Slip cast nitride-bonded silicon carbide bodies

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Abstract

The dispersion behaviour of SiC, Si and their mixtures, in deionised water, was studied as a function of pH by sedimentation, viscosity, rheology and zeta potential measurements. Slips of SiC + Si mixtures (3:1, 1:1 and 1:3 weight ratios) with 1 wt.% of Fe2O3 (with respect to Si), conditioned in the pH range 8–9.5 were slip cast to 56–65% dense green bodies. These on nitridation under 0.18 MPa pressure of high-purity nitrogen at 1400–1450 °C for 2–4 h resulted in nitride-bonded SiC bodies having 30–76 vol.% of Si3N4 bond, densities of 2.1–2.4 g cm−3 and 3-point flexural strengths of 60–220 MPa. The phase analyses of the products were carried out by XRD and microstructure by SEM studies. © 2002 Published by Elsevier Science B.V.

Keywords: Slip casting; Nitridation; Nitride-bonded silicon carbide; SiC–Si3N4

1. Introduction

Si3N4 and SiC ceramics have been recognised as potential candidates for high-temperature structural applications, e.g., in advanced heat engine parts, in heat exchangers, in friction and wear-resistant components, etc. [1]. However, the principal disadvantage, which limits their mechanical applications, is their marked brittleness. In a promising approach to improve the toughness of monolithic ceramic materials, Si3N4–SiC composites have attracted attention mainly due to their improved high temperature strength and fracture toughness [2,3]. Si3N4-bonded SiC ceramics (NBSC) have generated a sustained interest for their use in the field of refractories as well as for high-temperature structural applications for a long time [4–7]. Generally, NBSC products consist of 5–45 vol.% Si3N4 bonding phase with the remainder being the inert SiC phase. These ceramics are known to possess remarkable erosion, corrosion and chemical resistance at high temperatures as well as good thermal shock resistance and hence they find specific applications in metallurgical, chemical, ceramic and aerospace industries [7–10]. The lower cost of Si powders (compared to Si3N4) and the lower temperature of consolidation (nitridation) are added attractions of the reaction bonding process in addition to the near-net-shaping possibility [11,12]. Several investigators have studied the physical, chemical, mechanical and microstructural behaviour of the NBSC products [4,6,8,9,13–17]. Contrary to the NBSC products, the reaction-bonded silicon nitride (RBSN) reinforced with SiC particles or platelets, studied by few investigators [4,18–21] consists ~5–30 vol.% of SiC phase dispersed in the RBSN matrix. Such RBSN-SiC composites are much stronger and tougher than monolithic RBSN and they retain their room-temperature properties up to 1400 °C, wherein the properties are mainly controlled by the microstructure and micro-chemistry of the interface between the matrix and the reinforcing agent. This study was focused on investigating the reaction nitridation process of colloidal processed and slip cast SiC + Si mixture compacts in the weight ratios of 3:1, 1:1 and 1:3, to develop NBSC or SiC-RBSN composites having various amounts of Si3N4 as bonding phase.

2. Experimental

Commercial SiC (type G1200, M/s Grindwell Norton, Bangalore, India) and Si (type RQ, M/s Keminox Industries, Norway) powders used in this study were characterised for phase purity by X-ray diffraction (XRD). X-ray Diffractometer, PM 9002, M/s Phillips, Holland. The dispersibility of SiC, Si and SiC + Si mixtures in deionised water as a function of pH was investigated by studying their particle/floc size distribution, electrokinetic behaviour, sedimentation and viscosity rheological behaviours and the details were presented elsewhere [22–24]. For slurry characterisation, the powders were dispersed in deionised water with continuous magnetic stirring (5–20 min) and the pH of the slurry was adjusted in the range 2–12 using HNO3 and NH4OH solution for alkaline ranges, respectively. The particle/floc size distributions of the powders (5 wt.% slurry) were measured as a function of pH, by
3. Results and discussion

