

Mechanical Properties of Electroformed Copper

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1 Introduction

Copper (Cu) is used extensively as electrical wiring due to its excellent electrical conductivity, in plumbing due to its malleability and as heat sinks due to its good thermal conductivity. However, the strength of pure copper is considered too low to be used in load bearing applications therefore its uses are limited. Recently, Morganic Metal Ltd has developed nanocrystalline copper manufactured by an electroforming process that has shown signs of being much stronger than normal bulk copper. The work aims to improve the current understanding of the structure and mechanical properties of the metal.

At this initial development stage, characterisation of the material is the central issue. With soft metals such as Cu and nickel, the metallurgy – namely the grain size and chemistry maybe questioned. Therefore, these properties must be characterised with the appropriate experimental methods before the mechanical properties can be determined. This report describes the chemical, metallurgical and mechanical characterisation of this electroformed copper.

Chemical characterisation was carried out using energy dispersive X-ray spectroscopy (EDS) as well as X-ray diffraction (XRD). Metallurgical characterisation was carried out using mainly transmission electron microscopy and scanning electron microscopy. Mechanical tensile testing of these samples was carried out using the British Standard for tensile testing of metals ¹. Elastic properties were determined by a variety of methods (Impact Resonance and Surface Acoustic Wave at NPL², and nanoindentation at QMUL³). Thermal tolerance was investigated by heat treating samples and determining tensile mechanical properties.

2 Materials and Methods

Morganic Metal provided the copper electroforms of 0.8mm thickness manufactured into 3mm disks for TEM, 30×5mm dog bone specimens for tensile testing and 15×30mm plate for acoustic wave and nanoindentation testing. These shapes were electrodeposited onto a stainless steel plate electrode through a glass fibre reinforced plastic mask with the required shapes cut out from it. The copper is electrodeposited onto the electrode and grows outwards from it so that the thickness of the samples is controlled by the time it takes to deposit the copper. The electroforms were easily removed from the electrode to provide net shape samples.

2.1 Microstructural Characterisation

2.1.1 Scanning Electron Microscopy (SEM)

Surface preparation for SEM involved etching the copper with a suitable etchant. Haynes (1984) suggested that one of the best etching agents for copper is alcoholic ferric chloride⁷. This was prepared by adding 2ml of hydrochloric acid into 98ml of methanol and dissolving 5g of ferric in this mixture. The samples were immersed in the etching agent until the specimen changed colour. The prepared samples were examined in a JEOL 6300F (Field Emission) scanning electron microscope operating at 15 or 20kV accelerating voltage⁸.

2.1.2 Transmission Electron Microscopy (TEM)

Characterisation of the internal microstructure and therefore identification of the grain size and shape of the grains of the nanocrystalline copper was achieved using TEM. Electron transparent thin sections are very weak, so creating a stable section from an inherently soft metal is difficult⁸. Previous attempts to produce these thin sections using ion beam milling were not successful. Therefore, for this experiment, we used an electropolishing method.

Thin foils were prepared by mechanically polishing preformed 3mm diameter discs to 100µm thickness. Thin areas were created using a Metalthin Mk3 made by Materials Science North West Ltd., Lytham, which was a twin-jet electropolishing unit that sprayed electrolyte onto the sample from both sides. The electrolyte and a constant electric current were passed through the sample to facilitate electropolishing. It had an automatic foil perforation detection system that stopped electropolishing when light from the other side of the foil was detected (see figure 1). This produced a sample with decreasing thickness profile and a tiny hole in the middle.

The electropolishing conditions for copper as listed in the Metalthin Operating Instructions manual was to use 20% nitric acid in methanol at a temperature of -40°C , dc current of 200mA and a pump speed of 4. The thinning cell was placed in a bath of methanol and cooled down using liquid nitrogen. A thermometer displayed the temperature of the electrolyte and when the temperature of the electrolyte was at -40°C . The pump was started and the electrolyte was jetted onto the sample. The potential across the sample was increased until the current becomes 200mA. The current decreased as the sample was thinned, so the potential was constantly

increased to maintain the current at 200mA. The electropolisher also gave us the option of tweaking the electropolishing conditions that improved the quality of the sample such as rippling the dc supply $\pm 20\%$ across the sample to provide a rippling effect and adjusting the sensitivity of the potential.

