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EFFECT OF ZIRCONIUM ADDITION ON MICROSTRUCTURE AND PROPERTIES OF PURE TI PRODUCED BY POWDER METALLURGY

Hussein H. Kadhum[1], and Mohsin T. Mohammed[2]

[1] **Materials Engineering Department, Faculty of Engineering, University of Kufa, Najaf, Iraq. Email: husseinkadhim297@gmail.com**

[2] **Production Engineering and Metallurgy Department, University of Technology, Baghdad, Iraq. Email: mohsin.t.mohammed@uotechnology.edu.iq**

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ABSTRACT

Titanium (Ti) and its alloys are frequently employed in the biomedical industry because they have a high corrosion resistance in addition to being lightweight, non-toxic, and having excellent biocompatibility. In this work, the microstructure and some required properties were evaluated for binary Ti-15Zr alloy produced by powder metallurgy (PM) for biomedical applications; the obtained results were also compared to that of commercially pure Ti (CP-Ti). The major goal of this paper is to study the impact of Zr addition on the microstructure, micro-hardness, and corrosion resistance of Ti alloy.

KEYWORDS: Biomedical applications; Corrosion resistance; Micro-hardness; Powder metallurgy; and Titanium.

1. INTRODUCTION

It is well known that metallic medical implants should have desirable features including exceptional biocompatibility, superior strength, low elastic modulus, in addition to an impressive resistance to corrosion. Because of the particular qualities that some metals and alloys offer, they are frequently utilized in the field of biomedicine (Trevisan et al., 2018). Among metallic biomaterials, Ti and its alloys are attractive materials since they provide a combination of exceptional properties, such as mechanical performance, non-toxicity, and biocompatibility, which are extremely required for substituting materials for hard tissues. The broad application of Ti alloys in medical implants has generated a significant need to design and develop new classes of Ti alloys with higher bio-properties within the human body. As a direct consequence of this, new Ti alloys with significantly enhanced characteristics have been produced as a result of the addition of a variety of various alloying elements. Ti-6Al-4V and Ti-Ni (Nitinol) alloys are two materials that find widespread use in the biomedical industry. However, the release of various metallic ions from the alloy, particularly Al, V, and Ni, may induce some undesired results such as allergies, cytotoxicity, and neurological diseases (Sidhu et al., 2021). Therefore, the utilization of β-stabilizer elements like Nb, Mo, and Ta, etc., is a vital option for the development of contemporary Ti-based alloys with higher bio-preference (Mohammed et al., 2014). In this sense, zirconium (Zr) has been recognized as an element that is not toxic and does not cause allergic reactions. It shares the identical group in the periodic table of the elements as Ti, which helps to explain why both elements have similar chemical structures and physical characteristics (Tang et al., 2022). It is important to note that Zr is a neutral element, but it becomes a β-stabilizer element when combined with other elements (Hsu et al., 2009; Correa et al., 2014). In recent years, binary Ti-Zr alloys that are designed to be used exclusively in biomedical applications have been developed owing to their commendable corrosion resistance and biocompatibility. Hence, these alloys are the typical medical Ti materials for dental implants (Badranet al., 2017). The adding of Zr (as a strengthening alloying element) to CP-Ti is a viable course of action since it can increase the clinical performance of the produced Ti alloys (Han et al., 2014). The production of components of this kind of alloys can be achieved using several procedures, including wrought processing, solidification/casting methods, and powder metallurgy (PM) approaches (Semiatin, 2020). Among them, PM technique provides a cost-effective and efficient means of producing Ti implants (Carman et al., 2011). It is of practical consequence to clarify the effect of Zr on the structure and bio-performance of Ti implants. Therefore, in this study, the impact of Zr addition on microstructure, micro-hardness, and corrosion resistance of pure Ti was examined. The ultimate aim is to develop a binary Ti alloy system (Ti-15Zr) with higher performance for medical applications.

2. METHDOLOGY

This work involved the fabrication of disc-shaped samples of pure Ti and Ti-15Zr alloy using the PM technique. The dimensions of produced samples were 15 mm and 3 mm for diameter and thickness, respectively, as shown in Fig. 1. The powder combinations were mixed for 4 hours, mechanical blended through cold compaction at a pressure of 700 MPa, followed by sintering at a temperature of 1300 ^{o}C for 1 hour.

