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Gelcasting of concentrated aqueous silicon carbide suspension

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Abstract

Gelcasting of high concentrated aqueous silicon carbide suspension with 50 vol.% solids loading is discussed in this paper. It is found that SiC powder is suitable for being suspended in basic solution, provided that a proper pH value is chosen for it. The rheological property of SiC suspension is also affected by solids loading. When SiC slurry is cast at 70°C, reaction between free Si on the surface of SiC powder and an organic base used as dispersant gives out H_2 gas, which produces pores in green bodies. However, by vacuum pumping and controlling pH value of the suspensions, complicated shapes of uniform SiC green bodies without pores are prepared. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Gelcasting; Suspensions; Microstructure-prefiring; SiC

1. Introduction

Silicon carbide possesses a variety of virtues, such as high mechanical strength, high chemical stability, high temperature of decomposition, good thermal conductivity and semi-conductivity.[1] The development of advanced SiC ceramic materials is technologically important in a broad range of applications, which include medical biomaterials, high temperature semiconductors, synchrotron optical elements and light weight/high strength structure materials.[2] The latter category, i.e. structural SiC ceramics is widely studied[3,4] and considered as one of the promising candidate materials for various applications: diesel engines, gas turbines, industrial heat exchangers, high-temperature energy conversion systems and many other devices.[1,5] In recent years, complex-shaped silicon carbide components with high uniformity, high performance, and thus high reliability, have been receiving increasing attention largely due to those applications.

The preparation of high-quality complex-shaped ceramic parts is one of the most important problems that ceramists have been trying to resolve. The brittle nature of ceramics precludes deformation method,[6] so the cost-effective way is to form complex-shaped green bodies and then sinter them rather than to form simple-shaped green bodies and then machine them into complicated shapes after sintering. However, the conventional forming processes, e.g. dry pressing and hot pressing, have limitations in meeting the requirements because of inherent problems.[7]

The in-situ consolidation colloid forming processes, such as temperature induced flocculation,[8] direct coagulation casting,[9,10] and gelcasting[7,11] are promising techniques for complex shapes of structural ceramics. The approaches are able not only to prepare complicated shapes, but also to decrease or eliminate defects, such as hard agglomerates, pores and cracks, which would result in relatively low reliability as structural components. Compared to other colloidal processes, e.g. slip casting and tape casting, the outstanding advantage of those techniques is that their slurries can be in-situ consolidated, which results in near-net-shape forming. Among those in-situ processes, gelcasting is the best for practical application because the method is capable of preparing uniform green bodies with high strength, which opens up the possibility of machining them.

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Gelcasting is a generic process. Ceramic parts from more than a dozen different compositions (ranging from alumina-based refractories to high performance silicon nitride) have been produced by it,[12] but there is no paper that reports the study on gelcasting of silicon carbide component with its high concentrated (solids loading $\geqslant$ 50 vol%) slurry.

This study focuses on investigating colloidal behavior of SiC powder in aqueous solution, preparing high concentrated aqueous silicon carbide slurries and casting complicated shapes of uniform SiC green bodies.

2. Experimental procedure

2.1. Materials and reagents

The silicon carbide used is a commercially available powder (Rs07, Huamei abrasive and sharpener Corporation, P.R. China), which was manufactured by carbothermic reduction method. Table 1 shows its physical and chemical characteristics. Yttria and alumina powders (Jiangsu Wuxian Special Ceramics Plant, P.R. China), serving as sintering aids for silicon carbide, have the average particle size of 1 μm, with purity more than 99%. Acrylamide, $C_2H_3CONH_2$(AM) and N,N′-methylenebisacrylamide, $(C_2H_3CONH)_2CH_2$ (MBAM) are applied in the process of gelcasting as monomers for polymerization, which is initiated by an initiator, ammonium persulfate $[(NH4)_2S_2O_8]$ and accelerated by a catalyst, N,N,N′,N′-tetramethylethylenediamine (TEMED). All of these reagents are chemically pure.

