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Fabrication and properties of reaction-bonded SiC prepared by gelcasting

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The properties of green and reaction-bonded SiC (RBSC) samples prepared by a gelcasting technique are investigated in this paper. The results show that solid loading and monomer content of the suspension in the gelcasting process are the main factors that effect the density and shrinkage of the green bodies. A slurry with a solid loading of 58 vol% was solidified in situ to a green body with a linear shrinkage of 1.1% and flexural strength of 27 ± 2 MPa. SEM micrographs show that the SiC and C particles in the green body were closely compact by a connection of the polymer network. The maximum density and flexural strength of samples reaction sintered at 1700 °C in vacuum were 2.97 g/cm^3 and 378 ± 12 MPa respectively.

Key words: Gelcasting, Reaction-bonded SiC, Property, Sintering.

Introduction

Due to their excellent properties at elevated temperature, silicon carbide ceramics have been widely used for high temperature applications. Among various silicon carbide ceramics, reaction-bonded silicon carbide (RBSC) ceramics have considerable advantages from an economic viewpoint since the costs of production and raw materials are relatively low [1-3]. RBSC ceramics are made by reactive melt infiltration of silicon (Si) or its alloys into microporous silicon carbide and carbon preforms. For the manufacture of RBSC products, it is usual to adopt conventional forming techniques, e.g. slip casting and cold isostatic pressing. However, products with complex shapes and accurate dimensions are difficult to produce by these procedures without subsequent machining.

Gelcasting is a novel near-net-shape ceramic forming method as a synthesis of concepts derived from traditional ceramics and polymer chemistry. The process is based on polymerization of organic monomers and simultaneous solidification of a concentrated slurry to green body. The major two advantages of the gelcasting method are the low content of the organic binder (3-5 wt%) and the relatively high dried green body strength that allows machining in the green state. Other advantages include a short processing time, a more homogenous distribution of organic binders and easy binder removal [4-6].

In the present study, a gelcasting process was utilized to prepare RBSC bodies using SiC powder and carbon as starting materials. A concentrated SiC/C slurry suitable for aqueous gelcasting was obtained, and a high quality RBSC green body and dense RBSC ceramics were fabricated. The density, linear shrinkage and flexural strength of the green bodies as well as the flexural strength of sintered bodies were studied. In addition, the microstructures of green and sintered bodies were examined using scanning electron microscope (SEM).

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Experimental Procedure

Commercially available SiC powders (Weifang Liuhe Co. Ltd., China) and carbon black (Weifang Zhida Co. Ltd., China) were used as the raw materials. In order to reach a high packing density, the starting materials consisted of coarse silicon carbide powder and fine silicon carbide powder. The weight ratio of coarse powder R320 and fine powder R1200 was 1 : 3. The characteristics of SiC powders and carbon black are shown in Table 1 and Table 2 respectively.

For the gelcasting process, acrylamide [$C_2H_3CONH_2$, AM] was used as the monomer, *N,N'*-methylene-bisacrylamide [$(C_2H_3CONH)_2CH_2$, MBAB] as a coupling agent, and ammonium persulphate [$(NH4)_2S_2O_8$, APS] as an initiator. All the chemicals mentioned above were supplied by Tianjin Chemical Company, China. To improve the dispersion of the powders and the fluidity of the suspension, polyvinyl pyrrolidone [$C_3H_6CONC_2H_3$, PVP] and tetramethylammonium hydroxide [$(CH_3)_4NOH$, TMAH] were used as dispersants for carbon black and silicon carbide respectively.