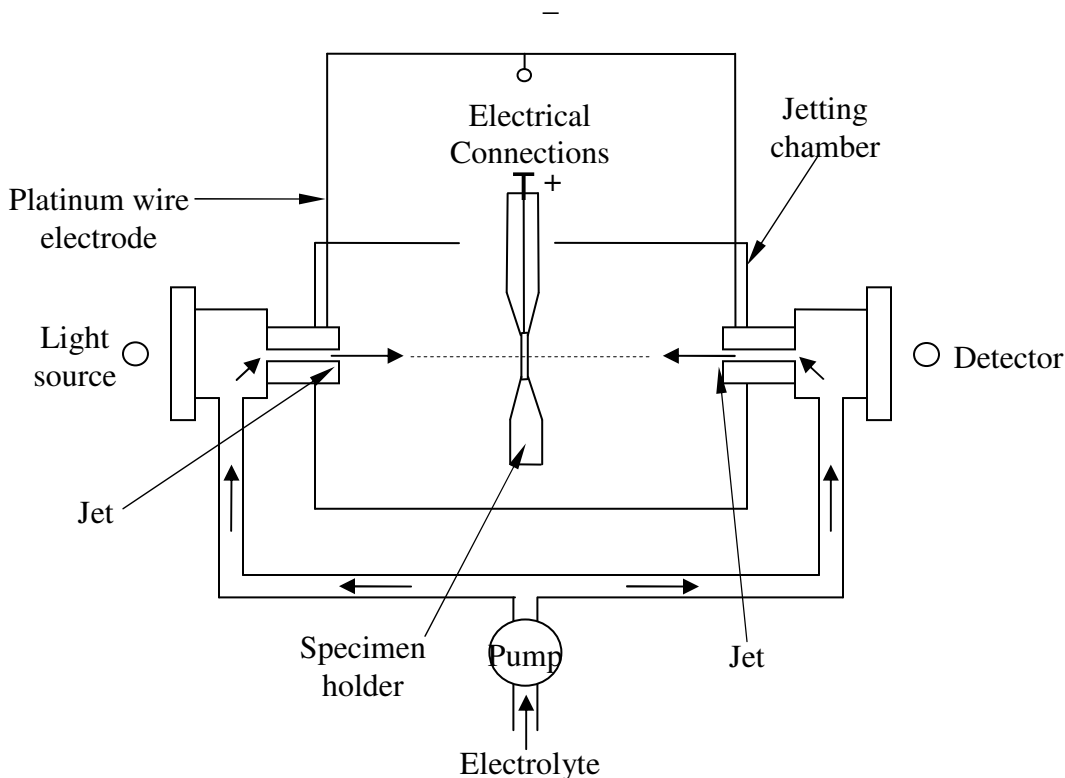


Figure 1. Schematic of the thinning cell. Showing jetting directions, electrical connections and perforation detector system.

Circular 3mm discs were punched out of an electroformed thin foil of nominally 20 micron thickness to be mounted on the TEM specimen holder. The 3mm discs were first electropolished with 20% nitric acid in methanol at a temperature of -40°C using a Metalthin electropolisher. The prepared sample was stored in a desiccated container and examined in a JEOL 2010 instrument operating at 200kV accelerating voltage within 3 days to avoid oxidation. The sample was mounted on a double axis tilt specimen holder to enable double axis tilt.

2.1.3 Chemical Analysis

Chemical analysis was investigated using Energy Dispersive X-ray Spectroscopy (EDS) on a JEOL 6300 SEM with an Oxford Instruments INCA EDS detector and analysis system.

2.1.4 Crystal Structure

Standard θ - 2θ diffraction experiments were conducted on a Siemens/Bruker AXS D5000 diffractometer using $\text{Cu K}\alpha$ radiation.

2.2 Mechanical and Physical Characterisation

2.2.1 Density

Density of the electroform was determined as mass / volume for a plate with approximate dimensions 30mm × 15mm × 0.8mm. Dimensions were determined with a micrometer to 0.001mm and mass was determined using a Sartorius balance to 0.00001g (c/o NPL).

2.2.2 Elastic Properties

Elastic modulus was determined by 3 separate methods using a plate with approximate dimensions 30mm × 15mm × 0.8mm in the as-received condition:

- i) Impact excitation (IE)² using the first 4 resonant frequencies, measures Young's modulus directly (c/o NPL).
- ii) Surface acoustic wave (SAW)² using laser excitation, requires input of values for density and Poisson's ratio (c/o NPL).
- iii) Nanoindentation (NI)³ using 5µm and 21µm radius spherical indenters with the partial unloading method, requires input of Poisson's ratio.

Poisson's ratio was assumed to be 0.34 in ii) and iii).

2.2.3 Tensile Properties

Mechanical tensile testing was carried out to BS EN 10002-1: 2001. Tensile dog bone specimens were grown to net shape as described above and burrs and built-up edges removed with SiC abrasive paper. Strain gauges were aligned axially on both sides of the specimens (type FLA-1-11, Tokyo Sokki Kenkyujo Co., Ltd. Japan). The specimens were abraded with #240 SiC paper and cleaned with acetone to remove grease and any particulates. The recommended cyanoacrylate adhesive was used to bond the strain gauges to the specimens. The strain gauge resistance was recorded by a multi-channel strain gauge bridge / data logger (Spider 8, Hottinger Baldwin Messtechnik, Germany). An Instron 5584 screw-driven machine was used together with a 1kN Instron load cell, taking care to align the specimens on the loading axis. Dimensions of the copper samples were input into the software that controls the Instron. The software controlled the rate of extension to give a constant stress rate of 2MPa/s, as specified by the standard.

2.3 Thermal Tolerance

Tensile dogbone samples were annealed in a laboratory furnace at temperatures between 200°C and 400°C for up to 2 hours. No attempt was made to control the atmosphere during annealing. Oxidation of the surface was removed with abrasive paper before tensile testing.

