



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, 50-200 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
- Lower density
- 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.

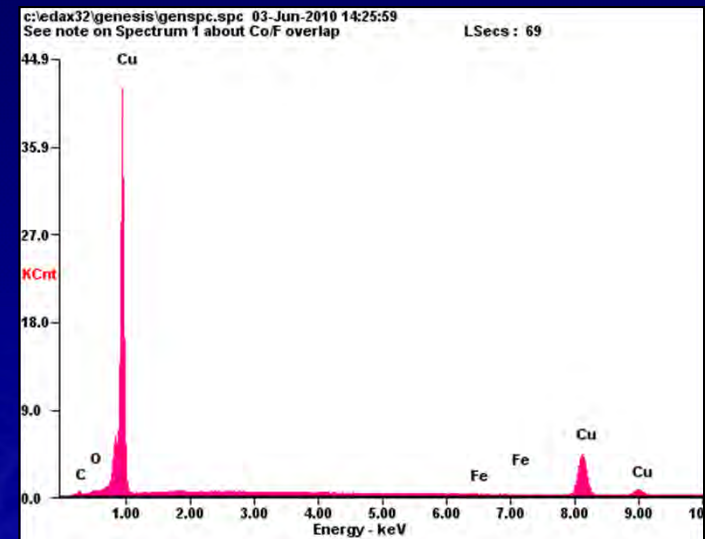
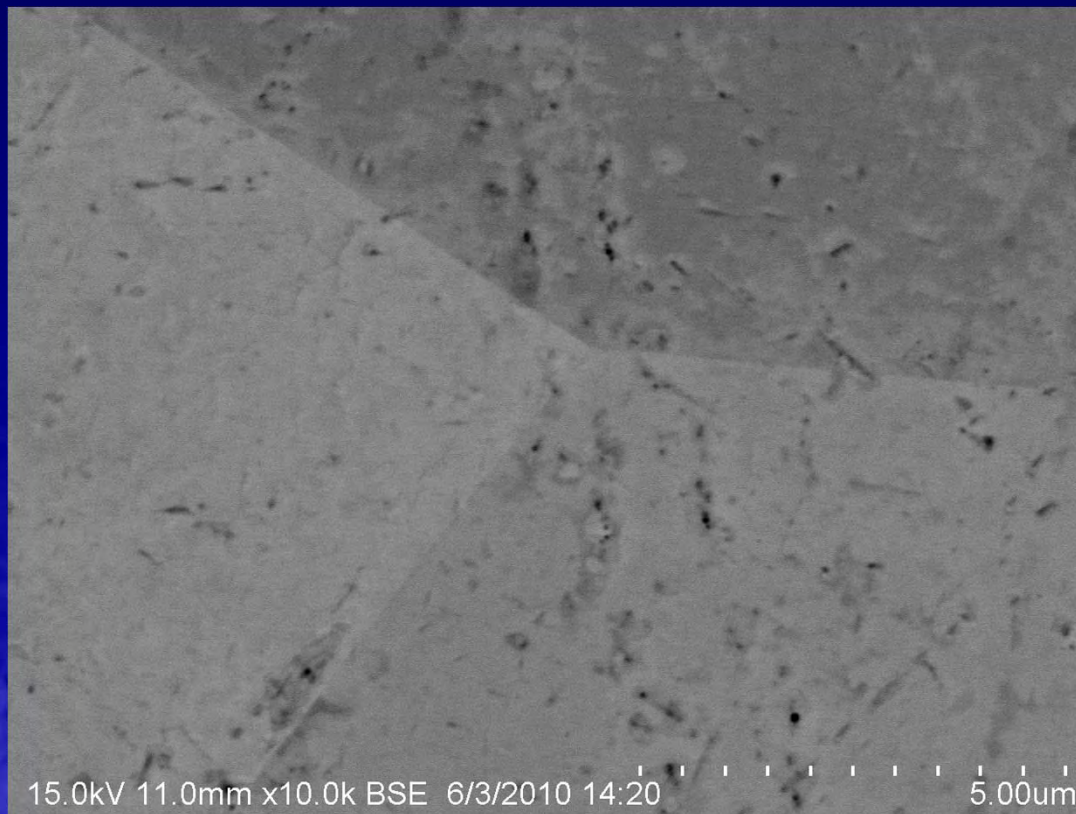
E K Athanassiou , R N Grass and W J Stark, "Large-scale production of carbon-coated copper nanoparticles for sensor applications," *Nanotechnology*, v. 17, no. 6, 28 March 2006.

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

- 50-200 nm diameter particles
- Well-dispersed
- Remain intact upon remelting and resolidification

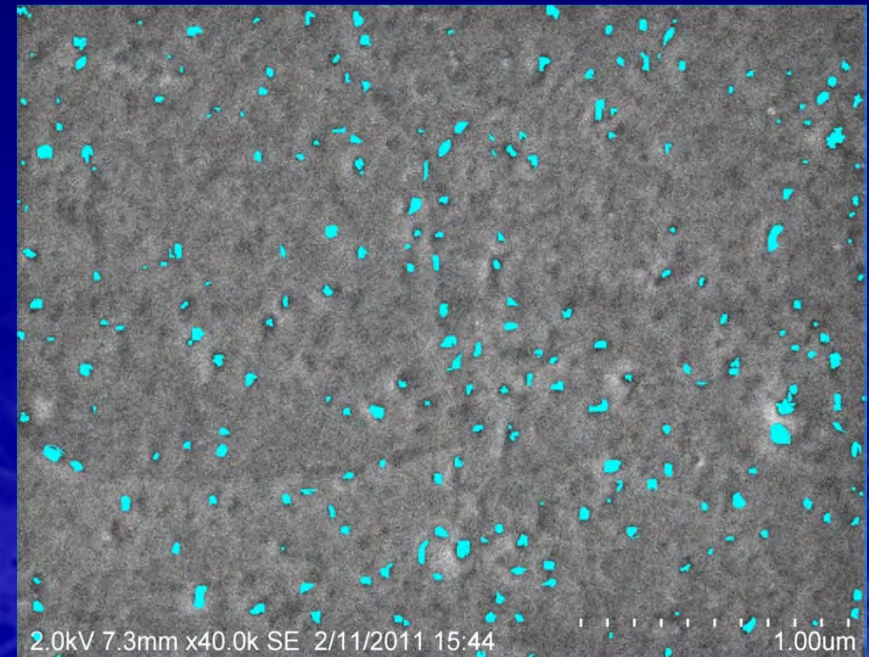
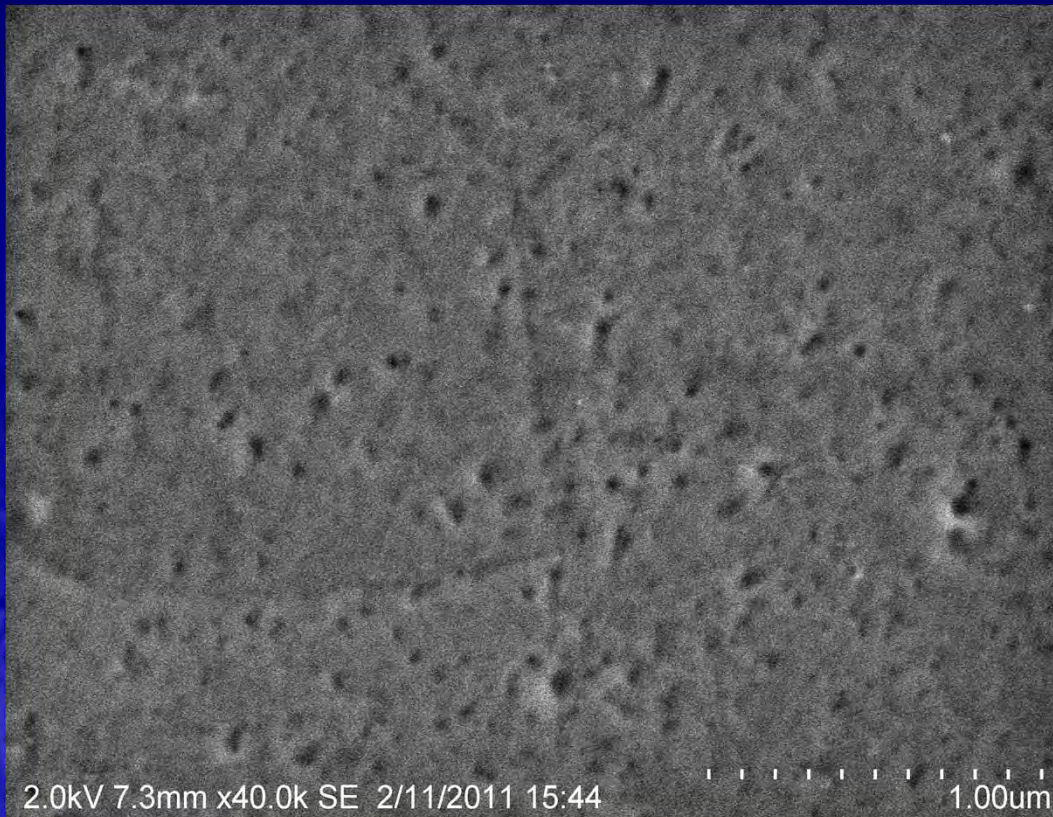


