

# Novel Metal-Matrix Composites with Integrally-Bound Nanoscale Carbon

David R. Forrest<sup>\*</sup>, Iwona Jasiuk<sup>\*\*</sup>, CAPT Lloyd Brown<sup>\*\*\*</sup>, Peter Joyce<sup>\*\*\*</sup>,  
Azzam Mansour<sup>\*</sup>, Lourdes Salamanca-Riba<sup>\*\*\*\*</sup>

<sup>\*</sup>Naval Surface Warfare Center, Bethesda, MD, david.r.forrest@navy.mil, azzam.mansour@navy.mil

<sup>\*\*</sup>U. of Illinois at Urbana-Champaign, Urbana, IL, ijasiuk@illinois.edu

<sup>\*\*\*</sup>United States Naval Academy, Annapolis, MD, lbrown@usna.edu, pjoyce@usna.edu

<sup>\*\*\*\*</sup>University of Maryland, College Park, MD, riba@umd.edu

## ABSTRACT

We characterized the chemical, thermophysical, and mechanical properties of nanomaterials with up to 5 wt% nanocarbon (aka “covetics”) in aluminum and copper metals. The nanocarbon is detectable by EDS and XPS but not by analytical methods such as LECO and GDMS. Nanocarbon raises the melting point and significantly alters surface tension, and thus porosity, during solidification. Open questions remain about the observation of higher density than would be predicted by the rule of mixtures. In aluminum alloys, we observed an increase in as-rolled strength and hardness with increasing amounts of nanocarbon. In copper, thermal conductivity was anisotropic: up to 50% higher in the extrusion direction and at least 25% lower in the transverse direction, and was different between transient and steady state test conditions. In aluminum, we observed a significant increase in electrical conductivity with nanocarbon, from 47 to 67% IACS. These materials are commercially promising because they are produced by conversion of inexpensive carbon powder to nanocarbon in the melt—paving the way for the production of nanomaterials in pyrometallurgical operations with economies of scale.

**Keywords:** nanocarbon, covetic, nanomaterial, metal-matrix composite

## 1 BACKGROUND

Recent advances in nanomanufacturing have made it possible for large amounts (> 6 wt.%) of nanoscale carbon to be retained in metals such as aluminum and copper. The dispersion of carbon is highly stable despite its presence not being predicted in phase diagrams, and it remains intact after remelting and resolidification. A complementary paper describing the structure of these unusual materials is provided in these proceedings [1].

## 2 ANALYTICAL METHODS

There are no standard analytical techniques or reference materials for covetics, so we have experimented with the application of various existing methods. Analysis of the

nanocarbon content in covetic materials is complicated by an unusually tenacious bonding between the carbon phase and the metal matrix. The nature of the interface between the phases is currently not well understood, and it has only been recently that the various forms of the carbon in the material were characterized at atomic resolution [1]. The nanocarbon has been seen in the form of ribbons, intra-lattice structures, and particles. An example of the latter is shown in Figure 1.

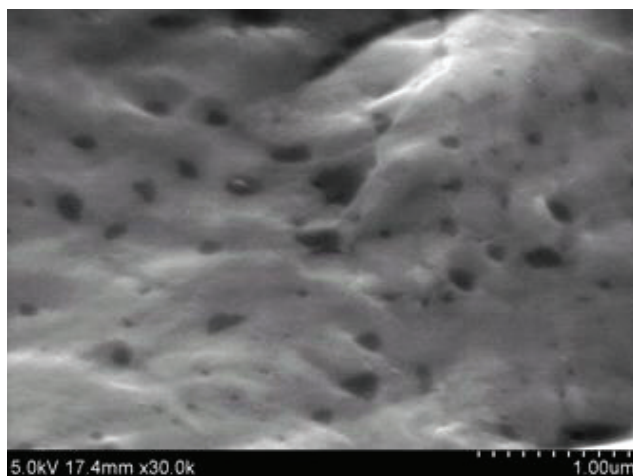


Figure 1. Nanocarbon particles measuring 5-200 nm diameter, seen as dark features in this tensile fracture surface of a 3 wt.% C AA6061 covetic.

### 2.1 LECO Method

In one carbon determination procedure, ASTM E1019-08 (“LECO” method), metal samples are heated to sufficient temperatures where the carbon in the metal is combusted with oxygen to form CO and CO<sub>2</sub>. These gases are then catalyzed to 100% CO<sub>2</sub> and measured using infrared absorption spectrometry. Unlike virtually all other forms of carbon and carbon compounds in metals, the nanocarbon in the covetics did not combine with oxygen at these temperatures. Instead, it remained in the melt, bound to the metal. We learned that we can, however, use the LECO method to detect carbon that is not in nanocarbon form.

