SYNTHESIS REPORT

FOR PUBLICATION

CONTRACT No: BRE2. Cw2. 0352

PROJECT No: BE(W74 -91

TITLE: THE DEVELOPMENT OF A NEW Low COST ROUTE FOR MAKING TOUGH CERAMICS

PRomE'cT COORDINATOR: w J cuEGG
UNKVERSHY OF CAMBRIDGE

PARTNERS:

(XLM'VIIQLIES El' COMPOSmES
DAIMILER BENZ
VOLVO AERO CORPORATION
MOTOR UND TLJRBHW3N UNION
TIOXIDE SPECM.LH'IES
'SVENSKA KEMMINSTITUTET
uNPmRsrrY OF cAIMBRmGE

REFERENCE PERIOD FROM i .1.93 to 31.12.95

starting Date:J .1.93

Duration: 36 months

PROJECT FUNDED BY THE EUROPEAN COIWV'IUNITY UNDER THE l$RrrE/EuRAM lPRoG!RAiw?m

A Simple Way to Make Tough Ceramics

W,J. Cleggl, G. Andrees2, E. Carlstr6m3, B. Grievson4, R. Lundberg5, A. Kristoffersscm3, E. Menessier~, R. Meistring7, A. Schoberth7 and M. Bougoin6

[1] Department of Materials, University of Cambridge, U. K.; [2]Motoren und Turbinen Union, Germany; [3]the Swedish Ceramic Institute, Sweden; [4]Tioxide Specialties, U. K.; [5]V01v0 Aero Corporation, Sweden, @ramiques at Composites, France; [7]Daimler-Benz, Germany.

Abstract

AittioLigh high toughness ceramic composites have been avaiiabie for many years they have found litde industrial application due prtlnariiy to their high cost, associated both with the $bres and with the processing techniques. Recently the possibility of preventing catastrophic failure by using layered ceramic structures has been demonstrated. The aim of this work is to inves~igate whether such materials have usefui properties under reaiistic conditions. This has been done by studying the behaviour of these materiais under the conditions in a combustor, where resistance to thermal shock, thermal cycling and and vibration is required. Initial laborato~ tests showed that iaininates had greatly improved thermal shock properties compared with the monolith and that the presence of the crack deflecting interlayers did not lead to a degradation in the fatigue behaviour, These improvements were borne out in the operating performance of a combustor lining made from laminated tiies.

Introduction

The most successful method to date for producing high toughness ceramic composites has been the chemical vapour infiltration (CVI) of continuous fibre preforms 1. Unfortunately the complexity of the process and the length of time required render these materials so expensive that despite their good properties they have found only very limited application. Furthermore the fibres themselves are expensive and do not have satisfactory performance at high temperatures. Recently an alternative approach, based on a biological analogue, has been demonstrated where ceramic powders are formed into thin sheets or fibres and then coated before compacting together and sintering without any pressure to give the structures shown in Figure 13~4.

However preliminary work showed that, although crack deflection occurred, the properties of these materials were different to those of fibrous composites. In particular, laminates give no benign failure in tensions and any improvement in properties is restricted to the situation in which cracks are traveling in the direction transverse to the crack deflecting interlayers. Furthermore, the presence of continuous interfaces suggests that these materials will be weak in shear, whilst fatigue in bending might Iead to delamination of the interlayers. It is clear that the properties of laminates are not as good as those of composites. However because fibrous ceramic composites are so difficult to make, the question arises as to whether the properties of ceramic laminates are good enough for certain applications. The objective of this programme is to see whether such Iaminated materiaIs offer useful properties by designing and making a suitable component and then testing it under reaiistic conditions.

Toughening ceramics either by lamination (or by incorporating fibres) increases the work required to break the material but does not increase the maximum strength when compared with a monolithic ceramic. Toughened ceramics are therefore most likely to find uses in components which carry high thermal loads (where a given strain is applied) and relatively small mechanical loads (where a given stress is applied).

