Metallographic preparation of copper and copper alloys

Struers

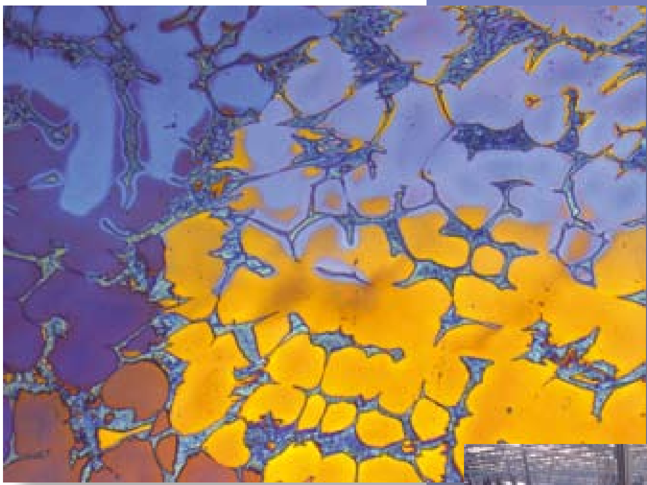
Application Notes

Copper, together with gold and tin were the first metals put to use by ancient man. The ease with which it could be shaped and formed, its attractive colour and its corrosion resistance were among some of the reasons why it found widespread use in the manufacture of early weaponry, jewellery, liturgical vessels and everyday domestic objects.

Metallic copper has been known since about 9.000 BC and was widely used by 5.000 BC. When its value as an alloy with tin was recognised, the birth of the Bronze Age initiated a profound cultural and economic development in Europe and the Mediterranean countries.

Historically, casting of bronze has a long tradition, but it is only since the 1920s that hot rolling and extrusion of copper and its alloys have been practiced. Nowadays, most of the copper produced is in wrought form, and with its high electrical conductivity copper is much used as cables, switchgear components, transformers, motor windings, and generators. Oxygen free copper is mainly used in the electro-nics industry.

The corrosion resistance and high thermal conductivity of copper make it suitable for tubes, vessels and heat exchangers in the chemical, and food and beverage industry. Apart from the traditional applications of copper for water and heating pipes, architects have in recent years discovered the appeal of designing facades with oxidised copper sheets.



Aluminium bronze, CuAl8, shows dendritic structure with α-δ eutectoid. Colour etching according to Klemm, pol. light, 100x.

The metallography of copper and its alloys is used for grain size measurement and purity checks by qualifying and quantifying the copper oxide content. On occasion, in certain brasses, the distribution of lead is determined as it can influence the machining process. In cast alloys the general microstructure and distribution of eutectic or lead is evaluated as well as the presence of shrinkage cavities or porosity.

Difficulties in the preparation of copper and its alloys

Pure copper is soft and ductile, easy to deform and prone to form scratches.

Bronzes, and even some of the harder brasses, may be susceptible to severe scratching.

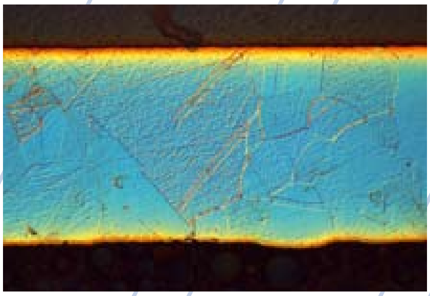


Fig.1: Pure copper wire, with final polish of OP-S, DIC, 200x.

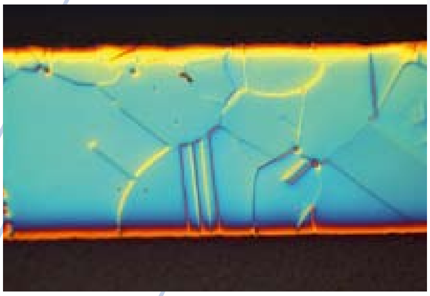


Fig. 2: Same sample as Fig.1 with final polish of OP-S-ammonia water-hydrogen peroxide-mixture, DIC, 200x.

