Covalently bonded organosilicon and organoaluminium dispersants for silicon carbide

J. R. FOX, M. J. UNGUREIT, H. K. BOWEN
Ceramics Processing Research Laboratory, Materials Processing Center, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

Covalently bonded organosilicon and organoaluminium compounds were used as dispersants for SiC powder and whiskers in hexane. The improved dispersion resulted in a threefold increase in whisker packing density in sedimented compacts. Comparison experiments with organosilanes having the formulas $RSi(OCH_3)_3$ and $RSiCl_3$ showed that the chlorosilanes were much more effective than their alkoxy counterparts in dispersing SiC powder. The aluminium alkoxy carboxylate aluminium *sec*-butoxide stearate was also a much more effective dispersant for SiC than the alkoxysilanes. Fourier transform infrared spectroscopy and solid-state ^{13}C nuclear magnetic resonance were used to characterize the organometallic dispersants grafted to the surface of the SiC.

1. Introduction

The dispersion of submicrometre ceramic particles is a key step in the processing of both structural and electronic ceramics. In high-dielectric-constant liquids such as water, dispersion usually occurs as a result of electrostatic stabilization. In low-dielectric-constant liquids such as hexane and toluene, the mechanism of dispersion is most often steric in nature. In many cases, the interaction of the dispersant molecule with the surface occurs as a result of acid–base interactions and is reversible. In other cases, the dispersant may react irreversibly with the ceramic particle, forming a covalent bond that anchors the molecule to the surface.

The introduction of grafting groups has been shown to improve the ability of a variety of organic polymers to act as dispersants [1]. Since a covalent bond is formed between the dispersant and the ceramic particle, the dispersant molecule cannot be displaced from the particle surface by other constituents of the dispersion medium. Recently, covalent attachment of monomeric organotitanates has been used to improve the dispersion of barium titanate ($BaTiO_3$) powders in non-aqueous media [2, 3]. The use of organotitanates produced a more stable dispersion than the corresponding carboxylic acids, and resulted in higher powder sediment densities. As steric stabilizers, the organometallic monomers were as effective as organic polymers with molecular weights an order of magnitude higher.

The use of grafted organometallic dispersants may also provide a means for the controlled introduction of desired dopant elements or densification aids into monolithic or composite ceramic green bodies. In the case of $BaTiO_3$, for example, it is plausible that oxidative removal of the grafted organotitanate would leave some residual TiO_2 at the surface, which could influence the electrical properties of the $BaTiO_3$ powder.

In the present work, organosilicon and organoalu-minium dispersants were used to sterically stabilize non-aqueous dispersions of SiC powder and whiskers. Although SiC is a non-oxidic ceramic, it typically possesses a hydroxylated, silica-like surface. The organosilicon and organoaluminium compounds employed in this study contained reactive chloro and alkoxy groups capable of reacting with the SiC surface hydroxyl groups, covalently bonding the dispersant to the SiC. The surface-modified powders and whiskers described herein should be useful in the fabrication of monolithic and composite SiC-based advanced ceramics.

2. Experimental procedure

The SiC powder employed in this study was a commercial, submicrometre α-SiC (GC No. 10 000, Fujimi Kenmazai Kogyo Co. Ltd, Nagoya, Japan) with a surface area of $16\,m^2\,g^{-1}$. The SiC whiskers used were obtained commercially (Silar Grade SC-9, Arco Metals Co., Greer, South Carolina) and had a typical length and diameter of 45 μm and 0.6 μm, respectively. The organoaluminium and organosilanes were also obtained commercially (Petrarch Systems Inc., Bristol, Pennsylvania and Alfa Products, Danvers, Massachusetts) and were used as received. Dispersions were prepared by sonicating the SiC powder (1 g) or SiC whiskers (0.5 g) and the organometallic dispersant with hexane (8 ml) in a 12 ml graduated centrifuge tube in an ultrasonic bath. Neat organosilane was injected by microlitre syringe prior to sonication. The more viscous aluminium *sec*-butoxide stearate (AlBS) had to be diluted before use. The concentration of dispersant was based on the weight of the SiC powder or whiskers.

The dispersions were allowed to gravity-sediment to constant volume and the packing density was calculated as a percentage of theoretical using $3.2\,g\,ml^{-1}$ as the density of SiC. Filter-cake compacts were prepared by filtering the dispersions using house vacuum through two pieces of filter paper and two 0.45 μm

membrane filters supported inside a polypropylene tube 17 mm in diameter.

