Influence of varied process parameters on the microstructure, densification and microhardness of spark plasma sintered Ti-6Al-4V/h-BN binary composite

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Abstract. The influence of varied process parameters involving three levels of temperature, pressure, heating rate and dwell time on the microstructure, densification and microhardness of spark plasma sintered Ti-6Al-4V/h-BN binary composite was studied. Taguchi design method was adopted to randomize the SPS process parameter levels. The microstructure was analyzed by optical microscopy, densification was determined based on the principle of Archimedes and Vickers microhardness tester was used to evaluate the microhardness of the sintered composite. The consolidation of Ti-6Al-4V powder and nanoparticles of 3 wt.% of h-BN via SPS produced nearly full theoretical densification of 99.77% and the sintered composite gave a microhardness value of 710.37 HV which is more than 200% that of the monolithic alloy. The best combination of relative densification and microhardness were obtained at the sintering parameters of 1000 °C of temperature, 40 MPa of pressure, 100 °C/min heating rate and 15 min of dwell time. Generally, it was found that improved microstructure, densification and microhardness were influenced by the high temperature of sintering and low rate of heating that gave room for adequate diffusional mass transport resulting in solid bonding between the particles of the matrix and the ceramic reinforcement.

1. Introduction

Ti–6Al–4V alloy combines high strength-to-weight ratio, excellent corrosion resistance, good high-temperature strength, stiffness, good toughness, moderate density, low modulus and good biocompatibility. Thus, the alloy gains enormous attention in the aerospace, chemical and petrochemical, marine, energy and biomaterials industries. Nevertheless, the alloy still suffers from inadequate wear, hardness and poor antifriction properties demonstrated in certain service conditions which have limited its general usage [1-2]. Recently, titanium matrix composites (TMCs) have been developed which possess high strength, good wear resistance, high-temperature stability owing to the added reinforcement. Most sought after set of mechanical properties are commonly realized when fine and thermally stable ceramic particulates are added to a Titanium Matrix Composite [3-4].

Hexagonal boron nitride (h-BN) ceramic is the most stable BN phase widely employed in various field of aerospace, high temperature technology, electrotechnology, metallurgical and chemical engineering applications [5-6] due to its excellent lubrication properties, low density, high temperature stability, chemical inertness, high thermal conductivity and non-toxicity [7-8]. In recent years, many studies showed creditable mechanical, chemical, lubricating and high-temperature properties of
hexagonal boron nitride [9-10]. Consequently, h-BN has been conceived to be an effective reinforcement to compensate for the present shortcomings of Ti-6Al-4V alloy. However, due to the poor sinterability of h-BN, it is continuously difficult to manufacture its dense products by using conventional consolidation methods [9-11]. Yang et al. [11] reported successful densification of hexagonal boron nitride through self-densifying mechanism via spark plasma sintering (SPS). SPS can process advanced nanomaterials with controlled grain growth, rapid heating/cooling rates, reduced sintering times, enhanced microstructure, better densification combined with improved mechanical properties [12-13]. Moreover, the production technology of hexagonal boron nitride–reinforced Ti–6Al–4V alloy has hardly ever been reported.

A major concern in a production line is the quality of products and the success of an industry is determined by the consistency and high production rate of quality products. The process parameters and the quality of the products are well connected. Inappropriate combination of process parameters can cause defects in products and optimal combination of process parameters can improve the products quality meaningfully [14,15]. The basic SPS process parameters comprise the temperature, pressure, heating rate and dwell time. These parameters are key to the quality of the sintered products. Hence, it is imperative to randomize these parameters to obtain optimal sintered product quality characteristics and maximize scarce resources concurrently. A very useful method employed in the randomization process is Taguchi method. Taguchi method is a simple, economical, quick and feasible method in designing high-quality processes and in recognizing proper process parameters to achieve optimal results [14,16-17].

In this work, the authors studied the influence of varied process parameters involving three levels of temperature, pressure, heating rate and dwell time on the microstructure, densification and microhardness of spark plasma sintered Ti-6Al-4V/h-BN binary composite. Taguchi design method was adopted to randomize the SPS process parameter levels.

2. Materials and methods

Commercially pure Ti-6Al-4V powder (>99%, 45-90 µm spherical particle sizes by TLS Technik, Germany) and h-BN (>99%, 100-200 nm hexagonal crystal form by Hongwu International Group Ltd., China) were used as the matrix and reinforcements respectively. The powders were measured according to the stoichiometric proportion of Ti6Al4V-3% h-BN with a high precision scale and mixed in a tubular mixer rotating at a speed of 100 rpm for 10 hours to achieve homogeneity.

