Strength and electrical resistivity of heavily worked copper

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Abstract. Copper and its alloys are a topic of interest for various cryogenic conductor applications. Often, it is used as a supporting matrix for superconducting filaments requiring that it have good strength and high conductivity. One of the best methods to increase strength while preserving conductivity is work hardening. In this study, CDA101, CDA110, and C182 copper were processed by a severe plastic deformation (SPD) procedure called equal channel angular extrusion (ECAE). In this study we explore the relationships between the levels of plastic strain and annealing with tensile and hardness properties, grain size, and electrical resistivity. While C182 has the highest strength, it also has the lowest conductivity. CDA101 and CDA110 both retain over 95\% of their conductivity in the fully worked state, while C182 has about 40\% of the IACS value. Saturation of strength occurs around 3-4 ECAE passes. It is concluded that a lower amount of plastic strain via ECAE is best for creating a material with the highest combination of strength and conductivity, and is suitable for high strength high conductivity applications.

1. Introduction

In the relatively recent past, the needs of higher strength materials have prompted an increase into studies dealing with the manufacture of ultrafine-grained (UFG) and nanocrystalline (NC) metals [1]. Additionally, in cryogenics communities dealing with low temperature superconducting wires and electromagnets, electrical conductivity plays a most important role [2]. In electrical applications, copper and aluminum are the most commonly used metals due to their availability and high electrical conductivity. Pure copper is often the preferred choice because of strength and compatibility issues. Copper also has superior creep resistance when compared to aluminum, which decreases the possibility of wire failure. However, pure annealed copper does not have a particularly high strength, which would help for most superconducting wires. The problem is to find a method to increase the strength of copper while not decreasing its superior electrical conductivity. Methods to strength a material can include precipitation hardening, introduction of nanoparticles to metal matrix, heat treatment schedules, and plastic deformation. Some of these methods have the possibility of additionally increasing material conductivity as well [3-5].

One of the easiest methods to increase the strength of a material, while not heavily sacrificing electrical conductivity, is through severe plastic deformation (SPD). Some of the more common methods of severe plastic deformation include high pressure torsion, accumulative roll bonding, twist extrusion, and equal channel angular extrusion (ECAE). ECAE has a few advantages over the other SPD processes.
mentioned. First, ECAE is a repeatable process that does not change the initial dimensions of the work piece (billet), allowing for multiple extrusions, meaning you can accrue large amounts of strain. Second, there is not a geometric requirement, meaning you can extrude bars, cylinders, plates, or even tubes. Third, ECAE is easy to perform, and could be easily implemented in manufacturing facilities.

Equal channel angular extrusion can produce bulk ultrafined grained metals by subjecting a thin layer of material at the crossing planes of the die to simple shear. This process refines the grain structure, and introduces dislocations into the material, both of which increase strength. A schematic of the ECAE process is shown in Figure 1.

![Figure 1: Schematic of ECAE deformation showing primary planes, directions, and the shear zone.](image)

While many studies have been done with regard to strengthening copper and some of its alloys via SPD processes, relatively few have studied the impact ECAE has on the electrical resistivity. In previous works of SPD by ECAE, studies reported increases in hardness and strength, sometimes by up to as much as 300%. Torre et al. [6], reported tensile strengths as high as 455 MPa for copper extruded via route Bc (Routes are described later in Materials and Methods section). Similarly, Xue et al. [7] found an increase in strength to approximately 445 MPa for route Bc processed copper. Microhardness results are similar and multiple studies have obtained fully work hardened values for copper that fall in the ranges of 130-150 Vickers hardness [6-7]. Testing of copper alloys has been done by Wei et al. [5] and Ko et al. [8], who found that both alloys had significantly increased strength with only a small drop in resistivity following ECAE. Ko et al, concluded that after SPD processing and a proper heat treatment, both the mechanical and electrical properties of the Cu-0.5wt.% Cr alloy could be increased.

Other studies have focused more on the microstructure and recrystallization behavior of copper and its alloys. Torre et al. [6] and Etter et al. [9] have all reported grain sizes for ECAE processed copper in the ranges of 200 nm to 500 nm for routes Bc for both 4 and 8 pass samples. Additionally, for routes Bc the microstructure was found to be more equi-axed when compared to other routes such route A. In almost all studies, the impact ECAE has on grain size is the most drastic for the first 2 passes, and then levels off with only a slight decrease after 4 passes.

