Effects of refractory nitride reinforcements on the microstructure, densification and microhardness of Ti6Al4V-based binary composites produced by spark plasma sintering

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Abstract. The effects of different refractory nitrides: aluminium nitride (AlN), titanium nitride (TiN) and hexagonal boron nitride (h-BN) reinforcements on the microstructure, densification and microhardness characteristics of spark plasma sintered Ti6Al4V-based binary composites were studied. The microstructure was examined by optical microscopy, densification was evaluated according to the method of Archimedes and the microhardness of the sintered composites was measured by Vickers microhardness tester. The SPS technique was successfully used to consolidate Ti6Al4V powder and 3 wt.% nanoparticles of AlN, TiN and h-BN respectively. The binary composites produced attained nearly full theoretical densification (98.22 to 99.54%) due to enough diffusional mass transport ensuing in solidly bonded compact of the matrix and the refractory nitride reinforcements. Ti6Al4V-3h-BN composite gave the optimal combination of relative densification and microhardness values of 99.54% and 7.03 GPa which exceeds 200% that of the monolithic alloy and about 48% superior to both composites with TiN and AlN reinforcements.

1. Introduction
Titanium and its alloys find wide use in airframes, jet engine and automotive structures owing to their exceptional combination of properties: moderate density, high structural properties (e.g. strength, stiffness, toughness and fatigue resistance), creep strength, and excellent resistance to corrosion and oxidation [1-2]. Of the many types of titanium alloys with different compositions in use today, the most important is Ti6Al4V. The alloy is comprised of both α-Ti and β-Ti, and therefore, regarded as α+β-Ti alloy [1,3]. Despite the undeniable benefits, extensive applications of Ti6Al4V alloy in the automotive and aerospace industries has been restricted because of low hardness and poor tribological properties, characterized by a high friction coefficient, weak self-lubricating property and severe adhesive wear, and insufficient high-temperature oxidation resistance [4-6]. The last five decades have witnessed new developments in titanium matrix composites (TMCs) which possess high strength, good wear resistance, high temperature stability owing to the added reinforcement. Superior desirable set of mechanical properties are obtained when fine and thermally stable ceramic particulates are dispersed in a TMC [5,7-8].

In recent times, studies have shown tremendous advantages of applications of refractory nitrides reinforcements in the development of materials meant for use in the automotive and aerospace industries. These nitrides are of a strong structural and chemical nature especially in applications involving high
temperature and/or corrosive environments where most metals are no longer suitable. Refractory nitrides consist of the nitrides of Ti, V, Zr, Nb, Hf, Ta, B, Al and Si [7-8]. Ray et al. [8] fabricated Al-based composites with 10 and 30 wt.% titanium nitride (TiN) by using pressureless sintering and hot-pressing techniques. The presence of titanium nitride (TiN) particles at grain boundaries played an important role in improving the densification, and results in improved mechanical properties. de Araujo et al. [9] reinforced Al with aluminium nitride (AlN) and silicon nitride (Si₃N₄) separately by mechanical alloying, cold uniaxial compaction and vacuum sintering. The results showed better Vickers hardness as mass fraction of reinforcements were increased. Yang et al. [10] and Matizamhuka [11] reported the frequent challenges manufacturers encounter in the synthesis of nanosized materials by conventional sintering methods. However, at the instance of the development of spark plasma sintering (SPS) technology, such recurrences are no more menacing. For instance, two dissimilar materials of Al and BN which cannot be prepared in a composite form via conventional powder metallurgical method as reported by Du et al. [12] were successfully achieved by Firestein et al. [13] where Al-based composite with BN nanoparticles reinforcement was synthesized via spark plasma sintering method. Kgoete et al. [14] also produced Ti6Al4V- Si₃N₄ composite by using spark plasma sintering process. In all these studies, incredible improvement in the mechanical properties of the MMCs were achieved. Besides, SPS offers rapid densification, with minimal grain growth, enhanced microstructure combined with improved mechanical properties and more within reduced sintering times in contrast to the conventional hot-pressing technology [11,15].