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## 2.2 Comparison of Analytical Methods

For one lot of copper covetic material, we used four different methods to measure the carbon concentration: LECO, Glow Discharge Mass Spectrometry (GDMS), Direct Current Plasma Emission Spectroscopy (DC-PES), and X-Ray Photoelectron Spectroscopy (XPS). In the first three methods we employed commercial analytical laboratories. Table 1 shows that LECO and GDMS were only able to detect trace amounts, while DC-PES and XPS found concentration levels two orders of magnitude greater (although there was still a significant discrepancy between these two methods).

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

Table 1. Summary of results of different analytical methods for carbon determination in copper covetic.

In a second lot of copper covetic, with higher carbon concentration, we found good agreement between XPS (collected using a Physical Electronic model 5400 spectrometer equipped with Mg K $\alpha$  X-rays) and Energy Dispersive X-Ray Spectroscopy (EDS) using an Apollo 40 Edax system in our Hitachi SU6600 Field Emission Scanning Electron Microscope. Table 2 shows that the values obtained agree to within 8% on a relative basis.

Method	Result (wt. % C)
SEM-EDS	3.78
XPS	3.5

Table 2. Comparison of EDS vs. XPS results, Cu covetic.

## 3 MELTING POINT

Nanoscale carbon increases the melting temperature of copper and aluminum covetics. Evans Analytical measured the melting point of the 0.21 wt% C copper covetic and the 3 wt% C 6061 covetic using Thermal Gravimetric Analysis. The Cu melted at 1105°C, which is 20°C higher than the literature value of 1085°C [3]. Nanoscale carbon raised the solidus temperature of AA6061 from the literature value of 582°C [4] to 619°C.

## 4 DENSITY

We used volume and mass results from a Quantachrome Ultra Pycnometer 1000 to calculate the density of the 3.5 wt. % Cu covetic material. This instrument measures the volume of the sample using helium gas, and can therefore compensate for porosity or other geometric nonuniformities. Some error may result if the material contains pores that are completely closed, so we hot

compressed the specimen prior to testing. The results showed that the copper covetic's density was 8.7894 g/cm<sup>3</sup> prior to compression, and 8.8777 g/cm<sup>3</sup> afterwards. This compares with 8.94 g/cm<sup>3</sup> for pure copper. Thus, the covetic's density was only 0.7% less than that of pure Cu. With 3.5-3.8% carbon (measured using XPS and EDS), we would expect a ~10% reduction in density based on the rule of mixtures and assuming 2.25 g/cm<sup>3</sup> for the carbon. Whether the carbon assumes the form of a new high density phase or seats itself in metal lattice structures remains an open question.

## 5 THERMAL CONDUCTIVITY

The thermal conductivity of copper covetic was determined for a copper covetic extrusion using two different methods, ASTM E1225 (which is a comparison method measuring conductivity at steady state), and ASTM E1461 (laser flash diffusivity), by Energy Materials Testing Laboratory. The carbon concentration of this material was measured to be 0.057 wt. % C via XPS. The results, shown in Tables 3 and 4, reveal significant differences between the two methods. The flash diffusivity method yielded conductivities about 50% higher than that of the base metal steady state conductivities at all temperatures. The E1225 results revealed significant anisotropies in thermal conductivity, with transverse values measuring about 20% lower than longitudinal results.

Temperature (°C)	Longitudinal W/m-K	Transverse W/m-K	Pure Cu W/m-K
23	415	334	401
200	401	329	389
400	386	324	379
600	371	318	366
750	360	314	355
900	350	310	344

Table 3. Thermal conductivity of 0.057% Cu covetic vs. pure Cu (ASTM E1225, steady state).

Temperature (°C)	Longitudinal W/m-K	Pure Cu W/m-K
23	612	401
200	630	389
400	614	379
600	594	366
750	587	355
900	591	344

Table 4. Thermal conductivity of 0.057% Cu covetic vs. pure Cu (ASTM E1461, laser flash diffusivity).

## 6 ELECTRICAL CONDUCTIVITY

We measured the electrical conductivity of 12.5 mm diameter AA6061 material using a 4-wire digital

multimeter (Agilent Model 34420A Nano Volt/Micro Ohm Meter) according to ASTM B193 procedures at 20°C. The results are shown in Table 5. In the as-extruded condition, the nanocarbon alloy had a higher electrical conductivity than the best electrical grade aluminum. There was, however, significant scatter in the results depending on heat treatment condition and even depending on the surface condition of the specimens. Standard practice is to clean the surface and sand or otherwise remove any oxide layer immediately before testing. Beyond this practice, however, the machining technique itself seemed to have a bearing on the results. This could have been a source of the data scatter. For example the same sample yielded 47.8% International Annealed Copper Standard (IACS) with a ground surface, but 56% IACS with an Electrical Discharge Machined (EDM) surface.