Recrystallization behavior have been studied for copper with the recrystallization temperature falling between 200°C and 300°C depending on the total amount of accumulated strain [5]. Grain sizes were reported for recrystallized microstructures in the ranges of 0.75 μm to 3 μm for fully worked copper samples depending on the temperatures and length of heating [5]. Some studies have seen dynamic recrystallization occurring at room temperature after samples were subjected to rolling, whereas the purely ECAE processed microstructure apparently remains stable up to 150°C [10].

In this study oxygen free high conductivity (OHFC) copper (CDA101), commercially pure copper (CDA110), and a copper chromium alloy (C182), were processed via ECAE. Testing to determine
tensile and yield strength, microhardness, recrystallization temperature, microstructure characteristics, and electrical resistivity were conducted. The testing results were used to determine if work hardening is indeed a suitable process to increase the strength of copper and its alloys, while maintaining the high conductivity needed in cryogenic applications.

2. Materials and Methods
The three different copper alloys studied, CDA101, CDA110, and C182, were purchased as 30 mm by 30 mm cross section bars. CDA101 with 99.99% Cu content was obtained from ThyssenKrupp Materials North America. CDA110 and C182 were purchased from New Southern Resistance Welding (NSRW). CDA110 possess 99.9% Cu content (silver counted as copper) and 0.04% oxygen. C182 contains 99.1% Cu content (Cu+Ag) and 0.6-1.2% Cr content.

The square cross section copper bars were first cut to 254 mm lengths and then recrystallized. The CDA101 and CDA110 bars were annealed at 350°C for one hour in a muffle furnace and then furnace cooled. The C182 was annealed at 990°C for 45 minutes and then quenched in room temperature water. Heat treatments were performed at 1 atm. Bars were then machined to 25.4 mm x 25.4 mm cross section.

Samples were ECAE processed though a square 90° sliding wall die at an extrusion speed of 2.54 mm/s at room temperature. The routes examined included routes A, B, Bc, and E, all processed to 8 passes. Route Bc was processed additionally to 16 passes. Between each pass, some flash on the bars was removed in order for the billet to fit back in the ECAE die. Table 1 summarizes the rotation angle between successive passes for each ECAE route. A more detailed description of the different routes can be found in Segal’s paper “Material processing in simple shear” [11].

| Routes of ECAE | Route A | Route B | Route Bc | Route E |
|----------------|---------|---------|----------|---------|
| Odd passes-beginning at pass #3 | 0° | +90° | +90° | +180° |
| Even passes | 0° | -90° | +90° | +90° |

After the bars were processed by ECAE, 12.7×6.4×3.2 mm samples were cut from the flow plane via wire electric discharge machining (EDM) for heat treatment to determine recrystallization behaviour and to characterize the recrystallized microstructure. The CDA101 and CDA110 samples were subjected to temperatures ranging from 100°C to 500°C in a sand bath for 1 hour. The C182 samples were heat treated from 350°C to 500°C for 10 minutes. Recrystallization temperatures to determine recrystallized grain sizes in CDA101 Cu were 350°C, 275°C, 250°C, and 225°C for 15 minutes in a sand bath for 1 pass, 2 pass, 4 pass, and 8 pass samples respectively.

The 12.7×6.4×3.2 mm samples wire EDM cut from the CDA101 billet flow plane were mechanically ground starting from 320-grit emery paper to 1200-grit, followed by electrolytic polishing for microscopy. Electrolytic polishing was achieved using an electrolyte solution of 82.5 mL of 85% H3PO4 solution mixed with 17.5 mL of distilled water, applying a cell voltage of 2 V for 15 minutes. The solution was constantly stirred at low speed. Samples were cleaned with water then ethanol before imaging. Scanning electron microscope images were then taken with an accelerating voltage of 13 kV and a working distance of 10 mm. Additionally, Vickers hardness measurements were taken on the same sample to determine recrystallization behaviour.

Electrical resistivity measurements on the Cu alloy and CDA110 Cu were made using the four-point probe method on 3.2x3.2x50.8 mm samples using currents of 2.6 A at room temperature (298 K). The voltage drop was measured by a Keithley Model 181 nanovoltmeter and the resistivity calculated by equation 1 below. The distance between voltage taps was 25.4 mm, and the current leads being connected at the two ends.