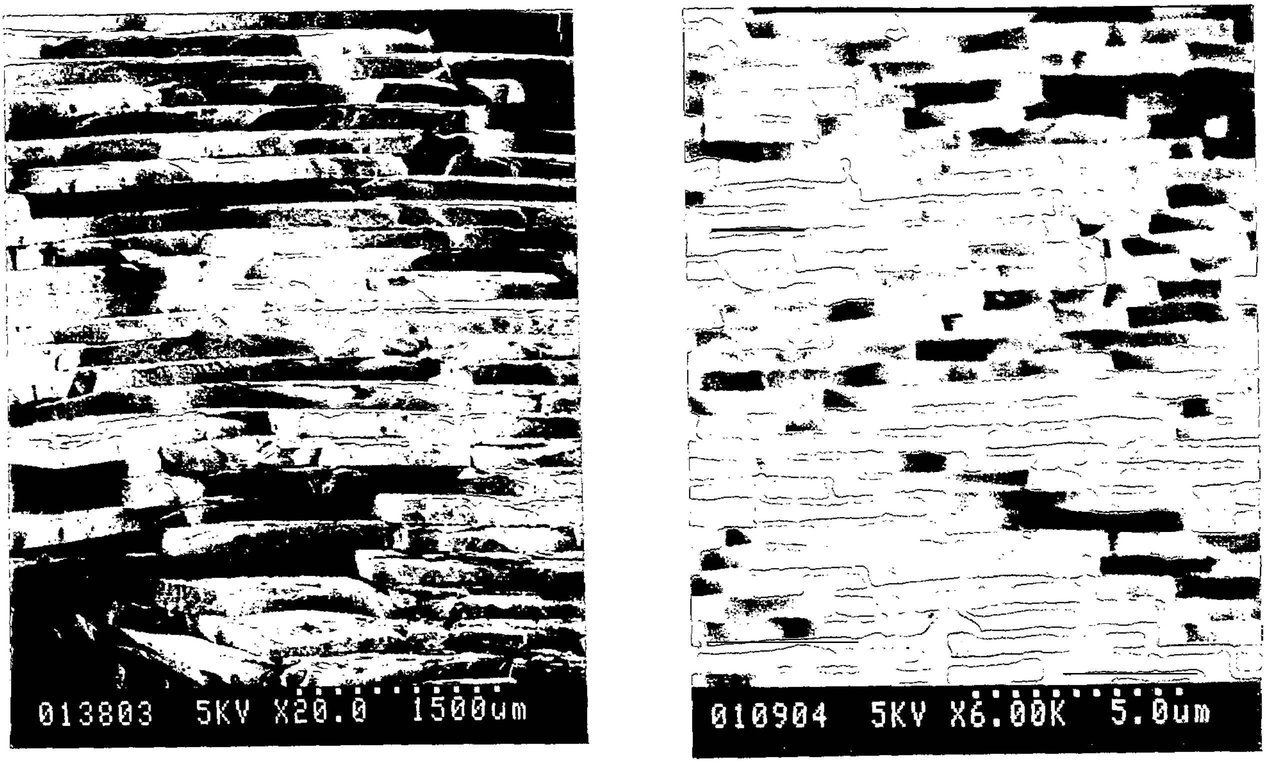


Figure 1 – Showing the fracture surfaces of (left) a laminate made of silicon carbide laminae and graphite interlayers and (right) the mollusc shell Pinctada *Margarit$era.*

A ceramic combustor lining for small land based gas turbines was chosen as a suitable demonstrator. Such turbines are likely to be used for power generation in hotels and hospitaIs allowing the recovery of the waste heat. This is thought to be the major area of market growth for turbines. Although existing combustors are made from superalloy, their use is only possible by forcing cooling air through the walls of the component and over the internal, that is the hot, surfaces. Where this cooling air impinges on the flame the local temperature rises allowing the reaction between oxygen and nitrogen in the air to take place more rapidly and increasing the emissions of nitrous oxides produced by the turbine. Overcoming these problems requires the development of a combustor lining which does not require film air cooling. LTnfortunately monolithic ceramics fracture under the severe thermal shock and thermal cycling which these components must withstand whilst composites, although possible, are too expensive for such a large scale application.

Previous work had shown that the thermal stresses cause the component to be loaded essentially in bending. This gives rise to shear stresses on the mid-plane of the component, which is also subject to vibration, effectively high cycle fatigue in bending. In this way it will be possible to see whether problems arise due to a reduction in the shear and fatigue properties, whilst testing the component subjected to stresses where advantages might be obtained, that is in bending.

The combustor lining has the added advantage that existing designs use a tile construction made of single and double curved tiles, allowing testing under rig conditions to be carried out with the minimum of effort.

Experimental

Specimen Fabrication

A &silicon carbide powder doped with 0.4910 boron (Superior Graphite, HSC-059S) was mixed with approximately 4070 by volume of an aqueous polymer solution (Nippon Gohsei, KH17s) using a Z-blade mixer from which the air had been evacuated. The resulting plastic mix was then rolled into sheets approximately 200 ~m thick and coated with colloidal graphite (Aquadag). The dried sheets were then stacked and pressed together under a pressure of 10 MPa. The resulting plaque was then heated at 1 K per min to 450 “C to pyrolyse the polymer before heating to 2050 “C under flowing argon for 30 minutes. The resulting plates had densities at least 95% that of the theoretical density, taken as 3.21 Mg m-s.

