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Study on gelcasting and properties of recrystallized silicon carbide

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Abstract

Gelcasting of recrystallized silicon carbide (RSiC) was described in this paper. The Zeta potentials of recrystallized silicon carbide powders dispersing in aqueous solution and the rheological property of the suspension were investigated. A concentrated suspension of solid loading as high as 75 vol.% for gelcasting was prepared successfully. At the same time the complex green bodies with uniformity of density and high flexural strength were fabricated by gelcasting through this kind of suspension. The performance and microstructure of green bodies and sintered samples was measured and observed. Recrystallized silicon carbide parts were prepared by gelcasting. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: B. Microstructure; Gelcasting; Recrystallized silicon carbide; Rheological property

1. Introduction

Recrystallized silicon carbide (RSiC) has been widely used in metallurgy, aerospace and other industry due to its high temperature strength, outstanding erosion resistance and oxidation resistance. Together with the high thermal conductivity and the low coefficient of expansion this material is especially designed for the use as kiln furniture [1]. For the complex compact forming of this material, slip casting has been employed to shape green bodies. However, slip casting requires rather long period for the process and the strength of green bodies is weak. In addition, density gradient in the thick green bodies is easily caused.

Gelcasting is a novel near-net-shape forming process, which was developed by M.A. Janney et al. at Oak Ridge National Laboratory [2–4]. In the process, ceramic powders are dispersed in the pre-mixed monomer solution to prepare a stable high solid loading suspension with low viscosity. The polymerization of monomers form a cross-link network by applying with the initiator and catalyst. The particles and water in slurry are held together with such a network of polymers. The notable merit of gelcasting is that green bodies are very uniform and strong compared to slip casting. This promising process has been applied to various fine ceramics, including oxides and non-oxides [5–8], where ultrafine ceramic powders (sub-micrometer or nanometer) are used. However, gelcasting of silicon carbide with coarse particles for producing recrystallized silicon carbide refractory has not been reported.

In the present paper, gelcasting of recrystallized silicon carbide is investigated. The influence of dispersant and solids loading on rheology of coarse silicon carbide suspension was studied. High solids loading suspension was obtained and used to form complex-shape green body with uniform structure and high strength. In addition, the microstructure of sintered samples was examined.

2. Experimental procedure

2.1. Materials and chemicals

The starting materials consisted of coarse silicon carbide and fine silicon carbide powders to reach a high parking density. The ratio of coarse powder to fine powder is 70:30 wt.%. Main impurities of the powders include Fe 520 ppm, O 1.17 wt.%, Si 0.26 wt.% and free carbon 0.35 wt.%. The particle size of mixture containing coarse and fine SiC powders ranges from 0.2 to 350

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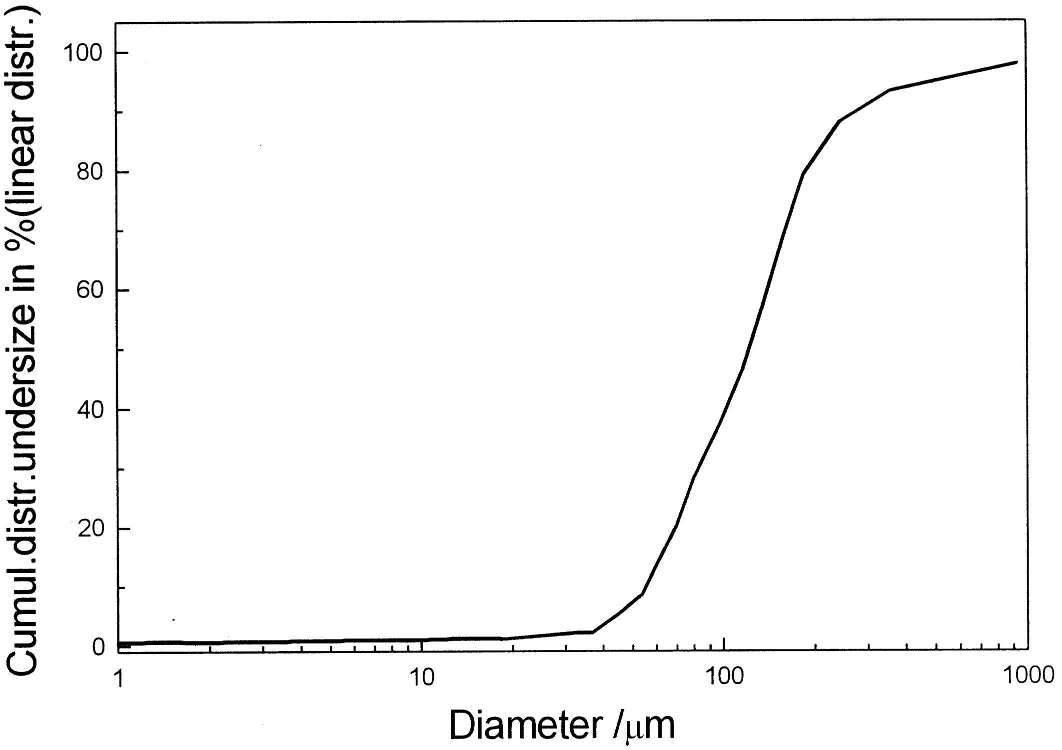


