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Preparation of boron carbide–aluminum composites by non-aqueous gelcasting

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Abstract

Gelcasting is an attractive forming process to fabricate ceramic parts with near-net-shape. In the present work, non-aqueous gelcasting of boron carbide (B_4C)–aluminum (Al) composites was studied. A stable B_4C–Al slurry with solids loading up to 55 vol.% for gelcasting was prepared. The slurry was solidified in situ to green body with the mean value of relative density of 64% and flexural strength of 21 MPa. The SEM images showed that powders in green body compact closely by the connection of polymer networks. B_4C–Al samples were also obtained by the process of gelcasting and sintering at 1300 °C for 1 h in 0.1 MPa Ar atmosphere. The average bulk density of sintered body was 2.05 g cm^{-3}.

Keywords: Gelcasting; Boron carbide; Aluminum; Non-aqueous

1. Introduction

Boron carbide (B_4C) is a valuable non-oxide ceramic material. This is mainly because of its high melting point, extremely high hardness, low density, and excellent corrosion resistance [1]. However, its two major drawbacks are the low fracture toughness and the very high sintering temperature for pure B_4C ceramics. On the other hand, aluminum possesses low density, low melting temperature and high ductility. Therefore, it is expected to lower the sintering temperature, increase the sinterability and improve the fracture toughness of pure B_4C.

According to Halverson et al. [2], a low contact angle of solid–liquid phases is particularly important for wetting which ensures the reaction during processing, when the driving force for wetting is a reduction in free energy of the reaction system. The contact angle is lower than 10° when processed in the condition of 1300 °C in vacuum only after about 2 min. The contact angle of B_4C–Al in this work was low enough for reaction.

Gelcasting is a near-net-shape forming technique as a synthesis concept derived from traditional ceramics and polymer chemistry. The process is based on the in situ polymerization of organic monomers to form green ceramic body [3]. Gelcasting can be used to prepare ceramic parts with complex-shaped, which can reduce the huge machining cost. In recent years, aqueous gelcasting has been widely studied to produce ceramic materials, including alumina [3–6], silicon carbide [7–9], etc. In our survey, only alumina ceramic was prepared by non-aqueous gelcasting [10]. Furthermore, there are few papers about non-aqueous gelcasting of boron carbide–aluminum composites.

In the present work, non-aqueous gelcasting of B_4C and Al powders was studied. The influence of the dispersant and solid loading on rheology of B_4C–Al slurry was evaluated. In addition, the properties of composites were also investigated.

2. Experimental procedure

2.1. Materials and process

The raw materials used in gelcasting process were listed in Table 1. According to Table 1, the size of B_4C and Al powders were very different: B_4C 1.5 μm and Al 45 μm, respectively. To fill small B_4C (1.5 μm) into the voids of large Al (45 μm) could enhance the solid loading of the slurry, which was benefit to obtain stable and compact samples. The schematic of gelcasting process was described in Fig. 1. Table 2 displayed the name and mass of each constituent of the sample in Fig. 1.

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Table 1
Lists of boron carbide powder and additives.

Raw material	Abbreviation	Purity	Functionality
Boron carbide	B_4C	90.81%	Powder
Aluminum	Al	99.00%	Powder
n-Octanol	$CH_3(CH_2)_6CH_2OH$	Analytical	Solvent
Trimethylol propane triacrylate	TMPTA	Analytical	Monomer
Hexanedioldiacrylate	HDODA	Analytical	Cross-linker
Benzoylperoxide	BPO	Analytical	Initiator
CH-10S	–	Analytical	Dispersant

B_4C: Mudanjiang Jingangzuan Boron carbide Co., Ltd., China, W1.5 with average particle size 1.5 μm; Al: Beijing Haoyun Industry Co., Ltd., China, with average particle size 45 μm; $CH_3(CH_2)_6CH_2OH$: Tianjin Bodi Chemical Co., Ltd., China; TMPTA and HDODA: Shanghai Baorun Chemical Co., Ltd., China; BPO: Shanghai Qinwei Chemical Co., Ltd., China; CH-10S: Shanghai Sanzheng Polymer Material Chemical Co., Ltd., China.

