Advanced Ceramics Progress

Research Article

Journal Homepage: www.acerp.ir

Microstructure of spark plasma sintered TiB_2 and TiB_2–AlN ceramics

Z. Ahmadi[1], Z. Hamidzadeh Mahaseni[2], M. Dashti Germi[2], M. Shahedi Asl[2*]

[1] *Ceramic Department, Materials and Energy Research Center (MERC), Karaj, Iran*
[2] *Department of Mechanical Engineering, University of Mohaghegh Ardabili, Ardabil, Iran*

PAPER INFO

Paper history:

Received 20 June 2019
Accepted in revised form 9 July 2019

Keywords:

Titanium diboride
Aluminum nitride
Spark plasma sintering
Microstructure
Densification

ABSTRACT

In this research study, the effects of aluminum nitride (AlN) additive on the densification behavior and microstructure development of titanium diboride (TiB_2) based ceramic matrix composite were investigated. In this way, a monolithic TiB_2 ceramic and a TiB_2–5 wt% AlN ultrahigh temperature ceramic composite were fabricated by spark plasma sintering (SPS) process at a temperature of 1900 °C for a dwell time of 7 min under an externally applied pressure of 40 MPa in vacuum conditions. The relative density measurements were carried out using the Archimedes principles for evaluation of bulk density and rule of mixtures for calculation of theoretical one. Compared to the additive-free monolithic TiB_2 ceramic sample with a relative density of ~96%, the addition of AlN as a sintering aid greatly improved the sinterability of TiB_2 matrix composite so that a near fully dense sample with a relative density of ~100% were obtained by the spark plasma sintering process. The removal of harmful oxide impurities of titania (TiO_2) and boria (B_2O_3) from the surfaces of starting TiB_2 powder particles and in-situ formation of new phases such as aluminum diboride (AlB_2) and Al_2Ti as an intermetallic compound of aluminum and titanium, not only improved the sinterability of the composite ceramic, but also significantly prevented the extreme growth of TiB_2 grains.

1. INTRODUCTION

TiB_2 is one of the ultra-high temperature ceramics that has extraordinary properties such as high melting point, good abrasion resistance and high hardness [1-5]. Because of the aforementioned properties, it is suitable for many applications such as cutting tools, wear-resistant parts and aluminum evaporator boats [6, 7]. However, the scope of its application is limited due to difficulties in fabricating fully dense TiB_2 even with applying high external pressure at high temperature [7, 8]. The high sintering temperature increases the grain growth which leads to decrease the fracture toughness [9, 10]. Its high melting point, low self-diffusion coefficient, strong covalent bonding, and presence of oxygen-rich layer on the surface of the TiB_2 powder are the main causes of weak sinterability [11, 12]. Several densification routes have been used for fabrication of TiB_2 ceramics such as pressureless sintering (PS), hot pressing (HP) and spark plasma sintering (SPS). SPS is a newly developed sintering method to manufacture the UHTCs at lower temperatures compared to the HP and PS [13-15].

In performed studies, in order to achieve fully dense TiB_2, various additives have been used. Additives can be divided into metallic and non-metallic categories. In metallic additives (such as Fe, Cr, etc.), sinterability of TiB_2 can be increased by forming liquid-phase. Nevertheless, these additives may also degrade high-temperature properties. Therefore, many researchers have studied non-metallic additives (SiC, AlN, Si_3N_4, $MoSi_2$, $TiSi_2$, etc.) [12, 16-19].

In some articles, the influence of nitride additives on densification of boride ceramics has been examined. It was reported that addition of 5 wt% silicon nitride (Si_3N_4) as a sintering aid in the spark plasma sintering process at 1900 °C for 7 min under 40 MPa pressure increases the densification of TiB_2 [4]. It was also shown that the sinterability of TiB_2 is improved by adding 2.5 wt% Si_3N_4 as a sintering aid to the matrix in the hot pressing possess (at 1800 °C for 1 h) [8]. The main role of this additive is the removal of the oxide layer on the

* *Corresponding Author Email: shahedi@uma.ac.ir*

surface of the initial powder that improves the densification [4, 20]. Another research shows when a small amount (<= 5 wt%) of AlN was added to TiB_2 and hot pressed at 1800 ℃ for 1 h, the sinterability of TiB_2 was improved and density reached 98% when the added amount of AlN was 5 wt% [21].

