Covetic Materials

CPS Agreement Number: 28418

Argonne National Laboratory/ORNL & NETL - Albany

Aug. 2014 – Sept. 2016

U. (Balu) Balachandran
Argonne National Laboratory

U.S. DOE Advanced Manufacturing Office Program Review Meeting
Washington, D.C.
May 28-29, 2015

Project Objective

- Covetic nanomaterials are metals that have been infused with nano carbon particles using a unique electrical process. Covetic nanomaterials conduct heat and electricity more efficiently than conventional metals, offering potential for significant energy savings in numerous applications from high-voltage electrical wires to solar cells and batteries.
- **There are unique challenges:**

  - Combination of analytical methods needed to measure carbon content and characterize the microstructure/nanostructure

  - High variability in carbon distribution in samples made so far

  - Variability in property measurements

  - Covetic materials display unusually strong bonding between the carbon particles and their metallic matrix, but the exact nature of the attraction is still unknown
- **Objective:** Establish structure-property correlation using samples made under controlled conditions at ORNL & NETL by: 1) Using advanced electron microscopy & synchrotron-based X-ray microscopic techniques (including 3D tomographic visualization, spectroscopic elemental and chemical mapping, micro-diffraction-based structural analysis, and coherent methods for nanomaterials imaging) to investigate the nanocarbon form, distribution, and carbon/metal interface, 2) Measuring thermal and electrical conductivities of covetic materials.

Fabrication of Covetic Materials – Nanocarbon Infusion

- Melt the metal, stir in carbon powder, apply electrical current
- Works with a range of metals (Al, Cu, Au, Ag, Zn, Sn, Fe); could work with all metals – but we don't know and we need to find out!
- Stable after covetic conversion
- Conventional furnaces, electrodes, electromagnetic or gas stirring. Infrastructure readily available for high throughput processing
- Can re-melt, dilute, alloy…

Technical Approach

Unusual Characteristics of Covetic Materials ("covalent" & "metallic" bonds)

- It is possible to add unusually high amounts of nanocarbon to metals – above 6% (well beyond thermodynamic stability limits reported in conventional phase diagrams)
- The carbon particles are a secondary phase --- not precipitates
- The particles are highly stable in the melt and do not float out or agglomerate, although there may be regions in which they are more concentrated
- The nanocarbon is highly resistant to oxidation in the melt in the presence of air
- Depending on processing, covetic nanomaterials can exhibit increased electrical conductivity, increased thermal conductivity, and higher strength
- A surprising (and as yet, unexplained) characteristic is that the nanocarbon does not significantly affect the density of the metal
- Nanocarbon form, distribution, and carbon/metal interface are not understood

DoD Research on Covetic Materials:

- 40% increase in the electrical conductivity of AA6061 (Al alloy)
- 50% increase in the thermal conductivity of Cu
- 30% increase in the yield strength of warm-worked Al and as-cast Cu
- Density remains unusually high -- only 0.7% reduction in density (vs. 10% expected) for sample with 3.8 wt. % C

Technical Approach (Contd.)
Open Questions & Opportunities

- 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?
- What is the role of oxygen, and how is its distribution related to that of the nanocarbon?
- What is the best analytical method(s) to determine carbon content in covetic materials? nanocarbon doesn't reoxidize. LECO & GDMS do not seem to detect covetically bonded carbon. SEM-TEM/EDXS & XPS appear to be best techniques.

Opportunities:

- 3D tomography using the hard X-ray nanoprobe at ANL's advanced photon source (APS) provides an excellent opportunity to answer questions regarding the fine structure and elemental composition of the covetic materials at the interface between the metal and infused carbon.
- ORNL and NETL-Albany have expertise/facilities to fabricate covetic & reference samples in controlled conditions.

"Extraordinary claims require extraordinary evidence." – Carl Sagan

Technical Approach (Contd.)

- The Hard X-ray Nanoprobe at the advanced photon source (APS) at ANL is a combination of scanning probe and full-field imaging microscope that incorporates fluorescence mapping, nano-diffraction and transmission imaging with absorption and phase contrast. The nanoprobe beam line will be used to map the elemental composition at the interface between the metal and infused carbon.
- Nano-tomographic images will be obtained to answer questions regarding the fine structure of covetic materials.
- SEM will be done to obtain morphological information to distinguish carbon-rich phase, oxides, etc. Elemental analysis will be done by SEM - TEM/EDXS. Focused ion beam (FIB)/SEM work will be carried out to isolate the region of interest to examine under synchrotron radiation.
- We will measure the thermal and electrical conductivity of covetic metals (made at both NETL and ORNL and samples from NSWC-Carderock) and control samples under applied stress gradient. Anisotropy of the thermal conductivity will be explored.
- Carbon analysis by XPS, EDXS, LECO, & ICP-OES will be done to determine “free” & covetically bonded carbon in the samples.

