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ALLOY DESIGN AND PROPERTY EVALUATION OF TI-MO-NB-SN ALLOY FOR BIOMEDICAL APPLICATIONS

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Abstract
Ti-Mo alloy containing Nb and Sn were arc melted and composition analyzed by EDX. The XRD analysis indicates that the crystal structure and mechanical properties are sensitive to Sn concentration. A combination of Sn and Nb elements in synergy hindered formation athermal ω phase and significantly enhanced β phase stability. The low elastic modulus and good ductility as observed implied that this alloy can be more suitable for biomedical application than the conventional metallic biomaterials from better mechanical compatibility perspective.

Keywords: Alloy, biomedical, biocompatibility, Young's modulus, microstructure.

1. Introduction

Biomaterials are used in medical devices, particularly in those applications for which the device either contacts or is temporarily or permanently in the body [1]. A variety of artificial materials such as metals, polymeric materials, composites and ceramics, are being explored for use as biomaterials [2-4]. In particular, metallic implant materials example, SUS316L stainless steel, Co-Cr-Mo-type alloys, titanium and titanium alloys (e.g. Ti-6Al-4V) are widely used as orthopaedic and dental implant materials. Among these, titanium and some of its alloys are preferred due to their relatively low modulus, excellent strength to weight ratio, good fracture toughness and superior biocompatibility and corrosion resistance [5-8]. Brunette et al [9], have shown in their research, "titanium in medicine", that titanium and some of its alloys are well accepted by human tissues compared to other metal materials. Niinomi [8], also reported that titanium and its alloys are getting much attention for biomaterials because they have excellent specific strength and corrosion resistance, no allergic problems and the best biocompatibility among metallic biomaterials. Titanium is relatively a new material used for surgical purposes compared to stainless steel and cobalt-chromium alloys. It was not until the 1960s that the titanium alloys were used as surgical implant material [10, 11].

As well as being biocompatible, Titanium alloys for surgical implants need to be mechanically compatible [12]. For orthopaedic implants, high strength in conjunction with a low elastic modulus is critical in order to reduce detrimental "stress shielding" effects [12]. Titanium undergoes an allotropic transformation from a hcp structure (α-phase) to a bcc structure (β-phase) at 880 $^{\circ}$C [13]. As a result of this structural change, titanium alloys fall into three classes: α alloys, $\alpha + \beta$ alloys and β alloys. The $\alpha + \beta$ alloy Ti-6Al-4V is the most frequently used titanium alloy for biomedical and structural applications [14]. However, there have been concerns that vanadium is potentially toxic [15] and aluminium can contribute to the development of Alzheimer's disease [16], especially with long time implantation. Furthermore, the elastic modulus of titanium also tends to increase with increasing aluminium content and increasing volume fraction of α phase [17]. Ti-6Al-4V for example, has an elastic modulus of approximately 110 GPa, which is significantly higher than the human bone, which has modulus in the range of 10-40 GPa. [18]. When joined to bone, either adhesively or mechanically, such large mismatches in elastic moduli result in the formation of large stresses at the bone/implant interface, which can lead to crack nucleation and early fracture [19]. Alloys containing primarily β phase tend to exhibit significantly lower modulus values than α and $\alpha + \beta$ alloys [17].

Some metastable ß Ti-Mo alloys have outstanding mechanical and physical properties, such as a high strength, a low thermal expansion and good workability [19-23], as well as good biocompatibility and corrosion resistance [22-24]. Because of these special properties, these alloys have attracted a lot of attentions recently as metallic biomaterials for use in artificial bones or implant [25-28], which requires low Young's modulus (10-30GPa) and high strength when subjected to cyclic loading under complicated conditions [29-32]. However, the Ti-Mo alloys are said to be susceptible to omega phase embrittlement, which has been a main concern to their applications.

Recently, many researchers have actively investigated separately the effect of the Sn, Si and Zr content on the phase stability and mechanical properties in the Ti-Nb and Ti-Mo systems [19-30]. For instance, Zain et al. [30], reported a better superelasticity due to a higher critical stress for slip deformation and a total recovery strain by ternary addition of Mo in Ti-Nb alloy, while and Sutou et al. [32] observed low Young's modulus by Sn additions to Ti-Mo. Considering the potential use as a biomaterial, and the goal of this work, we have cumulative investigated the effect of Nb and Sn on the phase stability and mechanical behaviours of Ti-Mo alloy system at cast condition, to improve the mechanical properties and ensure low Young's modulus at ambient temperature.