In the present paper, the effect of AlN as a sintering aid on the microstructural evolution of TiB_2-based ceramics was investigated. Monolithic TiB_2 and TiB_2-5 wt% AlN ceramic samples were fabricated by the spark plasma sintering at a temperature of 1900 °C for 7 min under 40 MPa pressure in a vacuum atmosphere. The chemical reactions and microstructural variations of samples were accomplished by x-ray diffractometer, scanning electron microscope, and thermodynamic assessments.

2. MATERIALS and METHODS

Commercially available TiB_2 powder (particle size: 3-8 µm, purity: 99.9%, Xuzhou Hongwu Co., China) as the matrix and 5 wt% of AlN powder (particle size: 1-2 µm, purity: 99%, Xuzhou Hongwu Co., China) as a sintering aid were prepared as raw materials. The powders were mixed in ethanol media for 30 min using an ultrasonic bath (Daihan WUC-D10H, Korea). Then, the slurry of TiB_2-AlN mixture was heated on a hot plate magnetic stirrer (Heidolph MR 3001 K, Germany) at 120 °C for 3 h and completely dried for 24 h in an oven (Memmert Universal Oven Um, Germany). Afterward, the dried powder mixture was milled and passed through a sieve. Finally, a graphite die with 30 mm inner diameter and 5 mm height was filled with the powders separated with graphite foils. Sintering process was accomplished at 1900 °C for 7 min under 40 MPa in a vacuum hot-press spark plasma (Nanozint 10i, Khalapoushan Felez Co., Iran). Furthermore, the monolithic TiB_2 sample was sintered at the identical processing status using the as received TiB_2 powder directly.

Archimedes method (ASTM B962) was utilized to measure the relative density and the theoretical density was calculated by the mixtures rule. Field emission SEM (Mira3, Tescan, Czech Republic) analyses were carried out for the microstructural investigations of spark plasma sintered ceramics of polished and fracture surfaces. The grain size of TiB_2 matrix was approximated by image processing software (ImageJ, Wayne Rasband, USA). The elemental analysis was carried out by an energy dispersive spectroscope (EDS: DXP-X10P) coupled with the SEM system. The phase composition analysis of as-sintered ceramics was carried out by an X-ray diffractometer (Philips PW1730).

3. RESULTS AND DISSCUSSION

Fig. 1 displays the result of measured relative densities of spark plasma sintered of pure TiB_2 and TiB_2-AlN samples. As can be seen, compared to the monolithic TiB_2 ceramic with a relative density of 96%, the AlN-doped TiB_2 ceramic reached its full density with a relative density of 100% so that both of them were sintered at same processing conditions. The results show that the porosity is equal to 4% and 0% for the monolithic TiB_2 and the AlN-doped TiB_2 composite, respectively. These results are in agreement with the water absorption test as the additive-free sample had 0.02% content, while the AlN-doped TiB_2 ceramic absorbed only 0.01% water.

SEM micrographs of the polished surfaces of spark plasma sintered monolithic TiB_2 and AlN-doped TiB_2 sample are presented in Fig. 2 (a) and (b), respectively. Addition of AlN significantly promoted the densification and developed microstructure of TiB_2 compared to the additive-free sample. As can be seen in Fig. 2, the occurrence of sintering phenomenon between the particles had taken place and several necks formed between neighbor particles. A few porosities in the microstructure can be related to the grains broken out of the main body of the sample during of polishing process.

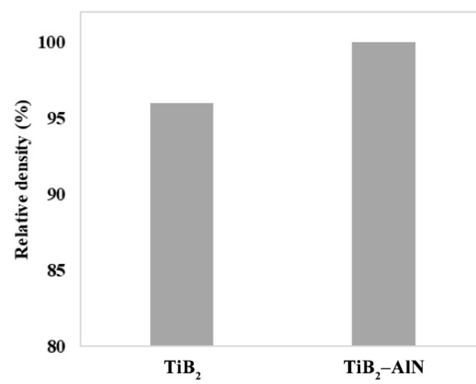

Figure 1. The relative density of the spark plasma sintered ZrB_2-based ceramics

Kim et al. [13] have reached a 95% relative density for TiB_2-AlN by pressureless sintering of a mechano-chemically processed Ti, Al, and BN powder mixture at 1800 °C for 60 min under 30 MPa. However, a relative density of 96.82% is reported by Yue et al. [14] for TiB_2-AlN composite that hot-pressed at 2000 °C under 25 MPa pressure for 2 h.