In the Taguchi design, four parameters: temperature, pressure, heating rate and dwell time, were chosen at three levels: A (800°C, 900°C and 1000°C), B (30MPa, 40MPa and 50MPa), C (100°C/min, 300°C/min and 300°C/min) and D (5mins, 10mins and 15mins). Minitab 19 was used to generate Taguchi L9 3^4 orthogonal array with four columns and nine rows, indicating a total of nine runs of experiment as shown in table 1 where A represents the temperature in °C, B represents the pressure in MPa, C represents the heating rate in °C/min, and D represents the dwell time in min. Correspondingly, 1 represents the least, 2 represents the average, and 3 represents the greatest of the parameters.

The admixed powders were measured in a graphite die of φ30mm to produce 10mm thickness of the composite and consolidated according to the design in Table 1 by using spark plasma sintering machine (SPS FCT Systeme GmbH, Germany) under argon atmosphere. 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%.

Later, the samples were first grinded by using 120-4000 grit papers and then polished by using diamax powder (6 µm, 3 µm and 1 µm) in solution to achieve mirror-like polish. Afterward, Kroll’s reagent was used to etch the samples, and the surfaces were observed under an optical microscope.

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 of the samples.
Table 1. Taguchi L9 $3^4$ orthogonal array generated for the experiment and symbols.

| Experiment run | SPS parameters and levels | Symbol  |
|----------------|---------------------------|---------|
| 1              | A1B1C1D1                  | A1B1C1D1|
| 2              | A1B2C2D2                  | A1B2C2D2|
| 3              | A1B3C3D3                  | A1B3C3D3|
| 4              | A2B2C3D1                  | A2B2C3D1|
| 5              | A2B1C2D3                  | A2B1C2D3|
| 6              | A2B3C1D2                  | A2B3C1D2|
| 7              | A3B1C3D2                  | A3B1C3D2|
| 8              | A3B2C1D3                  | A3B2C1D3|
| 9              | A3B3C2D1                  | A3B3C2D1|

A = temperature in °C, B = pressure in MPa, C = heating rate in °C/min, and D = dwell time in min. 1 = least, 2 = average, and 3 = greatest of the parameters.

3. Results and discussion

The details of the results of the experiment obtained for relative densification and microhardness measurements and microstructure study is seen in table 2 and figure 1, while the individual effect of temperature, pressure, heating rate and dwell time on relative densification and microhardness results was evaluated by calculating the arithmetic means of all the relative densification and microhardness values for the same category of levels of the parameters as shown in table 3 and figures 2-5 respectively.

The optical micrographs of the sintered composite at various sintering parameters are observed in figure 1 (a-i) in order to reveal the dispersion of h-BN nanoparticles and its influence on the densification and hardness property of the matrix. The relative densification of the spark plasma sintered monolithic alloy calculated from an effective density of 4.42 g/cm$^3$ and theoretical density of 4.50 g/cm$^3$ and Vickers microhardness were 98.22% and 331.8 HV respectively. Among the experimental runs of varied parameters and levels in table 2, A3B2C1D3 gave the best quality characteristics in terms of highest relative densification of 99.77% and microhardness of 710.4 HV.

Table 2. Densification and microhardness measurements results.

| Experimental run | SPS parameters and levels | Effective density (g/cm$^3$) | Theoretical density (g/cm$^3$) | Relative densification (%) | Microhardness (HV0.3/15) |
|------------------|---------------------------|-----------------------------|-------------------------------|----------------------------|--------------------------|
| 1                | A1B1C1D1                  | 4.33                        | 4.38                          | 98.86                      | 614.9                    |
| 2                | A1B2C2D2                  | 4.30                        | 4.38                          | 98.17                      | 623.2                    |
| 3                | A1B3C3D3                  | 4.14                        | 4.38                          | 94.52                      | 467.0                    |
| 4                | A2B2C3D1                  | 4.28                        | 4.38                          | 97.72                      | 519.1                    |
| 5                | A2B1C2D3                  | 4.25                        | 4.38                          | 97.03                      | 479.3                    |
| 6                | A2B3C1D2                  | 4.31                        | 4.38                          | 98.40                      | 630.1                    |
| 7                | A3B1C3D2                  | 4.34                        | 4.38                          | 99.09                      | 702.6                    |
| 8                | A3B2C1D3                  | 4.37                        | 4.38                          | 99.77                      | 710.4                    |
| 9                | A3B3C2D1                  | 4.32                        | 4.38                          | 98.63                      | 662.8                    |
Figure 1. Optical micrographs of the sintered composite at varied process parameters and levels: a. A1B1C1D1, b. A1B2C2D2 c. A1B3C3D3 d. A2B1C2D3 e. A2B2C3D1 f. A2B3C1D2 g. A3B1C3D2 h. A3B2C1D3 i. A3B3C2D1.

