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Mechanical characterisation of mullite-based ceramic matrix composites at test temperatures up to 1200°C

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Abstract

Nextel 610 fibre-reinforced mullite-based matrix fabricated by Dornier Forschung was characterised at DLR Institute of Materials Research. The material was produced by the polymer route after coating the fibres with a 0.1 μm thick carbon layer. The composite was manufactured by infiltrating the fibres with a slurry containing a diluted polymer and mullite powder, curing in an autoclave and subsequently heat treating and pyrolysis of the polymer. A final heat treatment in air is performed to remove the carbon coating and to reduce the residual stresses. A $(0/90/0/90/0/90)_s$-laminate was produced with an average fibre volume fraction of 45.6% and a porosity of 15.9%. Dog-bone-type tensile specimens with a width of 10 mm were cut from the plate by water jet and tested at temperatures up to 1200°C in air. The tensile strength at room temperature measured 177.4 MPa and linearly decreased to 145.2 MPa at a temperature of 800°C. A stronger decrease occurred at 1000 and 1200°C. In contradiction to ceramic matrix composites manufactured by the CVI-route the stress–strain behaviour is nearly linear up to failure. The modulus of the composite (at room temperature 108.8 GPa) is analysed on the basis of the expected moduli of the fibres and the mullite matrix. It can be concluded that the contribution of the matrix to the modulus of the composite is low, caused by porosity and components other than mullite. The intralaminar shear strength at room temperature measured 36 MPa. This value reflecting shear transfer capability of fibre to matrix limits the amount of fibre pull-out.

Keywords: Aluminosilicate fibres; Composites; Laminates; Mechanical properties; Mullite matrix

1. Introduction

Ceramic matrix composites (CMCs) are under development for high temperature applications as e.g. in aero engines, rocket nozzles and re-entry heat shields. In comparison with monolythic ceramics these fibre reinforced ceramics are attractive due to the increased toughness and decreased flaw sensitivity. First generation CMCs were usually produced on the basis of chemical vapour deposition (impregnation) making use of fibres surrounded by a carbon coating. These CMCs show on loading multiple matrix cracking which leads to a gradual loss of the contribution of the matrix to the composite stiffness.[1] This so-called quasi-ductility is reached due to the fact that matrix cracks do not penetrate the fibres but deflect at or in the C-layer. The main drawback of these CMCs is, that in high temperature oxidative environments the carbon layer is consumed giving rise to a loss of the crack deflective capability, if interfacial reaction products increase fibre/matrix bonding. Application of protective coatings is a possibility to reach short and medium term oxidative resistance.[2,3]

Long term oxidation resistance for thousands of hours, however, can only be reached if the material system is composed of components each of which is oxidation resistant. For this reason in recent years CMCs with oxide fibres and oxide matrices have drawn much attention. In the absence of weak layers surrounding the fibres a different crack deflection mechanism must be activated as is for example possible on the basis of a different coefficient of thermal expansion of fibre and matrix and a special geometrical arrangement of closely packed fibres in a finescale porous matrix.[4]

Crack deflection in the usual sense can be realized with

- crack deflective materials (e.g. monazites [5,6])
- porous interphases [5,6]
- fugitive interphases.

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In the present work the mechanical behaviour of a mullite-based CMC with oxide fibres (Nextel 610) and a fugitive interface is characterized. The material is produced by Dornier Forschung by the polymer route and tested at DLR.

2. Materials and experiments

The material investigated (designated Nextel 610/Umox) is produced by Dornier Forschung. The manufacturing technique is based on the polymer infiltration and pyrolysis process.[7,8] It comprises three steps. First, the fibre bundles are coated with a carbon layer of about 0.1 μm thickness. The fibres are pulled through a vessel containing a solution of a carbon precursor polymer. Thus, a polymer film on each single fibre is produced and subsequently converted into a carbon layer by pyrolysis in a furnace.

The infiltration technique is similar to the production of fibre reinforced plastics. The fibres can be infiltrated by filament winding (as shown in Fig. 1), resin transfer molding or wet lamination with the slurry out of a diluted silicon polymer and mullite powder. After infiltration, the polymer is cross-linked and densified in an autoclave to form a solid green body.

Subsequently the polymer is pyrolyzed in an oven with an inert atmosphere. Thus, a ceramic matrix is produced that consists of mullite and a Si–O–C phase. To minimize porosity, the composite is reinfiltrated with the polymer, which is also cross-linked and pyrolyzed. One to three reinfiltration cycles show the best results. As a final process, the composite is annealed in air to reduce internal stresses and to remove the carbon coating on the fibres. The microstructure of the composite is shown in Fig. 2. The matrix is characterized by a homogeneous distribution of the mullite and the Si–O–C phase and a small grain size of the particles compared to the fibre dimensions.

