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Thermal Characterization of Carbon Fiber-Reinforced Carbon (C/C)

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Carbon fiber-reinforced carbon (C/C) composites consist in a carbon matrix, which holds carbon or graphite fibers together. Their physical properties are determined by the fibers, matrix materials, layer buildup, as well as the material preparation and processing. They are designed as materials of high performance for highly demanding applications, looking for low thermal expansion, low density, high resistance to thermal shock, very good creep resistance at elevated temperatures, good chemical stability, among others. The complex structure of the C/C composites causes that mechanical, electrical, and thermal properties have different values related to the orientation of the fibers axis. In this work, we use Laser Flash Technique to study the thermal diffusivity and thermal conductivity of carbon fiber-reinforced carbon (C/C) composite consisting in laminates of weaved bundles of carbon fibers, forming a regular and repeated orthogonal pattern, all of them built into a matrix of graphite. Experimental data were fitted to mathematical model for the effective thermal conduction based on the solid heat transfer contribution and the radiative contribution. Results show that the values on thermal diffusivity and thermal conductivity measured in the perpendicular plane to the fiber axis decreases almost six times with respect those obtained in the parallel plane of laminate. It is also shown that in the temperature range from 373 to 1673 K, the thermal conductivity of the C/C composites remains almost constant at the value of 5.28 ± 0.42 W/mK in the direction perpendicular to the fiber axis.

Keywords: Carbon fiber-reinforced carbon, Solid thermal conductivity, Radiative conductivity, Rosseland extinction coefficient

Introduction

Carbon fiber-reinforced carbon (C/C) composites are ideally suited to applications where strength, stiffness, and others mechanical characteristics have critical requirements[1],[2]. Carbon fibers consist in long thin filaments composed mostly of carbon atoms joined together to form microscopic crystals (graphitic planes) aligned in parallel along the fiber axis[3],[4]. Graphitic planes exhibit a highly anisotropic due to the difference between in-plane and out-of-plane bonding of carbon atoms. This fact makes that the thermophysical properties of the fibers are more longer in the plane than it is perpendicular to the plane[5], [6]. Carbon fibers can reach values in modulus, thermal and electrical conductivity in the order of 900 GPa, 1000 W/mK, and 10^6 S/m, respectively and a very low mass density (1.75 - 2.0 g/cm³)[7], [8]. C/C composites consists in laminates of bundles weave of carbon fibers those forming a regular and repeated pattern, these are contained within a carbon matrix. The addition of the fibers in to the matrix contributes to the high degree of mechanical stability to the material[9], [10]. Individual properties of C/C composites are determined by the fiber (type, volume fraction, and orientation), the architecture (layer buildup, pores distribution, etc.) and thermal treatment that includes carbonization and graphitization[6]; graphitization process improves some of the composite material's properties such as thermal diffusivity, electrical conductivity, thermal stability and resistance to both oxidation and corrosion. In other hand, the number of impregnation and re-baking implies changes on physical properties such as inter-laminar shear strength, flexural and tensile strength, bulk density, pore volume and Young's modulus, compressive strength, and resistance to alternating loads. The appropriate selection of the production parameters as well as the constituent materials allows us to obtain C/C composites with physical and mechanical properties suitable for a wide range of applications[11]–[14].

Application of C/C composites materials in high temperature technology includes solar technology [15], furnace construction and heat treatment, internal combustion engines, aerospace technology, among others[2], [16]. The vibrations of the crystal lattice are the main source of heat conduction in C/C composites[17], crystal lattice vibrations can be described by the phonon interactions and they are divided in: phonon–phonon interaction, phonon–defect interaction and phonon–interface interaction. It is well known that at low temperature the energy of the optic phonon is small and can be ignored[18], so heat transfer mainly depends on the acoustic phonon (the elastic wave interacting with matter). In phonon–phonon interaction, the mean free path is very sensitive to temperature[19], this is because at low temperatures phonons do not scatter frequently with other phonons and defects, so the mean free path is limited mainly by the boundary of the sample. Thermal conductivity of C/C composites at elevated temperature exhibits an important growth since the amplitude of atomic vibrations in crystalline lattice increases with temperature, therefore increases the phonon–phonon interaction which is responsible for thermal conductivity. Also, at elevated temperature T heat capacity is independent of temperature and the number of phonons are proportional to T , then the mean free path λ is proportional to $1/T^2$ [20][21], at intermediate temperature phonon scatter from defects and other phonons. In this work, we present the results obtained in the thermal and optical characterization of carbon fiber-reinforced carbon, thermal diffusivity and thermal conductivity at the perpendicular direction to the fibers axis, heat capacity was determined by means of an indirect method[22], all of them were obtained in the range of temperatures from 298 to 1700 K with the Laser Flash Technique (LFT)[23]. Due to the anisotropy of the C/C composites samples, both the thermal diffusivity and thermal conductivity were obtained in three different directions (two parallel to fibers axis and another perpendicular) with a calorimetric method[24]. Additionally, solar absorptance and thermal emittance were obtained in the UV-VIS-NIR-MIR wavelength range, to know the response of the material under solar radiation and its behavior at elevated temperature surrounding.

Materials and methods

Heat transfer in any composite that comprises an orthogonal arrangement of fibers within a matrix will be governed by the thermal conductivities of the two components, their relative volume fraction and their geometrical arrangement[3], when the matrix contains porosity (cracks or pores) it is necessary taking into account a third phase due to a pore is a barrier to heat flow and its presence and distribution has an important influence in heat transfer[25]–[27]. Photothermal techniques are based on the heating of the material under test, the material response to that excitation depends on their thermophysical properties. Laser flash technique (LFT) is a dynamic method used in order to measuring the thermal diffusivity of solid materials in a wide range of temperature[28]. In general, LFT consists on illuminating one side of a sample by impinging a laser pulse of short duration, the laser energy absorbed by the sample surface causes local heating which is transmitted through the sample and a temperature increase occurs on the opposite side[29]; this increment in temperature is measured as a function of time using an infrared detector located just in front of the sample [30]. The recorded temperature signal is processed using adequate mathematical models, to obtain the thermal diffusivity. LFT has its theoretical basis on the solution of the differential equation for heat conduction in transient regime [31]. The simplest model for describe the temperature field at the opposite side of the sample was proposed by Parker et al. [23], assuming one-dimensional heat transfer with adiabatic boundary condition[32]. Parker's model is valid only if the sample is homogeneous, heat flux is predominantly one-dimensional, heat losses are negligible and uniform absorption of the laser energy, and short pulse length of the laser compared to the heat transport times[33]. These last are ideal situations since there are generally radial heat losses[34] which depends of the material as well the dimensions. Under these conditions, it is essential to make the necessary corrections to the mathematical fitting model[35], [36]. In order to obtain the thermal properties of C/C samples in the direction parallel and perpendicular to the plane of laminate, we implemented an experimental set based on the modified Angstrom method[24]. This method involves heating periodically one end of a bar and monitoring the temperature oscillations at the opposite end of it, phase lag of the signal is related with material's thermal diffusivity [37]. From the measurement of the thermal diffusivity (α) we can determine the thermal conductivity (κ) when knowing the data of specific heat (c) and mass density (ρ). C/C composites samples consist on disks (25.2 mm in diameter and 1.6, 2.1 and 5.2 mm on thickness) and rods (30.2 x 9.6 x 5.2 mm), bulk density: $1.509 \pm 0.012 \text{ g/cm}^3$, fiber volume fraction: 60 %, porosity: 8 % [38]. Figure 1 shows an image of C/C composite material, it consists in laminates of weaves of bundles (tows), everyone containing approximately 12 000 filaments of carbon fibers forming a regular and repeated orthogonally pattern, all of them are contained within a carbon matrix. Samples were darkening by applying a thin layer of graphite (GRAPHIT 33, CRC Industries Europe NV), this treatment is usually applied in the laser flash technique; it was done to ensure the uniform absorption on the sample surface of the laser energy and the emission of infrared energy[39].

