Nanoscale Carbon in Metals for Energy Applications

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Summary

- There is a new class of materials: Covetic
  - Third Millennium Metals, LLC; 12-yr development
  - “Immortal” nanocarbon phase, 5-200 nm, to 6 wt. % C
  - Well-dispersed, not graphite/diamond/fullerene
- Chemically bound to metal in a way we still need to understand; probably a new nano-effect
- Combination of analytic methods needed for C
- Nanoscale carbon raises the melting point
- Higher as-worked strength
- Higher thermal conductivity
- Higher electrical conductivity

Focus of Talk

- Background
- Form and distribution of carbon
- Analytical methods
- Properties
  - AA6061
  - Copper
- Applications

Background

- Third Millennium Metals, LLC
- Under development since 1999
- Conversion occurs in melt
  - Al, Cu, Au, Ag, Zn, Sn, Pb and Fe
  - Carbon powder → nanoscale C
- Stable after conversion
- Process development and scale up is ongoing
- Producing laboratory quantities now, 10-15 lb heats → 100-lb heat capacity soon

Examples of nanoscale effects between metals and C

Zhou, et al., “Copper Catalyzing Growth of Single-Walled Carbon Nanotubes on Substrates,” *Nano Letters 2006*, Vol. 6, No. 12, p. 2987-2990

Schaper, et al., “Copper nanoparticles encapsulated in multi-shell carbon cages,” *Applied Physics A: Materials Science & Processing*, v. 78, no. 1, p. 73-77 (2004).

Feng, et al., “Optical and structural studies of copper nanoparticles and microfibers produced by using carbon nanotube as templates,” (Proceedings Paper), Nanophotonic Materials III, Zeno Gaburro; Stefano Cabrini, Editors, Proceedings Vol. 6321, 30 August 2006.

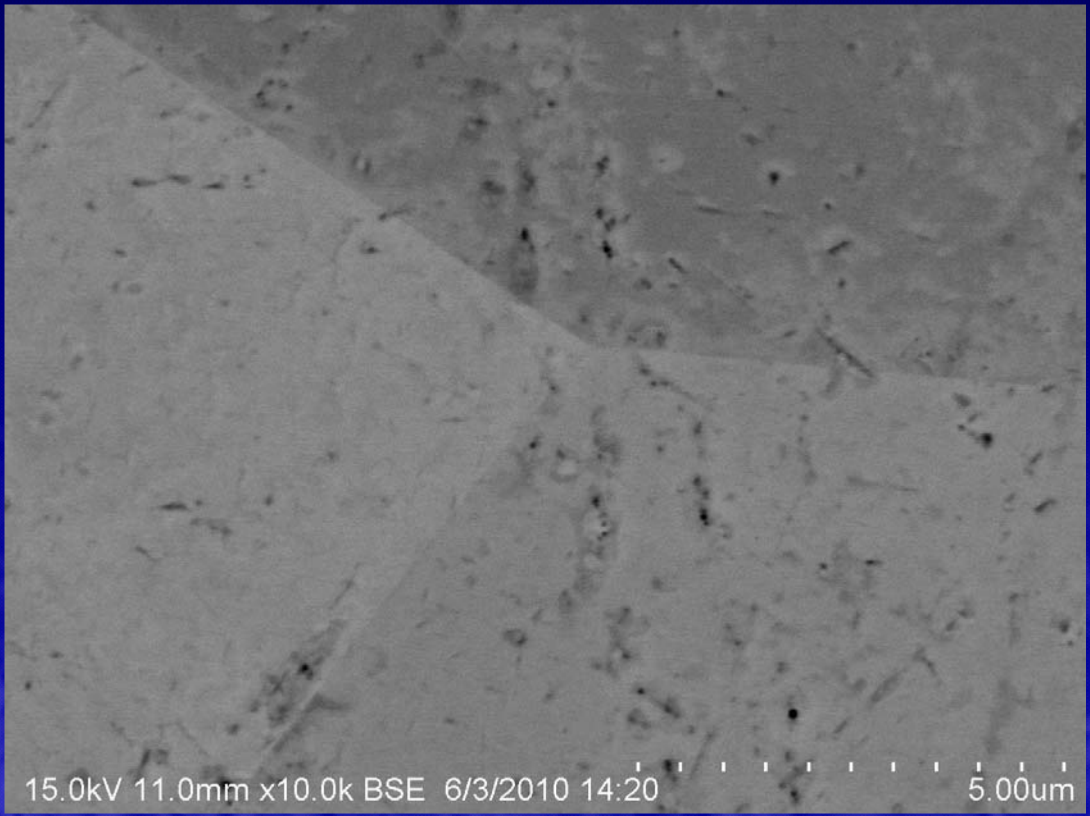
E K Athanassiou , R N Grass and W J Stark, “Large-scale production of carbon-coated copper nanoparticles for sensor applications,” *Nanotechnology*, v. 17, no. 6, 28 March 2006.

E. A. Sutter and P. W. Sutter, “Giant Carbon Solubility in Au Nanoparticles,” *Journal of Materials Science*, v. 46, p. 7090-7097 (2011).

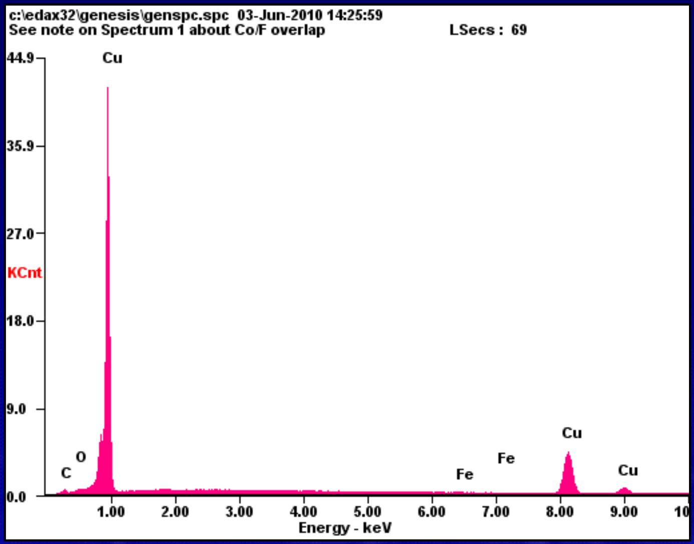
Distribution and Form of Carbon

SEM – Cu covetic, as-cast, 3.8% C

- 5-200 nm diameter particles
- Well-dispersed
- Remain intact upon remelting and resolidification



