Book Chapter

Experimental Investigation to Study the Feasibility of Fabricating Ultra-Conductive Copper Using a Hybrid Method

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Abstract

Ultra-Conductive Copper (UCC) has an enormous potential to disrupt the existing Electrical and Electronic Systems. Recent studies on Carbon Nanotubes (CNTs) a new class of materials showed the ballistic conductance of the electricity. Researchers around the world are able to demonstrate Ultra-conductivity at micro and millimeter length sections using various processing techniques by embedding CNTs in the Copper matrix. Although multiple methods promised the possibility of producing copper-based-nanocomposites with gains in electrical conductivity, thus far scaling up these results has been quite a challenge. We investigated a hybrid method of both hot-pressing followed by rolling in order to produce the UCC wire. Cu/CNT billets of 1/10%, 1/15%, and 1/20% are hot-pressed and the conductivity results are compared to a hot-pressed pure copper billet. Our results indicated that this method is not a viable approach as the gains in electrical conductivity are neutralized followed by attenuation of the wire cross-section.

Keywords

CNTs, Electrical Conductivity, Nanocomposites, Electrical Conductors, Ballistic Conductors, Cu/CNT Composites

Introduction

Today the world is heavily dependent on electricity in all aspects of life from lightening a house to lightening the International space station, running a car on the Earth to running a rover on the Mars. Electricity and Electronics are so integrated in our everyday lives, it is difficult to imagine the world without them. Not limiting to the current applications, more and more applications are coming forward everyday owing to the growing global electrification and advances in the electrical and electronic technologies. Although the demand for electricity exceeds the supply [1], newer methods of harvesting electrical power at large are disrupting the world every day [2]. Apart from generation of electricity, Electrification also involves the transmission and distribution of electricity which demands for an efficient conductor.

Traditionally copper and aluminum are the most widely used electrical conductors. Aluminum is used for the transmission of electricity from power grids to substation and transformers. Copper on the other hand is used in appliances, house/industrial wiring, and other electrical connectors. Since the invention of voltaic cells copper played a pivotal role in the Electrical conduction. Copper being a non-precious metal and with its wide range of properties, is the best material for electrical conduction. Copper is by far considered as the most commonly used metal for electrical applications. According to 2021 US geological Survey Mineral Commodities, 21% of mined copper is used for electrical or electronic products directly [3]. According to Copper Development association more than half of the copper produced is used for electrical or electronic applications [4]. In 1914 the United States Circular of the Bureau of the Standards determined the international annealed copper standard (IACS) as 1.7241 microohm-cm at 20^0 C [5]. This is the value of the electrical resistivity of annealed copper. This value is still in effect and IACS electrical conductivity is $58x10^6$ S/m. Owing to the technological advancements in purifying and processing copper, the Oxygen-free high purity copper guarantees 102% IACS. On the other hand, the electrical conductivity of the fully cold worked copper is only 5.63 x 107 S/m which corresponds to

97% IACS. We used IACS representation in this report to avoid misinterpretations with standard annealed copper, Oxygen-free Copper and/or other forms of Copper metal. Not much development was made in this field since the earliest conductors (Copper). As we are entered into new age of technology where electricity and electronics are used almost in all aspects, better conductors with that are capable of carrying higher currents and low resistance are in demand.

Collins and Avouris [6] observed in the Multi-Walled Carbon nanotubes (MWCNTs) all the shells in a MWCNT are contributing for the electrical conduction. This breakthrough discovery opened the channels for developing ultra-conductive materials by using MWCNTs as the high conductive filler material. Frank et al [7] reported the ability to quantize the conductance of MWCNTs and observed a high stable current density of $>10^7$. They reported the nanotubes conduct the electricity ballistically with no heat loss. Wei et al [8] also recorded the ability of MWCNTs to carry eelctrical current of magnitude higher than 10^9 A/cm2 at elevated temperatures of 250^0C. They also reported the Nanotubes showed no observable failure and no measurable change in the resistance detected. Li et al [9] reported in their experimental observations that MWCNTs have the capability to carry higher currents at low bias voltage with perfect ohmic contacts. They reported the behavior of MWCNT is due to quasi-ballistic conductance of inner walls of the CNT. Their experimental results showed higher conductance of MWCNT compared with theoretical value of Single-Walled Carbon Nanotubes (SWCNT). Hjortstam et al [10] in their famous article “Can we achieve ultra-low resistivity in carbon nanotube-based metal composites?” explains the possible challenges in the paths of developing Ultra-conductive materials. This article also guides the researchers in the possible ways to work towards achieving Ultra-conductive conductors.

