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Effects of Mo content on the microstructural and mechanical properties of as-cast Ti-Mo alloys

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Abstract: The effects of Mo content on the mechanical and microstructural properties of as-cast Ti-10Mo wt.% and Ti-15Mo wt.% alloys were measured in order to evaluate their possible use in biomedical applications. The microstructure and phase analysis of as-cast specimens were studied using an optical microscopy and X-ray diffraction (XRD). The micro-Vickers hardness properties of the alloys were examined using Vickers equipment and the elastic modulus was determined using the tensile test. Results indicated that the Mo content influenced the structure-property relationship. The relative density increased significantly with the addition of Mo, the optical microscopy results showed that CP Ti was characterised with an α'-phase lamellar structure and with the addition of Mo, the microstructure composed of β phase with equiaxed grains of different sizes with sub-grain boundaries were observed. The measured XRD patterns showed that the CP Ti consisted of α'-phase and with the addition of Mo, the resultant alloys consisted of the β-phase. The micro-Vickers hardness and elastic modulus increased significantly after the addition of 10 wt.% Mo and then decreased significantly when the Mo content was raised to15 wt.%.

1. Introduction

Commercial pure titanium (CP Ti) and Ti6Al4V alloy are state-of-the-art implant materials with excellent specific strength, biocompatibility and low elastic modulus as compared to stainless steel and cobalt alloys [1–3]. However, more recently published reports have highlighted increasingly alarming risks associated with CP Ti and Ti6Al4V alloys implants because of implant failure and biomechanical incompatibilities [4–7].

Titanium implants are typically directly fixed to the host bone material during orthopaedic surgery. Ideally, the mechanical interlock of the bone tissue and implant surface at the bone-implant interface zone is expected to strengthen with no other adverse. However, CP Ti and Ti6Al4V alloys suffer from biomechanical incompatibility due to their elastic modulus (~ 110 GPa) that is significantly higher than that of the cortical bone (10 ~ 30 GPa) [5,8,9]. The elastic moduli mismatch may eventually lead to severe stress shielding and ultimate implant failure due to insufficient integration [6,7,10].

In addition to mechanical failure, the reported release of V- and Al-ion from Ti6Al4V in the body environment further limits the biomedical use of Ti6Al4V and similar alloys. Reported adverse health issues associated with toxic ions release include Alzheimer and neuropathy diseases [4,5] and allergic reactions.

Broad research has been focused on the development and design of metastable β-type Ti alloys that are non-toxic and have a low young's modulus. The development and design of non-toxic β-type Ti alloys with modulus comparable to the cortical bone is also a contemporary research topic in the area of advanced biomedical materials. According to Mohammed, Khan and Siddiquee [11], and other recently published reports [3,7,12,13], β-type Ti alloys typically possess young modulus values as low as 50-90 GPa (significantly lower than that of Ti6Al4V). Consequently Recent studies have shown that β-type Ti alloys with alloying elements such as tungsten (W), niobium (Nb), zirconium (Zr), tantalum (Ta), tin (Sn) and molybdenum (Mo) have a low elastic modulus, biocompatibility, relatively good mechanical properties and corrosion resistance [12,14]. This article is limited to the study of the microstructure, mechanical properties of Ti-Mo binary alloys with Mo content of up to 15 wt.% after Ho *et al.* [15] and Oliveira *et al.* [16].

In this work, the alloy compositional design was carried out using three different methods: firstly, the Mo equivalent (Mo_{eq}) value method after Gordin *et al.* [17]; secondly, the average electron concentration (*e/a*) after Ikehata *et al.* [18]; and thirdly, the beta stabilizing index (K_β) after Moiseev and Antipov [19]. The Mo_{eq} value, calculated according to Eq. (1) below, is defined as the sum of the weight averages of the elements (wt.%) present in an alloy, according and is increasingly used to determine the stability of the β-phase in Ti alloys [17,20,21]. According to Bania, a Mo_{eq} value of greater than 10 wt.% is needed to stabilize the isomorphous β phase in Ti-Mo alloys.

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

K_β is yet another approach used to determine the β-phase stability in Ti alloys [19,22]. K_β is given in Eq. (2) as:

$$K_\beta = \frac{C_i}{\beta_{ci}} \quad \text{Eq. (2)}$$

where C_i is the composition of β stabilizing element and β_{Ci} is the critical beta concentration or the concentration at which β phase is expected to be stable [19].

