# MICROSTRUCTURAL CHARACTERISTICS OF AS CAST Ti-Zr ALLOYS

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***Abstract**: For many years casting alloys are widely used in dental applications. Among them, titanium and its alloys reveal the best properties for this purpose. However, the casting is difficult but it may be improved by alloying. This research deals with titanium-based alloys with zirconium additions. Investigated alloys were prepared by melting and casting in an electro-arc furnace under argon atmosphere. In order to identify the phases present in alloys, structural analysis was performed by X-ray diffraction method. It was showed two-phases microstructure of alloys. Further, zirconium addition in higher percentage contributes to formation of the beta phase of titanium which possesses more adequate properties then alpha titanium. Microstructural observations by scanning electron microscopy and energy-dispersive spectrometry showed that phases have similar chemical composition. Measured Vickers hardness values were lower than for pure titanium and are acceptable for dental applications.*

***Key words**: Ti-Zr ALLOYS, DENTAL ALLOYS, MICROSTRUCTURE, CRYSTAL STRUCTURE, VICKERS HARDNESS*

## *1. Introduction*

Casting alloys are widely use for dental products making for many years. Among them, titanium and titanium-based alloys reveal the most adequate properties and continues to be the first choice for dental treatments [1]. Therefore are used for full-cast, metal-ceramic, and removable partial denture frameworks, dental crowns and bridges, endosseous dental implants and plates for oral maxillofacial surgery. However, the casting is difficult in these cases, because of titanium high melting point and its high reactivity with oxygen and impurities at elevated temperatures and because of need for special casting machines and investments [2,3]. To solve these problems as well as to improve mechanical properties, titanium is alloyed. Titanium alloys of interest to dentistry exist in three structural forms: alpha (α), beta (β) and alpha-beta. The alpha (α) alloys have a hexagonal closely packed (hcp) crystallographic structure stable at lower temperatures, while the beta alloys (β) have a body-centred cubic (bcc) form which is stable at high temperatures [4]. The phase α/β transformation takes place at 863 °C. Alloying elements affect this temperature, so α-stabilizing elements (Al, O) increase phase transformation temperature, while β-stabilizing elements (Mo, V) decrease it [5]. Zirconium is neutral element, which slightly lowers or decreases temperature of phase transition, depending on its content added to titanium [6]. Beta titanium is preferred against the alpha titanium since it has better properties acquired for dental use.

## *2. Materials and methods*

In this investigation titanium alloys with 13 and 20 at. % of zirconium were prepared by casting and then examined. Zirconium was selected as alloying element since it improves mechanical properties of titanium and corrosion resistance as well as biocompatibility of titanium [7]. Preparation of alloys was performed by melting the pure elements (Ti 99.99% and Zr 99.9% in purity) in a laboratory arc furnace under argon protective atmosphere. Melting was realized by electro-arc established between the tungsten cathode and copper anode which was served as mould and it was rapidly water cooled. In order to achieve homogeneity, samples were remelted for five times. Obtained samples were in a form of “buttons” and then were casted in a cylindrical shape, 8 mm in diameter and 25 mm in a high. These cylinders were cut in pieces to acquire a several samples for examinations by different methods. Structural analysis, i.e. identification of present phases was performed by X-ray difractometry (XRD) using a Philips PW3040/60 X’Pert PRO diffractometer with $Cu_{K\alpha}$ radiation generated at 40 mA and 45 kV. For microstructural characterization samples were metallographically prepared by grinding and polishing followed by etching in a Kroll’s reagent. Microstructures of etched samples were observed by light microscope Olympus GX51 with digital camera. Detailed microstructural examinations were performed by scanning electron microscope (SEM) Tescan Vega TS 5136 MM and Bruker’s energy dispersive spectrometer (EDS). Hardness of alloys was determined for polished samples by Vickers method at applied loads of 1.96 N (HV0.2) and 19.60 N (HV2) during 10 s. Diagonals of Vickers pyramids indented in samples were measured at 500 x magnification.