Fig. 1. Particle size distribution of R-SiC.

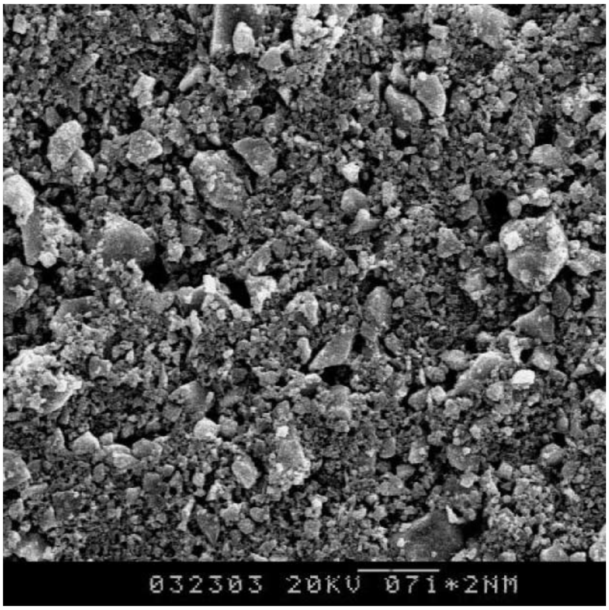


Fig. 2. SEM micrograph of SiC powder.

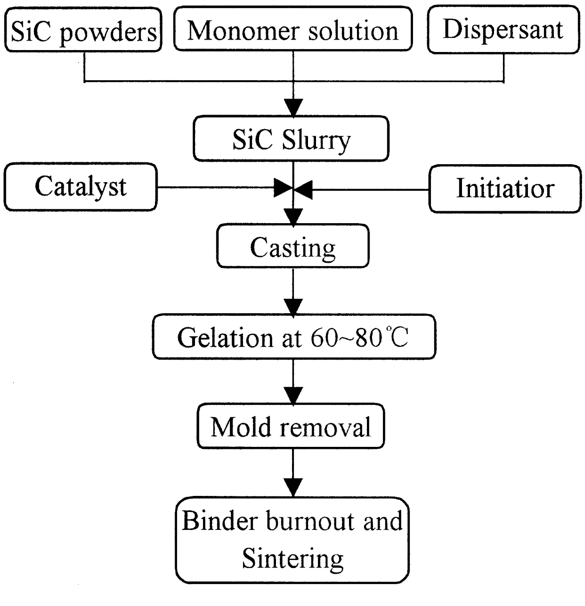


Fig. 3. The process flowchart of R-SiC gelcasting.

μm (as shown in Fig. 1). SEM photograph (Fig. 2) of the raw material shows the morphology of the particles.

For the gelcasting process, acrylamide (AM) is used as monomer, difunctional *N,N′*- methylenebisacrylamide (MBAM) as coupling agent. The initiator is ammonium persulphate, and the catalyst is *N,N,N′,N′*-tetramethylethylenediamine (TEMED). A kind of dispersant, namely tetramethylammoniumhydoxide solution (TMAH), is used to prepare stable suspension with high solid loading and low viscosity.

2.2. Gelcasting process of RSiC

The schematic forming process of gelcasting is described in Fig. 3. First, the silicon carbide powders and dispersant were added to premix solution of organic monomer. After mixing for around 30 min, the initiator and catalyst were applied to the slurry. Then it was cast into metal mould at room temperature. Afterwards the mould was moved into an oven at temperature of 60–80 °C, and the consolidation of suspension formed a green body. After demoulding and drying, the binders were removed by burnout before green bodies were sintered. Recrystallized silicon carbide parts were obtained by sintering in an oven at 2450 °C for 10 h in Ar.

