Properties of reaction bonded silicon nitride obtained from slip cast preforms

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Abstract. Fabrication of silicon preforms of high green density ($> 1.2 \text{ g/cm}^3$) by slip casting of silicon (in aqueous medium) has been studied. The nitridation product consists of 59–85% α - Si_3N_4 , 7–22% β - Si_3N_4 and 7–23% $\text{Si}_2\text{N}_2\text{O}$ phase. The amounts of un-nitrided silicon were negligible. The microstructure is either granular or consists of needle-like grains (α - Si_3N_4) and whiskers deposited in the large pores. MOR values of the specimens are almost constant up to 1000°C or 1400°C or show slight increase up to 1000°C or 1200°C . In some cases a little dip around 1200°C , then a sharp increase in MOR up to 1400°C was observed. K_{ic} values are almost constant up to 1000°C , and thereafter increase sharply.

Pore size distribution, existence of $\text{Si}_2\text{N}_2\text{O}$ phase and oxidation of RBSN at high temperatures have been considered for the explanation of the observed behaviour.

Keywords. Reaction-bonded silicon nitride; slip cast silicon preforms.

1. Introduction

Slip casting or injection moulding via aqueous slip of silicon permits fabrication of complicated shapes (Parr and May 1967; Mclean 1982). Slip casting of silicon has been studied previously. The main problem in slip casting is to achieve high green density ($> 1.2 \text{ g/cm}^3$) in the cast body. The present study is related to (a) the study of slip casting of Si as regards silicon loading, pH, ageing of the slip and casting time, and the effects of these on green density and (b) the effect of the possible formation of SiO_2 layers on the reaction-bonded silicon nitride (RBSN) as regards phase composition, and its mechanical properties.

2. Experimental

Silicon lumps (low-calcium content) obtained from Indian-metals and Ferro-alloys, Bhubaneswar, were successfully ground to fine powder in a pulveriser and vibratory ball mill and particle of size less than $10 \mu\text{m}$ were separated out by fractional sedimentation. An aqueous suspension of silicon at a pH of about 9 was allowed to settle for about 35 min (as obtained from a predetermined sedimentation curve) in a column of height 20 cm, when all particles larger than $10 \mu\text{m}$ settled. The particle size distribution was as follows, 14% between 10 and $5 \mu\text{m}$, 48% between 5 and $1 \mu\text{m}$ and the rest (38%) less than $1 \mu\text{m}$. The specific surface area of this powder was $5.07 \text{ m}^2/\text{g}$ as determined by the BET nitrogen adsorption method (Micromeritics, GA, USA) with an equivalent spherical diameter of $0.51 \mu\text{m}$. Major impurities in the powder by weight % were, Fe: 0.22; Al: 0.08; Ca: 0.004; Mg: 0.02 (Na + K): 0.09.

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Silicon billets of rectangular shape ($47 \times 21 \times 10 \text{ mm}^3$) were made by solid casting of silicon slips. A preliminary experiment on the sedimentation of silicon particles from its suspension was carried out using sedimentation balance in the pH range of 3–11. Silicon suspension was made using 50 g of silicon in distilled water with Na-alginate (1% by weight of silicon) solution as a defloculating agent. The amount of silicon deposited was directly read out from a Mettler balance (Mettler ME 100). Acidic and alkaline pH levels of the suspension were maintained using HCl and liquid ammonia solutions respectively.

For solid casting, a silicon slip of pH around 9 was made, having a silicon to water weight ratio of 5:6 to 5:7, and an ageing time of 5 to 7 days. Air bubbles were removed by keeping the slip in a vacuum dessicator. Casting was carried out in a plaster mould.

A laboratory-made sintered alumina-tube furnace capable of working in a controlled atmosphere was used for nitridation. Iolar-2 grade nitrogen gas supplied by Indian Oxygen and containing 4 ppm each of O_2 and H_2O and 1 ppm of the oxide of carbon was used for nitridation. A typical nitridation schedule was 24 h at 1200°C , 24–28 h at 1300°C and 20–24 h at 1350°C , followed by 10–16 h at 1380°C .