Much is unknown regarding the nature of the nanocarbon phase, its size & spatial distribution, and particularly the structure of the metal-carbon interface at the atomic scale. The APS at ANL provides a unique opportunity to study the fine structure and answer some of these fundamental questions.

Technical Approach (Contd.)

What is innovative about our project & approach?

- Team includes ORNL (Metallurgy & Carbon Research groups), NETL - Albany (Metallurgy), and ANL (Materials Scientists)
- Samples are made under controlled conditions in this project. Details of sample preparation conditions, variation in process parameters, etc. were not known to previous researchers
- Owing to a confluence of improvements in synchrotron source brightness, focusing optics fabrication, detection, and data analysis, nanoscale X-ray imaging techniques have moved only recently (within last couple of years) beyond proof-of-principle experiments to play a central role in synchrotron user programs with high-impact applications to materials science questions
- Compared with traditional electron microscopy, helium ion microscopy does not suffer from a large interaction volume, and hence can provide better-contrast sharp images of carbon nanostructures in covetic materials

Collaboration between ANL, ORNL, and NETL - Albany is an essential part of the program.

Argonne NATIONAL LABORATORY OAK RIDGE National Laboratory NETL

Transition and Deployment

- This is pre-competitive research. Results will be published and presented.
- Three National Laboratories (ANL, ORNL, NETL – Albany) are collaborating to verify earlier claims about covetic materials and find answers to open questions.
- Covetic nanomaterials are commercially important because the process is scalable to tonnage quantities with widespread implications for energy savings in thousands of potential applications from high-voltage electrical wires to solar cells and batteries.
- This project applies the expertise/facilities at three National Laboratories to make covetic materials under controlled conditions, and uses advanced analytical tools (Advanced Photon Source, Electron Microscopy Center, XPS, etc.) to understand and validate the covetic materials' superior performance.
- Covetics can be processed using many traditional methods for melting, casting, deforming, and heat treating metals; therefore, it is amenable to scalable high-throughput processing.
- National Laboratories have an excellent track record in commercializing innovative technologies that have been developed at the Labs. As part of the overall DOE-EERE requirement, Technology-to-Market (T2M) teams have been created at the Labs to ensure that the R&D conducted is consistent with the ultimate objective of deploying the technology.

Measure of Success: Impact of Research

- The covetic process is well suited to improve the electrical and thermal conductivities of metals, particularly those alloys where higher conductivity will improve performance, yielding significant energy savings.
- The covetic process offers a new metallurgical pathway to alloy development: use traditional alloying elements to increase the mechanical strength of metals, then use nanocarbon to restore/enhance the thermal and electrical conductivity.

Potential applications include:

Application	Benefits
High-voltage power transmission cable	Higher strength, 40% higher conductivity → $10B annual savings for US power grid
Substitution of covetic aluminum for conventional copper in electrical wiring and motor windings	Weight reduction and improved efficiency, especially on aircraft, but also on transportation systems of all types. Cu: 50 lbs/car→ Al: 20 lbs/car
Heat exchangers	Higher efficiency for a $12B annual market
Nuclear fuel rods	Reduce thermal gradients to improve service performance (less cracking)
Fuel cell and supercapacitor electrodes	Higher efficiency electrodes (greater conductivity through oxide layers)
Thermal management in microelectronics	Higher currents, faster switching at elevated temps.