Nayfeh [11] et al reported electrical conductivity of 113% IACS by copper nanocomposite produced by using die-casting method. These results encourage researchers in pursuit of developing Nano composites which can exhibit higher electrical conductivity. Furthermore, other methods for fabricating Ultra-conductive conductors are also investigated [12]. Chen [13] investigating a specific electrolytic co-deposition process showed an increase in the electrical conductivity of Copper/CNT composite by 200% of copper. Many others follow this route for fabricating Copper/CNT composite for developing ultra-conductive materials. Cambridge University researchers are developing methods to produce Copper/CNT composite by developing CNT-fiber bundles and infiltrate them onto copper by using vapor deposition or electrodeposition. Recently researchers from Shanghai Jiao Tong University [14] demonstrated the ability to produce ultra-conductive copper by embedding graphene in copper. Graphene is applied on both sides of copper and thus copper is sandwiched in between graphene. A stack of such layers pressed there by creating an electron path channel. They showed the material is able to measure 116% IACS.

Researchers are able to demonstrate the ultra-conductivity, but the results are not consistent, and the length of the ultra-conductive zones are limited to the ranges of millimeter long sections [11-14]. Albeit, multiple methods are being investigated, thus far scaling up these results has been quite a challenge [12,15]. In this paper we are reporting the experimental findings of using a hybrid method developed in order to synthesize Copper/CNT nanocomposite with enhanced electrical conductivity.

Materials and Methods

The CNTs used in this study are MWCNTs, which are obtained from Applied Sciences Inc., Cedarville, Ohio. The CNTs are functionalized with Magnesium as described in US Patent#8,347,944. Copper powder of 99.5% purity is supplied by Alfa Aesar Inc., USA (Lot No.: H05U037).

The magnesium functionalization process involves the mixing of anhydrous $MgCl_2$ with deionized water in a ratio of 1:4 by weight to form $MgCl_2(H_2O)_x$. Graphitized MWCNTs (25% (wt/w) are added to the $MgCl_2(H_2O)_x$ solution. This suspension is rigorously agitated using a mechanical agitator at 150rpm for six hours. Following the mechanical stirring, the $MgCl_2(H_2O)_x$ / CNT suspension is agitated by 20kHz ultrasonication technique. The 20kHz ultrasonication was performed with a solid probe (25 mm diameter, titanium alloy) connected to a 20 kHz oscillator (750 Watt, Vibra-cell VCX 750, Sonics & Materials Inc.) for 6 hours. The sonicator is operated in a pulsed mode 10s on and 20s off.

Following the ultrasonication, the slurry of CNTs and MgCl2 is heat treated in two phases. During the Phase-1 heat treatment the slurry is held at an elevated temperature of 200ºC for four hours in a Isotemp Vacuum Oven 282A. The resultant product after the first stage of heating is a dense material. It is broken down into smaller fragments and prepared for the Phase-2 heating treatment. The Phase -2 heating is conducted in a high vacuum chamber. A two-step heat treatment method is programmed for this operation. In step-one, the temperature of the furnace is increased at the rate of 5°C per minute until it reaches 300°C and is held for one hour, this is necessary for the $MgCl_2$ to decompose into magnesium and chlorine. After holding for an hour, step-two heating where the temperature of the furnace is programmed to increase until it reaches 900°C at 20°C per minute. The decomposed Chlorine will evaporate during this phase. The material obtained after the second stage of heating is a softer material and easy to sift. The final powder-like product after sifting is the CNT-precursor material, which, used in the hot-pressing operation.