3 Results

3.1 Chemical Characterisation

3.1.1 Electron Dispersive X-ray Spectroscopy (EDS)

Chemical purity of the copper electroforms was investigated using EDS. EDS on a few different growths confirmed that they are 100% copper. No impurities could be detected anywhere in the samples. Annealed samples were subjected to spot analyses at the grain boundaries to investigate the possibility of a concentration of impurities during grain growth. No other elements were detected to the limit of sensitivity ($\approx 1\%$) in these regions (excitation volume $\approx 1\mu\text{m}$ diameter).

3.1.2 X-ray Diffraction (XRD)

Figure 2 shows the intensity versus 2θ for the electroformed copper scanned through 2θ range from 0° to 140° . The peaks correspond with the correct interplanar spacing for pure copper. The absence of other peaks indicates that no other crystalline phases are present. Additionally, the peaks corresponds with the position of randomly oriented copper so did not detect significant preferential orientation in the copper samples, ruling out structures such as columnar grains. The measured lattice parameter is very close to the accepted values in literature⁶. However, the diffractometer was not calibrated to investigate residual strain. So an estimate of residual strain could not be made. It also does not show if any part of the sample is amorphous.

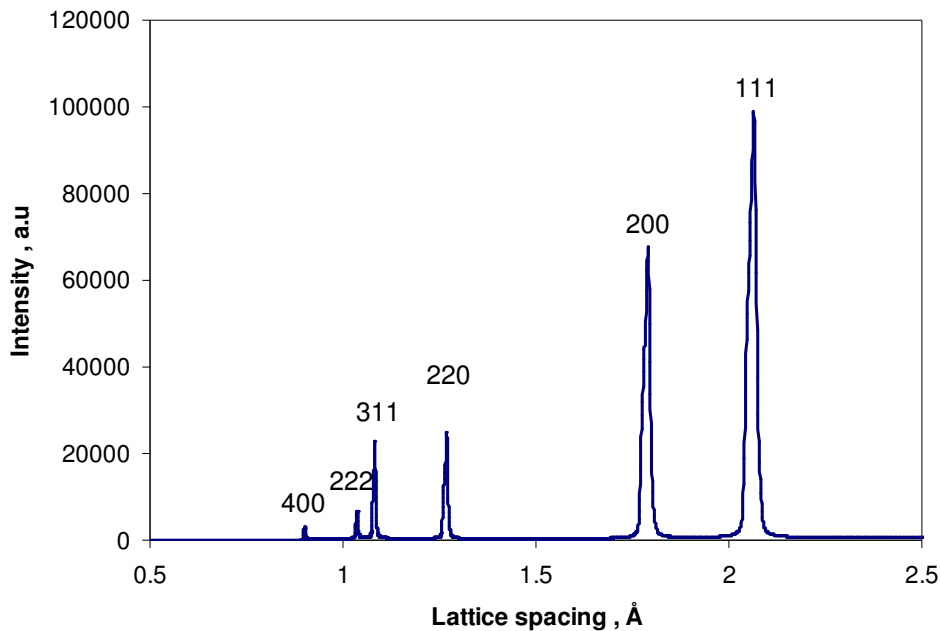


Figure 2. XRD of electroformed copper from $2\theta = 0^\circ$ to 140° . Peaks correspond to the lattice spacing of the usual planes of face centred cubic copper (labelled).

3.2 Microstructural Characterisation

Normal bulk copper, polished and etched using the methods described in section 2.1.1 revealed a typical microstructure in optical microscopy (figure 3) with grain sizes in the range 10 – 50 μm , many of which exhibit twinning.



Figure 3. Typical optical image of normal bulk copper prepared in the same method described in section 2.1.1.

TEM was used to determine the size of grains of as grown electroformed copper. A conventional bulk copper sample was prepared from copper sheet using the methods described in section 2.1.2. The resulting microstructure is shown in figure 4 (scale bar indicates 200nm in each micrograph). Bulk samples looked very similar to published micrographs of copper. The field in figure 4 shows a single crystal with dislocations in a well organise cell pattern, the dark bands between the veins representing bend contours.

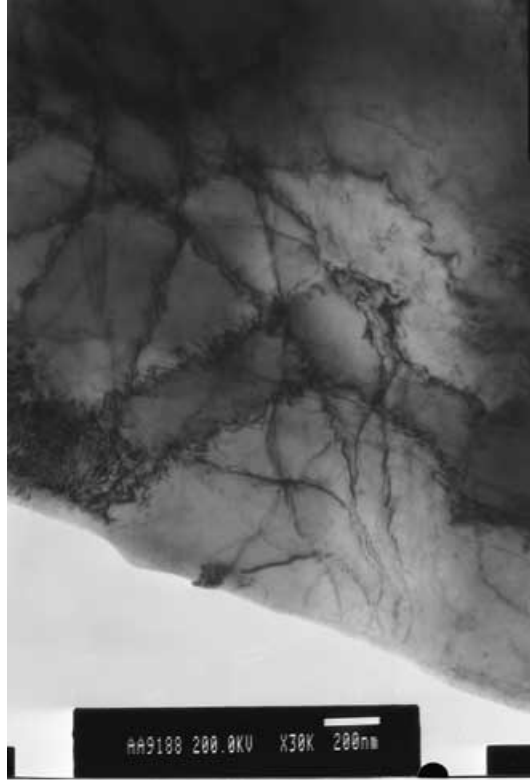


Figure 4. TEM image of normal bulk copper.

