The Influence of Sn addition on the microstructure and mechanical properties of the new β-type Ti-Mo-Nb based alloys for implant material

C Sutowo¹, G Senopati¹, S Supriadi², A W Pramono³, B Suharno¹
¹Metallurgy and Material Engineering Department, Faculty of Engineering
Universitas Indonesia, Depok 16424, Indonesia
²Mechanical Engineering Department, Faculty of Engineering
Universitas Indonesia, Depok 16424, Indonesia
³Research Center of Metallurgy and Material, Indonesia Institute of Sciences,
Kawasan Puspiptek Serpong, Tangerang Selatan 15314, Indonesia

Email :csutowo@yahoo.com, suharno@metalurgi.ui.ac.id

Abstract. Titanium alloys are very interesting for biomedical applications due to excellent biocompatibility, corrosion resistance, lower density, and lower young modulus compared to cobalt and stainless steel alloys. However, compared to bone, young modulus of pure titanium and Ti-6Al-4V are still relatively high and the mechanical properties are still insufficient to meet the needs of biomaterials replacing the hard tissues. In this paper, a newly Ti-Mo-Nb based alloys were designed and the effect of Sn content in Ti-6Mo-6Nb-xSn alloys (x=0,4,8 and 12 wt%) after homogenized on microstructure, hardness, and young modulus were investigated. The alloys were produced by electric vacuum arc furnace with non-consumable tungsten electrode then homogenized at 1100 °C for 7 under controlled argon atmosphere. Optical microscope, scanning electron microscopy, x-ray diffraction hardness test and ultrasonic test were used for alloys characterization. The results showed that Ti-6Mo-6Nb-xSn has equiaxed structure and Sn addition could promote the formation of β phase. The elasticity modulus of Ti-6Mo-6Nb-xSn alloy with the addition of 12% Sn was 88 GPa, this is better since it is below the elastic modulus of Ti6Al4V implant material.

1. Introduction
The biomaterial is a synthetic biocompatible material to replace or improve the function of body tissues, one of which is a bone replacement [1]. The basic properties that must be possessed by orthopedic implants, namely biomechanical properties and biomedical properties. The biomechanical properties of orthopedic implants must match the body's tissues without the rejection reaction of body tissues when applied [2-4].

Selection of titanium as an implant material has been done since it has several advantages such as light-weight nature, high strength, good corrosion resistance and lower modulus of elasticity compared to other biomaterials such as stainless steel and cobalt alloys [5]. In addition to its superior mechanical properties, another reason is that stainless steel and cobalt alloys contain harmful elements such as Ni, Cr, Co. However, commercial pure Titanium (cp Ti) has limitations and is considered insufficient to meet the needs of biomaterials that require high strength, for example to replace hard tissue so that it is developed in the form of alloys [3].
The titanium alloy currently popular on the market is the Ti-6Al-4V with the α-β phase, but the fact that the release of small amounts of vanadium and aluminum ions from this alloy into the human body is detrimental. V and Al can induce possible cytotoxic and neurological effects causing serious health problems if they enter the human body [6,7] having problems with allergies [3]. The development of titanium alloys has been carried out using molybdenum or niobium as a vanadium substitute which functions as a beta phase stabilizer [8].

Besides that, the presence of aluminum can increase the potential for Alzheimer's disease development[9-10]. Several studies have been carried out by substituting vanadium element using molybdenum and niobium but alpha-beta type titanium alloys still have the relatively high modulus of elasticity [11,12].

The development of the latest titanium alloy is done by replacing V and Al as well as adding another β (beta) phase stabilizing element so that it can function to increase strength and decrease the modulus of elasticity [13,14].

Beta type single phase titanium alloys are still in the research and development stage to reduce the modulus of elasticity so that it can avoid the effect of shield states on bone repair. Stress phenomenon shielding effect takes place because of the inequality between the nature of the elastic modulus of the implant material and that of the bone so that the load is seemingly received solely by implant material. Consequently the osteoporosis bone decreases and the bone that is not cracked will experience re-fracture due to the stress concentration around the implant. Some elements that have good biocompatibility and are not toxic to beta-type titanium alloys include Ta, Nb, Zr, Mo, W, Sn [4]. The purpose of this study was to design a new titanium alloy type β (beta) through the addition of beta phase stabilizer elements of niobium and molybdenum and to investigate the effect of adding low-cost stannum elements to reduce or substitute the use of niobium and molybdenum.