Compared to gelcasting of fine ceramic powders such as alumina with narrow and submicron particle size, ball-milling and degassing were omitted for coarse silicon carbide gelcasting. This is due to the wide range of particle sizes of the starting powders from 0.2 to 350 μm, which make it easy to mix completely and break down agglomerates under the condition of mechanical stirring. So it is unnecessary to ball-mill the slurry. In addition, recrystallized silicon carbide is used as porous materials, so degassing is totally meaningless.

2.3. Testing method

The viscosity of the recrystallized silicon carbide slurries at various shear rates was examined with a control-rate rotary rheometer (MCR300, Physica, Germany) and a concentric cylinder measurement device with a 1.13 mm gap was employed. Vane geometry was used for all tests. The vane had a diameter of 13.33 mm. The sample volume was 23 ml of fluid. The measurements were performed within the shear rate range of 0.1–250 s^{-1} at a constant temperature of 25 °C.

Zeta potential of the fine silicon carbide was calculated from the measured electrophoretic mobility using electrophoretic light scattering (ELS) with 5 mW laser source. The bulk density measurements of specimens at different stages, namely after drying and sintering, were determined with the Hg immersion method based on Archimedes' principle.

The room-temperature flexural strength of both green body and sintered samples were examined. A three-point bending method was employed for the test, with a cross-head speed of 0.2 mm/min and a span of 30 mm. The bars of green samples and sintered samples were commonly 5×6×36 mm. Fracture surfaces of the specimens of green and sintered samples were examined with scanning electron microscope (SEM).

3. Results and discussions

3.1. Effect of dispersant on the colloidal behaves of RSiC suspension

The Zeta potentials of SiC powder dispersed in the organic monomer solutions are shown in Fig. 4. It is found that the isoelectric point (IEP) of recrystallized silicon carbide in deionized water is 3.9. At strongly basic pH values, the absolute values of Zeta potentials are relatively high. With the addition of 0.2 vol.% dispersant (TMAH, based on organic monomer solutions), IEP of silicon carbide is shift to around 2.8. Meanwhile, the absolute Zeta potentials are increased considerably in the range of pH from 2 to 12. The electrostatic interparticle repulsion is increased when TMAH is adsorbed on the particle surface.

Regarding the above Zeta potential shift it can be considered as follows. During the synthesis process of the silicon carbide powder, it is inevitably oxidized,

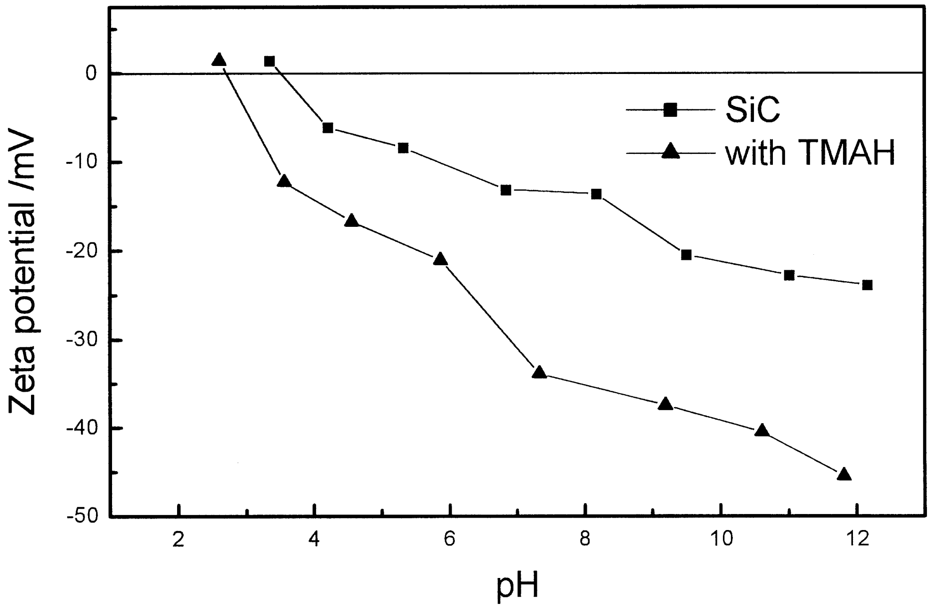


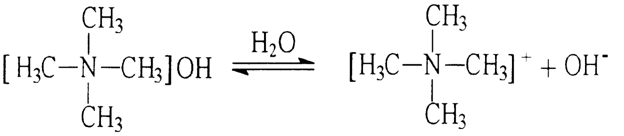
Fig. 4. Zeta potential versus pH value of SiC suspension with and without dispersant of TMAH.