Suspension was prepared by dispersing boron carbide and aluminum powders in the premixed solution, which was made by dissolving trimethylol propane triacrylate (TMPTA) and hexanedioldiacrylate (HDODA) (3:5 mass ratio) in *n*-octanol. TMPTA and HDODA were used as organic monomer and cross-linker to form network structure and consolidate the slurry. During the mixing, CH-10S (Shanghai Sanzheng Polymer Material Chemical Co., Ltd., China) was applied to improve the dispersibility and the stability of the slurry. The CH-10S was a hyperdispersant, which belonged to the ether family. The stable suspension of B_4C–Al with 55 vol.% solid loading could be prepared via mechanical stirring for 2 h. After the mixing period, a certain amount of BPO (benzoylperoxide, initiator of the reaction) solution was added into the suspension,

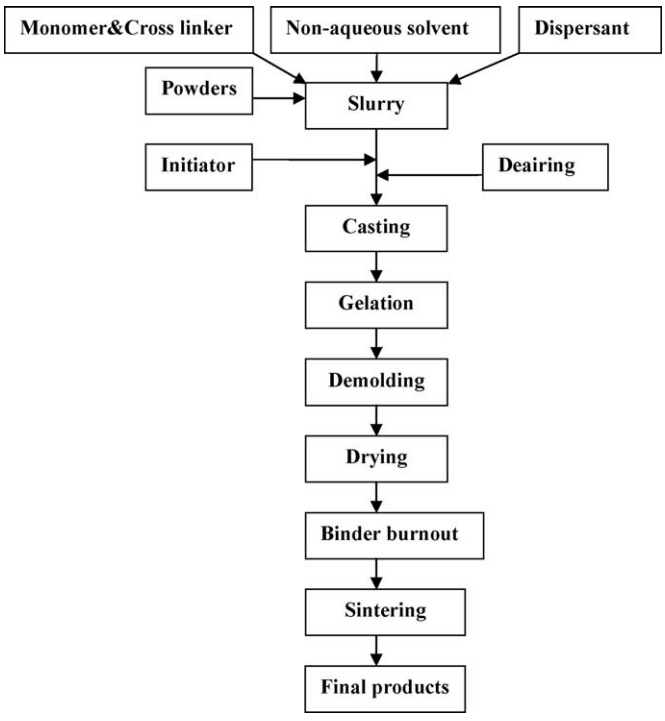

Fig. 1. Schematic of gelcasting process.

Table 2
Lists of constituents and masses of the sample in Fig. 1.

Constituent	function	mass/g
n-Octanol	Non-aqueous solvent	36.22
CH-10S	Dispersant	5.36
Trimethylol propane triacrylate (TMPTA) and hexanedioldiacrylate (HDODA)	Monomer and cross-linker	1.00
Benzoylperoxide:BPO	Initiator	4.03
B_4C–Al	Powders	141.60

which was deaired for 10 min before it was cast into the mould. Afterwards, the mould was moved into an oven at 100–130 °C for 5–30 min and the consolidation of the suspension could take place by polymerization and crosslink of the monomer and cross-linker, and the time of reaction depended on the amount of the initiator. The solidified green body was then demolded and dried at 150 °C for 5 h to remove organic solvent from the green body.

2.2. Test method

The viscosity of the concentrated B_4C–Al slurry was measured by rotary rheometer (NDJ-79, Shanghai Changji Dizhi Instruments Co., Ltd., China). All the slurries for viscosity measurements were prepared via mechanical stirring for 2 h and the measurements were performed at a constant temperature of 25 °C. The bulk densities of green and sintered body were determined by Archimedes principle. The flexural strength of green body was measured by three-point bending method with a span of 30 mm. The test bars of green samples were normally 3 mm × 4 mm × 36 mm. Microstructures of green and sintered samples were investigated by scanning electron microscope (JSM-840, JEOL, Japan). The elements of the sample were detected by energy dispersive X-ray spectroscopy (Oxford Instruments' INCA EDS system).