Table 1. Descriptions of ECAE routes.
\[ \rho = \frac{VA}{IL} \]  

where V and L stand for the voltage drop and the distance between the voltage taps, A is the cross section of the sample, and I is the current that passes through the sample. Resistivity ratios for the CDA101 material were determined by supplying a constant 1 A current and measuring the voltage drop across 2 mm diameter cylinders 25.4 mm long while immersed in liquid helium (4.2 K), liquid nitrogen (77 K), and an ice bath (273 K). The two voltage taps had a 12 mm distance between them, with current leads again being at the two ends of the sample.

Microhardness measurements were taken using a Leco Microhardness Tester LM 300AT. The samples required the same polishing procedure as described previously. The samples were tested with a 300 g indenter load with a dwell time of 5 seconds. The hardnesses presented are an average of 10 separate measurements.

Dogbone samples were cut via wire EDM for tensile testing. The dogbones were 26 mm in total length with an 8 mm gauge length and 7 mm long tabs. The radius of the curve connecting the tab to the gauge length was 2 mm. The width of the tab was 7 mm and the width of the gauge length was 3 mm. The thickness of the samples was approximately 1.25 mm. The samples were tested using an MTS machine coupled with an 11 kN Interface 1010AF load cell and Epsilon Model 3442-008m-020-LHT strain gauge. The tests were run at 0.01 mm/second until fracture. Three separate tests were done for each processing condition and the averages reported. Only CDA101 copper was tensile tested for this study.

3. Results

The average starting grain size for the CDA101 copper after the pre-processing anneal was found to be 29.5 µm. After a single ECAE pass the grain size decreased to 0.978 µm. With additional processing, grain size continued to reduce but much less drastically, coming to a near minimum with 4 pass route Bc at 0.412 µm. Recrystallized grain sizes follow a similar trend with route Bc having the smallest value ~1.3 to 1.9 µm, and the lower pass samples having the largest. Table 2 and Figure 2 summarize and show the changes in the microstructures after ECAE.

| Route | Accumulated Strain | Grain Size (micron) | Standard Deviation (micron) | Recrystallized Grain Size (micron) | Standard Deviation (micron) |
|-------|-------------------|---------------------|-----------------------------|-----------------------------------|-----------------------------|
| As Received | 0 | 29.5 | 14.4 | N/A | N/A |
| 1A | 1.1 | 0.98 | 0.67 | 6.3 | 4.5 |
| 2A | 2.3 | 0.75 | 0.24 | 4.4 | 2.7 |
| 4A | 4.6 | 0.58 | 0.20 | 2.2 | 1.2 |
| 4B | 4.6 | 0.49 | 0.11 | 2.5 | 1.6 |
| 4Bc | 4.6 | 0.41 | 0.13 | 1.9 | 0.8 |
| 4E | 4.6 | 0.47 | 0.14 | 2.1 | 1.2 |
| 8Bc | 9.2 | 0.42 | 0.16 | 1.4 | 0.7 |
| 8E | 9.2 | 0.53 | 0.20 | 1.7 | 1.2 |
| 16Bc | 18.5 | 0.42 | 0.13 | 1.3 | 0.7 |

Recrystallization based on Vickers hardness testing was studied for all three cases of copper for route 8Bc. CDA 110 and CDA101 showed a drop in hardness after heat treatment at 150°C. The C182 copper saw decreases in hardness starting after heat treatment at 400°C. Figure 3 gives examples of Vickers hardness for all the alloys at certain heat treatment temperatures.

Mechanical testing was performed for all routes for the CDA101 copper billets. Yield strength, tensile strength, and elongation to failure are presented in Table 3 along with total accumulated strain and microhardness. The lowest tensile strength is seen in the annealed as-received material, while the
The highest tensile strength of CDA101 Cu ECAE deformed samples comes from routes 4B, 4E and the three Bc routes. Generally, as the number of ECAE passes increase, the strength increases, but after 4 passes, the increases are small. Interestingly, route E gives a decrease in strength from 4 to 8 passes.

