Thermophysical Properties of a High Density Carbon/Carbon Composite from Ambient to Ultra-High Temperatures

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Abstract

Carbon/Carbon (C/C) composites are currently the material of choice for use on advanced thermal protection systems for high speed flight vehicles due to their excellent thermophysical properties, high specific stiffness and strength in hypersonic flight operational environments. Understanding the ultra-high thermophysical properties of C/C is essential for design purposes, especially where limited data exists for the temperature range of interest. To address this need, the thermophysical properties of a nominated high density C/C composite material were characterized. Properties such as specific heat, thermal diffusivity, thermal expansion and thermal conductivity for the material in all three material orientations (x,y,z) were investigated between ambient temperature to 2600°C.

The thermophysical assessment of the C/C composite is provided in two parts, the first set of thermal properties were determined for the material in its untreated state (no heat treatment), and the second set demonstrates the effect of heat treatment on the thermal properties. The coefficient of thermal expansion (CTE), diffusivity and conductivity of the composite exhibit a distinctive shift in the material properties in the temperature range of 1300-1500°C. Subsequent thermal analyses beyond that temperature range is markedly different and indicative of the thermophysical properties expected if the composite be subjected to heat treatment. Analyses of the same specimens (pre- and post-heating) were also conducted using X-ray diffraction (XRD) in order to investigate the resultant variation in thermophysical properties as a result of repeated heat treatments. The findings were useful to assess the performances of the C/C composite in extremely high temperature conditions for the potential applications of hypersonic vehicle structure and components.

Keywords: Carbon/Carbon Composites, Thermophysical Properties, Heat Treatment, Ultra-High Temperature, X-Ray Diffraction

Nomenclature

C/C – Carbon/carbon
C_p – Specific heat capacity
CTE – Coefficient of thermal expansion
HF – Heat flow
L_0 – Initial length
T – Temperature
d – Linear thermal expansion
m – Mass
s – Specimen thickness
t – Time
α – Thermal diffusivity

ΔL – Change in length
λ – Thermal conductivity
ρ – Density
sam – Sample
spr – Sapphire
XRD – X-ray diffraction

1. Introduction

Carbon/carbon (C/C) composites are a family of advanced composite materials that consist of carbon fibers embedded in a carbon matrix. C/C composites are currently the material of choice for use on advanced thermal protection systems for high speed flight vehicles due to their light weight, excellent thermophysical properties and high specific stiffness and strength in hypersonic flight operational environments. The ultra-high thermophysical properties of C/C are essential for design purposes, especially where limited data exists for the temperature range of interest.

However, the thermophysical properties of C/C composites have been shown to vary greatly with current manufacturing processes, composition, and lay-up. C/C composites consist of complex structures, and the thermal properties are influenced by the fiber (type, volume fraction, and orientation), the architecture and manufacturing process technologies (layer build-up, pores distribution, etc.), as well as the heat treatment (carbonization and graphitization) [1]. To assess the suitability for high speed flight applications, the thermophysical properties of a nominated high density C/C material were characterized. Properties such as specific heat, thermal diffusivity, and thermal expansion for the material in all three material orientations (x,y,z) were investigated, and the thermal conductivity was determined between ambient temperature to 2600°C.

Furthermore, the effect of heat treatment on the thermophysical properties of the designated C/C composite were investigated. Analyses of the same specimens pre- and post-heating were also conducted using X-ray diffraction (XRD) to investigate the resultant variation in thermophysical properties as a result of repeated heat treatment. The detailed thermophysical properties and associated mechanism to interpret the experimental finds were presented and discussed in following sections.

2. Experimental Process and Methods

2.1 Material

The nominated C/C material has a density between 1.5-1.9 g/cm^3 and consists of a multiaxial continuous fibre form joined together using a needling technique, and strengthened using a pyrocarbon infiltration process.

2.2 Specific Heat

The specific heat was measured using a simultaneous thermal analyser which measures both differential scanning calorimetry (DSC) and thermogravimetric analysis simultaneously (Netzsch STA 449 Fx Jupiter) [2]. In this technique, the DSC curve measures the difference between the heat flow of the material of interest and a known reference sample while being subjected to a controlled temperature profile in order to determine how the material's heat capacity varies with respect to temperature [3]. Specific heat measurements were conducted on a total of six specimens weighing between 20-40mg, with at least two heating cycles for each specimen. The C/C specimens were prepared with a flat face to ensure good contact with the bottom of the crucible. The samples were heated to 1400°C at a rate of 20K/min in an inert atmosphere. The specific heat can be obtained using the heat flux equation [4]:

$$C_{p,sam} = \frac{m_{spr}}{m_{sam}} \frac{HF_{sam}}{HF_{spr}} C_{p,spr} \tag{1}$$

Where *m* is the mass, *HF* the heat flow, and subscripts *sam* and *spr* refer to the sample and sapphire respectively.

