Effective metallographic techniques have been developed for revealing copper microstructures through color etching.

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Copper is an extremely malleable and ductile metal with high electrical conductivity, good corrosion resistance, and reasonable strength. Copper alloys date from antiquity and include a wide range of brasses, bronzes, and other alloys. Most copper alloys are in the annealed or cold-worked condition, because they work harden and remain ductile. A few alloys, such as beryllium bronze and Kunial brass, can be age hardened to high strength levels.

Copper has a face-centered cubic crystal structure, and relatively pure copper is available in several variants. Metallographers usually encounter tough-pitch (TP) copper, which is electrolytic or chemically refined, or has small silver or arsenic additions. Other fairly common variations are oxygen-free electronic or oxygen-free, high-conductivity copper; and phosphorus-deoxidized copper, which may contain additions of arsenic or tellurium. This article describes traditional copper specimen preparation methods, then presents examples of “contemporary” techniques that reduce the preparation time and are more effective in revealing the microstructure of interest.

Specimen preparation
In general, preparing copper and copper alloy specimens is not difficult, at least to a level where the true structure can be seen. However, removing...

Fig. 1 - This annealed cartridge brass, Cu-30Zn, was prepared using the traditional method, and the process included multiple etch-polish cycles (Klemm’s I reagent, 100X).

Fig. 2 - Annealed cartridge brass prepared by the traditional method, followed by vibratory polishing with an attack polish agent in colloidal silica with multiple etch-polish cycles. This yielded a scratch free surface by excessive relief (Klemm’s I reagent, 20X, DIC).

Fig. 3 - Annealed electrolytic tough-pitch copper prepared by the contemporary method plus a brief vibratory polish (Klemm’s II reagent, 50X, crossed-polarized light with light use of sensitive tint.)

Fig. 4 - Annealed and cold drawn arsenical, phosphorus-deoxidized copper prepared with the contemporary approach (Klemm’s I reagent, 50X, crossed-polarized light plus sensitive tint.)
all scratches can be quite challenging, and the structure of cold-worked specimens may not be easy to render sharply. In particular, the grain structure of annealed specimens is very difficult to fully reveal by etching. Many copper-base alloys contain minor additions of elements such as lead and tellurium for machinability, and retention of these precipitates in the specimen can also be a real challenge. Likewise, retaining the Cu₂O present in TP copper is not an easy task. Electrolytic polishing is a possible option, but it tends to attack these phases.

Immersion and swab etchants are the most widely selected for copper and its alloys. The most common etchant is a mix of equal parts of ammonium hydroxide, hydrogen peroxide (3% concentration), and water (addition of water is optional). Although a bit smelly, it works very well by swabbing, but has a very short useful life and, of course, must be made fresh each time.

Many different etchants are based on mixtures of ferric chloride, hydrochloric acid, and water or ethanol, and some are based on ammonium persulfate, etc. These can be found in standard sources. Color etching techniques are highly effective for copper and its alloys. The most common etchant is a mix of equal parts of ammonium hydroxide, hydrogen peroxide (3% concentration), and water (addition of water is optional). Although a bit smelly, it works very well by swabbing, but has a very short useful life and, of course, must be made fresh each time.

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**Traditional techniques**

The tried-and-true “traditional” approach to specimen preparation is shown in Table 1. This practice works to a limited extent, but is not really effective for removing persistent fine scratches. To get “good” color etching results, the last preparation step must be repeated after an unsuccessful etch, and the specimen must be re-etched. The must be repeated over and over to get good results, a technique that is an endurance test for metallographers. To improve results, many metallographers added an attack polish agent to the final polishing abrasive. For example, an aqueous 1% solution of ferric nitrate has been found to help. However, undesirable relief is a consequence of the repeated etch-polish cycles. Furthermore, the relief usually becomes excessive if the scratches are ultimately controlled. Figure 1 shows a soecimen of annealed cartridge brass, Cu-30% Zn, prepared manually using repeated etch-polish cycles with a ferric nitrate attack-polishing agent. This works much better than traditional methods, but problems remain.

