate from the β phase field into the α+β field. Then the size of α colonies as well as thickness of the individual α plates are smaller than after the slow cooling rates. Further, α colonies nucleated at β grain boundaries cannot fill the whole grain interior, so they start to nucleate on boundaries of other colonies. This type of structure is observed more often in alloys which contain higher concentrations of β stabilizers [1]. The microstructure of alloy with 17 at.% of zirconium consists of β phase with large grains and martensitic needle-like α'' phase in minor extent.

For qualitative and quantitative analysis of prepared alloys EDS analysis in point was applied. Results of qualitative EDS analysis show peaks for only titanium and zirconium (Figure 4.) meaning that preparation was carried out in a satisfactory manner without contamination.

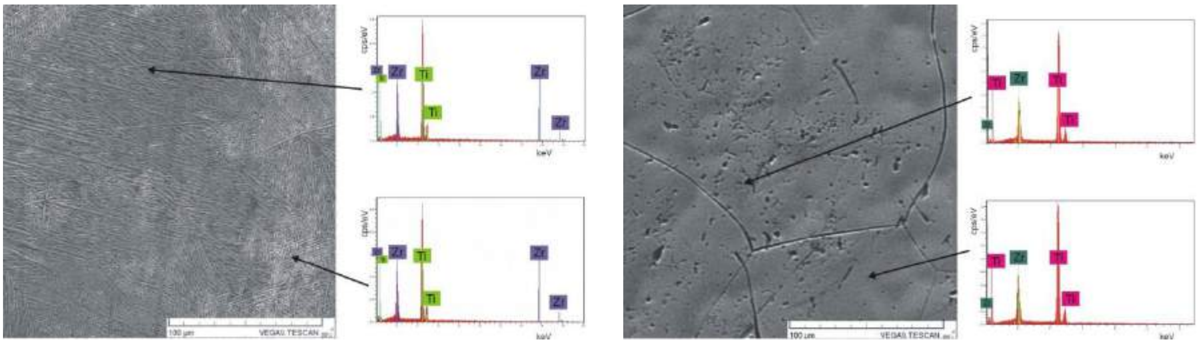


Figure 4. SEM and EDS point analysis of $Ti_{90}Zr_{10}$ and $Ti_{83}Zr_{17}$

The results of quantitative EDS analysis are given in Table 1. They indicate that formed solid solutions (αTi,Zr) and (βTi,Zr) have similar chemical composition which corresponds to chemical composition of alloy. Also, these results show that only transformation of crystal lattice was occurred, without change in the chemical composition. These ascertainment were confirmed by EDS line analysis (Figure 5).

Table 1. Results of EDS point analysis

Alloy, at.%	Element	Chemical composition of phases		
		α phase, at.%	β phase, at.%	α'' phase, at.%
$Ti_{90}Zr_{10}$	Ti	90	91	-
	Zr	10	9	-
$Ti_{83}Zr_{17}$	Ti	-	83	84
	Zr	-	17	16

Different areas in the microstructure of both alloys were scanned by electron beam along the line and the results show that there is no significant change in concentration of elements which are constituents of investigated alloys (Ti and Zr). This is a confirmation of the change in crystal structure without change of chemical composition.