The CNT-precursor material obtained after magnesium functionalization is mixed with the copper powder at different ratios. The CNT-precursor material is mixed with Copper powder in the ratios of 0%, 1/10% (w/w), 1/15% (wt/w), 1/20% (wt/w). The mixtures of different concentrations are hot-pressed at 750 ^{O}C with the pressing pressure of 2000psi. The billet obtained after hot-pressing has a diameter of φ15mm and height 10mm. The billets are later subjected to the rolling operation. The φ15mm billet is rolled down to φ2mm and φ1mm wires. Further the φ1mm wire is rolled down to a 0.1mm thickness and 2.74mm wide ribbon. A commercially available oxygen free billet of φ15mm billet is also rolled for calibrating our test equipment. This is essential to eliminate the errors in measurements. Table 1 describes the list of billets and the concentration of CNTs.

Table 1*:* list of billets and the concentration of CNTs.

Product	Description
Billet-1	Commercially available O2 free Copper
Billet-2	100% copper hot-pressed and rolled
Billet-3	Copper billet hot-pressed with 1/20 % MWCNTs
Billet-4	Copper billet hot-pressed with 1/15 % MWCNTs
Billet-5	Copper billet hot-pressed with 1/10 % MWCNTs

Furthermore, in this current study the Electrical conductivity of copper is measured by using four-point resistivity measurement technique. The four-point resistivity measurement technique involves flowing a fixed amount of current between the outer two probes/pins and measuring voltage is measured between the two inner probes/pins. The resultant electrical resistivity is calculated using the measured voltage and the current. The Keithley Data acquisition system consisting of a Keithley ultra-sensitive current source series 6200 model 6221, and a Keithley Nanovoltmeter model 2182A is used for this purpose. A 100mA current is applied to the wire and the voltage measurements are recorded. The voltage measurements are recorded for each 5-cm length of the wire. Equations 1-5 are used in computing the mass conductivity of the wire using the voltage measurements. The mass conductivity will give the true electrical conductivity of the sample by eliminating the density factor. From our density analysis we determined that the density of the hot-pressed billets is lower than the commercially available copper rods/wire. Table 2 shows the theoretical and measured densities of the billets. Furthermore, equation-4 will mitigate the effect of temperature on the measured resistance by normalizing the readings to 20^0C. The resistance obtained from equation-4 is the effective resistance of the wire at 20^0C.

Table 2. Theoretical and Measured Densities of the Billets.

Part No.	**Theoretical Density (g/cm³)**	**Measured Density (g/cm³)**
Billet-1	8.96	8.92
Billet-2	8.96	8.53
Billet-3	8.93	8.52
Billet-4	8.92	8.46
Billet-5	8.90	8.37

$$R = \frac{V}{I} \quad (1)$$

$$R = \frac{R_T}{1+\alpha\left(T-20\right)} \quad (2)$$

$$\rho_v = \frac{RA}{L} \quad (3)$$

$$\sigma_v = \frac{1}{\rho_v} \quad (4)$$

$$\sigma_m = \frac{\sigma_v}{d_m} \quad (5)$$

where:

V = voltage measurement
I = current
R = Resistance
T = Temperature of the room while recording the voltage measurements
R_T = Resistance of the wire at temperature T
ρ_v= Resistivity of the wire
A = Cross-sectional Area of the wire
L = Length of the wire segment (5cm)
σ_v = Electrical Conductivity of the wire
σ_m = Mass Electrical Conductivity of the wire

The Mass conductivity of a metal provides the conductivity of the metal after factoring it for the density factor. It is obtained by dividing the electrical conductivity with density of the metal. At 100% IACS the mass conductivity of annealed copper at 20^0C is 6524 Sm^2/kg. The mass conductivity is a useful indicator since this value compensates for the effective porosity. The metal with mass conductivity above 100% IACS exhibits higher conductivity and below this value will indicate low conductivity or metal with impurities [16].