2.3   Thermal Diffusivity

The thermal diffusivity of the designated C/C was measured using a laser flash analyser (Netzsch LFA 427) at temperatures between 25°C and 2600°C in an inert atmosphere [5]. With the laser flash method, a dispersed laser pulse is applied to the front surface of the specimen, and an infra-red detector is used to measure the transient temperature rise on the back surface of the specimen. The temperature rise across the back surface as a function of time is thereby determined, and assuming adiabatic conditions, the diffusivity of the material can be expressed using the following equation [5]:

$$t_{1/2} = 0.1388 \times \frac{s^2}{\alpha} \qquad (2)$$

where:

α = temperature diffusivity in mm^2/s
s = thickness of the specimen in mm
$t_{1/2}$ = time (s) at half the maximum temperature rise at the rear surface of the specimen

Three samples of dimension 10mm x 10mm x 2mm for each given material orientation were examined in accordance with ASTM E1461 [6]. Each specimen was coated on both surfaces with a thin graphite layer in order to increase the surface absorptivity and emissivity. Three measurements were made for each temperature step and for each of the samples to ensure consistency of measurements. The Penetration diffusivity model was used to correct the measurements due to its suitability in accounting for materials exhibiting rough surfaces and porous interlaminar structure [5].

2.4   Thermal Expansion

The thermal expansion of the designated C/C was measured using a vertical pushrod dilatometer (TA Waters DIL822HT) at temperatures between 25°C and 1900°C in an inert atmosphere [7]. Three samples of dimension 20mm x 5mm x 5mm were heated at a rate of 10K/min for each given material orientation while the push rod displacement was being logged in accordance with ASTM E228 [8].

The linear thermal expansion, d%, is simply the linear dimensional change of the material with respect to a temperature change, and is expressed as:

$$d\% = \frac{\Delta L}{L_0} \qquad (3)$$

Where ΔL is the change in sample length and L_0 is the initial sample length.

The coefficient of linear thermal expansion, CTE, is a measure of the fractional linear change with respect to the fractional temperature change, and is expressed as:

$$CTE = \frac{\Delta L}{L_0 \Delta T} \qquad (4)$$

3.   Thermophysical Property Results and Analysis

3.1   Behaviour of Specific Heat up to 1400°C

A curve of best fit was derived from the specific heat measurements of the C/C samples and plotted in Fig. 1 below. As can be seen, the C/C composite follows the characteristic specific heat trend of conventional carbon and graphite materials, with an increase of specific heat with increased

temperature. For comparison, the data for graphite is also included in Fig. 1. It was observed that below 1000°C the specific heat measurements for all six samples appeared to be in good agreement, whereas at higher temperatures the rise in measurement scatter is quite significant. The increased deviation in the measurements at higher temperatures is believed to be the result of the porous nature and interwoven structure of the C/C material. In addition, during measurements at higher temperatures, the contact between the sample mass and the crucible liner becomes compromised and this presents as increased scatter in the measurements. For this reason the specific heat values for the C/C were extrapolated for temperatures above 1000°C through to 2600°C using the characteristic Debye model to calculate the thermal conduction of the C/C composite material as presented in Section 3.4.
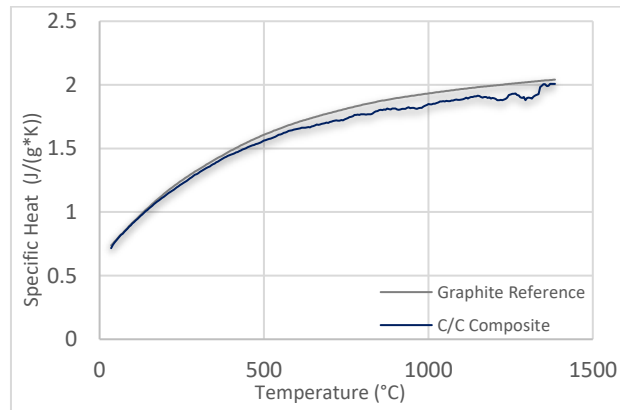

Fig. 1 Temperature-dependent specific heat measurements of C/C and graphite reference to 1400°C.

