Additive Manufacturing of Carbon Nanotube Metal Matrix Composites

Presenters:
Robyn L. Bradford-Vialva --- University of Dayton
Fred Herman --- SHEPRA Inc.

Fred.Herman@shepra.com
817 233 1942

Navy STTR: N16A-T007
Army SBIR: A17A-033

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Value Proposition

- Process to incorporate Carbon Nanotubes into Powder Metal to:
  - Improve Stiffness and Strength through “long fiber” load transfer in a matrix
  - Reduce / eliminate thermal tear in non-eutectic alloys by forming nucleation sites
  - Improve laser power absorption by acting as surface coating to shift wavelength response

Before Carbon Nanotubes

After mixing with Carbon Nanotubes

Carbon Nanotube absorption >0.97
Takeaways

- Carbon nanotube metal matrix composites have been investigated through Navy STTR (17-4 stainless steel) and Army SBIR (aluminum) programs
  - Key threshold objectives were demonstrated in stiffness and strength improvements
- More research and development is required
  - Currently at TRL 3 / MRL 3
  - Utilized commercial raw materials and AM processing equipment
  - Entire process is industrial scalable
- Carbon nanotubes provide “long fiber” reinforcement within a metal matrix
  - Strengthening mechanism has been applied to other metal systems
  - Key is dispersion of the carbon nanotubes within the metal matrix
UD-SHEPRA Project Team

Robyn L. Bradford-Vialva

Fred Herman

Dr. Charles Browning

Dr. Li Cao

Dr. Don Klosterman
Background Research
Methodology

• Reviewed academic literature for peer reviewed work on carbon nanotube metal matrix composites

• Captured key performance metrics
  o Elastic Modulus
  o Yield Strength
  o Ultimate Tensile Strength
  o Strain to Fracture

• Tracked key input conditions
  o Matrix Material
  o Manufacturing Process
  o Mixing Process
  o Dispersion Quality
  o Carbide Formation
  o Volume Fraction of Carbon Nanotubes

• 41 different papers with 170 data points

• All data was normalized to reported control data

Table 1: Breakdown of Raw Data

<table>
<thead>
<tr>
<th>Matrix Material</th>
<th>Number of Papers</th>
<th>Number of Experimental Data Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum (pure)</td>
<td>18</td>
<td>61</td>
</tr>
<tr>
<td>Aluminum Alloys</td>
<td>10</td>
<td>48</td>
</tr>
<tr>
<td>Titanium (pure)</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>Magnesium Alloys</td>
<td>6</td>
<td>22</td>
</tr>
<tr>
<td>Copper Alloys</td>
<td>4</td>
<td>21</td>
</tr>
</tbody>
</table>
Elastic Modulus Ratio

Positive trend between elastic modulus and volume loading
Trend applies to all metals

Good dispersion of carbon nanotubes results in statistically significant improvement in Elastic Modulus
Mechanical Properties vs. Dispersion

Good dispersion versus bad dispersion analysis of variance (ANOVA) for:
- Modulus
- Yield Strength
- UTS

Multiple metal matrix materials

P-values
- Modulus: 0.214
- Yield Strength: 0.009
- Ultimate Tensile Strength: 0.000
Composite Theory vs. Modulus Ratio of Pure Aluminum

Comparison of various long fiber composite “rule of mixture” based models to published data for carbon nanotube/pure aluminum composites

<table>
<thead>
<tr>
<th></th>
<th>Multiwalled Carbon Nanotube</th>
<th>1050 – O Aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus (Gpa)</td>
<td>1,000</td>
<td>70</td>
</tr>
<tr>
<td>Yield Strength (Mpa)</td>
<td>--</td>
<td>28</td>
</tr>
<tr>
<td>Ultimate Tensile Strength (Mpa)</td>
<td>1000</td>
<td>76</td>
</tr>
<tr>
<td>Shear Modulus (Gpa)</td>
<td>--</td>
<td>26</td>
</tr>
<tr>
<td>Shear Strength (Mpa)</td>
<td>--</td>
<td>62</td>
</tr>
<tr>
<td>Poisons Ratio</td>
<td>--</td>
<td>.33</td>
</tr>
<tr>
<td>Density (g/cm3)</td>
<td>1.35</td>
<td>2.71</td>
</tr>
<tr>
<td>Length (micron)</td>
<td>5</td>
<td>--</td>
</tr>
<tr>
<td>Diameter (Nm)</td>
<td>10</td>
<td>--</td>
</tr>
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</table>
Summation of Study Results

