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Dispersion, Slip Casting and Reaction Nitridation of Silicon–Silicon Carbide Mixtures

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Abstract

The dispersing behaviour of silicon, silicon carbide and their mixtures in aqueous media were monitored by particle size, sedimentation, viscosity and zeta potential analyses as a function of pH of the slurry. The pH values for optimum dispersion were found to be 4 and 8 for silicon, 10 for SiC and 9 for Si + SiC mixtures. Optimum slips of Si + SiC mixtures were slip cast to obtain green compacts which were nitrided once at 1450°C for 2 or 4 h or successively and cumulatively for 8 (2 + 6) and 10 (4 + 6) h in a resistively heated graphite furnace. The binding phases in the nitrided products were found to be fibrous/needle like α-Si_3N_4*, flaky grains of* β-Si_3N_4 *and* Si_2ON_2*. The products containing 19–47% of silicon nitride as bond/matrix possessed flexural strength (three-point bending) values of 50–85 MPa. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: nitridation, slip casting, suspensions, SiC, Si.

1 Introduction

Silicon nitride bonded silicon carbide ceramics have generated a sustained interest for their use in the field of refractories as well as in the field of high temperature structural applications for a long time.[1,2] These ceramics are known to possess remarkable erosion, corrosion, chemical and high temperature thermal shock resistances. They find specific applications in metallurgical, chemical, ceramic and aerospace industries (e.g. as aluminium reduction cell linings, as molten metal thermocouple shields, as high temperature refractory bricks, as refractory crucibles, as kiln furniture, as rocket nozzles, as high temperature turbine blades and as hot gas filters, etc.).[3,4] In addition, nitride bonded silicon carbide has the added advantage of forming near net shape bodies via the direct nitridation of silicon + SiC powder mixture compacts. The economic advantage of using low cost silicon powders compared to Si_3N_4 powders and the low reaction nitridation temperatures required are added attractions for producing these materials for their intended applications.

Nitride bonded silicon carbide composites were prepared by nitriding silicon green bodies containing SiC grains of different mesh sizes in a high purity N_2 atmosphere between 1350 and 1450°C so that the silicon nitride formed in-situ interlocks and bonds the silicon carbide grains.[2,3] Several authors prepared nitride bonded silicon carbide composites by the above method and studied the physical, chemical, mechanical and micro-structural behaviour of the products.[2–8] Reaction bonded silicon nitride (RBSN) reinforced with SiC filaments, fibers or whiskers have been more recently studied by many authors.[9–12] They found that the composites are much stronger and tougher than monolithic RBSN and they retain their room temperature properties up to 1400°C. The properties are mainly controlled by the microstructure and micro-chemistry of the fiber/matrix interface. The enhancement of strength and fracture toughness of Si_3N_4 matrix has been achieved by incorporating SiC in the form of powders, platelets or whiskers, along with or without sintering additives. Consolidation of the green Si + SiC bodies is done by reaction nitridation, by sintering at high temperatures or by subjecting the reaction nitrided products to hot pressing or hot isostatic pressing to improve the density and mechanical properties of the product.[13–20]

In almost all the above studies the composites have been fabricated either by uniaxial dry pressing followed by nitridation/sintering or by hot pressing/hot isostatic pressing. Even though the colloidal consolidation technique has proved to be a promising method to obtain well dispersed high

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solid-loaded slips which yield high green density bodies sinterable to dense products in the case of monolithic silicon carbide[21–25] and silicon,[26–30] very little study has been reported on wet slurry processing of silicon + silicon carbide mixtures[31] as a route to generate their green bodies. This paper presents the results of a study directed towards preparation of most optimal aqueous slips of silicon + silicon carbide mixtures. Their slip casting and nitridation to obtain Si_3N_4 bonded SiC composite bodies has been explored in this study.

2 Experimental Procedure

Commercial silicon (types HQ and RQ, M/s Keminord industries, Norway) and silicon carbide (type G1200, M/s Grindwell Norton, Bangalore, India) powders used in this study were characterised for their phase contents by X-ray diffraction (X-ray diffractometer, model PM 9002, M/s Philips, The Netherlands) studies. The slips of these powders were prepared in de-ionised water and their dispersability as a function of pH was investigated by studying the particle/floc size distribution (Sedigraph, Model 5100, M/s Micromeritics, USA), electrokinetic behaviour (Zeta potential analyser, Model 1202, M/s Micromeritics, USA), sedimentation behaviour and rheological/viscosity behaviour (Rotational viscometer, Searle type, Viscotester, Model VT-500, M/s Haake, Germany). The experimental details were presented earlier elsewhere.[25] The powders were dispersed in deionised water using magnetic stirring and the pH was adjusted to different values ranging from 2 to 12 using HNO_3 (for acidic) and NH_4OH (for basic) solutions, respectively. The particle/floc size distributions of the powders were determined by using 5 wt% solid loaded suspensions. The viscosity and rheological measurements were made for SiC-G1200 and Si-HQ/RQ slips with varying solid loadings of 47–62 wt% and at different shear rates in the range 27–2700 s^{-1} as a function of pH of the slurry. The rheological behaviour of the 52 wt% solid loaded slips made from SiC + Si mixtures in 3:1 and 1:1 weight ratios designated as 3SCS and SCS were also studied as a function of pH and shear rates. The sedimentation behaviour of the slips were studied as a function of time at different pH values (2–12) using 20 wt% solid loaded slips. The electrokinetic behaviour of the silicon carbide and silicon powders were characterised by measuring the electrophoretic mobilities as a function of pH for 20 wt% suspensions using a mass transport apparatus (zeta potential analyser) and then calculating the zeta potential values using Smoluchowski equation.[32]

