Spray Deposition of Coal-Derived Graphene-Copper Nanocomposites for Advanced Conductors

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Project Overview

- **Funding (DOE and Cost Share):**

  DOE share: $1,000,000; cost share: $255,742

- **Overall Project Performance Dates:**

  8/1/2023 to 7/31/2025

- **Project Participants:**

  Tennessee Technological University (TTU)

  Tennessee State University (TSU)

  Copperweld Bimetallics, LLC (Copperweld)

  Eastern Plating, LLC (EPL)

Project Overview

– Overall Project Objectives

This project aims to develop high-performance copper-graphene (Cu-Gr) nanocomposites using coal-derived Gr via a low-cost spray deposition process.

1. Optimize the spray deposition and post-deposition processes to achieve a Cu-Gr composite with uniform Gr distribution.
2. Improve interfacial bonding between Gr and Cu via minor alloying additions in the Cu melt or electroless Ni plating on the Gr particulates.
3. Perform a techno-economic analysis (TEA) to demonstrate the cost-effectiveness of the developed process.

Technology Background

- Both Gr and carbon nanotubes (CNTs) have low density and exceptional mechanical, electrical & thermal properties, which are critical for advanced Cu-matrix composites.
- Compared with CNTs, Gr is more cost-effective and easier to disperse into the Cu matrix.
- Gr particulates are being developed using coal as raw material.

Physical and Mechanical Properties at Room Temperature

Material	Density (g/cm^3)	Electrical Conductivity (S/m)	Thermal Conductivity (W/m·K)	Tensile Strength (GPa)	Young's Modulus (GPa)
Cu	8.96	58×10^6	394	0.2-0.4	118-132
CNT	1.58-2.16	$\sim 10^6$-10^7	~3000	100-200	~1000
Gr	2.26	up to 100×10^6	~5000	130	~1000

Cu-Gr metal matrix nanocomposites offer potential advantages of light weight, high strength, and good thermal/electrical properties.

Technology Background

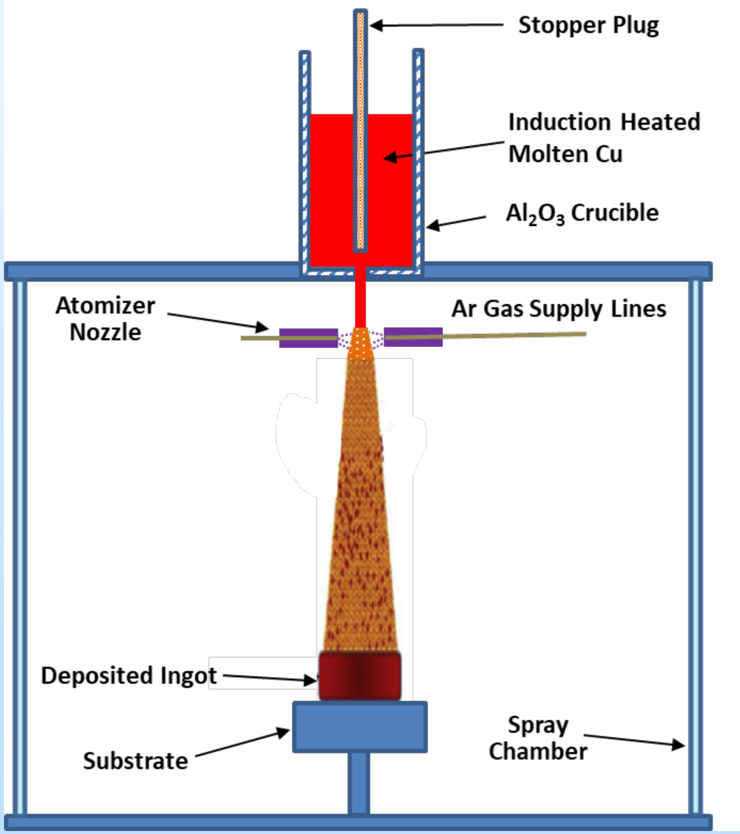
– **Why Spray Deposition for Cu-Gr Composites?**

Process Category	**Typical Process**	**Pros**	**Cons**
Solid State Processes	Powder Metallurgy (P/M)	• Well-controlled volume fraction of Gr	• High production cost & porosity • Nonuniform distribution of Gr at high vol.%
	Shear Assisted Processing & Extrusion (ShAPE)	• Capability of fabricating parts such as wires • Uniform Gr distribution • No or low porosities	• Limited vol.% of Gr that can be incorporated • Not suitable for complex-shaped components
Electro-chemical Processes	Electro-codeposition	• Relatively high vol.% of Gr (up to 20%) • Uniform distribution of Gr	• Not for mass production of bulk parts • More suitable for composite coating production
Two-Phase (Solid/Liquid) Processes	**Spray Deposition**	• **Relatively low-cost** • **High production rate** • **Potential uniform Gr distribution**	• **No work reported so far for Cu-Gr composites**

Technology Background

– **Spray Deposition for Cu and Cu-matrix Composites**
  - Molten Cu is separated into fine droplets by an atomizing gas jet.
  - Depending on the deposition conditions, fine Cu powder or solid Cu ingot can be obtained.