TEM of thick areas requires a very intense electron beam to penetrate the sample because inelastic scattering, diffraction and absorption are proportional to thickness. Objective apertures used to increase contrast also serve to decrease the brightness. Therefore, only the largest aperture is used to image these samples. Taking away the objective aperture gives bright images without much contrast whereas smaller apertures make the image too dark. Furthermore, the sample is tilted so that the grain is diffracting strongly. This makes the grain darker than the surrounding material and hence easier to see.

Figures 5 to 13 are a selection of micrographs of the thick regions of the electroformed copper. The highly diffracted grains in most figures are usually around half a micron in size with a range from around 600nm to around 100nm. However, smaller grains are present in the micrographs as shown in all figures except figures 9 and 10 because these micrographs are at a very low magnification.

The calculated grain size of selected grains is shown in Table 1.

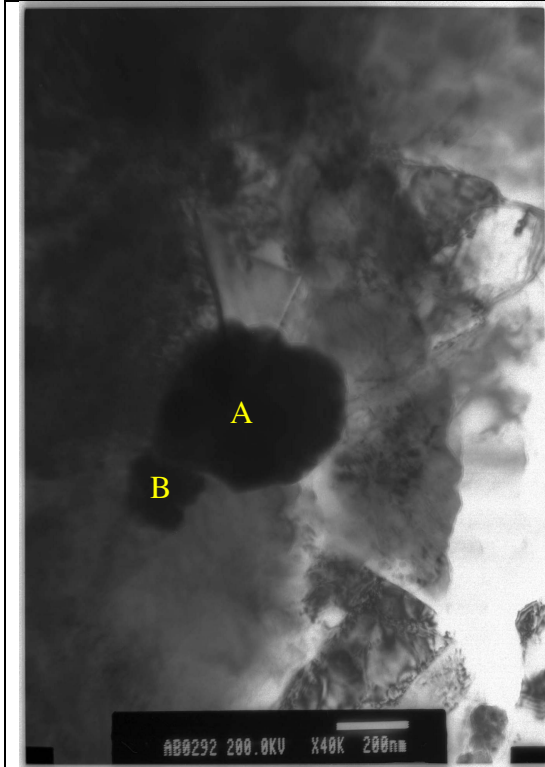


Figure 5. X40k magnification.

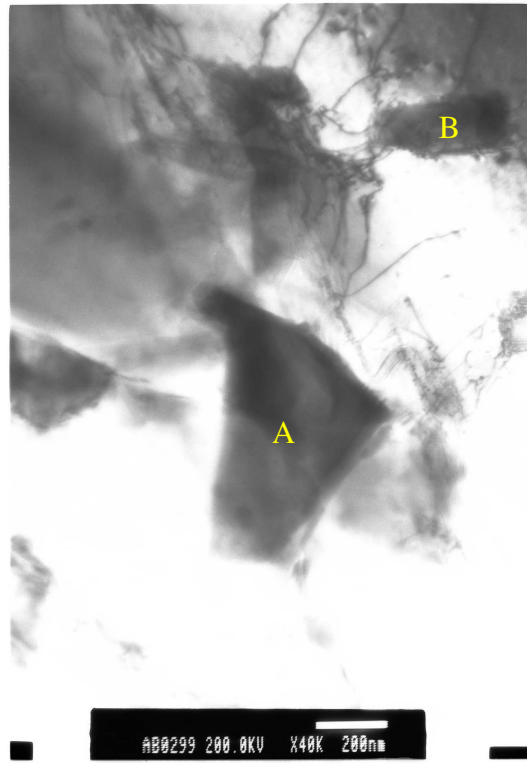


Figure 6. X40k magnification.

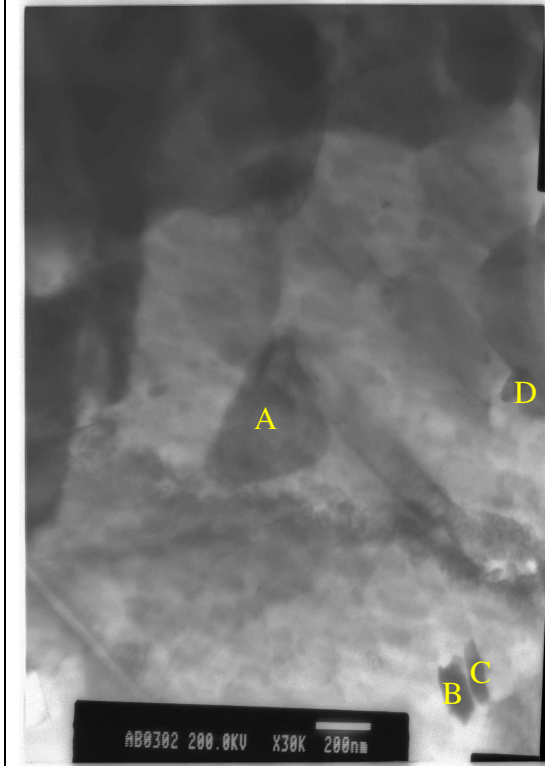


Figure 7. X30k magnification.

