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Preparation of High Strength Ceramic Fibre Reinforced Silicon Nitride Composites by a Preceramic Polymer Impregnation Method

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Abstract: High strength ceramic composites, reinforced with Si–N and Si–B–O–N ceramic fibres, were prepared by the preceramic polymer impregnation method. Low-viscosity polysilazanes with a 70–90 wt% ceramic yield, were used as a matrix precursor. To obtain dense composites, the impregnation, curing and firing processes were repeated. Three-point flexural strength of the UD and 2D (cross-ply) ceramic fibre reinforced ceramic composites were shown to be as high as 1000 and 600 MPa, respectively. This resulted from the dense silicon nitride matrix and controlled fibre/matrix interface. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Ceramic fibre reinforced ceramic matrix composites (CMCs) are being developed as excellent materials with high strength and oxidation resistance at high temperature. Several processes, including preceramic polymer impregnation (PCPI),[1–3] chemical vapour infiltration (CVI),[4,5] reaction bonding and hot-pressing,[6] have been employed for the fabrication of continuous fibre reinforced composites. The strength of the composite that is obtained by the CVI process is relatively low, because the density of the matrix is as low as 70–80% of the theoretical value. The reaction bonding method provides residual metal in the product, so the strength decreases at elevated temperatures. The hot-pressing method will degrade the fibre reinforcement through treatment at high temperature and pressure, and is not amenable to the production of complex shapes.

PCPI is the fabrication process of CMCs derived from organometallic or inorganic precursors. The advantages of PCPI are as follows: (1) There is no damage to the reinforcement because the firing process is at low temperature and atmospheric pressure. (2) There are no aids in firing, so high purity ceramics are readily obtained. (3) Can be applied to complex and near-net shaped parts. (4) Dense and homogeneous matrices are readily obtained. Accordingly, with high expectation of PCPI, our development activity has continued. In addition, TONEN's preceramic polymer technologies have provided stoichiometric, homogeneous and high purity silicon nitride fibre (SNF).[7–9] The SNF has excellent properties, including high strength and oxidation resistance at high temperature. Recently, progress in continuous silicon boron nitride fibre (SNBF) that has good potential at elevated temperatures was described by Funayama *et al.*[10] We have reported on unidirectional (UD) carbon fibre reinforced composites and UD SNF reinforced composites, prepared by PCPI.[3,11] Schwab *et al.* have reported on 2D (plain weave laminate) silicon carbide fibre reinforced composites by a similar process.[12] An initial attempt is made in this paper to apply SNF and SNBF in the fabrication of 2D (cross-ply) composites. Furthermore, this paper describes the influence of polysilazanes on the properties of resultant products.

2 EXPERIMENT

2.1 Matrix precursor

Perhydropolysilazane (PHPS) and methylhydrooligosilazane (SNC) were used as matrix precursors. PHPS was synthesized by ammonolysis of a dichlorosilane–pyridine adduct. SNC was synthesized by coammonolysis of a dichlorosilane–pyridine adduct and a monomethyldichlorosilane–pyridine adduct.[13] The properties of PHPS and SNC are shown in Table 1. These polymers are transparent liquids with low viscosity, and have a thermosetting property. By heating to 100–300°C, a thermal crosslinking proceeds, and glass-like hard solids are obtained. By firing to 800–1500°C in nitrogen or inert gases, the cured products convert to amorphous silicon nitride based ceramics with 70–90 wt% yield. The yield is extremely high in comparison to other preceramic polymers (e.g. polycarbosilane, polysilastylene, etc.) that have 50–60 wt% yield. The differences between PHPS and SNC are shown in the composition. The ^{1}H NMR spectrum of SNC exhibits a peak corresponding to SiMe due to the addition of a monomethyldichlorosilane. SNC consists mainly of structured units of SiH_2NH and SiHMeNH.

2.2 Ceramic fibre

Two kinds of ceramic fibres, produced by TONEN, were used as reinforcements. SNF is derived from perhydropolysilazane. SNBF is derived from polyborosilazane.[10] The properties of both fibres are shown in Table 2. The surfaces of these fibres were coated with a C-rich layer by chemical vapour deposition ($SiCl_4$–CH_4 gases system). The purpose of this fibre coating is not only to prevent reaction between fibre and matrix, but also to give adequate interface shear strength. The thickness of the coated layer was about 0.1 μm.