Project Management & Budget

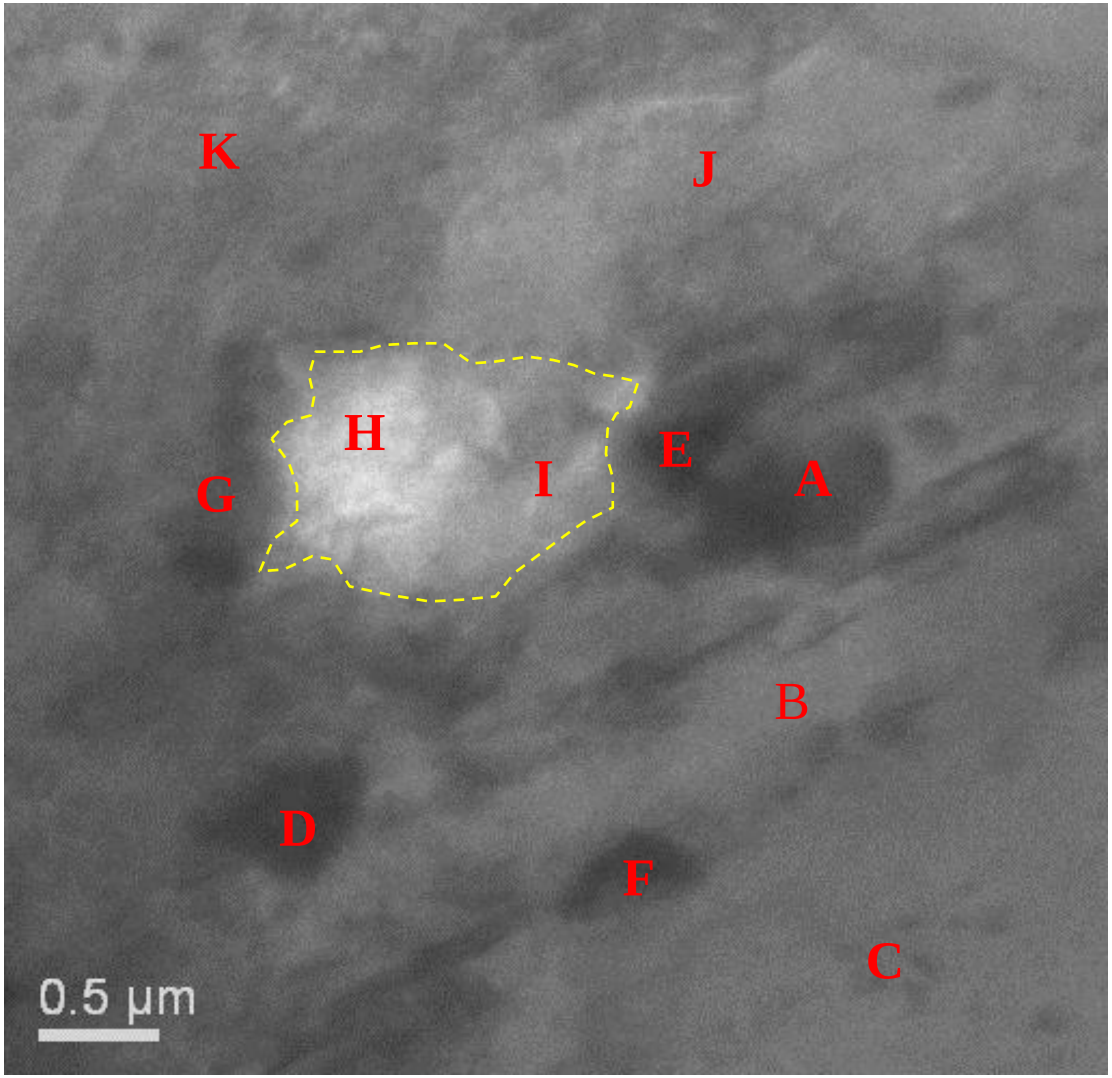
- Project is ongoing: Aug. 2014 - Sept. 2016

