

MICROSTRUCTURE DEVELOPMENT OF SPARK PLASMA SINTERED Ti-Nb ALLOY BY HEAT TREATMENT

The β -phase Titanium (β -Ti) alloys have been under the spotlight in the recent past for their use as biomedical prosthetic materials owing to their excellent properties such as low elastic modulus, high corrosion resistance and tensile strength. Recently, Niobium (Nb) has gained a lot of attention as a β -phase stabilizing element in Ti alloys to replace Vanadium (V) due to its excellent solubility in Ti, low elastic modulus and biocompatibility. In this work, low cost Ti-20Nb binary alloy has been fabricated via powder metallurgy procedures. The blended powder mixtures of Ti and Nb were sintered at 900°C for 20 mins by the Spark Plasma Sintering (SPS) with an applied uniaxial pressure of 40 MPa. The heating rate was fixed at 50°C/min. The sintered alloy was subject to heat treatments at 1200°C in vacuum condition for various time durations. The characterizations of microstructure obtained during this process were done using FE-SEM, EDS and XRD. By increasing heat treatment time, as understood, the volume of residual Nb particles was decreased resulting in accelerated diffusion of Nb into Ti. Micro hardness of the alloy increased from 340 to 355 HV with the increase in β phase content from 30 to 45%. The resultant alloys had relatively high densities and homogenized microstructures of dispersed lamellar β grains in α matrix.

Keywords: TiNb alloy; Spark plasma sintering; Heat treatment; Microstructure; β -phase Titanium

1. Introduction

Titanium and its alloys are a group of endeared materials due to their attractive properties for structural and nonstructural applications. However, in spite of their lucrative properties such as high strength to weight ratio, resistance to corrosion, fracture toughness, the deployment of these alloys have been limited in the industry. The industry is currently dominated by Steel and Aluminum. The obvious reason behind this fact is the high production cost of Ti based parts. Many factors contribute to the high cost of Ti alloys. Mainly high cost of pure Titanium production and poor machinability contribute to the spike in price. In addition more than 80% of Ti metal goes into scrap [1]. These factors cause an unrecoverable increase in prices of Ti products rendering them unfavorable for most industrial applications. The aforementioned factors demand an approach for fabrication route which eliminates price increasing factors. Hence, in recent times there has been a growing emphasis on achieving desired alloys using powder metallurgy route. The key feature of powder metallurgy process is that we can fabricate near-net-shape and ready-to-use component which require little to no post fabrication processing. This relieves us from costly processing as well as greatly reduces the loss of material to scrap [2].

Although Ti alloys have still long way to go before being able to compete with other metals and alloys in many industrial application, their use in biomedical field has surely surpassed

the main competitors such as stainless steels and Co-Cr alloy. For a long period of time Ti-6Al-4V has assumed the driving seat for its use in dental as well as orthopedic implants due to its excellent balance of mechanical properties desired for such applications [3]. However, long term use of such implants has shown adverse effects on the health of its users. These problems are associated with cytotoxicity of Vanadium and Aluminum ions which cause diseases such as Alzheimer, Osteomalacia, and neuron damage [4,5]. In addition, even though the stiffness of Ti-6Al-4V (~120 GPa) is considerably lower than its counterparts such as Stainless Steel and Co-Cr (~230 GPa), it is still considerably higher than that of bone (~10-40 GPa). This stiffness mismatch causes what is known as “Stress-shielding” which causes bone resorption and failure of implant. Since the increase in life expectancy and growing need of such implants in much younger consumers, it is of prime importance that these issues must be dealt with in order to improve the implant lifetime and avoid painful revision surgeries. These concerns have propelled the researchers in hunt for an alloy composition that not only is free of Vanadium and Aluminum but also have stiffness comparable to that of bones. It has been revealed by comprehensive research that the stiffness is inversely proportional to amount of β phase present in the Ti alloy. In addition alloying addition such as Niobium, Tantalum, Molybdenum and Zirconium present superior corrosion resistance in body fluid [6,7]. For such purpose Niobium based Ti alloys have been under development and

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have proven to be an exciting prospect for biomedical as well as other industrial applications due to their outstanding properties.

