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The microstructural and mechanical characterization of the β -type Ti-11.1Mo-10.8Nb alloy for biomedical applications

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Abstract. Ti-Mo alloys are promising biocompatible materials with lower elastic modulus than the extensively used Ti-6Al-4V alloy. However, research work done on these alloys indicate that their elastic modulus is still higher than that of the bone, even after the execution of numerous heat treatment procedures. Therefore, this study was aimed at adding Nb (non-toxic β stabilizer) to Ti-Mo system followed by the characterization of its microstructural and mechanical properties in the as-cast condition. This study will provide systematic preliminary information towards the design and development of novel biomedical components. The microstructure and phase analysis were carried out using optical microscope, SEM, and XRD. Mechanical tests were conducted using the uniaxial tensile test machine and Vickers microhardness tester. The as-cast Ti-11.1Mo-10.8Nb alloy consisted primarily of β phase and a possible small volume fraction of ω phase. The Vickers micro-hardness, elastic modulus, bending strength were measured as 311.62 HV_{0.5}, 56.9 GPa 1671.4 MPa, respectively. The Ti-11.1Mo-10.8Nb alloy also exhibited ductile fracture behaviour during bend testing. The Ti-11.1Mo-10.8Nb design is a promising alloy for biomedical applications.

1. Introduction

The most widely used biomaterial today is probably Ti6Al4V, owing to its low-weight, high corrosion resistance, high specific strength and availability [1–4]. However, in addition to low wear resistance [5], two particularly serious concerns are often raised in more recent years. Firstly, the Ti6Al4V alloy has an elastic modulus of 110 GPa, which is significantly higher than that of the human bone (10 – 40 GPa) [1–4,6]. This difference in the elastic moduli between an implant and a bone can cause bone degradation ('stress shielding effect') and resorption. This drawback puts serious limitations on their performance as implant materials [6]. Secondly, The release of Al and V ions from the alloy into the human body might cause genotoxic and cytotoxic responses from the human body such as the potential for the



development of Alzheimer's disease, peripheral neuropathy, and osteomalacia especially in long-term implantation cases [5,7,8].

Therefore, strategies to design next-generation Ti-based biomaterials with lower elastic modulus from biocompatible elements are developed [1–4,9]. Global research into next-generation Ti alloys has focussed on the lower elastic modulus β -type than α -type Ti alloys - their cubic crystal symmetry incidentally makes them processable too [9]. The β stabilizing elements are classified as isomorphous (form continuous solid solution with limited solubility in α phase like Mo, Ta, Nb, and V) and eutectoid (form continuous solid solubility in α and β phases like Zr and Hf) [6,10]. Amongst these β -stabilizers, Mo is the strongest β stabilizer, is the cheapest, can improve strength and corrosion resistance at lower elastic modulus and it can regulate the pH balance in the body [11].

The design of these β -type alloys can be carried out using several approaches amongst them being the Mo equivalence (Mo_{eq}) and the average valence electron concentration (e/a) ratio approaches. The Mo_{eq} is a parameter used in Ti alloy compositions to characterize the contribution of alloying elements on the β -phase stability [10], [12]–[15]. The proposal of the Mo_{eq} formula as a measure to compare the elemental contributions to that of Mo, the most β -stabilizing element, was presented by Bania as follows:

$$Mo_{eq} = 1.0 Mo + 0.67 V + 0.44 W + 0.28 Nb + 0.22 Ta + 2.9 Fe + 1.6 Cr + 0.77 Cu + 1.11 Ni + 1.43 Co + 1.54 Mn + 0.0 Sn + 0.0 Zr - 1.0 Al \text{ (wt\%)} \quad \text{Eq. 1}$$

For each alloying element, the coefficient value is the least amount of an alloying element that can suppress the formation of martensitic phases (α' and α'') and retain a single β -phase microstructure at room temperature upon water quenching – it's also known as a critical value (β_c) for that alloying element. The value of β_c experimentally determined by Bania was is approximately 10 wt% Mo [14–16]; that is a single β phase with equiaxed grains can be stabilized at Mo content of 10 wt% or more [7,17,18]. Hence, Wang *et al* (2015) proposed a new Mo_{eq} model for the characterization of the critical stability limit of multicomponent β -type Ti-based alloy systems, where the critical lower limit for β stabilization is 11.78 wt% [14].

$$Mo_{eq} = 1.0 Mo + 1.25 V + 0.59 W + 0.28 Nb + 0.22 Ta + 1.93 Fe + 1.84 Cr + 1.5 Cu + 2.46 Ni + 2.67 Co + 2.26 Mn + 0.30 Sn + 0.47 Zr + 3.01 Si - 1.47 Al \text{ (wt\%)} \quad \text{Eq. 2}$$

