Copper and its alloys

Subjects of interest

- Introduction/Objectives
- Extraction of copper from ores and refining of copper
- Classification of copper alloys
- The wrought copper
- Copper zinc alloys (brass)
- Copper tin alloys (bronze)
- Copper aluminium alloys
- Copper silicon alloys
- Copper beryllium alloys
- Copper nickel alloys

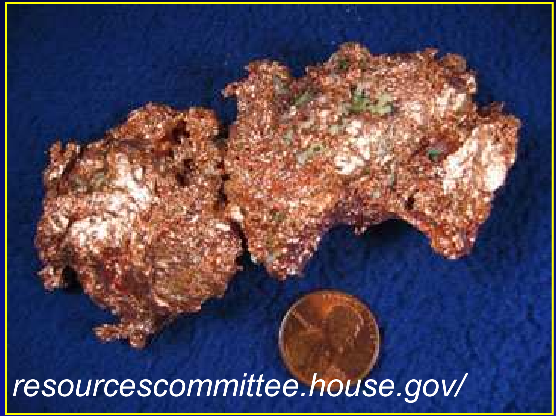
Objectives

• This chapter provides fundamental knowledge of different methods of productions / heat treatments of copper alloys and the use of various types of cast and wrought copper alloys.

• The influences of alloy composition, microstructure and heat treatment on chemical and mechanical properties of copper alloys will be discussed in relation to its applications.

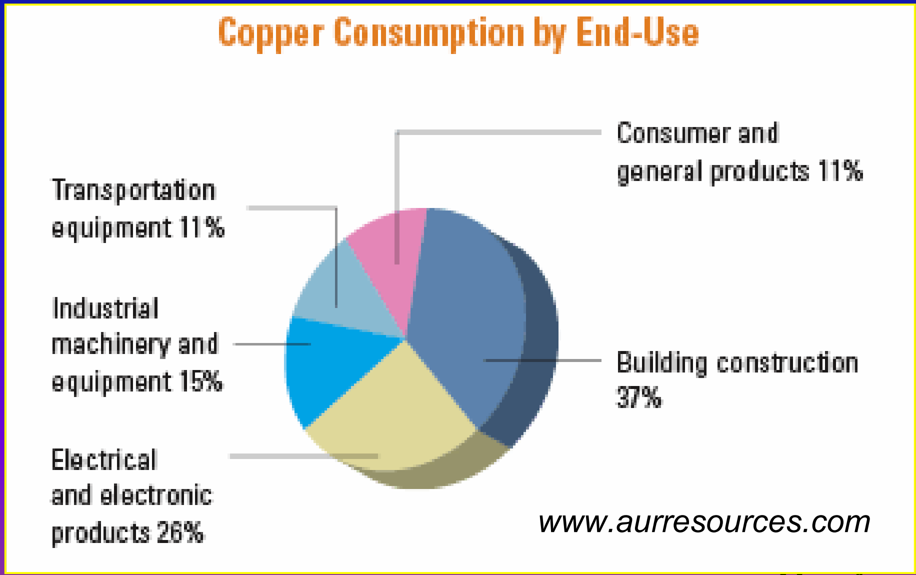
Introduction

- ***Copper*** is an element and a mineral called ***native copper***.
- Found in Chile, Indonesia and USA.
- Found in Loei and Khonkhan (but not much).
- Copper is an industrial metal and widely used in unalloyed and alloyed conditions. (second ranked from steel and aluminium).
- Used mostly in ***building constructions*** and as ***electronic products***.



Native copper

Copper mine in new mexico



Introduction – Applications of copper

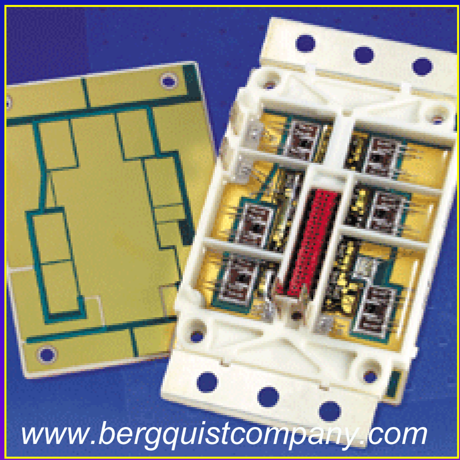
Properties:

- High electrical conductivity
- High thermal conductivity
- High corrosion resistance
- Good ductility and malleability
- Reasonable tensile strength

Applications:

Only second to silver for electrical conductance

Copper trolley wires



Electronic products

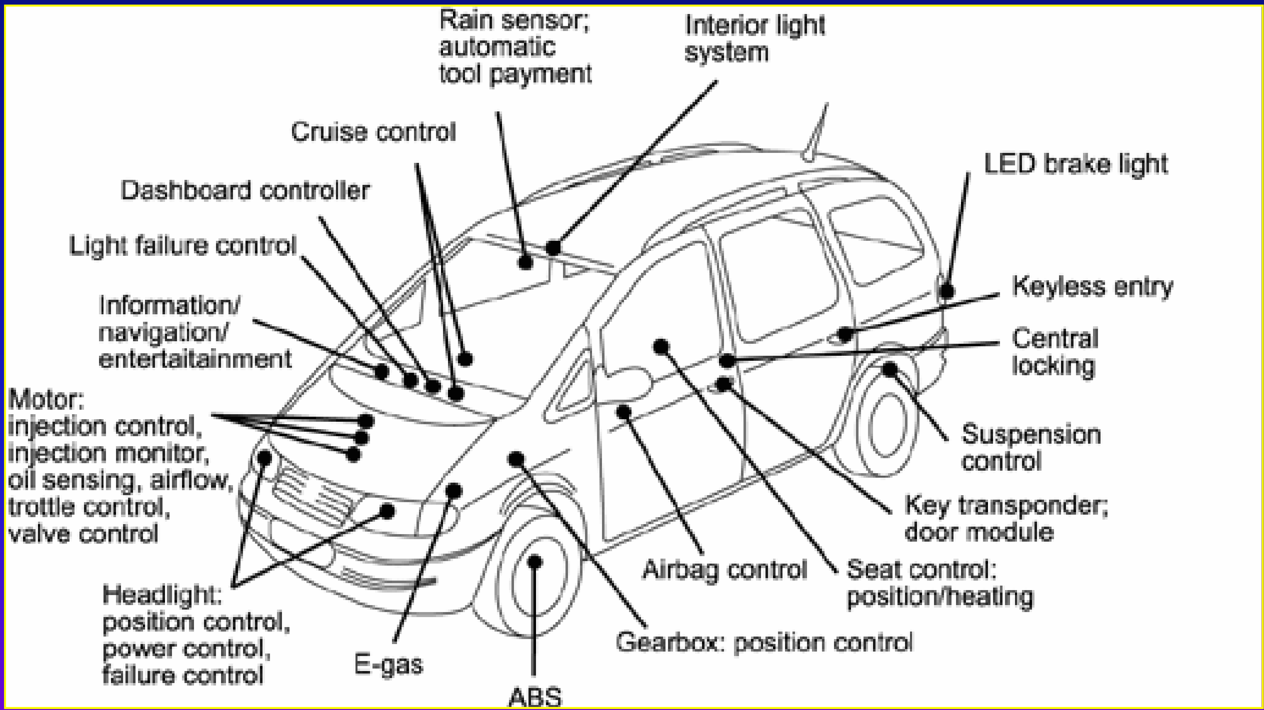
Copper finish parts

Copper plating

Application of copper in automotives

Copper: working behind the scenes in automotive applications.

• Increasing use of electronic parts in cars raise the amount of copper used per vehicle.



Copper prices

July 2006

Metals	US dollar/LB	Metals	US dollar/LB
Aluminum	1.1195	Nickel	12.1109
Alum Alloy	1.0183	Lead	.4717
NA Alloy	1.0115	Tin	3.7195
Copper	3.4332	Zinc	1.4451

Metalprice.com

Copper price is rising, which might affect companies producing electrical products

- **The price of copper has risen to nearly $7,000 a tonne on the back of strong demand and worries over supply.**
- **The rise in metal prices, including copper which is used in construction and electronics, has been prompted by growing demand from developing nations.**
- **Copper prices also rose following concerns that supplies could be disrupted by strike action in mines in Mexico and Chile.**

April 2006

news.bbc.co.uk

Extraction of copper from ores

- ***Copper ores*** are normally associated with ***sulphur*** in which ***copper*** can be extracted from ***chalcocite Cu_2S***, ***chalcopyrite $CuFeS_2$*** and ***cuprite Cu_2O***.

Chalcocite (Cu_2S, copper sulphide)

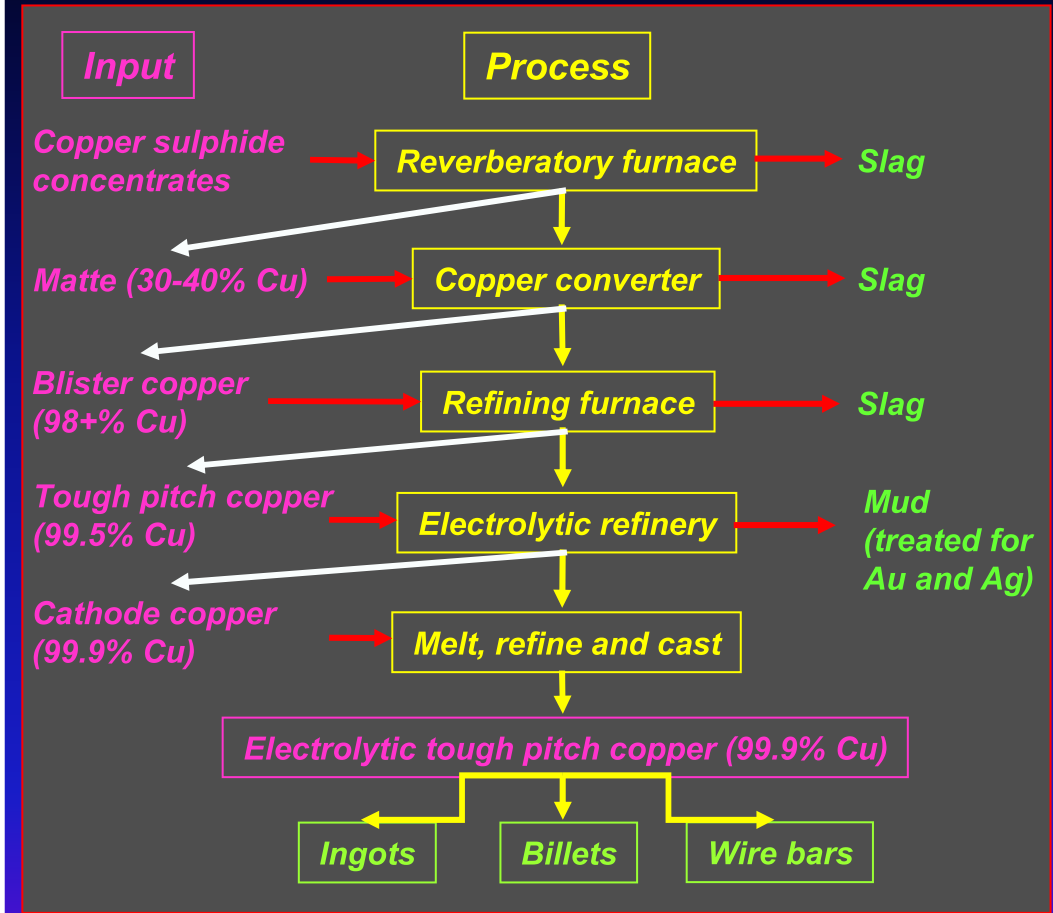
Chalcopyrite ($CuFeS_2$, copper iron sulphide)

Cuprite (Cu_2O, copper oxide)

Extraction processes:

- ***Pyrometallurgical*- for copper sulphide based ores.**
- ***Hydrometallurgical*- for oxide or carbonate ores.**

Pyrometallurgical process



- ***Copper sulphide concentrates*** are produced through different ore dressing processes (crushing→ washing→ screening → roasting).
- The concentrates are ***smelted*** in a ***reverberatory furnace*** to produce matte (mixture of copper& iron sulphides, and slag (waste).
- ***Matte*** is then converted into ***blister copper*** (elemental copper with impurities) by blowing air through the matte in a ***copper converter***.

$$2Cu_2S + 2O_2 \rightarrow 4Cu + 2SO_2$$

Note: *Iron sulphide is oxidised and slagged of while some copper is also oxidised.*

Refining of blister copper

• ***Blister copper*** is later ***fire-refined*** in the process called ***poling*** to produce ***tough pitch copper***, which can be used for some applications other than electrical applications.