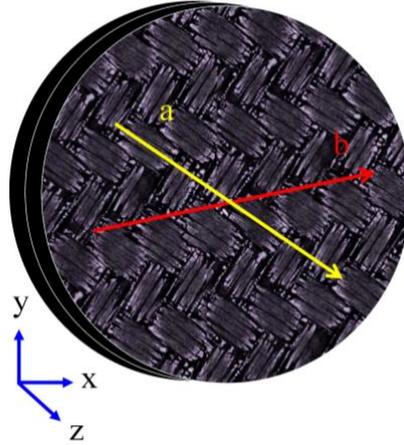


Figure 1. C/C composite material that consisting in laminates of weaves of bundles (tows) of carbon fibers forming a regular and repeated orthogonally pattern, all of them are contained within a graphite matrix.

Results

Figure 2 shows the values of the thermal diffusivity measured perpendicular to the plane of the laminate (through-thickness direction) in the C/C composites and a disk of standard graphite (thickness: 2.01 mm, mass density: 1.79 g/cm³, mass: 1.79 g) in the temperature range from 298 to 1673 K with the LFT. Measurements were performed with a laser flash apparatus (LINSIES, LFA1000). Materials with anisotropic structures such as C/C composite samples have different linear expansion coefficients in different directions[18], as result of this; the total volumetric expansion is distributed unequally among the three axes. Bulk density as function of temperature was determined by using the relation $\rho(T)=\rho_0/(0.9965-1.3192\times 10^{-5}T+4.5842\times 10^{-8}T^2-4.9752\times 10^{-11}T^3)$ [40] being ρ_0 the value of mass density at 298 K. To calculate the heat capacity of the C/C composites samples, we implement an indirect method, where the maximum of the temperature raise in the sample is compared to the maximum of the temperature raise of the reference sample (standard graphite) both, the composite and the reference samples are measured under the same conditions [22] so the energy of the laser pulse and the sensitivity of the infrared detector are the same for both measurements. Since the energy is the same for sample (*sam*) and reference (*ref*), the heat capacity of the sample can be calculated according the following relation:

$$c_{sam} = \frac{c_{ref}\Delta T_{ref}m_{ref}}{\Delta T_{sam}m_{sam}} \quad (\text{Eq.1})$$

Where ΔT is the raise in temperature (K), m is the weight (g) and c is the heat capacity (J/gK), Value of heat capacity as a function of temperature for the C/C composites samples presents an exponential behavior. It can be fixed to $c(T) = 1.8946 - 4.164 \exp(-T/254.7)$. Results are consistent whose are reported in literature[41][42], see Fig. 2. Once the thermal diffusivity has been obtained we can determine the thermal conductivity as a function of temperature $\kappa(T)$ with data of specific heat[38] and mass density according to: $\kappa(T)=\alpha(T)c(T)\rho(T)$. Values on thermal diffusivity as a function of temperature for the C/C composites samples as well as standard graphite measured through-thickness direction plane presents an exponential decay behavior, $\alpha(T)=0.01825+0.1307 \exp(-T/195.9)$ for C/C composite and $\alpha(T)=0.14808+0.84719 \exp(-T/238.86)$ for standard graphite. Fig. 3 presents the thermal conductivity obtained for the C/C composite samples and a sample of standard graphite. As can be seen from this Fig. 3, in the temperature range of 373 to 1673 K the thermal conductivity of C/C composites samples remains almost constant in the value of 5.28 ± 0.42 W/mK. Experimental data obtained in thermal conductivity for standard graphite can be fit to $\sim 1/T^x$ (being $x=0.6$) in the temperature range from 800 K to 1800K.

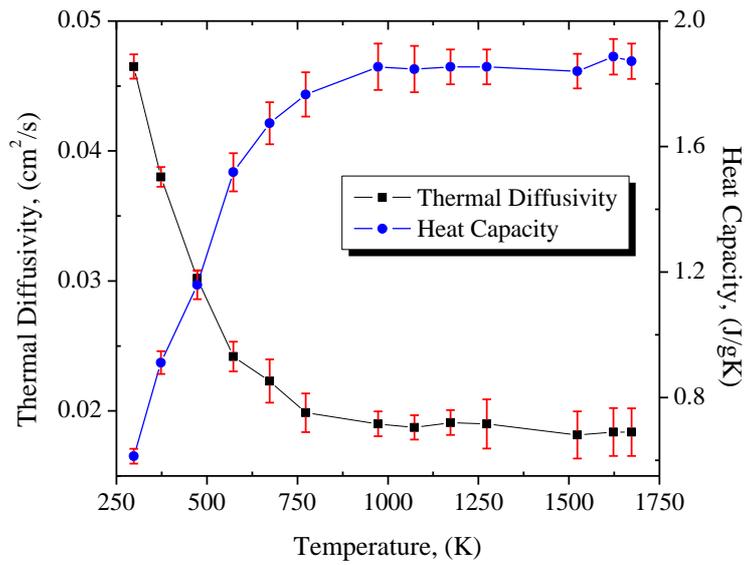


Figure 2. Values of the thermal diffusivity measured perpendicular to the plane of the laminate (through-thickness direction) and heat capacity in the temperature range from 298 to 1673 K with the LFT.

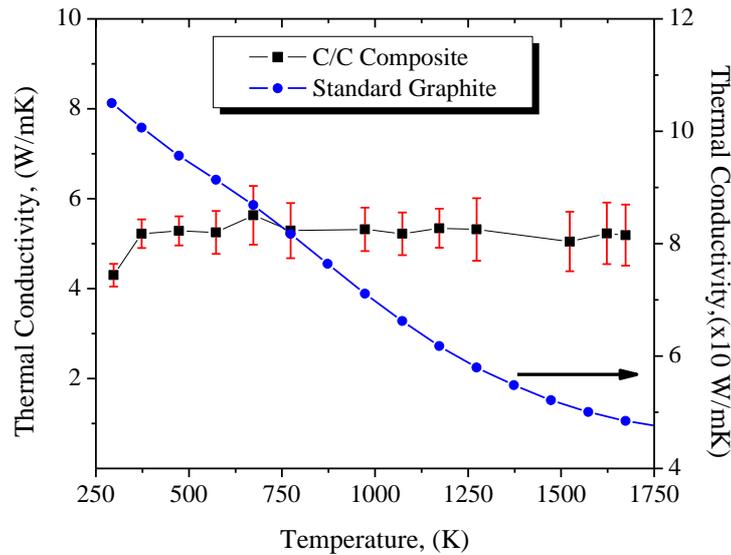


Figure 3. C/C composite's thermal conductivity measured perpendicular to the plane of the laminate (through-thickness direction) and the reference sample (standard graphite) in the temperature range from 298 to 1673 K with the LFT.

Thermal diffusivity of C/C composite was measured in three directions; a and b in the plane of laminate (x - y plane), and c perpendicular to the plane of laminate (through thickness, z plane). For this purpose, we implement a colorimetric method and specimens like bars of length L were prepared (table 1), periodic heating frequency was 0.048 Hz [37]. Table 1 shows the results obtained in C/C composite characterization. There is not a significant difference in thermal diffusivity values in a and b directions, due to the fiber counts in the warp and weft directions are equivalent and that there is no preferential formation of porosity in either direction. As result of these, the thermal conductivity will be invariant in the plane of the weave [43]. In other hand, through the plane (c direction), thermal diffusivity drops one

order of magnitude compared with in plane measurements. The last result implies that there is an anisotropic behavior in sample's heat conduction, which is related with its laminate structure. The heat flows better in the laminated planes than through the volume (perpendicular to the planes), this last is due to large number of long fibers provide the continuous path for the phonon transmission, however in the c direction, the phonon movement is readily obstructed[18]. The thermal conductivity measured in the direction parallel to the laminate plane is close to five times greater than that obtained in the plane perpendicular to the laminate, this result agrees with is reported in literature[18], [41], [44], [45].

