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Materials Characterisation and Mechanical Properties of Cf-UHTC Powder Composites

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Abstract

Ultra-high temperature ceramic composites based on carbon fibre, Cf, preforms impregnated with hafnium diboride, HfB₂, powder and then densified with carbon by chemical vapour infiltration, CVI, have been mechanically tested to measure the room temperature flexural, interlaminar shear, compressive and tensile strengths. The latter was also measured at 1000°C. All the composites suffered a degree of delamination during the different mechanical tests but the strength values obtained were at least equal to, or better than, those previously reported in the literature for ultra-high temperature ceramic (UHTC)-based composites. Importantly, in spite of the oxidation of the tensile samples tested at 1000°C, similar tensile strength values were obtained at both temperatures, suggesting that the materials can resist elevated temperatures. The samples tested at higher temperature did show greater evidence of fibre pull out, possibly due to a weaker fibre-matrix interface as a result of oxidative degradation. The results also suggested that the 0° orientation plies in the Cf preform structure offered greater resistance to mechanical stresses; this suggests that composites can now be designed to offer even greater strength values.

Keywords: UHTC composites, carbon fibre, mechanical properties

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1. Introduction

Advanced materials offering a temperature capability significantly exceeding 2000°C in extreme, highly corrosive environments are required for a range of aerospace and other applications where oxidation and/or erosion resistance is needed at very high temperatures¹. Ultra-high temperature ceramics (UHTCs), which are typically based on the borides, carbides and nitrides of refractory transition metals, including hafnium, zirconium and tantalum amongst others¹⁻³, not only offer extremely high melting points of over 3000°C, but their oxides also typically have melting points over 2500°C. Both hafnium and zirconium diborides, HfB₂ and ZrB₂, in particular have been extensively studied as innovative thermal protection systems (TPS)⁴⁻⁶ and sharp leading edge components⁷⁻⁹ for aerospace vehicles. They have typically been investigated as monolithic components; however they exhibit both poor thermal shock and oxidation resistance¹⁰.

The use of fibre reinforcement can significantly improve the performance of engineering ceramic materials and carbon fibres have received much attention due to their excellent high-temperature strength in reducing or neutral atmospheres, high thermal conductivity, low coefficient of thermal expansion (CTE), excellent thermal shock resistance and good ablation resistance¹¹⁻¹³. They do suffer badly from oxidation, however, even at temperatures below 1000°C^{14,15}. The impregnation of UHTC particles into carbon fibre preforms has been shown to be a good method of improving the oxidation resistance of the carbon fibres and the thermal shock resistance of the UHTCs at ultra-high temperatures^{16,17}. In terms of enhancing the protection of fibres against oxidation, a new injection vacuum impregnation route (IVI) has been developed, increasing the homogeneity of the powder distribution in the preforms¹⁸. More data are needed, however, on the mechanical properties* of such composites and how the composite's structure affects them; designers need such information to be able to define practical temperature and other limits beyond which the thermal, mechanical and other properties are potentially degraded to such a point that the material can no longer perform its required function. The mechanical performance constraints may be associated with more than one type of stress limit, depending on the mode of loading: tensile, compressive or shear. Maximum stress

* And the thermal properties, but this is covered in a forthcoming paper.

limits are usually obtained from mechanical failure data¹⁹. Most of the mechanical property data available in the literature relates to the fracture strength of monolithic UHTCs^{8,20-22}, with some information also available for SiCf- or Cf-UHTC composites²³⁻²⁷ under flexural testing. The purpose of this work was to obtain mechanical property data for Cf-UHTC composites under flexural, interlaminar shear, compressive and tensile stresses and to relate this to a microstructural characterisation of the composites with a view to allowing real components to be designed for subsequent application in hypervelocity vehicles.

