ELECTROCHEMICAL CORROSION AND PROPERTIES OF NEW Β-Ti-6Mo-4Zr-2Sn ALLOY WITH PLIABLE QUALITY FOR DENTAL AND SPINAL FIXATION APPLICATIONS

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Abstract

Ti-6Al-4V alloy is mostly used for dental and hard tissue implants, due to its high strength to weight ratio, high corrosion resistance, and relatively low elastic modulus. However, apart from health concerns of V ions release and higher Young's modulus (~120 GPa) than human bone (~30 GPa), recent research indicates day-to-day cyclic loading instead of a single-load event such as a fall, might be the consequence of inherent stiffness of fixation implants. In this study, Ti-6Mo-4Zr-xSn (at.%) alloy with pliable quality was developed and fabricated to efficiently avoid the potential hazards of fragility fracture and spinal spurs that pinch the spinal cord or its nerve roots and can cause weakness or numbness in the arms or legs-has been a long-term clinical quest. The evidence of its bone matching modulus, pliable mechanical behavior, excellent wear, corrosion and cytotoxicity properties are desirable potentials for future clinical therapy.

Keywords: Alloy design, titanium alloys, electrochemical properties, young's modulus, biomaterials

1. INTRODUCTION

Biomaterials research has attracted great attention owing to the increasing economic development leading to improved living standard, and attended consequences, such as increased number of senile aged people who, due to degenerative diseases such as arthritis, may need medical assistance in maintaining their convenience of mobility, increased volume of transportation in terms of the number of cars and associated traffic accidents, and increased amount of leisure time channeled to sports that have a higher than average risk of injuries. All these require orthopaedic surgeries and cause increased consumption of biomedical materials [1]. Although, some of the medical devices have been used in clinical practice over several decades, and most perform satisfactorily, which have significantly improved the qualities of life for the recipients, nonetheless, some of these them have a failure rate due to various problems, such as biocompatibility, stress shielding effect and corrosion resistance, at the moment, the relative low strength. Ti and the higher strength Ti-6Al-4V are the most prevalent titanium alloy for dentistry and in load bearing orthopaedic applications [1-3], respectively. However associated concerns about structural integrity and biocompatibility, has been identified as a major hurdles to the success of these implant materials [4-6]. For instance, low strength, poor machinability and poor wear resistance of cp-Ti restricts its use for high load application; high elastic modulus (110 GPa) of Ti-6Al-4V alloys when compared to human bone (~30 GPa) leads to stress shielding and bone spurs complication after most implant replacement surgery. There are also health concerns due to vanadium as well aluminum ions release, for which neurological side-effects [3], and genotoxic effects [7] have been reported in Ti-6Al-4V on the long term [1, 8-9].

For the above, Zr and Sn elements identified as being non-toxic and non-allergic, when compared with Ta [7], Al [9], V, Co, Ni, Cu or Nb [3] in the design of biocompatible Ti alloys) were exploited to facilitate the design of a novel low rigidity biocompatible Ti-alloys, with unusual cyclic loading behavior for dental and hard tissues implants. Considering the fact that human body environment as an extremely complicated electrolyte, which contains many erosive species that specially facilitated the electrochemical mechanisms of corrosion and hydrolysis, the corrosion performance of any biomaterial to be used in human body is crucially important. This study focuses on the corrosion and wear performance of this newly developed pliable Ti-6Mo-4Zr-7Sn alloy in a simulated physiological environment. The result indicate the newly developed β titanium (Ti-6Mo-4Zr-7Sn) alloy have better electrochemical and wear behavior hen compared to Ti-6Al-4V alloy.

2. EXPERIMENTAL

2.1. Materials and procedures

The designed ingots were fabricated from commercially pure Ti, Mo, Zr and Sn metals of high quality (~99.97 % purity) by vacuum electric arc-melting method. The temperature of the electric arc is about 3000 °C, while the melt was at the centre has a peak temperature of 1830-1850 °C in order to assure complete dissolution of the Ti, Mo and Zr elements. The electric arc method provided an intense stirring effect, but to ensure good standard, the ingots (30 g) were inverted and remelted at least four times to ensure an optimal chemical and structural homogeneity, before casting into cylindrical rods 40 mm x 8 mm for length and diameter. The compositions of the resulting ingots were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES) at the lab of Metallurgical and Materials Engineering, University of Nigeria, Nsukka, (atomic percent are used here and throughout the text unless otherwise specified). The results are presented in **Table 1**.

