Lecture 20: Copper Alloys

MMat 380

Over time, the copper roofs of Canada's Parliament Buildings and the statue of liberty become covered with a layer of copper acetate, which produces the green colour and prevents further corrosion.

Copper in pennies (USA)

- 1793-1837 US penny made from pure Cu
- 1837-1857 US penny bronze (Cu-Sn)
- 1857 penny 88% Cu + 12%Ni (whitish appearance)
- 1864-1962* US penny bronze (95% Cu+5% Zn and Sn)
- 1962-1982 - 95 percent Cu + 5% Zn
- 1982-present Cu-plated Zn (97.5%Zn + 2.5% Cu)

*In 1943, the coin's composition was changed to zinc-coated steel - due to the critical use of copper for the war effort.

Copper in pennies (Canada)

- Until 1997 mostly Cu (98%) with small amount of Zn (~2%)
- 1997-2000 Cu-plated Zn (Cu 2%, Zn 98%)
- 2000 – present Cu-plated steel (94% steel, 4.5% Cu, 1.5% Ni)

Other Coin Composition

- Nickel: 2000 - present, Ni-plated steel (94.5% steel, 3.5% Cu 2% Ni)
- Dime: 2000 - present, Ni-plated steel (92% steel, 5.5% Cu, 2.5% Ni)
- Quarter: 2000 – present, Ni-plated steel (94% steel, 3.8% Cu, 2.2% Ni)
- Loonie: 1987 – present, aureate bronze plated on pure nickel
- Toonie: 1996 – present, Bi-metallic - outer ring Ni and inner core is Al bronze (92% Cu, 6% Al, 2% Ni).

Topics in Copper

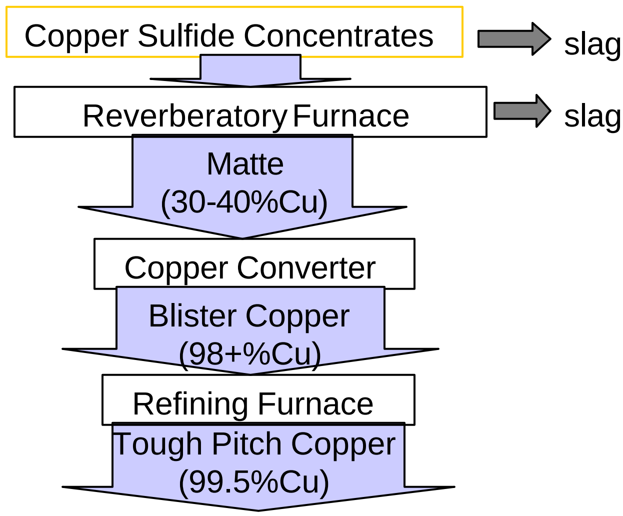
- “pure”
  - Extraction and terminology of “grades”
  - hydrogen embrittlement, deoxidizers
  - phosphor free (P reduces conductivity)
- Pros and cons of Cu
- Alloys
- Brasses
  - Stress corrosion cracking
- Bronzes
  - dezincification
- Cu-Ni alloys
- Cu-Be

Copper and copper alloys

- Used for ~11,000 years, bronze (Cu-Sn first alloy)
- Melting point: 1083 °C
- Density: 8.89 gm/cm^3 (3xAl)
- Crystal structure: FCC
- E= 130 GPa
- Mechanical Properties:
  - UTS Annealed: 173 MPa
  - Cold worked: 413 MPa

Processing:

Production of high-purity Cu from CuS concentrates



Processing:

