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

COPPER COLOR METAL

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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 arr oxygen-free electronic or exygen-free, high-

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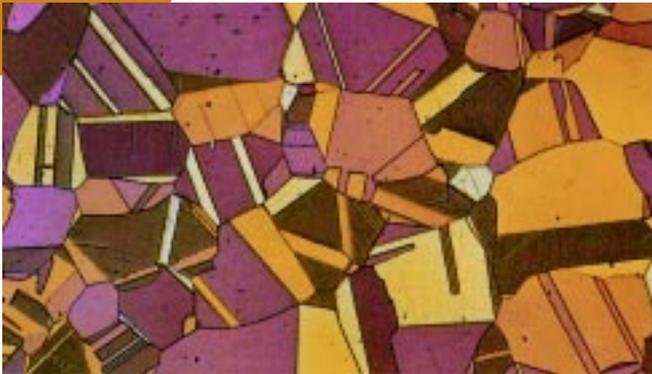
Fig.1 - This annealed cartridge brass, Cu-30Zn, was prepared using the traditional method, and the process included multiple etch-polish cycles (Klemm's I reagent, 100X).

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).
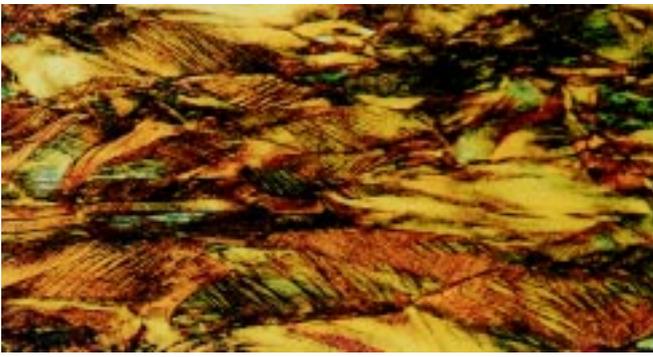
Fig. 5 - Cold worked cartridge brass, Cu-30Zn, prepared by the contemporary method, showing heavy slip deformation (Klemm's I reagent, 100X, nearly crossed-polarized light with sensitive tint.)
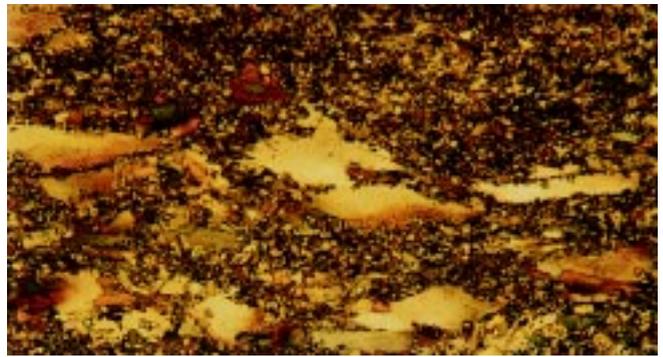

Fig. 6 - Partially recrystallized cold-worked cartridge brass, prepared by the contemporary approach (Klemm's III reagent, 100X, nearly crossed polarized light).

LOGRAPHY

all scratches can be quite challengin, 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 Cu_2O 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, but successful application depends mainly on the ability to remove fine polishing scratches and any minor damage remaining from sectioning or grinding. The as-polished surface could look perfect before etching, but tint etching would reveal a maze of scratches, always a frus0 trating discovery. In addition, color etchants fully reveal the grain structure, as well as any segregation or residual deformation.

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 presistent 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

Table 1 - Taditional preparation procedure, manual or automated

Step	Surface/Abrasive	rpm	Direction	Load, lb (N)	Time, minutes
1	120-grit SiC*	240-300	Comp.	5-6 (22-27)	U.P
2	240-grit SiC*	240-300	Comp.	5-6 (22-27)	1
3	320-grit SiC*	240-300	Comp.	5-6 (22-27)	1
4	400-grit SiC*	240-300	Comp.	5-6 (22-27)	1
5	600-grit SiC*	240-300	Comp.	5-6 (22-27)	1
6	6-mm diamond paste on canvas** cloth	120-150	Comp.	5-6 (22-27)	2
7	1-mm diamond paste on billiard** cloth	120-150	Comp.	5-6 (22-27)	2
8	Coloidal silica on Microcloth® Pad***	120-150	Comp.	5-6 (22-27)	2

Notes:Load is per specimen; Comp = complementary (head and platen rotate in same direction); U.P = until all surface are at the same plane and cutting damage is removed.
* Water is used as the coolant
** Metadi Fluid is used as the lubricant extender.
*** Step 8 replaced the previously used two steps with 0.3- and 0.05mm alpha- and gamma-alumina, respectively, slurries on Microcloth pads.