Table 1 Alloy composition (at.%)

Alloy/elements	**Mo**	**Zr**	**Sn**	**C**	**Nb**	**Al**	**Si**	**O**	**V**	**Ti**
Ti-6Mo	5.98	-	-	0.018	0.001`	0.02	0.004	0.010	-	balance
Ti-6Mo-Zr-Sn	5.98	3.96	1.99	0.018	0.001`	-	0.004	0.010	-	balance
Ti-6Al-4V	-	-	-	-	-	5.98	-	-	4	balance

2.2. Microstructure observation and mechanical behaviour

The microstructural characterization was investigated by scanning electron microscopy (SEM) after using standard metallographic techniques and then etched in Krol's reagents (3 ml HF, 6 ml HNO_3 and 100 ml H_2O). The tensile tests were carried out on an Olsen 8500 series testing machine, using "Dog-bone" specimens, which has be machined cut by wire spark erosion resulting in a strain gauge with dimensions 25 mm × 5 mm ×1 mm. A series of such dog-bone specimens was cycled under load control for 3 cycles, using an Olsen Tensile/Compression Module equipped with a 10 kN load-cell, between 0 and 2700 N (i.e. 0-550 MPa) with 10 mm/sloading/unloading rate. The load was measured by the load cell and the specimen's elongation was recorded by the company-calibrated elongation gauge (according to ASTM D882-11).

2.3. Evaluation of electrochemical behaviour

Electrochemical experiments were conducted in a three-electrode (CH instrument 660D) glass cell, the working electrode area of ~10 mm^2, a platinum counter electrode and the Ag/AgCl as a reference electrode. Working electrolyte was ~50 ml of unstirred naturally aerated Hank's balanced physiological solution, with a subsequent $NaHCO_3$ addition (details of Hank's composition has been discussed elsewhere [7], maintained at 37±1 °C. Before the potentiodynamic studies, cathodic treatment was carried out at -0.9 V for 600 s in order to remove any oxide films present on the surface of each specimen. The measurements were performed using the potentiostat (model VersaSTAT 4). Potentiodynamic polarization scan was performed on the samples at the rate of 0.335 mV/s in the potential range of -1 to 2 V vs SCE, and a step size of 1 mV, after reaching a steady state. To ensure good standard, the experiment was repeated for three times with different samples after polishing using waterproof emery papers before each test and undertaken in stirred solution maintained at 37±1 °C (i.e. normal body temperature) and pH of 7.4.

3. RESULTS AND DISCUSSION

3.1. Evaluation of chemical and microstructure analyses

The average values of the compositional analyses determined by XRF and EDX techniques are presented in **Table 1**. The results show that the actual chemical composition of the alloys is close to their nominal values and agree with ASTM F-67. As can be seen, all the alloys are within (±1 %) variance when the experimental and nominal values are compared. The chemical composition of the alloys was homogeneous and no expressive differences were found between the bulk and surface of the samples, which indicates a good homogenization of the studied alloys. Typical SEM microstructures of the new Ti-6Mo-4Zr-2Sn alloys (**Figure 1b**) along with the initial Ti-6Mo sample, is shown in **Figure 1**. **Figure 1(a)** is the microstructure of the initial Ti-6Mo alloy, consisting of mainly large equiaxed β grains with a size of about 231±79 μm in diameter. Also a significant amount of different sizes of acicular martensitic α´´+β structure can be distinguished in the alloy. In contrast to the large grain sizes observed in the initial Ti-6Mo alloy, it is evident from the alloyed microstructures (**Figure 1**) that significant microstructural sensitivity was apparent with Zr and Sn micro-additions to the alloy.