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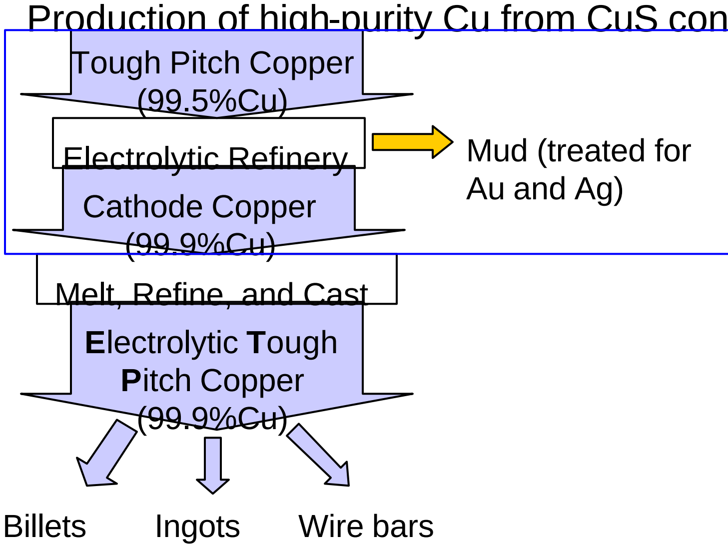
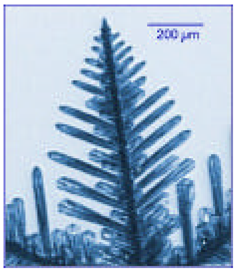
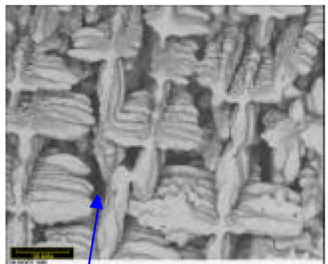


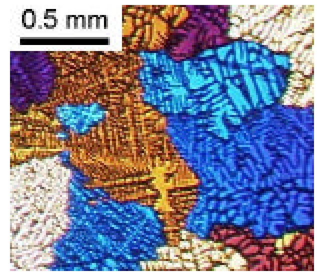
Interdendritic space: dendrites and solidification



Growth of dendrite in ice crystal



3D solidification in progress



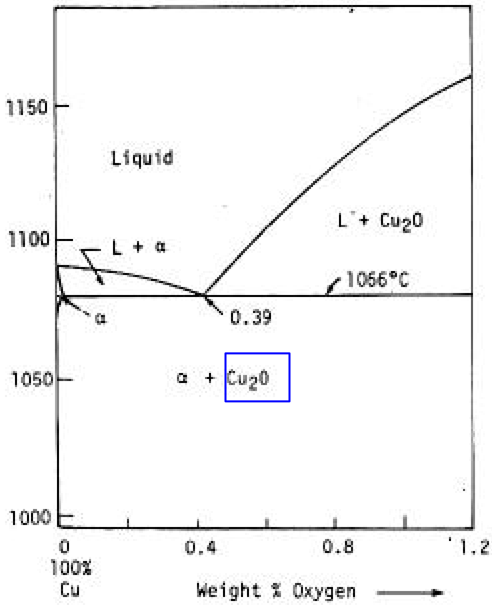
2D image of grains: showing dendritic structure

Interdendritic space

What would happen to material properties of something brittle was segregated to interdendritic space? What would failure look like?

Information from phase diagram's

- Is there a crystal change?
  - Hardening from heat treatments taking advantage of this: CCT diagrams, critical cooling rate to form a metastable phase…
- Solubility of one phase in another
- Can it be age hardened?
  - a supersaturated solution upon cooling which will permit fine dispersion of precipitates to form
- Phases to avoid, poor properties?
  - Brittle phases, regions susceptible to corrosion



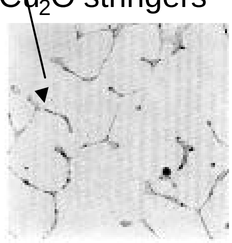
Cu-O phase diagram

Why oxygen makes alloy non-weldable: hydrogen embrittlement

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

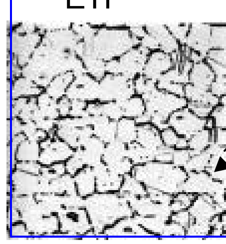
Insoluble in Cu: holes form

As cast ETP, interdentdritic Cu_2O stringers



After exposure to hydrogen at 850ºC for 30 min.