Solution

- Avoiding coarse grinding abrasives
- Thorough diamond polishing with soft cloths
- Chemical-mechanical fine polishing

Production and application

Fig. 3: Electrolytic refining

Although metallic copper occurs naturally, it is mainly extracted from sulphide ores in a metallurgical smelting process. A small amount of copper is also produced by hydro-metallurgical process. A brief description of the four steps in the copper production process is provided below.

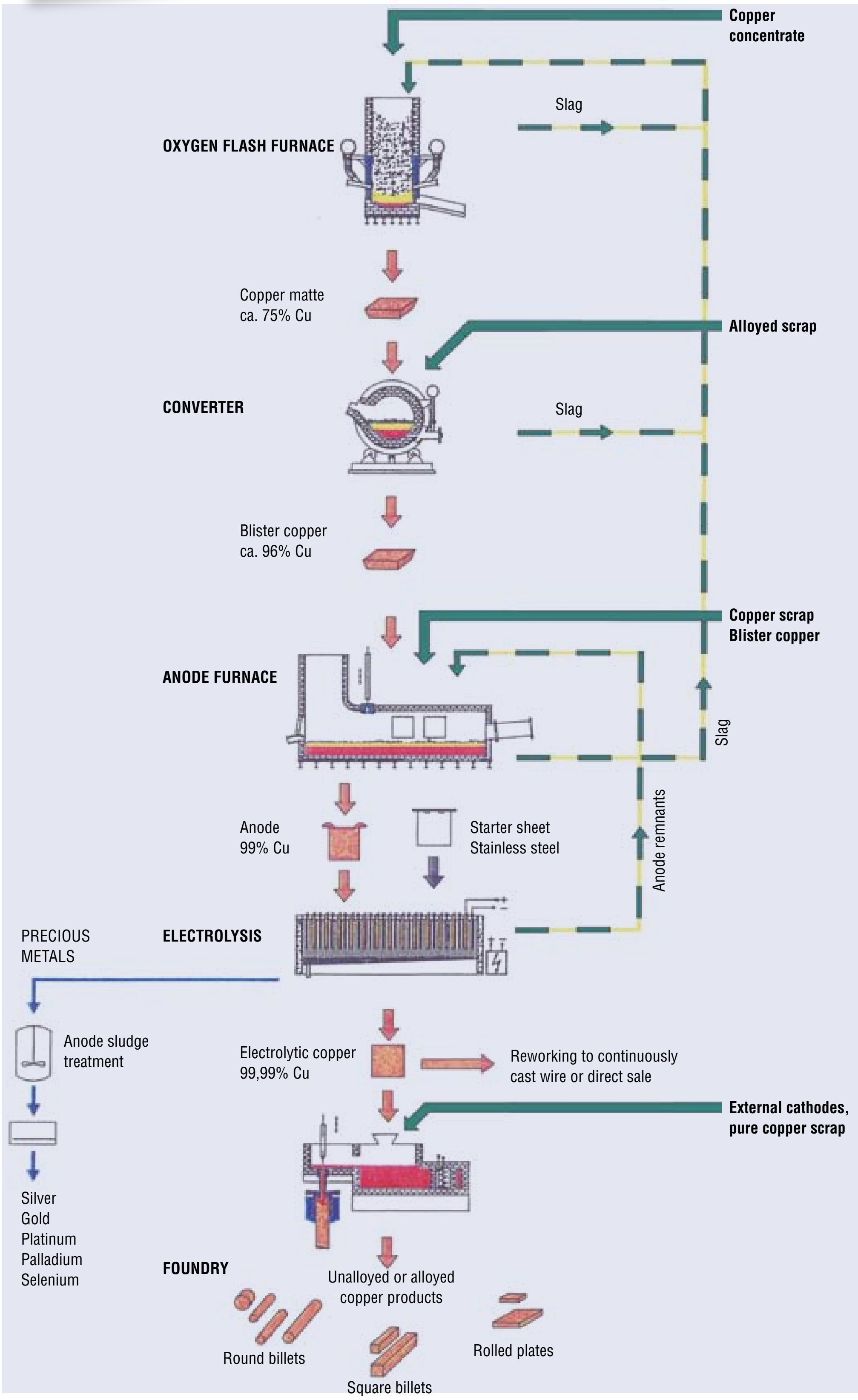
1. Copper matte, 75% Cu:
In this first smelting process for extraction, copper concentrates, mainly chalcopyrite ($CuFeS_2$), are roasted and melted with fluxes in an oxygen flash furnace to matte copper. Matte is a mixture of copper sulphide and iron sulphide and contains approx. 75% copper.