Aqueous slips of Si + SiC mixtures containing 0 to 85 wt% of silicon carbide were prepared by dispersing the two powders in de-ionised water using a magnetic stirrer. The pH of the slip was adjusted to a value between 8 and 9·5 (for reasons to be stated in the succeeding section) and milled in a polythene jar for 16 h using alumina balls as milling media and then cast as bars (50×9×9 mm) and discs (25×10 mm) into plaster of Paris molds. The cast bodies were nitrided at 1450°C for periods ranging from 2 to 10 h (either in one step or in a cumulative manner) in a resistive graphite furnace (M/s Dynatech Engineering, Bombay) under a constant static pressure (0·18 MPa) of high purity nitrogen. The nitrided products were characterised by (i) their percentage of nitridation (ii) percentage of Si_3N_4 bond formed (derived from sample weight gain after nitridation), (iii) the nitrided density (from weight and volume measurements of the nitrided products) and (iv) apparent porosity (by water displacement method). The different crystallographic phases formed during nitridation were analysed by X-ray diffraction techniques. The three-point flexural strengths were measured for rectangular bar specimens (50×9×9 mm) using a span width of 40 mm and cross head speed of 0.5 mm min^{-1} in a Universal Testing Machine (Electrohydraulic Universal Testing Machine, Model 6025, Instron, UK). The microstructures of the fractured surfaces were observed on a scanning electron microscope (Model JSM 35, M/s Jeol, Japan).

3 Results and Discussion

3.1 Slurry characterisation

The particle size distributions (PSD) measured as a function of pH of the slurry for silicon carbide and silicon powders depicted in Fig. 1 show that at the pH of optimum dispersion, the particle size distribution curve is shifted to the extreme right, i.e. towards the finer particle size ranges. On the other hand at the pH conditions where the particles are agglomerated, the curve is shifted towards coarser range (to the left) with a narrow size distribution. Silicon carbide powders used in this study show optimum dispersion at pH = 10 with particle size distribution of $d_{10} = 0{\cdot}6\,\mu m$, $d_{50} = 2{\cdot}5\,\mu m$ and $d_{90} = 8{\cdot}0\,\mu m$. For silicon, conditions of optimum dispersion occurred at the two pH values of 4 and 8 with $d_{10} = 0{\cdot}72\,\mu m$, $d_{50} = 2{\cdot}9\,\mu m$ and $d_{90} = 4{\cdot}8\,\mu m$ as shown in Fig. 1(c). These results show that SiC has wider size distribution than silicon and having considerable amount of coarser particles (SiC = 23% in the range 5–20 μm, Si = 10% in the range 5–8 μm).

When a ceramic powder dispersed in a liquid medium allowed to settle freely under gravity, the particle settling rate manifested in terms of an increase of sediment height or sediment volume as a function of time gives a measure of the state of dispersion and its stability. The sedimentation heights measured after 24 h for silicon carbide and silicon powder suspensions at different pH values are plotted in Fig. 2. The two silicon powders (HQ and RQ) show a similar state of dispersion with minima in sedimentation heights at pH values of 4 and 8, while the silicon carbide shows only one minimum in the pH range 9–10. The minimum in sedimentation heights indicates good dispersion of particles where the particles settle into tightly packed sediments leading to ideal packing. Higher sedimentation heights in a loose lumpy form, however, are ascribable to loose packing of agglomerates. The results of sedimentation experiments while matching with PSD results, are also supported by the results of viscosity measurements carried out on the silicon and silicon carbide slips.

The viscosity values measured for the 52 wt% silicon and silicon carbide slips at the shear rate of 972 s^{-1} are presented in Fig. 3. While silicon slips show viscosity minima in two regions of pH (namely 4–5 and 8), the silicon carbide slurry shows a minimum viscosity in the pH region of 9–10. Minimal viscosities of the slips are attributed to the state of good dispersion of powder particles in the medium. At other pH regions, significant agglomeration of particles coupled with entrapping

