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Effect of Rheological Behavior on Properties of Cast and Sintered Silicon Carbide

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Abstract: This paper describes the rheological behavior of suspensions for two types of SiC powder, termed G-SiC and S-SiC, with different contents of dispersant. In addition, examination of the suspension property and the cast density of the green compacts, together with the mechanical strength of the sintered body, was conducted. Experimental results show that a stable SiC suspension with the lowest viscosity is obtained by controlling the dispersant content at, e.g. ~0·1 wt% and ~0·25 wt% for 30 vol% of SiC phase for the G-SiC and S-SiC powders, respectively. Cast densities of as high as 68% of theoretical were attainable by using the finer S-SiC powders (having a mean particle size of 0·48 μm). The suspension with the lowest viscosity associated with the highest cast density cannot be fully considered as a true representation of the final sintered microstructure. Instead, a suspension with appropriate viscosity is needed for optimizing both particle arrangement and packing structure during casting toward a uniformly consolidated compact and sintered structure. The flexural strength of the sintered SiC ceramics is strongly related to the residual pore content, obeying an exponential power law dependence.

INTRODUCTION

Silicon carbide ceramic is frequently a strong candidate material for many advanced applications due primarily to possession of excellent properties such as high resistance to erosion, strength retention at elevated temperatures, high hardness, and excellent resistance to corrosion. Furthermore, its higher values of thermal conductivity make an important contribution to the integral circuits industry.[1,2] For many applications in ceramic processing it is desirable to obtain a fine-grained and fully dense microstructure by sintering at relatively low temperatures. One promising method is by using colloidal suspension followed by slip or pressure casting or other reliable methods[3] to obtain a uniformly consolidated compact. Ceramic powder compacts with dense packing of the particles are important in obtaining a high-density sintered body with lower concentration of defects, particularly voids. The presence of such defects not only prolongs the sintering time required for full densification, but also frequently reduces the mechanical properties of the sintered body.

Studies concerning the preparation of suspensions have been mostly on alumina;[4,5,6] available reports regarding the SiC suspension, particularly in an aqueous system (i.e. SiC–water) are limited in the open literature. Liden *et al.*[7] obtained a good SiC suspension by modifying the surface property of the SiC particles with the aid of Al-alkoxide agent through a well-controlled hydrolysis and polymerization surface reactions. However, no further report on the green density of their SiC compacts was available. Okuyama *et al.*[8] dispersed a number of SiC powders in a variety of organic solvents, followed by colloidal pressing. The green packing density of the colloidally pressed compacts was reported to be as high as ~62% of theoretical density. However, the investigations aforementioned were in non-aqueous media. The purpose of this study was to obtain a well-dispersed SiC ceramic suspension in aqueous system containing a polymeric dispersant (denoted as A) which was one of the best dispersing agents selected from a number of commercial and synthesized dispersants through a four-week sedimentation test. The properties and microstructure of the cast and the sintered SiC bodies were examined.

EXPERIMENTAL PROCEDURES

Two types of SiC ceramic powder were used, namely G-SiC (Nanko, GC-8000, mean particle size 2 μm) and S-SiC (Showa Denko, 0·48 μm in size). SiC suspensions containing 30–40 vol% of the SiC powder, deionized water, and 0·1–2 wt% (based on the weight of the SiC powder) of Na-containing polymeric dispersant A (having a molecular weight of ~2000), were prepared. The suspensions were blended thoroughly by ball milling (SiC balls) for 48 h. The viscosity of the suspension was measured by a viscometer (Brookfield, Model DV-II) with shear rates ranging from 10 s^{-1} to 100 s^{-1}.

The suspension was poured into a plastic plate with inner dimensions of 5 cm × 5 cm × 2 cm placed on a plaster substrate to form a cast compact. For purpose of uniform casting, the inner wall of the plate was lubricated with a silicone grease. After oven-drying at 120°C for two days, the green density of the cast compacts was measured by mercury porosimetry. The resulting cast density is expected to constitute a fundamental criterion related to the suspension property. The microstructure of the compacts was examined by scanning electron microscopy (Cambridge Instruments, S-360).