If the value of K_β lies in the 1.0 to 1.5 range ($1.0 < K_\beta < 1.5$), then the β-phase in the alloy was found to be metastable, beyond this value the β phase found to be stable [22]. The *e/a* ratio is used to predict the formation of the athermal omega-phase in Ti alloys [18,23]. The ratio is the average number of the valence electrons in each atom of Ti-Mo binary alloys. According to Ikehata *et al*., the formation of the athermal omega-phase is at its maximum when the *e/a* ratio is equal to 4.13 and at its minimum when the *e/a* ratio is 4.30 and above this minimum point the β-phase becomes dominant [18]. Ho *et al.* [15] and Oliveira *et al.* studied a series of binary arc melted Ti-Mo alloys using microstructural analysis and mechanical properties [15,16]. Their experimental results showed that the microstructure was strongly dependent on the molybdenum content, Ti-15Mo alloy had a lower elastic modulus than that of CP Ti, but was higher than that of Ti-7.5Mo alloy. The current study aims to investigate the effects of Mo content on the mechanical and microstructural properties of as-cast Ti-Mo alloys.

2. Experimental Methods

2.1 Material preparation

Ti-Mo ingots were fabricated by vacuum arc melting furnace technique using high purity CP Ti (99.9% and ASP of 28.07 μm) and high purity Mo (99.9% and ASP of 16.84 μm) powders as raw materials. Each ingot was re-melted at least three times and flipped between each melting to ensure chemical homogeneity. The nominal composition of the Ti-10Mo and Ti-15Mo alloys which are denoted as alloys AA and AB, respectively are shown in Table 1. The calculated values of Mo_{eq}, *e/a* ratio and K_β stabilizing of the alloys are also listed in Table 1.

Table 1: Composition of Ti-Mo binary alloys.

Alloy ID	**Composition [wt.%]**	Mo_{eq} **[wt. %]**	***e/a* ratio**	K_β
CP Ti	100 CP Ti	0	4	0
AA	Ti-10.02 Mo	10.00	4.24	1.0
AB	Ti-15.05 Mo	15.00	4.3	1.51

2.2 Characterization of as-cast ingots

2.2.1 Microstructural characterization

The microstructures of the as-cast Ti-Mo alloys were observed by means of the Leica DMI500 M optical microscope (Leica GmbH, Germany). Samples for optical microscopy observation were prepared by following the metallographic preparation technique and etched using Kroll solution (85 ml distilled water, 5 ml HNO_3 and 10 ml HF). The apparent densities were determined by Archimedes principle (OHAU). XRD was used for phase identification. The diffraction patterns were measured at room temperature in the Bragg-Brenton geometry (continuous scanning at a rate of 0.01°/s) using the PW3064/60 XPERT PRO diffractometer system (PANalytical BV, The Netherlands) and Cu Kα (45 kV, 40 mA, $\lambda_1 = 0.1540598$ nm, $\lambda_2 = 1.544426$ nm and $5° \leq 2\theta \leq 90°$) radiation conditions. The diffraction patterns were analysed using X'Pert HighScore Plus computer software (PANalytical BV, The Netherlands).

2.3 Mechanical testing

Micro-hardness was measured using a Vickers micro-indenter (FM-700, Japan) with a load of 500 g for 15 s on the sample. Ten different measurements were taken and the minimum and maximum values were discarded before averaging. Specimens for tensile tests were cut using an electro-discharge machine. The dimensions of the tensile specimens were 3.0 mm in thickness and 4.0 mm in width, and a length of 35 mm; the specimens had a gauge of 3 mm × 4 mm × 30 mm. The Instron^{TM} 1342 tensile test machine was utilised with an appropriate extensometer to record the stress-strain response of the alloys until fracture. The Young's modulus of the studied alloy was analysed therefrom.

3. Results and Discussion

3.1 Microstructural Characterization

The effect of Mo contents on the phase constitution and microstructure of the as-cast ingots is presented in Figures 1 and 2. Figure 2 (a - c) and (d - f) specifically combines the OM and SEM micrographs of the as-cast alloys, in that order.

Figure 1 illustrates the XRD spectra of the as-cast CP Ti, Ti-10Mo and Ti-15Mo alloys. The as-cast CP Ti XRD profiles are characterised by typical fully α' hexagonal-phase with peaks matching those attained by Ho *et al.* [15] and Oliveira [16] in the as-cast condition. From Figure 1, the addition of 10 wt.% (alloy AA) of Mo into CP Ti, resulted in the retention of the β-phase and nucleation of a small volume fraction of the α" phase. Further, the addition of 15 wt.% Mo (alloy AB) results in the retention of the majority β-phase and the suppression of the formation of α" phase. These results are in accordance with the experimental findings of Oliveira [16].