Type of Material	Condition	%IACS	Test Lab
0%C 6061	Conventional 6061, T6 <sup>1</sup>	47.4	USNA
3%C 6061	T6 ground surface	47.8	USNA
3%C 6061	T6 EDM surface	56.1	USNA
<b>3%C 6061</b>	<b>As-Extruded</b>	<b>67.3</b>	<b>USNA</b>
<b>3%C 6061</b>	<b>As-Extruded</b>	<b>54</b>	<b>U. Md</b>
EC-1350	Electrical grade Al	61.8	literature[5]

<sup>1</sup> Surface of extruded bar was not fully machined, just sanded.

Table 5. Summary of electrical conductivity measurements.

## 7 HEAT TREATMENT AND HARDENING

### 7.1 Aluminum Alloy 6061

We measured the tensile properties of AA6061 with 0% and 3 wt% nanocarbon. The material was provided in the form of 12.5mm diameter as-extruded rods, processed at 400°F. In this condition, the 3% nanocarbon material exhibited a yield strength about 30% higher than the non-covetic (Figure 2).

However, 6061 is normally prepared in the heat treated condition to much higher strength levels. For example, treated to the T6 condition by solutionizing at 985°F, water quenching, and aging at 350°F. After this heat treatment, there was virtually no difference in tensile properties (Figure 3). Based on grain size data, which revealed significant coarsening in as-extruded conventional 6061, we believe that the higher as-extruded covetic strength was due to improved resistance to grain coarsening at the extrusion temperature of 400°F. Subsequent heat treatment apparently removed any significant microstructural differences—at least in terms of grain size effects and the precipitate system. How the alloy can contain 3% nanocarbon with no effect on heat treated tensile strength remains an open question.

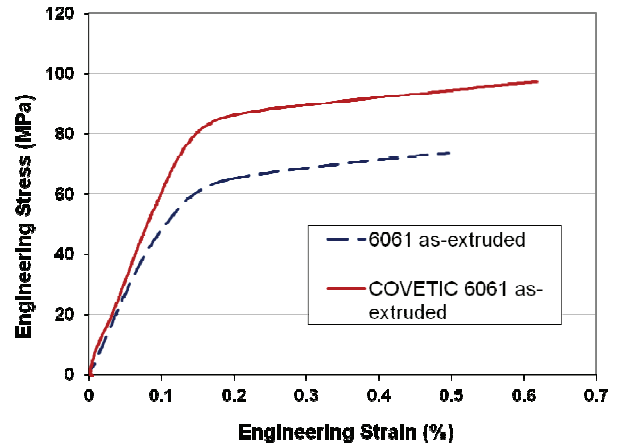


Figure 2: The yield strength of as-extruded 6061 covetic was approximately 30% higher than that of non-covetic.

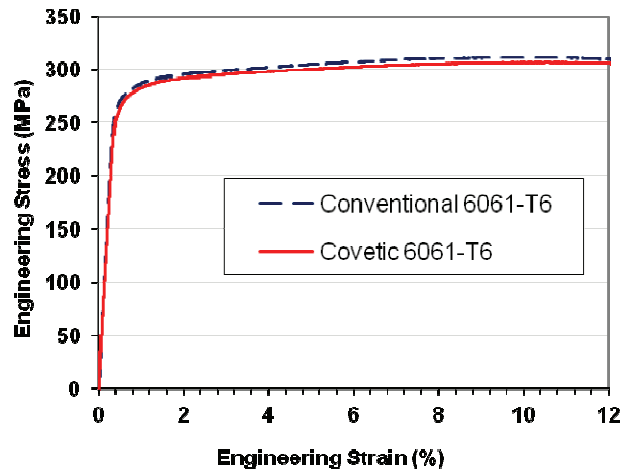


Figure 3: In the T6 condition, the tensile curves of 6061 covetic and non-covetic were virtually identical.

### 7.2 Aluminum Alloy 7075

We evaluated the tensile properties of AA7075 containing 0.84 wt%, 2.2 wt% and 4 wt% nanocarbon. The material was provided in the form of ~1mm thick sheet that had been processed in non-standard fashion: direct rolled from elevated temperatures down to finish gage at cooler temperatures. While we cannot separate the processing variable effects from the compositional effects, the general trend shows that increasing amounts of nanocarbon resulted in higher strengths (Figure 4).