3. Results and discussion

3.1. Rheological properties of the boron carbide–aluminum slurry

3.1.1. Effect of CH-10S amount

Fig. 2 showed the influence of CH-10S concentration on the viscosity of 55 vol.% B_4C–Al (7:3 volume ratio) slurries at a shear rate of 344 s^{-1}, where the mass ratio of CH-10S to B_4C–Al slurry was 0.5, 1, 2, 3, 4 and 5, respectively. It can be seen that the slurry viscosity rapidly reduced with the increase in the concentration of CH-10S up to 3 wt.%. However, when CH-10S concentration continued to increase, the slurry viscosity kept almost constant, which indicated that CH-10S was effective and necessary to improve the fluidity of concentrated B_4C–Al slurry in a certain range of concentration. Comparing the influence of various concentrations of CH-10S on the viscosity, the slurry with optimum fluidity was obtained with 3 wt.% of CH-10S based on B_4C–Al slurry.

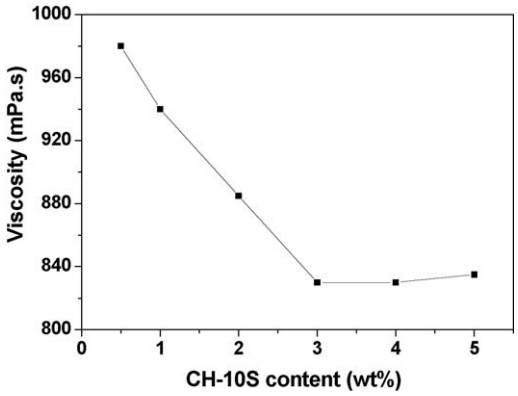

Fig. 2. Influence of CH-10S concentration on the viscosity of 55 vol.% B_4C–Al (7:3 volume ratio) slurry at a shear rate of 344 s^{-1}.

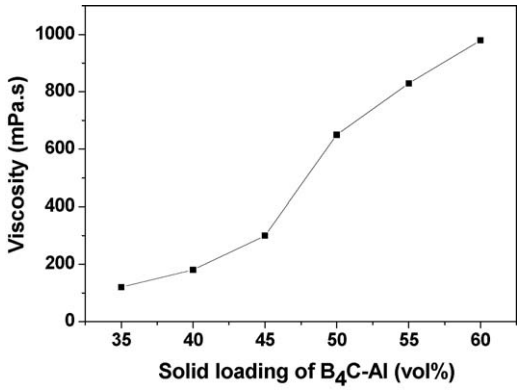

Fig. 3. Influence of different solid load on the viscosity of B_4C–Al (7:3 volume ratio) slurry at a shear rate of 344 s^{-1}.

3.1.2. *Effect of solid content*

Slurry for gelcasting should always meet two requirements: good fluidity and high solid loading. On the one hand, the slurry with good fluidity has uniform structure and ensures that the slurry can be poured into mold successfully. On the other hand, high solid loading can minimize shrinkage and warpage during drying and enhance high sintered density. Therefore, in gelcasting, it is desirable to have slurry with at least 50 vol.% solid loading, which is fluid and pourable at the same time. Fig. 3 showed the influence of different solids loading on the viscosity of B_4C–Al (7:3 volume ratio) slurry after adding 3 wt.% CH-10S at a shear rate of 344 s^{-1}. It can be observed that the slurry viscosity strongly depended on the amount of solid concentration. With the solid loading increasing from 35 to 60 vol.%, the slurry viscosity also increased significantly. When the solid loading of the slurry raised to 55 vol.%, the slurry showed low viscosity and high solid loading relatively, which was suitable for gelcasting in our experiments.