To examine the adsorption of the dispersant onto the SiC particles, part of the solutions were centrifuged at 6000 rpm for 3 h to separate the solid phase from the suspension. The resulting supernatant was examined using Induced Couple Plasma-Atomic Emissive Spectroscopy (ICP-AES) to detect the residual amount of dispersant (with respect to Na content). Standard solutions containing different pre-determined dispersant concentrations were prepared for calibration purposes. For accurate estimation, a supernatant which was centrifuged from the suspension containing no dispersant was employed as a blank.

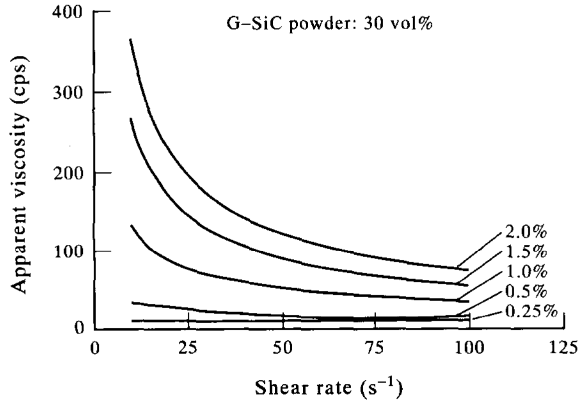

Fig. 1. Viscosity of suspension with 30 vol% of G-SiC powder under various shear rates.

Small amounts of sintering aids (6·3% Al_2O_3 and 3·7% Y_2O_3, based on the weight of SiC powder) were added to other batches of suspensions, prepared in exactly the same way as the original suspensions, for densification purposes. The cast compacts were then sintered at 1900°C for 2 h in vacuum condition (4 × 10^{-5} torr), followed by characterization of the mechanical strength.

RESULTS AND DISCUSSION

Suspension properties

Typical shear-thinning behavior for the suspensions containing 30% G-SiC powder with varying concentrations of dispersant A is shown in Fig. 1. In certain cases at dispersant concentration below approximately 0·5%, the degree of the viscosity–shear rate dependence became weak and nearly Newtonian behavior, i.e. viscosity independent of shear rate, was observed at 0·25% (the data for the dispersant content below 0·25% are omitted for clarity). Part of the dispersant was adsorbed onto the SiC particle surface, and the rest was distributed in the supernatant. The former causes particle separation and facilitates the sliding of the SiC particles past one another, leading to a decreased suspension viscosity; the latter increases the suspension viscosity. The increasing degree of shear-thinning behavior at higher dispersant content may either be 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 a slightly flocculated suspension. In the latter case, increase of the dispersant concentration induces further flocculation.

To evaluate the amount of the dispersant A adsorbed onto the SiC particles, (the rest of the

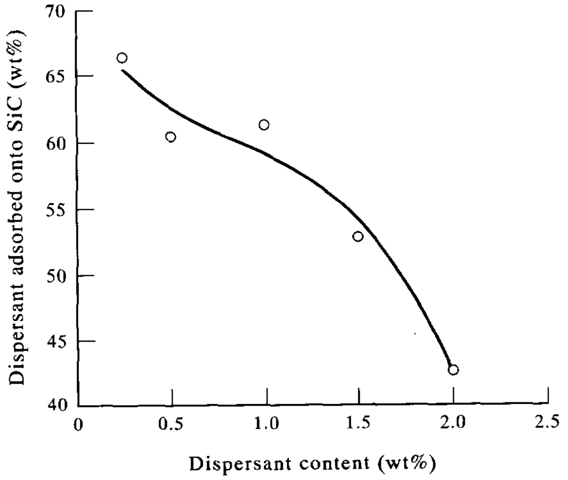

Fig. 2. Adsorption percentage of the dispersant A onto the G-SiC particles as a function of dispersant content.

