Thermal conductivity of individual carbon nanofibers

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ABSTRACT

In the present paper, we present results of thermal conductivity measurements in commercially-available, chemical vapor deposition grown, heat-treated and non-heat-treated individual carbon nanofibers (CNFs). The thermal conductivity measurements are made using the T-type probe experimental configuration using a Wollaston wire probe inside a high resolution scanning electron microscope. The results show a significant increase in the thermal conductivity of CNFs that are annealed at 2800 °C for 20 h when compared with the non-heat-treated CNF samples. When adjusted for thermal contact resistance, the highest measured thermal conductivity is 449 ± 39 W/m-K. The average thermal conductivity of the heat-treated samples is 163 W/m-K, while the average thermal conductivity of the non-heat-treated samples is 4.6 W/m-K. The results demonstrate the importance of the quality of the CNFs, in particular their heat treatment (high temperature annealing), in controlling their thermal conductivity for thermal management applications.

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1. Introduction

Although a relatively large body of literature exists for thermal conductivity measurements in large diameter carbon fibers (CFs) [1-6], only a few measurements of thermal conductivity have been reported in individual carbon nanofibers (CNFs) [7]. The individual CFs for which thermal conductivity measurements are available in the literature have outer diameters ranging from 4 to 71.4 μm [1,2], and their room temperature thermal conductivities range from 12 to 1950 W/m-K [1-6]. This relatively large variation in the measured thermal conductivity of CFs can be attributed to the differences in sample diameter, synthesis method employed, resultant defect structure, and heat treatment [1,2,7]. Heremans and Beetz [2] were the first to show that heat-treatment of CFs (at 3000 °C) significantly improved their room temperature thermal conductivity. The high thermal conductivity of the heat-treated CFs suggest the potential use of CFs and perhaps CNFs as thermal interface materials [3,4,8].

Most CFs and CNFs are synthesized in any one of the following three ways: (1) carbonization of spun polyacrylonitrile (PAN-based fibers), (2) carbonization of spun petroleum pitch (pitch-based fibers), and (3) carbon chemical vapor deposition (CVD), usually using methane or benzene [1]. The simplicity of the CVD process suggests that the production of vapor grown CFs and CNFs can be much less expensive than for their PAN-based and pitch-based counterparts [8]. The opportunity for wide-spread use of CVD grown CNFs along with their potential for dramatic improvement in thermal conductivity by heat treatment provide the motivation for the present study.

While a number of thermal conductivity measurements have been made on heat-treated and non-heat-treated CFs, to the best of authors' knowledge only one previous study

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has analyzed thermal conductivity of individual CNFs [7]; the CNFs used in the study had a diameter of approximately 152 nm and a room temperature thermal conductivity of 13 W/m-K. Moreover, the CNF samples analyzed in [7] were as received, and thus non-heat treated. The dramatic increase in thermal conductivity of CFs after the high temperature annealing step suggests that CNFs may also show improvement in thermal conductivity with annealing heat treatment. Heat treatment of CFs, CNFs, and multiwall carbon nanotubes (MWCNTs) at temperatures up to 3000 °C has been shown to remove defects and impurities, such as left over metal catalysts, as well as increase the crystallinity of the graphite planes [9–12]. More continuous graphene planes as well as removal of defects increases the phonon mean free path, and consequently the thermal conductivity of the annealed samples [9]. In the present study we focus on the extent to which heat treatment improves the thermal conductivity in CVD grown CNFs.

Many studies have explored thermal properties of test specimens by measuring the third harmonic voltage in a 3ω experimental set-up as the sample is Joule heated with an alternating current [9,13,14]. The “T-type probe” is one method that can employ third harmonic voltage detection to make thermal conductivity measurements. For the T-type probe method, a suspended wire of known electrical resistivity and temperature coefficient of resistance is Joule heated by a current source until it reaches a steady-state. A sample is attached, and the reduction in the spatially averaged temperature of the probe wire is measured via the change in voltage. The sample thermal conductivity is determined from the average temperature drop and the sample geometry. The method has been used to great effect in studying thermal transport in individual nanostructures, including CFs and multi-walled carbon nanotubes [3,4,9,13]. In the present study thermal conductivity of both heat-treated and non-heat-treated CNF specimens is determined using the 3ω, Wollaston wire, T-type probe method.

2. Experimental methods

2.1. Three omega analysis

In the present study, thermal conductivity measurements are made in individual CNFs using a Wollaston wire T-type probe inside a scanning electron microscope (SEM) [9,13]. The Wollaston wire is Joule heated using an alternating current, and the third harmonic voltage across the wire is measured. The thermal resistance and thermal conductivity of the specimen are deduced from an analytic model that relates the third harmonic voltage, the drop in average temperature of the wire when the sample is attached, and the thermal conductivity of the sample [3,4,9,13].

