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Preparation and Properties of SiC Fibre Reinforced SiAlON Ceramic Composite

Kazuo Ueno & Takahiro Inoue

Osaka National Research Institute, Midorigaoka 1-8-31, Ikeda-shi 563, Japan

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Abstract: Polymer-derived SiC fibre (Nicalon)/SiAlON($Si_3Al_3O_3N_5$)-matrix composite was fabricated by a filament-winding technique, followed by hot-pressing at 1350 °C. SiC fibres with and without carbon coating were used and the effect of carbon coating on the composite properties was investigated. The composite reinforced with non-coated SiC fibre indicated improved bending strength (600 MPa) and apparent fracture toughness (12.8 $MPam^{0.5}$) compared with those of monolithic SiAlON (389 MPa, 3.6 $MPam^{0.5}$), while the composite with carbon-coated fibre showed delamination fracture. The composites with non-coated and carbon-coated fibres both exhibited a remarkably higher fracture energy (9.8 kJ/m^2 and 11.1 kJ/m^2, respectively) than that of monolithic SiAlON (0.1 kJ/m^2). © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Ceramic matrix composite (CMC) reinforced with continuous fibre has high fracture resistance when the incorporated fibres are intact and the fibre/matrix interface is susceptible to bond and slide under limited stress.[1,2] Otherwise the fibre fails with the matrix cracking, resulting in brittle fracture of the composite. Therefore, it is important to maintain the reinforcement fibre strong enough to bear applied load after its process and control the bonding characteristics of the fibre/matrix interface, in order to obtain a CMC with high fracture resistance.

As an inorganic heat-resistive fibre, commercially available polymer-derived SiC fibre is often used for ceramic and glass matrix composites.[3–7] The fibre has a good oxidation resistance but shows serious thermal degradation. For example, when a composite is fabricated by sintering at over 1500 °C, the fibre strength degrades significantly.[8] It is reported that the fibre contained quite a large amount of oxygen (< 13%) after the curing process, and releases it as CO and SiO at high temperatures. Structural transformation from amorphous to crystalline state by the oxygen release causes thermal degradation of the fibre.[9] A fibre with improved heat resistance has been developed by curing with electron beam irradiation.[10] Even such a sophisticated fibre cannot stand the high temperatures, over 1600 °C, which are required by normal sintering of non-oxide ceramics. To avoid such thermal degradation, several noble routes have been evolved for low-temperature processing of ceramic-matrix composite fabrication. They are the chemical vapour infiltration (CVI) process,[11–13] the polymer-precursor infiltration method,[14–17] or their combination.[18] The CVI process scarcely damages the fibre, but it requires quite a long processing time, i.e. several hundred hours, to get a dense matrix. The polymer-precursor method can be applied to fabricate a large-size specimen with complicated shape, when the CVI process is hardly applicable, but it also requires a repeated time-consuming process to get a solid matrix. The problem is that the polymer-derived matrix is often not strong enough, so that the composite suffers from poor performance. Therefore, a process that doesn't damage the fibre and gives a matrix strong enough to bear the stress, and transfers it to fibres, is desirable. The aim of this article is to apply conventional hot-pressing to get a dense matrix at a temperature low enough not to degrade the fibre. SiAlON is selected as a matrix, because it has

excellent resistance against oxidation and corrosion, and good properties at high temperature such as heat and thermal shock resistivity. A unidirectional SiC fibre (Nicalon)/SiAlON matrix composite has been fabricated by hot-pressing at 1350 °C in order to minimize the fibre damage. The effect of fibre coating to enhance the interface debonding was studied by comparing the mechanical performance of the composite with carbon-coated and non-coated SiC fibres.

