Approaches to High Performance Conductors

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Summary

- AMO supports development of high performance conductors
  - SBIR
  - Potential NGEM solicitation
  - National Laboratory research on covetics

- Range of approaches:
  - Carbon fiber in metal
  - Powder processing
  - Extrusion processing
  - Electrodeposition
  - Melt processing

- Applications including power transmission and lightweight motors
"ACF's unique, high-performance fibers will enable our clients to dominate their marketplace"

"We make materials lighter, stronger, and more tolerant to heat, fatigue, stress, and corrosion." The photo shown left represents a block of aluminum with alpha silicon carbide/carbon fibers integrated into the metal. These unique fibers multiply the tensile strength of the aluminum 20 times!
Approaches—CVD, carbon on metal nanoparticles

- Carbon nanofibers and graphene on copper

Fig. 1 (a) Temperature dependence of the sample weight after 20 min treatment with different carbon sources resulted in the formation of (b) CNFs in the presence of acetylene and (c) a few-layered graphene in the presence of ethylene.
Approaches — Deposition on nanoparticles

- Powder compaction and deformation processing
- Hardness increase with both graphene and carbon nanofibers. . . Conductivity not reported

Fig. 4 The results of mechanical tests of Cu-3%C composite materials: (a) hardness (HB), (b) elongation (bending test).
Approaches—CVD of aluminum on carbon nanotubes

- Proof of concept, 10 micron thick Al on nanotube array
- Bulk properties not measured, no wire produced
Approaches — Ball milling Al powder plus CNT and nanodiamond

- Kwon; ball milling then hot pressing
- Improved strength, slight conductivity increase
Approaches — Copper powder hot extruded with CNT

- Taysir Nayfeh, Cleveland State U.
- Nanotubes aligned
- Up to 2X conductivity increase reported

FIG. 10
Approaches — Electrodeposition

- Quanfang Chen, U. Central Florida
- Co-deposition of nanotubes and copper
- 1.8X thermal conductivity increase reported
- Electrical conductivity 1.4X increase

Table 1 — Measured electrical resistivity of samples produced by Electrolytic Co-Deposition [4]

<table>
<thead>
<tr>
<th>Material Deposited</th>
<th>Electrical Resistivity (μΩcm)</th>
<th>Electrical Conductivity (% IACS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/SWCNT composite</td>
<td>1.22</td>
<td>141</td>
</tr>
<tr>
<td>Pure copper</td>
<td>1.72</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 4: Schematic drawing showing the electrolytic cell reported by Chen [4]

Figure 5 - Other mechanical and physical properties reported by Chen [4]

a) Strength and ductility
b) Coefficient of thermal expansion
Covetic Process

- Melt the metal, stir in carbon powder, apply voltage
- Works with a wide range of metals (Al, Cu, Au, Ag, Zn, Sn, Pb, and—they claim—Fe);
- Conventional furnaces, electrodes, electromagnetic or gas stirring, infrastructure readily available
- Can remelt, dilute, alloy
- Particularly promising because of scalability
Background

- GDC Industries, LLC
- Proprietary process
- Conversion occurs in melt
  - Al, Cu, Au, Ag, Zn, Sn, Pb, Fe
  - Carbon powder → nanoscale C
  - Converted under high voltage
- Stable after conversion
- Process development is ongoing
- Producing research quantities now, ~100 lbs Al, ~300 lbs Cu per heat
Increased melting point (DTA)

AA6061 solidus: 582°C → 619°C
Copper: 1085°C → 1105°C
Thermal conductivity: Anisotropic and rate-dependent

As-extruded Cu Covetic (0.057 wt % C)

- Steady state longitudinal → increased with nanocarbon
- Steady state transverse → decreased with nanocarbon
- Transient longitudinal → 50% increase with nanocarbon
- Consistent with independent results (Khalid Lafdi, U. Dayton)
Electrical Conductivity of Al increased

- High conductivities seem possible
- Causes of variability require further study

