53rd International Conference on Environmental Systems
21-25 July 2024, Louisville, Kentucky ICES-2024-198

Graphene-Copper Hybrid Thermal Straps for Cryogenic Instruments and Optical Systems

Dan Wang,[1] Timothy Hall,[2] Stephen Snyder,[3] Maria Inman,[4]
Faraday Technology Inc., Englewood, OH, 45315

and

Jessica Godwin,[5] Nick Roberts[6]
Department of Mechanical and Aerospace Engineering, Utah State University, Logan, UT, 84322

The development of next generation materials with enhanced thermal and/or electrical conductivity will be beneficial for both terrestrial and space applications, ranging from thermal links for conduction cooling of cryogenic instruments and optical systems, mirror substrates for space telescopes, coolant tubes for heat exchangers and deployable radiators, space landing systems, to high powered electronics and beyond. The cryogenic cooling systems enable new capabilities on sensors, detectors, and accelerators, and thus be beneficial for the near- and mid-IR instruments on SmallSats and CubeSats for Earth and Lunar observations, and for extracting heat dissipation of superconducting radio frequency cavity and optics. High conductive thermal straps play a critical role in balancing heat dissipation and reaching the operating temperature of the instruments.

Within this context, in collaboration with Utah State University, Faraday Technology are developing an efficient, scalable, manufacturing-ready approach to produce high conductive graphene-copper hybrid foils and demonstrate their application in thermal straps for the conduction cooling of cryogenic instruments and optical systems. This technology utilizes the intrinsic physiochemical, thermal, and mechanical properties of graphene and copper matrix, combined with advanced electrodeposition techniques for hybrid material fabrication. The manufacturing process is based on the use of pulsed electric fields and the combination of electrodeposition and electrophoretic deposition. The fabricated graphene-Cu hybrid foil exhibited enhanced thermal conductivity and mechanical strain for fast conduction cooling processes. We are currently working on the scalp-up production of graphene-copper hybrid foils for thermal strap fabrication.

---

[1] Principal Research Scientist, Faraday Technology Inc., Englewood, OH 45315
[2] Research Director, Faraday Technology Inc., Englewood, OH 45315
[3] Senior Research Engineer, Faraday Technology Inc., Englewood, OH 45315
[4] Vice President, Faraday Technology Inc., Englewood, OH 45315
[5] Undergraduate Student, Department of Mechanical and Aerospace Engineering, Utah State University, Logan, UT, 84322
[6] Associate Professor, Department of Mechanical and Aerospace Engineering, Utah State University, Logan, UT, 84322

Nomenclature

CTAB = Cetyltrimethyl Ammonium Bromide
CVD = Chemical Vapor Deposition
EPD = Electrophoretic Deposition
LaRC = Langley Research Center
PVP = Polyvinylpyrrolidone
R = Thermal Resistance
RGO = Reduced Graphene Oxide
SAGE = Stratospheric Aerosol and Gas Experiment
SDL = Space Dynamics Lab
SRF = Superconducting Radio Frequency
TJNAF = Thomas Jefferson National Accelerator Facility

I. Introduction

The increasing performance of cryogenic cooling systems enable new capabilities of the sensors, detectors, and/or accelerators, which are essential for the advancement of terrestrial and space science missions. The development of next generation materials with enhanced thermal and/or electrical conductivity will be beneficial for a variety of applications, ranging from thermal links for conduction cooling of cryogenic instruments and optical systems, coolant tubes for heat exchangers and deployable radiators, space landing systems, to high powered electronics and beyond. High conductive thermal straps play a critical role in balancing heat dissipation and reaching the operating temperature of the instruments, such as superconducting radio frequency (SRF) cavity for accelerators (Figure 1A)[1], optics and detectors (Figure 1B)[2] on SmallSats and CubeSats for Earth and Lunar observations, etc. Copper, aluminum, and graphite are the traditional materials for thermal straps due to their thermal and mechanical properties.[3] The sluggish conduction cooling rate of conventional thermal straps made from copper, aluminum, or graphite hinders the application of thermal straps on the cryogenic cooling systems**.**