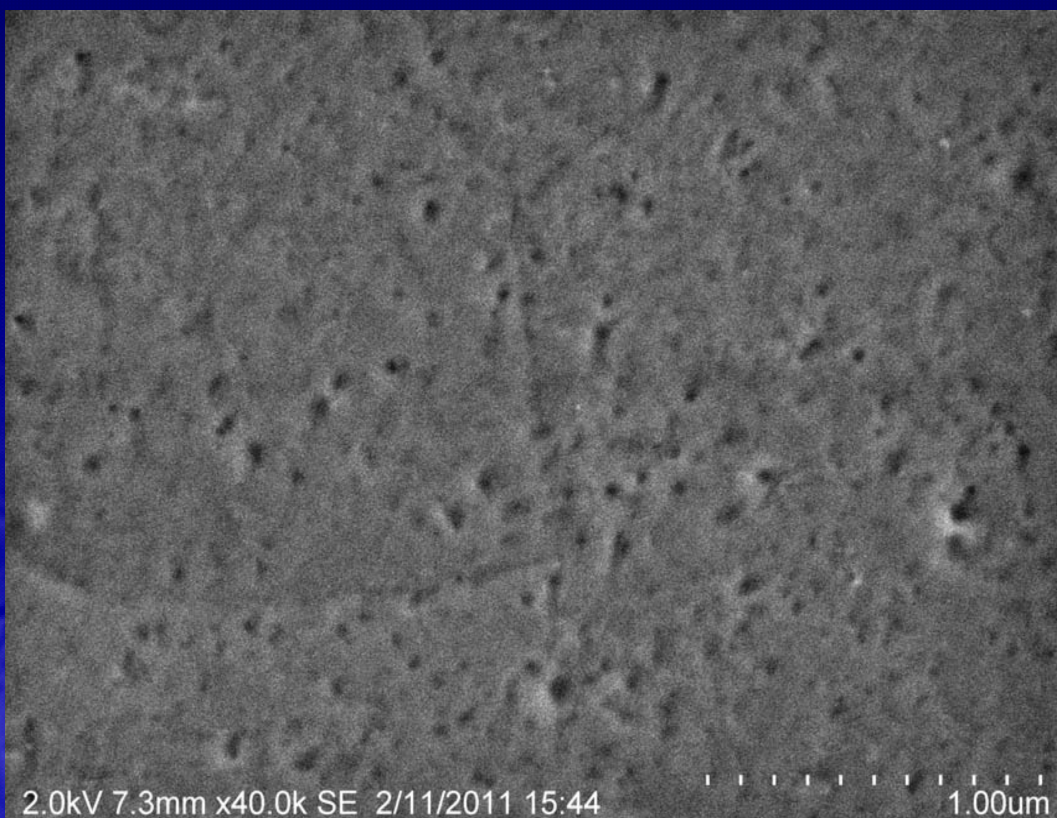
Metallographically as-polished surface

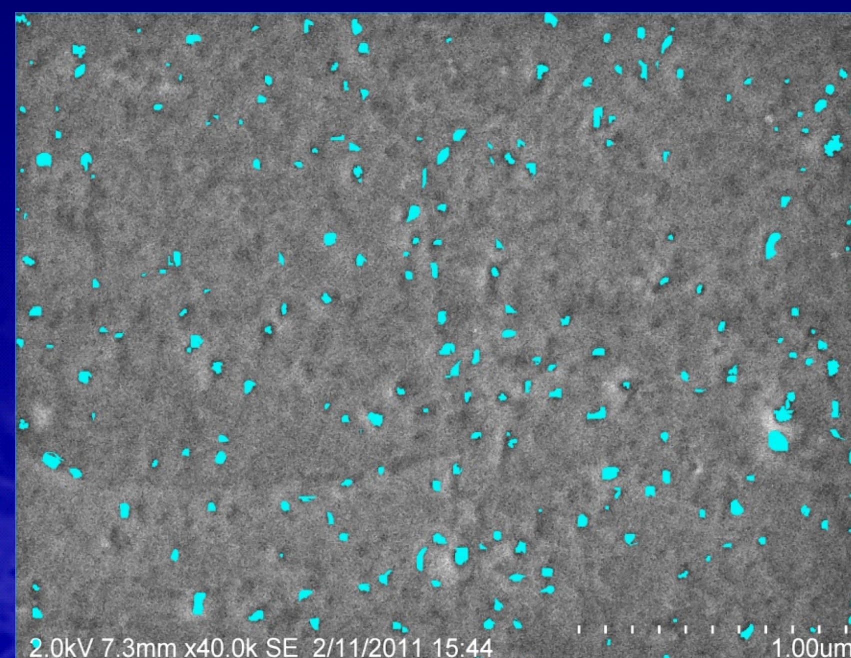


Element	Wt %	At %
C K	03.78	16.65
O K	01.29	04.25
FeK	00.32	00.30
CuK	94.61	78.79

SEM – AA6061 as-extruded, 2.7% nanoC

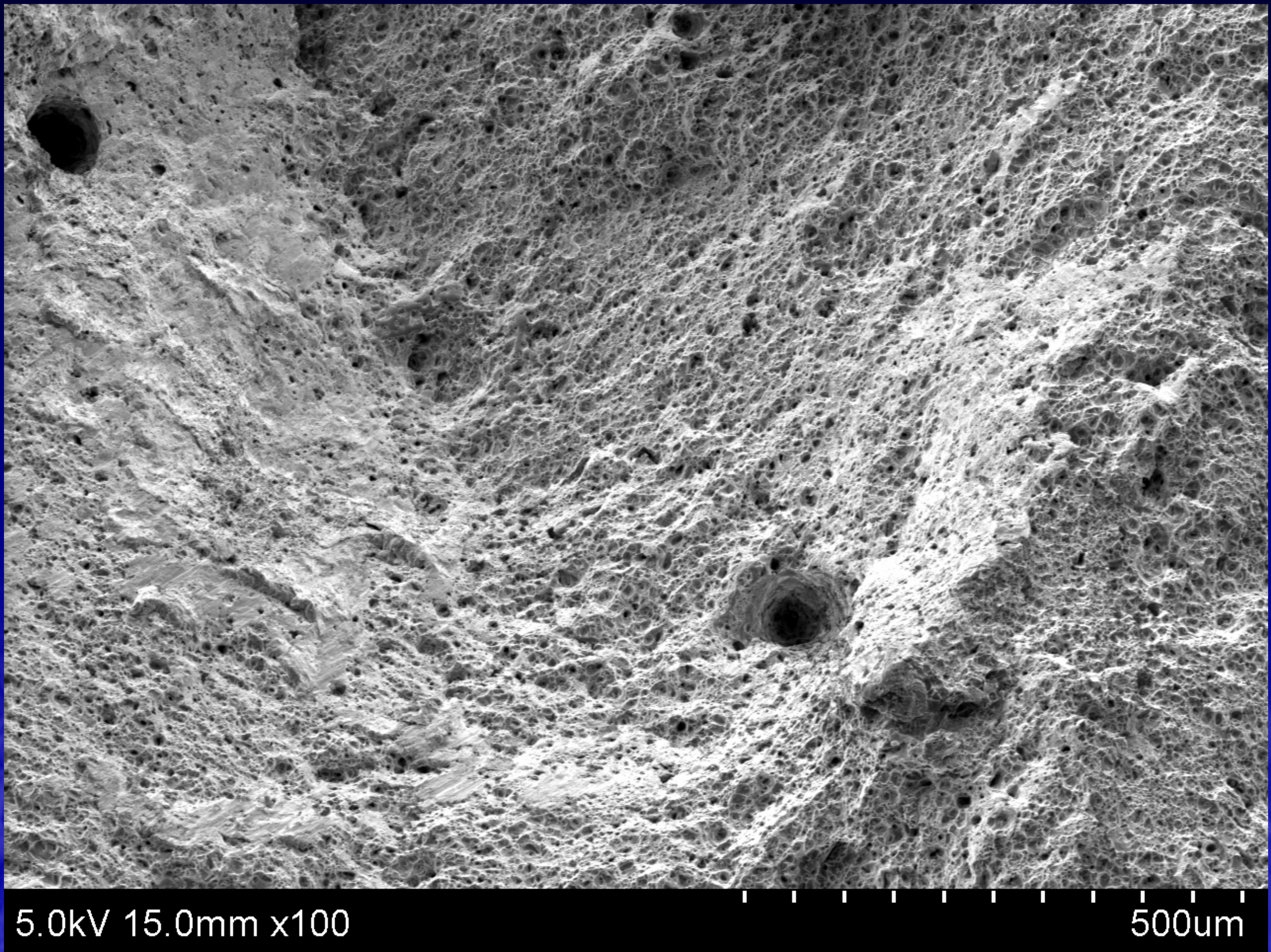
- 5-200 nm diameter particles
- Well-dispersed
- Remain intact upon remelting and resolidification
- Image analysis showed 1.1 – 2.6% C



