Spark plasma sintered Ti-35Nb-7Zr-5Ta-1Cu alloy

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Abstract. Beta-titanium alloys composed of non-toxic and non-allergic alloying elements are the material of choice for biomedical applications. The effects of Cu addition and heat treatment on the microstructural evolution and phase transformation of Ti-35Nb-7Zr-5Ta alloys were thoroughly investigated. The spark plasma sintering (SPS) was used to fabricate Ti-35Nb-7Zr-5Ta with a micro-addition of 1 wt.% Cu. Field Emission Scanning Electron Microscopy (FE-SEM) and X-ray diffractometry (XRD) were used to investigate microstructural evolution and phase transformation. Microstructures obtained include a predominant BCC β-phase and a two-phase area (α+β) with a large grain boundary of β-phase without the intermetallic phase, implying a positive effect on the mechanical properties of the alloy. The sintered alloys exhibited excellent corrosion resistance and may be suitable candidates for biomaterial applications.

Keywords: Ti-alloy, Biomaterials, Microstructures, Crystallography Electrochemical analysis

1. Introduction

Ti and its alloys have been recognized as appropriate biomedical implants for bone repair and/or replacement, orthopaedic devices, and other applications due to their good performance, such as excellent mechanical properties, corrosion resistance, and high biocompatibility. Ti implants serve as the foundation for the development of artificial organs and medical devices to improve people's lives [1-3]. Conventional alloys and the most commonly used CpTi, Ti-6Al-4V, and Ti-6Al-7Nb still suffer from some problems such as the mismatch of Young's modulus between the bones (10–30 GPa) that leads to stress shielding and premature failure of the implant and the release of Al and/or V ions from the alloy, which may cause long-term health issues. Ti64 alloy has significantly poor wear resistance and low antibacterial activity, which may result in the early degradation of long-term prostheses [4].

To address these issues, antibacterial metals such as silver and copper have been proposed [5, 6]. According to Lei et al., and Wang et al., [7, 8], a high level of antibacterial activity can be obtained with the addition of less than 5% wt of Cu or Ag. Because Cu is a trace element in the human body and participates in various biological and physiological human functions, it is preferred as an additional alloying element in Ti alloys [4, 9]. Cu CA also be removed from the human body via bile and has several favourable impacts on biological processes. β types of Ti alloys have a low Young modulus with full biocompatibility [2]. The Ti-35Nb-7Zr-5Ta (TNZT) alloy is considered a β-type Ti alloy with a Young modulus

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of approximately 60 GPa. The TNTZ alloy with the addition of 1wt% Cu is fabricated using the Spark plasma sintering (SPS) technique. The SPS is a technique for producing a homogenous alloy for an element that has a high melting temperature.

2. Methodology

2.1. Powder preparation and consolidation

High-purity elementary powders of Ti, Nb, Zr, Ta and Cu powders supplied by Alpha Aesar were used as starting materials to produce Ti-35Nb-7Zr-5Ta-1Cu alloy. The powders were prepared using an MB 200B ECO glove box under an inert argon atmosphere to avoid oxidation and weighed in percentage. The powders were mixed for 8 hours prior to sintering using a T2F Turbula Shaker Mixer at a rotational speed of 49 rpm. The mixed powders were loaded into a 20 mm diameter cylindrical graphite die and punch, with a thin graphite foil placed between the powders and the die to reduce friction between powders in contact with the die walls during the consolidation process and for smooth removal of the sintered alloys after sintering. The graphite foil was coated with cubic boron nitride to serve as a thermal barrier against the diffusion atoms from the graphite punches into the powders during sintering. Sintering was carried out in a vacuum at 1200 °C and 50 MPa pressure, with a heating rate of 100 °C/min and a dwell time of 10 min using the spark plasma sintering (SPS) technique.

Table 1. Raw powders data.

Powder	**Particle size**	**Purity (%)**	**Density (g/cm^3)**	**Melting Point (°C)**
Titanium	-150 Mesh	99.9	4.51	1668
Niobium	-325 Mesh	99.8	8.4	2477
Zirconium	2-3 Micron	The powder was supplied and stored in water and the purification depends on the drying process.	6.49	1855
Tantalum	-325 Mesh	99.9	16.69	3020
Copper	-325 Mesh	99	8.96	1085

2.2. Heat treatment

The sintered alloy was sand blasted to remove the attached graphite from the alloys and was sectioned into small pieces of a rectangle with dimensions of 0.5 cm x 1 cm using a wire cut. The sectioned two pieces of the alloy were heat treated using the solution and aging treatment. The sintered alloy was solution-treated in a high-purity argon (Ar) atmosphere in a Tube Furnace for 1 hour. The alloy was placed in a ceramic crucible and solution treated at a temperature of 900 °C above the β-transition at a heating rate of 10 °C/min and cooled in the furnace (furnace cooling (FC)) [10]. The solution treatment is performed before the aging treatment to improve phase changes and mechanical properties. Solution treatment allows the alloys to be homogenized, resulting in a stable phase [11]. The sintered alloy subjected to solution treatment was then aged for 4 hours at 400 °C with a heating rate of 10 °C/min and furnace cooled to improve the mechanical properties. Teddai et al conducted a similar study in which the aging treatment was carried out at a temperature of 600 °C for 4 to 6 hours and observed that the volume fraction of α precipitates increased and is homogeneously distributed throughout the β matrix [12].