2 EXPERIMENTAL PROCEDURES

β-SiAlON is formulated as $Si_zAl_{6-z}O_zN_{8-z}$ ($z < 4.2$). With an increasing z-value, mechanical properties such as strength or fracture toughness degrade but oxidation resistance and sinterability improve. As a starting matrix powder, β-SiAlON powder with $z = 3$, that is, $Si_3Al_3O_3N_5$, supplied from Ube Industry Co. Ltd (product number; SN-SZ3) was used. It has a composition of Si 29.6%, Al 25.8%, O 17.6% and N 23.4%, specific surface area of 5.7×10^3 m^2/kg, and an average diameter of 0.35 μm. To facilitate liquid phase sintering at 1350 °C, 5 mass% MgO (Iwatani Chemistry Co., MTK-30, purity: >99.9%) and 5 mass% MgF_2 (Morita Chemistry Co., Guaranteed grade) were added to the SiAlON powder. Polymer-derived SiC fibre, supplied from Nippon Carbon Co. Ltd, was used as reinforcement. SiC fibre without coating (NL-212) and the fibre with carbon-coating (NL-607) have filament numbers of 250 and 500, respectively. The thickness of the carbon coating is 0.3–0.5 μm. The density of Nicalon is 2.55 Mg/m^3. The oxygen content is about 11 mass%. The sizing agent was removed in a vacuum furnace by heating up to 500 °C. Nicalon fibre reinforced composite was fabricated by a filament-winding method comprising slurry infiltration, winding on a drum, warm-pressing to form a unidirectional green sheet compact, pyrolysis of organic binder and hot-pressing. The slurry was prepared by mixing starting SiAlON and sintering additives with ethanol with polyvinyl butyral and polyethylene glycol as binder, dibutyl phthalate as plasticizer, and linseed oil as dispersing agent. After slurry infiltration and drying, the green compact was formed by pressing the slurry-impregnated fibre sheets at 250 °C under a pressure of 30 MPa. Organic binder was pyrolysed in a vacuum furnace by gradual heating up to 700 °C. The completion of pyrolysis was checked by monitoring a vacuum gauge equipped with the furnace. Hot pressing was carried out at 1350 °C for 60 min. under a pressure of 20 MPa in nitrogen atmosphere. Bulk density and open porosity of the surface-ground sintered composite were measured by water immersion method. Three-point bending strength at room temperature, 1000 °C and 1200 °C in air was measured for three test pieces of 1.5 mm thick, 4 mm wide and 39 mm long (span 30 mm; crosshead speed 0.5 mm/min). The tensile surface of the test piece was polished with #800 diamond paste. Fracture toughness was measured by SENB (single edge notched beam) method for four test pieces of 4 mm thick, 3 mm wide and 19 mm long (span 16 mm; crosshead speed 0.5 mm/min). Straight-through notch was introduced at the centre part of the test beam with a depth of about 1.5 mm by a 100 μm thick diamond blade. Fracture energy was calculated from the area surrounded by the load–deflection curve obtained at the fracture toughness measurement. Volume fraction of the fibre was estimated by means of image analysis of the cross-sectional plane perpendicular to the fibre axis.

3 RESULTS

3.1 Density and microstructure

Table 1 shows bulk densities and open porosities of monolithic SiAlON, uncoated Nicalon/SiAlON and carbon-coated Nicalon/SiAlON composite (hereinafter referred to as sample S, sample UNC and sample CNC, respectively). Considering the open porosity, sample S is nearly full-densified by the sintering at 1350 °C, that is remarkably lower as compared with the normal sintering temperature required for dense SiAlON, i.e. 1600–1800 °C. This could be attributed to the magnesium fluoride that facilitates the sintering of Si_3N_4 at low temperature.[19] Gauckler reported that the calculated density based on X-ray data and the measured bulk density of SiAlON with $z = 3$ were 3.07 and 3.16 Mg/m^3, respectively.[20] The latter value corresponds well to the bulk density

Table 1. Fibre volume fraction, bulk density, assumed theoretical density, relative density and open porosity of monolithic SiAlON, UNC and CNC composites. (UNC, uncoated Nicalon composite; CNC, carbon-coated Nicalon composite)

	Fibre fraction (vol %)	Bulk density (Mg/m^3)	Theoretical density (Mg/m^3)	Relative density (%)	Open porosity (%)
SiAlON	0	3.13	3.16*	99.0	0.14
UNC	42	2.66	2.88	92.4	8.7
CNC	48	2.41	2.85	84.6	15.4

*Reported by Gauckler *et al.*[20]

of SiAlON studied here. Composites UNC and CNC have lower bulk densities than that of monolithic SiAlON. The open porosity is 8.7% and 15.4% for UNC and CNC, respectively.