Table 3. Individual influence of temperature, pressure, heating rate and dwell time on relative densification and microhardness results.

| Parameter | Temperature (°C) | Pressure (MPa) | Heating rate (°C/min) | Dwell time (min) |
|-----------|------------------|----------------|-----------------------|------------------|
| Level     | 800              | 900            | 1000                  | 30               | 40   | 50   | 100  | 200  | 300  | 5    | 10   | 15    |
| Mean relative densification (%) | 97.18 | 97.71 | **99.16** | 98.56 | 98.32 | 97.18 | **99.01** | 98.17 | 96.88 | 98.17 | **98.55** | 97.34 |
| Mean microhardness (HV) | 568.4 | 542.8 | **691.9** | **612.2** | 604.3 | 586.6 | **651.8** | 601.7 | 549.6 | 568.6 | **652.0** | 565.5 |

Optimum levels of process parameters and results are designated by bold values.
Figure 2. Plot of temperature against mean relative densification and mean microhardness values.

Figure 3. Plot of pressure against mean relative densification and mean microhardness values.

Figure 4. Plot of heating rate against mean relative densification and mean microhardness values.

Figure 5. Plot of dwell time against mean relative densification and mean microhardness values.

This can be attributed to adequate mixing of the powders where the nanoparticles of h-BN filled up pore spaces within the matrix which are the primary causes of poor densification and the effectiveness of the consolidation method which enables the development of dense products [18] as seen in Figure 1h (A3B2C1D3). In addition, there is an indication of a slight grain refinement and disappearance of pores and grain boundaries which explain the reason for the complete densification [17] in contrast to Figure 1c (A1B3C3D3) where the porosity is highest (5.48%) which is significant enough to affect the material properties and led to low relative densification of 94.52% and microhardness of 467 HV. In general, it is realized that improved microstructure, densification and microhardness are promoted by the high temperature of sintering and low rate of heating that gave room for adequate diffusional mass transport resulting in solid bonding between the particles of the matrix and the ceramic reinforcement. Moreover, the significant improvement in the hardness property of the produced composite suggests that SPS facilitates the production of ceramic reinforced metal matrix composites with superior characteristics useful for many engineering applications [18].

From table 3 and figures 2-5, it can be seen that an increase in relative densification and microhardness was noticed when temperature was raised from 800 to 1000 °C and dwell time was
raised from 5 to 10 min, whereas a general reduction in relative densification and microhardness was noticed when pressure, heating rate and dwell time were raised from 30 to 50 MPa, 100 to 300 °C/min and 10 to 15 min respectively. A critical consideration of the various results obtained from assessing the individual influence of each parameter on the relative densification and microhardness of the sintered composite as presented in Table 3 and figures 2-5 gives the needed information on the most important parameter levels that gave the optimum combination of quality characteristics in the experiment. Hence, the optimum process parameter levels are determined to be the temperature of 1000 °C, pressure of 30 MPa, heating rate of 100 °C/min, and dwell time of 10 mins (A3B1C1D2). This suggests that an inappropriate combination of the parameters can potentially lead to a very poor-quality product [15-16] as seen in A1B3C3D3 with 94.52% and 467 HV and A2B2C3D1 with 97.03% and 479.3 HV relative densification and microhardness respectively; in contrast to other improved product qualities with the best being A3B2C1D3 with relative densification of 99.77% and microhardness of 710.4 HV.

4. Conclusion
1. The consolidation of Ti6Al4V powder and nanoparticles of 3wt.% of h-BN via SPS produced nearly full theoretical densification of 99.77% and the sintered composite gave a microhardness value of 710.4 HV which is more than 200% that of the monolithic alloy.
2. An increase in relative densification and microhardness was noticed when temperature was raised from 800 °C to 1000 °C, whereas a general reduction in relative densification and microhardness was noticed when pressure, heating rate and dwell time was raised from 30 to 50 MPa, 100 to 300 °C/min and 10 to 15 min respectively.
3. According to the experiment, the best combination of relative densification and microhardness were obtained at the sintering parameters of 1000 °C of temperature, 40 MPa of pressure, 100 °C/min of heating rate and 15 min of dwell time, whereas results show that the optimal parameter levels were obtained at 1000 °C of temperature, 30 MPa of pressure, 100 °C/min heating rate and 10 min of dwell time.
4. Generally, it is found that improved microstructure, densification and microhardness were influenced mostly by the high sintering temperature and low heating rate.