Spray Deposition System at TTU

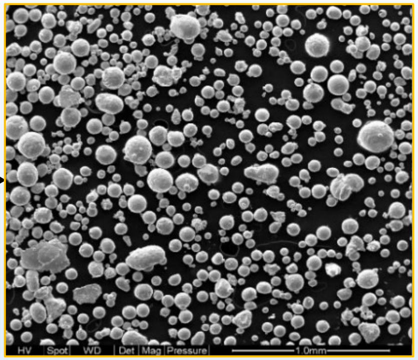


Schematic of Spray Deposition System

Technology Background

– **Spray Deposition for Cu and Cu-matrix Composites**

Fine Cu Powder



Cu Ingot

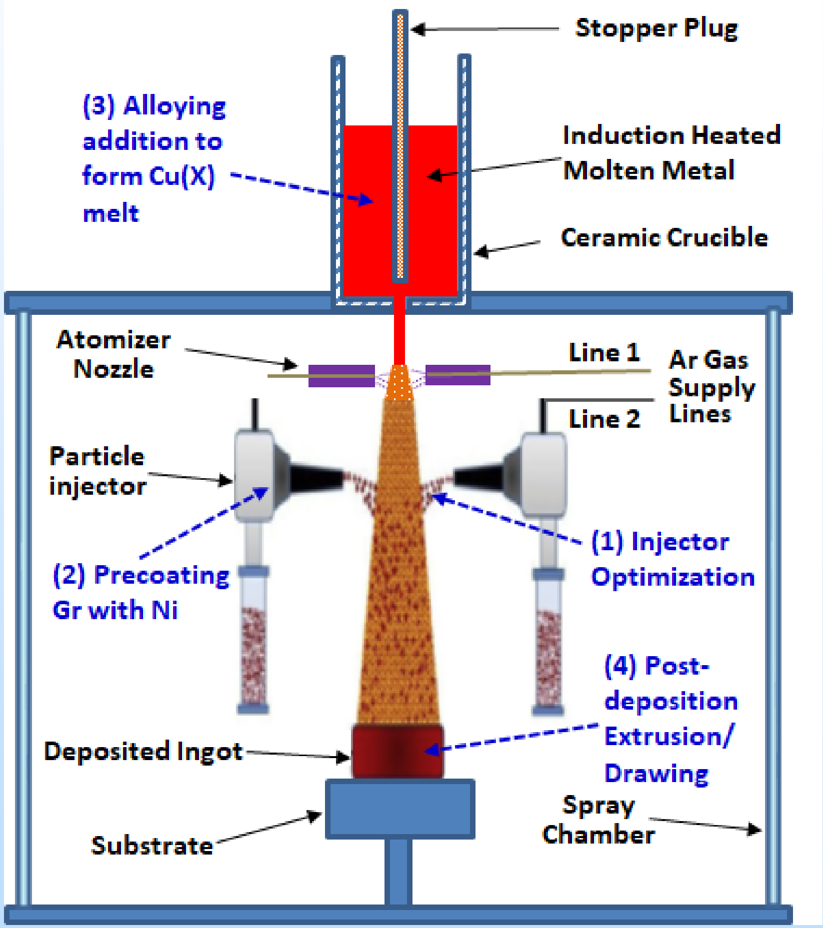
Cu-Gr Composites

- How can Gr particulates be incorporated into the Cu stream?
- How much Gr can be added to the Cu matrix?
- Can uniform Gr distribution in the composite be achieved?

Technical Approach/Project Scope

a. Experimental Design or Project Steps and Work Plan

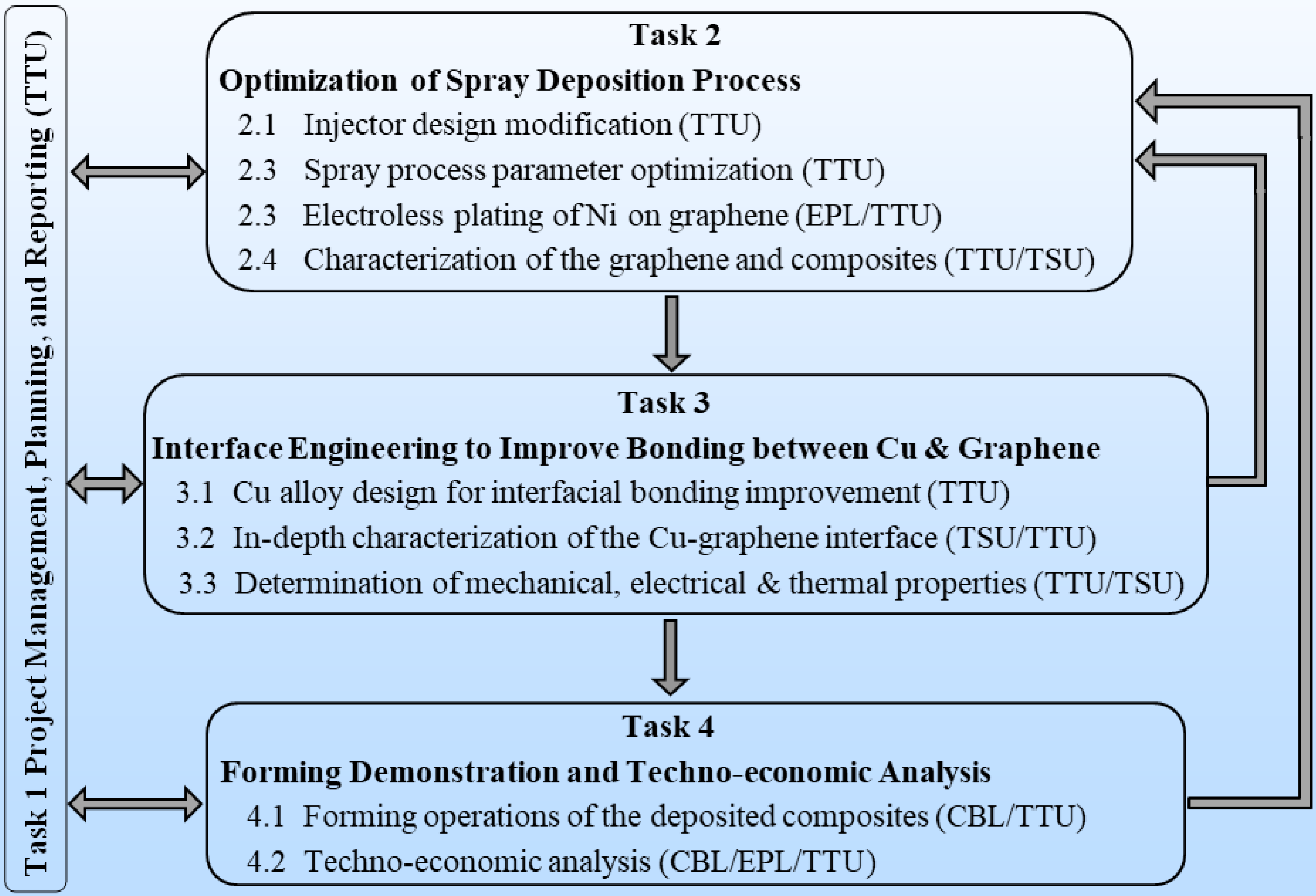
- Co-deposition of Cu and Gr particle streams to form Cu-Gr.
  - Utilization of a particle injector to inject Gr into the molten Cu droplets to form a Cu-Gr mixture.
  - Electroless plating of Ni on Gr particles to improve its distribution during spraying.
  - Alloying with a transition metal X to form Cu(X) alloy to enhance the wettability of the melt on Gr.
- Post-deposition deformation to better align the Gr particles in the microstructure.



Spray Deposition with Unique Features

Technical Approach/Project Scope

a. Experimental Design or Project Steps and Work Plan



Technical Approach/Project Scope

Budget Period	Task #	Milestone Title & Description	Planned Completion Date	Actual Completion Date	Verification Method
1	1	Milestone #A: Revised PMP	8/31/2023	8/16/2023	PMP file
1	1	Milestone #B: Kickoff meeting	8/31/2023	8/16/2023	Presentation file
1	2.3	Milestone #C: Completion of Ni electroless plating	5/31/2024	In progress	Gr particulates with desired Ni coating thickness and uniformity are obtained.
1	2.2	Milestone #D: Optimization of spray deposited Cu-Gr	7/31/2024	In progress	Cu-Gr composites with the desired Gr level & microstructure are synthesized
2	3.1	Milestone #E: Completion of Cu alloy design	10/31/2024	In progress	Optimal Cu alloy composition is identified for improved Cu/Gr bonding
2	3.3	Milestone #F: Completion of property assessment	1/31/2025		Hardness/tensile test data and electrical conductivity values for the composites are obtained.
2	4.2	Milestone #G: Completion of TEA	7/31/2025		TEA is completed and advantages over state-of-the-art are assessed.