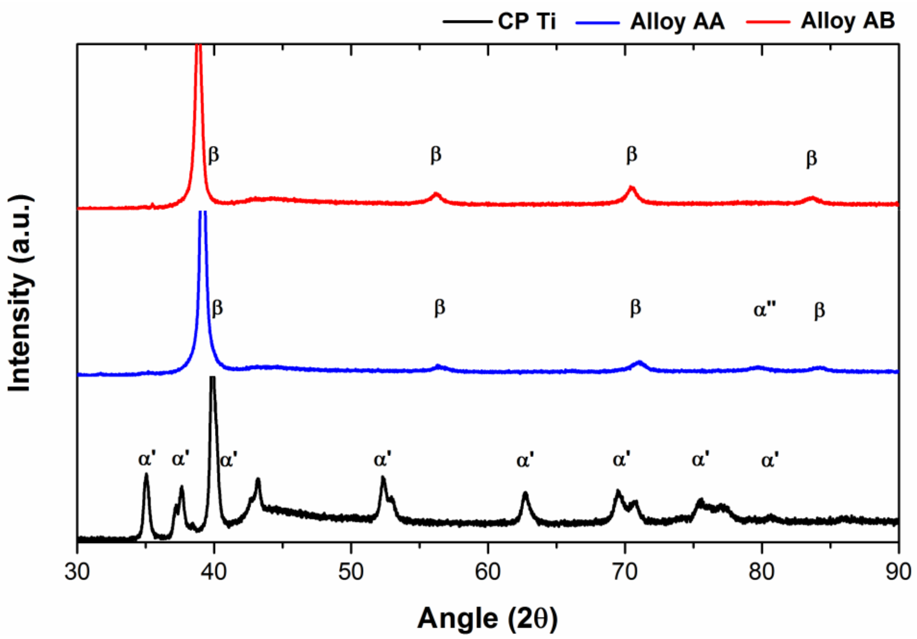

Figure 1: The XRD patterns of as-cast CP Ti, alloy AA, and alloy AB.

The OM as-cast CP Ti micrograph Figures 2(a) is characterised by a homogeneous and typical metastable ‘feather-like’ microstructure consisting of coarse plates with partitioned regions filled with small secondary plates and matches the one obtained by Bania [21]. The same microstructure was obtained after SEM characterization as seen in Figure 2(d). OM micrographs shown in Figures 2(b) and 2(c) confirm that the addition of 10 wt.% Mo (alloy AA) to CP Ti plays an important role in the formation of sub-grains of martensitic α" phase and equiaxed β phase microstructure with grains of various sizes. Observations of the suppression of other phases with increasing Mo content further to 15 wt.% (alloy AB) are consistent with findings presented by Chen *et al.* [24] and by Zhang *et al.* [25] which also investigated as-cast alloys. Figure 2(e) is the SEM micrographs of Ti-10Mo wt.%, also show equiaxed β-grains with sub-grains inside the grains and acicular α" structures nucleating on the β grain boundaries. Figure 2(f), SEM micrographs of Ti-15 wt.% Mo, on the other hand, revealed a microstructure with β equiaxed grains and but not the nucleation of the sub-grain microstructures.
Increasing Mo content appears to stabilize the β-Ti phase and the stability of the β-phase is in line with the predictive models (Table 1) where the K_β index of both alloys AA and AB ranges from 1.0 - 1.5.

