Morphology and mechanical properties fabricated from Ti, Nb and HA by powder metallurgy method

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Abstract. Hydroxyapatite (HA) is a bioactive ceramic material with poor mechanical properties which hinders its application in bone implant. However, HA has a similar structure to bone and can promote the growth of natural tissues. Combining the low modulus \(\beta\)-type Titanium (Ti) based alloy (e.g: Ti-40Nb) which has excellent mechanical properties and non-toxic composition with HA is considered as a good candidate to expand its biomedical applications. In this current work, Ti, Ti-40Nb and Ti-40Nb-15HA (wt.\%) was compacted under 500 MPa using powder metallurgy process. The mixtures were performed by high energy milling and sintering in a tube furnace with temperature of 1200\(^\circ\)C/2 h under argon flow. The aim of this research is to investigate the morphology and the mechanical properties of metal alloys. Images obtained by SEM show a homogeneous morphology of voids with smooth surface for Ti and Ti-40Nb while Ti-40Nb-15HA show the presence of pores located at grain boundary and exhibit rough surface appearance. Ti-40Nb-15HA alloy was found to give a favourable compression strength and low density at 171.93 MPa and 5.086 \(g/cm^3\), respectively. Thus, considering its mechanical properties, Ti-40Nb-15HA was found ideal for orthopaedic implant materials as it has properties closed to human bone.

1. Introduction

Titanium (Ti) and its alloys have been widely used for biomedical implants. However, the mismatch between Ti and the surrounding natural bones make the bone insufficiently loaded and becomes stress shielded resulting in bone resorption and lead to implant failure. Thus, a material with an excellent combination of high strength and low modulus closer to the bone has to be used for implantation to avoid loosening of implants and give higher service period [1]. The ultimate compressive strength, yield strength and Young's modulus of human cortical (dense) bone are \(\sim\) 130-180 MPa, 104-121 MPa and 10-30 GPa, respectively [2]. This mechanical properties of Ti alloys can be achieved by selecting an alloy composition with low Young's modulus (e.g:\(\beta\)-type alloy). The elastic modulus of pure Ti is 100...
GPa while Ti-6Al-V alloy ($\alpha + \beta$ type) which is the most used Ti-based alloy in bone implant has 110 GPa and β-Ti alloys has 55 GPa [3]. Thus, the β-Ti alloys display more compatible elastic behaviour with human bone. In terms of binary Ti-Nb alloys, the stability of β phase is enhanced with the increase of Nb content to 40 wt% which lead to the more stable β-Ti phase, minimizing the precipitation of ω phase and lowering the elastic modulus [4]. Therefore, the composition of β-type Ti-40Nb was chosen for the present work due to its unique combination of mechanical properties, especially its low elastic modulus, non-toxic and excellent corrosion resistance [5]. Among the factors that affect the mechanical properties of bone is its material properties [6]. In this study, our approach is to incorporate Hydroxyapatite (HA) into β-type Ti-Nb to form a new metallic biomaterials. HA has been widely used as a bone replacement material due to its chemical and crystallographic structure being similar to the bone mineral which result in excellent biocompatibility [7]. Furthermore, it has a good bioactivity and osteoconductivity [8-9]. However, HA cannot be used for load bearing implants due to its low strength and brittle nature [10]. Combining HA with the excellent mechanical properties of low modulus β-type Ti-Nb (non toxic metal) is considered to be a promising approach to fabricate most suitable biomaterial for medical implant applications. This comparative study is about the morphological and mechanical properties of Ti, Ti-40Nb and Ti-40Nb-HA15 (wt.%) which was produced by powder metallurgical approach. The aim of this study is to reduce the mechanical properties (e.g.: compressive strength) of Ti of the implants to the level approaching human bones which may decrease the stress shielding and reduce the failure of implants. Compressive strength is necessary for the development and growth of the bone which must be taken into account in producing new biomaterial. Therefore, in this study, mechanical properties under compressive stress has been mainly considered and investigated.

2. Experimental study

The elemental powder of Ti, Nb and HA was weighed with an electronic balance according to nominal compositions of Ti, Ti-40Nb and Ti-40Nb-15HA (wt.%). The mechanical milling was performed in a high-energy Fritsch Pulverisette P-5 planetary ball mill with stainless steel jar under argon atmosphere. To obtain a complete uniform mixture, the powders were milling for 2 hours at a weight ratio (balls to powder) of 10:1 at a rotation speed of 200 rpm. 3% n-heptane solution was added prior to milling process to avoid excessive cold welding of the elemental alloy powders. The mixture was uniaxially pressed at a pressure of 500 MPa into green compacts. Pellets of approximately 10 mm in diameter were fabricated. Finally, the green compact samples were sintered in a Lenton tube furnace at 1200°C for 2 hours in an argon atmosphere. These samples were mechanically polished using SiC abrasive papers from grade 100 up to 2000 grits, followed by a 0.05 μm diamond finish. The morphology of metal alloys was performed by VPFESEM SUPRA 35VP. Several magnifications were focused to obtain a good viewing point on the samples. The density of the sintered samples were determined by Archimedes method. Compression test was carried out to investigate the compressive strength of samples which was prepared using Universal Testing Machine (UTM) INSTRON 5982 at a crosshead speed of 1 mm/min at room temperature. Samples were subjected to 100 kN.