Figure 2: SEM images of as-worked 4A (a), as-worked 4Bc (b), recrystallized 4A at 250°C (c), and recrystallized 4Bc at 250°C (d)

Figure 3: Vickers hardness as a function of temperature after 1 hour heat treatment for route 8Bc CDA101, CDA110, and C182 copper
Table 3: Summary of tensile strength and hardness data for CDA101 copper

| Route | Accumulated Strain | Vickers hardness (VH<sub>300</sub>) | Yield Strength (MPa) | Tensile Strength (MPa) | Strain to Failure |
|-------|--------------------|-------------------------------------|----------------------|------------------------|------------------|
| AR    | 0                  | 54 ± 1                              | 181 ± 2              | 248 ± 2                | 0.38 ± 0.02      |
| 1A    | 1.1                | 126 ± 2                             | 323 ± 5              | 349 ± 4                | 0.14 ± 0.01      |
| 2A    | 2.3                | 132 ± 5                             | 364 ± 1              | 383 ± 4                | 0.14 ± 0.03      |
| 4A    | 4.6                | 137 ± 2                             | 372 ± 1              | 397 ± 2                | 0.16 ± 0.01      |
| 4B    | 4.6                | 145 ± 4                             | 399 ± 4              | 442 ± 4                | 0.16 ± 0.01      |
| 4E    | 4.6                | 143 ± 3                             | 402 ± 1              | 438 ± 2                | 0.19 ± 0.01      |
| 4Bc   | 4.6                | 144 ± 2                             | 383 ± 17             | 421 ± 6                | 0.16 ± 0.02      |
| 8Bc   | 9.2                | 141 ± 4                             | 373 ± 3              | 437 ± 6                | 0.20 ± 0.01      |
| 8E    | 9.2                | 145 ± 2                             | 382 ± 2              | 427 ± 1                | 0.15 ± 0.01      |
| 16Bc  | 18.5               | 136 ± 2                             | 357 ± 3              | 438 ± 3                | 0.18 ± 0.01      |

Resistivity measurements for CDA101, CDA110 and C182 samples as well as resistivity ratios for the CDA101 copper case are presented in Table 4. The CDA101 and CDA110 copper samples had starting conductivity values matching almost exactly with the international annealed copper standard (IACS) value. After becoming fully worked, both CDA101 and CDA110 had conductivity that fell a maximum 4-5% below that of the IACS value. The C182 copper alloy had a starting conductivity of approximately 60% of the IACS value. After becoming fully worked, the C182 alloy had a final conductivity of approximately 40% of the IACS number.

The residual resistivity ratio (RRR) for the annealed CDA101 copper is 91. After one pass of ECAE, the RRR drops to just above 50. The RRR continually drops as more strain is accumulated within the material reaching a minimum 19.2 for route 16Bc. Table 4 gives a summary of conductivity, resistance ratio (RR), and RRR measurements for the CDA101, CDA110, and C182 copper materials. Figure 4 graphically represents the change in conductivity compared to the IACS value with the different routes as well as illustrates the correlation of tensile strength to RRR measurements on CDA101 for selected routes. The correlation is very linear, with R² values of just over 0.96, indicating that as you increase in tensile strength the RRR values decrease indicating a lower conductivity.

Table 4: Summary of conductivity and RRR measurements

| Processing | %IACS | %IACS | %IACS | %IACS | RR (77K/4.2K) | RRR (273K/4.2K) |
|------------|-------|-------|-------|-------|---------------|-----------------|
| As Received| 59.6  | 100.7 | 103.4 | 11.2  | 91.0          |                 |
| 1A         | 41.2  | 97.0  | 98.2  | 7.40  | 51.6          |                 |
| 2A         | NM    | NM    | NM    | 6.05  | 36.4          |                 |
| 2B         | 41.4  | 97.2  | 96.9  | NM    | NM            |                 |
| 4A         | NM    | NM    | NM    | 4.94  | 30.8          |                 |
| 4Bc        | 40.4  | 96.5  | 95.6  | 4.14  | 24.5          |                 |
| 4E         | 41.8  | 97.1  | 97.1  | 4.79  | 30.0          |                 |
| 8Bc        | 39.1  | 96.5  | 95.4  | 3.64  | 21.1          |                 |
| 8E         | 41.4  | 97.2  | 97.0  | 4.28  | 27.3          |                 |
| 16Bc       | NM    | NM    | NM    | 3.48  | 19.2          |                 |
4. Discussion

