Synthesis of Ti-6Al-4V alloy with nano-TiN microstructure via spark plasma sintering technique

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Abstract. The effect of nano-TiN dispersion strengthened Ti-6Al-4V via spark plasma sintering method has been investigated. Ti-6Al-4V with 4 vol. percent of nano-TiN were mixed in a Turbula shaker mixer for 8 h at a speed of 49 rpm and the admixed powders were sintered at sintering temperature range of 1000 - 1100 °C, holding time of 10-30 mins, heating rate of 100 °C/min under an applied pressure of 50 MPa. The morphology of the as-received and sintered compacts was examined by scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) and phase analysis was done by X-ray diffractometry (XRD). The sintered compacts without nano-TiN reveal lamellar structure while reinforced Ti-6Al-4V with nano-TiN shows a bimodal structure and titanium nitride has a great influence on α grain growth at high temperature. Furthermore, the microstructural formation mechanism was investigated. With the addition of the content of Ti-6Al-4V with 4 vol.% of nano-TiN, the micro-hardness also improved and this was due to homogenous distribution of TiN in Ti-6Al-4V matrix.

1. Introduction

Powder metallurgy (PM) has gained attention over the conventional methods for the fabrication of composites reinforced with particles by applying new powder metallurgy processes such as using spark plasma sintering (SPS) [1-3]. The advantageous of powder metallurgy which includes better control on the microstructure, uniform dispersion of reinforced particle (second) in the sintered composite [3, 4]. The powder metallurgy technique has been proven for the production titanium alloys and their composites [5]. Furthermore, spark plasma sintering (SPS) method has been developed as a newly versatile technique to rapidly fabricate a number of materials including metals, composites and ceramics. [6-8]. Compared with other conventional methods of processing titanium alloys and composites, which takes longer time, required higher temperature and higher density is produced [9, 10]. However, longer time of sintering could cause grain growth, which is detrimental to the properties and microstructure of the composite material [11, 12]. Recent development in technology allows materials to be sintered with a reduction in time, temperature with the positive impact on the economic aspect of the fabrication of composite.

Titanium and its alloys are widely used due to their specific properties they possess like hardness, high specific strength and high corrosion resistance for various applications [13, 14]. Furthermore, Ti-6Al-4V remains the most widely used in various applications due to its extreme combination of mechanical

properties as well corrosion resistance Among the various titanium alloys, Ti-6Al-4V alloy is still the most commonly used one due to its favourable combination of mechanical properties and corrosion resistance [15]. Reinforcing titanium alloys with hard precipitates in sintered matrix composites such as titanium nitride helps with the improvement of corrosion and wear resistance of the materials. The aim of this research is to investigate the effect of reinforcement in the sintered materials in terms of increase in strength and hardness of titanium materials by developing a novel titanium matrix composite and dispersion-strengthened titanium material.

2. Experimental procedure

The materials used in the present composite production are a commercially pure Ti-6Al-4V powder (99.9%, 25 μm by TLS-Technik, Germany) and TiN (97%, 20 nm supplied by Nanostructured & Amorphous Material Inc., Texas, USA) were used as reinforcement phase. A composite mixture of Ti-6Al-4V was added to TiN while, turbula mixer was used to blend the powders according to varying ratios of 4 vol.% TiN for 8 h at a speed of 49 rpm so as to achieve a homogeneous mixture of titanium matrix composite. The mixed powders were sintered using a spark plasma sintering equipment (HHPD-25 FCT type SPS, Germany), the mixed powders were fed into a graphite die mould and then pressed with a pressure of 10 MPa. The die with an internal diameter of 30 mm and thickness of 5 mm was put into the SPS chamber machine. The sintering temperature range of 1000 - 1100 ºC for 10 and 30 min, while the heating rate was 100 ºC/min, and the applied pressure of 50 MPa used from the start to the end of the sintering operation. Sintered titanium composites produced were then characterized by XRD and SEM analyses.

The sintered density of the samples was carried out by Archimedes principle using an electronic balance with an accuracy of ±0.001 g. The micrograph of the synthesized composites was evaluated using field emission scanning electronic microscope (JEOL JSM-7600F) equipped with energy dispersive X-ray spectroscopy (EDS) at an accelerating voltage of 15 kV. An X-ray diffraction (PW1710 Philips diffractometer, with monochromatic Cu K radiation at 40 kV and 20 mA) was performed to identify the presence of the constituent phases of the sintered composites using an highscore X'Pert Software. Prior to observation, the surface of the sample was prepared by silicon carbide with the grit size of 320 and then polished with diamond paste to 0.2 μm. Kroll's reagent was used as an etching solution for 10–30 s in accordance with ASTM E3-11 ASTM standard [16] in order to reveal the grain boundaries of the sintered composites.