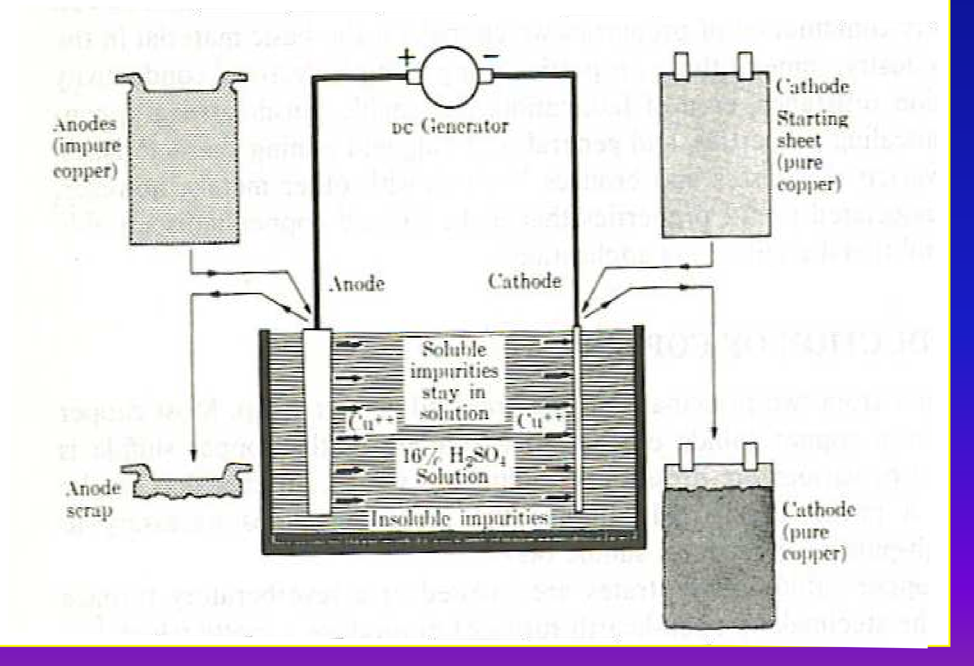
• Most impurities are oxidized and slagged off.

$$\boxed{M + Cu_2O \rightarrow MO + 2Cu}$$

• The remained ***copper oxide Cu_2O*** is reduced using ***coke or charcoal and green tree trunks*** until the copper oxide content is about 0.5% then stop.

Electrolytic refining of tough pitch copper

- Further refining of copper to about 99.95% is for ***electronics applications***.
- ***Electrolytic refining*** converts fire-refined copper at ***anode*** into high-purity copper at ***cathode***.
- ***Electrolyte*** used is $CuSO_4$ + H_2SO_4
- This ***high-purity copper*** is subsequently melted and cast into shapes.



Electro refining of impure copper

Physical properties of copper and copper alloys

Crystal structure	FCC
Atomic number	29
Atomic weight	63.546
Density ($g.cm^{-3}$)	8.933
Melting point (^{o}C)	1084.62

29 FCC
Cu
Copper
63.546

Metal	Relative electrical conductivity (copper = 100)	Relative thermal conductivity (copper = 100)
Silver	106	108
Copper	100	100
Gold	72	76
Aluminum	62	56
Magnesium	39	41
Zinc	29	29
Nickel	25	15
Cadmium	23	24
Cobalt	18	17
Iron	17	17
Steel	13–17	13–17
Platinum	16	18
Tin	15	17
Lead	8	9
Antimony	4.5	5

Electrical and thermal conductivities of pure metals at RT

- High ductility, formability.
- High electrical and thermal conductivities.

Classification of copper and copper alloys

Copper and copper alloys are designated according to the [Copper Development Association] (CDA).

Wrought alloys

- C100-C799

Cast alloys

- C800-C999

Wrought alloys	
C1xx	Coppers[1] and high-copper alloys[2]
C2xx	Copper-zinc alloys (brasses)
C3xx	Copper-zinc-lead alloys (leaded brasses)
C4xx	Copper-zinc-tin alloys (tin brasses)
C5xx	Copper-tin alloys (phosphor bronzes)
C6xx	Copper-aluminum alloys (aluminum bronzes), copper-silicon alloys (silicon bronzes) and miscellaneous copper-zinc alloys
C7xx	Copper-nickel and copper-nickel-zinc alloys (nickel silvers)
Cast alloys	
C8xx	Cast coppers, cast high-copper alloys, the cast brasses of various types, cast manganese-bronze alloys, and cast copper-zinc-silicon alloys
C9xx	Cast copper-tin alloys, copper-tin-lead alloys, copper-tin-nickel alloys, copper-aluminum-iron alloys, and copper-nickel-iron and copper-nickel-zinc alloys

[1] "Coppers" have a minimum copper content of 99.3 percent or higher.

[2] High-copper alloys have less than 99.3% Cu, but more than 96 percent, and do not fit into the other copper alloy groups.

Classification of copper and copper alloys

1) Unalloyed copper

2) Brass

Copper – Zinc alloys → brasses

Copper – Lead alloys
Copper – Zinc alloys with Tin and Aluminium additions

→ Alloy brasses

3) Bronze

Copper – Tin alloys
Copper – Aluminium alloys
Copper – Silicon alloys
Copper – Beryllium alloys

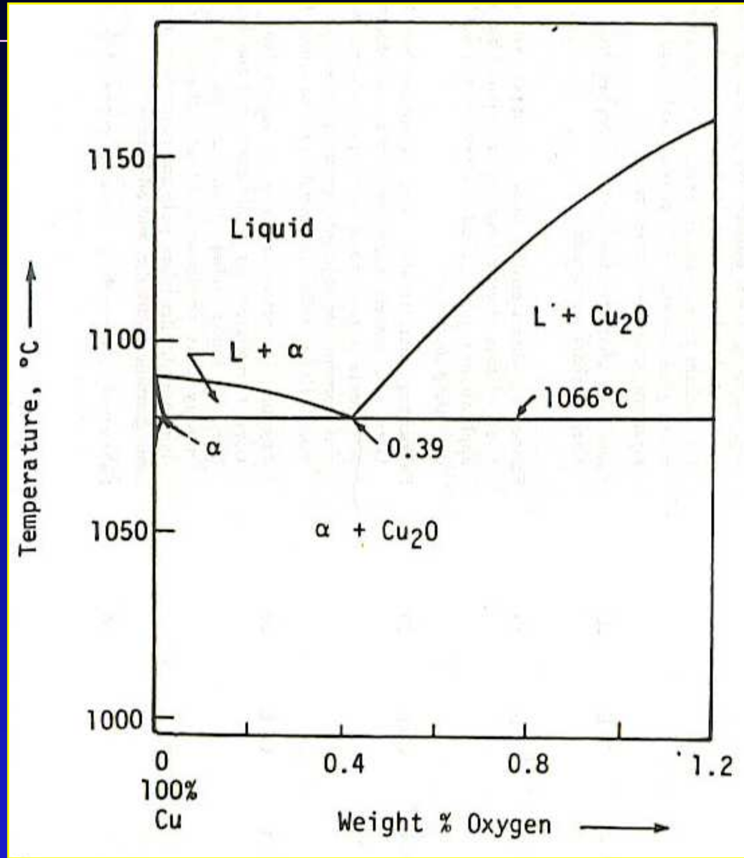
4) Cu-Ni based

Cupronickel (Cu-Ni)
Nickel silver (Cu-Ni-Zn)

The wrought coppers

Unalloyed copper

- Good electrical, thermal conductivities
- High corrosion resistance
- Easily fabricated
- Reasonable tensile strength
- Controllable annealing properties
- Good soldering and joining properties

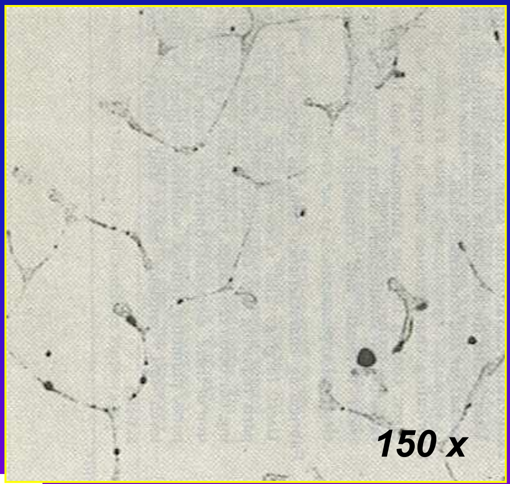


Copper-oxygen phase diagram

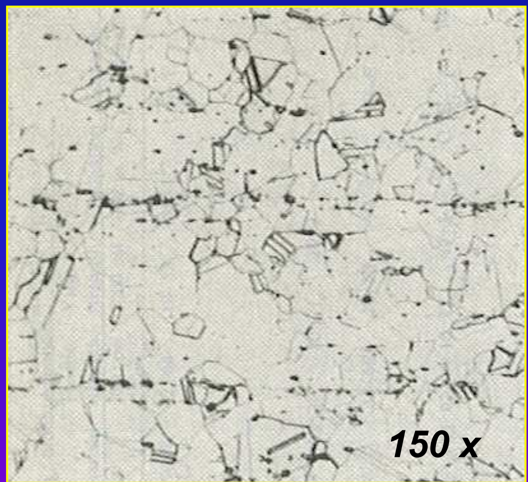
- ***Wrought coppers*** are classified according to ***oxygen*** and ***impurity*** contents.
- Can be roughly divided into;
  - ***Electrolytic tough pitch***
  - ***Oxygen – free***
  - ***Phosphorus deoxidised***