Element	Wt %	At %
C K	03.78	16.65
O K	01.29	04.25
Fe K	00.32	00.30
Cu K	94.61	78.79

Metallographically as-polished surface

SEM – AA6061 as-extruded, 2.7% nanoC

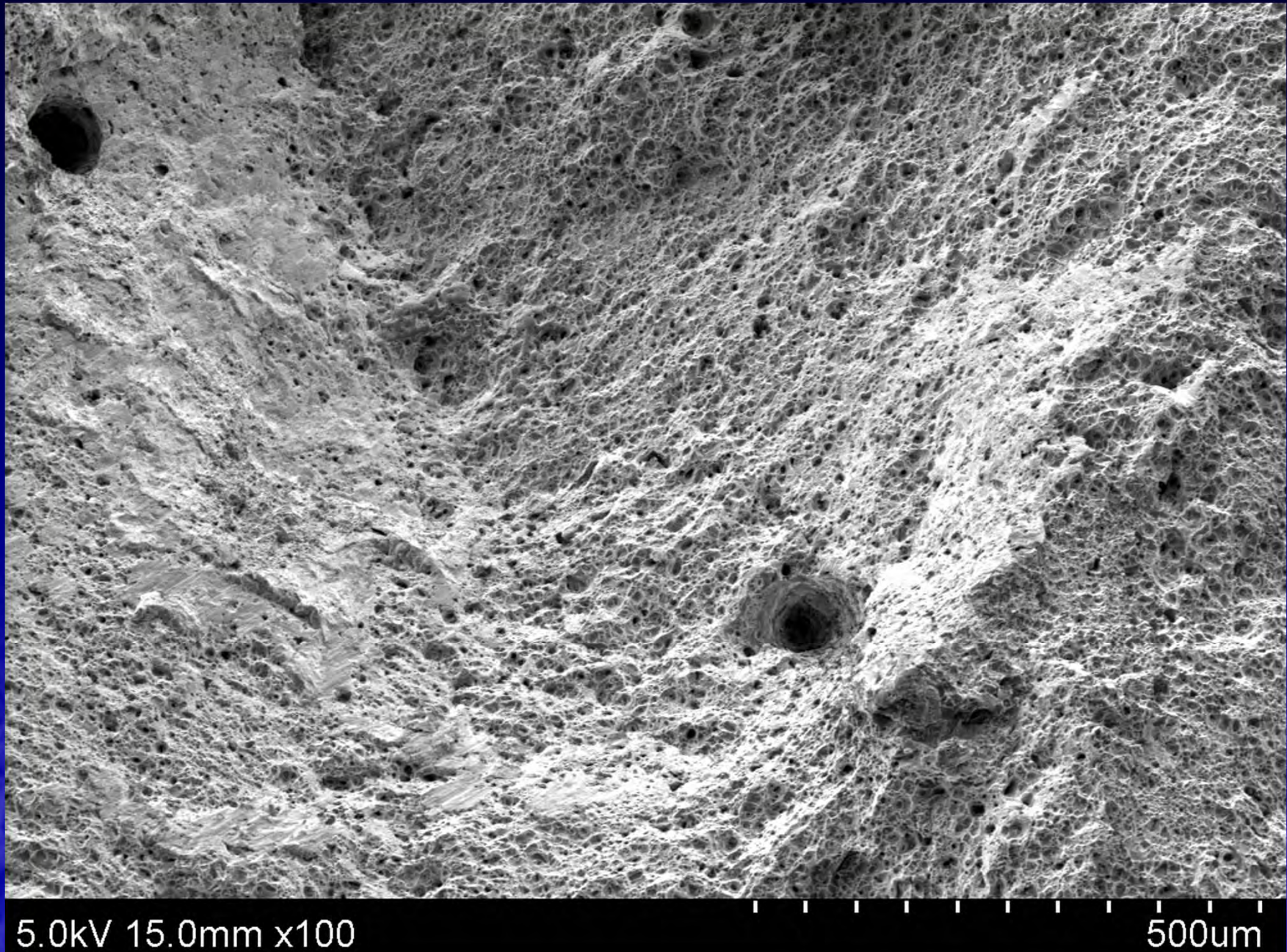
- 50-200 nm diameter particles
- Well-dispersed
- Remain intact upon remelting and resolidification
- Image analysis showed 1.1 – 2.6% C



