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Sintering Performance and Corrosion behavior of biomedical Ti-24Nb-4Zr-8Sn alloy produced using SPS in various simulated body solutions

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Abstract. In this study, the Ti-24Nb-4Zr-8Sn (Ti2448) alloy was produced using spark plasma sintering technique and its behaviour in 0.9% NaCl, Hank's solution and cell culture medium were investigated using open circuit potential and potentiodynamic polarization techniques. The results were compared with that of CP Ti and Ti-6Al-4V alloy. Relative densities above 99.0% were achieved for all three systems. CP Ti and Ti64 had both 100% relative density, and Ti2448 showed a slightly lower density of 99.8%. Corrosion results showed that all three materials exhibited good corrosion resistance due to the formation of a protective passive film. In 0.9% NaCl Ti2448 had the highest current density (9.05 nA/cm2), implying that its corrosion resistance is relatively poor in comparison to Ti (6.41 nA/cm2) and Ti64 (5.43 nA/cm2), respectively. The same behaviour was observed in Hank's solution. In cell culture medium, Ti2448 showed better corrosion resistance with the lowest current density of 2.96 nA/cm2 compared to 4.86 nA/cm2 and 5.62 nA/cm2 of Ti and Ti64 respectively. However, the current densities observed are quite low and insignificant that they lie within acceptable ranges for Ti2448 to be qualified as a biomaterial.

1. Introduction

Biomaterials are materials used for making devices that can interact with biological systems to coexist for longer service with minimal failure. They are widely used in the repair, replacement, augmentation of diseased or damaged parts of the musculoskeletal system such as bones, joints and teeth. Titanium alloys are the most suitable candidates used as metallic biomaterials due to their biocompatibility, low Young´s modulus and good corrosion resistance [1]. Ti-6Al-4V is one of the most widely used alloys for orthopaedic implants [2], although it suffers from some drawbacks: adverse health effects arise from the release of Al and V ions into the human body [3] and this alloy exhibits relatively high Young's modulus as compared to that of bone [1]. These limitations are overcome through the development of non-toxic β-stabilizing alloys in order to improve both biochemical and biomechanical compatibility. By favouring the formation of β phase, Young's modulus of the alloy can be decreased to facilitate the load transfer from the implant to the bone, avoiding bone resorption and final loosening of the implant. The Ti-Nb-Zr (TNZ) alloys are particularly interesting since not only do they consist of nontoxic elements but also possess Young's modulus amongst Ti alloys [4]. An improved corrosion resistance was reported in binary Nb-Zr alloy due to Nb content, and an increase in wear resistance in Ti-Nb-Zr-Ta (TNZT) alloy. Moreover, additions of tin (Sn) to these alloys serves to improve their densification and ultimately beta phase formation [6].

2. Experimental Procedure

2.1. Sample preparation and fabrication

The selected alloys for the present study were as follows: commercially pure titanium (grade 2), Ti-6Al-4V and Ti-24Nb-4Zr-8Sn. The alloy composition is given in weight per cent. Appropriate amounts of powder metals of defined purity and particle size (Table 1) were mixed and subsequently tubular mixed (Tubular T2F) for 30 minutes at 320 rpm prior to mechanical alloying. The three alloy systems were then milled using high energy ball mill (Simoloyer CM100, CSIR) under an argon protective atmosphere at room temperature. The grinding media was made of zirconia. The ball to powder ratio was approximately 10:1. Milling was performed at the rotation speed of 500 rpm for 5 hours without the addition of any process control agent.

Prepared powders were consolidated at the Tshwane University of Technology using SPS apparatus (FCT System-GmbH HHP-D5). The powder in a graphite die was heated to 1200 °C at a heating rate of 100 °C/min with a pressure of 50 MPa. The holding time was 10 min. Hussein et al. [5] reported that the heating rate and holding time of 100 °C/min and 10 min respectively minimize grain growth. According to Hussein et al. [5] sintering at 1200 °C allows the complete dissolution of Nb and the attainment of the homogenized nanocrystalline structure with better mechanical properties. Moreover, according to Hussein et al [5], nanostructured alloys have better compatibility compared to their coarse-grained counterparts. These powders were sintered to 40 mm diameter discs and 2 mm thick. The relative density of the compacts was measured by the Archimedes method. The sintered samples for scanning electron microscope (SEM) (FE-SEM JEOL 6000, CSIR) observation was prepared by the standard metallographic method. The polished samples were etched with Kroll's reagent.

