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Investigation of dispersion behaviour of SiC in water for slip casting of SiC

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The aim of the present work was to identify the conditions for the preparation of stable SiC slurries for fabrication of slip cast object and to correlate the slurry properties to the final properties of the ceramics. An ammonium salt of polymethacrylic acid was used as dispersant for SiC slurry. The effects of dispersant concentration and pH on the rheological behaviour of SiC suspension were studied. The slurry stability was evaluated by measuring settling of the powder as a function of time. The addition of dispersant improved the dispersion by increasing the negative zeta potential of SiC particles. The best conditions of stable slurry were selected on the basis of low viscosity and minimum settling of the powder. It was observed that 1 wt% dispersant resulted lowest viscosity for the slurry of 70 wt% solids loading. The properties of the slip cast object were compared with powder pressed object and it was observed that slip cast object exhibited better mechanical strength due to homogeneous powder packing.

Key words: Colloidal suspension, Dispersant, Rheological study, Slip cast, Mechanical property.

Introduction

Porous materials like SiC have now attracted considerable interest due to its excellent structural properties, high strength, high hardness, excellent mechanical and chemical stabilities at harsh atmospheric condition. The SiC ceramics is of significant techno-logical interests because of its application possibilities as, catalyst supports [1-2], gas sensors [3], hot gas filters [4-6], high temperature membrane reactors, [7] etc. These types of applications are limited by critical and complicated manufacturing technologies. As ceramics are highly sensitive to flaws, it is necessary to avoid those flaws as minimum as possible in order to achieve the best of properties for a reasonable performance and service life [8]. One promising method is by using colloidal suspension followed by shaping processes such as slip casting, tape casting, gel casting or spray drying, etc. [9-17].

Dispersion of ceramic powder in a medium is usually obtained by the addition of optimum amount of dispersant. Dispersion is achieved through electrostatic mechanism, steric mechanism or a combination of both. When polyelectrolyte are used as dispersing agent, the colloidal stability is achieved by a combination of electrostatic/ or steric mechanism [18]. Available reports regarding the SiC suspension particularly in aqueous system are limited in the open literature. Rao *et al*. have used ammonia or sodium hydroxide solutions to adjust the pH of the suspension [19] while Li *et al*. used tetramethylammonium hydroxide (TMAH) [20]. In both the cases the aim was to maximize the zeta potential of the SiC particles in aqueous suspension. Zhang *et al*. have reported the dispersion of as received SiC using the cationic dispersants like Hyamine 2389 (HY) and polyethyleneimine (PEI) with later being the superior as a result of generating stronger electro-steric interaction [21]. However literature exists on aqueous processing of SiC for fabrication of high density sintered body [22], a systematic study of dispersion of coarse SiC powder and aqueous processing of SiC for fabrication of porous SiC ceramics is needed for its technological importance. In the present study, the aim was to identify the conditions for the preparation of stable SiC slurries with moderate solid loading for the production of porous slip cast object with improved properties. The best optimum condition was selected by characterizing the suspension using sedimentation test and rheological studies. As far as the rheological characterization is concerned the system which produced minimum viscosity and near Newtonian flow behaviour was selected as the best dispersant condition. Finally the most dispersed slurry was used for slip casting to obtain a rectangular bar which on subsequent sintering at low temperature produced porous network. The properties of the slip cast and powder pressed sintered objects are examined.

Experimental

A commercially available α-SiC powder (M/S Superior Graphite, USA SiC 98.5%, purity) was used in this work. The mean particle size distribution of SiC powder was determined by Malvern laser particle size analyzer (MASTERSIZER 2000 MU, UK) and d_{10}, d_{50}

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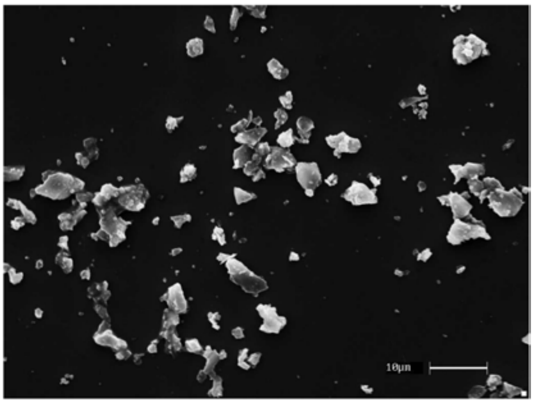

Fig. 1. Particle morphology (SEM) of the SiC particles.

Table 1. Characteristics of Darvan-CN.

pH (5% solution)	7.5-9.0
Specific gravity	1.10-1.12
Total solids	24-26%
Viscosity (Brookefield at 25 °C)	75 cps maximum
Molecular weight	10000

and d_{90} was found to be 0.95 μm, 6.26 μm, 17.93 μm respectively. Fig. 1 shows the SEM photographs of the SiC powder.