forming an oxygen-rich layer on its surface. The oxidized layer is chemically similar to the silicon surface [9]. When the powder is exposed in the ambient conditions or dispersed in deionized water, the layer is hydrated, causing silanols (Si–OH) on the surface of SiC particles. Silanols are amphoteric, relatively strongly acidic and weak alkalescent [10]. In all but low pH range (pH < 3.9), silanols react with OH^-, leaving $Si–O^-$ with negative Zeta potentials. At low pH range, silianols react with H^+, yielding $Si–OH_2^+$ with positive charge on the surface of SiC powders, resulting in positive zeta potentials. The reactions are expressed as following [11]:

$$Si-OH + OH^- \rightarrow Si-O^- + H_2O$$

$$Si-OH + H^+ \rightarrow Si-OH_2^+$$

Since silianols are of relatively strong acidity, and thus, easy to react with OH^-, the absolute values of zeta potential for SiC powder are higher at strong basic pH than at strongly acidic pH. When dispersant, namely TMAH, is added to the suspension containing silicon carbide powder, it is ionization according to the following reaction:



$$[H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_3]OH \xrightleftharpoons{H_2O} [H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_3]^+ + OH^-$$

As a result, a certain concentration of OH^- was provided and higher pH value was produced, which resulted in an adsorption of OH^- on the particle surface. A higher repulsive force between the recrystallized silicon carbide particles was obtained.

According to DLVO theory [12,13] and steric stability theory [14], higher zeta potential is necessary for stable and low viscosity slurry. The addition of TMAH as well as the strong basic condition is very helpful to prepare the stable suspension of recrystallized silicon carbide with low viscosity for the forming process of gelcasting.

3.2. Rheological properties of the RSiC suspension

The rheological property of aqueous ceramic suspensions strongly depends on pH values, solid loading and dispersant type. Fig. 5 shows that viscosity of the silicon carbide suspension changes with pH values for a solid loading of 60 vol.%. The pH values of suspension were adjusted by addition of an alkaline dispersant (TMAH). when the volume ratio of the organic monomer solutions to dispersant changed from 1 ml:10 µl to1 ml:60 µl, the pH value of suspension ranged from 9.5 to 12.5. It can be noticed that rheological properties of suspension is very sensitive to pH values as discussed above. When the pH value is lower than 9.5, viscosity increases dramatically with the decrease of pH value. This is due to the lower absolute value of Zeta potential of recrystallized silicon carbide in lower pH values. While the pH value reached 11.9 (ranges from 9.5 to 12.5), the viscosity of suspension is only around 0.12 Pa s and the suspension possesses good rheological property. However when pH value is higher than 12.5, ionic strength in the suspension is too high, causing increase of viscosity of the suspension. Therefore, the suspensions need a proper pH value ranging from 9.5 to 12.5.

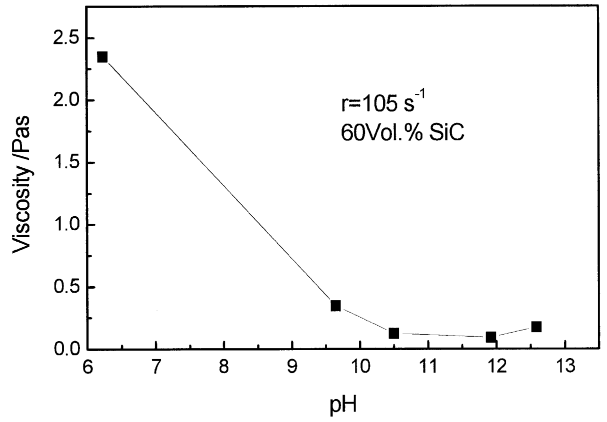


Fig. 5. Effect of pH on the viscosity of SiC suspension.

The influence of dispersant (TMAH) on rheology of slurry containing 70 vol.% solid loading is shown in Fig. 6. Where the volume ratio of the organic monomer solutions to dispersant is 1 ml:10 µl, 1 ml:20 µl, 1 ml:40 µl, 1 ml:60 µl and without dispersant. Clearly, viscosity is considerably reduced when TMAH is employed. Compared to the effect of various amounts of TMAH on viscosity, the lowest viscosity was obtained when the ratio of monomer solution to TMAH is 1 ml:20 µl.

