Aqueous processing of boron carbide powders

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The present study was performed to determine suitable processing conditions to obtain optimized boron carbide slurries for gelcasting. We examined how dispersant, pH and other factors function in boron carbide slurries. The effect of the dispersant on the slurry stability was characterized in terms of zeta potential, sedimentation, and rheology measurements. Subsequently, the optimum conditions for the preparation of stable slurries with high solid content were determined. Gelcasting was used to consolidate the slurries. The effect of monomers on the slurry properties was studied. The properties of green and sintered B₄C samples were also investigated.

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1. Introduction

Because of their unique physical and chemical properties such as ultrahigh hardness, low density, excellent chemical stability and high neutron absorption capability, boron carbide (B₄C) materials have found a wide application in aerospace, nuclear energy and high-temperature thermoelectric conversion, blasting, polishing and more.¹⁾ However, their widespread applications have been restricted mainly due to their low mechanical reliability, high machining cost as well as poor sinterability due to a low self-diffusion coefficient. Several additives have been investigated in order to promote the sinterability of B₄C. The addition of carbon has been found to be effective in improving the densification of B₄C.²⁾

Gelcasting is an attractive near-net-shape ceramic-forming technique which can effectively increase materials reliability and lower the manufacturing costs of complex-shaped ceramic parts.^{3)–5)} The process involves preparation of high solid loading ceramic slurries with monomers, catalysts and initiators. Gelling is initiated after the slurry is cast in a mold. The organic component can serve as carbon source in the subsequent sintering process. In gelcasting process, particle dispersion is often the limiting factor, affecting both rheology and homogeneity of the suspensions.⁶⁾

Up to now, there are no reports about the dispersion and gelcasting of B₄C. In this study, the dispersion of B₄C slurries was studied in term of zeta potential, sedimentation and rheological tests. The properties of gelcasted B₄C samples were further studied.

2. Experimental procedure

The powder used was boron carbide (Mudanjiang Jingangzuan Boron Carbide Co., Ltd.) with the average particle size as 0.93 μm and a specific surface area as 10.78 m^2/g . Tetramethylammonium hydroxide (TMAH) was used as the dispersant. Aqueous suspensions were prepared by adding ceramic powders to deionized water in the presence of different amount of dispersant. The pH of suspensions was adjusted by HNO₃ and NaOH.

In the process of gelcasting, N, N-dimethyl acrylamide (DMAA) and N, N'-methylenebisacrylamide (MBAM) were applied as organic monomers for polymerization. 2, 2'-azobis [2-(imidazolin-2-yl) propane] dihydrochloride (AZIP·2HCl) was used as the initiator. In our study, the ratio of AZIP to DMAA is fixed at 1:130 by mass after screening. To avoid the possible coagulation of the suspensions, a dilute AZIP solution (5 mass%) was used as the initiator source. The gel casting process was well addressed in literature.⁶⁾ Typically, An aqueous solution containing 12 mass% of DMAA and MBAM (Aldrich) in 13/1 ratio in the presence TMAH as the dispersant was used as the dispersing medium. The slurries were prepared by adding B₄C powder to the premix solutions and ball milled for 24 h. Then the suspension was transferred to a flask followed by the addition of the initiator (AZIP). After degassing and casting, the moulds were put in water bath at 80°C for 30 min in order to gel the system. The gelled pieces were carefully dried to avoid cracking.

2.1 Zeta potential test

Zeta potential of the B₄C particles was measured through Zetaplus (Brookhaven Instruments Corporation). Ceramic suspensions (0.01 vol%) were prepared in the absence and presence of dispersant at various pHs. The ionic strength of each slurry was adjusted with 0.001 M KCl solution.

2.2 Settling experiments

Sedimentation measurements were carried out on 10 vol% B₄C suspensions. After pH adjustment, suspensions were poured into graded tubes. Reading of the sedimentation volume was recorded during 7 d.

2.3 Rheological measurements

The suspensions were placed in milling jars and roll-milled for 24 h before analysis. Apparent viscosity of the suspensions under different shear rate was examined under steady shear conditions by ascending and descending shear rate ramps respectively using a stress controlled rheometry (SR-5 Rheometric scientific instrument company, USA.).

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2.4 Microstructure, mechanical and other properties

After gelcasting and drying, binder burnout for all samples was carried out at 800°C for 2 h in vacuum. Sintering was performed in Ar atmosphere and hold for 1h for all samples. Tests of flexural strength were performed by three point bending from specimens of size $3 \times 4 \times 36 \text{ mm}^3$. The microstructure of all samples was observed by SEM. The composition of B₄C powder and the as-sintered B₄C samples was also determined by chemical analysis.

3. Results and discussions

3.1 Surface properties of B₄C

The zeta potential curves of B₄C powder are shown in **Fig. 1**. In the absence of TMAH, B₄C particle is negatively charged in the pH range studied (from pH 1.7 to 12). When the pH was increased, the zeta potential decreased and the minimum value appeared around pH 9. Further increase in pH will result in an upward trend of this curve. Therefore, the B₄C particles can be stabilized around pH 9 by electro-static force. After the addition of TMAH, an increase in zeta potential was observed. The dissociation of TMAH in aqueous solution can be described as the following⁷⁾

As TMAH is positive-charged in water, the association of TMAH on negatively charged B₄C particle surface is highly possible. As shown in Fig. 1, in the presence of TMAH, the pH_{IEP} of B₄C powder shifts slightly toward high pH, this might be due to the adsorption of TMAH. However, the zeta potential did not show a significant change, and the pH_{IEP} just increase slightly, so it is proposed that TMAH is mainly served as a pH adjusting agent, and the adsorption of TMAH on B₄C particle surface is not so high, similar to the case for SiC.⁸⁾

The stability of B₄C suspensions is evaluated from change of sedimentation volume as a function of pH and time. As shown in **Fig. 2**, the stability of B₄C suspension can be achieved in the pH range from 5.5 to 8.5. At lower (pH < 4) or higher (pH > 9) pH region, an increased sedimentation is induced, which might be due to the low surface charge of B₄C particles (see Fig. 1).