2.3 Fabrication procedure

2.3.1 UD (Unidirectional fibre reinforced composites)

PHPS and SNC were used as matrix precursors. UD composites, SNF/PHPS and SNF/SNC, were fabricated as shown in Fig. 1. A unidirectional SNF aligned preform was prepared by winding a strand, which was infiltrated with precursor, on to a mandrel. The preform was pressed to a thickness of ≈5 mm, and cured in a N_2 atmosphere with a pressure of 0.05–0.1 MPa at 100–300°C for 1–3 h. The cured body was then fired in a N_2 atmosphere to 1350°C. To densify the product, the impregnation, curing and firing processes were performed repeatedly.

Table 1. The properties of the TONEN poysilazanes

	Molecular weight (M_n)	Density	Viscosity (mPa·s) at 30°C
PHPS	800–1000	1.1–1.2	10–50
SNC	800–1000	1.1–1.2	40–80

Table 2. The properties of the TONEN fibres

		SNF	SNBF
Tensile strength (GPa)		2.2	2.2
Tensile modulus (GPa)		200	200
Density		2.5	2.5
Typical composition (%)	Si	59.6	48.0
	B	—	5.5
	N	37.1	32.8
	C	0.4	5.4
	O	2.7	7.6

2.3.2 2D (Cross-ply composites)

SNC was used as a matrix precursor, because the UD composite, SNF/SNC, showed higher flexural strength than the SNF/PHPS. SNF and SNBF were used as reinforcement. 2D (cross-ply) composites were fabricated as follows. A unidirectional fibre aligned preform was prepared by winding a strand, which was infiltrated with SNC, on to a drum. To obtain a UD prepreg, the preform was pressed to a thickness of ≈0.2 mm.

The prepreg was then cut and stacked in the structure of $[0/90/90/0]_2$. The stacked prepregs were cured in a N_2 atmosphere with a pressure of 0.05–0.1 MPa at 100–300°C for 1–3 h. The cured body was then fired in a N_2 atmosphere to 1350°C. To densify the products, the same repeating process as in the UD composites was performed.

2.4 Characterization

The densification of the fired material in the repeating process was monitored by measuring bulk densities. The products were characterized by SEM, AES, X-ray diffraction analysis, and a three-point bending test at room temperature. (For cross-ply composites, the high temperature strength was measured at 1250°C in a N_2 atmosphere.) The three-point bending test was performed in accordance with JIS R1601 except for thickness of sample. Samples were cut into 1.0–1.2 × 4 × 40 mm bars and tested with a span length of 30 mm at a cross-head speed of 0.5 mm/min. JIS R1601 is not always advantageous to continuous fibre reinforced composites which show non-brittle failure, since this method shows a complex fracture mixed with tensile

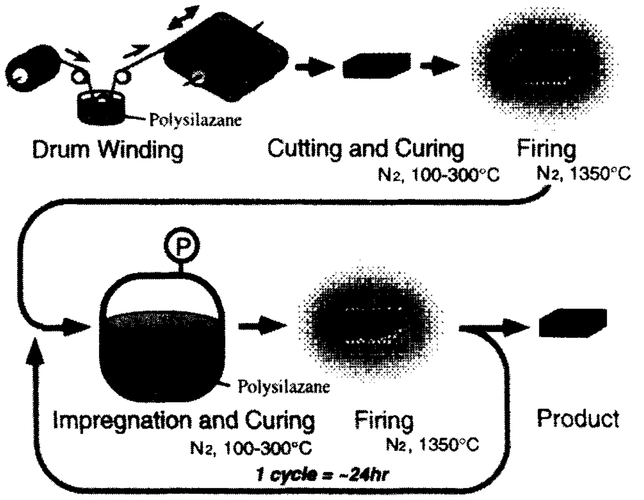

Fig. 1. Fabrication process of continuous fibre reinforced Si–N composite.

