The microstructure and mechanical hardness of cast Ti-30Nb-5Sn after solution treatment

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Abstract. This work reports the investigation on the development of microstructure and the resulting mechanical hardness of a metastable β Ti-30Nb-5Sn alloy as a result of solution treatment. The solution treatment was conducted at 1000°C for 5 h followed by water quenching. The microstructure was studied by a field emission-scanning electron microscope (FE-SEM) which equipped with EDX analysis for identifying the elemental composition. The phase change occurred in the alloy was analyzed by XRD while the mechanical hardness was measured by Vickers’s hardness technique. The results showed that the solution treatment induced the nucleation of intragranular α-phase precipitation in the alloy which formerly composed of only single β-phase with dendritic structure in the as-cast condition. The α-phase exhibited a micro size plate-like morphology distributed randomly in the metallic grain and along grain boundaries of the solution-treated alloy. The α phase precipitate contained a significantly lower Nb concentration (25.07 wt%) than the surrounding matrix (33.78 wt.%). The presence of α-phase precipitate enhanced the mechanical hardness from 274.3 to 335.8 HV. The results implied that the microstructure and hardness of the Ti-30Nb-5Sn were significantly altered by the solution treatment.

1. Introduction
The current commercial metallic biomaterials used in the clinic are made of stainless steel, Co-Cr alloy, pure-Ti, and Ti-6Al-4V. Two major problems which are found to be the reason for implant failure in the application are toxicity and stress shielding effect [1-4]. Ti and its alloys exhibited high specific density, good mechanical properties, and excellent corrosion resistance in a harsh human body environment [5]. The alloying elements of Al and V in commercial Ti-6Al-4V was reported to cause neurological disorders and nerve’s disease [6-7]. There some research investigating the development of Ti composite by mixing Ti and ceramic or glass material which revealed a good biocompatibility but counteracts by the significantly increased hardness [8]. Recent investigations of Ti alloy was focused on the development of non-allergic alloy with low elastic modulus such as the metastable β Ti which includes Ti-Mo, Ti-Nb, and Ti-Zr [9-11]. A large difference in elastic modulus between implant material and the adjacent bone may lead to stress shielding effect.

The β Ti-Nb-Sn alloys are extensively investigated [9-14] in recent years considering their non-toxic property and excellent biocompatibility. Niobium serves as a β stabilizer while the Sn prevents the precipitation of α phase resulting in the lower elastic modulus [9]. Both Nb and Sn had been proved to have a good cytocompatibility [12]. An optimization of the concentration of Nb and Sn in the alloy is
necessary to avoid the phase transformation of the β-phase. Previous work [13] had shown that the stable β-phase in Ti-30Nb was achieved by alloying with 5 wt% Sn. Besides, the concentration of the alloying element, the microstructure of Ti-Nb-Sn alloy was sensitive to a heat treatment which further affected the mechanical properties. The ω precipitate was reported [14] to form in Ti-35Nb as a result of aging for short time at 573-773 K but returned to its original properties at room temperature. The formation of ω precipitate resulted in a superelasticity phenomenon where the modulus elasticity dropped significantly. The ability to exhibit superelasticity shows potential for application as a shape memory alloy.

This work aimed to investigate the effect of heat treatment at 1000°C for 5 h on the microstructure and mechanical hardness of Ti-30Nb-5Sn. The treatment is typically performed to obtain homogeneous distribution of alloying element in the alloy, which is also called as solution treatment. The phase transformation which may occur as a result of solution treatment was analyzed by X-ray diffractometer.

2. Experimental Procedure
The Ti-30Nb-5Sn alloy was prepared from raw materials of Ti scrap (99.5%), Nb rod (99.8%), and Sn scrap (99.99%). The raw material was weighed 100 g in total to make an alloy. The arc vacuum furnace was used to melt the material and cast into an ingot. The ingot was remelted 5 times to ensure the homogenization of the components. The fabrication method was similar to an earlier report [13]. Some of the as-cast alloys was further solution treated at 1000°C for 5 h followed by water quenched. The solution treatment was conducted in a furnace under air exposure.

Prior further use, the specimen was ground with #800 to #2000 grit paper and then polished with alumina paste until mirror finished. The specimen was then washed in DI water. Before using for characterization, the specimen was degreased in acetone and ethanol in an ultrasonic bath for 3 min.

For microstructure observation, the specimen was etched in 5 M HF solution and desmutted in 30% HNO₃ solution. The microstructure was studied by FE-SEM (FEI Inspect F-50). The alloy composition was confirmed by EDX. The crystalline phases existed in the alloy was analyzed by using X-ray diffractometer (XRD, Panalytical X’Pert Pro MPD). Meanwhile, the mechanical hardness was measured by means of Vickers microhardness indenter (Struers DuraScan). Five-points measurements were conducted on each specimen to obtain the average value.

3. Results and Discussion
The composition of the as-cast alloy was analyzed by EDX on a large area on the specimen to make sure the ratio of each component. The alloy composition is listed in Table 1. The concentrations of Nb and Sn were slightly higher at 36.8 wt% and 6.9 wt%, respectively, but still in the tolerable range. The EDX analysis was done at three points on the specimen and the results were not so different indicating that the distribution of the element was homogeneous. The alloying element, in particular, Sn was volatile at a high temperature under vacuum condition inside the arc furnace chamber, which potentially caused significant mass loss during the process. However, the EDX result confirmed that the Ti-30Nb-5Sn alloy was successfully fabricated by using an arc furnace.

| Element | Wt% | At% |
|---------|-----|-----|
| Nb      | 36.8| 24.3|
| Sn      | 6.9 | 3.6 |
| Ti      | 56.3| 72.1|

Table 1. Elemental composition of the Ti-30Nb-5Sn alloy.