2. Blister copper, 96-98% Cu:
In a converter air is blown into the liquid matte to oxidise the sulphides. The resulting blister copper contains approx. 96-98% copper.

3. Anode copper, 99% Cu:
Blister copper is refined in the anode furnace. It is melted with copper scrap and rests of anodes from the electrolytic refining. Air blowing the melt, produces an oxidizing atmosphere which reduces the impurities that are then discharged as slag. The high oxygen content of the melt needs to be lowered to less than 0.1% as copper oxides make the copper brittle. The oxygen content is lowered by blowing natural gas into the melt, which reduces the copper oxide to copper, releasing steam and carbon dioxide. The resulting copper is 99% pure and cast into anodes that are subsequently used for electrolytic refining.

4. Electrolytic refining, copper cathodes, 99.99% Cu:
The copper anodes are still contaminated with metals such as Ni, Pb, Ag, Pd and Au. During the electrolytic refining process, high purity copper is produced whereby the impurities drop to the bottom of the electrolyses cell and are recovered. A solution of sulphuric acid and copper (II) sulphate, functions as electrolyte. Using direct current, the oxidation occurs at the anode, which is dissolved, and the pure copper is deposited at the cathode "starter sheet" of

Copper
from raw material to electrolytic copper



Simplified schematic diagram of copper production

Fig.4:
Control valve for the distribution of potable water.

Fig. 5: Copper with red copper oxides, dark field, 500x.

Fig. 6: Oxygen free copper, etched with ammonium peroxydisulfat, 100x.

Danish Embassy, Berlin, cladded with oxidised copper plates.

Courtesy: Danish Foreign Ministry

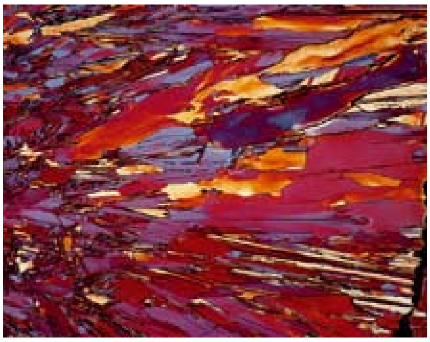


Fig. 7: Copper cathode, etched according to Klemm, 100x.

pure copper or stainless steel, from which it is mechanically removed.

The cathode plates of this very pure copper are melted with 50% pure copper scrap and cast into plates, round and square billets which are then converted to sheets, pipes, wire and casts. (Almost half the demand of copper today is covered by copper scrap and recycled copper.)

With increasing purity, the electrical and thermal conductivity, as well as the price of copper increase. Therefore the use of pure copper depends on the application of the product. Due to its excellent properties, oxygen free copper for electronics (OFE) is used as a basic material for semi conductors, switches and sealing rings in vacuum technology and electron tubes.

The largest amount of copper is used in construction for facades, roofs, potable water pipes and heating installations, as well as the electrical parts industry for motor coils, generators and power supply systems. Additional fields of applications are cryogenics and air conditioning technology, chemical industry and beverage and brewing technology.