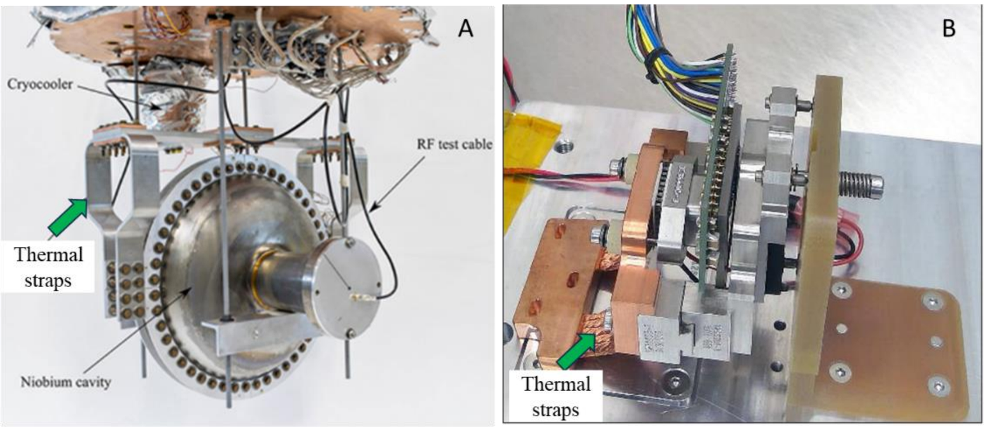

Figure 1. **Thermal straps for (A) SRF accelerator (Image from DOE Fermilab) and (B) SAGE-IV detector (Image from NASA/LaRC, SAGE-IV Team)**

Graphene are two-dimensional (2D) carbon materials with excellent physical and chemical properties, such as thermal and electronic conductivity, high mechanical strength, and large specific surface area.[4-6] Graphene and its derivatives have shown great potential in applications ranging from thermal management, energy storage, corrosion, to sensors.[5-9] Conjugated systems of composite materials may have collective properties that are drastically different than a simple combination of individual components. The intrinsic physiochemical properties of graphene and a metal (copper) matrix, combined with advanced fabrication techniques, could tailor graphene-copper hybrid properties and make the hybrid as ideal thermal strap materials for conduction cooling of cryogenic instruments and optical systems.

Graphene-metal hybrid materials can be synthesized through approaches such as chemical vapor deposition (CVD), electrical conversion process, powder metallurgy, electrodeposition, etc. Graphene has been directly grown on the surface of copper foil via CVD. However, the high synthesis temperature (> several hundred Celsius) limits its large-scale synthesis and industrial applications. In addition, graphene materials grown on the surface of copper foil are not only easily scratched during mechanical operation, but delaminate in operational environments due to different thermal expansion for graphene and copper during thermal cycling. Metal-carbon covetic materials have been produced using an electrical conversion process by applying electrical current into carbon materials infused molten metals. Covetics have shown higher thermal and electrical conductivity and higher strength compared to conventional metals.[10-12] However, challenges are high variability in carbon distribution in the metal matrix, high concentrations of micropores, and thermal stability of carbon materials in molten metals.[13] These challenges may result in the variability in property measurements and inconsistent conversion yields of covetic materials.[13] Due to the agglomeration of graphene, powder metallurgy remains the challenge on the interface creation between graphene and metal matrix.[14] Metal-carbon composites have been synthesized via electrochemical deposition.[14,15] Electrochemical approaches are particularly practical because they are cost-effective processes with simple equipment for large-scale manufacturing. The carbon materials are dispersed in the electrodeposition solution, to be well distributed in the metal matrix. In this work, we are developing an pulsed electrochemical deposition based, scalable manufacturing approach for producing high-performance graphene-Cu hybrid foils/coatings, and demonstrated their applications in thermal straps.

II. Experimental

A. Chemicals and Materials:

Copper sulfate solution (Maxu-pure) was purchased from Univertical. Reduced graphene oxide nanosheets were purchased from cheaptubes. Cetyltrimethyl Ammonium Bromide (CTAB), polyvinylpyrrolidone (PVP), and polyethylene glycol (PEG) were purchased from Sigma-Aldrich. Copper plates/foils and stainless steel substrates were obtained from McMaster-Carr.

B. Preparation of graphene-Cu plating bath

Reduced graphene oxide (RGO) nanosheets were chosen as graphene contents. Cetyltrimethyl Ammonium Bromide (CTAB) and polyvinylpyrrolidone (PVP) were used as dispersants for dispersing RGO nanosheets in Cu plating bath. CTAB also provides the positive charges for RGO sheets. Ultrasonication was used for dispersing the reduced graphene oxide sheets in the electrolytes. As shown in Figure 2 A and C, a clear Tyndall light scattering was observed by a side-incident light, indicating the presence of RGO nanosheets in the suspension/plating bath. The light is invisible (Figure 2 B) in the Cu plating bath without RGO contents. In a typical plating bath for graphene-Cu hybrid foil fabrication, the concentration of copper sulfate is ~ 90 g/L, the concentration of RGO, CTAB, and PVP are 5 mg/L.