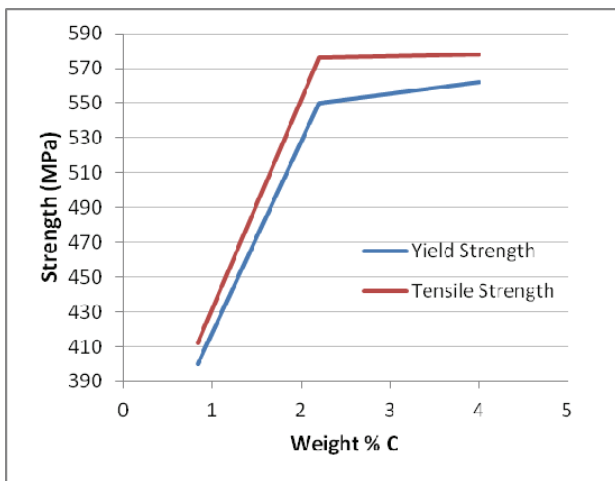


Figure 4: Increasing levels of nanocarbon appeared to increase the strength of continuously rolled sheet.

### 7.3 Copper

We evaluated the tensile properties of 0.21 wt% C copper covetic. Because the as-received ingot material contained a significant volume fraction of porosity, we remelted and recast some of the material in the centrifugal caster at NSWCCD. While the covetic copper initially exhibited a significantly higher yield strength than the conventional copper reference material (also centrifugally cast), it failed prematurely (likely due to increased levels of porosity) and we were unable to produce a full stress-strain curve (Figure 5). The covetic material began to deflect from linear elastic behavior at approximately 12,000 psi vs. 9,000 psi for conventional copper.

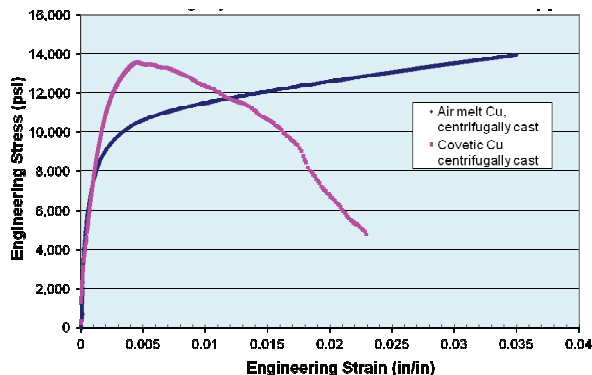


Figure 5: Tensile stress strain curves for centrifugally cast covetic vs. pure copper.

## 8 CONCLUSIONS

The covetic materials that we have studied to date have yielded some surprising properties and phenomena not seen in conventional metals: increased electrical and thermal conductivity in metals that are already highly conductive, anisotropic thermophysical properties, and a phase that defies conventional extractive metallurgy refining techniques and whose density appears to challenge the rule

of mixtures. The nanocarbon increased the material's strength (in some cases) and increased the melting temperatures.

We have confirmed the ability of the nanocarbon to be retained after remelting in air and recasting. This property offers a variety of potential benefits, such as the capability to arc weld covetic nanomaterials, and to perform pyrometallurgical refining operations to remove unconverted carbon. These materials are commercially promising because they are produced by conversion of inexpensive carbon powder to nanocarbon in the melt—paving the way for the production of nanomaterials in pyrometallurgical operations with economies of scale. There is considerable need for further investigation—of both the structure, and of the physics behind the phenomena we have reported.

## 9 ACKNOWLEDGEMENTS

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## REFERENCES

- [1] L. Salamanca-Riba, et al., "A New Type of Carbon Nanostructure Formed Within A Metal Matrix," Proceedings of Nanotech Conference and Expo 2012, 18-21 June 2012, Santa Clara, CA, in press.
- [2] L. Brown, P. Joyce, D. Forrest, J. Wolk, "Physical and Mechanical Characterization of a Nano Carbon Infused Aluminum-Matrix Composite," Proceedings of the SAMPE Fall Technical Conference, Ft. Worth, TX, 17-20 October 2011.
- [3] Metals Handbook, 9<sup>th</sup> Edition. v. 2, Properties and Selection: Nonferrous Alloys and Pure Metals ASM International, Metals Park, OH, p. 728.
- [4] Metals Handbook, 9<sup>th</sup> Edition. v. 2, Properties and Selection: Nonferrous Alloys and Pure Metals, ASM International, Metals Park, OH, p. 116.
- [5] Properties of Aluminum Alloys, MWS Wire Industries, Aug 2011.  
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