2.2. Procedure

The gelcasting process is similar to that of previous studies.[7,11] First, SiC powder (with or without sintering aids) was suspended in a premix solution, which has been prepared by dissolving AM and MBAM in deionized water. To improve dispersion of the powder and fluidity of the suspension, an organic base, tetramethyl ammonium hydroxide $[(CH_3)_4NOH$, TMAH] was applied as dispersant. The slurry was then degassed for 10 min after having been milled for 16 h. Two degassing methods, mechanical vibrating and vacuum pumping, were employed to compare their effect. The suspension was degassed for another 3 min when the initiator and catalyst were added. All the above operations were carried out at room temperature. Afterwards, the slurry was cast into a nonporous mold, which was then kept at 70°C. After monomers polymerized, the green bodies were demolded and dried at room temperature under controlled humidity to avoid cracking and nonuniform shrinkage due to rapid drying. Binder burnout was operated before sintering, which is not discussed in this paper.

2.3. Physical and chemical property measurements

Zeta potentials of the SiC powder were measured by Zetaplus (Brookhaven Instruments Corp., USA). Dilute HCl and TMAH solutions were used for pH adjustment. The apparent viscosity of suspensions was examined by a rotary viscometer (Model NXS-11, Chendu Instrument Plant, P.R. China). The microscopic morphology was observed by SEM (CSM950, OPTON, Germany). During the processing, pores were discovered in green bodies, which were supposed to be as a result of a kind of gas given off by reaction between SiC powder, the dispersant and the premix solution. A self-made gas gathering device, shown in Fig. 1, was then designed to ascertain the reaction. Gas gathered was analyzed by gas chromatography (Gas Chromatograph 3400, Beijing Analytical Instrument Plant, P.R. China). The condition of the reaction is similar to that of polymerization except that the experiments for collecting gas continue longer. Reagents (SiC powder, premix solution or dispersant) were contained in a gastight reactor immerged in a 80°C water bath. The reagents were agitated by a magnetic stirrer and the experiment lasted for 30 min. A certain volume of air was pressurized as gas vehicle in the reactor, so the volume of the resultant gas can be calculated by detecting the volume ratio of the resultant gas to N_2 in the collected gas.

3. Results and discussion

3.1. Colloidal behavior of SiC powder

The pH-dependent zeta potentials of the SiC powder in aqueous solutions are shown in Fig. 2. As the figure illustrates, the IEP of silicon carbide in deioned water is acidic, below which zeta potentials are positive, above which zeta potentials are negative; at strongly basic pH value, the absolute values of the zeta potentials are relatively high.

During synthesis, transportation and storage, silicon carbide powder is inevitably oxidized, forming an oxygen

Table 1
Physical and chemical characteristics of SiC powder

d_{50} (μm)	S_{BET} (m^2/g)	SiC (wt%)	Free Si (wt%)	O (wt%)	Free C (wt%)	Fe_2O_3 (wt%)
1.48	4.19	> 98	0.45	0.49	0.66	< 0.5

rich layer on its surface. The oxidized layer is chemically similar to the surface of silica[13]. When the powder is treated with water vapor or dispersed in deionized water, the layer is hydrated, causing silanols (Si–OH) on the surface of SiC powder. Silanols are amphoteric, relatively strongly acidic and weak alkalescent.[14] In all but low pH range(< pH3.3 in Fig. 2), silanols react with OH^-, leaving $Si–O^-$ with negative charges on the surface of the powder, resulting in negative zeta potentials. In low pH range, silanols react with H^+, yielding $Si–OH_2^+$ with positive charges on the surface of SiC powders, resulting in positive zeta potentials. The reactions are expressed as following:

$$\mathrm{Si{-}OH + OH^- \rightleftharpoons Si{-}O^- + H_2O}$$

$$\mathrm{Si{-}OH + H^+ \rightleftharpoons Si{-}OH_2^+}$$

Since silanols are of relatively strong acidity, and, thus, easy to react with OH^-, the absolute values of zeta potential for SiC powder are higher at strongly basic pH than at strongly acidic pH.