In this study, Ti20Nb binary alloy has been developed using novel electric current assisted sintering technique commonly known as Spark Plasma Sintering (SPS) which has shown great prospect in attaining superior properties in comparison with the other sintering process including Hot Isotactic Pressing, Hot Pressing and Pressure less Sintering [8]. The resultant alloy underwent heat treatment for microstructure homogenization and the resultant microstructure development was observed. Micro hardness of the heat treated alloy was measured

2. Experimental Procedures

Titanium and Niobium powder of irregular morphology and 325 mesh ($<45\ \mu\text{m}$) size provided by Alfa-Aesar were used as starting materials in this study. The powders were weighed in 80 wt% Ti and 20 wt% Nb under vacuum conditions and ball milled for 24 hours to achieve homogeneous mixture. A calculated amount of ball milled powder was put into a graphite die of 20 mm diameter. Spark Plasma Sintering was used to sinter the ball milled powder at 900°C with 40 MPa. After sintering, the resultant body was subjected to heat treatment. The heat treatment facilitated the dissolution of Niobium and increased the β -phase content in the microstructure. High vacuum sintering furnace was used to carry out the heat treatment at 1200°C with vacuum of larger than 10^{-5} torr. The microstructure development

was studied as the heat treatment was done from 0 to 6 hours. Micro Vickers hardness was done on the alloy to investigate the effect of heat treatment. Samples were collected, polished and analyzed using X-ray diffraction (XRD; D8-Advance, Bruker Miller, USA) with a Cu-K α target operated at 40 kV and scanning electron microscope (FEG-SEM; JEOL, JSM-7100F, Japan) equipped with energy-dispersive spectrometry.

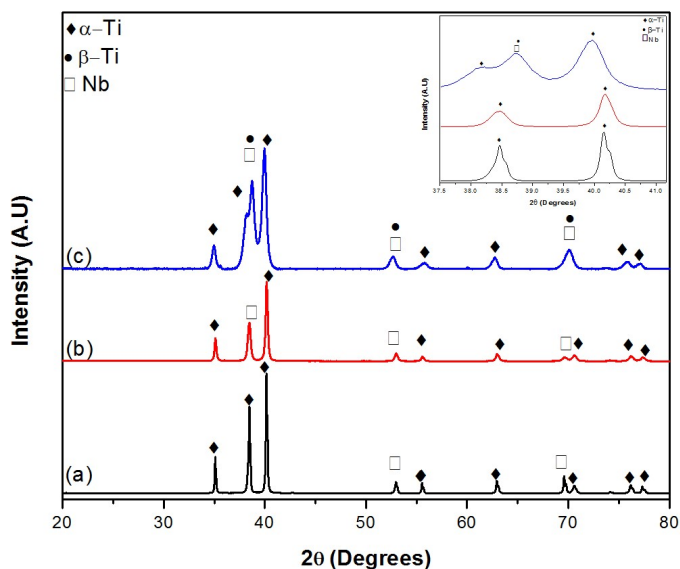


Fig. 1. XRD profiles of the (a) unmixed powder, (b) blended powder and (c) sintered sample at 900°C . Inset picture shows the peak broadening of powder after blending and peak shift that occurred after sintering

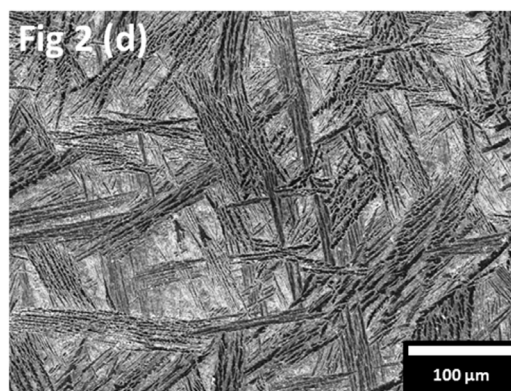
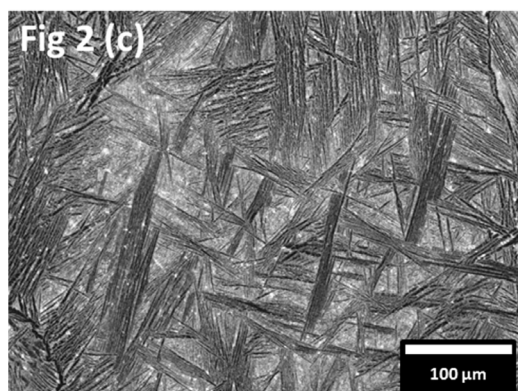
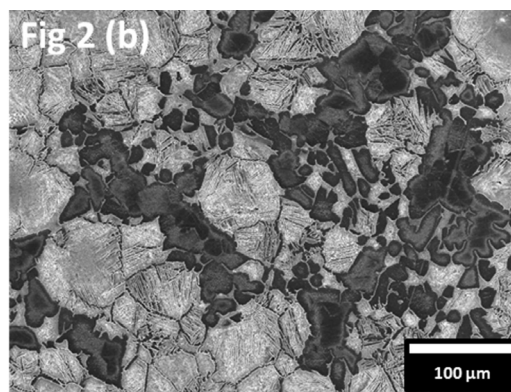
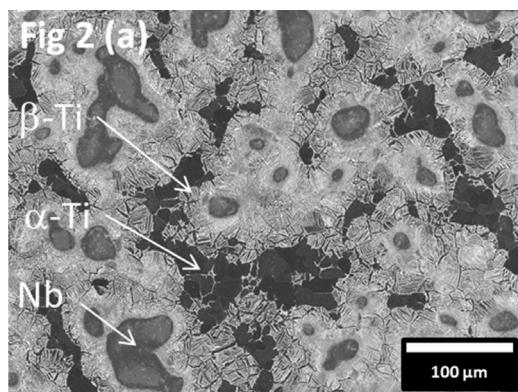


