Pressureless densification and properties of TiB_2–B_4C composite ceramics with Ni as additives

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Titanium diboride–boron carbide (TiB_2–B_4C) composite ceramics were prepared using different amounts of Ni as sintering aids by pressureless sintering at 2100°C for 60 min under an argon atmosphere. This study focused on the effects of different amounts of Ni as additives on densification and mechanical and thermal properties of TiB_2–B_4C composite ceramics. Results showed that the relative density, hardness, flexural strength and thermal conductivity of obtained composite ceramics with 1.3 wt% Ni addition were 98%, 20.4 GPa, 330 MPa and 30 W/m K, respectively. However, fracture toughness was 6 MPa $m^{1/2}$ when the content of Ni was fixed at 2.2 wt%.

1. Introduction: Titanium diboride (TiB_2) and boron carbide (B_4C) are potential candidate materials for structural applications due to excellent performances such as high melting point, high hardness, and exceptional corrosion and erosion resistance [1–5]. Basically, both TiB_2 and B_4C have poor sinterability owing to their high melting temperature and low diffusion coefficient [6, 7]. However, sintering behaviours could be enhanced through adding B_4C powders into the TiB_2 matrix because point defects are easily introduced by different thermal expansion coefficients between reinforcements and matrix. Numerous additives were added into TiB_2–B_4C composite ceramics in order to obtain dense composite ceramics, including metals [8–10] (Al, Fe, Ni etc.), oxides [11] (Al_2O_3, Y_2O_3, ZrO_2 etc.) and non-oxides [12, 13] (W_2B_5, ZrB_2, TiC, Si_3N_4 etc.). Actually, TiB_2–B_4C composite ceramics are able to remain good sintering characteristics and chemical properties of both TiB_2 and B_4C ceramics, and therefore can be used for extensive applications such as armour materials, cutting tools, spray nozzles and wear resistant materials [14–16]. Graziani *et al.* [17] found that B_4C–TiB_2 composite ceramics with Ni as the additive could be successfully prepared at 1500–1600°C under a pressure of 30 MPa, the fracture toughness, flexural strength and hardness of which were measured at 6.4 MPa $m^{1/2}$, 1000 MPa and 24.7 GPa, respectively. Huang *et al.* [18] discovered that the obtained hot-pressed B_4C–TiB_2 composite turned out to be a combination of high flexural strength (867 MPa) and high hardness (29 GPa), while the fracture toughness was modest (4.5 MPa $m^{1/2}$). The studies also showed that hot-pressing sintering process could contribute to achieving higher densification of B_4C–TiB_2 composite ceramics, but was not suitable for preparation of ceramics with complicated shapes due to the fixed shape of graphite dies and inflexible pressing directions. For this reason, the pressureless sintering process is developed for sophisticated ceramics and has drawn huge attention from many researchers. Mashhadi *et al.* [9] studied the influence of Al addition on the densification behaviour, physical and mechanical properties of pressureless sintered B_4C–TiB_2 composites. It was shown that the B_4C–30 wt%TiB_2 composite with 5 wt% Al addition possessed the optimal properties of flexural strength, elastic modulus, hardness and fractured toughness at 450 MPa, 500 GPa, 35 GPa and 6.2 MPa $m^{1/2}$, respectively. Metallic additives like Al or Ni could promote densification because of the generation of liquid phases at high temperatures, accelerating the liquid solid mass transfer process, and therefore the effect of Ni addition on performance of TiB_2–B_4C composite ceramics was investigated in details in our work. In this Letter, based on the optimised sintering temperature (2100°C) and holding time (60 min), we studied the densification behaviour, thermal and mechanical properties of TiB_2–B_4C composite ceramics with different amounts of Ni as additives via pressureless sintering method.

