COPPER-MULTIWALL CARBON NANOTUBES
AND COPPER-DIAMOND COMPOSITES FOR
ADVANCED ROCKET ENGINES

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JANNAF Meeting, Colorado Springs, Co
April 29, 2013
Overview

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• Experimental Procedure
  – Blending, Sintering
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Introduction

- Liquid-fueled rocket engine combustion chamber liners are regeneratively cooled and require high thermal conductivity material to maintain a low surface temperature.
- NARloy –Z (Cu-3wt%Ag-0.5%Zr alloy) is the state-of-the-art alloy used for liners.
- Single and Multiwall Carbon Nanotubes (SWCNT and MWCNT) are reported to have very high thermal conductivity, up to 10X that of NARloy-Z.

**Research goal:**
To improve the thermal conductivity of combustion chamber liner material NARloy-Z by 2X by embedding high thermal conductivity MWCNT in NARloy-Z matrix
Research Team

- **Biliyar N. Bhat**
  - NASA-MSFC, Principal Investigator
- **David L. Ellis**
  - NASA-GRC, Co-Investigator
- **Vadim Smelyanskiy & Michael Foygel**
  - NASA-ARC
- **Jogender Singh and Aaron Rape**
  - Applied Research Laboratory, Pennsylvania State University
- **Yogesh Vohra & Vinoy Thomas**
  - University of Alabama Birmingham
- **Deyu Li and Kyle Otte**
  - Vanderbilt University
Approach to Improving Thermal Conductivity Using MWCNT

- Significant effort has gone into thermal conductivity improvement using MWCNTs, but with limited success
- **Problem:** contact thermal resistance between MWCNT and matrix is high due to differences in thermal conductivity mechanisms
  - Copper: largely electronic conductor
  - MWCNT: conductivity by phonons (lattice vibrations)
  - Cu-MWCNT composites show lower thermal conductivity than copper
- **Challenge:** how to provide a low contact thermal resistance interface between Cu and MWCNT
- **Approach:** use carbide forming metallic elements (such as Cr, Ti, Zr) in the Cu-matrix to react with carbon in MWCNT to form a metal carbide
  - Metal carbides are believed to provide a higher contact conductance
  - Supported by literature in Copper-Diamond (Cu-D) system in which thermal conductivity improvements were reported by using Ti and Cr
- **NARloy-Z was selected as matrix alloy**
  - Logic: Zr in the NARloy-Z-matrix will react with MWCNT to form ZrC at the MWCNT interface
  - ZrC at MWCNT interface should improve contact conductance
Quantum Mechanics-Based Modeling of Contact Conductance (ARC)

(Left) Contact Conductance of Metals with Carbon Modifications: $d = 1$ (CNT), $d=2$ (graphene, $G$), $d = 3$ (diamond, $D$). Here $\theta_m$ – temperature at maximum phonon frequency ($kT = h \times$ frequency where $k$ is Boltzmann’s constant and $h$ is Planck’s constant) – Debye’s temperature is used for $\theta_m$ as an approximation. (Right) Contact thermal conductance for various interfaces

Observations:
- CNTs and diamond show similar contact conductance behavior at $T/\theta_m > 1$
- $D/ZrC/Cu$ contact conductance is significantly higher than direct CNT/Cu contact (by $>3.5x$)

Approach: Study NARloy-Z-MWCNT and NARloy-Z-D in parallel
## NARloy-Z-MWCNT and NARloy-Z-D Composites Studied

<table>
<thead>
<tr>
<th>Material/Process</th>
<th>Vol.% (CNT/D)</th>
<th>Wt.% (CNT/D)</th>
<th>Density (gm/cc)</th>
<th>Characterization</th>
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<tr>
<td>NARloy-Z baseline (FAST)*</td>
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<td>9.13</td>
<td>Thermal conductivity, mechanical, microstructure</td>
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<td>NARloy-Z-MWCNT (FAST)*</td>
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<td>9.06</td>
<td>Thermal conductivity</td>
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<tr>
<td></td>
<td>2</td>
<td>0.5</td>
<td>8.99</td>
<td>Thermal diffusivity</td>
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<tr>
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<td>5</td>
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<td>8.44</td>
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<td>20</td>
<td>5</td>
<td>7.75</td>
<td>Thermal diffusivity, microstructure</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>10</td>
<td>6.38</td>
<td>Microstructure</td>
</tr>
<tr>
<td>NARloy-Z-MWCNT (Extrusion)</td>
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<td></td>
<td>Microstructure, electrical resistivity</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.25</td>
<td></td>
<td>Microstructure, electrical resistivity</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.5</td>
<td></td>
<td>Microstructure, electrical resistivity</td>
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<tr>
<td>NARloy-Z-Diamond (FAST)*</td>
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<td></td>
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<td>7.75</td>
<td>Thermal conductivity, microstructure</td>
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<tr>
<td></td>
<td>40</td>
<td>10</td>
<td>6.38</td>
<td>Thermal conductivity, microstructure</td>
</tr>
</tbody>
</table>