Fig. 7 shows the rheological properties of recrystallized silicon carbide suspension vs. solid loading. It can be seen from the curves that the suspension shows relative low viscosity when solid loading is below 75 vol.%. With solid loading increased up to 75 vol.%, viscosity is 16.8 Pa s under shear rate of 72 s^{-1}. Viscosity of slurry with solid loading of 78 vol.% reaches the

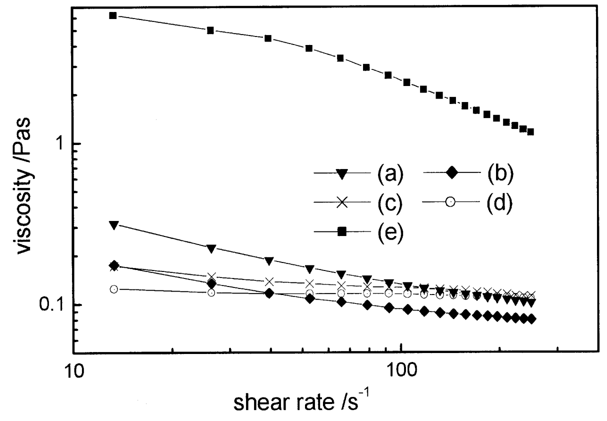


Fig. 6. Viscosity of SiC suspension with dispersent versus shear rate.

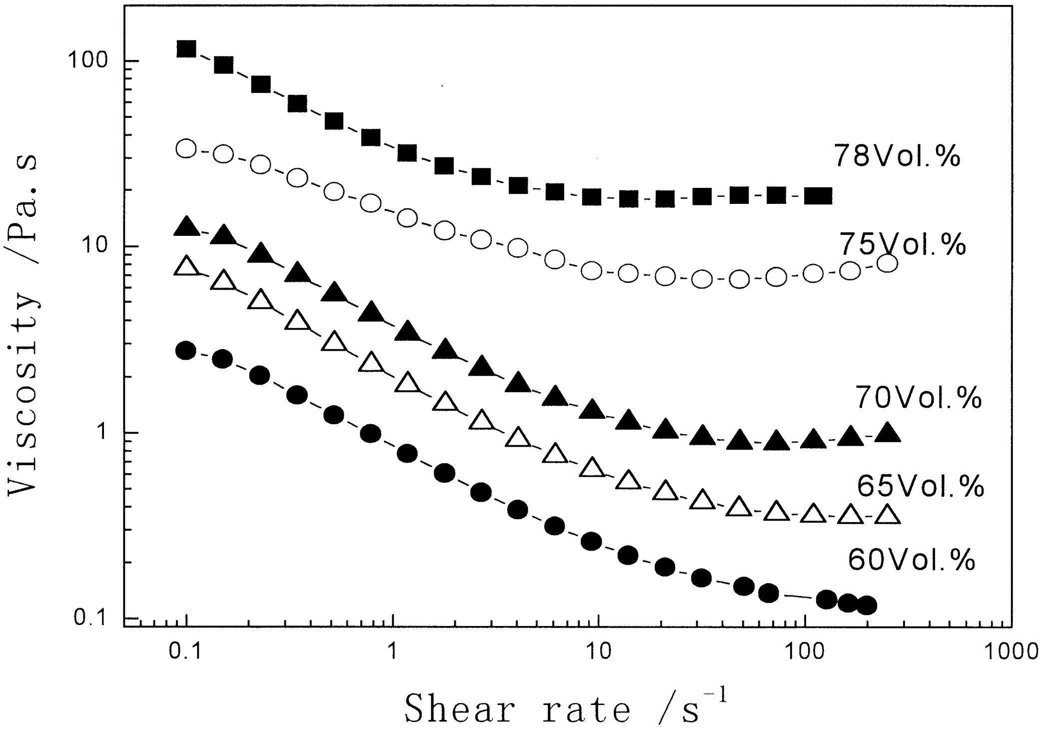


Fig. 7. Viscosity versus shear rate for SiC suspension with different solid loading.

value of around 100 Pa s, which is not suitable for gelcasting processing. The results show that much higher solids loading can be reached for the coarse powder compared to ultrafine ceramic powder.