For the combustor single and double curved tiles were also required. Single curved tiles could be simply produced by pressing the coated sheets in a suitable mould, giving a plaque of the appropriate shape. Sintering was usually carried out in a shaped graphite die,

Fabrication of the double curved shapes was more complex. In this case the shape cannot be formed simply by shaping the sheets around a die without the formation of wrinkles. This is a problem well known in the forming of polymer composites One possibility would be to stretch the sheets of silicon carbide filled polymer around a die of the appropriate shape. Unfortunately the sheets were not sufficiently plastic to allow the stretching of the form from a flat sheet. The alternative, that was adopted here, is to remove the material that wm.dd otherwise form the wrinkles, by cutting V-shaped portions from that part of the sheet which is to become the double curve. The double curved parts were then formed by making an appropriate lay-up of the cut sheets, before hot pressing and sintering as before. The resuiting combustor Iining made of both singIe and double curved tiles is shown in Figure 2.

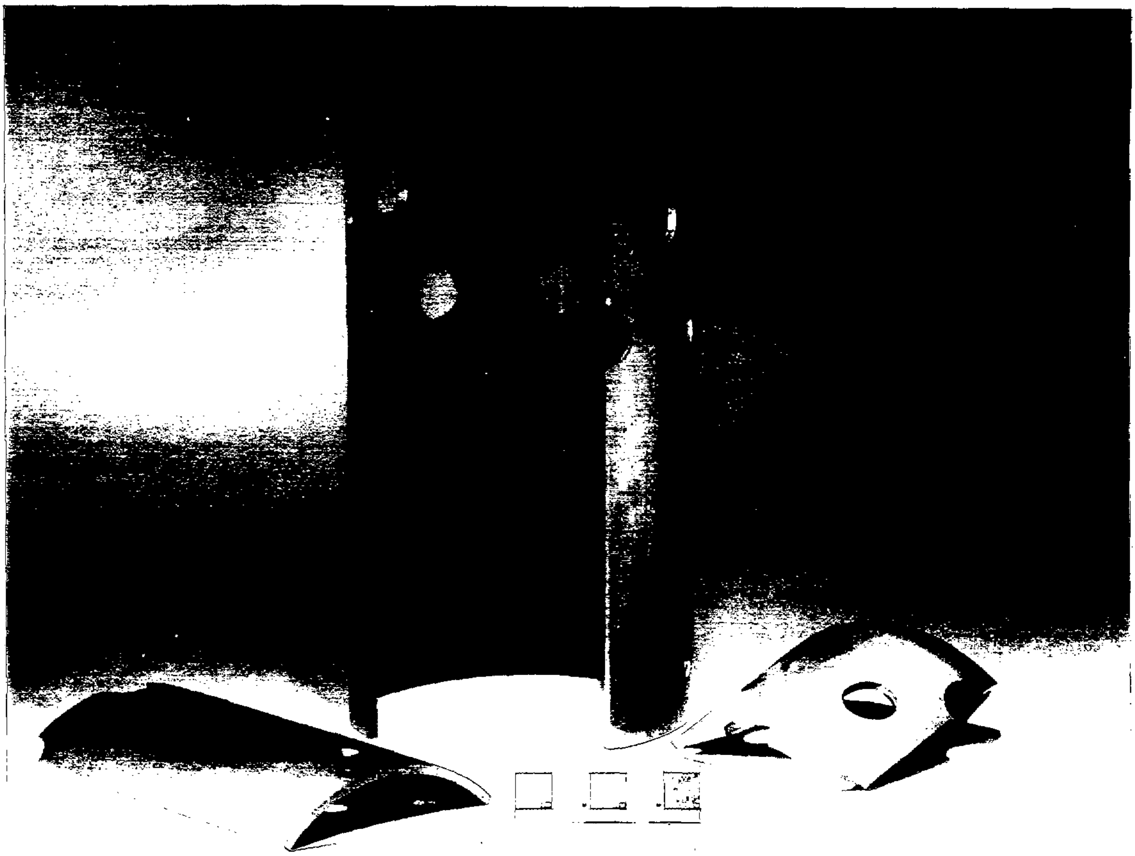


Figure 2 – Showing the combustor iining made from laminated tiles before coating.