*Parameters used for FAST: Temperature: 975°C, Pressure: 65 MPa, Heating rate: 10°C, Holding time at temperature: 20 minutes, Furnace cooled
Blending and Sintering of NARloy-Z-MWCNT

Attritor used for blending NARloy-Z and MWCNTs (GRC)

Left: Attritor in operation
Right: Attritor parts

Field Assisted Sintering Technology (FAST) (ARL – Penn State)

Left: FAST Apparatus
Right: Sintering at high temperature
Thermal Property Measurement

- Thermal diffusivities ($\alpha$) of sintered NARloy-Z-MWCNT composites were measured by laser flash technique
  - Thermo-Physical Research Laboratory (TPRL) – Thermal diffusivity and thermal conductivity
  - NASA-MSFC -- Thermal diffusivity only
- Bulk density ($\rho$) was calculated from mass and geometry
- Specific heat ($C_P$) was measured using a differential scanning calorimetry
- Thermal conductivity ($\lambda$) was calculated using the equation

$$\lambda (T) = \alpha(T) \, C_P(T)\rho$$
Thermal conductivities of MWCNTs used in this study (provided by Pyrograf, Inc.) and from other suppliers was measured at Vanderbilt University

**Method used:**
- Individual MWCNT sample was placed between two suspended membranes with integrated platinum coil serving as heat source and heat sink
- Platinum coil serves as both electric heater and resistance thermometer
- Dimension of sample was determined by electron microscopy
- Thermal conductivity of sample was calculated
- Contact resistance between sample and membrane is considered and sometimes eliminated by making measurements on two different lengths of the same sample
Results: Ball Milling

Observations:
- NARloy-Z powder particles work hardened quickly during milling and started to grind after 60 minutes.
- Blending time was limited to 45 minutes to prevent damage to MWCNT.
- Portion of MWCNT was left on the powder particle surfaces.
- It was not possible to completely embed the MWCNTs in NARloy-Z.
NARloy-Z-MWCNT Tensile Properties

<table>
<thead>
<tr>
<th>% MWCNT</th>
<th>Average Yield (MPa)</th>
<th>Average UTS (MPa)</th>
<th>Average Elongation (%)</th>
<th>Average R.A. (%)</th>
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<tr>
<td>0</td>
<td>88.2</td>
<td>271.7</td>
<td>31.3</td>
<td>61.2</td>
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<tr>
<td>5</td>
<td>105.9</td>
<td>124.7</td>
<td>1.6</td>
<td>1.2</td>
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<td>10</td>
<td>97.8</td>
<td>107.5</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Stress-strain curves for baseline pure NARloy-Z (0% MWCNT) and NARloy-Z-5% MWCNT
NARloy-Z-MWCNT Tensile Fracture Surfaces

NARloy-Z-MWCNT tensile specimens

NARloy-Z-MWCNT tensile fracture surfaces
The graph shows the thermal conductivity of NARloy-Z-MWCNT materials as a function of temperature. The x-axis represents temperature in Kelvin (K), ranging from 200 to 1400 K. The y-axis represents thermal conductivity in W/cm-K, ranging from 1.5 to 4.0 W/cm-K.

- **0% MWCNT**: The line with diamond markers indicates the thermal conductivity for 0% MWCNT samples. The conductivity decreases as temperature increases.
- **5% MWCNT**: The line with cross markers represents 5% MWCNT samples, showing a similar trend to 0% MWCNT but slightly higher conductivity.
- **10% MWCNT**: The line with square markers demonstrates 10% MWCNT samples, with the highest conductivity among the three, and it also decreases with increasing temperature.

The graph includes markers for various samples labeled as SAMPLE 1, SAMPLE 2, SAMPLE 3, SAMPLE 1532, and SAMPLE 1537, indicating different compositions or batches of the materials.
NARloy-Z-MWCNT Thermal Diffusivity (TPRL)

Thermal Diffusivity ($\alpha$) (cm²/s)

Temperature (K)

- 0% MWCNT
- 0% MWCNT
- 1% MWCNT
- 2% MWCNT
- 5% MWCNT
- 5% MWCNT
- 10% MWCNT
NARloy-Z-MWCNT Thermal Diffusivity (MSFC)

Thermal Diffusivity vs. Temperature

- 0% CuMWCNTs Avg
- 5% Cu MWCNTs Avg
- 10% Cu MWCNTs Avg
Thermal Conductivity of NARloy-Z-D Composites at Room Temperature (ARL)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vol. % Dia</th>
<th>Thermal Conductivity (W/mK)</th>
<th>Density, ρ (gm/cc)</th>
<th>λ/ρ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAgZr (NARloy-Z)</td>
<td>0</td>
<td>315</td>
<td>9.13</td>
<td>34.50164</td>
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<tr>
<td>CuAgZr+10 vol % D</td>
<td>10</td>
<td>351</td>
<td>8.44</td>
<td>41.58768</td>
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<tr>
<td>CuAgZr + 20 vol % D</td>
<td>20</td>
<td>422</td>
<td>7.75</td>
<td>54.45161</td>
</tr>
<tr>
<td>CuAgZr + 40 vol % D</td>
<td>40</td>
<td>533</td>
<td>6.38</td>
<td>83.54232</td>
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</tbody>
</table>
Microstructure Analysis