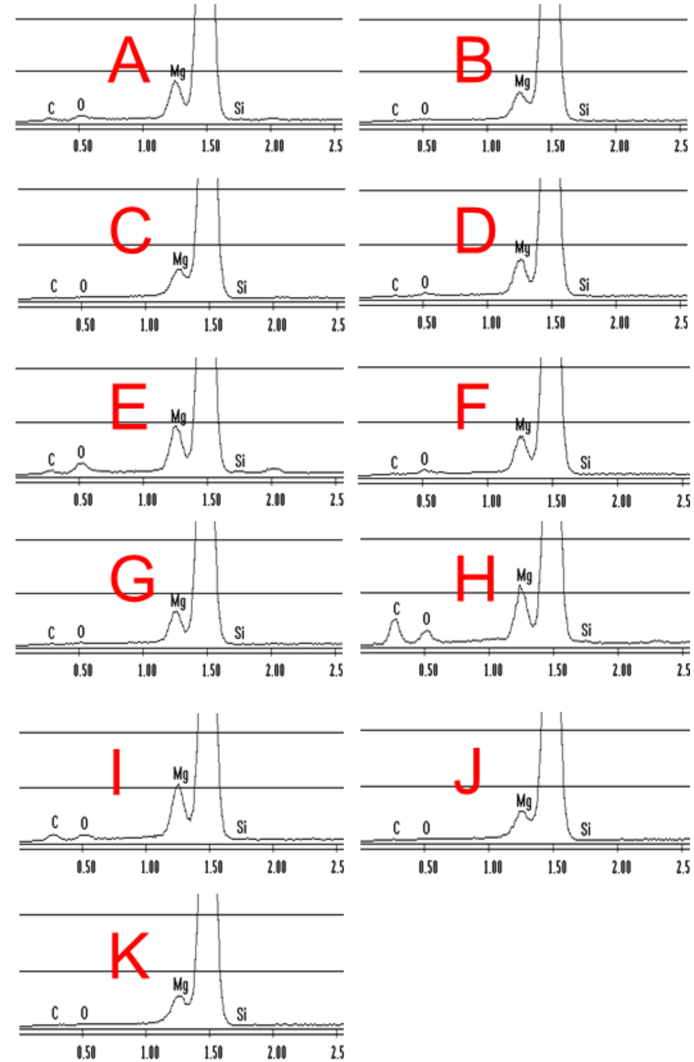
Task/Milestone Schedule

Task description	Target date	Progress note
Collect nano-tomographic images of covetic materials	06/31/2015	3D tomographic image reveals nanofeatures in covetic copper alloy
Measure electrical and thermal conductivities of covetic materials	09/30/2015	Thermal conductivities of pure Cu and covetic Cu alloys measured; components for electrical conductivity measurement being procured
Measure metal/nanocarbon interface strain using synchrotron radiation technology	03/31/2016	On-schedule
Develop processing - structure-property correlation for select covetic metals	09/30/2016	On-schedule

Total Project Budget	
DOE Investment	$612K
Cost Share	$0 (This a pre-competitive program)
Project Total	$612K

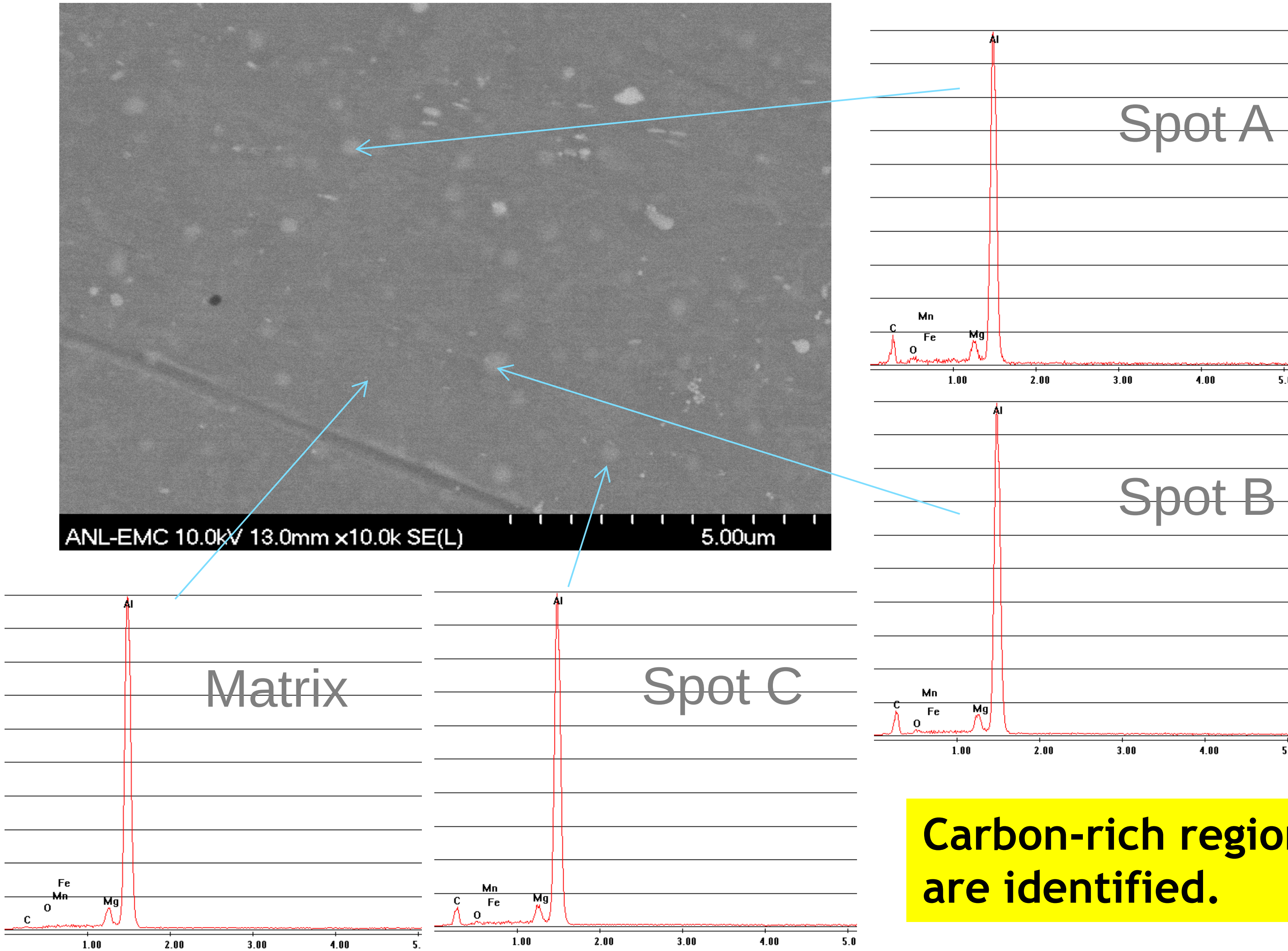
Results and Accomplishments: Bright field TEM image and EDS of nano-carbon cluster in covetic aluminum alloy (NC4A)