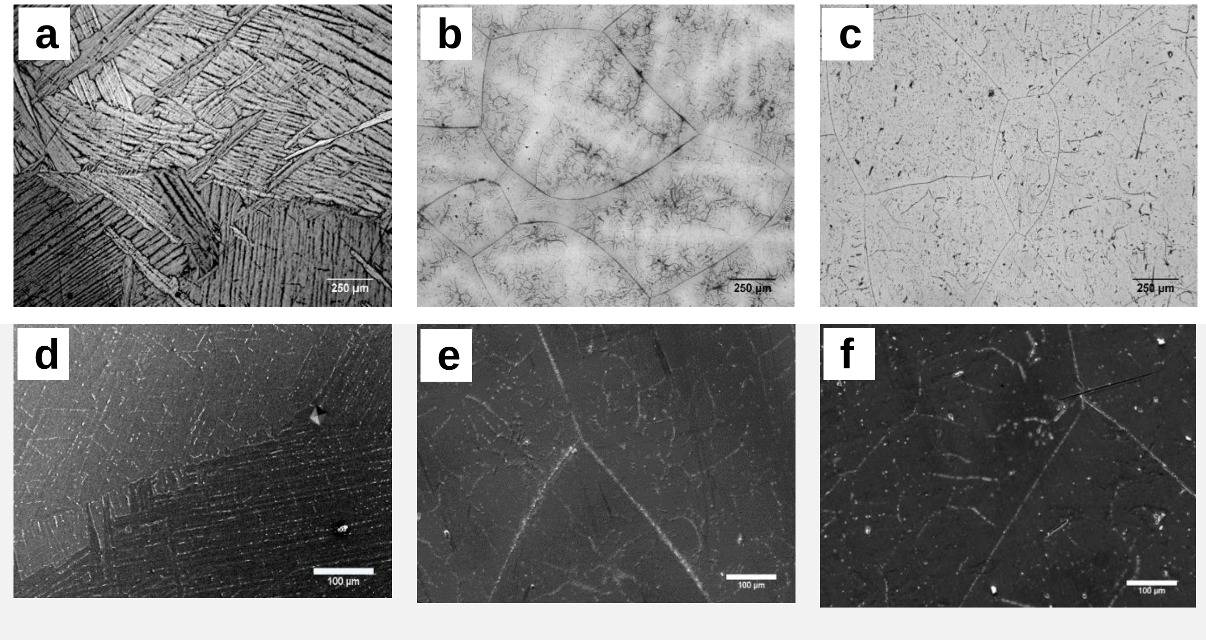

Figure 2: The optical micrographs of CP Ti (a), alloy AA (b), and alloy AB (c) respectively. The corresponding BSE SEM micrographs of CP Ti (d), alloy AA (e), and alloy AB (f).

3.2 Mechanical Properties

The relative density values of as-cast specimens are shown in Figure 3(a) below. The addition of Mo to CP Ti tends to significantly increase the relative density of alloys AA and AB. Figure 3(b) also demonstrates the micro-hardness of as-cast CP Ti, alloy AA and alloy AB. The micro-hardness properties values of the Ti-Mo alloys are comparable with findings prior reported by Ho *et al.* [15]. While the addition of Mo is expected to significantly increase in the micro-hardness of the alloys due to the solid solution effect [26], the interpretation of the observed increase is rather peculiar. According to Bagariatsikii *et al.* [27], the observed increase in the micro-hardness with increasing Mo content is due to the precipitation of the omega (ω) phase during cooling.

XRD and SEM analyses (in Figures 1 and 2) do not hint of the existence of this ω-phase (possibly hiving rise to the hardening effect) tentatively due to the phase's nanometer-sized domains or small volume fraction well below the detection limit of the conventional XRD [28]. According to Ikehata *et al.* [18], *e/a* ratio values (between 4.13 and 4.30) predict the possible existence of the ω-phase; alloy AA's *e/a* ratio predicts the presence of ω-phase while AB shows that the β phase is metastable, Moiseev and Antipov reported that the K_β stabilizing index of alloys AA and AB ranges from 1.0 - 1.5 and this shows that β is metastable at those alloys (Table 1) [19].