2. Experimental Procedures

2.1 Alloy design

The phase stability has been calculated by combining Morinaga et al calculation [31-33] with e/ratio calculations [34] of electronic structures. The theoretical method has been widely and successfully used to design and develop new Ti alloy by combining these three parameters to show the overlap population of the electrons between atoms, and hence a measure of the covalent bond strength between Ti and added alloying elements, and the metal d-orbital energy level (Md) which correlates with the electronegativity and metallic radius of elements. The (e/a), Bo and Md values are calculated by taking the compositional averages of the component elements, denoted as follows:

$$\frac{e}{a} = \frac{\sum_{i=1}^{I}(\chi_i n(s+d)_i)}{\sum_{i=1}^{I}\chi_i} \quad (1)$$

$$\overline{Bo} = \sum_{i=1}^{n} x_i\,(Bo) \quad (2)$$

$$\overline{Md} = \sum_{i=1}^{n} \chi_i\,(Md)_i \quad (3)$$

where, X_i is the atomic fraction of the alloying elements, i^{th} component ={1 … … I}, of the individual outer s+d contributed by the metal atoms. A series of high purity titanium alloys containing Ti-5M0-4Nb-2Sn (here and subsequently the atomic content of element(s) is given) were selected for the study. The average value of the (e/a), Bo and M_d values of the alloys are listed in Table 1 following our design process as seen in Fig.1.

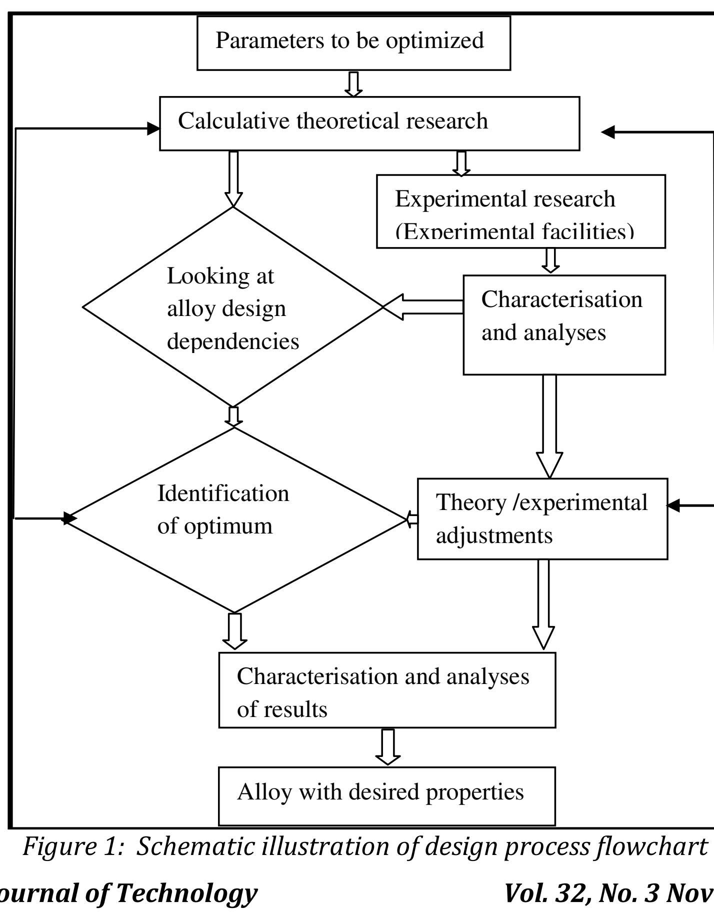

Figure 1: Schematic illustration of design process flowchart

Table 1: Alloy composition parameters (in atomic percent).

Elements	Mo	Nb	Sn	Ti	Md	Bo	e/a
Concentration	5	4	2	Bal.	3.48	2.38	4.115
Concentration	10	-	-	Bal.	3.55	2.36	4.2

2.2 Material preparation
The experimental alloys were fabricated by an arc-melting method using pure Ti, Nb, Mo and Sn as raw materials. To ensure homogeneity, the ingots were inverted and remelted at least six times before casting into cylindrical rods. Machined specimens for X-ray diffraction (XRD) measurement and tensile tests were subjected to solution treatment at 1273 K for 1 hours under high vacuum condition followed quenching into ice water. Following this, the specimens were acid etched to oxide skin.