Table 1. Thermal diffusivity and thermal conductivity measured in three different directions, two parallel to the plane of the laminate (a and b) and the other one perpendicular to the plane of the laminate (c direction). Temperature of the sample was 308 K in average[37]. Values for heat capacity and mass density were 0.652 ± 0.024 J/gK and 1.509 ± 0.012 g/cm³, respectively. (i) Values of the thermal conductivity and thermal diffusivity measured with LFT technique in the c direction.

Direction	Thickness (mm)	Thermal Diffusivity (10^{-2} cm ² /s)	Thermal Conductivity (W/mK)
a (x-y plane)	30.1±0.1	14.8±0.9	14.5±1.5
b (x-y plane)	30.2±0.1	15.1±1.1	14.8±1.7
c (z plane)	5.2±0.1	2.6±0.1	2.6±0.2
c (z plane) (i)	2.1±0.3	4.5±0.5	4.6±0.8

The effective thermal conductivity as a function of the temperature of the composite C/C is determined by the sum of the solid thermal conductivity and radiative conductivity. In a simple model for heat transfer in C/C composites the overall heat transfer is the sum of three contributions: solid heat conduction, radiation heat transfer and, heat transfer through the gas present in the pores[46], in present work thermal conduction by gas convection is ignored due to its low value with respect to the other heat conduction mechanisms. The effective thermal conductivity as a function of the temperature of the composite C/C is determined by (see appendix A Eq. A14):

$$\kappa_{eff}(T) = (1 - p)^2 \kappa_{me}(T) \left[\alpha(T) + \frac{1}{2} \beta(T)^2 + \beta(T) \sqrt{\alpha(T) + \frac{\beta(T)^2}{4}} \right] + \frac{16}{3} \sigma_{SB} \frac{n^2(T)}{\sigma_e(T)} T^3 \quad (\text{Eq.2})$$

In Fig. 4, the values of the experimental data obtained from the thermal conductivity and the fitting of such data with the equation 2 can be observed, the best fit is obtained for values of thermal conductivity in a temperature range higher than 750 K, this it is because the data of the conductivity of the fibers in the temperature range below 750 K is not entirely reliable (Eq. A8).

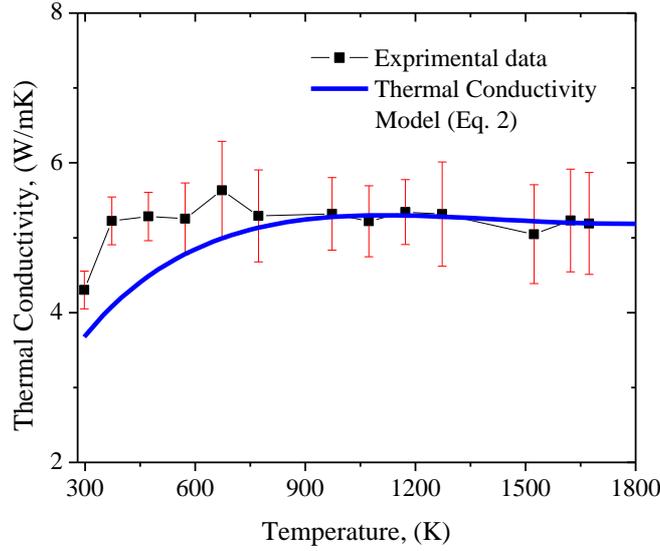


Figure 4. Experimental data values obtained for the thermal conductivity and the equation 2, the best fitting is obtained for values of thermal conductivity in a temperature range higher than 750 K

Reflectance spectroscopy

Reflectance spectroscopy is a powerful tool for characterizing the optical properties of a great diversity of materials applied in solar technology [47]–[50]. The analysis can be done in two wavelength ranges of interest: Ultraviolet/visible/near infrared and medium infrared, where solar spectrum radiation wavelengths and infrared emission range are located respectively. Reflectance spectra were obtained in the range of 0.3 to 2 microns using two UV-VIS-NIR spectrometers (Avantes, model AVASpec2048 and model AvaSpec-NIR256-2.5), in both cases, measures were performed with an integrating sphere (Avantes, model 50-LS-HAL). The reflectance spectra in the range of 2 to 15 microns were obtained with an FTIR spectrometer (Perkin Elmer, model Frontier NIR / MIR) equipped with an integrating sphere (PICO, model IntegratIR). In Fig. 4, the reflectance spectrum is shown in the range from 0.3 to 15 microns and the solar irradiance spectrum [51]. Values on solar absorbance ($\alpha(\lambda)$) were calculated in the range from 0.3 to 2.5 microns by weighting the reflection spectra data against the solar irradiance spectrum ASTM G173-03[51]. Whereas, values on thermal emittance ($\varepsilon(T)$) were determined in the range of 2 to 15 microns by weighting the IR spectra data against the black body radiation (I_{BB}) at 373.2 K. Both, solar absorbance and thermal emittance were calculated with the following relations [52]:

$$\alpha(\lambda) = \frac{\int_{0.3}^{2.5} I_{SUN}(\lambda) \cdot [1 - R(\lambda)] d\lambda}{\int_{0.3}^{2.5} I_{SUN}(\lambda)} , \varepsilon(T) = \frac{\int_2^{15} I_{BB}(\lambda, T) \cdot [1 - R(\lambda)] d\lambda}{\int_2^{15} I_{BB}(\lambda, T)} \quad (\text{Eq.3})$$

Where $I_{SUN}(\lambda)$ is the solar irradiance spectrum, $R(\lambda)$ is the reflection spectra data and $I_{bb}(\lambda)$ is the black body radiation function. Values obtained for solar absorbance and thermal emittance were $78.5 \pm 2\%$ and $59.4 \pm 1\%$, respectively. Spectral selectivity η (solar absorbance α to thermal emittance ε relation) has been determined using different methods in accordance with the operating temperature[53]–[55][56]. One of the simplest methods uses the relation $\eta = \alpha/\varepsilon$, but this method is not very reliable since it has been reported that a high absorption properties at low wavelengths have a stronger influence on the spectral selectivity than a low emittance at longer wavelengths[57]. Due this, solar absorbance effect is more important than the thermal emittance for the spectral selectivity, a more accurate way of determining spectral selectivity is to use the relation $\eta = \alpha - 0.5\varepsilon$ [58], this equation reflects in a better way the weight factor of solar absorbance on the spectral selectivity. Fig. 4 (inserted graphic) shows the thermal emittance (Eq.3) calculated as function of the thermal emission of a black body in the temperature range from 373 to 3073 K. In concertation ratios over 600 suns [59] the influence of thermal emittance

(operating temperatures above 1500 K) is less important, and in operating temperatures higher than 2000 K thermal emittance is almost independent of temperature.