Results

Figure 1 shows the relationship between the mass electrical conductivity and the size of the billet 1. It is observed that the conductivity of the billet 1 at 2mm thickness has a mean of 102.17 %IACS and standard deviation of 0.88. Furthermore, at 1mm and 0.1mm thickness, the conductivity has a mean of 103.26 %IACS and 103.52 %IACS with standard deviation of 1.52 and 1.71 respectively. This graph represents a more accurate representation of the conductivity measurements. The widespread at 0.1mm should not be confused with the higher conductivity rather the errors due to the thickness of the 0.1mm ribbon. The thickness of this ribbon is not uniform, and it is a limitation of the rolling process. Moreover, we are looking at the big picture to see the feasibility of the rolling operation in producing UCC wire therefore not much study is directed towards producing uniform thick ribbons.

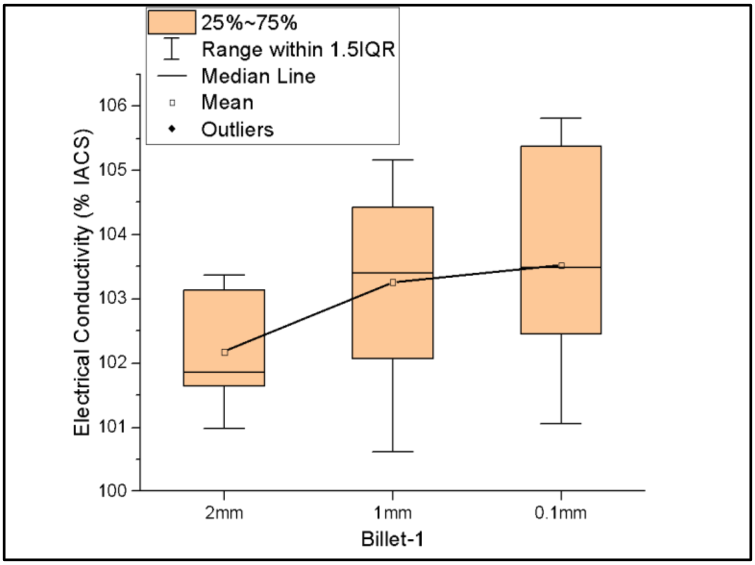

Figure 1: The Electrical Conductivity of the billet-1 at different cross-sectional sizes.

Figure 2 shows the relationship between the mass electrical conductivity and the size of the Billet-2. The measurements are taken over the wires of thickness 2mm, 1mm and 0.1mm thick ribbon. The resultant mean conductivity of the wire with decreasing thickness are 95.10% IACS, 95.22% IACS and 96.76% IACS with the standard deviation of 0.69, 1.15 and 1.01 respectively. Although the conductivity values of the Billet-2 are lower than the Billet-1, these values are still within the expected values. Unlike the rest of the billets used as feedstock for rolling operation, the Billet-1 is not hot-pressed. The hot-pressed billets consist of higher amounts of porosity which is reflected on the conductivity measurements. The Billet-2 has 0% CNT-precursor material embedded, therefore the conductivity results from this billet are used as the benchmark while comparing with the other billets with embedded CNT-precursor material.