Figure 1 shows the gelcasting procedures for the preparation of RBSC green bodies. First, the carbon black and dispersant PVP were added to a premix solution of organic monomer AM and coupling agent MBAM. After ball milling for 2 h in an alumina jar, the SiC powders and the dispersant TMAH were added to the carbon black slurry. The weight ratio of silicon carbide and carbon black was 9. Homogenization of

Table 1. Chemical and physical characteristics of SiC (wt %)

Type	SiC	Fe_2O_3	C	d_{50} (μm)
R320	98.96	0.14	0.08	29.2 ± 1.5
R1200	98.10	0.19	0.11	3.0 ± 0.8

Table 2. Physical characteristics of carbon black

Density (g/cm^2)	Specific surface area (m^2/g)	Particle size (nm)	pH value
1.9	100	200	9

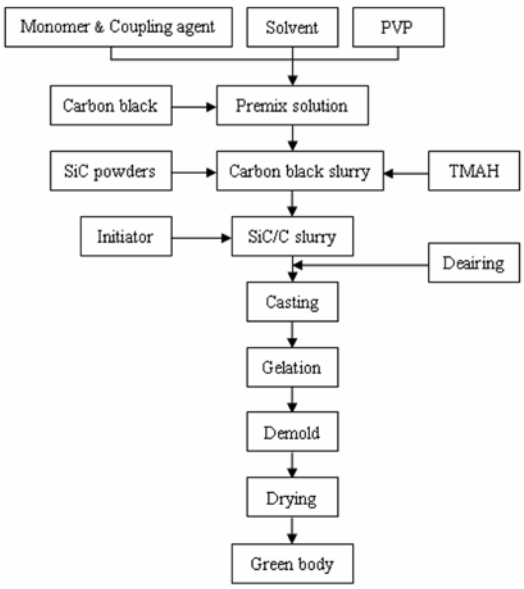


Fig. 1. Flowchart of gelcasting process.

SiC/C slurry was carried out for another 6 h. Afterwards, the initiator APS was applied to the slurry. The slurry was degassed for 10 minutes and then it was cast into nonporous molds. After the monomers polymerized, the gelled bodies were demolded and dried below 80 °C for 24 h. Finally, the green bodies were reaction-bonded at 1700 °C in vacuum. Binder burnout was carried out before sintering, which is not discussed in this paper.

The bulk density of the green and sintered bodies was measured according to Archimede's principle with deionized water as the immersion medium. For the flexural strength, a three-point flexural test was used on 3 mm × 4 mm × 36 mm bars with a span of 30 mm and a loading rate of 0.5 mm/minute. The microstructure of fractured surfaces was observed with a scanning electron microscopy (SEM JSM-6380LA, Hitachi, Japan).

Results and Discussion

The effect of initiator and temperature on gelation rate

The factors that strongly influence the rate of gelation are the content of initiator APS and gelling temperature when the solid loading and content of carbon black are fixed. The relationship of idle time with initiator content and gelling temperature is shown in Fig. 2. It can be

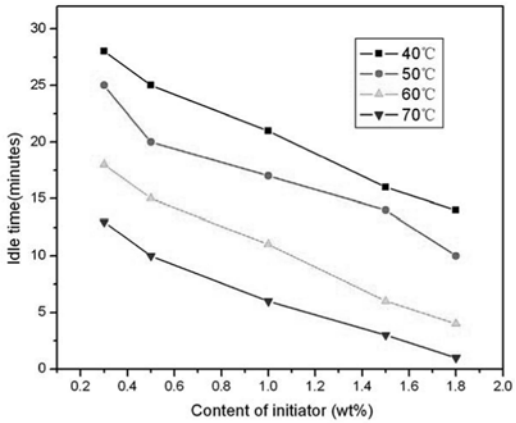


Fig. 2. Idle time as a function of initiator content and gelling temperature.

seen from Fig. 2 that the idle time ranged from 1 to 28 minutes by controlling the initiator content and gelling temperature. These data clearly show that gelation is accelerated by an increase in initiator content or temperature.

