Approaches to High Performance Conductors

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Next Generation Electric Machines Workshop
NIST, Gaithersburg, MD

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Summary

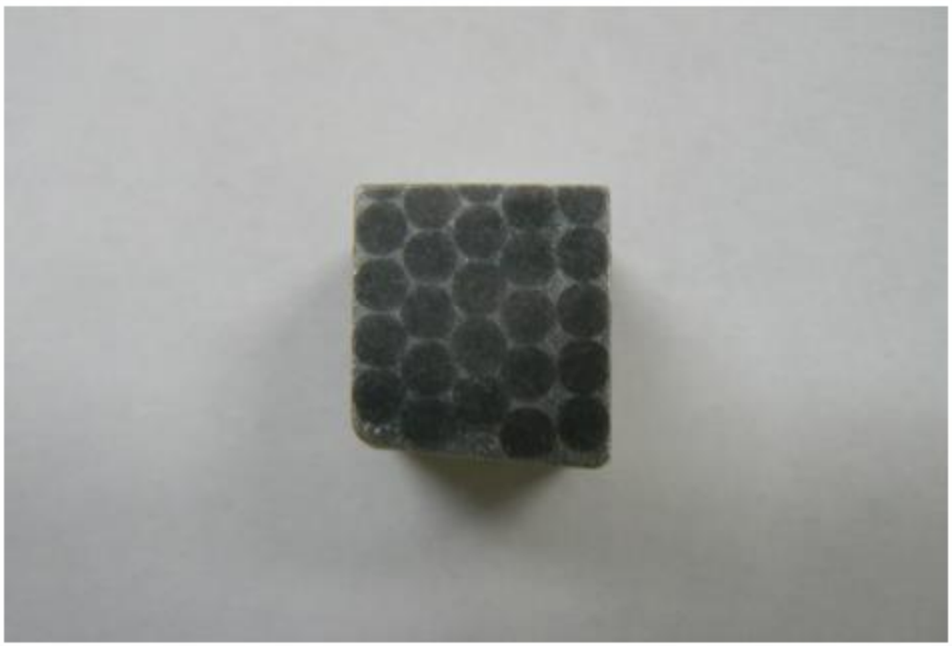
- AMO supports development of high performance conductors
  - SBIR
  - Potential NGEM solicitation
  - National Laboratory research on covetics
- Range of approaches:
  - Carbon fiber in metal
  - Powder processing
  - Extrusion processing
  - Electrodeposition
  - Melt processing
- Applications including power transmission and lightweight motors

Approaches – ACF

ACF

ADVANCED CERAMIC FIBERS, LLC
TRANSFORMING THE REINFORCED MATERIALS MARKETPLACE

HOME PRODUCT INFORMATION MARKET APPLICATIONS TECHNICAL REPORTS NEWS/UPDATES CONTACT US



"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

- Koltsova, et al., Journal of Materials Science and Engineering B 2 (4) (2012) 240-246
- Carbon nanofibers and graphene on copper

242 New Hybrid Copper Composite Materials Based on Carbon Nanostructures

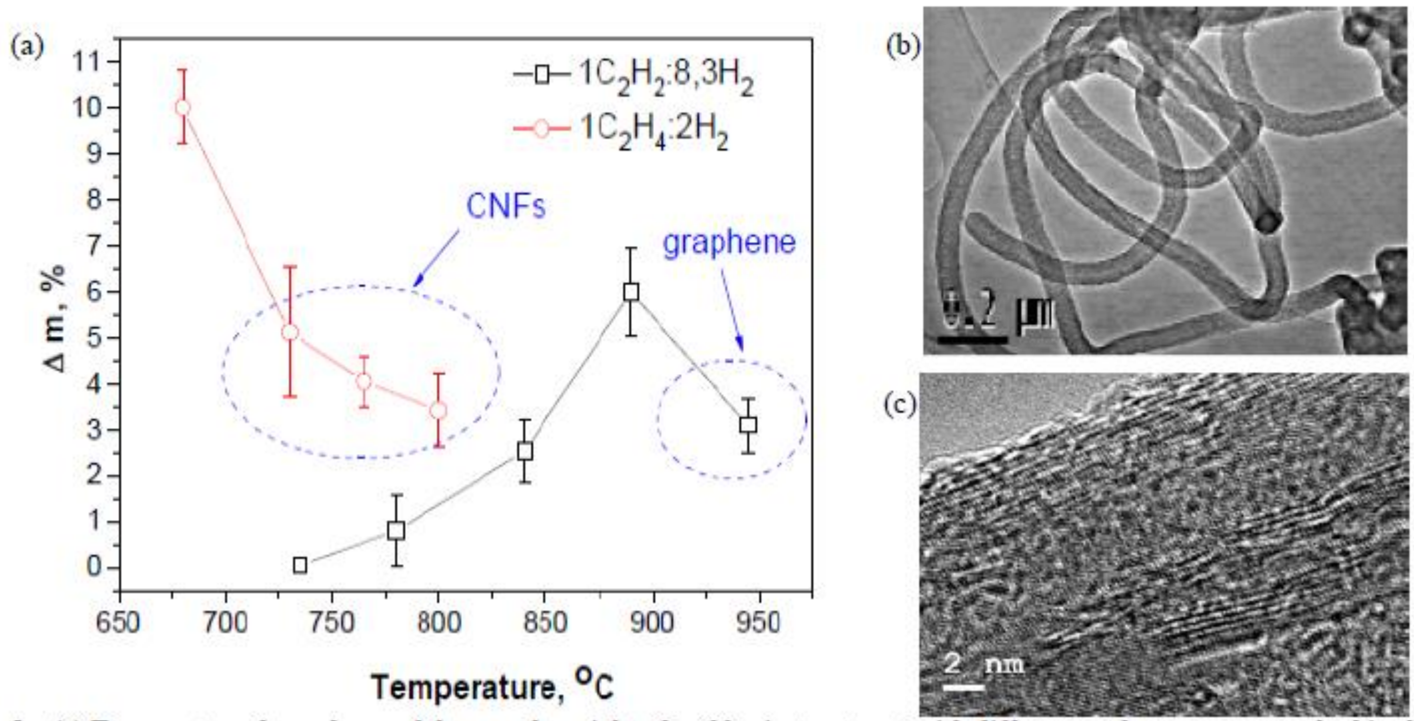


Fig. 1 (a) Temperature dependence of the sample weight after 20 min treatment with different carbon sources resulted in the formation of (b) CNFs in the presence of acetylene and (c) a few-layered graphene in the presence of ethylene.

Approaches – Deposition on nanoparticles

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

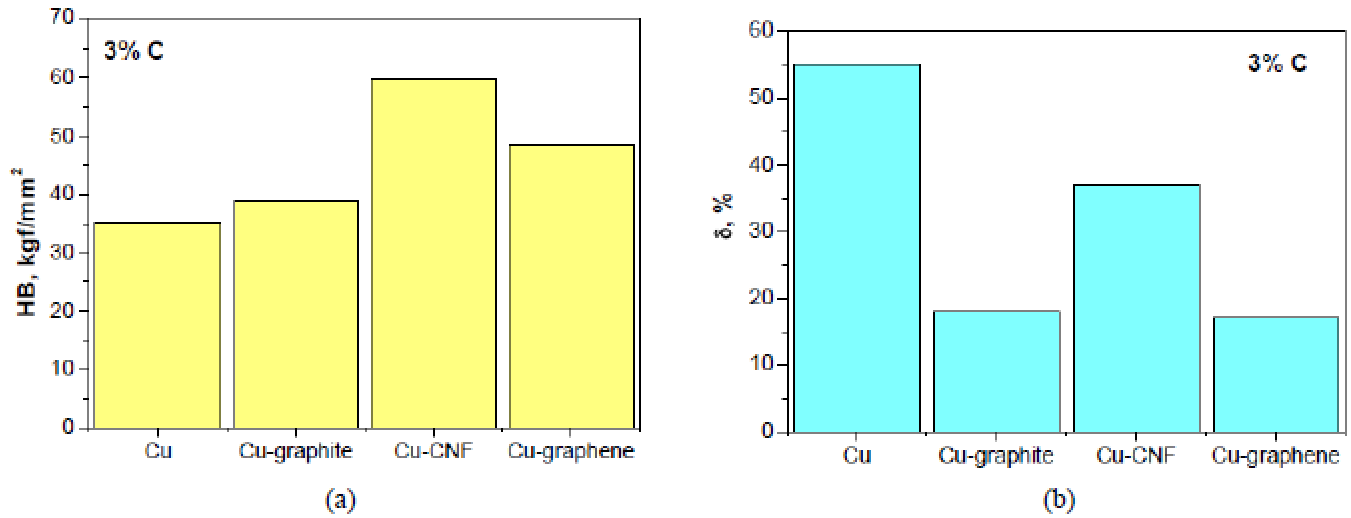


Fig. 4 The results of mechanical tests of Cu-3%C composite materials: (a) hardness (HB), (b) elongation (bending test).

Approaches—CVD of aluminum on carbon nanotubes

- Proof of concept, 10 micron thick Al on nanotube array
- Bulk properties not measured, no wire produced

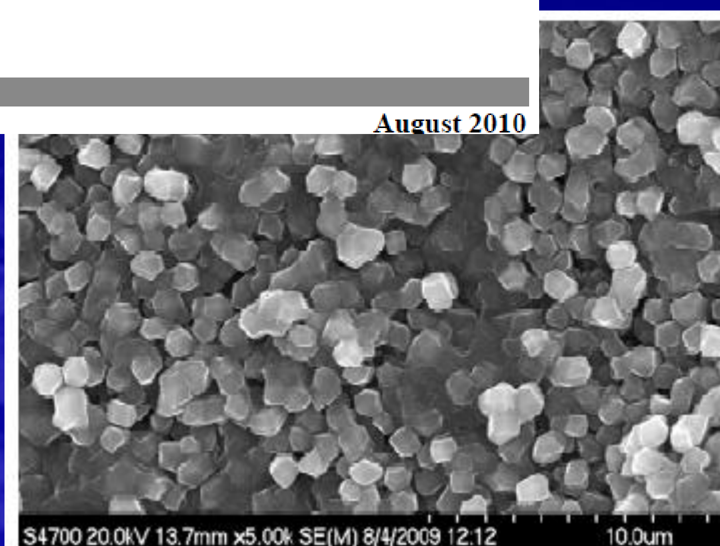
ARMY RESEARCH LABORATORY

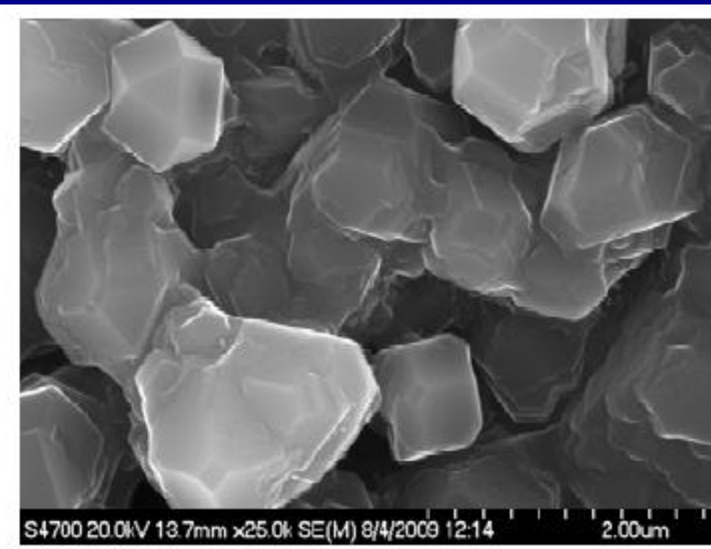
ARL

Carbon Nanotube Aluminum Matrix Composites

by Brent J. Carey, Jerome T. Tzeng, and Shashi Karna

ARL-TR-5252 August 2010





Approaches – Ball milling Al powder plus CNT and nanodiamond

- Kwon; ball milling then hot pressing
- Improved strength, slight conductivity increase

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journal homepage: www.elsevier.com/locate/msea

Mechanical properties of nanodiamond and multi-walled carbon nanotubes dual-reinforced aluminum matrix composite materials

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[a] Department of Materials System Engineering, Pukyong National University, 365 Shinseonro, Nam-gu, 608-739 Busan, Republic of Korea
[b] Empa, Swiss Federal Laboratories for Materials Science and Technology, Advanced Materials Processing, Feuerwerkerstrasse 39, CH-3602 Thun, Switzerland

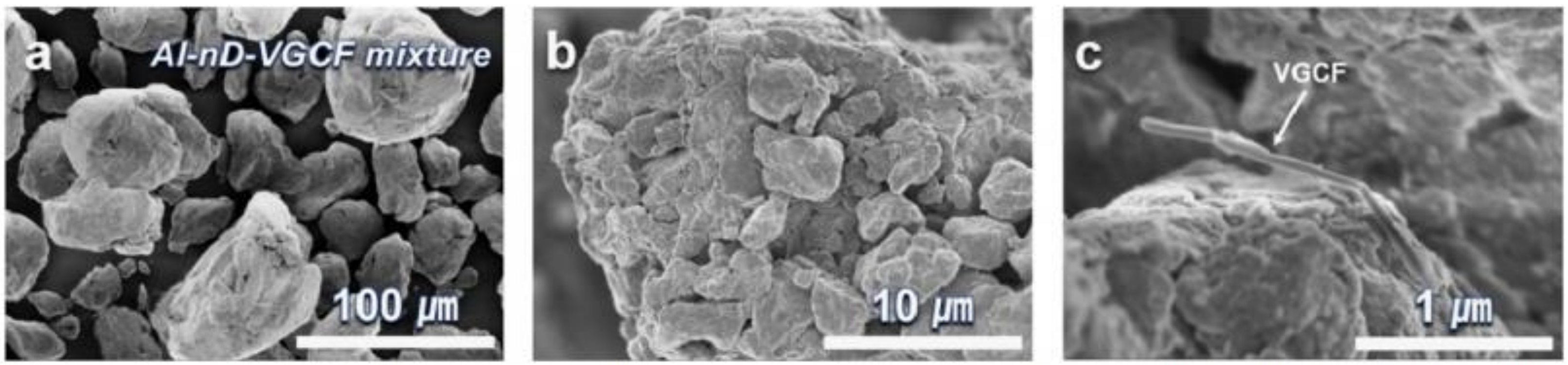


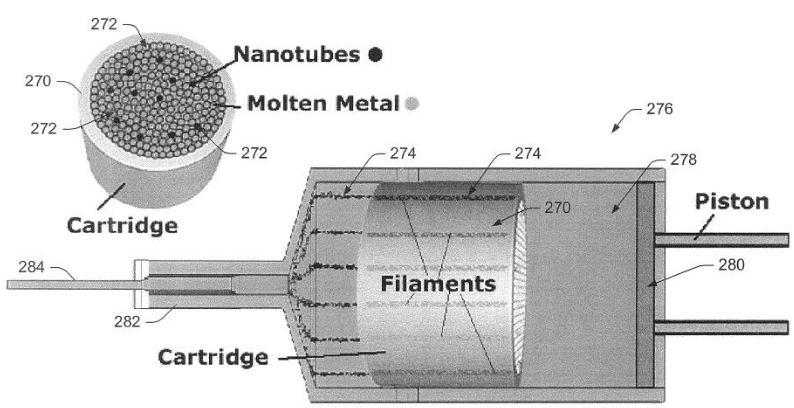
Fig. 2. FE-SEM micrographs of (a and b) pure Al–1 vol%nD–1 vol%VGCF composite powders after ball milling process. (c) High magnified image of a single VGCF in the composite powders.

Table 1
Some properties of the hot-pressed pure Al and the single and dual nanoparticle-reinforced composite materials.

Samples	Density (g/cm^3) ± 0.2%	Hardness (HV10)	Flexural strength (MPa)	0.2% offset Yield Strength (MPa)	Deflection (mm) ± 0.08	Crystallite size (nm) ± 10%	Lattice strain (%) ± 10%
Pure Al Bulk	2.70 (100%)	27 ± 2	-	70 ± 1.5	1.50 (Stop)	240	0.08
Al–1 vol%nD composite	2.689 (99.3%)	109 ± 1	391 ± 5	160 ± 2.3	0.47	105	0.14
Al–1 vol%VGCF composite	2.693 (100%)	97 ± 1	550 ± 7	315 ± 3.5	1.50 (Stop)	127	0.13
Al–1 vol%nD–1 vol%VGCF composite	2.693 (99.4%)	127 ± 2	759 ± 12	Prime: 150 ± 2.1 Second: 302 ± 3.2 Third: 600 ± 8.2	1.40	Powder: 48 Bulk: 78	Powder: 0.27 Bulk: 0.18

Approaches—Copper powder hot extruded with CNT

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



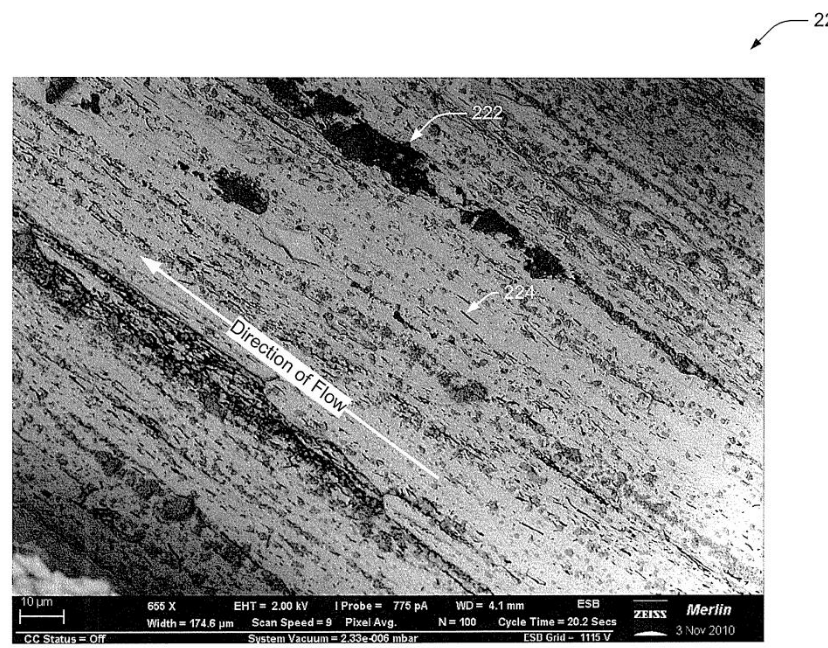


FIG. 10

Approaches – Electrodeposition

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

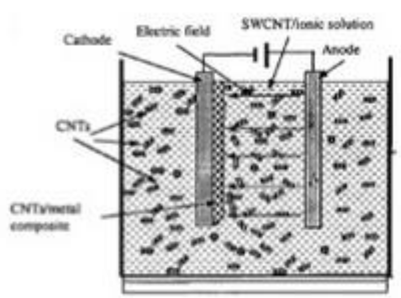


Figure 4: Schematic drawing showing the electrolytic cell reported by Chen [4]