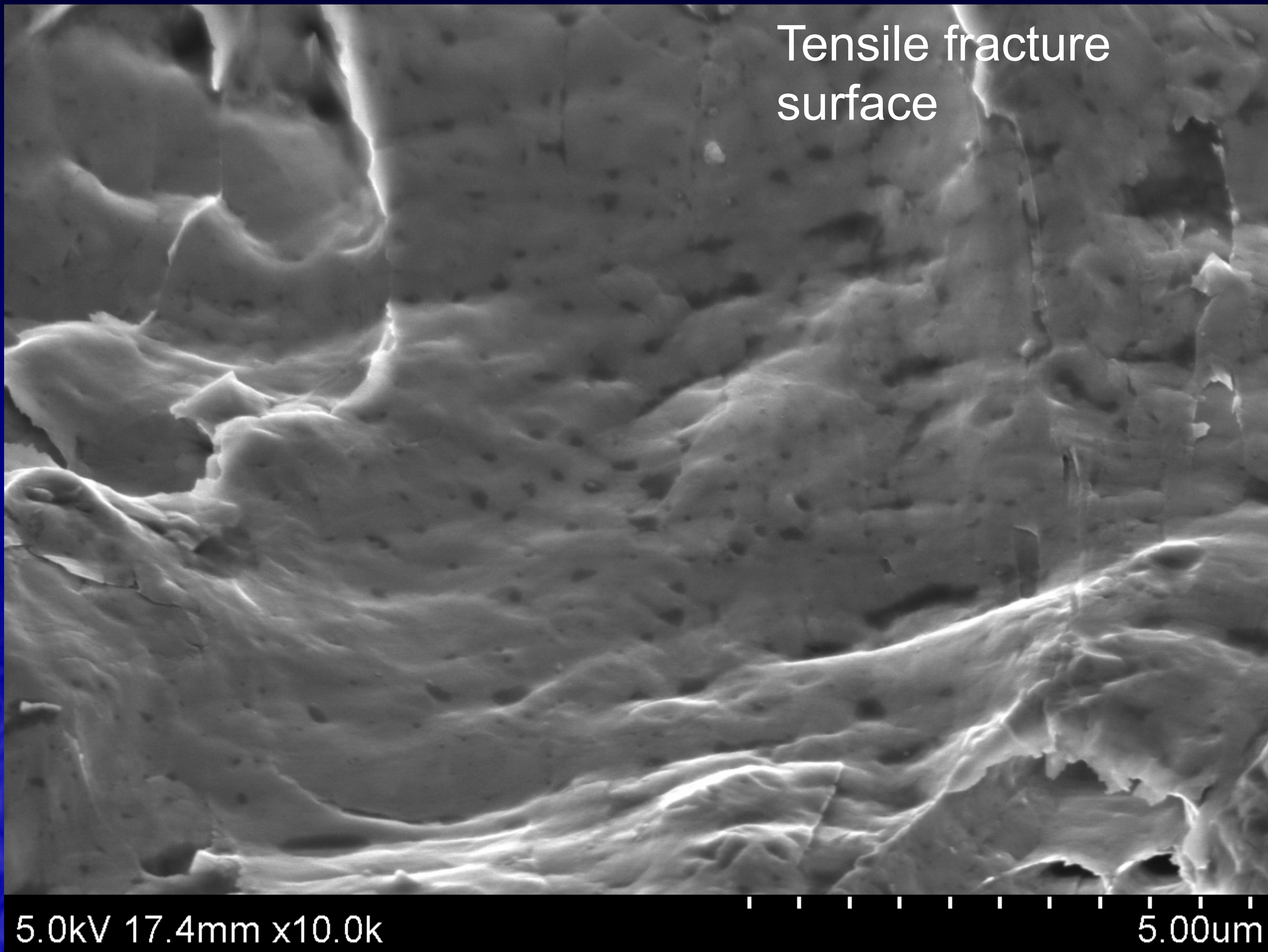


Metallographically polished surface

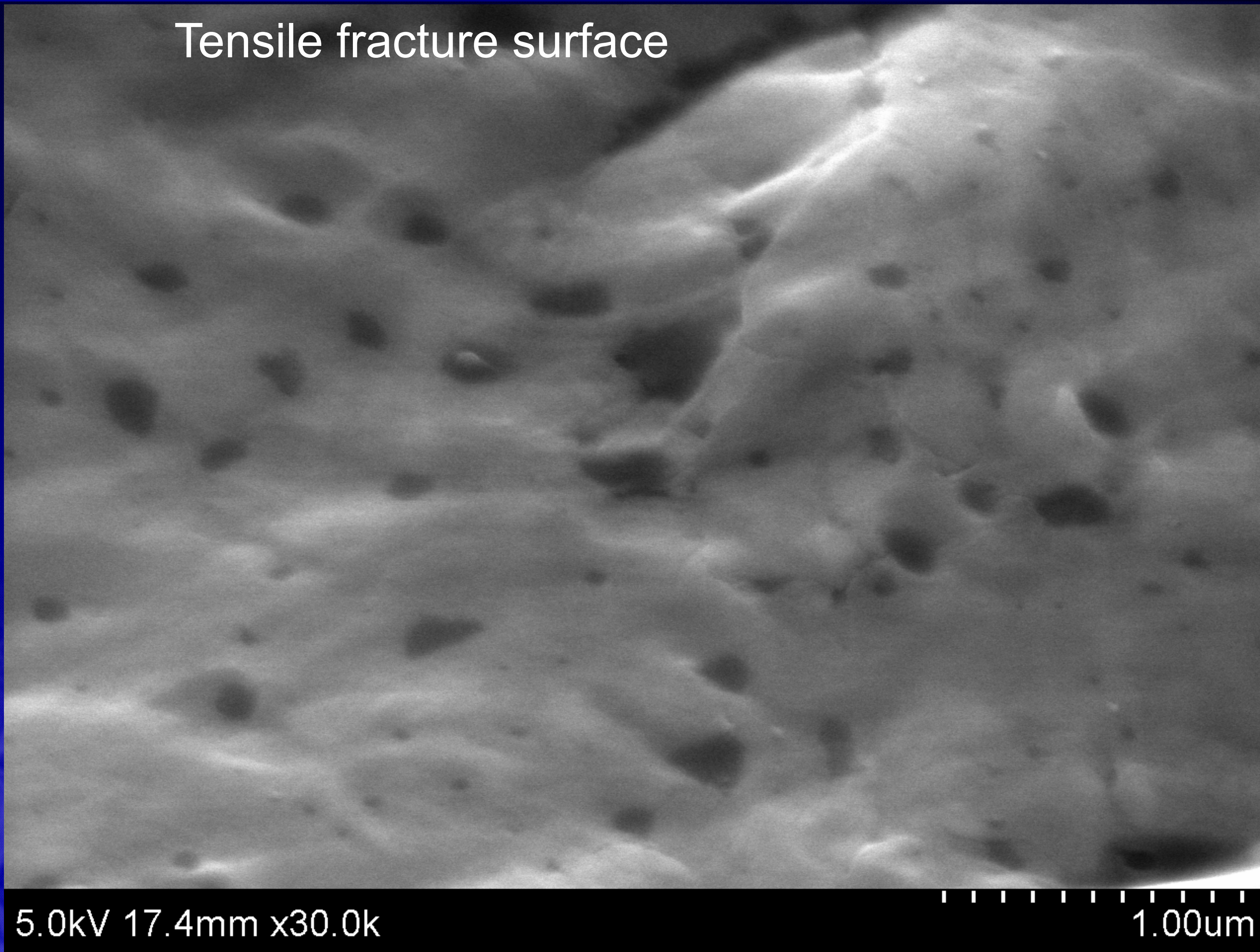
6061 as-extruded, 2.7% nanoC
Tensile fracture surface: ductile