## *3. Results and discussion*

According to the equilibrium phase diagram, zirconium and titanium form solid solutions in the entire range of concentrations. Precisely, low-temperature (αTi,Zr) and high-temperature (βTi,Zr) solid solution [6]. Diffractograms of investigated alloys, obtained by XRD analysis, are displayed in Figure 1. Phase identification was performed by matching each peak with JCPDS-ICDD files [8]. As can be seen on identified XRD patterns shown in figures 1 both alloys consist of two phases. In alloy with lower Zr content (Fig.1a) alpha Ti and martensitic α’ phase are present meaning that 13 at. % of zirconium is not enough to achieve β phase of titanium. Higher zirconium content (20 at. %) led to phase transformation α→β and this β Ti was retained at room temperature (Fig.1b) due to fast water cooling of alloy through a copper mould. Since the alpha and alpha’ phases of titanium as well as beta titanium show diffraction peaks at similar 2Theta values, it was necessary to observe micrographs of alloys for confirmation of present phases.

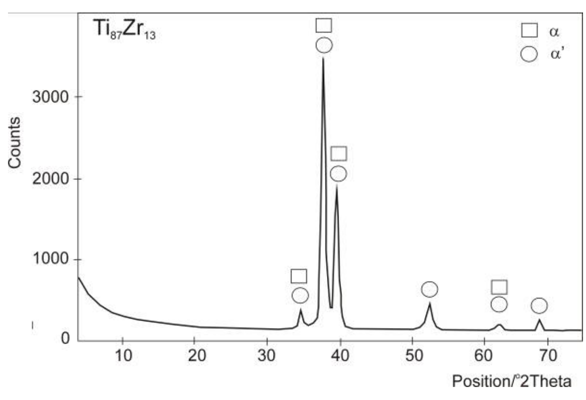


***Fig.1a** XRD analysis of alloy containing 13 at.% Zr*

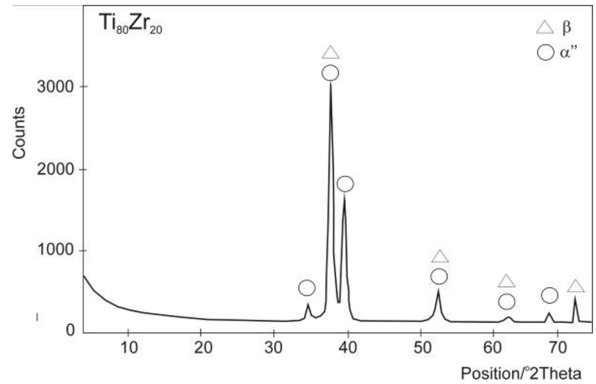


***Fig. 1b*** *XRD analysis of alloy containing 20 at.% Zr*

Micrographs of investigated alloys are presented in Figure 2. It can be seen that microstructure of alloy with lower Zr content is two-phases indicating the martensitic α' phase (light area) within the matrix of α Ti grains (gray area). Dark area is not a phase, but presents the spots of stronger activity of etching agent. In figure 2b two phases are visible, but lighter one is in a much less extent.

