Three-dimensional-linked carbon fiber-carbon nanotube hybrid structure for enhancing thermal conductivity of silicon carbonitride matrix composites

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Abstract
In this paper, a novel three-dimensional-linked (3D-linked) carbon fiber-carbon nanotube (Cf-CNT) hybrid structure is presented to improve the through-thickness thermal properties of polymer derived silicon carbonitride matrix composites. Comparing with pristine plain woven carbon fiber, the pores in the criss-cross position are fully filled with carbon nanotubes (CNT) in the presented Cf-CNT hybrid structure. CNT can be integrated in between the plain woven carbon fibers and generate a 3D-linked Cf-CNT hybrid network structure. Thanks to the percolating network of CNT and the densification effect, the through-thickness thermal conductivity of the resultant ceramic matrix composites is improved significantly, which is enhanced by 10% with short CNT and by 31% with long CNT, respectively. The thermal conductivity is found to increase with temperature from 100 to 900 °C for these composites. Multiphysics simulation is conducted to reveal the effects of the 3D-linked Cf-CNT hybrid structure on the thermal conductivity at various temperatures, which are consistent with experimental results.

1. Introduction
Carbon fiber reinforced ceramic matrix composites have recently attracted much attention for high-temperature structural applications due to the excellent properties, such as high strength, low density, and chemical inertness, which demonstrate significant performance improvement over traditional brittle ceramics [1–3]. However, there are still several key issues limiting the composites from broader applications, such as limited functionality [4]. In order to further increase the mechanical properties of carbon fiber composites, as well as to achieve the desired thermal/electrical properties, various approaches have been explored to introduce carbon nanotubes (CNT) into carbon fiber as the second-phase reinforcement [5–10]. CNT has attracted tremendous attention and interests due to their extraordinary unique properties, such as the remarkable intrinsic mechanical, electrical and thermal properties [11–14]. By introducing reinforcements with different magnitude orders, the mechanical and physical properties of the resultant ceramic composites can be significantly improved [6,15].

Several methods have been tried to place vertically aligned or random CNT on fiber surface [16–23]. The most common existing method to grow multi-walled carbon nanotubes on carbon fiber is chemical vapor deposition (CVD) [24]. The surface of carbon fiber are modified by growing CNT directly on carbon fibers. When embedded in a polymer matrix, the change in length scale results in a multiscale composite. Researches about polymer matrix composites show that with the inclusion of CNT, mechanical and thermal/electrical properties can be improved significantly [10,25]. Although CVD method is one of the main processes to add CNT into carbon fiber sheets, this method has its own inevitable drawbacks, such as the initial surface oxidation treatment of carbon fibers by nitric acid and catalysts. The strength and structure of carbon fiber can be damaged by the chemical reaction which deteriorates the resultant composite property.

In this paper, a novel three-dimensional-linked (3D-linked)
carbon fiber-carbon nanotube (Cf-CNT) hybrid structure is developed to improve the through-thickness thermal property of ceramic matrix composites. There is no chemical reaction involved in using this method, and CNT can be embedded within interbundle spaces of the carbon fiber sheet and are also infiltrated in between each two adjacent carbon fiber sheets. Effect of CNT with different lengths on the through-thickness thermal conductivity of the resultant ceramic matrix composites is characterized and simulated. The unique Cf-CNT hybrid reinforcement structure in ceramic matrix composite enables it dissipating heat much faster and extending the life time of the material system substantially. Multiphysics simulation is established to reveal the effects of the 3D-linked Cf-CNT hybrid structure on the thermal conductivity at temperatures from 100 to 900 °C.

2. Experimental

2.1. Materials

In this research, two dimensional (2D) plain woven carbon fiber sheets (3K, T300, Toray Industries, Japan) were chosen as the starting materials. Two types of CNT with different lengths were used in our research to study the effect of carbon nanotube length on the through-thickness thermal conductivity of the resultant composites: Short CNT (SCNT, Sigma-Aldrich, USA) and long CNT (LCNT, General Nano, USA). Both of them are multi-walled carbon nanotubes and the detailed information is shown in Table 1. They have similar outside diameter but different aspect ratios: LCNT is 200 times longer than SCNT. Sodium dodecyl sulfate (SDS, Sigma-Aldrich Corporation, USA) was used as the surfactant to help disperse CNT in water. Polysilazane (KION Defense, USA), a liquid thermosetting resin, was used as the liquid preceramic precursor of silicon carbonitride (SiCN) to prepare the carbon fiber reinforced ceramic matrix composites and 4 wt% dicumyl peroxide (Sigma-Aldrich Corporation, USA) was used as the thermal initiator.