The simple shear applied by ECAE across the intersecting planes of the die refined the microstructure and induced dislocations into the crystal structure. The SEM results shown in Figure 2 and grain size shown in Table 2 illustrate how the fully worked material has a much smaller grain size than the starting annealed material. With a smaller grain size and large number of dislocations, the material gains a much higher tensile strength and hardness. This is due to the numerous dislocations and grain boundaries inhibiting dislocation motion, meaning a larger force would need to be applied to deform the lattice. In the case of C182, the Cr precipitates inside the matrix also greatly increase hardness and strength due to the precipitates also blocking dislocation motion. It can be seen that the mechanical properties of copper are positively influenced by ECAE as seen by Table 3. As previously stated, through grain refinement and increasing the dislocation density in the material, dislocation motion is blocked. ECAE produces diminishing returns when looking at tensile strength increases. After ~4 passes, grain size and strength remain relatively constant. Fully worked samples of route Bc material show an increase in tensile strength of 78% with an increase in hardness of 166% when compared to the annealed starting material.

Another factor affected by ECAE processing is recrystallization. The required energy to start short range diffusion powered by elevated temperatures that leads to recrystallization has an inverse relationship to the amount of accumulated strain. The more strain and energy stored within the lattice, the easier the sample to recrystallize. The recrystallization temperature for route 8Bc is found to be 225°C as indicated in Figure 3. Additionally, for the higher applied strains, the recrystallization grain size is smaller compared to the lower strain samples. This is easily seen by Table 2. Route Bc, and E to some extent, have the lowest recrystallized grain size when compared to other samples with the same amount of strain. This could be due to the equiaxed nature of the grains. In the case of odd numbered passes, or routes that do not have full rotation, favourable sites for nucleation are more prevalent. However, if the grains stay equiaxed, the more common triple junction in the microstructure inhibits grain boundary migration, corresponding to a more stable structure [6-9,10]. Additionally, evidence of dynamic recrystallization can be seen by the decrease in strength after more processing in route E.

Resistivity testing indicates that as you increase the amount of cold work, the resistivity of the sample increases as shown in Table 4 and Figure 4. This is due to the scattering of electrons off numerous dislocations and grain boundaries. For the pure copper samples CDA101 and CDA110, the effect of extrusion on the conductivity is relatively minor. Fully worked samples retained, at a minimum, 95% of the conductivity compared to the IACS value. In comparison, the C182 alloy had a much lower conductivity when compared to its starting IACS value of 60%, only retaining 40% when fully worked. This is largely due to the alloy forming a solid solution which is particularly detrimental to easy electron flow through the material. There is still an effect due to increasing grain boundaries and dislocations,

![Figure 4: a) Tensile strength vs RRR for CDA101. b) Percent of international annealed copper standard (IACS) vs ECAE route for CDA101, CDA110, and C182 at 298 K](image)
but it is relatively minor when compared to the effect from the chromium. Similar results were seen by Wang et al. [10].

When trying to select the best material for a high strength high conductivity application, a figure of merit can be considered in evaluating both strength and conductivity. By multiplying the microhardness values by their respective IACS percentage conductivity, and taking the largest value, we see that the best ECAE processing route and material is CDA101 copper processed by route 2B. When finding a similar figure of merit using the RRR measurements for the CDA101 copper, the tensile strength was multiplied by the RRR, and for this case route 1A is calculated to be superior. However, this is assuming that the importance of resistivity and strength are the same. If the need is for a material that is as strong as possible, and the 5% losses to conductivity are not critical, one of the 4 pass routes would most likely be chosen for high strength, yet still reasonable high conductivity.

5. Summary and Conclusions
In this study, different numbers of passes and routes of equal-channel angular extrusion (ECAE) were successfully applied to oxygen-free high conductivity (OFHC) copper (CDA101), commercially pure copper (CDA110), and copper chromium alloy (C182). The hardness, tensile properties, and electrical conductivity of the materials were measured. The main findings are:

- Near saturation of hardness and tensile strength occur at 3-4 ECAE passes.
- Obtaining a tensile strength of 500 MPa or greater could be possible with additional post processing techniques such as cold rolling
- Route Be is a preferred method for creating the smallest grains possible in both as-worked and recrystallized conditions.
- Alloying, while good for increasing mechanical properties, causes a severe decrease in conductivity.
- A lower number of passes is best for creating a material with a high strength to resistivity ratio.

6. References
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