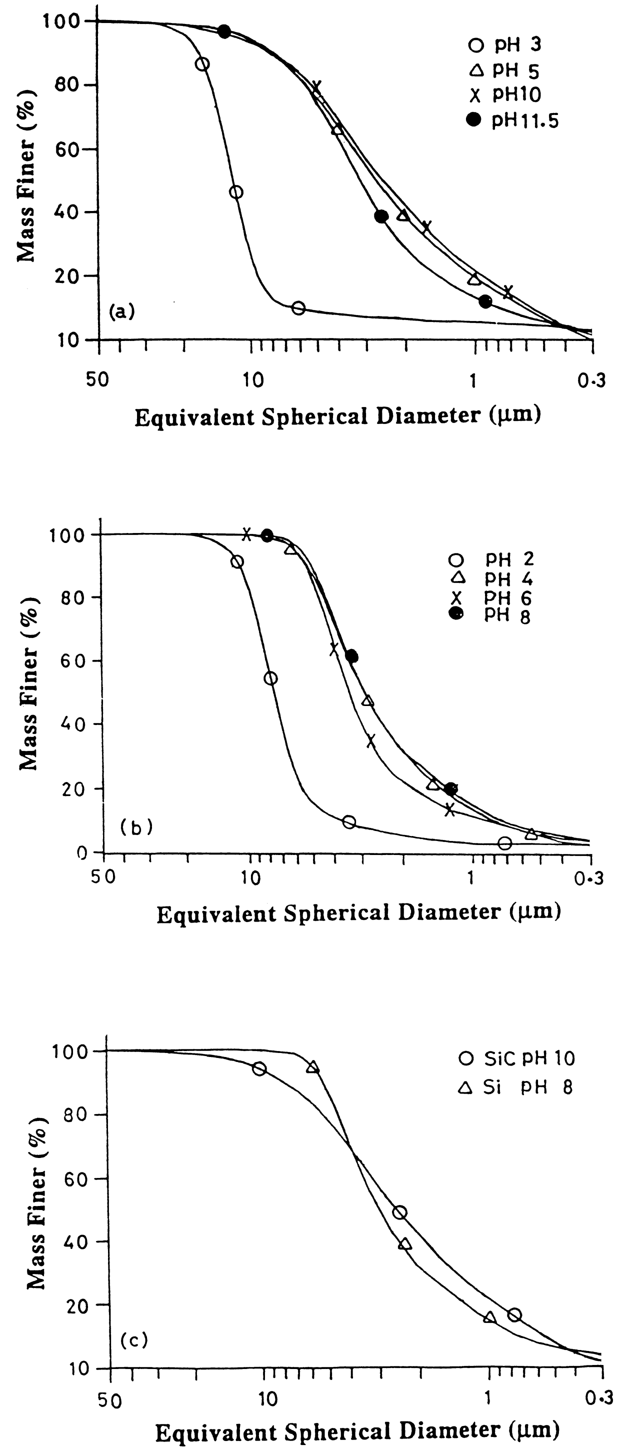

Fig. 1. Particle size distribution of (a) SiC G1200 and (b) Si-RQ under different pH conditions; (c) particle size distribution of pH optimised slips of SiC G1200 (o-o-) and of Si RQ (Δ-Δ-).

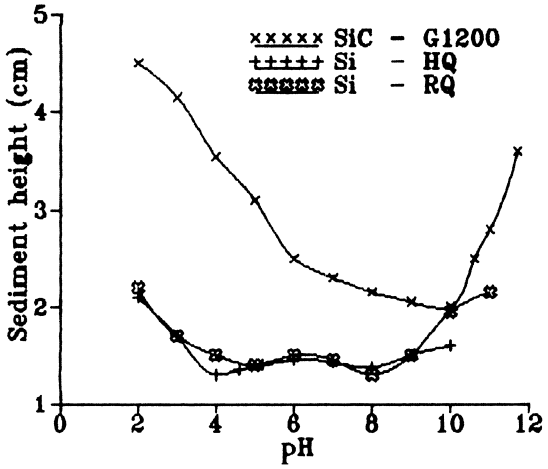

Fig. 2. Sedimentation height for silicon carbide and silicon powders (24 h) as a function of pH.

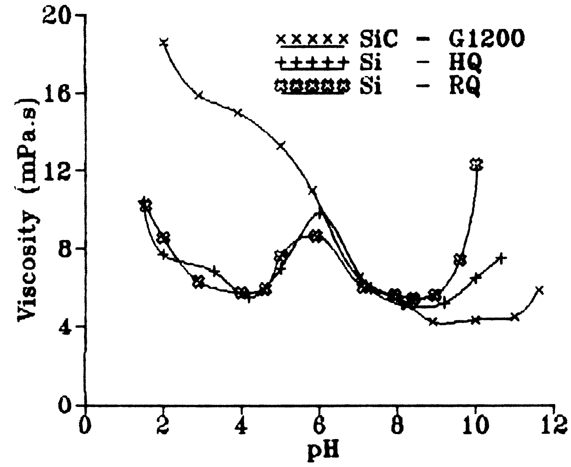

Fig. 3. Viscosity as a function of pH for SiC G1200 and Si-HQ/RQ at a shear rate of 972 s^{-1}.

of liquid in the interparticulate pore spaces increased the effective solid loading and thereby the slip viscosity. Further the rheological behaviour of SiC G1200 and Si-RQ slips (52 wt% solid loading) at different pH were studied by measuring the viscosity and shear stress as a function of shear rates.[25,33] The viscosity values plotted as a function of pH of the slips follow the same trend at different shear rates.[33] The flow curves obtained by plotting shear stress versus shear rate for SiC G1200 and Si-RQ slips are presented in Figs 4 and 5, respectively. The linear shear stress versus shear rate curve passing through the origin for SiC slip at pH = 10 shows the newtonian behaviour indicating a well dispersed, homogeneous slip. The shear thinning at pH 3 and 5 and slight shear thickening (dilatant) at pH 8 and 12, the characteristics of non newtonian flow are attributable to the high agglomeration/flocculation of the fine particles and/or high solid loading[25] of the slurry. On the other hand the silicon slips show near newtonian flow behaviour at pH 5, slightly non-newtonian shear thickening behaviour at pH values 3, 8 and 10 (Fig. 5). Thus the results of particle size distribution, sedimentation and viscosity studies on silicon and silicon carbide slurries indicate that the silicon powders are well dispersed in aqueous media in the pH regions around 4 and 8 and silicon carbide around pH = 10.