Technical Approach/Project Scope

b. **Project Success Criteria**

- Demonstration of a Cu-Gr nanocomposite with the desired microstructure via spray deposition
- Improved mechanical, electrical and thermal properties over Cu and/or P/M counterparts
- Verification of techno-economic feasibility of the developed technology

c. **Project risks and mitigation strategies**

Technical/Scope Risks	**Probability** (Low, Moderate, High)	**Impact** (Low, Moderate, High)	**Risk Management Mitigation and Response Strategies**
a. Uniform distribution of Gr in the nanocomposite	**Moderate**	**High**	**(1) Optimization of Gr injection mechanism (2) Optimization of key spray deposition parameters (3) Electroless Ni plating on Gr or microalloying addition in Cu melt to improve the Cu-Gr interaction**
b. Formability of Cu-Gr nanocomposite with desired Gr vol.% levels	**Low**	**Moderate**	**(1) Exploration of different forming operations (2) Increase in forming operation temperature (3) Optimization of the amount and distribution of Gr in the composite**

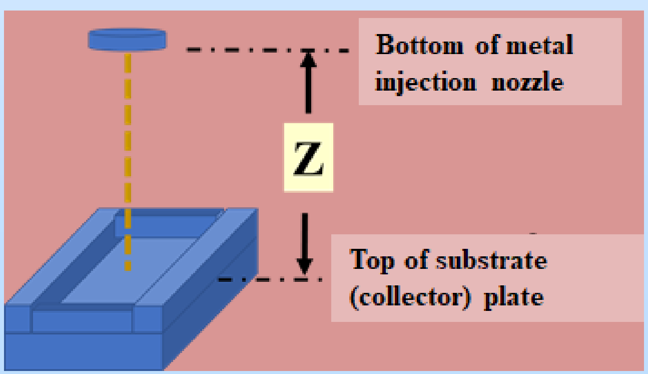
Progress and Current Status of Project

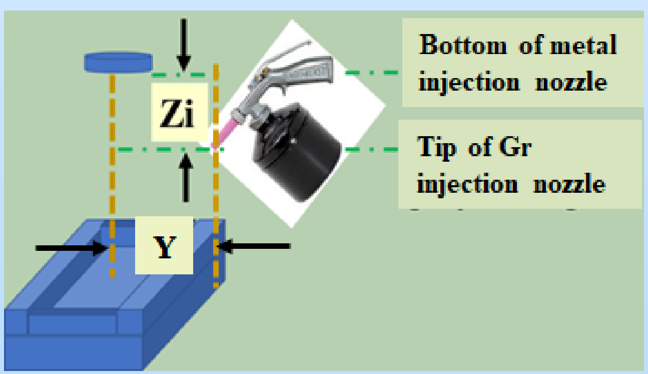
a. Design of the Gr Injector and Collector (Substrate)

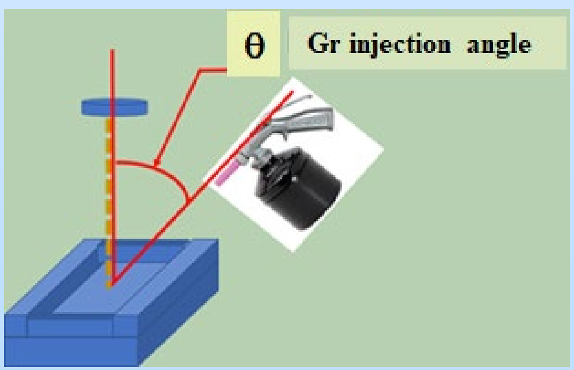
A number of spray runs have been conducted under different spray depositions.

Spray Deposition Conditions Used in the Experimental Runs

Run #	Injection Angle θ (°)	Z (in.)	Z_i (in.)	Y (in.)	Superheat Temperature (°C)	Gr Injector	Substrate Cooling
1	90	15.0	4.3	1.25	1240	Gen-1	No
2	90	20.0	4.3	1.25	1190	Gen-1	No
3	90	15.0	4.3	1.25	1190	Gen-2	Yes







Progress and Current Status of Project

a. Design of the Gr Injector and Collector (Substrate)

With the Gen-1 Gr injector, the Gr injection speed changed during deposition, likely leading to undesired Gr distribution in the nanocomposite.

0 sec

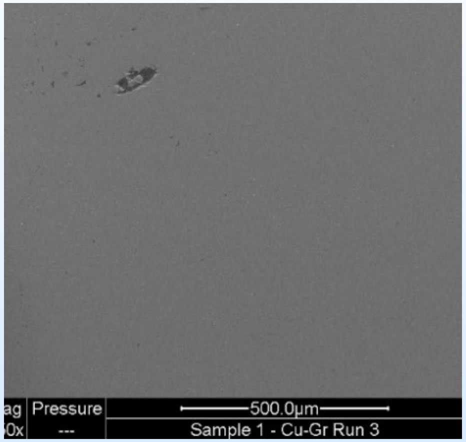
5 sec

Gr Injection in Action (with 100 psi Ar) with Gen-1 Gr Injector

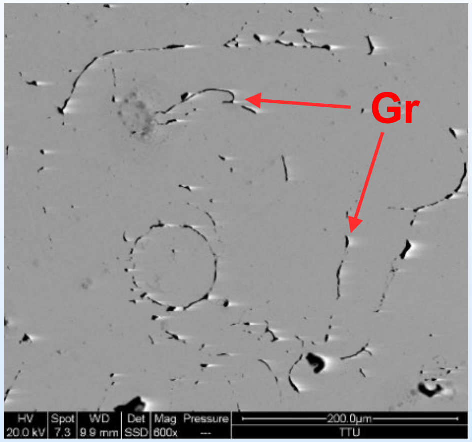
Progress and Current Status of Project

a. Design of the Gr Injector and Collector (Substrate)

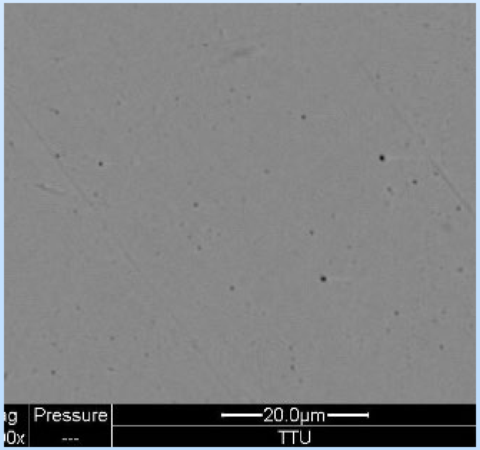
- With the Gen-1 Gr injector and uncooled substrate, the deposit in the center region was melted after impacting the substrate, resulting minimal Gr incorporation in the composite, while Gr was detected near the edge of the deposit in Run #1.
- With the increase in Z (distance between the Cu injection nozzle and substrate) from 15 to 20” and the decrease in superheat temperature from 1240 to 1190°C in Run #2, no noticeable improvement was achieved.