2.2. Cf-CNT hybrid structure preparation

The Cf-CNT hybrid structure was prepared by the vacuum filtration method. Firstly, CNT suspension was prepared by sonication and sodium dodecyl sulfate (SDS, Sigma-Aldrich Corporation, USA) was used as the surfactant to help disperse CNT in water. Polysilazane (KION Defense, USA), a liquid thermosetting resin, was used as the liquid preceramic precursor of silicon carbonitride (SiCN) to prepare the carbon fiber reinforced ceramic matrix composites and 4 wt% dicumyl peroxide (Sigma-Aldrich Corporation, USA) was used as the thermal initiator.

<p>| Table 1 |</p>
<table>
<thead>
<tr>
<th>Name</th>
<th>Catalog number</th>
<th>Types</th>
<th>Outside diameter/mm</th>
<th>Length/μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCNT</td>
<td>724769</td>
<td>Multi-walled</td>
<td>6−9</td>
<td>5</td>
</tr>
<tr>
<td>LCNT</td>
<td>GN-N8</td>
<td>Multi-walled</td>
<td>6−8</td>
<td>1000</td>
</tr>
</tbody>
</table>

2.3. Ceramic matrix composites preparation

After the Cf-CNT hybrid structure was obtained, as shown in Fig. 1(b), ten layers of this hybrid structure were stacked together to make ceramic matrix composites by polymer impregnation and pyrolysis (PIP) process. During this process, three different composites could be obtained: carbon fiber reinforced silicon carbonitride (Cf/SiCN) composites, carbon fiber with short CNT reinforced silicon carbonitride (Cf-SCNT/SiCN) composites, and carbon fiber with long CNT reinforced silicon carbonitride (Cf-LCNT/SiCN) composites.

Firstly, the liquid polysilazane precursor was infiltrated into pristine carbon fiber sheets and the Cf-CNT hybrid structure by vacuum process. Then, they were cured separately into a solid preceramic network by thermal crosslinking at 140 °C for 24 h under different pressures and the pressure was applied to control the volume of the final composite, as well as the volume fractions of carbon fiber and CNT in the final composites. Finally, the three composites were obtained after pyrolysis at 1000 °C for 1 h in N2 atmosphere. After five times of PIP cycles, the final composites were produced for subsequent characterization. To meet the requirements of the three-point bending strength test, the composites were cut into the specified size (3 mm × 2 mm × 30 mm) using diamond blades and the test was performed on a screw-driven load frame (AGS-J, Shimadzu Scientific, Inc.) with a crosshead speed of 0.5 mm min⁻¹ and a 500 N load cell. The composite specimens were tested at room temperature using the three-point bending fixture with a 20 mm span. The value of the bending strength was obtained by taking the average value of five tests. The microstructures of the Cf-CNT hybrid structure and the final composites were observed using scanning electron microscopy (SEM, Zeiss ULTRA-55 FEG, Carl Zeiss, Germany).

2.4. Thermal conductivity characterization and simulation method

Thermal conductivity was measured by laser flash thermal conductivity measurement system (Netzsch LFA 457, Germany). To simulate thermal conductivity of composite, a multi-scale simulation method was implemented for three sample cases: Cf/SiCN, Cf-SCNT/SiCN and Cf-LCNT/SiCN composites. A bottom-up scheme is prescribed to make a close-to-reality structure of composite by performing separate simulations for constitutive parts. Thermal conductivity of each part is calculated in all three directions before implementing into universal simulation of composite. For parts with carbon fiber inside CNT/SiCN, a former simulation is conducted to calculate thermal conductivity of CNT/SiCN. To do so, a box of 45 μm long filled with SiCN is considered with CNT of 20 μm and 40 μm long for small CNT and long CNT, respectively. Width and depth of simulation box are set to meet the weight ratio specified by experimental condition. Periodic boundary condition is considered in lateral directions for all simulations but universal simulation.

