

## Effect of microstructure on the high temperature strength of nitride bonded silicon carbide composite

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**Abstract.** Four compositions of nitride bonded SiC were fabricated with varying particle size of SiC of  $\sim 9.67$ ,  $\sim 13.79$ ,  $\sim 60$   $\mu$  and their mixture with Si of  $\sim 4.83$   $\mu$  particle size. The green density and hence the open porosity of the shapes were varied between 1.83 to 2.09 g/cc and 33.3 to 26.8 vol.%, respectively. The effect of these parameters on room temperature and high temperature strength of the composite up to 1300°C in ambient condition were studied. The high temperature flexural strength of the composite of all compositions increased at 1200 and 1300°C because of oxidation of Si<sub>3</sub>N<sub>4</sub> phase and blunting crack front. Formation of Si<sub>3</sub>N<sub>4</sub> whisker was also observed. The strength of the mixture composition was maximum.

**Keywords.** Nitride bonded silicon carbide composite; nitridation; microstructure.

### 1. Introduction

Nitride bonded silicon carbide (NBSC) composite is a promising high temperature refractory material for its high strength at high temperature, good fracture toughness, excellent thermal shock and oxidation resistances (Reddy and Mukerji 1991). As SiC has a tendency for oxidation to occur in service at high temperature, a silicon nitride bond offers protection to SiC grains by preferentially oxidizing to silica which also reduces the porosity (Davidge *et al* 1972; Pick 1979). Among the various fabrication techniques, reaction bonding process has been found attractive because of its near net shaping capability (Chiang *et al* 1989) and reduced cost of production because of low processing temperature (Rakshit and Das 1996). Compositing of SiC (whisker or particulate) with silicon nitride in a dense product was found to improve both fracture toughness and flexural strength (up to 1400°C) compared to dense monolithic Si<sub>3</sub>N<sub>4</sub> (Buljan *et al* 1987; Pizzotti *et al* 1989). The extensive use of nitride bonded silicon carbide refractory in the area of (i) iron and steel industry, (ii) non ferrous industry, (iii) kiln furniture, (iv) coal fired power plants etc are well known.

The present work includes study of the effect of microstructure and possible existence of silica (cristobalite) in the matrix (after hot MOR) on the strength improvement at high temperature.

### 2. Experimental

Commercial grade Si powder (97.5% purity, obtained from Indian Metals and Ferroalloys, Bhubaneswar, India) of mean particle size  $\sim 4.83$   $\mu$  and SiC powder (98%

purity from Grindwell Norton, India) of three varieties having average particle sizes of  $\sim 9.67$   $\mu$ ,  $\sim 13.79$   $\mu$  and  $\sim 60$   $\mu$  (considered as fine, medium and coarse varieties, respectively) were selected in this study. Each variety of powder and one batch containing appropriate mixture (fine : medium : coarse = 30 : 35 : 35 by weight) of the three were mixed with fixed amount of Si powder (100 : 30 w/w) separately and wet blended in a "V" mixer for 6 h. Test bars were made by uniaxial pressing at 23.5 MPa to a small rectangular shape of 45 × 6 × 5 mm size. The test bars were reacted with high purity nitrogen gas (O<sub>2</sub> and H<sub>2</sub>O vapour,  $\sim 4$  ppm each, oxides of carbon,  $\sim 1$  ppm) at 1 atm pressure. The details of preparative method followed was similar to those given earlier (Reddy and Mukerji 1991; Rakshit and Das 1996); bulk density and open porosity of the nitrided samples were determined by water immersion process. Mean pore diameter ( $d_{50}$ ) was determined from cumulative pore size distribution by mercury intrusion porosimeter (Quantachrome, Model No. Autoscan 60, USA). Existence of phases (a-, b-Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub>, etc) were determined by XRD technique. Both room temperature and high temperature MOR were determined by 4-point loading in a bending strength tester (Netzsch, Model No. 422 S, Type B-3, Germany) using fixture with larger and smaller span of 40 mm and 20 mm and cross head speed of 0.03 mm/sec. At least 5 samples were tested in each case. Microstructure was observed on fractured surface of both RT and HT piece in an electron microscope (Leo Cambridge, SE 440, UK).

### 3. Results and discussion

Table 1 shows the results of four different batches of nitride bonded SiC (NBSC) in respect of density,

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**Table 1.** Properties of nitride bonded SiC composite materials.