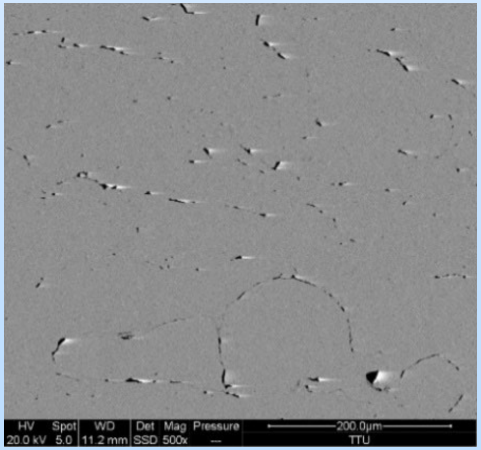
Center, Run #1



Edge, Run #1



Center, Run #2

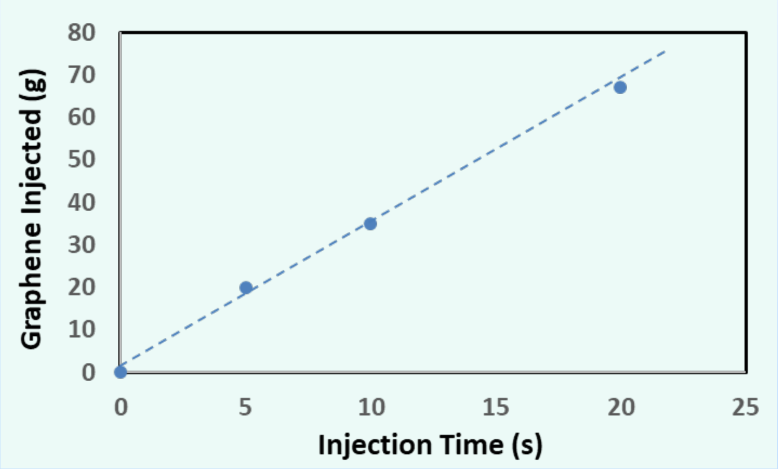


Edge, Run #2

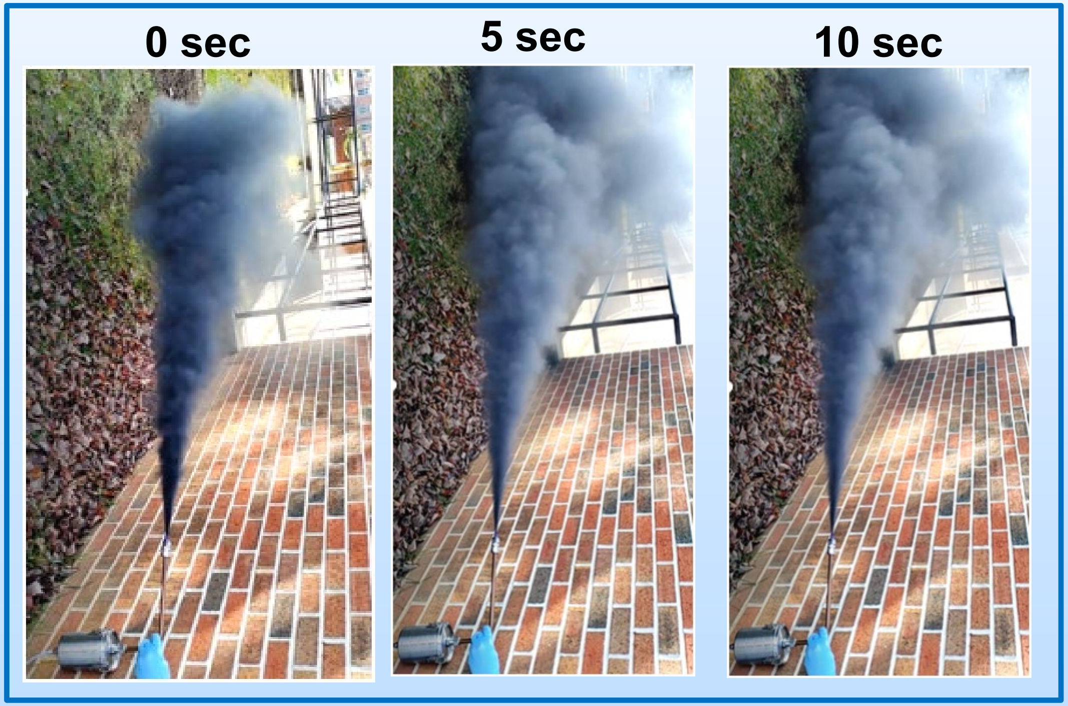
Progress and Current Status of Project

a. Design of the Gr Injector and Collector (Substrate)

With the change of the Gr injection mechanism used in the Gen-2 injector, the Gr injection speed was constant during deposition.



Gr Injected vs. Injection Time with the Gen-2 Injector at 100 psi Ar Pressure

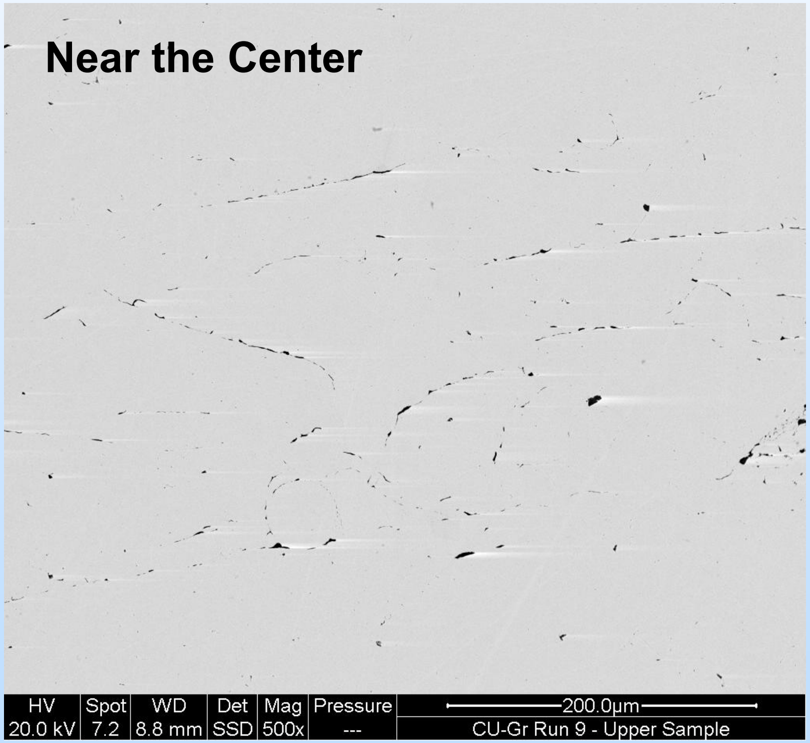


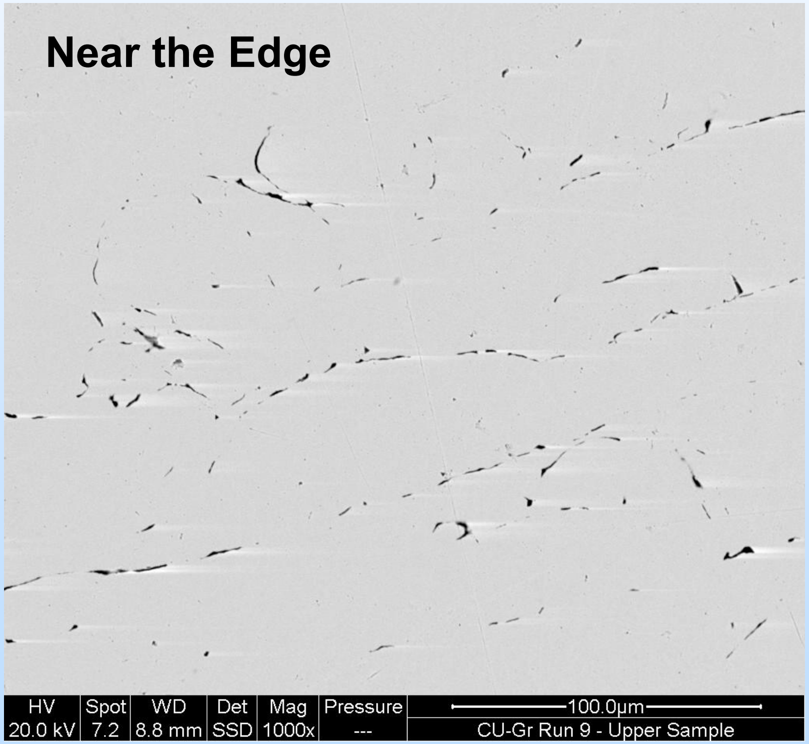
Gr Injection in Action (100 psi Ar) with the Gen-2 Gr Injector