Diffuse reflectance Fourier transform infrared spectra (Model 85 FTIR, IBM; Spectratech, Stamford, Connecticut, diffuse reflectance stage) and solid-state nuclear magnetic resonance (NMR) spectra were obtained from samples of vacuum-dried compacts. Solid-state cross polarization/magic angle spinning (CP/MAS) ^{13}C NMR spectra were acquired on a 100 MHz instrument (Model Nicolet S-100, General Electric Co., NMR Instruments, Fremont, California) using a boron nitride rotor spun at approximately 3000 r.p.s. A 2 sec delay and a contact time of 2 msec were used during data acquisition. Fourier transform/magic angle spinning (FT/MAS) spectra were acquired using a 35° pulse and a 10 sec delay.

3. Results

3.1. Dispersion and sedimentation of SiC powder with organosilanes

The organosilicon dispersants employed in this study were trifunctional organosilanes of the general formula $RSiX_3$, where R is a straight-chain alkyl group with 8 or more carbons and X is a hydrolysable group such as chloro or methoxy. Fig. 1 compares the sediment density obtained for the SiC powder in hexane with various concentrations of the octadecyl silanes $C_{18}H_{37}$ $Si(OCH_3)_3$ and $C_{18}H_{37}SiCl_3$. In pure hexane, the powder flocculated very rapidly and packed to a density less than 10% of theoretical. In the presence of the alkoxysilane, a slight increase in sediment density was observed as the concentration of the dispersant was increased; however, even at 50 wt % dispersant the SiC powder packed to only 12% of theoretical density. In contrast, when suitable quantities of chlorosilanes such as $C_{18}H_{37}SiCl_3$ were added, the sediment density of the powder increased from less than 10% of theoretical in pure hexane to over 30%.

Fig. 2 summarizes the results of dispersion experiments in which the carbon chain length of the chlorosilane dispersant was varied from 8 to 18. In general, packing densities increased as the length of the alkyl group increased. The data also reveal that only small amounts of the chlorosilanes, i.e. less than 2 wt % of
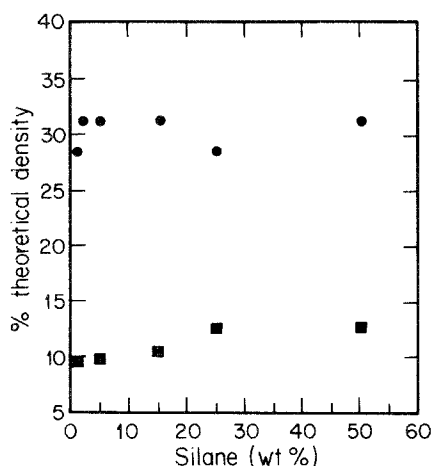
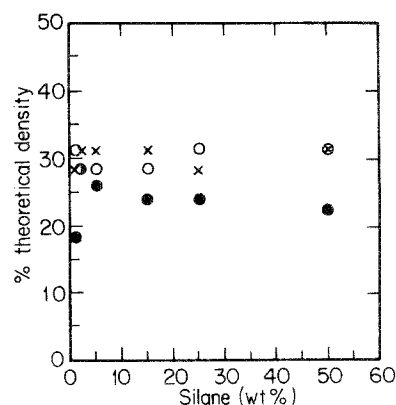*Figure 2* Packing density against silane content for SiC powder dispersed with (●) $C_8H_{17}SiCl_3$, (○) $C_{12}H_{25}SiCl_3$ and (×) $C_{18}H_{37}SiCl_3$.

the C_{12} and C_{18} derivatives, were necessary to achieve packing densities approaching 30% of theoretical. Increasing the concentration of these silanes only marginally improved the sediment density. Centrifugation of the gravity sediments at 3000 r.p.m. increased the packing density to between 40 and 42% of theoretical.

It was also observed that the sedimentation time of the SiC powder dispersions lengthened considerably when chlorosilane dispersants were used. In pure hexane the SiC powder flocculated rapidly, but with the addition of the organosilanes the dispersion quality improved markedly such that sedimentation occurred over the better part of a day. Filter-cake compacts prepared from these dispersions exhibited packing densities approaching 50% of theoretical.

Fig. 3a is a solid-state FT/MAS ^{13}C NMR spectrum of the SiC powder treated with $C_{18}H_{37}SiCl_3$. The resonances between 10 and 25 p.p.m. are due to the three distinct types of carbon that exist in the unit cell of α-SiC [4]. The less intense resonances between 30 and 40 p.p.m. can be attributed to carbons in the octadecyl substituent of the organosilane [5]. The cross-polarization technique (CP/MAS) enabled the carbons attached to hydrogens in the octadecyl group to relax more rapidly, and led to a dramatic enhancement in these resonances (Fig. 3b) relative to those due to SiC itself.