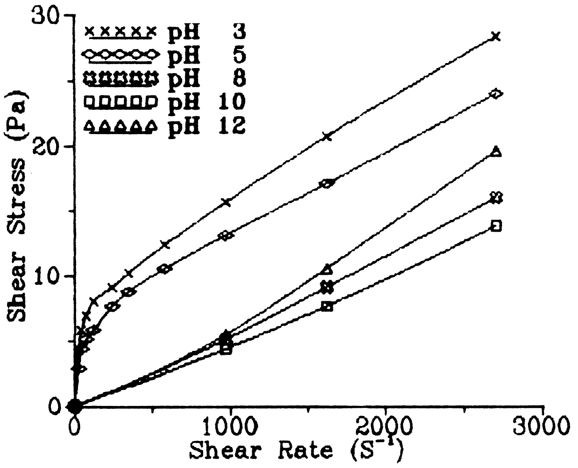

Fig. 4. Shear rate versus shear stress flow curves for SiC G1200 slurry (52 wt%) as a function of pH.

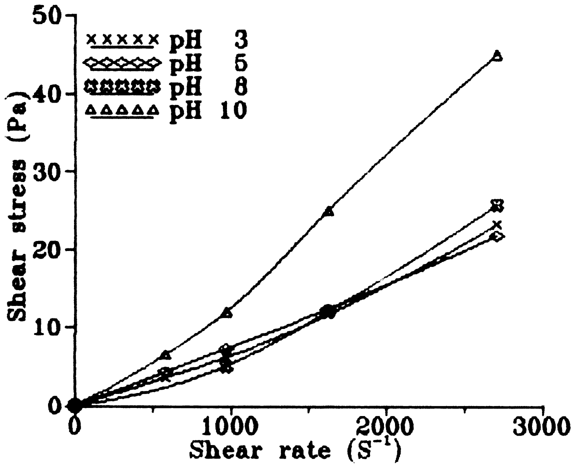

Fig. 5. Shear rate versus shear stress flow curves for Si-RQ slurry (52 wt%) as a function of pH.

The above results are the direct manifestation of the existence of surface charges on the powder particles. When the particles dispersed in a medium develop similar surface charges, they result in interparticulate electrostatic repulsion. When the electrostatic repulsive forces overcome the Van der Waals forces of attraction between the particles, the particles remain separated (unagglomerated/deflocculated) leading to a homogeneous and well dispersed slip exhibiting a minimum of viscosity and of sedimentation heights. Another property with which the condition of the dispersability of slips could be discerned is their zeta potential. The Zeta potential arising out of net effective surface charge on the particles in the suspension, directly reflects the dispersability levels of the particles in a medium. The zeta potential measured as a function of pH for silicon and silicon carbide powders presented in Fig. 6 show that silicon powders develop higher surface charges in the pH ranges around 4 and 8 while SiC powders do so in the pH range around 10 indicating these as the pH regions of their optimum dispersion. The isoelectric points for SiC and Si powders at the pH values of 3·3 and 2·4 are in accord with the reported[25–27] values, leading to higher agglomeration of the respective powder particles which in turn results in higher sedimentation heights, higher viscosity and non-newtonian flow behaviour for the slips. The reason for the relatively higher Zeta potential values at extreme pH conditions for SiC slips are not clear at present. However these can be attributed to the unusually higher values of conductivity resulting from excess

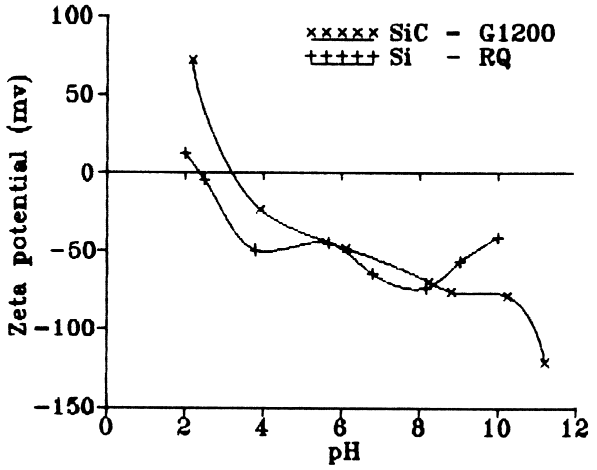

Fig. 6. Zeta potential versus pH for SiC G1200 and Si-RQ as a function of pH.

amount of electrolytes (acid/alkali) added to achieve extreme pH conditions or may be due to electrolysis in the measuring cell.

