EFFECT OF SINTERING TIME AND TEMPERATURE ON THE MICROHARDNESS OF TITANIUM-ZIRCONIUM ALLOY

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Abstract

Titanium and titanium alloys have been widely used in medicine as implant materials for the last 50 years. The reason for this could be found in a unique combination of biocompatibility and strength of these alloys. The main advantage of titanium is the ability to bind to bone and grow into the implant. Due to the high cost of production, titanium is not used in large quantities, and therefore research are focused on finding new, more economical alloys. For these reasons, the aim of this paper is to analyze the effect of powder metallurgy process parameters in the production of titanium alloy containing 20% zirconium. Starting elemental powders were a ball milled and then compacted using the hydraulic press. Sintering process was performed under the different values of time and temperature. Starting powders were characterized using the scanning electron microscope. Porosity was analyzed using the light microscope. It was found that it could be decreased by increase in sintering temperature. Microhardness of polished sintered samples was determined by Vickers method. Results showed that higher microhardness values were obtained in samples sintered at higher temperature. Finally, results show that titanium-zirconium alloy produced by this route of powder metallurgy could be potentially used in a biomedicine.

Keywords: Titanium-zirconium alloy, powder metallurgy, biomedical materials, microhardness

1. INTRODUCTION

As human life expectancy increases with age, the need for biomaterials, which in certain medical indications can improve the quality of life and/or prolong it, increases. Therefore, the development of new biomaterials is an increasingly important topic from a research point of view [1,2]. Biomaterials are commonly used as implants in the human body as a replacement for their lost or diseased biological structures [3,4]. Titanium alloys that include elements such as niobium (Nb), tantalum (Ta), zirconium (Zr), molybdenum (Mo) and palladium (Pd), elements that are non-toxic, are also being studied for their mechanical strength and good biocompatibility. Alloys with zirconium (Zr) are characterized by good corrosion resistance, good mechanical strength, and the biocompatibility of these alloys is better than that of Ti CP [5]. Problems related to casting as well as the high cost of the final products are the reasons why titanium alloys are not widely used [6,7]. In this sense, powder metallurgy technology has proven to be a successful alternative for the production of titanium alloys and final products [8,9]. The aim of the research is to analyze the effect of time and temperature of sintering on the Vickers microhardness of titanium alloy with the addition of 20 at% zirconium for potential use in a dental medicine.

2. MATERIALS AND METHODS

Chemical composition of investigated alloy is: 80 at% of titanium and 20 at% of zirconium (Ti-20Zr). The reasons why in this research zirconium was chosen as an element for adding to titanium are as follows: zirconium poses similar chemical properties that are derived from the same group of the periodic table as titanium; it is completely soluble in both (alpha and beta) allotropic Ti-phases; it lowers the alloy melting point and reduces the titanium reactivity with oxygen; due to the similar size of the Ti and Zr atoms, effect of solution hardening is minimized. Finally, zirconium can improve some properties of Ti-alloys that are crucial for biomedical use, such as: biocompatibility and corrosion resistance [10-12].

Ti-20Zr alloy was produced by powder metallurgy technology. Characteristics of used starting powdersare listed in **Table 1**.

Table 1 Characteristics of starting powders

Material	Purity (%)	Particle size (μm)	Density (g/cm^3)
Ti powder	99.8	125-250	4.51
Zr powder	99.8	<45	6.49

After the weighing of titanium and zirconium powders, their mixing and milling was carried out in a ball mill for a period of 30 minutes at room temperature. Grinding jar was made of hard metal as well as balls. Ball-to-powder ratio was 10:1 and rotation rate was 200 rpm. To prevent the oxidation of powders the inert atmosphere of argon was used. No lubricant was added.

The compaction of the powders was carried out by uniaxial pressing on a hydraulic press. Four disc-shaped samples were obtained by applying the same compacting pressure of 80 MPa. Samples were then sintered under different processing parameters, listed in **Table 2**.