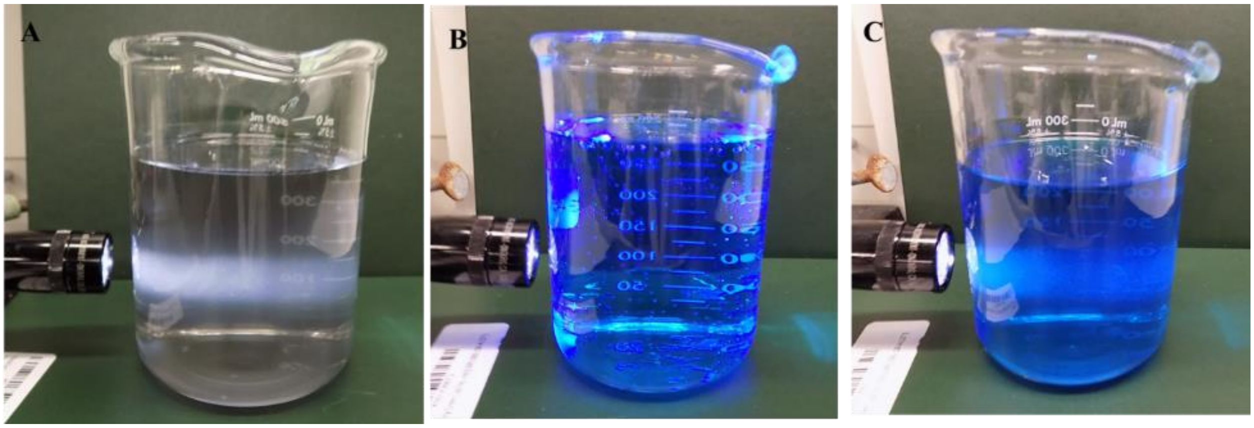

Figure 2. Photographs of (A) reduced graphene oxide (RGO) dispersion; (B) Cu plating bath without RGO; (C) Cu plating bath with dispersed RGO.

C. Fabrication of incorporated graphene-Cu hybrid foils

The incorporated graphene-Cu hybrid foils were fabricated *via Pulsed Electro-CoDeposition.* Electro-CoDeposition is a method for incorporating small particles of different materials (e.g., graphene or CNT) within a metal matrix (e.g., copper or aluminum) applied by electrophoretic deposition (EPD). *Pulsed Electro-CoDeposition* differs from conventional DC Electro-CoDeposition via a user defined, periodically interrupted waveform permitting benefits such as enhanced deposit properties (*e.g.*, hardness, wear and corrosion resistance), improved foil uniformity (via more homogenous current distribution obtained through waveform and process parameter control), and increased average deposition rates.

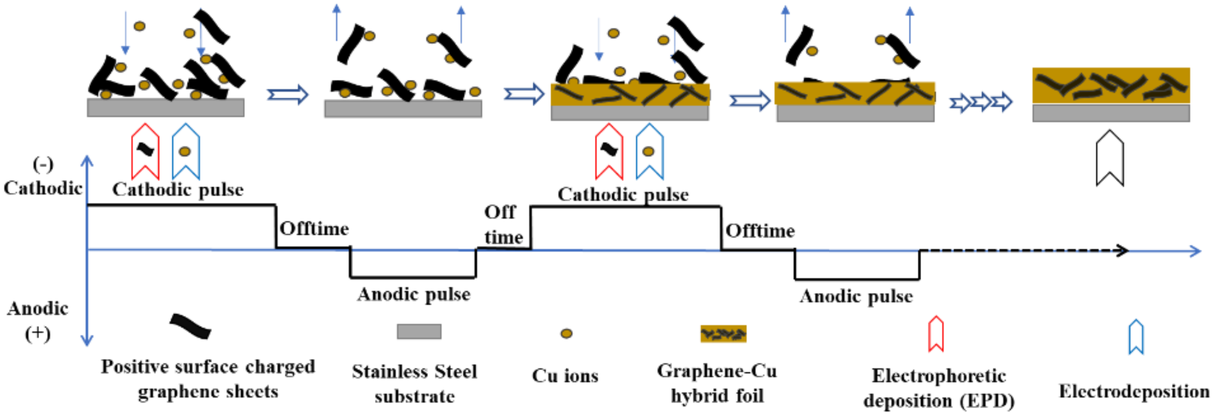

Figure 3. The scheme of Pulsed Electro-CoDeposition approach for fabricating incorporated graphene-Cu hybrid foils

