Characterizing Metallic Microstructure

Cu-Based Alloys and Precious Metals

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Equilibrium Phase Diagrams
Ag – Cu Equilibrium Phase Diagram

Ag – 20% Cu, diagram and microstructure (CrO$_3$ – H$_2$SO$_4$ – Water)
Ag – Cu Equilibrium Phase Diagram

Ag – 28 Cu, diagram and microstructure, Klemm’s I.
Ag – Cu Equilibrium Phase Diagram

Ag – 40% Cu, diagram and microstructure (CrO$_3$ – H$_2$SO$_4$ – Water)
Ag – Cu Equilibrium Phase Diagram

Ag – 45% Cu, diagram and microstructure (CrO$_3$ – H$_2$SO$_4$ – Water)
Ag – Cu Equilibrium Phase Diagram

Ag – 65% Cu, diagram and microstructure, Klemm’s I.
The copper-phosphorus binary phase diagram. The following slides show the microstructure of hypoeutectic, eutectic and hypereutectic compositions at 4.5, 8.4 and 10.5% P, respectively.
As-cast hypoeutectic Cu – 4.5% P tint etched with Klemm’s II reagent which colors the copper-rich proeutectic dendrites and the α-copper portion of the eutectic. Polarized light plus sensitive tint has changed the appearance, compared to bright field. The copper dendrites are yellow and the last region to solidify, just above the eutectic temperature, has the same color, blue, as the copper in the eutectic. The copper phosphide, Cu$_3$P in the eutectic is colored by the sensitive tint filter. Original at 200X.
As-cast hypoeutectic Cu – 4.5% P tint etched with potassium dichromate reagent which colors the copper-rich proeutectic dendrites and the alpha-copper portion of the eutectic. Note that the color variations indicate compositional differences in the growing dendrites. Between the Cu dendrites is the eutectic of copper (colored) and copper phosphide, Cu₃P (white). Original at 200X.
As-cast eutectic Cu – 8.4% P tint etched with potassium dichromate reagent which colored the alpha-copper portion of the eutectic of alpha copper and copper phosphide, Cu₃P (white). Original at 200X.
As-cast hypereutectic Cu – 10.5% P tint etched with Klemm’s II reagent which colors the $\alpha$-copper phase in the eutectic of Cu and copper phosphide. The large white particles are proeutectic copper phosphide, $\text{Cu}_3\text{P}$ and the white, unetched part of the eutectic is copper phosphide. Original at 500X.
As-cast hypereutectic Cu – 10.5% P tint etched with Beraha’s PbS reagent which colors the alpha-copper phase in the eutectic of Cu and copper phosphide. The large white particles are proeutectic copper phosphide, Cu₃P and the white, unetched part of the eutectic is copper phosphide. This etch reveals mechanical twins in the copper phosphide. Original at 500X.
Casting
Dendrites in as-cast Monel (Ni – 30% Cu) revealed using Beraha’s reagent (50 mL water – 50 mL HCl – 2 g ammonium bifluoride – 1 g potassium metabisulfite). Originals at 50X (left) and 100X (right). Magnification bars are 200 and 100 µm long, respectively.
Dendritic microstructure of phosphorous-deoxidized copper (Cu – 0.02% P) in the as-cast condition revealed by Klemm’s I reagent (original at 50X in bright field illumination).
Microstructure of sand-cast Cu – 4% Sn etched with Beraha’s PbS tint etch revealing the dendritic cast structure. 63 HV.
Microstructure of sand cast Cu – 37% Zn revealing some beta phase between the alpha dendrites using Nomarski DIC and an as-polished specimen.
As-cast microstructure of chill-cast Cu – 5% Sn revealing a finer dendritic cast structure. Klemm’s II etches faster than Klemm’s I and yields a wider color range.
Cast High-Lead Tin Bronze

Lead morphology and size in high-lead tin bronze, as-polished condition.
Dendritic as-cast microstructure of high-Pb tin bronze alloys revealed using Beraha’s PbS tint etchants.
Cast Sterling Silver, ≥ 92.5% Ag

Microstructure of as-cast sterling silver (≥ 92% Ag) revealed by etching with equal parts of water, ammonium hydroxide and hydrogen peroxide (3% conc).
Hot Working

Hot working occurs at a temperature that is relatively close to the melting point of the metal or alloy. This temperature is normally well above the normal recrystallization temperature. A homogenization cycle may be used prior to hot working to permit alloy diffusion and enhance chemical homogeneity. Too high a temperature must be avoided so that “burning” or grain-boundary liquation (incipient melting) does not occur. The temperature during the last hot working pass is also important as it controls the grain size in the as-rolled microstructure and may influence problems such as “banding” in steels. If the finishing temperature is low, recrystallization will not occur and the grain structure will be coarse and elongated and will contain residual deformation (dislocations). “Warm” working occurs below the recrystallization temperature.
P-Deoxidized Copper

Microstructure of as-cast and hot extruded and cold drawn (interior) phosphorous-deoxidized copper tint etched and viewed with polarized light plus sensitive tint.
Microstructure of as-cast and wrought, annealed tough – pitch copper, Cu – 0.04% O (FCC grains with annealing twins and stringers of cuprous oxide) viewed with polarized light.
Cuprous oxides in extruded tough pitch copper (Cu – 0.04% O) revealed in dark field illumination by their ruby-red color (as polished).
Wrought Silver