3.2   Effect of Repeated Heating on C/C Thermal Diffusivity

The thermal diffusivity measurement average values from three measurements for each C/C orientation are shown in Fig. 2 and Fig. 3. The thermal diffusivity in the fibre orientations (x,y) were in agreement as expected, ranging from 5.5-10.8 mm^2/s, whereas the diffusivity measurements through the plane (z) were significantly lower, ranging from 3.5 - 7.1 mm^2/s. For all three orientations, the thermal diffusivity showed a decrease between room temperature to 1200°C and then increased with rising temperature. This distinctive increase in diffusivity as the composite is heated above 1200°C appears to highlight the onset of a permanent material change in fibre and matrix during the first heating cycle for each of the specimens. This behaviour is likely a result of insufficient heat treatment of the C/C composite which was not elevated to a temperature exceeding 1300°C during the manufacturing process. Interestingly, subsequent heating cycles for the same C/C, as shown in Fig. 3, result in a significant increase in diffusivities for a given temperature, while the diffusivities decrease with the temperature increase. In addition, the diffusivity measurements in the in-fibre orientations appear to diverge particularly at lower temperatures. Diffusivities range between 9.8 - 55.4 mm^2/s for in-fibre (x), 9.3 - 50.8 mm^2/s for in-fibre (y), and 6.8 - 43.3 mm^2/s for the through-plane (z) orientation.
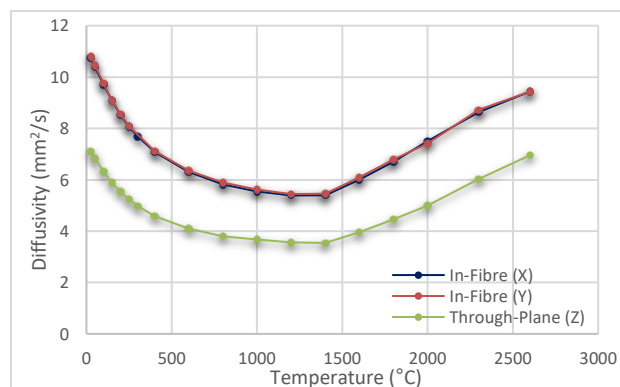

Fig. 2 Temperature-dependent diffusivity measurements of C/C from room temperature to 2600°C.
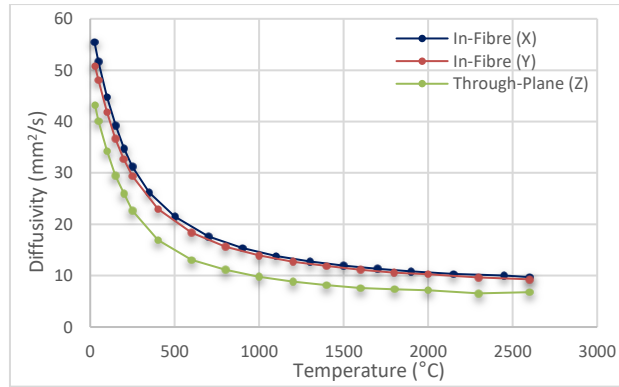
Fig. 3 Subsequent temperature-dependent diffusivity measurements of C/C from room temperature to 2600ºC.