The configuration, technique, and analysis used in this study for making the thermal conductivity measurements of CNFs are described in detail by Bifano et al. [9]. The platinum probe wire is heated by an alternating current \( I(t) = I_{\text{rms}} \sin \omega t = I_{\text{rms}} \sqrt{2} \sin \omega t \), where \( I_{\text{rms}} \) is the current amplitude, and \( I_{\text{rms}} \) is the RMS current. The Joule heating in the wire is given by

\[
Q(t) = I^2(t)R_{\text{eo}} = I_{\text{rms}}^2 R_{\text{eo}} (1 - \cos 2\omega t),
\]

where \( R_{\text{eo}} \) is the electrical resistance of the probe wire at zero current. The spatially averaged temperature of the wire above the ambient temperature, \( \bar{T}(t) \), is directly proportional to the Joule heating by the thermal transfer function \( Z_\theta \) such that

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Fig. 1 – SEM images of CNF batches from which individual samples are selected. (A) and (B) are representative of US Nanomaterials Research heat-treated batch US 4460). (C) and (D) are representative of US 4450.
The electrical resistance of the probe wire changes according to
\[ R(t) = R_{eo}\left[1 + a h(t) / C_{138}\right] \]
where \( h(t) = Z_0 Q(t) \).

The RMS Joule heating is defined to be \( Q_{\text{RMS}} = I_{\text{RMS}}^2 R_{eo} \). When the wire is Joule heated, the third harmonic voltage across the wire is given by
\[ V_{3\text{RMS}} = \frac{1}{2} a Z_0 I_{\text{RMS}}^2 Q_{\text{RMS}} R_{eo}. \]

The thermal transfer function is determined experimentally by measuring the slope of \( R_{3\text{RMS}} \) versus \( Q_{\text{RMS}} \) versus.

2.2. Theoretical considerations: thermal transfer function

The steady state response of the probe wire is modeled in one dimension by
\[ k_\text{p} \frac{d^2 \theta}{dx^2} = \frac{Q_{\text{RMS}}}{A_{\text{P}}} R_{\text{th},\text{P}} \]
where \( x \) is the position marked from the midpoint of the wire, \( k_\text{p} \) is the thermal conductivity of the wire, \( A_\text{p} \) is the cross-sectional area of the wire, and \( L_\text{p} \) is the length of the wire. Heat loss due to convention and radiation can be neglected because the experiments are conducted in vacuum in a high resolution SEM and involve only small temperature rises. Using constant ambient temperature boundary conditions at the ends of the wire and a heat flux out of the wire where the sample is attached, the spatially averaged temperature is given as
\[ \theta = \frac{1}{12} Q_{\text{RMS}} R_{\text{th},\text{P}} \left[1 - \frac{3}{4} (1 + \eta^{-1})^{-1}\right] = Q_{\text{RMS}} Z_0, \]
where the thermal resistance of the probe and sample are given by \( R_{\text{th},\text{P}} = L_\text{p} / k_\text{p} A_\text{p} \) and \( R_{\text{th},\text{S}} = L_\text{S} / k_\text{S} A_\text{S} \), respectively. The ratio of thermal resistances, \( \eta \), is defined by \( \eta \equiv R_{\text{th},\text{P}} / 4R_{\text{th},\text{S}} \).

2.3. Experimental procedure

When no sample is attached, i.e. \( \eta = 0 \), the thermal resistance of the probe wire is deduced using Eqs. (4) and (6) to be
\[ R_{\text{th},\text{P}} = \frac{24}{32} \left( \frac{\Delta R_{3\text{RMS}}}{\Delta Q_{\text{RMS}}} \right) \]
The ratio of the slopes is then defined as
The thermal conductivity of the sample can then be determined from \( k_S = \frac{L_S}{R_{\text{th},s} A_S} \), where the cross-sectional area is \( A_S = \pi \left( r_o^2 - r_i^2 \right) \). Many studies have shown CNFs to have hollow cores, like tubes [5,15–17], with inner diameters shown to be in the range from 2 to 50 nm [17]. In the present study, the inner radius, \( r_i \), is taken to be much smaller than the outer radius, \( r_o \), such that \( r_i^2 / r_o^2 \ll 1 \). The effective cross-sectional area of the sample can therefore be approximated as \( A_S \approx \pi r_o^2 \).

3. CNF samples

The two sample groups examined in this study are: (1) CNF samples grown using thermal CVD, and (2) CNF samples grown using thermal CVD, which are then thermally annealed at 2800 °C for 20 h. The as-grown CNFs were procured from US Nanomaterials Research (US4450) and are referred to as "non-heat-treated" samples. The thermally annealed or "heat-treated" samples were obtained from US Nanomaterials Research, Inc. (Serial number US4460).