2. Materials and methods

3 precursor materials were used, viz. hafnium diboride, HfB₂, powder from two different sources, carbon fibre preforms and phenolic resin. The coarser HfB₂ (325 mesh, d₅₀ = 7.6 μm) was procured from ABCR GmbH & Co, Karlsruhe, Germany whilst a finer particle size HfB₂ (d₅₀ = 3.4 μm) powder was purchased from Treibacher Industrie AG, Althofen, Austria (via ABSCO Ltd, Haverhill, UK). A range of 2.5D needled Cf preforms of different dimensions, but all containing 23 vol% fibres and having a density of 0.37 g cm⁻³, were obtained from Surface Transforms Plc, Ellesmere Port, UK. Cellobond J2027L phenolic resin, with a carbon content of ~43.3% at 800°C under an inert atmosphere, was obtained from Hexion UK Ltd, Penarth, UK.

The structure of the Cf preforms consisted of layers of fabric stacked in an arrangement of random/0°/random/90°/random orientation fibres, where 0° and 90° are unidirectional layers and the random layers were formed as a result of Surface Transform's needling process. Prior to further processing, the preforms were characterised using micro-CT (Phoenix X-Ray 225 kV Microfocus system with a Real-Time Digital Detector Array) at 200 kV and 200 μA. Figure 1 shows the structure of the Cf preforms.

The HfB₂ powders and phenolic resin were subsequently turned into a slurry by ball milling them in acetone in a plastic container using alumina milling media for 48 h. A typical slurry composition consisted of 28 g of coarse HfB₂, 12 g of fine HfB₂, 20 g of phenolic resin and 12.5 g of acetone. The first step was introduce the UHTC slurry into the preform by injection. Subsequently a standard vacuum impregnation step

was required to increase the powder loading in the external layers. Following an extensive preliminary investigation (to be published elsewhere¹⁸), Cf preforms were injected manually with the slurry using a 2.5 ml Terumo syringe and 21G Terumo Agani needle (0.8 x 38 mm). The distance between each injection was 5 mm in both the x and y directions and the amount of slurry injected at each injection point was calculated with respect to the volume of the samples to achieve a 2.5 g cm^{-3} density in the as-prepared samples. The injection procedure was to insert the needle from the top to the bottom of the preform and then to inject the slurry as the needle was withdrawn at a constant velocity and with a constant pressure on the syringe to achieve an homogeneous distribution of the slurry across the full thickness of the sample. After injection the preforms were cleaned using tissues and acetone, then dried in an air oven at 75°C for 12 h and cured at 175°C for 2 h.

The partially loaded Cf preforms were subsequently impregnated with the slurry using vacuum impregnation; details of the process have been provided elsewhere^{28,29}. The remaining porosity in the impregnated preforms was subsequently filled with carbon using chemical vapour infiltration (C-CVI) from methane by Surface Transforms Ltd. After 4 CVI runs the samples were machined to achieve the final shape by Gledco Engineered Materials, Leeds, UK. The change in mass of the samples was recorded after each stage in the preparation process and the bulk density of the composites was measured geometrically. The degree of impregnation after C-CVI and machining of samples were characterised by SEM (Philips XL-30), EDS (Oxford Inca) and the porosity by mercury porosimeter (PoreMaster, PR-60GT, Micromeritics, USA).

A total of four different sizes of sample were prepared for the mechanical tests, these are illustrated in figure 2. Table 1 summarises the numbers of preforms prepared, sample type, preform dimension, numbers of samples tested and the final dimension of the samples after C-CVI and machining.

With respect to the mechanical property measurements, 4 point flexural tests were performed in accordance with the ASTM C 1341-13 standard (Test geometry IIB) using an Instron 1185 testing machine, a 10 kN load cell (ref: UK 1086) and a deflectometer (ref: GT62; range of measurement +/- 5 mm). The diameter of the loading and support rollers was 10 mm, the distances between the support span and

loading span were 96 mm and 32 mm respectively, and the rate of cross head motion was 16.8 mm min^{-1} . All the samples were tested at room temperature and a relative humidity of 42-47%. The test samples were positioned so that a 0° ply surface was oriented downwards on the support span for all samples.

Interlaminar shear tests were developed in accordance with the ASTM C 1292-00 standard using an Instron 1185 with a 10 kN load cell and no extensometer. The rate of cross head motion was 3 mm min^{-1} . All the samples were tested at room temperature and a relative humidity of 43%.