The viscosity curves for the slips of SiC + Si mixtures designated as 3SCS and SCS (52 wt% solid loading) measured as a function of pH at the shear rate of 972 s^{-1} are reproduced in Fig. 7 in comparison with the curves for SiC and Si slips. It can be observed that the flow behaviour of the mixtures is the combined characteristic of both individual components with distinct minima around the pH values of 5 and 9 (as against the pH values of 4 and 8 for silicon and 10 for SiC alone). The contribution of individual components on the flow behaviour of the slips made of SiC + Si can be explained more effectively from the plots of shear rate versus shear stress depicted in Figs 8 and 9. While the slips of 3SCS show shear thinning non-newtonian behaviour at pH values of 3 and 5 similar to that of SiC slurry (Fig. 4), the slips of SCS is slightly shear thinning at pH = 3 and near newtonian at pH = 5. At the pH value of 8 the 3SCS slurry behaves as near newtonian and SCS shows shear thickening behaviour. Both the compositions of 3SCS and SCS show non newtonian shear thickening behaviour at pH values of 9 and 10. These results clearly indicate the complex rheological behaviour of the SiC + Si slurry with contributions both from silicon and silicon carbide. The sedimentation behaviour of SiC + Si mixtures (1:1 wt%, SCS) in deionised water studied as a function of pH is presented in Fig. 10. The slips show minimum sedimentation heights in the pH range 5 to 10 at all times indicating good dispersion while higher sedimentation heights at extreme pH values of ≤ 4 and ≥ 10 are attributable to higher levels of agglomeration. A small percentage of SiC is found settled preferential to silicon initially at all pH conditions. This is attributed to the coarser fraction of SiC particles [Fig. 1(c)] present in the mixture. Otherwise at all pH ranges silicon carbide and silicon are found to sediment almost simultaneously irrespective of small difference in their density (SiC = 3·2 g cm^{-3}, Si = 2·33 g cm^{-3}). From

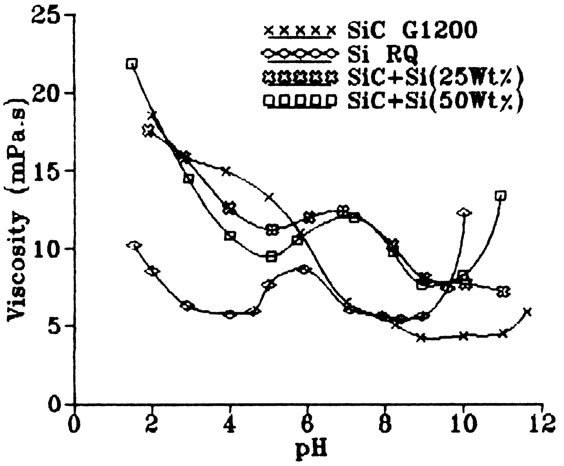

Fig. 7. Viscosity versus pH curves for SiC G1200, Si-RQ and their mixtures at 52 wt% solid loading (shear rate 971 s^{-1}).

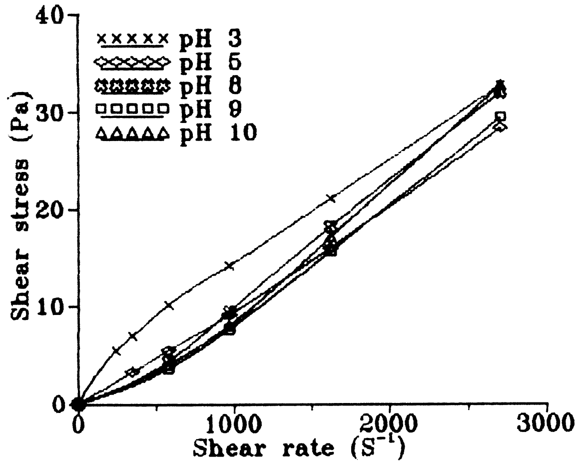

Fig. 9. Shear rate versus shear stress curves for SiC + Si (1:1 wt%) slips (52 wt%) as a function of pH.

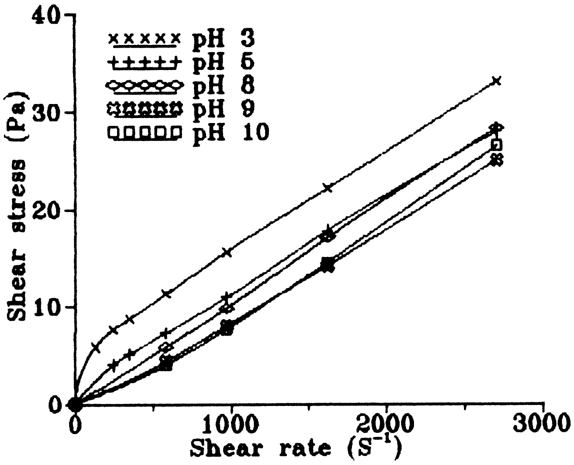

Fig. 8. Shear rate versus shear stress curves for SiC + Si (3:1 wt%) slips (52 wt%) as a function of pH.