As we know, solid loading for fine ceramic powders, whose diameter is in scale of micron or submicron, can reach no higher than 60 vol.%. Generally oxides and non-oxide powders can be prepared into slurry with solid volume from 45 to 60 vol.% [15,16]. However, a solid volume fraction of 75 vol.% can be prepared by recrystallized silicon carbide. Meanwhile the suspension has a good fluidity. This is attributed to the broad distribution of particle diameters, which improve the parking density.

In the case of silicon carbide suspension, viscosity increases exponentially with the increase of slid loading. It can be described with Newtonian fluid and Power law equations [17]:

$$\tau \ = \eta\gamma \tag{1}$$

$$\tau = K\gamma^{n} \tag{2}$$

where $n = \mathrm{d}(\lg\tau)/\mathrm{d}(\lg\gamma)$ named non-Newtonian index, γ is the shear rate, τ is shear stress, η is the viscosity, K and n are constants.

It is concluded from Eqs. (1) and (2):

$$\eta = \tau/\gamma = K\gamma^{n-1} \quad d\eta/d\gamma = K(n\text{-}1)^{n-2}$$

If $n = 1, d\eta/d\gamma = 0$ Newtonian fluid;

If $n < 1, \ d\eta/d\gamma < 0$ pseudoplastic fluid.

A pseudoplastic fluid mold with $n<1$ is observed in Fig. 7 where the suspension shows shear thinning. In the case of the suspension containing 60 vol.%, there is the strongest pseudoplastic flow behaviour. With the increase of solid loadings, pseudoplastic flow behaviour was weakened. For example, near Newtonian fluid was shown when shear rate was higher than 10 s^{-1} shear rate for the suspensions containing 78 and 75 vol.% solid loadings.

3.3. Preparation and properties of RSiC materials

3.3.1. Properties and microstructure of RSiC green bodies gelcasted

According to Fig. 3 a stable suspension of silicon carbide with 75 vol.% solid loading was prepared by dispersing silicon carbide powders in the organic monomer solutions. After mixing it was cast into a metal mould. With appropriate amounts of initiator and catalyst, the consolidation of the suspension was completed in about 20 min at 60 °C. Some complex shape parts with smooth surfaces and fine features were produced and samples are shown in Fig. 8 (pH = 11.9±0.2, 75 vol.%).

Flexural strength of the green bodies and bulk densities were measured. The results were presented in Fig. 9, in which a highest flexural strength of 35±1.9 MPa was obtained. The green strength is much higher that of slip cast samples. It was found that flexural strength reduced with the solids loading when monomer content is fixed. The flexural strength varies from 35±1.9 to 15±2.1 MPa as the solids loading ranges from 55 to 75 vol.%. This is largely because the strength of green body is related to the adhesion of the polymer network between particles. With solid loading increased, polymer networks were used to keep more particles together, and the cross-link of powders was weakened, which results in the decrease of green strength with solid loading increase. Bulk density strongly depends on solid loading as shown in Fig. 9. It varies from 2.16 to 2.37 g cm^{-3}, when the solids loading change from 55 to 75 vol.%. The density of green body is 73.8% of theoretical density of recrystallized silicon carbide.

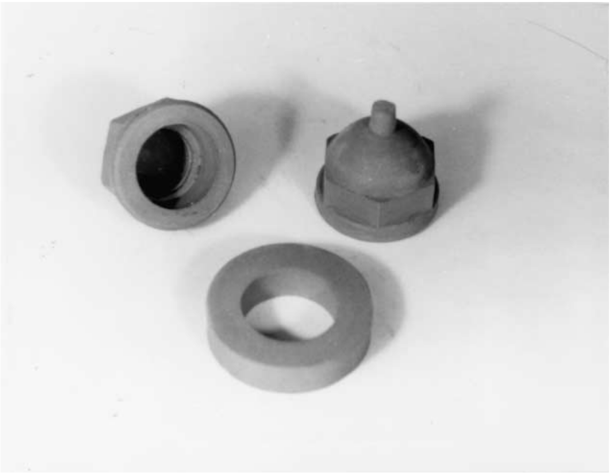


Fig. 8. Complicated shapes of SiC green bodies prepared by gelcasting.

The microstructure of green body was examined by SEM. From the micrograph shown in Fig. 10, it can be seen that powders are connected by polymer networks, which present the green body's high strength.