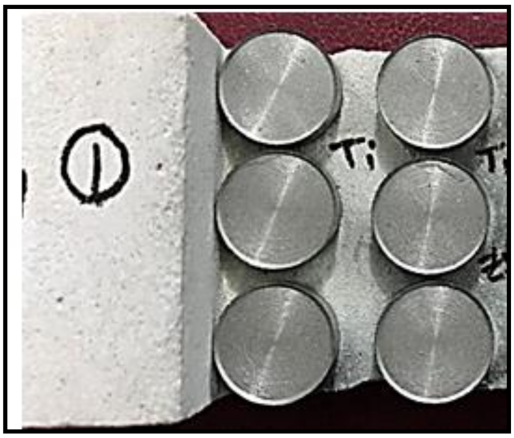

Fig. 1. Pure Ti and Ti-15Zr alloy samples produced by PM technique.

This process was carried out at a vacuum level of 10^{-3} Pa under an inert environment. The heating and cooling speeds were established at 6 ^{o}C/min and 10 ^{o}C/min, respectively. The sintering process was conducted through multi-stage periods as shown in Fig. 2.

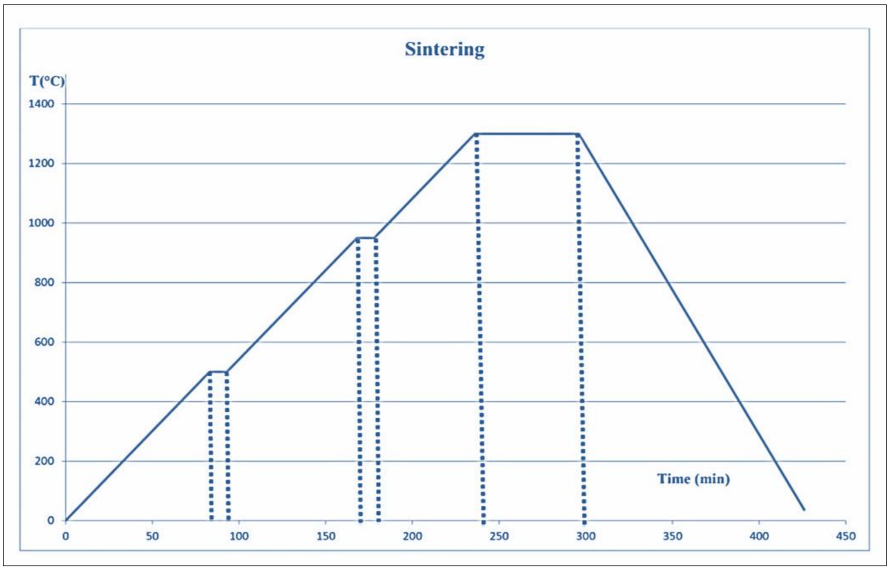

Fig. 2. Sintering process used in this study.

In order to examine the microstructure, the sintered samples were subjected to standard grinding and polishing procedures. The grinding process was performed on the mounted samples, first with the use of sandpaper at various grit sizes (400, 600, 800, 1000, 1200, 2000, and 2500). Subsequently, a fine cloth was employed, along with a 3μm diamond paste, to achieve a mirror like surface. Subsequently, the samples were etched by immersing them in a solution of Kroll's Titanium Etch (92% distilled-water, 6% nitric acid, and 2% hydrofluoric acid) for a duration of 15 seconds.

The microstructure characterization of the Ti samples was conducted using optical microscopy (NMM-800RF) and scanning electron microscopy (AxiaChemi SEM, USA). Energy-dispersive spectrometry (EDS) attached to SEM was also utilized for determining the chemical composition of the investigated samples. Besides, X-ray diffraction analysis was conducted using (SHIMADZU Lab XRD-6000, Japan) instrument to ascertain the constituent phases present in the generated Ti samples with a 2θ ranging from 10 to 100 degrees.

Vickers micro-hardness (HV) test was carried out using (TH715 digital micro Vickers hardness tester, China). The micro-hardness measurements were obtained by applying a load of 2.94 N for 15 seconds in different positions for each sample. A minimum of about five measurements were performed to quantify the hardness over the polished surface of each sample; the outcome is displayed here using the average value in units of kg/mm^2.