<table>
<thead>
<tr>
<th>Type of Material</th>
<th>Condition</th>
<th>%IACS</th>
<th>Test Lab</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% C 6061</td>
<td>Conventional 6061, T6¹</td>
<td>47.4</td>
<td>USNA</td>
</tr>
<tr>
<td>3% C 6061</td>
<td>Covetic T6 ground</td>
<td>47.8</td>
<td>USNA</td>
</tr>
<tr>
<td>3% C 6061</td>
<td>Covetic T6 EDM</td>
<td>56.1</td>
<td>USNA</td>
</tr>
<tr>
<td>3% C 6061</td>
<td>Covetic As-Extruded</td>
<td>67.3</td>
<td>USNA</td>
</tr>
<tr>
<td>3% C 6061</td>
<td>Covetic As-Extruded</td>
<td>54</td>
<td>U. Md</td>
</tr>
<tr>
<td>EC-1350</td>
<td>Electrical grade Al</td>
<td>61.8</td>
<td>Literature</td>
</tr>
</tbody>
</table>

High conductivities seem possible. Causes of variability require further study.
### Example Application

<table>
<thead>
<tr>
<th>Example Application</th>
<th>Benefit</th>
</tr>
</thead>
<tbody>
<tr>
<td>High voltage power transmission cable</td>
<td>Higher strength, 40% higher conductivity → $10B annual savings for US power grid</td>
</tr>
<tr>
<td>Substitution of nanocarbon aluminum for copper in electrical wiring, buses, and motor windings</td>
<td>Weight reduction, improved efficiency, especially on aircraft, but on transportation systems of all types. Cu 50 lbs/car → 20; 737 bus bar 600lbs.</td>
</tr>
<tr>
<td>Thermal management in microelectronics</td>
<td>Higher currents, faster switching at elevated temps</td>
</tr>
<tr>
<td>Heat exchangers</td>
<td>Higher efficiency, $12B annual market</td>
</tr>
<tr>
<td>Copper motor brushes</td>
<td>Better wear resistance, greater efficiency</td>
</tr>
<tr>
<td>Electrical contacts and switches</td>
<td>Cooler operation, possibly increased wear resistance</td>
</tr>
<tr>
<td>Transparent conductor thin films for electrodes in photovoltaics</td>
<td>Higher conductivity than conventional metal films, easier deposition than graphene</td>
</tr>
<tr>
<td>Nuclear fuel rods</td>
<td>Reduce thermal gradients to improve service performance (less cracking)</td>
</tr>
<tr>
<td>Heat pipes</td>
<td>Improved thermal uniformity along length</td>
</tr>
<tr>
<td>Thermal insulators</td>
<td>Improved through-thickness thermal resistance</td>
</tr>
<tr>
<td>Fuel cell and supercapacitor electrodes</td>
<td>Higher efficiency electrodes (greater conductivity through oxide layers)</td>
</tr>
</tbody>
</table>

**Open questions:**
- How much of the periodic table?
- Can we make a high conductivity steel?
- Ceramics? Intermetallics?
- Thin films? Oxide layers? Oxides?
- Is the electrical conductivity directional?
Density remains unusually high
Naval Academy, CAPT Lloyd Brown

3.8 wt % Cu Covetic

- Compressed 50% in Gleeble to consolidate porosity
- Ultrapycnometer 1000
- Before compression = 8.7894 g/cm³
- After compression = 8.8777 g/cm³
- Compared with $\rho_{\text{Cu}} = 8.94$ g/cm³
- Only 0.7% reduction in density with 3.8 wt % C vs. 10% expected
Carbon Atoms in Between Metal Atoms

Lourdes Salamanca-Riba, U. Maryland College Park
SEM — Cu covetic, as-cast, 3.8% C

- 5 -200 nm diameter particles
- Seem to occur in connected clusters
- Remain intact upon remelting and resolidification

Metallographically as-polished surface

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>03.78</td>
<td>16.65</td>
</tr>
<tr>
<td>O K</td>
<td>01.29</td>
<td>04.25</td>
</tr>
<tr>
<td>FeK</td>
<td>00.32</td>
<td>00.30</td>
</tr>
<tr>
<td>CuK</td>
<td>94.61</td>
<td>78.79</td>
</tr>
</tbody>
</table>
SEM – AA6061 as-extruded, 2.7% nanoC
Lourdes Salamanca-Riba