Sample	Density (g/cm <sup>3</sup> )		Open porosity (vol.%)	Mean pore dia. ( $d_{50}$ $\mu$ )	MOR (MPa)		
	Green	Nitrided			RT	1200°C	1300°C
C <sub>1</sub>	1.83	2.10	33.3	0.36	31.9 ± 4.9	59.4 ± 5.1	68.9 ± 2.4
C <sub>2</sub>	1.90	2.20	30.4	0.27	41.4 ± 5.3	71.9 ± 14.5	79.3 ± 13.6
C <sub>3</sub>	2.09	2.33	26.8	0.52	26.4 ± 7.2	56.9 ± 6.0	64.0 ± 12.4
C <sub>4</sub>	2.04	2.25	28.5	0.21	46.5 ± 6.4	70.2 ± 9.4	90.5 ± 1.9
S <sub>1</sub>	1.20	2.21	23.3	—	88.7 ± 8.6	118.0 ± 4.4	116.6 ± 11.0*
S <sub>2</sub>	1.37	2.39	18.0	—	122.1 ± 12.5	153.7 ± 19.1	131.8 ± 16.9*
S <sub>3</sub>	1.43	2.44	16.2	—	135.0 ± 4.4	166.4 ± 22.8	147.1 ± 13.2*

C<sub>1</sub> → Si + fine SiC, C<sub>2</sub> → Si + medium SiC, C<sub>3</sub> → Si + coarse SiC, C<sub>4</sub> → Si + mix SiC.

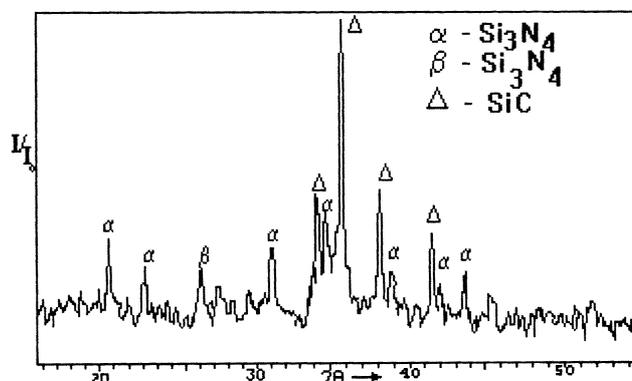
S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub> → RBSN samples of same dimension as NBSC samples. Green shapes were made by uniaxial pressing at 23–31 MPa. \*Strength measured at 1400°C.

porosity, average pore diameter ( $d_{50}$ ) and flexural strength both at room temperature (RT) and high temperatures (HT).

Since the bonding phase, Si<sub>3</sub>N<sub>4</sub>, is almost fixed (32 wt%) in each batch, the bulk density of the composites increases and open porosity (vol.%) decreases as the green density increases. In composite C<sub>3</sub>, containing coarse variety of SiC, mean pore diameter ( $d_{50}$ ) is the largest among the other batch compositions, which is least ( $d_{50} = 0.21 \mu\text{m}$ ) in C<sub>4</sub> containing a mixture of fine, medium and coarse varieties of SiC particles although the open porosity is least (26.8%) in the former case. Therefore, batch composition containing multimodal particle packing would result in material with maximum number of fine pores as explained in the earlier work (Rakshit and Das 1996). Figure 1 shows the XRD patterns of composite (C<sub>4</sub>) material showing the existence of exclusively **a** Si<sub>3</sub>N<sub>4</sub> with a little amount of **b**-Si<sub>3</sub>N<sub>4</sub> as nitridation product instead of major SiC phase. The absence of Si indicates that nitridation is completed. Figure 2 is the XRD pattern of the same material (C<sub>4</sub>) after MOR tested at 1300°C. The results are almost identical, only difference is in the existence of silica (cristobalite) and silicon oxynitride in the latter case. This is due to oxidation of nitride bonded SiC composite preferentially at Si<sub>3</sub>N<sub>4</sub> grains in the matrix.

A low value of MOR at room temperature of C<sub>3</sub> containing coarse variety of SiC particle and high room temperature MOR value of C<sub>4</sub> containing mixture of SiC particles are attributed to porosity and pore size distribution of the materials in general agreement with our results reported earlier (Rakshit and Das 1996).