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 addition to colloidal silica. Not bad, but certainly not perfect.

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

Step	Surface/Abrasive	rpm	Direction	Load, lb (N)	Time, minutes
1	240-grit SiC*	240-300	Comp.	5-6 (22-27)	U.P.
2	p-μm diamond paste on Ultra-Pol Cloth**	120-150	Comp.	5-6 (22-27)	5
3	3-μm diamond paste on Trident Cloth**	120-150	Comp.	5-6 (22-27)	3
4	1-μm diamond paste on Trident Cloth**	120-150	Comp.	5-6 (22-27)	2
5	Colloidal silica on Microcloth or Chemomet cloth	120-150	Contra	5-6 (22-27)	1.5-2

Notes:Load is per specimen; Comp. = complementary (head and platen rotate in same direction);
Contra = head and platen rotate in opposite directions;
U.P. = until all surfaces are at the same plane and cutting damage is removed.
* Water is used as the coolant
** Metadi Fluid is used as the lubricant/extender, after polishing commences, diamond of the same size range

Table 3 - Compositions of tint etchants

Composition	Comments
50 mL saturated aqueous sodium thiosulfate, 1 g potassium metabisulfite	Klemm's I reagent. Immerse until surface is colored
50 mL saturated aqueous sodium thiosulfate, 1 g potassium metabisulfite	Klemm's II reagent. Immerse until surface is colored. Good for alpha brass.
5 mL saturated aqueous sodium thiosulfate, 45 mL water 20 g potassium metabisulfite	Klemm's III reagent Immerse until surface is colored. Good for bronzes
1000 mL water, 240 g sodium thiosulfate, 30 g citric acid, 24 g lead acetate	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.

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 series of micrographs illustrates the microstructure of cartridge brass, Cu-30Zn, a very difficult metal to prepare scratch-free when in the annealed condition. Figure 5 shows a specimen that was cold-reduced in thickness by 30%. The twins and alpha grains are distorted by cold rolling, and slip lines are evident everywhere. Figure 6 shows the microstructure of a partly recrystallized, cold-worked alpha grain structure after annealing at 371°C for 30 minutes. The large elongated grains are the non-recrystallized grains, while the background is a mass of very fine, newly recrystallized grains. Figure 7 shows a fully recrystallized grain structure with grain growth after annealing at 704°C for 30 minutes. This is the same specimen as shown in Fig. 1 and 2, but examination of tint-etched specimens in polarized light can add further information to the examination.

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 Cu_3Sn. Some voids (shrinkage cavities) are also present and appear

Fig. 7 - Annealed cartridge brass (same specimen as Fig. 1), prepared with the contemporary approach (Beraha PbS reagent, 50X, crossed-polarized light plus sensitive tint.)
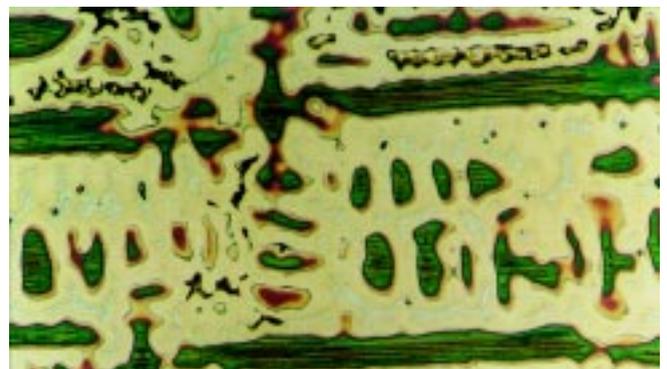

Fig. 8 - This photomicrograph shows the dendritic as-cast microstructure of chill cast tin bronze, Cu-10Sn, prepared with the contemporary method (Klemm's I reagent, 500X, bright field).

black; these are often associated with this inter-metallic phase.