The corrosion resistance of the examined Ti materials was assessed through the utilization of potentiodynamic polarization measurements, using (DY2321 potentiostats). The samples were submerged in Ringer's solution at ambient temperature for duration of 1200 seconds, during which the open circuit potential (OCP) was brought to a stable state. Ringer's solution is employed as a simulated bodily fluid (SBF) with a PH range of (5.0-7.0). The constituents and concentration of Ringer's solution are illustrated in Table 1. Potentiodynamic polarization test was performed on all investigated Ti samples; with a scan rate of 0.02 V/s. Potentiostats software was utilized in order to determine the values for the parameters associated with corrosion, which include the corrosion rate, as well as the corrosion potential (E_{corr}), and the corrosion current density (i_{corr}).

Table 1. Constituents and concentration of Ringer's solution used for corrosion test.

Constituent	Concentration g/l
NaCl	8.60
KCl	0.3
$CaCl_2$, $2H_2O$	0.33

3. RESULTS AND DISCUSSION

As is well identified, the microstructure and phases exhibited by an alloy play a crucial role in dictating its diverse range of characteristics (Poondla et al., 2009). The XRD patterns of the Ti-15Zr alloy and CP-Ti (reference material) are attained in order to examine the influence of Zr addition on the phases formed in the microstructure, as shown in Fig. 3. It can be seen that the CP-Ti exhibits diffraction peaks of a singular phase, commonly referred to as the α-phase. The Ti-15Zr alloy also shows an α-Ti type structure without any distinct existence of secondary phases, i.e. β phase, or any intermediate phases, which fits perfectly with the expected phases from the phase diagram. In other words, the microstructures of the samples of CP-Ti and Ti-15Zr alloy exhibited the hexagonal crystal shape that is often associated with the α phase. Indeed, this indicates that the adding of Zr to Ti does not cause any possibility to form other phases.

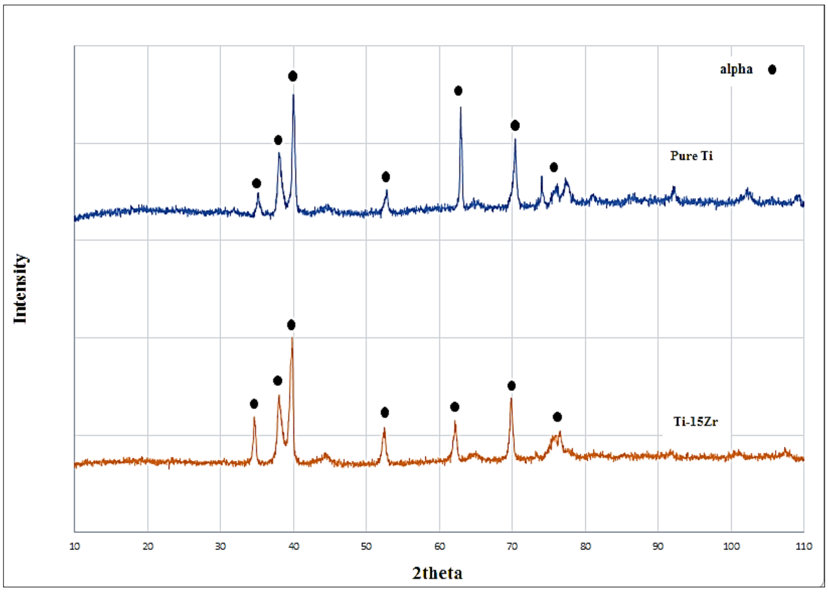

Fig. 3. XRD results of CP-Ti and Ti-15Zr alloy samples.