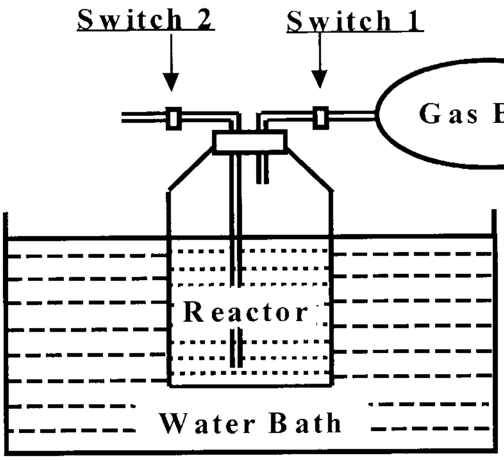

Fig. 1. Sketch map of the device for gathering resultant gas.

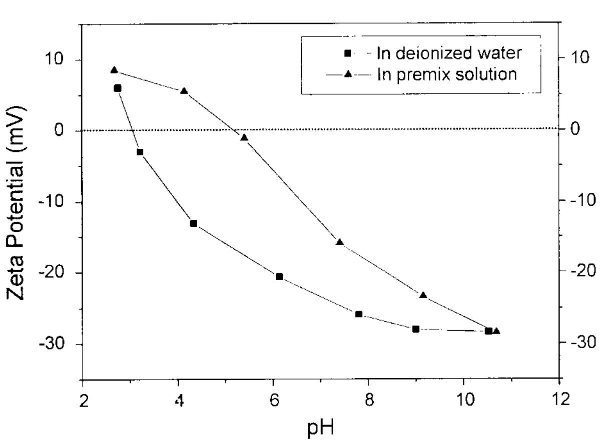

Fig. 2. The pH-dependent zeta potential of SiC powder.

The zeta potential curve for SiC powder in premix solution is in analogy to that of SiC particles in deioned water. However, IEP of the former is higher than that of the latter, while the gradient in zeta potential at the IEP of the former is lower than that of the latter. The adsorption of monomers on the surface of the SiC particles, with a high probability, contributes to the shift of IEP.

Anyway, when SiC powder is suspended in aqueous solution, the absolute values of its zeta potentials are larger at high pH, inducing larger electrostatic interparticle repulsion, which is important to establish a colloidally stable suspension. So SiC powder is easy to disperse in alkaline solution.

3.2. Rheological property of SiC suspension

Fig. 3 shows curves for rheological property of slurries (at 50 vol.% solids loading) with various pH values. The slurry with pH 10.60 or 11.38 possesses good rheological property. When pH value is lower than 10.1, zeta potential of SiC particle is not sufficient to establish a stable suspension, so the slurry is of shear-thickening and increases sharply in viscosity at high shear rate. When pH value is higher than 11.92, ionic strength in the suspension is too high, causing viscous slurry. Therefore, the suspensions need a proper pH value range (10.5–11.5), that is, the dispersant of TMAH should be added to slurries in a proper amount.

Fig. 4 includes curves for rheological behavior of SiC slurries (at pH 10.5) at different solids loading. As shown in the figure, when their solids loading are less than 50 vol.%, the viscosity of the SiC slurry increases gently with increase in solids loading, but when they are more than 50 vol.%, the fluidity decreases sharply with increase in solids loading. The operation in gelcasting process is responded to shear rate at 100 s^{-1}, so the suspension at 51 or 52 vol.% does not fit gelcasting.