The hardness and fracture surface of the sintered composites were carried out in order to determine the level of mechanical properties.   The micro indentation test was done by using a Vickers micro hardness tester (FALCON 500 series) at room temperature upon a polished surface at a load of 100 gf (0.98 N) and dwell time of 15 secs, while the fracture surfaces were observed by using a SEM to check the morphology.

3. Results and discussion

Figure 1a. present SEM micrograph of Ti-6Al-4V while Figure 1b demonstrates SEM morphology of admixed Ti–6Al–4V and TiN powders subjected to intensive, periodically pulsating motions (rotation, translation and inversion) [17]. It could be seen that TiN diffuses into Ti–6Al–4V. Turbula mixing of Ti–6Al–4V with nano-sized titanium nitride powder resulted in even dispersion within the titanium alloy powder. The effectiveness of mixing process is usually described by the homogeneity of the mixed powder [9].
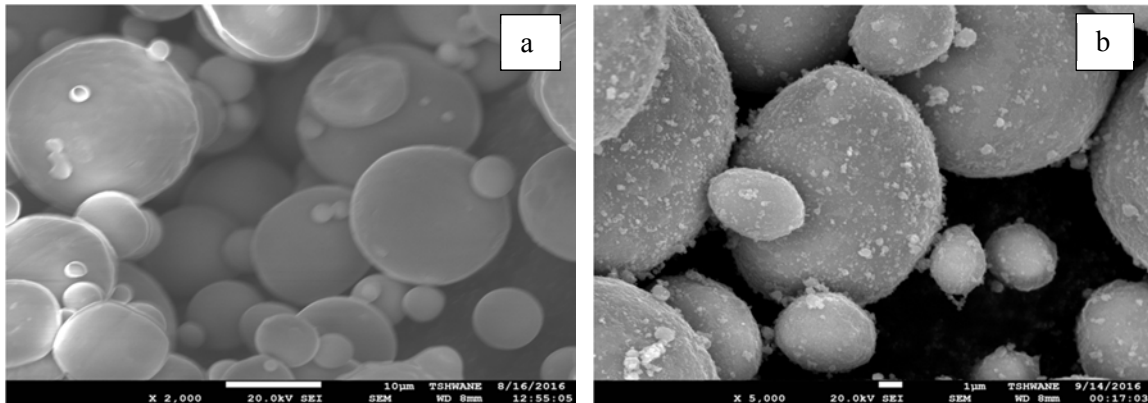
Figure 1. (a) SEM morphology of Ti–6Al–4V powder and (b) SEM morphology of Turbula mixed powders.

Figure 2 present the effect of sintering temperature and holding time on the displacement of punches during sintering and this demonstrates the deformation of the samples at an applied pressure of 50 MPa. Firstly, a sintering temperature of 250 – 300 ^{o}C was maintained constantly for 240 to 420 s. Thereafter, it was increased to 1000 ^{o}C and 1100 ^{o}C respectively and maintained for 600 to 900 s. At the initial stage, the displacement increases from 0.3 to 0.5 mm under the effect of applied pressure exacted on it, although the initial temperature was too low to have an effect on the material. The displacement observed was as a result of cold compaction of the powder. Displacement begins to increase as a result of rising in temperature thereby causing rearrangement of the particles. The effect of pressure becomes stronger which causes the escape of trapped air from the green compact. The densities of samples sintered at 1000 – 1100 ^{o}C for 10 and 30 mins respectively resulted in the theoretical density of 97–99% upon the addition of titanium nitride. The increase in densification with increase in temperature can further lead to the grain growth which therefore leads to gradual closure of pores in the material [18].
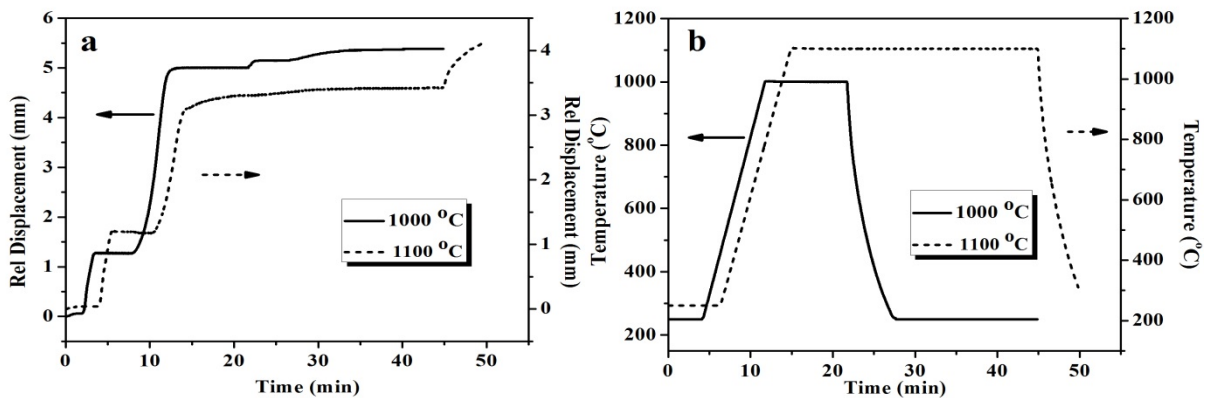