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

Material Deposited	Electrical Resistivity (μΩcm)	Electrical Conductivity (% IACS)
Cu/SWCNT composite	1.22	141
Pure copper	1.72	100

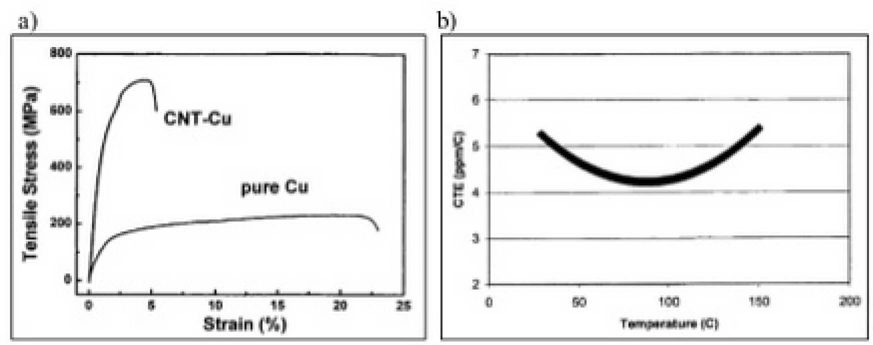


Figure 5 - Other mechanical and physical properties reported by Chen [4]
a) Strength and ductility
b) Coefficient of thermal expansion

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

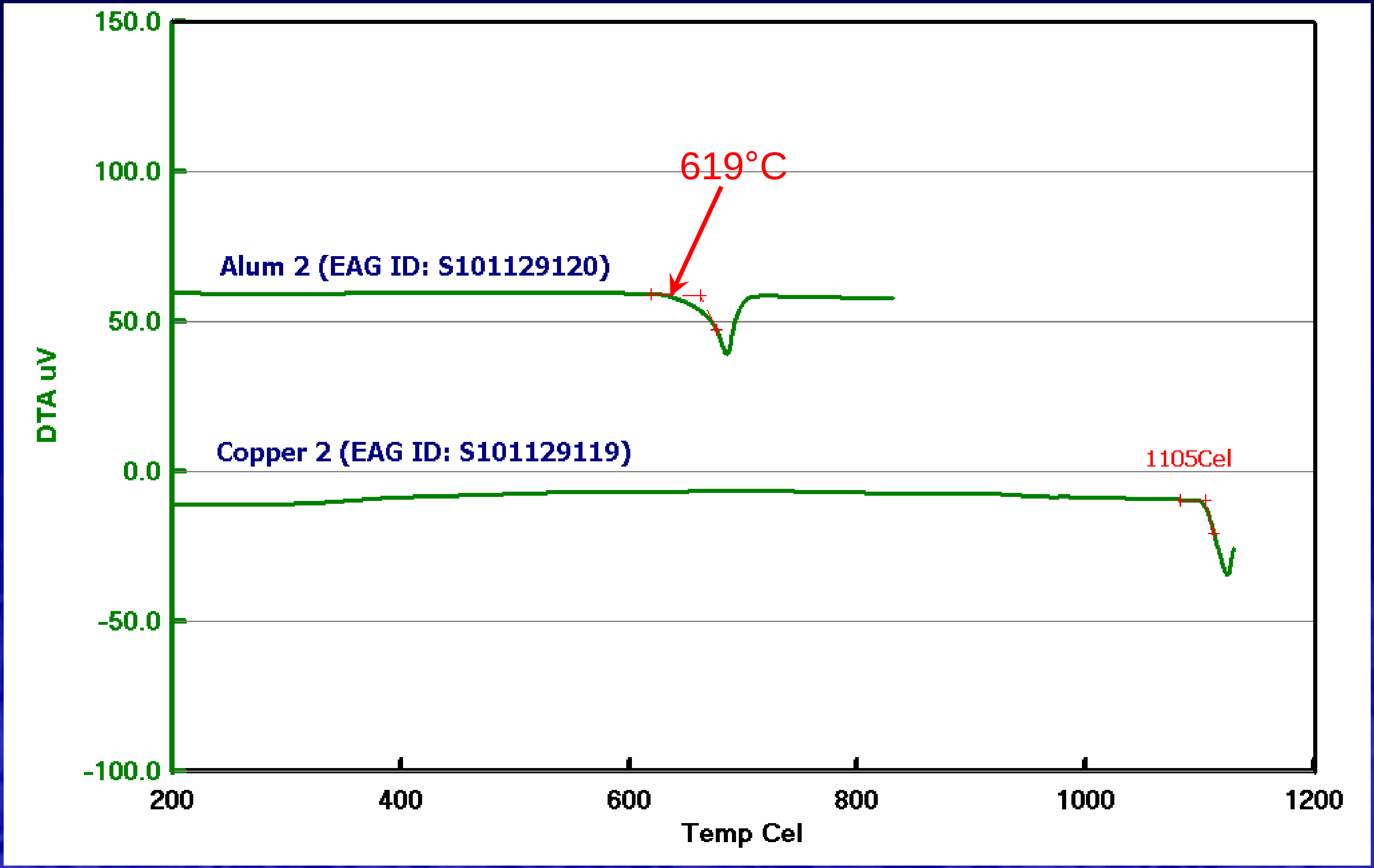
Background

- 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

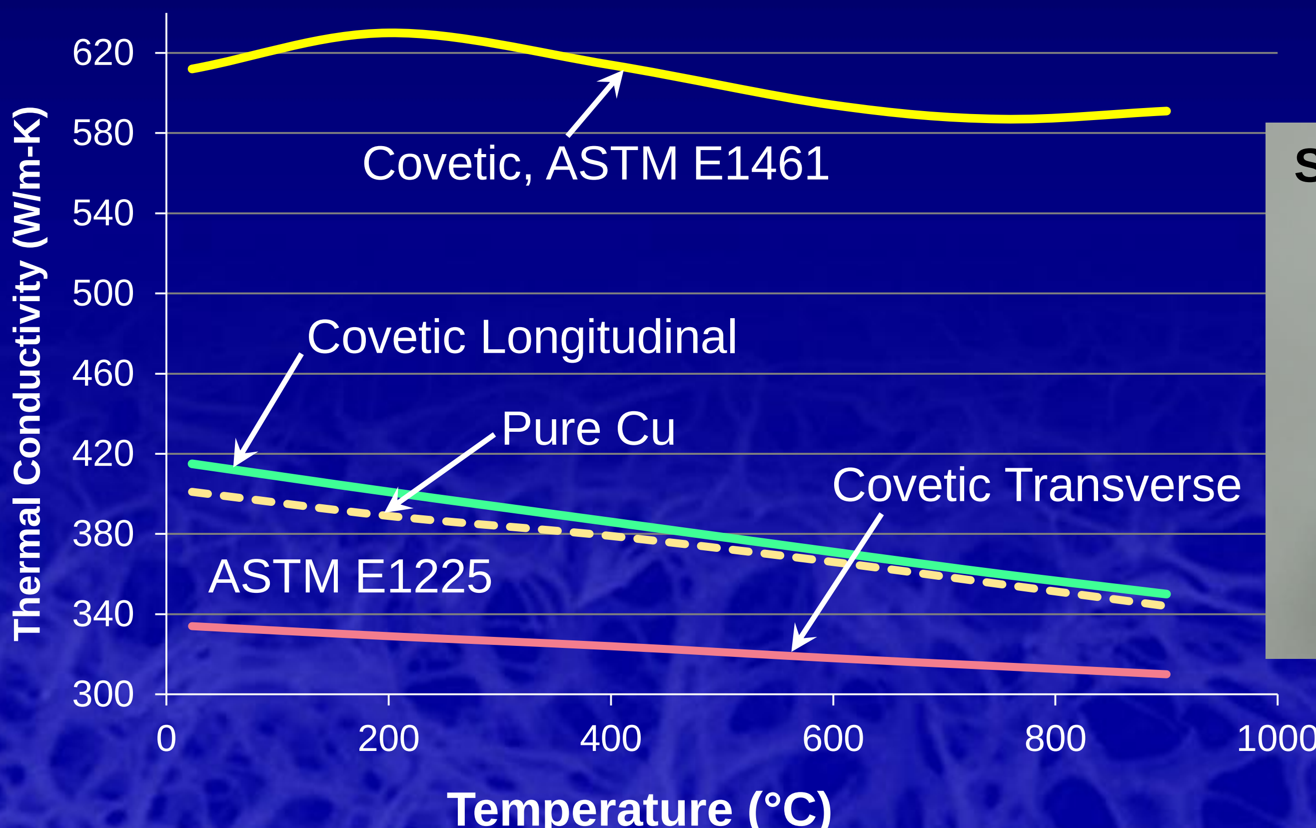
Copper: 1085°C → 1105°C



Thermal conductivity: Anisotropic and rate-dependent

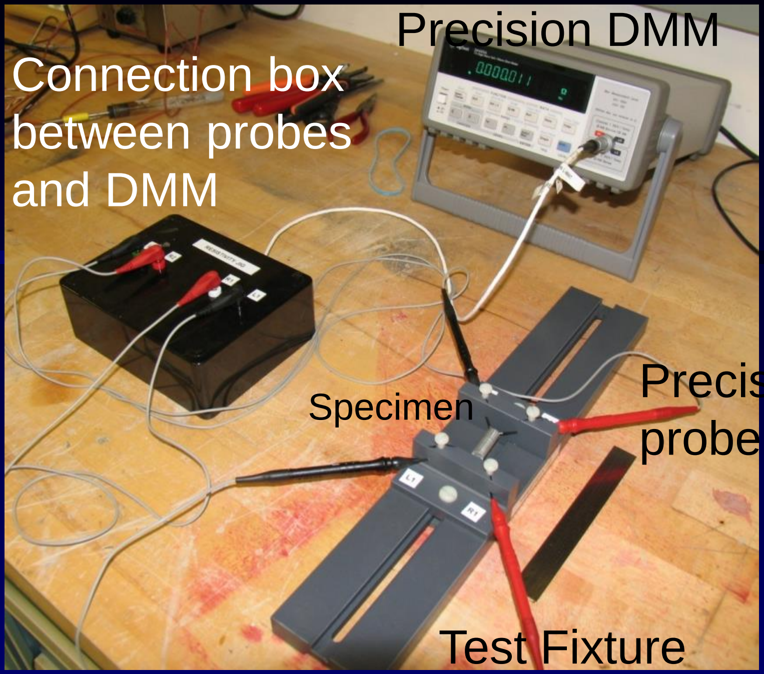
As-extruded Cu Covetic (0.057 wt % C)

- 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

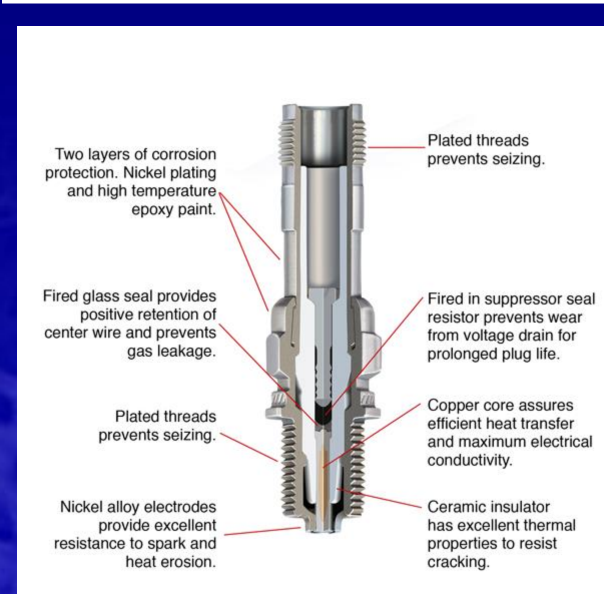
- High conductivities seem possible
- Causes of variability require further study



Type of Material	Condition	%IACS	Test Lab
0%C 6061	Conventional 6061, T6[1]	47.4	USNA
3%C 6061	Covetic T6 ground	47.8	USNA
3%C 6061	Covetic T6 EDM	56.1	USNA
3%C 6061	Covetic As-Extruded	67.3	USNA
3%C 6061	Covetic As-Extruded	54	U. Md
EC-1350	Electrical grade Al	61.8	**Literature**

Broad, Significant Impact

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

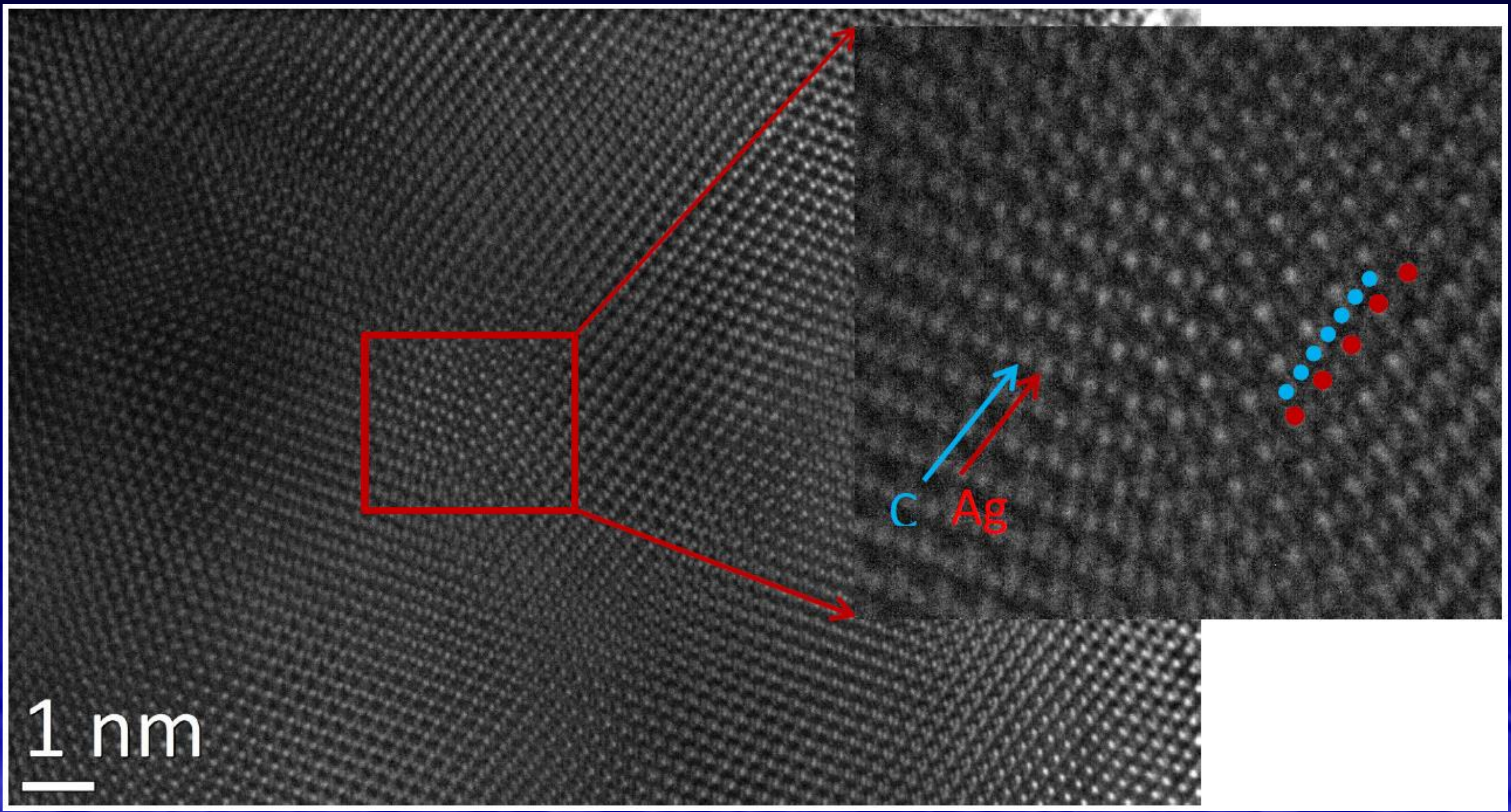


Density remains unusually high
Naval Academy, CAPT Lloyd Brown

3.8 wt % Cu Covetic

- Compressed 50% in Gleeble to consolidate porosity
- Ultrapycnometer 1000
- Before compression = 8.7894 g/cm^3
- After compression = 8.8777 g/cm^3
- Compared with ρ_{Cu} = 8.94 g/cm^3
- Only 0.7% reduction in density with 3.8 wt % C vs. 10% expected