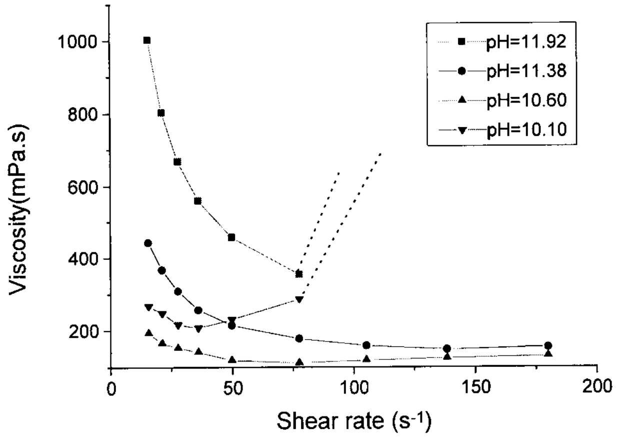

Fig. 3. Rheological behavior of SiC suspensions at different pH values (at 50 vol.% solids loading).

The suspensions, with a formulation of 91 wt% SiC, 6 wt% Al_2O_3 and 3 wt% Y_2O_3, were developed for consolidation in the study. The viscosity of those slurries are not increased because alumina and yttria powders are also well dispersed in basic solution, as demonstrated in Fig. 5.

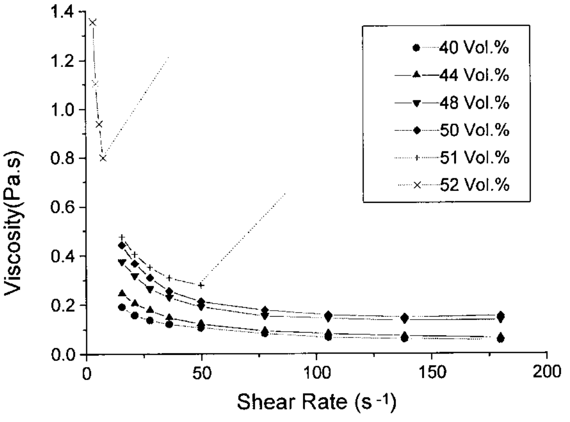

Fig. 4. Rheological behavior of SiC suspensions at different solids loading (at pH 10.5).

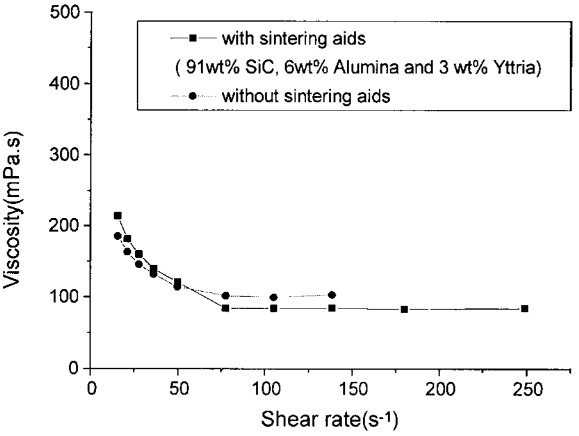

Fig. 5. Effect of sintering aids on rheological behavior of SiC slip (at 50 vol.% solids loading and pH10.5).

3.3. Consolidation of SiC suspension

When cast into a mold at constant temperature of 70°C, SiC suspensions were consolidated within 10 min. Fig. 6 are scanning electron micrographs of the fracture surfaces of the SiC green bodies, which were cast from slurries, at 50 vol.% solids loading and pH 11.52, degassed by the two methods. Sample A was prepared by mechanical vibration, sample B via vacuum pumping. As shown in Fig. 6, there are more and larger pores in sample A; fewer and smaller ones in sample B.

When milled or added initiator and catalyst, the SiC slurries are inevitably puffed, leaving air bubbles in them. If not excluded, the air bubbles will be inflated and yield pores in green bodies when suspensions were consolidated at 70°C. On the other hand, acrylamide reacts with TMAH and discharges NH_3, the reaction is expressed as:

$$C_2H_3CONH_2 + OH^- = C_2H_3COO^- + NH_3(g)$$

At room temperature, the degree of the reactivity is very low and the NH_3 gas is dissolved in the suspensions due to its high solubility.[15] But at 70–80°C, the reaction is strong and the solubility of NH_3 decreases greatly. If the rate at which the reaction gives out NH_3 is higher than the rate that slurries discharge the gas, pores will form in green bodies. Because of the two causes above, degassing must be applied before casting slurries.