Compressive tests were carried out in accordance with the British Standard BS EN 658-2:2002 using an Instron 1185 testing machine, a 100 kN load cell (ref: UK 411) and extensometer CAT No. 2620-601 serial No. 1529 (gauge $1/L_0 = 25 \text{ mm}$). The rate of cross head motion applied was 1 mm min^{-1} . All the samples were tested at room temperature and a relative humidity of 43%. The compressive samples were prepared in two different orientations, $0^\circ/90^\circ$ and Z (along and across the plies, respectively), see figure 2.

The tensile testing was carried out in air at both room temperature and 1000°C . In both cases the standard ASTM C 1275-15 was followed. The measurements were carried out using an Instron 6025 testing machine, a 100 kN load cell (ref: UK 375), a longitudinal extensometer, CAT No. 2620-601 serial No. 3156, and a transversal extensometer, CAT No. 2620-601 serial No. 1529 for measuring the strain. The cross-head speed was 0.5 and 2 mm min^{-1} at room temperature and 1000°C respectively. The tests at 1000°C were performed using two, 6 kW infra-red heating panels; this offered a high heating rate of $\sim 500^\circ\text{C min}^{-1}$. The temperature at the surface of the tensile sample along the gauge length was measured using an optical pyrometer (IMPAC IN5, LumaSense technologies GmbH, Frankfurt, Germany) that had been calibrated against a type K thermocouple placed inside a tensile sample previously tested at room temperature. The emissivity of the optical pyrometer was adjusted to 0.88.

After testing, the two samples with the highest and lowest values from each different mechanical property test were characterised by SEM (JEOL JSM-6060 LV, JEOL Ltd, Tokyo, Japan) to determine the failure mode. It was noteworthy, though, that the

modes of failure were consistent for each type of mechanical test, thus this publication only shows the images that illustrate the failure mode most clearly.

3. Results

3.1 Processing

The original bulk density of the Cf preforms was 0.37 g cm^{-3} and the bulk densities of the composites after HfB_2 impregnation, carbon infiltration by CVI and machining are summarised in table 2. The samples showed consistent density values, $2.4 \pm 0.1 \text{ g cm}^{-3}$ after HfB_2 slurry impregnation, and $3.0 \pm 0.2 \text{ g cm}^{-3}$ after carbon CVI densification. The final composite thus contained $\sim 60 \pm 2 \text{ wt\% HfB}_2$ and $\sim 12 \pm 1 \text{ wt\%}$ carbon fibre. The distribution of the powder into the preform was uniform throughout the entire thickness, see figure 3a. The random orientation layer retained a much higher amount of powder than either oriented layer due to its higher porosity and larger pores. Figure 3 also shows SEM images of the different ply orientations after C-CVI and final machining. In the images, a light grey colour corresponds with HfB_2 powder whilst the darker grey regions show carbon from the range of different sources, viz. carbon fibres, phenolic resin and infiltrated carbon from the CVI process. Figure 3e clearly shows carbon filling the intra-tow porosity and a low amount of HfB_2 powder present. The aim of the impregnation process was to fill the inter-tow and large pores in the random orientation layers whilst retaining enough porosity to allow the penetration of the reactive gases involved in the CVI process so that the finer intra-tow porosity could be filled with carbon to achieve a high degree of densification of the composites. Figure 4 shows an EDS analysis of a random orientation layer. Area 1 corresponds with HfB_2 powder particles from the impregnated slurry; it also shows carbon and oxygen from the pyrolysed phenolic resin. Areas 2 and 7, which correspond to the $7\text{-}10 \text{ }\mu\text{m}$ diameter carbon fibres, show carbon with traces of oxygen, whilst area 3 relates to the carbon deposited by the CVI process; the high purity is notable. Areas 4, 5 and 6 are all related to the pyrolytic carbon originating from the phenolic resin; it again shows higher amounts of oxygen, together with some Hf and B content from the powder present in the slurry.

The porosity was measured by mercury porosimeter for the final composite samples prepared on $0^\circ/90^\circ$ and Z orientations, both showed similar values of $\sim 12 \pm 1 \text{ vol.\%}$.

The size distribution of the pores was also evaluated, see figure 5, indicating a preponderance of porosity that was $<1 \mu\text{m}$ in size as desired. The aim had been to eliminate the presence of large, potentially strength-limiting pores, whilst retaining sufficient fine porosity to allow the penetration of the methane during the CVI process.