Metallographically polished surface

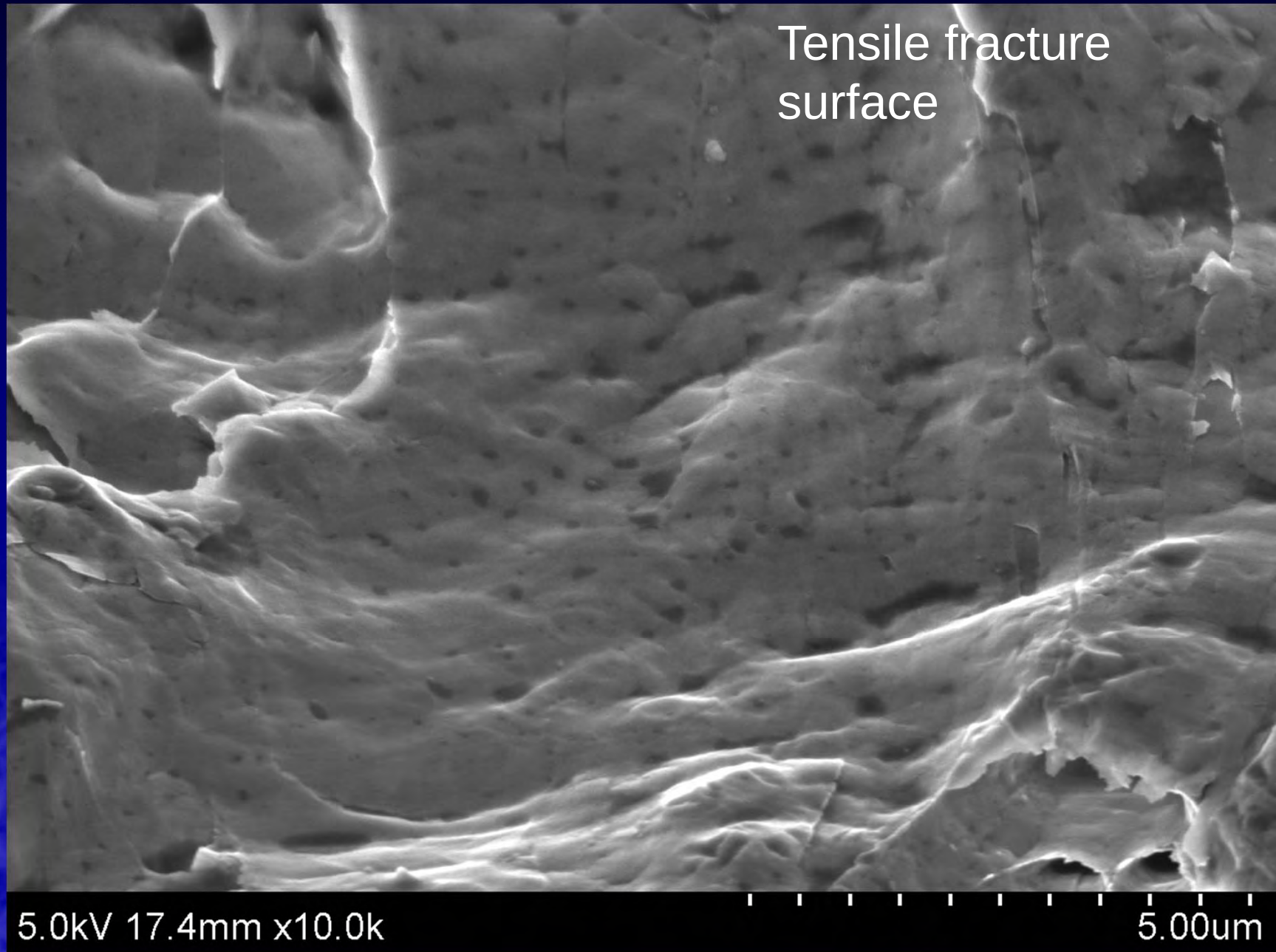
6061 as-extruded, 2.7% nanoC

Tensile fracture surface: ductile



SEM — AA6061 as-extruded, 2.7% nanoC