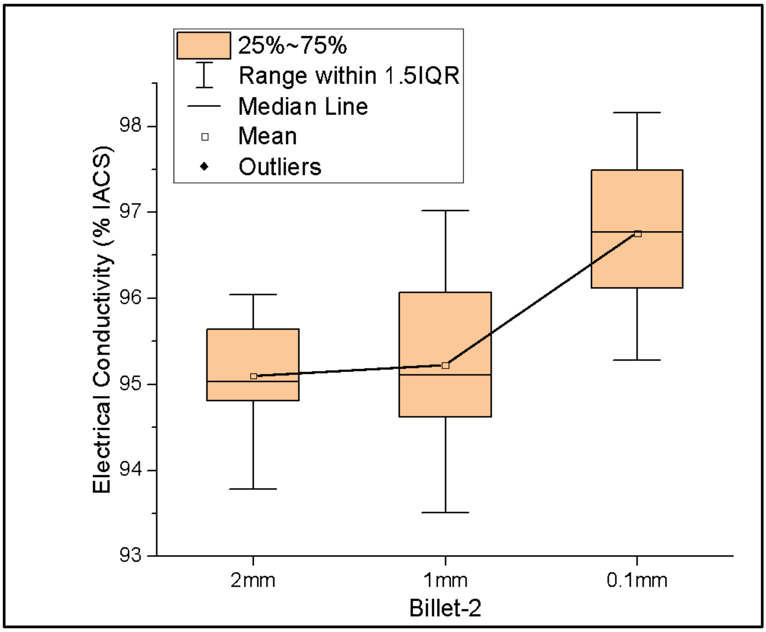

Figure 2: The Electrical Conductivity of the billet-2 at different cross-sectional sizes.

Figure 3 shows the relationship between the mass electrical conductivity and the size of the Billet-3. The Billet-3 showed a mean conductivity of 95.31% IACS, 94.72% IACS and 94.17% IACS with standard deviation of 1.11, 3.08 and 1.79 for the thickness of 2mm, 1mm and 0.1mm wire respectively. Although it looks as if the conductivity is decreasing with decreasing thickness, it is presumptive to conclude it, since the difference between the mean values is less than 1.5%. Therefore, we consider the conductivity measurements to be uniform at different thickness. It is noticed that the results of the Billet-3 are close to the Billet-2 results. This indicates the CNT-precursor material is not contributing to the overall bulk conductivity and/or there is not a significant amount of CNT-precursor material within the wire to contribute to the electrical conductivity of the copper.

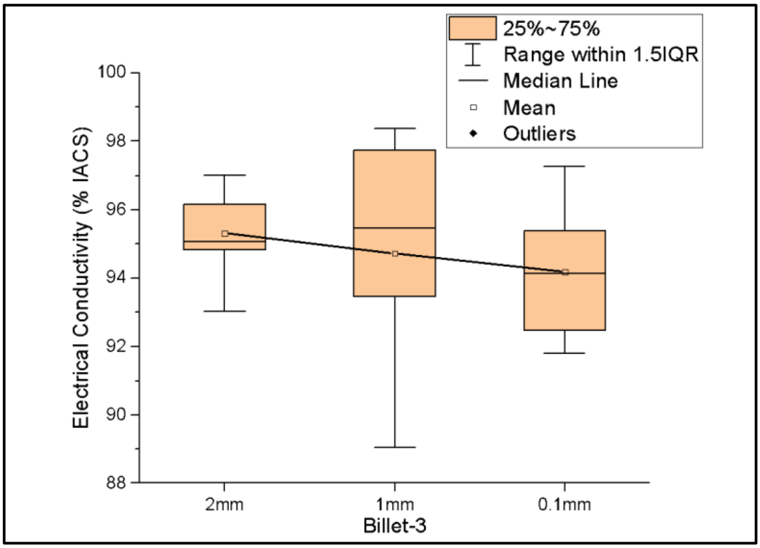

Figure 3: The Electrical Conductivity of the billet-3 at different cross-sectional sizes.

Figure 4 shows the relationship between the mass electrical conductivity and the size of the Billet-4. The Billet-4 showed a mean conductivity of 101.91% IACS, 93.33% IACS and 92.97% IACS with standard deviation of 5.70, 4.17 and 1.96 for the thickness of 2mm, 1mm and 0.1mm wire respectively. The results from the Billet-4 show remarkable increase in the electrical conductivity of the 2mm wire compared with the Billet-2 and Billet-3 but upon further rolling the conductivity fell down to 85% IACS at 1mm thickness and 84.68% IACS at 0.1mm thickness. This observation shows the CNT-precursor material contributed to the bulk conductivity at 2mm wire thickness and upon further rolling the CNTs probably either destroyed or the ohmic path between the CNTs increased and thereby resulted in lower conductivity or the CNT acted as an impurity in the copper matrix.