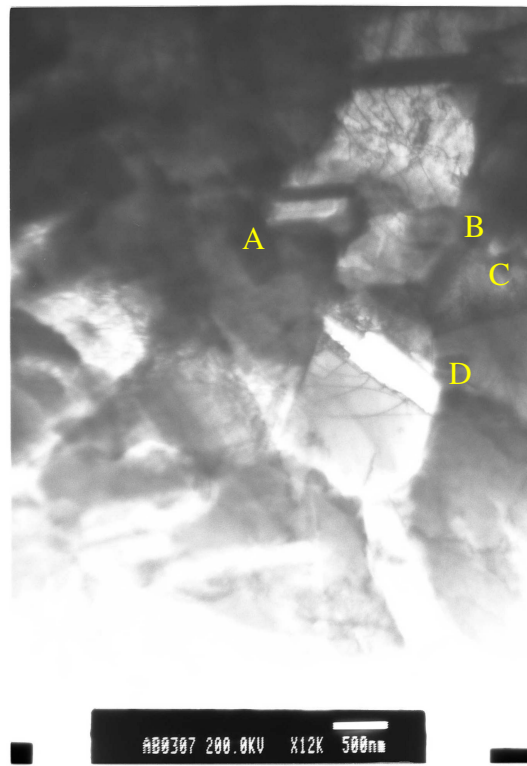


Figure 8. X12k magnification.

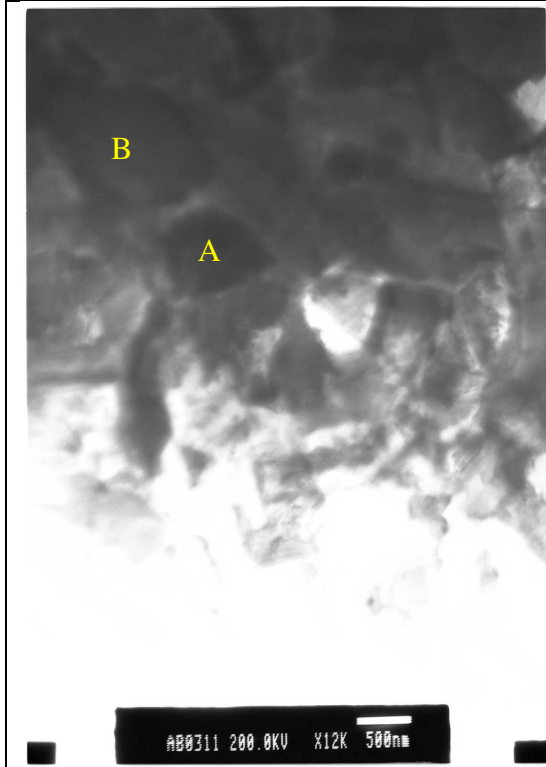


Figure 9. X12k magnification.

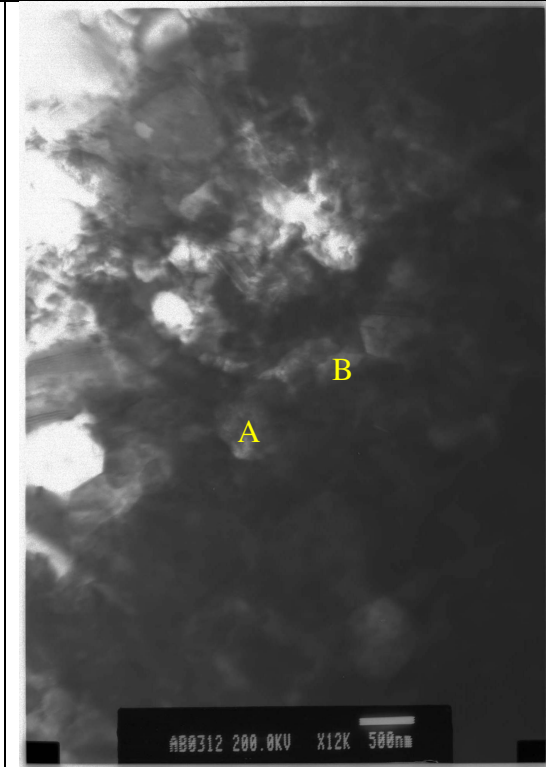


Figure 10. X12k magnification.

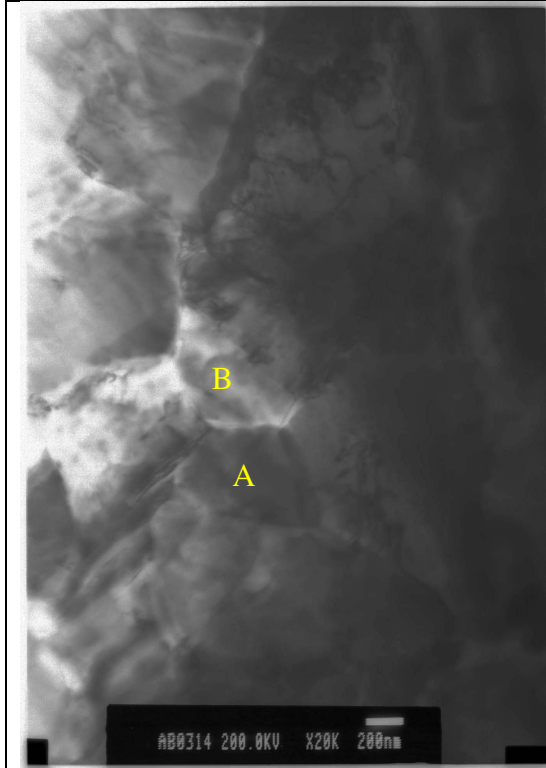


Figure 11. X20k magnification.