Figures 1(a) and (b) show an optical cross-sectional view perpendicular to the fibre axis for samples UNC and CNC, respectively. Each SiC fibre filament is surrounded by the matrix, meaning that the slurry has been infiltrated successfully into the fibre tow in these composites. One can observe a small amount of pores at the part where fibre filaments are close together. In sample CNC, a large amount of pores is observed within the fibre bundle as compared with sample UNC. This result corresponds well with the bulk density of each composite.

3.2 Room and high temperature bending strength

Table 2 shows the bending strengths at room and high temperature of samples S, UNC and CNC. Their load–deflection curves obtained from bending test at ambient temperature are illustrated in Fig. 2. The mean strength of monolithic SiAlON (sample S) is 389 MPa, which is slightly lower than the reported value, 400–450 MPa.[20] Sample S shows a typical brittle fracture.

UNC composite with non-coated fibre exhibits a mean strength of 605 MPa, showing a remarkable improvement in strength. It deforms linearly up to nearly matrix fracture stress, but the compliance increases over this point. This indicates that toughness enhancement mechanisms by incorporated fibres, such as fibre bridging or fibre pull-out, have been activated. The ultimate stress is higher than the fracture stress of monolithic SiAlON.

CNC composite with carbon-coated fibre, in contrast, shows quite a different fracture behaviour. The specimen fails at lower stress compared with the UNC composite. Shear fracture along the fibre-orientation direction (delamination) proceeds. Delamination fracture propagates from the edge plane of the test specimen. The calculated shear strength is 4.2 MPa.

Optical microphotos near the tensile surface after the bending test are shown in Fig. 3(a) and (b). In the UNC composite (Fig. 3(a)), cracks propagate some distance from the tensile surface and then deflect along the fibres bundles. One can observe that plenty of fibre pull-out occurs along the crack surface. In CNC composite (Fig. 3(b)), no distinctive crack propagation crossing fibre planes is observed. As described above, delamination fracture takes place, so that many multiplex shear fractures along the fibre/matrix interface occur.