The dispersant used for the slurry stabilisation is known by its commercial name Darvan-CN (R.T.Vanderbilt Co, Norwalk, CT USA). It is an ammonium salt of poly methacrylic acid with a low tendency to foam. The dispersant is completely water soluble and is provided by the manufacturer in the form of aqueous solution. The characteristics of the dispersant are summarised in the table 1.

Dispersion studies were carried out with 40-70 wt% of SiC powder in deionised water using and 0-4 wt% dispersant (based on the weight of the SiC powder). As our aim was to fabricate porous SiC object by slip casting route, solid loading was restricted to maximum 70 wt%. The suspension was than subjected to ball milling for 24 hours with alumina as grinding media. Immediately after this, each sample was taken in a graduated measuring cylinder for sedimentation testing. Slurry viscosity was determined with a rotating spindle viscometer (Malvern, USA). Sets of measurements with a specific spindle were taken at all shear rates where reading of viscosity at each shear rate could be obtained. Homogenous suspension of solid concentration 1 mg ml^{-1} was prepared by ultrasonification for 10 min at different pH to measure the zeta potentials with the help of a zetasizer (Malvern Instruments, Malvern, U.K). On the basis of low viscosity and minimum settling of the powder, the best condition of stable slurry was selected. Thereafter, the best dispersed suspension was used for slip casting to produce rectangular bar shape configuration ($48 \times 19 \times 12.0$ mm^3). Green rectangular samples ($50 \times 20 \times 16$ mm^3) were also prepared by pressing SiC powder mixed with 10% solution of polyvinyl alcohol (Loba Chemie, India) at 23 MPa pressure in a stainless steel die to compare the slip cast object with the object prepared by conventional *powder metallurgical technique*. This would included i) powder mixing, ii) pressing of green shape, and iii) sintering. Finally all the slip casted and pressed samples were heat treated at 1500 °C for 4 h in air in high temperature electrically heated furnace (TE-3499, Therelek Engineers Pvt. Ltd., Bangalore, India) with a programmed heating and cooling rate of 1 °C min^{-1}. The weight and dimensions of sintered samples were measured, density and porosity were determined by the Archimedes method (water immersion method) and pore size distribution was determined by Hg-intrusion porosimetry (Model 60, Poremaster, Quantachrome Instruments Inc., Florida, USA). Phase Identification of different phases of the sintered specimens was done by X-ray diffractometry technique (XRD, PW 1710, Philips, Holland, with Cu Kα radiation, $\lambda = 1.5406$Å). Morphology and distribution of phases of the sintered specimens were examined by a Field emission scanning electron microscopy (FESEM, CARLZEISS, SUPRA™ 35 VP, Germany). For mechanical property evaluation the sintered specimens were sliced to produce rectangular pieces of cross section of 4.75×3.25 mm^2. They were ground and polished up to 10 μm finish and tensile surfaces were champhered. The room temperature flexural strength was determined in a three-point mode (with a span of 40 mm, speed of 0.5 m min^{-1}) in an Instron Universal Testing machine (Model 1123, Instron, Canton, MA, USA). The deflection was monitored through LVDT with a resolution of 0.05% of full scale and from the load-deflection data Young's modulus was determined using standard software (Instron Bluehill-2, UK).

Results and Discussion

Sedimentation behaviour of the SiC suspension

Slurry stability was evaluated by measuring the settling of powder (sediment height as percentage of the total suspension height) for different amount of dispersant. Figure 2 shows the sediment volume of SiC suspension after 24 h with varying amount of solid loading and dispersant. Sedimentation of suspension with low solid loading is obvious while at high solid loading cannot even observed. The slurry with no dispersant settled promptly after ball milling. It is observed that increasing the concentration of the dispersant from 0 to 1.5 wt% makes the sediment volume to first decrease gradually up to a minimum value observed for 1 wt% dispersant, followed by increase for further addition. The result indicate that a more consolidated structure is progressively formed up to the optimum amount (1 wt%), followed by a small decrease in sediment packing density due to an over

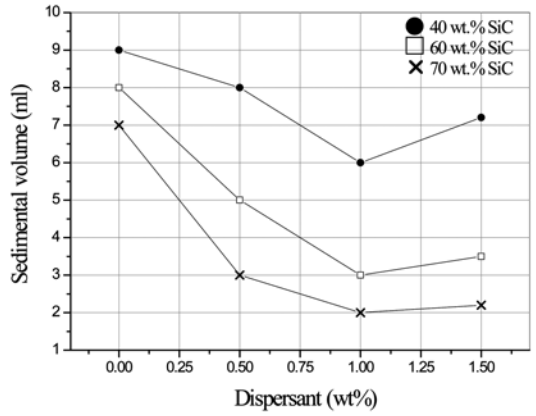

Fig. 2. Settling of powder as a function of dispersant concentration.