3.3   Effect of Repeated Heating on C/C Thermal Expansion

The average thermal expansion properties for the C/C composite material in the fibre (x,y) and through the plane (z) orientations are shown in Fig. 4 Temperature-dependent expansion measurements of C/C from room temperature to 1900ºC. for the first heating cycle, and the corresponding coefficient of thermal expansion values are shown in Fig. 5 for the repeated heating. The thermal expansions along the x and y direction of the C/C composite are significantly lower than that through the plane. The composite appears to expand following a consistent trend with increased temperature till about 1300°C, after which there is a distinctive contraction from 1300°C to 1500°C before increasing again until the maximum heating temperature of 1900°C. This turning-point from 1300°C to 1500°C for the first heating cycle is consistent with that of the first heating thermal diffusivity presented previously in Section 3.2. Following the material contraction between 1300°C to 1500°C, the material exhibits a higher coefficient of thermal expansion through to 1900°C.
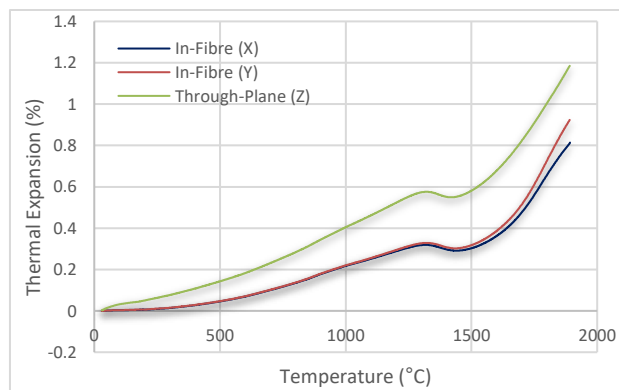

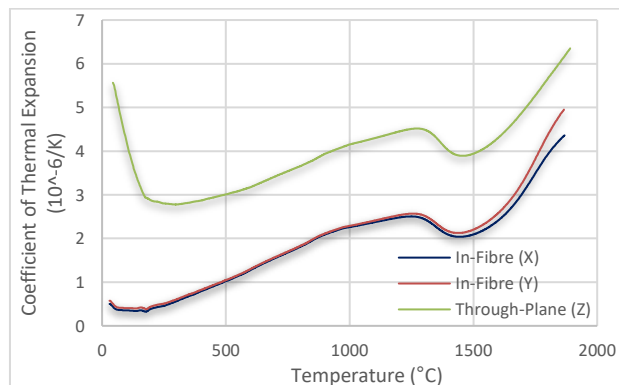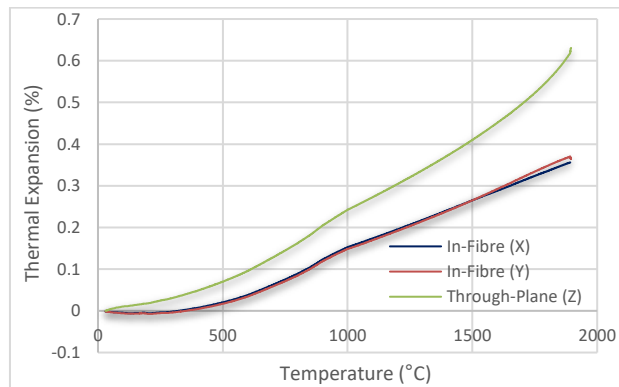**Fig. 4** Temperature-dependent expansion measurements of C/C from room temperature to 1900ºC.
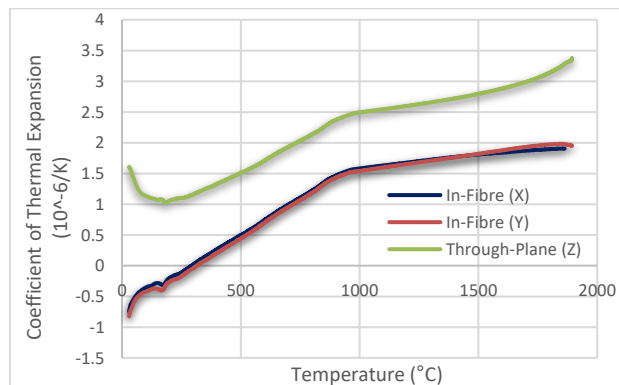
Fig. 5 Coefficient of thermal expansion of C/C from room temperature to 1900ºC.

The average thermal expansion properties for C/C in the fibre (x,y) and through the plane (z) orientations for subsequent heating cycles are shown in Fig. 6, and the corresponding coefficient of thermal expansion values shown in Fig. 7. The thermal expansion in all three material orientations is reduced by about a factor of two when compared to the original expansion behaviour of the composite during the first heating cycle. In addition, the distinctive material contraction observed in the first heating cycle between 1300°C to 1500°C is no longer present. Instead the composite appears to expand following a consistent trend with increased temperature till about 1000°C, after which the expansion appears to follow a somewhat linear trend between 1000°C to 1900°C. This behaviour is also consistent with that of thermal diffusivity during the second heating cycle presented previously in Section 3.2.

Fig. 6 Subsequent temperature-dependent expansion measurements of C/C from room temperature to 1900ºC.