Fig. 4 is a Fourier transform infrared (FTIR) spectrum of the SiC powder treated with $C_{18}H_{37}SiCl_3$, then washed thoroughly and dried. The strong absorbances near 3000 cm^{-1} are associated with C–H stretching vibrations, and are further evidence that the organosilane remained attached to the SiC surface.
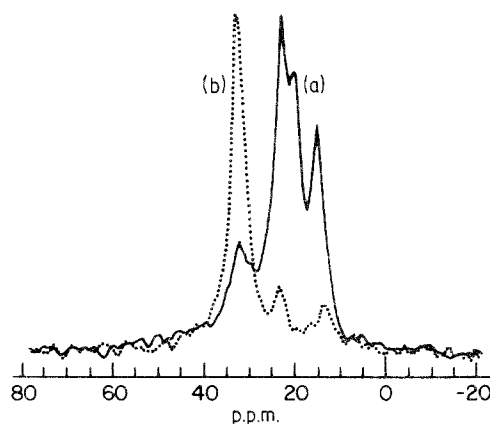
Figure 1 Packing density against silane content for SiC powder dispersed with C_{18} alkoxy and chlorosilanes: (■) $C_{18}H_{37}Si(OCH_3)_3$, (●) $C_{18}H_{37}SiCl_3$.

Figure 3 Solid-state ^{13}C NMR spectra of SiC powder treated with $C_{18}H_{37}SiCl_3$: (a) FT/MAS spectrum, (b) CP/MAS spectrum.
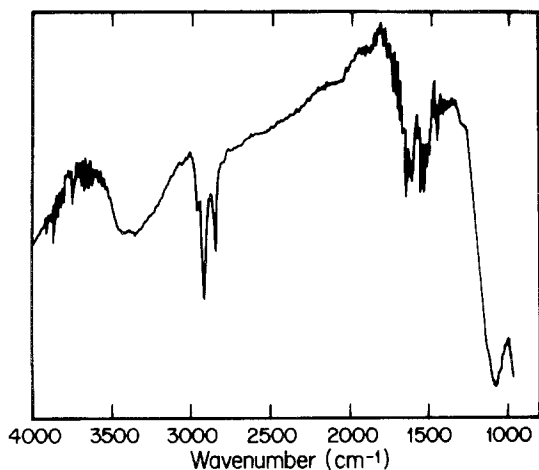
Figure 4 FTIR spectrum of SiC powder treated with $C_{18}H_{37}SiCl_3$.

3.2. Dispersion and sedimentation of SiC powder and whiskers with AlBS

The organoaluminium dispersant AlBS employed in this study is an aluminium alkoxy carboxylate with the molecular formula $Al_5(sec\text{-}OC_4H_9)_{13}(C_{17}H_{35}COO)_2$. AlBS was also investigated as a dispersant for the SiC powder in hexane; results are summarized in Fig. 5. With concentrations of less than 1 wt % AlBS, a slight decrease in sediment density was observed, but as the concentration of AlBS was increased the sediment density of the powder increased more than threefold. A maximum sediment density of 33% of theoretical was achieved with 10 wt % AlBS. Fig. 6 is a solid-state CP/MAS ^{13}C NMR spectrum of a powder compact with grafted AlBS and shows a strong resonance at 29 p.p.m. with several weaker upfield resonances all characteristic of the stearic chain, but there is no evidence of downfield resonances due to carbons in residual alkoxy groups.

The use of AlBS as a dispersant for SiC whiskers was also examined; results are summarized in Fig. 7. In pure hexane, the whiskers packed to less than 3% of theoretical density. Adding small amounts of AlBS steadily increased the sediment density to a maximum of between 7 and 8% of theoretical. Due to the whiskers' large size and cylindrical geometry, the packing density remained quite low relative to the SiC powder. However, the two- to three-fold increase observed with AlBS indicates that its presence improved whisker dispersion.
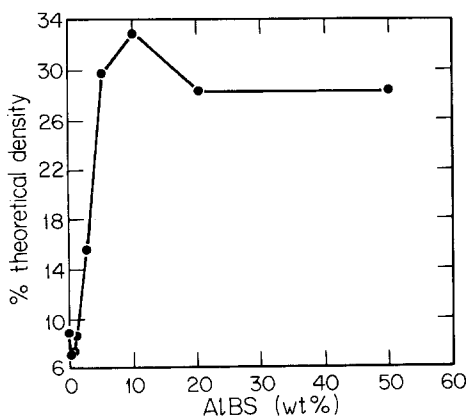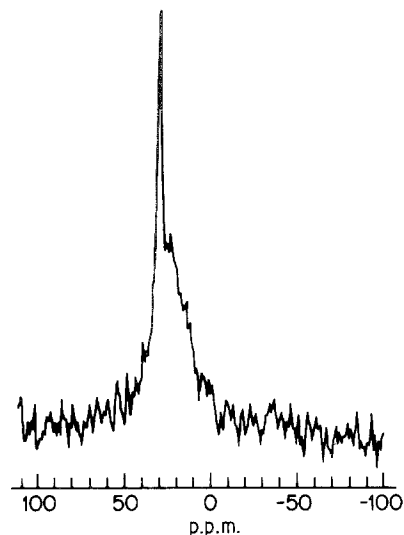