Comparing sample A to B, it can be concluded that vacuum pumping plays a better role on degassing, but it still cannot eliminate holes in green bodies. The pores in sample B are probably the result of the resultant gas going out from an unexpected reaction due to the high pH 11.52 of the slurry.

To confirm the reaction discharging the resultant gas in suspensions, a series of experiments was designed for gathering the gas. It is difficult to collect the gas during consolidation since the gas will be trapped in the green bodies, so the experiments for gathering the gas produced by Si-hydrolysis in suspensions are operated in

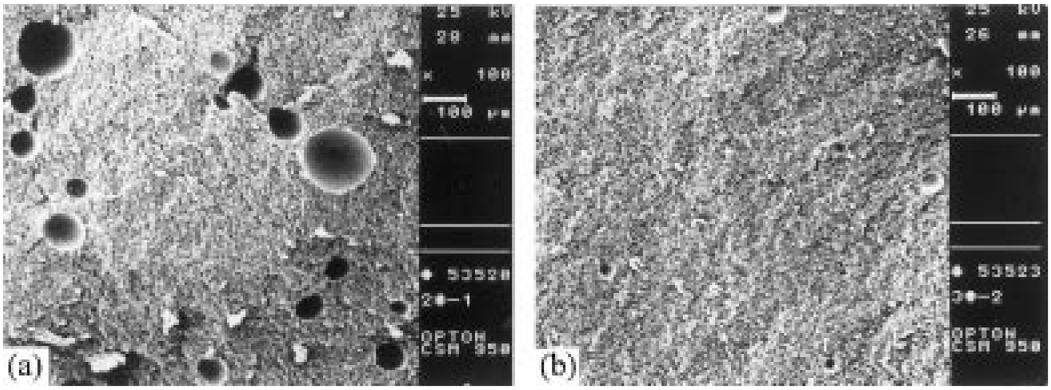

Fig. 6. The fracture surfaces of the SiC green bodies (cast form slurries at 50 vol.% solids loading and pH 11.52): (a) by mechanical vibrating; (b) by vacuum pumping.

Table 2
The results of experiments for gas chromatography

No.	Reactants (reacting at 80°C for 30 min)		H_2
	Powder	Solution	(ml)
1	SiC/200 g	Premix solution[a]/25O ml, TMAH[b]/12.5 ml	195.7
2	SiC/200 g	Premix solution/25O ml	none
3	SiC/200 g	H_2O/250 ml, TMAH/12.5 ml	291.3
4	Si/0.25 g	H_2O/250 mL, TMAH/12.5 ml	280.9
5	Oxidized SiC/200 g	H_2O/250 ml, TMAH/12.5 ml	4.08
6	SiC/200 g	Premix solution/250 ml, TMAH/25 ml	380.4

[a] Premix solution: Acrylamide[$C_2H_3CONH_2$(AM)], *N,N′*-methylenebisacrylamide [$(C_2H_3CONH)_2CH_2$ (MBAM)] and deionized water.
[b] TMAH: tetramethyl ammonium hydroxide [$(CH_3)_4NOH$], 10 wt%.

suspensions with lower solids loading and for longer time without initiator and catalyst. Table 2 shows the results. The solution formulation in experiment 1 is that of slurry with pH 10.5 after milling. Its result suggests that the suspensions do give off extra gas — H_2 gas at 70–80°C. The NH_3 is not detected because of its high solubility in water. Experiment 2 and 3 clarify that the H_2 is the result of SiC powder reacting with TMAH. According to chemical compositions of SiC powder, free Si is the only possible substance that is able to react with TMAH, which is authenticated by experiment 4.