2. Experimental procedure: TiB_2 powders (Beijing Global International Science and Technology Co., Ltd.), B_4C powders (Zhengzhou Songshan Boron Technology Co., Ltd.), Ni powders (Hebei Maijie Hard Alloy Technology Co., Ltd.), and phenolic resin (PF, Laiwu Runda New Material Co., Ltd., theoretical carbon content 40.0 wt%, acting as the binder and C source) were used as raw materials. The mass fraction of TiB_2, B_4C, Ni and PF in the mixture was 54.3–52.9, 36.2–35, 0.5–3.1 and 9 wt%, respectively, shown in Table 1. The synthetic process of composite ceramics was shown in Fig. 1. A brief description of the process was as follows. The starting powders were mixed by ball milling for 30 min in an alumina pot, using B_4C balls as the milling media and ethanol as the binder, where the mass ratio of balls to powders was 5:1. After dried at 60°C for 24 h, crushed and sieved, the powder batches were compacted into cylinder-shape green bodies with a diameter of 65 mm and a height of 5.5 mm by uni-axial pressing under a pressure of 30 MPa. Subsequently, in order to obtain relatively uniform dense green bodies, all compacts were isostatically pressed under a pressure of 200 MPa for 200 s. Then, the samples were placed in a graphite resistance furnace for sintering at 2100°C for 60 min under Ar atmosphere. After that, the sintered samples were machined into cylinders with approximate dimension of 5 mm × ~Φ55 mm. The bulk density of samples was determined by Archimedes' method. Relative density was defined as the ratio between the bulk density and theoretical density. The sintered samples were ground and cut with a diamond saw into bars of 3 mm and 2 mm × 4 mm × 40 mm, and then were mirror polished using diamond slurries in order to proceed with the three-point flexural strength measurement that was determined by an Electromechanical Universal Testing Machine (CMT 5105,

Table 1 TiB_2–B_4C composite ceramic with different amounts of Ni

No.	TiB_2, wt%	B_4C, wt%	Ni, wt%	PF, wt%
TB001	54.3	36.2	0.5	9
TB002	53.8	35.9	1.3	9
TB003	53.3	35.5	2.2	9
TB004	52.9	35	3.1	9

Shenzhen Suns Technology Co., Ltd.) at a speed of 0.5 mm/min with a span of 20 mm at room temperature. The fracture toughness of the compacts was examined by the three-point loading and single-edge notched beam technique with a notch of 0.1 mm width and 1.0 mm depth, a span of 20.0 mm and a speed of 0.05 mm/min. Hardness was measured by the Vickers indentation method (DHV-1000, Shanghai Caikon Optical Instrument Co., Ltd.) at a load of 5 N for a dwell time of 15 s on the mirror-polished surface. Microstructural observation was carried out by the field high resolution scanning electron microscope (SU-70, Hitachi). Thermal conductivity was measured by the thermal conductivity measuring instrument (TC3000, Xi'an Xia Xi Electronic Technology Co., Ltd.).

3. Results and discussion

3.1. Microstructure of TiB_2–B_4C composite ceramics: Fractured surface images of TiB_2–B_4C composite ceramics with different Ni addition were shown in Fig. 2. It was clearly seen from Fig. 2*a* that the sample turned out to be porous while adding 0.5 wt% Ni because the content of liquid phase was too limited to fill the pores. As shown in Fig. 2*b*, the ceramic with 1.3 wt% Ni addition as additives had the least porosity among four samples. Owing to enough Ni as the liquid phase to fill the pore and its further diffusion between TiB_2 and B_4C particles, porosity of composite ceramics significantly decreased. Furthermore, as exhibited in Figs. 2*c* and *d*, grains size had increased because of the generation of the excessive liquid phase by adding 2.2 and 3.1 wt% Ni as additives and the porosity also increased due to the growth of anisotropic TiB_2 and B_4C grains caused by different thermal expansion coefficients.

3.2. Mechanical properties of TiB_2–B_4C composite ceramics: The block diagrams of relative density, hardness, flexural strength and fracture toughness of TiB_2–B_4C composite ceramics with different Ni addition were presented in Fig. 3. As shown in Fig. 3*a*, the relative density of TiB_2–B_4C composite ceramics increased firstly and then decreased, where the relative density peaked at 98% when 1.3 wt% Ni was added, which was consistent with the variation trend of the porosity in Fig. 2. The pore had low resistance with the external pressure, and therefore the high porosity resulted in low mechanical properties. Similarly, by adding 1.3 wt% Ni as additives, the highest hardness (20.4 GPa) and flexural strength (330 MPa) of composite ceramics were achieved. As the liquid Ni could be formed at a high sintering temperature, the diffusion among the surface, lattice and grain boundary was promoted by the particle migration during the sintering process. Volume diffusion and mass transferring were generally known as the main mechanisms to enhance the sinterability through the rearrangement of grains to reduce the pores in composites. As exhibited in Figs. 3*b* and *c*, it could be observed that hardness and flexural strength of the composite ceramics with 1.3 wt% Ni addition reached the maximum at 20.4 GPa and 330 MPa, respectively. However, as displayed in Fig. 3*d*, the highest toughness fracture was