Observed nanocarbon clusters in covetic aluminum alloy.

Results and Accomplishments: SEM EDX of polished covetic aluminum alloy (NC4A)



Carbon-rich regions are identified.

Results and Accomplishments: X-ray micro image of covetic copper alloy taken at Advanced Photon Source nanoprobe beamline

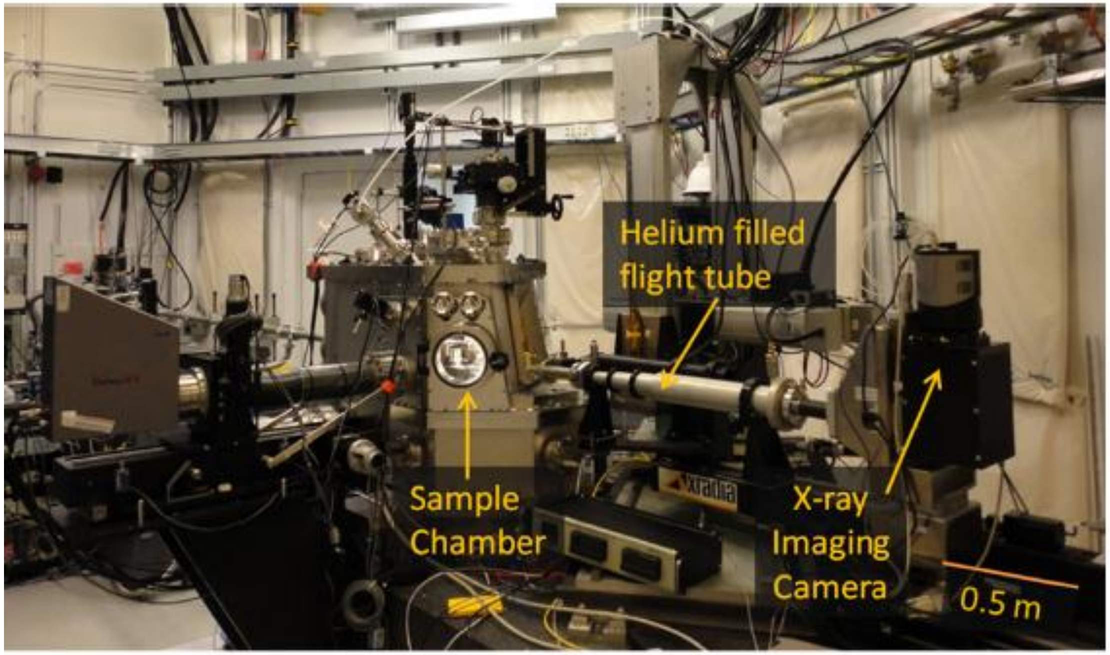
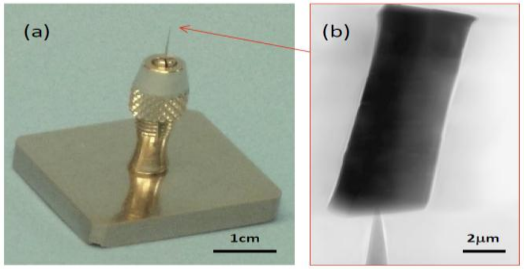
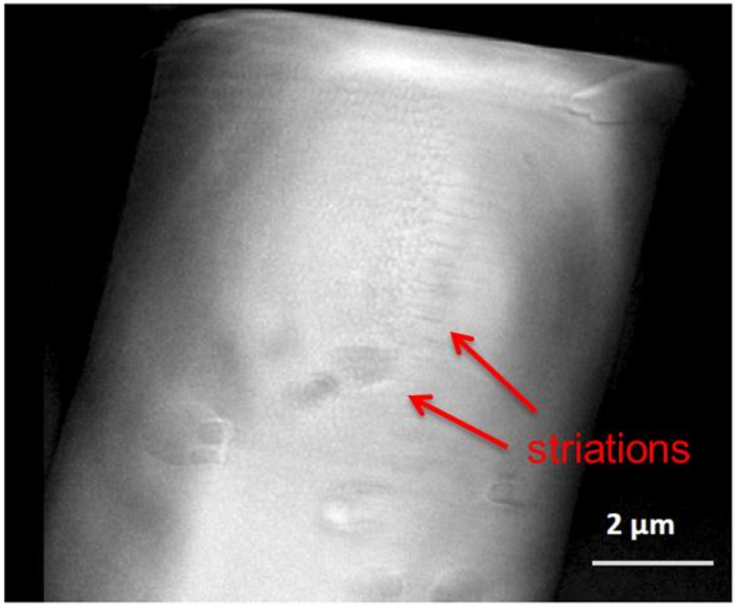