To evaluate thermal conductivity a variation of ±10 centigrade is applied on opposite sides of simulation box with a convention coefficient of 10000 W/(m²-K) in the corresponding boundaries. Choice of fixed boundary condition over enforcing of temperature values at boundaries is to minimize length effects that can be significant in our calculations. Stationary Equations (1) and (2) of heat transfer are solved by Comsol Multiphysics software in all three directions:

\[ \rho C_p u \cdot \nabla T + \nabla \cdot q = 0 \quad (1) \]

\[ q = -k \nabla T \quad (2) \]

where \( \rho \) is density, \( C_p \) is specific heat capacity, \( T \) is temperature, \( k \) is intrinsic thermal conductivity, \( u \) is normal direction to plane of heat transfer, and \( q \) is transferred heat. To obtain thermal conductivity of
simulated structure average temperature of opposite planes is measured along with integration of transferred heat through the surface to plug into:

$$k = \frac{QL}{A\Delta T}$$  \hspace{1cm} (3)

where \(L\) is length of box in measured direction, \(A\) is area of (transverse) plane, \(Q\) is total heat transferred through the plane and \(\Delta T\) is difference in the temperature of opposite planes.

3. Results and discussion

3.1. Microstructure of the Cf-CNT hybrid structure

Although CVD is the most common method currently to grow multi-walled carbon nanotubes on carbon fiber, CNT can only be formed on the surface of single carbon fiber or on the surface of carbon fibers sheets [24]. Big pores inevitably will be left in the carbon fiber sheets [10]. It is hard for composites densification as infiltrated polysilazane will shrink back to the rim of the big pore and big pores will remain there.

Fig. 2 shows the schematic of plain woven carbon fibers and our presented Cf-CNT hybrid structure. As shown in Fig. 2(a) and (c), the warp and weft are aligned to form a simple criss-cross in the plain woven pattern. Each weft thread crosses the warp threads by going over one then under the next. The next weft thread goes under the warp thread first and then over the next one. It is unavoidable that there are some big pores in the criss-cross position in the plain woven pattern, as well as the interspaces between the mutual perpendicular carbon fiber bundles along the vertical direction. During our proposed Cf-CNT hybrid reinforcement preparation, the CNT suspension is infiltrated through carbon fiber sheets and filter paper, as shown in Fig. 1(a). The pores in the criss-cross position and interspaces along the vertical direction in the plain woven carbon fibers will be fully filled by CNT, and there is no big pore left in the Cf-CNT hybrid reinforcement structure, as shown in Fig. 2(b) and (d).

Fig. 3 illustrates the SEM images of carbon fiber bundle and Cf-CNT hybrid structure. It can be found that there are macro-sized pores between the mutual perpendicular carbon fiber bundles, as shown in Fig. 3(a). In the Cf-CNT hybrid structure, these pores in pristine carbon fiber sheets are filled with CNT, as shown in Fig. 3(b) and (c). In larger magnified pictures (Fig. 3(d) and (e)), it is shown that the macro-sized pore is divided into numerous nano-sized pores by CNT. The microstructure of the CNT zone looks different with different length of CNT. For the long CNT zone, it looks smoother than the short CNT zone.

Fig. 3(b) also shows that there are still some interspaces between the mutual perpendicular carbon fiber bundles and between each carbon fiber for Cf-SCNT hybrid structure and the surface looks rough. The reason is that short CNT is easier to flow through carbon fiber bundles. Some CNT are left on the surface of carbon fiber bundles and form a CNT layer. In contrast, long CNT can be held much more uniformly to fill the interspaces in carbon fiber sheet and large pores are fully filled by CNT, as shown in Fig. 3(c).

3.2. Mechanical properties and microstructure of the resultant ceramic matrix composites

After CNT is embedded within the inter-bundle of carbon fibers, PIP process is applied to prepare the ceramic matrix composites. In this paper, Cf-CNT/ScCMT stands for ceramic matrix composites with carbon fibers and CNT, not indicating whether CNT is long or not. During material preparation, in order to achieve a certain volume fraction of carbon fibers and CNT for the three sample cases, firstly, the thickness of the final ceramic composite is set to a certain value (3 mm). As the diameter of our sample is controlled to 35 mm, the total volume (\(V_{\text{total}}\)) of the resultant composites is set to be a constant. To obtain the volume fraction of carbon fibers and CNT, their volume is divided by the whole volume of the composites as shown in Equations (4)–(6).