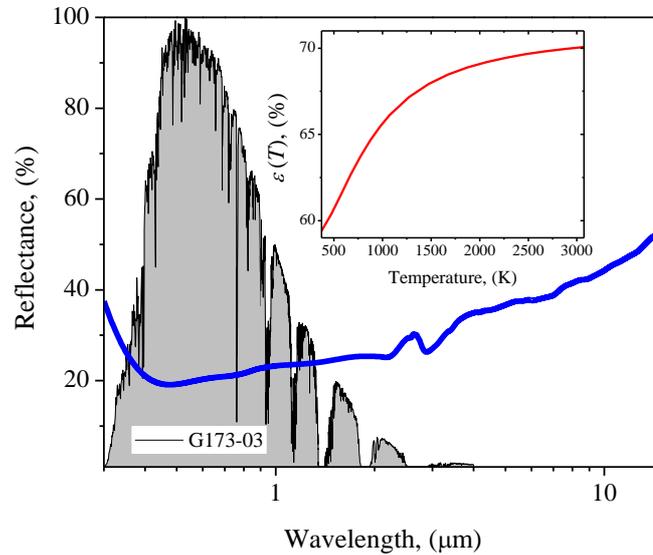


Figure 4. Reflectance spectrum of the samples of carbon composite in the range of 0.3 to 15 microns and the sun radiation spectrum ASTM G173-03[51]. The inset graphic corresponds to the thermal emittance (Eq.3) calculated as function of the thermal emission of a black body in the temperature range from 373 to 3073 K.

Conclusions

In this work, we have determined the thermal conductivity of carbon fiber-reinforced carbon (C/C) composite, for this purpose, a mathematical model for the effective thermal conduction based on the solid heat transfer contribution and the radiative contribution has been developed. Results show that solid heat conduction is the principal contributor to the overall heat transfer, but its influence decreases when the temperature increases, this last is due to the sum of different scattering process. However, these scattering processes are predominantly dominant at different temperature ranges, for temperatures above 1000 K, the influence of radiative conduction becomes more important in the overall heat transfer. Using a calorimetric method, we found that values on thermal diffusivity and thermal conductivity measured in-plane to the fiber axis decreases almost six times with respect those obtained out-plane of laminate.

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References

- [1] S. Chand, "Carbon fibers for composites," *J. Mater. Sci.*, vol. 35, no. 6, pp. 1303–1313, 2000.
- [2] W. Krenkel and F. Berndt, "C/C-SiC composites for space applications and advanced friction systems," *Mater. Sci. Eng. A*, vol. 412, no. 1–2, pp. 177–181, 2005.
- [3] T. Tian, "Anisotropic Thermal Property Measurement of Carbon-fiber / Epoxy Composite Materials," University of Nebraska-Lincoln, 2011.
- [4] C. Sauder, J. Lamon, and R. Pailler, "The tensile behavior of carbon fibers at high temperatures up to 2400 °C," *Carbon*, vol. 42, no. 4, pp. 715–725, Jan. 2004.
- [5] D. F. Pedraza and P. G. Klemens, "Effective conductivity of polycrystalline graphite," *Carbon*, vol. 31, no. 6, pp. 951–956, 1993.
- [6] X. Huang, "Fabrication and properties of carbon fibers," *Materials (Basel)*, vol. 2, no. 4, pp. 2369–2403, 2009.
- [7] M. L. Minus and S. Kumar, "The processing, properties, and structure of carbon fibers," *JOM J. Miner. Met. Mater. Soc.*, vol. 57, pp. 52–58, 2005.
- [8] S. Ghosh, I. Calizo, D. Teweldebrhan, E. P. Pokatilov, D. L. Nika, A. A. Balandin, W. Bao, F. Miao, and C. N. Lau, "Extremely high thermal conductivity of graphene: Prospects for thermal management applications in nanoelectronic circuits," *Appl. Phys. Lett.*, vol. 92, no. 15, 2008.
- [9] S. Y. Fu, B. Lauke, E. Mäder, C. Y. Yue, and X. Hu, "Tensile properties of short-glass-fiber-and short-carbon-fiber-reinforced polypropylene composites," *Compos. Part A Appl. Sci. Manuf.*, vol. 31, no. 10, pp. 1117–1125, 2000.
- [10] S. Y. Fu, B. Lauke, E. Mäder, X. Hu, and C. Y. Yue, "Fracture resistance of short-glass-fiber-reinforced and short-carbon-fiber-reinforced polypropylene under Charpy impact load and its dependence on processing," *Mater. Process. Technol.*, vol. 89–90, pp. 501–507, 1999.
- [11] E. T. Thostenson, W. Z. Li, D. Z. Wang, Z. F. Ren, and T. W. Chou, "Carbon nanotube/carbon fiber hybrid multiscale composites," *J. Appl. Phys.*, vol. 91, no. 9, pp. 6034–6037, 2002.
- [12] Z. Zhang, Z. Wu, Y. Sun, and F. Li, "Design aspects of the Chinese modular high-temperature gas-cooled reactor HTR-PM," *Nucl. Eng. Des.*, vol. 236, no. 5–6, pp. 485–490, 2006.
- [13] J. Fukai, M. Kanou, Y. Kodama, and O. Miyatake, "Thermal conductivity enhancement of energy storage media using carbon fibers," *Energy Convers. Manag.*, vol. 41, no. 14, pp. 1543–1556, 2000.
- [14] M. Balat-Pichelin, D. Hernandez, G. Olalde, B. Rivoire, and J. F. Robert, "Concentrated Solar Energy as a Diagnostic Tool to Study Materials Under Extreme Conditions," *J. Sol. Energy Eng.*, vol. 124, no. August 2002, p. 215, 2002.
- [15] P. G. Loutzenhiser, A. Meier, and A. Steinfeld, "Review of the Two-Step H₂O/CO₂-Splitting Solar

- Thermochemical Cycle Based on Zn/ZnO Redox Reactions,” *Materials (Basel)*, vol. 3, no. 11, pp. 4922–4938, Nov. 2010.
- [16] T. Lin, D. Jia, P. He, M. Wang, and D. Liang, “Effects of fiber length on mechanical properties and fracture behavior of short carbon fiber reinforced geopolymer matrix composites,” *Mater. Sci. Eng. A*, vol. 497, no. 1–2, pp. 181–185, 2008.
- [17] N. Burger, A. Laachachi, M. Ferriol, M. Lutz, V. Toniazzo, and D. Ruch, “Review of thermal conductivity in composites: Mechanisms, parameters and theory,” *Prog. Polym. Sci.*, vol. 61, pp. 1–28, 2016.
- [18] R. Luo, T. Liu, J. Li, H. Zhang, Z. Chen, and G. Tian, “Thermophysical properties of carbon/carbon composites and physical mechanism of thermal expansion and thermal conductivity,” *Carbon*, vol. 42, no. 14, pp. 2887–2895, 2004.
- [19] J. Heremans, I. Rahim, and M. S. Dresselhaus, “Thermal Conductivity and Raman spectra of carbon fibers,” *Phys. Rev. B*, vol. 32, no. 10, pp. 6742–6747, 1985.
- [20] P. Gonnet, “Thermal Conductivity and Coefficients of Thermal Expansion of SWNTs/Epoxy Nanocomposites, Master’s thesis,” The Florida State University, 2004.
- [21] B. Nysten, J.P. Issi, R. Barton, D.R. Boyington, and J.G. Lavin, “Determination of lattice defects in carbon fibers by means of thermal-conductivity measurements,” *Phys. Rev. B*, vol. 44, no. 5, pp. 2142–2148, 1991.
- [22] K. Shinzato and T. Baba, “A Laser Flash Apparatus for Thermal Diffusivity and Specific Heat Capacity Measurements,” *J. Therm. Anal. Calorim.*, vol. 64, pp. 413–422, 2001.
- [23] W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, “Flash method of determining thermal diffusivity, heat capacity, and thermal conductivity,” *J. Appl. Phys.*, vol. 32, no. 9, pp. 1679–1684, 1961.
- [24] N. M. Jackett, T. H. Sein, D. D. Allred, and J. U. Trefny, “Thermal Diffusivity by the Modified Angstrom Technique,” *Proceedings of the Fifth International Conference on Thermoelectric Energy Conversion*. pp. 116–119, 1984.
- [25] A. J. Whittaker and R. Taylor, “Thermal transport properties of carbon-carbon fibre composites III. Mathematical modelling,” *Proc. R. Soc. Lond. A*, vol. 430, pp. 199–211, 1990.
- [26] W. Woodside, “Calculation of the Thermal Conductivity of Porous Media,” *Can. J. Phys.*, vol. 36, no. 7, p. 815, 1958.
- [27] R. Yang, G. Chen, and M. S. Dresselhaus, “Thermal conductivity of simple and tubular nanowire composites in the longitudinal direction,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 72, no. 12, pp. 1–7, 2005.
- [28] A. Cezairliyan, T. Baba, and R. Taylor, “A High-Temperature Laser-Pulse Thermal-Diffusivity Apparatus,” *Int. J. Thermophys.*, vol. 15, no. 2, pp. 317–341, 1994.
- [29] H. Shibata, A. Suzuki, and H. Ohta, “Measurement of Thermal Transport Properties for Molten Silicate Glasses at High Temperatures by Means of a Novel Laser Flash Technique,” *Mater. Trans.*, vol. 46, no. 8,