Photo taken inside the hutch showing the experimental setup for nanotomography using the Hard X-ray Nanoprobe at APS



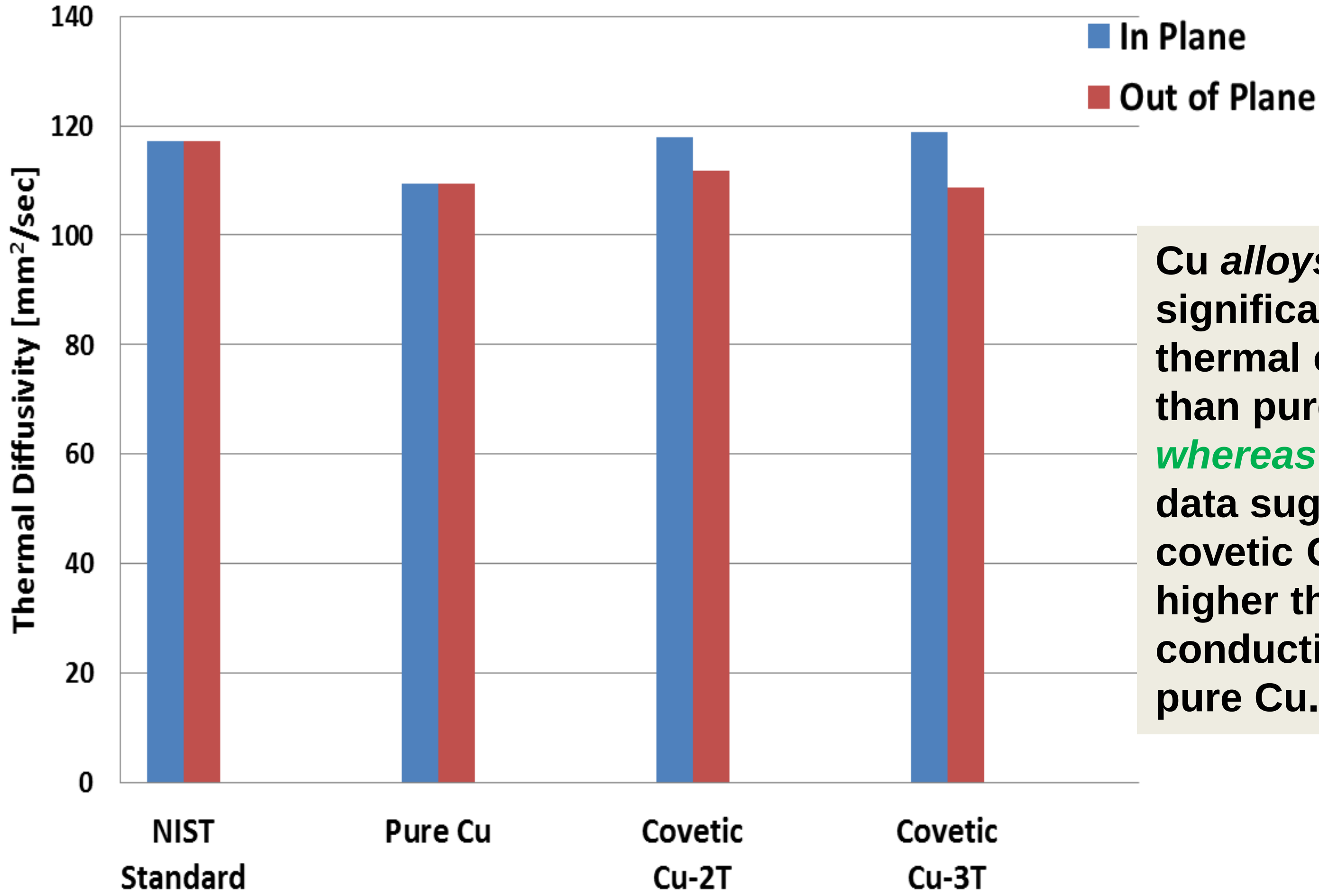
Photograph of the sample stage & micrograph of mounted Cu covetic sample