A crossply laminate $(0/90/0/90/0/90)_s$ with, in total, 12 layers was produced. The average thickness of the plate was 2.00 mm (ply thickness 0.167 mm), the fibre volume fraction and the porosity measured $V_f = 0.456$ and

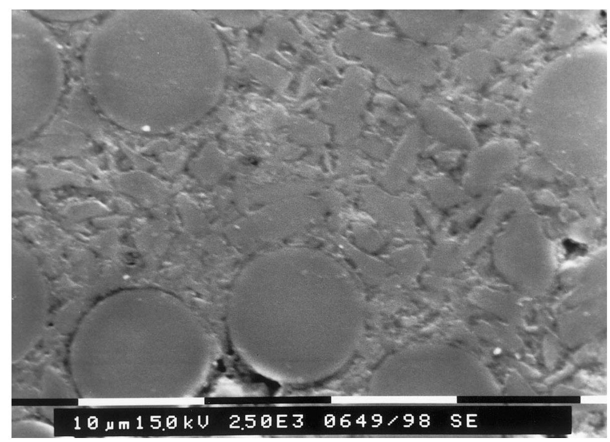

Fig. 2. Macrostructural details on polished surface of a Nextel 610/Umox crossply laminate.

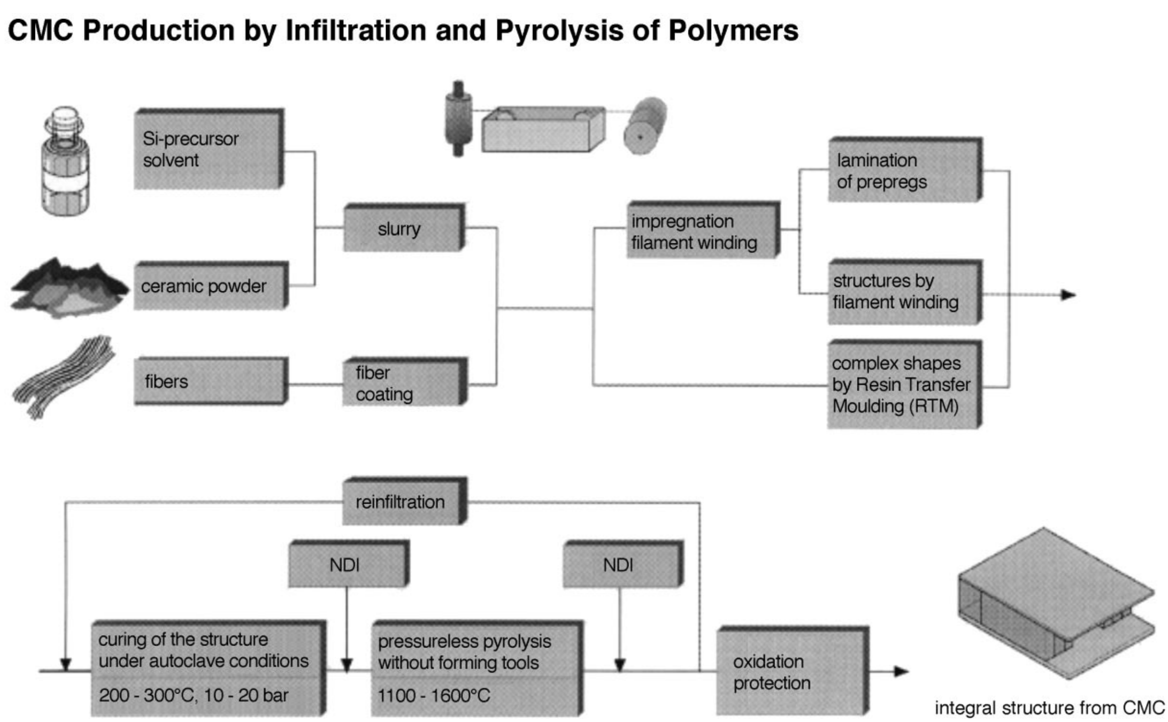

Fig. 1. Production of mullite/mullite CMCs by poylmer impregnation and pyrolysis.[7]

$V_p = 0.159$, respectively. The density of the plate reached 3.0015 g/cm^3. Dog-bone type specimens were cut from the plate in 0°-direction by waterjet. For a first test series waisting of the specimens from a width of 15 mm in the grip range to a 10 mm wide gauge section was performed according to the dimensions in Fig. 3 and Table 1. As most of the specimens tested in the first test series broke near the radius the shape of the specimen was adapted to give a smoother change of width. The *x–y* coordinates for the changed specimen shape is given in Table 2.