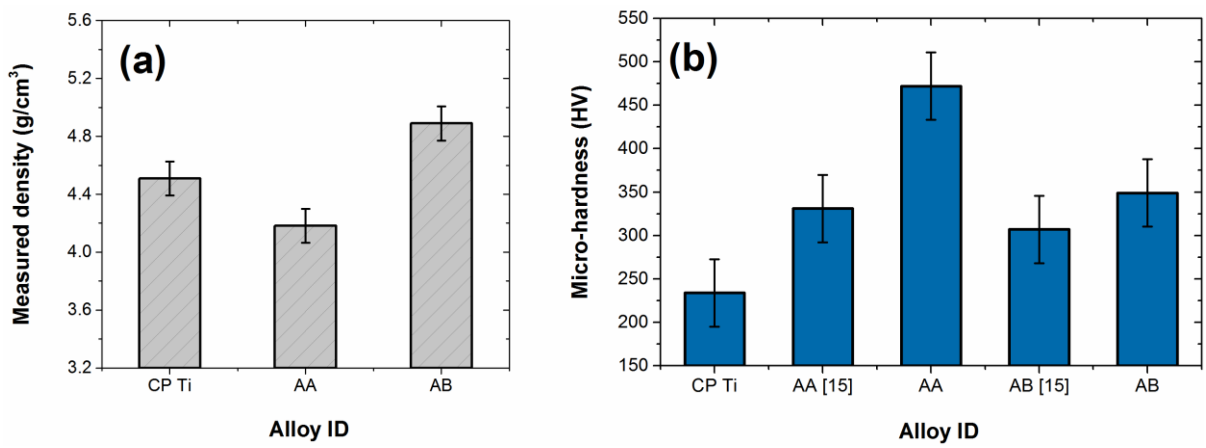

Figure 3: (a) Relative density of as-cast CP Ti, AA and AB and (b) Micro-hardness of as-cast CP Ti, AA and AB in comparison to prior reported values for alloys AA and AB [15].

The presence of the ω-phase in the Ti-Mo alloy is characterised by increase the mechanical properties [5,29]. The elastic moduli of as-cast CP Ti, alloy AA and alloy AB are illustrated in Figure 4; likewise, an increase in the Mo content is associated with a significant decrease in the measured elastic modulus that was attributed to the stabilization of the β-phase and suppression of the ω phase. The elastic modulus values obtained from this study are consistent with those obtained and reported by Gabriel, Nunes and Soares [30] and Ho [31] in the literature.

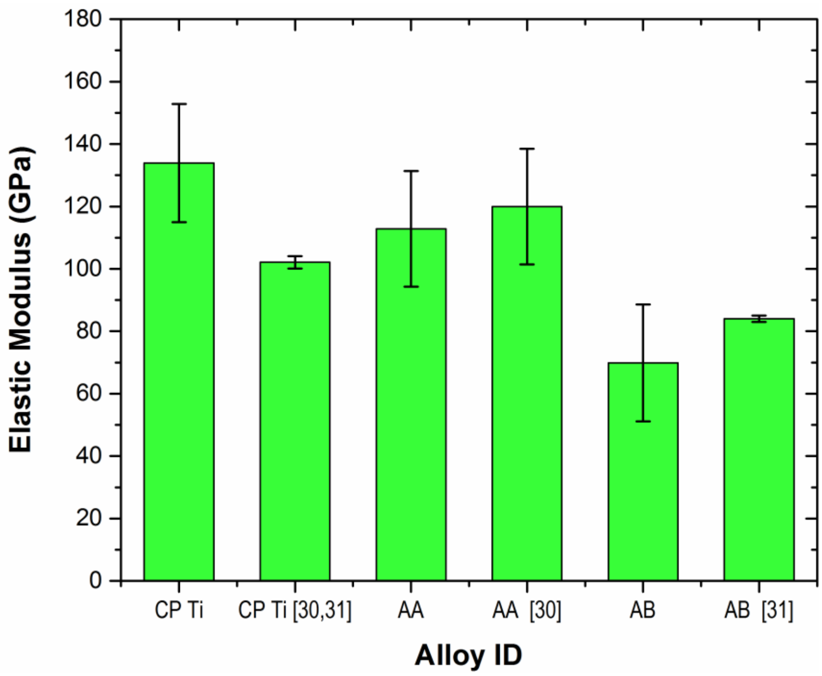

Figure 4: The Elastic modulus of as-cast CP Ti, AA and AB

4. Conclusions
Based on the density, microstructures, phase constituent and mechanical properties of the studied alloys, the following conclusions were drawn:

- The K_β stability index revealed that both alloys AA and AB had a beta stabilizing index in the range of 1.0-1.5 which indicated the formation of metastable β phase, while the *e/a* ratio predicated the ω-phase nucleation in alloy AA and its suppression in Alloy AB.
- The microstructure of CP Ti showed lamellar; with the addition of Mo, dendrites formed within the beta grains. As the Mo content increased, the dendritic structure decreased and the β equiaxed structure became the dominated phase.
- The micro-hardness of the binary Ti-Mo alloys was found to be higher than that of CP Ti. The addition of 10 wt.% Mo to CP Ti increased the hardness significantly due to the presence of the ω-phase, the hardness significantly decreased after the addition 15 wt.% Mo.
- The elastic modulus of CP Ti was higher than that of binary Ti-Mo alloys. With the addition of Mo, the elastic modulus decreased until Mo content of 10 wt.% the increase in the Mo content is due to the presence of the ω-phase as they have a tendency of increasing the modulus of elasticity and the strength. The elastic modulus then decreased as the Mo content increased to 15 wt.%.

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