ETP



holes

Oxygen-free Cu

Deoxidizers

- Li, Na, Be, Mg, Bo, Al, C, Si and P can be used
- Ca, Mg and Zn sometimes normally other roles
- Requirements of a deoxidizer
  1. affinity for oxygen in molten copper
  2. relatively inexpensive compared to copper and any other additions

Examples of deoxidizers

- Zn normally solid-solution strengthener, sometimes added in small amounts as deoxidizer
- In tin bronze, traditionally use P thus “**Phosphor bronzes**”
- In chromium-coppers Si not P:
  - **P severely reduces electrical conductivity**

"Pure" copper

Electrolytic tough pitch copper (~0.045 O_2)

- Least expensive of the coppers
- Oxide does not appreciably affect conductivity
- H_2 from torch when welding diffuses into metal and interacts with oxide to form steam
- Metal may become "gassed" and therefore weak and brittle

Phosphorous deoxidized copper

- < 0.09%P therefore oxygen absent
- Suitable for torch welding and brazing
- Good for plumbing, gas
- Not used for electrical conductivity (i.e., 0.025%P in solution lowers the conductivity to 85% IASC)

Relative electrical and thermal conductivites of commercially pure metals (at 20°C)

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

Pros and Cons of Cu and Cu Alloys

Advantages

- Good corrosion resistance
- Excellent electrical and thermal conduction
- Variance in colour with alloy addition (aesthetic value)
- Ease of fabrication due to excellent ductility (rolled stamped, drawn)

Disadvantages

- Susceptibility to hydrogen embrittlement, stress corrosion cracking
- Relatively low strength/weight ratio
  - (when compared to Al or steel)
- Properties are subject to dramatic changes with varying alloy content
  - (i.e. conductivity decreases substantially with increasing impurity content)

Copper and its alloys

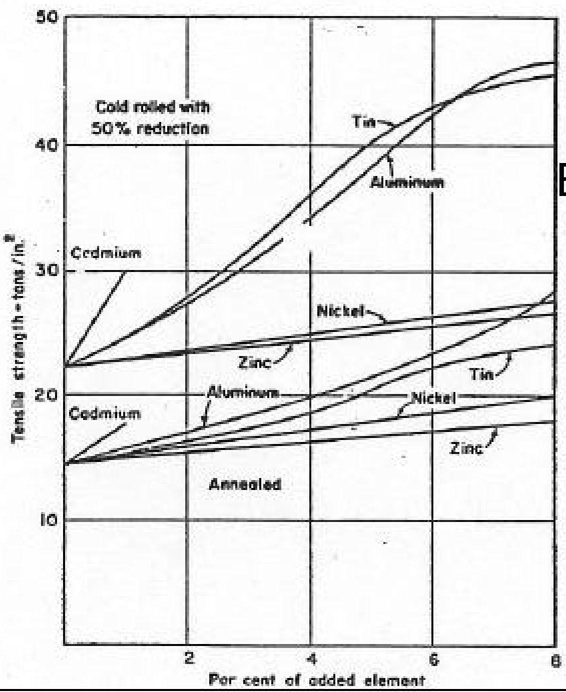
- Pure Cu
- Cu with minor additions
- Brasses
- Bronzes – Sn, Al, Si, Mn
- Cu-Ni alloys
- Cu-Be

Copper and its alloys

Family	Alloying element	Solid solubility at%
Brasses	Zinc (Zn)	37
Phosphor bronze	Tin (Sn)	9
Al bronze	Aluminum (Al)	19
Si bronze	Silicon (Si)	8
Cu-nickel, Nickel-silver	Nickel (Ni)	100%