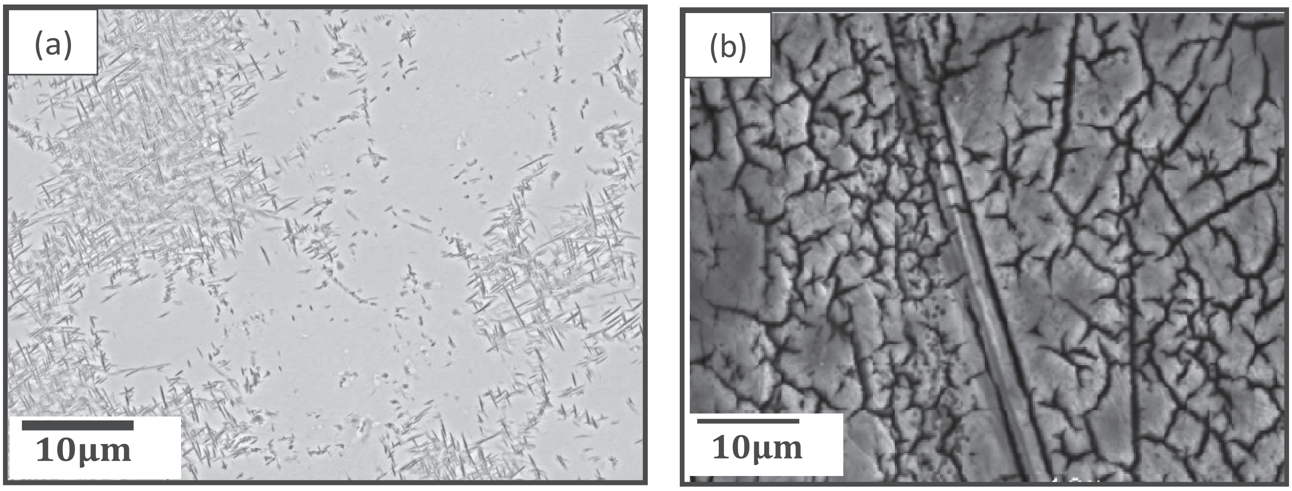

Figure 1 SEM microstructure of the studied alloys (a) binary Ti-6Mo alloy, (b) multicomponent Ti-6Mo-4Zr-2Sn alloy

3.2. Mechanical behavior analyses

As mentioned in the previous section, ultrasounds technique was employed for determining the elastic modulus: In comparison to the strain gauge measurement, the ultrasound tests showed small elastic moduli values of 52 GPa and 79GPa for Ti-6Mo-4Zr-2Sn and Ti-6Mo alloy samples, respectively, with an estimated error of ±3 %, while the former indicated 60 GPa; and 76 GPa, respectively. The relationship of the shape recovery ratio (pliability) and the elastic strain of the Ti-6Mo-4Zr-2Sn is shown in **Figure 2**. Just like other SMAs, the recovery ratio decreases with the increasing of the pre-strain, but spectacularly improved better than most Ti alloys when the strain is up to 2 %, the specimens can completely recover to the original shape, and after more than 20 times deformation cycling, the recovery ratio is still more than 6 %.