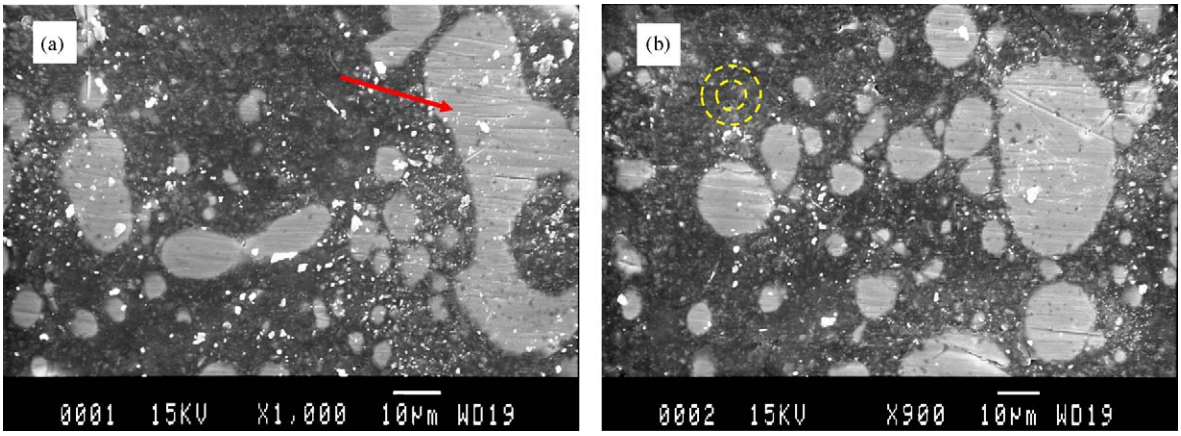

Fig. 4. SEM micrographs of green body on a polished surface.

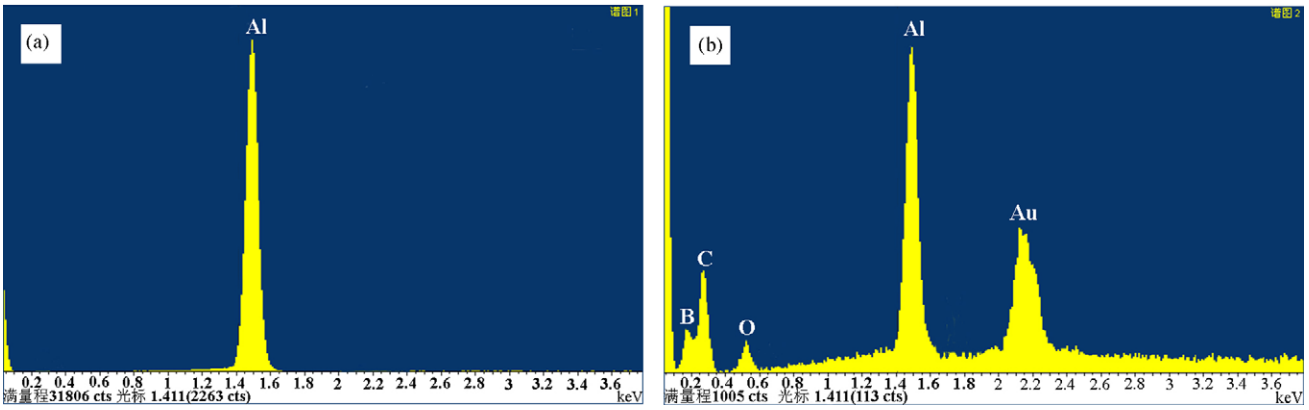

Fig. 5. EDS results of green body.

