

DEFORMATION AND FRACTURE OF CERAMIC MATRIX COMPOSITES

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Abstract. A survey is presented of research aimed at an understanding of the relation between microstructure, interface properties and mechanical behaviour of a range of silicate (glass ceramic) and nitride matrix composites.

For silicate CMCs, hot-pressing cycle (P/T) in relation to matrix chemistry and fibre type is critical in avoiding mechanical and chemical damage of fibres with consequent reduction in ultimate CMC strength.

'Graceful' failure, typified by 3 stage stress-strain curves, may be obtained for interface debond energies Γ and shear stresses τ up to $\sim 20 \text{ Jm}^{-2}$ and $\sim 50 \text{ MPa}$, respectively.

Interface-oxidation-induced property degradation occurs at intermediate temperatures (400-800°C) but is suppressed at higher temperatures by passive oxidation of SiC fibre ends which prevents further carbon interface removal by channelled reaction.

Higher temperature SiC (Textron CVD) monofilament based CMCs with Si_3N_4 (SRBSN) matrices have been fabricated using tape-cast matrix preforms. Although oxidation of carbon interfaces is a limiting problem for creep and stress rupture, these properties are superior to turbine superalloys.

1. INTRODUCTION

It is now generally recognised that for 'high-risk' engineering applications the use of probabilistic failure criteria, intrinsic to brittle monolithic ceramics, is not acceptable. An alternative solution is the use of long-fibre ceramic matrix composites (CMCs).

The concept of 'damage-tolerance' via stress-transfer to high modulus aligned fibres following matrix microcracking in a service overload transient has been repeatedly demonstrated in CMCs. The classical 3 stage stress-strain response of long-fibre CMCs has also been modelled theoretically, consisting of a linear elastic range followed by a reduced modulus during progressive matrix cracking, reaching an ultimate stress at which fibre failure initiates and a final reduced-stress range associated with energy absorption during fibre pull-out. However, there are major problems in the application of CMCs concerning the difficulty and cost of fabrication,

availability of small diameter ($\sim 10\mu\text{m}$) fibres with high temperature stability during fabrication or service and the synthesis of chemically-compatible and environmentally stable fibre/matrix interface layers which have a suitable debond and shear property within a range of high-temperature matrices.

Most current CMCs based on polymer-precursor SiC-based fibres (Nicalon and Tyranno type) have a fortuitous combination of composition (Si-C-O) and non-crystalline structure which produces a controlled reaction with silicate matrices during fabrication, resulting in carbon-rich interfaces with appropriate debond/shear property. Based on the earlier work of Prewo et al [1], aluminosilicate glass composites such as $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ (LAS) have been used as matrices, in model composites, which form low thermal expansion phases on crystallisation (e.g. spodumene). More recently $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ (CAS) matrix composites have been produced commercially (Corning,

USA) and used in many basic studies of mechanical behaviour. However, relatively few research programmes have concentrated on the systematic variation in interface, matrix and processing parameters in comparing a wider range of microstructure with theoretical prediction. This has been the theme of a number of projects at Warwick which are reviewed in this paper. The research concerns a range of glass and glass-ceramic (silicate) matrix CMCs with differing chemistry and processing parameters together with higher-temperature CMCs composed of CVD SiC monofilaments within silicon nitride or sialon matrices.

2. GLASS AND GLASS-CERAMIC MATRIX COMPOSITES

2.1 Ultimate Fracture Stress

The ultimate theoretical strength (σ_u) of a unidirectional CMC has to be less than that given by the unrealistic assumption of equal load-sharing by all fibres in the cross-section;

$$\sigma_u = V_f \bar{S}, \text{ where } V_f = \text{fibre volume fraction} \quad (1)$$

and \bar{S} = mean fibre strength

More realistic theories involve the statistics for fibre strength (specified by the Weibull modulus m); the treatments of Rosen [2] and, more recently, Thouless et al [3] yield similar values for σ_u but are based on differing assumptions about stress-distribution within fibres in relation to their failure origin. The Thouless et al analysis requires a knowledge of fibre/matrix interface

shear stress τ and matrix microcrack spacing D in addition to m , fibre radius R and strength S ;

$$\sigma_u = V_f S \exp \left[\frac{1 - (1 - \frac{\tau D}{RS})^{m+1}}{m+1 [1 - (1 - \frac{\tau D}{RS})^m]} \right] \quad (2)$$

Using measured values for Nicalon fibres in various glass (borosilicate) and glass ceramic matrices these 'lower-bound' values for σ_u may be compared with experimental values from 3 point bend specimens (typical size 50mm X 3mm depth). In making this comparison it is clear that whereas the higher temperature fabricated glass ceramic matrix composites (GCMCs) provide reasonable agreement with equation 2, with lower temperature glass matrices σ_u , may approach the upper limit (Fig.1). A simplistic explanation is that of thermal degradation of fibre strength and Weibull modulus which is known to occur in the isolated fibre state. Another possibility is that of surface mechanical damage induced by premature crystallisation and absence of totally viscous-flow-densification during hot-pressing. These observations have prompted a more detailed study and refinement of composition and processing variables in relation to fibre surface condition, covering a series of GMCs and GCMCs.