dispersant distributed in the supernatant can be deduced directly from a mass balance calculation), the centrifugally separated supernatant was then characterized by ICP-AES to measure the Na concentration. The resulting dispersant concentration was obtained by subtracting the concentration of dispersant-containing supernatant from that of the blank solution, followed by calibration with the standard solutions. Figure 2 illustrates the percentage of the dispersant adsorbed onto the SiC particles, which decreases with increasing concentration of the dispersant. The dispersant left in the supernatant thus increases with increase of the dispersant content. This causes an increase in suspension viscosity and/or degree of flocculation, corresponding to an increased resistance to flow, which results in a more pronounced shear-thinning behavior at higher dispersant concentration.

In most cases, a monolayer coverage of the particle by the dispersant molecule is estimated by using the specific surface area of the particle and the surface coverage per molecule. In this case, the G-SiC particle, having surface area of 4·2 m^2/g and a surface coverage per molecule of the dispersant A assumed to be 100 Å^2, the minimum amount of the dispersant required for a monolayer coverage of the G-SiC particles is 1·4 wt%. In a similar approximation, the S-SiC powder has a surface area of 15 m^2/g, corresponding to 4·9 wt% of the dispersant for a monolayer adsorption. In fact, a concentration greater than the estimated amount required for each powder is essentially needed to achieve a saturation equilibrium of the suspension. Based on this calculation, it is obvious that the dispersant used in the present study is considerably below the minimum amount required for a complete coverage of the S-SiC powder but may satisfy the requirement for the G-SiC powder. The latter case implies that a monolayer adsorption may be achievable onto the G-SiC powder in the range of dispersant content studied. A further calculation deduced from Fig. 2 leads to a relationship illustrated in Fig. 3 which shows that the amount of dispersant adsorbed onto the G-SiC particles increases with dispersant content. The degree of the adsorption amount of the dispersant onto the G-SiC particles tends to decline toward an equilibrium state of adsorption at dispersant concentration > 2·0 wt%, greater than theoretical concentration of ~1·4%. Therefore, a substantially larger amount of the dispersant A is needed for a complete coverage of the S-SiC particles.

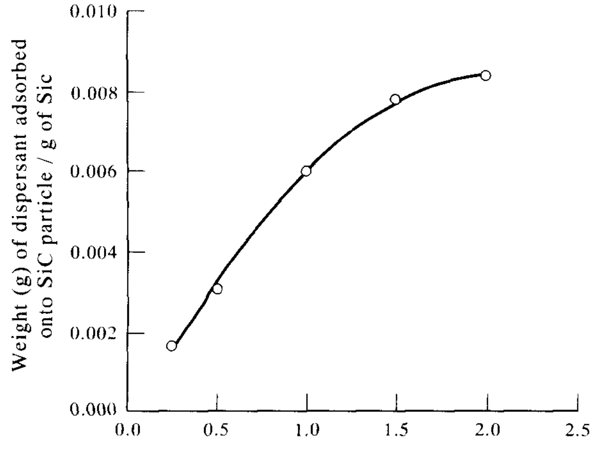

Fig. 3. Amount of the dispersant A adsorbed per gram of G-SiC powder for various dispersant contents.

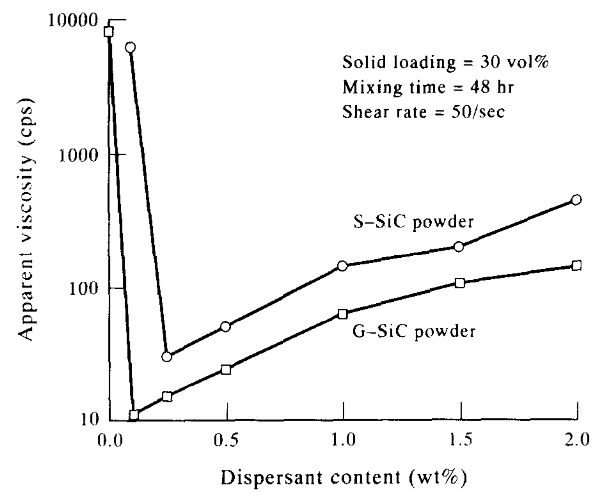

Fig. 4. Effect of dispersant content on suspension viscosity for both G-SiC and S-SiC powders at a fixed shear rate of 50 s^{-1}.