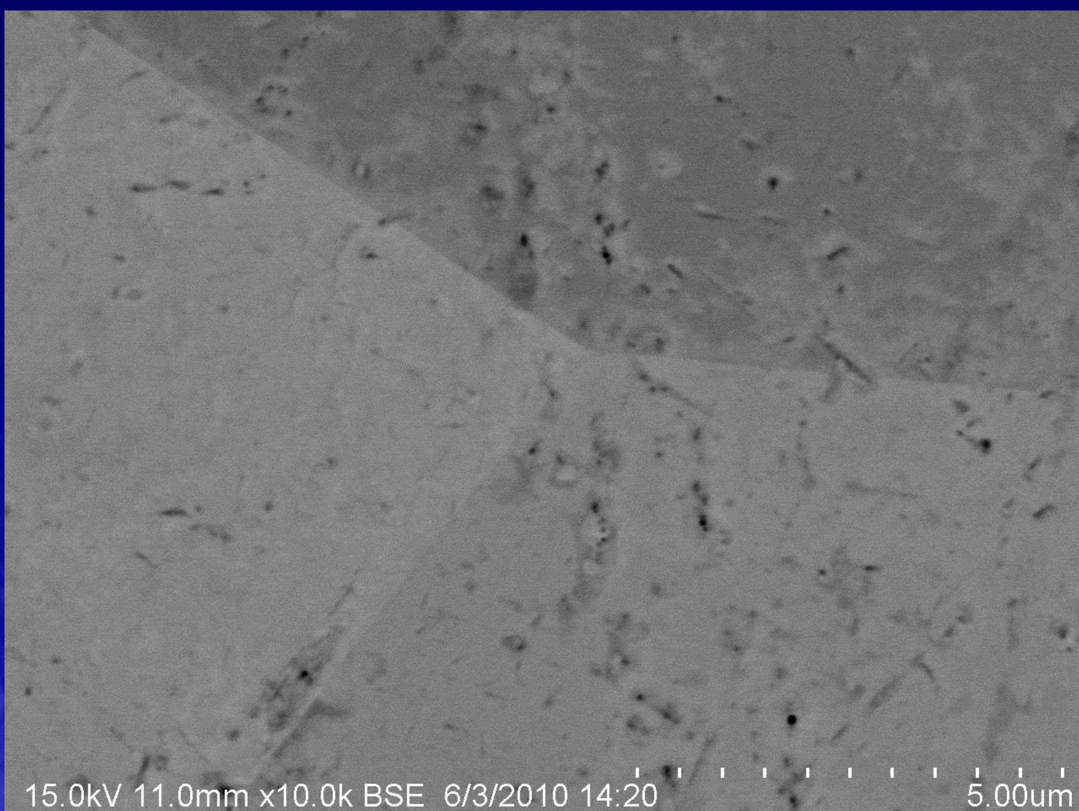
Carbon Atoms in Between Metal Atoms



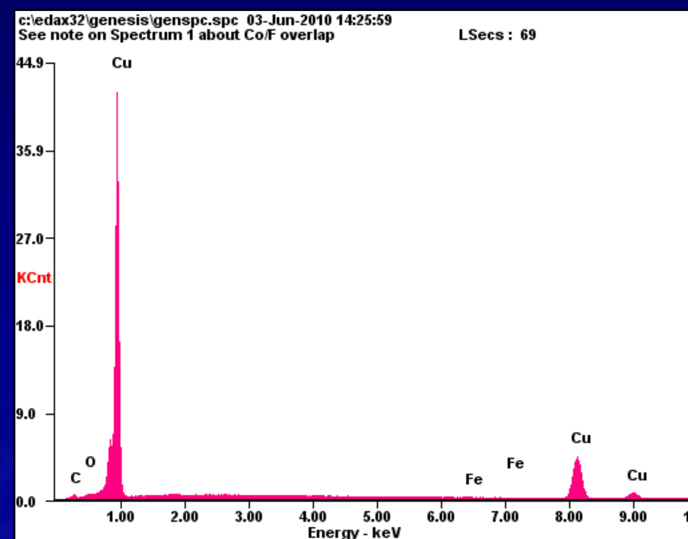
Lourdes Salamanca-Riba, U. Maryland College Park

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

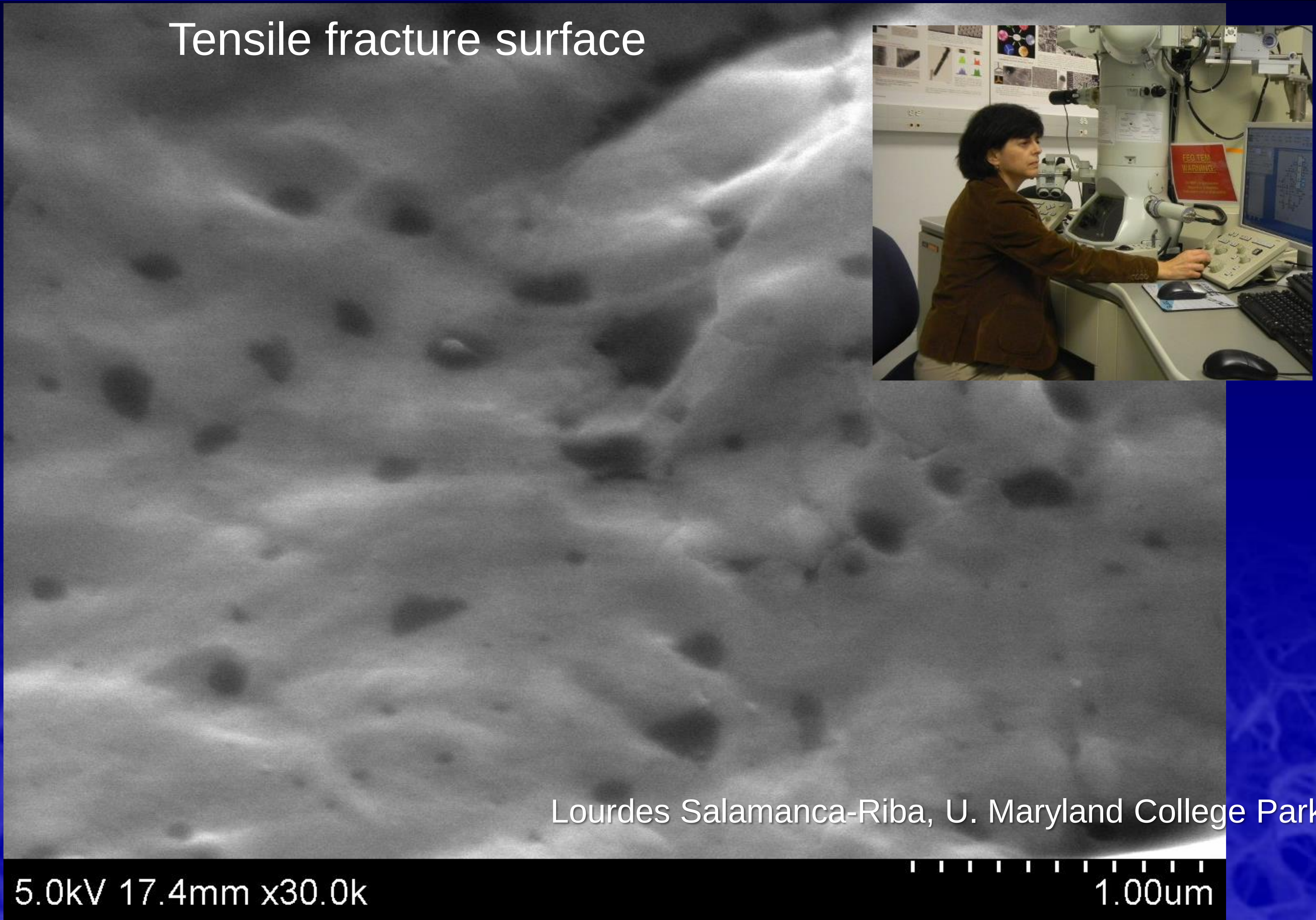


Metallographically as-polished surface

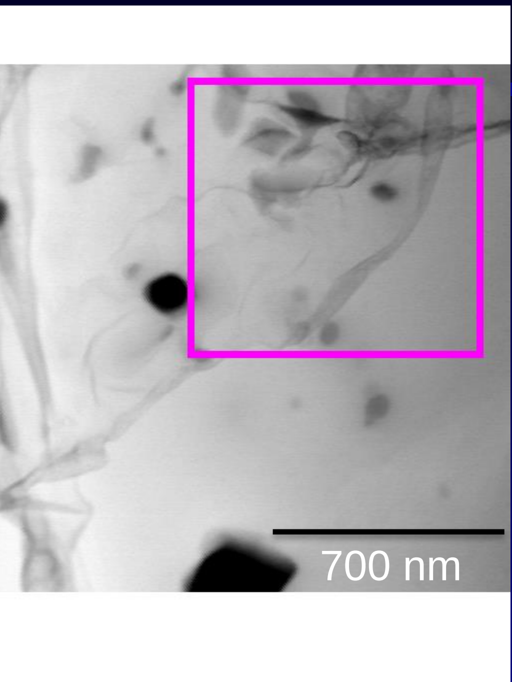


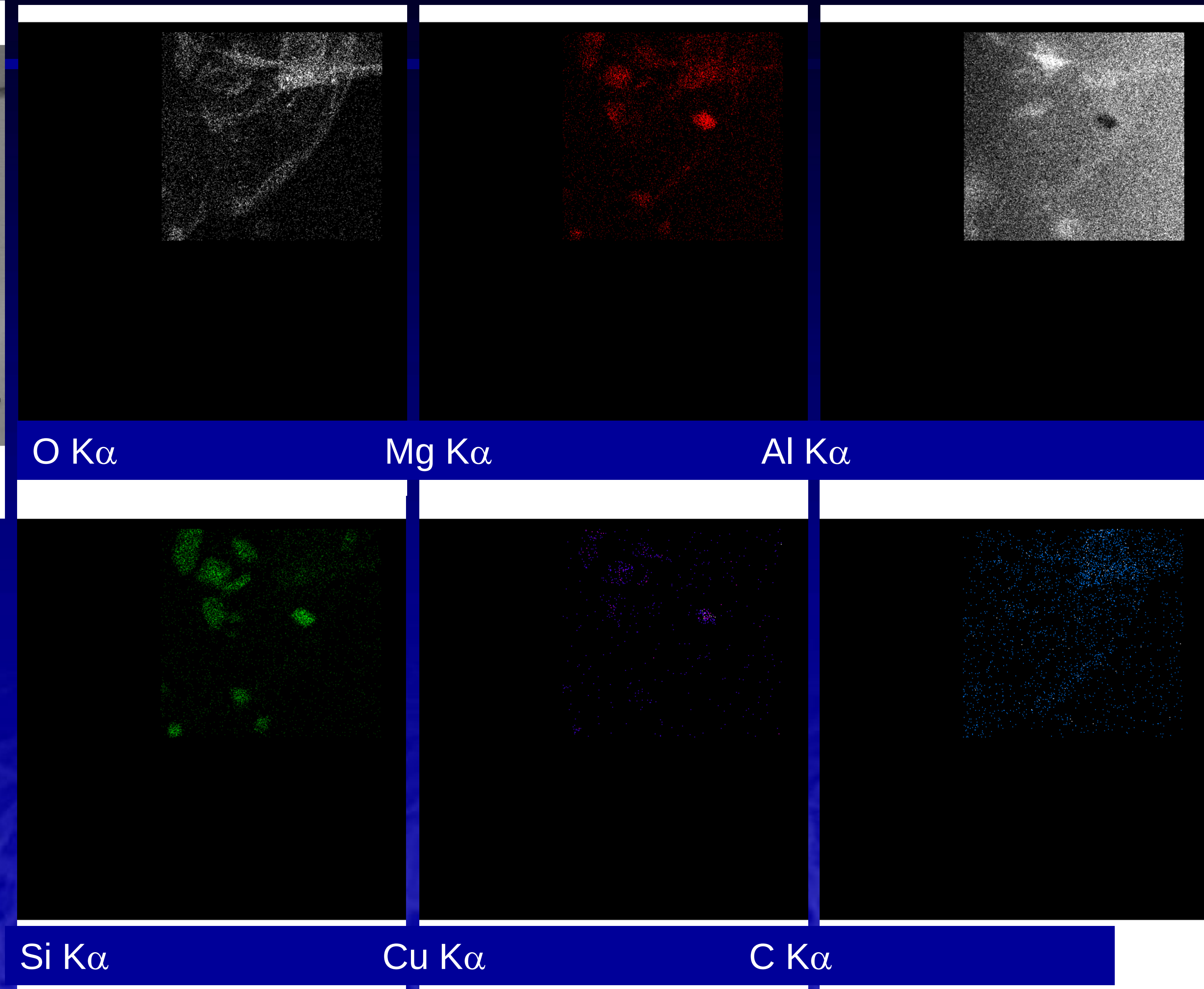
Element	Wt %	At %
C K	03.78	16.65
O K	01.29	04.25
FeK	00.32	00.30
CuK	94.61	78.79

SEM – AA6061 as-extruded, 2.7% nanoC Lourdes Salamanca-Riba



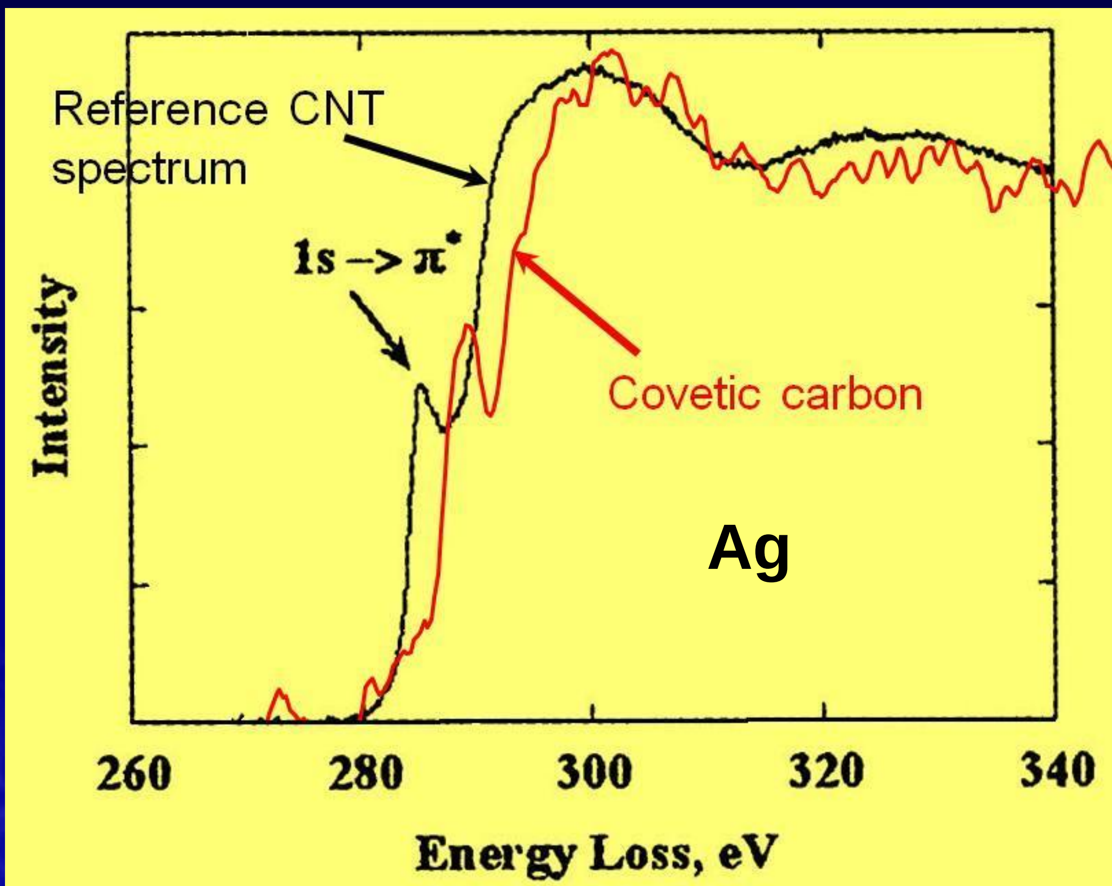
EDS Map of Ribbon in Al 6061 cv 3%

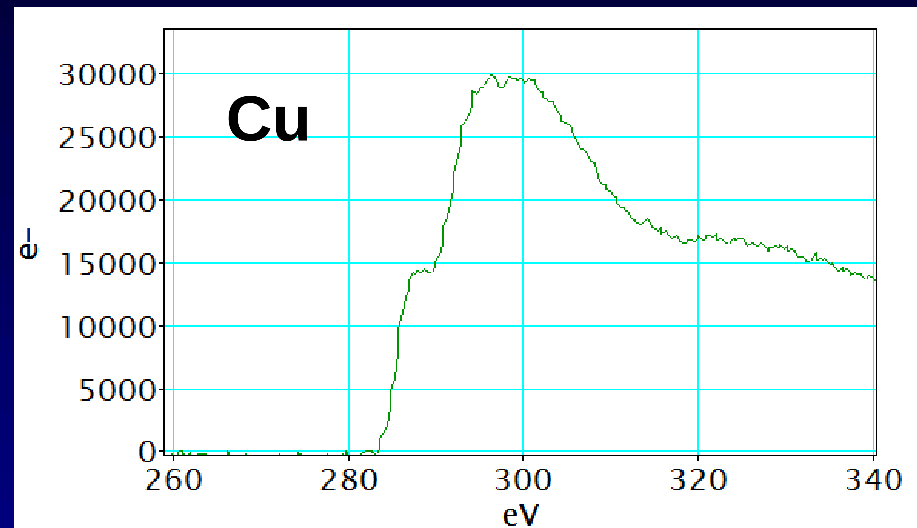


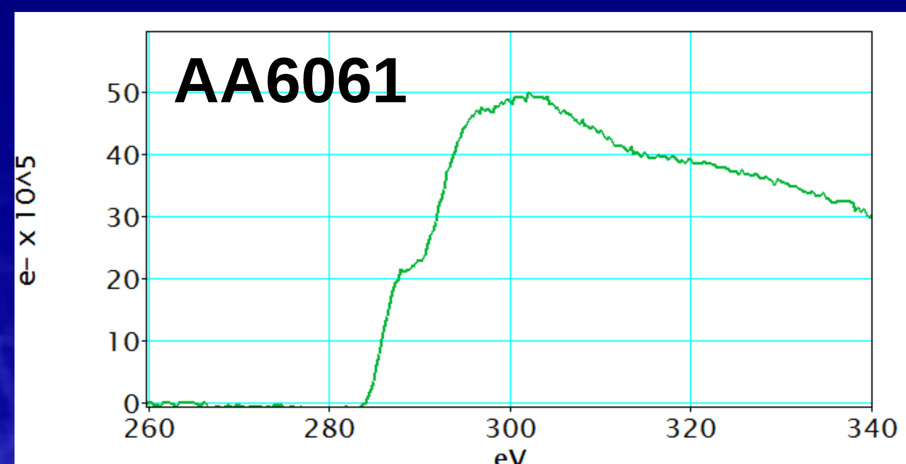


- Ribbon has high C and O content.
- Particles have Mg, Si and Cu.