Copper alloys

There are a large range of copper alloys; however, zinc (brass) and tin (bronze) are the most important alloying elements for copper. Some of the most important alloys and their applications will be briefly described in the following section.

Brasses are copper alloys with 5 - 45% zinc. Copper has a high solubility for zinc and the alloys are very homogenous. Brass with less than 28% zinc is called red brass and is especially suitable for machining. With increasing zinc content the reddish copper colour changes to the yellow of brass. Alloys up to 37% zinc consist of α - solid solution and are suitable for cold forming. With increasing zinc content the brass becomes harder and therefore easier to machine. From 38% zinc, the alloys display a two-phase α - β microstructure which is suitable for hot forming. By adding aluminium, manganese, iron, nickel and tin, special types of brass, which have specific chemical or mechanical properties, can be produced. Additions of small amounts of lead improve the machinability of brass.

Depending on the zinc content, different brasses are used in various fields of application: from watches and jewellery to electro-technology (CuZn5), to springs, screws, pins, die forged parts (CuZn30), to armatures (CuZn40) and bearings for sea water resistant pump housings (CuZn10Sn2).

Fig. 8: Anti-friction and roller bearing brass cages

Fig. 9: Wrought bronze tubes and profiles

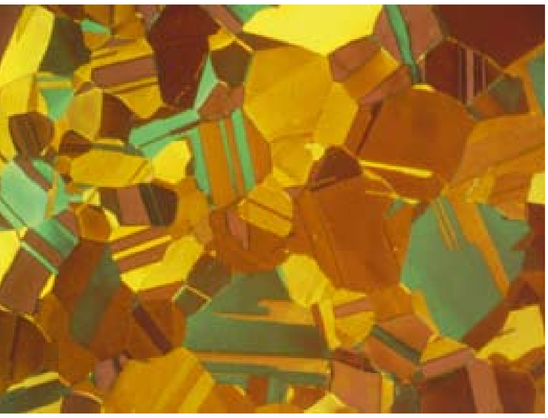


Fig.10: α-brass, colour etched, 200x.

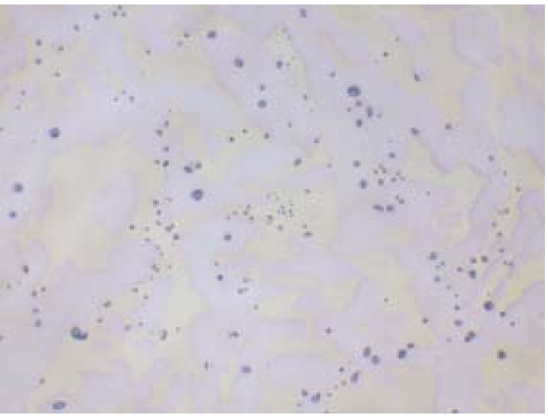


Fig. 11: α-β-brass cast (CuZn40Pb2) with grey-blue lead inclusions, unetched, 500x.

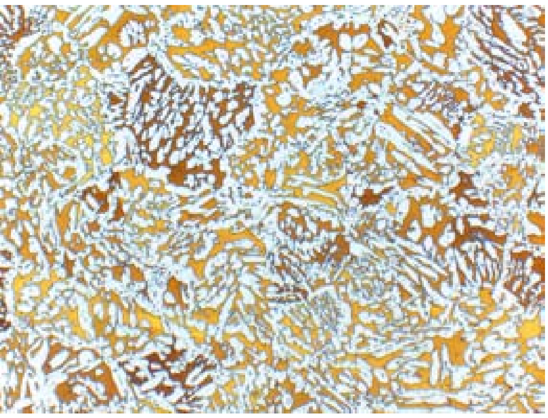


Fig.12: α-β-brass cast, etched according to Klemm, light α-solid solution in dark matrix of β-solid solution, 100x.