2. Material and Method

Design of Ti-6Nb-6Mo-(x)Sn alloy with variations in Sn composition (x=0, 4, 8, and 12 wt%) in this study pure titanium (99, 9%), pure molybdenum (99.9%), pure niobium (99.9%) and pure stannum (99.9%). Melting process was performed using electric arc vacuum furnace in argon environment. The melting process was carried out five times to get homogeneity of the solid solution in the resulting ingot. The specimen produced in the remelting process was a button ingot weighing about 20 grams with 20 mm in diameter and 5 mm in thickness. The chemical composition of titanium alloy produced was tested using standard Q4 Mobile Broker testing.

The ingot was further homogenized by heating in a tube furnace with argon at 1100°C for 7 hours followed by furnace cooling. The purpose of homogenization is to increase uniform distribution of the element in the titanium alloy.

The sample was then mounted to facilitate grinding and polishing. The grinding of sample was carried out using wet emery papers no 80, 120, 400, 800 and 1200, while the polishing used alumina micropolish up to 0.3μ followed by etching with Kroll's reagent solution (5 ml HF, 10 ml HNO₃, and 85 ml H₂O). Microstructure examination was conducted using optical microscope Meiji Techno Japan and scanning electron microscope (SEM/EDS) by JEOL JSM5390A. X-ray diffraction (XRD) measurements for phase analysis was conducted using Rigaku smart-lab diffractometer at room temperature using Cu Kα radiation and operating at 30kV/15mA. The hardness value was measured using the Mitutoyo Hardness Testing Machine HM-200 with a load of 0.3N for 12s. The elastic modulus was examined using the DM4 DL Krautkramer ultrasonic test and DA312B type probe with the ASTM-E494-95 standard [15].

Ultrasonic test will be obtained in the form of ultrasonic longitudinal velocities (V₁), the calculation of elastic modulus using equation 1, while the relationship between ultrasonic longitudinal velocities and shear wave velocities (V₉) with poisson ratio is shown in equation 2 [16].

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E = \rho V_1^2 \frac{(3V_1^2 - 4V_9^2)}{V_9^2 - V_1^2}
\]

(1)
3. Results & Discussion

The material used in this study was as-cast Ti-6Mo-6Nb-(x)Sn alloy, with the chemical composition shown in Table 1.

Table 1. Chemical composition of Ti-6Mo-6Nb-(x)Sn

| Unsure wt% | Ti    | Mo  | Nb  | Sn | Cr  | Fe  | V   | Cu  | Si  |
|------------|-------|-----|-----|----|-----|-----|-----|-----|-----|
| Ti-6Mo-6Nb | 93.2  | 3.15| 2.79| -  | 0.02| 0.05| 0.45| 0.09| 0.04|
| Ti-6Mo-6Nb-4Sn | 84.8  | 5.75| 4.55| 3.93| 0.03| 0.05| 0.59| 0.11| 0.04|
| Ti-6Mo-6Nb-8Sn | 81.5  | 5.06| 3.92| 8.06| 0.04| 0.04| 0.50| <0.01| 0.04|
| Ti-6Mo-6Nb-12n | 76.9  | 5.25| 4.92| 12.20| 0.03| 0.05| 0.42| 0.06| 0.04|

(a). Sample 1, Ti-6Mo-6Nb  
(b) Sample 2, Ti-6Mo-6Nb-4Sn  
(c) Sample 3, Ti-6Mo-6Nb-8Sn  
(d) Sample 4, Ti-6Mo-6Nb-12Sn

Figure 1. The microstructure of Ti-6Mo-6Nb-(x) Sn as-cast homogenized, etching using Kroll’s reagent solution (5 ml HF, 10 ml HNO₃, and 85 ml H₂O).