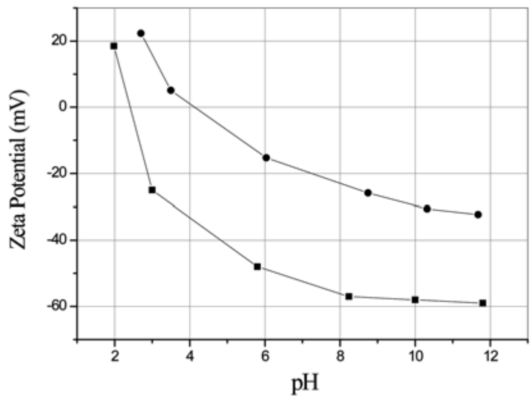

Fig. 3. Zeta potential versus pH : SiC powder dispersed ● -without; ■ - with Darvan CN.

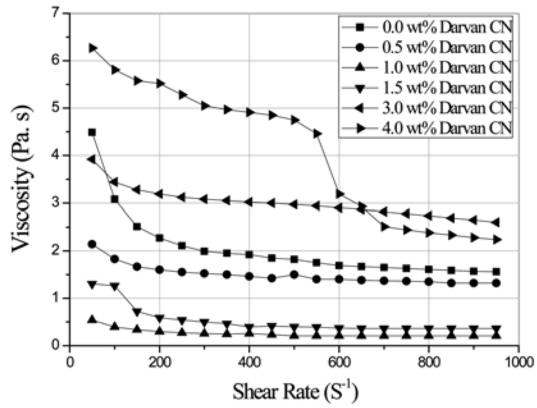

Fig. 4. Effect of dispersant amount on the viscosity of the slurry of 70 wt% SiC suspension under various shear rate.

deflocculation effect. It is also seen that the stability of the sample has further improved with the increase in the concentration of the powder. For 70 wt% solid loading, there is no much change in the sedimentation height over the entire range of dispersant from 0.5-1.5 wt% because of the flocculated network formed due to the high solid content.

Zeta potential measurements

The variation of zeta potential versus pH for suspension of as received SiC powder without and with 1 wt% Darvan CN are plotted in Fig 3. Normally oxygen rich layer is formed due to usual oxidation during synthesis of silicon carbide powder. The oxidized layer is chemically similar to the silicon surface. In aqueous medium, silicon layer get hydrated and forms silanol on the surface of the SiC particles, which at low pH (~ pH < 4) reacts with H^+ ions and form $Si\text{-}OH_2^+$ and at higher pH silanol reacts with OH^- and form $Si\text{-}O^-$[23]. Figure 3 shows the charge development at different pH condition, which is in agreement with the above phenomena of charge development. The variation of surface charge with pH was observed in both the cases of with or without addition of dispersant except the value of negative charge has increased many folds due to adsorption of the dispersant on SiC surface. The isoelectric point of SiC changed from pH 4.2 to 2.4 with addition of dispersant. The use of the dispersant provided a wider range of pH within which the suspension is stable and produced high absolute zeta potential values and polyelectrolyte stabilization, which is helpful for the more stable suspension. These observations suggest that SiC suspension should experience progressive deflocculation with increase in pH. Similar observations were also reported by other researchers [19, 23-24].

Optimisation of rheological properties of the slurry

As it was seen from the sedimentation test that the 70 wt% slurry was relatively more stable at less amount of dispersant, the rheological properties of the 70 wt% slurries with varying amount of dispersant (0-4 wt%) were studied in detail. Figure 4 shows the viscosity with varying amount of dispersant as a function of shear rate.

High slurry viscosity is seen for the suspension without dispersant. With addition of dispersant the viscosity values were found to decrease and with further addition of dispersant slurry viscosity increased sharply. The lowest viscosity was produced with 1 wt% dispersant. For the dispersant concentration 0.5-1.5 wt%, the degree of the viscosity-shear rate dependence became weak and nearly Newtonian behaviour was observed. The increasing degree of shear thinning behaviour at higher dispersant content may be either due to the excess of the dispersant in the supernatant or is associated with the formation of bridging effect between separated particles through the polymeric chain causing slightly flocculated suspension.