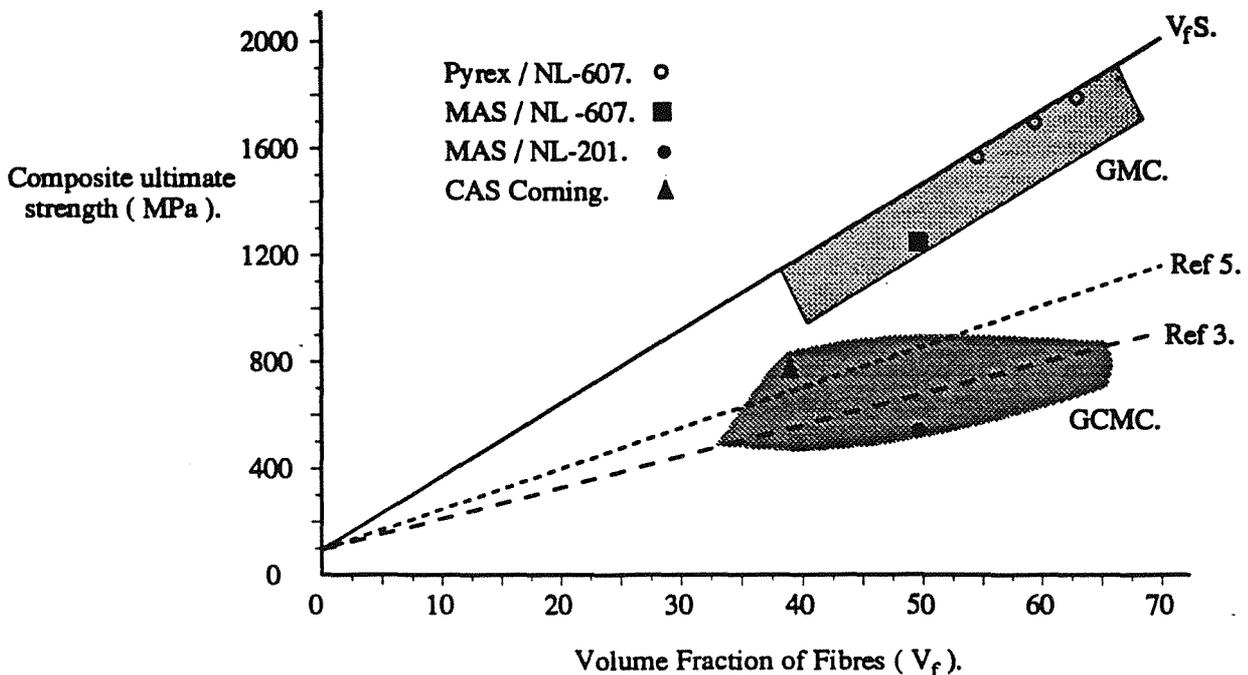


Fig.1 A sample of ultimate bend fracture stresses (σ_u) for GMCs and GCMCs illustrating the improvement in σ_u for MAS compositions relative to borosilicate matrix composites with optimised processing. The reference lines represent typical $\sigma_u - V_f$ relations for tensile fracture according to theory [3,5].

Critical features of the pressure/temperature cycle during hot pressing were a delayed pressure application until beyond the glass softening temperature and a critical choice of pressing isotherm in relation to crystallisation kinetics for GCMCs. Some of these features are summarised in Fig.2 which compares P and T profiles with the 'C-curve' for initiation of crystallisation. There is some control of the latter, and of glass softening range by selection of off-stoichiometric silicate compositions; the most convenient choice is near a eutectic join between primary phase (e.g. low thermal expansion aluminosilicates CAS-anorthite or MAS-cordierite) and binary silicate (wollastonite, CaSiO_3 or enstatite, MgSiO_3). This also facilitates control of matrix thermal expansion α relative to that of the fibre [4], for example cordierite ($\alpha \sim 2.6 \times 10^{-6}$) in phase-mixture with enstatite ($\alpha 8 \times 10^{-6}$) may span the range from negative to positive values with respect to SiC (Nicalon $\alpha \sim 3.1 \times 10^{-6}$).