EELS: Similar to spectrum of SWCNT in Ag, more like amorphous C in Cu and AA6061







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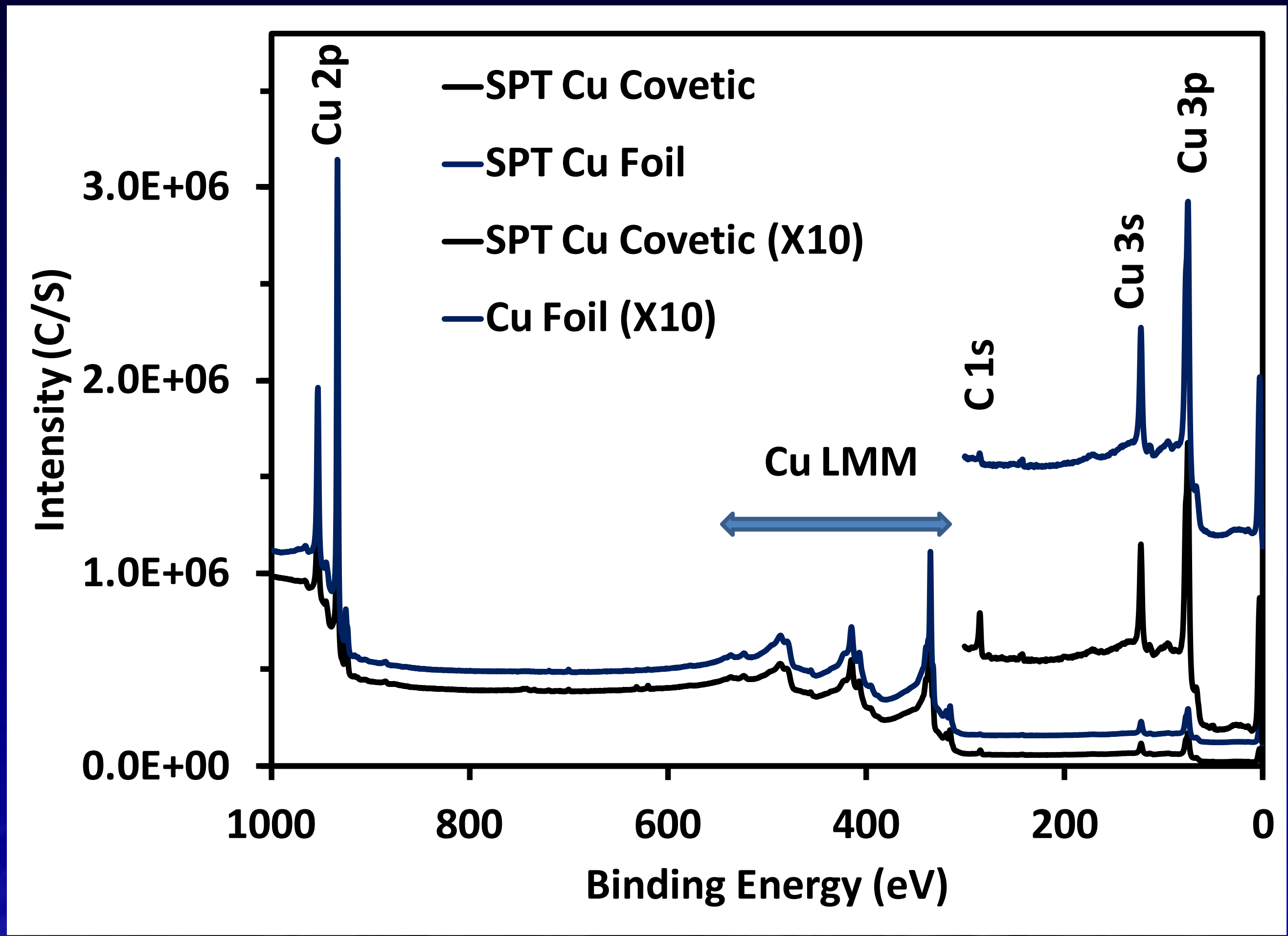
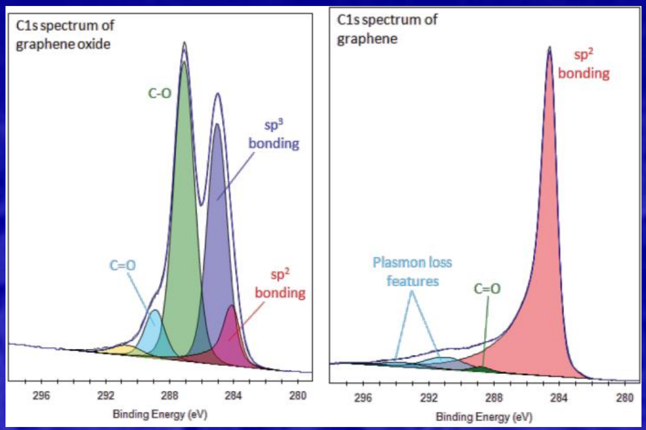
Schlittler, et al., “Single Crystals of Single-Walled Carbon Nanotubes Formed by Self-Assembly,” Science, New Series, Vol. 292, No. 5519 (May 11, 2001), pp. 1136-1139

In bulk,
Covetic virtually identical to pure Cu

XPS:

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

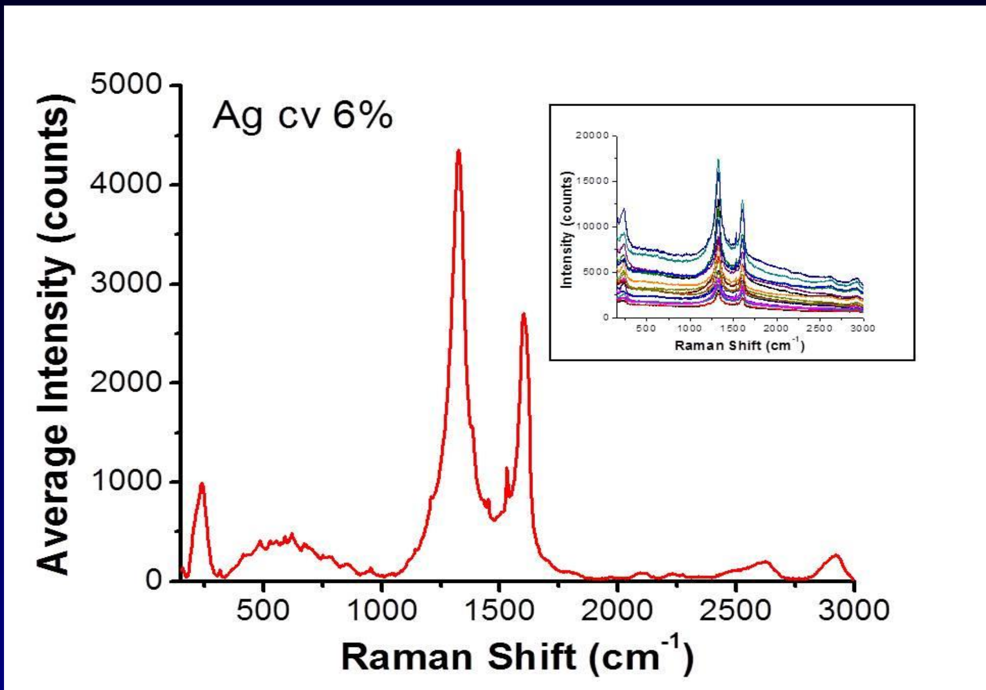


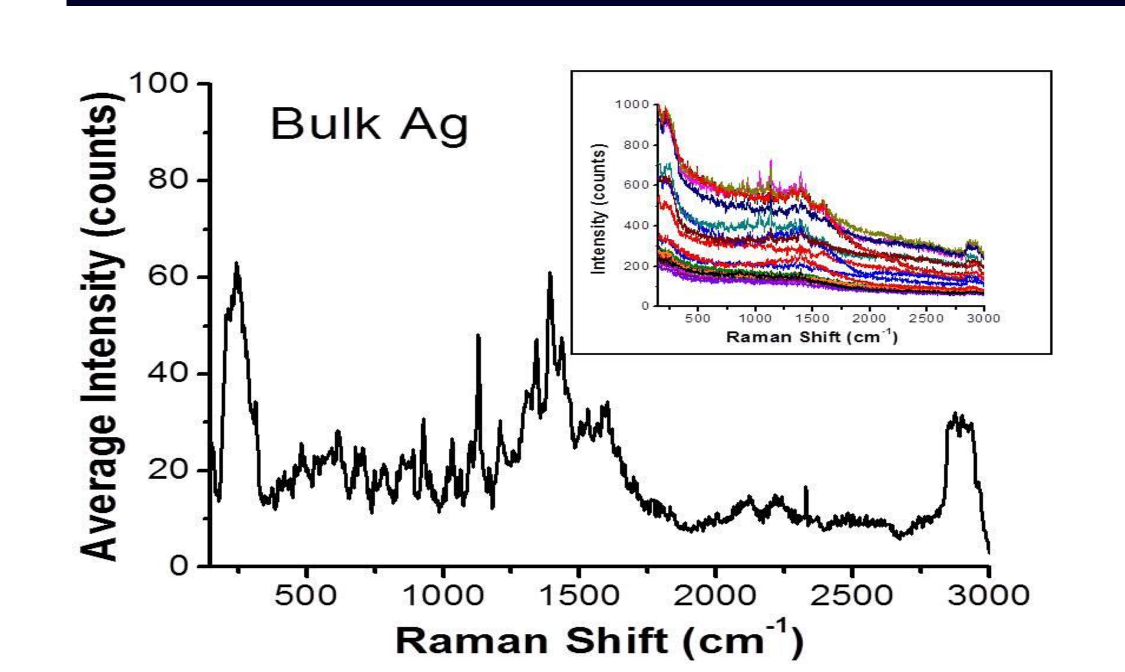


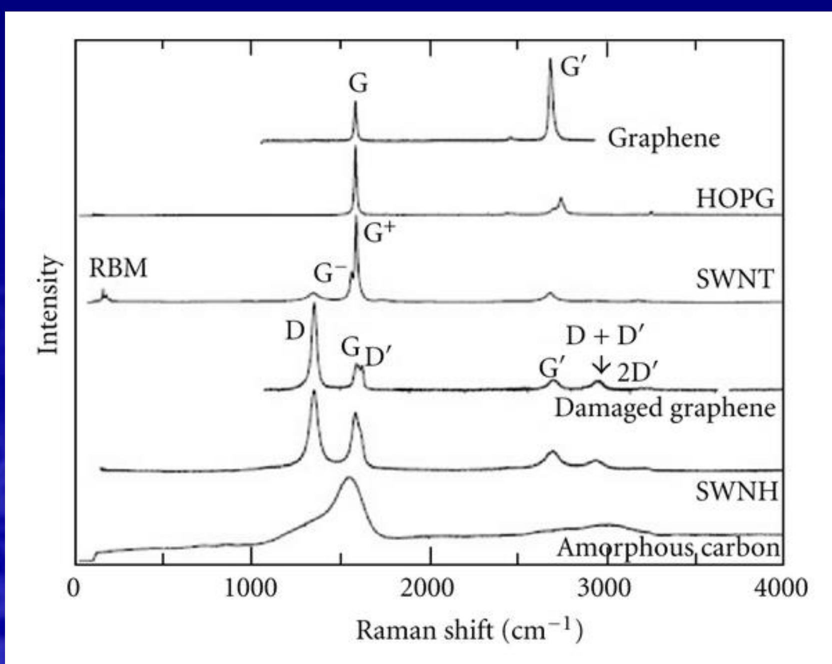
Foil: 0% C

Covetic: 3.5 wt% C

Evidence of *sp2* Carbon in Covetics



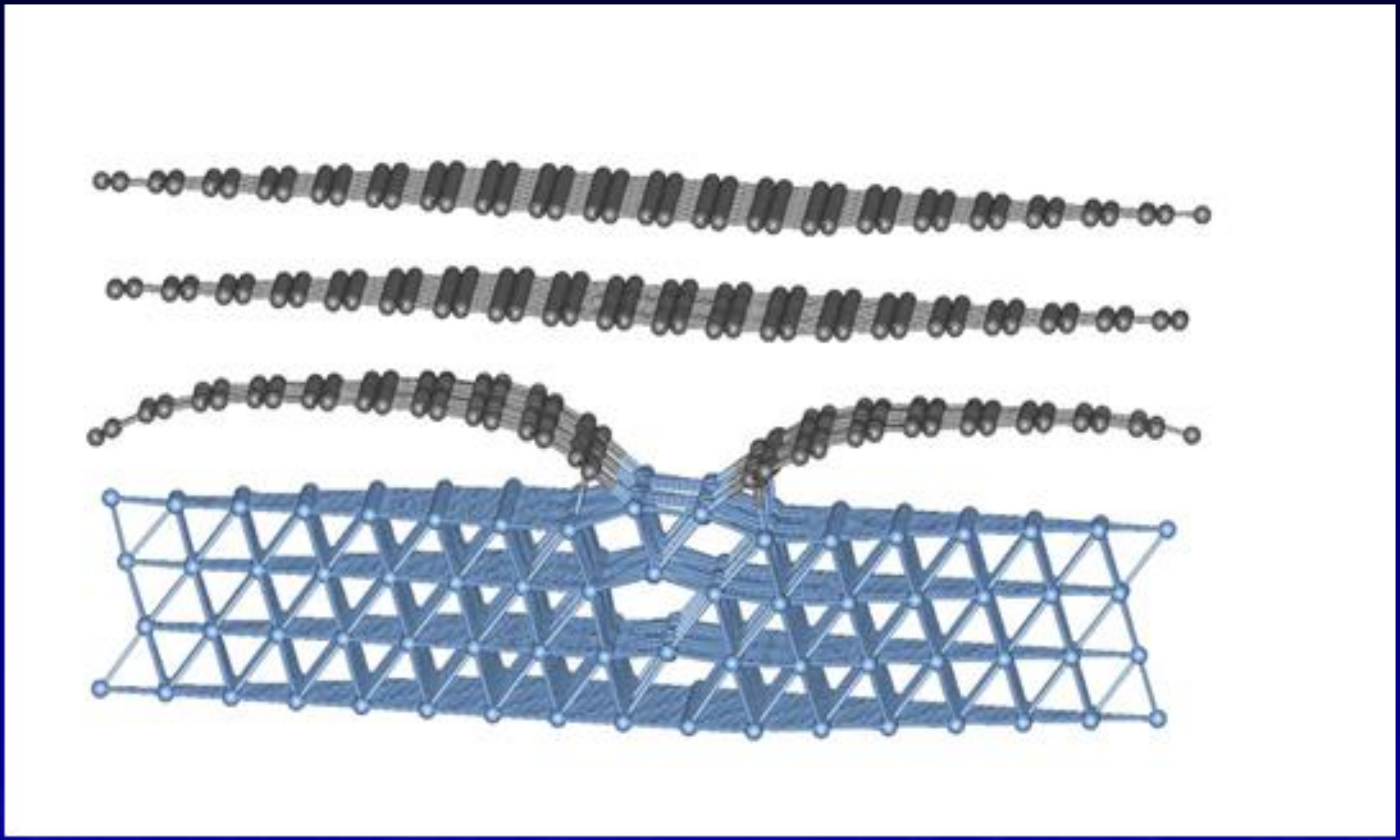




- Ag covetic shows clear D and G peaks at ~1,300 and 1,600 cm^{-1} in all 20 points of the sample.
- Ag metal shows weak signal in this region in all 20 points.
- Good match to single wall carbon nanohorn and to damaged graphene.

Melbs Lemieux

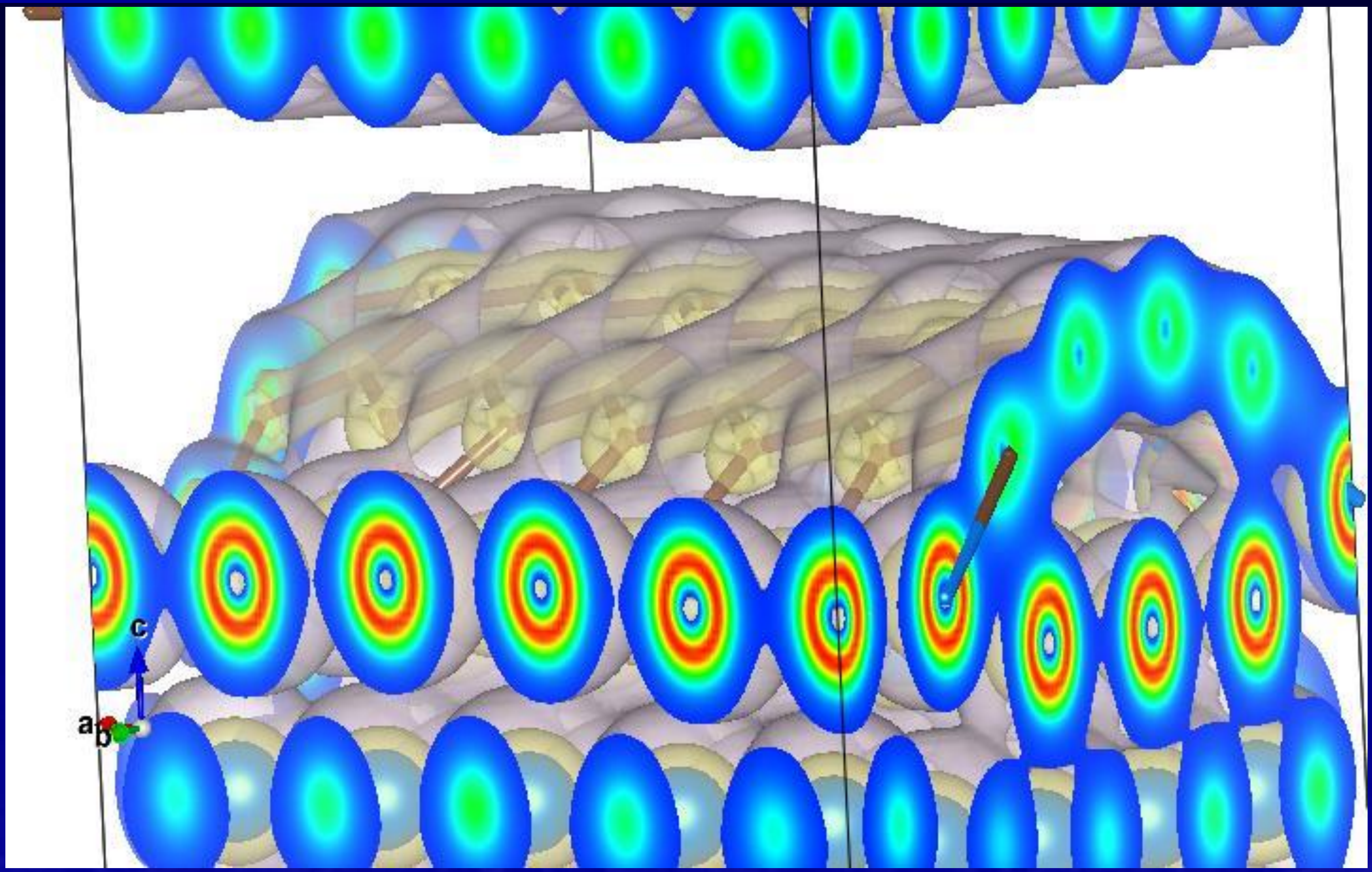
DFT: Graphene in Ag Covetic



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

Maija Kukla,
University of Maryland. (DARPA funding)