The average valence electron concentration (e/a) approach is also used to design alloys. The e/a ratio is defined as the average number of valence electrons in each atom of an alloy and the precipitation of the metastable omega (ω) phase occurs between the range 4.13 and 4.30 [14,19]. This phase is formed under the three conditions: upon quenching above the β transus via a diffusionless (shuffle) mechanism, during ageing in the temperature range 100 °C to 500 °C in the regions lean in the alloying elements through a diffusion-controlled process and deformation at room temperature [20]. The formation of the β -phase is dominant at e/a ratios above 4.30 [14,19].

Mo and Nb are known to segregate easily in β -Ti alloys during solidification and extensive research is being carried out to hinder this problem [21,22]. In this study, a novel β -type Ti-Mo-Nb alloy with high strength and low elastic modulus was designed using the Mo equivalence and the average valence electron concentration ratio approaches. The microstructural characteristics and mechanical properties of the alloys in as-cast condition were investigated. This study will provide systematic preliminary information towards the design and development of novel biomedical components.

2. Materials and Methods

2.1. Alloy design

The β -type Ti-11.1Mo-10.8Nb alloy used for this study is shown in Table 1 below. The alloy formulation was designed using a combination of the Mo equivalence and the average valence electron concentration ratio approaches. The investigation will also be carried out on CP Ti and Ti-11.78Mo binary alloy. Their

calculated Mo equivalence and e/a ratio values are listed in table 1. The designed alloy is classified in the β metastable category [7] and according to references [17,23], the precipitation of ω phase is expected in Ti-11.78Mo and Ti-11.1Mo-10.8Nb alloys, but not in CP Ti.

2.2. Material Preparation

The three Ti-based alloys of 100 g each were prepared from elemental powders of CP Ti (99.9%), molybdenum (99.5%) and niobium (99.8%). Green compacts of each alloy composition were first cold-pressed and then melted in a water-cooled copper crucible with a tungsten electrode using a commercial arc melting vacuum-pressure casting system. The evacuation and purging of the melting chamber with argon was carried out before melting. The ingots were each turned-over and remelted three times to promote chemical homogeneity [24].

Table 1. Compositions of CP Ti, Ti-11.78Mo and Ti-11.1Mo-10.8Nb alloys.

Alloy Name	(MoEq)Bania	(MoEq)Qing	e/a Ratio
	[wt%]	[wt%]	
CP Ti	0	0	4
Ti-11.78Mo	11.78	11.78	3.8
Ti-11.1Mo-10.8Nb	14.19	13.65	4.3

2.3. Microstructural Characterization

An optical microscope (Leica CTR4000) and a Scanning electron microscope (SEM) (JEOL: JSM-6510) were used to observe the microstructure and elemental composition in the alloys. Samples were precision cut from the vacuum arc-melt as-cast ingots, mounted, ground using silicon carbide papers up to 2400 mesh, polished using 3 μm diamond suspension and colloidal silica (final polishing) and etched with Kroll's reagent (85 ml of distilled water, 15 ml of Nitric acid and 5 ml of hydrofluoric acid). The polished samples were then etched with Kroll's reagent (85 ml of distilled water, 15 ml of nitric acid and 5 ml of hydrofluoric acid), consecutively. Phase identification was carried out via X-ray diffractometry (XRD) XPERT-PRO diffractometer with Cu K_α radiation and graphite monochromator operated at an accelerating voltage of 45 kV and a current of 40 mA. The various Ti phases were identified by matching the observed XRD profile peaks with the Joint Committee on Powder Diffraction Standards files or in prior published work.

2.4. Mechanical Testing

The density measurements produced specimens were carried out using Archimedes method. The Vickers micro-hardness measurements were conducted using a Vickers micro-hardness tester (FM-700) with a load of 500 g for 15 s. At least ten different indentation measurements were taken and the average was calculated. Tensile specimens with the dimensions illustrated in Figure 1 were prepared from the vacuum arc-melt as-cast ingots via electrical discharge machining (EDM). The stress-strain data was recorded at room temperature using the InstronTM 1342 model apparatus.