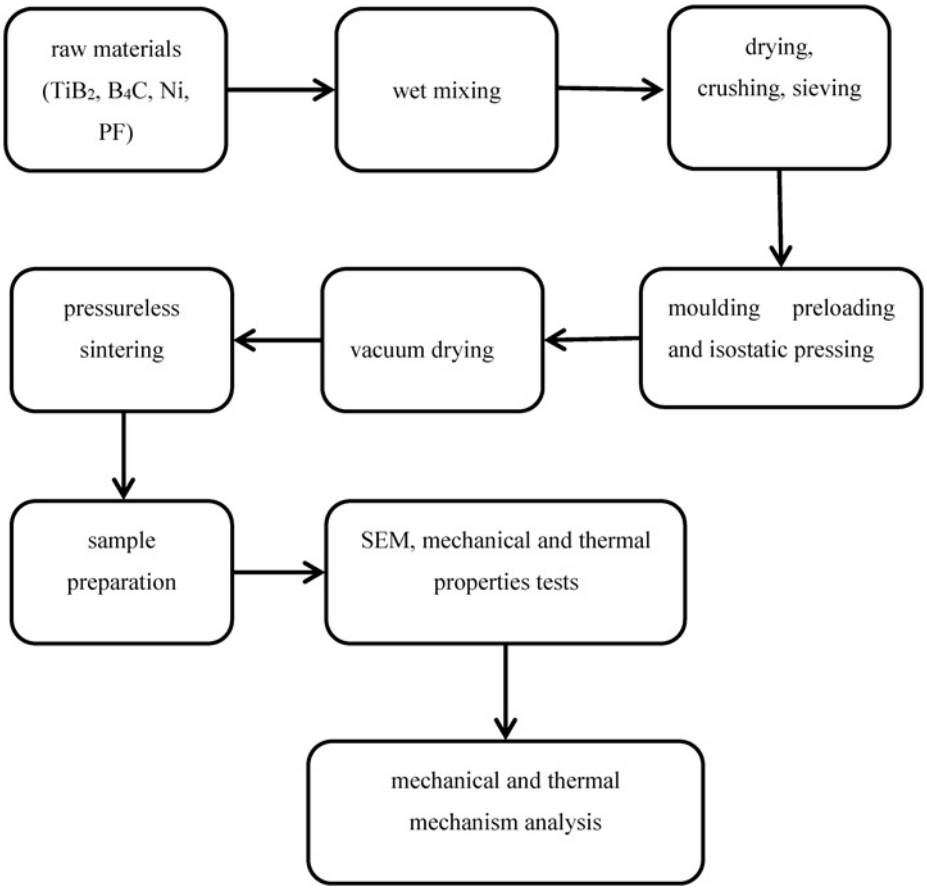

Fig. 1 *Flowchart of sample preparation and measurements*

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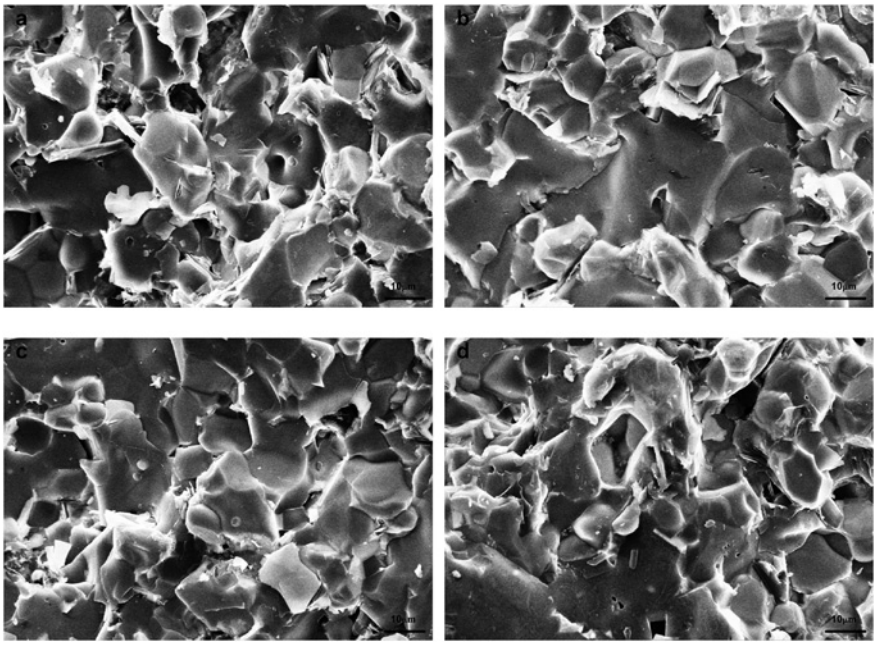

Fig. 2 *SEM micrographs of TiB_2–B_4C composite ceramics with different amounts of Ni*
a 0.5 wt% Ni