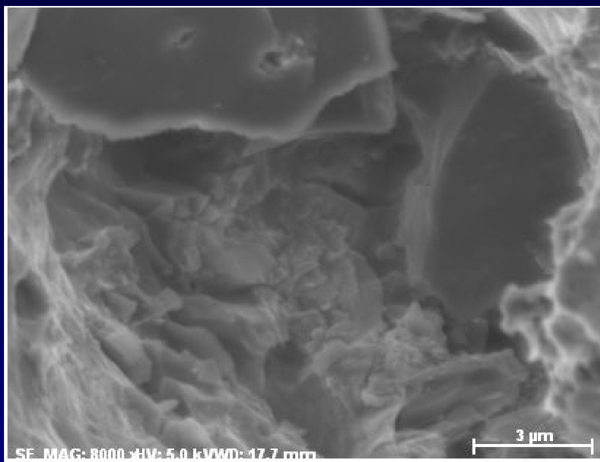
SEM – AA6061 as-extruded, 2.7% nanoC Lourdes Salamanca-Riba



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



SEM – AA6061 as-extruded, 2.7% C



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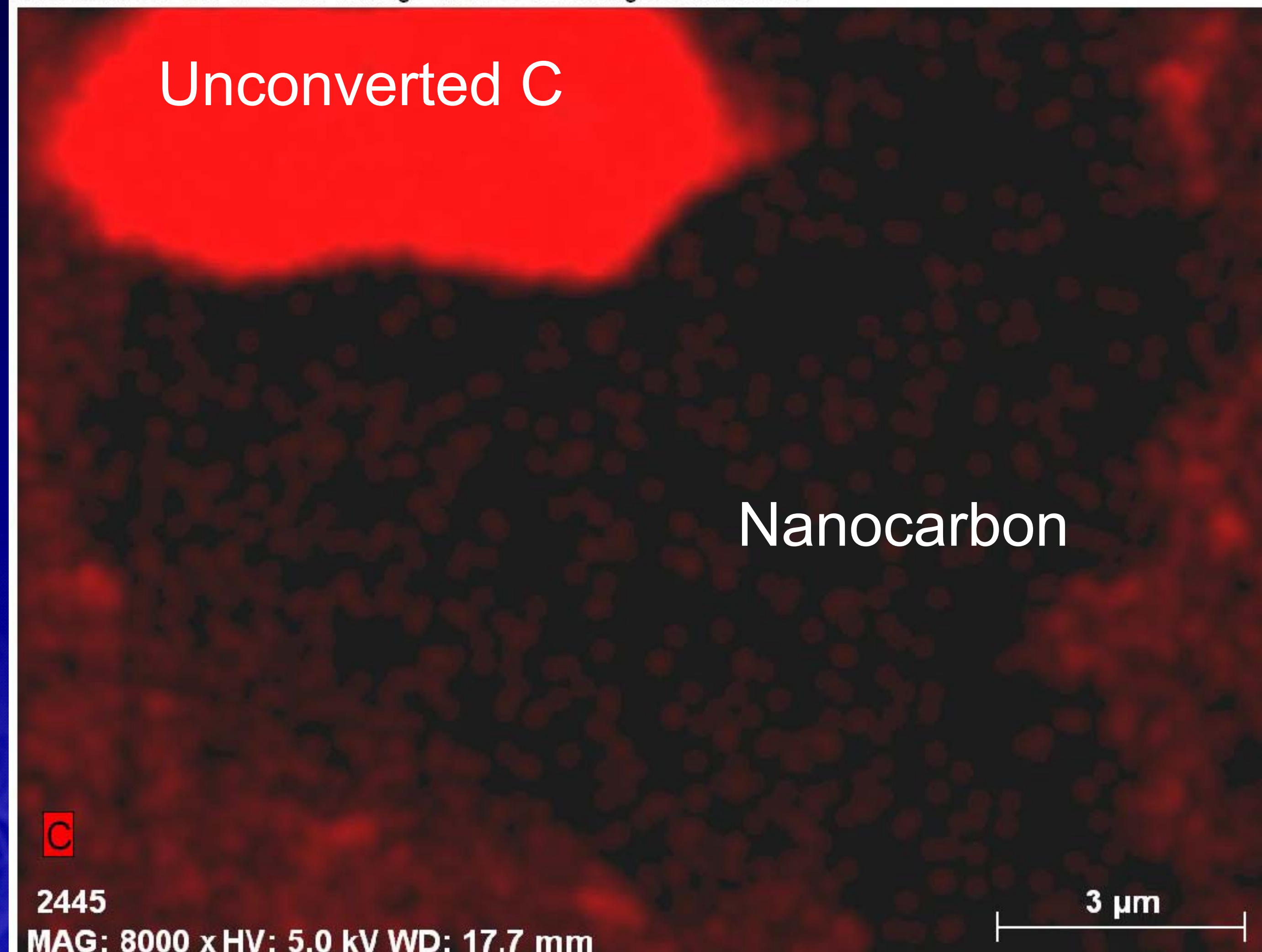
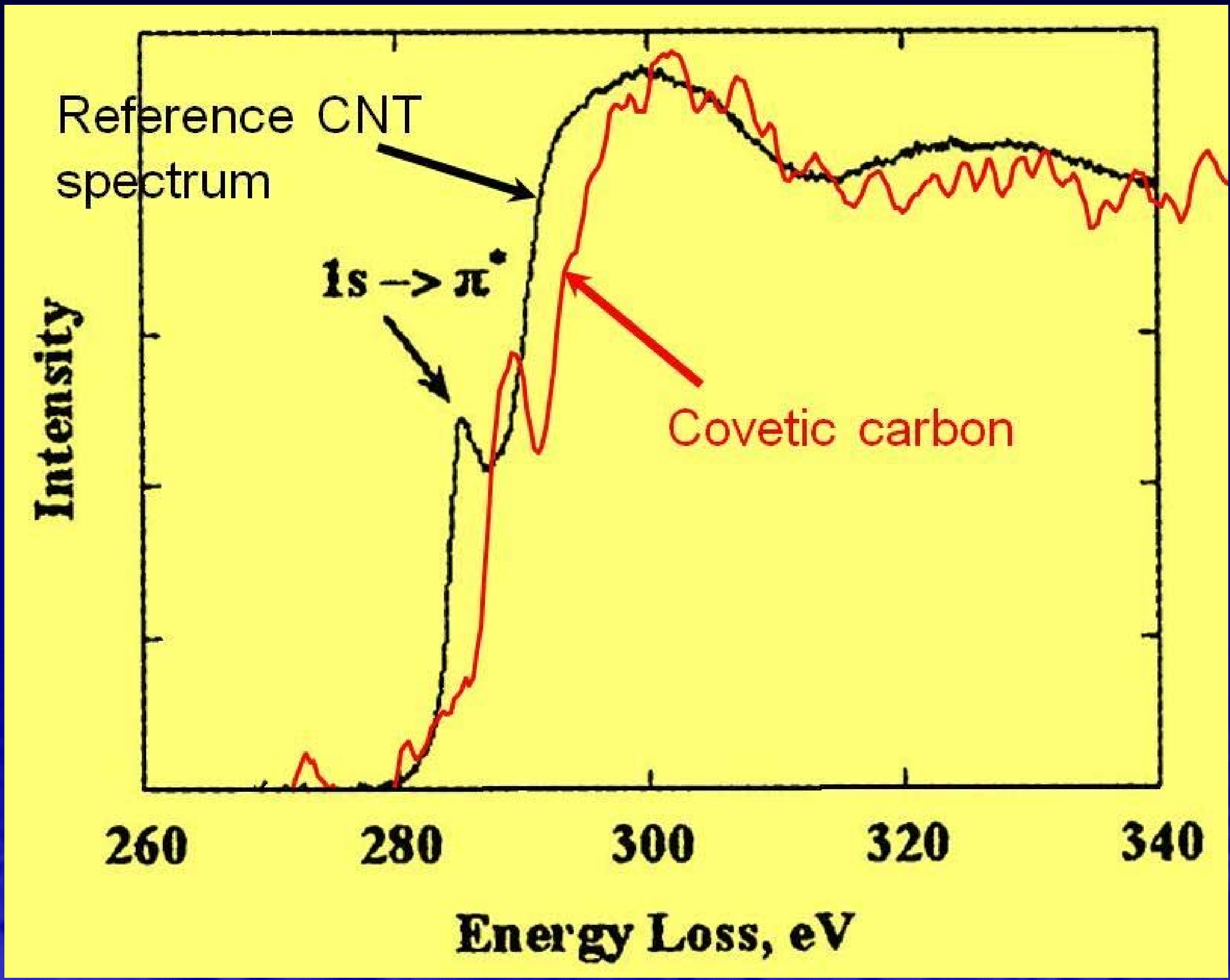