3.2 Characterisation

The results obtained from the mechanical tests are summarised in table 3, whilst the actual stress strain curves are shown in figure 6.

Flexural strength

The flexural strengths varied from 96 to 166 MPa, whilst the flexural modulus varied from 23 to 34 GPa. Observations revealed that, for the majority of the test pieces, tensile failure, with delamination, occurred in the stressed area between the rollers of the loading span as expected. The quality of the preform, in terms of homogeneity of the structure along the entire batch of samples, played an important role in obtaining consistent results. The scatter in the data is believed to be explained by the inherent capacity of the each preform to absorb the slurry, which was observed to vary slightly in terms of the mass gain during vacuum impregnation from preform to preform, and also the slight 'waviness' of the plies (see figure 1). The latter were not always entirely flat and this waviness effect had significant impact during the machining process since it meant that, post machining, not all the samples had the same number of complete plies.

Since the failure mode was the same for each type of sample, only the strongest and weakest were selected for SEM characterisation. This consisted of analysing the cross-section and surface at the location of the fractures, see figure 7. The images of the fractures are shown in figure 8. The cross-sectional views of the samples are showed in figure 8a & c and the surface view in figure 8b & d. The strongest sample, figure 8a & b, had the structure; R/0/R/90/R/0/R, which means that there were twice as many 0° orientation fibre layers as 90° orientation layers and the top layer consisted of a random oriented fibre layer. The cross-section shows how the crack crossed the 90° ply vertically and the 0° orientation layer horizontally as the crack found the weakest path through each layer that broke. In some cases, the weak

point was a pore produced by separated fibres. The top view shows a uniform fracture crossing the entire random orientation ply at the surface. The fracture was produced on the same axis and in the direction of the applied force. The weakest sample, figure 8c & d, had the structure half 0/R/90/R/0/R/90/R, which means 1.5 layers of 0° orientation fibres (sample machining removed half of the outermost layer) and 2 layers of 90° orientation fibres. As can be observed, the failure mode was the same as for the strongest samples. After analysing the samples it was observed that the 0° orientation layers showed more resistance to flexural stresses. Higher flexural strengths corresponded to the sample with more 0° orientation layers, whilst the presence of more 90° orientation layers lead to a lower strength. This suggests that the number of 0° orientation layers present should be maximised.

Interlaminar shear strength

The interlaminar shear strengths varied from 38.2 to 22.3 MPa, see table 6. The degree of scatter in the results is relatively high, which is not unusual for ceramic matrix composites. All the interlaminar shear samples split in two during testing with the same failure mode, so again only the strongest and weakest samples were selected for SEM characterisation of the fracture. Figure 9 shows the two locations at which the fracture was analysed by SEM. Note that, as can be appreciated from figure 10, for neither the strongest nor weakest samples were the fibres actually broken, rather the samples delaminated. Figure 10a & c shows the strongest sample delaminated at the end of the slot cut in each part that corresponded with the 0° orientation ply. The delamination was produced in the middle of the 0° orientation ply and the fracture surface, figure 10b & d, showed 0° orientation fibres in both halves.

Figure 10e & g shows the cross-sectional fracture view of the weakest sample. The sample failed in a random orientation layer, at the interface with a 90° orientation fibre layer at the end of the slot. Both surfaces showed random and 90° orientation fibres, figure 10f & h.

After the analysis of the samples was complete, it was observed that failure occurred in the ply that corresponded with the end of the slot and that the strength of samples where the slot finished in a 0° orientation fibre ply was higher than when the slot finished in a random or 90° orientation fibre ply. This may be explained by the fact

that the composite offered more resistance to the applied stress when the fibres were oriented in the same direction as the force. Once again, this suggests that the number of 0° orientation fibre plies should be increased to improve the shear strength of the material. Indeed, the improvement might be even higher if 3D carbon fibre structures were used as a result of the structural strength provided by including Z orientation fibres. This is being investigated in current research being undertaken via funding from the European Community C3Harme, Horizon 2020, programme.