To prevent oxidation of the graphite layer and enable testing. in air at high temperature, the sample was coated with a layer of crystalline /3-silicon carbide iaid down by chemical vapour deposition from a mixture of hydrogen and trichloromethyl silane at 1200 “C. This was found to give complete oxidation protection even in extended heat treatments lasting thousands of hours. Clearly the use of an interlayer material which could be removed within minutes if the coating cracked, leading to the compIete disintegration of the component, is highly unsatisfactory for use in any real application. However it does allow the idea that there might be improvements in the properties to be studied in the laboratory. More recently the possibility of using porous interlayers has been demonstrated, giving rise to substantial improvements in oxidation behaviour[8,9] as well as removing the potential for interracial crack growth due to differences in the thermal expansion coefficients between the matrix and the interlayer material as has been identified in some systems.

A range of mechanical properties were measured. For successful operation of the combustor lining the material must have sufficient resistance to thermal shock and thermal cycling as well as vibration, which is equivalent to high cycle fatigue in bending. The latter was an especial concern, as a driving force exists for the growth of cracks from the ends of the sample, whilst the resistance to interface cracking has been reduced by the presence of the crack deflecting graphite interlayers. Some shear testing was also carried out.

Shear Testieg

Shear testing was carried out using either the cut shear test or the doub~e notch shear test. In the case of the cut shear test a macroscopic shear stress is applied by two blades moving parallel to the plane of the interlayers. The samples tested were 25 mm thick, with a width transverse to the plane of the iriterlayer of 12 mm. The double notch shear test 10 is similar in concept to that of the lap shear test, [1]1 except that the applied loads are compressive rather than tensile, as shown schematically in Figure 3. Specimens were tested with ratios of specimen length to notch separation varying between 4.5 and 6.5. All samples were tested uncoated.

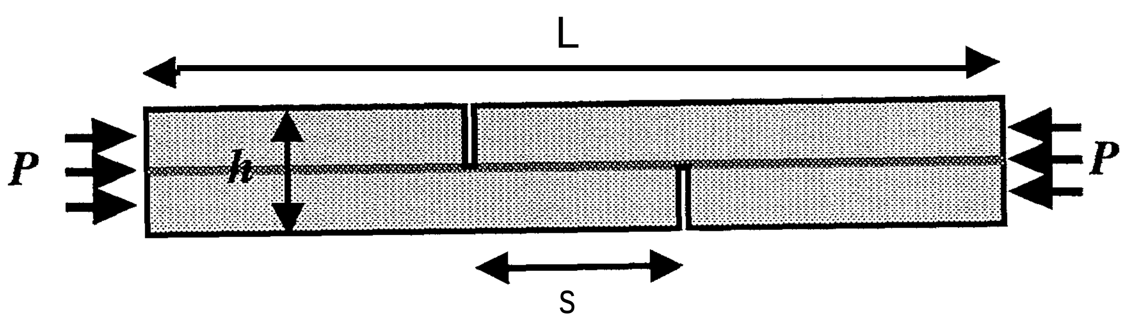


Figure 3 – Schematic of the specimen geometry in the double notch shear test.

Fatigue **Testing**

Initial experiments were carried out in three-point bending on samples with a thickness of 3.3 mm and a loading span of 60 mm. The load was cycled in a sinusoidal fashion with the maximum stress being set between 65% and 100% of the mean strength under monotonic loading. The minimum stress was always 10% of the maximum. Tests were discontinued after 3 x 10$ cycles if the samples had not failed. Such samples were then monotonically y loaded to investigate whethel any strength reduction had occurred during fatigue.

The resistance of both coated and uncoated materials to vibration in the engine was simulated by cycling the samples at their fundamental frequency through a given deflection. Samples 3 mm thick, 10 mm wide and 100 mm long were gripped in steel jaws with an intermediate plastic foil to minimise any contact stresses. The test wouid stop if there was a decrease in the frequency of more than 1%. If after 106 cycles the sample had still not failed the amplitude was increased.

Thermal shock and cycling

ThermaI shock and thermal cycling were carried out using an upright combustor, equipped with a sIiding sampie holder above the hot gas nozzle. Two samples at a time weree mounted on the rig, one being located in the stream of hot gas, and the other over the cold air nozzie. The temperature changes are generated by moving the samples. Tests were carried out on samples approximately 3 mm thick, 12 mm wide and 100 mm iong by heating for 5 minutes in the hot gas followed by cooling in the stream of cold gas also for 5 minutes before being returned again to the hot gas.