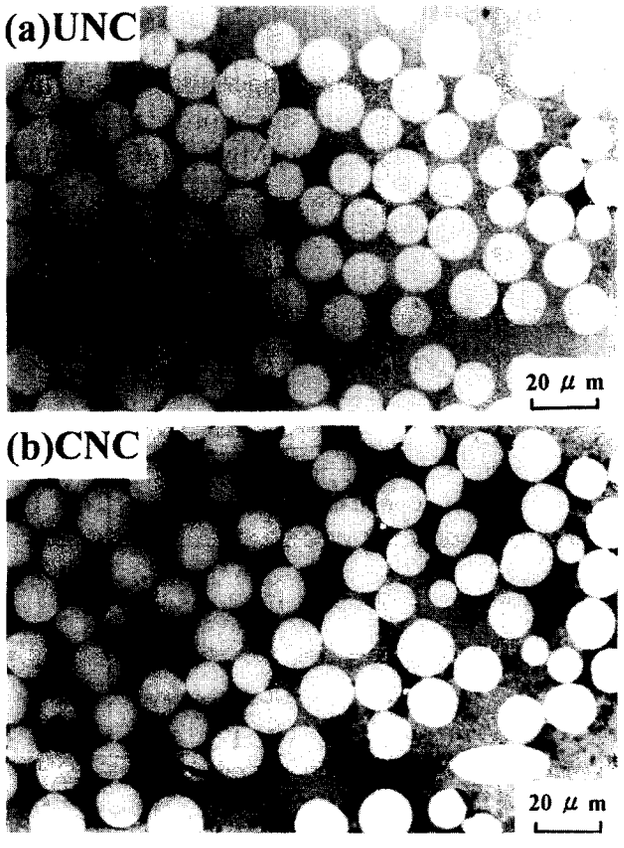

Fig. 1. Optical cross-sectional views perpendicular to the fibre axis for sample (a) UNC and (b) CNC. (UNC, uncoated Nicalon composite; CNC, carbon-coated Nicalon composite).

Table 2. Bending strengths at ambient and high temperatures of monolithic SiAlON, UNC and CNC composites. UNC, Uncoated Nicalon Composite; CNC, Carbon-coated Nicalon Composite.

	Ambient temp.	1000 °C	1200 °C
Monolithic SiAlON	389	240	13
UNC	605	214	185
CNC	163*	216	158

*Delamination fracture has taken place.

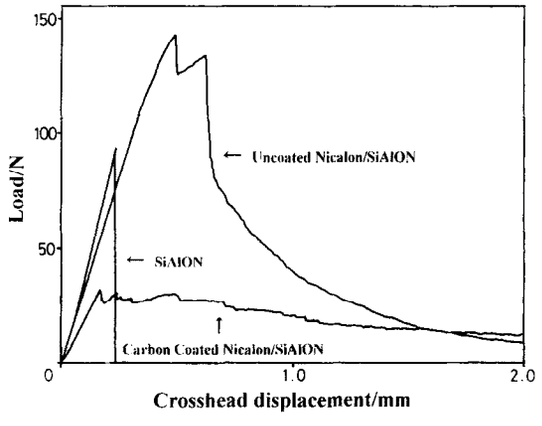

Fig. 2. Load–deflection curves obtained from bending tests at ambient temperature for monolithic SiAlON and the composites.

High temperature bending strengths have been measured at 1000 °C and 1200 °C in air. The typical load–deflection curves for monolithic SiAlON and the composites are shown in Fig. 4(a) and (b) for the tests at 1000 °C and 1200 °C, respectively. Sample S shows a brittle fracture, but indicates quite large strength degradation at 1000 °C. At 1200 °C it deforms plastically. This is probably because of grain boundary softening. The phase diagram of $MgO–MgF_2$ suggests that a liquid phase appears at 1214 °C.[21] This is confirmed by the fact that a trace of liquid oozing was observed on the specimen surface after the test at 1200 °C.

Sample UNC exhibits quite large strength degradation at high temperatures. The strength decreases to almost one third of that at room temperature. Non-linear deformation, even from low load, is observed at 1000 °C, as shown in Fig. 4, although the matrix deforms elastically at the temperature. Sample CNC holds higher strength than that at room temperature. In this case, tensile fracture takes place at first, but is later followed by delamination fracture that occurs after the strain exceeds a certain range. At 1200 °C, both composites deform plastically because of matrix softening. The strengths based on the ultimate stress are much higher than that of monolithic SiAlON.