3. Electrochemical analyses

The electrochemical behaviour of the sintered and heat-treated TNZT alloys was performed using AUTO LAB Gamry Potentiostat. The alloys were mounted in resin with copper wire and were metallographically polished to investigate the corrosion behaviour in terms of the corrosion current density (icorr) and corrosion potential (Ecorr) from potentiodynamic polarization tests. The electrochemical cell consists of three electrodes, a working electrode, platinum as a counter electrode, and Ag/AgCl saturates calomel electrodes (SCE) as the reference electrode. The electrochemical tests were carried out at room temperature with alloys immersed in Hank's balanced salts solution (HBSS) as electrolytes for 7200 s for an open-circuit potential. Potentiodynamic analyses were performed at a potential range of -1.5 V to +1.5 V vs SHE for the open circuit potential of each alloy with a scan rate of 0.00167mV/s.

4. Results and discussion

4.1 Microstructural and crystallographic phase analyses of the sintered and heat-treated alloys

Figures 1 and 2 show SEM micrographs and crystallographic phase analyses of sintered admixed Ti-35Nb-7Zr-5Ta-xCu alloys after being subjected to solution and aging heat treatments. The microstructure of the sintered alloy shows a dark grey and brighter region, where the dark grey regions are the Ti-rich and Cu matrix, while the surrounding brightly coloured regions are the combination of Zr, Ta, and Nb layers. The microstructure of the sintered alloy microstructure exhibited full densification with a relative density of 98.34% as evidenced by a slight porosity of 1.66%. The microstructure of both heat treatment ST and AT illustrates a full dissolution of alloying elements in the Ti-matrix, demonstrating the chemical homogenization of the alloy. The XRD analyses for spark plasma sintered (SPSed) , solution treated (STed) and aged treated (ATed) revealed a BCC β phase as a predominated phase with a minor α phase present. It is noticed that both SPSed , STed and ATed possess similar diffraction peak patterns, indicating that their phase compositions are the same. The predominated BCC β-phase is due to the β-stabilizers (Nb and Ta) dissolved in the titanium matrix**.** The two-phase area (α+β) was also detected homogeneously distributed in a Ti-rich matrix of both solution and age-treated alloys. The alloys showed substantial grain boundaries of β-phase with α-phase without intermetallic phases. Hussein et al., 2019 [10] reported that decreasing the cooling rate by cooling in air or furnace after STed above β-transus increases the volume fraction of the α-phase. The alloys' XRD analyses revealed no evidence of intermetallic phases of α'' martensite and ω-phase. This indicates a good combination of phases, mechanical characteristics, and densification.

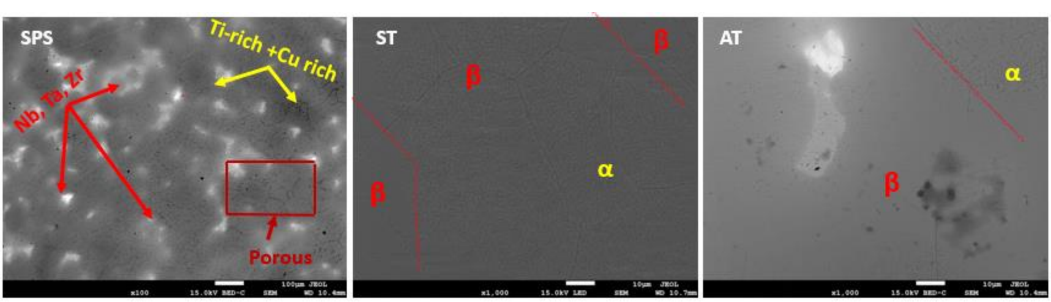

Fig. 1. SEM micrographs of Sintered (SPS), Solution Treated (ST) and Age Treated (AT) Ti-35Nb-7Zr-5Ta-1Cu alloy.