Bulk density as well as %pore (open) volume of nitrided specimens were determined. Poresize distributions of RBSN specimens were determined using a 'Mercury Intrusion porosimeter' (Micromeritics, USA, Model No. 1300). Microstructures of fired samples were examined by both optical and scanning electron microscopy. For optical microscopy, polished sections were prepared by mounting the sample in epoxy and grinding successively with – 220 mesh and – 400 mesh SiC powder followed by – 600 mesh emery. Polishing was done with 20 micron and then 5 micron Al_2O_3 powder on felt in a vibratory polisher. The fracture surface was examined by SEM after gold coating. Flexural strength (room temperature and high temperature) was measured using 4-point flexural specimens of $45 \times 4.5 \times 3.5 \text{ mm}^3$ size. Silicon nitride fixtures were used for sample support (Mukerji *et al* 1985). Fracture toughness was measured using a single edge notched beam specimen in 4-point geometry, having a notch-width of 0.2 to 0.3 mm. The normalised notch width (a/w) was in the range 0.3 to 0.5. Fracture toughness (K_{Ic}) was determined using the equation recommended by ASTM (Brown and Srawley 1966).

3. Results and discussion

3.1 Green and fired densities

The green-density (D_g), fired density (D_f), nitriding temperature, % weight gain and porosity, as determined by the water absorption method, are given in table 1. The D_g of cast products was found to depend on the ageing time, casting time and pH of the silicon suspension. Results are shown in tables 2 and 3. The results of the sedimentation experiments at different pH values are shown in figure 1. From the curve of figure 1, a graph is plotted for sedimentation rate vs pH (figure 2). It is evident that better suspension can be expected at pH 4 and pH 9. The suspension is least stable at a pH around 2 and 12 (figure 2). Accordingly, casting time is less (~ 50 min) and the rate of casting is fast for the silicon suspension of high acidic (pH < 3) or high alkaline (pH > 10) medium. A longer casting time (> 3 h) was observed for a slip of pH range 7.5 to 10.5. The longer casting-time of a particular slip favours higher green

Table 1. Properties of green compacts and nitrided products after firing at 1380°C under 101 kPa N₂ gas atmosphere.
Particle size < 10 µm

Sample	D_g (g/cm ³)	D_f (g/cm ³)	Weight gain (%)	P^* (%)
S ₁	1.28	2.08	51.2	28.2
S ₂	1.36	2.16	51.3	26.1
S ₃	1.35	2.25	52.6	22.0
S ₄ [†]	1.39	2.34	56.1	17.7
S ₅ [†]	1.45	2.48	54.4	14.8

[†] Argon treatment before nitridation

* Free (open) volume.

Table 2. Dependence of green density of the 'slip-cast' specimens on 'casting time' and 'ageing time'.
Starting silicon powder < 10 µm; pH of the slip is approximately 9.

Ageing time (days)	Casting time (min)	Water/silicon ratio (by wt)	Green density (g/cm ³)
1	80	1.3	1.22
1	300	1.4	1.30
3	130	1.3	1.28
3	140	1.3	1.32
4	110	1.4	1.25
4	140	1.4	1.26
5	145	1.4	1.31
5	180	1.4	1.40
6	75	1.4	1.20
6	300	1.4	1.44
7	135	1.3	1.40
7	300	1.4	1.45

Table 3. Dependence of 'casting time' and 'green density' on the pH of the silicon slip.
Silicon particle size < 10 micron

pH of the slip	Casting time (min)	Water/silicon ratio (by wt.)	Green density (g/cm ³)
1.9	17	1.4	1.14
2.9	50	1.4	1.19
4.2	150	1.4	1.22
5	195	1.4	1.20
7.5	255	1.4	1.28
8	300	1.5	1.30
9	135	1.3	1.40
9	300	1.4	1.45
9.4	220	1.5	1.29
10	250	1.5	1.23
10.4	180	1.5	1.19
11.2	75	1.4	1.16

Figure 1. Amount of deposition of silicon particle per unit area (g/cm^2) from silicon suspension (Si particle size $< 10 \mu\text{m}$)

Figure 2. Dependence of silicon particle sedimentation on the pH of the suspension.

density as the particles also get a chance to distribute themselves in the voids. An optimum green density was observed for a slip having a silicon–water weight ratio of 5:6 to 5:7, an ageing time of 5 to 7 days and a pH of about 9.

