CARBON FIBERS FROM MESOPHASE PITCH: Processing and Properties

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Potential Applications

**Ultra High Thermal Conductivity Composites**
Ten years from now, chips will run at 30 GHz and churn a trillion operations per sec. Unfortunately, with today’s technology, that would lead to chips putting out the same amount of heat, proportionally, as a nuclear power plant … *Intel CTO Pat Gelsinger*

**Gen IV Nuclear Reactor:** Structural materials needed to build the advanced reactor; structural carbon-carbon composites needed for High Temperature Internals (>1200°C) … *Dr. Bill Corwin, Natl Tech Director for Matls, ORNL*
BARRIERS TO HIGH VOLUME APPLICATIONS

• Current price of carbon fibers ranges from ~$1000/pound for high thermal conductivity carbon fibers to $15/lb for low modulus fibers.
• For electronic applications the cost of high thermal conductivity fibers must be reduced to $100/pound.
• Mesophase pitch precursors for carbon fibers with controllable molecular properties
• Process models for control and the optimization of molecular structure within fiber during processing for balance of properties
Carbon fibers made from mesophase pitch

- Excellent tensile modulus 800 GPa
- Outstanding thermal conductivity 1100 W/m-K
- Moderate tensile strength (2000 MPa)
- Poor compressive strength (700 MPa) and
- Poor transverse properties (10 W/m.K)
Topical Outline

- Molecular Structure
- Flow Behavior and Processing
- Microstructure and Texture
- Mechanical and Transport Properties
Precursors: Mesophase Pitch

MW $\sim$ 500
MALDI Analysis

Mitsubishi AR-HP: Synthesized from Naphthalene using BF$_3$/HF catalysts

Kundu,… Ogale, *Carbon*, 2008
MALDI Analysis

Petroleum Pitch-derived Experimental
Molecular Structure: AR-HP Mesophase Pitch

Rigaku 2-D diffractometer (Rigaku/ MSC) Cu-Kα 45 KV and 0.67 mA.
Azimuthal Scans

Kundu, Naskar, Ogale, Anderson, Arnold, CARBON 2008

Azimuthal profiles of 25° and 7° peaks display off-set by 90°
Processing of Mesophase Pitch-Based Carbon Fibers

Liquid crystalline pitch precursor $\xrightarrow{\text{Melt-spinning}}$ precursor fiber $\xrightarrow{200-300^\circ \text{C}, \ 1-24 \text{ h}}$ Stabilized fiber $\xrightarrow{\text{Graphitization} \ 2000-3000^\circ \text{C}, \ \text{inert atmosphere}}$ Carbon fiber

“Carbon-Carbon Materials and Composites”
NASA Reference Publication 1254, Buckely and Edie, Eds., 1992
Transient Rheo-structural Evolution

The local maximum in shear stress is a consequence of yielding of initial texture

Kundu, Grecov, Rey, and Ogale, J. Rheology, 2009
Flow-Microstructure Relationship: Converging Section

- Vortex formation was observed in the contraction region.
- Vortex formation typically associated with viscoelasticity of the material.
- Dynamic rheology for this material indicated low elasticity\(^2\).

*Kundu and Ogale, Rheologica Acta 2010*
Melt-Spinning

Single-shot batch extruder

12 capillary hole spinneret
Capillary diameter = 150 µm,
L/D = 5

Spinning temp ~ 200-220°C  Winding speed ~ 100-600 m / min
Ultra High Temperature Heat Treatment

Graphitization furnace: 2700°C

Ultrahigh temperature press: 10 Tons and 2100°C
Carbonization under tension

Fiber tows

Tungsten weight
EM images of AR-MP carbon fiber

SEM and TEM images of ARMP carbon fibers heat treated at (a) 2600, (b) 2100, (c) 1500, & (d) 1200°C.
Carbon fibers: Stress-strain plots

Figure 1 Stress-strain response of AR-MP pitch based carbon fibers heat treated at various temperatures
## Table 1 Tensile properties of AR-MP fibers

