Fabrication And Analysis Of Thin-Film Copper Multilayers

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Abstract*: Thin-film copper multilayers were produced by cyclic cold rolling of pure copper. Resistivity and yield strength were estimated using the Fuchs thin-film resistivity model and the Hall-Petch relation. It appears feasible to produce nanostructured copper using the cold rolling method described here.*

Introduction

Conductors in high field magnets are subjected to intense Lorentz forces. The resulting stress on the conductor can cause failure. One possible source of stronger conductors is the realm of nanostructured materials. The Hall-Petch relation:

$$\sigma_y = \sigma_0 + K_{H\text{-}P} d^{-1/2}$$

describes increasing yield strength in materials (σ_y) as average grain size (d) decreases. The strengthening is attributed to grain boundaries acting as barriers to dislocation motion. This relation is well defined in coarse-grained materials.

Extrapolation of the Hall-Petch relation implies that materials with nanoscale (1-100 nm) grains are stronger than materials with microstructured grains. Experiments have found that nanostructured materials do have much higher strength than their coarse-grained counterparts.[i] Since copper is widely used as a conductor, nanostructured copper could be of value in applications (such as high field magnets) where high strength and conductivity is of value.

However, there are conflicting reports about the validity of the Hall-Petch relation at the nanoscale level. There are reports of normal Hall-Petch behavior at nanoscale sizes, but some observations suggest that at sufficiently small grain sizes (estimated < 15 nm) an inverse Hall-Petch behavior is in effect - that as grain size decreases further, the strength of the material begins decreasing.[ii] One explanation is that the grain size becomes too small to support a dislocation pileup. Another suggested mechanism is that the grain boundaries bind together to form a single continuous matrix, with each grain embedded in the matrix.[iii]

The resistivity of copper increases as average grain size decreases, in accordance with the Mayadas-Shatzkes resistivity model.[iv] Nanograin sizes in nanostructured copper can be less than the mean free path of an electron. At this grain size, electron scattering off grain boundaries becomes a dominant mechanism of resistivity. The result is greatly increased resistivity in the material.

Research on materials with nanograins has attracted great interest in both nanoscience and materials science. Copper is a good subject for nanocrystalline analysis because of its versatility and its well-known bulk properties.

In this report, thin-film copper multilayer foil was produced by repeated cold rolling of pure copper. The cold rolling fabrication technique in use was refined, and both the mechanical and electron transport properties of pure nanostructured copper were estimated.

Method of fabrication

Cyclic cold rolling *(Fig. 1)* was used because of comparative advantages over other fabrication techniques. Cold rolling does not introduce porosity

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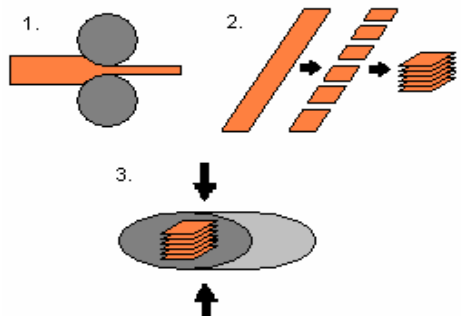

Fig. 1: *Cyclic cold rolling of pure copper. (1) Copper is rolled between two steel rollers. (2) Copper foil is cut and stacked. (3) Stack is placed in a stainless steel sheath, compressed and rerolled.*

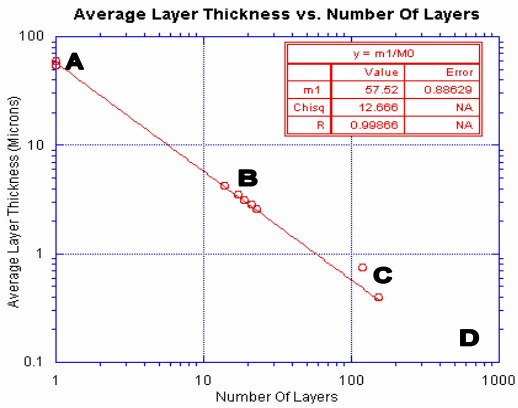

Fig. 2: *Graph of the relationship between average layer thickness and the number of layers. Region A: A single layer of foil after one rolling. Region B: Multilayer samples produced by two rollings (one packing). Region C: Multilayer samples produced by three rollings (two packings). Region D: Estimated region of samples after four rollings (three packings).*

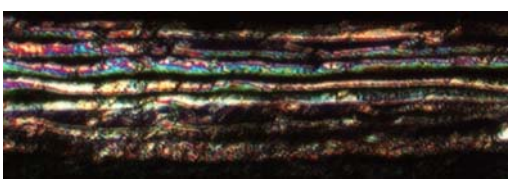

Fig. 3: Image of a cross section of a final copper multilayer. The total thickness of the sample is 60 microns. In this sample there are 8 layers of 19 layers, for a total of 152 layers. Average layer thickness is about 400 nm. There was poor binding from the second packing stage (8 layers are distinct).

and gaseous impurities like deposition techniques, and rolling is more controlled than ball milling. Cold rolling is also relatively inexpensive and can be scaled up for greater production.