2.3 Microstructure Observation, XRD and SEM analyses
Specimens for microstructure observation were mechanically polished with standard metallographic preparation procedure and etched in the Kroll's reagent (5% HF +10% HNO_3 + 85% H20) to reveal the microstructure. The microstructure observation was performed on a JOEL 6400 SEM machine. The phase constituents identification was characterized using Siemens D5000 Diffractometer using a Ni filtered Cu Kα (λ=1.5406nm) radiation operated at 40KV and 30mA, at a slow scanning rate of 0.005 in the angular (2θ) range of $20^o \sim 90^o$. The lattice parameter determination and peak indexing utilized a least square interactive method [35]. The tensile test were carried out on an Olsen 8500 series testing machine, using tensile specimens of 12 mm x 8mm for length and diameter (according to ASTM D882-11) at a cross head speed of 8.2 x 10-6 ms-1 at room temperature. These experiments were performed in triplicates to minimize experimental errors. The E, was calculated from the relationship $E=\rho\upsilon_E^2$ where ρ is the density of the alloy υ_E is the velocity of ultrasonic waves along the materials. υ_E^2 was measured with a purse-echo technique at room temperature [36]. The density, ρ, of the samples was measured by the Archimedes method. The estimated error was around 1%.

3. Results and discussions
3.1 X-ray Diffraction Analysis
The X-ray diffraction profile of the solution treated Ti-5Mo-4Nb-2Sn alloy is shown in Figure 2. As shown in this figure, only the β phase can be identified in the alloy. The diffraction peaks of the isothermal ω phase were not detected, although the intensity of ω phase is not always high enough to provide evidence of the presence of ω phase, if the ω phase has quite a small size or volume fraction. The significant retention of the β phase is observed for the alloy as verified by the X-ray analysis. β Phase retention is reminisce of Ti alloys with higher Mo concentrations in accordance with results presented earlier by Davis [37], who reported that in Ti-Mo systems, martensitic structures changes from hexagonal α′ to orthorhombic α′′ at Mo rates of 6 %. And more recently, Bania [38] showed that a minimum of 10% Mo was required to completely stabilize the β phase at room temperature. Thus, the observed increase in β phase stability can be ascribed to the combined influence of Nb and Sn additions. This is evident in the lattice parameter of 0.31nm compared to the lattice parameter of β phase (usually 0.32nm), due to contraction in the binding metallic bonds due to alloying leading to an increase in the intensity of and slight shifting of the β peaks.
As pointed out earlier by Hao et al [39], knowing the microstructure of biomedical materials, such Ti alloys is very important because the phase have a direct influence on their Young's modulus as well as the biocompatibility.

3.2 Microstructure Characterization
Typical microstructure of the solution-treated alloy at 1273 K for 1 hours followed by ice water quenching is shown in Figure 3. The microstructure consists of large β grains with a size of around 500 μm. No significant evidence of other phase can be confirmed from the microstructure observation. Though, the presence of athermal ω and α phases has been predicted by e/a ratio values between 4.1and 4.2 of Ti alloy having a similar Mo content. However, the mean e/a ratio value of Ti-5M0-4Nb-2Sn alloy were calculated to be 4.113, which is beyond the range mentioned above (See Table 1). A reasonable explanation may be combined alloying influence and or the homogeneity of chemical composition of the ingot.