The influence of TMAH on the stability of B₄C suspensions was further characterized in term of apparent viscosity, see **Fig. 3**. With the addition of TMAH, the viscosity of B₄C slurries initially decreased with the increase of TMAH up to the TMAH to B₄C mass ratio of 5 mg/g, reached a minimum point and

Fig. 1. Zeta potential of B₄C powder.

Fig. 2. Sedimentation test with 10 vol% B₄C slurries.

Fig. 3. Viscosity of 50 vol% B₄C slurries (shear rate 350 s⁻¹).

increased thereafter (the shear rate is 350 s⁻¹). From Fig. 3, it can be concluded that TMAH could help to improve the slurry stability. This might be mainly due to the electrostatic force developed among B₄C particles because an increase in surface charge density was resulted in the presence of TMAH, see Fig. 1. The optimal TMAH content can also be determined (at the TMAH/B₄C mass ratio of ~5 mg/g).

Subsequently, 57 vol% B₄C slurries were prepared around pH 7 with the TMAH/B₄C mass ratio as 5 mg/g. The rheological properties were shown in **Fig. 4**. B₄C slurries exhibited a shear thickening behavior at higher shear rate (> 292 s⁻¹). A stable

Fig. 4. Rheological properties of 57 vol% B₄C slurries.

suspension tends to behave as a pseudoplastic fluid with low viscosity at low shear rates which may suddenly increase at a critical shear rate: shear thickening (dilatancy).⁹⁾ Figure 4 showed that B₄C slurries were in well stabilized state. This can also be correlated to the zeta potential, sedimentation tests and would confirm that TMAH was effective for obtaining well stabilized B₄C slurries.

After the addition of monomers, the slurry stability was also studied. The results are shown in Fig. 4. The addition of monomer and initiator showed very limited effect on the slurry stability. After degassing, the concentrated slurries showed good fluidity for the gelcasting process. After casting, gelation and drying, well-shaped green bodies were obtained. No obvious contraction and cracking was observed. The samples showed enough strength for demoulding and handling. The relative density of green samples was 64%. The mechanical properties of green samples are high. This high strength comes from the cross-linked gel network, which adhered to B₄C particles and bound them together. Pores with different sizes in the green bodies were also observed. The pore diameter distribution, obtained by Hg intrusion porosimetry, showed a monomodal distribution type with the peak around 156 nm, see Fig. 5. Figure 5 confirmed a homogeneous microstructure of B₄C green bodies by gelcasting.

The relative density of sintered samples at 2250°C was 91.6%, similar to that shown in literature using 1–3 mass% C as the sintering additives and sintered at 2325°C (the relative density is in the range of 90–91%).¹⁰⁾ The fracture strength is 261 ± 39 MPa. Schwetz et al reported the preparation of B₄C ceramics using 4 mass% carbon as the sintering additives, the relative density and flexural strength was 96.4% and 475 MPa respectively after pressureless sintering at 2150°C.²⁾ However, this high carbon addition might have deleterious effects on the mechanical properties of B₄C samples.¹¹⁾ The low density in our study might be due to the lack of sintering additives. Table 1 showed the carbon content in the powder and sintered samples. A slight increase in carbon content was observed after sintering. This extra carbon might come from the monomers, which could

Fig. 5. Pore size distribution of B₄C green samples.

Table 1. Composition of Starting Powder and as-Sintered B₄C Samples

Elements	Content (mass%)	
	B ₄ C powder	B ₄ C sintered sample
C	23.54	24.23
B	75.45	75.02
O	1.01	0.75

Fig. 6. XRD pattern of as sintered B₄C samples.

Fig. 7. Micrographs of as-sintered B₄C samples.

not be removed completely from the samples after binder removal. However, the carbon content is too low for the densification process. The XRD patterns showed the pure phase of B₄C according to PCPDFWIN Card No. 35-0798, Fig. 6. Micrographs of the fracture surface of B₄C sintered samples are shown in Fig. 7. A transgranular fracture type is observed. The fracture surface shows the presence of both fine and large pores, in agreement with the relative density value. Up to now, no literature about the colloidal processing of B₄C materials. Further study on the sintering and microstructure control is in process.

4. Conclusions

The stability of B₄C powder in aqueous media was studied using TMAH as the dispersant. Zeta potential showed that B₄C particles were negatively charged in the whole pH range investigated. Sedimentation test showed that B₄C powder can be stabilized in the pH range of 5.5–8.5. Viscosity and rheological measurement showed that TMAH was effective for obtaining stable B₄C slurries. After addition of monomers and initiators, the slurry stability was well kept and meets the requirement for gelcasting. The green samples exhibited a homogeneous microstructure with the relative density as high as 64%. Results showed that TMAH is a good dispersant for the gelcasting of B₄C ceramics.

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