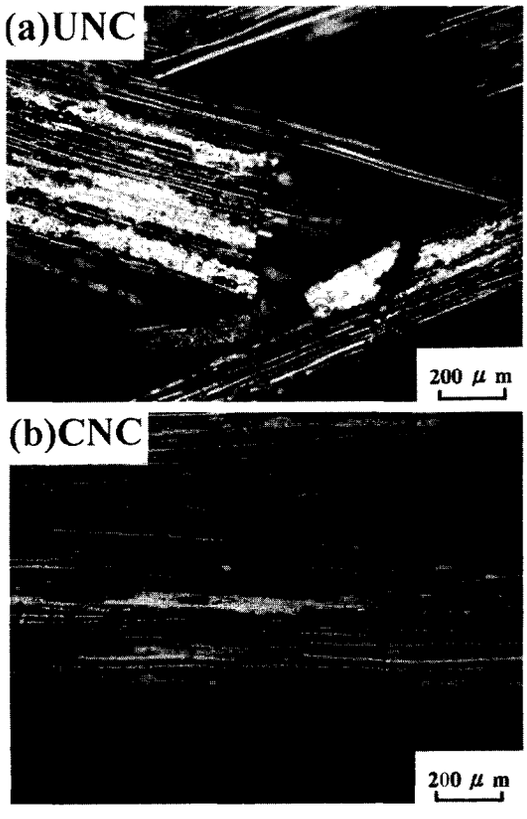

Fig. 3. Optical microphotos near the tensile surface after the bending test of (a) UNC and (b) CNC. (UNC, uncoated Nicalon composite; CNC, carbon-coated Nicalon composite).

3.3 Fracture resistance

Table 3 shows the fracture toughness and the fracture energy of the monolithic SiAlON and the composites. UNC composite has an improved toughness of 12.8 $MPam^{0.5}$, as compared with 3.6 $MPam^{0.5}$ of sample S. Note that this high fracture toughness is only an apparent value, as linear fracture mechanics cannot be applied for such heterogeneous material. Delamination has not been observed in this composite. Sample CNC showed delamination fracture from the notch tip, so that the toughness was not calculated.

Fracture energy is a measure of the fracture resistance of the material and includes all energy consumption accompanied with the fracture. Monolithic SiAlON has the fracture energy of about 0.1 kJ/m^2, while the UNC composite has 100 times higher value, 9.8 kJ/m^2, than this. A lot of fibre pull-out consumed quite a large amount of energy accompanied with the fibre/matrix debonding and the fibre sliding friction along the matrix sheath. In CNC composite with carbon-coated fibre, only delamination fracture occurs, so that the maximum stress is relatively low, but the composite can bear applied stress for an anomalously large strain. The fracture energy of sample CNC is 11.1 kJ/m^2.

4 DISCUSSION

To lower the processing temperature of SiC fibre reinforced SiAlON composite in order to minimize thermal damage to the fibre, $MgO–MgF_2$ additives

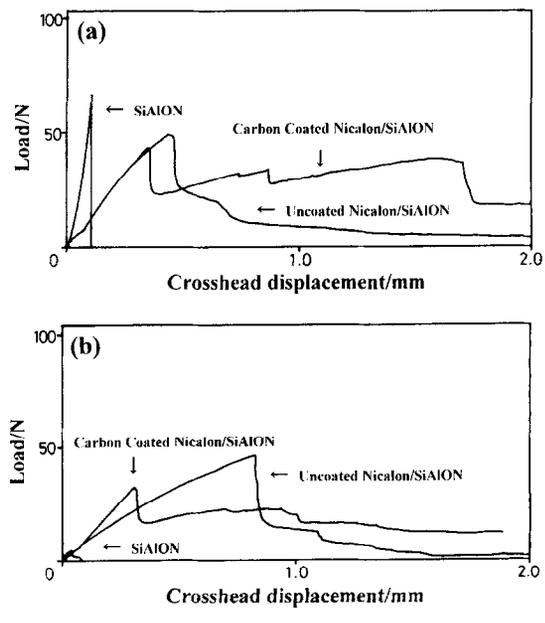

Fig. 4. Load–deflection curves obtained bending tests at (a) 1000 °C and (b) 1200 °C for monolithic SiAlON and the composites.