The microstructure of Ti-6Mo-6Nb-(x)Sn alloy in Figure 1 shows as-cast microstructure after homogenized at 1100°C for 7 hours with slow cooling in the furnace, which aims to eliminate segregation and to achieve uniform microstructure. The microstructure of the globular alloy is the result of static recrystallization due to the cooling process after homogenized which occurs along with the decrease in temperature of the β-transus. The results showed that Ti-6Mo-6Nb-xSn have equiaxed structure and Sn element addition could promote the formation of β phase, the higher the Sn content the less the alpha phase contained in the beta matrix.
The influence of the homogenization results in a large amount of grains evenly distributed in various compositions, but the material of Ti-6Mo-6Nb-12Sn with a 12% Sn have smaller grain size average about 500 microns causing the increase in hardness.

Figure 2 shows diffraction patterns of as-cast Ti-6Mo-6Nb after homogenization consisting of β phase. The XRD results showed that in the Ti-6Mo-6Nb alloy without Sn, beta stabilizer was still not sufficient to form the beta phase as seen from the intensity peak that is still more dominant in the phase α than the β phase. The addition of Sn has an effect on increasing the phase volume fraction of β, as evidenced by the increasing peak/intensity of the β phase in the alloy containing Sn.

Further observations on the microstructure of the alloy were carried out using SEM / EDS. The sample grain size is almost the same as sharing the variation of Sn elemental content. In the Ti-6Mo-6Nb-4Sn alloy with the addition of Sn = 4% and Sn = 8%, the appearance of α precipitates in the β matrix is still obvious; whereas in the sample with Sn = 12% does not indicate the presence of precipitates/α phases. In EDS observation the presence of precipitate alpha is marked by the higher dominant content of the alpha phase stabilizer.

Yang et al (Huet al., 2008) have investigated the effects of alloying elements of Nb, Zr, and Sn on the stability of Ti alloy and the results show that Sn is a beta phase stabilizer stronger than Nb, and an additional amount of Sn can reduce the elasticity modulus of alloy by suppressing the formation phase ω in the Ti-Nb-Zr-Sn alloy.
Figure 3. SEM photograph of the Ti-6Mo-6Nb alloy, etching using Kroll's reagent solution (5 ml HF, 10 ml HNO$_3$, and 85 ml H$_2$O).

Figure 4 shows the average Vickers hardness value of as cast Ti-6Mo-6Nb before and after homogenization condition. The effect of homogenization on Ti-6Mo-6Nb and Ti-6Mo-6Nb-4Sn alloy causes a decrease in the value of Vickers’ hardness whereas in the Ti-6Mo-6Nb-8Sn and Ti-6Mo-6Nb-12Sn alloy with higher Sn content (x=8% and x=12%) the hardness increased.

Figure 4. Vickers hardness value of Ti-6Mo-6Nb-(x)Sn alloy.
Figure 5 shows the modulus of elasticity before and after the homogenization process. In the study of P. Majumdar et al, it is said that the β phase in titanium can reduce the elastic modulus compared to the α phase [16].

Elasticity modulus of titanium alloy is related to alloy composition and phase constitution. In the Ti-6Mo-6Nb-based alloy, the elastic modulus is determined by the phase and volume fraction. The modulus of elasticity of titanium alloy is lower with increasing Sn content. This proves that the addition of Sn element can promote the formation of phase β, as shown in the figure 2 which shows the increase in beta phase intensity as the Sn content increases. In the Ti-6Mo-6Nb-12Sn alloy with 12% Sn, the lowest achieved modulus of elasticity is 88 GPa and increases after homogenization to 92 GPa.

![ELASTICITY MODULUS](image)

**Figure 5.** Elasticity modulus of Ti-6Mo-6Nb-(x)Sn alloy.

In the homogenized samples, the modulus of elasticity is relatively higher compared to that of the as-cast samples. This indicates the occurrence of phase changes due to the cooling effect in the furnace. So that the alloy samples with the addition of Sn homogenization experience an increase in the value of the modulus of elasticity compared to the as cast sample as shown in figure 5.

4. Conclusion

The results of the x-ray diffraction analysis of Ti-6Mo-6Nb alloy after homogenization showed the increase of peak intensity of β phase in the alloy with the addition of Sn. Phase intensity β increases with increasing percentage of Sn. The hardness value off the alloy has increased with the addition of 12% Sn and has increased further with the homogenization. The elasticity modulus of Ti-6Mo-6Nb alloy with the addition of 12% Sn was 88 GPa, this value is better than other implant material even below the elastic modulus of Ti6Al4V.

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