Microstructure of wrought fine silver (left) and wrought sterling silver (right) revealed by etching with equal parts of 10% NaCN and 10% ammonium persulfate (left) and with equal parts of water, ammonium hydroxide and hydrogen peroxide, 3% conc., (right).
Cold working occurs at temperatures below the recrystallization temperature. Typically, it is performed at room temperature. For low-melting point metals and alloys, deformation at room temperature can be above the recrystallization temperature. There are a variety of cold working methods, such as rolling, swaging, extrusion and drawing. Cold worked structures normally exhibit deformed grain structures with considerable slip (bcc and fcc metals) or mechanical twinning (hcp metals).
Cu–30% Zn, Hot Extruded, Annealed and Cold Rolled

Cold Reduced 15%; \(126.0 \pm 11.3\) HV

Cold Reduced 30%; \(159.8 \pm 10.4\) HV

Microstructure of wrought cartridge brass after cold reduction, Klemm’s III, 3 min., polarized light and sensitive tint. Note: the hardness of the starting annealed specimen was \(57.9 \pm 4.8\) HV.
Cu–30% Zn, Hot Extruded, Annealed and Cold Rolled

Cold Reduced 40%; 185.5 ± 6.2 HV
Cold Reduced 50%; 194.0 ± 2.1 HV

Microstructure of wrought cartridge brass after cold reduction, Klemm’s III, 3 min., polarized light and sensitive tint.
Cu–30% Zn, Hot Extruded, Annealed and Cold Rolled

Cold Reduced 60%; 199.6 ± 5.2 HV
Cold Reduced 70%; 231.9 ± 7.9 HV

Microstructure of wrought cartridge brass after cold reduction, Klemm’s III, 3 min., polarized light and sensitive tint.
Native Copper

Microstructure of native copper (112 HV). Note the extensive slip lines. Color micrograph was taken with crossed polarized light plus sensitive tint.
Cold rolled 18-karat gold (75% Au – 22% Ag – 3% Ni) etched with equal parts of 10% NaCN and H₂O₂ (30% conc.).
Annealing
Cu–30% Zn, HE, CR 50%, Annl. 704 °C – 30 min.

Microstructure of wrought cartridge brass, Cu – 30% Zn, cold reduced 50% and annealed at 704 °C (1300 °F) – 30 min. producing a fully recrystallized, and grown, equiaxed FCC grain structure with annealing twins. Polarized light and sensitive tint.
Cu – 22% Zn – 2% Al, CD, Annealed 600 & 750 °C

Microstructure of wrought aluminum brass, Cu – 22% Zn – 2% Al, cold drawn and annealed producing equiaxed alpha grains containing annealing twins. Tint etched with Beraha’s PbS.
Microstructure of wrought aluminum brass, Cu – 22% Zn – 2% Al, annealed at 850°C (1562 °F) producing equiaxed alpha grains containing annealing twins. 57 HV; ASTM 00.
Microstructure of Muntz Metal, Cu – 40% Zn (α-β brass) heated to various temperatures in the α+β phase field and quenched showing an increase in beta phase (colored) and a decrease in preferred orientation. Tint etched with Klemm’s I reagent (bright field).
**Cu – 40% Zn, “Muntz Metal”**

Microstructure of Muntz Metal, Cu – 40% Zn, heated to 716 °C (1320 °F), held 1 h and water quenched (left) producing still more beta phase (colored), of larger size, and with less preferred orientation. Microstructure of specimen heated into the all beta field (right), 843 °C (1550 °F) and air cooled producing alpha and ordered beta.
Cast and Wrought Microstructures of Cu-Based Alloys and Precious Metals

Single-Phase Microstructures
Microstructure of wrought, fine silver (≈100% Ag) revealed by etching with equal parts of 10% NaCN and 10% ammonium persulfate.
Wrought 18-karat gold (75% Au – 22% Ag – 3% Ni) after attack polishing and etching with equal parts of 10% NaCN and H₂O₂ (30% conc.).
Martensite in Nonferrous Alloys

Substitutional-type martensite, rather than interstitial, and relatively low strength and hardness.
Wrought, eutectoid aluminum bronze, Cu – 11.8% Al, heat treated (Heat to 900 °C (1652 °F), hold 1 h, water quench) to form martensite. Specimen was not etched. Original at 200X. Viewed with cross polarized light.
Cu – 26% Zn – 5% Al

β1 martensite formed in fcc alpha phase in a Cu – 26% Zn – 5% Al shape memory alloy (both un-etched).
Microstructure of Spangold, Au – 19% Cu – 5% Al, a new jewelry alloy using martensite formation to create a rippled ("spangles") on the surface. The specimen was polished, heated to 100 °C for 2 minutes, and quenched in water to form martensite, which produces shear at the free surface. This roughness can be seen using Nomarski DIC without etching. The criss-crossed pattern is produced by forming martensite, polishing and then forming new martensite.
Two-Phase Microstructures
Microstructure of Muntz metal, Cu – 40% Zn, heated into the alpha + beta phase field at 716 °C, held 1 hour and water quenched, producing an alpha/beta grain structure. The specimen was etched with Klemm’s I to color the beta phase (left, in bright field). Imaging of this field with Nomarski DIC (right) reveals annealing twins in the non-colored alpha phase.
Annealed and cold drawn Naval Brass (Cu – 39.7% Zn – 0.8% Sn) viewed with polarized light on a transverse plane after etching with Beraha’s selenic acid reagent, which colors the alpha phase (note annealing twins) and the beta phase (color is non-uniform).
Microstructure of hot extruded and cold drawn Muntz metal, Cu – 40% Zn, tint etched with Beraha’s selenic acid reagent for copper which colored the twinned FCC alpha grain structure shades of yellow and red and non-uniformly colored the beta phase (note light blue border around the beta phase). Viewed in bright field.