Figure 1 shows the plane-view FE-SEM images of the Ti-30Nb-5Sn alloy before and after solution treatment. The as-cast alloy exhibited a lamellar with branching structure forming dendrites (Fig. 1a). The space between lamellar was about 30 μm. A higher magnification image in the inset Fig. 1a shows...
more clear the dendrites. The structure indicated that alloy had only a single phase. Diffusion of the molten alloy during casting gave lamellar and dendrites path in the microstructure [5]. Meanwhile, after solution treatment, the dendritic structure did not exist any longer. The microstructure of the alloy after solution treatment showed a clear metallic grain structure decorated by plate-like precipitates of about 10 µm size. The discontinuous grain boundaries exhibited similar morphology as the plate-like precipitates. The plate-like precipitates and the grain boundaries corresponded to the α-phase. Both grain boundaries and precipitates appeared darker indicating lower average atomic weight than the surrounding matrix. A higher magnification image in the inset Fig. 1b revealed some grain boundary lines existed inside the precipitates. Similar plate-like morphology of the α-phase precipitates was reported [11] to form as a result of aging at temperature 500° and 600°C.

![Figure 1. FE-SEM images of the a) as-cast and b) solution treated Ti-30Nb-5Sn alloy showing the transformation in the microstructure.](image)

To confirm the composition of the plate-like precipitate, EDX point analysis was conducted on the precipitate as well as the matrix for comparison purpose. The results are presented in Fig. 2. The Nb concentration in the precipitate was only 25.07 wt% which was 8.71 wt% lower than that of the matrix. Oppositely, the Ti concentration was higher at 67.43 wt% at the precipitate than at the matrix (59.77 wt%). The low Nb and higher Ti concentration proved that the precipitate consisted of α-phase. It was reported that the martensitic α-phase typically has low Nb and higher Ti content [7, 11]. The low Nb concentration at the precipitate reduced the average atomic weight and hence gave darker appearance than the surrounding matrix.
Figure 2. FE-SEM images and the corresponding EDX point analysis at the a) matrix and b) plate-like precipitate.

Figure 3 shows the XRD pattern of the Ti-30Nb-5Sn alloy as-cast and after solution treatment. The as-cast specimen composed of mainly \( \beta \)-phase. The distinct peaks corresponded to the \( \beta \)-phase aroused at the angles of 38.9°, 55.9°, 69.5°, and 82.1° in the as-cast specimen. The as-cast alloy entirely composed of \( \beta \)-phase. Meanwhile, the XRD pattern of the solution-treated specimen exhibited numerous peaks of \( \alpha \)-phase in addition to the \( \beta \)-phase. The \( \alpha \)-phase was identified by the serial peaks appeared at the angles of 32.5°, 35.9°, 41.1°, 54.1°, 55.4°, 62.7°, 68.9°, and 75.8°. The XRD results were in agreement with the FE-SEM images in Fig.1 that the solution-treated specimen consisted of \( \beta \)-phase and numerous \( \alpha \)-phase precipitates while the as-cast specimen composed only \( \beta \)-phase. The solution treatment conducted on the Ti-30Nb-5Sn induced the formation of \( \alpha \)-phase precipitates in the metastable \( \beta \)-phase matrix.

Figure 3. X-ray diffraction pattern of as-cast and solution-treated Ti-30Nb-5Sn alloys.
Table 2 shows the effect of solution treatment on the mechanical hardness of Ti-30Nb-5Sn alloy. The presence of α-phase precipitates in the metallic grain of β-phase of Ti-30Nb-5Sn alloy enhanced the mechanical hardness of the alloy. The as-cast alloy which exhibited a hardness of 274.3 HV became significantly harder with hardness value 335.8 HV after solution treatment. The presence of α-phase as a result of solution treatment enhanced the mechanical hardness of about 61.5 HV. The martensitic α phase is brittle and hence tends to raise the hardness of Ti alloy [10, 11].

| Specimen           | Microhardness (HV) |
|--------------------|--------------------|
| As-cast            | 274.3              |
| Solution-treated   | 335.8              |

4. Conclusion
The effect of solution treatment on the microstructure and hardness of Ti-30Nb-5Sn alloy have been investigated. Surface characterization and elemental analysis unambiguously showed that the solution treatment induced the formation of α-phase precipitates as confirmed by the XRD analysis. The precipitate existed in the form of micro-size plate-like morphology segregated in the metallic grain of β-phase. The α-phase was also enriched along the grain boundaries. Prior to solution treatment, the as-cast alloy exhibited a lamellar and dendritic structure of single β-phase. The presence of α-phase precipitate in the solution-treated specimen resulted in an increase of mechanical hardness from 274.3 to 335.8 HV. The microstructure of metastable β-phase is very sensitive to heat treatment. The α-phase played an important role in the precipitation hardening mechanism of the β Ti alloy which opened the possibility to control the mechanical properties of β Ti alloy.

5. References
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