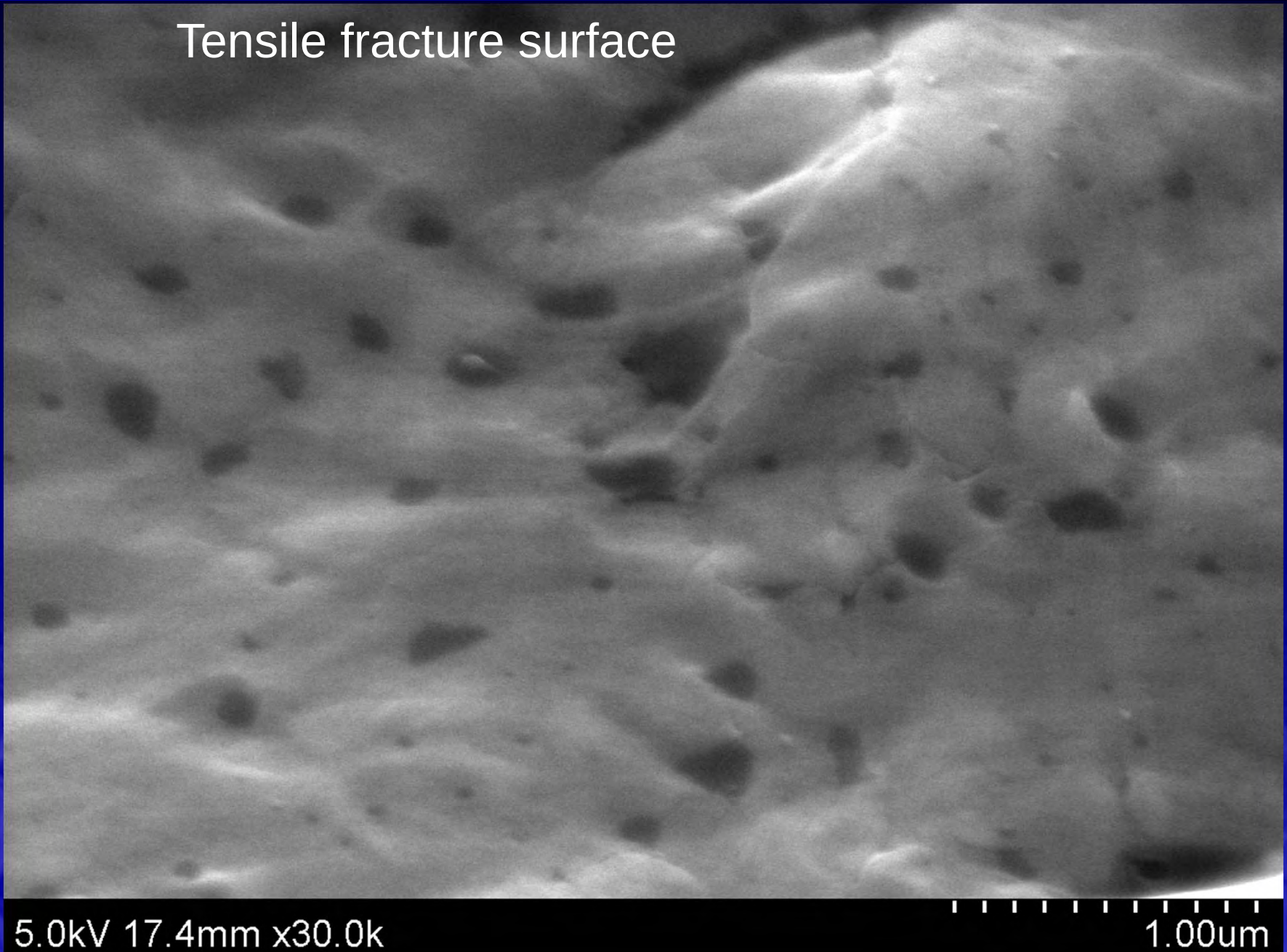
Lourdes Salamanca-Riba



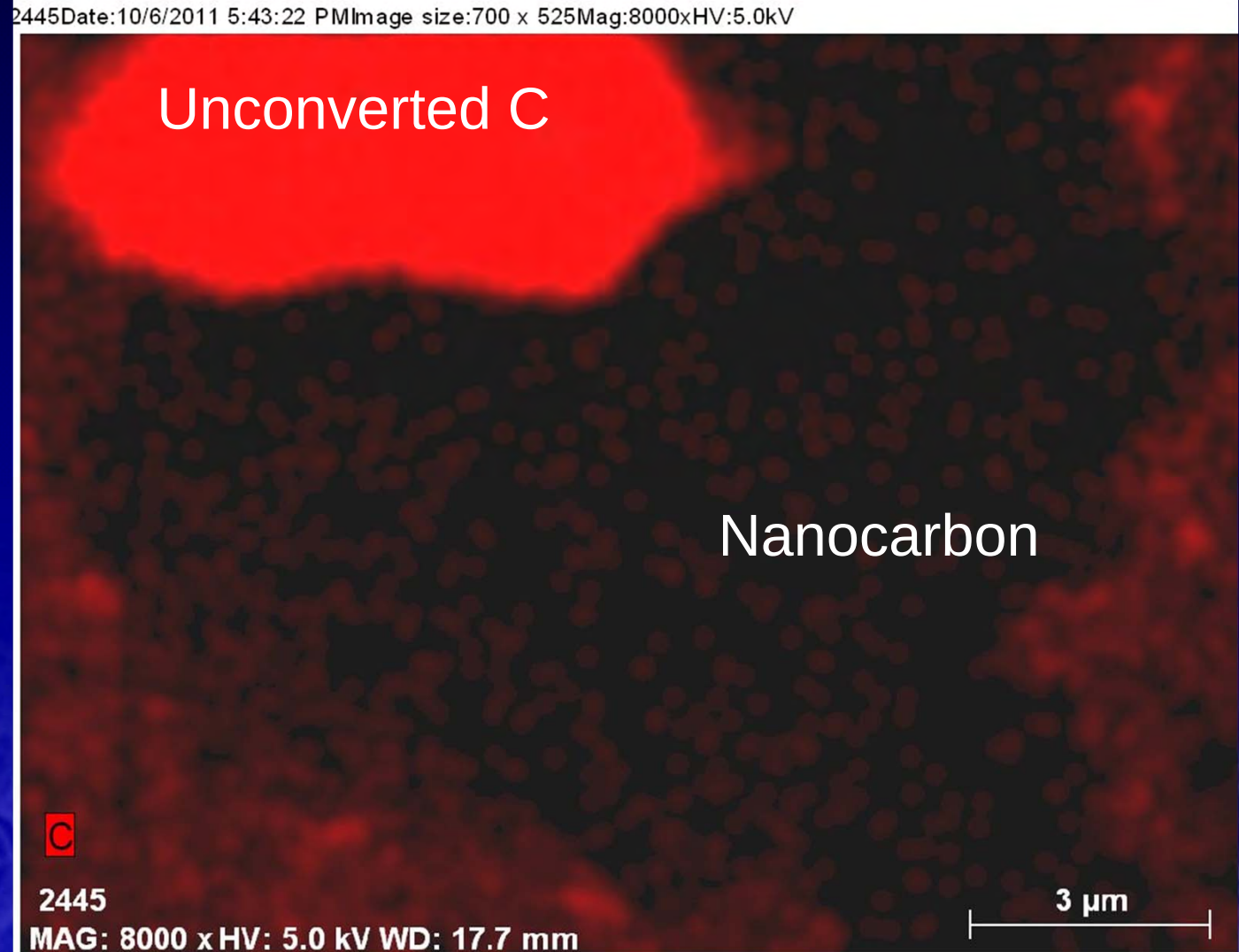
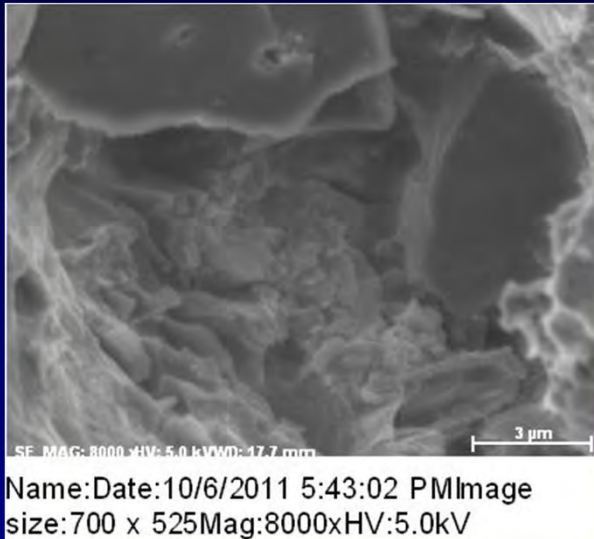
SEM — AA6061 as-extruded, 2.7% nanoC