U. Maryland EELS Covetic Spectrum vs. Reference Spectrum of SWCNT



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

C Analysis in Cu Covetic

- Some techniques do not detect nanoscale C
- SEM-EDS and XPS best
- Standardization work needed

Method	Result (wt. %)
LECO	0.0016
DC-PES*	0.56
GDMS	0.0060
XPS (similar sample)	0.21

* Direct Current Plasma Emission Spectroscopy ASTM E1097 to detect Cu

6061 Covetic (wt. %)

- Total carbon (3%) is detectable by EDS and XPS
- Unconverted carbon via LECO and GDMS
- LECO measurement: 0.300 wt. % C

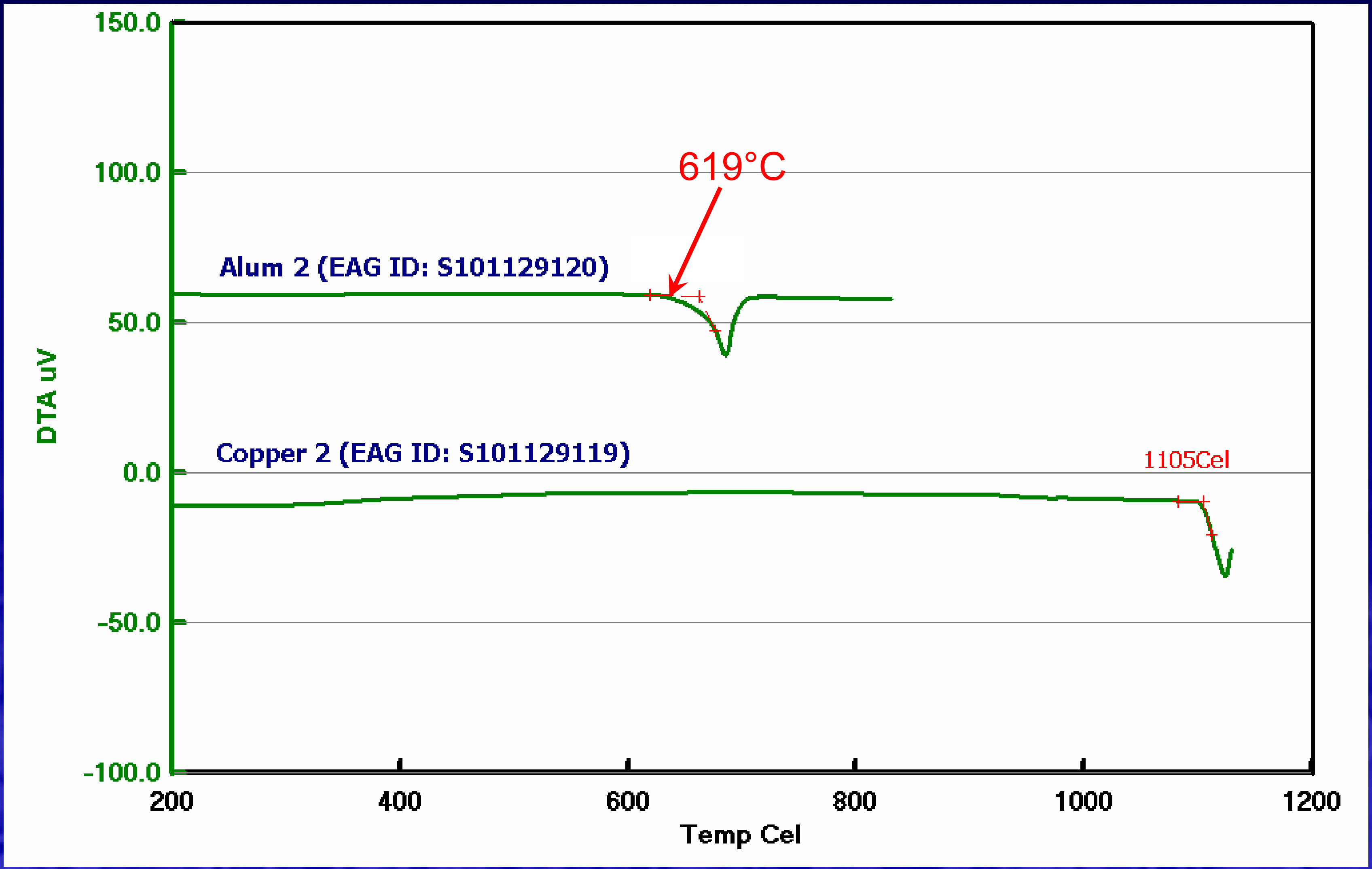
	6061-0	H-49 Covetic	ASTM B211
C	0.003	0.300	0.05 max
Si	0.72	0.71	0.4 – 0.8
Fe	0.25	0.24	0.7 max
Cu	0.18	0.18	0.15 – 0.40
Mn	0.061	0.064	0.15 max
Mg	0.99	1.03	0.8 – 1.2
Cr	0.054	0.057	0.04 – 0.35
Zn	0.080	0.084	0.25 max
Ti	0.088	0.099	0.15 max
V	0.0072	0.0074	0.05 max

Mechanical and Thermophysical Properties

Increased melting point (DTA)