Copper and its alloys

- Solid solution alloys (Zn, Sn, Al, Si)
- Age-hardenable alloys (Be, Zr, Cr)
- Insoluble alloying elements (lead, tellurium, selenium)
- Deoxidizers (Li, Na, Mg, B, Al, C, Si and P)

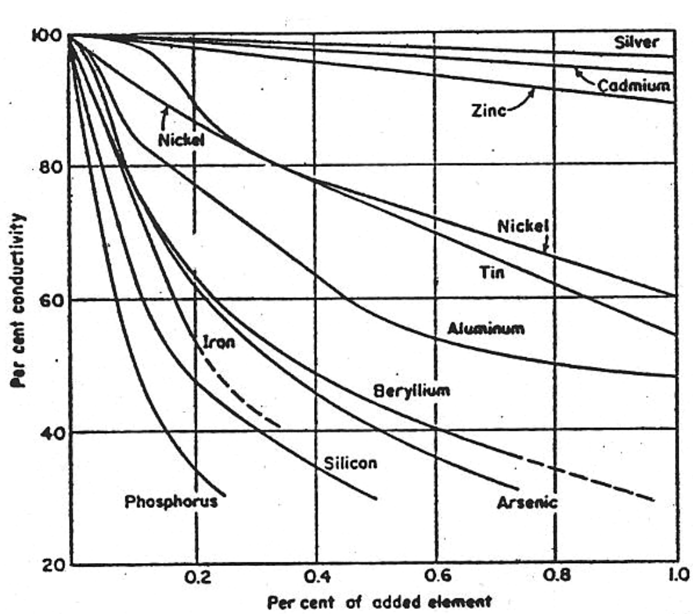


Effect of additions on strength

All increase strength

especially Cd, Sn, Al

Effect of additions on conductivity



All decrease conductivity

especially P

Then Si, Fe, Ar, Be

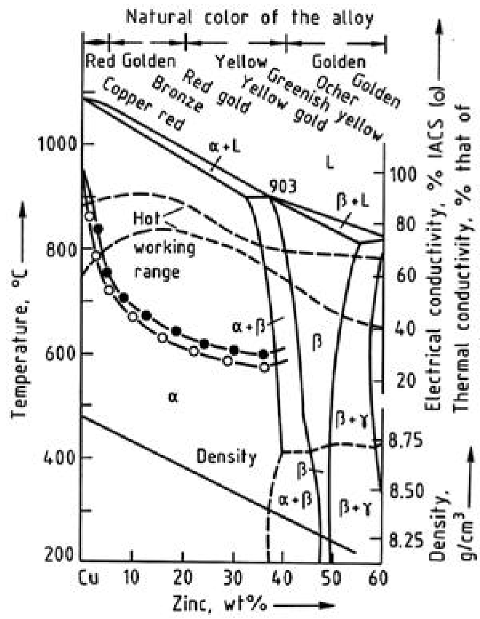
Typical applications Cu alloys

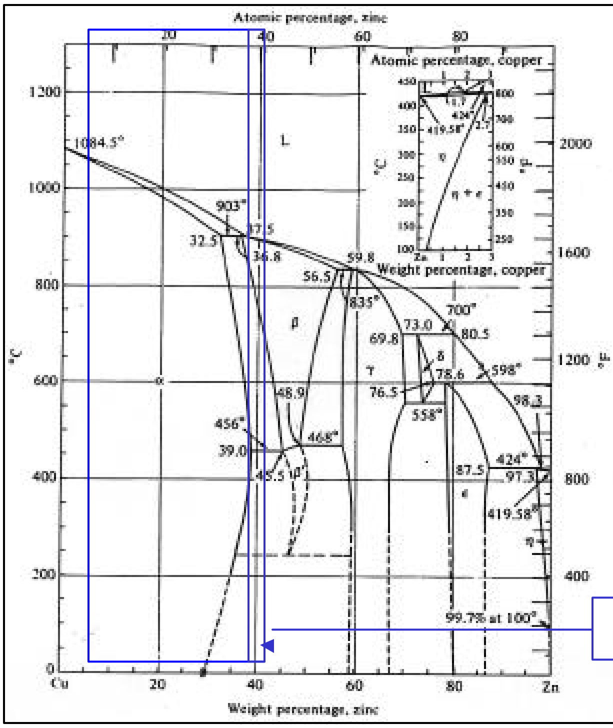
- Electricity conduction (power/data transmission)
- Heat conduction (radiators)
- Marine condensers, or exposed marine fixtures (heat/salt water exposure)
- Coin blanks (pennies)