The SEM fractographs of spark plasma sintered AlN-free and AlN-doped TiB_2 ceramics are shown in Fig. 3. Full connection of the grains to each other in the as-sintered sample is a sign of the excellent effect of AlN on the sinterability of TiB_2. As shown in Fig. 3, the average size of the TiB_2 grains is around 5 µm which is smaller than monolithic TiB_2 grains (9.2 µm). Therefore, the AlN addition prevents extreme grain growth. In the case of pressureless sintered TiB_2-based ceramics, grains were in the size range of 1-1.5 µm that were reduced compared to the starting powders [13].

The phase composition of the prepared sample was analyzed by its XRD pattern. Figure 4 shows the characterized XRD pattern of as-spark plasma sintered sample. As can be seen in Fig. 3, besides the TiB_2 and AlN as the starting materials, there are some peaks of AlB_2 and Al_2Ti as an intermetallic compound of aluminum and titanium. However, Li et al. [17] have reported that the titania (TiO_2) presented on the surface of the TiB_2 powder is eliminated by a reaction with AlN to form TiN and Al_2O_3.

AlN additive can react with the oxide impurities presented on the surface of TiB_2 powders (B_2O_3 and TiO_2) and produce the AlB_2 and Al_2Ti according to Eqs. (1) and (2), respectively.

$$2AlN + 2B_2O_3 = 2AlB_2 + N_2 + 3O_2 \quad (1)$$

$$2AlN + TiO_2 = Al_2Ti + O_2 + N_2 \quad (2)$$

Theoretically, based on the chemical reactions of Eqs.1-2 under standard conditions, regarding weights of starting materials used in this research work, the volumes of as-released N_2 and O_2 gases were estimated 1.28 and 3.20 lit, respectively. However, due to the applied vacuum during the SPS process, it seems that such gaseous byproducts have mainly escaped from the sintering chamber. This hypothesis can be logical concerning the high relative densities of as-sintered samples.

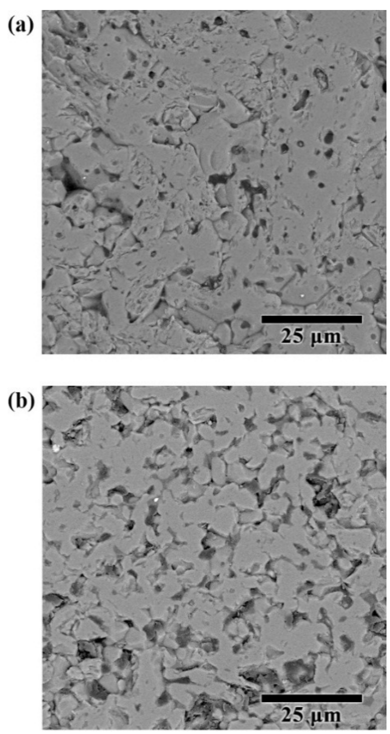

Figure 2. SEM images of the polished surface of (a) monolithic TiB_2 and (b) TiB_2–AlN ceramics

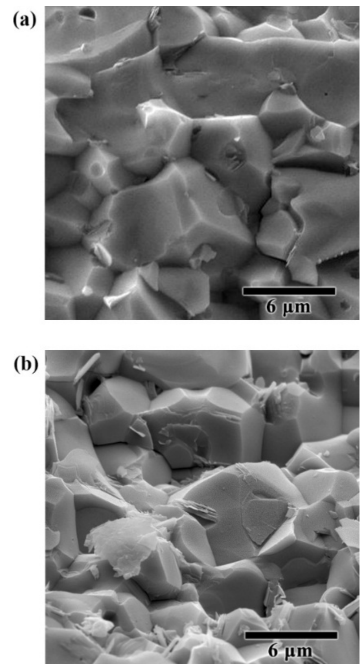

Figure 3. SEM fractographs (SE mode) of (a) monolithic TiB_2 and (b) TiB_2–AlN ceramics

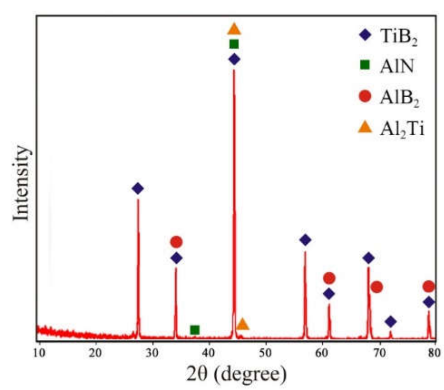

Figure 4. XRD pattern of AlN-doped TiB_2 ceramic

These reactions lead to the removal of surface oxides and result in new products that promote the densification. The applied external pressure during the sintering pushes the formed gasses (N_2 and O_2) out, and inhibits them of intensifying the porosity formation.