Fig. 10. SEM micrograph of fracture surface of the gelcast RSiC green bodies.

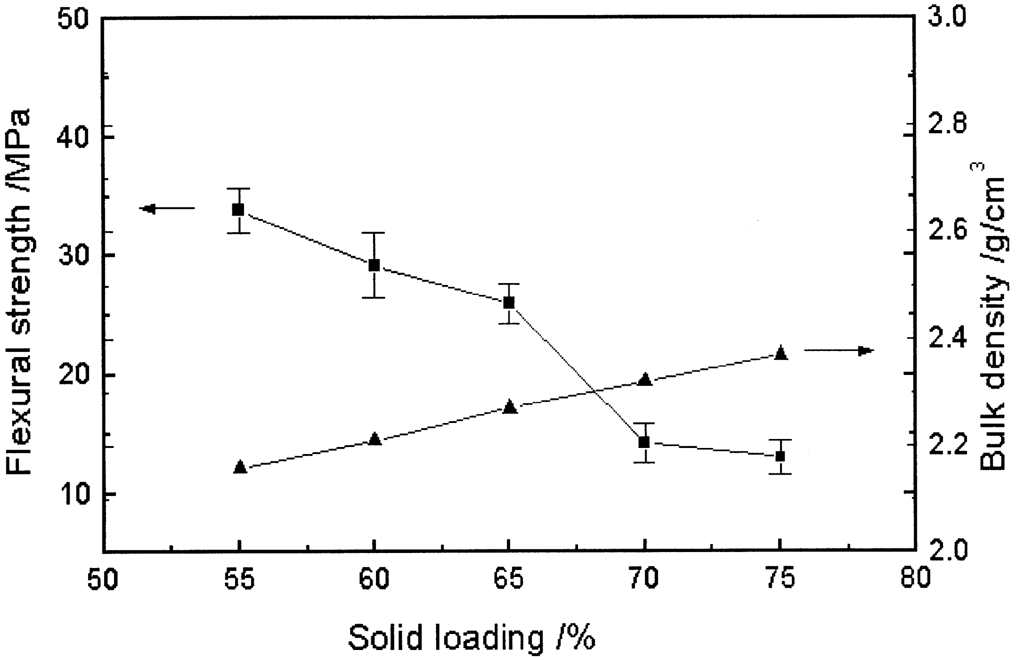


Fig. 9. Flexural strength and bulk density of green bodies versus solids loading of suspension.

3.3.2. Performance and microstructure of sintered RSiC samples

Fracture surfaces (SEM) of sintered samples are shown in Fig. 11. It can be seen from Fig. 11 that the microstructure consists mainly of coarse recrystallized silicon carbide grains and pores. The RSiC grains with average size of 100–150 μm are homogeneously distributed. All of them show hexagonal morphology in the form of RSiC at high temperature of 2450 °C. As compared with the microstructure of as starting powders (as shown in Fig. 2), finer particles disappeared. This is attributed to the average grain size increase. During the sintering process there is a tendency for material transfer because of the differences in surface curvature and consequently the differences in vapour pressure at various parts of the system. The silicon carbide, which lies on convexity of granules, was vaporized and the vapour of silicon carbide was condensed on concave and flat surfaces in packed SiC granules at temperatures as high as 2450 °C. The reason is that on the surface of a particle there is positive radius of curvature so that the vapour pressure is somewhat higher than that in concave or flat surface. This transfer of substance results in symbiotic phenomenon, which takes place on the place of contact of granules and SiC was recrystallized. The relationship between the bulk density of the sintered sample and the solid loading of the suspension is shown in Fig. 12. Sintered density increases from 2.34 to 2.52 g cm^{-3}, when the solids loading changes from 55 to 75 vol.%, behaviour which is similar to that of the green density (as shown in Fig. 9). Both flexural strength and bulk density of sintered samples increased with solid loading (as shown in Fig. 12), and the highest strength of 55.4±2.8 MPa was obtained for the samples with highest density of 2.52 g cm^{-3}. The strength of the material strongly depends on the number of contact points of grains after sintering. It should be noticed that gelcast green strength (as shown in Fig. 9) decreased with increase of green density where the bonding force between SiC particles mainly depends on polymer networks. And a