In addition to P/T cycle and matrix composition, choice of fibre is important in minimising surface 'chemical' damage; carbon pre-coated Nicalon 607 inhibits interfacial cross-diffusion associated with the formation of C-rich layers by in-situ reaction and retains the pristine fibre surface topography and strength.

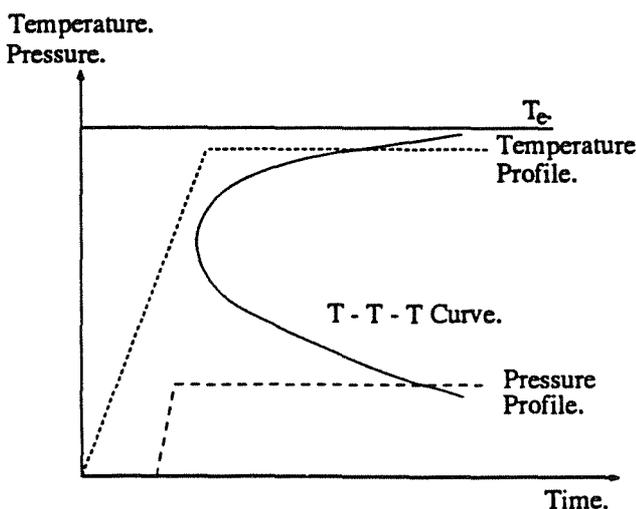


Fig.2 Typical pressure/temperature cycle for GCMC hot-pressing to optimise matrix densification and avoid fibre damage. Pressure application is delayed until glass softening and is followed by rapid densification in the interval before substantial matrix crystallisation (shown via the T-T-T curve in relation to liquidus temperature T_e).

The elevation in GCMC bend strength associated with these combined processing/chemistry changes is illustrated in Fig.1. The MAS matrix composites have an unsurpassed strength near to the upper-bound in

parallel with the borosilicate GMCs. A more limited range of processing variables have been applied to the CAS-matrix compositions but their strength is above that for near-stoichiometric CAS-matrix composites produced commercially (Corning, USA).

In comparing absolute values of ultimate strength with theory there are inevitable difficulties in using bend test data and the lack of precise data for fibre strength and Weibull modulus 'in-situ' after processing. However it is clear that there is little mechanical, thermal or chemical degradation in fibre properties with optimised processing since the lower bound strengths (assuming a Weibull modulus of 3) in Fig.1 use pristine fibre values of ~ 2.7 GPa. This data also supports the recent refinement to theory which assumes that broken fibres may support load by matrix stress-transfer at positions remote from the fracture origin. Curtin [5] has shown that such analysis may increase σ_u by $\sim 30\%$ for $m \sim 3-4$. It is also necessary to correct experimental data for variations in interfacial shear property (τ), although for existing theories (equation 2) σ_u is a relatively insensitive (slowly decreasing) function of τ .

2.2 Matrix Microcracking

In addition to ultimate strength, values of matrix cracking stress and interfacial debond/shear stresses are critical parameters which dictate composite design criteria, for example, the notch sensitivity of CMCs (Fig.3) [6]. In general high ratios of ultimate strength (σ_u) to microcracking stress (σ_m) are required and the latter is associated with low values for interfacial shear stress (τ) in systems with low interface debond energy

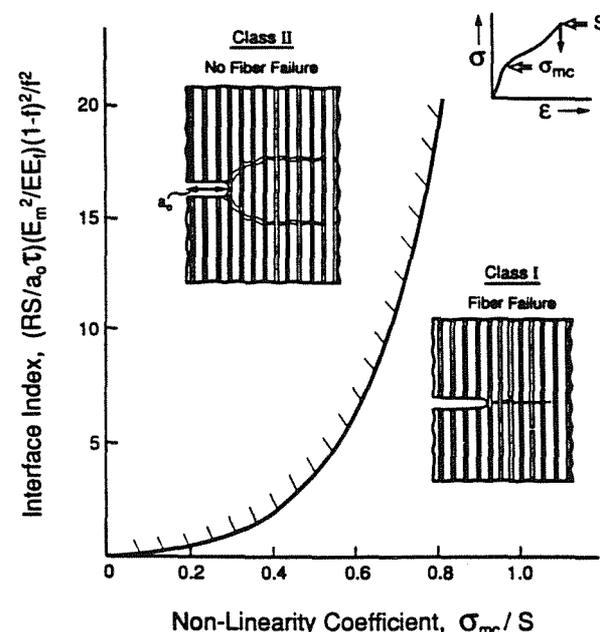


Fig.3. A mechanism map illustrating the influence of microcracking and ultimate stresses (together with interfacial shear stress) on notch sensitivity [6].