Bronzes are copper-tin alloys that are divided into wrought alloys, with up to 8.5% tin, and cast alloys, with usually 9-12% tin, and also so-called bell casts with up to 20% tin.

Depending on the required properties, small amounts of zinc and phosphorus can be added to the wrought alloys, e.g. for bearings. These alloys are called phosphor bronzes. Lead, nickel and iron are common additions to cast alloys.

Cu-Sn-Zn-alloys are called gun metal. They are often used for the manufacture of slide bearings, worm gears, bearing bushes; parts which need a bearing surface capable of withstanding high contact loads. As well as good corrosion resistance, Gun metal has a low friction coefficient which means it can operate under such conditions without seizure.

Aluminium bronzes are copper alloys with up to 11% aluminium, displaying high strength at elevated temperatures and very good corrosion resistance. They are suited for marine propellers, highly stressed rotors for pumps and water turbines, and bearings and parts for the chemical industry. Copper-aluminium wrought alloys are used in mechanical and light engineering.

Beryllium bronze has high strength and hardness, with the specific property of not producing sparks when striking or impinging other metals. Therefore this type of bronze is suited for tools in an explosive environment such as refineries.

Due to their excellent corrosion resistance, copper-nickel alloys are used in desalination plants, for coins, heating wires in toasters and hair driers. The copper-nickel-zinc alloys, called German silver, display high strength, are corrosion resistant and are easily formed. Fields of application are surgical instruments, food industry, base metal for silver cutlery, contacts in connectors and jewellery.

Fig.13: Cast bronze pump housing

Fig.14: Wrought bronze liners with graphite

Difficulties in the preparation of copper and copper alloys

With increasing purity, copper becomes softer and more susceptible to mechanical deformation and scratches. Consequently, grinding can cause deep deformation in high purity copper while grinding and polishing abrasives can be pressed into the surface. Copper alloys are harder, but still have a tendency to form scratches, which in some bronzes may only occur only in some individual grains.

Recommendations for the preparation of copper and copper alloys

For **sectioning** of copper a hard silicon carbide cut-off wheel is used that is generally suitable for non-ferrous metals.
For **mounting,** a phenolic resin is in most cases sufficient.

CitoPress Hot mounting press

Mechanical Preparation

Pure copper and copper alloys with low alloying contents.

Grinding

Step	PG	FG 1	FG 2	FG 3
Surface	SiC- Paper	SiC-Paper	SiC-Paper	SiC-Paper
Grit	320	800	1200	4000
Lubricant	Water	Water	Water	Water
rpm	300	300	300	300
Force (N)	150	150	150	150
Time	As needed	1 Min.	1 min.	1 min.

Polishing

Step	DP	OP
Surface	MD-Mol	OP-Chem
Suspen-sion	DiaPro Mol	Iron (III) nitrate*
rpm	150	150
Force (N)	150	90
Time	4 min.	1 min.

**Wet the polishing cloth with water and polish with a few drops of the etchant without any polishing medium.*
Formula: see table on page 6.

Copper alloys

Grinding

Step	PG	FG
Surface	SiC-Paper	MD-Largo
Körnung*/ Suspension	220 or 320	DiaPro Allegro/Largo
Lubricant	Water	
rpm	300	150
Force (N)	180	180
Time	As needed	4 min.

Polishing

Step	DP	OP
Surface	MD-Mol*	OP-Chem
Suspension	DiaPro Mol	OP-S**
rpm	150	150
Force (N)	150	90
Time	3 min.	1-2 min.

**Alternative: MD-Dac*

***96 ml OP-S, 2 ml ammonia water (25%), 2 ml hydrogen peroxide (3%)*

Mechanical grinding and polishing

It is recommended that plane grinding is carried out with the finest possible grit in order to avoid any excessive mechanical deformation. Hardness, size and number of samples have to be taken into account, but even with larger samples of pure copper, plane grinding with 500# SiC-paper is sufficient. Large cast parts of copper alloys can be ground with 220# or 320#. It is also important that the force for grinding is low to avoid deep deformation.

