

Production and Examination of Nanocrystalline Copper

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Abstract

325-mesh copper powder was ball milled under various conditions to produce copper samples of different grain sizes. One well-milled sample was annealed at varying temperatures and for different times to promote grain growth. These two procedures provide a range of grain sizes for study. Crystallite size was determined by analyzing x-ray diffraction peak broadening. Continuing research would include equal channel angular extrusion (ECAE) of the samples in an attempt to produce bulk nanocrystalline copper, allowing researchers to more easily determine the mechanical properties of this nanocrystalline metal.

Objective

Fabricate, consolidate, and examine nanocrystalline copper to determine how its mechanical properties vary with grain size.

Introduction

According to the Hall-Petch relationship, the yield strength and hardness of a metal depends upon the inverse square root of its grain size.¹ In recent years, however, some have come to question the relevance of this relationship at sufficiently small grain sizes. A study by S. Cheng et al. found that the Hall-Petch relationship held at least down to $d=20$ nm.² It would be interesting to observe the mechanical properties at sufficiently small grain sizes, to see if the Hall-Petch relationship could still be observed.

Obtaining a bulk piece of polycrystalline copper for mechanical testing without obliterating the nano-sized grains can prove to be quite challenging. S. Cheng et al. use the small copper pellets produced from their series of cryomilling and room temperature milling in their

mechanical testing.² These small pieces of copper may be useful for certain mechanical tests, but they are not large enough for many practical applications. Equal Channel Angular Extrusion, if able to fully consolidate nanocrystalline copper, could produce bulk nanocrystalline copper for practical use. The successful ECAE consolidation of copper powders in the 44 micron-100nm grain size range in a study by Haouaoui et. al. suggests a promising future in nanocrystalline (<100 nm) powder ECAE consolidation.³

Method

Ball milling 32- mesh copper powder

Three ball milling methods were used in an attempt to decrease the crystallite size of the 325-mesh copper. The first method was high-energy milling in the SPEX-8000 with a ball-to-powder mass ratio of 3:1. Milling time was 12 hours. No heating or cooling system was used to regulate the temperature of the specimen; the machine appears to heat up during milling, so the milling occurs slightly above room temperature.

Another procedure was room temperature milling in the Attritor, a lower-energy mill, for 80-93 hours with a 10:1 ball-to-powder ratio. Argon was pumped into the canister before milling began and a slight positive pressure was maintained throughout the milling process to avoid contamination from the air. Cool water circulated about the XRD canister to assist in maintaining a steady temperature throughout the process. Milling began at 400 rpm and increased over the first two hours to 500 rpm.

Cryomilling with liquid nitrogen in the Attritor was the third milling process. As in the previous procedure, a 10:1 ball to powder mass ratio was used. After loading the powder and balls into the canister, liquid nitrogen was poured in and the sample ran for 10 min at 600 rpm after which it was filled with liquid nitrogen and milled for 15 min. More liquid Nitrogen was added every 15 minutes for the next 80 minutes, and was added before the final 10-minute mill. The powder was cryomilled for two hours in total.

Annealing to Promote Grain Growth

To increase the range of grain sizes tested, some of the Attritor 93-hr. copper was annealed at 400° C, 600° C, and 800° C for one hour each and at 400° C for 10, 20, and 30 minutes. Small portions were annealed, often consisting of just enough powder to perform an XRD scan or to prepare an SEM or optical microscope sample.