Fig. 7 Subsequent coefficient of thermal expansion of C/C from room temperature to 1900ºC.

Interestingly, Wang et al [9] also reported similar findings when examining C/C composites heat treated at different temperatures to study the variation of CTE with increased heat treatment temperature. The study found that the CTE of untreated C/C composites increased gradually with increased temperature up to 1300ºC, then decreased from 1300°C to 1500°C, and then increased again at a higher coefficient of thermal expansion through to 1900°C. Furthermore, Wang et al [9] reported on the reduced CTE values for the C/C composites that were subjected to heat treatment. The distinctive variations in the CTE measurements for the C/C composites in the temperature range between 1300°C to 1500°C gradually diminishes as heat treatment temperature increases. Additionally, the CTE measurements are in agreement with the findings by Fitzer and Manocha [10] who have reported that C/C composites that are heat treated to graphitization temperatures tend to exhibit a lower thermal expansion in the material orientation.

3.4 Calculation of Thermal Conductivity

In the case of C/C composites, the thermal conductivity can be predominantly attributed to the vibration of the crystal lattice as a result of the phonon interaction of atoms [11].

The measured thermal diffusivity, specific heat, and density with respect to an increased temperature were used to derive the thermal conductivity, λ, of the C/C composite in accordance with the following relationship [5]:

$$\lambda(T) = a(T) \times \rho(T) \times C_p(T) \tag{5}$$

The average thermal conductivity of C/C in the fibre (x,y) and through the plane (z) orientations are shown in Fig. 8 Thermal conductivity of C/C from room temperature to 2600ºC. The thermal conductivity of C/C is higher in the in-fibre direction than through the plane. This is likely the result of the highly orientated fibres embedded within the matrix being crystalline and thereby conducting heat along their length. The matrix on the other hand provides pathways for heat transfer and thermal stability. In all orientations it was observed that after an initial rise in the thermal conductivity between room temperature and 400°C, the conductivity appears to remain constant till 1400°C. Measurements above 1400°C reveal a significant shift in the thermal response of the composite with the conductivity increasing somewhat linearly with an increase in temperature. Subsequent heating cycles for C/C, as shown in Fig. 9 Subsequent thermal conductivity measurements of C/C from room temperature to 2600ºC., have a significantly higher conductivity for lower temperatures. The conductivity decreases with increased temperature till 2600°C at which point the values are comparable with those for the first heating cycle.
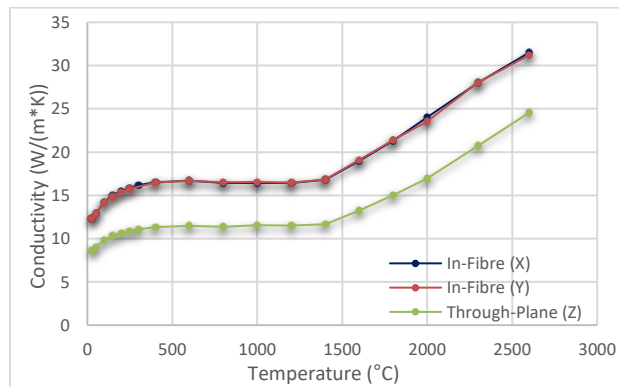

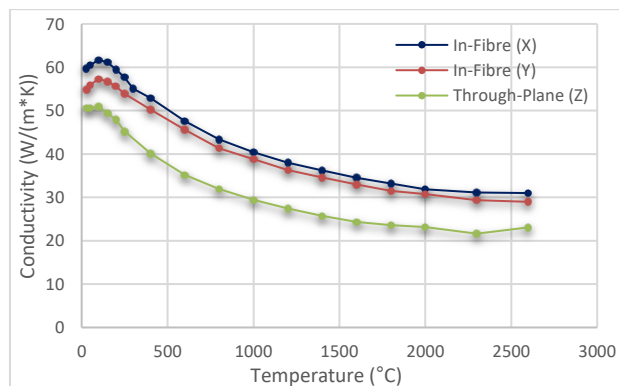**Fig. 8** Thermal conductivity of C/C from room temperature to 2600ºC.

Fig. 9 Subsequent thermal conductivity measurements of C/C from room temperature to 2600ºC.