Green density and linear drying shrinkage

The shrinkage that occurs during water elimination by diffusion towards the surface and evaporation is the critical character of the drying stage. Figure 3 shows the effect of solids loading on linear drying shrinkage and green density when the total amount of monomer was kept at 4 wt% for the powders. In accordance with previous reports [7, 8] about an acrylamide-based gelcasting system, the bulk density of the green body increased with solid loading and on the other hand, the drying shrinkage dec- reased with solid loading. There exists a linear shrinkage of about 1.1% and a density of 2.09 g/cm^3 can be obtained at a solid loading of 58 vol%, which indicates that a high solid loading resulted in a high packing density in the RBSC gelcasting process. Figure 4 shows the variation in linear shrinkage and green density of dried bodies with monomer content where the solid loading was kept at 55 vol%. As can be seen from Fig. 4, the density did not show an obvious change with an increase in the monomer content from 3 wt% to 4.5 wt%, while the linear shrinkage ranged from 2.41% to 1.9%. The reason for the decrease of linear shrinkage could be attributed to the strengthened three-dimensional polymeric network, which helped to resist further contraction

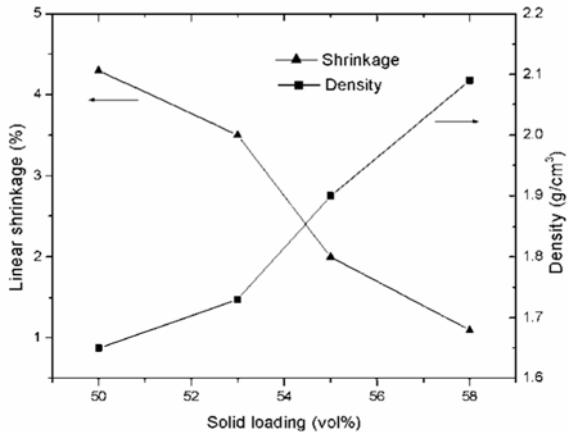


Fig. 3. Effects of solid loading on linear drying shrinkage and green density.

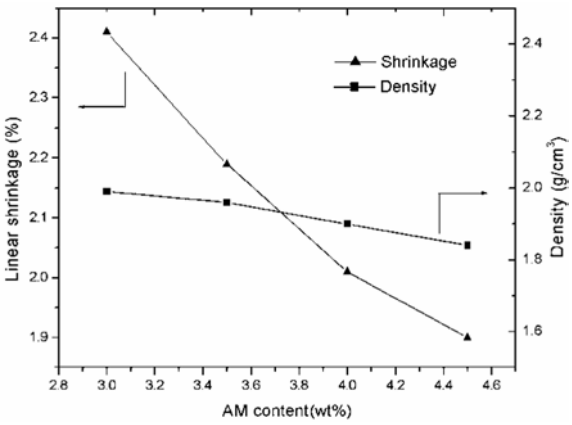


Fig. 4. Effects of monomer content on linear drying shrinkage and green density.

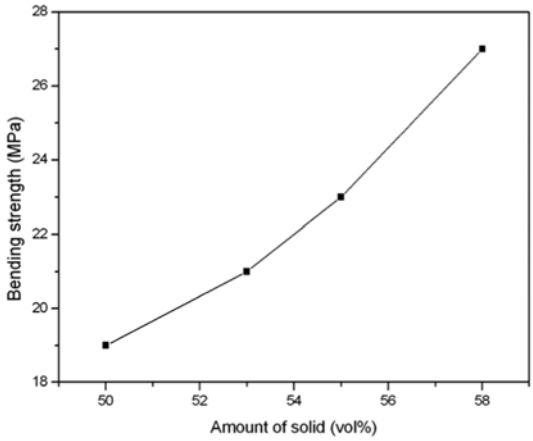


Fig. 5. Effects of solid loading on green strength.

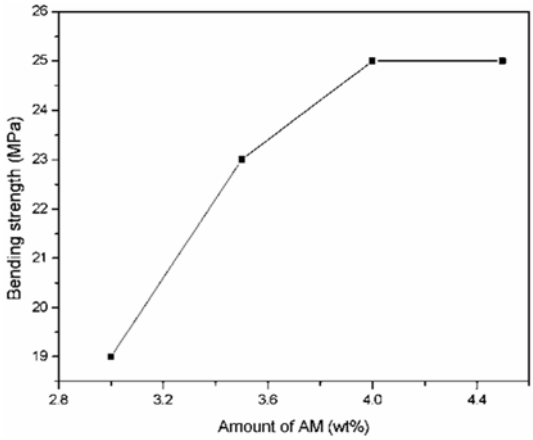


Fig. 6. Effects of monomer content on green strength.

caused by the water evaporation.