Brasses

%Cu	%Zn	Brass
95	5	Gilding metal
90	10	Commercial bronze
85	15	Red brass
80	20	Low brass
70	30	Cartridge brass
65	35	Yellow brass
60	40	Muntz metal (a+b)

Cu-Zn
phase diagram

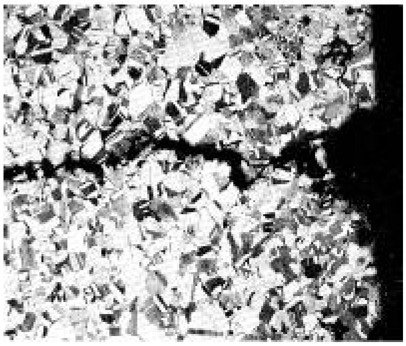




Cu-Zn
Phase
Diagram

Muntz metal and
Naval brass

Stress Corrosion Cracking



Intergranular s.c.c. crack in cartridge brass (70%Cu, 30%Zn)

Susceptible:

- cold worked α brasses
- with Zn>15%
- In presence of trace ammonia with oxygen and moisture

Alleviated by:

- Low-T stress relief

For Each Phase Diagram

- Is there a crystal change?
  – Hardening from heat treatments taking advantage of this: CCT diagrams, critical cooling rate to form a metastable phase…
- Solubility of one phase in another
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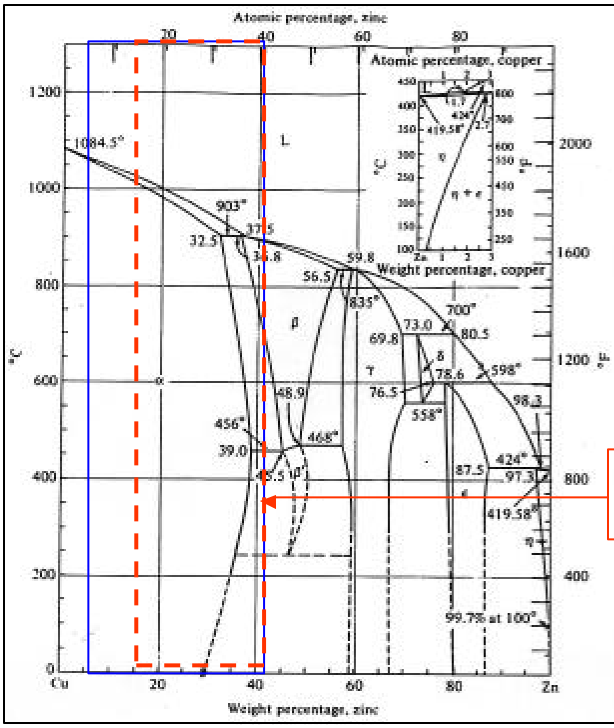
  – Brittle phases, regions susceptible to corrosion