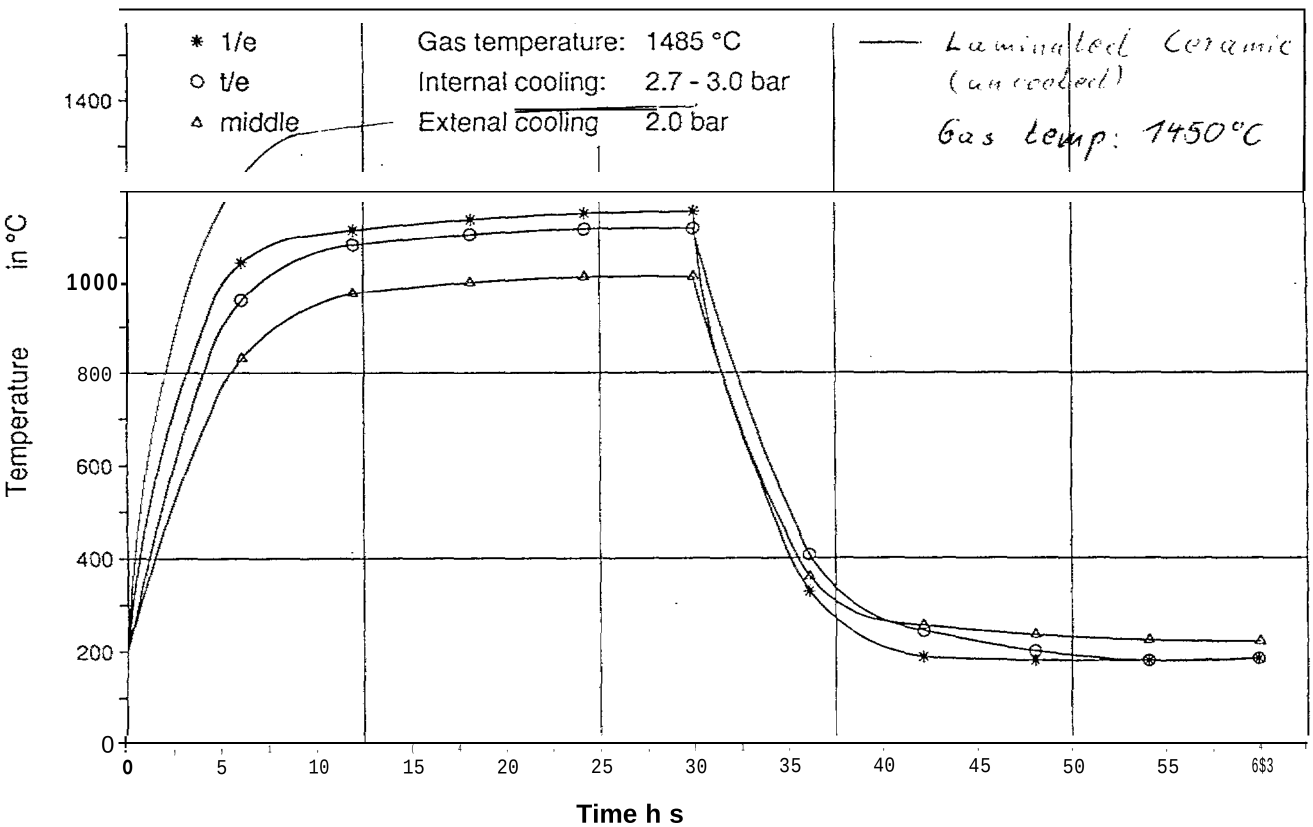


Figure 4 – Showitig how the surface temperature increases with time when a silicon carbide iaminate is put into the combustor flame.

The temperature of the hot gas was measured with a Pt/Rh-Pt thermocouple located inside the hot gas nozzle 20 mm from the discharge opening. The temperature can be controlled by maintaining a constant flow of fuel and adjusting the air flow. The rate at which the surface temperature of a sample increases with time after being put into the hot combustor flame with a gas temperature of 1450 ‘C was measured with a specimen where thermocouples had been fixed to the surface and is shown in Figure 4.

Table 1- Showing the test conditions for the combustion chamber.

Test number	1	2	3
Inlet Temp (K)	623	773	823
Outlet temp (K)	1523	.1800	1600
Gas pressure (bar)	2	2	4
Cycles	3	10	10
Test time (hr)	5	3.5	1.6

Testing the complete combttstor lining

The overall combustor is made up of three separate parts – an external metal supporting structure, a metal casing and eight internaI ceramic tiles. The tiles are suspended in such a manner so as to minimise any stresses due to assembly during the operation of the combustor. The details of the chamber and test method are described elsewhere.