Table 3. Fracture toughness and fracture energy of monolithic SiAlON, UNC and CNC composites. (UNC, uncoated Nicalon composite; CNC, carbon-coated Nicalon composite)

	Fracture toughness ($MPam^{0.5}$)	Fracture energy (kJ/m^2)
Monolithic SiAlON	3.6	0.11
UNC	12.8	9.78
CNC	—	11.1

were applied. The density of monolithic SiAlON ceramics suggests that the additives are effective to get full-densification at 1350 °C, which is significantly lower than that required normally, e.g. 1600–1800 °C. Concerning with the composite density, it is necessary to know the theoretical densities of their constituents. Supposing that the fully densified matrix in the composites has the same density as monolithic SiAlON (3.13 Mg/m^3), the theoretical density of UNC and CNC composite is 2.89 Mg/m^3 and 2.85 Mg/m^3, based on the fibre volume percentages of 42 and 48 vol%, respectively. The relative density calculated by dividing measured bulk density by theoretical density is 92.0% and 84.6%. Therefore, the bulk porosity is 8.0% and 15.4%, while the measured open porosity is 8.7% and 15.4% for UNC and CNC, respectively. They coincide with each other fairly well. This confirms that the estimated theoretical densities of the composites are correct and the matrix in then is densified fully.

The difference in porosities of the composites is probably due to the filament number per yarn, which is 250 and 500 for uncoated and carbon-coated fibres, respectively. It is more difficult for the matrix slurry to infiltrate the carbon-coated fibre bundle as compared to the uncoated fibre bundles. Another point we should consider is the wettability of the fibre surface. The surface free energy is 3–5 J/m^2[2,22] and about 0.12 J/m^2[2,23] for silicon carbide and graphite, respectively. Therefore, it is not surprising that the slurry can infiltrate into the non-coated fibre bundles more easily than into the carbon-coated fibre bundles, as the former fibres are wetted far better with the matrix slurry than the latter.

Concerning the mechanical properties, the composite with uncoated fibres shows an improved bending strength at ambient temperature, being about 1.5 times higher than that of monolithic SiAlON. At high temperatures, the composite has a load-bearing capability even at 1200 °C, while the monolith deforms plastically. However, the composite exhibits remarkable creep deformation. As SiAlON is known to have higher heat resistivity, such performance is not good for a high temperature engineering material. It is known that the additives that form the liquid phase and facilitate sintering at low temperature, cause grain boundary softening at high temperature. Development of a sintering additive that enables low-temperature processing and offers better performance at high temperatures is desired.

The most striking improvement among the composite properties is toughness. Although the value is not an exact fracture toughness as defined in linear fracture mechanics, it can be used as a measure of resistance against fracture for a material with a notch. It may be known as 'notch toughness'. The toughness of UNC with non-coated fibre is improved by over 3 times as compared to that of monolithic SiAlON. This result also suggests that the incorporated fibres have survived through the fabrication procedure, and are strong enough to activate various toughness enhancement mechanisms.

The effect of carbon coating of Nicalon fibre on the composite's performance is negative so far as the system studied here. As the fibre/matrix interface in ceramic-matrix composite dominates the fracture behaviour, surface modification of the fibre that is expected to introduce weaker interface bonding is carried out. In this case, however, carbon coating on Nicalon fibre makes the interface bonding too weak, so that the delamination fracture takes place overwhelmingly. It seems that original Nicalon has an adequate bonding with the SiAlON matrix.

5 CONCLUSION

Nicalon fibre/SiAlON ceramic composites were fabricated at quite low temperatures compared with conventional sintering temperatures, so that the incorporated fibre is intact after the fabrication. The composite with non-coated SiC fibre exhibits remarkably improved room temperature strength, notch toughness and fracture energy. Its fracture manner is not brittle but graceful, with quite a large energy consumption by debonding and fibre pull-out. The composite with carbon-coated SiC fibre has poor room temperature strength, as it fails under low stress. This should be caused by easy debonding at the fibre/matrix interface, which facilitates shear fracture along the interface under relatively low stress. These results suggest that the carbon coating results in a weak bond between the fibre and the matrix, while the original Nicalon fibre seems to have an adequate bonding. In order to optimize the properties, it is necessary to study the relation between the interface bonding strength and the mechanical behaviour of the composite more quantitatively.