Tensile fracture surface

Lourdes Salamanca-Riba, U. Maryland College Park

5.0kV 17.4mm x30.0k 1.00um
• Ribbon has high C and O content.
• Particles have Mg, Si and Cu.
EELS: Similar to spectrum of SWCNT in Ag, more like amorphous C in Cu and AA6061


Lourdes Salamanca-Riba, U. Maryland College Park
In bulk, Covetic virtually identical to pure Cu

XPS:

- Overall metallic character confirmed
- No difference in electron binding energies
- No evidence for carbide formation

Foil: 0% C
Covetic: 3.5 wt% C
Evidence of sp2 Carbon in Covetics

- Ag covetic shows clear D and G peaks at ~1,300 and 1,600 cm\(^{-1}\) in all 20 points of the sample.
- Ag metal shows weak signal in this region in all 20 points.
- Good match to single wall carbon nanohorn and to damaged graphene.

Melbs Lemieux
DFT: Graphene in Ag Covetic

• Wider graphene ribbons have flatter surfaces.
• Bonding between Ag and C occurs at edges of ribbons.

Maija Kukla,
University of Maryland. (DARPA funding)
Only under-coordinated carbon atoms positioned around vacancy and/or at the edges of graphene ribbons attach to Ag atoms.

Analysis indicates that C-Ag bond is a typical covalent bond (common electronic orbitals formation) similar to C-H bonds in hydrocarbons.
Carbon Atoms in Between Metal Atoms

1 nm

Lourdes Salamanca-Riba, U. Maryland College Park
Open Questions on Fine Structure
(and why we’re so keen on the ANL tomography)

➢ What is the proportion of carbon disks vs. ribbons? What is the 3D structure of the disks?

➢ What is the spatial distribution of the disks and ribbons?

➢ Do the ribbons form a network to provide conductive pathways?

➢ What is the nature of the interface between metal and nanocarbon phases? Is the registration edges-only or whole surface? If it’s the whole surface, how do the phases accommodate this while retaining their fundamental structures? e.g. first shell distance maintained for metal atoms and graphene-like structure for the nanocarbon

➢ What is the role of oxygen, and how is its distribution related to that of the nanocarbon?
Analytical Methods for C Determination

- LECO and GDMS do not seem to detect nanoscale C
- SEM-EDS and XPS best
- DC-PES may be better with higher carbon levels and provide better averaging with larger samples
- Standardization work needed
- Reference materials needed

<table>
<thead>
<tr>
<th>Method</th>
<th>Result (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LECO</td>
<td>0.0016</td>
</tr>
<tr>
<td>DC-PES*</td>
<td>0.56</td>
</tr>
<tr>
<td>GDMS</td>
<td>0.0060</td>
</tr>
<tr>
<td>XPS</td>
<td>0.13, 2.1</td>
</tr>
</tbody>
</table>

* Direct Current Plasma Emission Spectroscopy ASTM E1097 to detect Cu
AA5083
Remelting and Strand Casting

Induction furnace at Surface Treatment Technologies
Remelting and Strand Casting
Remelting and Strand Casting
Forging
Forging
Forging
Remelting and Casting
Friction Stir Welding
Extrusion
Extrusion
Hot Rolled
Porosity in Copper Covetic

Significant amount of porosity present, with severity increasing as radius decreases. Percent of porosity estimated at 18.9%.
Centrifugally-Cast Microstructure

C11000

Covetic
Surface Effects

Depth Profile Concentrations for Cu Covetic (# 021, Polished and Un-Polished Surfaces)
Mechanical Properties
Covetic YS 30% higher as-extruded 400F

Engineering Stress (psi) vs. Engineering Strain (%)

0% nanoC AA6061

3% nanoC AA6061

y = 7.650808731E+04x - 2.706069218E+00

y = 8.980792711E+04x + 8.054999174E+01
T6 condition:
No difference in tensile curves

![Graph showing tensile curves for 0% and 3% nanoC AA6061 with no significant difference.](image)
One cylindrical specimen (H49, extrusion number 14422, heat treated to T6 condition) was provided by NSWC Carderock.