Progress and Current Status of Project

a. Design of the Gr Injector and Collector (Substrate)

With the change of the Gr injection mechanism used in the Gen-2 injector and substrate cooling, a more consistent Gr distribution in the deposit was achieved.





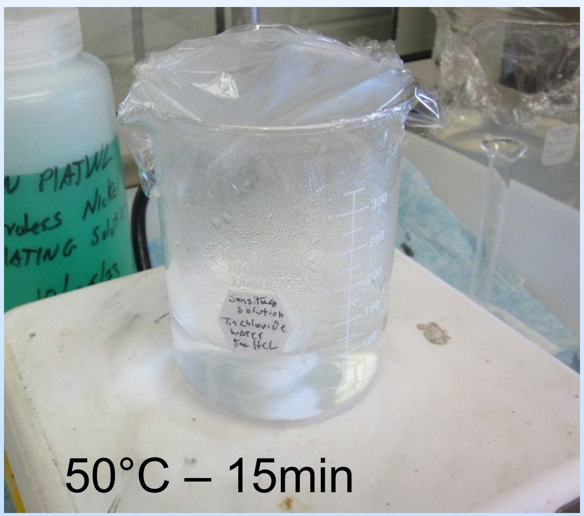
Cross-sectional Microstructure of the Deposit from Run #3

Progress and Current Status of Project

b. Approaches to Further Improving the Interface of the Gr and Cu

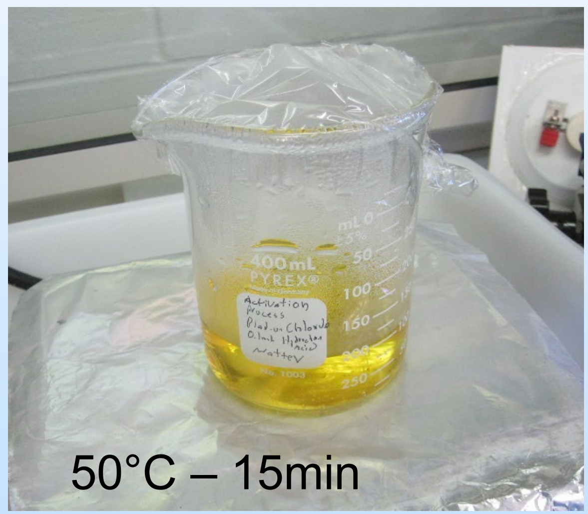
An electroless Ni-plating process was used to coat Gr with a thin Ni layer to improve Cu/Gr interfacial bonding.

The 3-Step Electroless Ni-Plating Process



1. Sensitizing

- 95mL DI Water
- 5mL HCL
- 1.0 (g) SnCl



2. Activation

- 99mL DI Water
- 1.0mL HCL
- 0.025 (g) $PdCl_2$

3. Plating

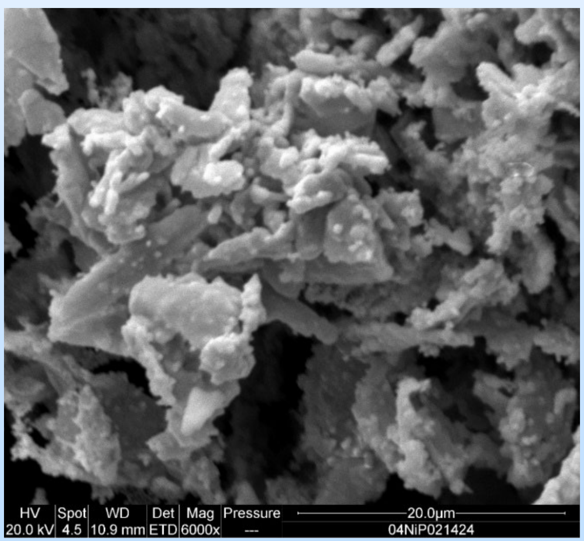
- EPL Ni Electroless Plating Solution

Progress and Current Status of Project

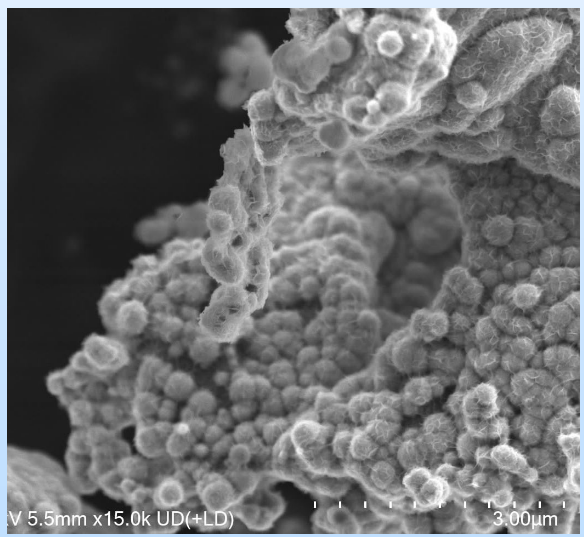
b. Approaches to Further Improving the Interface of the Gr and Cu

An electroless plating process is being optimized for coating Gr with an Ni layer

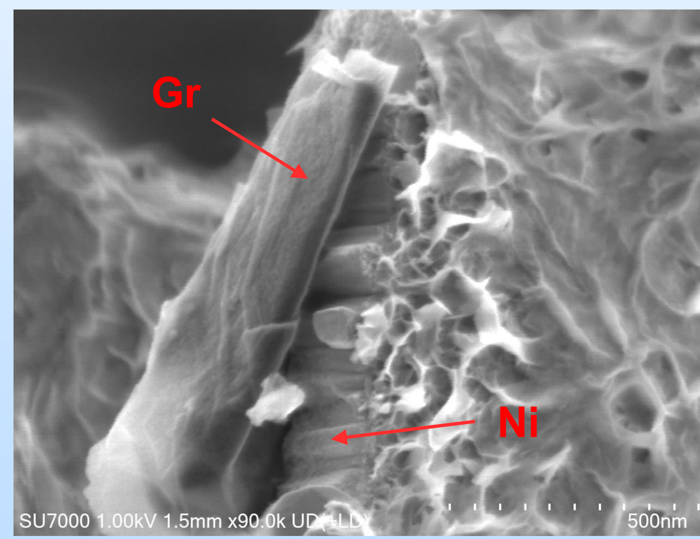
- The electroless Ni typically has a cauliflower-like surface morphology and columnar cross-sectional feature.
- The thickness of the Ni coating was reasonably uniform, ~150 nm around the Gr particulate.