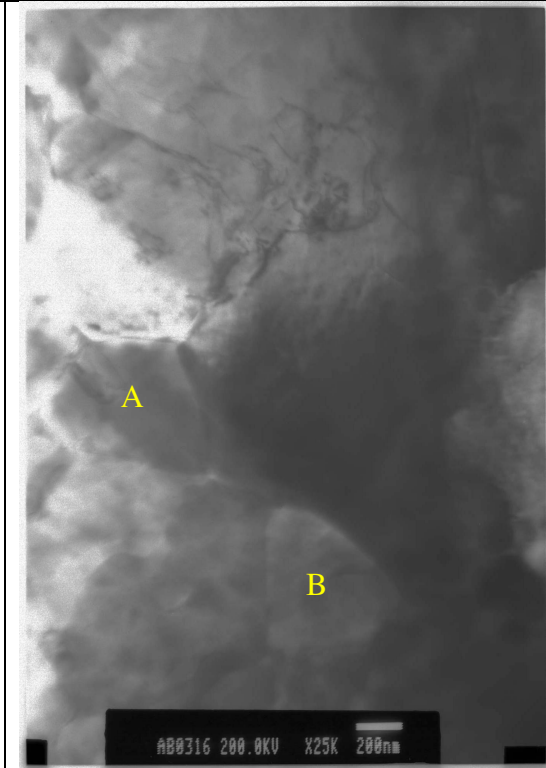


Figure 12. X25k magnification.

Table 1: Calculated grain size for selected grains. See figures for grain location.

	Grain Size / nm			
	A	B	C	D
Figure 5	461	192		
Figure 6	452	262		
Figure 7	438	142	130	111
Figure 8	477	204	189	189
Figure 9	689	1068		
Figure 10	477	287	469	
Figure 11	577	506		
Figure 12	592	562		

The majority of the grains shown here are approximately half a micron in size. The Hall-Petch plot in figure 13 shows that at 500nm, the datum for the as grown electroform conforms to the Hall-Petch law. Even though larger and smaller grains are shown to be present, it is the average grain size that determines the material yield strength.

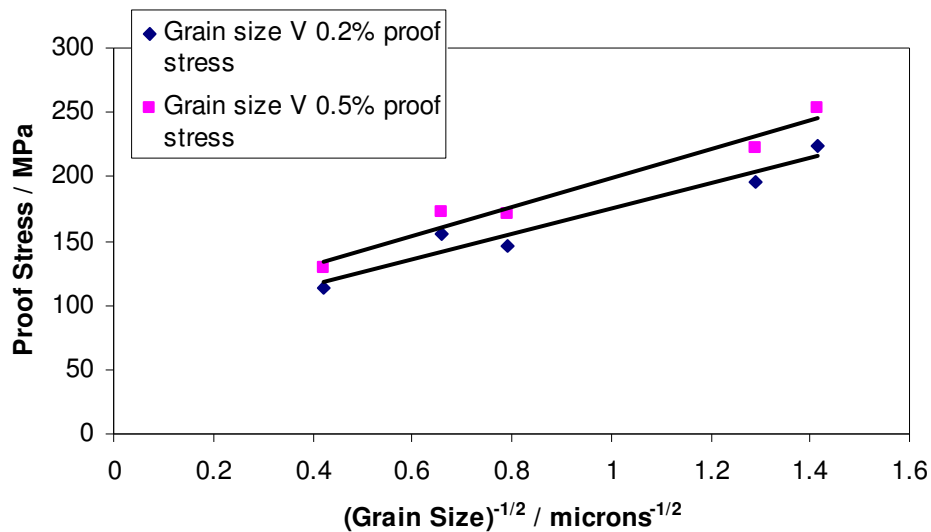


Figure 13. Hall-Petch relationship. Datum for the as grown electroform (furthermost right) lies on the Hall-Petch prediction.

Mechanical Properties

The results of mechanical property tests are summarised in Table 2 using the methods described in section 2.2. The value of shear modulus is calculated assuming a Young's modulus of 114GPa and a Poisson's ratio of 0.34. A typical example of a stress-strain curve for the electroformed copper is shown in Figure 14 below ('as grown'), from which tensile properties are derived.

Table 2: Results of mechanical property tests.

Property	Method	Mean	Standard Deviation	N
Density, ρ	Mass/volume	8.45 g/cm ³	0.038 g/cm ³	5
Young's modulus, E	IE	112.7 GPa	(\pm 3.38 GPa)	2
Young's modulus, E	SAW	118.8 GPa	1.41 GPa	
Young's modulus, E	NI	113.8 GPa	3.85 GPa	
Young's modulus, E	Tensile	99.3 GPa	9.7 GPa	
Shear Modulus, G	E = 114 GPa, ν = 0.34	42.5 GPa		
0.2% Proof Stress, $\sigma_{y(0.2)}$	Tensile	224.3 MPa	13.6 MPa	12
0.5% Proof Stress, $\sigma_{y(0.5)}$	Tensile	253.0 MPa	11.7 MPa	5
Ultimate Strength, σ_{UTS}	Tensile	311.9 MPa	8.0 MPa	12
Strain to Failure, ϵ_f	Tensile	20.62 %	2.77 %	8
Hardness, H	NI	1.2 GPa	0.2 GPa	42

3.3 Thermal Tolerance

Temperature dependence of electroformed copper is important because many modern applications require a material that is strong and stable over a wide range of temperatures. The annealed copper specimens were heat treated in a furnace at 200°C for 1 and 2 hours, 300°C for 1 hour and 400°C for 1 hour followed by tensile testing to determine mechanical properties.