• Carbon nanotubes have successfully improved mechanical properties of multiple metal materials

• Mechanism is “long fiber” load transfer within the composite matrix

• Carbide formation was not a statically significant factor on modulus, yield strength or UTS

• Dry mixing or wet mixing techniques was best in achieving dispersion of the carbon nanotubes
  – Use of ionic processes or surfactants was not successful in achieving dispersion

• Powder consolidation process was not a factor as long as porosity was addressed
Navy STTR Phase I / Phase I Option

Baseline Process

**Powder Metal**

**Carbon Nanotubes**
- Multiwalled Carbon Nanotubes (MWCNTs)
- Carbon NanoFibris (CNF)

**Mixing**
- Mix Methods, Mixing Parameters

**AM Processing**
- Laser power, scan rate, build height

**Post Processing**
- CNC Machining, Heat Treatment

### Requirements

<table>
<thead>
<tr>
<th></th>
<th>Heat Treatment</th>
<th>Yield Strength</th>
<th>Ultimate Strength</th>
<th>Hardness</th>
<th>Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Threshold</td>
<td>H1025</td>
<td>145 Ksi</td>
<td>155 Ksi</td>
<td>35 HRC</td>
<td>12%</td>
</tr>
<tr>
<td>Objective</td>
<td>H900</td>
<td>170 Ksi</td>
<td>190 Ksi</td>
<td>40 HRC</td>
<td>12%*</td>
</tr>
</tbody>
</table>

STTR: N16A-T007
Initial Results

- Use of Ni-MWCNTs eliminated the Lüders bands and increased yield strength by 20 Ksi
- Impurities in MWCNTs led to thermal tearing
Summary of Phase I Results

- Use of argon atomized 17-4 SS powder also eliminated Lüders bands
- Use of specially processed carbon nanofibrils (CNF) resolved thermal tearing issues and further improved mechanical properties
- Use of Solution Treatment and 1025 Heat Treatment achieved Threshold Requirements
Next Steps - Stainless Steel

- Leverage lessons learned from Army Phase I SBIR and apply to Navy Phase II STTR
  - Utilize special CNF processing on carbon nanotubes to prevent thermal tearing
  - AM processing parameters to decrease density
- Lessons learned from prior post-processing experiences
  - Machined surface finish required
  - Heat Treat using commercial processes

**SEMs of dispersed Carbon Nanotubes**

![Comparison to Threshold Requirement](chart.png)

- Ar_17-4 + 5% CNF
- N_17-4 + 5% Ni-MWCNT
- N_17-4 Sol Treat + 1025 HT

**Comparison to Threshold Requirement**

- Yield Strength
- UTS
Army SBIR Research
Army SBIR Phase I

- Leverage lessons learned from Navy STTR efforts
- Evaluated the use of lower cost aluminum (AlSi10Mg) metal powders
- Incorporate multiwalled carbon nanotubes
- Address porosity and thermal tearing issues that are inherent to AM processing of aluminum

<table>
<thead>
<tr>
<th></th>
<th>Specific Modulus MSI/ lb/in³</th>
<th>Shear Strength KSI</th>
<th>Elongation</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Threshold</strong></td>
<td>104</td>
<td>22</td>
<td>8%</td>
<td>90% of current cost</td>
</tr>
<tr>
<td><strong>Objective</strong></td>
<td>139</td>
<td>20</td>
<td>12%</td>
<td>75% of current cost</td>
</tr>
</tbody>
</table>

1/3rd Section of 25 mm Sabot
Stress-Strain Curves for Aluminum

Porosity had a significant impact on mechanical properties.

- 2.5% vol & 5% vol HHT-MWCNT / AlSi10Mg Best
  - 12-14-17 #2
    - SS: 650 mm/s ~98% dense
    - Modulus: 12.5 Msi
  - ARL Tested
    - 12-14-17 #4
      - SS: 650 mm/s ~95% dense
      - Modulus: 10.4 Msi
  - 12-14-17 #3
    - SS: 650 mm/s 98.51% dense
    - Modulus: 10.9 Msi

- 01-25-18 #2
  - SS: 400 mm/s ~96% dense
  - Modulus: 11.7 Msi

- 02-01-18 #4
  - DS: 400 mm/s 100.87% dense
  - Modulus: 12.2 Msi

- 2.5%vol HHT-MWCNT 02-22-18 #3
  - SS: 650 mm/s 98.03% dense
  - Modulus: 11.2 Msi

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Comparison to requirements & wrought 6061 Al