Since the two SiC powders used in the study have different particle sizes, corresponding to different particle surface areas, the amount of dispersant A for a minimum suspension viscosity should certainly be different. Figure 4 shows that at a fixed shear rate of 50 s^{-1}, the S-SiC powders exhibit higher suspension viscosity than G-SiC suspension at various dispersant concentrations and a minimum dispersant content for the suspension of the lowest viscosity is ~0·1% and ~0·25% for G-SiC powder and S-SiC powders, respectively. Increase of the solid loading increases the dispersant amount required for obtaining a low-viscosity suspension, as shown in Fig. 5, which is ~0·25, ~0·5, and ~0·75% for S-SiC of 30, 35 and 40% solid loading, respectively.

Properties of cast and sintered SiC bodies

The cast SiC compacts exhibit a packing density strongly related to the type of powder used and dispersant concentration, as shown in Fig. 6. The packing densities achieved with S-SiC powder are greater than those with the G-SiC powder, and

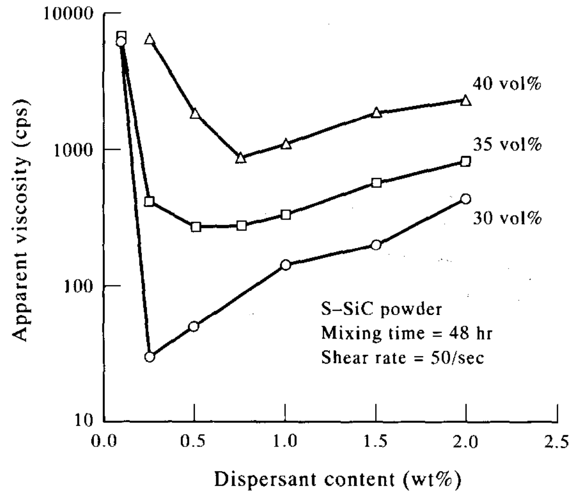

Fig. 5. Effect of dispersant content on suspension viscosity for various S-SiC powder loadings.

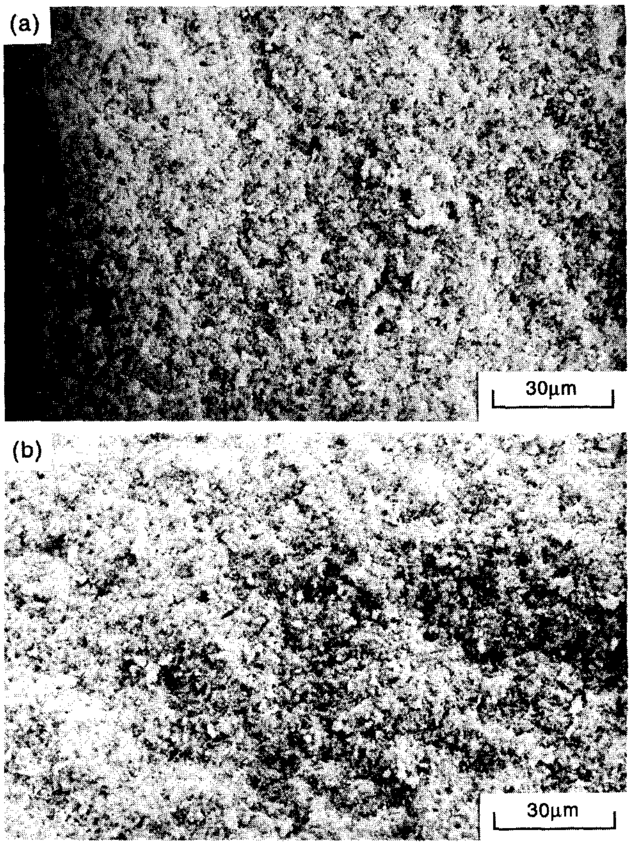

Fig. 7. Scanning electron micrograph of the broken surface of the cast S-SiC compact prepared at (a) 0·5% and (b) 2·0% dispersant.