- pp. 1877–1881, 2005.
- [30] T. Nishi, H. Shibata, H. Ohta, and Y. Waseda, “Thermal Conductivities of Molten Iron, Cobalt, and Nickel by Laser Flash Method,” *Metall. Mater. Trans. A*, vol. 34, no. December, pp. 2801–2807, 2003.
- [31] D. Almond and P. Patel, *Photothermal Science and Techniques*. London: Chapman & Hall, 1996.
- [32] W. N. Dos Santos, P. Mummery, and A. Wallwork, “Thermal diffusivity of polymers by the laser flash technique,” *Polym. Test.*, vol. 24, no. 5, pp. 628–634, 2005.
- [33] S. Min, J. Blumm, and A. Lindemann, “A new laser flash system for measurement of the thermophysical properties,” *Thermochim. Acta*, vol. 455, no. 1–2, pp. 46–49, Apr. 2007.
- [34] L. M. Clark and R. E. Taylor, “Radiation loss in the flash method for thermal diffusivity,” *J. Appl. Phys.*, vol. 46, no. 1975, pp. 714–719, 1975.
- [35] R. D. Cowan, “Pulse method of measuring thermal diffusivity at high temperatures,” *J. Appl. Phys.*, vol. 34, no. 1963, pp. 926–927, 1963.
- [36] J. A. Cape and G. W. Lehman, “Temperature and finite pulse-time effects in the flash method for measuring thermal diffusivity,” *J. Appl. Phys.*, vol. 34, no. 7, pp. 1909–1913, 1963.
- [37] J. Bodzenta, B. Burak, M. Nowak, M. Pyka, M. Szalajko, and M. Tanasiewicz, “Measurement of the thermal diffusivity of dental filling materials using modified Angstrom’s method,” *Dent. Mater.*, vol. 22, no. 7, pp. 617–621, 2006.
- [38] S. K. Gmbh, “Schunk–Carbon fiber-reinforced carbon (C / C),” Schunk Group, Heuchelheim, Germany.
- [39] S. K. Kim and Y. J. Kim, “Determination of apparent thickness of graphite coating in flash method,” *Thermochim. Acta*, vol. 468, no. 1–2, pp. 6–9, 2008.
- [40] H. Whittaker, A.J., Taylor, R. and Tawil, “Thermal transport properties of carbon-carbon fibre composites I. Thermal diffusivity measurements,” *Proc. R. Soc. Lond. A*, vol. 430, pp. 167–181, 1990.
- [41] C. W. Ohlhorst, W. L. Vaughn, P. O. Ransone, and H. T. Tsou, “Thermal Conductivity Database of Various Structural Carbon-Carbon Composite Materials,” Hampton, Virginia, 1997.
- [42] A. Cezairliyan and A. P. Miiller, “Specific Heat Capacity and Electrical Resistivity of a Carbon-Carbon Composite in the Range 1500- 3000 K by a Pulse Heating Method,” *Int. J. Thermophys.*, vol. 1, no. 3, 1980.
- [43] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*. London: Oxford University Press, 1959.
- [44] K. Sun, M. A. Stroschio, and M. Dutta, “Graphite C-axis thermal conductivity,” *Superlattices Microstruct.*, vol. 45, no. 2, pp. 60–64, 2009.
- [45] L. M. Manocha, A. Warriar, S. Manocha, D. Sathiyamoorthy, and D. Banerjee, “Thermophysical properties of densified pitch based carbon / carbon materials — I . Unidirectional composites,” *Carbon*, vol. 44, pp. 480–487, 2006.
- [46] R. . Baxter, R. . Rawlings, N. Iwashita, and Y. Sawada, “Effect of chemical vapor infiltration on erosion and thermal properties of porous carbon/carbon composite thermal insulation.,” *Carbon*, vol. 38, no. 3, pp. 441–

- 449, 2000.
- [47] Q. C. Zhang, "Recent progress in high-temperature solar selective coatings," *Sol. Energy Mater. Sol. Cells*, vol. 62, no. 1, pp. 63–74, 2000.
- [48] K. Gelin, T. Boström, and E. Wäckelgård, "Thermal emittance of sputter deposited infrared reflectors in spectrally selective tandem solar absorbers," *Sol. Energy*, vol. 77, no. 1, pp. 115–119, 2004.
- [49] S. Yue, S. Yueyan, and W. Fengchun, "High-temperature optical properties and stability of $\text{Al}_x\text{O}_y\text{-AlN}_x\text{-Al}$ solar selective absorbing surface prepared by DC magnetron reactive sputtering," *Sol. Energy Mater. Sol. Cells*, vol. 77, no. 4, pp. 393–403, Jun. 2003.
- [50] L. Rebouta, A. Pitães, M. Andritschky, P. Capela, M. F. Cerqueira, A. Matilainen, and K. Pischow, "Optical characterization of $\text{TiAlN/TiAlON/SiO}_2$ absorber for solar selective applications," *Surf. Coatings Technol.*, vol. 211, pp. 41–44, Oct. 2012.
- [51] American Society for Testing and Materials, "Standard Tables for Reference Solar Spectral Irradiances : Direct Normal and Hemispherical on 37 Tilted Surface," West Conshohocken, PA, USA, 2013.
- [52] J. A. Duffie and W. A. Beckman, *Solar Engineering of Thermal Processes*, Third Edit. New Jersey: John Wiley & Sons, 2006.
- [53] M. A. Leon and S. Kumar, "Mathematical modeling and thermal performance analysis of unglazed transpired solar collectors," *Sol. Energy*, vol. 81, no. 1, pp. 62–75, 2007.
- [54] F. Russell, "Heat Transfer Analysis and Modeling of a Parabolic Trough Solar Receiver Implemented in Engineering Equation Solver," *Natl. Renew. Energy Lab.*, no. October, p. 164, 2003.
- [55] C. K. Ho and J. E. Pacheco, "Derivation of a Levelized Cost of Coating (LCOC) Metric for Evaluation of Solar Selective Absorber Materials," *Energy Procedia*, vol. 69, pp. 415–423, 2015.
- [56] S. A. Kalogirou, "Solar thermal collectors and applications," *Prog. Energy Combust. Sci.*, vol. 30, no. 3, pp. 231–295, 2004.
- [57] K. Burlafinger, A. Vetter, and C. J. Brabec, "Maximizing concentrated solar power (CSP) plant overall efficiencies by using spectral selective absorbers at optimal operation temperatures," *Sol. Energy*, vol. 120, pp. 428–438, 2015.
- [58] Z. Chen, T. Boström, and Q. Nguyen, "Carbon Nanotube Spectrally Selective Solar Absorbers," *Proc. EuroSun 2014 Conf.*, no. September 2014, pp. 1–7, 2015.
- [59] J. Moon, T. K. Kim, B. VanSaders, C. Choi, Z. Liu, S. Jin, and R. Chen, "Black oxide nanoparticles as durable solar absorbing material for high-temperature concentrating solar power system," *Sol. Energy Mater. Sol. Cells*, vol. 134, pp. 417–424, Mar. 2015.
- [60] M. W. Pilling, B. Yates, M. A. Black, and P. Tattersall, "The thermal conductivity of carbon fibre-reinforced composites," *J. Mater. Sci.*, vol. 14, no. 6, pp. 1326–1338, 1979.
- [61] H. B. Shim, M. K. Seo, and S. J. Park, "Thermal conductivity and mechanical properties of various cross-