(Γ). However, for environmentally sensitive interfaces, such as carbon in oxidising conditions, it is preferable to maintain a moderate σ_m to minimise atmospheric exposure.

An attempt has been made to use GMCs and GCMCs to experimentally model microcracking response in relation to variations in interface microstructure and micromechanical measurements of debond and shear property. Microcracking stresses may be estimated from the thresholds for significant acoustic emission from bend specimens, which is considered more reliable than the detection of non-linearity in stress-strain. Fig.4 is an example of acoustic signal in comparison with a 3pt. bend stress/deflection relation from the high-strength MAS matrix composite.

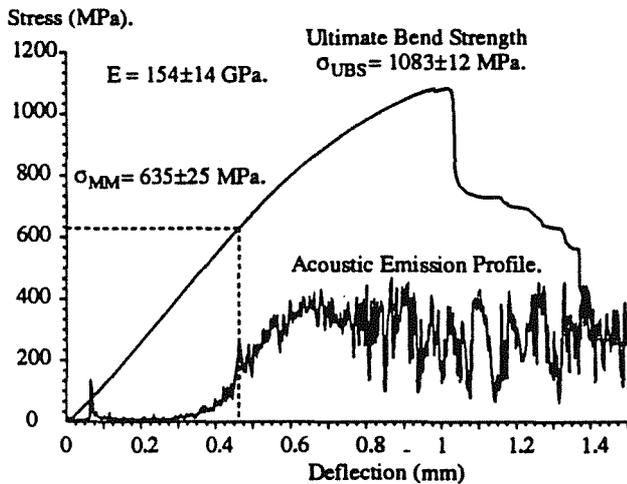


Fig.4 3 point bend stress/deflection plot for a high strength Nicalon 607/MAS matrix composite. Acoustic emission from the composite is recorded during the test to indicate the initiation of matrix cracking.

To measure τ and Γ the technique pioneered by Marshall and Oliver [7] using indentation 'push-down' of exposed fibre ends on transverse polished surfaces has been used. A novel indent system, operating within a scanning electron microscope (SEM), has been developed [8] which has a higher load capability than conventional 'nano indentors' (20N compared to 0.1N). A smaller radius diamond indenter also enables greater fibre sliding distances (u), measured to a positional resolution of < 10 nm using a capacitive gauge attached to the end of a computer-controlled piezo 'inchworm' translator. Load (F) is continuously monitored to a precision of < 1mN using a 'hard' piezo load-cell directly interfaced with the diamond mounting. Within the SEM a simultaneous monitoring of image enables an exact indenter positioning and a correlation of interface debond and sliding events with discontinuities in load/displacement curves. Software has been developed to facilitate the subtraction of displacements due to indent-plasticity and

to plot the F^2 vs u relation [8] from which Γ and τ are calculated using intercept and gradient, respectively. The indentation response is dependent on interface microstructure and, in turn, on processing parameters and matrix and fibre chemistry [9]. Values of 2Γ and τ are listed in Table 1, for a range of GCMCs and interface types, and used to compare theoretical and experimental microcracking levels.

The gradation in matrix microcracking stress (σ_m) follows that in τ but the precise correlation with theory is inhibited by the uncertainty in σ_m defined by the acoustic emission threshold. Using appropriate values for V_f (~40%), fibre and matrix moduli, fibre radius ($r = 7-8\mu\text{m}$ for Nicalon) and matrix fracture energy (Γ_m), combined with experimental values of τ , only moderate agreement with experimental σ_m values is obtained from the expression [10];

$$\sigma_m = \left[\frac{6\tau\Gamma_m E_f E^2 V_f}{r E_m^2 (1-V_f)} \right]^{1/3} - p \frac{E}{E_m}$$

(where p = longitudinal residual stress in matrix)

Typical composite behaviour (a 3-stage stress-strain relation) is observed for 2Γ and τ values up to $\sim 20\text{Jm}^{-2}$ and ~ 50 MPa, respectively. The theoretically-predicted debond condition Γ (interface)/ Γ (fibre) < 1/4 is apparently not obeyed, assuming typical Γ (fibre) values < 10 Jm^{-2} . Alternatively, measured values for Γ (interface) are too large.

The influence of thermal expansion mismatch between fibre and matrix on Γ and τ is visible in comparing LAS and CAS matrices which give rise to similar interface microstructures but a reversal (from -ve to +ve) in the α values relative to the fibre. For borosilicate matrices, which have similar α values to the fibre, the high Γ and τ values are dominated by the limited interface reaction thickness at the lower fabrication temperature.