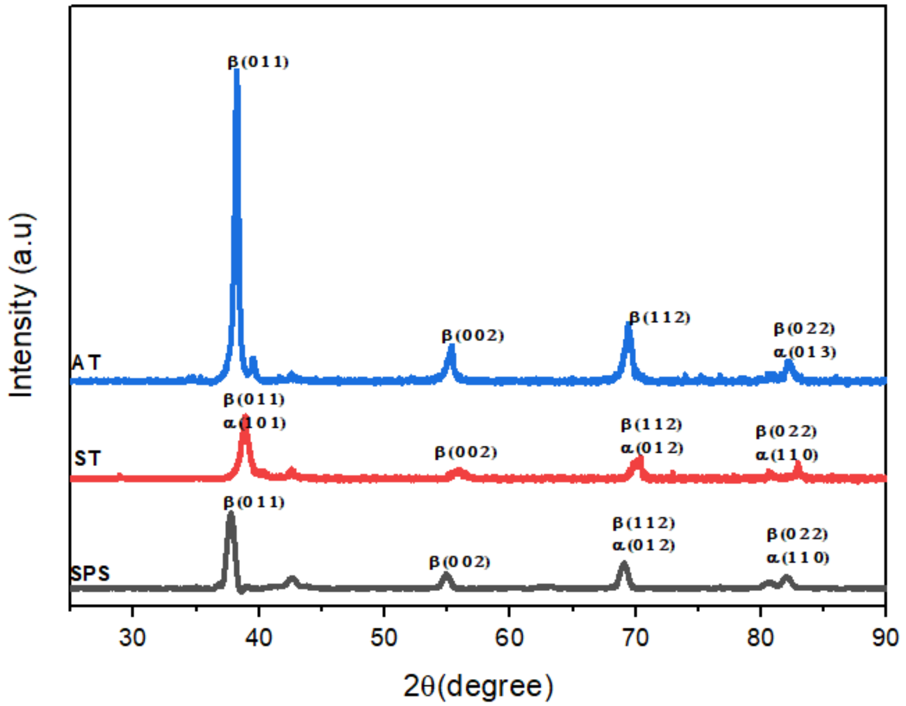

Fig. 2. XRD pattern of Sintered (SPS), Solution Treated (ST) and Age Treated (AT) Ti-35Nb-7Zr-5Ta-1Cu alloy

4.1. Electrochemical analyses of sintered, solution, and age-treated TNZT alloys

The electrochemical analyses were performed on the sintered, solution, and age-treated TNZT alloys in Hank balanced salts solution which is a simulation of human body fluids. A combination of open circuit potential (OCP) and Potentiodynamic polarization behaviour is displayed in Figure 3. The STed alloy exhibited the most negative OCP value, this is an indication that the alloy has a higher tendency to corrode while aged alloy exhibited less negative OCP, indicating excellent corrosion resistance. Furthermore, in the polarisation behaviour, the sintered alloy demonstrated a lower current density than the solution treated and aged. The lower the current density the higher the corrosion resistance and is indicative of the protectiveness of passive films. From the PDP graph, it's observed that the alloys were re-passivating. This indicates the formation of a protective oxide film against the progress of corrosion. The presence of β stabilizer elements (Nb and Ta) results in a stable pentoxide (Nb_2O_5 and Ta_2O_5) on the surface of the alloys [13]

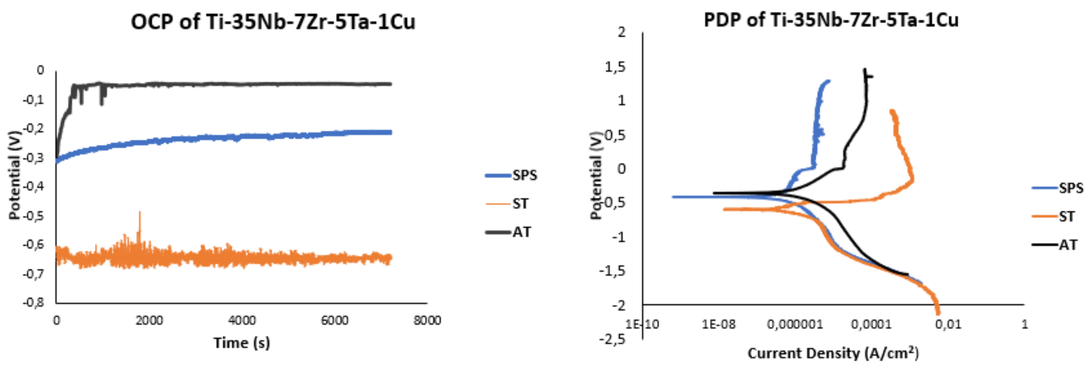

Fig. 3. Open circuit potential (OCP) and Potentiodynamic Polarisation (PDP) Sintered (SPS), Solution Treated (ST) and Aging Treated (AT) Ti-35Nb-7Zr-5Ta-1Cu alloys

5. Conclusion

The Ti-35Nb-7Zr-5Ta-1Cu alloy was fabricated by spark plasma sintering technique and the sectioned sintered alloy was subsequently, heat treated. The alloy exhibited complete densification of 98.34% as evinced by minor porosity of 1.66% on the surface of the microstructure. The microstructures of the heat-treated alloys revealed a complete dissolution of alloying elements into the Ti matrix indicating a chemical homogenization. The XRD also revealed a predominant BCC β phase with a minor α-phase. The BCC β-phase structure is attributed to the strong β stabilizing alloying elements Nb, and Ta. The sintered alloy exhibited excellent corrosion resistance with lower current density due to the present of porosity that create a barrier that limits the penetration of corrosive agents, thus enhancing corrosion resistance. The sintered alloy can be considered a suitable candidate for biomaterial applications.

Declaration of competing interest

The authors declare that they do not have any known competing financial interests or personal ties that could appear to have influenced the work disclosed in this study.

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