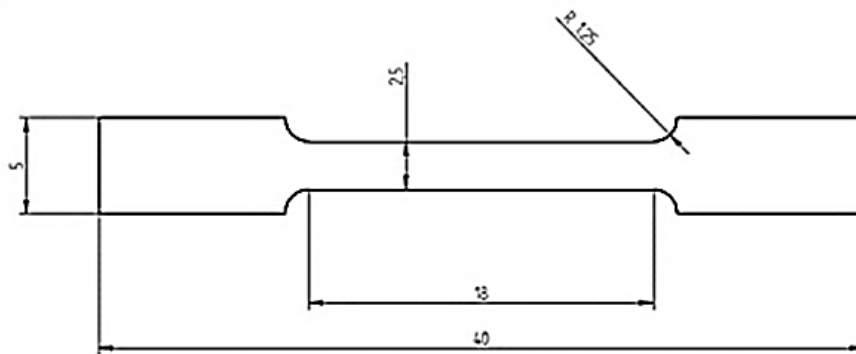


Figure 1. Schematic dimensions of the tensile specimen.

3. Results and Discussion

3.1. Microstructural Characterization

The XRD patterns of the as-cast CP Ti, Ti-11.78Mo and Ti-11.1Mo-10.8Nb with identified phases and indexed diffraction planes are exhibited in Figure 2. The as-cast CP Ti XRD patterns are characterised by martensitic orthorhombic α' phase peaks and these results are in agreement with Ho *et al*'s observations [25]. The optical micrographs of the as-cast CP Ti alloy presented in Figure 3(a) show coarse primary plates with partitioned regions filled with progressing small secondary plates and matches the one obtained by Davis *et al* [17]. The microstructure is characteristic of a fast-cooled metastable feather-like microstructure of hexagonal martensitic α' phase was observed in the CP Ti as in Ref [3].

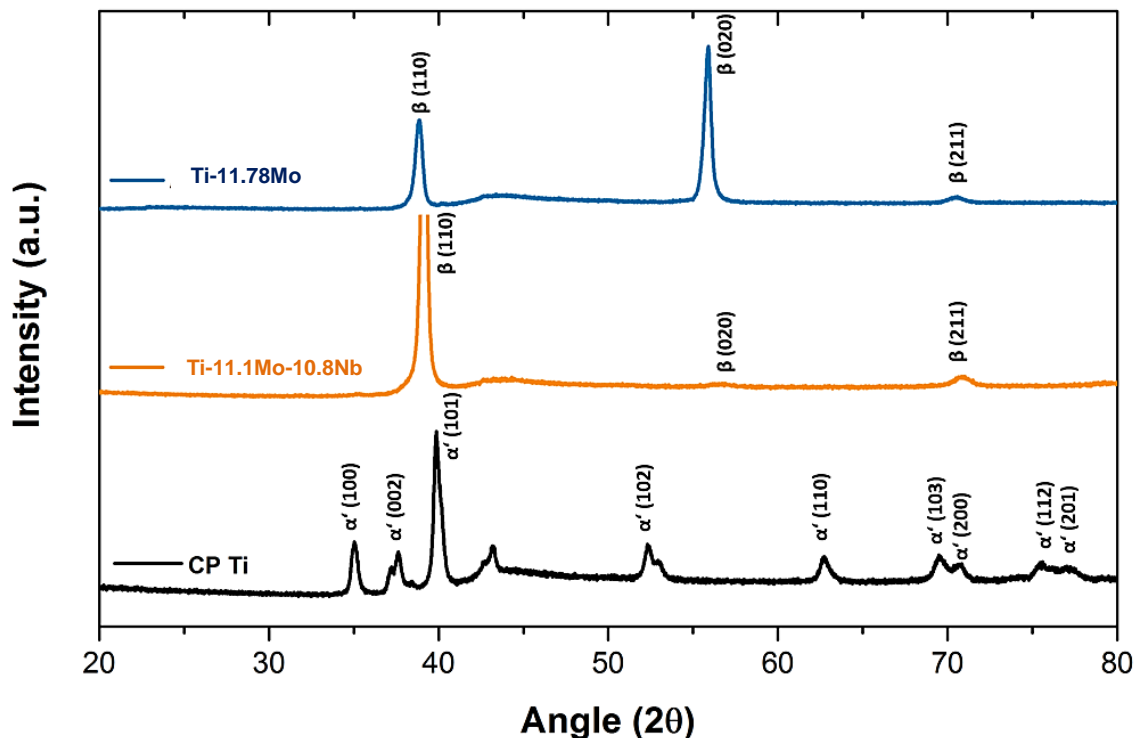


Figure 2: X-ray Diffraction (XRD) patterns of CP Ti, Ti-11.78Mo and Ti-11.1Mo-10.8Nb

Both the XRD patterns of alloys Ti-11.78Mo and Ti-11.1Mo-10.8Nb exhibit the existence of a single cubic β phase. The optical micrographs of alloys Ti-11.78Mo and Alloy are presented in Figures 3(b)

and c), respectively corroborate the experimental XRD results. With the addition of 11.78 wt% Mo to CP Ti in Ti-11.78Mo, the microstructure was composed of a significant amount of retained β -phase with equiaxed grains of various sizes. The grains of Ti-11.1Mo-10.8Nb were finer than those of Ti-11.78Mo. Therefore while the alloying of Ti-Mo alloy with Nb also contributed to the stabilization of the β phase it tentatively results in grain refinement the microstructure possibly due to the interaction of grain boundary that minimizes grain growth [21].