3.5 Microstructural Analysis using XRD

X-Ray Diffraction (XRD) analysis was conducted to investigate the effects of heating the C/C material to ultra-high temperatures. XRD analysis allows the sampling of a representative volume of the material, and the results offer insight into the bulk microstructural characteristics (averaged) of the material of interest. XRD analysis was conducted on two C/C specimens, one of which was in the unheated form while the other was subjected to two heating cycles from room temperature to 2600ºC. Fig. 10 presents the full diffraction patterns together with model fits for both specimens. XRD diffractions were analysed using the CarbonXS software package [12], which offers a graphitic crystal structure model developed by Shi et al. [13] which reasonably matches the experimental C/C diffraction patterns and thereby provides useful crystal lattice and microstructural parameters as summarised in Table 1. It is observed that the XRD peaks are broader for the unheated C/C when compared to the heated specimen which indicates that the heated specimen has an increased crystallinity. In addition, the shape of the in-plane reflections are asymmetric for both the heated and unheated samples which suggests that the C/C composite contains strain, defects or non-uniform size distribution.

Most notably, the in-plane lattice parameter d_{002} was used to estimate the increased degree of graphitisation, $\bar{g}$, of the C/C composite, from 0.60 to 0.77 as a result of heat cycling. XRD analysis of the C/C also revealed that in its unheated form, the composite consists of smaller crystallite sizes of L_a (in-plane) = 51˚A and L_c (along c-axis) = 105˚A when compared to the crystallite sizes of the heated C/C of L_a (in-plane) = 90˚A and L_c (along c-axis) = 175˚A. These findings are in agreement with Huang's [14] review, which reported that increasing the heat treatment temperature to above 2000ºC is responsible for the growth of the in-plane and along its c-axis crystallite structure, as well as the reduction of the interlayer spacing (i.e reduced material porosity). The increased crystallite sizes, together with an increase in local defects as a result of heating may impede on the strength of the C/C particularly in the fibre direction [15].
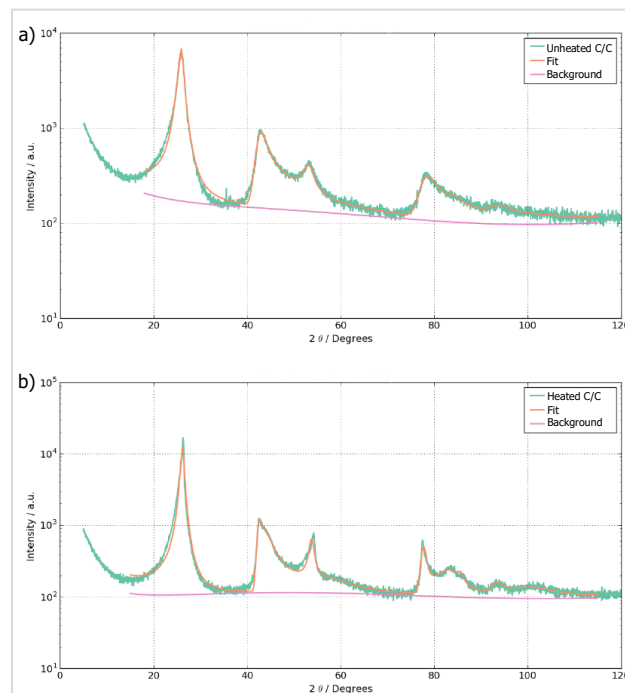

Fig. 10 X-ray diffraction patterns and model fittings of the a) unheated, and b) heated C/C composite.

Table 1. Comparison of microstructural parameters of unheated and heated C/C composite as determined from the CarbonXS fittings of the XRD data. Parameter values are reported as: value(uncertainty level).

Microstructural parameters	Unheated C/C	Heated C/C
d002 (Å) – Inter-plane lattice spacing	3.4364(1)	3.4009(0)
a (Å) – In-plane lattice constant	2.4501(4)	2.4579(2)
$\bar{g}$ – Degree of graphitisation	0.60(0)	0.77(0)
La (Å) – In-plane crystallite size	51(3)	90(1)
Lc (Å) – Crystallite size along c-axis	105(2)	175(2)
ζ – In-plane strain	0.012(1)	0.001(1)
δ – Inter-plane strain	0. 790(2)	0.942(0)
PRS – Probability of random stacking	0.987(7)	0.688(4)