- section types carbon fiber-reinforced composites,” *J. Mater. Sci.*, vol. 37, no. 9, pp. 1881–1885, 2002.
- [62] B. A. Newcomb, “Processing, structure, and properties of carbon fibers,” *Compos. Part A Appl. Sci. Manuf.*, vol. 91, pp. 262–282, 2016.
- [63] C.-W. Nan, R. Birringer, D. R. Clarke, and H. Gleiter, “Effective thermal conductivity of particulate composites with interfacial thermal resistance,” *J. Appl. Phys.*, vol. 81, no. 10, pp. 6692–6699, 1997.
- [64] D. A. G. Bruggemann, “Berechnung verschiedener physikalischer Konstanten von heterogenen substanzen,” *Ann. Phys.*, vol. 24, p. 636–679., 1935.
- [65] J. Ordóñez-Miranda and J. J. Alvarado-Gil, “Thermal conductivity of nanocomposites with high volume fractions of particles,” *Compos. Sci. Technol.*, vol. 72, no. 7, pp. 853–857, Apr. 2012.
- [66] C.-W. Nan, G. Liu, Y. Lin, and M. Li, “Interface effect on thermal conductivity of carbon nanotube composites,” *Appl. Phys. Lett.*, vol. 85, no. 16, pp. 3549–3551, 2004.
- [67] H. S. Huang, S. Ganguli, and A. K. Roy, “Prediction of the transverse thermal conductivity of pitch-based carbon fibers,” *J. Compos. Mater.*, vol. 48, no. 11, pp. 1383–1390, 2013.
- [68] C. Pradere, J. C. Batsale, J. M. Goyheneche, R. Pailler, and S. Dilhaire, “Thermal properties of carbon fibers at very high temperature,” *Carbon N. Y.*, vol. 47, no. 3, pp. 737–743, 2009.
- [69] C. Jie, X. Xiang, and X. Peng, “Thermal conductivity of unidirectional carbon/carbon composites with different carbon matrixes,” *Mater. Des.*, vol. 30, no. 4, pp. 1413–1416, 2009.
- [70] J. Michalowski, D. Mikociak, K. J. Konsztowicz, and S. Blazewicz, “Thermal conductivity of 2D C – C composites with pyrolytic and glass-like carbon matrices,” *J. Nucl. Mater.*, vol. 393, no. 1, pp. 47–53, 2009.
- [71] Z. Feng, Z. Fan, Q. Kong, X. Xiong, and B. Huang, “Effect of high temperature treatment on the structure and thermal conductivity of 2D carbon/carbon composites with a high thermal conductivity,” *New Carbon Mater.*, vol. 29, no. 5, pp. 357–362, 2014.
- [72] K. Guan, J. Wu, and L. Cheng, “Modeling of thermal conductivity of CVI-densified composites at fiber and bundle level,” *Materials (Basel)*, vol. 9, no. 12, 2016.
- [73] M. Spinnler, E. R. F. Winter, and R. Viskanta, “Studies on high-temperature multilayer thermal insulations,” *Int. J. Heat Mass Transf.*, vol. 47, no. 6–7, pp. 1305–1312, Mar. 2004.
- [74] P. Gong, P. Buahom, M. P. Tran, M. Saniei, C. B. Park, and P. Pötschke, “Heat transfer in microcellular polystyrene/multi-walled carbon nanotube nanocomposite foams,” *Carbon*, vol. 93, pp. 819–829, 2015.
- [75] J.-J. Zhao, Y.-Y. Duan, X.-D. Wang, and B.-X. Wang, “Experimental and analytical analyses of the thermal conductivities and high-temperature characteristics of silica aerogels based on microstructures,” *J. Phys. D. Appl. Phys.*, vol. 46, no. 1, p. 15304, Jan. 2013.

Appendix A

Thermal conductivity modeling

Mathematical models for determining the effective thermal conductivity of C/C composites are many and varied, effective thermal conductivity may be expressed in terms of the corresponding thermal conductivities of the fibers, and the matrix, fibers volume fraction[60], fiber mass fraction[61], graphitic planes direction[62], contact heat transfer rate between fibers[13], effective contact volume between two plates[5], some other models are based on the solid heat transfer contribution (κ_S), the radiation contribution (κ_R), and the contribution of the gas (κ_G) to the whole thermal conductivity [46]. Considering a composite made up of laminate bundles of fibers forming a regular orthogonal pattern embedded in a solid matrix, as shown in Fig. A1, if we assume that the delamination between fiber mats is regular; then the in-plane (κ_{\parallel}) and out-plane (κ_{\perp}) thermal conductivities of this bidirectional composite are given by:

$$\kappa_{\parallel} = n_v \kappa_{\parallel}(\theta) + n_h \kappa_{\parallel} \left(\frac{\pi}{2} - \theta \right) \quad (\text{Eq. A1a})$$

$$\kappa_{\perp} = \kappa_{1\perp} \quad (\text{Eq. A1b})$$

where $\kappa_{1\perp}$ is the composite thermal conductivity perpendicular to unidirectional fibers (see Fig. A1), n_v and n_h are the number fractions of fibers in the vertical and horizontal directions, and the in-plane thermal conductivity $\kappa_{\parallel}(\theta)$ in a direction making an angle θ with the axis of unidirectional fibers is defined by[43]:

$$\kappa_{\parallel}(\theta) = \kappa_{1\parallel} \cos^2(\theta) + \kappa_{1\perp} \sin^2(\theta) \quad (\text{Eq. A2})$$

Where $\kappa_{1\parallel}$ is the composite thermal conductivity parallel to unidirectional fibers, as shown in Fig. A1, considering that the numbers of fibers in vertical and horizontal directions in Fig. 1(a) are equal ($n_v = n_h = \frac{1}{2}$), Eqs. (A1a) and (A2) yields to:

$$\kappa_{\parallel} = \frac{1}{2} (\kappa_{1\parallel} + \kappa_{1\perp}) \quad (\text{Eq. A3})$$

Equation (A3) explicitly shows that the in-plane thermal conductivity of the composite in Fig. A1 is independent of the direction in which is measured, as was first predicted by Pilling et al.[60].