both, after reaching a maximum packing density of ~68% for the S-SiC and of ~65% for the G-SiC, show a decreased cast density as the content of dispersant increases. Available data (from both manufacturers) illustrated that the G-SiC powder has a wider particle size distribution (0·6–6 μm) than that of the S-SiC powder (0·2–2 μm). This indicates that suspensions containing narrow-sized and finer powders can be consolidated to green compacts with a higher cast density and is consistent with that reported by Roosen and Bowen in the alumina–water system.[9] The peak densities of the cast bodies were generally above ~65% of theoretical density (3·2 g/cm^3) for both powders, approximately the maximum achievable packing density of uniform particles. The cast densities for both powders decreased sharply with further increasing dispersant content, suggesting a poorly dispersed or even a flocculated suspension due to possible bridging effect by the dispersant.

It is interesting to note that the maximum cast density for both types of powders occurs when both the suspensions have certain viscosity, rather than having the lowest viscosity. This indicates that the rate at which the packing structure of the SiC particles is built up is too fast to achieve a dense packing for the suspension having the lowest viscosity, although the SiC particles slide much more easily over one another at the lowest viscosity than at higher viscosity. Therefore, it is more important for the suspension to have an optimal viscosity which is not too high for particle rearrangement and not too low for poor packing structure development

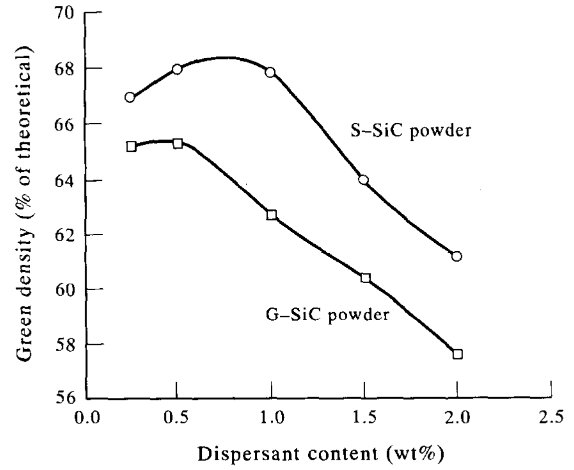

Fig. 6. Green density of the cast compacts as a function of dispersant content for G-SiC and S-SiC powders.

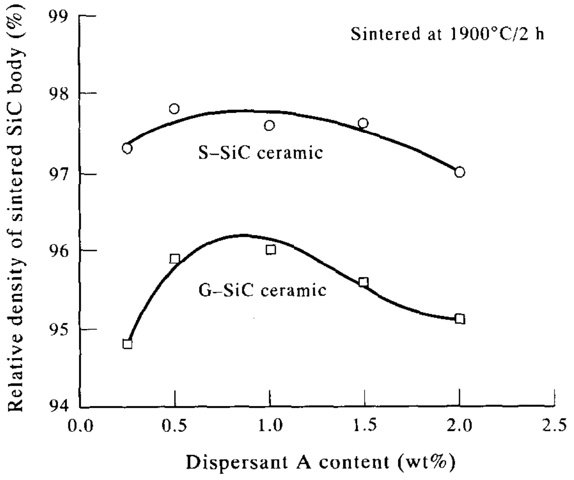

Fig. 8. Sintered density of the G-SiC and S-SiC ceramics, prepared at various dispersant contents.

during casting. Increase of the dispersant content gave rise to an increase in suspension viscosity, which subsequently suppressed the particle rearrangement toward dense packing and resulted in lower green density.