Determining Average Grain Size of Samples

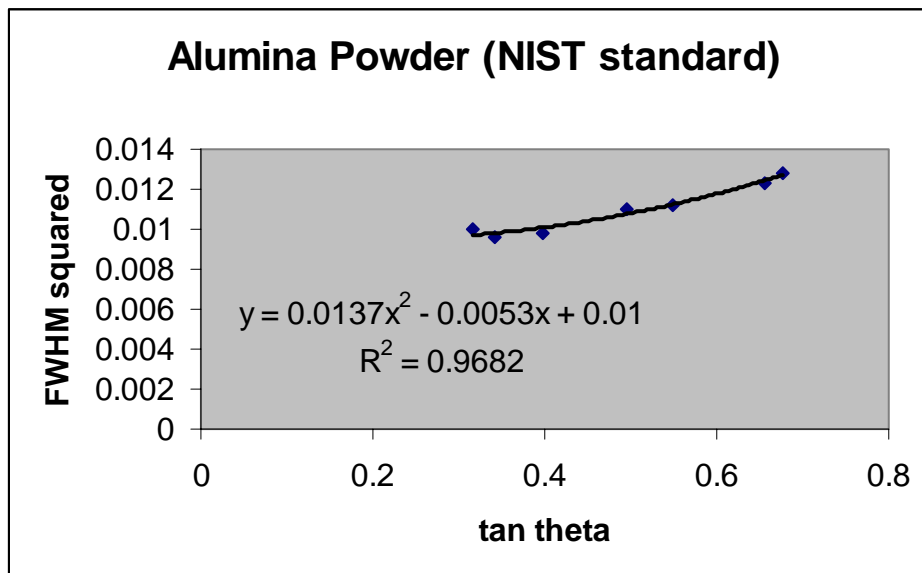
Specimens were scanned in a Siemens D-5000 x-ray diffractometer. Powder samples were readied for XRD analysis by sprinkling powder over a very thin, smooth layer of petroleum jelly on the tray. Often a flat, clean glass slide was pressed on top of the sample to ensure that the powder was level.

The non-powder specimen, SPEX-12hr. was set in Phenocure, ground, and polished. The sample was placed in an XRD sample holder with putty and was then made level with the surface of the sample holder.

Most samples were scanned from 2-Theta equals 30 degrees to 100 degrees with a step size of 0.02 degrees and a step time of 5 seconds. Some of these parameters were altered for certain scans, in part due to the availability of the instrument.

Peaks are refined and analyzed using EVA Diffrac Plus software. The software can remove $K\alpha_2$ peaks from the $K\alpha_1$ peaks. It can also provide FWHM and position, 2θ , for the four peaks. The Williamson-Hall technique can now be applied to determine grain size.³

First, instrumental broadening must be removed. To determine an equation for instrument broadening, an Alumina Powder standard was scanned. From its peak data, FWHM^2 was plotted versus $\tan\theta$. The coefficients of the quadratic equation of best fit of this graph are used to determine instrumental broadening at any angle. $\text{FWHM}_{\text{inst}} = \text{squareroot}(0.0137\tan^2\theta - 0.0053\tan\theta + 0.01)$



After instrumental broadening has been removed, the FWHM and 2θ values can be used to plot $B\cos\theta$ vs. $\sin\theta$ for each of the four peaks. A line of best fit can then be calculated. $(0.92) \cdot (0.154\text{nm})$ divided by the y-intercept of this line of best fit is equal to the estimated grain size of the sample.

Because the x-ray diffractometer is not sensitive to changes in crystallite sizes from 100-10,000 nm, other methods must be used to calculate grain size.⁴ Three polished samples, consisting of the 400° C 10, 20, and 30 minute anneals were etched for 4 seconds using a 4% nitric acid solution dissolved in methanol in preparation for optical microscopy. No pictures of the magnified specimens have been taken yet due to time constraints. (Samples 1-3 in table below.)

Hardness testing

Nine powder samples were put in EPOFIX, a cold-setting resin, to prepare them for hardness testing. The resins were then set in Phenocure after which they were ground and polished. Each Phenocure cylinder contained three samples set in resin. (See table below for sample identification.)

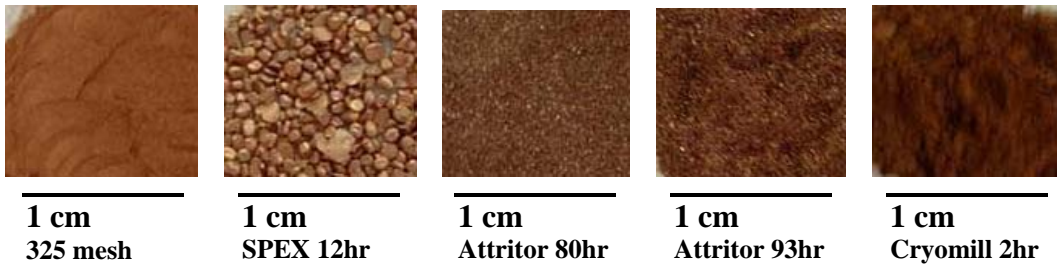
Number	Sample ID	Cylinder	Color
1	30min @400 C	A	black
2	20 min @400 C	A	green
3	10 min @ 400 C	A	red
4	cryomill dark	B	black
5	attritor 90	B	red
6	attritor 80	B	green
7	attritor 93	C	black
8	325 mesh Cu	C	green
9	cryomill dark	C	red