2.3 Environmental Stability

The influence of heat treatment in oxidising (air) environment on interface properties and on macromechanical response is generic for composites with C-enriched interfaces; a retention in strength with little change in interface behaviour above $\sim 1000^\circ\text{C}$ and a reduced strength with enhanced statistical spread in strength and interface property in the 400-800 $^\circ\text{C}$ interval.

The data, exemplified in Fig.5, may be explained by the active oxidation (CO or CO₂ loss) of C-rich interfaces

Table 1. Interface debond energies Γ and shear τ for various glass and glass-ceramic matrix composites together with experimental and theoretical matrix microcracking stresses, the latter calculated with and without residual stresses due to thermal mismatch.

Composite/processing condition	$2\Gamma/\text{Jm}^{-2}$	τ/MPa	σ_m/MPa	Theoretical σ_m/MPa	
				inc.res.stress	w/o res.stress
CAS/Nicalon as pressed	9.6 ± 1.2	25 ± 3	390 ± 30	450	370
MAS/Nicalon - 607 as pressed	12.4 ± 5.4	48 ± 15	640	690	530
Borosilicate/Nicalon 607 950°C, 20min.	17.8 ± 8.6	111 ± 108	1000		
Borosilicate/Nicalon 607 1100°C, 20min.	20 ± 7	51 ± 9	600	510	510
LAS/Nicalon - 607	2.2 ± 0.8	14.5 ± 10	-	230	350
BMAS/Tyranno as pressed	1.2 ± 1.6	25 ± 7	-	450	490

at intermediate temperatures by 'channelled', longitudinal, gas transport along fibre interfaces from exposed fibre ends. There is a limited fibre surface oxidative degradation and fibre-matrix 'bridging', giving reduced fibre strength and increased τ . Above 1000°C passive oxidation of SiC (SiO₂ formation) inhibits continued 'channelled' reaction from fibre ends. Further oxygen ingress is limited, in the absence of matrix cracking, to diffusion through the glass-ceramic [11, 12]. Matrix diffusion is surprisingly slow in well-crystallised glass ceramics and, for example, in the CAS composition interface oxidation is limited to a few fibre diameters (10-30 μm) from the free surface. In this surface layer fibre/matrix interfaces are totally 'bridged' by SiO₂ and exhibit immeasurably-high debond and shear levels consistent with zero interface crack deflection.

An important observation is the retention of composite (and hence fibre) strength in the protected state within silicate matrices even following long heat-treatment (> 100 hours) up to 1200°C. This is accompanied by a measurable change in order (or microcrystallite size) in Nicalon fibres and demonstrates that the key problem of strength-loss is related to changes in surface microstructure, probably oxidation-induced.

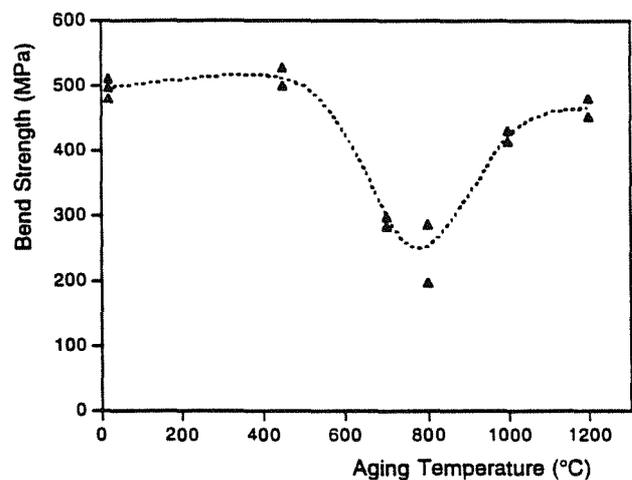


Fig.5(a) Variation in bend strength with oxidising heat treatment (100 hours) for CAS/Nicalon.

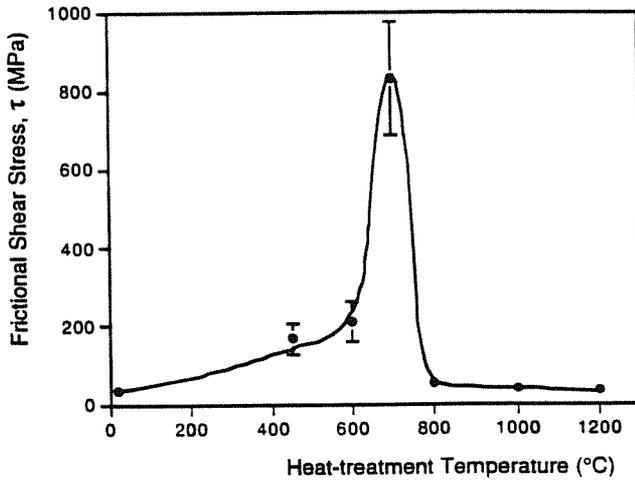


Fig.5(b) Interfacial shear stress τ for the CMCs tested in (a).