In several early investigations,[13,16,17] it was reported that Si had a tendency to hydrolyze in water, which is an exothermic reaction

$$Si(s) + 2H_2O = SiO_2(s) + 2H_2(g)$$

and that there were difficulties associated with Si processing in an aqueous environment. When mixing Si with aqueous solution, H_2 evolution was observed. The degree of reactivity increased with decreasing particle size and increasing alkalinity, and severe gassing was reported for pH values in excess of 10.[17] According to the authors' knowledge, there is no early paper reporting the reaction between SiC powder and alkaline solution, partly because free Si in SiC powder is commonly less than 1 wt% and, thus, the reaction is slow and inconspicuous; partly because in early researches, SiC slurries were not heated to as high as 70–80°C with pH value beyond 10.

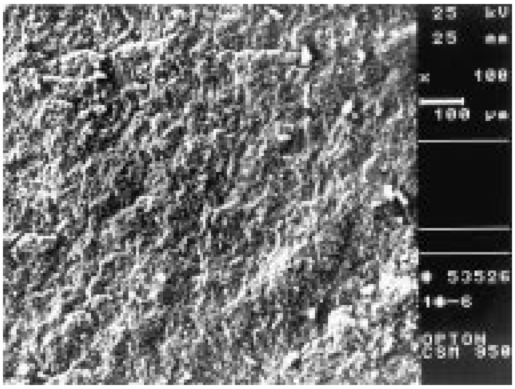

Fig. 7. The fracture surface of the SiC green body prepared by vacuum pumping (cast form slurries at 50 vol.% solids loading and pH 10.5).

Experiment 5 illustrates that when free Si on the surface of the powder is lessened by oxidization in air at 800°C for 2 h, there is less resultant H_2; while in comparison with experiment 2, experiment 6 shows that the rate of the reaction and, thus, the volume of H_2 are proportional to the concentration of TMAH. The two experiments indicate that there are at least two methods to decrease or even eliminate the resultant H_2 leading to pores in green bodies. One is to reduce the content of free Si on the surface of SiC powder by oxidization or other methods; the other is to decrease concentration of TMAH, viz. pH value of SiC suspensions.

Fig. 7 displays scanning electron micrographs of the fracture surfaces of the SiC green bodies cast from slurries degassed by vacuum pumping at 50 vol.% solids loading and pH 10.5. It shows a uniform green body without pores. Fig. 8 shows some complex shapes gelcast from the suspensions. The density of these bodies is 54% of theoretical, while their strength is 31.6 MPa (3×4×30 mm), which indicates that the green bodies

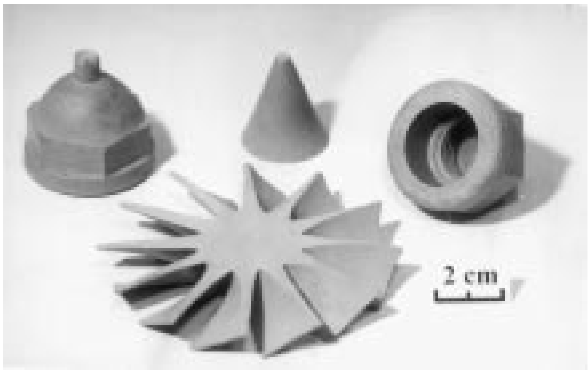

Fig. 8. Complex shapes of SiC green bodies by gelcasting.

are machinable. After binder burnout, there were no shrinkage, crack and distortion in them.

4. Conclusion

1. The surface of SiC powder is similar to that of Silica and, thus, its colloidal behavior is similar to that of silica. SiC is suitable for being suspended at basic solution, but a proper pH value should be controlled for it. Too low or too high pH value results in viscous slurries.
2. The rheological property of SiC slurry decreases with increase in solids loading. Slurries prepared at solids loading as high as 50 vol.% are of good fluidity and fit gelcasting.
3. When SiC slurry is cast at 70°C, free Si on the surface of SiC powder reacts with the dispersant, an organic base providing alkalescence, and gives out H_2 gas. If the reaction is violent, pores will come into being in green bodies. By vacuum pumping and controlling pH value of the suspensions, complicated shapes of uniform SiC green bodies are prepared.

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