REFERENCES

1. EVANS, A. G., *Mater. Sci. Eng.*, **A107** (1989) 227–239.
2. EVANS, A. G., *J. Am. Ceram. Soc.*, **73** (1990) 187–206.
3. MAH, T., MENDRIRATTA, M. G., KATZ, A. P., RUH, R. & MAZDIYASNI, K. S., *J. Am. Ceram. Soc.*, **68** (1985) C27–C30.
4. PREWO, K. & BRENNAN, J., *J. Mater. Sci.*, **15** (1980) 463–468.
5. PREWO, K. & BRENNAN, J., *J. Mater. Sci.*, **17** (1982) 1201–1206.
6. BRENNAN, J. & PREWO, K., *J. Mater. Sci.*, **17** (1982) 2371–2383.
7. MAHAND, T. & LIPSITT, H. A., NASA Conference Publication 2291. In *Proc. a Joint NASA/DOD Conf.*, Cocoa Beach, FL, 1983, p. 153.
8. PYSHER, D. J., GORETTA, K. C., HODDER, R. S. & TRESSLER, R. E., *J. Am. Ceram. Soc.*, **72** (1989) 284.
9. SHIMOO, T., SUGIMOTO, M. & OKAMURA, M., *J. Japan Inst. Metal*, **54** (1990) 802.
10. OKAMURA, M., SATO, M., SEGUCHI, T. & KAWANISHI, S., *J. Japan Soc. Powder & Powder Metallurgy*, **35** (1988) 170.
11. CAPUTO, A. J. & LACKEY, W. J., *Ceram. Eng. Sci. Proc.*, **5** (1984) 654–667.
12. STINTON, D. P., CAPUT, A. J. & LOWDEN, R. A., *Am. Ceram. Soc. Bull.*, **65** (1986) 347–350.
13. CAPUTO, A. J., STINTON, D. P., LOWDEN, R. A. & BESMANN, T. M., *Am. Ceram. Soc. Bull.*, **66** (1987) 368–372.
14. RICE, R. W., SPANN, J. R., LEWIS, D. & COBLENZ, W., *Ceram. Eng. Sci. Proc.*, **5** (1984) 614–624.
15. JAMET, J., SPANN, J. R., RICE, R. W., LEWIS, D. & COBLENZ, W. S., *Ceram. Eng. Sci. Proc.*, **5** (1984) 677–694.
16. BOISVERT, V. & DIEFENDORF, R. J., *Ceram. Eng. Sci. Proc.*, **9** (1988) 873–880.
17. HURWITZ, F. I., GYEKENYESI, J. Z. & CONTROY, P. J., *Ceram. Eng. Sci. Proc.*, **10** (1989) 750–763.
18. KIM, Y.-W., SONG, J.-S., PARK, S.-W. & LEE, J.-G., *J. Mater. Sci.*, **28** (1993) 3866–3868.
19. OSWALD, J. R., RILEY, F. L. & BROOK, R. J., *Brit. Ceram. Trans. J.*, **86** (1987) 81–84.
20. GAUCKLER, L. J., PRIETZEL, S., BODEMER, G. & PETZOW, G., In *Nitrogen Ceramics*. Noordhoff, Leyden, 1977, pp. 529–537.
21. HINZ, W. & KUNTH, P.-O., *Am. Mineralogist*, **45** (1960) 1204. (Ref. *Phase Diagram for Ceramists 1969 Supplement*, The American Ceramic Society, Inc., 1969, p. 447).
22. SCHLICHTING, J., CZACK, G., KOCH-BIENE-MANN, E., KUHN, P. & SCHRÖDER, F., In *Gmelin Handbook of Inorganic Chemistry*, 8th edn: *Silicon*, Supplement Vol. B2. Springer Verlag, Berlin–Heidelberg, 1984, p. 231.
23. UBBELOHDE, A. R. & LEWIS, F. A., In *Graphite and its Crystal Compounds*. Clarendon, Oxford, 1960, pp. 41.