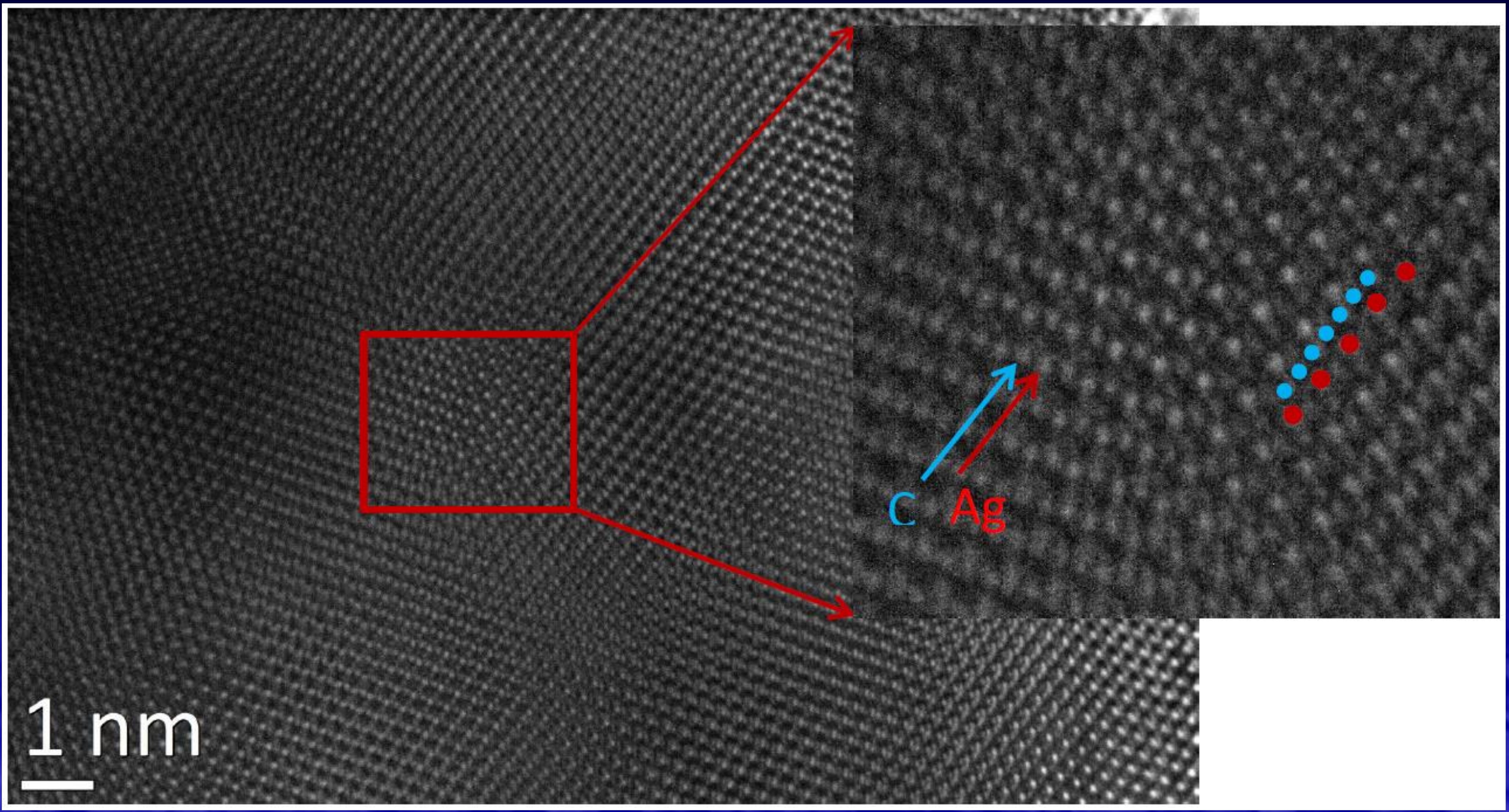
Nature of Chemical Bonding Between Graphene Layer and Surface Ag Atoms



➢**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



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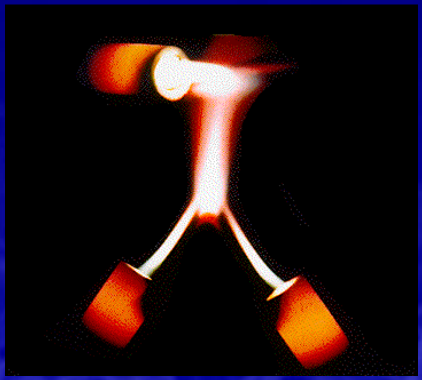
Open Questions on Fine Structure
(and why we're so keen on the ANL tomography)

- 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

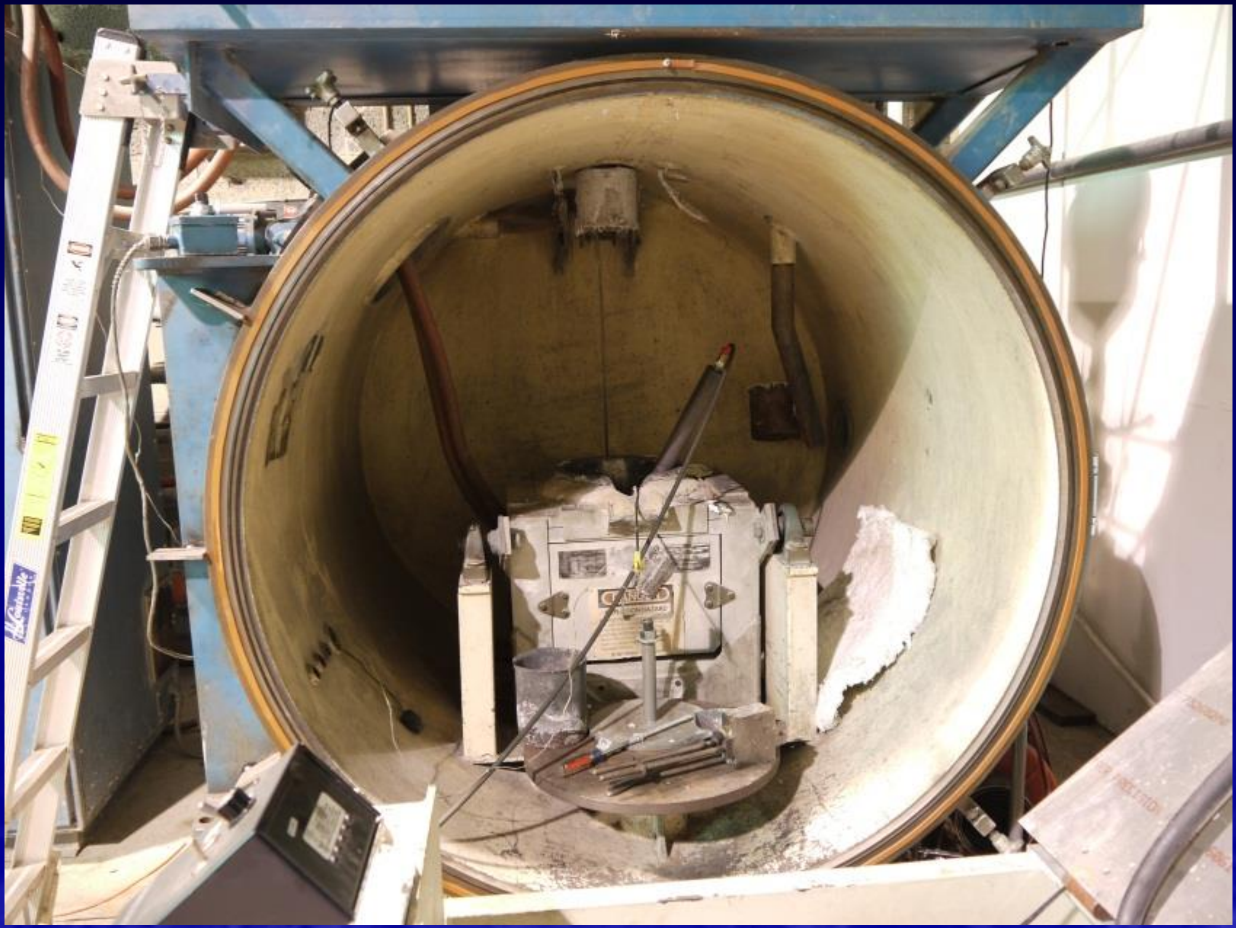
- LECO and GDMS do not seem to detect nanoscale C
- SEM-EDS and XPS best
- DC-PES may be better with higher carbon levels and provide better averaging with larger samples
- Standardization work needed
- Reference materials needed