b 1.3 wt% Ni
c 2.2 wt% Ni
d 3.1 wt% Ni

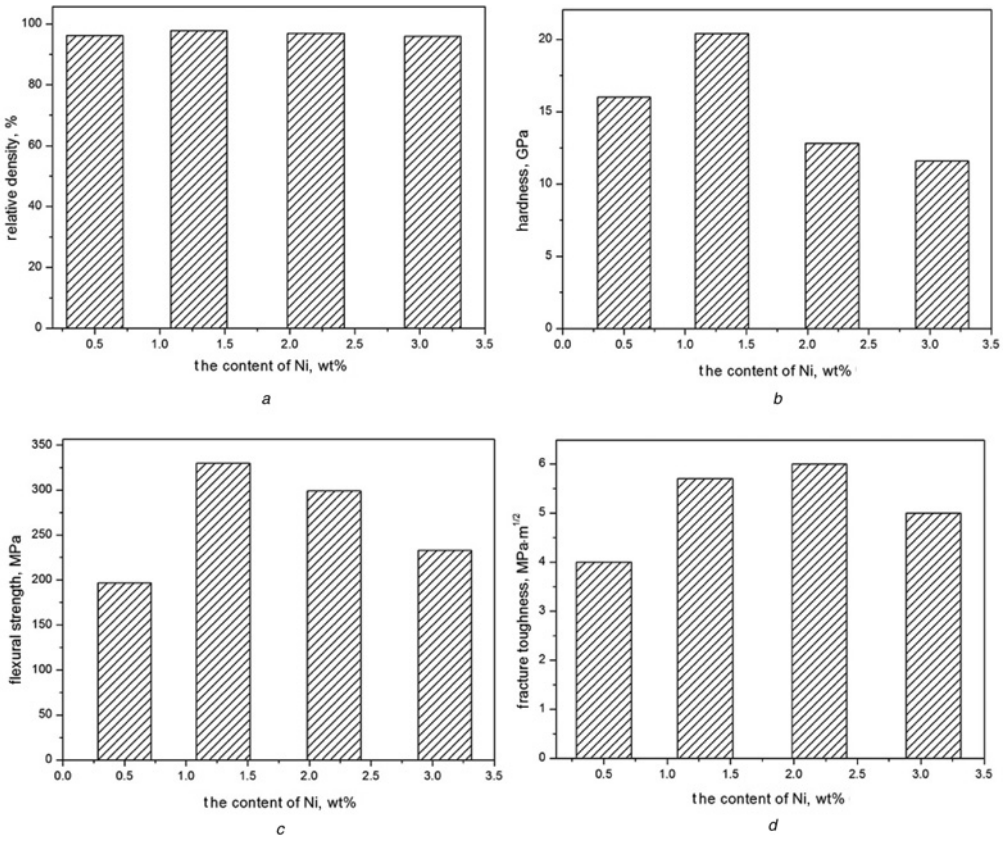

Fig. 3 *Relative density, hardness, flexural strength and fracture toughness of TiB_2–B_4C composite ceramics with different amounts of Ni*
a Relative density
b Hardness
c Flexural strength
d Fracture toughness