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2600°C</td>
<td>8.5 ± 0.7</td>
<td>0.11±0.04</td>
<td>1.9±0.7</td>
<td>482.1 ± 94.1</td>
<td>0.42 ± 0.2</td>
</tr>
<tr>
<td>2100°C</td>
<td>8.9 ± 1.0</td>
<td>0.16±0.05</td>
<td>2.7±0.5</td>
<td>412.0 ± 54.6</td>
<td>0.70 ± 0.1</td>
</tr>
<tr>
<td>1500°C</td>
<td>9.1 ± 0.5</td>
<td>0.15±0.05</td>
<td>2.3±0.6</td>
<td>205.7 ± 29.4</td>
<td>1.10 ± 0.2</td>
</tr>
<tr>
<td>1200°C</td>
<td>9.1 ± 0.7</td>
<td>0.13±0.04</td>
<td>2.0±0.7</td>
<td>173.8 ± 19.7</td>
<td>1.10 ± 0.3</td>
</tr>
</tbody>
</table>
# Electrical Conductivity

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Diameter, $\mu$m</th>
<th>Resistivity $\mu\Omega$-m</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1100</td>
<td>12</td>
<td>$1.4 \pm 0.2$</td>
</tr>
<tr>
<td>P100</td>
<td>12</td>
<td>$3.2 \pm 0.3$</td>
</tr>
<tr>
<td>AR-HP based</td>
<td>13</td>
<td>$3.5 \pm 0.6$</td>
</tr>
<tr>
<td>T300</td>
<td>7</td>
<td>$18.1 \pm 5.3$</td>
</tr>
<tr>
<td>Terpolymer</td>
<td>17</td>
<td>$31.7 \pm 11.1$</td>
</tr>
<tr>
<td>Rayon-based</td>
<td>12</td>
<td>$55.5 \pm 2.3$</td>
</tr>
</tbody>
</table>
Carbon fibers: electrical properties

Table 2 Electrical resistivities of AR-MP fibers

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Diameter [μm]</th>
<th>Area [m²]</th>
<th>Resistance [Ω]</th>
<th>Electrical Resistivity [μΩ·m]</th>
<th>Predicted* Thermal Conductivity [W/mK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2600°C</td>
<td>9.0 ± 1.1</td>
<td>7.1 × 10⁻¹¹</td>
<td>475.5 ± 138</td>
<td>3.2 ± 0.6</td>
<td>466</td>
</tr>
<tr>
<td>2100°C</td>
<td>9.3 ± 0.8</td>
<td>6.9 × 10⁻¹¹</td>
<td>1,200.3 ± 266</td>
<td>8.0 ± 1.2</td>
<td>120</td>
</tr>
<tr>
<td>1500°C</td>
<td>9.3 ± 0.5</td>
<td>7.2 × 10⁻¹¹</td>
<td>1,356.2 ± 228</td>
<td>9.6 ± 1.2</td>
<td>66</td>
</tr>
<tr>
<td>1200°C</td>
<td>9.6 ± 0.7</td>
<td>7.3 × 10⁻¹¹</td>
<td>1,524.0 ± 313</td>
<td>10.9 ± 1.8</td>
<td>31</td>
</tr>
</tbody>
</table>

*Lavin-Issi Correlation

\[ \kappa = \frac{440,000}{(\rho + 258)} - 295 \]

where \( \kappa \) [W/mK] and \( \rho \) [μΩ·cm]
## ER properties of 2400 °C HT fibers

<table>
<thead>
<tr>
<th>HT at 2400°C</th>
<th>Diameter [μm]</th>
<th>R [Ω]</th>
<th>ER [μΩ-m]</th>
<th>Predicted Thermal conductivity [W/mK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>thin fibers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AR</td>
<td>11.7 ± 0.8</td>
<td>541 ± 306</td>
<td>3.4</td>
<td>438</td>
</tr>
<tr>
<td>Ex2</td>
<td>9.8 ± 0.8</td>
<td>725 ± 265</td>
<td>4.4</td>
<td>338</td>
</tr>
<tr>
<td>Ex3</td>
<td>11.9 ± 0.7</td>
<td>316 ± 88</td>
<td>2.8</td>
<td>520</td>
</tr>
<tr>
<td>thick fibers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AR</td>
<td>16.0 ± 0.8</td>
<td>164 ± 27</td>
<td>2.8</td>
<td>521</td>
</tr>
<tr>
<td>Ex2</td>
<td>17.6 ± 1.3</td>
<td>180 ± 126</td>
<td>2.9</td>
<td>502</td>
</tr>
<tr>
<td>Ex3</td>
<td>15.9 ± 0.7</td>
<td>172 ± 26</td>
<td>2.3</td>
<td>603</td>
</tr>
</tbody>
</table>