Method	Result (wt. %)
LECO	0.0016
DC-PES*	0.56
GDMS	0.0060
XPS	0.13, 2.1

* Direct Current Plasma Emission Spectroscopy ASTM E1097 to detect Cu

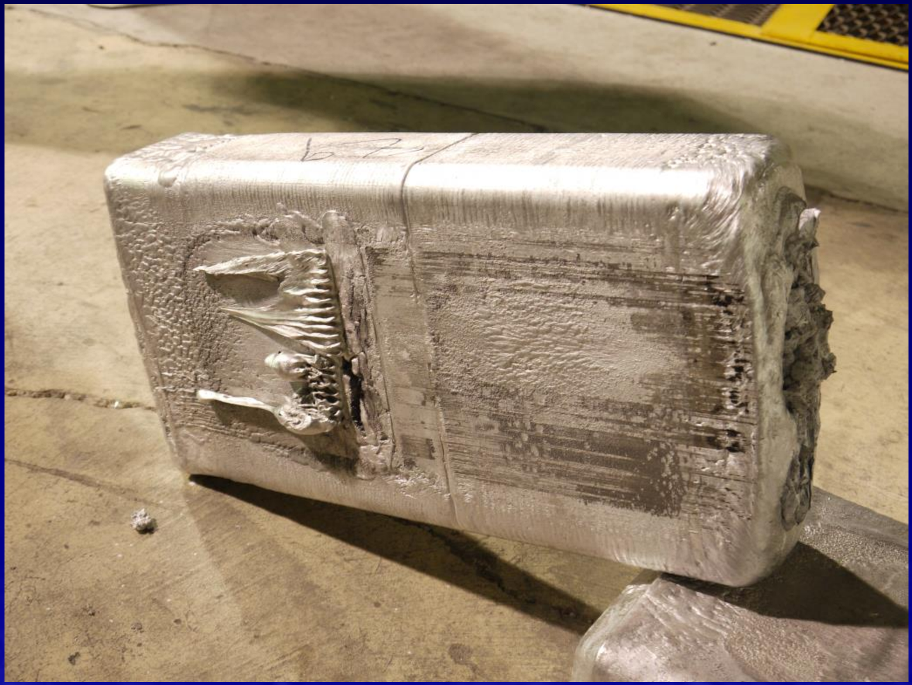
AA5083
Remelting and Strand Casting



Induction furnace at Surface Treatment Technologies

Remelting and Strand Casting

Remelting and Strand Casting

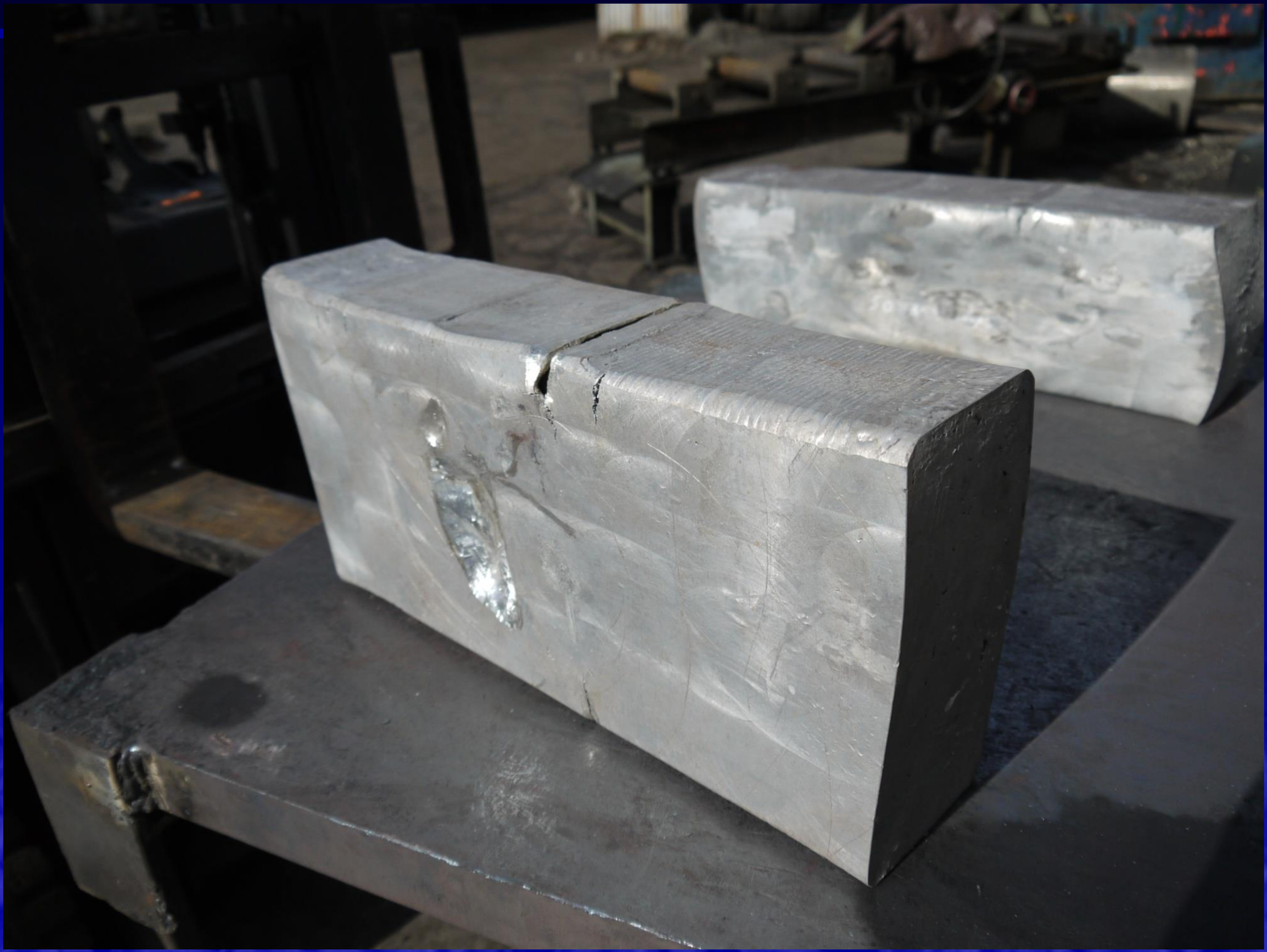


Remelting and Strand Casting

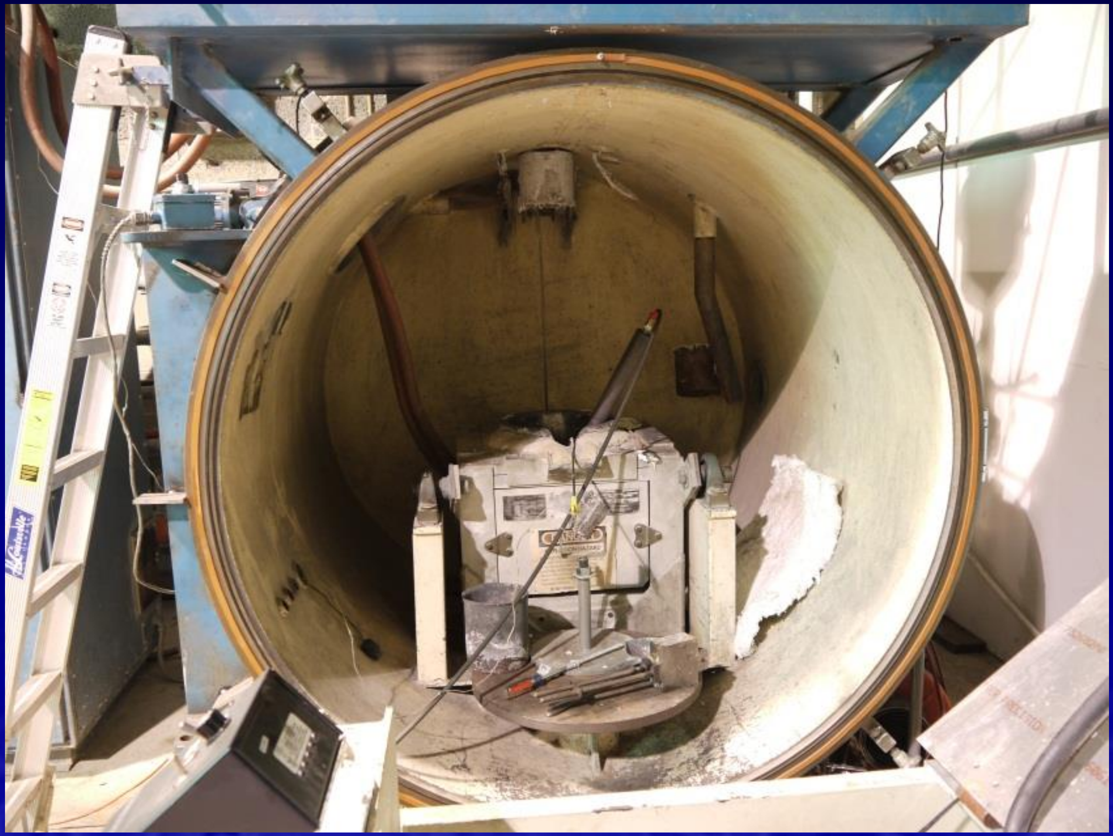
Forging

Forging

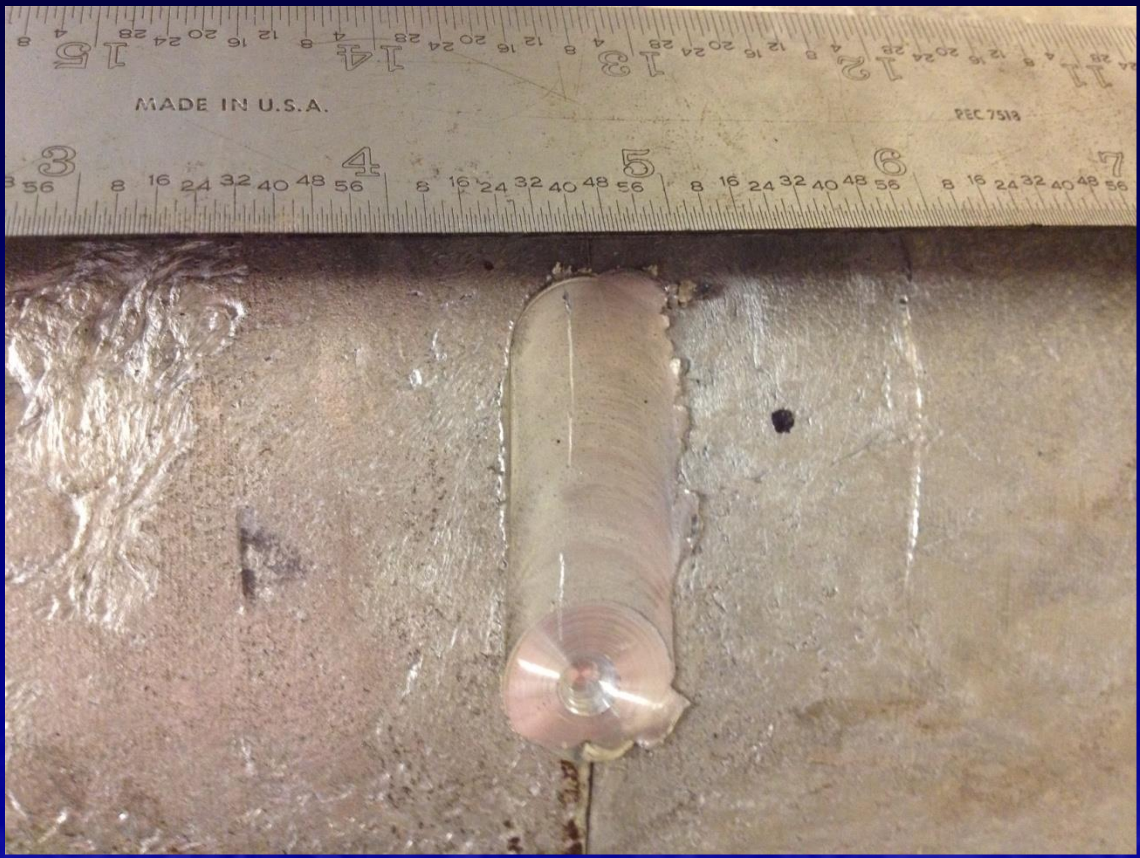
Forging



Remelting and Casting



Friction Stir Welding



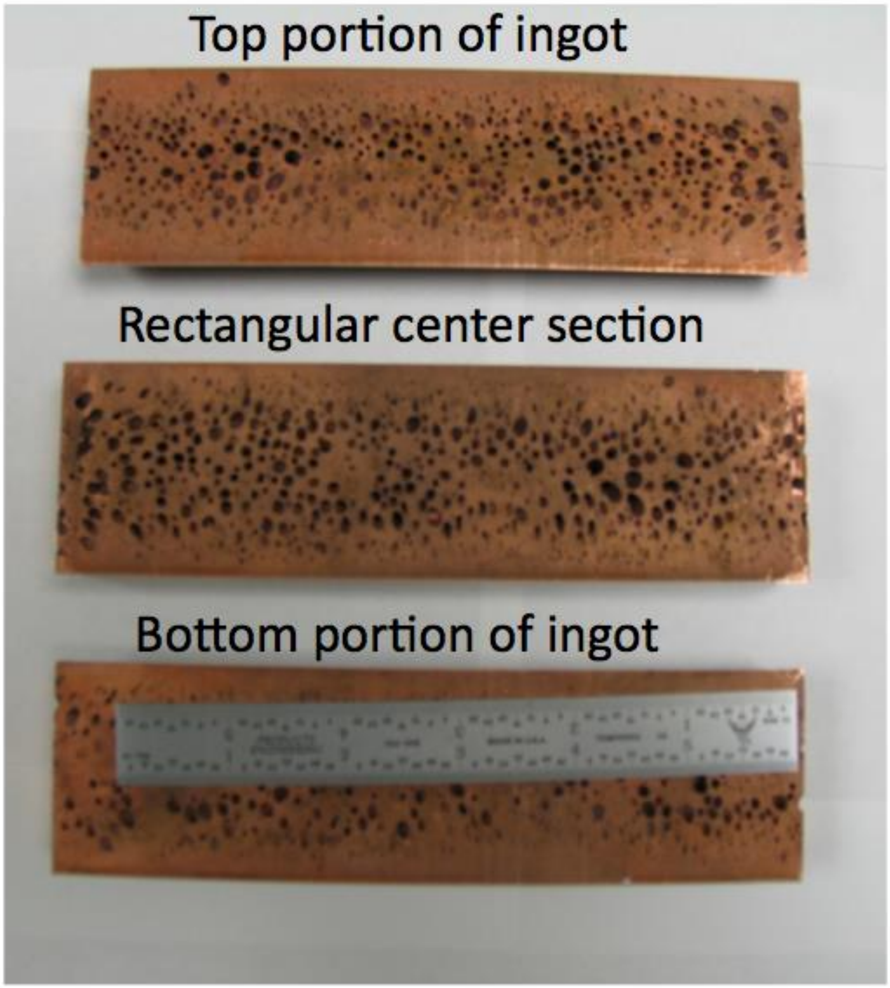
Extrusion

Extrusion

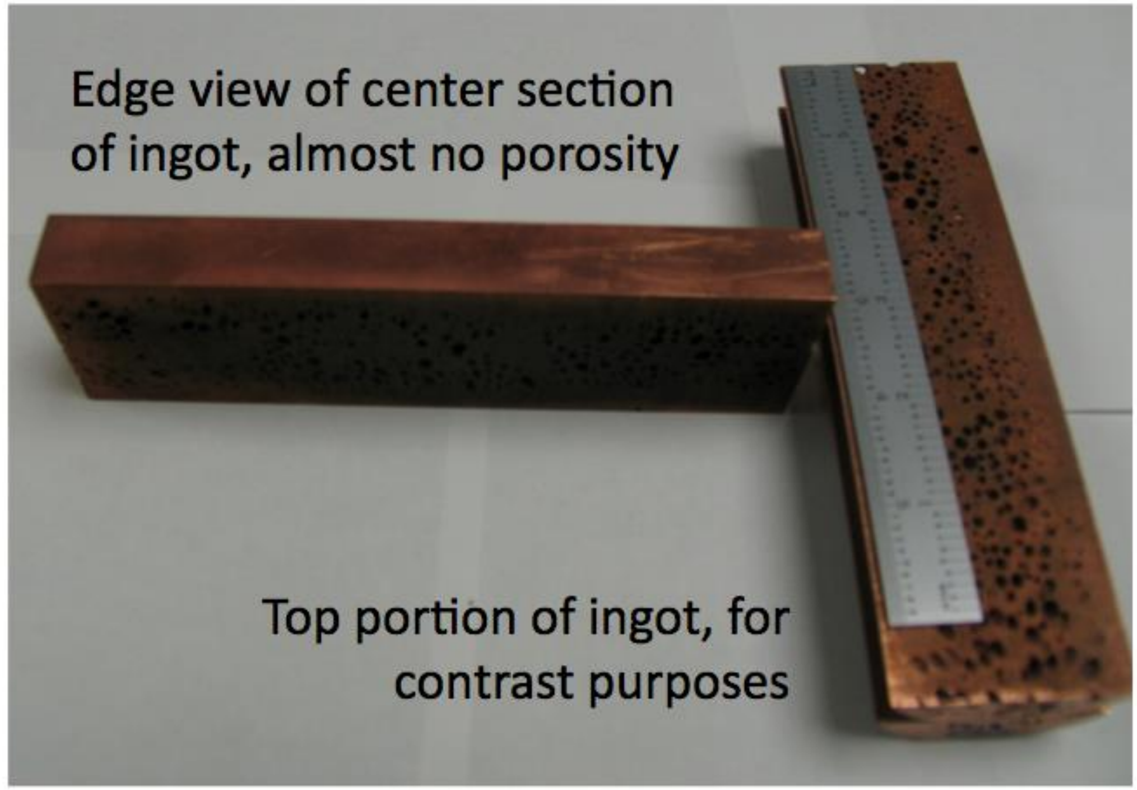
Hot Rolled

NC4-A
NC4-B
NC4-C
NC4-D
NC4-E
NC4
NC4-F
NC2-A
NC2-B
NC2-C
NC2-D
NC2-E
NC2-F
NC2

Porosity in Copper Covetic



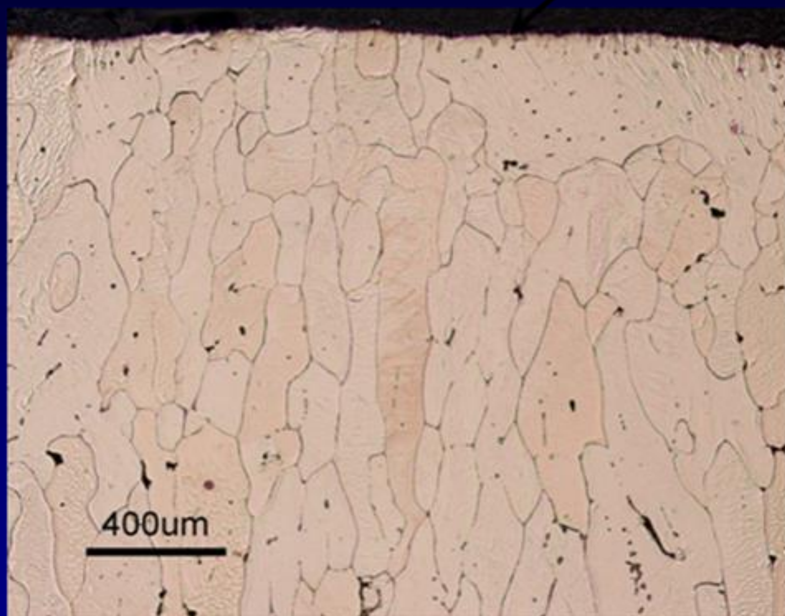
Center section dimensions: 6.62” X 1.895” X 0.730”

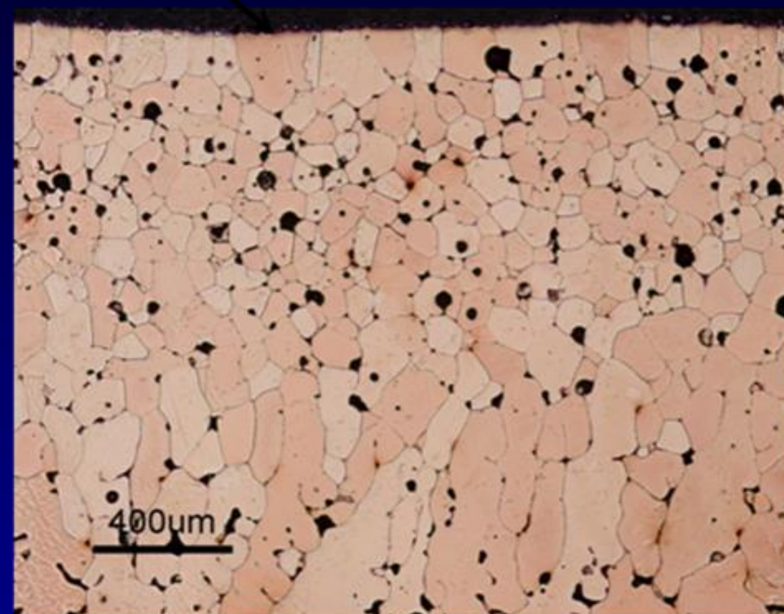


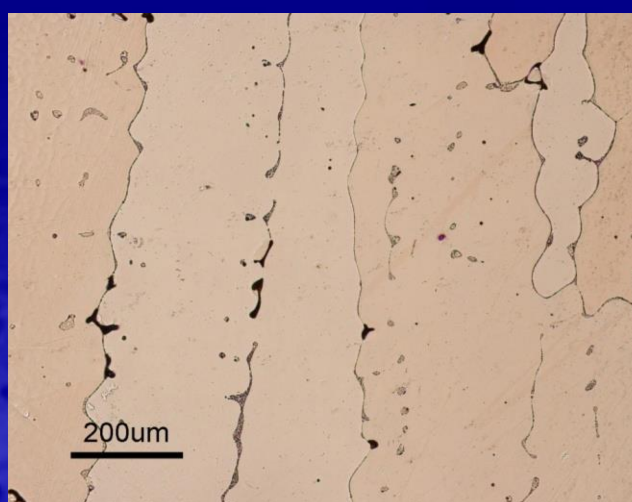
Significant amount of porosity present, with severity increasing as radius decreases. Percent of porosity estimated at 18.9%.