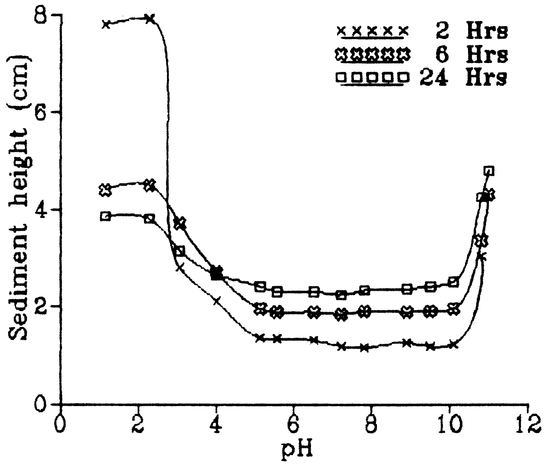

Fig. 10. Sedimentation height versus pH for SiC + Si (1:1 wt%) slips (20 wt%) as a function of time.

the results of the above studies (particle size distribution, viscosity, sedimentation and zeta potential measurements), pH values in the range 8·5–9·5 was used as the optimum dispersing condition for all Si + SiC mixtures in our further investigations.

3.2 Slip casting of Si + SiC mixtures

Slips of Si + SiC mixtures were slip cast into plaster of paris moulds to obtain green bodies for nitridation. The compositional density calculated by the rule of mixtures (using the density values of 3·2 and 2·33 g cm^{-3} for SiC and Si, respectively), the green density of mixtures computed from weight and dimensional measurements and the percentage theoretical density for different compositions of silicon + SiC (0–85 wt%) are depicted in Fig. 11. The green density is found to decrease with the in crease in silicon content in correlation with a concomitant decrease of compositional density. However, the percentage theoretical density of green bodies increases with silicon content which reveals the better packing efficiency of silicon powder particles as compared to that of SiC in the mixtures.

3.3 Nitridation of Si + SiC (0–85 wt%) compacts

The Si + SiC mixture (0–85 wt% SiC) compacts (made by slip casting their optimised slips) were nitrided at 1450°C separately for 2 and 4 h. As the products were found to be only partially nitrided they were renitrided additionally for 6 h at 1450°C by repeating the same heating cycles. The percentage nitridation (calculated from weight gain after nitridation) as a function of duration of nitridation is presented in Fig. 12. A systematic improvement in percentage nitridation is observed for all compositions with respect to increase in duration of nitridation. Compacts with smaller amounts of silicon (15–25%) nitrided to the extent of 70–88% for durations of $\geq$4 h. On the other hand compacts with higher percentages of silicon (75–100%) nitrided to a maximum of 42% even after nitridation for 4 + 6 h. The compacts with 33 and 50% of silicon in the green compacts nitrided to an intermediate range resulting in 70–76% nitridation after reacting for 4 + 6 h at 1450°C. These results prove that nitridation is a process which is a dependent function of time, temperature as well as the mass of silicon in the compacted mixture.

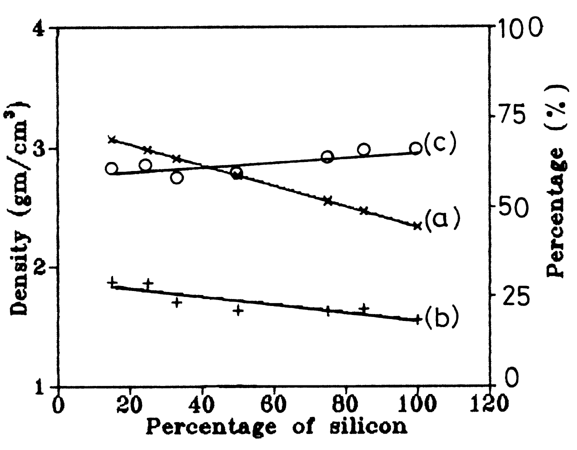

Fig. 11. Change of (a) compositional density; (b) bulk density; (c) percentage theoretical density of slip cast Si + SiC green compacts.

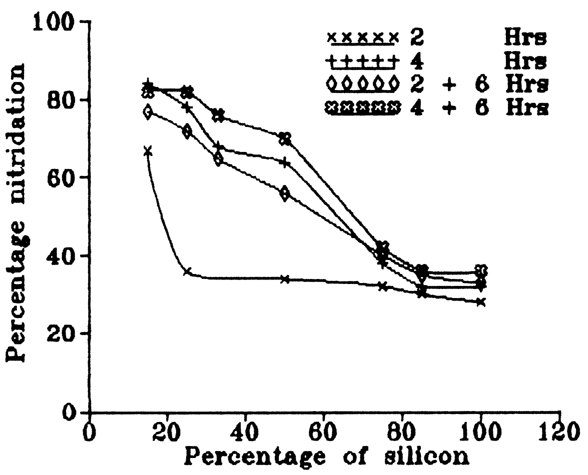

Fig. 12. Percentage nitridation of slip cast Si + SiC compacts as a function of duration of nitridation at 1450°C.

Another interesting observation of the present study is that the percentage nitridation achieved by reacting for 2 + 6 h is less than that achieved by reacting for 4 h alone, in compacts with 15–50% of silicon. This is due to the fact that the Si_3N_4 crystals grown during the first nitridation cycle could close up the pores on the periphery of the compacts and prevent the passage of nitrogen into the interior core of the compact during the successive cycles resulting in a decrease in the levels of the relative percentage of nitridation. The results indicate that the nitridation reaction should be continued for longer times at a single stretch at the same temperature rather than subjecting them to repetitive cycles of renitriding.