$$V_{\text{total}} = V_{\text{fiber}} + V_{\text{matrix}} + V_{\text{CNT}} + V_{\text{pore}}$$  \hspace{1cm} (4)

$$V_{\text{fiber}} = \frac{V_{\text{fiber}}}{V_{\text{total}}} = \frac{m_{\text{fiber}}}{\rho_{\text{fiber}} \times V_{\text{total}}}$$  \hspace{1cm} (5)

$$V_{\text{CNT}} = \frac{V_{\text{CNT}}}{V_{\text{total}}} = \frac{m_{\text{CNT}}}{\rho_{\text{CNT}} \times V_{\text{total}}}$$  \hspace{1cm} (6)

where \(V_{\text{total}}\), \(V_{\text{fiber}}\), \(V_{\text{matrix}}\), \(V_{\text{CNT}}\), and \(V_{\text{pore}}\) are the volume of the resultant composites, carbon fibers, ceramic matrix, CNT and pores separately; \(m_{\text{fiber}},\ \rho_{\text{fiber}}\) and \(m_{\text{CNT}}\) are the volume fraction, mass, and density of carbon fibers; \(V_{\text{CNT}},\ \rho_{\text{CNT}}\) and \(m_{\text{CNT}}\) stand for the volume fraction, mass, and density of CNT. With known density of carbon fiber and CNT, the weight of carbon fiber and CNT needed can be calculated. In our experiments, three types of ceramic matrix composites are prepared: one sample is reinforced by carbon fiber with the volume fraction as 45%, and the other two are reinforced by carbon fiber (volume fraction as 45%) and CNT (volume fraction as 10%) for both short CNT and long CNT. The volume fractions of carbon fiber are kept the same for all three samples and the introduction of CNT (short or long) helps the composite densification and improves the bending strength of the resultant composites.
During PIP process, the polymer precursor is transformed into a ceramic matrix by high temperature pyrolysis process. Shrinkage and densification of the matrix material occurs because the density increases significantly from 1.10 g cm\(^{-3}\) to 2.23 g cm\(^{-3}\) during the polymer-ceramic conversion from polysilazane to silicon carbonitrile in the pyrolysis process, and around 28% linear shrinkage.

Fig. 2. Schematic and optical images of plain woven carbon fibers and C\(_f\)-CNT hybrid structure: (a) Illustration of plain woven carbon fibers; (b) Illustration of C\(_f\)-CNT hybrid structure; (c) Optical images of plain woven carbon fibers; (d) Optical images of C\(_f\)-CNT hybrid structure. (A colour version of this figure can be viewed online.)

Fig. 3. SEM images of carbon fiber and C\(_f\)-CNT hybrid structure. (a) Carbon fiber bundle, (b) the surface of C\(_f\)-SCNT hybrid structure, (c) the surface of C\(_f\)-LCNT hybrid structure, (d) SCNT zone and (e) LCNT zone. (A colour version of this figure can be viewed online.)
results in a great volume reduction [26]. Fig. 5 illustrates procedures of our composites preparation by PIP process. Liquid polysilazane is used as the precursor of silicon carbonitride. After infiltration and curing processes, both pores in pristine carbon fiber sheets and Cf-CNT hybrid structure are filled by the solidified precursor. For case (a) with big pores in pristine carbon fiber sheets, the macro-sized pores have a negative impact on the densification process during the PIP process: it is hard to densify the composites because the matrix shrinks along carbon fiber and there are still big pores left in the resultant composites [27]. For case (b), before the infiltration process, the big pore in pristine carbon fiber sheets are divided into small pores by the embedded CNT. With the inclusion of CNT, the macro-sized pores in the inter-bundle of carbon fibers are divided into numerous nano-sized pores, which will be helpful for the infiltration/densification process.