Fortunately, a vibratory polisher can help. This very handy device can provide the final polishing step by applying colloidal silica and the 1% ferric nitrate attack-polishing agent. This works much better than traditional methods, but problems remain.

Figure 2 shows another micrography of the annealed cartridge brass specimen, at low magnification, it was prepared by repeated etching and vibratory polishing. This produced better scratch control but resulted in excessive relief.

Because the standard procedures could not develop the true structure to the level of perfection.
required for color etching, it was time to look at new methods and ideas. Metallographic preparation ideas have been evolving over the past decade, producing more streamlined procedures, often called “contemporary” procedures. Table 2 represents a current preferred method, which is usually followed by one- to two-hour vibratory polish with colloidal silica, but without attack polishing agents. Vibratory polishing is usually not required with ordinary black and white etchants, except for the most difficult alloys.

**Table 2 - Five-step contemporary preparation**

<table>
<thead>
<tr>
<th>Step</th>
<th>Surface/Abrasive</th>
<th>rpm</th>
<th>Direction</th>
<th>Load, lb (N)</th>
<th>Time, minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>240-grit SiC*</td>
<td>240-300</td>
<td>Comp.</td>
<td>5-6 (22-27)</td>
<td>U.P.</td>
</tr>
<tr>
<td>2</td>
<td>p-µm diamond paste</td>
<td>120-150</td>
<td>Comp.</td>
<td>5-6 (22-27)</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>3-µm diamond paste</td>
<td>120-150</td>
<td>Comp.</td>
<td>5-6 (22-27)</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>1-µm diamond paste</td>
<td>120-150</td>
<td>Comp.</td>
<td>5-6 (22-27)</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>Colloidal silica</td>
<td>120-150</td>
<td>Contra</td>
<td>5-6 (22-27)</td>
<td>1.5-2</td>
</tr>
</tbody>
</table>

**Notes:** Load is per specimen; Comp. = complementary (head and platen rotate in same direction); U.P. = until all surfaces are at the same plane and cutting damage is removed.

**Table 3 - Compositions of tint etchants**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Comments</th>
</tr>
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<tbody>
<tr>
<td>50 mL saturated aqueous sodium thiosulfate, 1 g potassium metabisulfite</td>
<td>Klemm’s I reagent. Immerse until surface is colored</td>
</tr>
<tr>
<td>50 mL saturated aqueous sodium thiosulfate, 1 g potassium metabisulfite</td>
<td>Klemm’s II reagent. Immerse until surface is colored. Good for alpha brass.</td>
</tr>
<tr>
<td>5 mL saturated aqueous sodium thiosulfate, 45 mL water</td>
<td>Klemm’s III reagent Immerse until surface is colored. Good for bronzes</td>
</tr>
<tr>
<td>20 g potassium metabisulfite</td>
<td></td>
</tr>
<tr>
<td>1000 mL water, 240 g sodium thiosulfate, 30 g citric acid, 24 g lead acetate</td>
<td>Beraha’s lead sulfide (PbS) reagent for copper and alloys. Mix in order given. Allow each to dissolve before adding next (the citric is impossible to dissolve, so mix well and add the lead acetate). Age 24 h in a dark bottle before using. Store in darkness. To use, pour about 100 mL in a beaker, do not remove precipitates. Immerse until the surface is colored.</td>
</tr>
</tbody>
</table>

**Color micrograph examples**

The first examples show the purest and most difficult to prepare copper grades. Figure 3 shows the microstructure of electrolytic tough pitch copper etched with Klemm’s II reagents (see Table 3 for the compositions of the reagents.) Note that one or two very fine scratches are barely visible, but no excessive relief is visible, and the inclusion stringers are fully retained. The twinned alpha grain structure is also fully revealed. Figure 4 shows the twinned alpha grain structure of phosphorus-deoxidized, arsenical copper (Cu-0.4As-0.04P). This specimen was cold drawn slightly after annealing. Note that a few grains exhibit slip lines.