Figures 7(a) and 7(b) show the microstructure of the broken surface of the cast compact for S-SiC powder at dispersant content of 0·5% and 2%, respectively. Both compacts contain voids of approximately 1–2 μm in size. Apart from some of the larger particles exhibiting irregular geometry, most of the S-SiC particles are nearly spherical in shape and some of them show close packing, which further substantiates the earlier discussions on achieving higher cast densities (Fig. 6)

For densification purpose, small amounts of sintering aids (Al_2O_3 and Y_2O_3) were added to the additional batches of suspensions, prior to casting. A slight reduction of suspension viscosity was found after the additions. After sintering at 1900°C for 2 h, the relative density of the sintered bodies was measured using Archimedes' method with water as medium. Figure 8 shows the sintered density of both types of SiC ceramic (identified as α-SiC) with respect to different dispersant contents. The S-SiC ceramic exhibits a higher density than the G-SiC ceramic, both of which correlate well with the trend related to the dispersant content as observed in cast density (Fig. 6), except in the case of G-SiC at 0·25% A which showed the lowest sintered density and no similar trend between the cast density and sintered density was found. An examination of the fractured surface for the sintered body at 0·25% and 1·0% of dispersant is shown in Figs 9(a) and (b), respectively. It can be easily visualized that the sintered G-SiC ceramic derived from the suspension with 1·0% dispersant shows a more uniform microstructure, particularly pore size and/or its distribution, than that for 0·25%, even though the latter results in the highest cast density. Therefore, the lowest suspension viscosity associated with the highest cast density may not be considered as fully characterizing the final sintered microstructure. Pore size as well as pore-size distribution within the cast compact are more critical factors governing the microstructure evolution and have been the subjects of many investigations.[9–12] The sintered densities presented in this study were greater than those prepared by Omori and Takei[13] with various proportions of Al_2O_3/Y_2O_3 as sintering aids, followed by pressureless sintering at 2100°C.

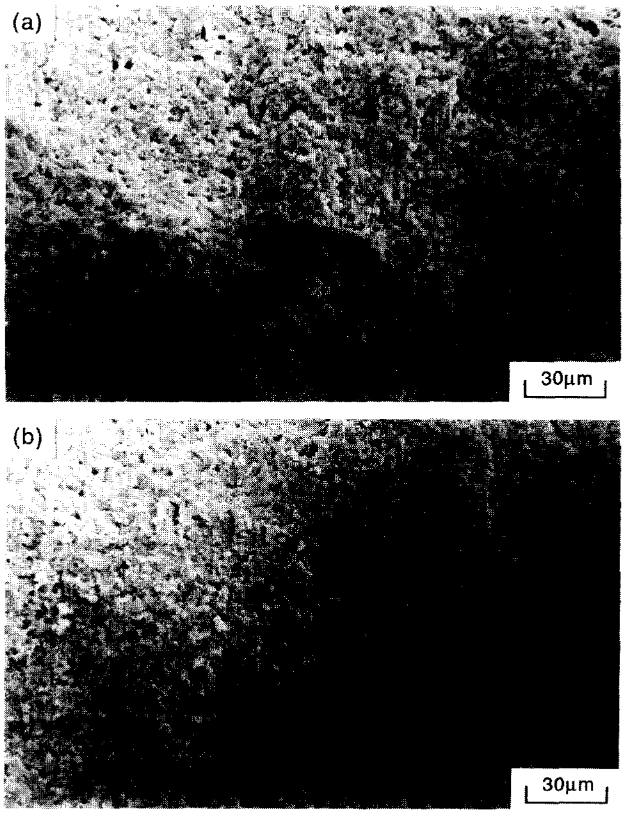

Fig. 9. Scanning electron micrograph of the fractured surface of the sintered G-SiC ceramic prepared at (a) 0·25% and (b) 1.0% dispersant.