3.1. Slurry characterisation of SiC + Si mixtures

The results of the studies on particle size distribution (PSD), sedimentation, viscosity and rheological behaviour of SiC and Si slurry in aqueous media as a function of pH are in good correlation with each other [22–24]. These results reveal that pH 10 is the condition of optimum dispersion for SiC and pH 4 and 8 for Si as manifested by a shift in the PSD curve to the finer range, lower sedimentation heights, minimum in viscosity and near-Newtonian flow behaviour. On the contrary, at other pH values the slips of SiC and Si show shifts in the PSD curves towards coarser range, higher sedimentation heights, higher viscosity and non-Newtonian flow behaviour. These properties are directly related to the zeta potential values presented in Fig. 1 as a function of pH. The zeta potential arising out of net effective surface charges on the particles directly reflects the dispersability levels of the particles in a medium. The high zeta potential values around pH 10 for SiC and around pH 4 and 8 for Si indicate the development of high surface charges around these respective pH values and hence the optimum dispersion due to inter-particle repulsion. The isoelectric points of 3.3 for SiC and 2.4 for Si represent the region of high agglomeration leading to higher sedimentation heights, higher viscosity and non-Newtonian flow behaviour for the respective slips [22–24]. The PSDs measured at the pH of optimum dispersion reveals that the SiC powder has slightly wider size distribution with standard deviations were calculated. The microstructures of the fractured surfaces were observed in a scanning electron microscope (Leo 440, M/s Leo Electron Microscopy, UK).

![Fig. 1. Zeta potential versus pH for SiC G1200 and Si RQ.](image)
the individual components, with distinct minima around the pH values of 4–5 and 8–10 as against the pH values of 10 for SiC [22] and 4 and 8 for Si [23]. Thus, the pH values in the range 8.0–9.5 could be considered as the optimum dispersing condition for slip casting of SiC + Si mixtures.

3.2. Slip casting and nitridation of SiC + Si mixtures

The slip casting conditions of SiC + Si mixtures, their compositional density as well as the bulk density of the slip cast green compacts are presented in Table 1. On the average, the slip casting duration was about 10–15 min for solid casting of rectangular bar (50 × (8–10) × (6–9) mm³) and disc (25 × 10 mm²) specimens. The lowest green density of the 50SCSN compacts may be attributed either to the least packing efficiency of SiC and Si powders in 1:1 weight proportion or due to slight shift in the dispersion condition of the slip from the optimum, leading to partial agglomeration and higher viscosity of the slip. However, a general trend of the increase in percentage theoretical density from 58 to 67% with increase in Si content from 25 to 100% could be attributed to the better packing efficiency of Si particles as compared to that of SiC, which is also confirmed earlier by slip casting of pure SiC, Si as well as their mixtures without Fe₂O₃ additions [22–24].

Generally, the packing of the particles and the green density of the slip cast compacts are the function of the PSD and the dispersibility of the powders. In this study, though a direct correlation of green density for slip cast SiC and Si compacts with the PSD of these powders is not evident, the variation in green density could be related to the dispersability of these powders in aqueous media which is controlled by the surface characteristics of the powders. In aqueous media, the Si particles are expected to produce more surface silanol groups due to oxidation and hydroxylation than SiC particles, wherein the surface hydroxylation depends upon the extent of surface silica present on the SiC particles. The

Table 1: Characteristics of slip cast SiC + Si compacts

<table>
<thead>
<tr>
<th>Sample identity</th>
<th>Initial composition</th>
<th>Compositional density a (g cm⁻³)</th>
<th>Bulk density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiC (wt.%)</td>
<td>Si (wt.%)</td>
<td></td>
</tr>
<tr>
<td>75SCSN</td>
<td>75</td>
<td>25</td>
<td>2.98</td>
</tr>
<tr>
<td>50SCSN</td>
<td>50</td>
<td>50</td>
<td>2.75</td>
</tr>
<tr>
<td>25SCSN</td>
<td>25</td>
<td>75</td>
<td>2.53</td>
</tr>
<tr>
<td>0SCSN (RBSN)</td>
<td>0</td>
<td>100</td>
<td>2.33</td>
</tr>
</tbody>
</table>

* By rule of mixtures (theoretical density of SiC = 3.2 g cm⁻³ and Si = 2.33 g cm⁻³).
The characteristics of the NBSC or SiC-RBSN composite bodies resulting from the nitridation of slip cast SiC + Si compacts are presented in Table 2. The XRD spectra of the products are presented in Fig. 5(a)–(c) and the microstructures of the fractured surfaces are depicted in Fig. 6(a)–(c).

The percentage of Si₃N₄ bond formed, free Si and the SiC content of the products are in good agreement with each other. Higher percentage of nitridation was observed for SiC-RBSN composites as compared to pure RBSN bodies due to lower mass of Si to be nitrided than in monolithic RBSN. The nitrided density and the apparent porosity of surface oxidation and hydroxylation of Si particles would be enhanced further by wet milling whereas it is less effective in the case of covalent SiC particles, leading to increased dispersion, reduced viscosity and hence increased packing and green density of the slip cast Si compacts.