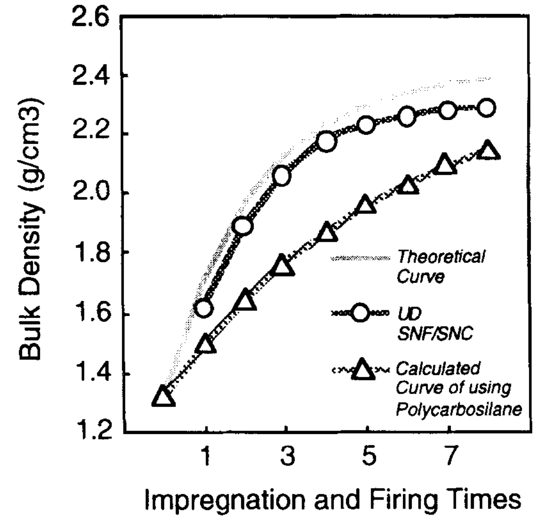

Fig. 2. Densification curve of UD composite.

and shear failure. In order to fracture samples by a tensile stress, the ratios of span to thickness were set to 25–30. In addition, for UD composites, an interlaminar shear strength (ILSS) test was also performed in accordance with JIS K7057. For the 2D samples, the direction of the fibre on a surface layer was aligned to the orientation of the tensile stress. A true density was measured with a pycnometer by using *n*-decane as the medium. The total porosity was calculated by the true density for 2D composites.

3 RESULTS AND DISCUSSION

3.1 UD (Unidirectional fibre reinforced composites)

The densification curves are shown in Fig. 2. Because of the shrinkage of precursors in firing, reimpregnation of polymers is required to densify the product. The curve for the product agrees well with the theoretical curve calculated from eqn (1). (The impregnation efficiency is assumed to be 0.9.) Equation (1) is defined as follows:

$$\rho_{c(n)} = \rho_m(1 - V_f) + \rho_f V_f - \rho_m P_{(n-1)} \qquad (1)$$

with

$$P_{(n)} = P_{(n-1)}(1 - ICY\rho_p/\rho_m) \qquad (2a)$$

$$P(0) = (1 - V_f) \qquad (2b)$$

where n is the number of firing times, ρ_c, ρ_f, ρ_m and ρ_p are the densities of composites, fibres, matrix (fired polymers) and polymers, respectively, V_f and P are the volume fraction of fibres and porosities, Y is the char yield of polymers, I is the impregnation efficiency and C is the polymer concentration.

As is obvious from Fig. 2, the steps of PCPI have theoretically proceeded.

Mechanical properties of UD composites are shown in Table 3. The stress–deflection curve is shown in Fig. 3. The SNF/SNC composite demonstrates a flexural strength of over 1 GPa at room temperature. We have reported the effect of coating on the fibre,[14] in the carbon coated case, 2D (plain weave laminate) silicon carbide fibre reinforced composite has demonstrated a non-brittle failure with fibre pull-out and a high flexural strength of 294 MPa. On the contrary, in the non-coated case, the composite has shown catastrophic failure and a relatively low flexural strength of 60 MPa. In this study, the SNF reinforced composites have also shown a non-brittle failure, similar to the one in the carbon coated case. Therefore, this suggests that the coating on the fibre is essential for an adequate interface shear strength in CMCs.

The auger depth profiles of coated SNF surface show that a carbon-rich layer, which is contaminated with silicon, is deposited (Fig. 4). In an attempt to perform auger analysis on the fracture

Table 3. The properties of CMCs prepared by the PCPI method

Type		UD		2D	
Firing condition		1350°C : 8 times		1350°C : 7 times	
Fibre		SNF	SNF	SNF	SNBF
Matrix precursor		PHPS	SNC	SNC	SNC
Bulk density		2.54	2.35	2.36	2.38
V_f (%)		43	54	57	58
Total porosity (%)		—	—	7.2	5.8
Flexural strength	R.T.	649	1049	618	627
(MPa)	1250°C	—	—	546	595
ILSS (MPa)		55.1	45.4	—	—
R^a (%)		80	85	95.5	94.5

[a] R: apparent effectiveness = $\sigma_c/(\sigma_f V_f A)$; A is assumed to be 1.0 (UD) and 0.5 (2D).