Electrolytic tough-pitch copper

- This copper contains 99.9% ***Cu*** with 0.045 ***O*** content.
- Used for the production of wire, rod plate and strip.
- ***Oxygen*** is almost insoluble in copper and forms Cu_2O interdendritic eutectic upon solidification.
- Hot-working process breaks up this Cu_2O network and appears as ***particles*** aligned in the working direction.
- Exposed to H_2 at $T > 400^oC$ leads to pressure build up at grain boundaries, causing fracture. (hydrogen embrittlement)

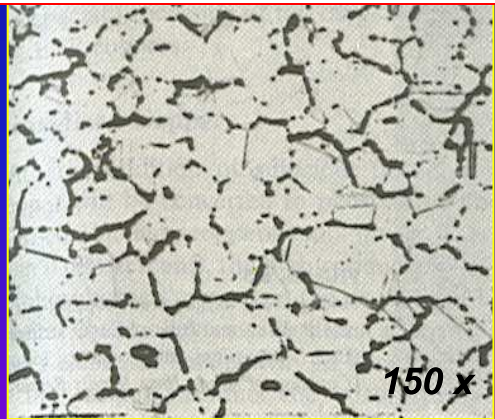


As-cast electrolytic tough-pitch copper



Hot-worked electrolytic tough-pitch copper

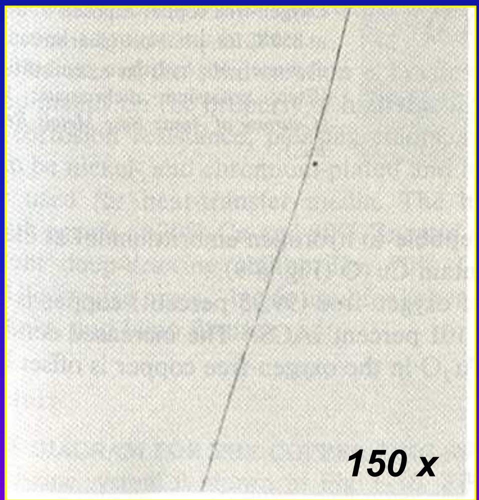
$$Cu_2O + H_{2(dissolved)} \rightarrow 2Cu + H_2O_{(steam)}$$



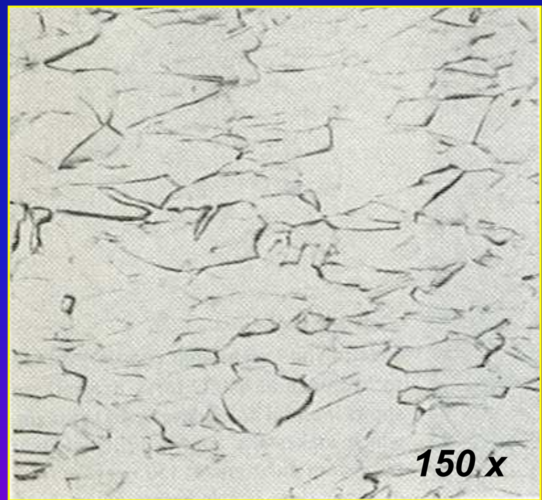
Electrolytic tough-pitch copper exposed to H_2 at $850^oC/.5h$

Oxygen free copper

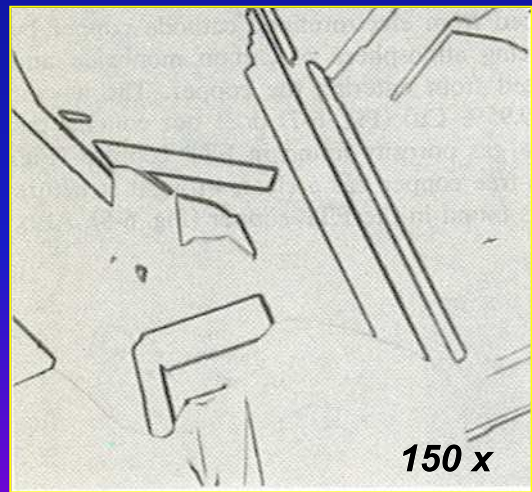
- ***Oxygen-free copper*** is produced from electrorefined cathode copper which is melt and cast in a ***reducing atmosphere*** of ***CO*** and ***N*** to prevent ***O***.
- Microstructure of ***as-cast oxygen free copper*** is free of interdendritic eutectic ***Cu_2O***
- Hot worked microstructure also shows a ***clear microstructure*** and not affected by ***hydrogen embrittlement***.



As-cast oxygen free copper



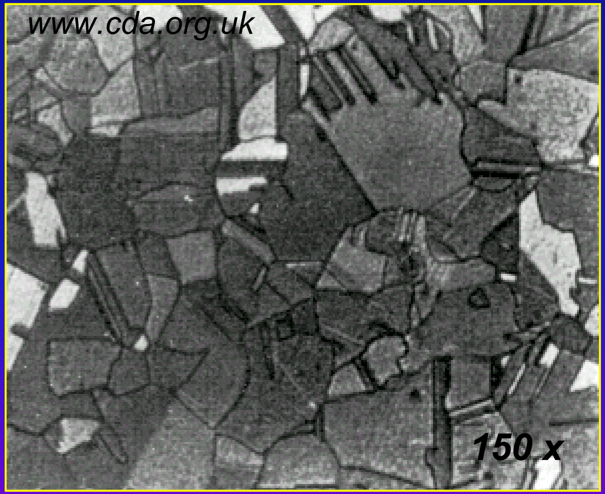
Hot-worked oxygen free copper



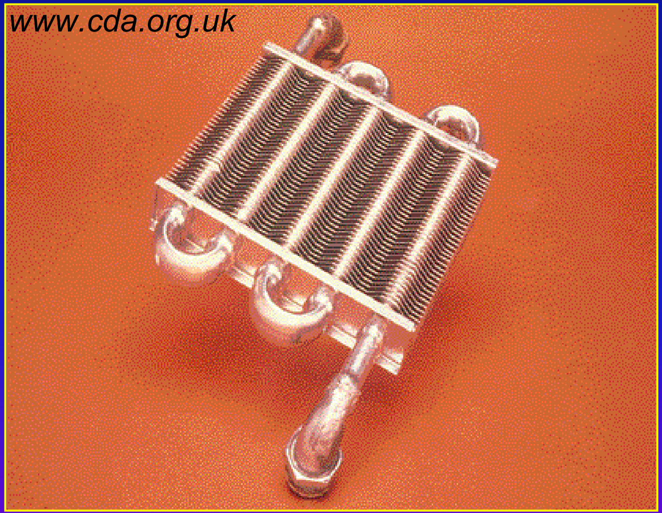
Hot-worked oxygen free copper exposed to H_2 at $850^oC/0.5h$

Deoxidized copper

- ***Phosphorus*** is sufficiently added to produce phosphorus pentoxide P_2O_5. This reduces the amount of ***O*** and give high conductivity copper such as ***deoxidized high phosphorus copper*** (***CDA 122***).
- The excess amount of the ***P*** lowers electrical conductivity (***IACS***).



Microstructure of hot rolled deoxidised copper



Phosphorus deoxidised copper used in pressure vessels or plumbing tubes for electrical purposes

Copper zinc alloys (brasses)

Different kinds of brasses

1) Gliding Metal (<5% Zn)

2) Commercial Bronze (~10% Zn)

3) Jewelry Bronze (~12.5% Zn)

4) Red Brass (~15% Zn)

5) Low Brass (~20% Zn)

6) Cartridge Brass (~30% Zn)

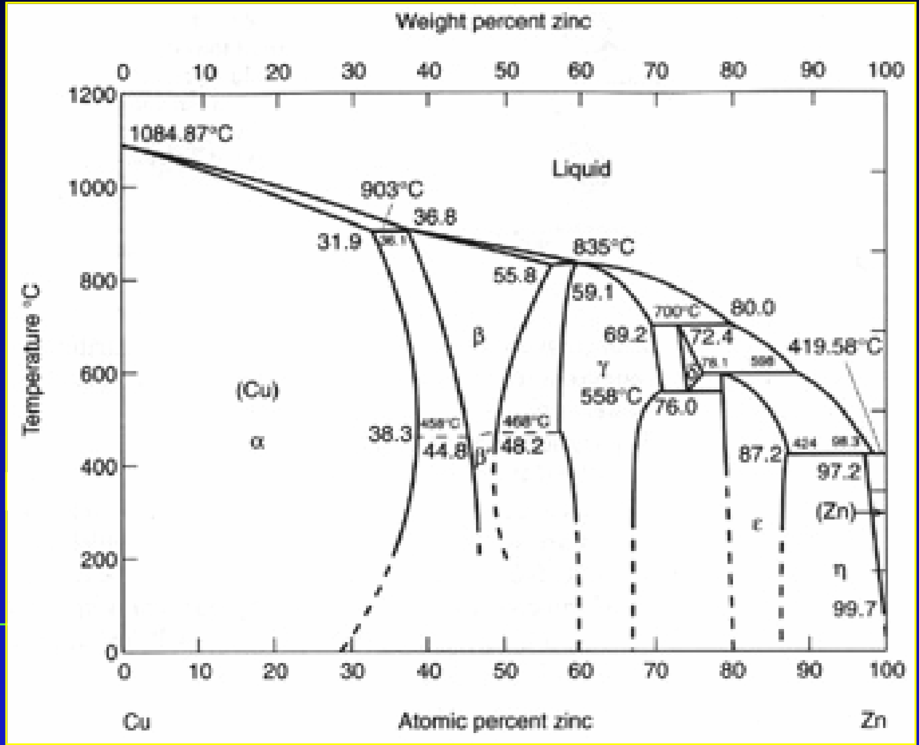
7) Yellow Brass (~ 35% Zn)

8) Muntz Metal (40% Zn)

Copper zinc alloys (brasses)

- ***Copper*** and ***zinc*** form solid solution up to ~ 39% zinc at 456°C, giving a wide rage of properties.
- ***Sn, Al, Si, Mg, Ni, and Pb*** are added elements, called '***alloy brasses***'.
- ***Commercially used brasses*** can divided into two important groups:

1) ***α brasses (hypo-peritectic) with α structure containing upto ~35% Zn.***
2) ***$\alpha+\beta$ brasses (hyper-peritectic) with $\alpha+\beta$ two phase structure, based on 60:40 ratio of Cu and Zn***

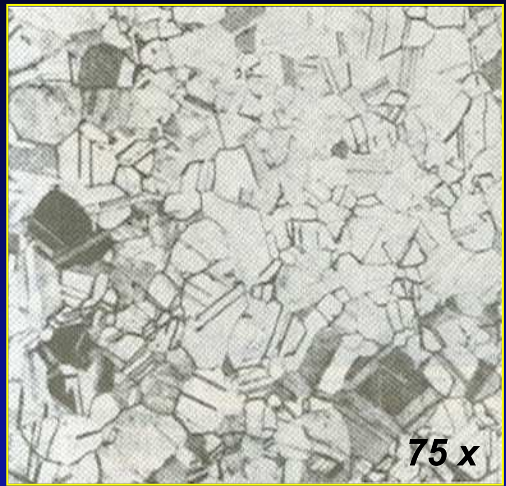


Phase diagram of Cu-Zn system

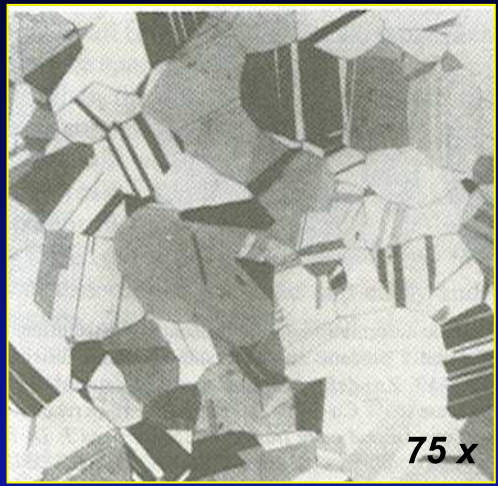
α phase – FCC structure
β phase – BCC structure (disordered)
β' phase – BCC structure (ordered)
γ phase – complex structure (brittle)

Microstructure of α brasses

- ***Microstructures*** of the single-phase α brasses consist of α solid solution.
- ***Annealing twins*** observed in the α ***grains*** increases with the ***Zn contents.***
- ***Dislocation structure*** also changes from ***cellular*** to well-defined ***planar array*** structure with ***increasing Zn***. (due to lowered stacking fault energy).