Compressive strength

This was measured along and across the plies, 0°/90° and Z respectively. The results are shown in table 3 and the compressive stress was calculated and plotted as a function of the strain measured by the extensometer, Figure 6. The compressive strengths varied from 179.0 to 221.4 MPa, whilst the compressive modulus varied from 23.9 to 25.3 GPa for the 0°/90° orientation plies. For the Z orientation plies, the composite displayed a similar compressive strength, from 146.7 to 219.0 MPa, but the compressive modulus was 50% lower than for the 0°/90° direction. The failure mode for both orientation plies was characterised by SEM after compression testing, the strongest and weakest samples from each test orientation being examined. Figure 11 shows a schematic illustrating the locations where the analysis of the samples took place. The cross-sectional images of the samples tested along the plies show cracks in the same direction as the applied force, producing delamination between the 0° and random orientation fibre layers that extended to the 90° orientation fibre plies, obliquely crossing them as is shown in figure 12 for both the strongest and weakest samples. No cracks were found in the middle of the 0° orientation fibre plies, again suggesting higher strength and indicating delamination as the main failure mode. Figure 13 shows the bottom of the samples after testing for the strongest and weakest samples parallel to the plies, revealing the same behaviour; delamination at the interface between the 0 and random orientation fibre layers. The cross-sectional characterisation of the compressive samples tested across the plies showed a shear failure mode, which is clearly recognizable in figure 14. The cracks crossed the different orientation plies obliquely. The bottom surface of the sample, figure 15, did not reveal any cracks since the latter were produced from the top of the sample, where the force was

applied, and only spread through about $2/3^{\text{rds}}$ of the thickness. This suggests that the use of a 3D carbon fibre preform might result in a reduction in the delamination of the composites for samples tested parallel to the plies.

Tensile strength

The tensile samples were tested at room temperature and 1000°C. The results are shown in table 3 and tensile stress was calculated and plotted as a function of the strain in figure 6. The tensile strength at room temperature varied across the range 70 to 88 MPa, whilst the tensile modulus ranged from 27 to 37 GPa. For the samples tested at 1000°C, the tensile strength did not decrease; it varied from 59 to 92 MPa – a larger range but with a very similar mean value, table 3. The tensile modulus, however, decreased by 25% compared with the value at room temperature, dropping from 32 to 24 GPa. As usual, the strongest and weakest samples tested at room temperature and 1000°C were characterised by SEM at 2 locations each, figure 16, to determine the failure mode.

The strongest sample tested at room temperature had the structure R/0/R/90/R/0/R/90/R/0/R, i.e. it contained three 0° orientation layers and two 90° layers with one of the latter at the top surface. Figure 17a shows how the crack crossed the sample vertically, showing a low degree of fibre pull-out, whilst figure 17b shows a single, straight fracture crossing the entire 90° orientation layer on the top of the sample. The equivalent views for the weakest tensile sample tested at room temperature are shown in figures 17c & d. The structure of this sample was R/90/R/0/R/90/R/0/R/90/R/0, i.e. it contained three 90° orientation layers and two complete 0° orientation layers, with an extra half layer at the top surface. The failure mechanism was the same as for the strongest sample; the crack crossed the sample vertically and low fibre pull-out behaviour was observed. The fracture on the top was uniform, crossing the 0° orientation fibres. Uniform distribution of HfB₂ was observed across the entire thickness of the samples.

Figures 18a & b shows the cross-section and top surface for the strongest tensile sample tested at 1000°C. The colour of the sample changed due to the oxidation that occurred during testing, converting the HfB₂ near the sample surfaces to HfO₂. The top layer was formed of 90° oriented fibres corresponding with the structure of the

sample being R/0/R/90/R/0/R/90/R/0/R/half 90°, i.e. it consisted of 3 layers of 0° orientation plies and 2.5 layers of 90° orientation plies. The cross-sectional view, figure 18a, shows a vertical crack crossing the sample and revealing a high degree of fibre pull-out, whilst figure 18b shows a uniform fracture across the entire 90° orientation ply at the top of the sample. The weakest tensile sample tested at 1000°C, figures 18c & d, had the same structure and failure mode as the strongest sample, i.e. the crack crossed the sample vertically.