The dog-bone specimens were loaded up to failure in a tensile test performed at different temperatures between room temperature and 1200°C as a maximum. In order to guarantee a homogeneous temperature distribution, a holding time of 10 min was applied after reaching the required temperature. Heating of the middle section of the specimen is realized by inductive heating of a susceptor. The temperature is measured with the aid of a thermocouple in the middle of the specimen. The heating coil with a height of 100 mm and consisting of 6 windings was adjusted in such a way, that the temperature in the 40 mm gauge length was as homogeneous as possible. The maximum temperature deviation in the gauge length of 40 mm measured +3% −0% at a temperature of 1200°C in the middle. Stress–strain behaviour at all temperatures is measured with the aid of a clip gauge with a gauge length of 20 mm as schematically presented in Fig. 4.

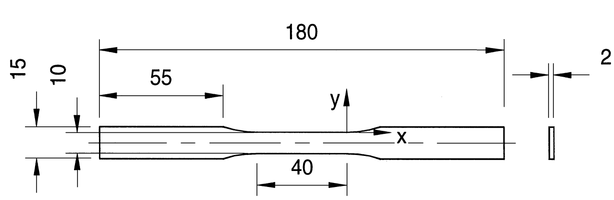

Fig. 3. Dog-bone specimen dimensions for $(0/90/0/90/0/90)_s$ tensile test.

Table 1
Radius of dog-bone specimen (grip length 55 mm)

X	0.000	1.612	2.955	4.567	5.830	7.782	9.000	9.931
Y	0.000	0.027	0.060	0.118	0.179	0.314	0.432	0.545
X	11.507	12.555	13.245	13.755	14.131	14.382	15.000	
Y	0.814	1.068	1.291	1.492	1.677	1.827	2.500	

Table 2
Radius of adapted dog-bone specimen (grip length 40 mm)

X	0.000	1.612	2.955	4.567	5.830	7.782	9.000	10
Y	0.000	0.027	0.060	0.118	0.179	0.314	0.432	0.54
X	15	20	25	30				
Y	1.03	1.52	2.01	2.5				

Parallel sided specimens with a width of 10 mm as indicated in Table 3 were also cut from the plates but now with the aid of a diamond wire machine. Specimens cut under an angle of 45° with respect of the 0°-direction are used to measure the shear modulus G and the intralaminar shear strength at room temperature. Further 10 mm wide specimens were cut transverse to the 0°-direction. After this these specimens were ground with a diamond wheel on both surfaces in order to remove the surface layers so that finally specimens with the orientation $90_{0.2}/0_2/90_{0.2}$ remain. The stiffness of the crossply specimens with two different relative amounts of transverse plies ($V_{90°} = 50\%$ and $V_{90°} = 16.6\%$ respectively) allows the determination of the moduli of the parallel and transverse ply ($E_{//}$, $E_{\perp}$).

3. Results and discussion

A calculation of the longitudinal and transverse ply stiffness $E_{//}$ and $E_{\perp}$ with the aid of the moduli of the two types of crossply specimens delivers the values indicated in Table 4. The modulus parallel to the fibres can be approximated very well by the rule of mixtures:

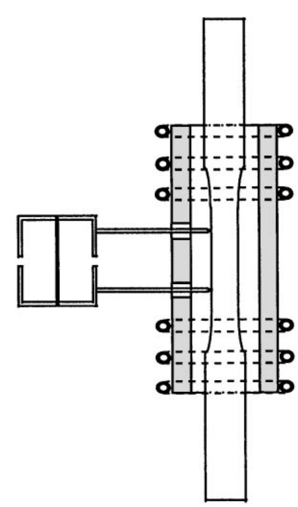

Fig. 4. Schematics of experimental set-up for high temperature tensile testing of Nextel 610/Umox.