The synthesis process of incorporated graphene-copper hybrid foils via pulsed electro-codeposition process are demonstrated in Figure 3. During the electro-codeposition process, the stainless-steel substrate and the counter electrode (Cu plate) will be fixed relative to one another and connected to a pulsed power source (Figure 4). Cu anode is a sacrificial counter electrode to maintain the Cu concentration constant during the fabrication process. With the positive charges, both RGO materials and Cu are deposited on the substrate under cathodic current. Under anodic current the hybrid coating is preferentially removed from areas exposed to higher current densities, to improve deposit uniformity. With alternate electrical fields under pulse current reverse process, RGO sheets were distributed and embedded in the copper matrix to form incorporated graphene-copper hybrids. Pure cooper foils were also fabricated using the Cu plating bath without RGO contents. The fabricated foils were then peeled off from the substrate (Figure 5) for further thermal reduction treatments and characterization.

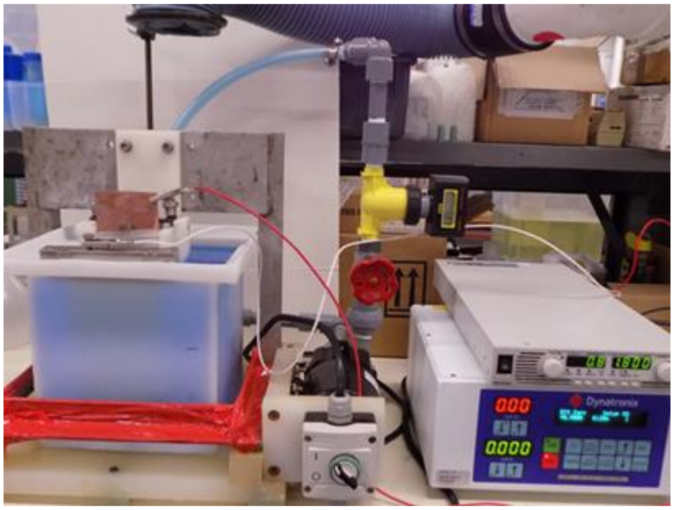

Figure 4. Pulsed Electro-CoDeposition setup for 4” x4” of graphene-copper hybrid foil fabrication.

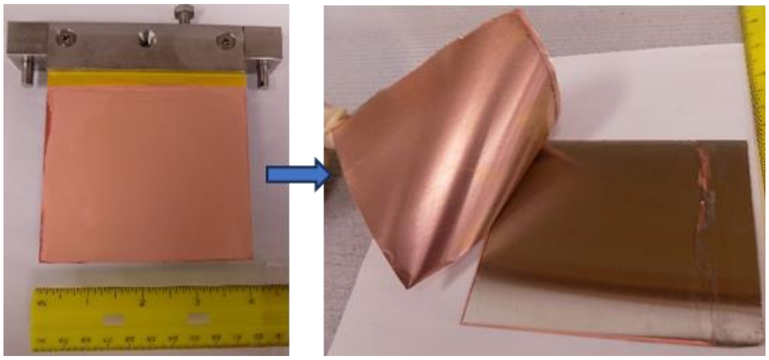

Figure 5. Fabricated foil peeled off from the substrate

Instead of pristine graphene, reduced graphene oxide sheets are used as graphene content in this solution phase -based approach. Due to the defects and/or oxygen containing groups, the thermal/electrical conductivity of RGO are decreased comparing with pristine graphene. Therefore, a post thermal reduction treatment for fabricated graphene-Cu hybrid foils was performed. In a typical thermal reduction process, the tube furnace system was evacuated for 20 min and then backfilled with reducing gas. Second, the tube furnace was heated to desired temperatures. Third, the selected samples were thermal reduced under reducing gas environment. Finally, furnace was opened and cooled down to room temperature, and the foils were then taken out from the furnace for thermal and mechanical property characterization.

D. Characterization

The hybrid foils were examined by Raman spectroscopy using the Renishaw inVia Reflex Micro-Raman with 514 nm laser excitation to confirm graphene composition in the hybrid foils. The thermal conductivity measurement method is a steady-state method that applies a known heat rate (0.25 W) across the foil along the in-plane direction. The foil sample is held in place in the sample holder that is mounted to the cold finger within a He Closed Cycle Cryostat. The heat rate is applied by a cartridge heater mounted on the hot-side (top) of the sample holder. The cartridge heater is rated to 25W of power and run at 1% (0.25W). Figure 6 shows the images of the thermal conductivity test device with the fabricated foil sample. The temperature sensors are mounted on the plates that secure the sample to the sample holder. The test device is approximately 2.5” tall by 2” wide. The dimensions of the test samples are cut to approximately 1” wide by 1.5” tall. Mechanical measurements were conducted on an INSTRON 5542 using the ASTM E345 testing standard. Sandpaper and tape were added at the grips to improve friction and minimize slipping of the foil samples during measurements. The mechanical measurements were performed at room temperature with a constant strain rate of 20 mm/min.