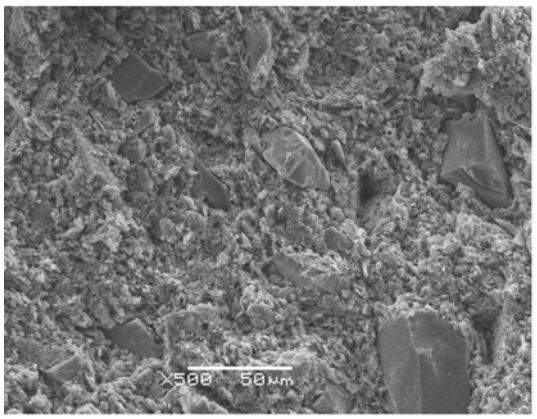
Strength of green bodies

The effects of solid loading and monomer content on the strength of SiC/C green bodies are shown in Fig. 5 and Fig. 6, respectively. Figure 5 shows that the green strength increased almost linearly with solid loading and varied from 19 to 27 MPa as the solid loading ranged from 50 to 58 vol%, which gives a reasonable strength for green machining [9]. According to Chen etal.'s study [10], the existence of carbon black inhibited the free-radical polymerization of acrylamide partially, which resulted in the lower conversion of polymerization in the SiC/C gelcasting system. This may be the cause of the lower green strength compared with SiC green bodies prepared by gelcasting [11]. The results in Fig. 6 show that the flexural strength of the green body reached a maximum strength of 25 MPa at a monomer content of 4 wt%, but higher amounts of monomer have little effect on the green strength. This is largely because the green strength is related to the adhesion of the polymer networks between particles. However, if the monomer content is higher than 4wt%, the superfluous will not contribute to the three-dimensional polymeric network structure and the green strength will hardly increase.

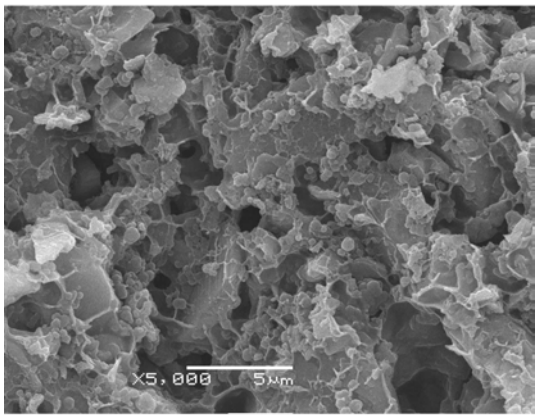
SEM micrographs of the fracture surfaces of the dried green body with 55 vol% solid loading are shown in Fig. 7. It can be seen from Fig. 7(a) that the coarse and fine silicon carbide particles have a relatively uniform distribution. From Fig. 7(b) it can be seen that a well-developed cross-linked network was formed and the SiC and C particles were connected by this polymer network.

Performance and microstructure of sintered RBSC samples

Figure 8 shows the variation of flexural strength and sintered density with the solid loading. As shown in Fig. 8, both flexural strength and bulk density of sintered samples increased with solids loading, and the highest strength of 378 ± 12 MPa was obtained for the samples with the highest density of 2.97 g/cm^3. In general, a high packing density would lead to better sinter ability and higher strength. However, this viewpoint may not be supported for the reaction bonding process of RBSC



(a)



(b)

Fig. 7. Micrographs of gelcast green body.