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References
[1] Ochonogor, O F, Akinlabi, E T, Nyembweb, K D, Pityana, S, & Shongwe, M B (2017). Particle variation and effect on the microstructure and microhardness of Ti6Al4V hybrid metal matrix system. International conference on sustainable materials processing and manufacturing, SMPM (pp. 616-621). Kruger National Park: Procedia manufacturing.
[2] Mouritz, A. P. (2012). Introduction to aerospace materials. Philadelphia New Delhi: Woodhead Publishing Limited.
[3] Kim, I. Y., Choi, B. J., Kim, Y. J., & Lee, Y. Z. (2011). Friction and wear behaviour of titanium matrix (TiB+TiC) composites. Wear 271, 1962-1965.
[4] Ray, A. K., Venkateswarlu, K., Chaudhury, S. K., Das, S. K., & Kumar, B. R. (2002). Fabrication of TiN reinforced aluminium metal matrix composites through a powder metallurgical route. Materials Science and Engineering A338, 160-165.
[5] Jiang, X., Weng, Q., Wang, X., Li, X., Zhang, J., Golberg, D., & Bando, Y. (2015). Recent Progress on Fabrications and Applications of Boron Nitride Nanomaterials: A Review. Journal of Materials Science & Technology 31, 589-598.
[6] Ertuğ, B. (2013). In Powder Preparation, Properties and Industrial Applications of Hexagonal Boron Nitride (pp. 33-56). IntechOpen.
[7] Lipp, A., Schwetz, K. A., & Hunold, K. (1989). Hexagonal boron nitride: fabrication, properties
and applications. *Journal of the European Ceramic Society*, 5, 3-9.

[8] Eichler, J., & Christoph, L. (2008). Boron nitride (BN) and BN composites for high-temperature applications. *Journal of the European Ceramic Society* 28, 1105–1109.

[9] Du, Y., Li, S., Zhang, K., & K, L. (1997). BN/Al composite formation by high-energy ball milling. *Scripta Materialia*, 36(1), 7-14.

[10] Firestein, K. L., Steinman, A. E., Golovin, I. S., Cifre, J., Obraztsova, E. A., Matveev, A. T., Golberg, D. (2015). Fabrication, characterization, and mechanical properties of spark plasma sintered Al–BN nanoparticle composites. *Materials Science & Engineering A* 642, 104–112.

[11] Yang, H; Fang, H; Yu, H; Chen, Y; Wang, L; Jiang, W; Wu, Y; Li, J. (2019). Low temperature self-densification of high strength bulk hexagonal boron nitride. *Nature Communications* 10, 1-9.

[12] Al-Aqeeli, N. (2013). Processing of CNTs Reinforced Al-Based Nanocomposites Using Different Consolidation Techniques. *Journal of Nanomaterials*, 1-10.

[13] Diouf, S., & Molinari, A. (2012). Densification mechanisms in spark plasma sintering: Effect of particle size and pressure. *Powder Technology* 221, 220–227.

[14] Matizamhuka, W. R. (2016). Spark plasma sintering (SPS) – an advanced sintering technique for structural nanocomposite materials. *The Journal of the South African Institute of Mining and Metallurgy Volume 16*, 1171-1180.

[15] Fei, N. C., Mehat, N. M., & Kamaruddin, S. (2013). Practical Applications of Taguchi Method for Optimization of Processing Parameters for Plastic Injection Moulding: A Retrospective Review. *ISRN Industrial Engineering*, 1-11.

[16] Athreya, S., & Venkatesh, Y. D. (2012). Application of Taguchi Method for Optimization of Process Parameters In Improving The Surface Roughness of Lathe Facing Operation. *International Refereed Journal of Engineering and Science*, 1(3), 2319-1821.

[17] Ujah, C. O., Popoola, A. P., Popoola, O. M., & Aigbodion, V. S. (2018). Optimisation of spark plasma sintering parameters of Al-CNTs-Nb nano-composite using Taguchi Design of Experiment. *The International Journal of Advanced Manufacturing Technology*, 1-11.

[18] Cavaliere, P., 2019. *Spark Plasma Sintering of Materials: Advances in Processing and Applications*. 1st ed. Switzerland: Springer Nature.