SEM images of NARloy-Z-CNT composites

NARloy-Z-5%MWCNT  NARloy-Z-10%MWCNT  NARloy-Z-20%MWCNT

Note the segregation of MWCNT at prior particle boundaries
SEM – EDS Analysis

Narloy-Z- 0% MWCNT
NARloy-Z-2%MWCNT
NARloy-Z-20%D
NARloy-Z –MWCNT and NARloy-Z-D composite showing Zr elemental map

Note the migration of Zr to MWCNT and D
XPS C 1s spectrum showing a small ZrC peak for a 1% MWCNT-NARloy-Z interface

XPS Analysis of NARloy-Z-1%MWCNT and NARloy-Z-20%D composites showing ZrC peaks.

Note: Peak height for ZrC is small because of thin ZrC layer
Separation of MWCNTs
To Prevent Agglomeration

Carboxylated MWCNTs disperse well in acid media

- Surface-carboxylation of MWCNTs by acid treatment in 1:3 HNO₃ :H₂SO₄, sonication for 1 h and then kept at room temperature for 24h. This process provides MWCNTs with more –COOH chemical groups on the surface and reduce the agglomeration of MWCNTs.

- Acid treated CNT is used for chromium coating by electroless plating (wet chemical method)
Electroless Coating
(Schematic – UAB)

Acid treated or Carboxylated MWCNTs

Sensitization by (0.1 M SnCl2 + 0.1 M HCl) sonication for 1h

Activation by (0.0014M PdCl2-0.25MHCl for 30 min)

Electroless deposition of Chromium from Chromium Acetate solution (2 days)

Reduction of the metal ions by Formaldehyde

By changing the metal salt solution concentration a uniform coating can be achieved
Coating of MWCNTs

Representative EDS scan of chromium electroless plated MWCNTs. Inset shows the corresponding SEM image MWCNTs. Sn from sensitization step can also be seen. Other elements are from SEM sample holder.

Cr seems to oxidize during the coating process
Note: Measured thermal conductivities were much lower than expected
MWCNT Quality: Raman Spectroscopy

Raman spectroscopy results for (a) Nanoshel CVD MWCNTs with a large D/G ratio and (b) Cheap Tubes graphitized MWCNTs with a lower D/G ratio.

**Note:** D/G ratio should be near zero for high quality MWCNTs.
TEM micrographs of a MWCNT at different positions. While the tube structure in (a) is good, there are significant structural defects in (b), which reduce the thermal conductivity.
Discussion: NARloy-Z-MWCNT Composite

- Ball milling did not produce desired microstructure in NARloy-Z-MWCNT composite
  - MWCNT were not detangled -- they segregated in prior particle boundaries
- FAST process produced fully dense composites, but the tensile ductility was lower because of poor microstructure
- Thermal conductivities of NARloy-Z-MWCNT composites were lower than baseline
  -- Tangled MWCNT acted as insulators and lowered the thermal conductivity
- Thermal conductivities of commercially produced MWCNTs were much lower than expected
  -- Attributed to poor quality of MWCNTs
  -- Contributed to low thermal conductivity of NARloy-Z-MWCNT composites
- Separation of tangled MWCNTs by acid treatment was effective, but Cr electroless coating to keep them separated produced highly oxidized coatings, not suitable for bonding with MWCNT or copper
  -- Should pursue alternate coating techniques such as pulsed laser deposition technique for coating Cr or Zr
  -- Copper over coating will be necessary to prevent oxidation of coating and will also help to improve blending during ball milling
Discussion: NARloy-Z-D Composite

- Narloy-Z-D composites showed significant improvements in thermal conductivity (69% at 40vol%D)
  - Such improvements are not observed in Cu-D system
- ZrC at Cu-D interface is essential for good contact conductance
- The results support the quantum mechanics based model of contact conductance
- Further improvement in thermal conductivity is possible by coating diamond with Zr by pulsed laser deposition technique and then over coating with copper
Recommendations

• Approach to improving the thermal conductivity of NARloy-Z-MWCNT composites should be changed for better results
  – Must use the highest thermal conductivity MWCNT (>2000 W/m-K)
  – Reliable source for high thermal conductivity MWCNT must be found
  – MWCNT clumps should be separated and coated with a carbide former such as Zr or Cr and then over coated with copper for best results
  – Dry techniques such as pulsed laser deposition should be used for coating the MWCNTs

• NARloy-Z-D system looks promising for further development for application in advanced rocket engines
  – Further optimization of diamond particle size and NARloy-Z-D interface is recommended
  – Development of mechanical property data is necessary for designing components
  – Demonstration at component level should be the next logical step