(a) Commercial bronze (90%Cu-10%Zn)

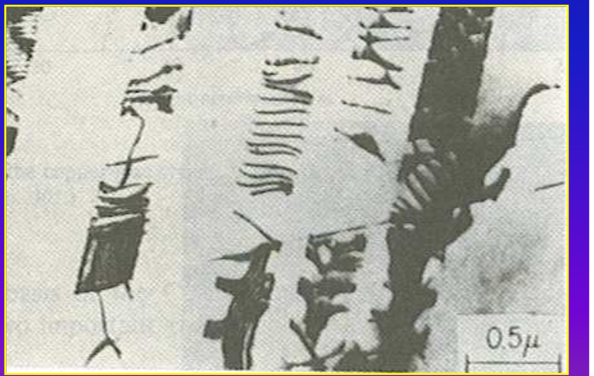


(b) Cartridge brass (70%Cu-30%Zn)

Increasing Zn content

Pure copper

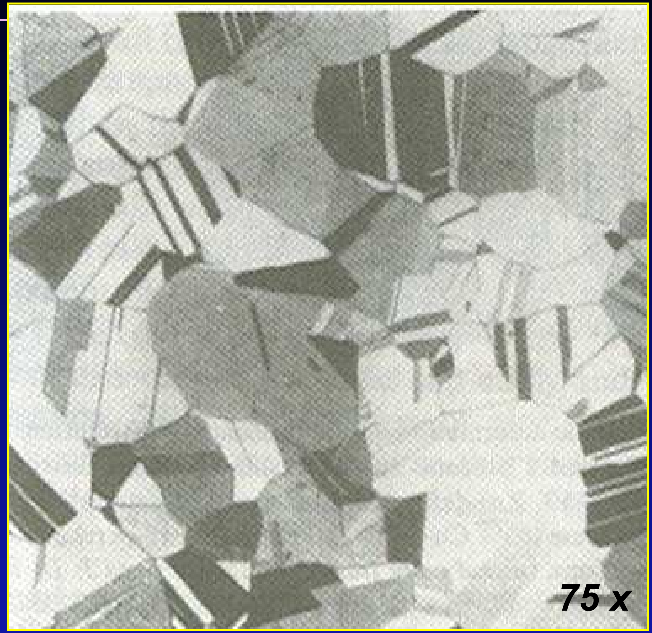
15% Zn



37% Zn

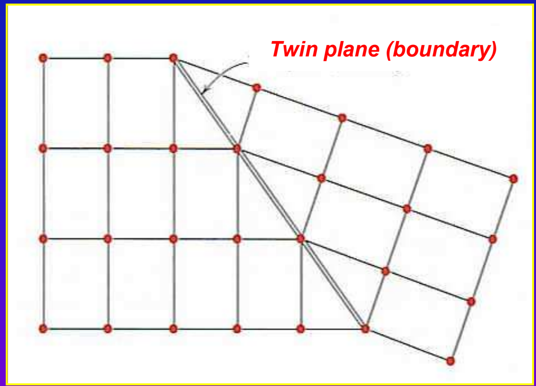
Annealing twins in α brasses

- ***Annealing twins*** can be observed in the α **grains** when the alloy has been cold worked and followed by annealing.
- Cold working introduces strain within the structure. After annealing, recrystallization occurs and produce twin bands or twin lines due to slip.

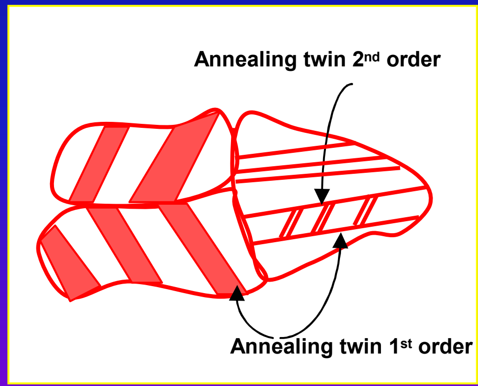


Cartridge brass (70%Cu-30%Zn)

- The twin interface is parallel to **{111} planes** which have the stacking sequence ..***ABCABC***.. on the other side of the twin boundary (mirror reflection), giving the sequence ***ABCABACBA***..across the boundary.



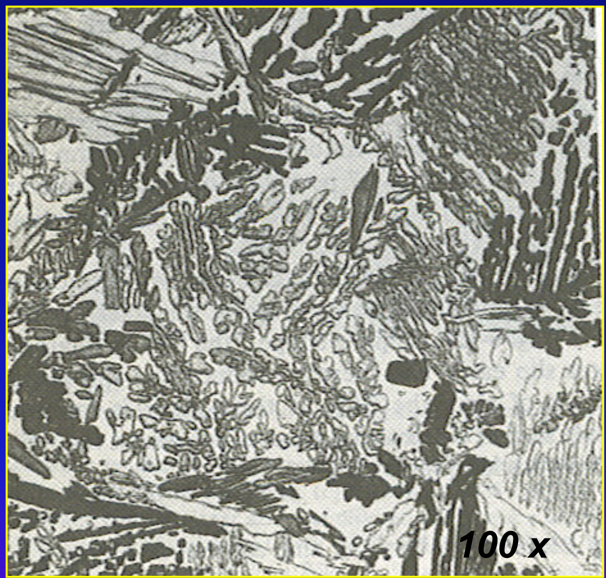
Twin plane or boundary



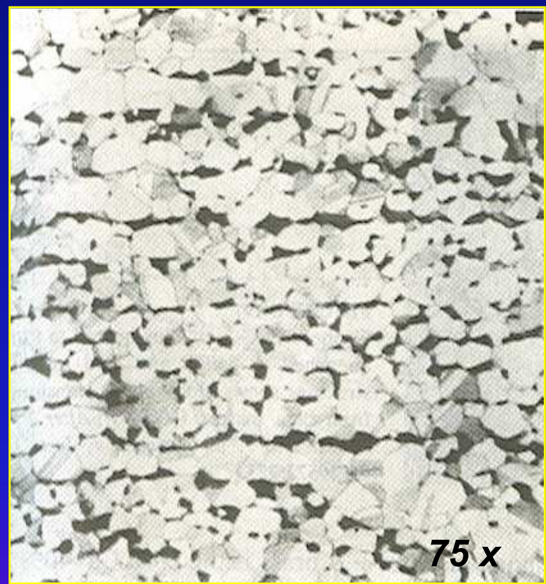
1st and 2nd order twins

Microstructure of $\alpha+\beta$ brasses

- ***40% Zn addition*** provides a complex structure of α and β ***phases***.
- ***60%Cu-40%Zn*** (***Muntz metal***) is the most widely used.
- β ***phase*** makes this alloy ***heat-treatable***.



(a) Cast structure shows dendrites of alpha (dark) in a matrix of beta (white)



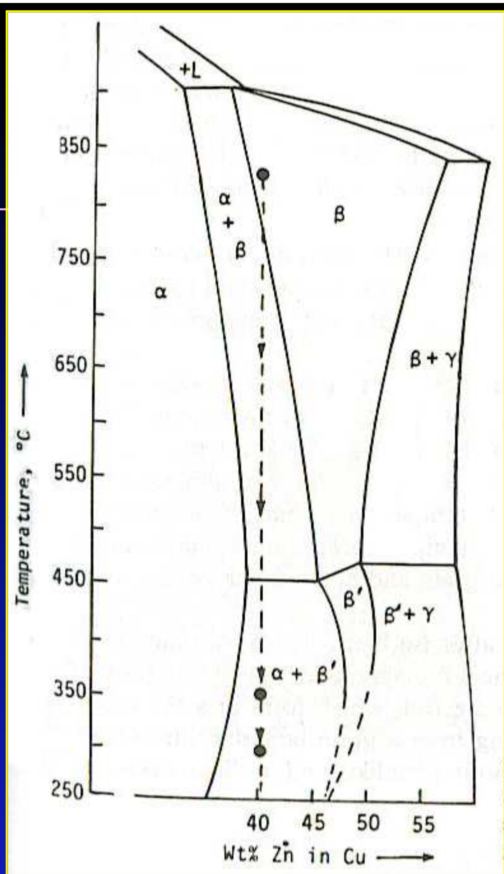
(b) Hot rolled Muntz metal sheet structure of beta phase (dark) and alpha phase (light)

Decomposition of β' in $\alpha+\beta$ Cu-Zn alloys

- Heat treating from 830°C and hot quenched to ~700-710°C causing an ***isothermal transformation*** of unstable ***β or β' to α phase***.
- There are two types of ***α phase*** formed during decomposition.