Table 2 shows that both Cf-SCNT/SiCN and Cf-LCNT/SiCN composites have smaller porosity (9.4% and 9.2%) than Cf/SiCN (11.2%), indicating improved densification. Fig. 6 shows the SEM images of the polished surface of Cf/SiCN and Cf-SCNT/SiCN composites. It is found that big pores still exist at the criss-cross position in Cf/SiCN composites (Fig. 6(a)); while those pores are filled with CNT entirely and after PIP process form a dense CNT/SiCN composites (Fig. 6(b)). The improved densification and inclusion of CNT enhance the thermal properties of the final composites, which will be explained in details in Section 3.3. Fig. 7 shows SEM images of the polished cross-section of the final composites (Cf/SiCN, Cf-SCNT/SiCN, and Cf-LCNT/SiCN). As discussed above, a CNT layer is formed in between of each adjacent carbon fiber sheets (for both Cf-SCNT/SiCN and Cf-LCNT/SiCN composites). However, for short CNT, the CNT layer in Cf-SCNT/SiCN composites is much thicker than Cf-LCNT/SiCN composites. The reason is that short CNT is easier to flow through carbon fiber bundles, as shown in Fig. 7(b). In contrast, long CNT is held within the interspaces in sheet. So the thickness of CNT layer in the Cf-LCNT/SiCN composites is smaller.

### 3.3. Thermal conductivity measurement and simulation result

To simulate thermal conductivity of composite, a multi-scale simulation method was implemented for three sample cases: Cf/SiCN, Cf-SCNT/SiCN and Cf-LCNT/SiCN composites. Cf-CNT/SiCN can stand for both Cf-SCNT/SiCN and Cf-LCNT/SiCN composites. The simulation structures have been constructed similar to real

<table>
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<th>Composites</th>
<th>Size</th>
<th>V_fiber/%</th>
<th>V_CNT/%</th>
<th>Density/(g cm$^{-3}$)</th>
<th>Porosity/%</th>
</tr>
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<tr>
<td>Cf/SiCN</td>
<td>35</td>
<td>3</td>
<td>45</td>
<td>0</td>
<td>1.80</td>
</tr>
<tr>
<td>Cf-SCNT/SiCN</td>
<td>35</td>
<td>3</td>
<td>45</td>
<td>10</td>
<td>1.76</td>
</tr>
<tr>
<td>Cf-LCNT/SiCN</td>
<td>35</td>
<td>3</td>
<td>45</td>
<td>10</td>
<td>1.77</td>
</tr>
</tbody>
</table>

**Fig. 4.** Three-point bending strength-displacement curve of the resultant ceramic matrix composites. (A colour version of this figure can be viewed online.)

**Fig. 5.** Illustration of the composites preparation by PIP process. (a) Cf/SiCN composites; (b) Cf-CNT/SiCN composites. (A colour version of this figure can be viewed online.)
samples, with dimensions determined by experimental microscopy measurements. The simulated structure for Cf/SiCN composite is shown in Fig. 8(a); while the simulated structure of Cf-CNT/SiCN is depicted in Fig. 8(b). In both samples main part of the structure is constructed by eight blocks. For Cf/SiCN each block has dimensions of 800 μm in 1600 μm and a thickness of 125 μm. Two layers of carbon fiber are simulated in the universal simulations, consistent with Fig. 8(a) and (b). Placing two blocks beside each other in the thickness direction we will have 250 μm thickness of woven carbon fiber sample. To make simulation box resemble the experimental structure, two boxes are shifted by 800 μm in the length direction so that they will cover a total length of 2400 μm with empty blocks of 800 μm at two ends. These two blocks will be filled by two other blocks orienting in the perpendicular direction. Following the same pattern a block of 2400 μm in 2400 μm with a free space of 800 μm in 800 μm in the center with a thickness of 250 μm is constructed. The middle box is filled with SiCN to complete the simulation box. This structure is consistent with the experimental images shown in Fig. 7 where thickness of box is aligned in the z direction of simulation setup. For Cf-CNT/SiCN, same blocks with the same dimensions and layout are used except that thickness of each block is reduced to 115 μm to have a layer of 20 μm of CNT/SiCN between two carbon fiber layers. This middle layer as well as the empty space of 800 μm in 800 μm is filled with CNT/SiCN composite whose thermal properties are calculated separately for CNT in SiCN matrix. This structure and corresponding experimental dimensions are shown in Fig. 8(b).