After analysing the samples, it was observed that the 0° orientation layers showed more resistance to tensile stresses; the samples with more 0° plies showed the highest strength values. Interestingly, the tensile samples tested at 1000°C showed very similar mean tensile strengths, though with a greater degree of scatter. The failure mode indicated more 'ductile' behaviour for samples tested at 1000°C, a higher degree of fibre pull-out was observed, presumably due to the degree of degradation of the carbon matrix and carbon fibres at elevated temperature, figure 19. Figure 20 shows the degradation of the carbon fibres and loss of carbon matrix after testing at 1000°C. It is possible that these resulted in a weaker matrix-Cf interface and so yielding greater 'ductile' behaviour²⁹. In terms of the degree of oxidation and degradation of the carbon fibres and carbon matrix, the replacement of the carbon matrix by a UHTC matrix could result in greater protection of the Cf and so this is another direction of current research.

4. Discussion

There are hardly any reports in the literature on the mechanical properties of UHTC-based composites, but the few results available describe similar behaviour to that observed here. With respect to flexural strength, previous work⁷ for ZrB₂-20 vol.% SiC reinforced with SCS-9a SiC fibres described cracks passing through the thickness during testing, resulting in composite delamination. Similar flexural strength values, 130 MPa, were obtained as reported in this work even though the composite composition involved was quite different. A different study³¹ involved a Cf / ZrB₂-SiC composite made by impregnating a ZrB₂ powder slurry into 2D Cf preforms, with the remaining porosity being filled with SiC by CVI. Unfortunately, the ZrB₂ powder seems to have blocked the channels for the CVI process leading to

interfacial debonding. This also resulted in a lower interlaminar shear strength than that obtained in the current work.

All of the four different mechanical tests undertaken yielded similar results; there was a relatively high degree of scatter in the data, which is not unusual for ceramic matrix composites, and the 0° orientation fibre layers were consistently shown to yield higher strengths than the 90° orientation fibre layers. With respect to the latter, it was clearly shown that the more of the 0° and fewer of the 90° layers that were present, the better the samples performed mechanically. The random layers, however, were the layers that absorbed the majority of the HfB_2 powder due to their higher porosity and larger pores; these are the layers, therefore, that will impart the greatest oxidation and ablation protection. These factors will allow future 2.5D-based $\text{C}_f\text{-HfB}_2\text{-C}_m$ composites to be designed so that the performance is enhanced.

In general, the fracture of the composites was due to cumulative damage processes involving matrix cracking, matrix-fibre debonding, fibre fracture and, mainly, delamination. The tensile tests were also carried out at elevated temperature and the results showed that both the carbon fibre and carbon matrix were partially oxidised; this resulted in a higher degree of fibre pull-out after mechanical testing. Despite this, however, the tensile strength of the composite at 1000°C was similar to that measured at room temperature suggesting that the composites are capable of withstanding at least moderate temperatures without degradation of their mechanical performance.

5. Conclusions

A very uniform $\text{C}_f\text{-HfB}_2$ powder composite developed using 2.5D carbon preforms impregnated with a HfB_2 powder / phenolic resin / acetone slurry and densified using carbon deposited via CVI has been mechanically tested. Flexural, interlaminar shear and compression strength were measured at room temperature and the strongest and weakest samples were analysed post-mortem to determine the failure mode of the composites. In general, the composites suffered a degree of delamination during testing and it was observed that the 0° orientation plies showed higher resistance to the different mechanical stresses than the 90° plies or the random orientation layers. This suggests that the inclusion of a greater proportion of the 0° plies in the preform

structure would enhance the mechanical properties of the composite. The design of 3D preform structures with a higher fibre content of 0° orientation plies might avoid the delamination issues.

The tensile strength was measured at both room temperature and 1000°C. The values obtained for both temperatures showed little difference; the mean values being 79 MPa and 78 MPa at room temperature and 1000°C respectively, however the behaviour of the material tested at 1000°C exhibited greater fibre pull-out, probably as a result of the partial oxidation of the carbon fibres and carbon matrix. As a result, current work is investigating the replacement of the carbon matrix by UHTC matrices, also deposited by CVI.

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