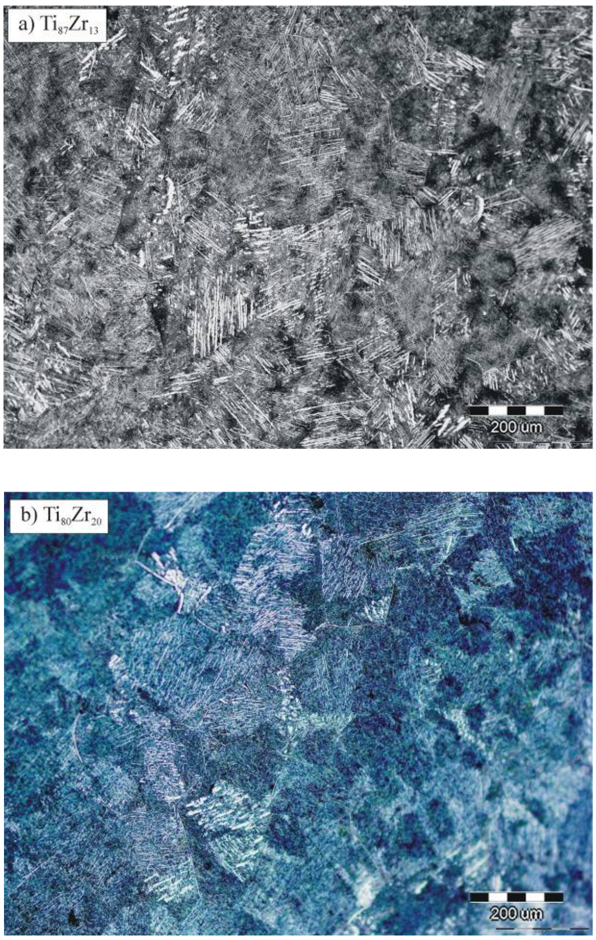


***Fig. 2*** *Microstructures of alloys*

It is known that alloy phases in titanium alloys depend on the chemical composition and cooling conditions during the casting. Therefore, if the cooling rate is a fast enough an acicular or lath-like martensite is formed. Martensitic transformation involves the movement of atoms in the groups using the shear process. This results in a microscopically homogeneous non-diffusional transformation of cubic volume centered crystal structure into the hexagonal close packed complex structure within the entire volume. This martensite with hexagonal structure is referred to as α' and occurs at high cooling rates and a small proportion of β-stabilizer. With the increasing content of alloying element distortion hexagonal structure of martensite takes place. From the crystallographic point of view, it loses its hexagonal symmetry, so it is described as a rombic and designated as α" [5,9].

Detailed examination of microstructure was conducted using the SEM and EDS. It is obvious on SEM micrographs (Figure 3) that microstructure of alloy with lower Zr content consists of two phases which are differ from these in figure 3b. Namely, it is clear that alloy with higher Zr content contains coarse β Ti grains and needle-like phase. This phase is an evidence of beta phase transformation into martensitic α'' phase which occurs during the fast enough cooling of an alloy [10-12].

EDS analysis in point showed peaks characteristic for only Ti and Zr, indicating that alloys were not contaminated during the preparation. It means that only solid solutions (αTi,Zr) and (βTi,Zr) were formed. Further, similar intensity of peaks pointed in different phases means the similar chemical composition of phases (Table 1).