AA6061 solidus: 582°C → 619°C

Copper: 1085°C → 1105°C

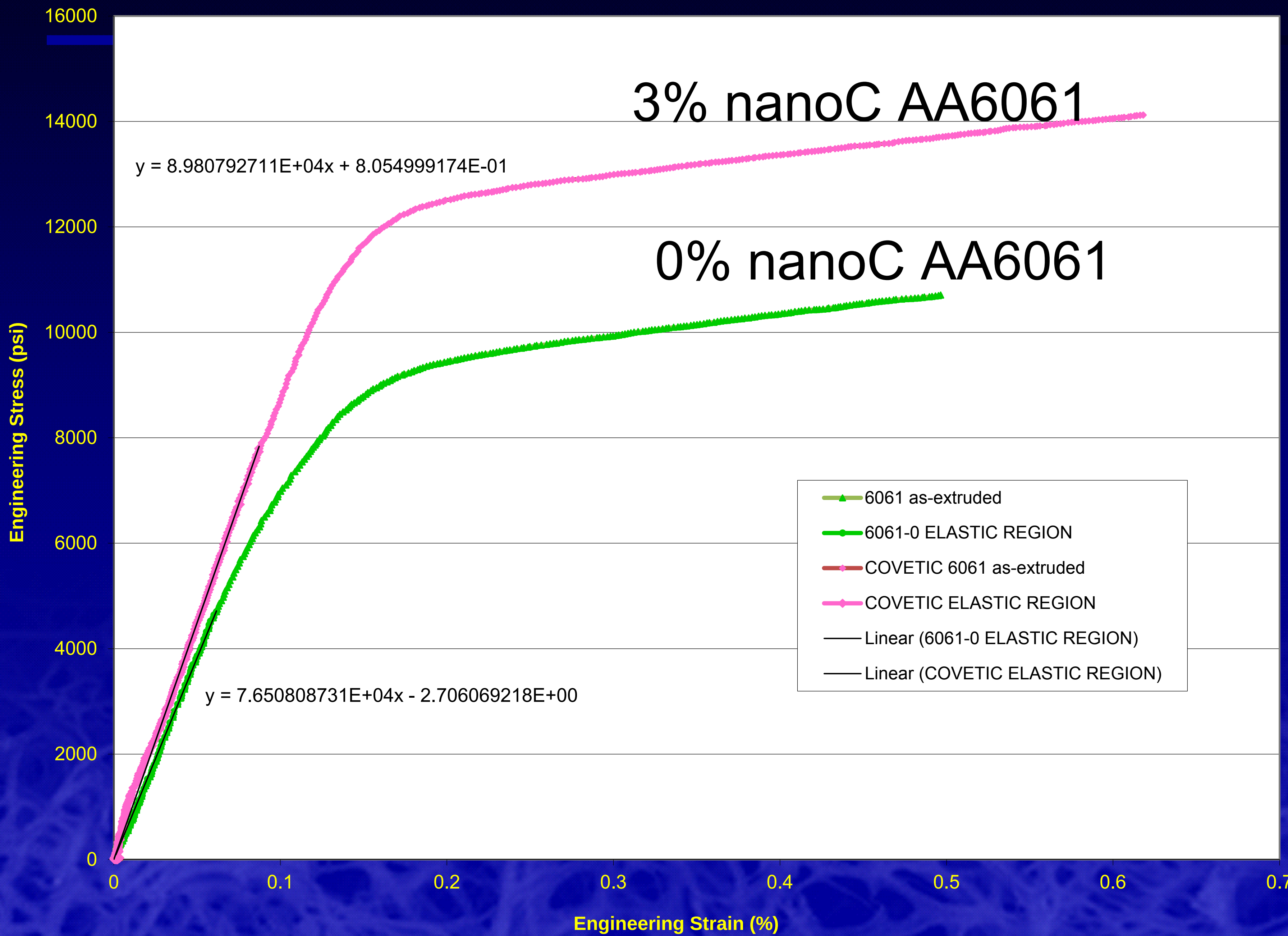


Density
Naval Academy, CDR Lloyd Brown

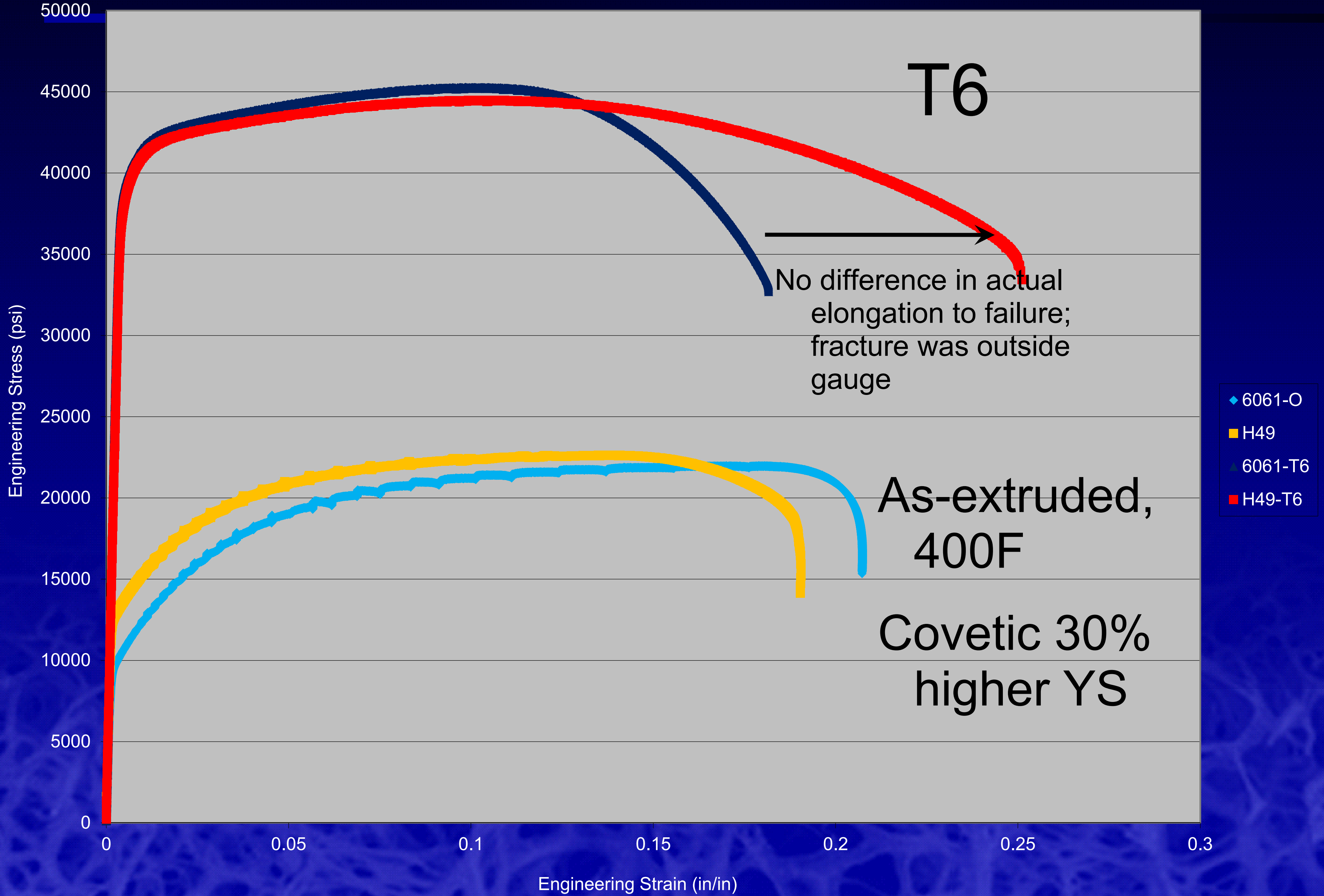
3.8 wt % Cu Covetic

- Compressed 50% in Gleeble to consolidate any porosity
- 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