Lourdes Salamanca-Riba

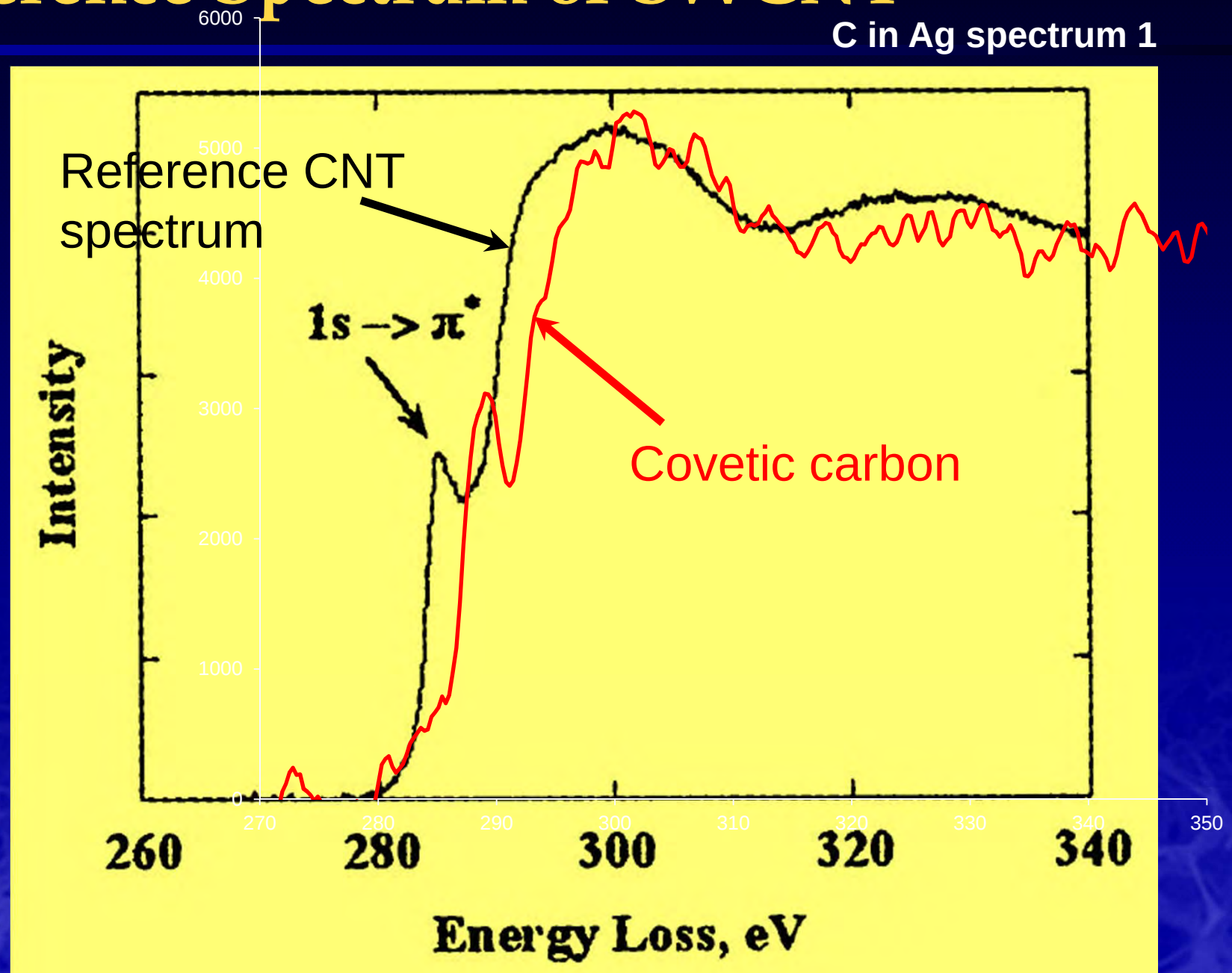
Tensile fracture surface



SEM – AA6061 as-extruded, 2.7% C



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



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
SEM-EDS	3.8
XPS (similar sample)	3.5
Density	< 4.3
% C reportedly added to the heat in the conversion process	5

* 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

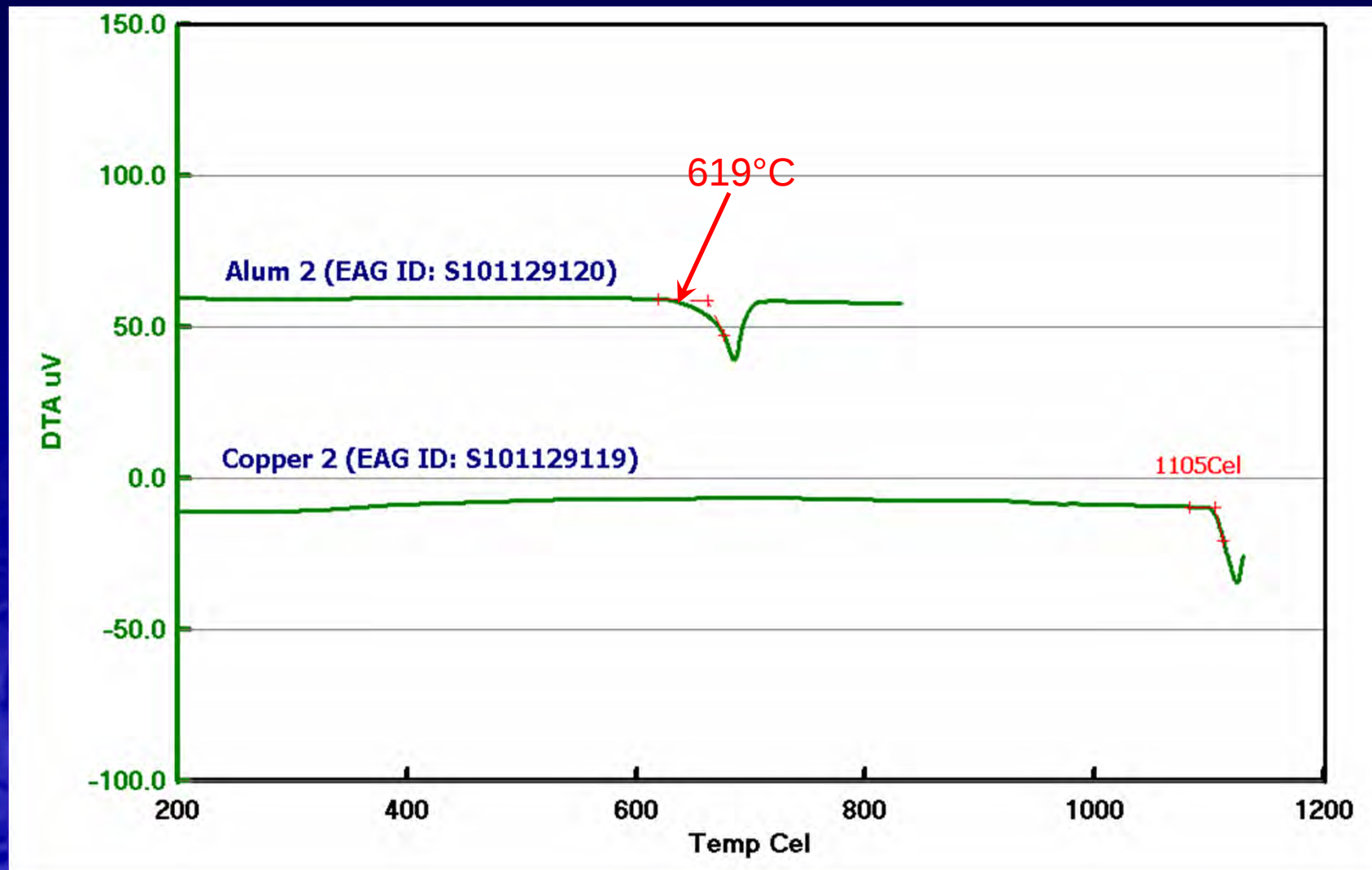
	6061-0	H-49 Covetic	ASTM B211
C	0.003	0.300	0.05 max
Si	0.72	0.71	0.4 – 0.8
Fe	0.25	0.24	0.7 max
Cu	0.18	0.18	0.15 – 0.40
Mn	0.061	0.064	0.15 max
Mg	0.99	1.03	0.8 – 1.2
Cr	0.054	0.057	0.04 – 0.35
Zn	0.080	0.084	0.25 max
Ti	0.088	0.099	0.15 max
V	0.0072	0.0074	0.05 max

Mechanical and Thermophysical Properties

Increased melting point (DTA)