Figure 6 Solid-state CP/MAS ^{13}C NMR spectrum of SiC powder treated with AlBS.

4. Discussion

Submicrometre SiC powders produced by the Acheson process typically possess a silica-like surface with hydroxyl groups that can interact with dispersant molecules in solution. The organosilicon and organoaluminium compounds employed in this study contained hydrolysable chloro and alkoxy groups, capable of reacting with the hydroxyl groups at the surface of the SiC to eliminate one or more molecules of HCl or alcohol and covalently anchor the dispersant. Although the alkoxysilanes possess reactive groups, the data in Fig. 1 show that they were essentially ineffective as dispersants for the SiC powder. The addition of a catalytic amount of acetic acid to assist the grafting reaction did not improve the dispersion quality or sediment density of the powder. Alkoxysilanes have been attached to the surface of silica gel, but significantly higher reaction temperatures were used to achieve grafting [6].

Grafting was accomplished at room temperature with the more reactive chlorosilanes. The data in Figs 1 and 2 indicate that the sediment density of the SiC powder was tripled to over 30% of theoretical with as little as 2 wt % of the organosilicon dispersant in hexane. As the chain length of the R group was increased, a slight improvement in sediment density was observed. The FTIR and solid-state ^{13}C NMR results obtained with $C_{18}H_{37}SiCl_3$ showed that the organosilane was grafted to the surface.
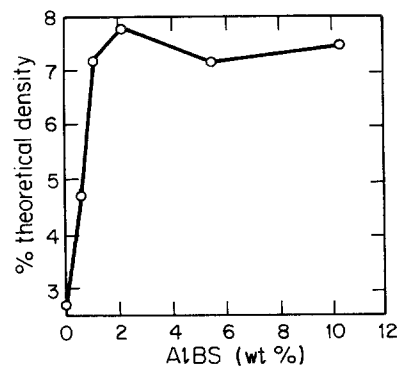

Figure 5 Packing density against AlBS content for SiC powder (AlBS = aluminium sec-butoxide stearate).

Figure 7 Packing density against AlBS content for SiC whiskers in hexane.

Similar improvements in the dispersion and packing behaviour of the SiC powder were obtained using AlBS. This aluminium alkoxy carboxylate could also be used to improve the dispersion of SiC whiskers. The higher reactivity of aluminium alkoxides relative to their silicon counterparts permitted grafting of the AlBS to occur at room temperature. At low concentrations, it was found that AlBS flocculated the SiC powder. This observation is consistent with the oligomeric nature of AlBS and the presence of many hydrolysable alkoxy groups that could interact with more than one ceramic particle.

Although these studies have shown that covalently bonded dispersants are helpful in improving dispersion quality, the effect of these dispersants in subsequent processing steps remains an area for future investigation. In the processing of SiC, where the presence of excess surface oxygen during sintering can be detrimental, oxidative removal of grafted dispersants could introduce undesirable surface oxides. For SiC and other non-oxide ceramics, decomposition of the covalently bonded dispersant under an inert atmosphere should be advantageous. The organosilanes employed in this study were chosen in light of the demonstrated success in forming SiC from polycarbosilanes [7, 8] and related precursors [9]. Under an inert atmosphere, it is possible that the organosilicon dispersants themselves might decompose to SiC. Future work will examine the decomposition of the grafted organosilanes and the sintering behaviour of silanized powders.

Efforts will also be directed toward determining the fate of the grafted AlBS and its effect on the microstructure and properties of monolithic and composite SiC ceramics. Previous studies have shown that addition of aluminium additives (AlN, Al_4C_3) can be used to hot-press- or pressureless-sinter SiC to high densities [10–12]. There is also considerable current interest in the fabrication of SiC whisker-reinforced Al_2O_3 composites [13]. In view of these studies, the decomposition of the grafted AlBS to a sintering aid for SiC powders and the use of AlBS as a coating/matrix precursor for SiC whisker composites will be investigated.

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