3.2 Weight gain on nitridation

A nitridation weight gain of 51–56% was achieved, the theoretical weight gain being 66.6%. The optical microscopic as well as XRD of the nitrided specimens showed

Table 4. Type and amount of phases present in slip cast RBSN.

Sample	Approximate amount of phases present (wt.%)			
	α -Si ₃ N ₄	β -Si ₃ N ₄	Si ₂ N ₂ O	Free-Si
S ₁	78.6	7.3	13.1	1
S ₂	63	14.2	22.8	—
S ₃	59	21.3	19.7	—
S ₄	84.1	9.1	6.8	—
S ₅	80.6	11	8.4	—

negligible amounts of unnitrided silicon. The low weight gain may be accounted for by the formation of Si₂N₂O during nitridation, which needs 50% uptake of nitrogen as compared to 66.6% for nitride formation. The formation of oxynitride is expected to be due to the reaction between nitrogen and silica layers on the surface of silicon particles. During the ageing of the slip for long periods fine silicon particles produce SiO₂ in the following way:

It was shown (Atkinson and Moulson 1976) that any native oxide layer on silicon particles can be removed by heat treatment under vacuum or under argon atmosphere when the following reaction takes place.

Thus a slipcast RBSN of higher weight gain (table 1) was achieved when argon treatment before nitridation was done, consequently the oxynitride phase was reduced from 23% to 7%.

3.3 Crystallographic phases

Quantitative phase estimation was carried out using the calibration curve of Jack and Thomson in which the XRD peak height ratio of $\beta(210)/\{\beta(210) + \alpha(201)\}$ was directly plotted against weight % β . The amount of free silicon and Si₂N₂O were determined from a similar calibration curve using the peak height ratio of Si (111)/{Si(111) + $\alpha(201)$ } and Si₂N₂O(201)/{Si₂N₂O(201) + $\alpha(210)$ } respectively. The type and amount of phases present are shown in table 4. The major crystalline phase was α -Si₃N₄. It was stated earlier that unconverted silicon could not be found either by optical microscopic observation or by XRD, but appreciable amounts (7–23%) of silicon oxynitride were detected and its existence has already been discussed in § 3.2.

3.4 Porosity and pore-size distribution

The total volume % porosity (open) as measured by the water absorption method is shown in table 1. The result of the pre-size distribution as measured by a Mercury Intrusion porosimeter is shown in figure 3. It is evident that about 96.2% of the pores lie between 0.2 and 0.008 μm , 3.8% pores are greater than 0.2 μm . Pore-size distribution depends on green (D_g) and fired density (D_f) of the nitrided products. For a

Figure 3. Pore-size distribution of RBSN samples. (a) S_3 , (b) S_4 and (c) S_5 .

Figure 4. Optical micrograph of slip-cast RBSN showing negligible amount of free silicon ($\times 280$).

sample (S_3) of $D_g - 1.35 \text{ g/cm}^3$, and $D_f - 2.25 \text{ g/cm}^3$, although 90% pores lie between 0.18 and 0.06 microns, most of the pores ($\sim 70\%$) are larger in size (> 0.1 micron) (figure 3a). Large pores (> 0.1 micron) are also found in another sample (S_4) of about 50% with a higher density (figure 3b) ($D_g - 1.39 \text{ g/cm}^3$ and $D_f - 2.34 \text{ g/cm}^3$). In a sample

(S_5) of much higher D_g (1.49 g/cm³) and D_f (2.48 g/cm³), most of the pores ($\sim 80\%$) are fine and lie between 0.06 and 0.007 microns, while large pores (> 0.1 micron) are only 3% (figure 3c). Therefore fine pores are in higher percentage for products of higher green and nitrided density.