To obtain the thermal properties of the subdomains, smaller scale simulation has been conducted to calculate the property of constitutive parts, which are then provided as input for large scale
composites structures. In particular, the thermal conductivity calculation of a bundle containing thirty carbon fibers in SiCN matrix is performed in Fig. 8(c). The thermal conductivity calculation of one CNT in SiCN matrix is performed in Fig. 8(d). Firstly thermal conductivity calculation of CNT in SiCN powder is performed. Then resultant value is used to simulate subdomain of carbon fiber inside the mixture of powder. Finally all the components are arranged in the corresponding structure shown in Fig. 8(a) and (b) for calculation of thermal conductivity along the thickness direction.

In subdomain thermal conductivity simulation of Cf/SiCN with the experiment, 10% pores have been added to structure. For this purpose, two pores have been placed as two columns of air centered on the top and bottom side of carbon fiber. As shown in Fig. 8(c) this simulation is consisted of 30 carbon fibers, each carbon fiber with a diameter of 7 μm and a length of 1200 μm surrounded in the middle of a box of 8.1 μm in 8.1 μm with a height of 1600 μm of SiCN or CNT/SiCN matrix. Two columns of air have the same diameter of carbon fiber and a height of 135 μm. These dimensions are compatible with volume fraction shown in Table 2. In thermal conductivity simulation of CNT/SiCN matrix, we simulate a single CNT of diameter 0.08 μm and length of 20 μm for short CNT and 40 μm for long CNT. For case of short CNT, nanotube is implemented in a box of 0.1 μm in 0.1 μm with a height of 45 μm. For long CNT a box of 0.14 μm in 0.14 μm with a height of 45 μm is considered. For this step of simulation, two approaches have been chosen: first, all boundary effects and scattering contributions have been ignored; second, thermal resistance has been considered in boundaries of CNT to account for scattering effects. Considering thermal resistance between CNT and SiCN matrix as a fitting factor, it has been shown that a factor of $8.5 \times 10^{-8} \text{K m}^2/\text{W}$ provides the best fit to experimental data.

Thermal conductivity of carbon fiber has been extracted from Wang et al. [28]. Thermal conductivity of CNT as a function of temperature has been obtained from Xie et al. [29]. Density and specific heat has been considered constant for all materials and mixing rule based on weight ratio has been applied where required. Properties of air have been considered for pores while all values have been fixed with respect to temperature for pores (thermal conductivity = 0.003 W/(m·K)). The relatively negligible thermal conductivity of air in the temperature range of $25-200 \, ^\circ\text{C}$ ($0.0025-0.0035 \, \text{W/(m·K)}$) compared to thermal conductivity of other parts (1.5 W/(m·K)) for SiCN as the least conductive material in the composite) makes the assumption of constant thermal conductivity legitimate.

Fig. 9(a) shows the temperature-dependent thermal conductivity of all three composites (Cf/SiCN, Cf-SCNT/SiCN, and Cf-LCNT/SiCN composites) along the through-thickness direction. All three composites exhibit an increasing trend when temperature increases from 100 °C to 900 °C. It is found in this study that the
through-thickness thermal conductivity of Cf-SiCNT/SiCN is improved by 10% and the value of Cf-LCNT/SiCN is improved by 31%, compared with Cf/SiCN composites. There are two reasons why the proposed Cf-CNT hybrid structure improves the thermal conductivity: firstly, the percolating network of CNT provides better heat conduction path; and secondly, big pores in carbon fiber sheet are filled by CNT in the Cf-CNT hybrid structure, which is beneficial for the densification process as well as reducing the porosity of the resultant ceramic composites (Table 2).

Fig. 9(b) demonstrates the simulated thermal conductivity values of Cf/SiCN, Cf-SCNT/SiCN and Cf-LCNT/SiCN composite. We ignore thermal resistance between carbon fiber bundles and SiCN, mainly due to low thermal conductivity of SiCN. We assume that low value of thermal conductivity for SiCN is the controlling factor in determining overall thermal conductivity of composite in meso-scale. This is due to the fact that value of thermal resistance between carbon fiber and SiCN is determined by the quality of bonding. Thermal resistance between parts of a composite can be a function of bonding and wetting agents [30]. They even demonstrate varying pressure will change thermal contact conductance of composite. Here we have filtration process which applies pressure to the composite in the first step of composite production process followed by pyrolysis; so we expect low thermal resistance between fiber and matrix coming from strong bonding between them. For Cf-CNT/SiCN composite, the thermal resistance between CNT and SiCN matrix are considered because CNT is in nano-scale and as shown in previous work, thermal resistance of CNT plays a major role in determining effective thermal conductivity of composite [31]. Also we do not expect to manipulate value of thermal resistance for nano-scale CNT by the process applied. The simulated values of thermal conductivity without considering thermal scattering case are much different from the experimental results. In fact, we found that the measured thermal conductivity of the composite is much lower than the value simulated under non-resistive boundary condition. Therefore, in the case of Cf-CNT/ SiCN, the thermal conductivity is dominant by the interface resistance coming from scattering on the CNT/SiCN boundary. In order to quantitatively understand the effects of CNT in the thermal conductivity of the composite, it is important to estimate the thermal resistance between CNT and SiCN. Here we treat thermal resistance as a fitting factor to fit to the experimental data.