Table 1. Characteristics of raw metal powders.

Component	**Purity (%)**	**Particle size (µm)**	**Density (g/cm^3)**	**Melting point (°C)**
Ti	99.9	44	4.51	1668
Al	99.5	44	2.70	660
V	99.5	44	6.0	1910
Nb	99.8	3	8.57	2648
Zr	99.5	149	6.49	1852
Sn	99.5	0.1	7.30	232

2.2. Corrosion test

The corrosion behaviour of the materials in artificial body fluids [Hanks solution (NaCl 8.0 g/L; KCl 0.4 g/L; KH_2PO_4 0.6g/L; $CaCl_2$ 0.14 g/L; $MgCl_2.6H_2O$ 0.1 g/L; $NaHCO_3$ 0.35 g/L; $NaH_2PO_4.2H_2O$ 0.06 g/L; $MgSO_4.7H_2O$ 0.06 g/L; Glucose 1.0 g/L at pH 7.4), 0.9% NaCl solution and E-MEM + 10% FBS) was carried out using potentiodynamic polarization technique. The specimens with a square surface area (8 x 8 mm) and 2 mm thick were used for tests. All electrochemical tests were conducted using a potentiostat (VersaSTAT3) controlled by a computer (VersaStudio) software for data acquisition. The cell used was a typical three-electrode consisting of the platinum counter electrode (CE), a working electrode (specimen) and silver/silver chloride reference electrode. The tests were performed using scan rate of 0.1667 mV/s and polarized from – 0.25 V to 1.5 V. All the electrochemical experiments were conducted in an incubator and the test temperature was controlled as 37 ± 1ºC. Two samples were used for each alloy group in each solution, and 10 ml test solution was used in every electrochemical test. The tests were conducted according to corrosion testing standard (ASTM F2129).

3. Results and Discussion

The average relative densities of the compacts are shown in Fig. 1. Commercially pure titanium and Ti-6Al-4V compacts achieved higher relative densities than Ti-24Nb-4Zr-8Sn. The reason is possibly due to the additions of the higher melting alloying elements such as Nb and Zr that results in incomplete densification.