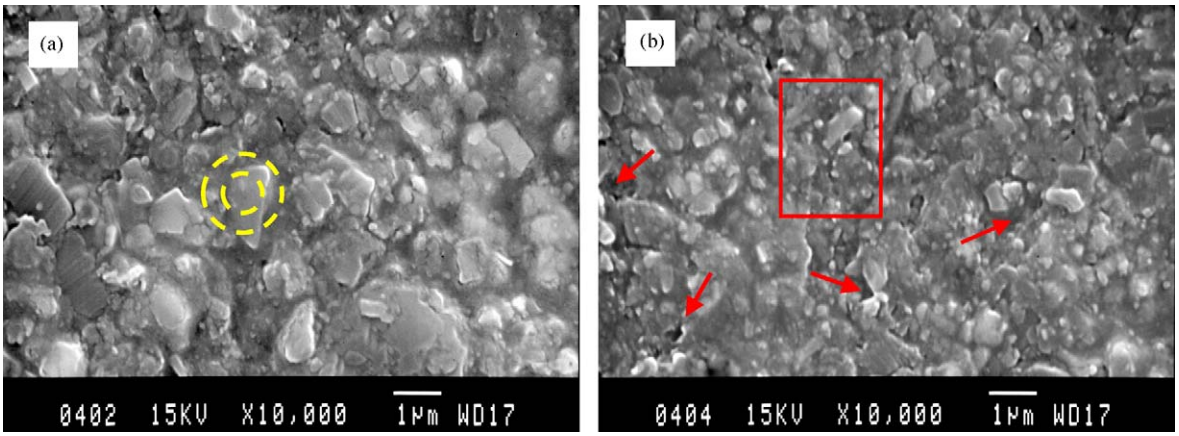

Fig. 6. SEM micrographs of sintered body on a polished surface.

3.2. Properties of boron carbide–aluminum composites formed by gelcasting

3.2.1. The strength and micrograph of green body

B_4C–Al green bodies with smooth surface and no visible defects can be produced by gelcasting. After drying in ovens, the mean value of relative density and the flexural strength of green body were 64% and 21 MPa relatively. The microstructures of the gelcast green body on a polished surface observed by SEM were showed in Fig. 4. It showed that powders in green body compacted closely and homogeneously. Particles in green body were connected by slender polymer networks, which improved the strength of green body even to afford machining. Moreover, the EDS results of green body on the polished surface were displayed in Fig. 5. According to Fig. 5(a), the big gray grains (corresponding to the arrow point in Fig. 4(a)) were Al. As to Fig. 5(b), the elements of B and C could demonstrate that the small black grains (corresponding to the circle part in Fig. 4(b)) were B_4C. The small white pieces in Fig. 4(a) and (b) were Al which fell from green body during milling. The O was the element of organic substances which added into the slurry. For Au element, it was detected because the sample was coated with Au to take SEM photographs firstly.

3.2.2. Phase composition and micrograph of sintered body

The sintering condition was at 1300 °C for 1 h in 0.1 MPa Ar atmosphere. Fig. 6 displayed the SEM micrographs of B_4C–Al samples on a polished surface. It showed that the microstructure was homogeneous, although with some pores (the arrows points in Fig. 6(b)) remained. Also, after sintering, the grains compacted closely and strongly. The phases in the sintered products were B_4C, Al_4C_3 and other unidentified phases. In addition, the EDS results of sintered body on the polished surface were shown in Fig. 7. According to Fig. 7(a), the gray grains (corresponding to the circle part in Fig. 6(a)) were aluminum compounds (the newly formed phase Al_4C_3), for the average at.% ratio of Al to C was 1.25, close to the atom ratio of Al_4C_3. To Fig. 7(b), the elements of B, C and Al showed the compositions in Fig. 6(b) (corresponding to the rectangle part) were Al_4C_3, B_4C and other unidentified phases. The presence of Al_4C_3 and other unidentified phase can be attributed to the vigorous reaction between B_4C and Al. These analyses were in good accordance with the results of Harverson et al., whose products were comprised of Al_4C_3, B_4C, $Al_4B_{1-3}C_4$ and unidentified X-phase [2]. The bulk density of sintered body was 2.05 g cm^{-3}. The main reason for the low density of B_4C–Al sintered body was that boron carbide and aluminum reacted to