The combustor testing carried out so far has been using a lining of four single curved tiles of laminated silicon carbide and four double curved tiles of monolithic silicon carbide inserted into the metal casing. Three tests were carried out under the conditions shown in Table 1.

Results

Shear Testing

Tests on the DNS specimens showed that the material deformed elastically, before rapid interracial crack growth took place from the notches. Attempts to use analyses such as those of Kendall for the lap shear jointl [1] and derive an interracial fracture energy gave results dependent on the specimen geometry and different from the values of interracial fracture energies obtained elsewhere over a wide range of lading states. However, dividing the failure load by the area of sample in between the transverse notches gave reasonable agreement between samples of differing values of specimen length to notch separation. Using this approach, the apparent shear strength of the interface, ~i , was measured as 26~7 MPa.

The cut shear tests gave rather lower vaIues of 6+1 MPa. The reason for the difference is not clear. As the interfaces are made in an identical fashion it might be expected that for an interface of a given fracture energy and defect size their strength would be similar. Possibly the effects are due to difference in loading state. However, the DNS test might be expected to give the lower failure load due to the occurrence of bending in the central portion caused by the misalignment of the neutral axes of the regions close to the transverse cracks and the remainder of the sample gives rise to a contribution to the interracial crack driving force.

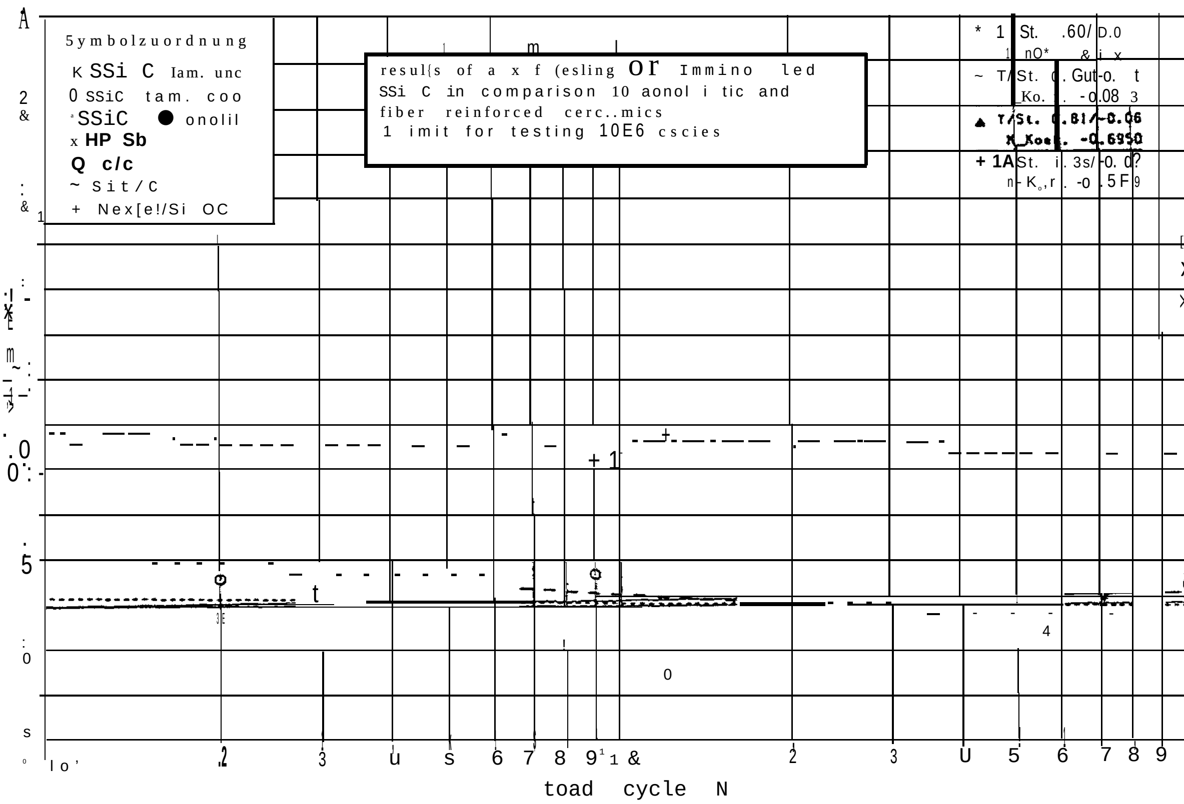


Figure 5 – Showing the amplitude multiplied by the frequency of the vibration plotted against the number of cycles to failure.