2.4 Creep Deformation

Data has been obtained for bend and tensile creep of GMCs and GCMCs at stress levels below σ_m within two temperature regimes; that where both fibre and matrix undergo measurable creep in the isolated state (above $\sim 1000^\circ\text{C}$ for Nicalon) and that where fibres exhibit only elastic deformation.

There is approximate agreement with theoretical prediction based on parallel spring/dashpot elements;

- (i) Creep rates ($\dot{\epsilon}$) are largely fibre-controlled and hence much smaller than matrix rates
- (ii) Nicalon/borosilicate glass composites are limited (by glass softening) to temperatures (400-600°C) where fibres are elastic and hence undergo transient creep; the rate of approach to zero creep is related to matrix creep rate and hence temperature, which agrees with theory [13];

$$\dot{\epsilon} = \alpha \dot{\epsilon}_m [1 - (V_f / \sigma) e]^n$$

$$\text{where } \alpha = \left[\frac{E_m(1-V_f)}{E_f V_f + E_m(1-V_f)} \right] (1-V_f)^n$$

and E_f, E_m are Young moduli of fibre and matrix, V_f = fibre fraction and n = matrix stress exponent

(iii) GCMCs above $\sim 1000^\circ\text{C}$ exhibit classical primary + steady state creep at a composite rate $\dot{\epsilon}_c$ dictated by load-sharing between fibre and matrix [14];

$$\sigma_c = \frac{\sigma_{fo} V_f \dot{\epsilon}_c^{\frac{1}{n}}}{\dot{\epsilon}_{fo}^{\frac{1}{n}}} + \frac{\sigma_{mo} V_m \dot{\epsilon}_c^{\frac{1}{m}}}{\dot{\epsilon}_{mo}^{\frac{1}{m}}}$$

where fibre and matrix creep rates ($\dot{\epsilon}_{fo}$ etc) for stresses (σ_{fo} etc) are measured in isolation and give stress exponents n and m , respectively.

There is evidence that oxidative interface reactions in the critical 400-800°C interval may be responsible for reduced stress-rupture lifetimes, due to loss of fibre strength, especially above σ_m .

3. HIGH TEMPERATURE NITRIDE-MATRIX COMPOSITES

3.1 Microstructure

In the quest for higher temperature performance there is a recognition that currently-available polymer-precursor fibres are intrinsically unstable above 1100-1200°C. Whereas the ultimate solution may rest with oriented oxide monofilaments, there have been a number of CMC studies using CVD SiC monofilaments (Textron SCS) which have a modest strength retention and microstructural stability to $\sim 1400^\circ\text{C}$. They may be incorporated within reaction-bonded silicon nitride (RBSN) at such fabrication temperatures [15] but matrix porosity results in a susceptibility to oxidation of pre-coated carbon-rich interfaces (typically using SCS6 grade filaments). A novel approach to matrix densification, at Warwick, utilises the SRBSN route of intermediate temperature nitriding/partial sintering, using a Si/Si₃N₄ powder mix containing a liquid-sintering aid, followed by a brief liquid sintering under pressure at $\sim 1700^\circ\text{C}$ [16,17]. Single layer filament + powder preforms are made by simultaneous filament winding and tape-casting which produces a regular microstructure on subsequent layer-stacking, nitriding and hot-pressing.

The CVD monofilaments appear to tolerate short excursions to the final sintering temperature with little change in the fine columnar SiC crystal size but with the appearance of microporosity (possibly due to free Si or C reaction/evaporation). A key to composite performance is the survival of part of the carbon precoating; the reaction $3\text{C} + \text{Si}_3\text{N}_4 \leftrightarrow 3\text{SiC} + 2\text{N}_2$ may be shown (using the MTDATA thermodynamic programme - NPL, UK) to proceed in favour of SiC above a critical temperature of $\sim 1400^\circ\text{C}$ at 1

atmosphere N_2 partial pressure. Continued reaction is limited by diffusion through the SiC reaction layer. The matrix is a typical liquid-phase sintered (SRBSN) microstructure of micron-sized βSi_3N_4 or β' Sialon crystals in a glassy residue of the sintering medium (MgO , Al_2O_3 and Y_2O_3 additives were used in varied combination [17]).

Interface microstructure is unstable for long heat-treatments in oxidising atmospheres (100-1000 hours in the 1000-1400°C interval) due to channelled reaction from fibre ends. Channel closure due to passive SiC/Si₃N₄ oxidation is less effective in these microstructures which have very large interface widths ($\sim 5 \mu m$ compared with $\sim 50 nm$ in GCMCs).