Figure 5a shows another SEM fractograph (in the back-scattered electron mode) of the TiB_2–AlN ceramic composite. The EDS spectrum of Al_2Ti phase, which is marked by arrow in Fig. 5a is presented in Fig. 5b indicating the presence of titanium and aluminum as well as oxygen that is associated with the oxide impurities.

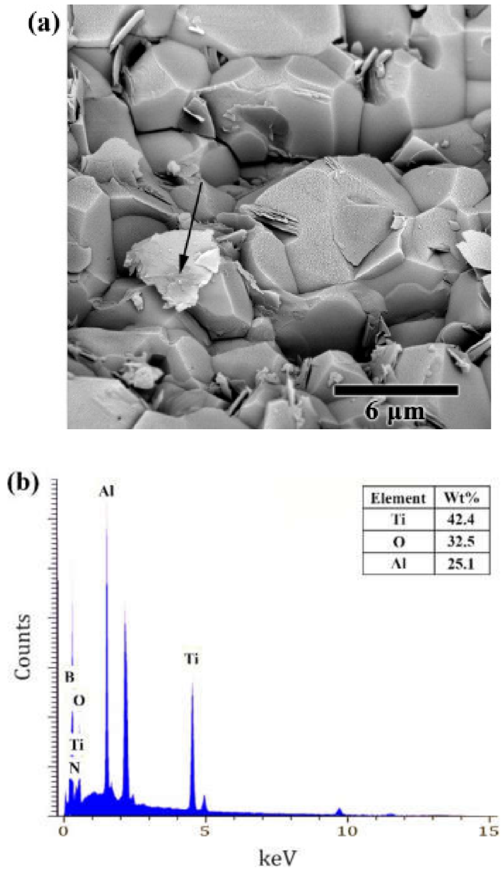

Figure 5. (a) SEM fractograph (BSE mode) of TiB_2–AlN composite and (b) EDS spectrum of the in-situ formed Al_2Ti phase

4. CONCLUSION

The effect of the AlN addition on the sinterability and microstructural evolution of TiB_2-based ceramic during the sintering process was studied and compared to the monolithic TiB_2. The TiB_2-based samples were prepared by the spark plasma sintering at 1900 °C for 7 min under 40 MPa pressure. The densification of TiB_2 was encouraged by adding 5 wt% of AlN as a sintering aid. Aluminum diboride (AlB_2) and Al_2Ti as an intermetallic compound of aluminum and titanium in the AlN-doped TiB_2 sample were formed by chemical reactions of AlN with the oxide layers (B_2O_3 and TiO_2) presented on the surface of TiB_2 particles. The removal of surface oxide impurities significantly hindered the excessive grain growth of TiB_2 matrix which resulted in refined microstructure and improved sinterability.

5. ACKNOWLEDGMENT

The authors would like to acknowledge the Fannavaran Arta Mavad Novin Pazhouh Company.