Centrifugally-Cast Microstructure

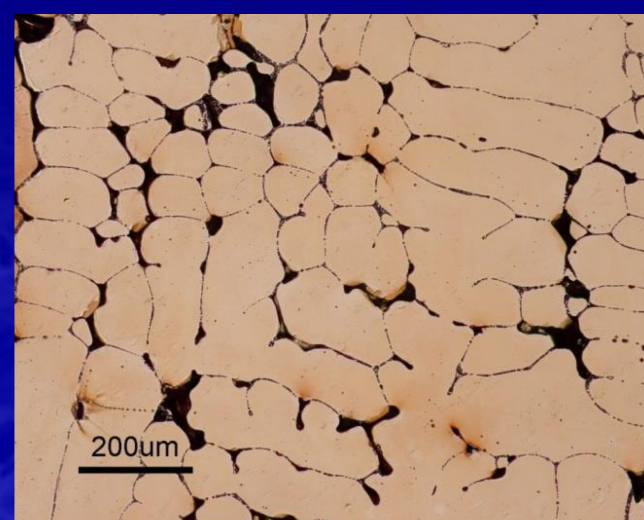
Ingot surfaces







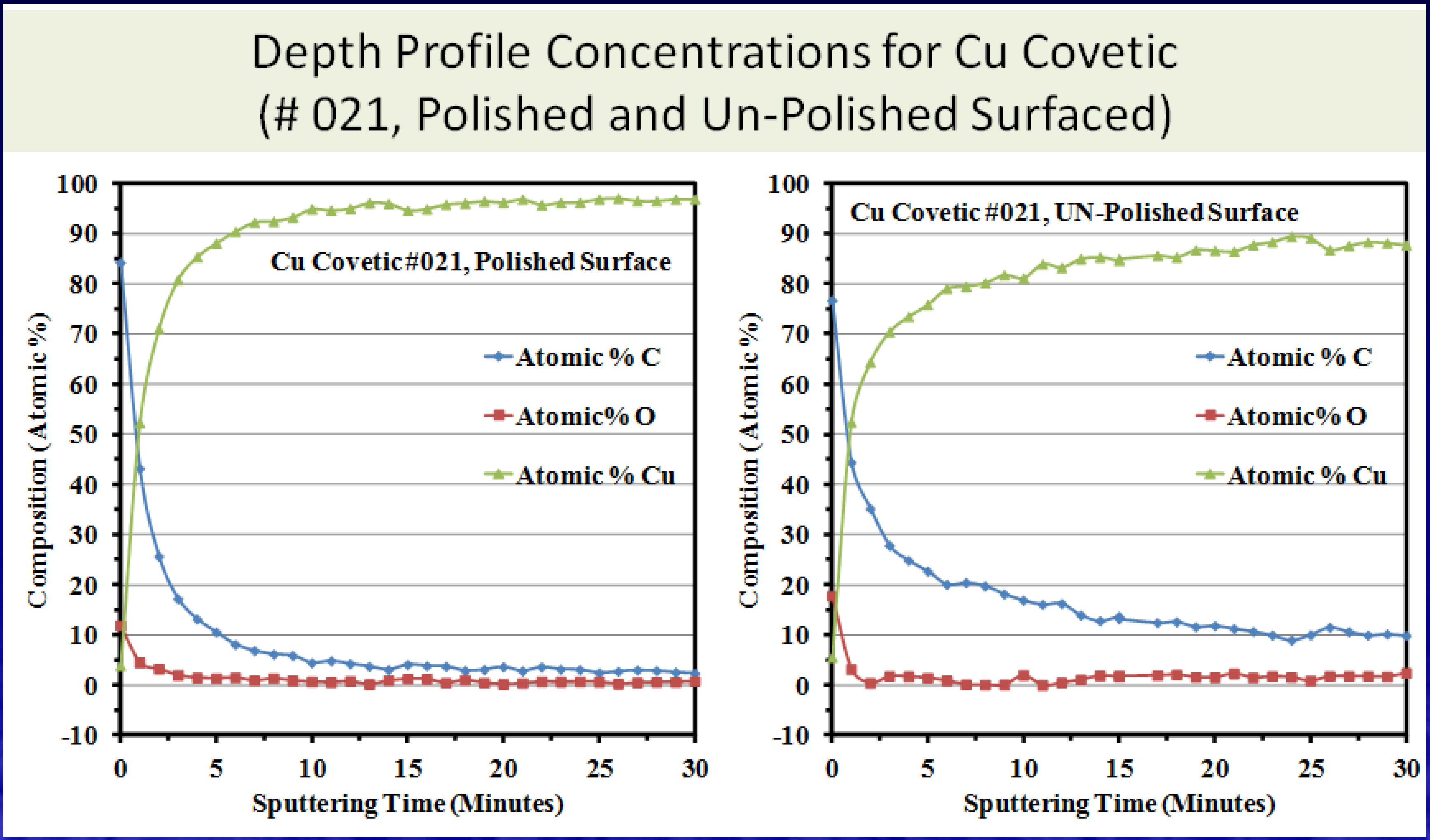
C11000



Covetic

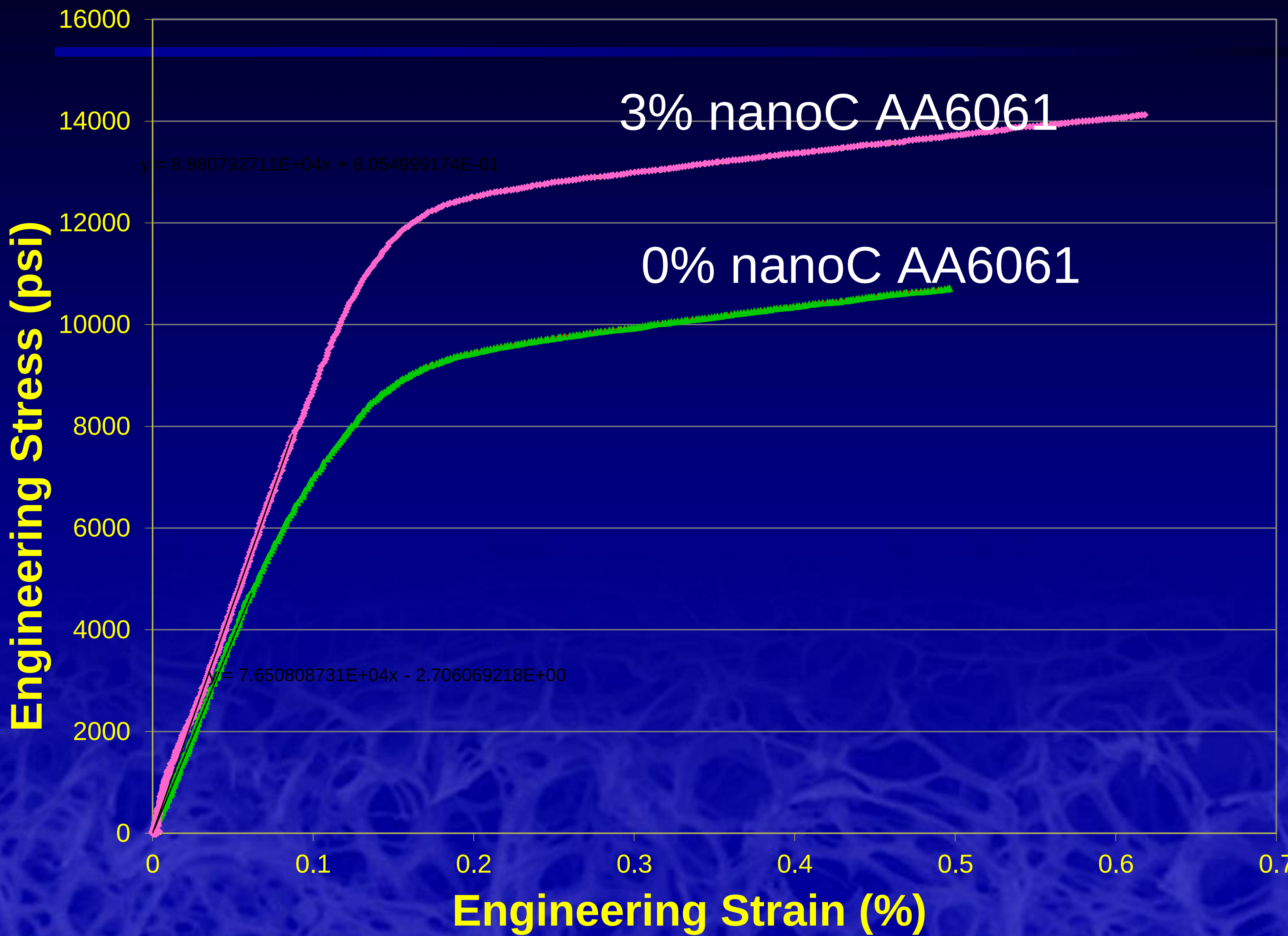
Surface Effects

Surface Effects

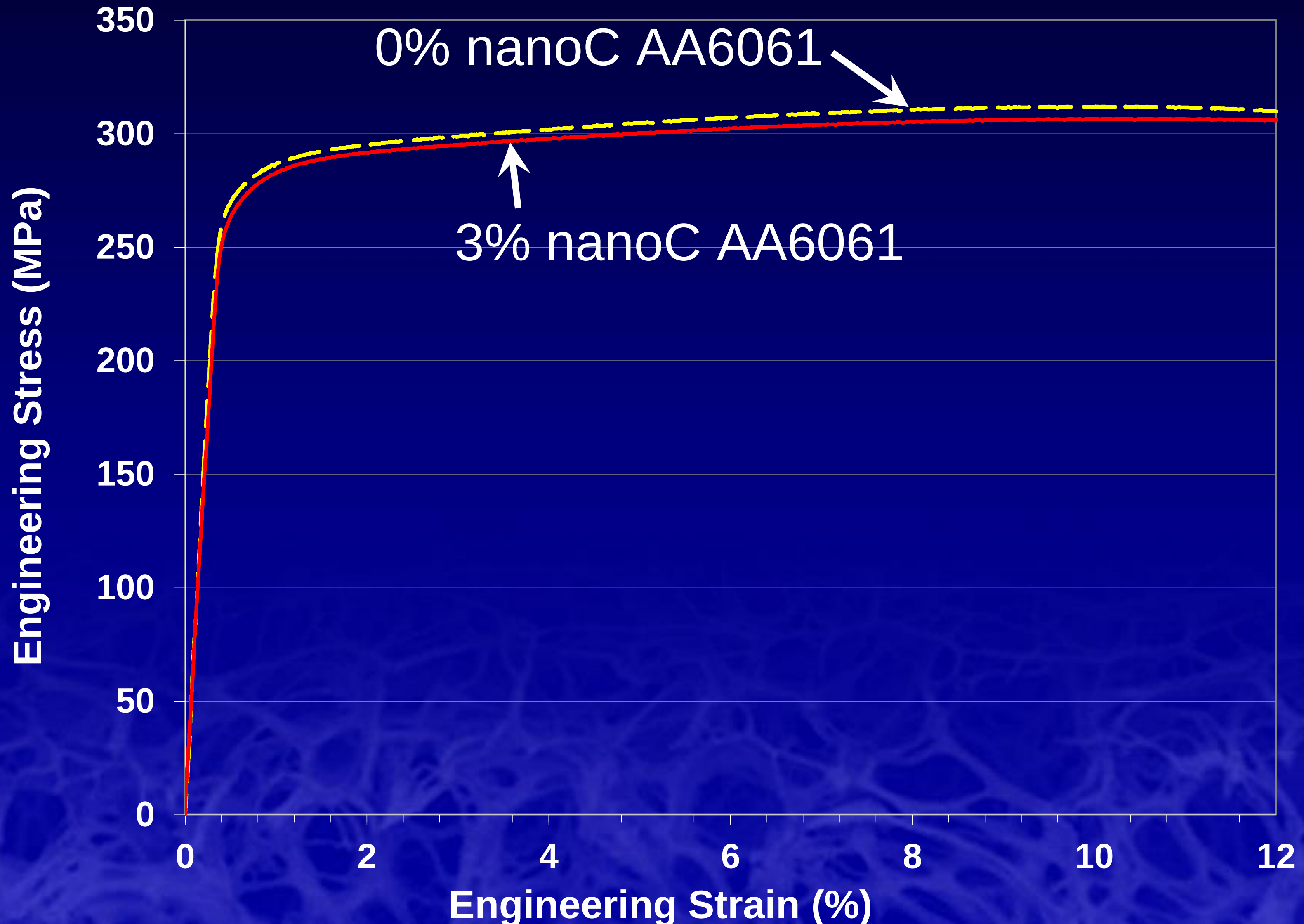


Mechanical Properties

Covetic YS 30% higher as-extruded 400F

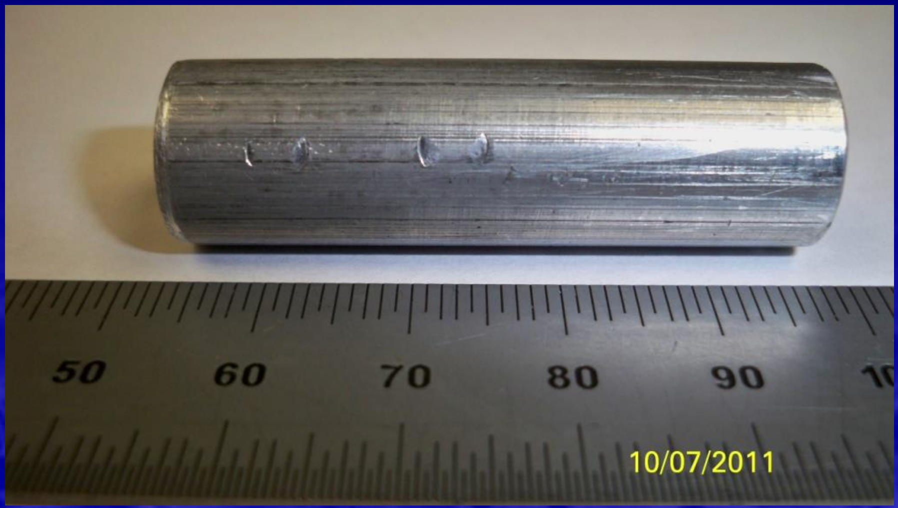


T6 condition:
No difference in tensile curves



6061 Cold Reduction (Naval Academy)

- 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



As received condition, prior to machining

6061 Cold Reduction (Naval Academy)

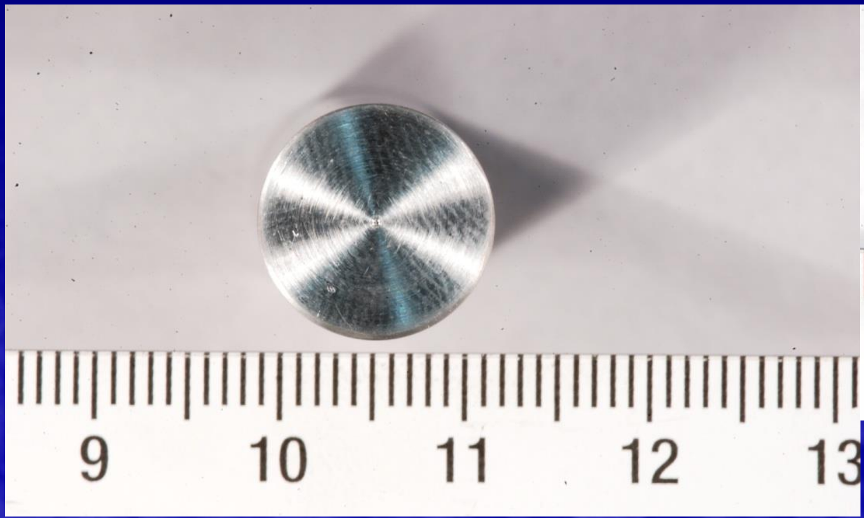
Initial Conductivity Measurement

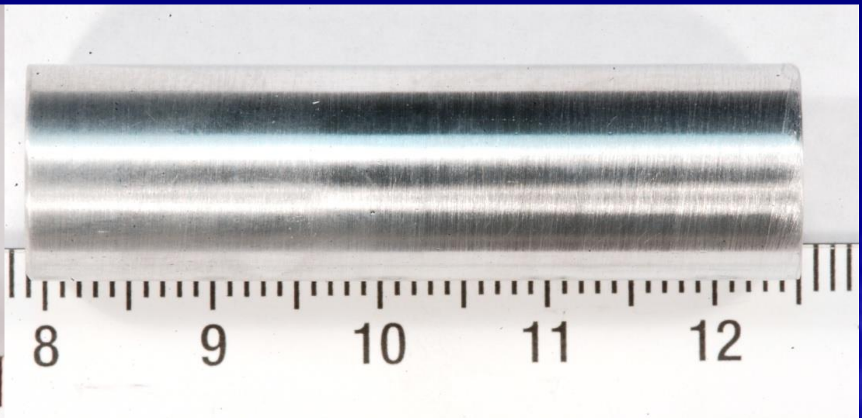
- Prior to H49 testing, resistivity was determined for a specimen of 6061 – T6. Resistivity was then converted to %IACS. The specimen was "off the shelf" and had a stock finish.
- 6061 – T6 %IACS = 48.44%
- Expected value: 40 – 45% (MATWEB)
- Value higher than expected, no explanation for variation.

6061 Cold Reduction (Naval Academy)

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.

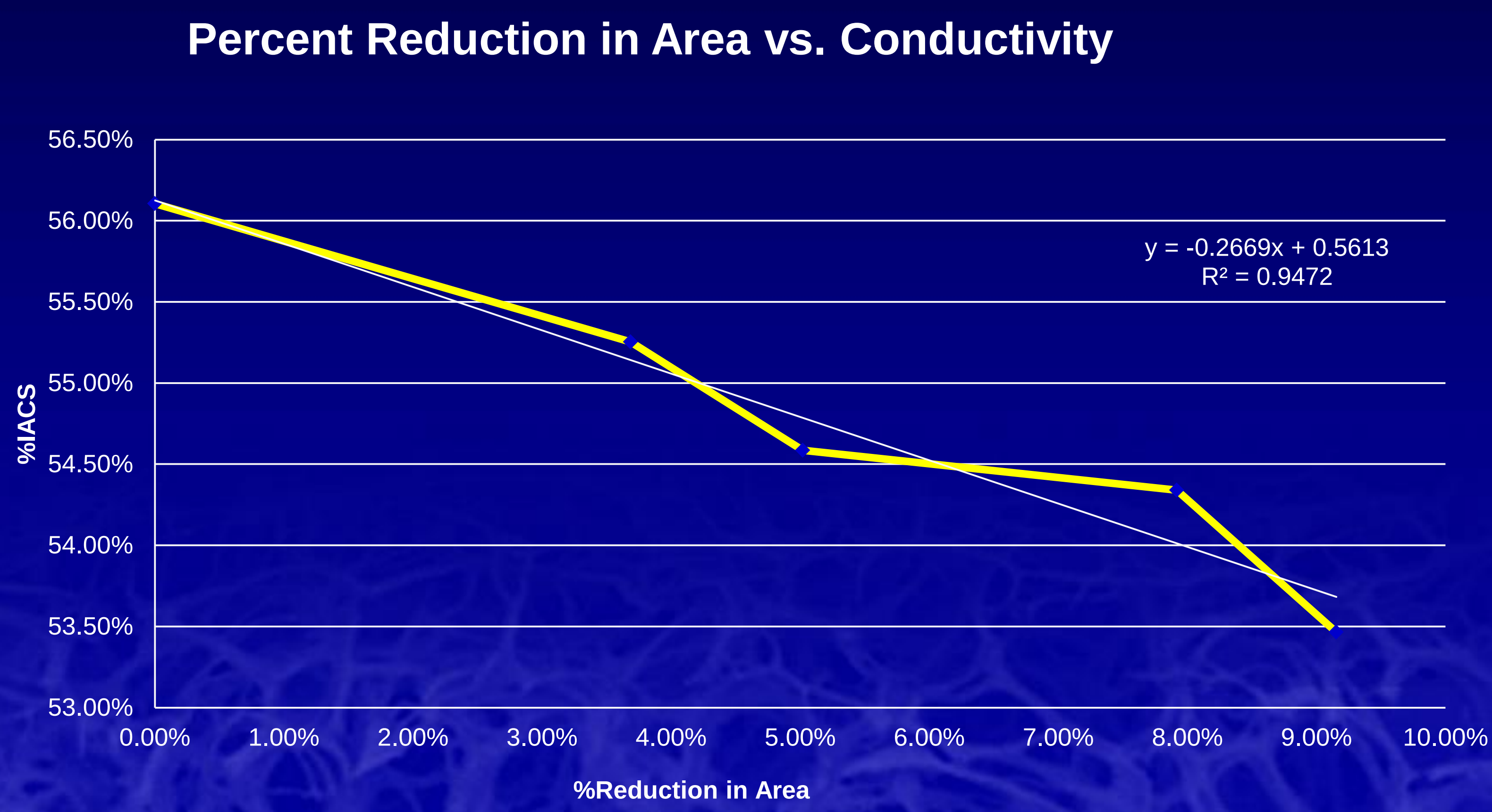
6061 Cold Reduction (Naval Academy)

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).

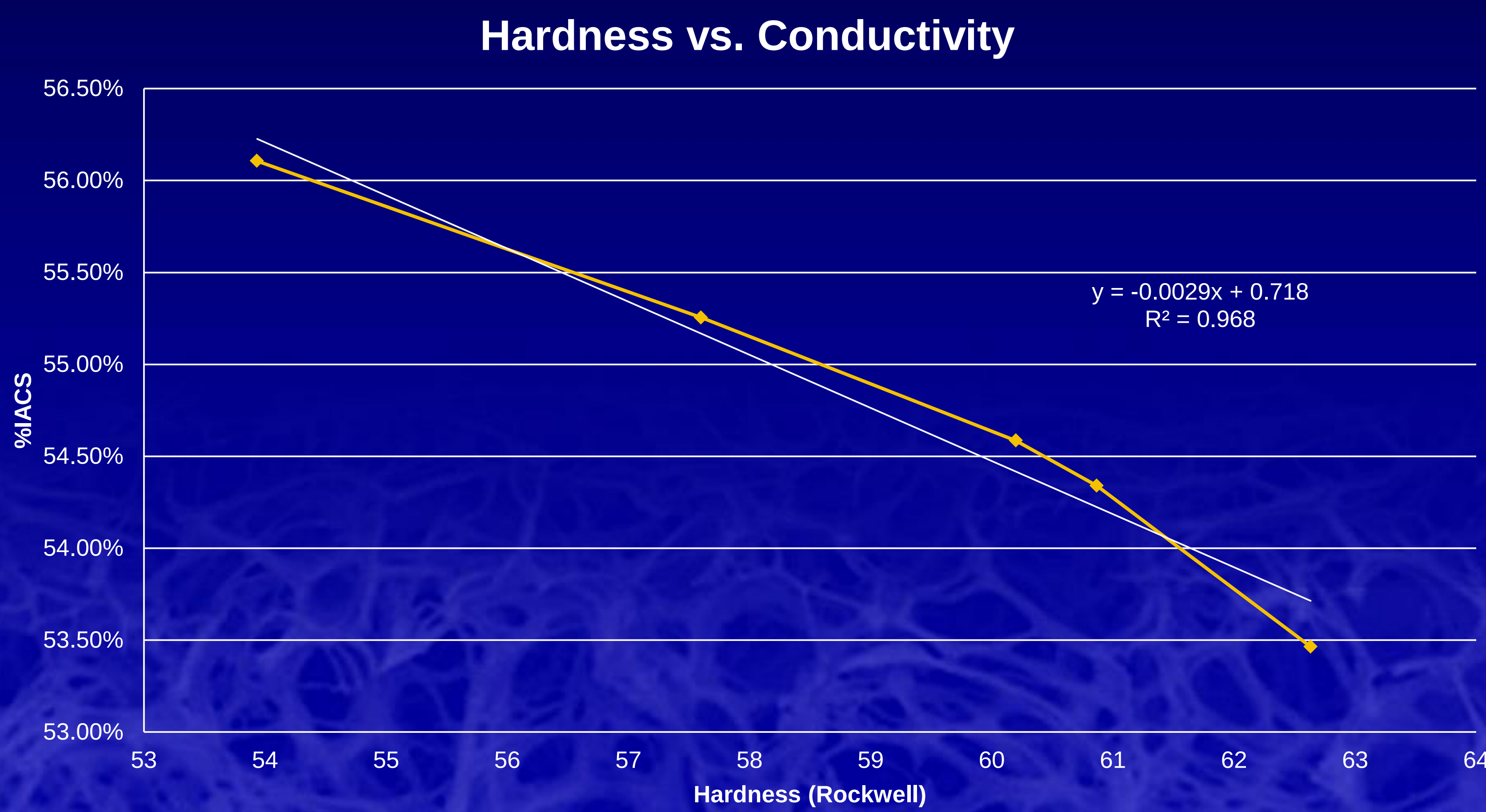
6061 Cold Reduction (Naval Academy)