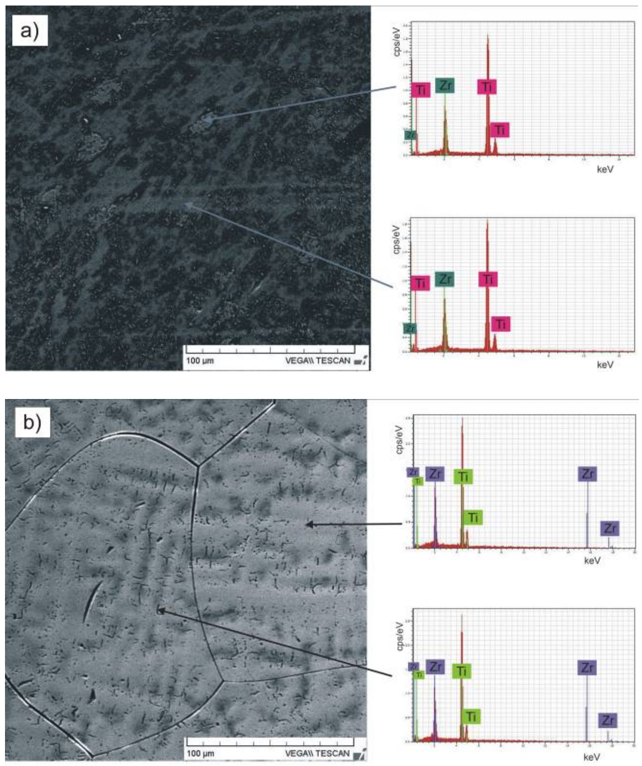


***Fig. 3*** *SEM and EDS point analysis of a) $Ti_{87}Zr_{13}$ and b) $Ti_{80}Zr_{20}$*

***Table 1****: EDS point analysis*

| Alloy, at.% | Element | Chemical composition of phases | | |
|---|---|---|---|---|
| | | α phase, at.% | α' phase, at.% | β phase, at.% |
| $Ti_{87}Zr_{13}$ | Ti | 86 | 87 | - |
| | Zr | 14 | 13 | - |
| $Ti_{80}Zr_{20}$ | Ti | - | 81 | 79 |
| | Zr | - | 19 | 21 |

Chemical compositions of phases in both alloys are very similar and correspond to chemical compositions of alloys. This could be explained by the fact that only transformation of crystal lattice was take place without the change in chemical composition. Also, these results indicate that α and β phase are solid solution consist of α titanium and β titanium respectively and zirconium.

Above results were confirmed by EDS line analysis (Figure 4). Namely, by scanning the samples surface across the all different areas line profiles of Ti and Zr were obtained. It is obvious that there is no visible change in concentration of Ti or Zr during the scan transition through the different area, i.e. phases. This is showed for both alloys indicating that all phases have the very similar composition. Accordingly, only crystal lattices are different.

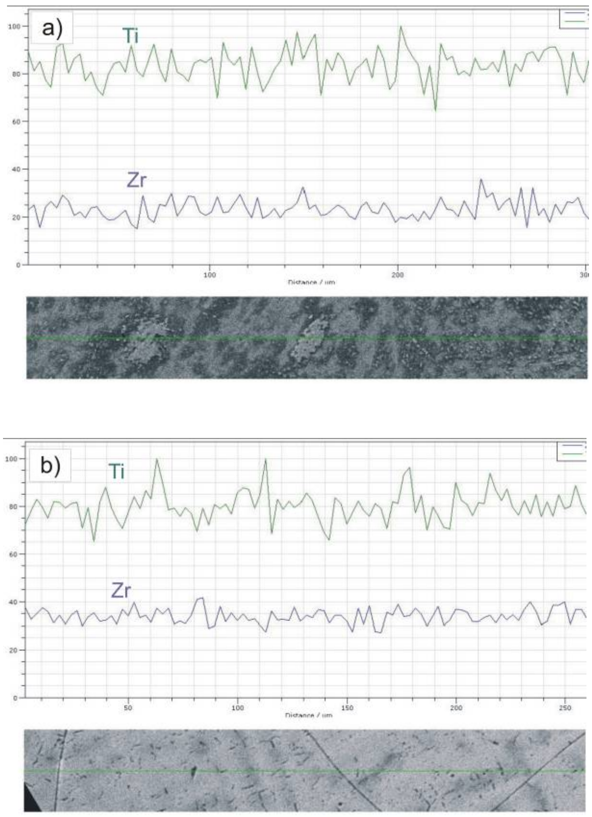


***Fig. 4*** *EDS line analysis of a) $Ti_{87}Zr_{13}$ and b) $Ti_{80}Zr_{20}$*

Hardness measurements were performed by Vickers method. For each alloy hardness was examined in five randomly chosen spots and mean values are given in Table 2. It can be seen that all values are lower than for pure titanium [5]. It is since the zirconium shows lower hardness than titanium [13].