Cu-Zn Phase Diagram

Susceptible to SCC if ammonia, O_2 and H_2O present

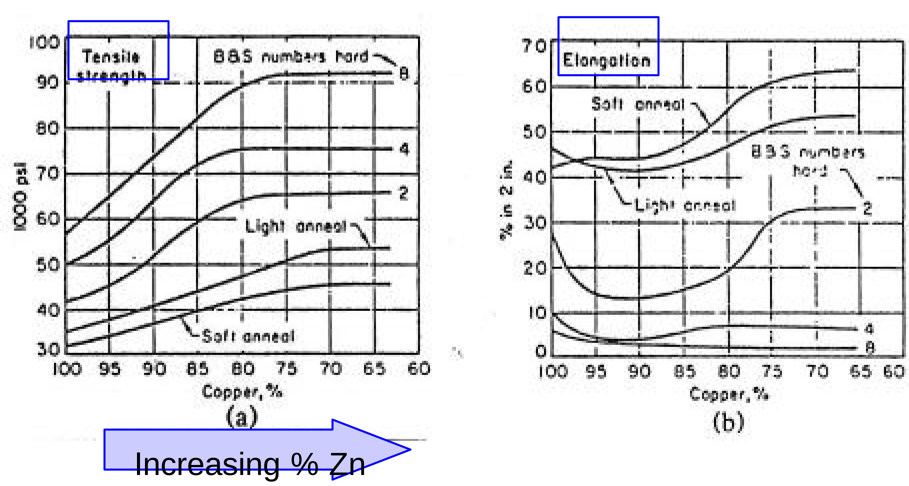
Brasses

- Alloys of Cu-Zn - cheaper than Cu
- Solid solution to ~38% Zn
- 3 alloys:
  - α (cold working alloys),
  - α+β,
  - β (hot working alloys)
- Strength increases a lot in the α+β region
- Ductility drops - β more brittle
- 70-30 or 65-35 brass:
  - high strength,
  - high ductility

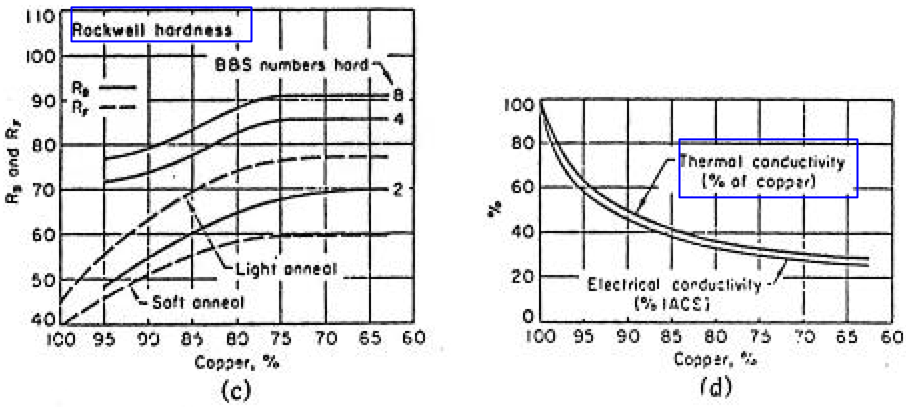
Corrosion: dezincification

- Porous Cu-rich plug forms
- Hi zinc brasses (>15%) susceptible
- when exposed to:
  - high temperature
  - certain environments