Table 3
Test specimens to characterize the mechanical behaviour of Nextel 610/Umox

Specimen	Specimen type	Test temperature	Mechanical properties
$(0/90/0/90/0/90)_s$	10 mm dog-bone	RT-1200°C	E, UTS
$90_{0.2}/0_2/90_{0.2}$	10 mm parallel	RT	E
$(+45/-45/+45/-45/+45/-45)_s$	10 mm parallel	RT	E(G), UTS(S)

Table 4
Elastic constants and intralaminar shear strengths of different CMCs with a porosity content of 10–15%

Process	Material	E_f GPa	E_m GPa	$E_{//}$ GPa	Matrix contr. to $E_{//}$%	$E_\perp$ GPa	$G_{//\perp}$ GPa	S MPa
PP	C/C	331	35	206	0	0	6	21.8
PP	N610/Umox	325	220	163	6	54.4	23.0	36
CVI	SiC/SiC	200	469	265	100	130	65	–

$$E_{//} = E_f V_f + E_m V_m \quad (1)$$

in the absence of porosity. Taking E_f (Nextel 610) = 331 GPa[9] and $E_m = 220$ GPa[10] for mullite the resulting modulus of $E_{//} = 271$ GPa is substantially higher than the value given in Table 4.

Due to porosity and the presence of the probably not continuous Si–O–C network in which the mullite particles are embedded, the matrix contributes only 6% of the theoretical modulus of mullite.

A comparison made in Table 4 with other CMCs (C/C and SiC/SiC) shows that this behaviour is characteristic for CMCs produced by the pyrolysis of a polymer matrix (PP). If the matrix is produced by chemical vapour impregnation (CVI) a continuous stiff matrix with a maximum contribution of the matrix $[= E_m(1 - V_p - V_f)]$ can be possible.[11]

The shear modulus $G_{//,\perp}$ can be determined with the aid of a tensile test on a ±45-specimen, if the strain in and transverse to the loading direction, ε_l and ε_t respectively, is measured. Fig. 5 shows the result of such an experiment. The shear modulus follows from:

$$G = \sigma/(\varepsilon_l - \varepsilon_t) \quad (2)$$

whereas the intra-laminar shear strength is given by

$$S = \sigma_{max}/2 \quad (3)$$

The results of the tensile tests at temperatures ranging from room temperature to 1200°C are indicated in Fig. 6. The strength of the $(0/90/0/90/0/90)_s$ specimens at room temperature measures 177.4 MPa and decreases linearly to 145.2 MPa at 800°C. Above 800°C a stronger drop occurs. The modulus is maintained around 100 GPa up to a maximum temperature of 1000°C. At 1200°C a strong drop in modulus takes place. The stress-strain curves at the different temperatures are practically linear up to failure with the tendency for larger non-linearity at larger temperatures. Non-linear type of failure giving rise to the before-mentioned quasi-ductility can be a result of

(a) matrix cracking
(b) fibre failure resulting in loose bundle type of failure.

It has been discussed, that the matrix contributes little to the modulus of the composite. Matrix cracking, thus, can hardly give rise to a quasi-ductile behaviour. The only phenomenon which can produce a substantial amount of non-linearity is fibre failure due to a loose bundle type of failure. Condition for this type of failure is a low capability of transferring stresses between fibre and the matrix.

This low stress transfer capability usually leads to a considerable pull-out. Microscopical observations of fracture surfaces, given in Fig. 7, indicate in agreement with the occurrence of little non-linearity only limited pull-out of broken fibres, mainly near porous areas. No substantial difference between the fracture surfaces produced at room temperature and e.g. at 800°C test temperature occurred. Fracture surfaces illustrate that a homogeneous fugitive interface with a theoretical thickness of 0.1 μm is not present around all fibres but local

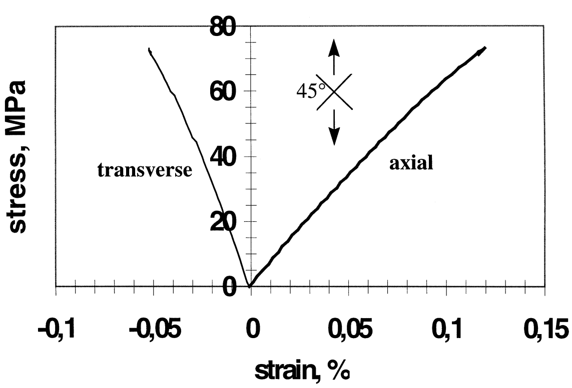

Fig. 5. Stress-strain curve of ±45° specimen at room temperature.

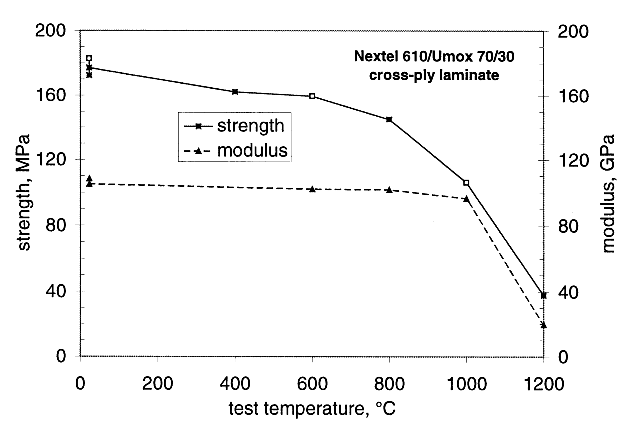

Fig. 6. Tenile strength and modulus of Nextel 610/Umox crossply laminate as a function of the test temperature.