1) *Rod-type α precipitate*

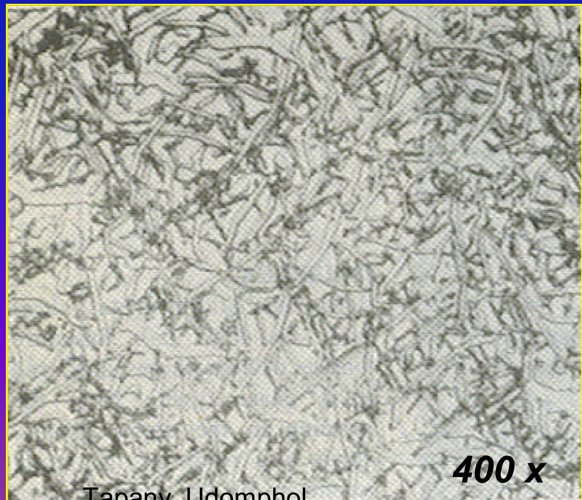
*Formed at higher temp (500-700°C) above the **B_s** (bainitic start) temperature.*



Section of Cu-Zn phase diagram

2) *Widmanstätten α precipitate*

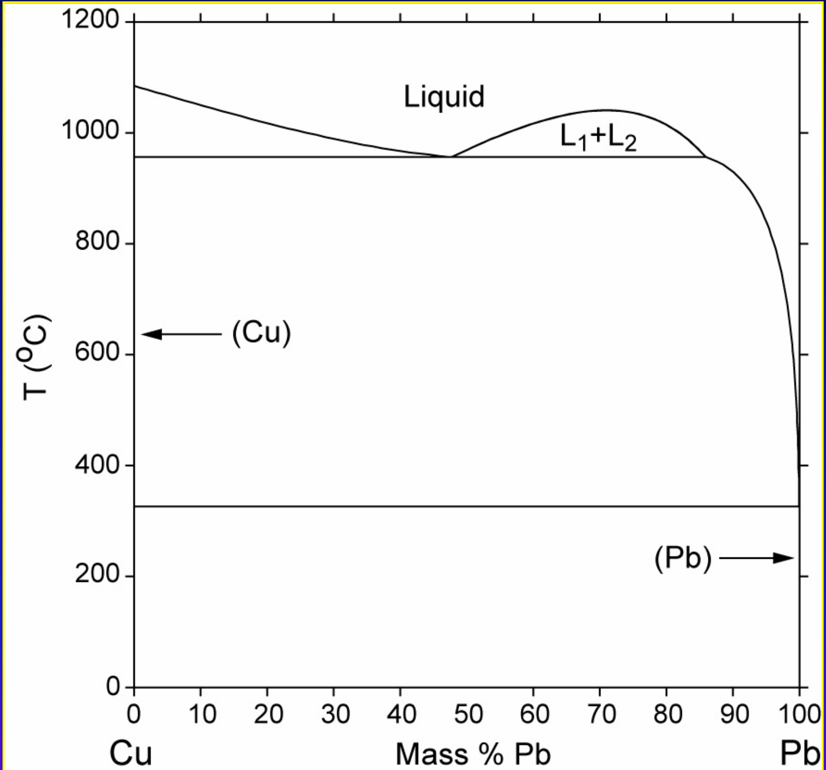
*Nucleated uniformly throughout the β **grains** and grew rapidly in the lengthwise below the **B_s** temperature.*



Cu-41.6% Zn heat treated to 830°C, quenched to 250°C and held for 20h shows a plates transformed from β matrix

Microstructure of alloy brasses

Copper-Lead alloys (Leaded brasses)



Cu-Pb phase diagram

- ***Lead*** is soluble in ***liquid copper*** at high temperatures but insoluble at ***RT***.

- ***Monotectic reaction*** occurs at 955^{o}C.

$$\boxed{Liquid_1(36\%Pb) \underset{955^o C}{\Leftrightarrow} \alpha(100\%Cu) + Liquid_2(87\%Pb)}$$

- ***Eutectic reaction*** occurs at 326^{o}C.

$$\boxed{Liquid_2(99.94\%Pb) \underset{326^o C}{\Leftrightarrow} \alpha(100\%Cu) + \beta(99.99\%Pb)}$$

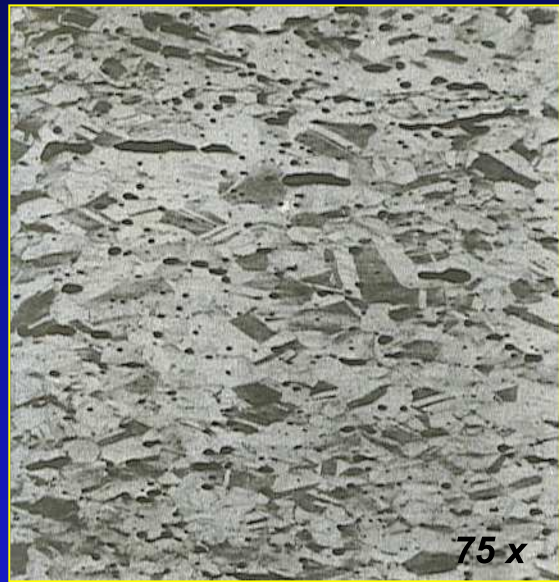
Microstructure of alloy brasses

Copper-Lead alloys (Leaded brasses)

• ***Leaded brasses*** has ***Small amounts of Pb (0.5-3.0%)*** which are added to many types of brasses to improve their machinability.

• Essentially pure lead (99.99%***Pb***) produced by the ***eutectic reaction*** will be distributed inter-dendritically in the copper as ***small globules***.

• Cold deformation makes these globules strung out.



Free-cutting brass extruded rod showing elongated lead globules with the remained α phase

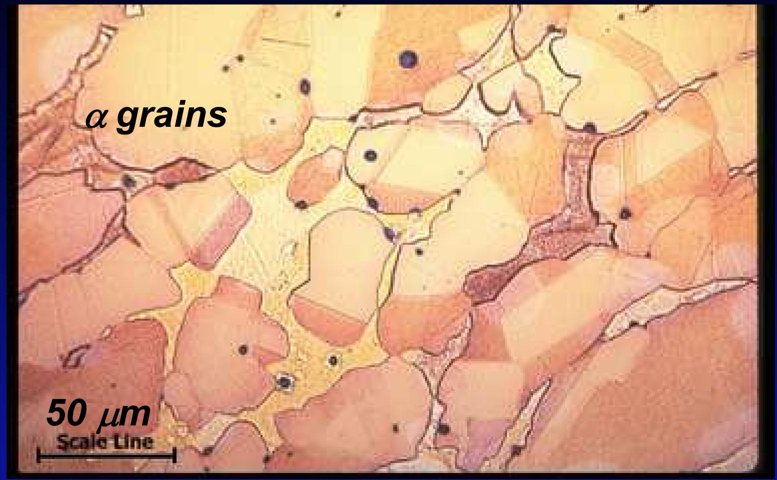
Microstructure of alloy brasses

Tin brasses

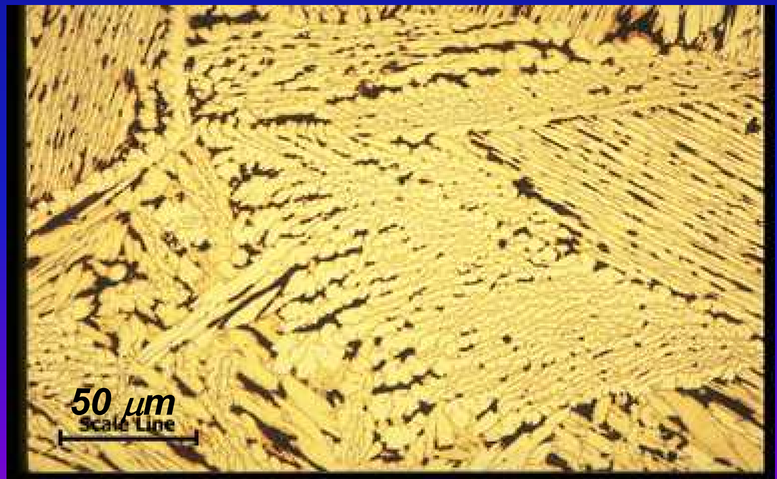
- Microstructure of low ***Zn*** and low ***Sn*** consists of single α ***phase***.
- Increasing ***Sn*** contents gives a lighter coloured microstructure of $\alpha+\beta$ multi-phase.
- ***1% of Sn*** addition in ***cartridge brass*** improve corrosion resistance in sea water.
- ***0.04% arsenic addition*** could almost eliminate ***dezincification*** (corrosion condition).

Note:

- *Replacing **Sn** with **Al** gives brass a **self-healing** protective oxide on its surface. → Called **Aluminium brasses***
- *corrosion resistance → used for marine condensers.*



Microstructure of cast and hot rolled tin brass.(Cu 59.0-62.0, Zn 36.7-40.0, Sn 0.5-1.0, Pb 0.20, Fe 0.10)



Increasing Sn content gives a microstructure of α phase (yellow) in β matrix (dark)

Mechanical properties of brasses

Low brasses (80-95%Cu, 20-5%Zn)

↑ **Zn content** ↑ **Strength**
Hardness
ductility

Colour change

Red → **Gold** → **Green yellow**

• Can be hot worked in 730-900°C temperature range.

• Annealed low brass is extremely ***ductile*** (40-50% at ***RT***) and ***malleable***.

High brasses (60-80%Cu, 40-20%Zn)

• ***Increased strength and hardness*** due to increasing ***Zn*** content.

• ***Decreased ductility*** due to the presence of the β ***phase*** (***BCC***).

• The $\alpha+\beta$ ***brasses*** are difficult to cold-work, due to increasing amount of β ***phase***.

Alloy brasses

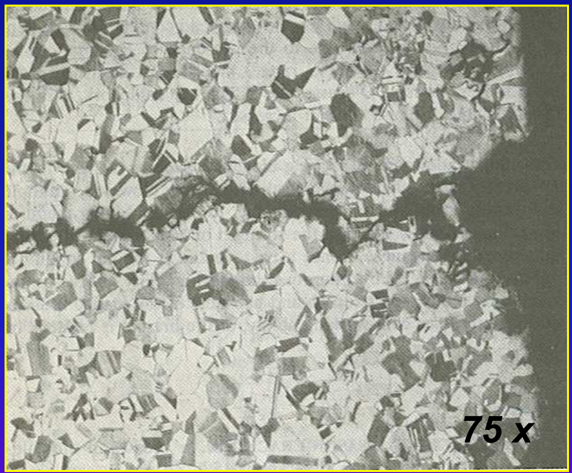
• Addition of 1% ***Sn*** to brass do not greatly affect mechanical properties.

• Multiple additions of ***Mn, Fe, Sn*** increase strength (manganese bronze).

Corrosion of brasses

Stress-corrosion cracking (season cracking)

• Occurs in brasses containing **>15% Zn** and appears at **grain boundaries** (intergranular cracking).