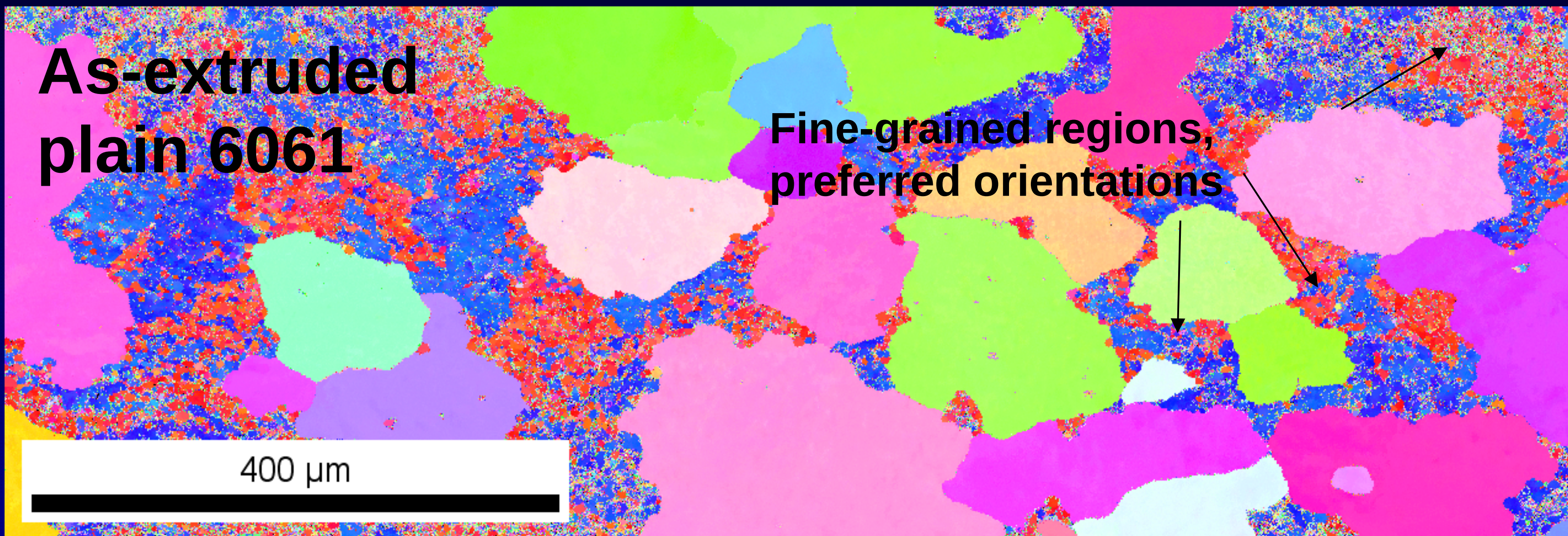
Covetic YS 30% higher as-extruded 400F

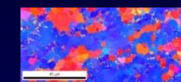


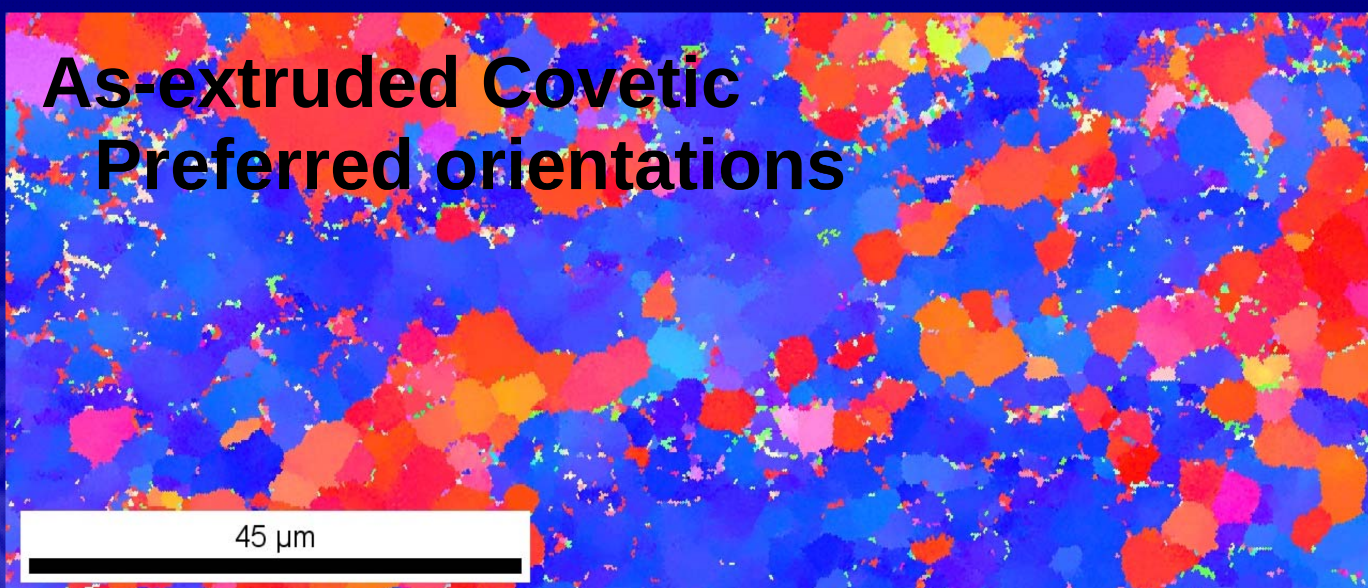
Tensile Curves:
No difference in T6 condition