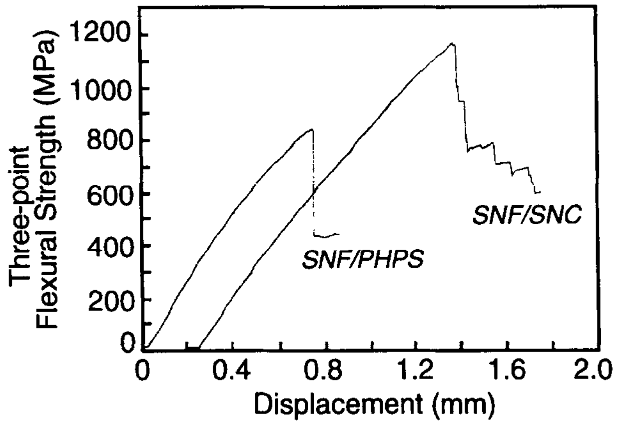

Fig. 3. Stress–deflection curves of UD composites.

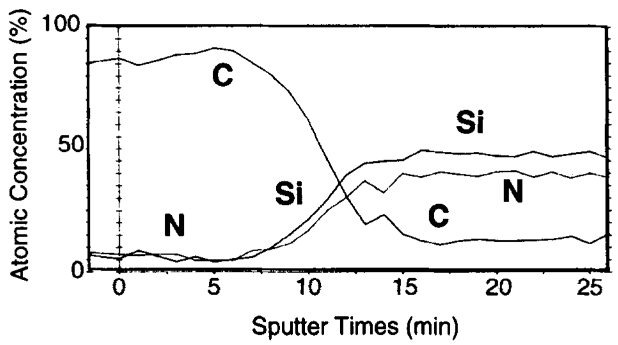

Fig. 4. AES depth profiles of coated SNF.

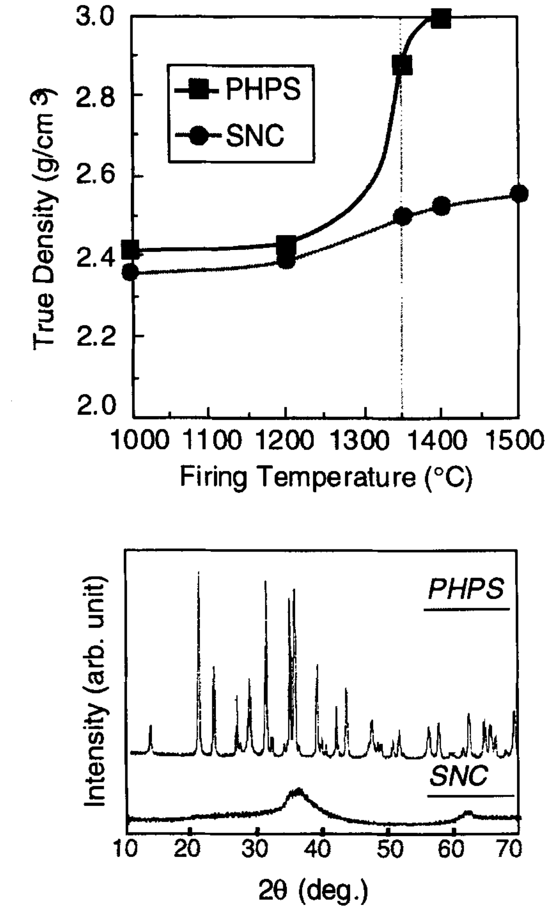

Fig. 5. The variation of polysilazanes in pyrolysis. (a) Plot of true density as a function of firing temperature. (b) XRD patterns of polysilazanes pyrolysed at 1350°C.

surface of the composite, the fibre pull-out has provided similar profiles as above. These results would suggest that the pulled out face is the interface between the coated surface and the matrix. It is reasonable to speculate that coating the fibre would give adequate interface shear strength by controlling the interaction.