A small sample (40mm x 25mm x 1mm) was cut from a sheet of pure high-conductivity copper. This sample was cold rolled to thickness 60 microns. This thickness was chosen to balance the need for high reduction in thickness and the need to be able to physically handle the multilayer. The copper foil was then cut into 15-20 pieces and stacked. The stack was placed in a sheath, compressed with a hydraulic press (P_{max} = 750 MPa) and rerolled.

Stainless steel was chosen as the material for the sheaths because it is soft enough to be rolled but still strong enough to hold the copper stack in place.

The product of the cyclic cold rolling was a copper multilayer – a strip of copper foil with as many as 152 layers. The copper multilayers were rolled 1 to 3 times for a reduction in thickness ranging from 20x to 2500x from the original 1mm-thick sample. The multilayers felt into distinct groups based on how many rollings were used *(Fig. 2)*.

The usable area of good binding in a final multilayer was approximately 2 cm x 10 cm. This section was cut into longitudinal and latitudinal cross sections and mounted in epoxy for observation with a Leica MeF4 inverted optical microscope. Visual inspection shows that good binding was achieved from the first packing stage, but there was poor binding from the second packing stage (*Fig. 3*). Because the material only had a small area of good binding after the first packing, there was only enough multilayer material for 8 layers in the stack for the second packing. Experience from the other samples suggests that at least 15 layers are needed in a stack for good binding between layers. Two methods can be used to increase the multilayer yield – increasing the original sample size, and combining two or more samples. The latter method was not used here because of concern about the feasibility of maintaining similar sample conditions.

The need for each packing stage to yield more multilayer material also led to a refinement of the shape of the sheath to minimize loss. Keeping the width of the sheath close to the width of the copper stack restricted the deformation of the copper was to two dimensions. Lengthening the sheath to over twice its original length (from 35mm to 90mm) solved the problem of copper being squeezed out of the sheath during rolling.

Resistivity model

Estimates were made of the resistivity and strength of the copper. Pękala *et. al* have previously found that the Mayadas-Shatzkes resistivity model accurately describes the resistivity of nanocrystalline copper.[iv] For simplicity, resistivity was estimated using the Fuchs theory for thin films:

$$\rho=\rho_i\left[1-(3/2\kappa)(1-p)\int_1^\infty\left(\frac{1}{t^3}-\frac{1}{t^5}\right)\frac{1-e^{-\kappa t}}{1-pe^{-\kappa t}}dt\right]^{-1}$$

where κ is the ratio of film thickness to the mean free path of an electron for the material, *p* is a parameter between 0 and 1 that is approximately 0 for polycrystalline films and ρ_I is the intrinsic resistivity of the material.

The solution of the Fuchs equation is that a 400 nm copper film is 1.6 times as resistive as bulk copper, much higher than what was hoped for. However, the Fuchs model is much simpler than the Mayadas-Shatzkes model, and is not as accurate. This calculation was made assuming each layer of copper in the nanostructured multilayer would act independently electrically; however, copper-copper boundaries (which are not described in the Fuchs model) may reflect electrons differently than copper-air boundaries as in a thin film. In addition, the parameter *p* may not be zero for a nanocrystalline material.

Strength model

Yield strength was estimated by using the Hall-Petch relation, assuming no softening behavior. For pure copper, σ_0 has a value of –8.6 MPa, K_{HP} has a value of 292 MPa(micron)$^{1/2}$, d is the grain diameter measured in microns and an additional temperature-dependent term has a value of –9.87 MPa at 300K.

Cold worked pure copper has a yield strength of 393 MPa. A sample with layer thickness and grain size 400 nm is estimated to have a yield strength of 443 MPa, slightly stronger than cold worked pure copper. Using the Hall-Petch relation for nanostructured copper predicts a yield strength of 900 MPa for 100 nm nanograins and 2.9 GPa for 10 nm nanograins.

Conclusions

Thin-film copper multilayers were produced by repeated cold rolling. The cold rolling process in use was refined. It appears feasible to use this procedure to fabricate nanostructured copper. The next step is to produce nanostructured copper with a fourth rolling and to confirm that it is nanocrystalline with scanning and transmission electron microscope observations. Strength and resistivity tests can then be performed on the nanostructured samples. The results of these tests can then be compared with the predictions of the Hall-Petch relation and the Mayadas-Shatzkes resistivity model.

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