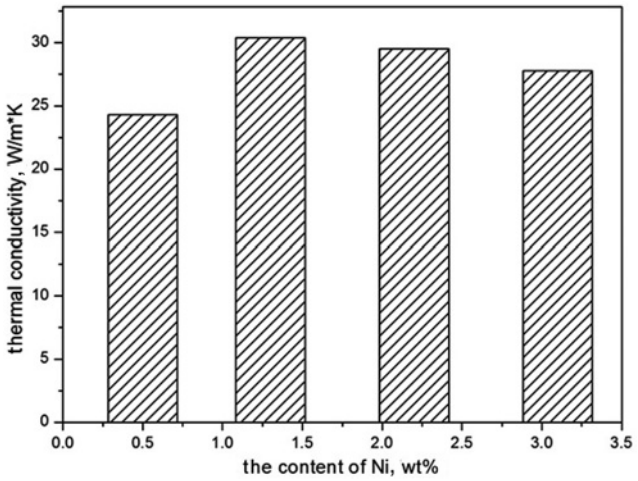

Fig. 4 *Thermal conductivity of TiB_2–B_4C composite ceramics with different amounts of Ni*

6 MPa $m^{1/2}$ when 2.2 wt% Ni was employed probably due to the high toughness of Ni.

In addition, the residual stress and micro-cracks were easily introduced in the sintering cooling process due to different thermal expansion coefficients between TiB_2 and B_4C, which could promote the fracture toughness of the compact. As observed from Fig. 2*c*, grains were pulled out in the course of fracture. It could be inferred that the intergranular fracture was converted into the mixed fracture (consisting of both intergranular and transgranular fracture), resulting in increasing toughness fracture of TiB_2–B_4C composite ceramics.

3.3. Thermal properties of TiB_2–B_4C composite ceramics: Fig. 4 shows the thermal conductivity of TiB_2–B_4C composite ceramics. Adding 1.3 wt% Ni into TiB_2–B_4C composite ceramics, it was obvious that the thermal conductivity reached the maximum at 30 W/m K. The heat carrier of inorganic non-metallic materials is mainly the phonons, which could be explained by the lattice vibration of the 'quantum'. The lattice thermal conductivity is calculated according to Debye's heat conduction theory [19], shown as

$$k = \frac{1}{3} C v_p l_p \tag{1}$$

where C is the specific heat per unit volume, v_p is the phonon velocity, and l_p is the mean free path of phonons.

The phonon transfers from one grain to another grain in theory. However, its transmission is bound by the phonon scattering due to the existence of pores, grain boundaries and dislocations. Thus, the continuity of the phonon transmission is damaged, reducing the average speed and the phonon mean-free path, which leads to the decrease of thermal conductivity. As shown in Figs. 2, 3*a* and 4, the thermal conductivity of samples with 1.3 wt% addition was the maximum (30 W/m K) among four samples because of the highest relative density (98%). Furthermore, when the content of Ni was >1.3 wt%, too much liquid phase promoted the growth of grains and the porosity. Moreover, excessive Ni caused lattice distortion and increased the phonon scattering.

4. Conclusion: The relative density, hardness, flexural strength and fracture toughness of TiB_2–B_4C composites were improved by adding 1.3 wt% Ni as additives, the optimal values of which were 98%, 20.4 GPa, 330 MPa and 30 W/m K, respectively. By contrast, fracture toughness of TiB_2–B_4C composite ceramics peaked at 6 MPa $m^{1/2}$ when 2.2 wt% Ni was added.