Table 2: Characteristics of SiC-RBSN composites

<table>
<thead>
<tr>
<th>Sample identity</th>
<th>Nitridation with respect to Si (%)</th>
<th>Si₃N₄ formed (wt.%)</th>
<th>Free Si (wt.%)</th>
<th>SiC in the product (wt.%)</th>
<th>Nitrided density (g cm⁻³)</th>
<th>Apparent porosity (%)</th>
<th>MOR (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75SCSN</td>
<td>83.7</td>
<td>30.6</td>
<td>3.6</td>
<td>61.8</td>
<td>2.078</td>
<td>32.5</td>
<td>69 ± 10</td>
</tr>
<tr>
<td>50SCSN</td>
<td>89.2</td>
<td>57.3</td>
<td>4.2</td>
<td>38.6</td>
<td>2.064</td>
<td>35.1</td>
<td>119 ± 25</td>
</tr>
<tr>
<td>25SCSN</td>
<td>87.0</td>
<td>76.2</td>
<td>6.4</td>
<td>17.4</td>
<td>2.333</td>
<td>21.4</td>
<td>168 ± 56</td>
</tr>
<tr>
<td>0SCSN (RBSN)</td>
<td>73.7</td>
<td>81.9</td>
<td>18.1</td>
<td>–</td>
<td>2.359</td>
<td>17.9</td>
<td>168 ± 33</td>
</tr>
</tbody>
</table>

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the products are related to the green density and percentage nitridation. The 50SCSN sample in spite of near-complete nitridation (~90%) resulted in lower nitrided density and higher apparent porosity due to its lower green density.

The mechanical properties of the above SiC-RBSN composite bodies developed by slip casting are found promising. The 3-point MOR values in the range 60–80 MPa for 75SSCN are comparable to or higher than those reported in the literature [4,6,8–10,13,14]. The strength values in the range 110–230 MPa, obtained for 25SCSN samples which contain about 17.4 vol.% of SiC as dispersed phase in the RBBS matrix are considerably higher than 85–130 MPa reported by Mukerji and Rakshit [18] for RBSN-SiC composites produced by isostatic pressing and having 5–20 vol.% SiC phase and density in the range 2.16–2.24 g cm\(^{-3}\). Further, our results are better than those reported (115 and 140 MPa) by Kosmac and Janssen [19] for composites having 20 vol.% SiC platelets processed by injection moulding and injection moulding + cold isostatic pressing, respectively. These better strength values irrespective of the considerably higher porosity (21–33%) and lower density (2.06–2.35 g cm\(^{-3}\)) could be attributed to the uniform and homogeneous microstructures of the green body wherein the formation of agglomerations has been prevented through slurry optimisation techniques. However, the large variation in strength values (110–230 MPa) of the 25SCSN samples could be attributed to the effect of critical furnace atmosphere, like high carbon activity, which leads to the formation of β-SiC on the surface layers of the samples as observed in earlier studies on the nitridation of pure Si compacts [25]. The MOR values of 119 ± 25 MPa observed for 50SCSN samples are higher than 85 MPa, reported for products (50NBSC) with similar composition produced without Fe₂O₃ addition [24]. This can be attributed to the higher percentage (89%) of nitridation, higher amount of Si₃N₄ bond (57%) and lesser amount of free Si (4%) in the 50SCSN sample as compared to 70% nitridation, 47% Si₃N₄ bond and 12% of free Si in 50NBSC sample [24]. Further, the more uniform nitridation leading to more homogeneous microstructure in SiC-RBSN samples (Fig. 6(a)–(c)), containing Fe₂O₃ might also contribute to the higher strengths. The SEM pictures reveal typical microstructures with fibre- and needle-shaped α-Si₃N₄ crystals and flaky particles of α- and β-Si₃N₄ as well as small amount of Si₃N₄O along with SiC particulate reinforcing phase.

4. Conclusions

The slips of SiC, Si and their mixtures were optimised for best dispersion in aqueous media by studying their sedimentation behaviour, viscosity, flow behaviour and zeta potential measurements as a function of pH. Using optimum dispersion conditions of pH in the range 8.0–9.5, the slips of SiC + Si in various proportions could be slip cast in plaster moulds to yield high green density (56–67%) products. The nitridation study has proved that the extent of nitridation is a function of temperature, time and the mass of Si to be nitrided. The SiC-RBSN composite bodies produced by nitridation of slip cast SiC + Si compacts having 30–76% of Si₃N₄ bonding phase showed a considerably higher 3-point MOR value of 60–220 MPa in spite of their lower bulk density (2.06–2.35 g cm\(^{-3}\)). This could make them useful for various refractory as well as high-temperature structural applications. The microstructural studies reveal a homogeneous distribution of different phases (α- and β-Si₃N₄ with dispersed α-SiC) in the composite bodies, which have contributed considerably to the higher mechanical strength of these products.

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References