Overall View of Ni-plated Gr



Surface Morphology of Ni on Gr



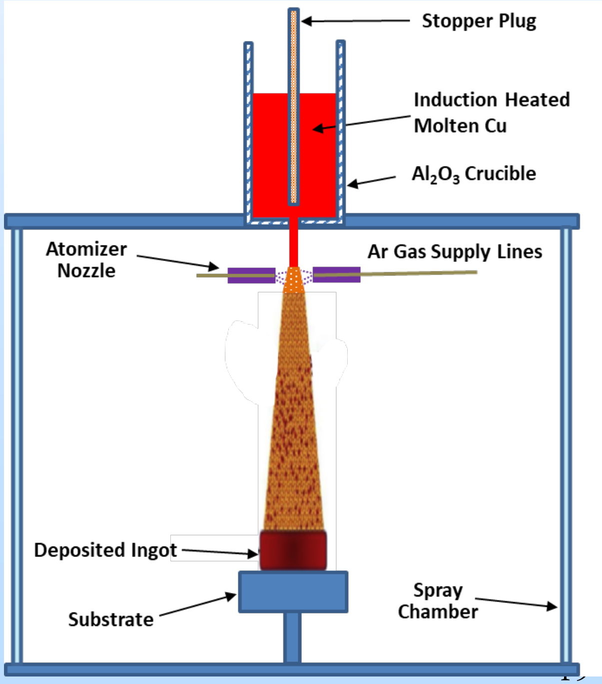
Cross-Sectional View of Ni Layer on Gr

Progress and Current Status of Project

b. Approaches to Further Improving the Interface of the Gr and Cu

Alloying addition of a transition metal X (X = Ti, Cr, etc.) into Cu to form an Cu(X) alloy can be used modify its wettability and interaction with Gr via the formation of a conductive carbide at the Cu-Gr interface.

- Cr or Ti pieces could be directly added to the Cu melt to form the desired alloy.
- Cu-Cr or Cu-Ti masteralloys could also be utilized.



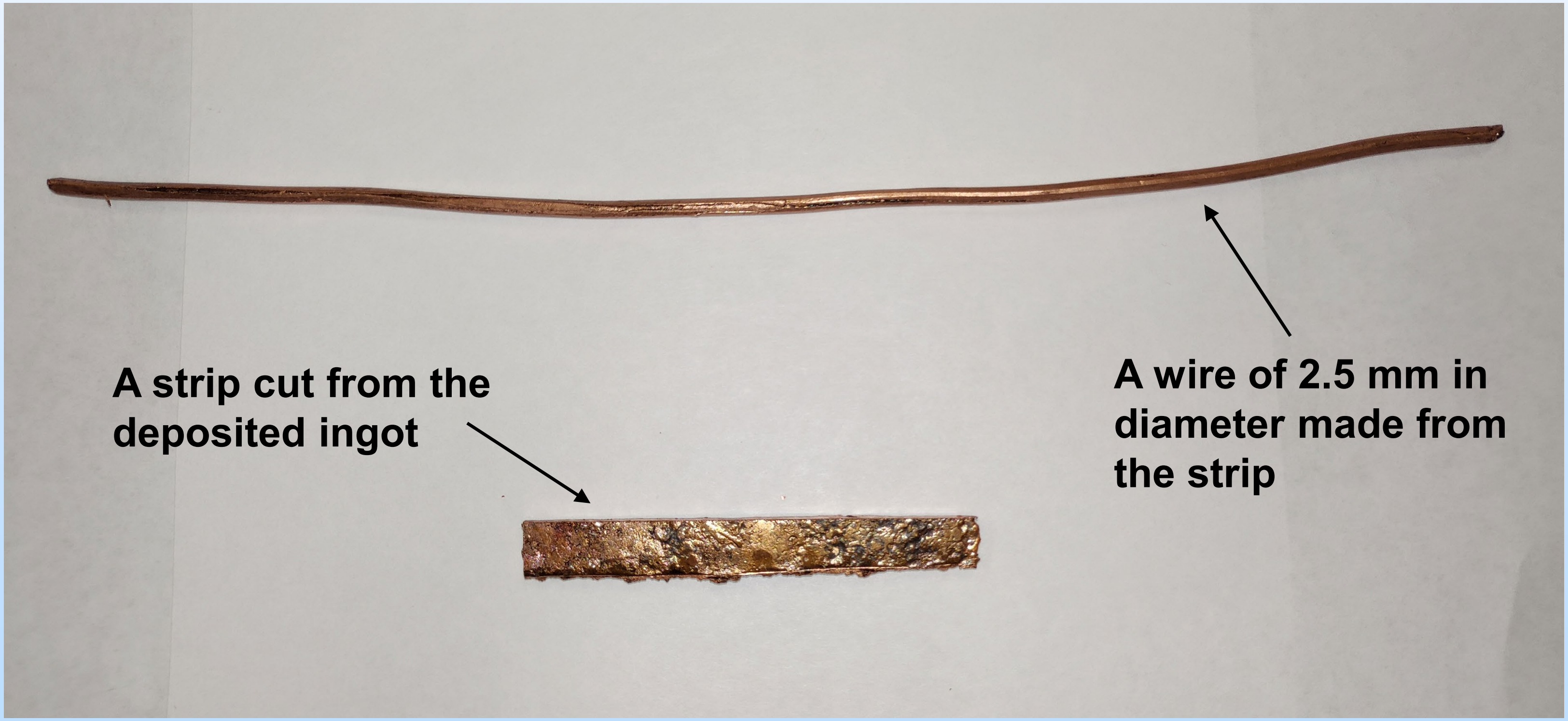
Chemical Compositions of Several Commercial Alloys and Masteralloys

Alloy	Cu (wt.%)	Cr (wt.%)	Ti (wt.%)	Vendor
C18200	99.1	0.9	—	AZO Materials
Cu-Cr Masteralloy	94-96	4-6	—	
Cu-Ti Masteralloy	70	—	30	American Elements
Cu-Ti Masteralloy	90	—	10	