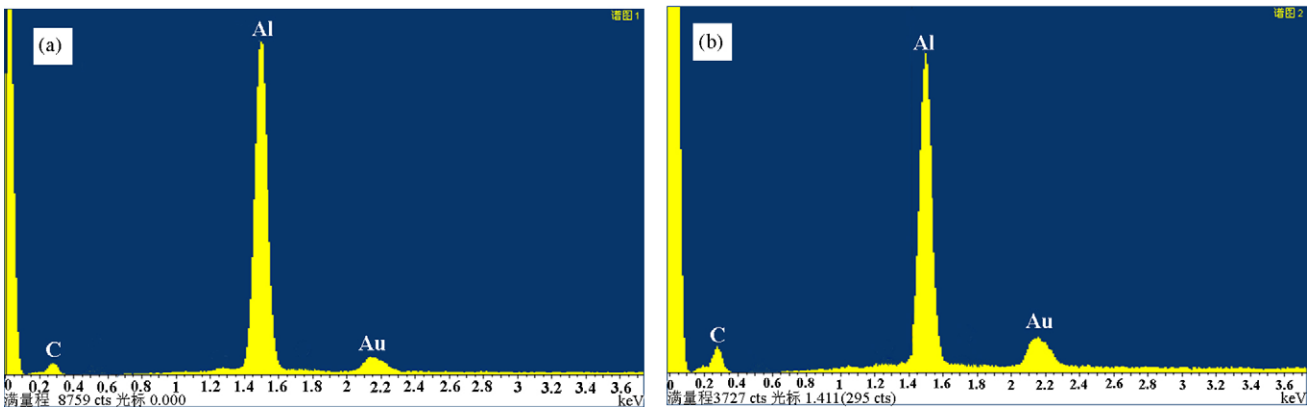

Fig. 7. EDS results of sintered body.

form huge amounts of new ceramic materials. Furthermore, the rate of reaction between B_4C and Al was greater than the rate of the movement of liquid aluminum throughout the B_4C agglomerates [11]. As a result, the densification was incomplete. B_4C–Al composites with high density could be obtained by reducing the sintering temperature and increasing the heat preservation time. Further study in this area is in progress in our group.

4. Conclusions

The present work reports the development of non-aqueous gelcasting using B_4C and Al powders. Stable uniform B_4C–Al slurry with 55 vol.% solid loading was obtained using 3 wt.% CH-10S. The mean value of relative density and flexural strength of green body is 64% and 21 MPa, respectively. The SEM images showed that ceramic and aluminum powders in green body compacted closely by the connection of polymer networks. The sintered samples were also obtained at 1300 °C for 1 h in 0.1 MPa Ar atmosphere. The bulk density of sintered body was 2.05 g cm^{-3}.

References

[1] F. Thévenot, Boron carbide—a comprehensive review, J. Eur. Ceram. Soc. 6 (4) (1990) 205–225.
[2] D.C. Halverson, M. Calif, A.J. Pyzik, I.A. Aksay, US Patent 4,605,440, 12 August (1986).
[3] A.C. Young, O.O. Omatete, M.A. Janney, P.A. Mechhofer, Gelcasting of alumina, J. Am. Ceram. Soc. 74 (3) (1991) 612–618.
[4] O.O. Omatete, M.A. Janney, R.A. Strehlow, Gelcasting—a new ceramic forming process, Am. Ceram. Soc. Bull. 70 (10) (1991) 1641–1649.
[5] O.O. Omatete, M.A. Janney, S.D. Nunn, Gelcasting: from laboratory development toward industrial production, J. Eur. Ceram. Soc. 17 (2–3) (1997) 407–413.
[6] K. Prabhakaran, C. Pavithran, Gelcasting of alumina using urea–formaldehyde: II. Gelation and ceramic forming, Ceram. Int. 26 (1) (2000) 67–71.
[7] Z.Z. Yi, Z.P. Xie, J.T. Ma, et al., Study on gelcasting of silicon nitride-bonded silicon carbide refractories, Mater. Lett. 56 (6) (2002) 895–900.
[8] L. Zhou, Y. Huang, Z. Xie, Gelcasting of concentrated aqueous silicon carbide slurry, J. Eur. Ceram. Soc. 20 (1) (2000) 85–90.
[9] T. Zhang, Z.P. Zhang, J.X. Zhang, et al., Preparation of SiC ceramics by aqueous gelcasting and pressureless sintering, Mater. Sci. Eng. A-Struct. 443 (2007) 257–261.
[10] M.A. Janney, US Patent 4,894,194, 16 January (1990).
[11] A.J. Pyzik, I.A. Aksay, US Patent 4,702,770, 27 October (1987).