4. Conclusions

In this work, the thermophysical property measurements for a nominated high density C/C material were investigated between ambient temperature to 2600°C. Properties such as specific heat, thermal diffusivity, thermal expansion and thermal conductivity for the composite in all three material orientations (x,y,z) have been determined experimentally. The results highlighted the effects of heat treatment on the thermophysical properties of the C/C material. The specific heat of the C/C composite increases with temperature and follows the characteristic trend of conventional carbon and graphite materials. During the first heating cycles of the C/C specimens, the diffusivity was found to reduce with increasing temperature until about 1200°C, followed by an increase in diffusivity with increasing temperature. The same shift in thermophysical properties was also observed in CTE measurements, which were shown to increase with increasing temperatures until 1200°C, followed by a decrease between 1300-1500°C. As a consequence, the same shift is observed in the deduced conductivity of the C/C. Subsequent thermal analyses on the candidate C/C composite reveal markedly different thermophysical properties which are to be expected should the composite be subjected to specific heat treatment before the application for hypersonic flight vehicle structures and components. The diffusivity of the C/C composite which had already undergone heat treatment was significantly higher particularly in the lower temperature range. Similarly, it was observed that the heat treatment of the C/C resulted in a significant decrease in the CTE measurements. Finally, the XRD analyses showed increased crystallite sizes, together with an increase in local defects as a result of heating the C/C to ultra-high temperatures up to 2600°C. Most notably, the in-plane lattice parameter d_{002} was used to estimate the increased degree of graphitisation, $\bar{g}$, of the C/C composite, from 0.60 to 0.77 as a result of heat cycling.

Acknowledgements

References

1. Lages, EN & Cavalcanti Marques, SP 2022, "Prediction of effective thermal conductivity of multiphase composites with periodic microstructures using an expanded micromechanical

model", International Journal of Thermal Sciences, vol. 171.

2. NETZSCH, "Operating Instructions STA 449 Fx Jupiter", 2021.

3. Höhne, G., Hemminger, W. F., and Flammersheim, H. J., 2003, Differential Scanning Calorimetry, Springer, Germany.

4. Q. Wang, H.P. Wang, D.L. Geng, M.X. Li, B.B. Wei, "A calorimetric study assisted with first principle calculations of specific heat for Si-Ge Alloys within a broad temperature range", Chin. Phys. Lett. 35, 126501-1-126501-4 (2018).

5. NETZSCH, "Operating Manual Laser Flash Apparatus LFA 427", 2021.

6. ASTM Standard E1461, 2007, "Standard Test Method for Thermal Diffusivity by the Flash Method," ASTM International, West Conshohocken, PA.

7. TA Instruments, "DIL821HT/DIL822HT Guidelines for Initial Startup", 2015.

8. ASTM Standard E228, 1995, "Standard Test Method for Linear Thermal Expansion of Solid Materials With a Viterous Silica Dilatometer," ASTM International, West Conshohocken, PA.

9. Pei Wang, Shouyang Zhang, Hejun Li, Jie Kong, Wei Li, Wajed Zaman, "Variation of thermal expansion of carbon/carbon composites from 850 to 2500°C", Ceramics International, Volume 40, Issue 1, Part A, 1273-1276, 2014.

10. Fitzer, E. Carbon Reinforcements and Carbon/Carbon Composites. Springer, (2013).

11. N. Burger, A. Laachachi, M. Ferriol, M. Lutz, V. Toniazzo, D. Ruch, "Review of thermal conductivity in composites: Mechanisms, parameters and theory", Progress in Polymer Science, Volume 61, 2016, 1-28.

12. L.-k. Tsui , F. Garzon , CarbonXS GUI, "a graphical front-end for CarbonXS," J. Appl. Crystallogr. 50 (6) (2017) 1830–1833 .

13. H. Shi , J.N. Reimers , J.R. Dahn, "Structure-refinement program for disordered carbons," J. Appl. Crystallogr. 26 (6) (1993) 827–836.

14. X. Huang, "Fabrication and properties of carbon fibers," Materials (Basel)., vol. 2, no. 4, 2369–2403, 2009.

15. Z. Wang, O. Muránsky, H. Zhu, T. Wei, Z. Zhang, M. Ionescu, C. Yang, J. Davis, G. Hu, P. Munroe, W. Windes, "Impact of pre-existing crystal lattice defects on the accumulation of irradiation-induced damage in a C/C composite," Journal of Nuclear Materials, Volume 564, 2022, 153684.