3.2 Mechanical Behaviour

Interfacial mechanical data, obtained from filament 'push-through' tests yield shear stresses, τ , of 2-4MPa, with little change from the relatively low debond shear stress. Debonding and shear occurs at the inner carbon interface of the fibre coating and not at the outer reaction interface. The low debond and shear values may result from thermally-induced separation over part of the interface due to the higher expansion coefficient of the fibre. There is little change in τ with oxidising heat-treatments up to ~ 100 hours at 1200°C, during which only partial carbon removal occurs. For longer times τ is reduced to negligible levels, with total filament debonding during specimen polishing.

observation of smaller pull-out lengths and reduced filament strength, probably due to atmospheric interaction (it is known that uncoated monofilaments suffer a 50% strength reduction [18]).

3.3 Creep and Stress-Rupture

Bend-creep has been studied at 1300°C for stresses between 150 and 300 MPa (i.e. below the matrix cracking stress in the linear part of the stress-strain plot for constant-imposed strain rate tests). For all stress levels the creep curves may be resolved into transient and steady state components consistent with a partial load transfer to the monofilaments which have been calculated, from literature data [19], to creep in the isolated state at a slower rate than the composite. All creep curves have a shape consistent with a temperature for measurable simultaneous creep of both matrix and fibre. Unlike GCMCs the disparity in matrix and fibre creep rates is not large.

Stress-rupture tests were conducted between 200 MPa and 400 MPa at 1300°C, using 500 MPa as a zero-time failure stress based on monotonic tests between 1200 and 1400°C. The composite appears to show an almost stress-independent failure limit at ~ 1000 hours. This is symptomatic of a time-dependent interface oxidation coupled with fibre strength degradation. The data has been plotted for comparative purposes in the form of a 'Larsen-Miller' diagram (Fig.7) which combines time (t) and temperature (T) on a single axis via a parameter

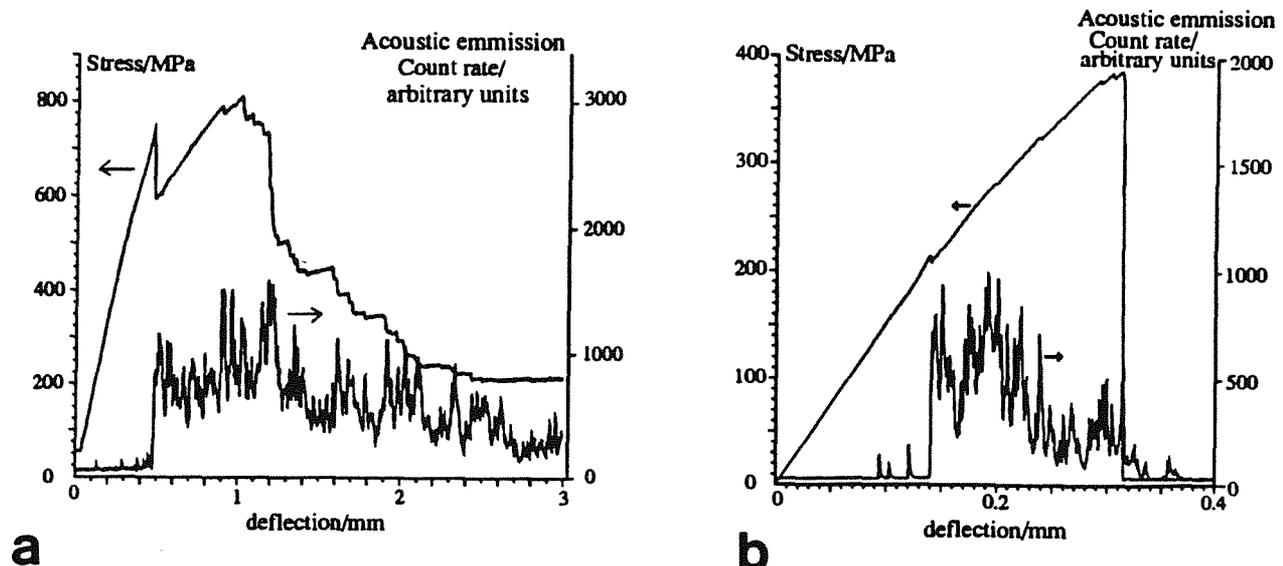


Fig.6 Stress-deflection and stress-elongation curves for 3 point bend (a) and tension (b) tests on a SiC monofilament/SRBSN matrix U.D. composite. Acoustic emission traces are used to detect matrix cracking for comparison with non-linearities in stress-strain plots.