Fig. 2. SEM image of the microstructure evolution during heat treatment: (a) 0 hour, (b) 2 hours, 1200°C , (c) 4 hours, 1200°C , (d) 6 hours, 1200°C

3. Results and discussions

XRD results of the starting powders, ball milled powders and alloy sintered at 900°C with 40 MPa pressure are shown in Fig. 1. As it can be seen in the XRD, peak broadening occurred in the milled sample indicating reduction in size of the ball milled powder. There were no peaks observed other than the starting material confirming the absence of any kind of oxides or impurities. After SPS there was a peak shift observed in the XRD, as it can be seen in Fig. 1, the peak for α -Ti shifted from 40.3° to 40.0°. This peak shift can be attributed to the alloy formation between Ti and Nb. Furthermore, the formation of β phase was confirmed by the characteristic peak observed around 38.7°. It is important to mention that the XRD peaks of β -Ti and Nb overlap and it is hard to distinguish the two from each other. Since undissolved Niobium was present in the alloy at this stage therefore the peak is attributed to both β -Ti and Nb.

Figure 2 shows microstructure evolution of the alloy as the heat treatment was done on the sintered samples until 6 hours. As it can be seen in Fig. 2a, sintered sample without heat treatment consisted of large amount of unreacted α -Ti grains while unreacted Nb grains homogeneously are spread across the matrix. As Niobium is a β phase stabilizer, Titanium grains in the locality of Niobium grains had started the transition from α to β phase. This showed that the diffusion of Nb into Ti grains had initiated at 900°C which was above β transus temperature. However, the diffusion at this temperature was extremely slow. Afterwards the sample was heat treated for 2 hours at 1200°C and the diffusion of Nb particles into Ti sped up as can be seen in Fig. 2b. Almost all the Nb particles had lost their discreet identity and had now converted into Nb rich core. Pure globular α -Ti grains were still observed in the matrix. Fig. 2c shows that after 4 hours of heat treatment was done the lamellar microstructure of α and β Ti had spread throughout the matrix. At this stage, no discreet Nb particles were observed with the microstructure now dominated by lamellar microstructure. Increasing the heat treatment time to 6

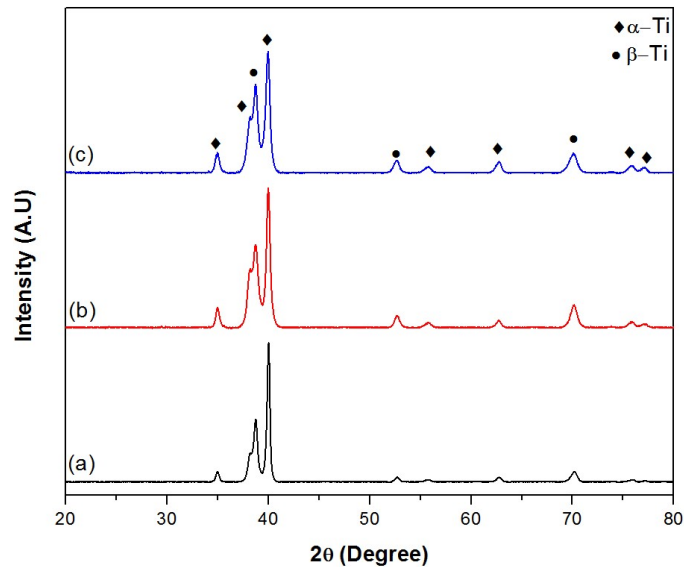


Fig. 3. XRD analysis of heat treatments at 1200°C for (a) 2 hours (b) 4 hours and (c) 6 hours

hours had no observable effect on the microstructure apart from coarsening of grains. Figure 3 illustrates XRD of the samples heat treated at 1200°C from 2-6 hours. It can be clearly seen that the intensity of β phase increased proportional to the heat treatment time. The peak intensity of β phase after 2 hours was about 30%. The percentage increased to 37% after 4 hours and 45% after 6 hours of heat treatment. Figure 4a,b depict the hardness of the sample heated for 4 and 6 hours; respectively.