Comparison of 5% MWCNT CNMMC & 6061 Al vs Requirements

- **Strength**: 97.50% for 5% MWCNT CNMMC, 75.14% for Threshold, 79.71% for Wrought 6061-T6 Aluminum
- **Specific Modulus**: 95.78% for 5% MWCNT CNMMC, 75.14% for Threshold, 73.84% for Wrought 6061-T6 Aluminum

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Next Steps - Aluminum

• Army phase II SBIR proposal submitted March 2018

• Porosity had a significant impact on mechanical properties, especially elongation to failure

• Address porosity through the following:
  – Adjust powder size and morphology to improve re-coating
  – Optimize build height, laser power, laser scan rate and number of laser scans

• Carbide formation and carbon nanotube thermal tear issues have been addressed

• Carbon nanotubes act as nucleation sites in the melt pool look at other aluminum alloy and metals

X-ray diffraction shows no formation of Aluminum Carbide or Aluminum Oxide
Conclusions

• Carbon nanotubes have demonstrate improve strength and stiffness in aluminum (AlSi10Mg) and 17-4 Stainless Steel
• Carbon nanotubes has been applied to strengthen & stiffen other metal systems
  – Key to success is dispersion
• More research and development is required
  – Currently at a TRL 3 / MRL 3
  – Utilized commercially purchased raw materials and AM processing equipment, Entire process is industrial scalable
  – Should Cost modeling indicates Army cost requirements can be met
6061 Aluminum
Initial 6061 Trials

Initial Design of Experiments Trial
On AM Processing Parameters

3 of 9 processing parameter sets were successful

Second batch of 6061 specimens using best available AM processing parameters

Wire brushed to remove top layer of unmelted metal powder
Copper
Initial Copper Trial

Used same DOE parameters as 6061 Al trial

Initial layers did not stick to the build plate

Subsequent layers were melted but swept aside by the re-coater blade.

Laser at max powder (95W), more laser power and additional laser scans per layers might be beneficial
Commercialization plan
Commercialization Plan

- Multiple commercial materials suppliers for raw materials
- Work with DOD services / DOD OEMs to establish “tech pull”
- Co-develop and license to AM system manufacturers and powder metal suppliers to establish sales channel

Core Technology is applicable to other Powder Metallurgy manufacturing processes such as die cast, metal injection molding.

Current Status:
TRL / MRL: 3
**Should Cost Modeling**

*"Should Cost" modeling performed on SolidWorks*

<table>
<thead>
<tr>
<th>Manufacturing Process</th>
<th>Raw Material</th>
<th>Material Cost</th>
<th>Labor &amp; Operations Cost</th>
<th>Tooling</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNC Machining</td>
<td>6061 Al-T6</td>
<td>$0.34</td>
<td>$8.54</td>
<td>$0.00</td>
<td>$8.88</td>
</tr>
<tr>
<td>Additive Manufacturing</td>
<td>2.5% MWCNT</td>
<td>$1.20</td>
<td>$2.55</td>
<td>$0.00</td>
<td>$3.75</td>
</tr>
<tr>
<td>Die Cast</td>
<td>2.5% MWCNT</td>
<td>$1.05</td>
<td>$3.40</td>
<td>$0.50</td>
<td>$4.95</td>
</tr>
</tbody>
</table>

- Use of Carbon Nanotubes not a significant cost increase
- TPOC validated, results are consistent with current production cost of sabots
- Some additional post-processing is required for AM

Machined 6061 Al does not meet performance requirements

Raw Material Cost

<table>
<thead>
<tr>
<th>Density (g/cm³)</th>
<th>$/Kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlSi10Mg Powder</td>
<td>2.68</td>
</tr>
<tr>
<td>MWCNT + Processing</td>
<td>1.5</td>
</tr>
<tr>
<td>2.5% MWCNT / AlSi10Mg</td>
<td>2.65</td>
</tr>
<tr>
<td>5% MWCNT / AlSi10Mg</td>
<td>2.62</td>
</tr>
</tbody>
</table>

* Price for laboratory quantity
Current Status / Next Steps

Current Status

• Navy STTR (17-4 SS): Passed DCAA audit, NAVAIR KO finalizing contract for phase II
• Army SBIR (aluminum): Submitted phase II proposal (3/30/18), surpassed 3 of 4 threshold requirements.

Next Steps

• Identify potential applications (DOD / commercial)
• Mix, Melt and Test
• Identify additional funding opportunities
• Look at additional metal alloys