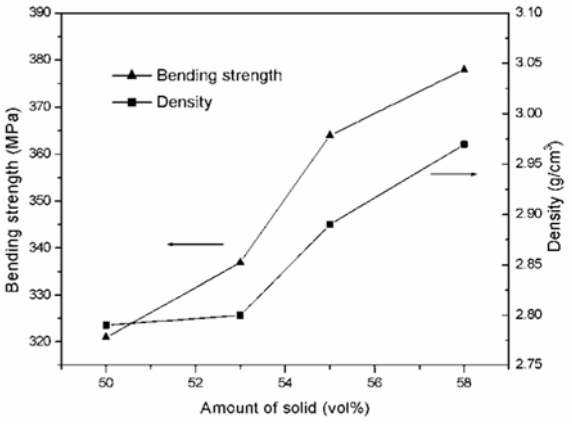


Fig. 8. Flexural strength and bulk density of sintered bodies versus solids loading.

ceramics. During the reaction bonding, the melted silicon reacts with carbon to form new silicon carbide, which bonds the original silicon carbide particles together [12]. Therefore, the fully dense preforms are not helpful to liquid silicon infiltration. But if the amount of pores is too much to be completely filled by the newly-formed silicon carbide, the residual spaces will be filled with free Si phase. The existence of free Si limits application

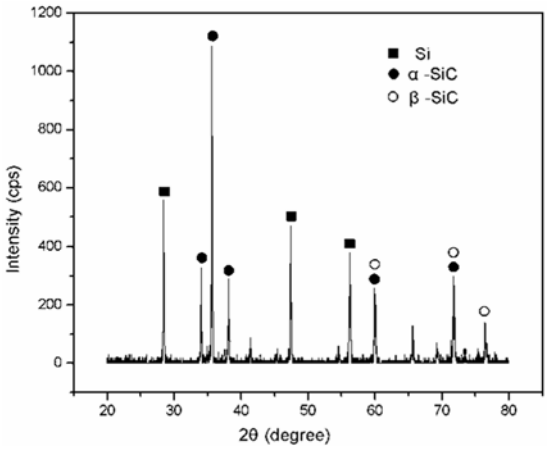


Fig. 9. XRD patterns of RBSC.

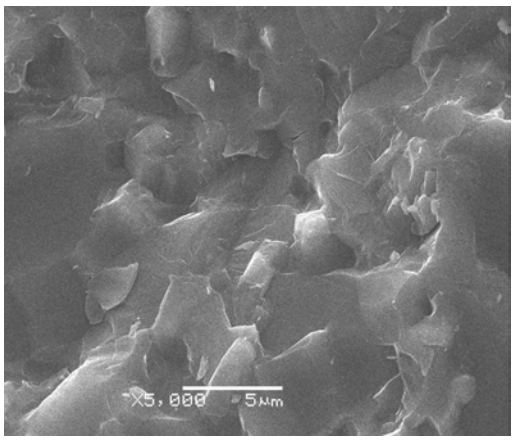


Fig. 10. SEM micrographs of fracture of RBSC obtained by gelcasting.

of the product because of the relatively low melting point and fracture toughness of Si. According to the results of Fig. 8, a higher solid loading and density of green bodies with a low porosity may lead to a lower proportion of free Si in the sintered samples, which exhibit better mechanical properties.

Figure 9 shows a typical XRD pattern of RBSC obtained by gelcasting (with a solid loading 58 vol%), which shows the presence of both α- and β-SiC and unreacted free Si. Fig. 10 is a SEM micrograph of the RBSC sintered samples. It can be seen from Fig. 10. that the microstructure is homogenous and there are few pores in the RBSC sintered body. However, obvious growth of fine silicon carbide can also been found and this phenomenon may be due to the dissolution and recrystallization of original SiC grains during the sintering [13].

Conclusions

Reaction-bonded silicon carbide (RBSC) ceramics were prepared successfully from silicon carbide and carbon black by a gelcasting process. The results showed that an increase of initiator ccontent as well as a higher gelling

temperature decreased the idle time of the gelcasting process significantly. The green bodies with a higher packing density (2.09 g/cm^3) and lower drying shrinkage (1.1%) have been obtained, which indicate that the gelcasting process results in the near-net-shape desired. SEM analysis shows that SiC and C particles in the green body were connected by a three-dimensional polymeric network, and coarse and fine silicon carbide particles were distributed homogeneously. The RBSC ceramics were fabricated by reaction sintering at 1700 in vacuum. The highest strength of 378 ± 12MPa was obtained for the sintered samples with the highest density of 2.97 g/cm^3.

Acknowledgements

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