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6 References

[1] Demirskyi D., Agrawal D., Ragulya A.: 'Tough ceramics by microwave sintering of nanocrystalline titanium diboride ceramics', *Ceram. Int.*, 2014, **40**, pp. 1303–1310
[2] Zhao G.L., Huang C.Z., Liu H.L., *ET AL.*: 'Microstructure and mechanical properties of TiB_2–SiC ceramic composites by reactive hot pressing', *Int. J. Refract. Met. Hard Mater.*, 2014, **42**, pp. 36–41
[3] Demirskyi D., Borodianska H., Sakka Y., *ET AL.*: 'Ultra-high elevated temperature strength of TiB_2-based ceramics consolidated by spark plasma sintering', *J. Eur. Ceram. Soc.*, 2017, **37**, pp. 393–397
[4] Pei L.Z., Xiao H.N.: 'B_4c/TiB_2 composite powders prepared by carbothermal reduction method', *J. Mater. Process. Tech.*, 2009, **209**, pp. 2122–2127
[5] Yamada S., Hirao K., Yamauchi Y., *ET AL.*: 'B_4C-CrB_2 composites with improved mechanical properties', *J. Eur. Ceram. Soc.*, 2003, **23**, pp. 561–565
[6] Li L., Kim H., Kang E.S.: 'Sintering and mechanical properties of titanium diboride with aluminum nitride as a sintering aid', *J. Eur. Ceram. Soc.*, 2002, **22**, pp. 973–977
[7] Kumar S., Sairam K., Sonber J.K., *ET AL.*: 'Hot-pressing of $MoSi_2$ reinforced B_4C composites', *Ceram. Int.*, 2014, **40**, pp. 16099–16105
[8] Yamada S., Hirao K., Yamauchi Y., *ET AL.*: 'High strength B_4C–TiB_2 composites fabricated by reaction hot-pressing', *J. Eur. Ceram. Soc.*, 2003, **23**, pp. 1123–1130
[9] Mashhadi M., Taheri-Nassaj E., Mashhadi M., *ET AL.*: 'Pressureless sintering of B_4C–TiB_2 composites with Al additions', *Ceram. Int.*, 2011, **37**, pp. 3229–3235
[10] Heydari M.S., Baharvandi H.R.: 'Effect of different additives on the sintering ability and the properties of B_4C–TiB_2 composites', *Int. J. Refract. Met. Hard Mater.*, 2015, **51**, pp. 61–69
[11] Heydari M.S., Baharvandi H.R., Dolatkhah K.: 'Effect of TiO_2 nanoparticles on the pressureless sintering of B_4C–TiB_2 nanocomposites', *Int. J. Refract. Met. Hard Mater.*, 2015, **51**, pp. 6–13
[12] Königshofer R., Fürnsinn S., Steinkellner P., *ET AL.*: 'Solid-state properties of hot-pressed TiB_2 ceramics', *Int. J. Refract. Met. Hard Mater.*, 2005, **23**, pp. 350–357
[13] Song J.P., Huang C.Z., Lv M., *ET AL.*: 'Effects of TiC content and melt phase on microstructure and mechanical properties of ternary TiB_2-based ceramic cutting tool materials', *Mater. Sci. Eng. A*, 2014, **605**, pp. 137–143
[14] White R.M., Dickey E.C.: 'Mechanical properties and deformation mechanisms of B_4C–TiB_2 eutectic composites', *J. Eur. Ceram. Soc.*, 2014, **34**, pp. 2043–2050
[15] Ran S.-L., Wang D.-W., Fan C.-G.: 'Research progress of B_4C-TiB_2 composite ceramics', *J. Synth. Cryst.*, 2013, **42**, pp. 2150–2155, (in Chinese)
[16] Sun J.-L., Liu C.-X., Wang B.-W.: 'Effect of mechanical propertieson erosion resistances of B_4C/TiB_2 matrix ceramic nozzles', *J. Synth. Cryst.*, 2009, **38**, pp. 529–534 (in Chinese)
[17] Graziani T., Bellosi A.: 'Production and characteristics of B_4C/TiB_2 composites', *Key Eng. Mater.*, 1995, **104**, pp. 125–132
[18] Huang S.G., Vanmeensel K., Malek O.J.A., *ET AL.*: 'Microstructure and mechanical properties of pulsed electric current sintered B_4C-TiB_2 composites', *Mater. Sci. Eng. A*, 2011, **528**, pp. 1302–1309
[19] Li Q.S.: 'Preparation and application research of high thermal conductivity SiC ceramics' (Shandong University, Jinan, 2016) (in Chinese)

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