Hardness values of 10 different points were taken by applying a load of 300 g on the sample. Average hardness value of 4 hours heat treated sample was 342 HV whereas the hardness of the material increased to 355 HV. The hardness values are considerable higher than the reported values of commercially Pure-Ti (~250 HV); in addition these values are similar to the reported hardness values of the prominent Ti alloy Ti-6Al-4V. The increase in hardness with the heat treatment time can be attributed to multiple factors.

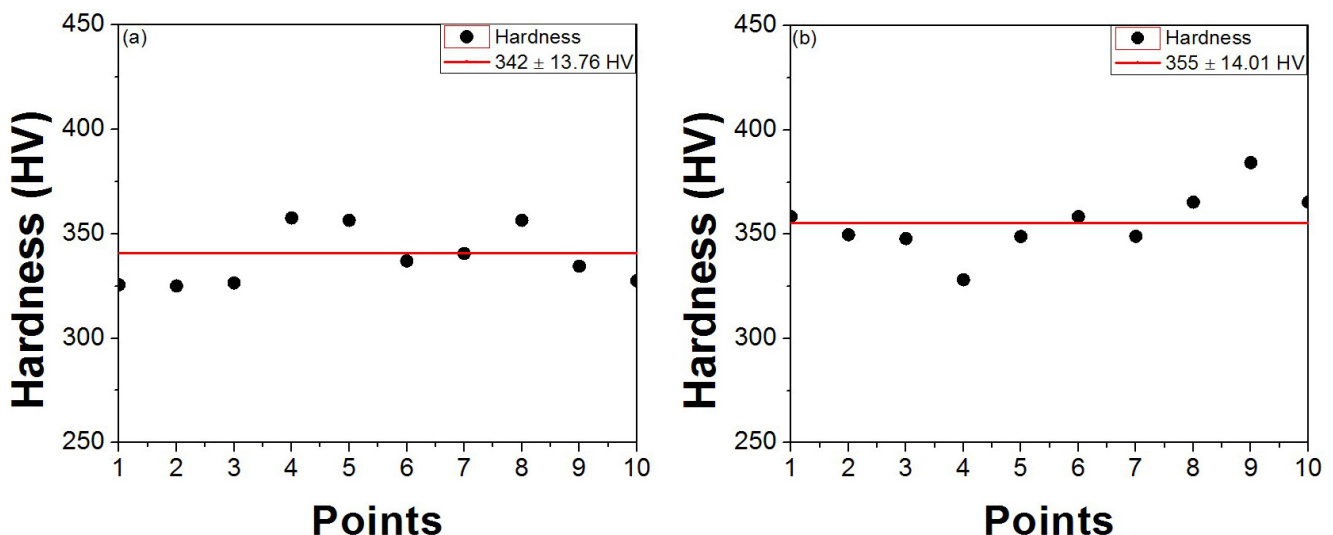


Fig. 4. Vickers micro hardness testing of heat treated samples (a) 4 hours, (b) 6 hours

The hardness can be affected by factors such as density, microstructure or phases [9-12]. Nazari et. al. reported that the increase in density of Ti-Nb alloy resulted in the increase in the hardness values [9]. Sieniawski et. al. argued that the β phase and lamellar morphology of the microstructure will improve the mechanical properties of the Ti alloys [10]. Lee et. al. suggested that the micro hardness of β phase is higher than that of α phase [11]. The density of the sample was around 4.95 g/cm^3 after heat treatment which was similar to the measurements done after sintering therefore it is presumed not to be a factor in hardness change. As it was observed in Fig. 2c,d both have similar lamellar morphology therefore the microstructure also did not affect the hardness change. Therefore it can be concluded that the phase change played a definite role in increasing the hardness. The increase in β phase peak intensity from 37 to 45% with heat treatment time caused the increased hardness keeping in good agreement with the aforementioned report [10,11]. We were able to achieve 355 HV using powder metallurgy which are similar to the values reported for cast Ti-Nb alloy [12]. These results indicate that by using powder metallurgy, we can achieve properties similar to the alloys achieved using costly conventional methods.

4. Conclusion

In this study, β -phase Titanium alloy containing Niobium as alloying element was designed using Spark Plasma Sintering and heat treatment method. The Niobium dissolution in Titanium matrix was observed as the heating of the alloy took place. Initially, before the commencement of heat treatment, microstructure mainly consisted of separate α -Ti grains and Nb grains with lamellar α and β structure on the interface between the two. As the heat treatment was done at 1200°C , the lamellar

microstructure began to grow. After 4 hours of heat treatment, the microstructure consisted of only lamellar morphology. The micro hardness of the sample increased with increasing the heating time.

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