3D micro image reveals nanofeatures in a covetic copper alloy (Cu-4T).



Micro image of Cu covetic sample

Results and Accomplishments: Measured Thermal Diffusivities of Pure Cu, Covetic Cu Alloy Samples & NIST standard data



Cu *alloys* have significantly lower thermal conductivity than pure Cu, *whereas* preliminary data suggests that the covetic Cu *alloy* has higher thermal conductivity than pure Cu.

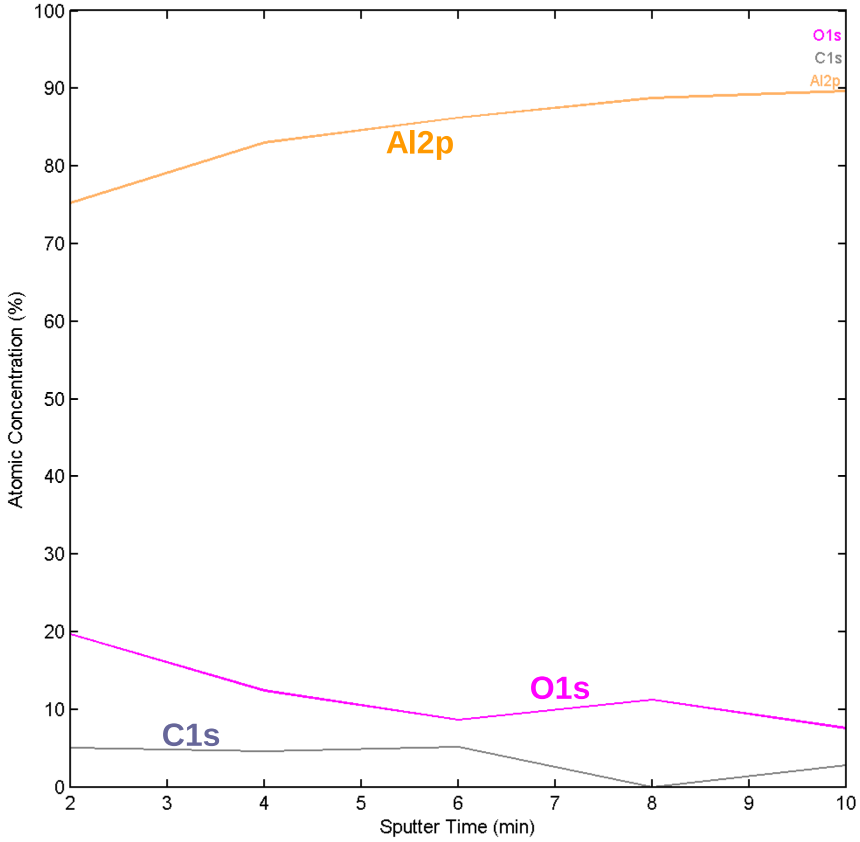
Thermal conductivity = Thermal diffusivity x Specific heat x bulk density

Thermal conductivity of covetic Cu alloy is higher than that of pure Cu; In-plane conductivity is higher than out-of-plane conductivity.