Fatigue Testing

The mean strength of monotonically loaded samples was 334~90 MPa and 327*44 MPa for coated and uncoated materiak respectively. Generally it was found that either that if failure did not occur during the first loading cycle, that is the strength of the sample under monotonic loading was less than the mean strength. In that case the samples survived fatigue, even where cycling loads were applied to 98?+0 of mean monotonic strength, suggesting that the material is insensitive to fatigue. This view is confhrned by examining the residual strength of samples after fatigue testing which show that there is no reduction in strength. This behaviour is typical of materials where irreversible deformation does not occur.

For the vibration tests the amplitude multiplied by the frequency is plotted against the number of cycles to failure. The results for the monolithic and laminated silicon carbides, both coated and uncoated, are shown in Figure 5 and compared with results for a hot pressed silicon nitride. Although the silicon nitride has a better fatigue resistance, the fatigue resistance of the laminated silicon carbide is not diminished compared with the monolithic material, indicating that the introduction of the crack deflecting layers is not damaging, as might be expected.

Thermal Shock and Th.errmd Cycling

Tests on uncoated materials resulted in complete delamination of the material due to oxidation of the graphite. Monolithic samples also fractured catastrophically. However, coa[ed laminates survived intact apparently undamaged. No cracks or defects were visible after testing as shown in Figure 6. This is clearly a considerable improvement over monolithic material. The reason for this behaviour is not understood. One possibility is that the presence of the compliant graphite layers somehow reduces the stresses within the thin silicon carbide layers. This seems unlikely as it has been observed elsewhere that small fIaws within the laminae grow under applied mechanical loads at stresses similar to those where there are no graphite layers. Even continued cycling gave rise to no further damage observable either metailographically or by measuring the residual strength of the test bars, as shown in Table 2.

Table 2- Showing the Young modulus and strength after therrmd cycling.

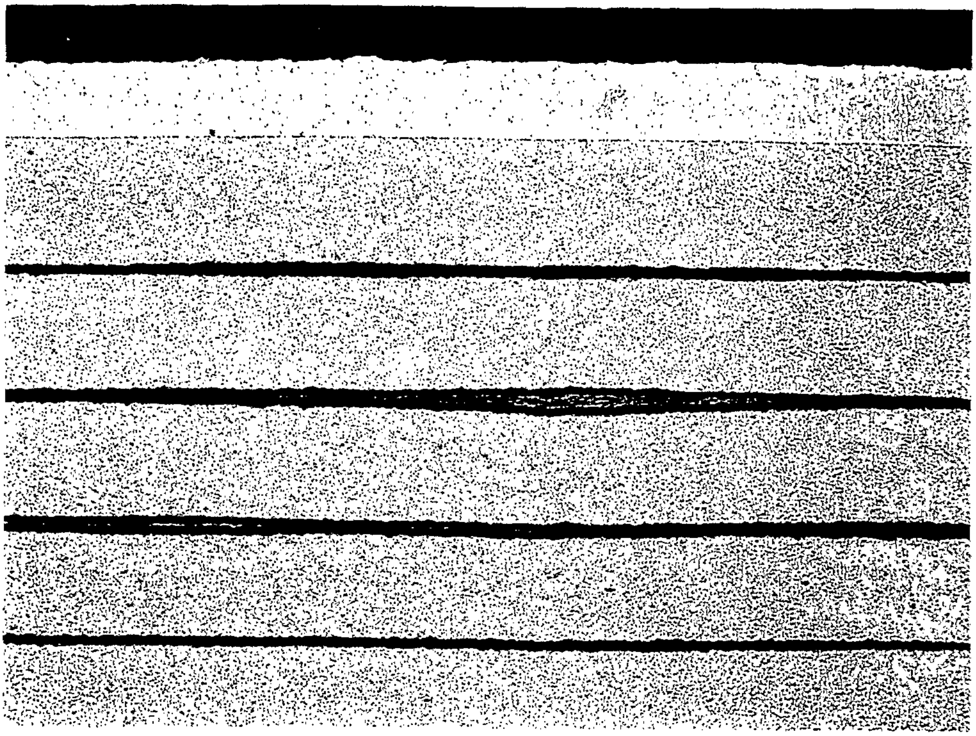
No of Cycles	Young Modulus (GPa)	Strength @lPa}
0	*332*	*348*
50	329	398
200	322	382
500	324	404

Testing of the Cornbtistor Lining

Three tests were carried out under the conditions shown in Table 1. For the first test with gas inlet and outlet temperatures of 623 K and 1523 K respectively and a pressure of 2 bar no damage was found on either the monolithic or the laminated tiles after a test time of 5 hours which included 3 cycles.