Figure 2. (a) Relative displacement with time and (b) Sintering temperature with time of SPS process.

The hardness value of all the composites was higher irrespective of the sintering temperature and time than Ti–6Al–4V alloy, which indicates that the addition of titanium nitride into titanium alloy really enhanced the hardness of the sintered composites from 389 to 531 $HV_{0.1}$. The microstructure contribution to the observed increase in hardness was as a result of the uniform distribution of TiN particles and Ti_2N hard phases in Ti–6Al–4V matrix. The increase in microhardness with increasing temperature and time may be attributed to decrease in porosity and increases in sintered density. Also, the increase can be explained by the increase in α volume fraction with hardness phase and presence of nitrogen in solid solution.

Figure 3 shows SEM microstructure of Ti–6Al–4V with an equiaxed structure with intergranular β and evidence of prior β grain boundaries, while figure 4 shows Ti–6Al–4V reinforced with 2 and 4 vol.% content of titanium nitride. The presence of TiN shows a relatively refined homogeneous distribution in the composite matrix which was located at the grain boundaries. Moreover, the α-nucleation sites show an increase when TiN particles were incorporated which further acted as a point of nucleation for the primary α-phase. Also obstructions which forestall those lamellae growth development in the microstructural transform. The introduction of nano-sized TiN in the titanium matrix is suggested to be responsible for the enhancement of Ti–6Al–4V alloy transforming to bimodal-structure. The composite were nearly free from porosity.
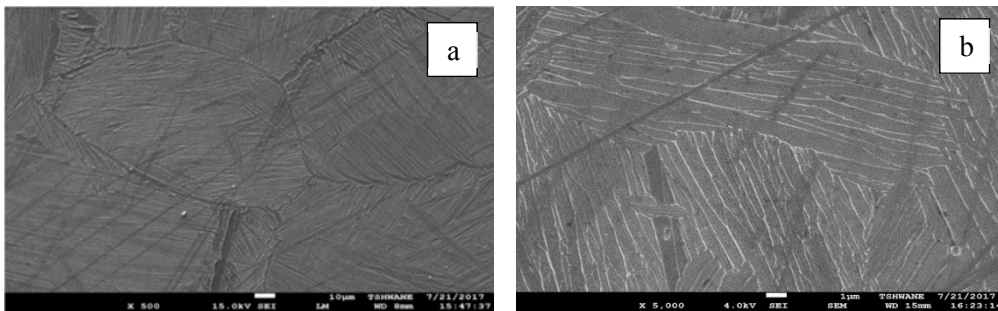