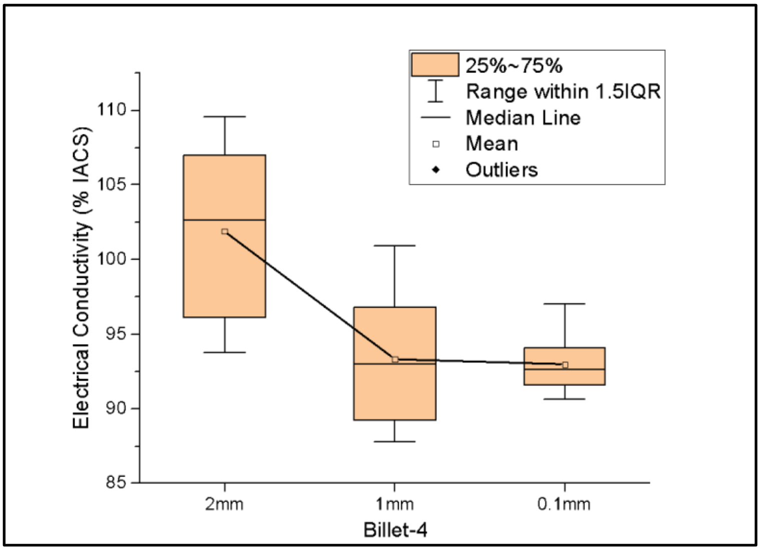

Figure 4: The Electrical Conductivity of the billet-4 at different cross-sectional sizes.

Figure 5 shows the relationship between the mass electrical conductivity and the size of the Billet-5. The Billet-5 showed a mean conductivity of 88.32% IACS, 91.22% IACS and 90.19% IACS with standard deviation of 1.92, 4.33 and 2.29 for the thickness of 2mm, 1mm and 0.1mm wire respectively. The deviation in electrical conductivity from the rest of the billets is clearly observed. The lower conductivity in the Billet-5 can be attributed to the improper dispersion of CNT-precursor material in the matrix. Rolling the wire from 2mm thickness to 1mm thickness the electrical conductivity is improved which can be explained by the breaking of agglomerants and dispersion of CNTs or looking at the standard deviation there could be a non-uniform thickness which resulted in the error in determining the thickness.

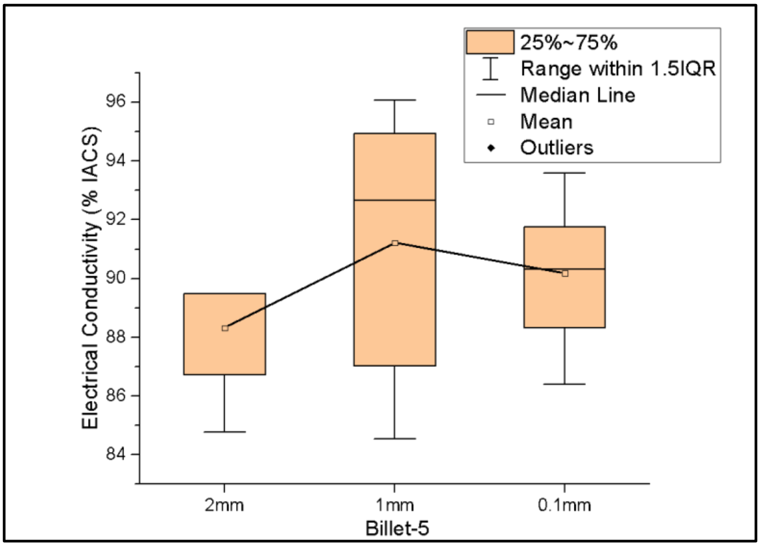

Figure 5*:* The Electrical Conductivity of the billet-5 at different cross-sectional sizes.

Figure 6-8 shows the graphs that summarize the electrical conductivity results on all billets at different thicknesses. It is noticed at 2mm thickness the conductivity of Billet-4 is closer to the Billet-1. This phenomenon is not possible unless the CNTs are contributing to the overall bulk conductivity of the wire. In all other cases the hot-pressed billets failed to exhibit higher conductivities close to the Billet-1. It is also noticed that electrical conductivity decreases as the content of the CNT-precursor material is increased. Furthermore, billet-2 with 1/20%(w/w) of CNT-precursor material showed no significant change in the electrical conductivity from billet-2, it indicates that the CNT-precursor material is not in significant quantity to contribute either constructively or destructively to the overall conductivity. The only deviation between the Billet-2 and Billet-3 is observed at 0.1mm thickness. This could be a result of the errors in determining the thickness of the 0.1mm thick ribbon. The probability of this error is high as we noticed the 0.1mm thick ribbon’s thickness change dramatically at different sections of the ribbon. The Billet-3 and Billet-4 did exhibit a behavior of decreasing conductivity and it can be attributed to the increasing content of the CNTs.