3.5 Microstructure

An optical micrograph of an RBSN specimen is shown in figure 4 showing negligible amounts of free silicon in the silicon nitride matrix, the scanning was done from the edge to the core. The material is composed of a continuous silicon-nitride phase with fine isolated pores. The scanning electron microscope (SEM) photographs of nitrided specimens are shown in figures 5 a–e. The microstructure of S_3 in low magnification shows fine and uniformly distributed pores (figure 5a). At high magnification the microstructure is essentially granular in nature with complete absence of wool and whiskers (figure 5b). The material is composed of about 20% Si_2N_2O , the α -phase as detected by XRD is also low (59%). The β - Si_3N_4 phase was 21%. A few large grains of β - Si_3N_4 with a few large pores (> 1 micron) are also found in the microstructure (figure 5b). The sample (S_4) has got a preponderance of elongated α -crystal and whisker deposit in the pores (figures 5c and d), large pores favour the deposition of α - Si_3N_4 whiskers and wool as these are formed essentially by vapour-transport; hence the α -phase was present to a larger extent ($\sim 84\%$), compared to β ($\sim 9\%$) and Si_2N_2O ($\sim 7\%$). The microstructure of the dense product (S_5), with 80% pores of less than 0.06 micron, is essentially grainy with some whiskers deposited in the large pores (figures 5e and f). The lower total porosity and grainy structure are responsible for the high room temperature flexural strength.

3.6 Mechanical properties

3.6a Transverse rupture strength

The four-point bending strength (σ) of RBSN samples (table 5) is found to increase exponentially with bulk density both at room temperature and high temperature (1200°C). Although increase in green density and nitridation weight gain are means of increasing nitrided density (and hence strength), it is very difficult to achieve a fired density of above 2.5 g/cm³, because fired density depends on green density and a green density of above 1.45 g/cm³ is very difficult to achieve by solid casting of silicon slip.

Figure 6 shows the flexural strength of RBSN samples and its variation with temperature. Some of the specimens (S_3, S_4) show a rise in MOR with temperature, others (S_1, S_5) show temperature independent values up to 1000°C. The former observation is similar to those observed by Ashcroft (1973) and Paar and May (1967) and the latter to those by Thomson and Pratt (1966) and Jennings *et al* (1978). A sharp increase in MOR above 1200°C followed by a dip at that temperature is observed for the samples S_1 and S_3 , but the constancy in values above 1200°C is found to be maintained by the specimen (S_5) with high density (2.48 g/cm³). A decreasing trend in MOR above 1200°C is found for sample S_4 . Above observations are identical with the work of Evans and Davidge (1970), Noakes and Pratt (1972) and Davidge *et al* (1972). Oxidation, pore-size distribution and microstructure of RBSN have been considered

Figure 5. a. SEM photograph of the fracture-surface of S_3 showing finely distributed pores. b. SEM photograph of the fracture surface of S_3 showing granular structure. c. SEM photograph of the fracture surface of S_4 showing needle like crystal and whisker. d. SEM

(d)

(e)

(f)

photograph of the fracture surface of S_4 in high magnification. e. SEM photograph of the fracture surface of S_5 showing granular structure with some amounts of whisker in the large pores. f. SEM photograph of the fracture surface of S_5 in high magnification.

Table 5. Room temperature (RT) and high temperature ($^{\circ}\text{C}$) flexural strength (4-point) data of slip cast RBSN specimens.Starting silicon powder $< 10\ \mu\text{m}$, D_f — fired density.

Sample	D_f (g/cm^3)	Flexural strength (MPa) at				Span (mm)	$(\alpha:\beta)$ ratio
		RT	1000	1200	1400		
S_1	2.08	82.0	79.0	75.0	95.0	40–20	10.76
S_3	2.25	152.0	174.0	172.0	188.0	40–20	2.76
S_4	2.34	119*	136.7*	139.7*	114.7*	20–7	9.24
S_5	2.48	197.3*	—	195.1*	—	20–7	7.32

*85% of the value obtained when span = 20 – 7 mm (15% reduction)

Figure 6. Dependence of flexural strength of slip-cast RBSN on temperature.

for the explanation of the above behaviour. Increase in strength with temperature is attributed to crack-healing by oxidation at the crack-tip. When the pores are very fine (as for the sample S_5) extensive oxidation is not possible because of the sealing of pores. No crack-healing would be possible at high temperature, hence no increase in strength with temperature is observed. The decrease in strength above 1200°C is due to viscous

Figure 7. Dependence of fracture toughness (K_{Ic}) of slip cast RBSN on temperature.