AA6061 solidus: $582^{\circ}\text{C} \rightarrow 619^{\circ}\text{C}$

Copper: $1085^{\circ}\text{C} \rightarrow 1105^{\circ}\text{C}$



Density

Naval Academy, CDR Lloyd Brown

As-cast Cu Covetic

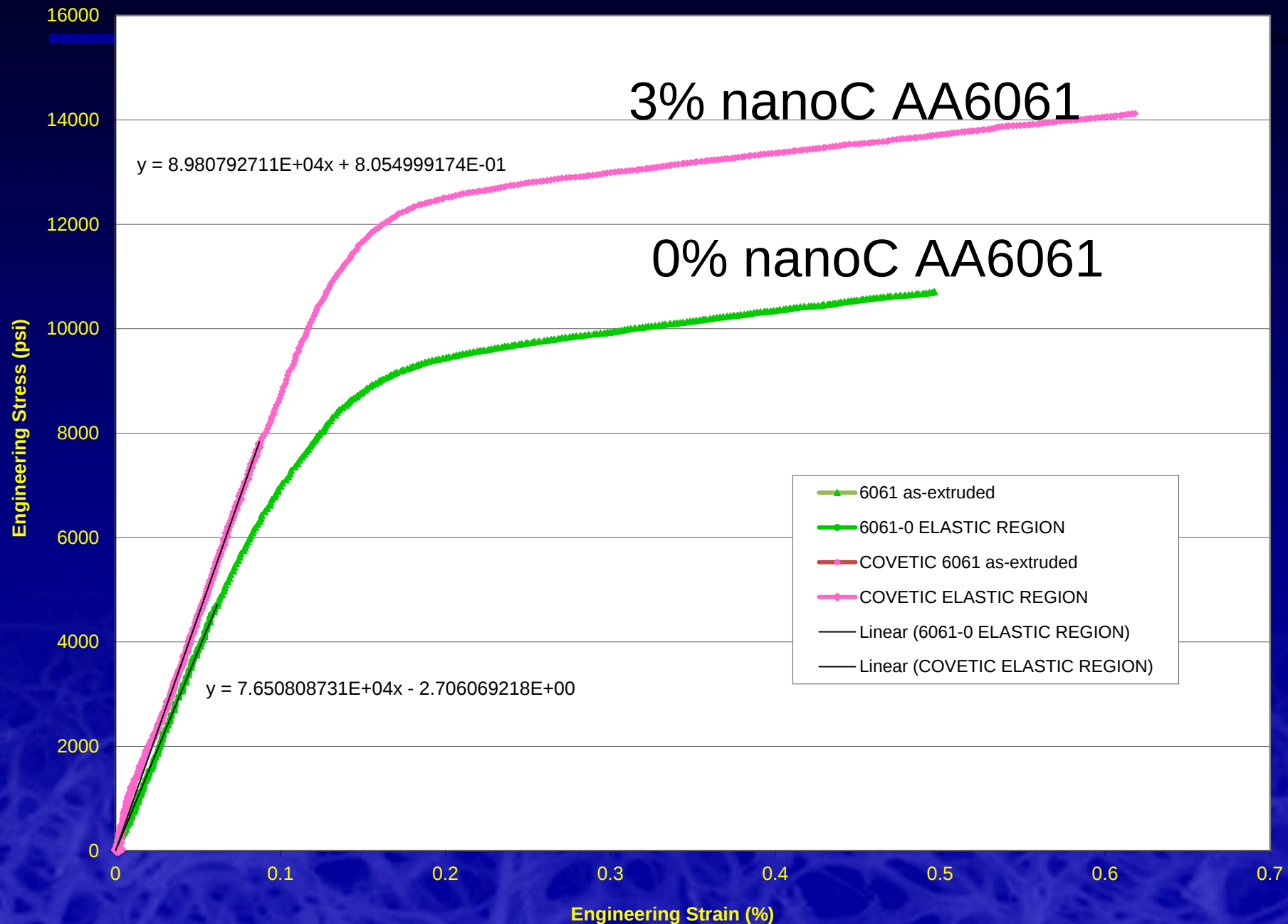
- Density = 7.92 g/cm³ covetic
8.94 g/cm³ pure Cu
- Assuming $\rho_{\text{Cu}} = 8.94 \text{ g/cm}^3$ and $\rho_{\text{C}} = 2.25 \text{ g/cm}^3$,
carbon content $\leq 4.33 \text{ wt}\%$
- Roughly consistent with EDS measurement = 3.8%



Extruded 6061

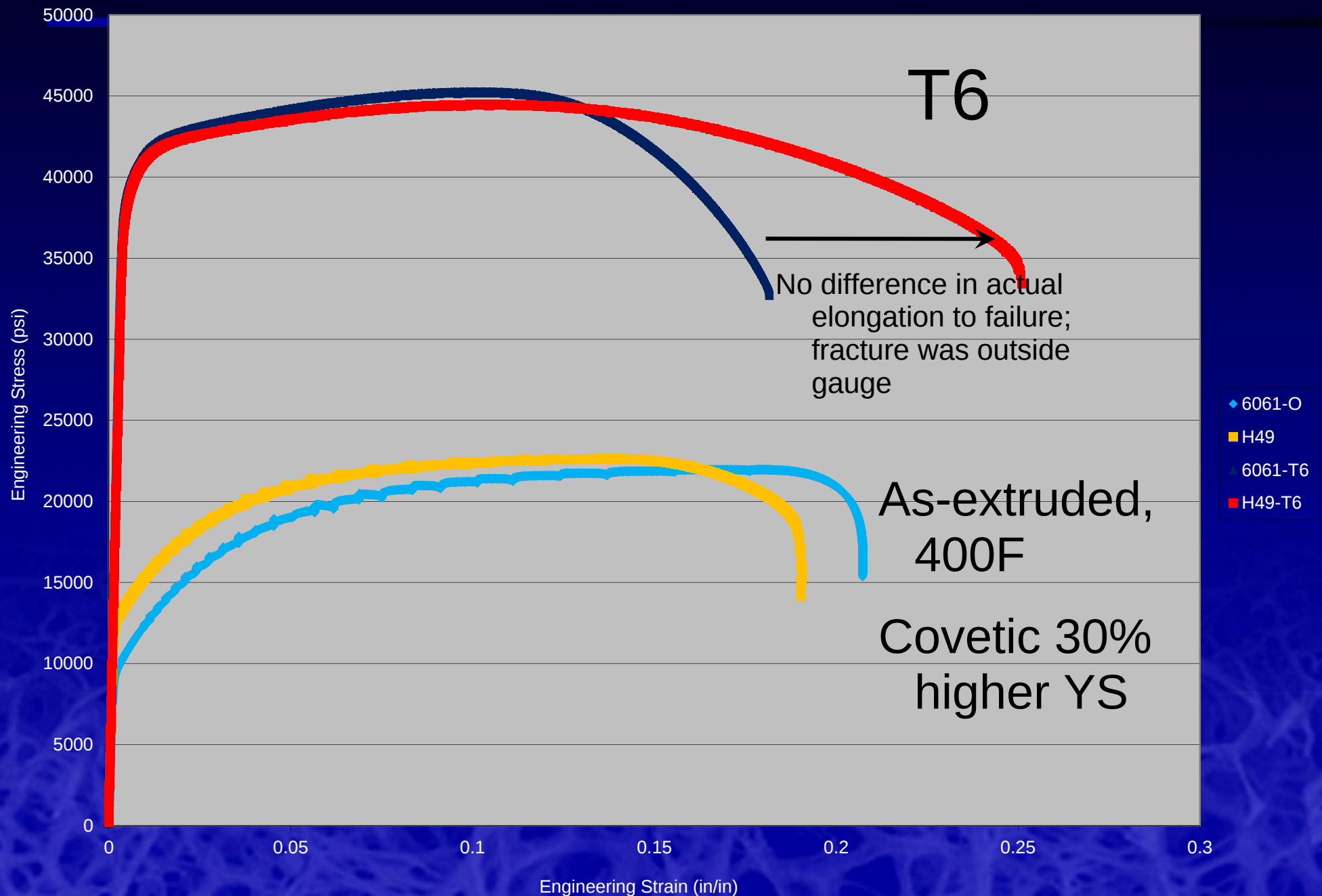
- Density = 2.6729 g/cm³ 3% C
2.6775 g/cm³ 0% C
- Assuming $\rho_{\text{C}} = 2.25 \text{ g/cm}^3$,
carbon content by density = 0.91 wt% vs 3