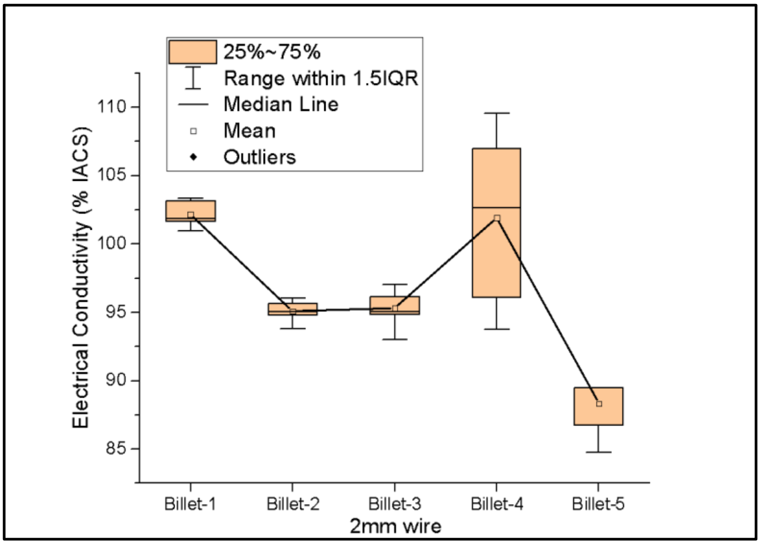

Figure 6: The Electrical Conductivity of all billets at 2mm thickness.

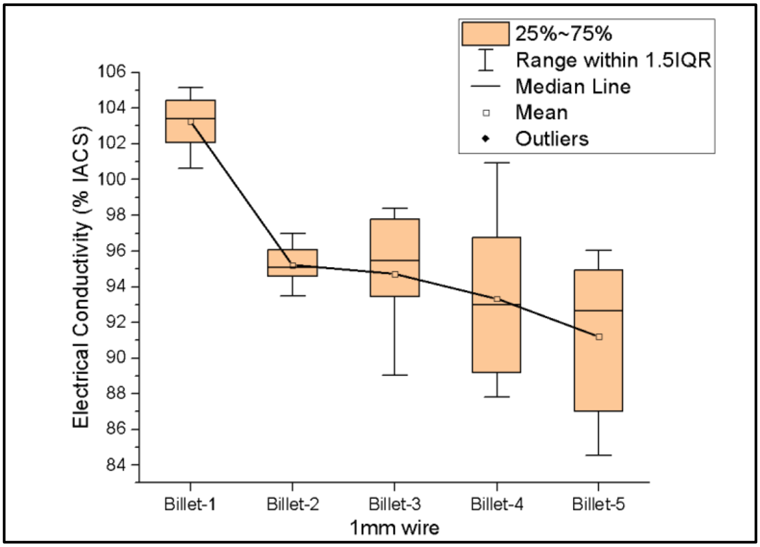

Figure 7: The Electrical Conductivity of all billets at 1mm thickness.