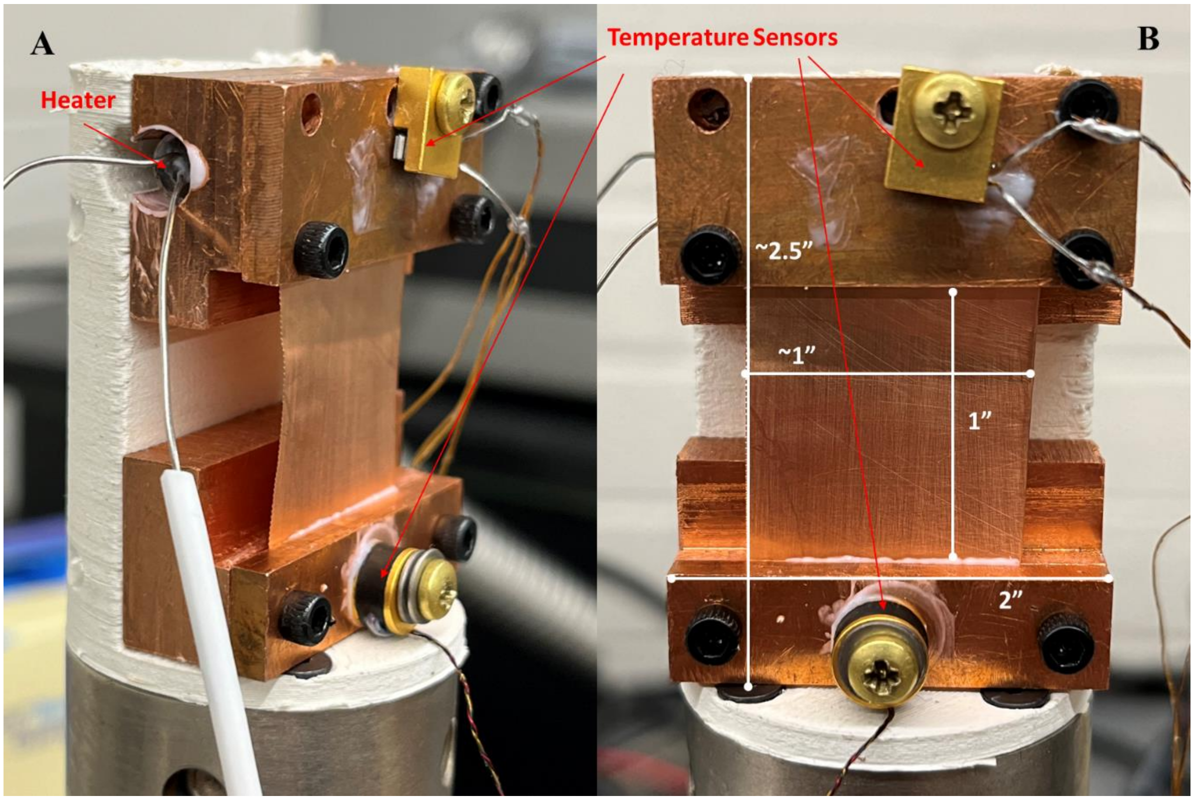

Figure 6: (A) Side and (B) front view of the thermal conductivity test device with the fabricated foil sample

III. Results and discussion

The graphene-Cu hybrid foils were peeled off from the substrates as free-standing graphene-copper hybrid foils for the characterizations. Raman spectrometry was used to confirm graphene composition in the hybrid foils. As shown in Figure 7A, the hybrid foil exhibited two peaks: the D band at ~1350 cm^{-1}; the G band at 1600cm^{-1}. The D band is attributed to defects in the graphene, and G band is associated with the tangential vibrations of sp^2 bonded carbon atoms. These two featured bands indicated the existence of graphene materials in the hybrid foils. As a comparison, electrodeposited pure copper foil is featureless across 1200 ~1800 cm^{-1} (Figure 7B).