In this work, SPS was utilized to synthesize Ti6Al4V-based composites reinforced with nanoparticles of AlN, TiN and h-BN. The effect of the refractory nitride reinforcements on the microstructure, densification and microhardness of the composites were also investigated.

2. Materials and methods
The raw materials in this work were commercially pure Ti6Al4V powder (>99%, 45-90 µm spherical particle sizes by TLS Technik, Germany) used as the matrix and AlN, TiN and h-BN (>99%, 100-200 nm by Hongwu International Group Ltd., China) as the reinforcements respectively. Three sets of Ti6Al4V-based powders of the same weight with each consisting 3 wt.% of each reinforcement and a control of pure Ti6Al4V were measured with a high precision scale and mixed in a tubular mixer rotating at a speed of 100 rpm for 10 hours to achieve homogeneous mixture. Some steel balls of approximately φ5mm were incorporated into the powder container at the ball-to-powder weight ratio of 2:5 during the mixing for better distribution of the reinforcement in the matrix. The admixed powders were measured into a graphite die of φ30mm to produce 10mm thickness of the composite and consolidated by using spark plasma sintering machine (SPS FCT Systeme GmbH, Germany) under argon atmosphere with optimized sintering parameters (1000 °C temperature, 30 MPa pressure, 100 °C/min heating rate and 10 min dwell time) obtained from an initial optimization experiment designed by Taguchi method. The density measurements of the sintered samples were carried out by using Archimedes’ principle where the average value of six repeated measurements was taken for each sample and recorded as the effective density and the theoretical density was calculated according to the rule of mixture. Subsequently, the relative densification of each sample was calculated as the ratio of the effective density and theoretical density multiplied by 100% [14,16].

Later, the samples were first grinded by using 120, 400, 500, 800, 1200, 2400, 4000 grit papers and then polished by using diamax powder (6 µm, 3 µm and 1 µm) in solution to achieve mirror-like polish. Afterwards, Kroll’s reagent was used to etch the samples, and the surfaces were observed under an optical microscope (Olympus BX 51 TRF, Japan). Finally, microindentation of the sintered samples was done by using Vickers microhardness tester (FUTURE-TECH FM-800 from Japan) with a dura scan diamond indenter and test load of 300gf for 15 seconds with a spacing of 0.5. The average value of five indentations was taken for each sample and recorded as the effective microhardness value.

3. Results and discussion
The details of the results of the experiment obtained for relative densification and microhardness measurement is shown in table 1 and figure 1 shows the graph of the comparison of the relative
densification and microhardness values of Ti6Al4V alloy, Ti6Al4V-3AlN, Ti6Al4V-3TiN and Ti6Al4V-3h-BN.

Table 1: Densification and microhardness measurement details

| Sample                | Effective density (g/cm³) | Theoretical density (g/cm³) | Relative densification (%) | Microhardness (GPa) |
|-----------------------|---------------------------|----------------------------|---------------------------|--------------------|
| Ti6Al4V alloy         | 4.42                      | 4.50                       | 98.22                     | 3.25               |
| Ti6Al4V-3AlN          | 4.41                      | 4.45                       | 99.10                     | 4.79               |
| Ti6Al4V-3TiN          | 4.44                      | 4.52                       | 98.23                     | 4.75               |
| Ti6Al4V-3h-BN         | 4.36                      | 4.38                       | 99.54                     | 7.03               |

Figure 1. Graph showing the comparison of the relative densification and microhardness values of Ti6Al4V alloy, Ti6Al4V-3AlN, Ti6Al4V-3TiN and Ti6Al4V-3h-BN.