Fig. 4 shows the SEM micrographs and EDS results of investigated CP-Ti and Ti-15Zr alloy samples. For both Ti samples, it can be seen that the microstructure consists of a lamellae structure, which is typical of α-Ti phase. This structure is associated with the inherent anisotropy of the hexagonal crystal structure of α phase (Cordeiroet al., 2017; Matuła et al., 2020). In general, the microstructure disclosed whole solid solution, as assumed from the phase diagram of binary Ti-Zr alloy system (Baker, 2006). However, it can be observed that the micrograph of the Ti-15Zr alloy has finer lamellae structure of grains compared to the CP-Ti sample. Consequently, increasing Zr concentration led to refine the grains; the microstructure of Ti-Zr system was extremely sensitive to Zr content (Eyyup et al., 2022). Also, for Ti-15Zr sample, stripes in white color with a distinct separation distance are evident, suggesting that the distribution of Zr in this sample is non-uniform (Tang et al., 2022). This means that the grain boundaries have a slight decrease of Ti and a slight increase of Zr. Moreover, macro and micro pores were observed at the microstructure of both CP-Ti and Ti-15Zr alloy. Moreover, EDS analysis displayed the existing of Ti and Ti with Zr for CP-Ti and Ti-15Zr alloy, respectively. The results demonstrated the higher purity of the produce samples as there is no other elements present in these samples.

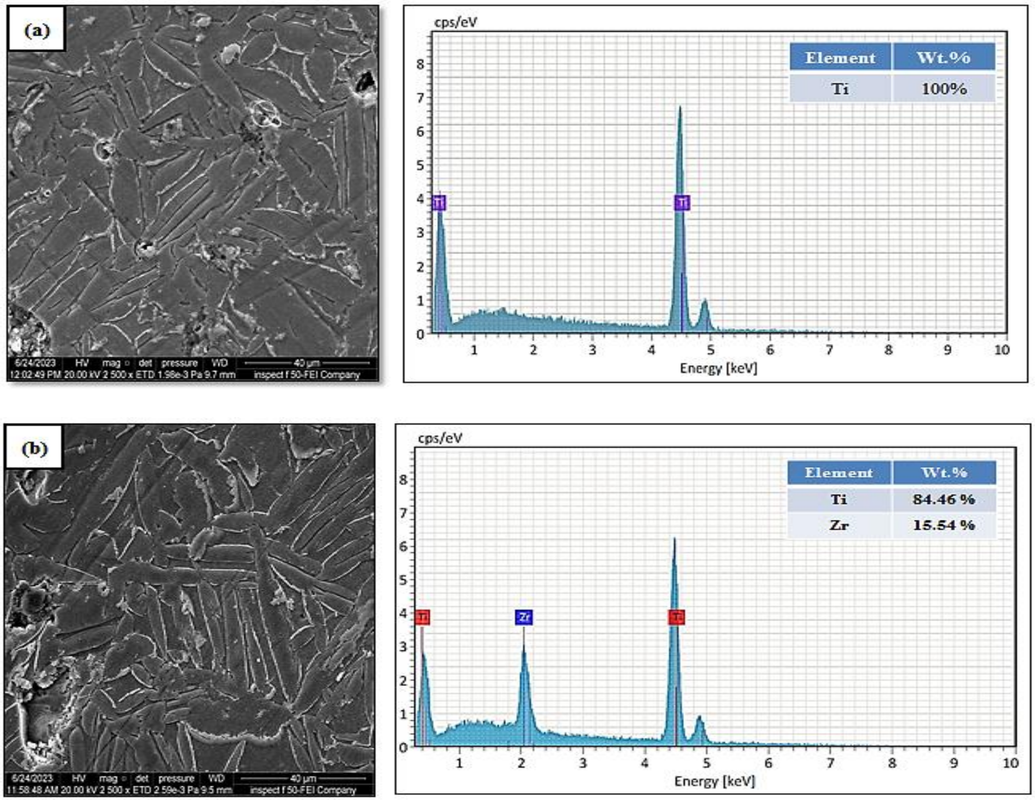

Fig. 4. SEM and EDS of investigated samples: (a) CP-Ti and (b) Ti-15Zr allo.

It is well known that the mechanical properties of implantable materials should be very close to those of human bone. Thus, to understand how the addition of Zr could alter the microstructure and mechanical properties, the micro-hardness test for CP-Ti and Ti-15Zr alloy samples was attained. Table 2 shows the average micro-hardness of the investigated. The results showed that the Ti-15Zr sample has higher value of micro-hardness (388.1 HV) compared to that of CP-Ti (311.4 HV). These results indicated that the hardness tends to rise with the addition of Zr. This means that the addition of Zr causes an effective increase in the micro-hardness of CP-Ti. In general, there are some parameters that may affect the hardness of any engineering material, such as its ability to atomic mobility, distortion of crystalline lattice and atomic displacement. Hence, adding of Zr resulted a crystalline lattice and atomic displacement, which induce greater micro-hardness of Ti-15Zr alloy (Ho et al., 2009; Correaet al., 2014). Also, this increase in the hardness may be related to the refinement in the microstructure of Ti-15Zr alloy, i.e. due to Hall–Patch effect (see Fig. 4) (Matułaet al., 2020).