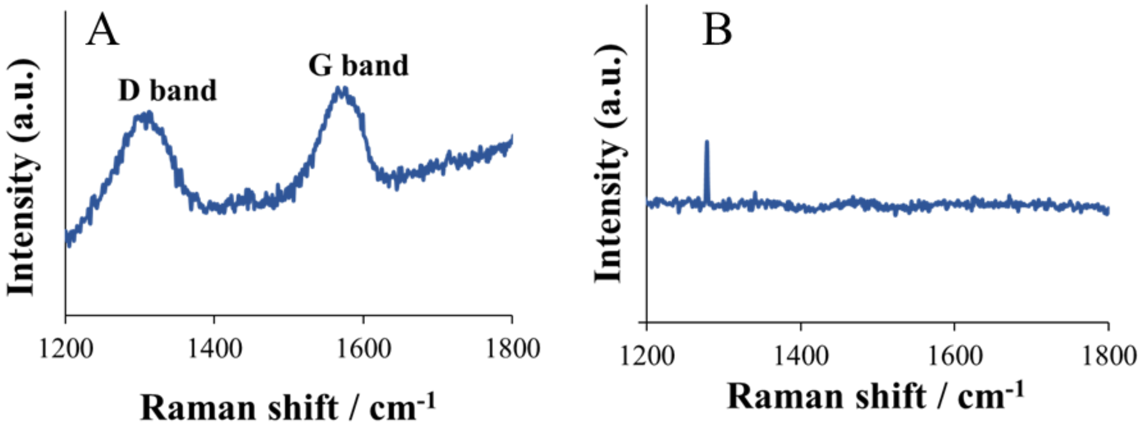

Figure 7. Raman spectra of (A) graphene-Cu hybrid foil and (B) Cu foil.

The thermal conductivity of the foils was measured via a steady-state method that applies a known heat flux across the foil along the in-plane direction. The calculation of the thermal conductivity is based on Fourier's Law of Heat Conduction. By applying a known heat rate from the cartridge heater and measuring the temperature difference across the foil using two Si-diode temperature sensors, the thermal conductivity can be calculated by treating the foil and sample holder as a parallel thermal resistance circuit. The sample holder thermal resistance has been quantified and is necessary to accurately calculate the heat flux through the foil. Some of the heat is transferred through the sample holder. The thermal resistance network consists of two parallel thermal resistance paths. One includes the foil and the thermal contact resistances between the sample holder and the foil. The thermal contact resistances are minimized by applying a vacuum compatible thermal grease. The second thermal resistance path is that of the sample holder. Based on a standard Cu foil, the thermal resistance of the sample holder is more than 50x greater than the foil for the most conductive foils, meaning 98% of the heat flux will conduct through the foil sample, providing an excellent temperature difference to have good signal to noise in the measurement which will allow us to minimize the heating rate, which can result in greater heat loss and thus higher uncertainty. The target temperature difference across the 2" foil is targeted to be 5-15 K, which is achieved with a fraction (1% in current tests) of the 25 W heater with the use of the temperature controller.

The measurement produces a total thermal resistance based on the measured temperature difference and the applied heat rate:

$$R_{tot} = \frac{\Delta T}{q}$$

The thermal resistance of the foil is determined by solving the following equation:

$$R_{tot} = \left[\frac{1}{R_{sh}} + \frac{1}{R_{foil}}\right]^{-1}$$

where R_{sh} is the thermal resistance of the sample holder, which is determined from previous measurements without a foil present. By knowing the thermal resistance of the individual foil, the thermal conductivity can be calculated based on the definition of the thermal resistance.

$$R_{foil} = \frac{L}{kA}$$

Where L is the length of the foil between the sample holder, A is the cross-sectional area of the foil sample along the direction of heat transfer and k is the foil thermal conductivity. Uncertainty in the measurement is included based on uncertainties of temperature, length, thickness, and width measurements. These vary from sample to sample based on the surface roughness and non-uniformity and the individual measurements and variations. More detailed uncertainty quantification is still needed, but we currently estimate the measured thermal conductivity values are within 10% accuracy of the actual thermal conductivity and the range of values given represents a 98% confidence interval of the thermal conductivity.

The thermal conductivity of commercial Cu foil (annealed, McMaster-Carr), both DC and pulsed electrodeposited Cu foils and Cu-graphene hybrid foils were measured and plotted in Figure 8. The Cu-graphene foils fabricated via Pulsed Electro-CoDeposition exhibited more than 50% enhancement in thermal conductivity compared to that of commercial Cu foil.

In addition, the thermal conductivity of Cu-Graphene foil after thermal reduction treatment exhibited 90% enhancement compared to commercial annealed Cu foil (Figure 8). We reason that the post thermal reduction treatment reduces the oxygen containing groups of reduced graphene oxides and the oxidation of Cu, and thus further improve hybrid foil conductivity.