The flexural strength of the sintered SiC bodies was measured as shown in Fig. 10. A strength as high as 515 MPa for the S-SiC ceramic is attainable at dispersant content of ~0·5 wt%, which exhibits the highest sintered density. The variation of the strength with respect to dispersant content closely resembles that of the sintered density (Fig. 8), and is believed to be due to the presence of residual porosity. Plotting the data of strength versus porosity for both SiC ceramics (shown in Fig. 11), the strength–porosity dependence is well described by an exponential power law which is given, with a correlation coefficient of as high as 0·94, by the following equation

$$\sigma_f = 695{\cdot}2\ e^{-0{\cdot}14\phi} \qquad (1)$$

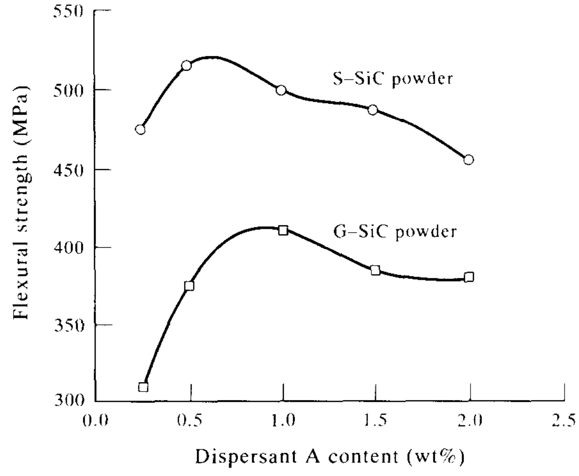

Fig. 10. Flexural strength of SiC ceramics made from S-SiC and G-SiC suspensions with different dispersant contents.

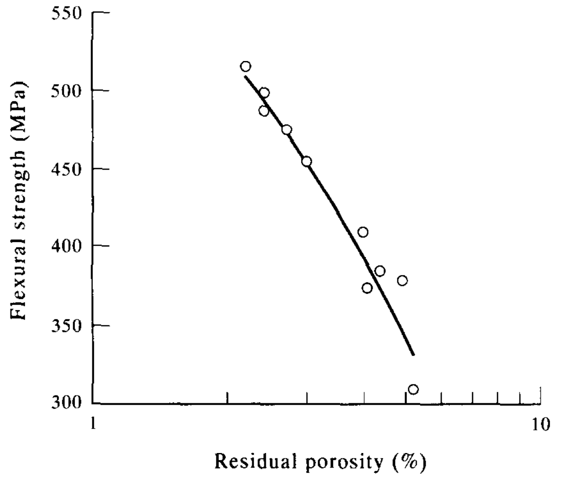

Fig. 11. Flexural strength of the sintered SiC ceramics prepared from both types of powders changes exponentially with porosity.

where σ_f represents the four-point flexural strength (MPa) and ϕ is porosity (%). The flexural strength of the SiC ceramic is strongly affected by the presence of porosity and a value of as high as ~695 MPa can be obtained according to eqn (1) for a pore-free SiC sintered body.

CONCLUSIONS

Rheological behavior together with the cast density of the suspensions for two types of commercially available SiC powders were investigated. A minimum amount of the dispersant A, i.e. ~0·1 wt% and ~0·25 wt% for the G-SiC and S-SiC powders, respectively, was required for obtaining the lowest viscosity suspension with 30 vol% of solid phase. Further increase of the dispersant concentration enhanced suspension viscosity. The cast density reached a maximum achievable cast density of ~65 and ~68% for G-SiC and S-SiC powders, respectively, which is close to the maximum achievable theoretical packing density of uniform particles. The lowest suspension viscosity and the associated highest cast density cannot be completely indicative of the uniformity of the final sintered structure. To our understanding, a narrow-sized and fine-particle-containing suspension with optimal viscosity facilitating particle arrangement and packing structure development is essentially important for obtaining a fine-grained, uniform sintered microstructure. The flexural strength of the SiC ceramics is directly related to the residual porosity within the sintered body and a maximum value of 515 MPa is attainable in the present study using the S-SiC powder. An exponential power law provides an excellent description for the strength–porosity dependence of the present SiC ceramics, which clearly reflects the profound effect of initial suspension rheology on the mechanical property of the final sintered SiC body.

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