REFERENCES

1. Castaing, J., Costa, P., “Properties and Uses of Diborides”, in *Boron and Refractory Borides*, Berlin, Heidelberg, Springer, (1977), 390-412.
2. Sabahi Namini, A., Seyed Gogani, S.N., Shahedi Asl, M., Farhadi, K., Ghassemi Kakroudi, M., Mohammadzadeh, A., “Microstructural development and mechanical properties of hot pressed SiC reinforced TiB_2 based composite”, ***International Journal of Refractory Metals and Hard Materials,*** Vol. 51, (2015), 169-179.
3. Farhadi, K., Sabahi Namini, A., Shahedi Asl, M., Mohammadzadeh, A., Ghassemi Kakroudi, M., “Characterization of hot pressed SiC whisker reinforced TiB_2 based composites”, ***International Journal of Refractory Metals and Hard Materials,*** Vol. 61, (2016), 84-90.
4. Hamidzadeh Mahaseni, Z., Dashti Germi, M., Ahmadi. Z., Shahedi Asl, M., “Microstructural investigation of spark plasma sintered TiB_2 ceramics with Si_3N_4 addition”, ***Ceramics International,*** Vol. 44, No. 11, (2018), 13367-1337.
5. Shahbazi, M., Tayebifard, S.A., Razavi, M., “Effect of Ni content on the reaction behaviour and microstructure of TiB_2-TiC/Ni cermets synthesized by MASHS”, ***Advanced Ceramics Progress***, Vol. 2, No. 2, (2016), 22-26.
6. Mukhopadhyay, A., Rajua, G.B., Basua, B., Suri, A.K., “Correlation between phase evolution, mechanical properties and instrumented indentation response of TiB_2-based ceramics”, ***Journal of the European Ceramic Society,*** Vol. 29, No. 3, (2009), 505-516.
7. Zheng, L., Li, F., Zhou, Y., “Preparation, microstructure, and mechanical properties of TiB_2 using Ti_3AlC_2 as a sintering aid”, ***Journal of the American Ceramic Society,*** Vol. 95, No. 6, (2012), 2028-2034.
8. Park, J.H., Koh, Y.H., Kim, H.E., Hwang, Ch.S., Kang, E. S., “Densification and mechanical properties of titanium diboride with silicon nitride as a sintering aid”, ***Journal of the American Ceramic Society,*** Vol. 52, No. 11, (2004), 3037-3042.
9. Zhao, G., zhen, Ch., Hanlian, H., Bin, L., Hongtao, Z., Wang, Zh.J., “Microstructure and mechanical properties of TiB_2–SiC ceramic composites by reactive hot pressing”, ***International Journal of Refractory Metals and Hard Materials,*** Vol. 42, (2014), 36-41.
10. Bhaumik, S.K., Divakara, C., Singh, A.K., Upadhyaya, G.S., “Synthesis and sintering of TiB_2 and TiB_2–TiC composite under high pressure”, ***Materials Science and Engineering: A,*** Vol. 279, No. 1-2, (2000), 275-281.
11. Shahedi Asl, M., Ahmadi, Z., Parvizi, S., Balak, Z., Farahbakhsh, I., “Contribution of SiC particle size and spark plasma sintering conditions on grain growth and hardness of TiB_2 composites”, ***Ceramics International,*** Vol. 43, No. 16, (2017), 13924-13931.
12. Brahma Raju, G., Basu B., “Densification, sintering reactions, and properties of titanium diboride with titanium disilicide as a sintering aid”, ***The Journal of the American Ceramic Society,*** Vol. 90, No. 11, (2007), 3415-3423.
13. Balak, Z., Zakeri, M., Rahimipour, M.R., Salahi, E., Azizieh, M., Kafashan, H., “Investigation of effective parameters on densification of ZrB_2-SiC based composites using taguchi method”, ***Advanced Ceramics Progress***, Vol. 2, No. 2, (2016), 7-15.
14. Balak, Z., Azizieh, M., “Oxidation of ZrB_2-SiC composites at 1600°C: effect of carbides, borides, silicides, and chopped carbon fiber”, ***Advanced Ceramics Progress***, Vol. 4, No.1, (2018), 18-23.

15. Irankhah, R., Zakeri, M., Rahimipour, M.R., Razavi, M., "In-situ fabrication of transparent magnesium aluminate spinel by spark plasma sintering", ***Advanced Ceramics Progress***, Vol. 3, No. 1, (2017), 6-9.

16. Raju, G.B., Basu, B., "Development of high temperature TiB_2-based ceramics", ***Key Engineering Materials***, Vol. 395, (2008), 89-124.

17. Kim, H. J., Choi, H. J., Lee, J. G., "Mechanochemical synthesis and pressureless sintering of TiB_2–AlN composites", ***Journal of the American Ceramic Society***, Vol. 85, No. 4, (2002), 1022-1024.

18. Yue, X.M., Zhang, G.J., Wang, Y.M., "Reaction synthesis and mechanical properties of TiB_2–AlN–SiC composites", ***Journal of the European Ceramic Society***, Vol. 19, No. 3, (1999), 293-298.

19. Dashti Germi, M., Hamidzadeh Mahaseni, Z., Ahmadi, Z., Shahedi Asl, M., "Phase evolution during spark plasma sintering of novel Si_3N_4-doped TiB_2–SiC composite", ***Materials Characterization***, Vol. 145, (2018), 225-232.

20. Park, J.H., Lee, Y.H., Koh, Y.H.. Kim, H.E., Baek, S.S., "Effect of hot-pressing temperature on densification and mechanical properties of titanium diboride with silicon nitride as a sintering aid", ***Journal of the American Ceramic Society***, Vol. 83, No. 6, (2004), 1542-1544.

21. Li, L.H., Kim, H.E., Kang, E.S., "Sintering and mechanical properties of titanium diboride with aluminum nitride as a sintering aid", ***Journal of the European Ceramic Society***, Vol. 22, No. 6, (2002), 973-977.