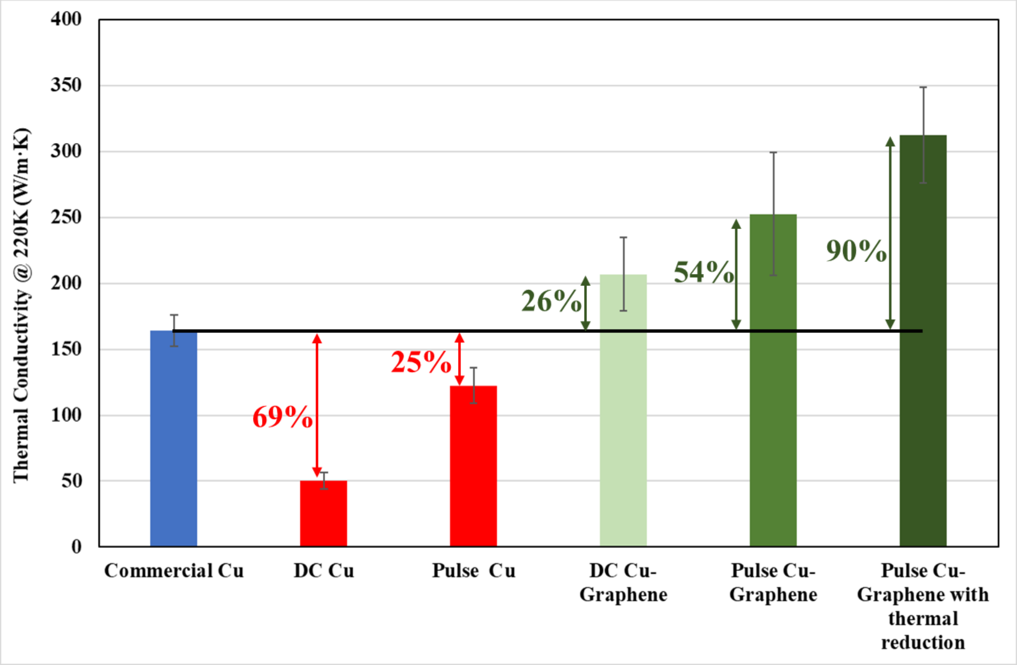

Figure 8. The comparison of thermal conductivity

The mechanical measurements were conducted on an INSTRON 5542 using the ASTM E345 testing standard and performed at room temperature with a constant strain rate of 20 mm/min. The Stress-Strain Curves of Cu foil and graphene-Cu hybrid foil are shown in Figure 9. The graphene-Cu hybrid foil exhibits ~50% increase in mechanical strain comparing with that of pure Cu foil.

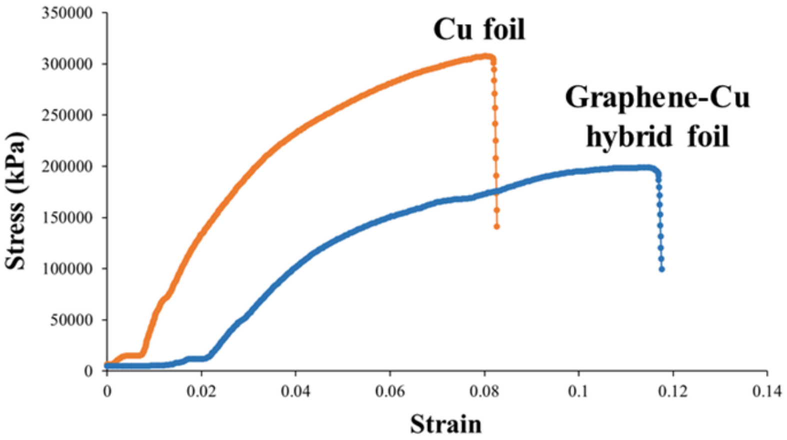

Figure 9. Stress-Strain Curves of Cu foil and graphene-Cu hybrid foil.

IV. Conclusion and Future Work

In this work, we developed a pulsed electrochemical deposition based, scalable and manufacturing-ready approach for production of high-performance graphene-Cu hybrid foils/coatings. We confirmed CTAB and PVP for dispersing graphene contents in Cu plating bath, and CTAB provides positive charges for graphene contents to avoid the aggregation or precipitation with Cu ion in the electrolyte due to electrostatic interaction. The thermal conductivity of Cu-Graphene foils is more than 50% higher than that of commercial annealed Cu foil. The thermal conductivity of Cu-Graphene foil is further enhanced by thermal reduction treatments, which exhibited 90% enhancement compared to commercial annealed Cu foil. The graphene-Cu hybrid foils also show ~50% mechanical strain increase.

Figure 10. The scale-up deposition system for graphene-Cu hybrid foil fabrication.