3.4 Characterisation of nitrided compacts of Si + SiC (50–85 wt%)

Some results on the typical nitrided products obtained from the Si + SiC mixture castings are presented in Table 1. The products are designated as *xx* NBSC (nitride bonded silicon carbide) based on the wt% of silicon present in the green compact. The percentage of nitridation (with respect to silicon in the green compact), the percentage of silicon nitride formed and the percentage of unreacted free silicon left in the nitrided product were calculated from the weight gained during nitridation and these data are depicted in Fig. 13 as a function of percentage of silicon present in the initial green compact. The three-point flexural strength values for the nitrided compacts are also plotted in Fig. 13.

Table 1. Characteristics of green and nitrided compacts of slip cast Si + SiC compositions

Sample identity	*Initial Si content (%)*	*Green density (%)*	*Nitridation w.r.t silicon (%)*	*Si_3N_4 formed (%)*	*Bulk density ($g\,cm^{-3}$)*	*Apparent porosity (%)*	*M.O.R (MPa)*
15NBSC	15	60·9	81·2	18·8	2·011	34·0	53
25NBSC	25	62·2	78·2	28·8	2·089	30·3	76
33NBSC	33	58·3	76·2	36·2	1·978	31·7	69
50NBSC	50	58·9	70·3	47·4	2·015	30·1	85

The increased amount of nitridation (and hence the silicon nitride formed) at higher percentages of silicon in the green compacts are responsible for the increase in flexural strength values. The flexural strength values obtained (55 to 85 MPa) are considerably higher than those reported by Albano *et al.*[5] and Reddy *et al.*[3] for SiC–Si_3N_4 refractory materials. These higher strength values in spite of lower nitrided densities (max: 2·1 $g\,cm^{-3}$) and higher porosity (30–34%) achieved in this study are attributable to the uniform and homogeneous microstructures of the green body in which the agglomeration and other inhomogeneities have been prevented from forming in the green bodies through slurry optimisation methods.

The X-ray diffraction patterns were taken for the Si + SiC (50–85 wt%) compacts (50×8×8 mm bar specimens) nitrided at 1450°C for 4 + 6 h, on their outer surface and at depths of 2 and 4 mm from the outer surface. The major crystalline phases present in the products were α-Si_3N_4, β-Si_3N_4 and Si_2ON_2 in addition to starting phase α-SiC and a minor fraction of unreacted silicon as revealed in the typical XRD spectra for 25NBSC taken at the core of the specimen (shown in Fig. 14). The presence of Si_2ON_2 phase can be attributed to the SiO_2 that could be present or introduced as a surface layer on both silicon and SiC during processing. The appearance of α-Si_3N_4 and β-Si_3N_4 in almost equal amounts for all the compositions suggest the possibility of both vapour as well as liquid phase reaction occurring during nitridation. The percentage of free silicon detected by XRD spectra increases from the surface towards the centre. While very small amount of silicon is detectable at the core of 25NBSC compact, considerable amounts are found at the core of 50NBSC. However, on the average, the free silicon content detectable by XRD in all the compositions are lower than that calculated from weight gain measurements (Table 1). This is probably attributable to the loss of silicon by vaporisation. In all the samples having higher percentage of silicon ($\geq$33%) in the green compacts, on nitridation a greenish layer was found on the outer most surface (to a depth of 1–2 mm from the outer surface) which had different morphology and colour than the interior core. Similar layers were observed in our earlier studies on the nitridation of pure silicon also. The greenish layer was then identified as β-SiC,[32] the formation of which, was promoted on the external surface of the samples due to the high carbon activity existing in the furnace.

The observation of the fractured surfaces of nitrided samples by scanning electron microscope revealed the morphology of the reaction products

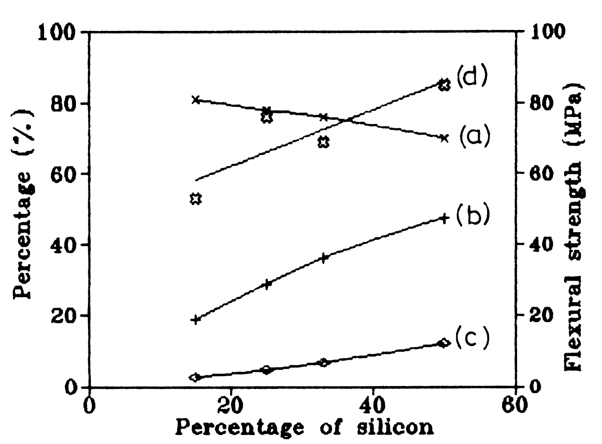

Fig. 13. Variation of percentage of (a) nitridation; (b) silicon nitride formed; (c) free silicon; and (d) three-point flexural strength for nitride bonded silicon carbide (NBSC) products.