SEM micrographs of the samples (Fig. 1) reveal large amounts of amorphous carbon throughout the heat-treated batch when compared with the non-heat-treated batch. SEM micrographs of individual CNFs also show the presence of amorphous carbon attached to the surfaces. In addition the comparison of the heat-treated and non-heat-treated sample
images indicate that the heat treatment process promotes fusion of adjacent CNFs.

3.1. **Raman spectroscopy**

Raman spectroscopy is used to examine the improvement in graphitization and reduction of defects in the heat-treated samples when compared to the non-heat-treated samples. The excitation wavelength used for this assessment was 785 nm. The analysis of the sample quality is made by observing the ratio of the D band peak intensity (~1330 cm\(^{-1}\)) and the G-band peak intensity (~1875 cm\(^{-1}\)). The D band is associated with the loss of symmetry of atoms at the graphene sheet boundaries, which appears in the form of defects and carbonaceous impurities [18]. The G band is associated with the sp\(^2\) bonding in carbon systems, and indicates the degree of graphitization in the sample [19]. Thus, a lower D/G ratio of band intensity indicates that the sample batch has fewer defects and a higher degree of graphite crystallinity. Since there are currently no standards for D/G ratio for CNFs by which to judge the quality of the batches, only a qualitative comparative study of the CNF batches can be conducted. It should also be noted that the band peaks are a result of an average of all of the samples in the area excited by the laser and not of individual samples.

Fig. 2A and B compare the Raman intensity of the heat-treated and non-heat-treated sample batches. The Raman intensities are normalized with respect to the D-peak. Fig. 2 shows evidence of significant defect healing and improved graphitization.

4. **Results and discussion**

4.1. **Thermal conductivity measurements**

To determine the effect that heat treatment has on CNF thermal conductivity, 15 heat-treated CNFs (Fig. 3) and 6 on non-heat-treated CNFs (Fig. 4) were tested in the present study. The heat-treated batch produced a mean thermal conductivity of 160 ± 139 versus 4.5 ± 3.1 W/m-K for the non-heat-treated samples. The large standard deviations associated with the average values reflect the large variation in individual sample thermal conductivity, not uncertainty in the measurements. The values of length, diameter, and thermal conductivity are listed in Tables 1 and 2 for the non-heat-treated and heat-treated samples, respectively.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Length (μm)</th>
<th>Average diameter (nm)</th>
<th>Thermal conductivity (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.5 ± 0.3</td>
<td>489 ± 39</td>
<td>9.7 ± 1.6</td>
</tr>
<tr>
<td>3</td>
<td>10.7 ± 0.3</td>
<td>446 ± 11</td>
<td>2.5 ± 0.3</td>
</tr>
<tr>
<td>4</td>
<td>12.7 ± 0.1</td>
<td>390 ± 23</td>
<td>2.5 ± 0.3</td>
</tr>
<tr>
<td>5</td>
<td>3.59 ± 0.06</td>
<td>292 ± 27</td>
<td>2.2 ± 0.4</td>
</tr>
<tr>
<td>6</td>
<td>19.9 ± 0.2</td>
<td>273 ± 20</td>
<td>7.2 ± 1.0</td>
</tr>
<tr>
<td>23</td>
<td>6.94 ± 0.06</td>
<td>151 ± 11</td>
<td>3.1 ± 0.4</td>
</tr>
</tbody>
</table>

**Fig. 4 –** SEM micrographs of non-heat-treated sample experiments. Each image shows the probe wire above the manipulator tip with the CNF connecting the probe wire to the manipulator. The samples representing the non-heat-treated group have measured thermal conductivities of (A) 9.7 ± 1.6 W/m-K, (B) 2.5 ± 0.3 W/m-K, and (C) 3.1 ± 0.4 W/m-K. The values are not corrected for thermal contact resistance.
A Welch’s T-test for unequal sample size and unequal variance produced a $p$-value of 0.0007, indicating that the heat treatment of the samples produced statistically significant differences in thermal conductivity.

The largest value of thermal conductivity is $434 \pm 38$ W/m-K, measured on a sample having an average diameter of 171 nm and a length of 26.1 µm. Even the maximum value for these samples is much lower than highest reported value for a vapor grown carbon fiber of 1950 W/m-K [1]. Fig. 5 plots the thermal conductivities versus the sample diameters.