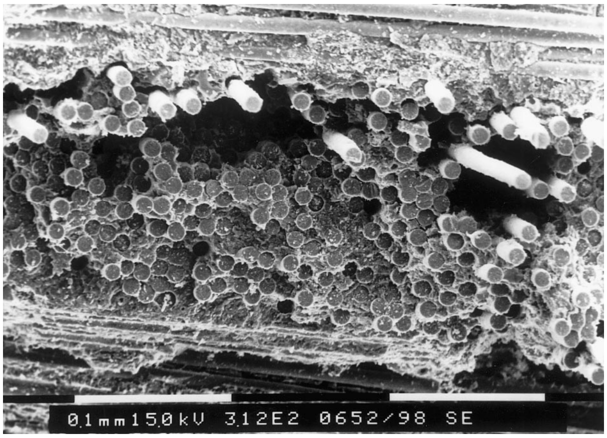

Fig. 7. SEM-picture of fracture surface of 0°-ply in crossply specimen tested at room temperature.

points of fibre/matrix contact are visible. These contact points realise fibre/matrix stress transfer quantified by the intra-laminar shear strength indicated in Table 4. A possibility to increase quasi-ductile effects is to increase the thickness of the fugitive interface, which however is accompanied by a reduction of the intralaminar shear strength.

4. Conclusions

A Nextel 610 fibre reinforced mullite-based ceramic matrix on the basis of a fugitive interface has been characterised. The crossply laminate $(0/90/0/90/0/90)_s$ with a room temperature strength of 177.4 GPa showed a moderate drop in strength up to 800°C and a stronger decrease up to 1200°C. The contribution of the matrix to the modulus of the laminate ($E_{0/90} = 108.4$ GPa at room temperature) is small, so that the matrix cannot contribute to a quasi-ductile stress–strain behaviour. The intra-laminar shear strength (at room temperature 36 MPa) is rather high, which leads to limited fibre pull out visible at fracture surfaces of crossply specimens.

References

1. Beyerle, D. S., Spearing, S. M., Zok, F. W. and Evans, A. G., Damage and failure in unidirectional ceramic matrix composites. *J. Am. Ceram. Soc*, 1992, **75**(10), 2719–2725.
2. Strife, J. R., Ceramic coatings for carbon–carbon composites. *Ceramic Bulletin*, 1988, **67**, 369–374.
3. Ohlhors, C.W., Vaughn, W.L. and Barratt, D.M., Current research in oxidation-resistant carbon–carbon composites at NASA Langley, NASA-Report N93-12456, 149–158, 1993.
4. Tu, W., Lange, F. F. and Evans, A. G., Concept for damage-tolerant ceramic composite with "strong" interfaces. *J. Am. Ceram. Soc.*, 1996, **79**(2), 417–424.
5. Marshall, D. B., Davis, J. B., Morgan, P. E. D. and Porter, J. R., Interface materials for damage-tolerant oxide composites. *Key Engineering Materials*, 1997, **127–131**, 27–36.
6. Cain, M. G., Cain, R. L., Tye, A., Rian, P., Lewis, M. H. and Gent, J., Structure and stability of synthetic interfaces in CMCs. *Key Engineering Materials*, 1997, **127–131**, 37–51.
7. Knabe, H., Haug, T , Schäfer, W. and Waldenmaier, T., *Oxide Ceramic Matrix Composites for Aerospace Applications*. Dornier GmbH und Dornier Luftfahrt GmbH, Friedrichshafen.
8. Duran, A., Aparicio, M., Rebstock, K. and Vogel, W. D., Reinfiltration processes for polymer derived fibre reinforced ceramics. *Key Engineering Materials*, 1997, **127–131**, 287–294.
9. Clemens, F., private communication.
10. Schneider, H., Okada, K., and Pask, J., *Mullite and Mullite Ceramics*, John Wiley & Sons, New York.
11. Peters, P. W. M., Martin, E. and Pluvinage, P., Influence of porosity and fibre coating on engineering elastic moduli of fibre-reinforced ceramics (SiC/SiC). *Composites*, 1995, **26**(2), 108–114.