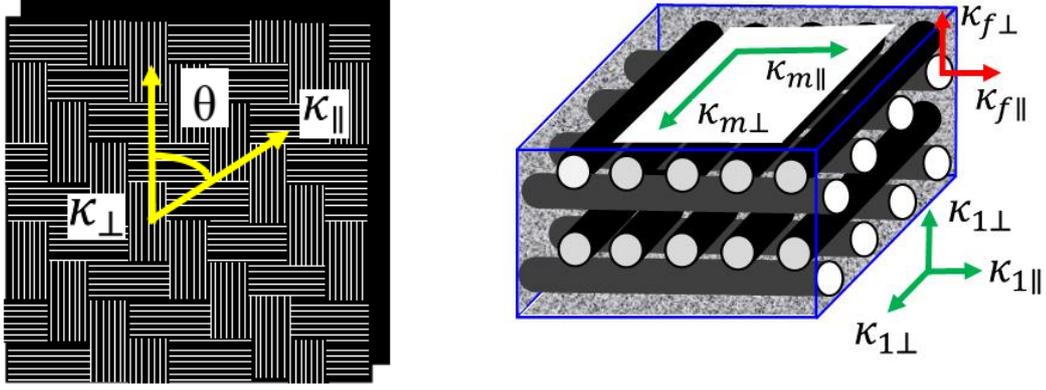


Figure A1. Two-dimensional twill woven fabric and 3D unit cell.

The thermal conductivity $\kappa_{1\parallel}$ of the unidirectional composite in Fig. A1 is simply given by the series model, as follows:[63]

$$\kappa_{1\parallel} = f\kappa_{f\parallel} + (1 - f - p)\kappa_{m\parallel} \quad (\text{Eq. A4})$$

where f and p are the respective volume fractions of the fibers and pores, while $\kappa_{f\parallel}$ and $\kappa_{m\parallel}$ are the fiber and matrix thermal conductivities in the axial direction of the fibers, respectively. On the other hand, the out-plane thermal conductivity $\kappa_{1\perp}$ can be determined by means of the Bruggeman's model[64] applied to cylindrical particles[65], as follows

$$\frac{\kappa}{\kappa_m} = a + \frac{1}{2}\beta^2 + \beta\sqrt{a + \frac{\beta^2}{4}} \quad (\text{Eq. A5a})$$

$$\beta = (1 - a)(1 - v) \quad (\text{Eq. A5b})$$

$$\alpha = \left(\frac{\kappa_m}{\kappa_p} + \frac{a\kappa}{a}\right)^{-1} \quad (\text{Eq. A5c})$$

where κ_m and κ_p are the respective thermal conductivities of the continuous (matrix) and discontinuous (fibers) phases interacting with an interface thermal resistance R , $a_\kappa = R\kappa_m$ is the Kapitza radius[66], a is the average radius of the fillers composing the discontinuous phase of volume fraction v and κ is the composite thermal conductivity. Considering the fibers and matrix like an effective matrix for the usually cylindrical pores present among the fibers (see Fig. A2), we take $\kappa_m = \kappa_{1\perp}$ ($p = 0$), $\kappa_p = 0$ (air thermal conductivity), $R \rightarrow \infty$ and $v = p$ in Eqs. (A5a) to (A5c), which render:

$$\kappa_{1\perp} = (1 - p)^2\kappa_{1\perp}(p = 0) \quad (\text{Eq. A6})$$

Equation (A6) indicates that the presence of pores reduces the effective thermal conductivity of the matrix and fibers ($\kappa_{1\perp}(p = 0)$) by a factor of $(1 - p)^2$. The thermal conductivity $\kappa_{1\perp}(p = 0)$ can now be calculated by reusing Eqs. (A5a) to (A5c) with $\kappa_m = \kappa_{m\perp}$, $\kappa_p = \kappa_{f\perp}$ and $v = \frac{f}{1-p}$ being the volume fraction of fibers in the solid matrix alone. After making these substitutions in Eqs. (A5a) to (A5c) and combining the result with Eq. (A6), one obtains:

$$\kappa_{1\perp} = (1 - p)^2\kappa_{m\perp}\left(a_{\perp} + \frac{1}{2}\beta_{\perp}^2 + \beta_{\perp}\sqrt{a_{\perp} + \frac{\beta_{\perp}^2}{4}}\right) \quad (\text{Eq. A7})$$

where β_{\perp} and a_{\perp} are defined by Eqs. (A5b) and (A5c), for $\kappa_{m\perp}$, $\kappa_{f\perp}$ and $v = \frac{f}{1-p}$. Equation (A7) considers the effects of the radius a and volume fraction f of the fibers, as well as of the porosity p and the interface thermal resistance R . The thermal conductivities κ_{\parallel} and κ_{\perp} of a composite with unidirectional fibers thus determine the overall thermal conductivities κ_{\perp} and κ_{\parallel} of the bidirectional composite shown in Fig. A1.

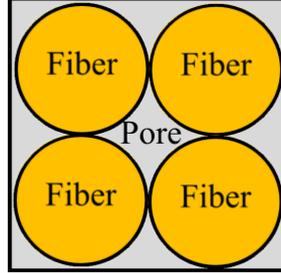


Figure A2. Scheme of the cylindrical pores present among the fibers.

In-plane and out-plane thermal conductivities of a simple carbon fiber

To calculate the thermal conductivity as a function of the temperature of the CC composites (Eq. A7) it is necessary knowing the data of the axial and transverse thermal conductivities of a simple carbon fiber and the pure matrix (without carbon fibers). The effective transverse thermal conductivity of the pitch-based carbon fibers, was predicted by H.S Huang et al.[67], they calculated the in-plane and out-plane thermal conductivity for straight graphite sheets. The value of the simulated equivalent transverse thermal conductivity was 50.8 W / mK for perfect fibers and the measured value for real fibers was 12 W/mK. Therefore, we can take the value of 26.74 for the anisotropy factor ($\kappa_{\parallel}/\kappa_{\perp}$) this value is consistent with those reported in literature[3]. We can also have assumed that this factor does not change significantly as function of temperature[61]. C. Pradere et al.[68] report the longitudinal thermal conductivity in the temperature range from 750 to 2000 K, of simple carbon fibers made with the same raw materials and exposed to a heat treatment similar those C/C composites examined in this work. Out -plane thermal conductivity of the fibers in the temperature range from 750 to 2000 K can be adjusted to the expression:

$$\kappa_p(T) = 5.5045 + 4.97 \times 10^{-3}T - 4.78 \times 10^{-6}T^2 + 1.20 \times 10^{-9}T^3 \quad (\text{Eq. A8})$$

Pure matrix thermal conductivity

There are different and varied methods to build C/C composites, usually these methods consist on impregnation of sheets of carbon fiber fabrics with precursors (i.e. phenol-formaldehyde resins or gas phase precursors such as propane) that give rise the matrix of the composite[69]. Once the sheets are impregnated, the composites are molded and cured, subsequently they are carbonized at 1000°C under vacuum. The processes of impregnation and carbonization are repeated several times to change the density and porosity of the composite. Under these conditions the thermal conductivity of the composite obeys the simple mixing rule for two phases system: $\lambda_c = \lambda_f V_f + \lambda_m V_{fm}$ (λ is the thermal conductivity, V is the volume fraction, and c, f , and m refer to composite, filler and matrix, respectively), due to $\lambda_f V_f \gg \lambda_m V_{fm}$, then $\lambda_c \sim \lambda_f V_f$. However, when the C/C composites are subjected to a High Temperature Treatment (HTT) at temperatures above 2000 °C, the experimentally thermal conductivity value of the composite increases significantly with respect to that calculated from the simple mixing rule[19], [62]. In addition, it has been demonstrated that after several HTT cycles, the thermal conductivity value of the C/C composite is no longer affected. Due to the thermal conductivity of the single fibers does not change significantly during the HTT cycles of C/C composites, because the fibers were previously subjected to a similar HTT and their structural parameters are well formed[6], then the increase of the thermal

conductivity of the C/C composite can be attributed to changes in the structural and microstructural parameters of matrix (d_{002} and L_c)[70]. For all the above, C/C composites with same fiber fabric and matrix precursors but subjected to different HTT may have different thermal conductivities[71], and this behavior is most noticeable at high temperature. One way to determine and to distinguish the effect of components in the C/C composite (carbon fibers and matrix), is by obtaining the thermal conductivity of samples of pure matrix (without carbon fibers). A good approximation to thermal behavior of the pure matrix is to consider it as glass-like carbon (GC) material [70], then the effective thermal conductivity of the matrix (κ_{me}) can be expressed by: $\kappa_{me} = \xi \kappa_{GC}$, where ξ is a constant that depends on volume fraction of solid matrix and porous, as well as the pore shape factor[72]. Effective thermal conductivity of the matrix out-plane can be expressed as[22]:

$$\kappa_{me}(T) = -0.219975 + 0.012285 T - 1.08x10^{-5}T^5 + 4.46x10^{-9}T^3 - 7.12x10^{-13}T^4 \quad (\text{Eq. A9})$$