Table 2 Processing parameters

Sample No.	Temperature of sintering (°C)	Time of sintering (h)
1	1100	2
2	1350	2
3	1100	4
4	1350	4

Sintering of Ti-20Zr alloy samples, a four green compacts, was performed in a tube furnace in an argon atmosphere. The sintering process was realized through three phases: first, samples were heated at rate of 10 °C/min to sintering temperature; then they were sintered according to data in **Table 2** and finally, the samples were cooled to the room temperature in a furnace to prevent oxidation in air. After metallographic preparation by mounting, grinding and polishing, samples were observed using the light microscope and digital camera in order to analyze the porosity. Microhardnessof the samples after sintering was determined on polished samples by the Vickers method. Indentation was realized by force of 0.490 N (HV0.05) during the 10 s. Diagonals of imprints were measured at the microscope. Measurements were performed on each sample at 5 different spots, after which the mean value was calculated.

3. RESULTS AND DISCUSSION

In order to determine the effect of time and temperature of sintering on the microhardness of titanium-zirconium alloy Ti-20Zr, first starting powders were characterized using the scanning electron microscope. As it can be seen in **Figure 1**, titanium powder particle shape is spherical (**Figure 1a**) while powder particles of zirconium are of irregular and angular shape (**Figure 1b**).

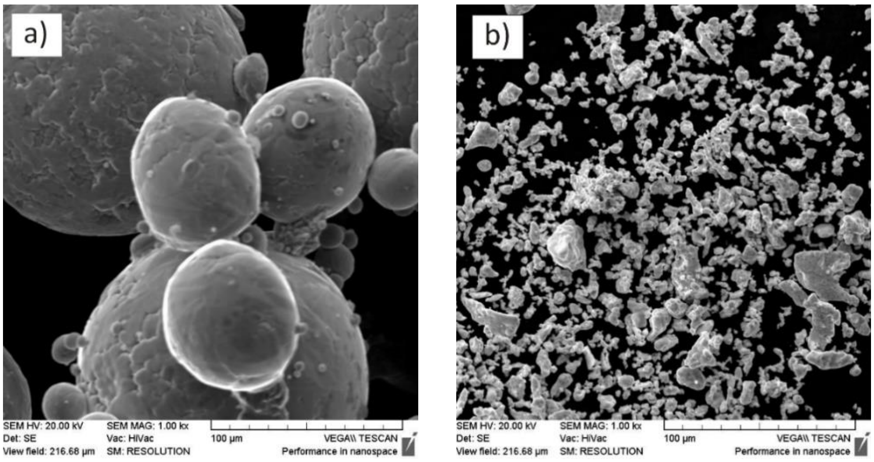
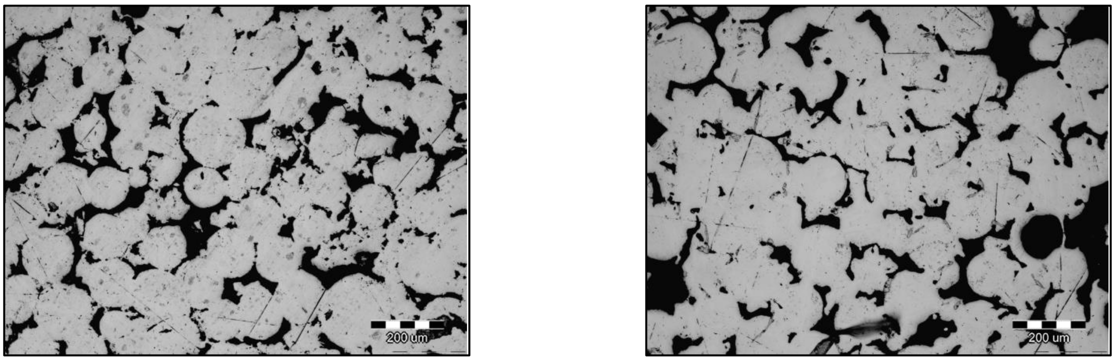