Intergranular stress-corrosion cracking in cartridge brass (70%Cu-30%Zn) due to exposure to corrosive atmosphere

Dezincification

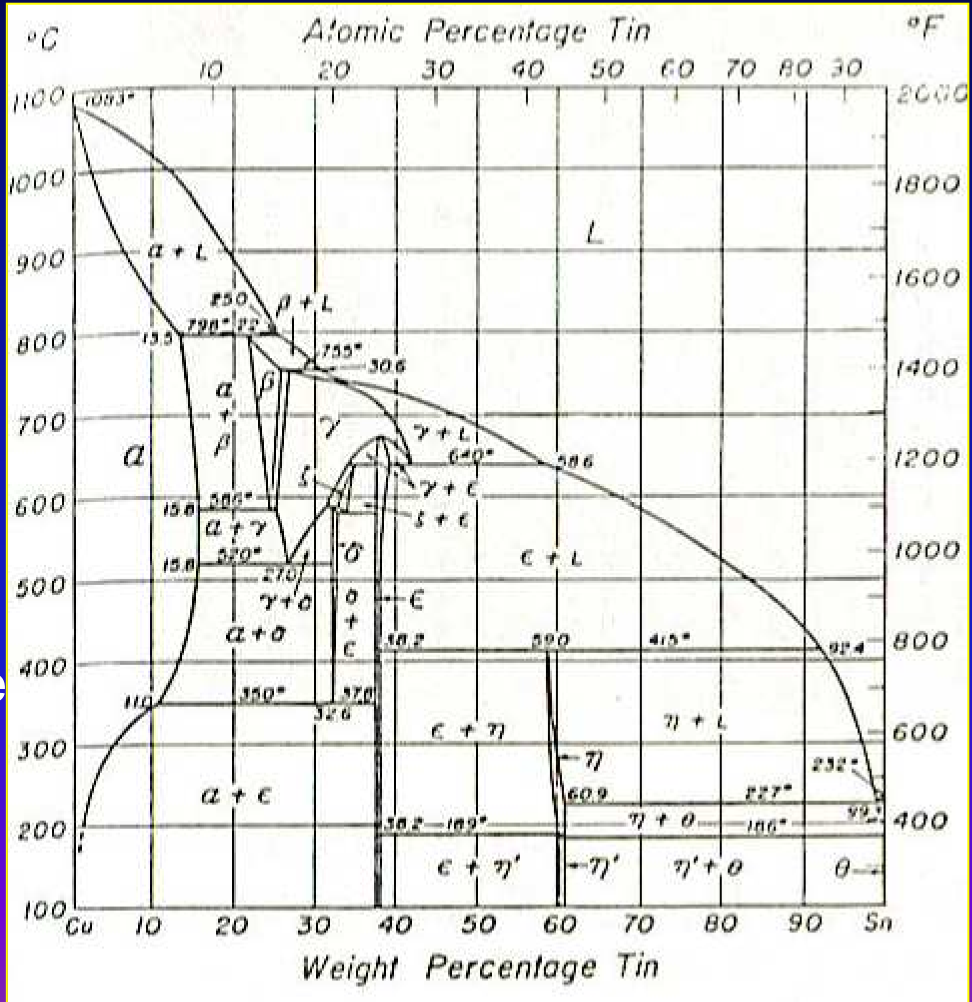
• The **Zn** corrodes preferentially and leaves a **porous residue of copper** and **corrosion products**.

Dezincification of cartridge brass (70%Cu-30%Zn)

Copper-tin alloys (Tin bronze)

- Contains principally of ***Cu*** and ***Sn***.
- ***P*** is usually added as deoxidizing agent → called ***phosphor bronzes***.

- ***Cu-Sn*** can form ***solid solution*** upto 15.8% at about 520-586^{o}C.
- Solid solubility limit of ***Cu-Sn*** is lower than that of ***Cu-Zn***
- Upto about 11% ***Sn***, precipitation of ε ***phase*** is found sluggished when cooled from above 350^{o}C to ***RT***, but the formation of metastable ε' has been observed.

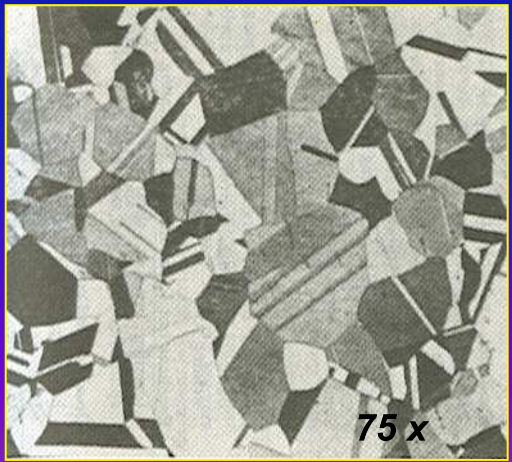


Cu-Sn phase diagram

Wrought and cast copper-tin bronzes

- Wrought ***Cu-Sn bronzes*** contain about 1.25-10% ***Sn*** with upto 0.1% ***P***; hence usually called ***phosphor bronzes***.
- ***P*** is added as ***deoxidizing agent*** to improve ***castability***.
- ***Microstructure*** of ***92%Cu-8%Sn*** consists of recrystallised α ***grains*** with ***annealing twins***.
- The wrought tin bronzes possess ***higher strength*** than brasses, especially in the cold-worked condition and has better corrosion resistance.

Microstructure of phosphor bronze 92%Cu-8%Sn-trace P, showing recrystallised α grains with annealing twins

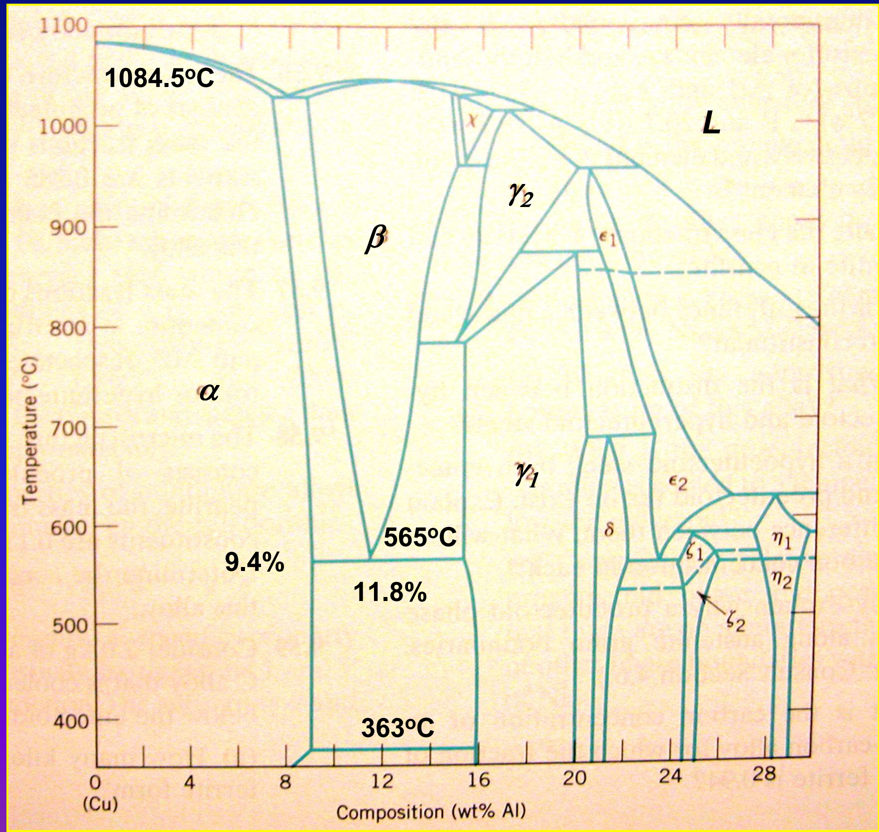


- ***Cu-Sn bronze castings*** containing up to 16% ***Sn*** are used for ***high strength bearing*** and ***gear blanks***.
- High ***Sn*** (>10%) gives strength but unworkable → ***casting***.

Copper-aluminium alloys (aluminium bronzes)

- ***Al*** forms solid solution in ***Cu*** ***(α phase)*** upto 9.4% at 565°C.
- Microstructure of ***α aluminium bronzes*** consists of single α phase solid solution.
- The solid solubility of the ***α phase*** increases with decreasing temp.
- Above 9.5% ***Al***, rapid quenching to ***RT*** produces ***martensitic transformation*** of ***metastable β' tetragonal*** structure.

Annealed microstructure of Cu-5%Al, showing α grains with twin bands.



Cu-Al phase diagram

Microstructure and heat treatment of the complex aluminium bronzes

- From ***Cu-Al phase diagram***, the β ***phase*** is introduced when the ***Al content*** is above 8% at ***T***> ~900^{o}C. → complex microstructure.

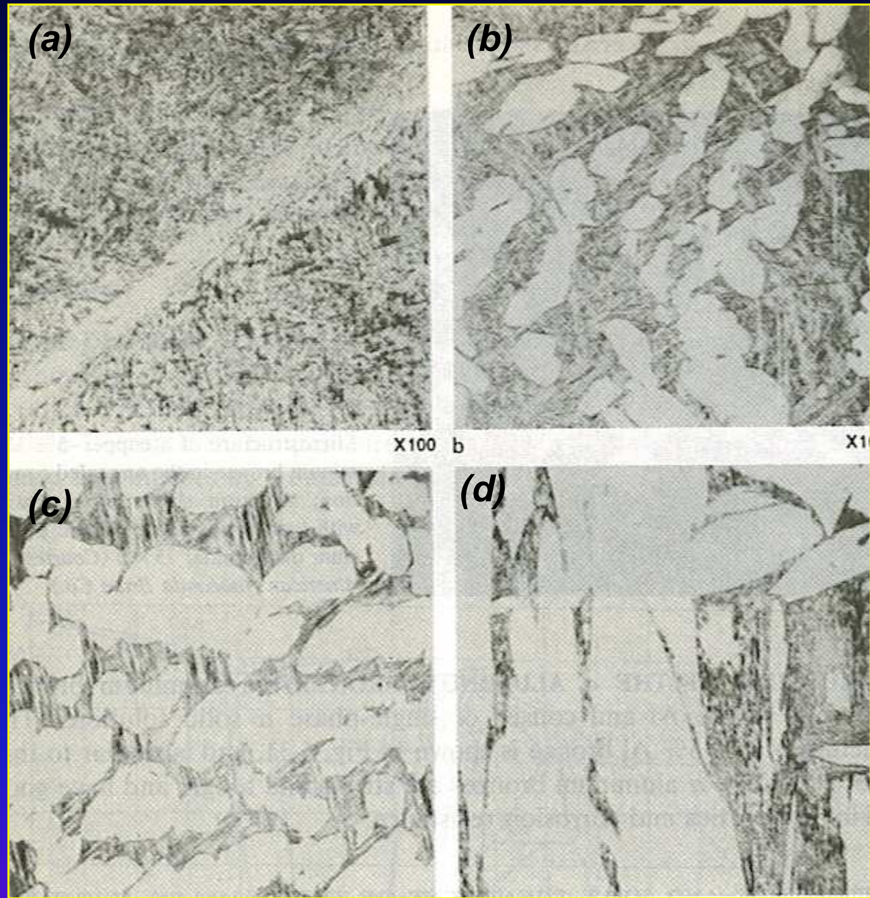
- Above 9.5% ***Al***, quenching from ~900^{o}C gives almost β' ***martensites***, ***fig (a).***

- Slowly cooled to 800 or 650^{o}C and quenched gives less β' ***martensites***, ***fig (b) and (c).***

- Cooled to 500^{o}C and quenched, the β ***phase*** will decompose to form α+γ_2, ***fig (d).***

$$\boxed{\beta \leftrightarrow \alpha + \gamma_2}$$ **brittle**

(aluminium bronze pearlite)