The small particle size of the powders made microhardness testing with the Vickers' hardness tester impossible. Nanoindentation also proved ineffective, since there seemed to be no way of distinguishing between the EPOFIX and the copper powder. The viewing screen showed simply the topography of the sample, so there was no way of knowing whether the indent was on the powder or on the epoxy.

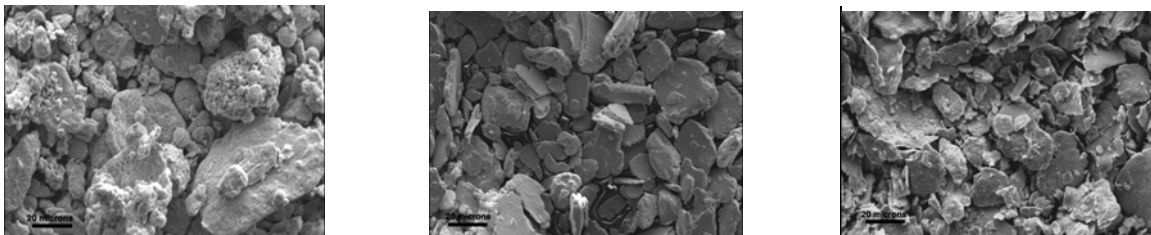
Results

Examination of Ball Milled Copper Particles

The samples milled in the Attritor were still powders when taken from the Attritor (both the cryomilled samples and the room temperature samples were powders.) However, the samples milled in the SPEX 8000 were more like small copper pellets when removed. (See pictures below)



The RT milling and cryomilling in the Attritor produces particles that look much flakier than the pieces that make up 325 mesh copper. (See SEM photos below.)



325 mesh Cu

Attritor 80 hr.

Cryomill 2 hr.

Grain Size Calculations

Found using Williamson-Hall technique.

<i>Sample</i>	<i>SPEX 12-hr</i>	<i>Attritor 80-hr</i>	<i>Attritor 90-hr</i>	<i>Attritor 93-hr</i>	<i>Cryomill 2-hr</i>
<i>Estimated Size (nm)</i>	<i>>100</i>	<i>28.34</i>	<i>19.95</i>	<i>40.48</i>	<i>41.67</i>

Improvements

It seems that calculating crystallite size from XRD peak broadening is not very precise. One would think that the three Attritor powder values would be very close in size, but the 93-hour milled grains are twice the size of the 90-hour milled grains according to the Williamson-Hall Technique. It could be very useful to supplement this data with grain size measurements using another instrument, such as a Transmission Electron Microscope.

On several XRD scans there are extra peaks corresponding to oxides and to iron. Because the ball milling involves steel balls colliding with each other, the sides of the canister, and the powder, there is no clear way to avoid some small amount of iron contamination. However, more care could be taken to prevent oxidation from occurring in the copper powder. Ensuring that seals are airtight and keeping a sufficient amount of Argon pumping into the canister would help. It may also be useful to use the glove box when loading and unloading samples.

Future Research

Continued research could include the consolidation of the copper powder through Equal Channel Angular Extrusion. Hopefully, multiple passes at a raised temperature (100°C or 200°C) will produce fully consolidated bulk nanocrystalline copper.

Following consolidation, the bulk specimen can undergo tensile, hardness, or other tests to determine its mechanical properties as functions of grain size.

References

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2. Cheng S et al, "Tensile properties of in situ consolidated nanocrystalline Cu," *Acta Materialia* 53 (2005) 1521-1533.
3. Meier M, "Measuring Crystallite Size Using X-Ray Diffraction, the Williamson-Hall Technique (Draft)." Department of Chemical Engineering and Materials Science, University of California, Davis. Feb. 22 2005.
4. Cullity B D, Elements of X-Ray Diffraction, p. 283, Addison-Wesley, 1978.