***Table 2****: Vickers hardness*

| Alloy | HV0.2 | HV2 |
|---|---|---|
| $Ti_{87}Zr_{13}$ | 550 | 459 |
| $Ti_{80}Zr_{20}$ | 387 | 379 |

Therefore, alloy with higher zirconium content shows lower hardness values HV0.2 (387 HVN) than alloy with lower zirconium content (550 HVN). That could be explained by the fact that revealed phases have primary effect on hardness along negligible solid solution hardening mechanism. Namely, it is known that beta phase of titanium shows lower hardness values than alpha phase [14]. Therefore, because of alpha phase precipitation, alloy with lower zirconium content showed higher hardness values. All resulted values are in the range of satisfactory hardness for dental applications [7,15].

## 4. Conclusions

In this paper, microstructural characterization of titanium alloys with 13 and 20 at.% addition of zirconium was presented. From the showed results it can be concluded that addition of 13 at.% of Zr to pure Ti resulted in two-phase microstructure consisting of α and α' phases. Further, β Ti was achieved by applied casting conditions together with addition of 20 at.% of zirconium. Simultaneously a certain quantity of α'' phase are obtained. All phases have similar chemical composition corresponding to composition of alloy. Only differ is in their crystal lattice. Vickers hardness values of experimental alloys are lower than for pure titanium and acceptable for potential dental use. Finally, zirconium addition resulted in a fluent casting of titanium alloys.

## 5. References

1. Grandin H. M., Berner S., Dard M. A Review of Titanium Zirconium (TiZr) Alloys for Use in Endosseous Dental Implants - Materials 5, 2012, 1348-1360
2. Ho W-F., Cheng C-H., Pan C-H., Wu S-C., Hsu H-C. Structure, mechanical properties and grindability of dental Ti–10Zr–X alloys - Materials Science and Engineering C 29, 2009, 36-43
3. Wataha J. C. Alloys for prosthodontic restorations - The Journal of Prosthetic Dentistry 87, 2002, 351-363
4. Osman R.B., Swain M.V. A critical Review of Dental Implant Materials with an Emphasis on Titanium *versus* Zirconia - Materials 8, 2015, 932-958
5. Lütjering G. Titanium, Berlin, Springer, 2003, (Lütjering G., Williams J. C.)
6. ASM Handbook Volume 3: Alloys Phase Diagrams, Ohio, ASM International, 2002.
7. Takahashi M., Kikuchi M., Okuno O. Grindability of Dental Cast Ti-Zr Alloys - Materials Transactions, 50 (4), 2009, 859-863
8. Powder Diffraction File Search Manual, JCPDS International Centre for Diffraction Dana, Swarthmore, 1982.
9. Boyer R., Welsch, Collings E. W. Materials Properties handbook: titanium alloys, Materials Park, ASM International, 199., 1051-1060
10. Majumdar P., Singh, S. B., Chakraborty M. Elastic modulus of biomedical titanium alloys by nano-indentation and ultrasonic techniques – A comparative study – Materials Science and Engineering A, 489, 2008, 419-425
11. Taneichi K. Taira M., Sukedai E., Narushima T., Iguchi Y., Ouchi C. Alloy design and property evaluation of new β type titanium alloy with excellent cold workability and biocompatibility – ISIJ International. 46 (2), 2006, 292-301
12. Kim H-S., Kim W-Y., Lim S-H. Microstructure and elastic modulus of Ti-Nb-Si ternary alloys for biomedical applications – Scripta Materialia, 54, 2006, 887-891
13. ASM Handbook Volume 2: Properties and Selection: Nonferrous Alloys and Special-Purpose Materials, Ohio, ASM International, 2002.
14. Weiss I., Semiatin S. L. Thermomechanical processing of beta titanium - Materials Science and Engineering A, 243, 1998, 46-65
15. Wang L., D'Alpino P. H. P., Lopes L. G., Pereira J. C. Mechanical properties of dental restorative materials: relative contribution of laboratory tests - Journal of Applied Oral Science, 11 (3), 2003, 162-7