The properties of composites are different according to the kinds of matrix precursor. The flexural strength at room temperature of SNF/PHPS and SNF/SNC are 649 MPa and 1049 MPa, respectively. This difference is due to the crystallization behaviour of the precursors. Though PHPS is selected as a high impregnation precursor with low viscosity, this PHPS contains excess Si compared with the stoichiometric composition of silicon nitride. The deviation from the theoretical Si/N ratio results in low crystallization temperature (≈1200°C). On the other hand, SNC's crystallization temperature is above 1500°C, because SNC does not contained excess Si, and its pyrolysis product has a stoichiometric composition of a complex silicon nitride and silicon carbide. The true density and X-ray diffraction patterns of pyrolysed polymers are presented in Fig. 5. In preceramic polymer, the crystallization would inherently cause an increase in density. Since both matrices are similar in Si based component and structure, densification (an increase in atomic density) would provide an increase in elastic modulus. The true density of fired SNC and PHPS are 2.5 and 2.8 g/cm^3, respectively. Therefore, it is presumed that the elastic modulus (E_m) of pyrolysed PHPS was much larger than that of pyrolysed SNC. If $E_f > E_m$, the stress in the fibre is greater than in the matrix, because the fibre bears the major part of the applied load. This effect results in an increase in the effectiveness of fibre strength to composite strength. The flexural strength of samples using SNC matrix has become high as noted above. To neglect the influence of the amount of scatter in the V_f on the composite strength, the apparent effectiveness of fibre strength to composite strength (R) is defined as follows:

$$R = \sigma_c/(\sigma_f V_f A) \qquad (3)$$

where σ_c and σ_f are the strength of composites and fibres, and A is the ratio of the fibre which is aligned to the orientation of the tensile stress. For UD and 2D composites, A is assumed to be 1.0 and 0.5, respectively.

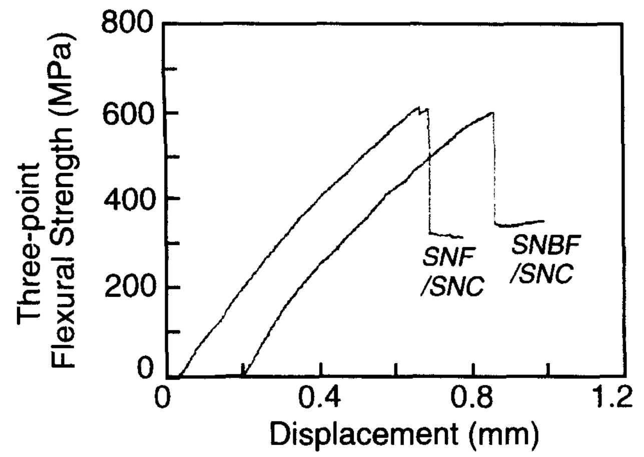

Fig. 6. Stress–deflection curves of 2D composites.

Thus, the high strengths of UD composites are due to improved interaction between coating on the fibre and adequate matrix.

3.2 2D (Cross-ply composites)

Polished cross-sections of cross-ply composites are shown in Fig. 7. The contrast of the fibre/matrix interface and microcracks, attributed to the back-scattered-electron intensity, are observed. From repetition of the impregnation and firing process, dense products are obtained. The properties of the samples are shown in Table 3. The excellent flexural strength (≈600 MPa) is obtained in samples of both SNF composite and SNBF composite. The stress–deflection curve is shown in Fig. 6. The fracture surface shows a non-brittle failure with fibre pull-out, as in the UD composites. The apparent effectiveness of fibre strength in 2D composites is also extremely high. This would be due to the following reasons: (1) The products with high volume fraction of fibre can be obtained easily. Since both the polymer rheology and the thermosetting nature are similar to organic thermosetting resin (e.g. epoxide phenolic resin), the FRP's fabrication process can be applied to the shaping process of PCPI. (2) To densify the matrix, shrinkage of the whole material, including reinforcement, is not necessary in PCPI. While in the hot-pressing method, UD composites could be densified easily because the degree of freedom of shrinkage is two. However, 2D composites could not be well-densified because the degree of freedom of shrinkage is only one (the direction of thickness).

In high temperature flexural tests, the strengths at room temperature are maintained to 1250°C (Fig. 8). There is no obvious difference in strength between the SNF composite and SNBF composite, because both fibres (SNF, SNBF) do not degrade at the present manufacturing temperature and pressure. In the fibre evaluation, SNBF has better properties at elevated temperatures than SNF. Therefore, SNBF is expected to be applied as the reinforcement of CMCs (target temperature is 1500°C or above).