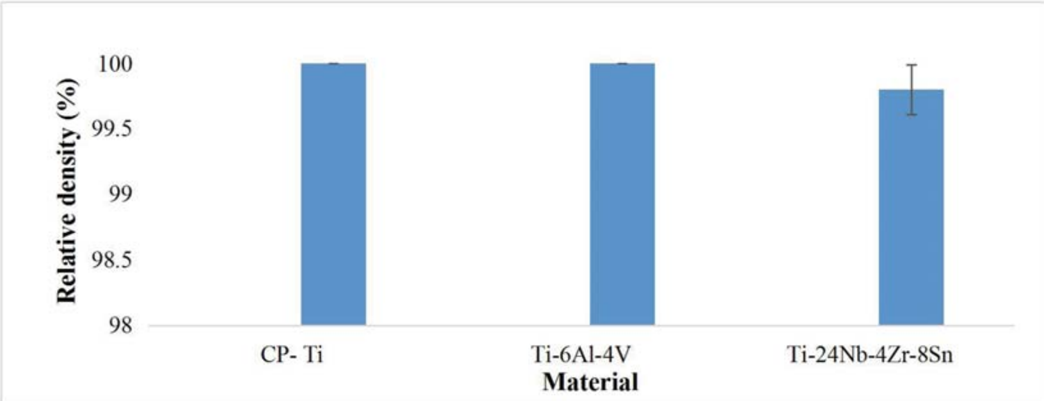
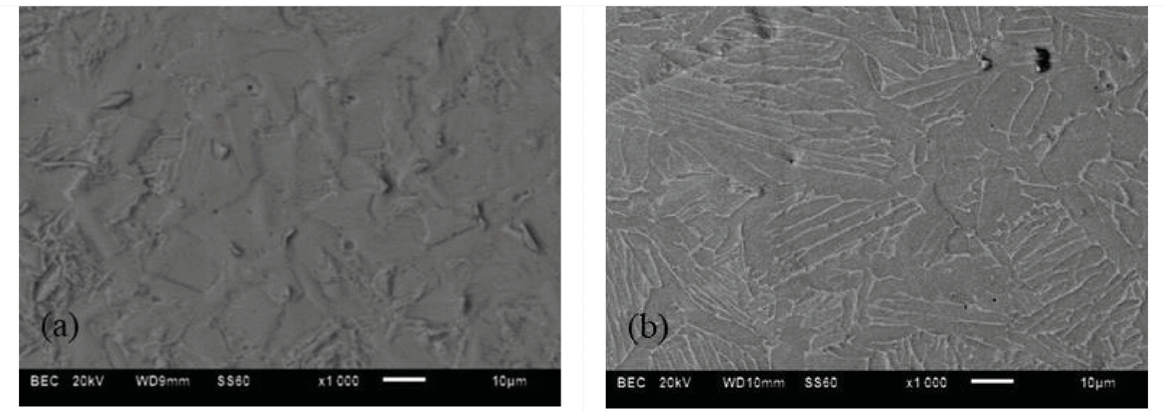
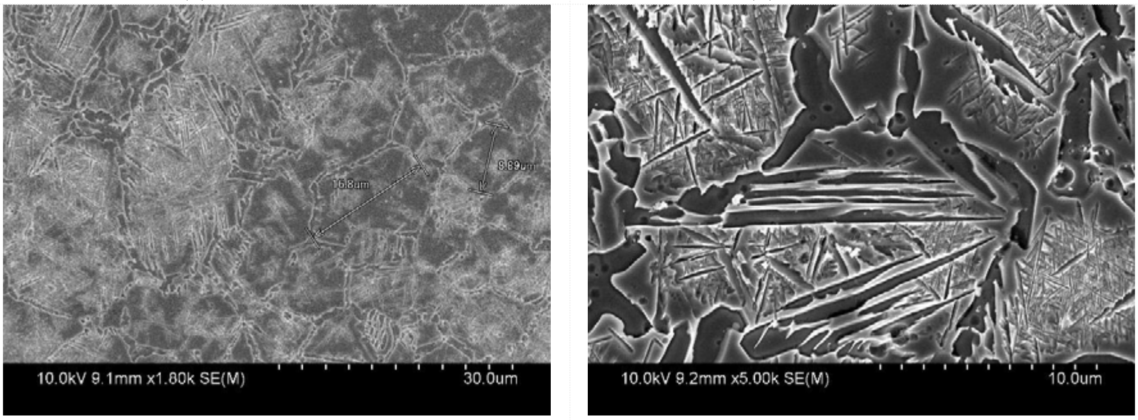


Figure 1: Average relative densities of CP Ti, Ti6Al4V and Ti-24Nb-4Zr-8Sn alloys after SPS.

Figure 2 illustrates the microstructures of the compacts sintered at 1200 ºC for 10 min. Refined microstructures can be observed in pure titanium as shown in Figures 2(c) and 2(d). This has been attributed to fast cooling during the SPS sintering cycle as also reported by Falodun et al [12]. Figures 2(a) and (b) show the typical CP Ti and Ti6Al4V microstructures – the α/β phases are more homogeneously distributed as expected. Figure 2(c) however exhibits porosity and an inhomogeneous distribution of the α/β phases in the microstructure of the sintered Ti2448 samples. Xia Li and co-workers [13] also recently observed similar microstructures in their studies of the fabrication of biomedical Ti-24Nb-4Zr-8Sn alloy with high strength and low elastic modulus via powder metallurgy– the insufficient diffusion of elemental powders was highlighted as the possible reasons. Further investigations are currently focused on studying the porosity and the homogenisation of the microstructures.



(a) Sintered CP Ti **(b)** Sintered Ti6Al4V



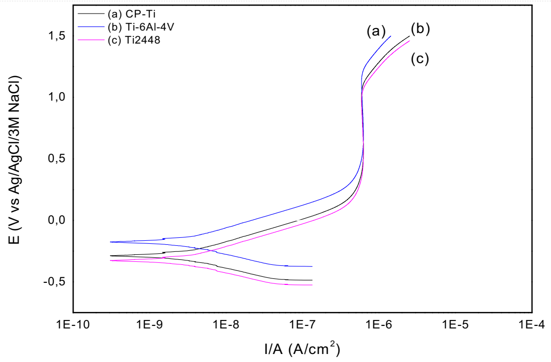
(c) Sintered Ti2448 **(d)** Sintered Ti2448 at high magnification