Figure 9 shows the microstructure of sane 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 Cu_3P, 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 com-position of the outer rim of the proeutectic alpha dendrites is essentially the same as the alpha in the eutectic. The proeuctectic 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). *Continued*
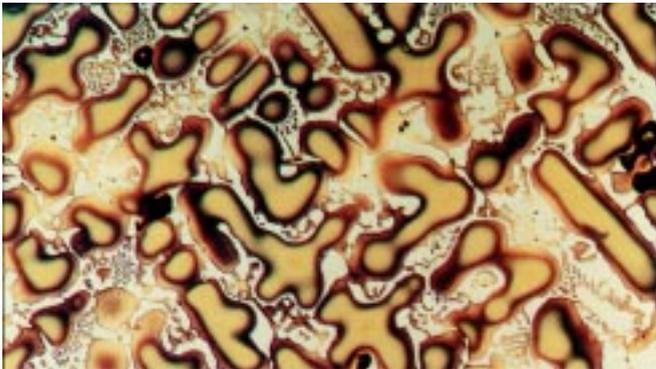

Fig. 9 - *This dendritic microstructure of sand-cast hypoeutectic Cu-4.5P was revealed when prepared by the contemporary method (Klemm's II reagent, 200X, bright field).*
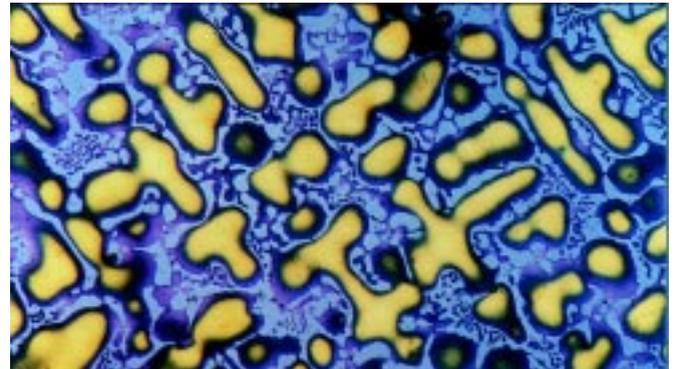

Fig. 10 - *Same specimen as shown in Fig. 9, but in cross-polarized light plus a sensitive tint plate.*
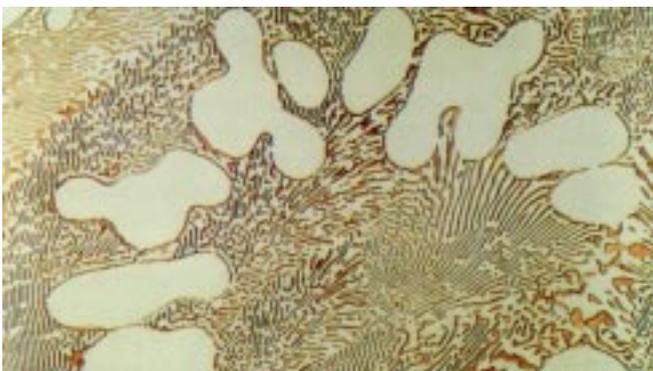

Fig. 11 - *Dendritic microstructure of sand-cast hypereutectic Cu-10.5P is clearly shown when prepared by contemporary method (Klemm's II reagent, 500X, bright field).*
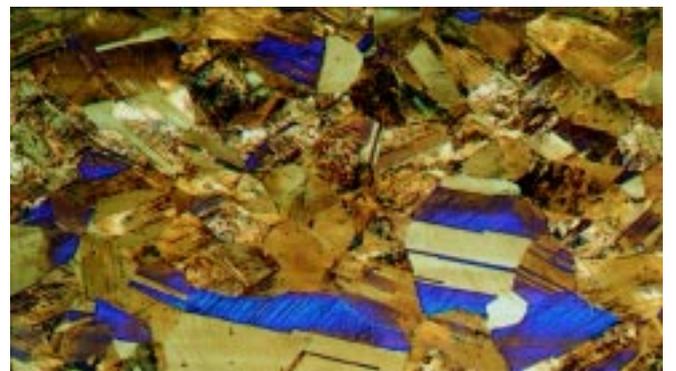