Solid thermal conductivity as a function of the temperature $\kappa_c(T)$ of the C/C composites (Eq. A7) can be rewrite as:

$$\kappa_c(T) = (1 - p)^2 \kappa_{me}(T) \left[\alpha(T) + \frac{1}{2} \beta(T)^2 + \beta(T) \sqrt{\alpha(T) + \frac{\beta(T)^2}{4}} \right] \quad (\text{Eq. A10})$$

Radiative thermal conductivity

Effective thermal conductivity in porous materials can be expressed in terms of the solid thermal conductivity and the radiative conductivity (thermal conduction by gas convection is usually ignored due to its low value with respect to the other heat conduction mechanisms). Radiative conductivity ($\kappa_r(T)$) is based on Rosseland diffusion approximation[73], and it can be expressed by[74]:

$$\kappa_r(T) = \frac{16}{3} \sigma_{SB} \frac{n^2(T)}{\sigma_e(T)} T^3, \quad (\text{Eq. A11})$$

where σ_{SB} is the Stefan-boltzmann's constant ($5.67x10^{-8} \text{ W/m}^2\text{K}^4$), n is the effective refractive index, and $\sigma_e(T)$ is the Rosseland mean extinction coefficient[75] which is an average value of the spectral extinction coefficient ($\sigma_{e,\nu}(T)$) weighted by the local spectral energy flux. Rosseland mean extinction coefficient is defined as follows :

$$\frac{1}{\sigma_e(T)} = \frac{\int_0^\infty \frac{1}{\sigma_{e,\nu}(T)} \frac{\partial I(T,\nu)}{\partial T} d\nu}{\int_0^\infty \frac{\partial I(T,\nu)}{\partial T} d\nu}, \quad (\text{Eq. A12a})$$

$$\frac{\partial I(T,\nu)}{\partial T} = \frac{2h^2\nu^4}{\kappa_B T^2 c^2} \frac{e^{\frac{h\nu}{\kappa_B T}}}{\left(e^{\frac{h\nu}{\kappa_B T}} - 1 \right)^2} \quad (\text{Eq. A12b})$$

Where $\partial I(T,\nu)/\partial T$ is the temperature derivative of Planck's function. For homogeneous media, and considering $\sigma_{e,\nu}(T)$ independent on thickness, according to Beer's law:

$$\sigma_{e,\nu}(T) d = -\ln[\tau_{n,\nu}(T)], \quad (\text{Eq. A13})$$

Being d the thickness of the sample composite and $\tau_{n,\lambda}(T)$ is the spectral transmittance percentage, which could be measured with a Fourier transform infrared (FTIR) spectrometer. Fig. A3 shows the spectral transmittance percentage ($\tau_{n,\lambda}(T)$) for two samples (600 and 800 ± 30 microns on thickness) obtained with a FTIR spectrometer (Perkin Elmer, model Frontier NIR / MIR), and the Rosseland mean extinction coefficient ($\sigma_e(T)$) calculated with Eq. A12a.

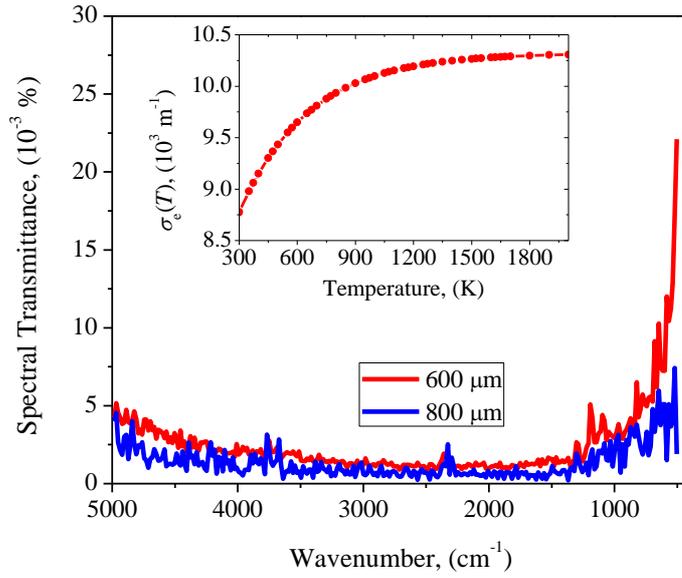


Figure A3. Spectral transmittance percentage ($\tau_{n,\lambda}(T)$) and Rosseland mean extinction coefficient ($\sigma_e(T)$)

The effective thermal conductivity as a function of the temperature of the composite C/C is then determined by the sum of the solid thermal conductivity ($\kappa_c(T)$) and radiative conductivity ($\kappa_r(T)$)

$$\kappa_{eff}(T) = \kappa_c(T) + \kappa_r(T) \quad (\text{Eq. A14})$$

Figure A4 shows the effective thermal conductivity (Eq. A14), the solid thermal conductivity (Eq. A10) and radiative conductivity (Eq. A11) as function of temperature. The effective thermal conductivity of the C/C composite for temperatures below 1000 K is dominated mainly by solid thermal conductivity (99.4%). However, for temperatures above 1000 K, the contribution of radiative conductivity increases appreciably until reaching the value of 4.5% of the effective conductivity of the C/C composite at 2000 K.

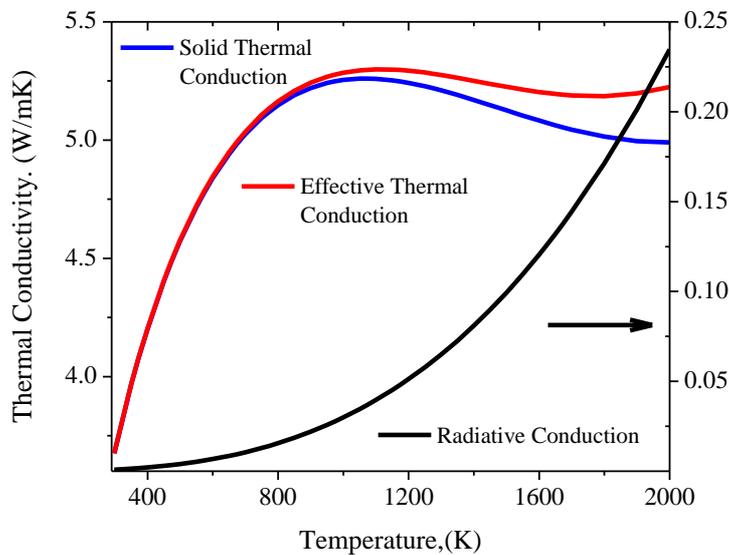


Figure A4. Effective thermal conductivity, the solid thermal conductivity and radiative conductivity as function of temperature.