The mechanical properties of the annealed electroformed copper were investigated by tensile testing. Figure 14 shows averaged engineering stress – engineering strain curves and figure 15 the proof stress values of the copper as a function of annealing temperature. The proof stress decreases when the copper is annealed at increasing temperatures as well as increasing periods of time. Even at 200°C, this effect degraded the proof strength of the copper. This behaviour is characteristically due to the microstructure of the material specifically, the grain size. Grain growth kinetics are governed by temperature and time. Larger grains give softer material. It is likely that electroformed copper gets its extraordinary strength from its small grain sizes. Therefore, if the grains become larger, then the strength of electroformed copper should degrade as shown in figure 15. Grain growth appears to be significant above about 130°C.

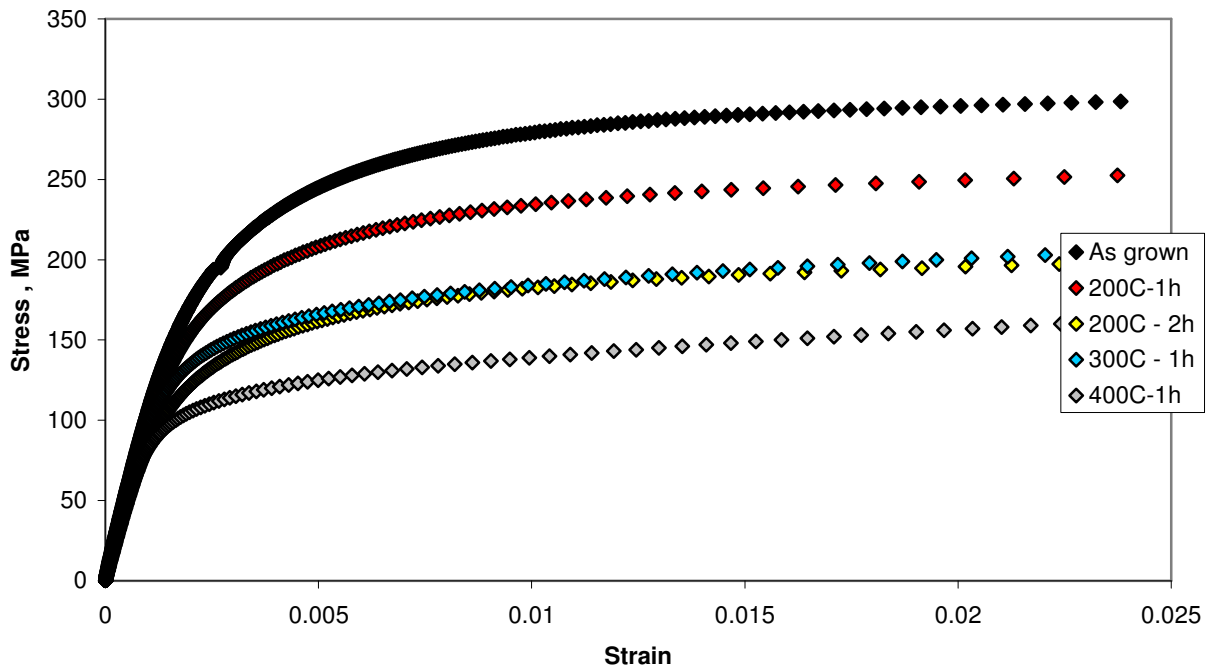


Figure 14. Engineering Stress – Engineering Strain curves of electroformed copper for different annealing conditions.

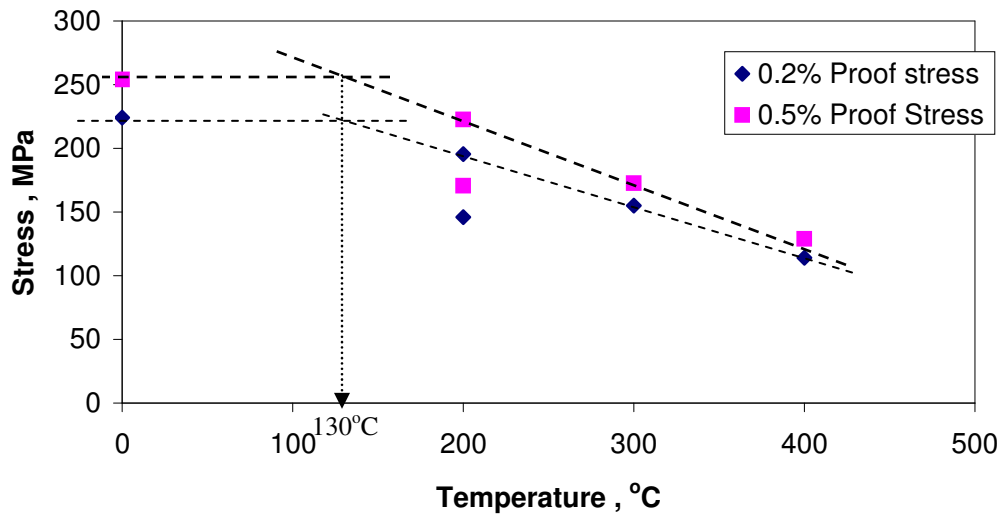


Figure 15. Yield stress as a function of annealing temperature.