β' martensite ↓ **strength** ↓ **Ductility** ↑

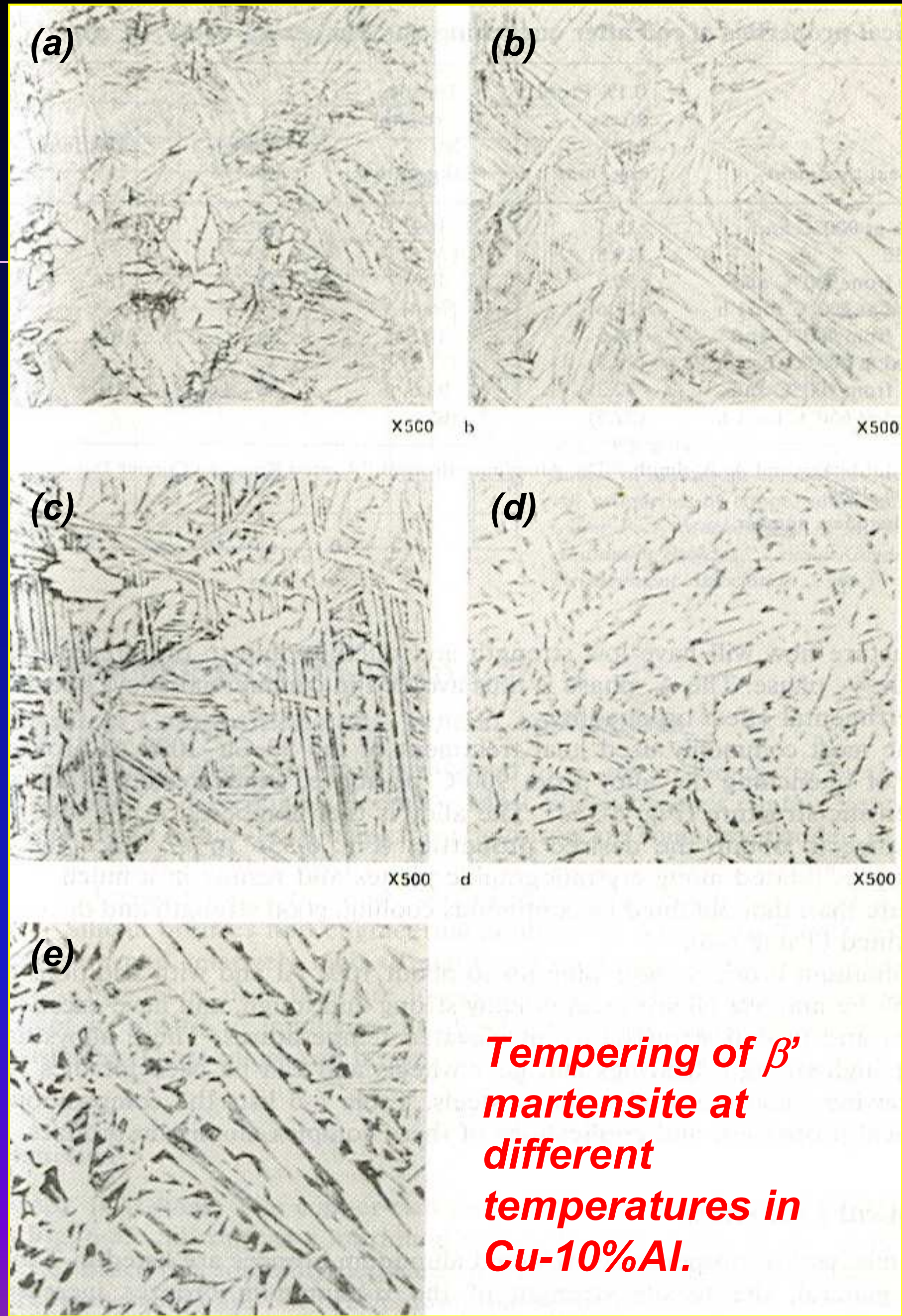
Tempering of β' martensite

• Good properties can be achieved by tempering ***β' martensite*** at 450-600^{o}C.

• Very fine ***α phase precipitates*** along crystallographic planes provide good strength and ductility.

Increasing tempering temperature → ***Larger microstructure***

(a) Soaked 1 h and quenching from 900^{o}C.
(b) Tempered 1 h at 400^{o}C.
(c) Tempered 1 h at 500^{o}C
(d) Tempered 1 h at 600^{o}C.



Tempering of β' martensite at different temperatures in Cu-10%Al.

Properties of aluminium bronzes

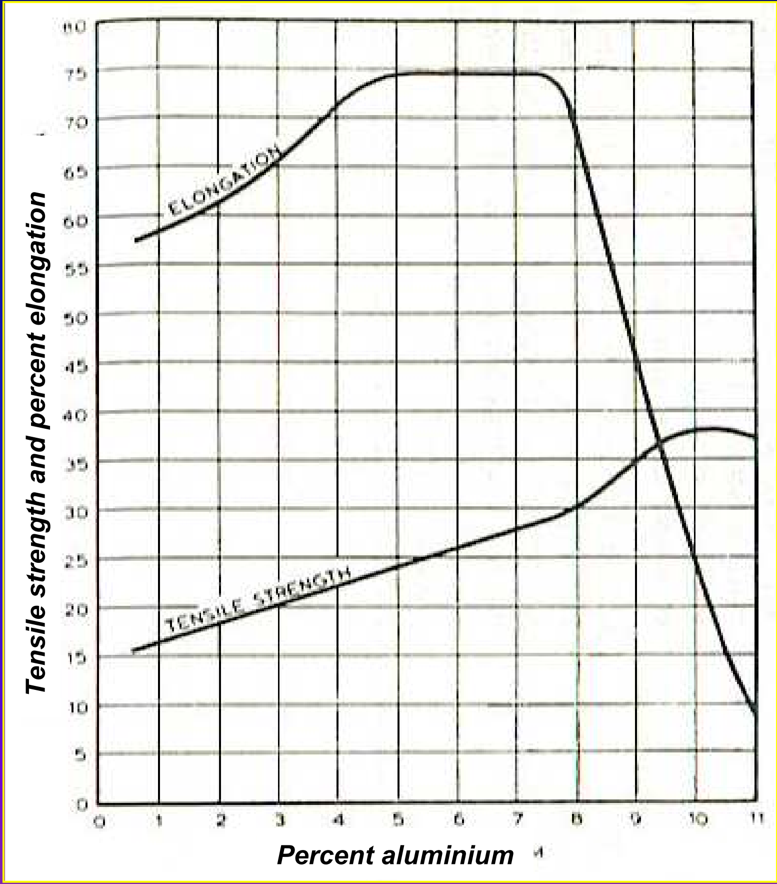
• ***Aluminium bronzes*** have high strength, excellent corrosion and good resistance to wear and fatigue.

• ***Self-healing*** surface film of aluminium oxide → excellent corrosion resistance.

• ***Tensile strength*** increases with increasing β ***phase*** while ductility drops off.

• Increasing ***Al content*** → increases ***tensile strength***.

• Tensile strength of ***10%Al*** varies from 300-680 MPa.



Effect of aluminium content on mechanical properties of Cu-Al bronze

Copper-silicon alloys (silicon bronze)

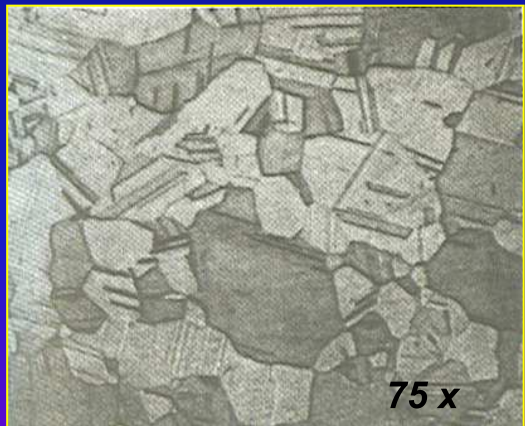
• ***Si*** has a maximum solid solubility with ***Cu*** at 5.3% at 843°C.

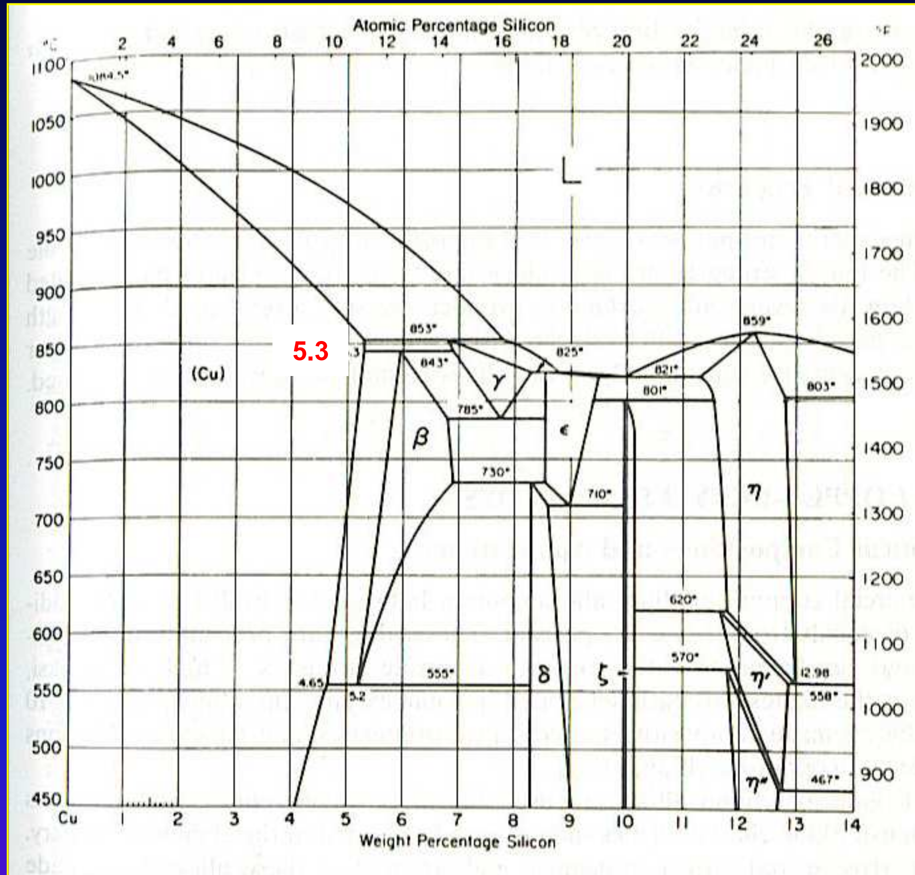
• Most ***silicon bronzes*** contain 1-3% ***Si***, which are not ***precipitation hardenable***.

• ***Mn*** and ***Fe*** are sometimes added to improve properties.

• Annealed structure of a bronze consists of α ***grains*** with ***twin bands***.