Carbon fibers based on experimental mesophase pitch showed smaller ER (thus higher thermal conductivity)
Stresses created by high-temperature heat treatment causes splitting, reducing the mechanical and thermal properties of the fibers.

(S. Kumar, SAMPE Qtr, 1989)
Ongoing Clemson Studies ...

Introduction of multi-walled nanotubes of high aspect ratio disrupts the otherwise highly ordered, radial structure of carbonized fiber derived from mesophase pitch


0% Nanotubes          0.1% Nanotubes          0.3% Nanotubes
Recoil Test: Large stress – compressive failure
### Fiber Properties: Mechanical

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>Diameter ($\mu$m)</th>
<th>Tensile Strength (GPa)</th>
<th>Compressive Strength (GPa)</th>
<th>Compressive/Tensile (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% MWNTs in MP</td>
<td>8.4</td>
<td>2.6 ± 0.4</td>
<td>0.77 ± 0.04</td>
<td>30</td>
</tr>
<tr>
<td>0.1% MWNTs in MP</td>
<td>8.0</td>
<td>1.8 ± 0.5</td>
<td>0.94 ± 0.06</td>
<td>53</td>
</tr>
<tr>
<td>0.3% MWNTs in MP</td>
<td>11.6</td>
<td>1.8 ± 0.3</td>
<td>1.13 ± 0.04</td>
<td>63</td>
</tr>
</tbody>
</table>


- Compressive strength as a ratio of tensile strength was improved for nanocomposite carbon fibers, suggesting a decrease in the anisotropic nature of the pitch-based carbon fiber
SEM images of the fractured cross section of (a) 0 wt% and (b) CB modified carbon fibers. White boxes correspond to the positions at which the high resolution images were obtained.

R. Alway-Cooper, D. P. Anderson, and A. A. Ogale, CARBON 2013
Two theta x-ray diffraction spectra of milled 0 wt% and CB modified experimental carbon fibers, as well as the highly graphitic, commercial grade K1100 (a) from 25 to 29° and (b) from 75 to 90°.

R. Alway-Cooper, D. P. Anderson, and A. A. Ogale, CARBON 2013
Conclusions

• MWCNT and carbon black was shown to modify the structure of mesophase pitch-based carbon fibers when added in dilute concentration of about 0.3 wt%. A decrease was observed in the number of fibers that exhibited “pac-man” splitting.

• Despite the cross-sectional textural changes, no significant reduction was observed in the d$_{002}$ spacing or L$_{a}$ indicating that the nano-modified carbon fibers retained a high degree of graphitic crystallinity.

• These mesophase-pitch based carbon fibers showed a strong graphitic development and excellent transport properties, which makes them suitable for high electrical and thermal conductivity industrial applications.
Carbon Fibers: Next Steps …

PROs: MULTI-FUNCTIONALITY
✓ Excellent Strength and Stiffness = high performance
✓ Light-weight = fuel-efficient
✓ Outstanding Electrical and thermal conductivity
✓ Fire-retardant

Con: COST
• Expensive on per pound basis ($ 10 to $ 1800/lb)

Current research directions:
alternative precursors and novel processing routes for reducing costs (at current fiber properties) OR improve properties (at current cost)
References


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Army Research Lab
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Center for Advanced Engineering Fibers and Films (CAEFFF)

CAEFFF Mission: To provide an integrated research and education environment for the study of high performance fibers, films, and composites for applications ranging from military to medical uses

• A Graduated NSF-ERC that secured over $30 million from NSF and other sponsors
• Interdisciplinary faculty team
• Served over 65 industrial members