Figure 2. Optical micrographs depicting the microstructure and representative diamond-shaped microindentation on the surface of: a. Ti6Al4V alloy b. Ti6Al4V-3AlN c. Ti6Al4V-3TiN d. Ti6Al4V-3h-BN.
The optical micrographs of the samples sintered at 1000 °C of temperature, 30 MPa of pressure, 100 °C/min of heating rate and 10 min of dwell time are given in figure 2 (a-d) in order to show the distribution of the reinforcement nanoparticles of AlN, TiN and h-BN and their effects on the densification and hardness property of the matrix. The relative densification of the matrix calculated from an effective density of 4.42 g/cm³ and theoretical density of 4.50 g/cm³ and Vickers microhardness were 98.22% and 3.25 GPa respectively. The micrograph in figure 2a shows a dominance of α-Ti lamellar (which is responsible for toughness and creep resistance) and little evidence of prior β-Ti grain boundaries (which is responsible for high strength and fatigue resistance) in the Ti6Al4V-rich matrix can be said to be the reason for the low microhardness value of the alloy [1,3] as shown by the large-sized diamond indentation. The relative densification results (98.22 to 99.54%) obtained as presented in table 1 and figure 1 indicate that the SPS consolidation technique applied to synthesize the Ti6Al4V-based composites was effective and produced nearly full theoretical densification with h-BN reinforcement (99.54%). Figure 2b presents the micrograph of a decent distribution of coarsened nanoparticles of AlN in the Ti6Al4V-rich matrix with a slightly increased microhardness value of 4.79 GPa than the TiN reinforcement as denoted by the relatively moderate-sized diamond indentation. This increase can be traced to the presence of hard AlN phase which imparted more hardness and acted as further nucleation points for strong β-Ti phase [17]. Similarly, the moderate microhardness value of 4.75 GPa of Ti6Al4V-3TiN as depicted in figure 2c can be ascribed to the formation of dendritic structure demonstrating a significantly coarsened TiN and a relatively refined homogeneous dispersion at the grain boundaries of the Ti6Al4V-rich matrix. However, Ti6Al4V-3h-BN binary composite gave the optimal combination of relative densification and microhardness values of 99.54% and 7.03 GPa which exceeds 200% that of the matrix (3.25 GPa) and about 48% superior to both composites with TiN and AlN reinforcements as ably characterized by the smallest diamond indentation in figure 2d. This phenomenon can be attributed to adequate mixing of the powders where the nanoparticles of h-BN filled up pore spaces within the titanium alloy matrix which are the primary causes of poor densification and the effectiveness of the consolidation method which enables development of dense products [18]. Besides, there is an indication of better closure of pores and refined grains which could be the reason for the complete densification [16]. In general, it is found that the hardness property is proportional to the relative densification which is promoted by enough diffusional mass transport ensuing in solidly bonded compact of the matrix and the refractory nitride reinforcements [19]. Likewise, the considerable improvement in the hardness property of the matrix suggests that SPS aids the synthesis of refractory nitride nanoparticles of AlN, TiN and h-BN reinforced titanium matrix composites with superior mechanical characteristics useful in the automotive and aerospace industries.

4. Conclusion
In this work, SPS was usefully applied to synthesize Ti6Al4V-based binary composites with three different refractory nitride nanoparticles of AlN, TiN and h-BN with desirable characteristics. The effects of these reinforcements on the microstructure, densification and microhardness of the sintered composites were studied. The following conclusions are therefore made:
1. The consolidation of Ti6Al4V powder and nanoparticles of 3 wt.% of AlN, TiN and h-BN by SPS produced nearly full theoretical densification (98.22 to 99.54%) of the sintered composites which gives credence to the effectiveness of the consolidation technique enabled by enough diffusional mass transport ensuing in solidly bonded compact of the matrix and the refractory nitride reinforcements.
2. Ti6Al4V-3h-BN binary composite gave the optimal combination of relative densification and microhardness values of 99.54% and 7.03 GPa which exceeds 200% that of the monolithic alloy (3.25 GPa) and about 48% superior to both composites with TiN and AlN reinforcements.

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