No peaks of martensitic or ω phases were observed on the XRD patterns. This is probably due to two tentative reasons; (i) the amount of the formed ω phase might be below the detection limits of the diffractometer and/or (ii) that the provision of sufficient beta-stabilizers suppressed the formation of the ω phase as well as other martensitic phases [10]. Our observations and interpretation are consistent with findings also available in the literature, specifically by Ho *et al.* [25], Gabriel *et al.* [26] and Xu *et al.* [27]. That means that Mo and Nb alloying elements contributed to the stabilization of the β phase by suppressing the formation of the martensitic phases. However, the single peak exists in the XRD patterns of all the alloys at $2\theta \approx 44.3^\circ$ could not be conclusively identified.

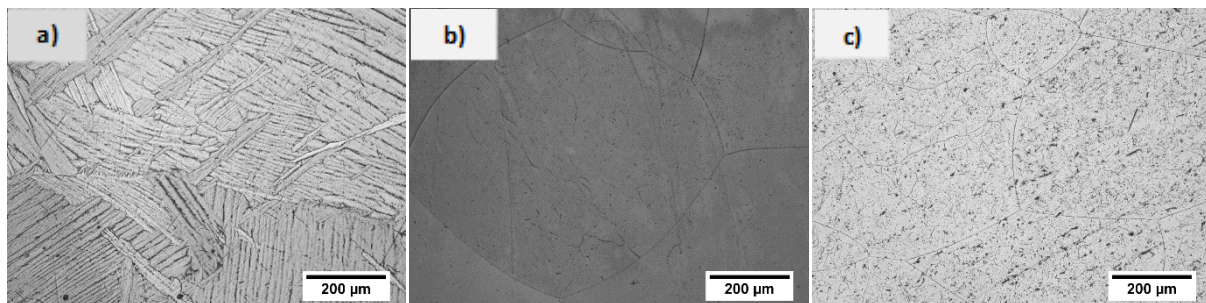


Figure 3: Optical micrographs of as-cast a) CP Ti, b) Ti-11.78Mo and c) Ti-11.1Mo-10.8Nb.

Mo and Nb are known to segregate easily in β Ti alloys during solidification [21]. Figure 4 shows the distributions of the key elements in the as-cast alloy Ti-11.1Mo-10.8Nb analysed using EDS mapping. Both the β stabilizing elements, Mo and Nb, are present and homogeneously distributed, with no significant enrichment or depletion of both beta stabilizers in the as-cast alloy.