3. Results and discussion

3.1 Morphology Observation

It can be seen from Figure 1 that the morphology of Ti, Ti-40Nb and Ti-40Nb-15HA (wt %) after milling was varies due to its different particle size and properties. The raw materials of the starting materials were broken down and reduced to smaller particles. Ti and Ti-40Nb powder appears as an irregular particle shape with different size. With the addition of HA content, the morphology of Ti-40Nb-15HA...
was changed and appeared as flower-like particles. The presence of small agglomerates of HA particles can also be observed (label at figure).

The thermal treatment at 1200°C leads to a sintering process of the mixture. Figure 2 shows SEM micrographs of the sintered Ti, Ti-40Nb and Ti-40Nb-15HA (wt.%) at 1200°C. After sintering, porosity was observed for Ti sample while for Ti-40Nb sample, the interconnected porosity with irregular shapes and various sizes was seen. Furthermore, there was a lack of fusion regions observed in Ti-40Nb which caused by its fusion temperature. The melting temperature of Ti and Nb was 1668°C and 2477°C, respectively. The energy needed to melt the metal powder increased, especially with Nb content increased. Due to incomplete melting of the metal powders, this lead to a lack of fusion of the sample which produce porosity. The pores also may result from entrapment of gas during the melting process [11]. When adding HA (e.g: 15 wt.%) into Ti-Nb40, the agglomeration phenomenon of HA powders occurred. This is due to the high surface activity and this phenomenon is more obvious, especially with the increase of HA content [12]. For Ti-40Nb-15HA, the agglomeration of the particle create porous structure. Different heights of grain, which exhibit high irregularity of sample surface was observed. The implant surface should be rough to enhance load bearing capacity and osseointegration which could allow for bone ingrowth [13].

![Figure 1. SEM images of the particle morphology obtained after 2 hours of milling: Ti (Figure 1a), Ti-40Nb (Figure 1b) and Ti-40Nb-15HA (Figure 1c).](image)

![Figure 2. SEM images of metal alloys sintered at 1200°C with different magnification: Ti (Figure 2a), Ti-40Nb (Figure 2b) and Ti-40Nb-15HA (Figure 2c).](image)

### 3.2 Density Measurement

As seen in Table 1, the density of Ti increase with the addition of Nb. The density of Nb is high which is around 8.6 g/cm³. Therefore, the addition of Nb into Ti-Nb40 give a significant increase to the density value. However, the addition of HA into Ti-40Nb-15HA which has a density of 3.156 g/cm³ has
significantly decreased the density of metal alloy due to its low density. The bulk density achieved for the samples are considered light and close to natural bones (1.8-2.1 g/cm$^3$), compared to other similar metallic biomaterials such as stainless steel (8 g/cm$^3$) or cobalt-based alloys (8.5 g/cm$^3$).

**Table 1.** Theoretical density (g/cm$^3$) and bulk density (g/cm$^3$) of Ti, Ti-40Nb and Ti-40Nb-15HA

|                | Theoretical Density (g/cm$^3$) | Bulk Density (g/cm$^3$) |
|----------------|--------------------------------|------------------------|
| Ti             | 4.510                          | 4.265                  |
| Ti-40Nb        | 5.569                          | 5.281                  |
| Ti-40Nb-15HA   | 5.160                          | 5.086                  |

### 3.3 Compressive Strength

The mechanical behaviour of metal alloys was studied by compression tests using cylindrical samples are shown in Table 2. It can be observed that the strength of Ti increase when added 40% Nb due to a solid solution hardening effect. This is consistent with observations by other author working with Ti-Nb alloys [14]. Ti-40Nb-15HA give the lowest strength compared to other sample. When the HA incorporated into Ti-40Nb, the strength of the sample decline drastically which related to the brittleness and agglomeration of HA. Besides, microcracks and pores on Ti-40Nb-15HA also affect its strength and fracture pattern. The lower compressive strength can supported by the fracture surface. The microstructure appears to be less dense and brittle in Ti-40Nb-15HA as compared to Ti and Ti-40Nb, which show ductile behaviour. This is shown on the morphology of fracture surface in Figure 3.

**Table 2.** Compressive strength of Ti, Ti-40Nb and Ti-40Nb-15HA

|                | Compressive Strength (MPa) |
|----------------|-----------------------------|
| Ti             | 1186.66                     |
| Ti-40Nb        | 1353.00                     |
| Ti-40Nb-15HA   | 171.93                      |

**Figure 3.** Fracture morphology of the samples after compression test: Ti (Figure 3a), Ti-40Nb (Figure 3b) and Ti-40Nb-15HA (Figure 3c).
4. Conclusion

In this paper, the metallic biomaterials were synthesized by mechanical milling of powder consisting of Ti, Nb and HA forming Ti, Ti-40Nb and Ti-40Nb-15HA. Then, the samples were fabricated by powder metallurgy method. The effect of Nb and HA content on microstructure and mechanical property were investigated. The main conclusions can be summarized as follows.

i. Ti and Ti-40Nb show a smooth surface morphology and ductile behaviour while Ti-Nb-HA15 exhibited rough surface and brittle behaviour.

ii. With the addition of Nb content, the strength of Ti-Nb increase due to solid solution strengthening effect. HA is brittle and this result in a reduction of mechanical strength for Ti-40Nb-15HA. Besides, excessive HA content would also reduce the mechanical properties even further.

Ti-Nb-HA15 not only has a low density of metal alloy but also display better results in terms of its mechanical properties. By establishing a balance between strength and elasticity with human bone, a successful performance of a load-bearing bone implant can be achieved.

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