The next several examples show as-cast copper alloys. Figure 8 illustrates dendritic solidification and “coring” segregation in a chill-cast Cu-10Sn bronze specimen. The high-magnification view shows the color variation within the dendrites due to variations in the tin and copper contents. Note also that another phase, left white, is between the dendrites. No attempt was made to identify this intermetallic phase, which may be Cu₃Sn. Some voids (shrinkage cavities) are also present and appear...
black; these are often associated with this intermetallic phase.

Figure 9 shows the microstructure of sand cast Cu-4.5P, which is not a commercial alloy. The tint etch reveals coring segregation in the colored alpha dendrites. Between the dendrites is a fine eutectic of alpha (colored) and Cu₃P, copper phosphide (uncolored). Again, shrinkage cavities are present. Figure 9 was taken in bright field illumination. An interesting effect results if the same specimen is viewed in cross-polarized light with a sensitive tint plate, Fig. 10 (different area). Note that the cored alpha primary dendrites are yellow in the center (richest in copper), and are rimmed by a violet color. The alpha phase in the eutectic is also violet in color, and is segregation-free, due to the nature of the eutectic transformation. We conclude that the composition of the outer rim of the proeutectic alpha dendrites is essentially the same as the alpha in the eutectic. The proeutectic alpha has precipitated just above the eutectic temperature, while the eutectic alpha has formed just below the eutectic temperature. Hence, these regions should be of similar composition.

This type of information cannot be revealed by standard etchants. If you look at Fig. 9 again, you can see that these same areas have the same color in bright field, but this chemistry difference is not as obvious as in Fig. 10. Figure 11 shows the microstructure of sand cast Cu-10.5P, another non-commercial alloy. The white dendrites are proeutectic copper phosphide, while the matrix is the eutectic of alpha copper (colored) and copper phosphide (not colored).
Cold-worked specimens

The next two specimens illustrate cold-worked copper alloys. Figure 12 shows the microstructure of an Outukumpu alloy called “Everdur,” Cu-3Si-1Mn, which has been cold drawn to the “half-hard” condition. Tint etching reveals that the cold work has not been uniformly distributed, as some grains exhibit relatively few slip lines compared with others that are heavily slipped. In comparison, Fig. 13 shows a more uniform distribution of slip, and substantial grain elongation in cold-drawn phosphor bronze (Cu-5Sn-0.15P).

Figures 14 and 15 illustrate the microstructure of aluminum bronze. In this case, the aluminum content is slightly below the eutectoid composition of 11.8%. Figure 14 illustrates an annealed structure in a wrought specimen. The specimen was heated high into the beta field, to 982°C, held for one hour, slow-cooled to 482°C in the furnace, and then air cooled. Figure 14 shows that the aluminum content was definitely lower than the eutectoid composition, because some proeutectoid alpha (white acicular shaped grains) are present in the matrix. The matrix is the $\alpha - \beta_2 (\text{Al}_4\text{Cu}_9)$ eutectoid, with a lamellar structure similar to pearlite in steels. Fine lamellar structures respond nicely to polarized light, regardless of the etchant. Figure 15 shows the same specimen heated into the beta field, but to only 900°C, held one hour, and water-quenched to form a metastable martensite. This specimen is unetched, because martensite responds nicely to polarized light without etching. Actually, this is the best way to examine martensite in a aluminum bronze, because etching produces a poorer image of the martensite, irrespective of the etchant.

As a final example of the color metallography of copper alloys, Fig. 16 and 17 show the microstructure of beryllium bronze, Cu-1.8Be0.3Co. Figure 16 shows the as-cast microstructure with alpha grains, an interdendritic mix of $\alpha$ and $\beta$ that is formed from the decomposition of the $\beta$ phase on cooling, and light-colored beryllides. A higher magnification view would reveal a light blue color. The striations in the alpha grains are caused by metastable precipitation of very fine phases, and these are not resolvable with the light microscope. Beryllium bronze can be hardened by heat treatment involving a solution treatment and an aging treatment. Figure 17 shows the microstructure of beryllium bronze heated to 790°C, held for one hour, oil quenched, aged at 315°C for two hours, and air-cooled to ambient. This microstructure responds beautifully to crossed-polarized light with almost any etchant. The striations are again caused by precipitation of sub-microscopic phases.

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**Bibliography**

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