4 Discussion

4.1 Microstructure

The electroformed copper appears to have very fine grain size, with grain sizes observed to have a range of 100-600nm. This appears to be the source of the unusually high strength for pure copper. Dislocations were only occasionally observed in the structure, and then only in the largest grains. There was little evidence of preferential orientation of grains and the same microstructure was observed in all parts and orientations of the electroform. Therefore it is suggested that the material is *bulk nanocrystalline*.

The measured density is about 95% of theoretical (8.94 g/cm³). Tensile modulus values of 99.3 GPa are about 86% of typical values for oxygen free Cu (115 GPa). Such a reduction in modulus is consistent with the reduction in density. For 5% porosity, Coronel *et al* (1990)⁴ give $E/E_o = 0.85$ for sintered glass. The MSA theory (mean solid cross-sectional area) gives $E/E_o = 0.78$. A reduced tensile modulus has been reported recently for micro-tensile tests on nanocrystalline metals with grain size less than 50nm, associated with a reduced density in these materials. Elastic modulus values for Cu are reported in the literature over the range 110GPa – 130GPa depending on the methods used and the purity of the Cu. Measurements of modulus from tensile testing tend to be less accurate due to the problem of reliably determining elastic strains. However, the values determined here are within a 10% of expected values thereby validating the other values determined from the tensile tests for yield stress, ultimate stress and strain to failure, where the plastic strains are much greater. The other methods used might be expected to provide a more representative measurement of elastic modulus. The Impact Excitation method has the advantage that it measures E directly. However, for relatively small samples out of plane resonances from the plate edges can introduce uncertainties in the results, estimated to be about 3% in this case. The Surface Acoustic Wave method is limited by the number of different wave path lengths possible on the relatively small sample and is very sensitive to velocity of sound in the material. Nanoindentation measurements can be effected by displaced material piling-up around the indentation, giving an error in the apparent contact area, which leads to an underestimate of modulus. This effect is less severe with spherical indenters. However, there was no significant difference in E values from 2 different sized spherical indenters, which might be expected if pile-up was a significant problem.

Comparing the properties of Morganic Metal's electroformed copper to typical properties of number of commercially available high purity metals (Table 3), the properties are comparable to cold worked copper (1/2 hard) with improved ductility, wrought Ti and low alloy carbon steels.

Table 3: Comparison of typical properties of various pure metals.

Metal	Designation	Condition	ρ g/cm ³	E GPa	σ_y MPa	σ_{UTS} MPa	ϵ_f %
Electroformed Cu ¹	QM1	As received	8.45	99.3	224	312	20.6
Cu (99.99%) ⁶	C10100 (OS050)	Annealed	8.94	115	69	220	45
Cu (99.99%) ⁶	C10100 (H 02)	Half hard	8.94	115	250	290	14
Al (99.99) ⁶	1199 (O)	Annealed	2.70	62	10	45	50
Ti (99.5%) ⁶	ASTM Grade 1	Annealed	4.50	103	170-240	240-330	30
Ni (99.9%) ⁶	270	Annealed	8.90	207	110	345	50
0.22% C steel ⁵	A285 (B)		7.85	207	185	345-485	25-28

ρ = density, E = tensile Young's modulus, σ_y = yield strength (0.2% proof stress)

σ_{UTS} = ultimate tensile strength, ϵ_f = strain to failure

Annealing electroformed copper causes grain growth (see figure 15). It is undisputable that annealing it at 200°C for 1 hour will degrade the strength by around 15%. So, this limits the range of applications to temperatures below 130°C. Extrapolating the Hall-Petch relationship of the annealed copper to include smaller grain sizes gives an average grain size value of around 500nm for the strength of as grown electroformed copper (dotted line). This is consistent with the Hall-Petch relation for grain size strengthening.

5 Conclusions

Electroformed copper is a pure form of copper that is made much stronger than bulk annealed copper by its ultra-fine grain structure. In the *as grown* form, the strength is similar to mild steel which is exceptional because copper in its pure form is inherently a soft metal. This improvement in strength does not make it as brittle as work hardened metals so it can be used in applications where strength and ductility are important.

The grain structure was shown to be around 500nm in size. The small grains did indicate some preferred orientation however, we could not extensively study the orientation of the grains nor if there was any residual strain.

The grains grow when they are annealed at 200°C for 1 hour, resulting in a 15% loss in strength. The effect of temperature on electroformed copper is a preliminary result but appears to be limited to temperatures above about 130°C. Subsequent annealing at higher temperatures and for longer times did reduce the strength further, in proportion to the increase in grain size.

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