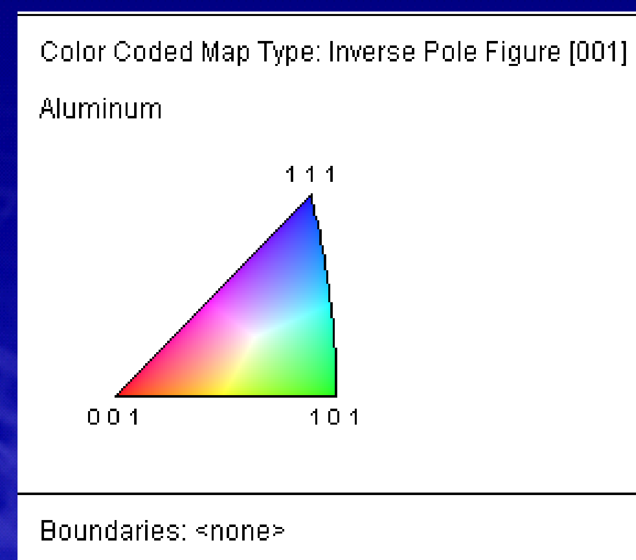


Electron Backscatter Diffraction (Wolk): Covetic resists grain coarsening



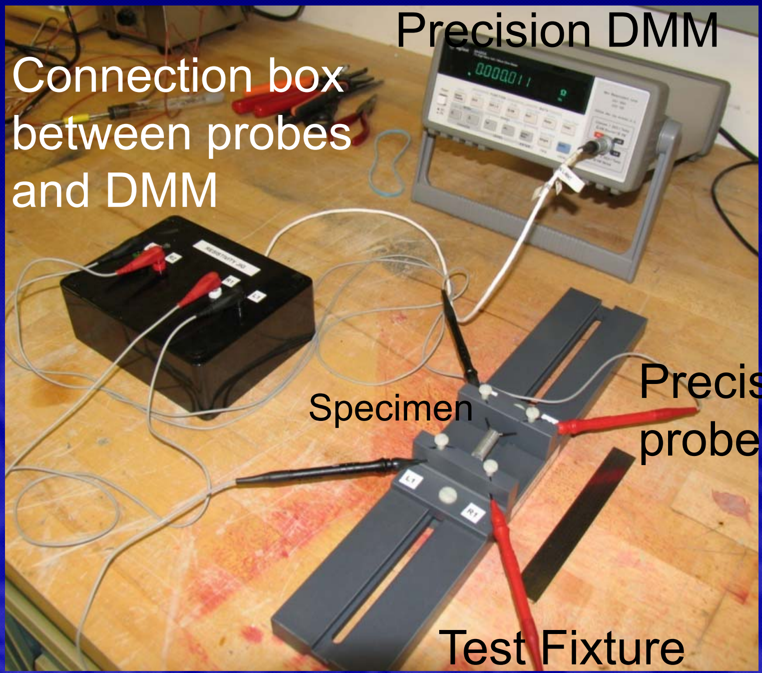




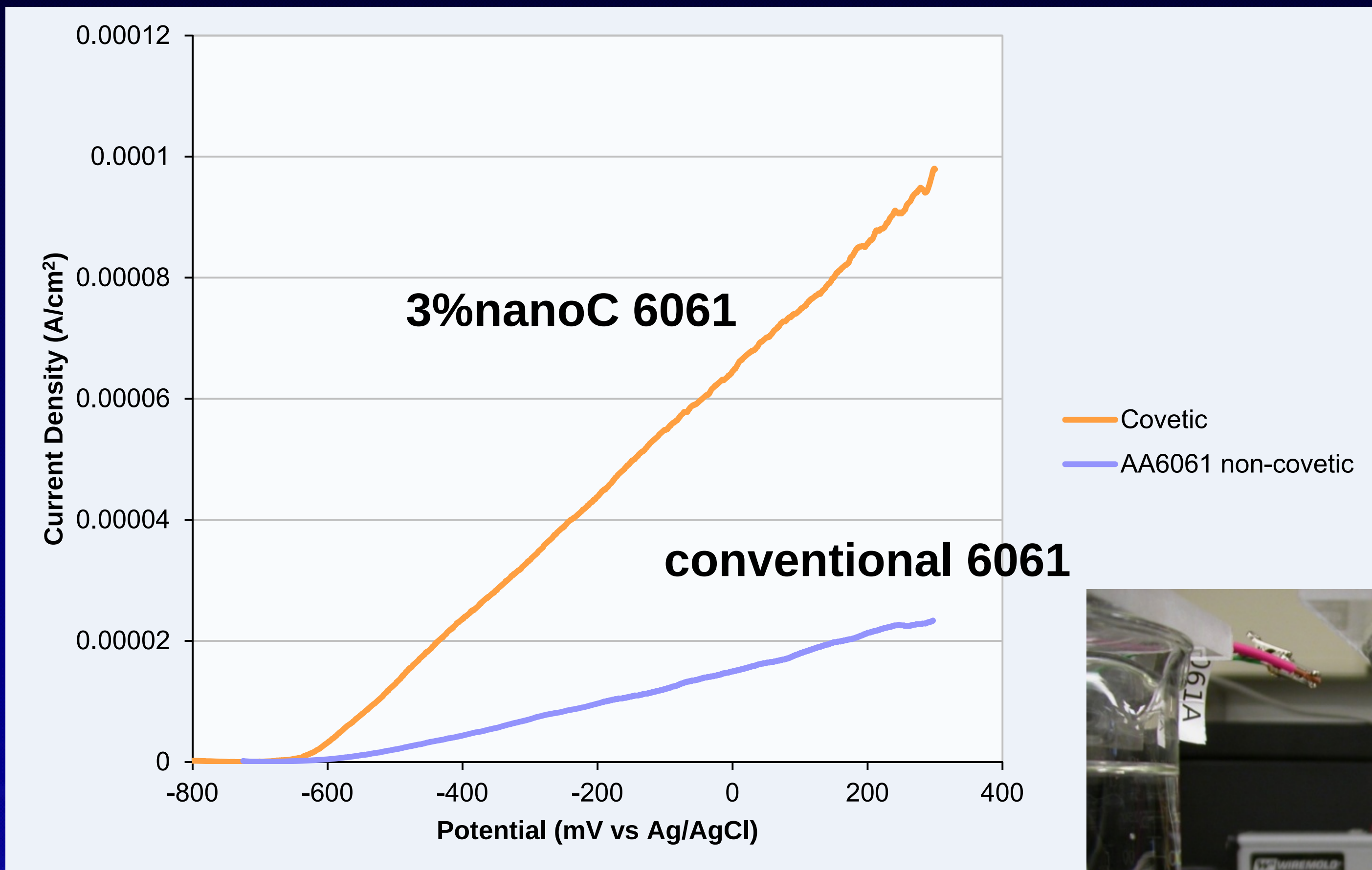


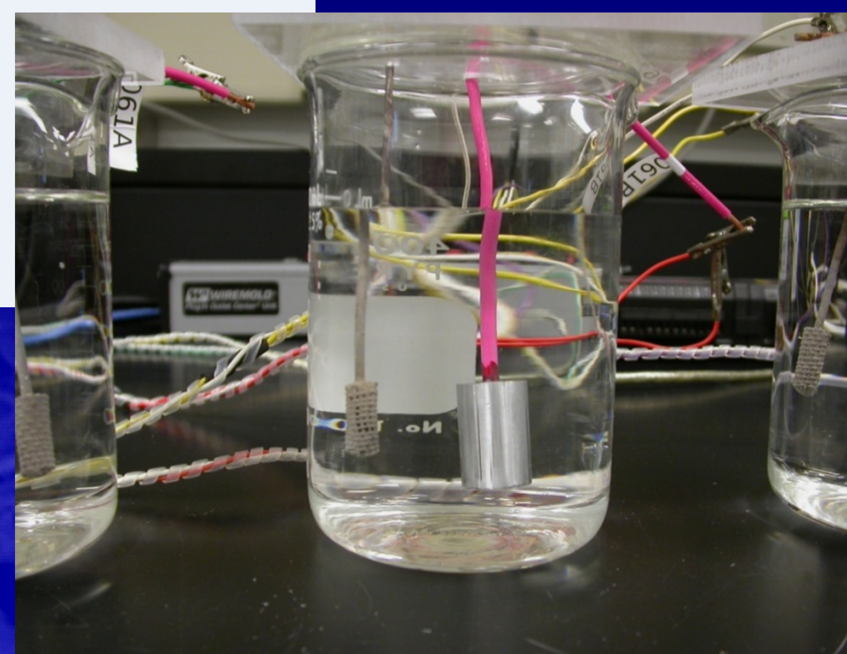
Electrical Conductivity, % IACS

0% C 6061	T6	47.4% Naval Academy
3% C 6061	T6	47.8% Naval Academy
3% C 6061	as-extruded	67.3% Naval Academy
"	"	54% U. Maryland
Electrical grade Al		61.8%



Anodic Polarization in Seawater





Factor of 5 increase in current in artificial seawater: Greater conductivity through the passive film?

Thermal conductivity

Khalid Lafdi (U. Dayton)

- Cold rolled copper
  - 0% nanoC 402 W/m-K
  - 3% nanoC 617 W/m-K in rolling direction
  - 3% nanoC 91 W/m-K orthogonal
- Normal 90Cu-10Ni: 71 W/m-K
  Covetic 90Cu-10Ni: 290 – 460 W/m-K

Energy Materials Testing Laboratory

- As-extruded Cu Covetic
  - 415 W/m-K in rolling direction vs. 402 annealed
  - 334 W/m-K orthogonal

Applications

- Anisotropic, high thermal conductivity Cu
  - Heat exchangers
  - Microelectronics
- High electrical conductivity aluminum
  - High tension lines
  - Electrodes and contacts

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