Figure 2: SEM micrographs of studied alloys

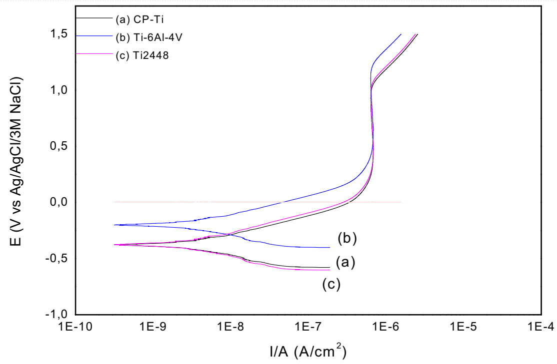
The potentiodynamic polarization curves for the studied alloys in 0.9% NaCl, Hank's and E-MEM + 10% FBS solutions at 37 ºC are shown in Figures 3(a-c). It is clear all the samples exhibit a typical active-passive characteristic. The corrosion potentials (Ecorr) were estimated from these curves and displayed in Table 2. There is no distinctive difference on the anodic polarization curves of these three alloys, indicating that the same anodic reaction occurred on their surface but with different rates. In 0.9% NaCl Ti2448 had the highest current density (9.05 nA/cm2), implying its corrosion resistance is relatively poor in comparison to Ti (6.41 nA/cm2) and Ti64 (5.43 nA/cm2), respectively. The same behaviour was observed in Hank's solution. In cell culture medium, Ti2448 showed better corrosion resistance with the lowest current density of 2.96 nA/cm2 compared to 4.86 nA/cm2 and 5.62 nA/cm2 of Ti and Ti64 respectively. However, the corrosion rates observed are quite low and insignificant that they lie within acceptable ranges for Ti2448 to be qualified as a biomaterial as provided in the corrosion testing standard (ASTM F2129).

Table 2: Corrosion parameters of the potentiodynamic polarization for the Ti2448, CP-Ti and Ti-6Al-4V alloy in different solutions at 37 °C.

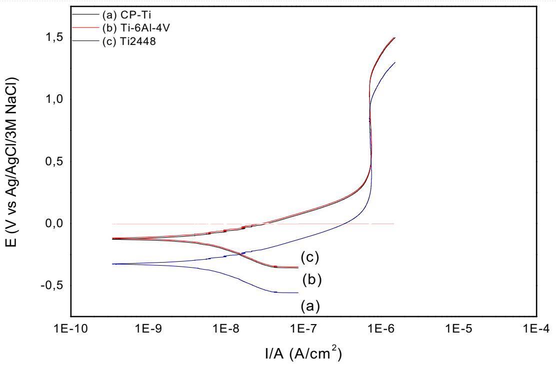
Materials	Solutions	I_{corr} (nA/cm^2)	E_p (V, Ag/AgCl 3M NaCl)
Ti2448	0.9 NaCl	9.0475	-0.253
	Hank's	4.048	-0.327
	E-MEM + 10% FBS	2.4805	-0.351
CP-Ti	0.9 NaCl	6.4105	-0.304
	Hank's	2.290	-0.348
	E-MEM + 10% FBS	4.859	-0.122
Ti6Al-4V	0.9 NaCl	5.427	-0.088
	Hank's	1.977	-0.257
	E-MEM + 10% FBS	5.618	-0.112



(a) 0.9 wt. % NaCl solution



(b) Hanks's solution



(c) E-MEM + 10% FBS

Figure 3: Potentiodynamic polarization curves in (a) 0.9 wt. % NaCl solution, (b) Hanks's solution and (c) E-MEM + 10% FBS, all conducted at 37 °C.

4. Conclusions

From the material preparation and corrosion behaviour analyses, the following conclusions have been made:

1. Higher relative densities were achieved for the three alloys indicating that the set sintering parameters were favourable.
2. Some instances of undissolved Nb were picked up. These suggest that the milling time was rather insufficient.
3. The Ti228 alloy presented a good passivation performance and its corrosion current density is comparable to that of CP-Ti and Ti-6Al-4V alloy.
4. Ti2448 alloy showed the highest current densities in both 0.9% NaCl and Hank's solution. However, its current density was the lowest in cell culture medium.

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