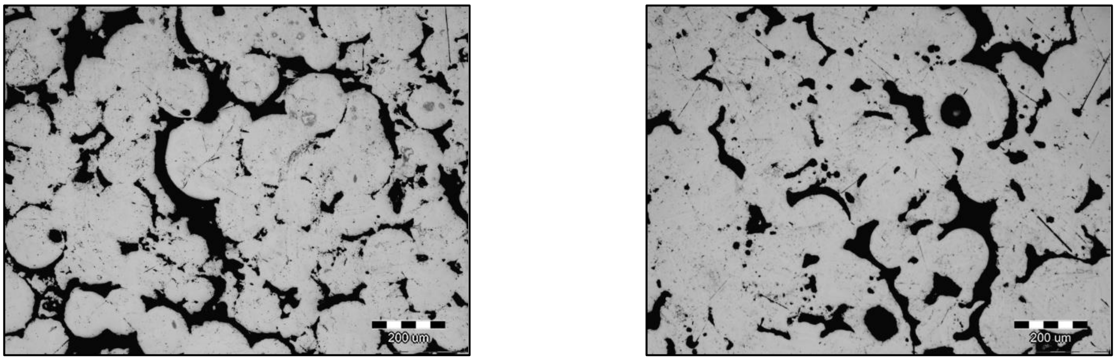
Figure 1 SEM images of starting powders: a) titanium and b) zirconium

The porosity of the sintered and polished samples was observed using a light microscope and recorded with a digital camera. The taken images are shown in **Figure 2**. It can be seen darkareas that represent the pores that are placed along the grain boundaries. In samples 1 and 3, sintered at a lower temperature (1100 °C), pores are in an irregular form andalso interconnected which may be the result of poor densification throughout the sintering. As a result, the interparticle boundaries are still clearly visible. This means that most of the thermodynamic energy of the system was spent on diffusion and homogenization of the chemical composition instead of densification. In samples 2 and 4, sintered at a higher temperature (1350 °C) there are spheroidized pores present indicating that higher sintering temperature is favourably to reach the minimal porosity. Furthermore, **Figure 2d** shows disconnected and spheroidized pores implying that the higher temperature as well as longer time of sintering are necessary to the last stage of sintering be finished.



a) Sample 1, sintered at 1100 °C for 2 h

b) Sample 2, sintered at 1350 °C for 2 h



c) Sample 3, sintered at 1100 °C for 4 h

d) Sample 4, sintered at 1350 °C for 4h

Figure 2 Pores in sintered samples

If we consider the amount of pores in relation to the applied compacting pressure, **Figure 2** implies that the pressure during the compaction could be higher in order to achieve degree of porosity as low as possible, i.e. a higher density of the powder mixture.

It is known that the hardness can be affected by the presence of oxides and contamination of the powder by grinding balls. Also, hardness can be influenced by the high porosity and the hardness measurement method used. Since no chemical analysis was performed, in this work microhardness was determined. The results of Vickers microhardness determination are given as mean values and are shown in **Figure 3**.