Figure 3. SEM micrograph of sintered Ti-6Al-4V at different magnifications.
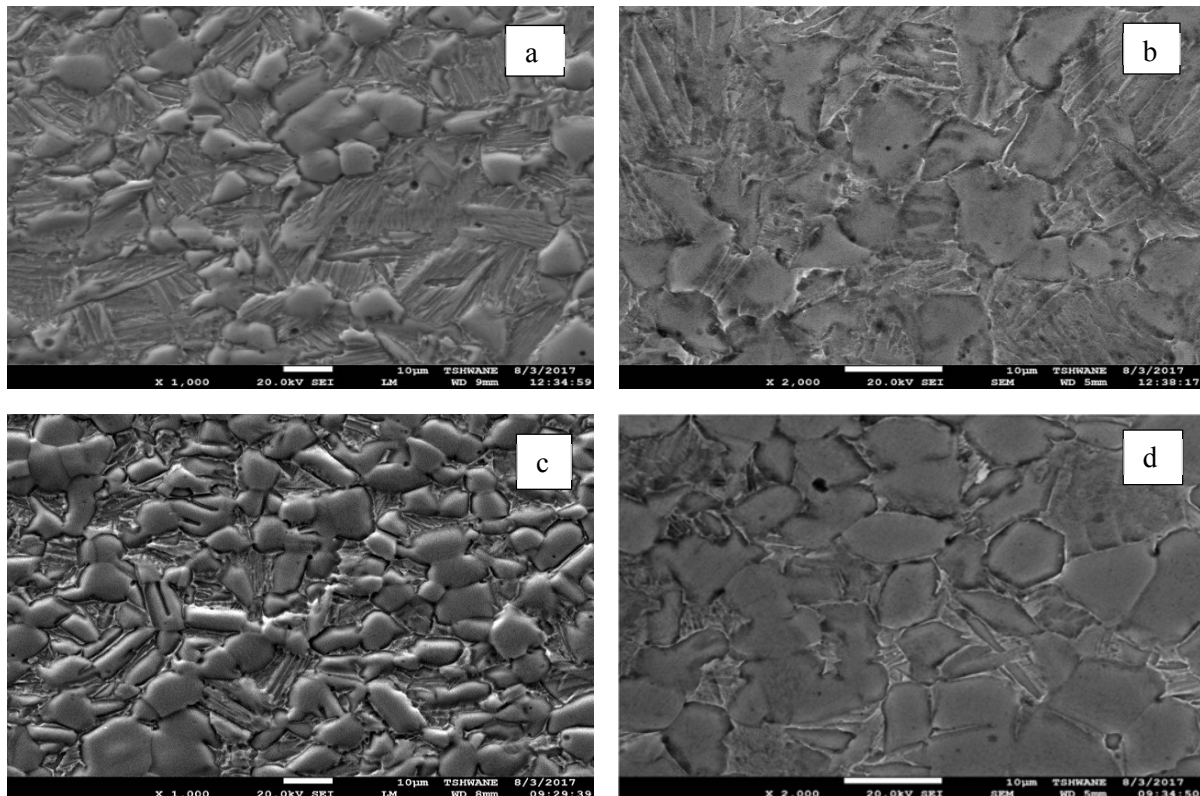

Figure 4. SEM images of Ti-6Al-4V with TiN: (a-b) 2 vol% TiN and (c-d) 4 vol% TiN.

Figure 5 reveals fracture morphology of the sintered Ti-6Al-4V with cleavage feature and dimples. Ti-6Al-4V reinforced with 4 vol.% TiN shows a transgranular pattern with fine dimples features and TiN grains thereby causing cleavage facets with a river pattern. This fracture mode remains a complex one.

These features may be as a result of TiN addition and which may improve the fracture hardness of the sintered composites.
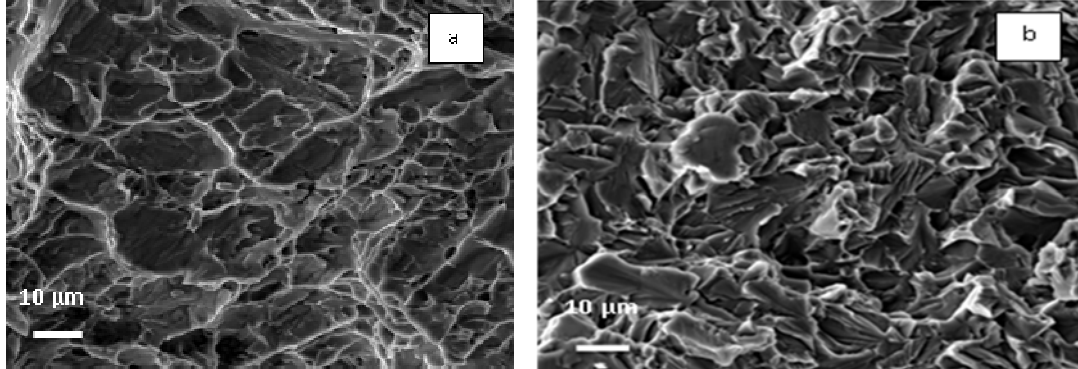

Figure 5. SEM fractographs of sintered (a) Ti-6Al-4V and (b) Titanium matrix composite with 4 vol.% TiN addition.

4. Conclusion
The sintering temperature and time have a critical impact on densification, microstructure, hardness and fracture surface of the sintered titanium matrix composites. Conclusions are as follows:

1.   For these materials, the relative density was between 97.53 – 99.89%. Sintering at higher temperatures and time tends to promote the formation and growth of new phases in the sintered matrix composites and microstructural transformation from lamellae to bi-modal structures.

2.   The microhardness of the sintered composites significantly increases from 389 HV and upon addition of 4 % volume fraction of TiN in the matrix increases to 531 $HV_{0.1}$.

3.   An intergranular was revealed with Ti–6Al–4V which further transform within the titanium matrix composite to transgranular with fine dimples features.

5. References
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