As indicated in the table with the preparation data, for the soft alloys fine grinding with SiC-paper with fine grits is recommended, whereas MD-Largo with diamond can be used for the harder alloys. Better planeness and edge retention is obtained using MD-Largo.

Diamond polishing has to be carried out until all deformation and embedded abrasives from grinding have been removed. The chemical-mechanical fine polishing with silicon dioxide is especially important as an almost scratch free surface can be achieved. For pure copper, the final polish with a solution containing iron nitrate has proven to give very good results, and for copper alloys, a mixture of OP-S suspension with hydrogen peroxide and ammonia water is recommended (Formula below the table). After 1 minute polishing the result is checked under the microscope. If necessary the polish should be continued for another minute and the result checked again. It is recommended to continue this polish/check sequence until the required quality of the result has been achieved. If the attack is too fast or too strong the mixture should be diluted with water.
(Approx. 30 sec before the end of polishing, water is poured onto the polishing cloth to rinse the sample as well as the cloth. Then the sample is washed again with clean water from the tap and then dried.)

The preparation data are for the automatic grinding and polishing of 6 mounted samples, 30 mm diameter, clamped into a holder.

Electrolytic Polishing is suited for pure copper and α - brass wrought alloys. Two-phase α - β - brass can also be polished electrolytically, but the results are not very well suited for quantitative analysis, especially if the alloy contains lead.
Prerequisite for a good electrolytic polish is a preceding fine grinding with SiC-paper up to 2400# or 4000#. Due to the different phases in cast alloys, they are not suited for electrolytic polishing.

Electrolyte:	**D2**
Area:	**0.5 cm²**
Voltage:	**24 V**
Flow rate:	**10**
Time	**20 sec**

Directly after polishing the sample can be etched with the same electrolyte for 4 seconds with 2-4 volts.

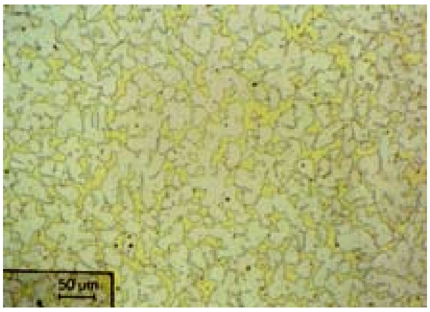


Fig.15: α-β-brass cast, mechanically polished, unetched, 200x.

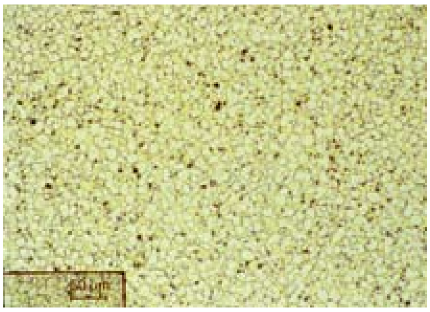


Fig.16: Same specimen as Fig.15 electrolytically polished, unetched, 200x.
The lead inclusions are pulled out and therefore appear larger and more numerous than in Fig.15.

Etching

There are numerous etchants for copper and its alloys that are relatively easy to apply. Most of the cast alloys are not difficult to etch. It can be more difficult to find the right etching solution for some of the wrought alloys, especially when they are severely cold worked. In these cases a colour etch can be helpful.
It needs to be pointed out that lead is attacked by the etchants and mostly only black voids remain. Micrographs that are to document the quantity and distribution of lead always have to be taken before etching. The colour of pure lead is grey-blue.