Effect of zinc on strength and ductility



Effect of zinc on hardness and conductivity



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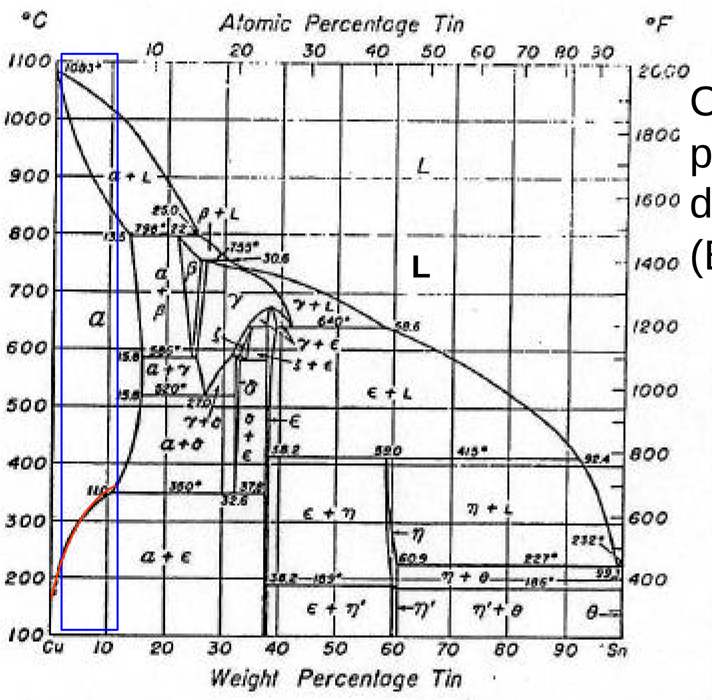
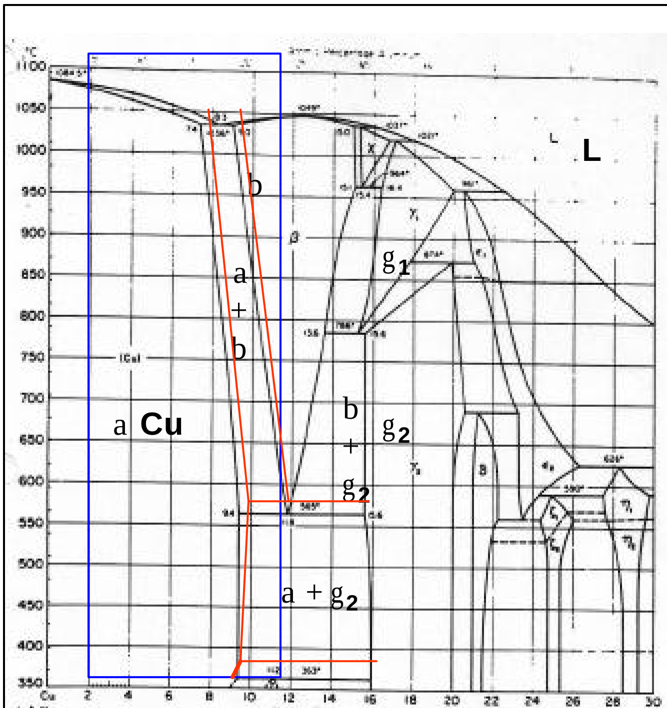
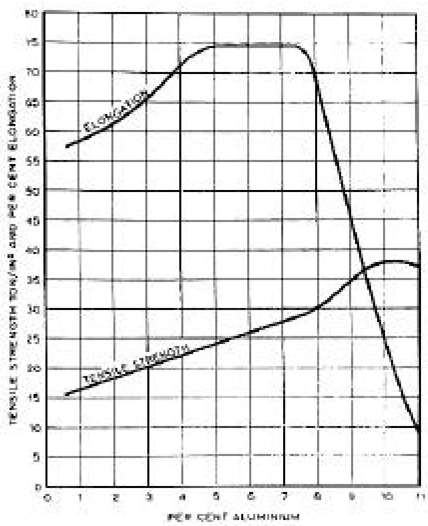


Cu-Sn phase diagram (Bronzes)



Cu-Al phase diagram aluminum bronzes

Influence of Al on properties of bronzes



- Increase ductility
  - (if adding < 8%)
  - what happens at 8%?
- Increase strength