Progress and Current Status of Project

c. Post-deposition Processing of Spray-deposited Materials

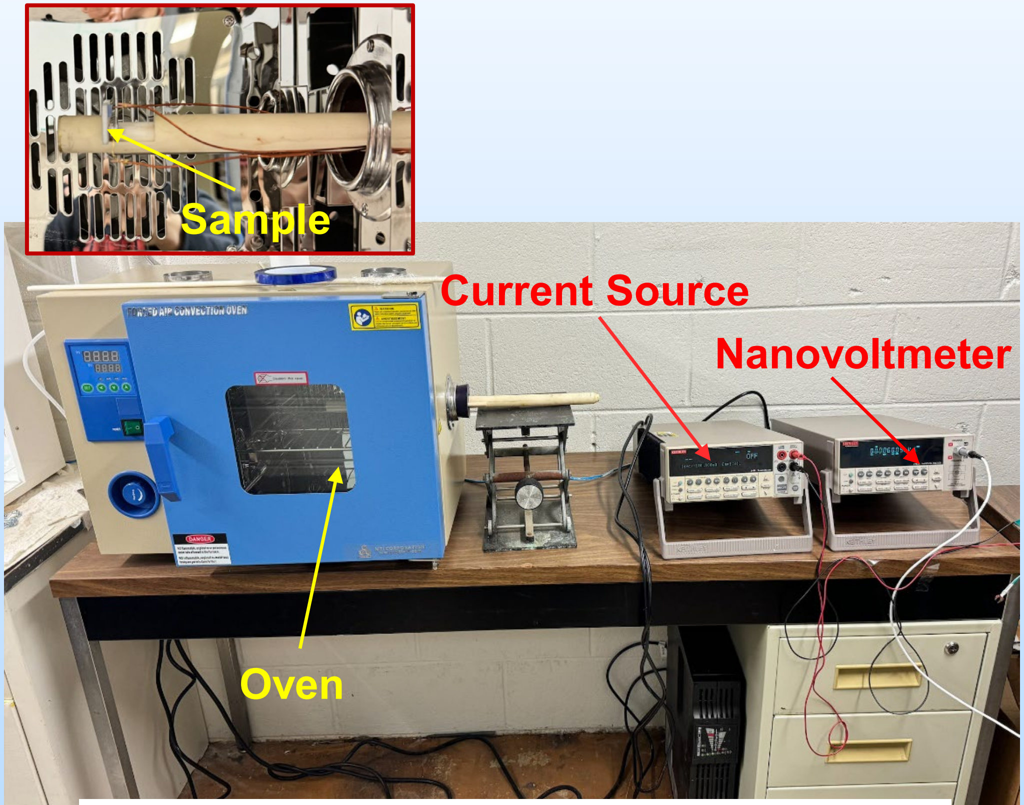
In collaboration with Copperweld, various post-deposition processes such as extrusion, drawing, rolling, etc., are being assessed to convert the deposited materials into wires with better Gr alignment for further evaluation.



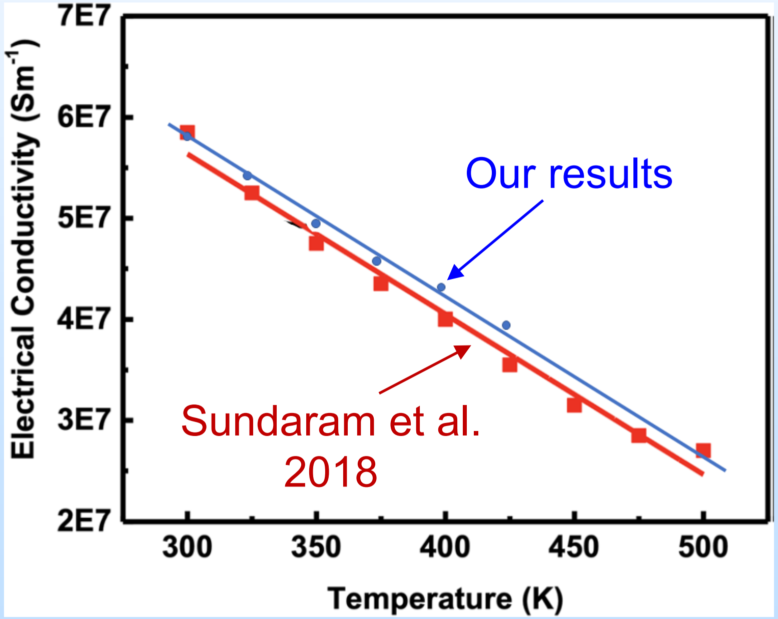
Progress and Current Status of Project

d. Characterization of Spray-deposited Composite Materials

A system has been successfully set up for the electrical conductivity measurement of highly conductive materials. Our preliminary results are promising.



Electrical conductivity measurement system at TTU

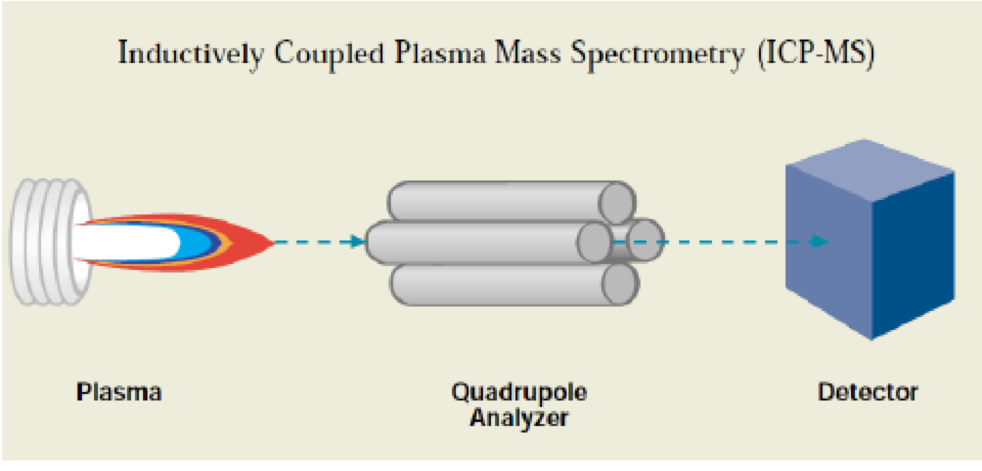


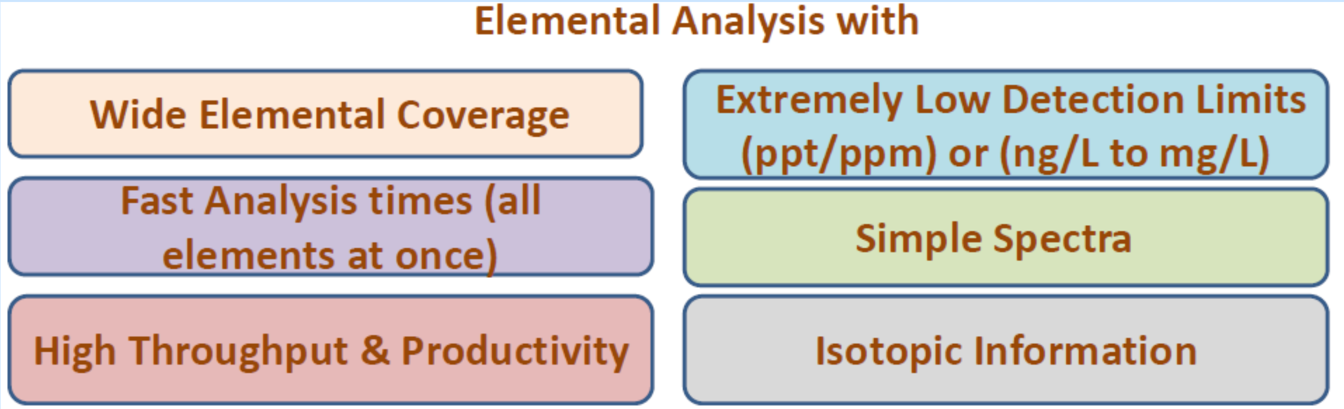
Electrical conductivity vs. temperature for pure copper using our test system

Progress and Current Status of Project

d. Characterization of Spray-deposited Composite Materials

- Inductively coupled plasma mass spectrometry (ICP-MS) is being used to assess the fate and quantity of impurity species (e.g., Hg, As, Se, Cd Sb, Pb, etc.) released from coal-derived Gr during processing.
- ICP-MS uses the ICP source to convert the atoms of the elements in the sample to ions which are then separated and detected by MS.