### 4.2. Thermal contact resistance

Bifano et al. [9] demonstrated the importance of improving the thermal contacts for the Wollaston wire, T-type probe experiments. To decrease the thermal contact resistance (TCR), samples are attached to the Wollaston wire by application of platinum electron beam induced deposition (EBID) inside of the SEM. The TCR for multi-wall carbon nanotubes (MWCNT) tested using the Wollaston wire, T-type probe method was calculated by utilizing an anisotropic diffusive mismatch model including the fin resistance due to the platinum EBID [9]. The calculated thermal contact resistance, when subtracted from the total thermal resistance, resulted in approximately a 5% increase in the thermal conductivity of the MWCNT samples [9]. By modeling the CNFs in the same way, as graphitic planes, a similar analysis can be conducted. The total thermal contact resistance for the CNF-wire contact and the CNF-manipulator contact can be written as

$$R_{TCR} = \frac{2}{\sqrt{hP_kS_A S_{P_tanh}}}$$

The heat transfer coefficient is $h = 1/R_b$, where $R_b$ is the boundary resistance. Bifano et al. [9] estimated boundary resistance values of $R_b = 5.79 \times 10^{-9}$ K-m/W for a pure platinum EBID and $R_b = 5.18 \times 10^{-8}$ K-m/W for an amorphous carbon EBID. The fin perimeter is $P = \pi D_o/2 + b$, where $D_o$ is the sample outer diameter, and $b$ is the contact width, estimated from the elastic properties of the sample and wire [9,20]. The sample-wire contact length, $L_c$, is measured inside the SEM.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Length (µm)</th>
<th>Average diameter (nm)</th>
<th>Thermal conductivity (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>9.28 ± 0.03</td>
<td>339 ± 70</td>
<td>24.5 ± 9.8</td>
</tr>
<tr>
<td>9</td>
<td>492 ± 2</td>
<td>536 ± 96</td>
<td>196 ± 67</td>
</tr>
<tr>
<td>10</td>
<td>100.4 ± 0.3</td>
<td>412 ± 30</td>
<td>134 ± 19</td>
</tr>
<tr>
<td>11</td>
<td>16.7 ± 0.4</td>
<td>226 ± 21</td>
<td>117 ± 22</td>
</tr>
<tr>
<td>12</td>
<td>102.5 ± 0.4</td>
<td>369 ± 15</td>
<td>66.8 ± 5.6</td>
</tr>
<tr>
<td>13</td>
<td>53.9 ± 0.2</td>
<td>187 ± 24</td>
<td>382 ± 97</td>
</tr>
<tr>
<td>14</td>
<td>50.5 ± 0.3</td>
<td>206 ± 13</td>
<td>378 ± 49</td>
</tr>
<tr>
<td>15</td>
<td>32.8 ± 0.2</td>
<td>235 ± 6</td>
<td>139 ± 8</td>
</tr>
<tr>
<td>16</td>
<td>26.1 ± 0.1</td>
<td>171 ± 8</td>
<td>434 ± 38</td>
</tr>
<tr>
<td>17</td>
<td>7.85 ± 0.08</td>
<td>200 ± 15</td>
<td>16.2 ± 2.5</td>
</tr>
<tr>
<td>18</td>
<td>31.4 ± 0.2</td>
<td>199 ± 8</td>
<td>241 ± 19</td>
</tr>
<tr>
<td>19</td>
<td>10.3 ± 0.1</td>
<td>112 ± 5</td>
<td>77.8 ± 7.3</td>
</tr>
<tr>
<td>20</td>
<td>204.8 ± 0.1</td>
<td>228 ± 40</td>
<td>48.5 ± 16.6</td>
</tr>
<tr>
<td>21</td>
<td>30.0 ± 0.2</td>
<td>244 ± 14</td>
<td>123 ± 14</td>
</tr>
<tr>
<td>22</td>
<td>28.2 ± 0.2</td>
<td>218 ± 36</td>
<td>24.4 ± 7.9</td>
</tr>
</tbody>
</table>

Fig. 5 – Thermal conductivity measurements of heat-treated and non-heat-treated samples plotted against sample length. The values are not adjusted for thermal contact resistance.
The TCR and adjusted thermal conductivity are obtained iteratively because the TCR requires a thermal conductivity for the calculation. For the CNF samples, the TCR accounted for an average 1.7% increase in the thermal conductivity. Fig. 6 shows the thermal conductivity adjusted for TCR. The average adjusted thermal conductivities for the heat-treated and non-heat-treated samples are 163 and 4.6 W/m-K, respectively. The highest thermal conductivity adjusted for TCR is 449 ± 39 W/m-K.

5. Summary

In the present study, thermal conductivity measurements are made in individual CNFs using a Wollaston wire, T-type probe method inside of an SEM [9,13]. The results of the study indicate that significant improvements in thermal conductivity are obtained by heat treatment of CNFs to 2800 °C for 20 h. The average measured thermal conductivity of the heat-treated batch is 160 W/m-K when compared to the much lower average of 4.5 W/m-K for the as-grown non-heat-treated samples. The highest measured thermal conductivity when adjusted for TCR is 449 ± 39 W/m-K.

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