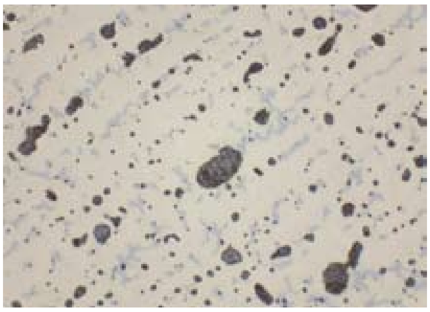


Fig.17: Bronze cast, CuSn8Pb, unetched, large and small blue-grey lead inclusions, pale blue α-δ eutectoid discernable, 500x.

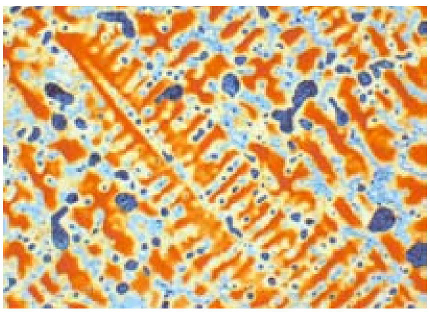
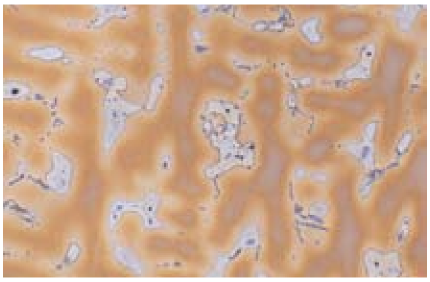


Fig.18: Same specimen as in Fig.17, colour etched according to Klemm, dendritic structure with light blue eutectoid and blue lead inclusions. Small lead inclusions can not be clearly differentiated, 500x.



Bronze cast, CuSn10, etched with iron (III) chloride, dendritic structure α-δ eutectoid, 200x.

Application	Etchant
Grain area etch for copper, brass and bronzes	100 ml water 10 g ammonium peroxydisulfate Use fresh!
All types of copper	100-120 ml water or ethanol 20-50 ml hydrochloric acid 5-10 g iron (III) chloride (concentration variable)
    Grain boundaries Grain areas	25 ml distilled water 25 ml ammonia water 5-25 ml hydrogen peroxide, 3% Less hydrogen peroxide More hydrogen peroxide
α-β brass Fast and good polish for pure copper Colour etch according to Klemm	120 ml Water 10 g copper (II) ammonium chloride Add ammonia water until precipitate dissolves 100 ml water 100 ml ethanol 19 g iron (III) nitrate 100 ml cold saturated sodium thiosulfate 40 g potassium metabisulfit

Summary

Due to its good formability, high electric and thermal conductivity and corrosion resistance, pure copper is mainly used in electric engineering, the electronics industry and in the food and beverage industry. The application of brass and bronze wrought and cast alloys ranges from small parts to sea water resistant pump housings. The metallography of copper and its alloys is used in quality control mainly for checking purity and grain size determination. In addition, cast alloys are examined for general structure evaluation. Copper is soft and ductile and particularly prone to mechanical deformation. Therefore care needs to be taken that for the first grinding step the finest possible grit is used. Diamond polishing is carried out on medium soft to soft cloths and can take relatively long for pure copper. Chemical-mechanical final polishing with OP-S suspension is essential and results in a scratch free surface. Lead free wrought alloys can also be electrolytically polished. Etching with the common etchants is fairly easy, whereby colour etching can reveal some attractive structures in cast bronzes.

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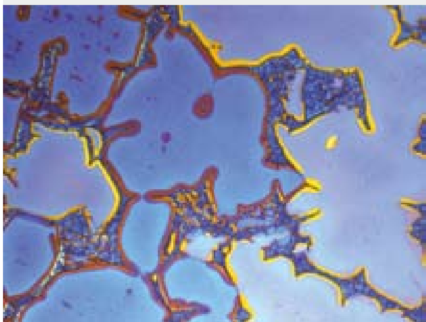

Aluminium bronze, colour etched according to Klemm, pol. light, 200x.

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