Specimen Dimensions: 1.8125” long, 0.523” diameter
Prior to H49 testing, resistivity was determined for a specimen of 6061 – T6. Resistivity was then converted to %IACS. The specimen was “off the shelf” and had a stock finish.

- 6061 – T6 %IACS = 48.44%
- Expected value: 40 – 45% (MATWEB)
- Value higher than expected, no explanation for variation.
Specimen Preparation

- H49 specimen was turned on lathe, after having ends cut clean, to a mirror finish.
- Conductivity measurement: 55.06%
- This value is higher than previous USNA measurements of conductivity for H49 in T6 condition. [47.81% -- Fall of 2010]
- The Fall 2010 measurement was taken with oxide still present on extrusion, but the specimen had been hand polished using emery cloth.
6061 Cold Reduction (Naval Academy)

Test Matrix

• H49 specimen cut into rectangular shape from original extrusion

• Conductivity then measured for the following nominal % RA values
  - 0%, 2.5%, 5%, 7.5%, 10 %
  - An attempt was made to roll to higher value, but specimen curved.
  - Rockwell B hardness measured at five locations after each rolling, then averaged.
Conductivity Comments

• Specimen was fabricated using EDM technique.

• Prior to rolling, conductivity was 56.11 %IACS, which was slightly higher than previous measurement in turned condition (55.06 %IACS), and significantly higher than in as extruded condition (47.81 %IACS).
6061 Cold Reduction (Naval Academy)

Conductivity vs %RA

Percent Reduction in Area vs. Conductivity

\[ y = -0.2669x + 0.5613 \]

\[ R^2 = 0.9472 \]
Conductivity vs Hardness

$y = -0.0029x + 0.718$

$R^2 = 0.968$
6061 Cold Reduction (Naval Academy)

At the Conclusion of Testing
Current Efforts at DOE

- Argonne (Balachandran):
  - Characterization of nanocarbon morphology, size, distribution, and interface
  - Thermal and electrical conductivity
  - Analytical methods

- ORNL (Feng): development of rapid synthesis methods, study process of conversion of carbon to tenacious nanocarbon

- NETL Albany (Jablonski): Replicate process for kilogram scale heats, develop methods to improve uniformity of carbon
Summary

- Covetic nanomaterials have potential to provide improved performance for electrical and thermal conductivity, amenable to scalable high throughput processing

- Covetics can be processed using many traditional metals processing methods for melting, casting, deformation, and heat treatment

- There are unique challenges:
  - Combination of analytic methods needed to measure C
  - High variability in carbon distribution
  - Porosity in castings
  - Variability in property measurements
  - Surface finish effects
Spare slides
Good correspondence: XPS and EDS

Copper covetic

<table>
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<tr>
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</tr>
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<tbody>
<tr>
<td>Energy Dispersive Spectroscopy</td>
<td>3.8</td>
</tr>
<tr>
<td>X-Ray Photoelectron Spectroscopy</td>
<td>3.5</td>
</tr>
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Composition vs. Sputtering Time

- Atomic % Cu
- Atomic % C
- Atomic % O
In bulk, Covetic virtually identical to pure Cu

EXAFS/Fourier transforms:
- Overall metallic character confirmed
- FCC structure
- Same structural parameters → no significant difference between atomic spacing of Cu atoms
- No evidence for a solid solution
- No evidence for carbon-Cu bonds except possibly at the interface region
Effect of carbon level on 7075 strength
Third Millennium Metals Rolling

![Graph showing the effect of carbon level on 7075 strength.](image-url)

- **Strength (MPa)**
- **Weight % C**
- **Yield Strength**
- **Tensile Strength**
Work Hardening of Cu: No difference
Cold Rolling at 0.21% C
Applications

• Anisotropic, high thermal conductivity, high strength Cu/Cu alloy
  - Heat exchangers
  - Microelectronics
  - Electrodes and electrical contacts

• High electrical conductivity, high strength aluminum alloy
  - High tension lines
  - Wiring
  - Electrodes and contacts

• Currently evaluating AA5083 covetic for naval structural applications
XPS Binding Energies for Graphene

C1s spectrum of graphene oxide

- C-O
- sp³ bonding
- C=O

C1s spectrum of graphene

- sp² bonding
- Plasmon loss features
- C=O