Potentiodynamic polarization curves were used to analyze the influence of Zr on the corrosion behavior of studied Ti samples when they were exposed to Ringer solution at 37 °C. The typical potentiodynamic polarization curves observed for a CP-Ti and Ti-15Zr alloy samples are depicted in Fig. 5. The primary electrochemical parameters obtained for the studied Ti samples are detailed in Table 2. As can be seen, the investigated Ti materials display typical active-passive transition and comparable passive manner. This confirms that a spontaneous oxide film was developed with passivation characteristics after immersion in SBF solution. Also, the findings revealed that the Ti-15Zr alloy sample exhibits better corrosion resistance as it has a lower I_{corr} and CR compared to that of CP-Ti. This indicates the greater resistance to corrosion attack offered by Ti-15Zr alloy in contrast to CP-Ti. These improvements in corrosion parameters may be attributed to the existence of alloying elements like Zr, which may induce a grain size refinement to increase the growth kinetics onto oxide layer with greater grain boundary area. As a result, the incorporation of Zr results in an increase in the corrosion resistance of the Ti alloy.This finding provides credence to the hypothesis that alloys with Zr additions tend to exhibit superior corrosion resistance, i.e. a more nobler electrochemical behavior (Wang et al., 2009).

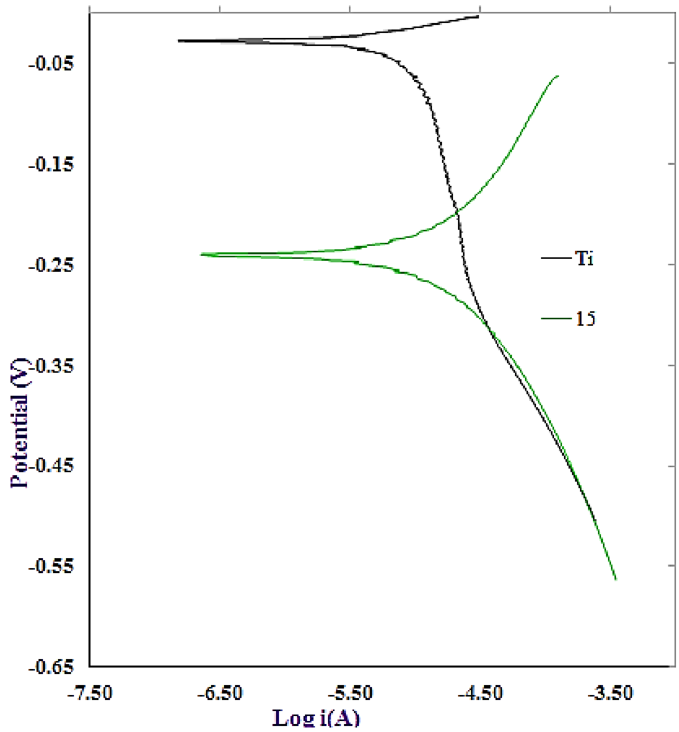

Fig. 5. Corrosion Curves of specimens.

Table 2. Electrochemical parameters for the investigated Ti samples.

Sample	E_{corr} (mV)	I_{corr}(μA.cm^{-2})	CR (mpy)
CP-Ti	-28	8.46	2.74
Ti-15Zr	-241	6.82	2.21

4. CONCLUSIONS

The current investigation employed the PM approach to fabricate samples of pure Ti and a Ti-15Zr alloy with the intention of its utilization in biomedical applications. The microstructure, phase composition, micro-hardness, and corrosion resistance of Ti materials were investigated. The main results of this study can be summarized as follows:

- The microstructure analysis indicates the presence of solely α-phase, suggesting that both materials possess a stable α structure.
- The addition of Zr into Ti structure has an effective effect for increasing the micro-hardness.
- The Ti-15Zr alloy exhibits a significant enhancement in its corrosion resistance when exposed to Ringer solution, as compared to pure Ti.

5. ACKNOWLEDGEMENT

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