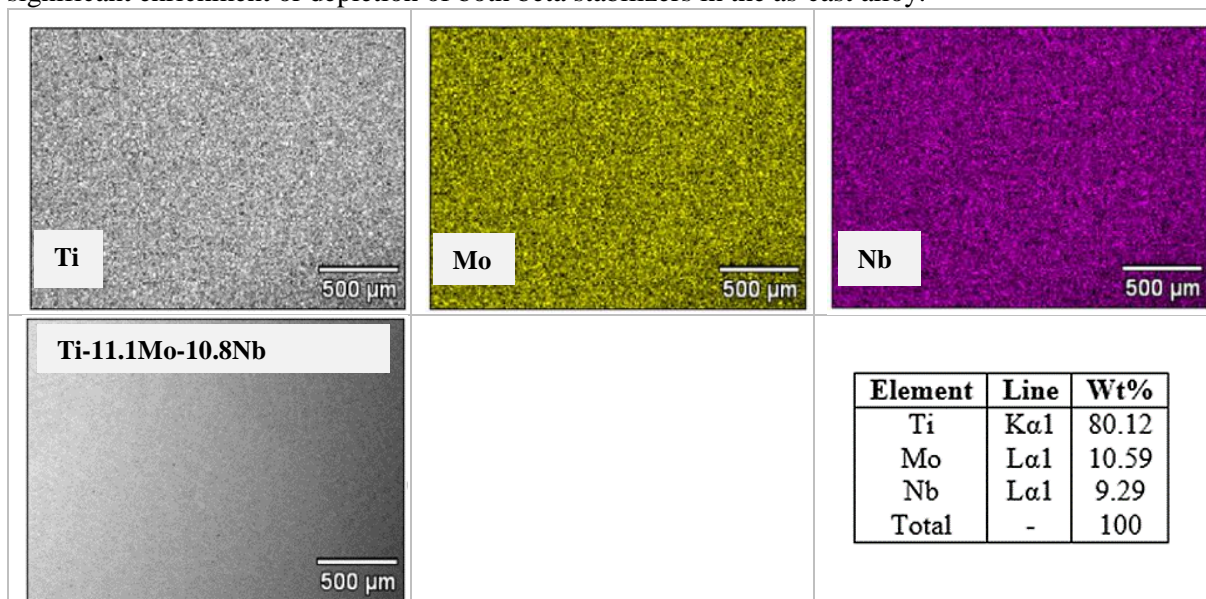


Figure 4: Energy dispersive spectroscopy (EDS) elemental mapping of Ti, Mo and Nb distribution and spectra of Ti-11.1Mo-10.8Nb

3.2. Mechanical Properties

Table 2 summarises the physical and mechanical properties of the studied alloys. The addition of 11.78 wt% Mo to CP Ti contributed to a significant increase in the micro-hardness while with Nb addition, the micro-hardness of Ti-11.1Mo-10.8Nb was significantly lower than of Ti-11.78Mo, but higher than that of CP Ti. The general increase can be attributed to the possible solution strengthening effect of the alloying elements as well as the tentative precipitation of the ω phase during cooling [10,17,23,25]. The addition of Nb possibly contributed towards the stabilization of β phase and the suppression of the formation of ω and/or the α' phases (in the Ti-11.1Mo-10.8Nb alloy), which has been reported to have lower hardness [25,28].

Table 2: Comparison of the mechanical properties of the designed alloys (Ti-11.78Mo and Ti-11.1Mo-10.8Nb) with other biomaterials.

Alloy Name	Rel. Density [g/cm ³]	Hardness [Hv]	Elastic Modulus [GPa]
Ti6Al4V ELI wrought [29]	-	-	110
Ti-12Mo-13Nb (hot swaged + aged) [30]	-	-	110 ± 2.62
Ti-10Mo-20Nb (cold swaged +/- or aged) [31]	-	267.36 - 333.28	100.12 - 101.32
Ti-12Mo-8Nb (hot swaged + annealed) [32]	-	275 ± 9	91 ± 0.53
CP Ti (this study)	4.5 ± 0.01	234.22 ± 14.77	133.7 ± 0
Ti-11.78Mo (this study)	4.8 ± 0.01	389.62 ± 32.22	133.15 ± 10.52
Ti-11.1Mo-10.8Nb (this study)	5.1 ± 0.01	311.62 ± 5.44	56.9 ± 3.08

The elastic modulus generally decreases with the increasing Mo equivalence [14]. It is evident that the increased $M_{o_{eq}}$ of Ti-11.78Mo did not have a significant influence on the elastic modulus of CP Ti. The elastic modulus of Ti-11.1Mo-10.8Nb alloy was decreased significantly by the Nb that contributed to increase in $M_{o_{eq}}$ and the stabilization of β phase, thereby suppressing the formation of ω phase. The mechanical properties show that this Ti-11.1Mo-10.8Nb is a promising β -type alloy for biomedical applications.

4. Conclusions

The design of Ti-11.1Mo-10.8Nb β -type alloy for biomedical applications was carried out using the Mo equivalence and e/a ratio approaches. Based on the microstructures, phase constitution and mechanical properties of the alloys studied, the following conclusions can be drawn:

- The microstructure of as-cast Ti-11.1Mo-10.8Nb alloy was composed primarily of β and possibly some ω phase, which were characterized by optical microscopy and XRD.
- The distribution of the β stabilizing elements (Mo and/or Nb) in the alloys was homogeneous and there was no significant enrichment or depletion of both beta stabilizers.
- The tentative precipitation of ω phase in the alloy contributed to the significant increase in micro-hardness compared to CP Ti.
- The addition of 11.78 wt% Mo decreased the elastic modulus due to the precipitation of ω phase during fast cooling, while the micro-alloying of Ti-Mo alloy with Nb contributed to the decrease in elastic modulus from 133.15 ± 10.52 GPa to 56.9 ± 3.08 GPa.
- This β -type Ti-11.1Mo-10.8Nb composition design is a promising alloy for biomedical applications.

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