In the second test, the gas inlet and outlet temperatures were increased to 773 K and 1800 K respectively. The test was run for 3.5 hours and included 10 cycles. However, this time it was found that the monolithic tiles had cracked, although the laminated tiles had remained intact. Some of the flame-sprayed metallic bushings had aiso begun to melt.

For the last test the metallic bushings were replaced with sintered silicon carbide parts. This time the pressure was increased from 2 bars to 4.2 bars, ‘with the air irdet and outlet temperatures being 823 and 1600 K respectively. During the tenth cycle, some irregularities were observed and the test was stopped immediately. However, the metallic housing had distorted and destroyed the tile assembly.



Neg. No. 94919 m=laax

Figure 6 – A laminate after thermal cycling in the combustor rig. Note the lack of any lamina or interf~cial cracking.

From these initial rig tests it is clear that the laminated tiles can withstand the severe combustor environment better than the monolithic tiles and further testing is now underway using a modified rig to investigate this difference in more detail.

Conclusions

This work has shown that it is possible to manufacture laminated components in a simple fashion. Flat and single curved tiles can be easily produced. Double curved tiles can also be made using a cutting technique. This could undoubtedly be improved perhaps by developing techniques which allow plastic forming of a stretched sheet, whilst keeping the layers intact or by building up layers in a different way for instance by electrophoresis. Despite these difficulties it has been possible to produce the combustor lining shown in Figure 2.

Experiments have shown that the shear strength of the material is relatively low. However laminated material has a markedly improved resistance to thermal shock and thermal cycling compared with monolithic material whilst the material appears to be unaffected by fatigue and shear stresses, at least under realistic conditions. Interestingly, cracking appears to be suppressed in thermal shock compared with the monolithic material. The reasons for this are not understood at present. These improved properties manifest themselves in an improved performance of laminated tiles compared with monolithic tihx in the rig testing of the combustor liner. It is therefore quite clear that the introduction of crack deflecting layers does give rise to useful properties.

Acknowledgements

The authors would like to acknowledge the support for project BE-6074-91 of both the Commission of the European Community, through the Brite-13uRam II programme, and that of N. U. T.E.K in Sweden.

References

1. P.J. Lamicq, G.A. Bernhart, M.M. Dauchier and J.G. Mace, *SiC/SiC Composite Ceramics,* J. Am. Ceram. Sot., 65[2], 1986, 336-38

2. A.G. EvarIs and D.B. Marshall, *The Mechanical Behaviow of Ceramic Matrix Cornposi~es,* Acts. Metall., 37, 1989, 2567-83

3. W.J. Clegg, K. Kendall, N.McN. Alford, T.W. Button and J.D. Birchall, *A Sirnp/e Way to Make Tough Ceramics,* Nature, 347, 1990,455-7.

4. W.J. Clegg, *The Fabrication and Failwe of I.arnirmr Ceramic Composites,* Acts Metall et Mater, 40[11], 1992, 3085-93.

5. R. Lundberg, private communication, 1992.

6. G.A. Schneider, K.G. Nickel and G. Petzow, *Thermal Shock and Corrosion of SiC-A Combustion Chamber Model Case Study,* in The Physics and Chemistry of Carbides, Nitrides and Borides (NATO ASI series E, 185), 1990, Kluwer Academic Publishers, The Netherlands, pp 387-401

7. R.K, okine, *Analysis of Forming Parts from Advanced Thermoplastic Compusite Sheet Materials,* J Thermoplastic Composite Materials, 2, 1989,50-76.

8. J.B. Davis, A. Kristoffersson, E. Carlstrdm and W.J. Clegg, Design *aizd Fabrication of Ceramics Madej?-orn Porous Layers, To* be submitted to J. Am Ceram. Sot.

9. J.B. Davis, N.A. Fleck and W .J. Clegg, *Crack Propagation in PoroLts Merlayei-s in* Ceramic Z.zmzinates, To be submitted to Acts Mater.

10. *N..T.-J.* Fang and T.TV. CIIou, *Characterization of Intedaminar Shear Strength of Cerwnic Matrix Composites,* J. Am. Ceram. Sot., 76[10], 1993,2539-48

11. K.KendaII, *Crack Propagation in Lap Shear Joints,* J. Phys. D (Appl. Phys) 8, 1975, .512-22.