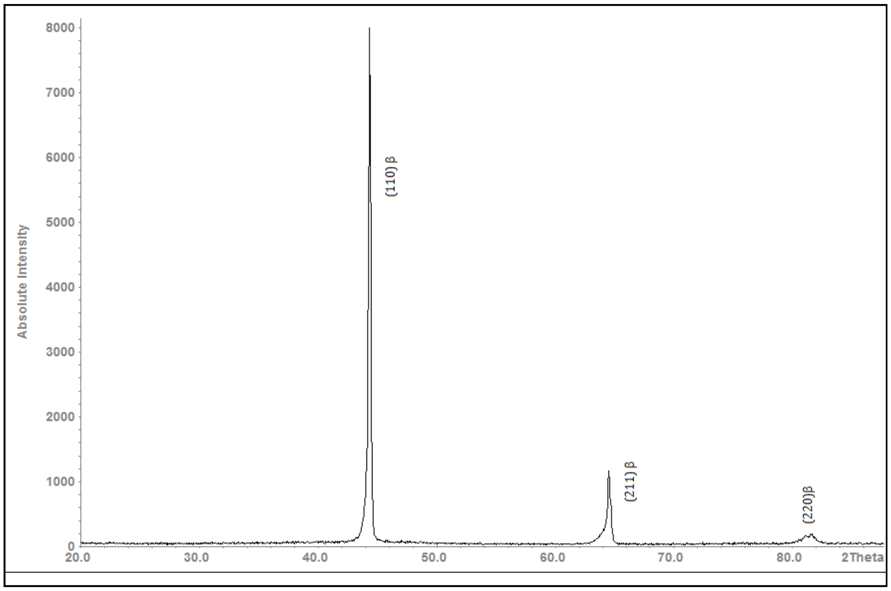

Fig. 2: X-ray diffraction profile of as cast, solution–treated Ti-5M0-4Nb-2Sn alloy produced for biomedical application

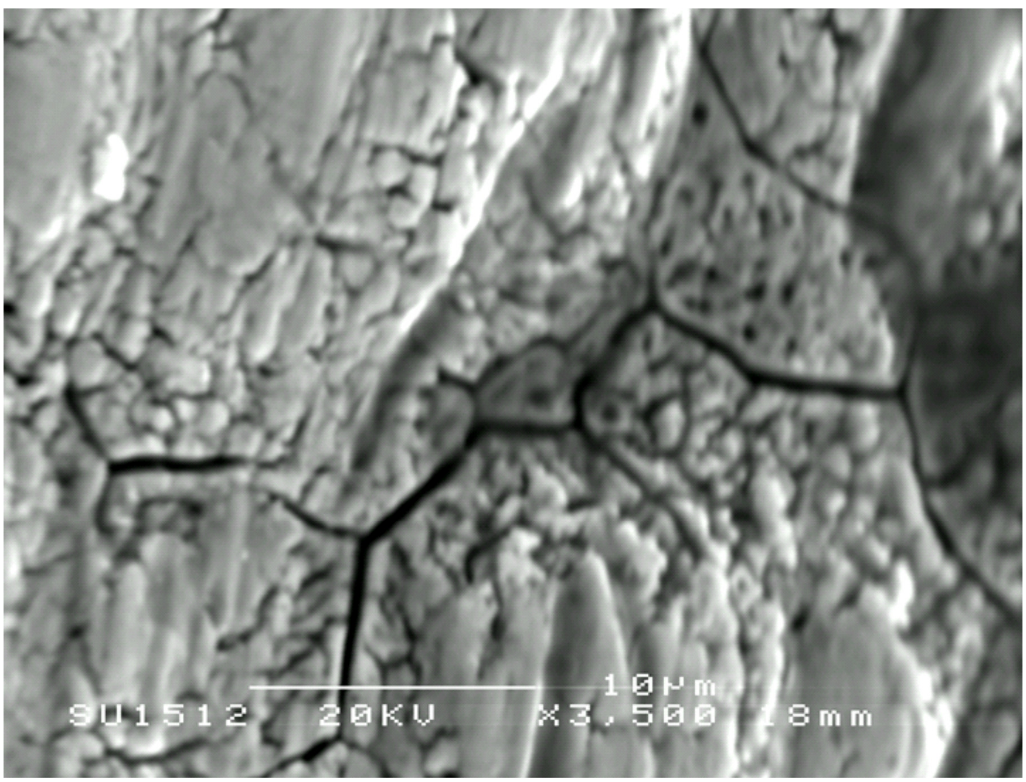

Fig. 3: SEM microstructure of as cast, solution–treated Ti-5M0-4Nb-2Sn alloy produced for biomedical application

3.3 Mechanical properties

Figure 4 shows the True stress–strain curve of the alloy in compression at room temperature. The curve exhibited considerable gentle slope in elastic region and outstanding work hardening after the yield. The elastic modulus carefully measured using strain gauge is approximately equal to 73 GPa, which 1.6% higher than ultrasonic wave measurement. This shows a good agreement in the two measurements recorded.