Currently we are working on the scale-up production of the graphene-Cu hybrid foils. We designed and built the scale-up deposition system as shown in Figure 10. The scale-up deposition system has the capacity for depositing graphene-copper hybrid foils on stainless steel panel substrates up to 24” x 24”. We will work with Space Dynamics Lab (SDL) for thermal strap fabrication using synthesized graphene-copper hybrid foils. The thermal and mechanical performance of the thermal straps will be evaluated at SDL and DOE Thomas Jefferson National Accelerator Facility (TJNAF).

Acknowledgments

The authors of this project would like to acknowledge the financial support from DOE SBIR program through grant No. DE-SC0021676 (Phase I&II).

References

---

[1] https://science.osti.gov/hep/Highlights/2018/HEP-2018-10-b

[2] https://www.eoportal.org/other-space-activities/sage-iv#instrument-design

[3] Trollier, T, Cryocoolers 19, 2016, https://cryocooler.org/resources/Documents/C19/595.pdf

[4] M.J. Allen, V.C. Tung, and R.B. Kaner; "Honeycomb Carbon: A Review of Graphene"; *Chem. Rev.* **110**, 132-145 (2010).

[5] A. Ambrosi, C. K. Chua, A. Bonanni, and M.Pumera; "Electrochemistry of Graphene and Related Materials"; *Chemical Reviews* **114**, 7150-7188 (2014).

[6] C. Cheng, S. Li, A. Thomas, N.A. Kotov, and R. Haag; "Functional Graphene Nanomaterials Based Architectures: Biointeractions, Fabrications, and Emerging Biological Applications"; *Chemical Reviews* **117**, 1826-1914 (2017).

[7] Jacob Lewis, T. Perrier, Z. Barani, F. Kargar, and A.A. Balandin. "Thermal interface materials with graphene fillers: review of the state of the art and outlook for future applications"; *Nanotechnology* 32 (2021) 142003

[8] Jackie Renteria, Denis L. Nika, Alexander A. Balandin; "Graphene Thermal Properties: Applications in Thermal Management and Energy Storage"; *Appl. Sci*. 2014, 4, 525-547;

[9] S. Ghosh, I. Calizo, D. Teweldebrhan, E. P. Pokatilov, D. L. Nika, A. A. Balandin, W. Bao, F. Miao, and C. N. Lau; "Extremely high thermal conductivity of graphene: Prospects for thermal management applications in nanoelectronic circuits"; *Appl. Phys. Lett*. 92, 151911 (2008)

[10] Mete Bakir, Iwona Jasiuk; "Novel metal-carbon nanomaterials: A review on covetics"; *Advanced Materials Letters*. 2017, 8(9) 884-890

[11] H.M. Iftekhar Jaim, Romaine A. Isaacs, Sergey N. Rashkeev, Maija Kuklja, Daniel P. Cole, Melburne C. LeMieux, Iwona Jasiuk, Sabrina Nilufar, Lourdes G. Salamanca-Riba; "Sp^2 carbon embedded in Al-6061 and Al-7075 alloys in the form of crystalline graphene nanoribbons"; *Carbon* 107 (2016) 56-66

[12] Lourdes Salamanca-Riba, Romaine A. Isaacs, Melburne C. LeMieux, Jiayu Wan, Karen Gaskell, Yeping Jiang, Manfred Wuttig, Azzam N. Mansour, Sergey N. Rashkeev, Maija M. Kuklja, Peter Y. Zavalij, Jaime R. Santiago, Liangbing Hu; "Synthetic Crystals of Silver with Carbon: 3D Epitaxy of Carbon Nanostructures in the Silver Lattice"; *Adv. Funct. Mater*. 2015, 25,4768-4777

[13] Beihai Ma, Uthamalingam Balachandran, Jie Wang, Jianguo Wen, Tae H. Lee, Stephen E. Dorris, and Adam J. Rondinone; "Structural hierarchy of nanocarbon in copper covetics"; *J. Mater. Sci*. (2018) 53:10173-10180

[14] Hrudaya Jyoti Biswal, Pandu R. Vundavilli, and Ankur Gupta; "Perspective—Electrodeposition of Graphene Reinforced Metal Matrix Composites for Enhanced Mechanical and Physical Properties: A Review"; *J. Electrochem. Soc.*, 2020, 167, 146501

[15] H. McCrabb, EJ Taylor, M. Inman, Christie Devlin and Matthew Leines; "Pulsed Electric Fields for Fabrication of Copper/Carbon Nanotube and Carbon Nanotube Films"; *ECS Transactions*, 28 (17) 85-101 (2010)