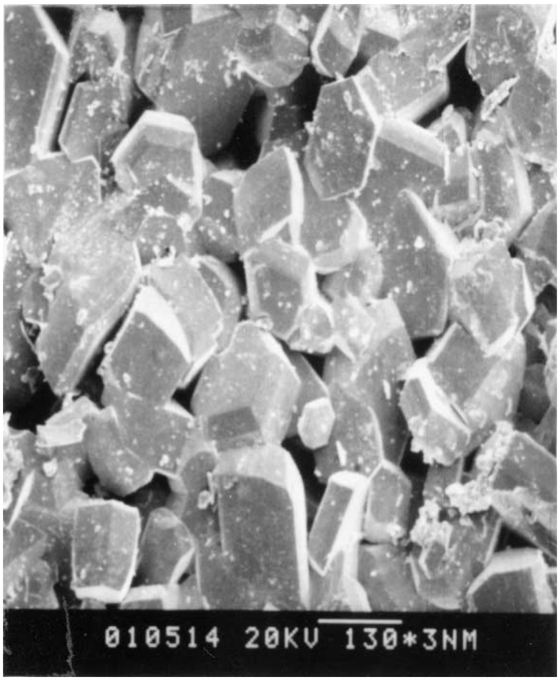


Fig. 11. SEM micrograph of sintered sample fracture surface.

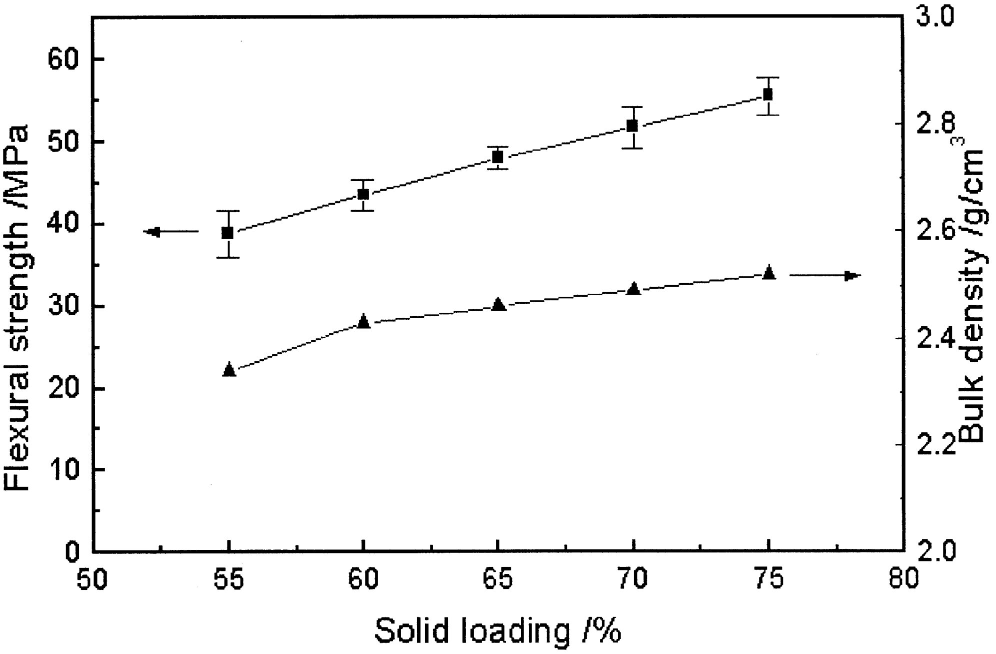


Fig. 12. Flexural strength and bulk density of sintered bodies versus solids loading of RSiC suspension.

stronger polymer network was easily established for the green body with lower solid loading.

4. Conclusions

The stable suspension with high solid loading of RSiC powder is prepared by water-based monomer solution. The dispersion and solids content could be improved by using dispersant, namely TMAH. When pH value is adjusted to about 11.9 by the dispersant, suspension of concentration as high as 75 vol.% solid loading was obtained. Consolidation of the suspension can be completed in 30 min at 60–80 °C by the proper amount of initiator additive, then can be removed from the mold while still wet.

High green strength of about 35±1.9 MPa was obtained from this gelcast RSiC green body, and consequently different green parts with complex shape and precise size were easily produced by this process. Recrystallized silicon carbide parts sintered at 2450 °C for 10 h in Ar show that the flexural strength increase from 38.2±2.3 to 55.4±2.8 MPa and bulk densities vary from 2.34 to 2.52 g cm^{-3} when the solids loading increases from 55 to 75 vol.%. A uniform microstructure with grain and pores were observed for the recrystallized silicon carbide.

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