From Table 2, it can be noted that with alloying additions of Sn and Nb in Ti-Mo system, the yield stress, the ultimate compressive stress and elongation increased while lower Young's modulus is evident when compared to Ti-6Al-4V [40].and other Ti based alloys [1-17] already being used for orthopedic implant applications. This is ascribed to increased resistance to dislocation flow arising from the resolution of the high volume fractions of Sn particles during solution treatment and increased solid solution hardening due to Nb additions in the microstructure matrix. Therefore by appropriate alloy optimization and solution treatment at temperature near to the β transus point can be an effective way to suppress the formation of athermal ω phase in the Ti-Mo alloys and exhibit much lower elastic modulus and higher ratio of strength modulus value.

Additionally, the alloying elements in this alloy have been developed as commercial biomaterials grades [39]. Sn can also decrease melting temperature thereby making melting process easy. Thus, this alloy is expected to be a promising candidate for biomaterials.

4.0 Conclusion

In this study, we investigated the microstructure and mechanical properties of cast Ti-Mo-Nb-Sn alloy solution treated for potential use in biomedical applications. The conclusions of the study are summarized as follows:

The microstructure, phase stability and mechanical properties of Ti-Mo alloys are dependent upon alloying additions. Combining Sn and Nb alloying elements in synergy, impeded formation of athermal ω phase which has been a main concern to their mechanical applications and which significantly improved β Phase stability of this Ti-5Mo-4Nb-2Sn alloy. It also improved the elastic modulus, while yield strength to modulus value remains high ~7.5. The alloy's high yield strength and good ductility indicate it's more suitable for biomedical application than the conventional metallic biomaterials from the better mechanical compatibility perspective

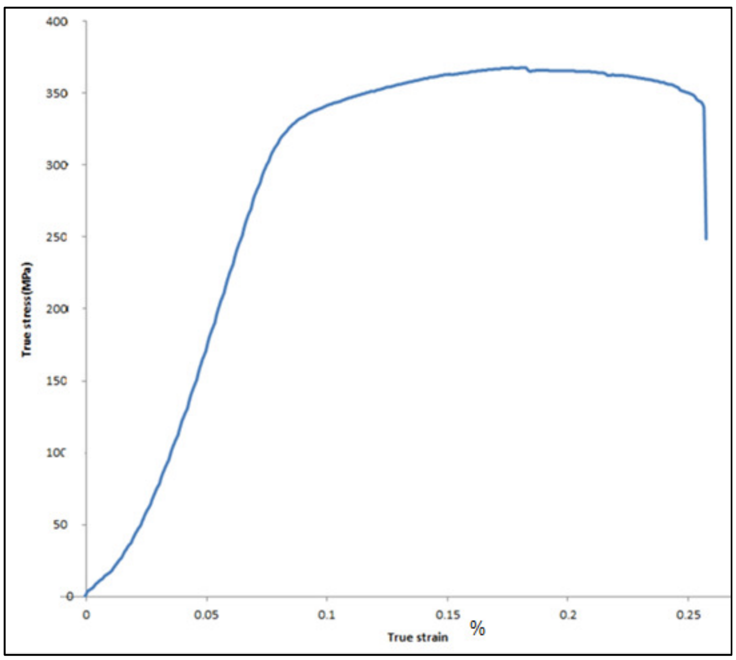

Figure 4: True stress Vs strain curve of as-cast, solution-treated Ti-5Mo-4Nb-2Sn alloy produced for biomedical application.

Table 2: Mechanical properties of Ti-Mo alloys and some typical metallic biomaterials

Alloys codes	Elastic modulus[E_{Mod}]	Yield Strength [$\sigma_{0.2}$ (MPa)]	Ratio of Strength to modulus [10^{-3}]	Elongation (ε=%]
CP –Ti[22]	103	170-485	1.7-4.7	15-24
Ti-6Al-4V[22]	110-114	825-869	7.2-7.9	6-10
ASTMF75[ ](Co-Cr-Mo)	220	448	2	8
Ti-10Mo [22]	93	412	7.4	30
Ti-15Mo [22]	78	544	7	21
Ti-20Mo [22]	75	428	5.7	15
Ti-5Mo-4Nb-2Sn [this work]	65	483	7.43	26

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