Plans for Future Testing/Development/ Commercialization

- Optimization of the spray deposition process is currently in progress to fabricate Cu-Gr nanocomposites with adequate Gr volume fraction, uniform Gr distribution, and minimal porosity.
- The improvement of the bonding between Cu and Gr will be explored through electroless Ni plating or alloying addition of transition metals such as Cr and Ti.
- The distribution and orientation of Gr in the composite will be further modified through secondary processing such as rolling, drawing, extrusion, etc.
- Electrical conductivity, thermal expansion coefficient, and mechanical properties of the nanocomposites will be evaluated.
- A TEA will be conducted to evaluate the cost-effectiveness of spray deposition compared to other processes (e.g., P/M).

Outreach and Workforce Development Efforts or Achievements

- Inclusion of diverse team members (female, veteran, etc.) to serve as role models to underrepresented communities
- Training of 2 graduate students and 6 undergraduate students so far, including the following:
  - ✓ 2 African Americans
  - ✓ 2 female students
  - ✓ 1 graduate student who started as an undergraduate research assistant on the project

- TTU
  - Co-PI: Female
  - Faculty Participant: African American
  - Lab Engineer 1: Veteran
  - Lab Engineer 2: Hispanic
- TSU: HBCU and surrounded by DACs
- Industry partners (CBL & EPL): small businesses in DACs

- Enhancement of a minority-serving institution (TSU)'s research capabilities in nanomaterials for clean energy applications
- Helping rural and low-income communities increase well-paid job opportunities and raise living standards

Summary

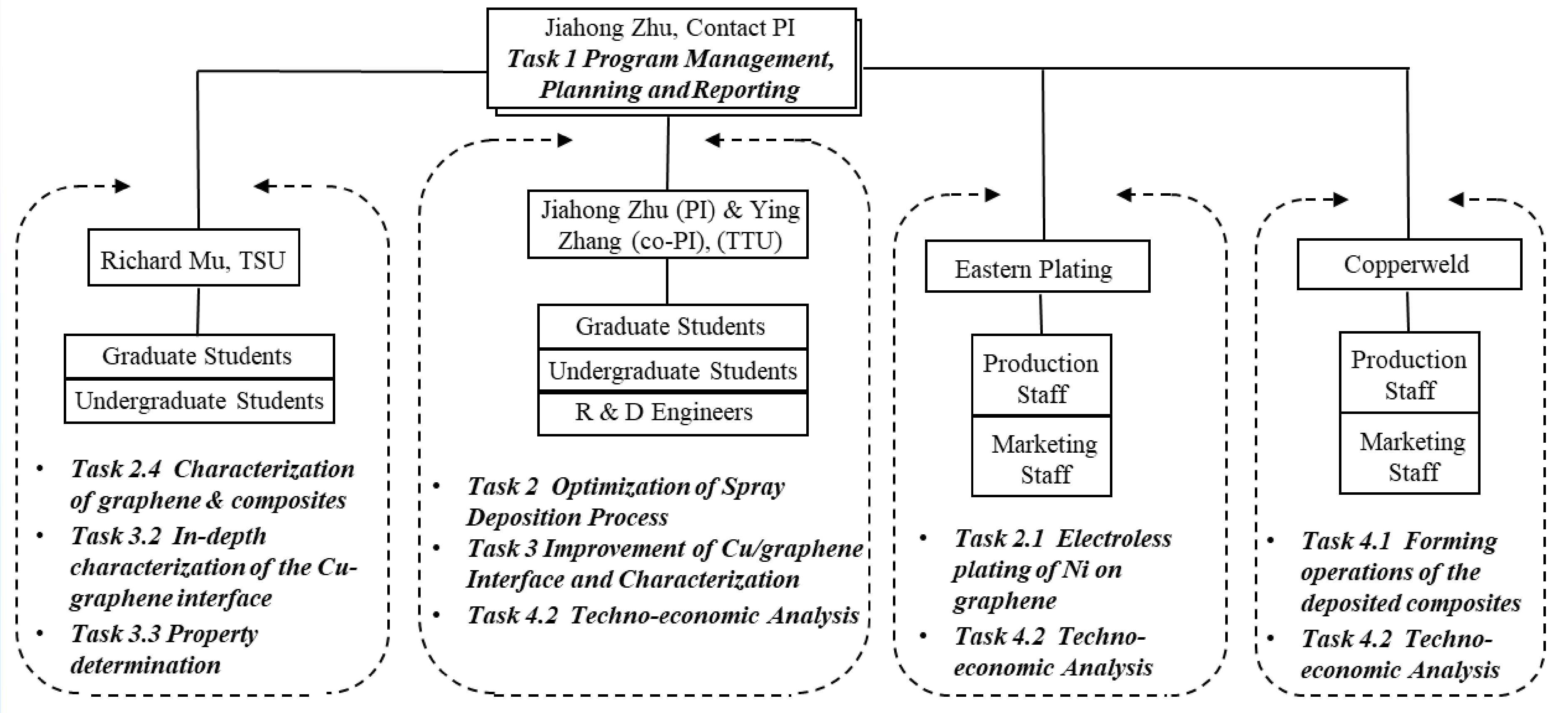
This research aims to develop high-performance Cu-Gr composites using coal-derived Gr via a low-cost spray deposition process.

- A new Gr injector design led to a consistent and uniform Gr stream during deposition.
- With the incorporation of a new Gr injector and water cooling of the substrate, a Cu-Gr composite with uniform Gr distribution was achieved.
- Electroless plating was utilized to deposit a uniform Ni layer onto the Gr particulates.
- Alloying addition to Cu is being explored to improve the Cu-Gr interface.
- Optimization of the spray deposition process is currently in progress for fabricating the Cu-Gr nanocomposites with adequate Gr volume fraction, uniform Gr distribution, well-aligned Gr, and minimal porosity.

Appendix

– These slides will not be discussed during the presentation but are mandatory.

Organization Chart



Project Team

- **Lead Institution:** Tennessee Technological University (TTU)
- **Academic Collaborator:** Tennessee State University (TSU)
- **Industrial Partners:** Copperweld Bimetallics (Copperweld) and Eastern Plating (EPL)

Gantt Chart

Task/ Subtask	Month after Start / Activity Description	Year 1				Year 2			
		3	6	9	12	15	18	21	24
1	**Project Management, Planning & Reporting**	AB							
2	**Optimization of Spray Deposition Process**								
2.1	*Injector design modification*								
2.2	*Spray process parameter optimization*					D			
2.3	*Electroless plating of Ni on graphene*				C				
2.4	*Characterization of graphene and composites*								
3	**Improvement of Cu/Gr Interface & Charact.**								
3.1	*Minor alloying additions in Cu*					E			
3.2	*In-depth interface characterization*								
3.3	*Determination of various properties*							F	
4	**Forming demonstration & TEA**								
4.1	*Forming operations of the composites*								
4.2	*Techno-economic assessment*								G

A, B, C, D, E, F, G - Milestone; ▲- Quarterly, Progress or Final Report