Fig. 12 - *Microstructure of Everdur, Cu-3Si-1Mn, cold drawn to half hardness, prepared by the contemporary method (Klemm's reagent, 100X, cross-polarized light plus sensitive tint).*
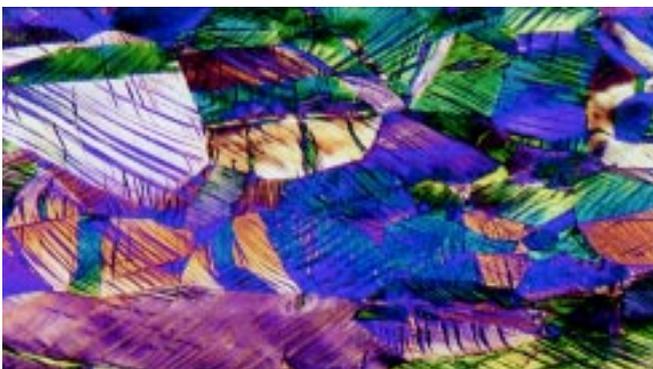

Fig. 13 - *Microstructure of cold worked phosphor bronze, Cu-5 Sn-0.15P, prepared using the contemporary method (Klemm's II reagent, 200X, crossed-polarized light plus slight sensitive tint.)*
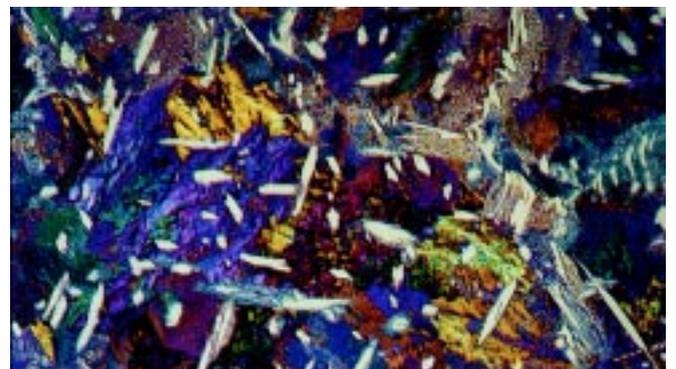

Fig. 14 - *Microstructure of annealed aluminum bronze, slightly hypoeutectiod, prepared by the contemporary method (equal parts NH_4OH and H_2O_2, 50X, crossed-polarized light.)*

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 conpared 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 filed, 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 α - β_2 (Al_4Cu_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, be-

cuase etching produces a poorer image of the martensite, irrespective of the etchant.

As a f inal 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 α and β that is formed from the decomposition of the β 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 ait-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 phasses. ∎

Fine lamellar structures respond nicely to polarized light.

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Fig. 15 - Martensitic microstructure of quenched aluminum bronze is revealed when prepared by the contemporary method (200X, crossed-polarized illumination plus light sensitive tint).

Fig. 16 - Microstructure of as-cast beryllium bronze prepared by the contemporary method (Klemm's I, 100X, bright field).
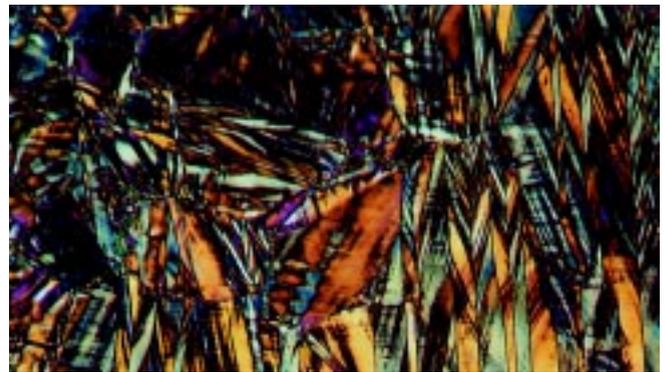

Fig. 17 - Microstructure of solution annealed and aged beryllium bronze prepared with the contemporary method (equal parts NH_4OH and H_2O_2, 200X, crossed-polarized light plus a sensitive tint plate).