Conductivity vs %RA



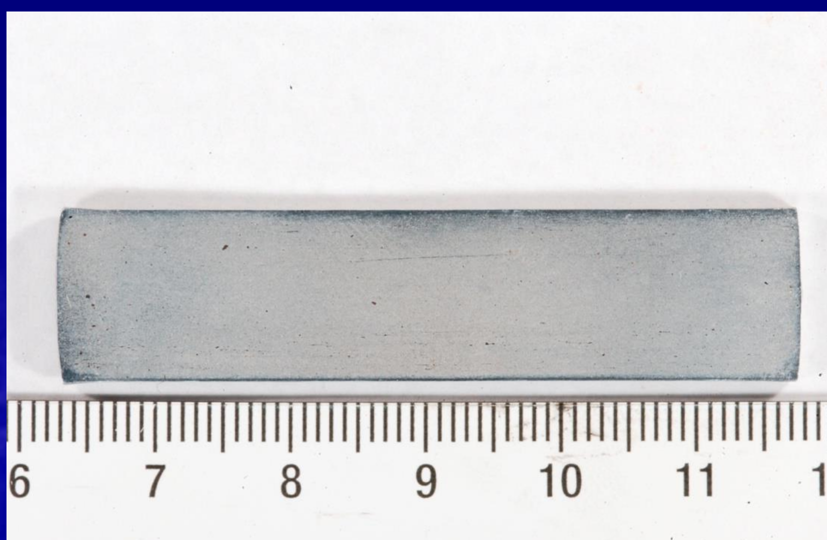
6061 Cold Reduction (Naval Academy)

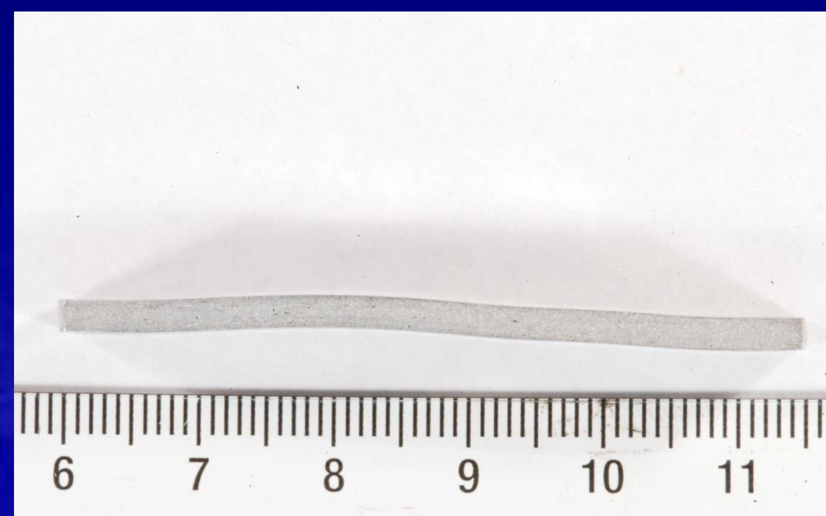
Conductivity vs Hardness



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

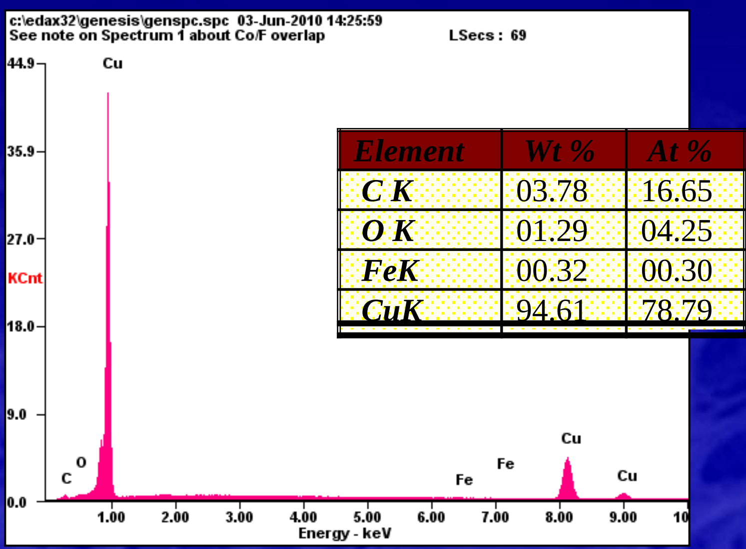
- Covetic nanomaterials have potential to provide improved performance for electrical and thermal conductivity, amenable to scalable high throughput processing
- Covetics can be processed using many traditional metals processing methods for melting, casting, deformation, and heat treatment
- There are 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

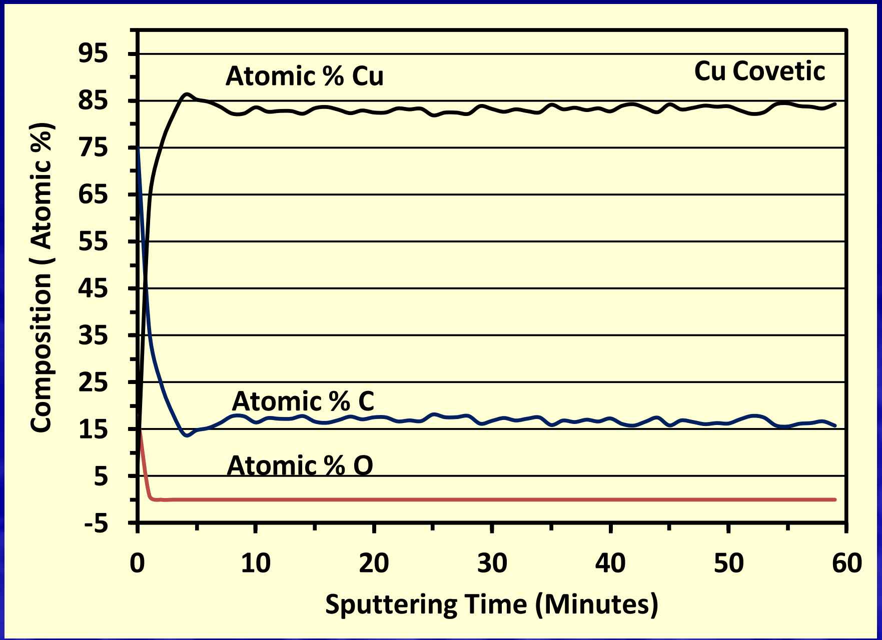
Spare slides

Good correspondence: XPS and EDS

Copper covetic

Method	Result (wt. %)
Energy Dispersive Spectroscopy	3.8
X-Ray Photoelectron Spectroscopy	3.5

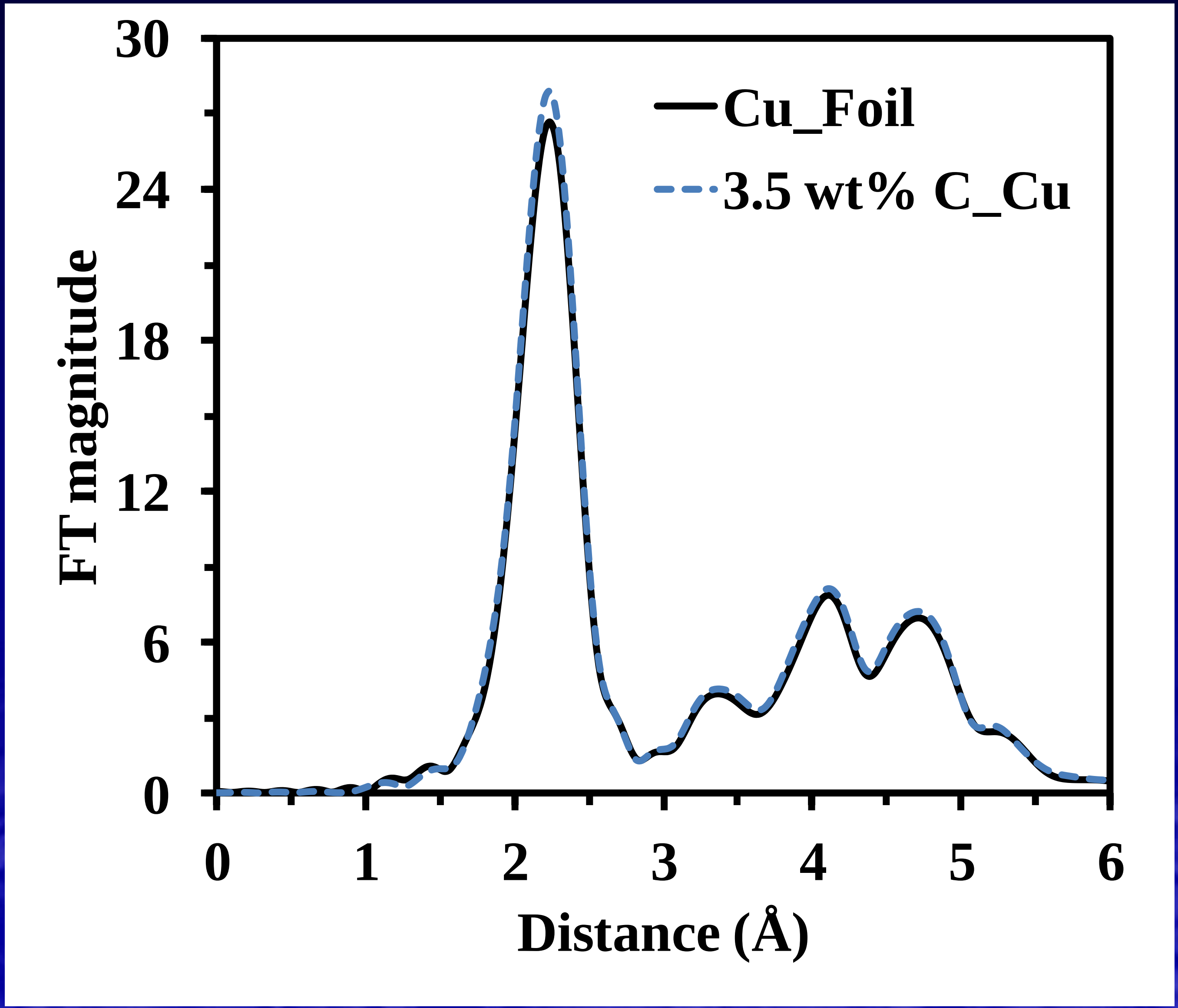




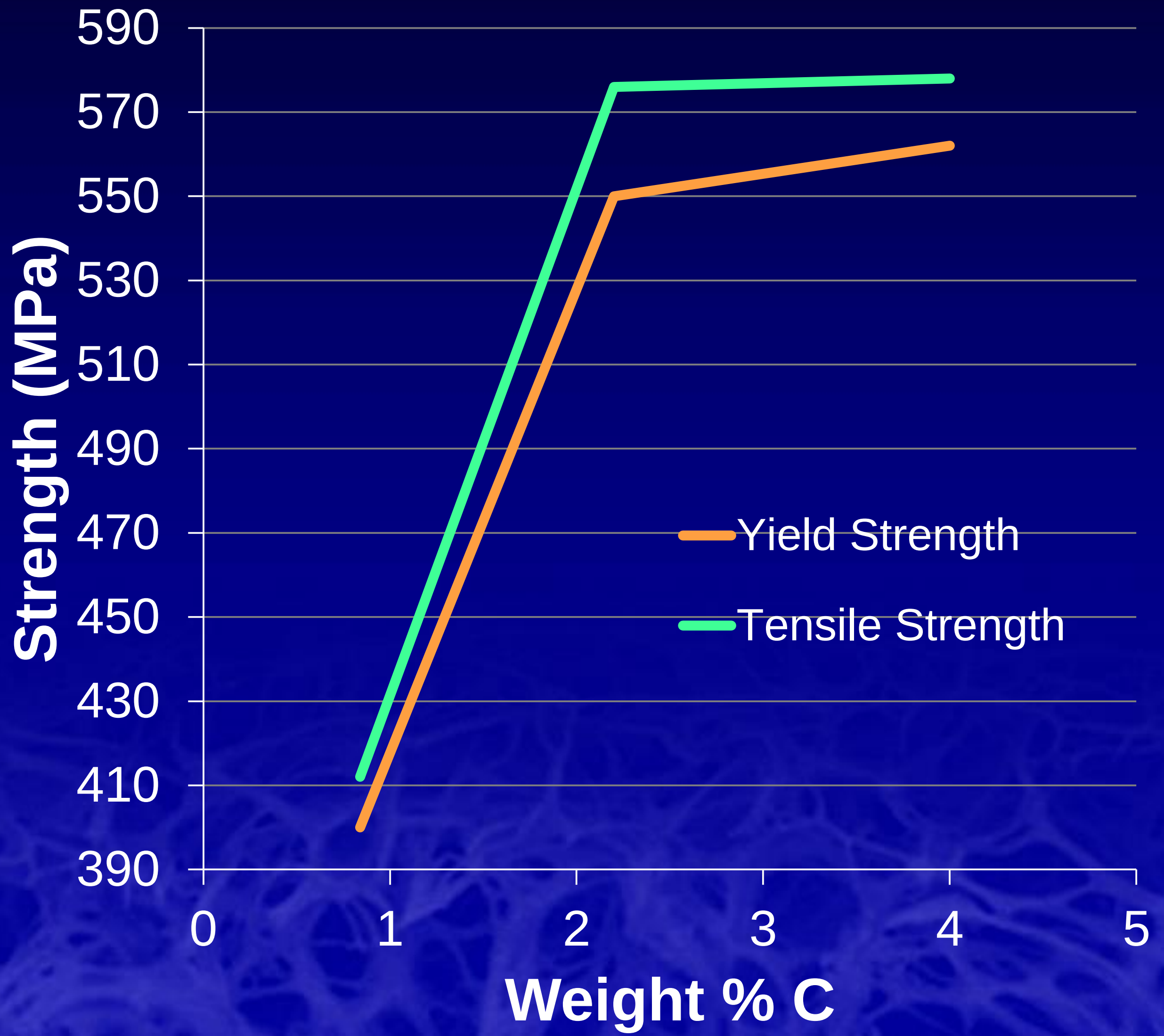
In bulk,
Covetic virtually identical to pure Cu

EXAFS/Fourier transforms:

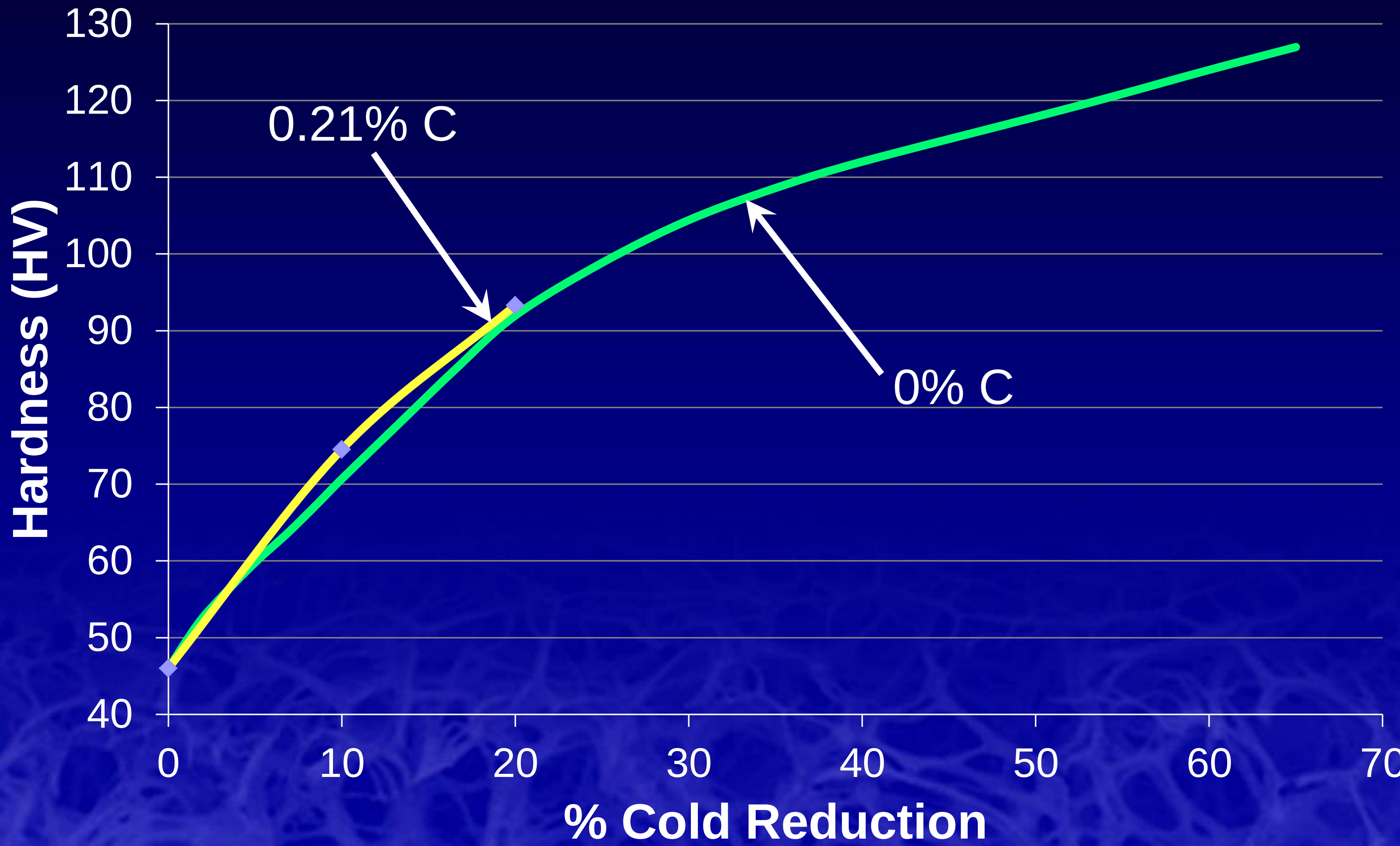
- Overall metallic character confirmed
- FCC structure
- Same structural parameters ⟶ no significant difference between atomic spacing of Cu atoms
- No evidence for a solid solution
- No evidence for carbon-Cu bonds except possibly at the interface region



Effect of carbon level on 7075 strength Third Millennium Metals Rolling



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