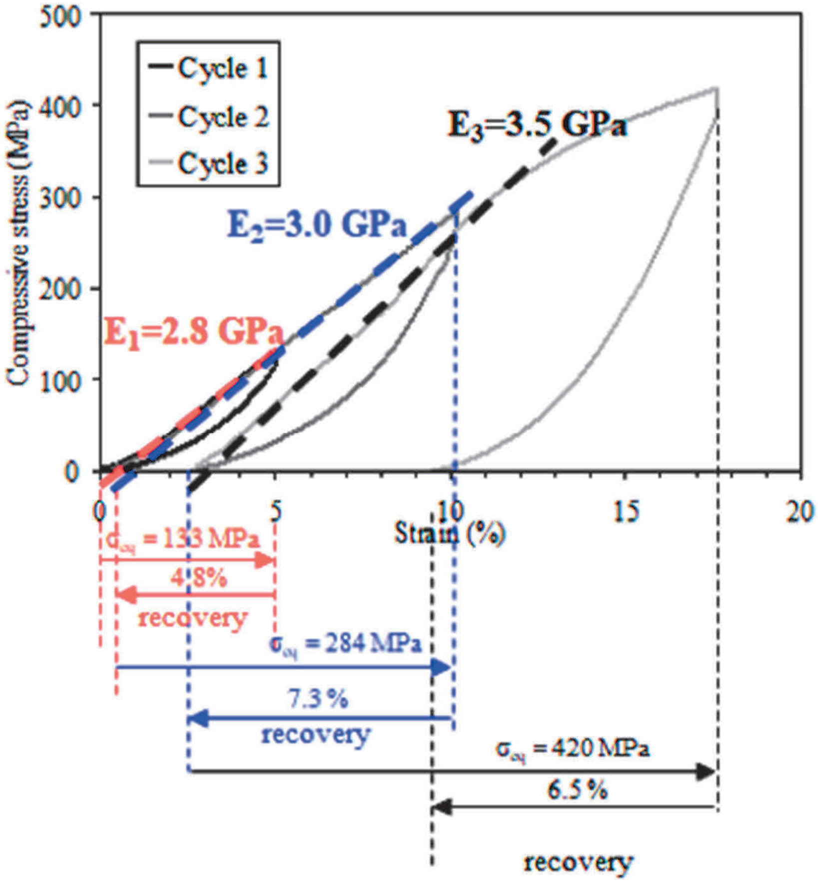

Figure 2 Pliable behaviour of the new Ti-6Mo-4Zr-2Sn-multicomponent alloy

3.3. Potentiodynamic polarization

On **Figure 3** is the potentiodynamic anodic polarization curves for the new alloy in comparison with the mostly used Ti-6Al-4V alloy, with respect to a saturated calomel electrode in naturally aerated Ringer's solution at 37 °C. The continuity, stability, and intensity of the passive Ti oxide film are analyzed by this technique. As can be seen from **Figure 3** and compared with cp-Ti and Ti-6-4 in **Table 2**, the polarization curves obtained for the two alloy samples show a typical active-passive characterization, a rising anodic current with increasing potential, and then transforming directly into the passive area from the Tafel curves.

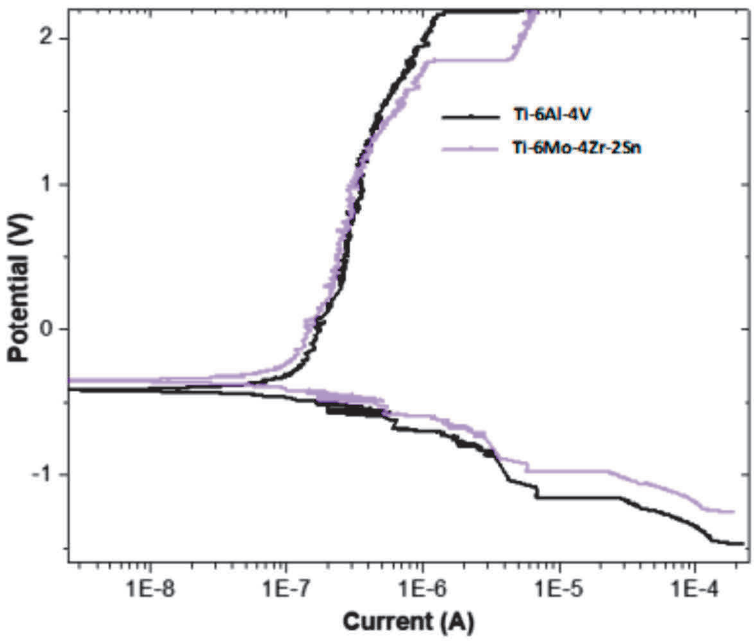

Figure 3 The current density of the new Ti-6Mo-4Zr-2Sn alloy compared with Ti-6Al-6V alloy in a Ringer's solution at 37 °C temperature for 1 hour

Table 2 Corrosion parameters (and standard deviation values) as determined from the potentiodynamic polarization analyses

Alloy	The corrosion parameters (and standard deviation values) of the new alloy compared with cp-Ti, Ti-6Al-4V alloys			
	E_{corr} (V_{SCE})	j_{corr} (μA·cm^{-2})	j_{pass} (μA·cm^{-2})	**Reference**
cp-Ti	-0.33 (0.021)	0.33 (0.07)	2.17 (0.04)	[6]
Ti-6Al-4V	-0.327 (-)	0.326 (-)	0.323 (-)	This work
Ti-6Mo-Zr-Sn	-0.301 (0.021)	0.214 (0.07)	1.9 (0.05)	This work

4. CONCLUSIONS

A new low elastic modulus pliable β-type Ti-6Mo-4Zr-2Sn alloy is presented in this study. The microstructure, mechanical properties, and corrosion resistance of this newly developed Ti alloy are characterized and the main results are summarized as follows:

i. The present study shows that Zr and Sn micro-addition to binary Ti-6Mo alloy led to microstructural refinement and tremendous reduction of elastic modulus to bone matching values of 40.8GPa based on the ultrasound measurement. This is very remarkable, with respect to the use of metallic biomaterial for orthopaedic implant applications.

ii. Although further studies may be considered, the outcome of the mechanical, biocompatibility and electrochemical tests show that this new Ti-6Mo-4Zr-2Sn can be a more favourable candidate for some biomedical applications than the commonly used biomaterials alloys

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