Covetic YS 30% higher as-extruded 400F

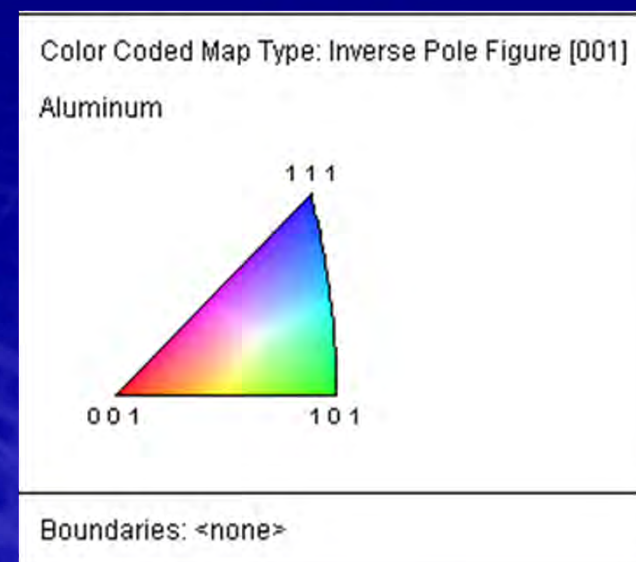
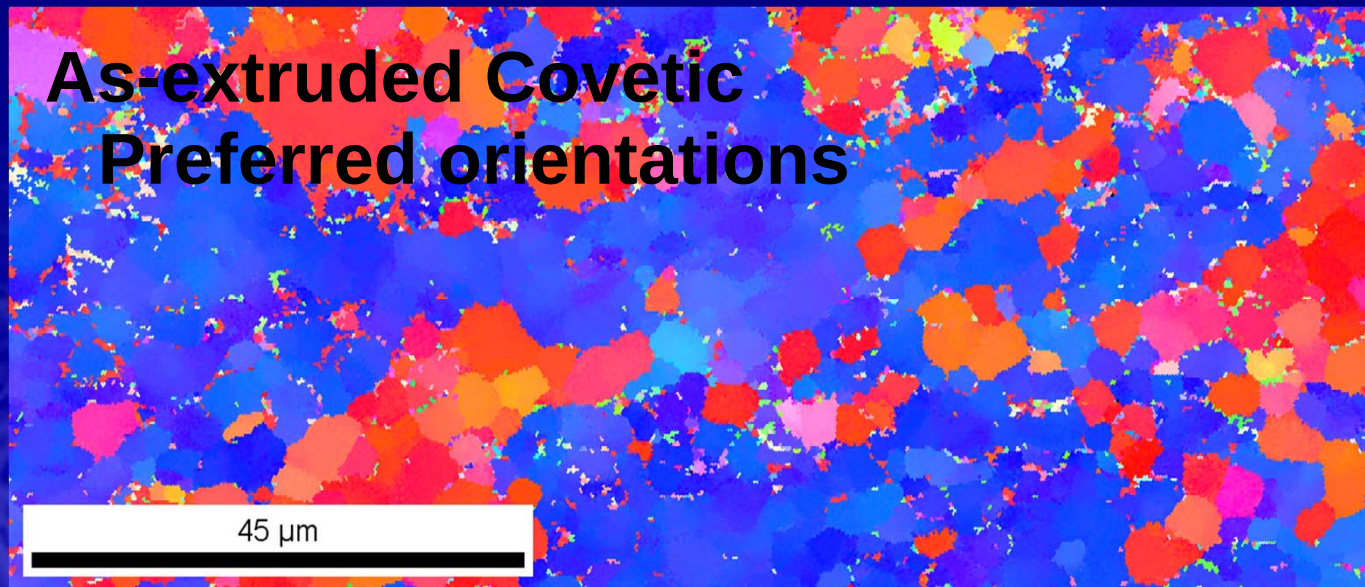
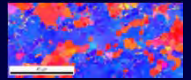
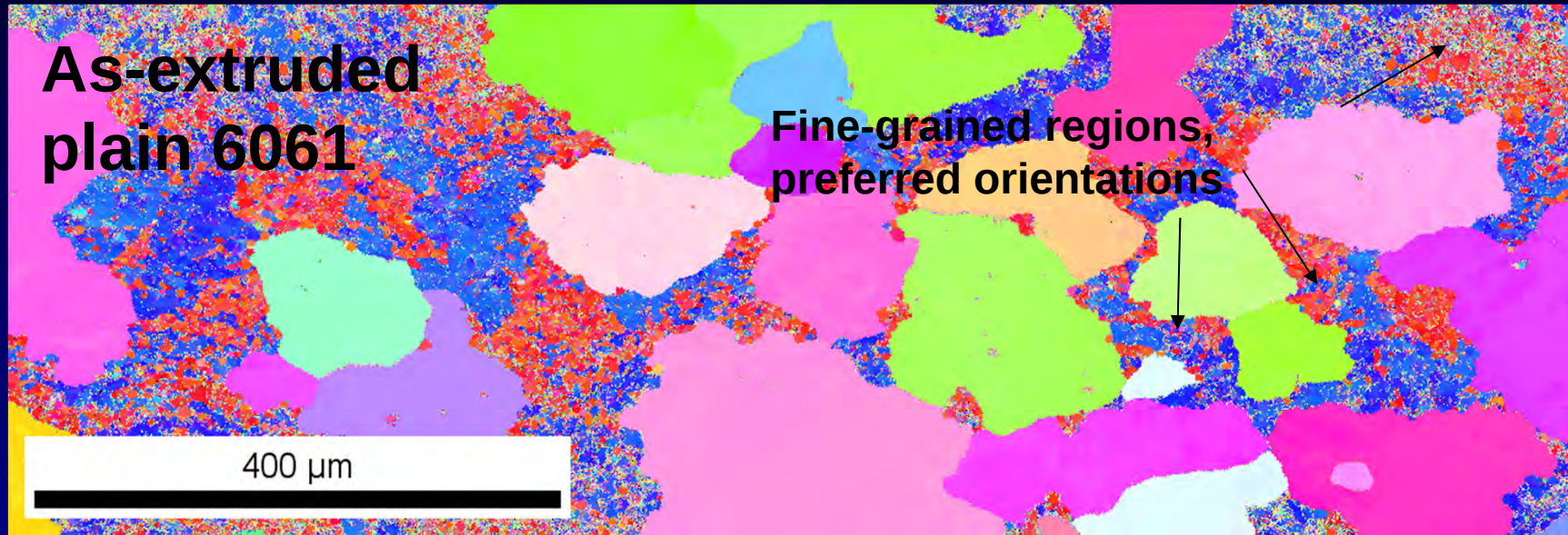


Tensile Curves:

No difference in T6 condition

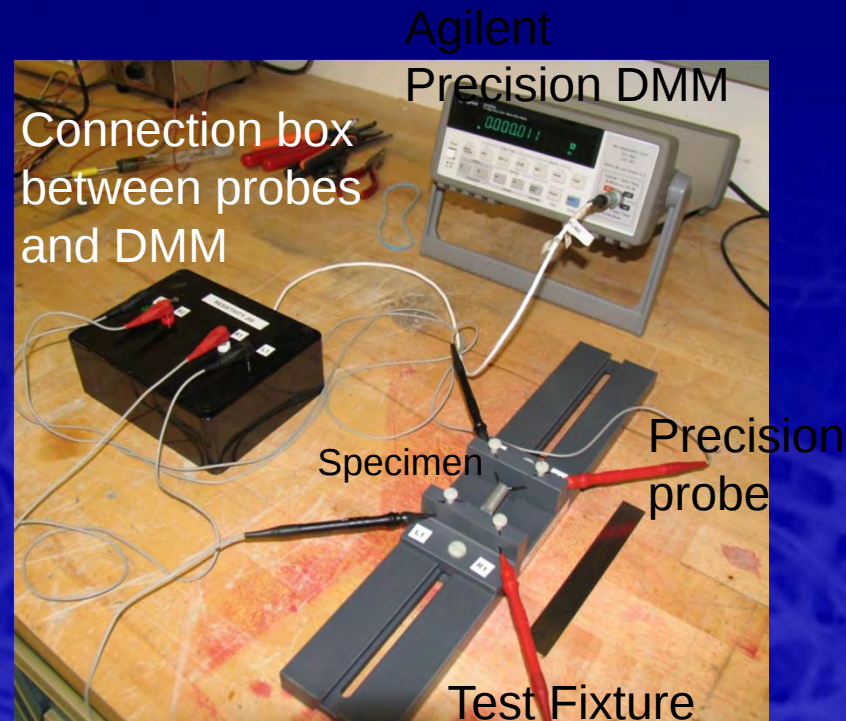


Electron Backscatter Diffraction (Wolk): Covetic resists grain coarsening

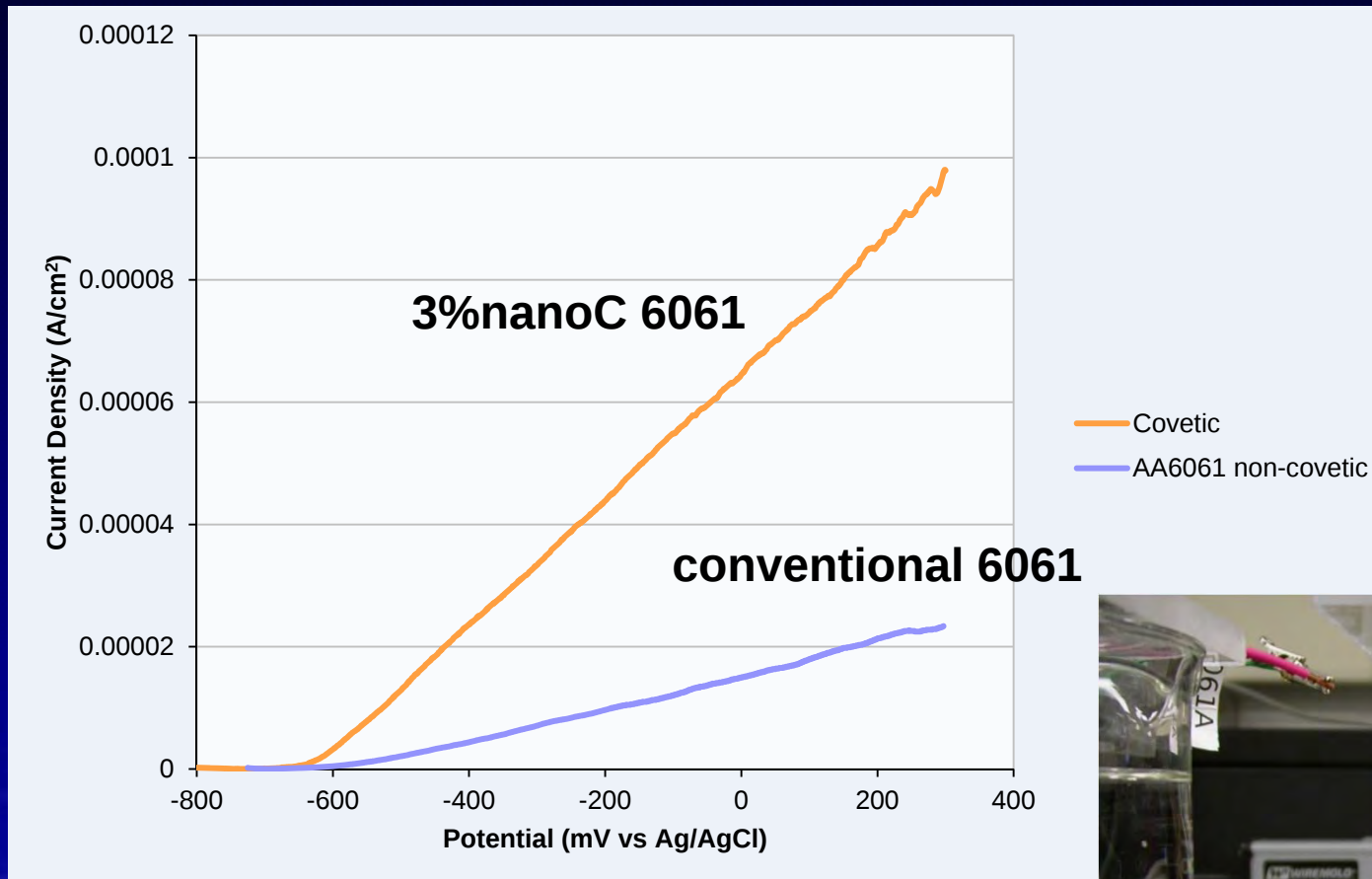


Electrical Conductivity, % IACS

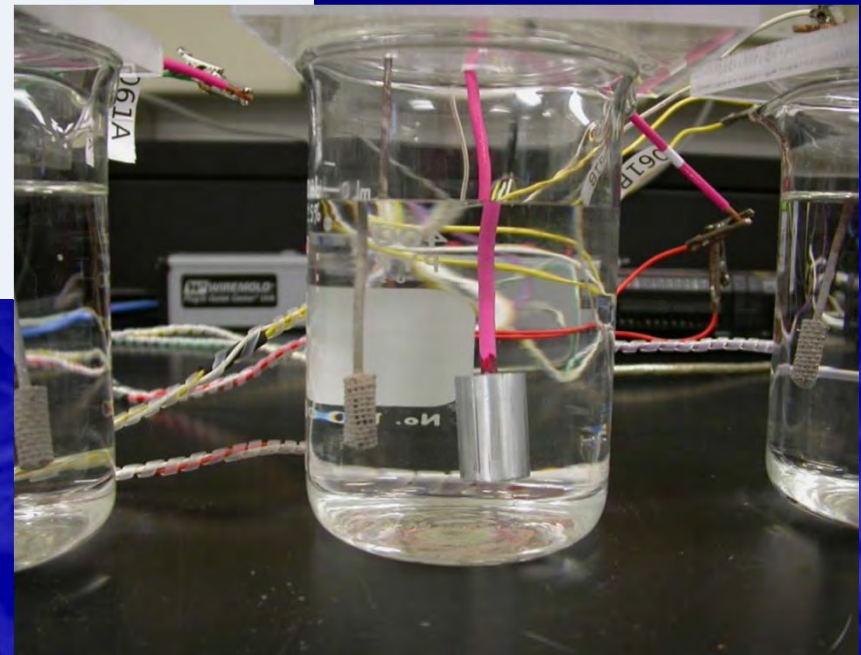
0% C 6061	T6	47.4% Naval Academy
3% C 6061	T6	47.8% Naval Academy
3% C 6061	as-extruded	67.3% Naval Academy
"	"	54% U. Maryland
Electrical grade Al		61.8%



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

- Lower density Cu with same electrical conductivity
 - Wiring, lightweight electrical motors
 - Ships, jets, helicopters, UAV's
- Anisotropic, high thermal conductivity Cu
 - Heat exchangers
 - Microelectronics
- High electrical conductivity aluminum
 - High tension lines
 - Electrodes and contacts

Summary

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