$P = T \log (C + t)$. The constant C is empirically adjusted to enable data from different temperatures to fall on the same line. The data for various stages in evolution of 'superalloy' turbine materials is compared

with that for the CMC which shows a significant increment in Larsen-Miller parameter P , at least for low stress levels.

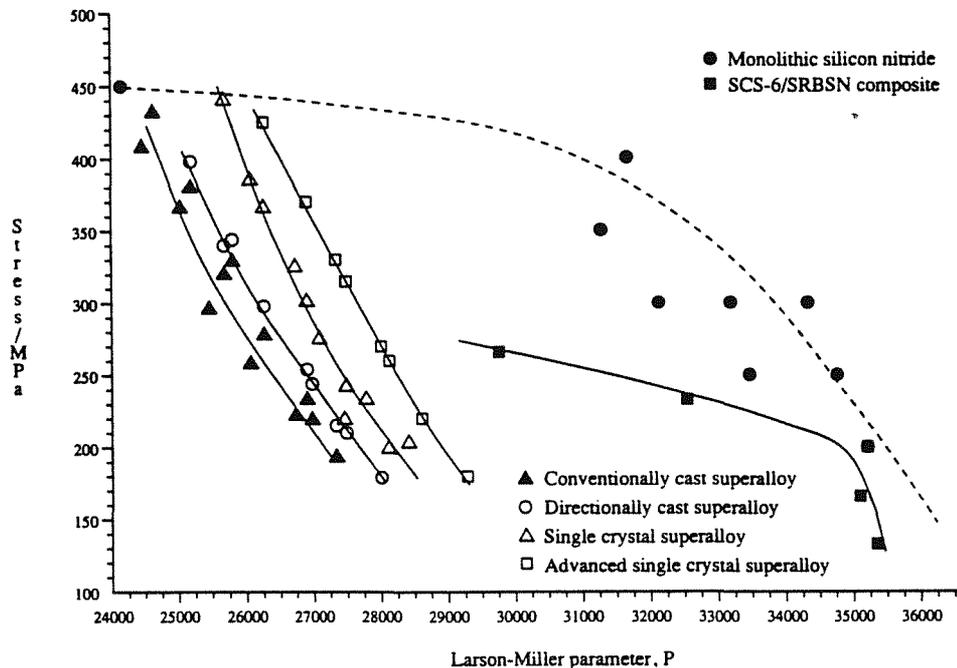


Fig.7 Stress-rupture data for a SiC monofilament/SRBSN matrix composite compared with that for a range of turbine superalloys and a typical monolithic silicon nitride (data from [20]). The Larsen-Miller parameter ($P = T \log [c+t]$) is used to compare the time/temperature influence on a single axis.

4. CONCLUSIONS

The selection of pressure/temperature cycle in relation to matrix chemistry and initial fibre condition is critical in avoiding mechanical and chemical damage to fibre surfaces during fabrication of CMCs. With optimised conditions GCMCs with ultimate bend strengths in excess of 1 GPa are obtainable. High ultimate strength is important in relation to an ability to maintain moderate ratios of σ_u/σ_m for varying σ_m . The value of σ_m in GCMCs is most conveniently controlled via interfacial shear stress τ which varies, typically, from 10-50 MPa and is a function of time and temperature of fabrication as well as chemistry and thermal expansion of matrix relative to fibre. Measured values of fibre-matrix debond energy are sometimes higher than the theoretical limits predicted for ideal composite response.

Interface oxidation is a critical problem at intermediate temperatures (400-800°C) due to channelled reaction from fibre ends. This mechanism is suppressed above ~1000°C by channel-blocking with the SiO₂ oxidation product of SiC. A silicate-coating or preoxidation treatment of exposed fibre ends may resolve the intermediate temperature problem but a stress limit remains that for microcrack exposure of interfaces.

Textron CVD SiC monofilament-reinforced Sialon and Silicon Nitride matrices have been explored as higher temperature CMCs. A novel preform-preparation method using matrix tape-casting has been used in conjunction with SRBSN matrix chemistry/processing. Composite response and moderate fracture energy may be achieved utilising a partially-sacrificial thick C-rich interface which has a very low τ value (2-4 MPa). The oxidation problem of C-rich interfaces is retained at higher temperatures than for GCMCs due to the difficulty in channel-blocking of thick interfaces. Despite the oxidation problem creep and stress-rupture properties exhibit useful increments over turbine superalloys.

ACKNOWLEDGEMENTS

The research surveyed in this paper has been supported by the SERC and Rolls-Royce plc. The use of unpublished data from research colleagues (A.M. Daniel, A. Chamberlain, A.G. Razzell, S. Sutherland, K.P. Plucknett and M.W. Pharaoh) is gratefully acknowledged.

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