Effect of pH on viscosity

Figure 5 shows the viscosity of 70 wt% SiC slurry containing 1 wt% dispersant measured as a function of pH at a constant shear rate 500 S^{-1}. The higher viscosity at the lower pH is the characteristics of

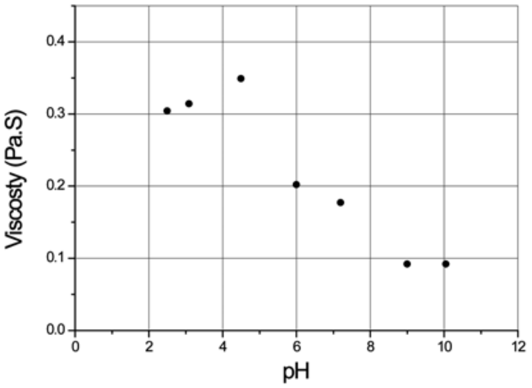

Fig. 5. Effect of against pH.

Table 2. Characteristics of the sintered samples.

Processing route	Density (g cc^{-1})	Porosity (%)	Max. Flexural stress (MPa)	Modulus (GPa)
Slip casting	1.95	28.47	31.57	15.69
Powder pressing	1.84	31.18	18.05	13.80

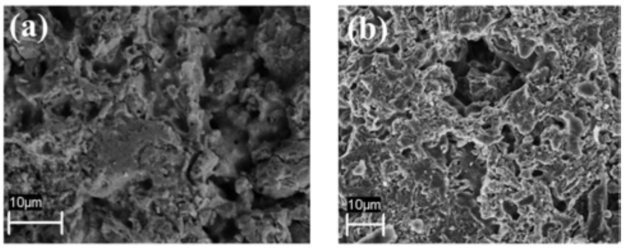

Fig. 6. Microstructure of porous SiC ceramics sintered at 1500 °C (a) powder pressing route (b) Slip casting route viewed under higher magnification.

agglomerated structure. Lower viscosity was observed at pH away from the IEP.s This result shows that the powder is well dispersed at higher pH.

Materials and mechanical properties of the pressed and slip cast sample

Sintered ceramics produced by slip casting and pressing exhibited no distortion in shape and their characteristics are summarized in Table 2. Slip cast samples exhibited slightly higher density compare to the pressed samples. From scanning electron microstructural images (Fig. 6), it is observed that better packing of the powders was achieved in case of slip cast sample compare to the pressed sample. In both the samples formation of SiO_2 bonds at regions of contacting SiC particles and well developed necks between SiC particles were clearly observed.

Mercury intrusion porosimetry results of samples prepared by powder pressing route and slip cast route are compared in Fig. 7. Broad distribution patterns were obtained which might be due to wide variation of starting SiC powder sizes. The effects of homogenous and close packing in slip cast sample are also reflected

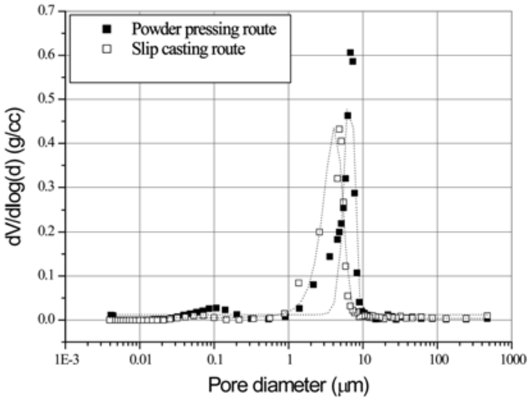

Fig. 7. Pore size distribution profile of the samples prepared by powder pressing and slip casting route.

in the pore size distribution results. A maximum pore size of around 6.7 mm and 4.2 mm was obtained for the samples processed by powder pressing route and slip casting route respectively. The slip cast sample with a porosity of 28.47% showed a flexural strength of 31.57 MPa while the pressed sample with a porosity of 31.18% showed a flexural strength of 18.05 MPa indicating homogenous closed packing of the particles in case of slip casting.

Conclusions

The first part of the work involved preparing stable silicon carbide slurries of moderate solid content to produce porous ceramics via slip casting. Dispersion behavior of Silicon Carbide powder was studied for 40-70 wt% solid loading using 0-4 wt% dispersant. The suspension stability was measured using rheological studies and sedimentation test. The best dispersion was obtained for 70 wt% SiC loading with 1 wt% Darvan-CN. The slurry exhibited lowest viscosity and was stable over a long time. The slurry was stable over a wide range of pH (6-12) and is more stable in the alkaline region than in the acidic region. The next part of the work involved slip casting the specimens using the most stable slurry. Slip cast specimens showed improved mechanical strength compared to the pressed samples indicating a homogenous powder packing. These results demonstrate that the colloidal suspension through the control of dispersant concentration and loading of SiC could be recommended route for well dispersed suspension which may also be used for fabrication of porous ceramics with improved properties.

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