For Each Phase Diagram

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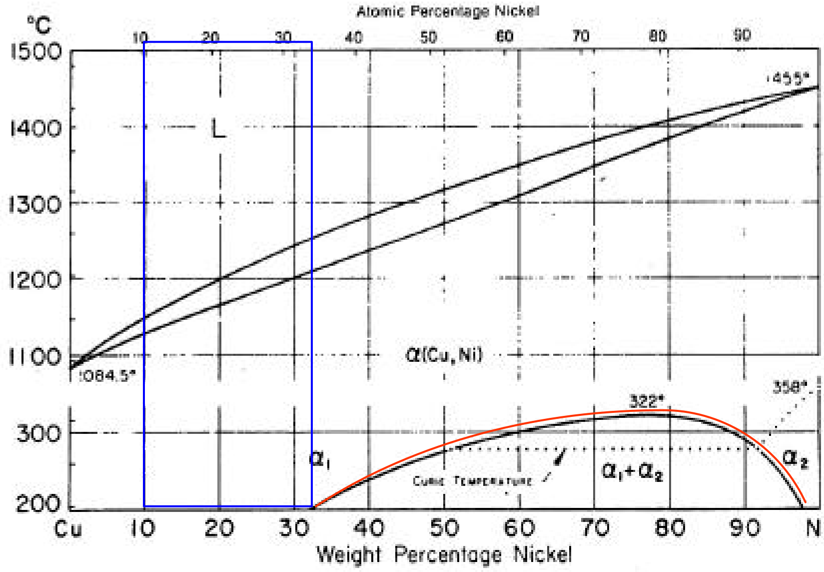
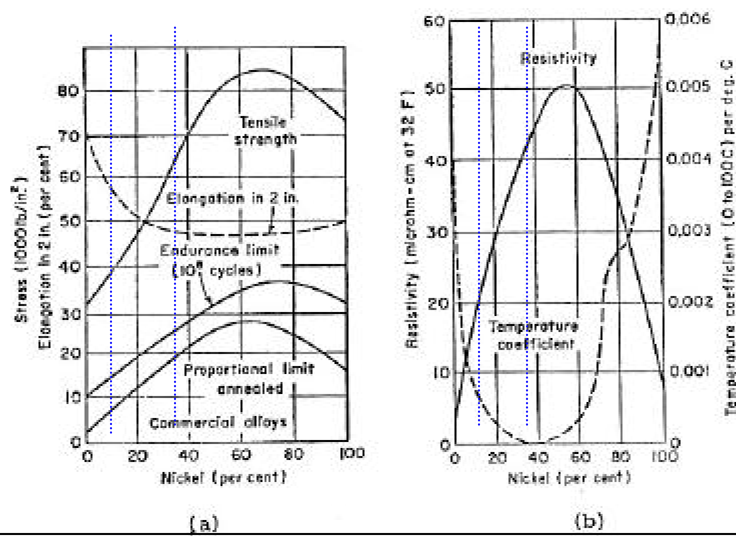
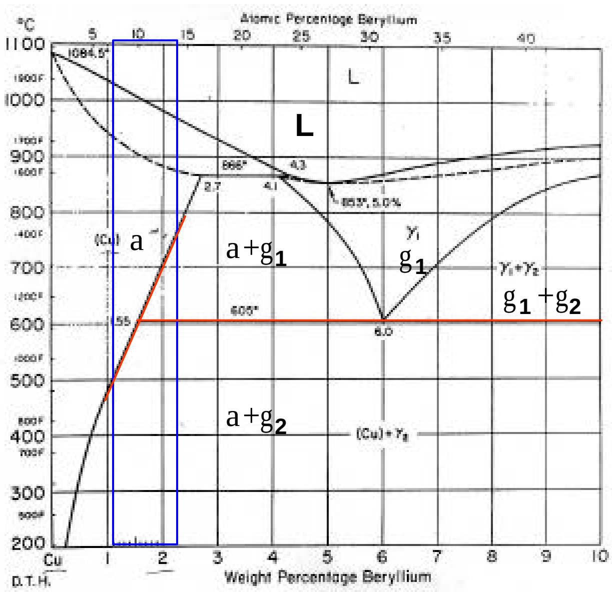
Cu-Ni phase diagram



Influence of Ni on properties



Cu-Be phase diagram



Cu-2%Be alloys:

- Age hardenable

1.87%Be solutionised @ 800ºC, quenched, aged 4h @ 350ºC.

γ'
intermediate CuBe phase