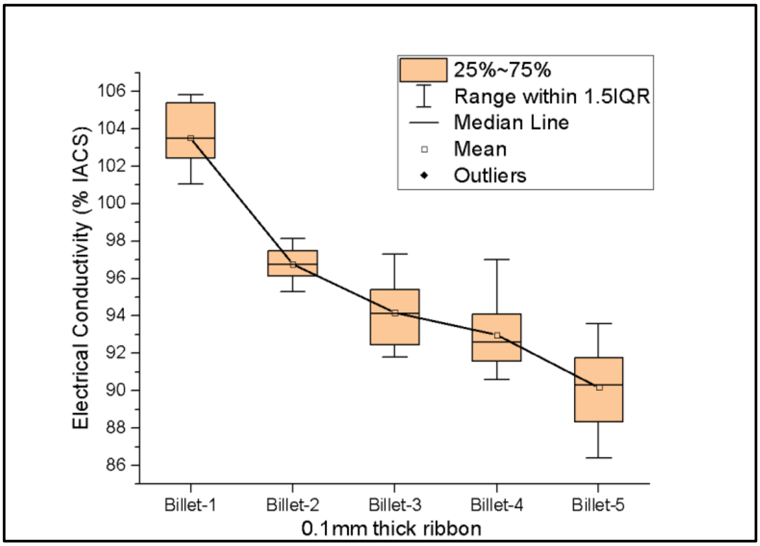

Figure 8: The Electrical Conductivity of all billets at 0.1mm thickness.

Summary and Conclusions

It is evident from the results that the conductivity of the CNT embedded copper changes dramatically at different reduction ratios. Although a remarkable improvement in the electrical conductivity is not observed, a trend of low and high conductive zones in the CNT-embedded copper wire is observed. A consistent conductivity measurement for both oxygen-free copper and hot-pressed billet with no CNT-precursor material at various stages of the rolling process is observed. The same effect is not observed on the CNT-embedded copper billets. Although we did not observe high conductive zones in all the billets, Billet-4 showed both high and low conductive regions. Especially with the Billet-4, the conductivity changed dramatically from an average of 101.91% IACS at 2mm thickness to 93.33% IACS and 92.97% at 1mm and 0.1mm thickness respectively. Even though it is still lower than an oxygen-free copper, it certainly adds to the excitement for further exploration of the UCC wire. Overall the current method needs improvements at various stages to achieve UCC wire. A more extensive study with collaborators from different fields is required. As of now the UCC wire is still in the early stages of scaling up the results.

Future works

The UCC wire is gaining attention in recent years and researchers are investigating feasible methods to achieve the UCC wire. There are many areas in our study that need improvement and more thorough research. Some of the areas that needs to be focused based on this study are as follows:

The effect of different grain sizes of copper powder (raw material) is not investigated in this study but in future works it is advisable to compare the results with multiple sizes of copper powder. This study will assist in lowering the porosity of the sintered CNT-embedded copper billet.

Using hot rolling/hot extrusion. This is vital in developing UCC wire. We know the fully cold worked material tends to exhibit lower electrical conductivity compared with hot worked and annealed. In this study we used cold rolling due to the fact that we had no other options available during the final stage of this overall program. In future work, it is essential to work with either hot rolling/ hot extrusion. Extrusion is preferred due to the ability to produce wire/rods by applying immense pressure which aids in the mechanical bonding of CNTs with the copper and greatly assists in maintaining intimate electrical contact between the nanotube ends and the matrix material.

Impact of grain size on Electrical Conductivity: This study is conducted with an intention to produce commercial scale UCC wire by investigating favorable manufacturing methods. A rigorous microstructural analysis with respect to how grain size impacts the electrical conductivity needs to be performed.

Determining a favorable reduction/extrusion ratio. This is possible only if we control the precursor material size. In this study we are able to observe the effects of extrusion ratio, as the conductivity of the CNT embedded copper wire changes drastically with the reduction ratio as the size of the agglomeration's changes and the Ohmic distance between the nanotubes increases.

Amount of CNT-precursor material mixed with copper powder. Our initial assumption that higher concentrations of CNTs will enable additional streaks of ultra-conductive paths was not viable. We faced difficulty in deagglomeration and dispersing the CNTs at lower concentrations. Further, the billets with higher concentration of CNT-precursor material fractured in our initial works which forced us to work with lower concentrations. This is a huge concern since the lower concentration of CNT might deagglomerate and disperse but their contribution to the bulk conductivity is difficult to measure and their overall contribution can be futile. A rigorous study is required in estimating the optimal concentration of CNT precursor material, size of CNT and the electrical conductivity of the wire formed.

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