Annealed 96%Cu-3%Si-1%Mn bronze, showing α grains with twin bands





Cu-Si phase diagram

• ***Silicon bronzes*** *have high corrosion resistance, high strength (~390-1000 MPa) and toughness.* ***Low-cost substitutes*** *to tin-bronze (due to high corrosion resistance to sea water).*

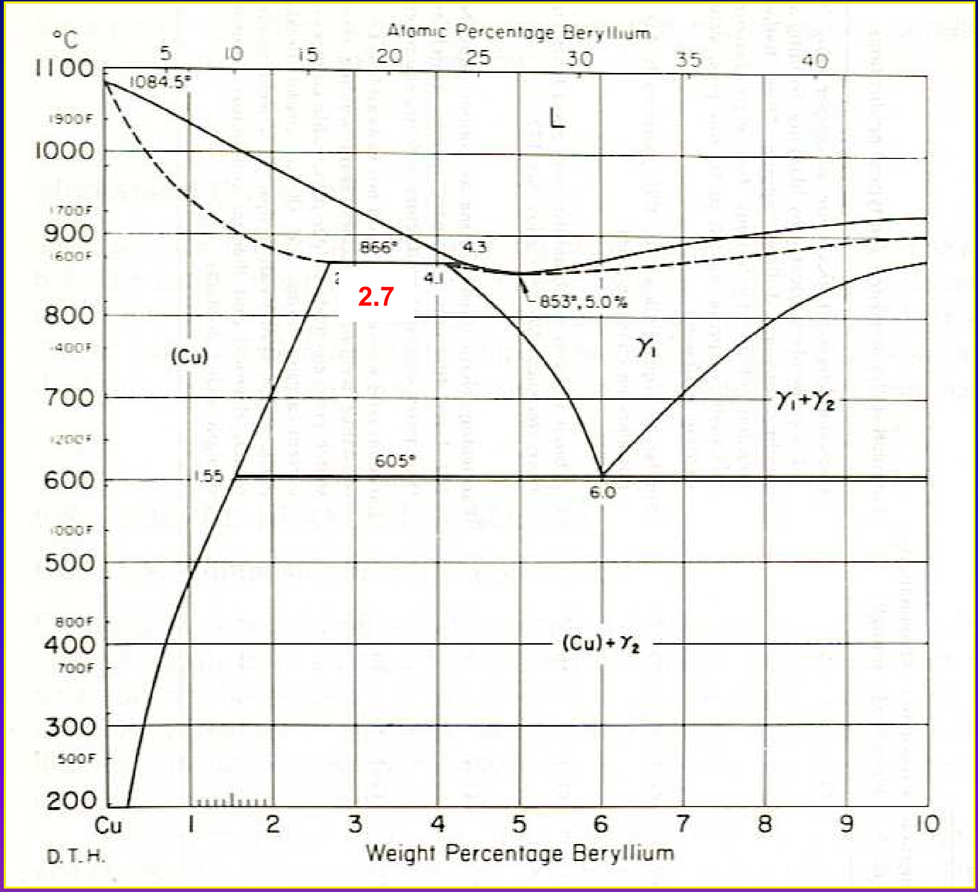
Copper-beryllium alloys

• ***Be*** has maximum solid solubility of 2.7% in ***Cu*** at 866^{o}C.

• ***Cu-Be alloys*** with upto 2% ***Be*** are ***precipitation hardenable*** due to a rapid decrease in ***Be*** solubility.

• ***Cu-Be alloys*** can be ***solution heat-treated*** (at ~800^{o}C) to produce the ***highest tensile strength*** (~470-1400 MPa) among commercial copper alloys due to precipitation hardening.

• The alloys are relatively ***high cost*** and can replace other lower cost copper alloys, which will not meet the property requirement.



Cu-Be phase diagram

Precipitation sequence and microstructure

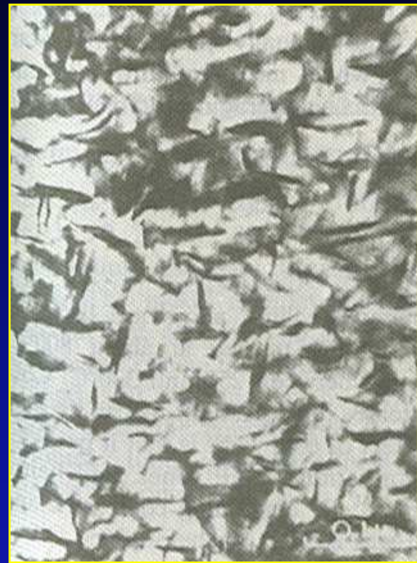
- General precipitation sequence in Cu-2%Be alloy.

$$SSSS \rightarrow \underset{(flat\ \ plate)}{GP\ \ zones} \rightarrow \underset{(rods, plates)}{\gamma'} \rightarrow \underset{CuBe(ordered)}{\gamma}$$

- The ***GP zones*** were first formed and then transform to partially coherent γ' precipitates while further ageing, ***fig (a).***

- Increasing ***ageing temperature*** (~380°C) produces ***equilibrium ordered BCC γ phase CuBe*** (eutectoid structure), ***fig (b).*** → ***overageing*** → ***decreased hardness.***

Intermediate ordered γ' of Cu-1.87% Be solution heat-treated at 800°C, quenched and aged at 350°C/4h



Cu-1.87%Be alloy solution heat-treated at 800°C, quenched and aged 16h at 400°C

Copper-nickel alloys (cupronickel)

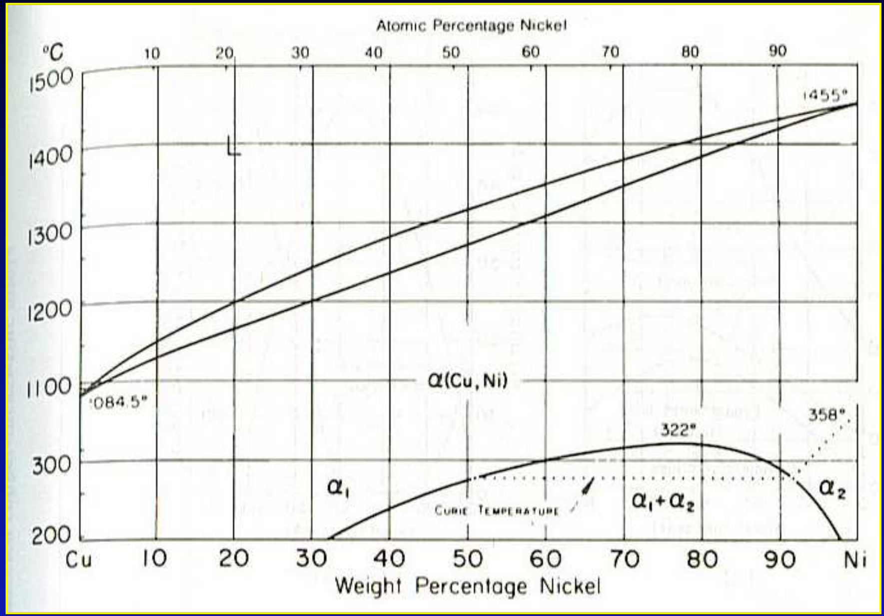
• ***Cu*** and ***Ni*** are both ***FCC*** and can form solid solution throughout.
• Microstructure consists of α ***phase solid solution***.

• ***Ni*** (10, 20, 30%) are added to ***Cu*** to form solid solution alloys, called ***cupronickel***.

• ***Ni addition*** improves strength, oxidation, and corrosion resistance.

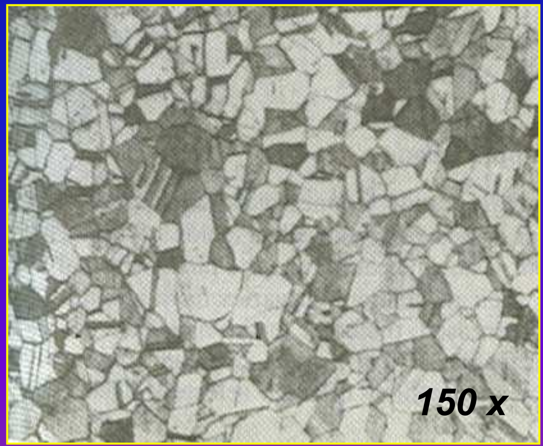
• ***Ni*** greatly increases ***electrical resistivity*** of ***Cu*** (ex:55%Cu-45%Ni) → used for wire-wound resistance for electrical instrument.

• ***Applications:*** condenser tubes and plates, heat exchangers, and chemical process equipment.



Cu-Ni phase diagram

Microstructure of cupronickel 70%Cu-30%Ni consisting of recrystallised α ***grain with twin bands***



Copper-nickel-zinc alloys (nickel silvers)

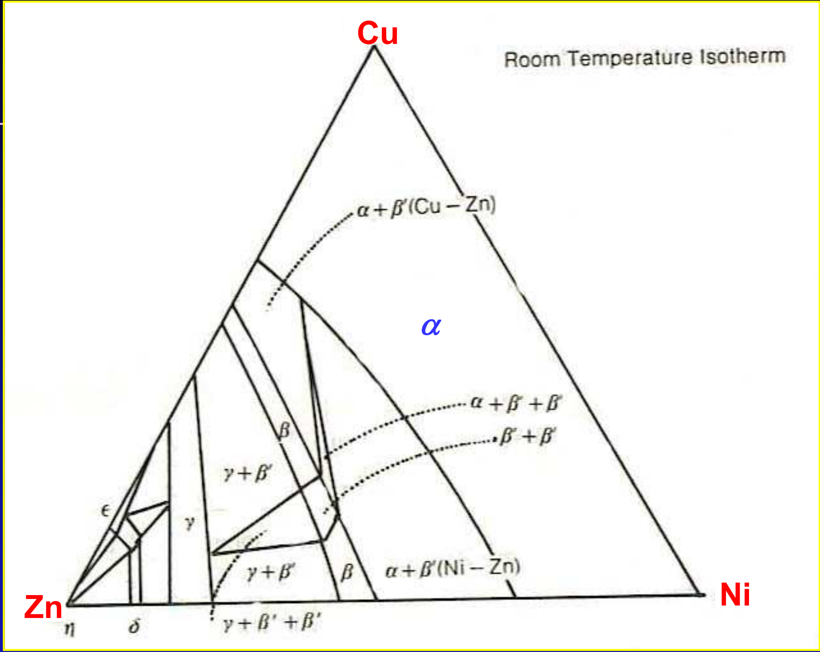
• ***Ternary Cu-Ni-Zn alloys*** or ***nickel silvers*** do not contain any silver but the colour.

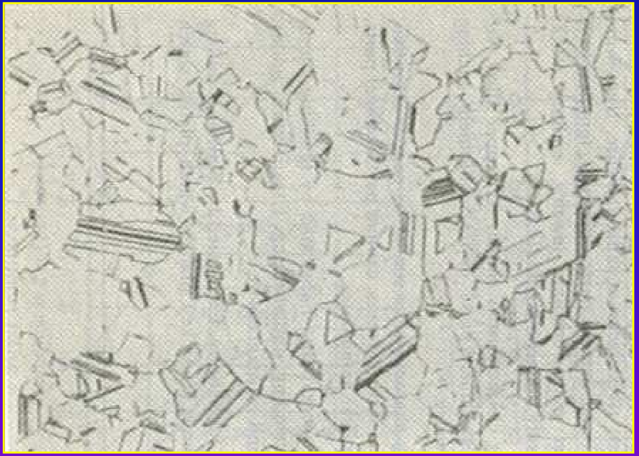
• Alloys contain 17-27%***Zn*** and 8-18% ***Ni***.

• The colour changes from ***soft ivory*** to ***silvery white*** with increasing ***Ni*** content.

• Microstructure consists of α ***phase solid solutions***.

- ***Properties:*** Medium to high strength, good cold-workability, good corrosion resistance.
- $\alpha+\beta$ structure alloys are used for medical devices, springs.





Annealed nickel silver alloy (65%Cu-10%Ni-25%Zn) structure of α ***grains with twin bands***

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