Table 6. Room temperature (RT) and high temperature ($^{\circ}\text{C}$) fracture toughness (K_{Ic}) SENB-4-point bending data of slip cast RBSN. Si powder $< 10\ \mu\text{m}$.

Sample	D_f (g/cm^3)	Fracture toughness (K_{Ic}) in $\text{MPa m}^{1/2}$ at				Span (mm)
		RT	1000	1200	1400	
S_4	2.34	2.15	2.01	2.24	3.14	20-7
S_5	2.48	3.04	3.02	3.26	—	20-7

flow of the grain boundary vitreous silica (Mukerji and Rakshit 1988). The sharp increase in strength above 1200°C for samples S_1 and S_3 is assumed to be due to the existence of high $\text{Si}_2\text{N}_2\text{O}$ ($\sim 20\%$) in the nitrified products. There must be some influence of $\text{Si}_2\text{N}_2\text{O}$ ($\sim 20\%$) on high temperature strength, because this behaviour is not found for samples (S_4, S_5) containing low $\text{Si}_2\text{N}_2\text{O}$ ($< 9\%$) (Mukerji *et al* 1985). The reason for the dip is not clear. A high room temperature MOR ($197.3\ \text{MPa}$) is observed for the specimen of density $2.48\ \text{g}/\text{cm}^3$ having a granular structure and lower porosity (14.8%). This result is superior to those observed by others (Davidge *et al* 1972), but inferior to that of Heinrich (1987).

3.6b Fracture toughness (K_{Ic})

Dependence of fracture toughness on temperature is shown in figure 7, for two slip-cast RBSN specimens (S_4 and S_5). The data is given in table 6. Like MOR, room temperature K_{Ic} values are higher for samples of higher bulk density. K_{Ic} values are found to be almost constant or decrease slightly up to 1000°C for both samples (S_4 and S_5), thereafter an increasing trend is observed. The room temperature and high temperature (1200°C) K_{Ic} of slip-cast RBSN of density $2.48\ \text{g}/\text{cm}^3$ are 3.04 and $3.26\ \text{MPa m}^{1/2}$ respectively and the result is comparable to that obtained by Barnby and Taylor (1972),

and superior to those observed by others (Thompson and Pratt 1966; Heinrich 1987; Burne and Tressler 1980). Increase in K_{ic} may be the effect of oxidation at the crack tip. The role of presence of $\text{Si}_2\text{N}_2\text{O}$ on the increase in K_{ic} cannot be explained at present.

4. Conclusions

(i) Fabrication of green-shape formation by solid casting, the criteria of silicon-slip to improve the density of the cast products and the properties of nitrided products have been described.

(ii) Total volume % porosity (open) and pore-size distribution are dependent on green and fired densities of RBSN specimens. High percentages of fine pores are found in specimen with high bulk density.

(iii) Microstructures are grainy as well as needle-like crystals with whiskers and wool in the large pores. Specimens with grainy structure and fine pores show better room temperature flexural strength.

(iv) MOR values are either constant up to 1000°C or 1400°C or show a rise with rise of temperatures up to 1000°C with a dip at 1200°C, then rising sharply above 1200°C. This behaviour is explained by oxidation induced crack-healing, the existence of the silicon-oxynitride phase and the pore-size distribution of specimens which control the oxidation.

(v) The K_{ic} values are almost constant up to 1000°C, thereafter increase with increasing temperature. The oxidation product of silicon nitride at high temperature, existence of a silicon oxynitride phase and the absence of free silicon are assumed responsible for the above behaviour.

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