4 CONCLUSION

By the PCPI method, dense SNF and SNBF reinforced silicon nitride composites were obtained. Three-point flexural strengths of the UD and 2D (cross-ply) composites were shown to be as high as 1000 and 600 MPa, respectively. This resulted from improved interaction between the coating on the fibre and an adequate matrix. Using SNC as the matrix precursor to fabricate these composites has

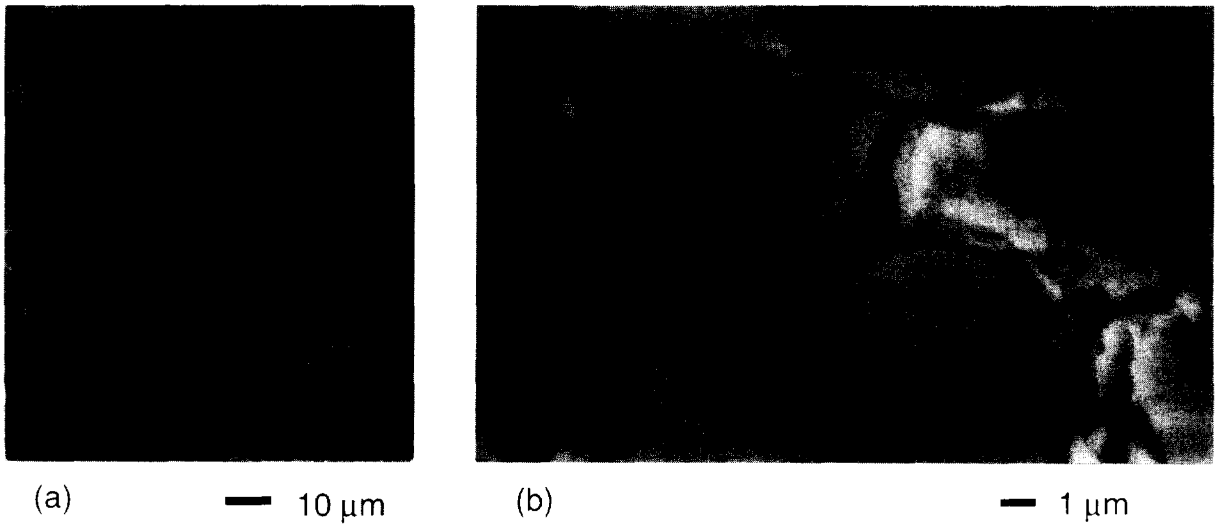

Fig. 7. Backscatterd electron image (composition) of polished cross-section of 2D SNBF reinforced composite. (a) Low magnification, (b) high magnification.

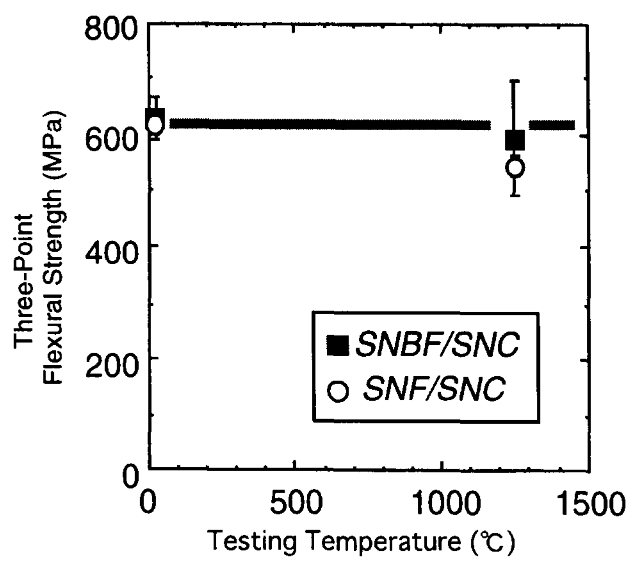

Fig. 8. High-temperature strength of 2D composites under an N_2 atmosphere.

taken an important role in the relation between E_f and E_m, because SNC maintained a relatively low density under the firing conditions.

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