Flexural strength of all composites in ambient condition shows an increasing trend with increase of temperature up to 1200°C (figure 3), similar to uniaxially pressed and nitrided reaction bonded silicon nitride (Mukerji and Rakshit 1988) and a sharp increase above 1200°C. Strength improvement is maximum (at 1300°C) in case of C<sub>4</sub> containing mixture of SiC particles. Unlike reaction bonded



**Figure 1.** XRD pattern of nitride bonded silicon carbide (NBSC) material (C<sub>4</sub>), containing Si + SiC mixture.

silicon nitride, in which a strength degradation was observed above 1200°C (table 1) [because of viscous flow of the grain boundary vitreous silica layer formed due to oxidation of Si<sub>3</sub>N<sub>4</sub> phase (Mukerji and Rakshit 1988)], no such degradation was observed in NBSC samples. Previous study on nitride bonded SiC (Mukerji 1984) where SiC was the predominant phase (80%) revealed the strength to increase continuously up to 1400°C. A number of inferences were made by different workers for improved strength of NBSC materials at elevated temperatures. Increase of strength with temperature (up to 1200°C) was accepted to be a result of oxidation and crack healing due to oxidation at the crack tip (Mukerji and Rakshit 1988). Further increase of MOR above 1200°C is attributed to the presence of Si<sub>2</sub>N<sub>2</sub>O on the surface of Si<sub>3</sub>N<sub>4</sub> grains (Mukerji and Rakshit 1988). Others (Mukerji and Reddy 1980) explained the case with the help of microstructure. According to them, whisker and woolly felt of **a**-Si<sub>3</sub>N<sub>4</sub> was converted into a consolidated hard intergranular phase of **a**-Si<sub>3</sub>N<sub>4</sub> when the product was under load at high temperature thereby resulting in an increase in strength.

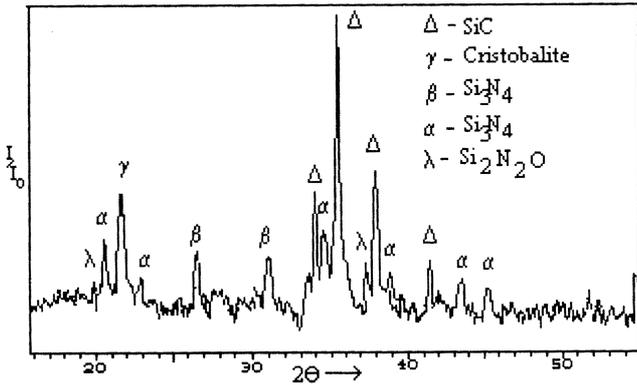


Figure 2. XRD pattern of nitride bonded silicon carbide (NBSC) material (C<sub>4</sub>), containing Si + SiC mixture, after hot MOR at 1300°C.

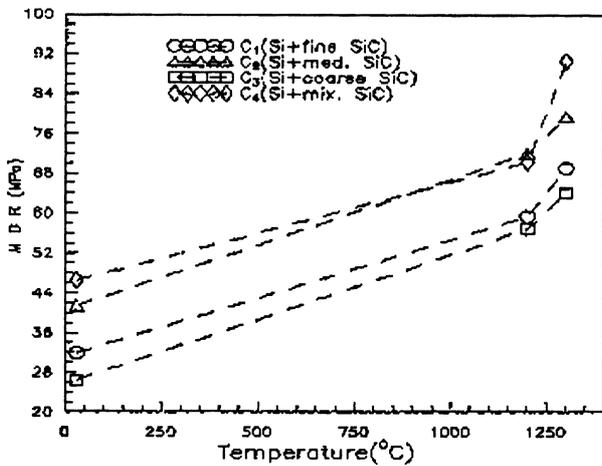


Figure 3. Dependence of MOR of NBSC materials (32 wt% nitride bond) with temperature.