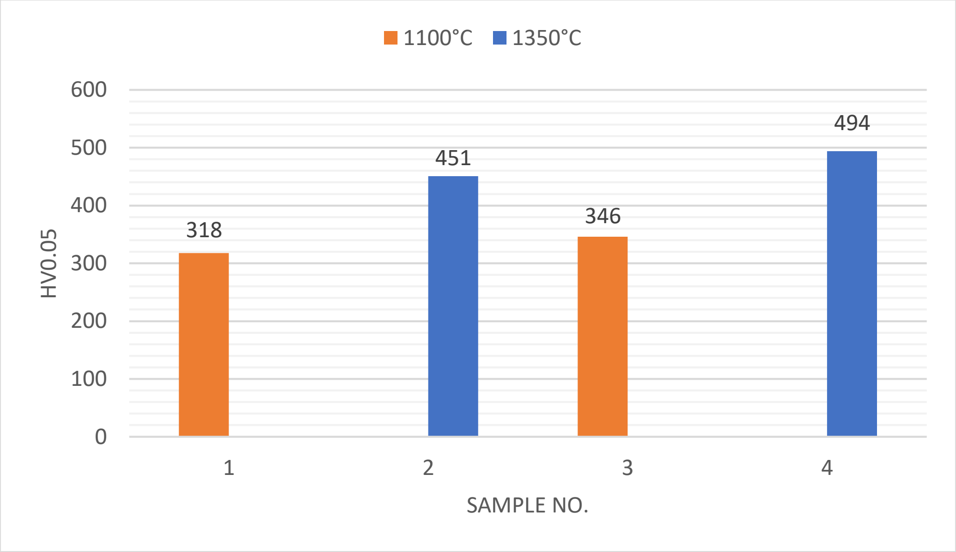


Figure 3 Dependence of microhardness on sintering temperature

Obtained mean values are between318 and 494 HV0.05. It is evidentin **Figure 3** that the HV0.05 values are lower for the samples sintered at a lower temperature (1 and 3) and accordingly higher for samples sintered at higher temperature (2 and 4). This is in line with the fact that as the sintering temperature increases, the microhardness increases. Namely, sintering at higher temperatures encourages additional binding of particles and more complete alloying due to higher diffusion and mass transfer rates.

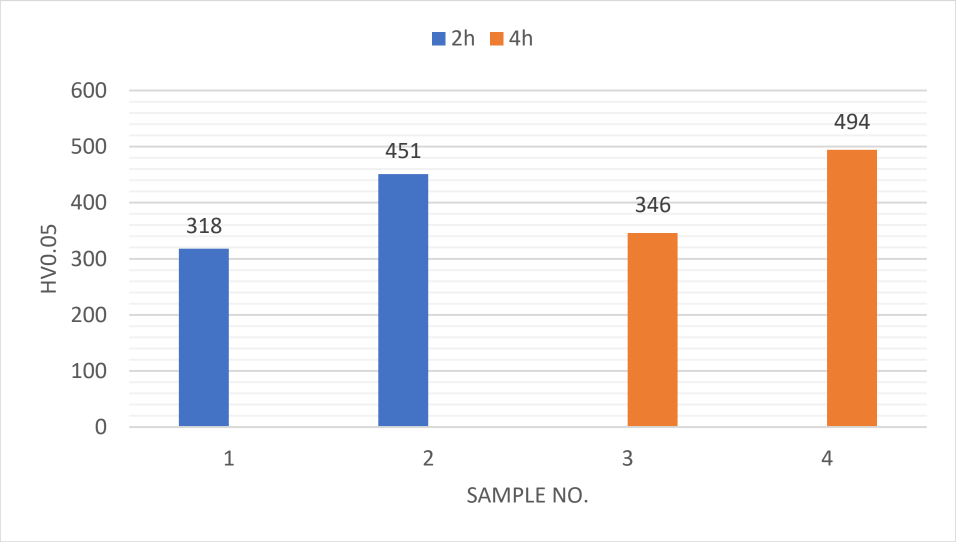


Figure 4 Dependence of microhardness on sintering time

Dependence of microhardness on the sintering time is graphically consider by **Figure 4**. In order to evaluate the influence of the sintering time on the microhardness, HV0.05 values for samples 1 and 3 were compared. Thus it can be observed thatsample 3 that was sintered for a longer time than sample 1, shows a higher value ofmicrohardness. Similarly, sample 4 was sintered for a longer time than a sample 2 and therefore shows higher microhardnes value. This behavior can be related to the fact that a longer sintering time ensures a more complete interparticle connection, i.e. alloying, which highlights the influence of the alloying element zirconium on the basic element titanium. Therefore, this increase in microhardness can be explained as hardening by the formation of a β(Ti,Zr) solid solution. Regarding the time and temperature of sintering effect on the microhardness values, it is obvious that temperature is a predominant factor for microhardness rather than time of sintering.

When pores presence and morphology are analyzed, it can be seen that they are the most interconnected just in sample 3, while in sample 4 they are spheroidized. Therefore, it is expected that sample 4 sintered at higher temperature for a longer time shows the highest microhardness value.

4. CONCLUSION

This paper presents the analysis of the sintering time and temperature effect on the hardness of Ti-20Zr alloy for potential use in biomedicine. From the obtained results it can be concluded that porosity can be reduced by sintering at a higher temperature as well as by applying the higher compacting pressure. Furthermore, simultaneously increase in time and temperature of sintering leads to the decrease of porosity as well as to the increase of microhardness. Still, this values are in the acceptable range for biomedical applications implying that processing parameters of powder metallurgy applied in this work can result in potentially biomedical titanium-zirconium alloy.

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