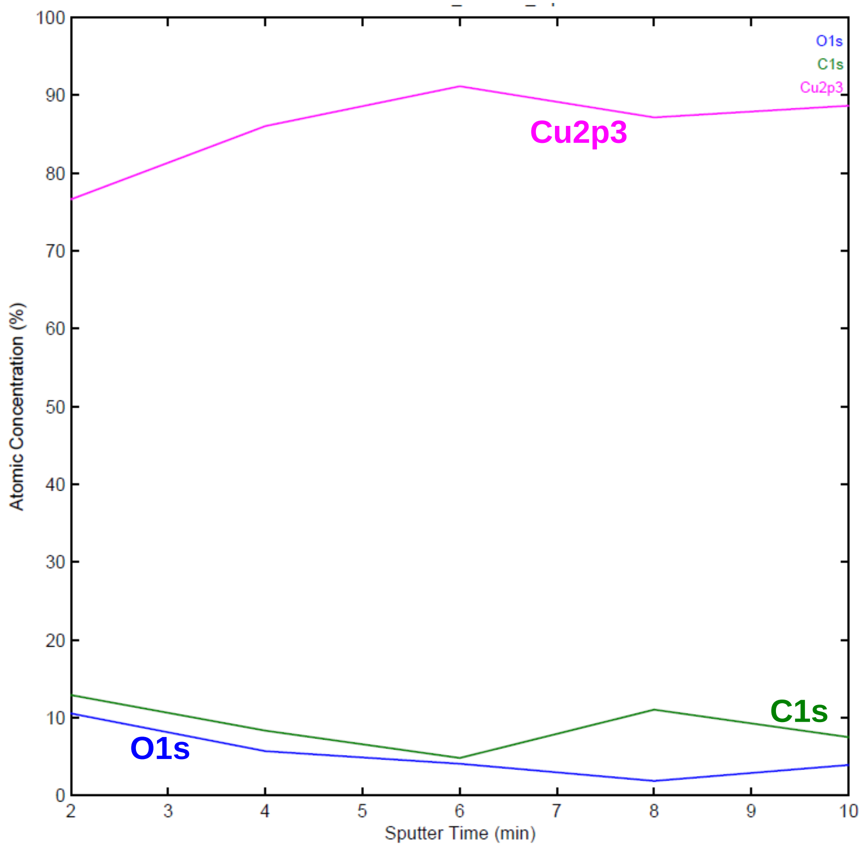
OAK RIDGE National Laboratory

Results and Accomplishments: XPS analysis of covetic Al and Cu samples

Covetic Al



Covetic Cu



Significant amount of carbon is present in all samples at the end of the sputtering cycle.

Future Plans

ORNL and NETL will provide samples that will be used to study the evolution of nanocarbon particles as they are formed; the fine structure work at ANL will provide new scientific knowledge regarding the nature of the conversion process. Specifically, our future work will be:

- Characterize the electrical and thermal conductivity of samples from ORNL and NETL, and explore the relationship between stress fields and conductivity; explore the directionality of conductivity measurements.
- Identify morphological features of nanostructure in covetic materials through electron microscopy.
- Utilize focused ion beam (FIB) analysis to probe and verify the existence of nanocarbon structures in metal matrixes.
- Use APS synchrotron source to visualize covetic nanostructures with high spatial resolution, and conduct spectroscopic elemental and chemical mapping and micro-diffraction-based structural analysis.
- Determine carbon content by multiple independent techniques, namely, LECO, direct current plasma emission spectroscopy, inductively coupled plasma optical emission spectroscopy, SEM-TEM/EDS, and XPS.

Building on capabilities at the National Laboratories to advance the development of covetic materials, which could have widespread implications for energy savings in thousands of potential applications.

Selected References

1. D. R. Forrest, et al., "The Production and Properties of Copper and Aluminum Covetic Nanomaterials", MS&T'14, Pittaburgh, PA, Oct. 15, 2014.
2. T. Knych, et al., "Fabrication and Cold Drawing of Copper Covetic Nanostructured Carbon Composites", Arch. Metallurgy and Materials, 59(4), 1283, 2014.
3. T. Knych et al., "Characterization of Nanocarbon Copper Composites Manufactured in Metallurgical Synthesis Process", Metallurgical and Materials Transactions B, 45B, 1196, 2014.
4. D. R. Forrest, et al., "Nanoscale Carbon in Metals for Energy Applications", MS&T '12, Columbus, OH, Oct. 19, 2012.
5. L. Salamanca-Riba, et al., "A New Type of Carbon Nanostructure Formed Within a Metal-Matrix", Nanotech 2012, Santa Clara, CA, June 18, 2012.
6. D. R. Forrest, et al., "Novel Metal-Matrix Composites with Integrally-Bound Nanoscale Carbon", Nanotech 2012, Santa Clara, CA, June 18, 2012.
7. L. Brown, et al., "Physical and Mechanical Characterization of a Nanocarbon Infused Aluminum-Matrix Composite", SAMPE Fall Technical Conference, Ft. Worth, TX, Oct. 17, 2011.
8. J. Shugart, "New Class of Metallic Nanocomposites", MS&T'09, Pittsburgh, PA, Oct. 25, 2009.