Scanning electron micrograph (SEM) of the fractured surface of the composite (C<sub>4</sub>) containing mixture of SiC particles both at room temperature and at high temperature (1300°C) are shown in figures 4–6, respectively. In figure 4, Si<sub>3</sub>N<sub>4</sub> bond appears as light grey boundaries around large SiC (deep grey) grain. No pullout of silicon nitride was observed, which indicates strong bonding between SiC and newly formed Si<sub>3</sub>N<sub>4</sub> grains. Figure 5 shows the formation of needle like whiskers of a Si<sub>3</sub>N<sub>4</sub> into the large pores by the side of large SiC grains. Unreacted Si could not be seen in the micrograph. At high temperature (1300°C), no such wool or whisker is observed (figure 6). They have been converted into consolidated grains of a Si<sub>3</sub>N<sub>4</sub> with a glassy (cristobalite) phase in between large SiC grains. The pores of oxidized material is rounded off by formation of silica reducing

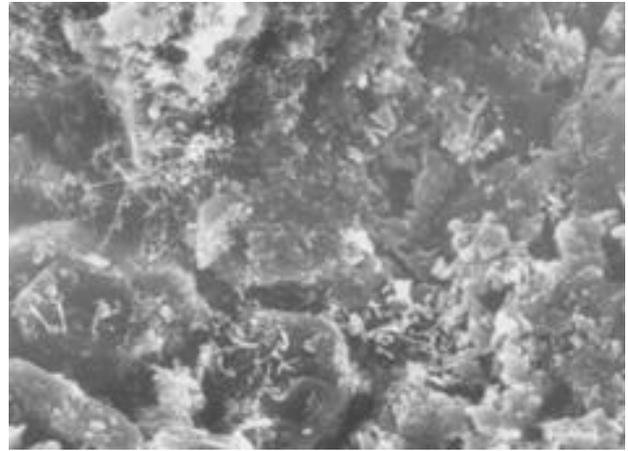


Figure 5. SEM photomicrograph of fractured surface of NBSC material (C<sub>4</sub>) showing needle like whiskers in large pores (bar = 2 μm).

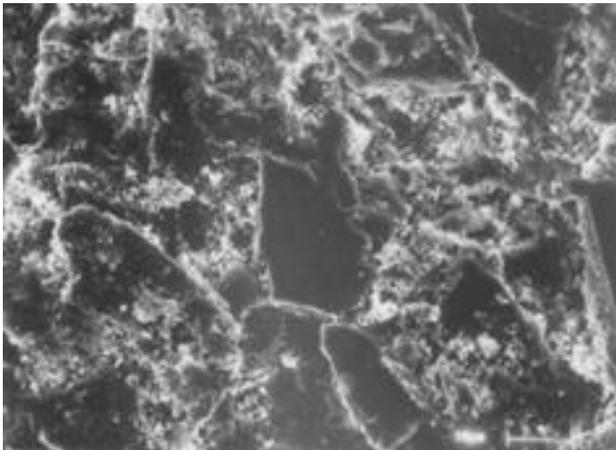


Figure 4. SEM photomicrograph of fractured surface of nitride bonded silicon carbide (NBSC) material (C<sub>4</sub>) showing light grey boundaries of Si<sub>3</sub>N<sub>4</sub> around large SiC grains (bar = 10 μm).



Figure 6. SEM photomicrograph of fractured surface of NBSC material (C<sub>4</sub>) after MOR testing at 1300°C showing glassy phase of cristobalite in between large SiC grains (bar = 2 μm).

the pore size of the original sample (figure 6), as a result of which the material showed high flexural strength at hot condition (Davidge *et al* 1972). The existence of  $\text{Si}_2\text{N}_2\text{O}$  as detected by XRD, could not be identified in the microstructure (figure 6). The formation of silicon oxynitride during oxidation reduces microstructural degradation of composite materials and could have an influence on improved mechanical property at high temperature similar to dense composite ( $\text{Si}_3\text{N}_4$ -SiC) materials (Klemm *et al* 1997).

#### 4. Conclusions

(I) Batch composition containing mixed SiC particle packing would result in a material with maximum number of fine pores.

(II) Low value of room temperature MOR is due to presence of large pores and not the total vol.% (open) porosity of the composite.

(III) Flexural strength of all composites in ambient condition showed an increasing trend with increase of temperature up to 1300°C. Oxidation and crack healing at the crack tip and also the existence of  $\text{Si}_2\text{N}_2\text{O}$  phase on the surface of  $\text{Si}_3\text{N}_4$  grains could be the cause of strength improvement at high temperature.

(IV) Needle like whisker of  $\alpha$   $\text{Si}_3\text{N}_4$  is converted into a consolidated grain of  $\alpha$   $\text{Si}_3\text{N}_4$  at high temperature

(1300°C) along with the presence of a glassy (cristobalite) phase in between large SiC grains.

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