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

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Overview

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• Research Team
• Analytical Modeling of Contact Conductance
• Experimental Procedure
  – Blending, Sintering
  – Thermal Property Measurements
  – Microstructure Analysis
  – Separation and Coating
• Results
• Discussion
• Recommendations
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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<td>40</td>
<td>10</td>
<td>6.38</td>
<td>Microstructure</td>
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<td></td>
<td>40</td>
<td>10</td>
<td>6.38</td>
<td>Thermal conductivity, microstructure</td>
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</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-MWCNTs

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.

Powder morphology evolution during ball milling for NARloy-Z-10%MWCNT.
- 30 minutes:
  - Secondary Electron Image
  - Backscattered Electron Image
  - Typical NARloy-Z – MWCNT Composite Powder Particle Surfaces

- 60 minutes:
  - Secondary Electron Image
  - Backscattered Electron Image
  - Typical NARloy-Z – MWCNT Composite Powder Particle Surfaces
### 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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<td>271.7</td>
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<td>5</td>
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<td>1.6</td>
<td>1.2</td>
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<tr>
<td>10</td>
<td>97.8</td>
<td>107.5</td>
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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
NARloy-Z-MWCNT Thermal Conductivity (TPRL)

Thermal Conductivity

Temperature (K)

<table>
<thead>
<tr>
<th>Sample</th>
<th>MWCNT Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLE 1</td>
<td>0% MWCNT</td>
</tr>
<tr>
<td>SAMPLE 2</td>
<td>5% MWCNT</td>
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<tr>
<td>SAMPLE 3</td>
<td>10% MWCNT</td>
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<td>SAMPLE 1532</td>
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<td>SAMPLE 1537</td>
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</tbody>
</table>
NARloy-Z-MWCNT Thermal Diffusivity (TPRL)

Thermal Diffusivity ($\alpha$) (cm$^2$/s)

Temperature (K)

- 0% MWCNT
- 1% MWCNT
- 2% 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

Temperature °C

Thermal Diffusivity (α) cm²/s
# Thermal Conductivity of NARloy-Z-D Composites at Room Temperature (ARL)

**Sample** | Vol. % Dia | Thermal Conductivity (λ), W/mK | Density, ρ (gm/cc) | λ/ρ  
---|---|---|---|---  
CuAgZr (NARloy-Z) | 0 | 315 | 9.13 | 34.50164  
CuAgZr+10 vol % D | 10 | 351 | 8.44 | 41.58768  
CuAgZr + 20 vol % D | 20 | 422 | 7.75 | 54.45161  
CuAgZr + 40 vol % D | 40 | 533 | 6.38 | 83.54232
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
NARloy-Z – MWCNT and NARloy-Z-D composite showing Zr elemental map

Note the migration of Zr to MWCNT and D
XPS Analysis

XPS C 1s spectrum showing a small ZrC peak for a 1% MWCNT-NARloy-Z interface

Note: Peak height for ZrC is small because of thin ZrC layer

XPS Analysis of NARloy-Z-1%MWCNT and NARloy-Z-20%D composites showing ZrC peaks.
Carboxylated MWCNTs disperse well in acid media

- Surface-carboxylation of MWCNTs by acid treatment in 1:3 HNO\(_3\) :H\(_2\)SO\(_4\), sonication for 1 h and then kept at room temperature for 24 h. 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 PdCl2-0.25M HCl 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
MWCNT Thermal Conductivity (Vanderbilt)

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