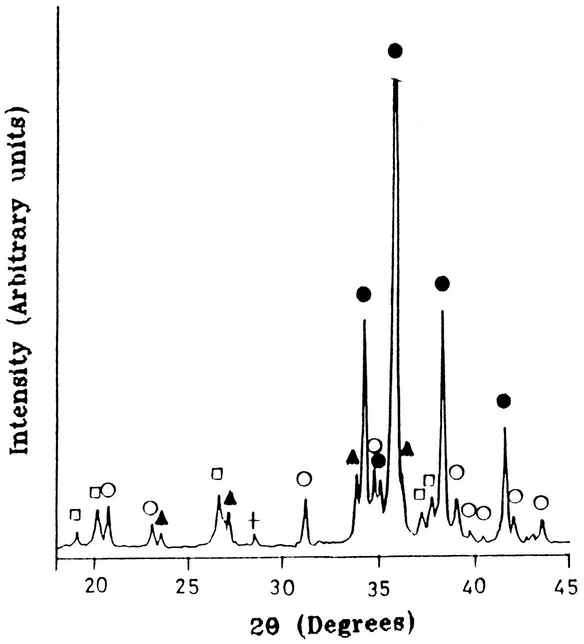

Fig. 14. XRD spectra of 25 NBSC product at the central core of a 50×8×8 mm bar specimen. Phases identified: ● = α-SiC, □ = Si_2ON_2, O = α-Si_3N_4, ▲ = β-Si_3N_4, + = silicon.

and thereby the reaction mechanisms of nitridation [Fig. 15(a)–(c)]. The SEM for 15NBSC sample in Fig. 15(a) reveals large amounts of long fiber like structures typical of α-Si_3N_4 crystals formed preferably by the vapour phase reaction of $Si_{(g)}$ or $SiO_{(g)}$ with nitrogen which envelop the SiC particles. In the case of 25NBSC and 50NBSC samples [Fig. 15(b) and (c)] small needle like crystals typical of α-Si_3N_4 are observed instead of longer fibers along with small flaky particles characteristic of β-Si_3N_4 as well as of Si_2ON_2 embedding the SiC grains.[2,8]

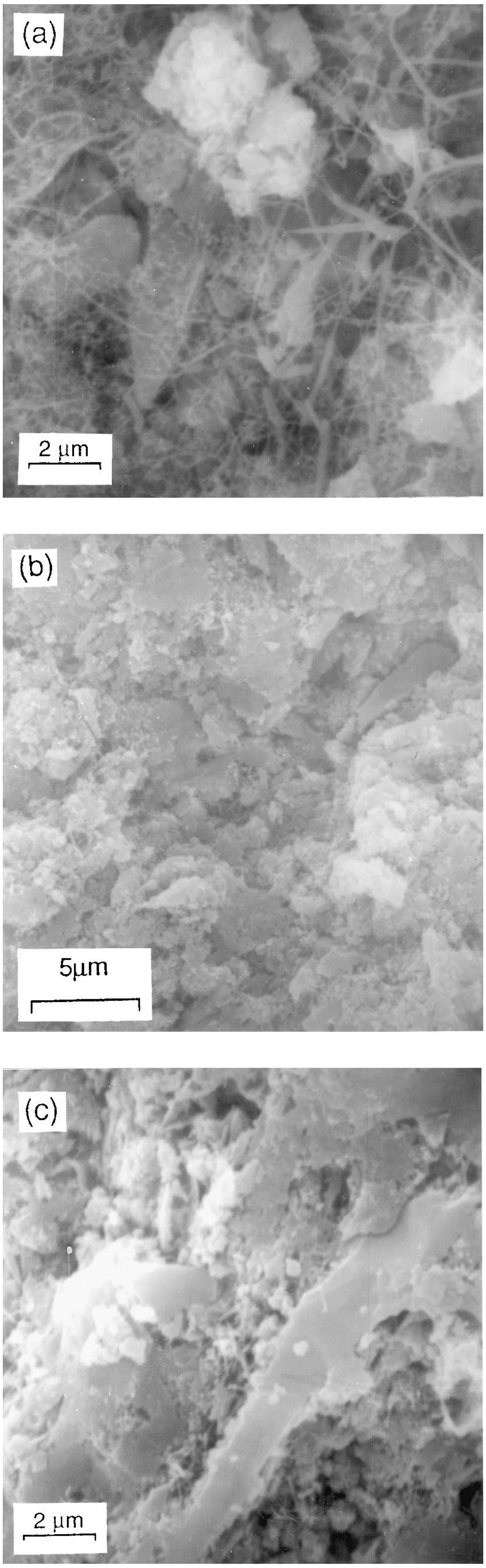

Fig. 15. Scanning electron micrographs of nitride bonded silicon carbide products: (a) 15NBSC; (b) 25NBSC; (c) 50NBSC.

4 Conclusion

Dispersion of silicon and SiC powders in aqueous media can be optimised by adjusting the pH of the medium. By using various techniques like particle size analysis, sedimentation, viscosity and zeta potential measurements, the optimum condition of dispersion for silicon is found to be either of the two pH values of 4 and 8 and for silicon carbide at the pH value of 10. Adjusting the pH value in the range 8·5 to 9·5 is found to give optimum, well dispersed, low viscosity slips of Si + SiC mixtures which when cast yield homogeneous high green density compacts.

The nitridation experiments have proved that the extent of nitridation is a function of temperature, time and the mass of silicon required to be nitrided. Compacts with higher percentage of silicon nitrided to a minimum value, while those with lower percentage of silicon nitrided to a maximum value. The binding phase in the nitrided product consisted of fiber and needle shaped crystals of α-Si_3N_4 and flaky grains of β-Si_3N_4 and Si_2ON_2. Considerably higher mechanical properties (three-point flexural strength) of 50–85 MPa irrespective of lower bulk density (2·0–2·1 $g\,cm^{-3}$) measured for these samples would make them useful for various refractory as well as high temperature applications.

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