As the accuracy of model for Cf/SiCN composite has been proven, we are allowed to use current model for Cf-CNT/SiCN composite. By this way, we found the value of $8.5 \times 10^{-8}$ (K m$^2$)/W for thermal resistance as the best fitting factor for the experimental results. It is interesting to see that a value of $8.3 \times 10^{-8}$ (K m$^2$)/W has been reported as the interface thermal resistance across the carbon nanotube matrix [32,33]. As discussed in literature [34–36], interfacial thermal resistance plays a major role in CNT composites, the reasonable value of thermal resistance between CNT and SiCN matrix enables a good estimation of thermal conductivity for the overall structure. As seen in Fig. 9(b), the thermal conductivity of Cf-SCNT/SiCN and Cf-LCNT/SiCN composites are about 10% and 33% higher than that of Cf/SiCN composites, respectively. The thermal conductivity increases monotonically with the temperature, which is consistent with the trend of the experimental results of CNT in Cf-CNT/SiCN composites (in Fig. 9(b)). Effective thermal conductivity goes high due to increase in the thermal conductivity of carbon fiber and SiCN with increasing temperature. It has a 20% increase in thermal conductivity of SiCN from 100 °C to 900 °C whereas thermal conductivity increases from 20 W/(m·K) to 85 W/(m·K) for carbon fiber in this temperature range [37,38]. The previous work also present an increase in thermal conductivity of CNT with increasing aspect ratio of nanotube [31]. Main contribution of long CNT in increasing thermal conductivity in this simulation comes from having heat travel in CNT with a thermal conductivity of three orders of magnitude higher than that of SiCN matrix over a longer distance. It is obvious that we expect a higher overall thermal conductivity for a sample where a big portion of heat transfer can be done with longer CNT in comparison with the sample where CNT has shorter length with SiCN matrix filling the gap between them. The value of experiment and simulation values are very close at temperature less than 700 °C. However, the difference between experiment and simulation data widens as temperature increases after 700 °C. This might be due to the following factors: the inaccurate thermal conductivity of CNT, carbon fiber and SiCN, and thermal scattering resistance value of CNT at high temperatures. Further works need to be done to build more accurate value of the thermal conductivity of CNT, carbon fiber and SiCN, and thermal scattering resistance of CNT at elevated temperatures.

4. Conclusions

This paper presented a new manufacturing method to fabricate a 3D-linked Cf-CNT hybrid structure to enhance the through-thickness thermal conductivity of ceramic matrix composites. Effect of CNT with different lengths on the thermal conductivity of the resultant ceramic matrix composites is characterized. Following the same processing procedure, the porosity of the ceramic composites is reduced from 11% to 9% after including CNT as the second-phase reinforcement. The macro-sized pores at the cross-section position in the plain woven carbon fiber sheets are divided into
numerous nano-sized pores in between each CNT, which is beneficial for the infiltration process and densification of the resultant ceramic composites. The percolating network of CNT provides much improved heat conduction path along through-thickness direction and the through-thickness thermal conductivity of the final composites is improved (10% with short CNT and 31% with long CNT). Thermal conductivity increases monotonically with elevated temperature (from 100 to 900 °C) for all three cases, e.g. C/SiCN, Cr-SCNT/SiCN, Cr-LCNT/SiCN composites. Multiphysics simulation was utilized to reveal the effects of the Cr-CNT hybrid structure on the improvement of thermal conductivity, which is consistent with experimental results. Thermal scattering between CNT and SiCN is found to be an important factor to decide the thermal conductivity of the Cr-CNT/SiCN composites.

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