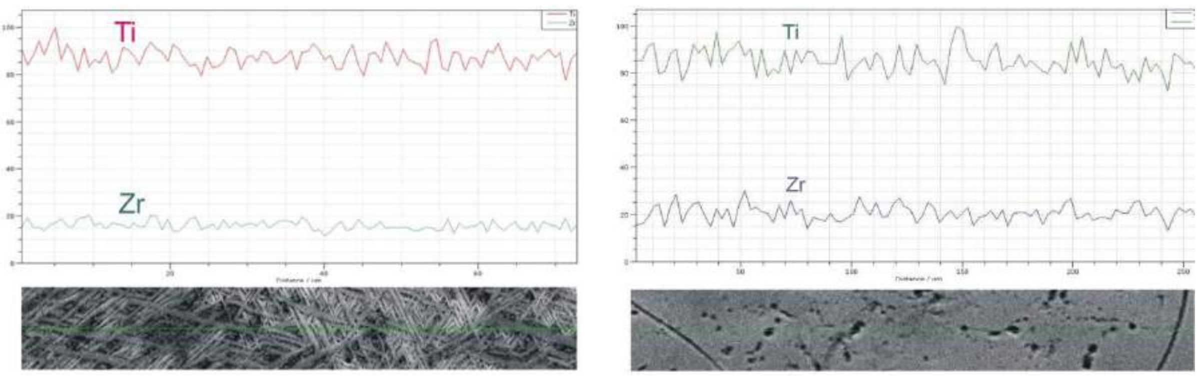


Figure 5. EDS line analysis of $Ti_{90}Zr_{10}$ and $Ti_{83}Zr_{17}$

Crystal lattice parameters for α and β phase which are dominant in the investigated alloys were calculated by the computer program CELREF using the results of XRD analysis.

Theoretical values for lattice parameters values of phases as well as calculated values are given in Table 2.

Table 2. Lattice parameters of phases

phase/parameter	a, nm	c, nm
α Ti	0,295	0,468
β Ti	0,330	-
α in $Ti_{90}Zr_{10}$	0,299	0,476
β in $Ti_{90}Zr_{10}$	0,331	-
β in $Ti_{83}Zr_{17}$	0,334	-

Since the atomic radius of zirconium (0.159 nm) is larger than that for titanium (0.145 nm), lattice parameters for present phases, i.e. solid solutions, are increased when compared to α and β titanium. Higher increase of lattice parameters is evident for alloy with higher zirconium content. Furthermore, this increase in parameters values could be assigned to the limited stresses in particular phase during the phase transformation.
Hardness of investigated alloys was determined by Vickers method on polished samples as well as on etched samples in both solutions. Measurements were performed in five randomly chosen spots in each alloy. The calculated mean values are given in Table 3.

Table 3. Vickers hardness

Alloy	Surface condition	HV0,2
$Ti_{90}Zr_{10}$	Polished	607
	Etched 1	561
	Etched 2	567
$Ti_{83}Zr_{17}$	Polished	381
	Etched 1	365
	Etched 2	375

Firstly, these results show that all obtained hardness values are lower than for pure titanium [1]. That means that zirconium as alloying element makes titanium more suitable for machining and surface treatment needed in the dental practice.
Polished samples show slightly higher values than etched probably because of softer compounds which were formed on surface of samples during the etching. There is no difference in hardness values regarding the chemical composition and volumes of ingredients of etching solutions.
Hardness values of alloy containing 10 at.% of zirconium are in the range from 567 HV0.2 up to 607 HV0.2 and are considerably higher than values for alloy with 17 at.% of zirconium (375 – 381 HV0.2). Evidently, higher amount of zirconium which shows lower hardness than titanium leads to lower hardness of alloy. Further, the microstructure of alloy with higher zirconium addition contains β phase which possesses lower hardness than α phase [8]. This is reflected in lower hardness values which satisfied requirements for dental use as implants [9, 10].

4. CONCLUSIONS

Presented investigation of structure and hardness of $Ti_{90}Zr_{10}$ and $Ti_{83}Zr_{17}$ alloys for potential dental use was resulted by following conclusions:

- Phase analysis by X-ray diffraction showed presence of two phases in each alloy. In alloy with 10 at.% of Zr α and β phases are present. In alloy with 17 at.% of Zr β and martensitic α" phases are present. Hence, XRD analysis showed that phase transformation due to higher zirconium addition occurred.
- Etchant 2 (1 cm^3 HF, 3 cm^3 HNO_3, 16 cm^3 H_2O) gave better results in revealing the microstructure.
- Microstructural analysis by scanning electron microscopy showed two-phase microstructure of investigated alloys. Microstructure of alloys with 10 at.% of Zr is characteristic so called „basket weave“ or Widmanstätten structure. In the microstructure of alloy with 17 at.% of Zr β phase with coarse grains is dominant and a certain quantity of martensitic α'' phase is present.
- Energy-dispersive spectrometry showed uniform chemical composition in all analyzed spots in microstructure indicating that all constituents have almost the same chemical composition, but different crystal structure.
- Higher zirconium content decreases the hardness of titanium which makes titanium-zirconium alloys suitable for potential dental applications.

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