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 (brass)
• 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*.
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 finish parts
- Copper trolley wires
- Copper plating

Electronic products
Copper finish parts
Copper plating

www.bergquistcompany.com
www.kme-extrusion.com
www.silvexinc.com

Tapany Udomphol
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

<table>
<thead>
<tr>
<th>Metals</th>
<th>US dollar/LB</th>
<th>Metals</th>
<th>US dollar/LB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>1.1195</td>
<td>Nickel</td>
<td>12.1109</td>
</tr>
<tr>
<td>Alum Alloy</td>
<td>1.0183</td>
<td>Lead</td>
<td>.4717</td>
</tr>
<tr>
<td>NA Alloy</td>
<td>1.0115</td>
<td>Tin</td>
<td>3.7195</td>
</tr>
<tr>
<td>Copper</td>
<td>3.4332</td>
<td>Zinc</td>
<td>1.4451</td>
</tr>
</tbody>
</table>

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.
Extraction of copper from ores

- **Copper ores** are normally associated with **sulphur** in which **copper** can be extracted from **chalcocite Cu₂S**, **chalcopyrite CuFeS₂** and **cuprite Cu₂O**.

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 off 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.

\[ M + Cu_2O \rightarrow MO + 2Cu \]

• 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 $\text{CuSO}_4 + \text{H}_2\text{SO}_4$
- This high-purity copper is subsequently melted and cast into shapes.
Physical properties of copper and copper alloys

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>FCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>29</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>63.546</td>
</tr>
<tr>
<td>Density (g.cm(^{-3}))</td>
<td>8.933</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1084.62</td>
</tr>
</tbody>
</table>

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

### Electrical and thermal conductivities of pure metals at RT

<table>
<thead>
<tr>
<th>Metal</th>
<th>Relative electrical conductivity (copper = 100)</th>
<th>Relative thermal conductivity (copper = 100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>106</td>
<td>108</td>
</tr>
<tr>
<td>Copper</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Gold</td>
<td>72</td>
<td>76</td>
</tr>
<tr>
<td>Aluminum</td>
<td>62</td>
<td>56</td>
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<tr>
<td>Magnesium</td>
<td>39</td>
<td>41</td>
</tr>
<tr>
<td>Zinc</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>Nickel</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>Cadmium</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>Cobalt</td>
<td>18</td>
<td>17</td>
</tr>
<tr>
<td>Iron</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>Steel</td>
<td>13–17</td>
<td>13–17</td>
</tr>
<tr>
<td>Platinum</td>
<td>16</td>
<td>18</td>
</tr>
<tr>
<td>Tin</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>Lead</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Antimony</td>
<td>4.5</td>
<td>5</td>
</tr>
</tbody>
</table>
Classification of copper and copper alloys

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

<table>
<thead>
<tr>
<th>Wrought alloys</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C1xx</td>
<td>Coppers(^1) and high-copper alloys(^2)</td>
</tr>
<tr>
<td>C2xx</td>
<td>Copper-zinc alloys (brasses)</td>
</tr>
<tr>
<td>C3xx</td>
<td>Copper-zinc-lead alloys (leaded brasses)</td>
</tr>
<tr>
<td>C4xx</td>
<td>Copper-zinc-tin alloys (tin brasses)</td>
</tr>
<tr>
<td>C5xx</td>
<td>Copper-tin alloys (phosphor bronzes)</td>
</tr>
<tr>
<td>C6xx</td>
<td>Copper-aluminum alloys (aluminum bronzes), copper-silicon alloys (silicon bronzes) and miscellaneous copper-zinc alloys</td>
</tr>
<tr>
<td>C7xx</td>
<td>Copper-nickel and copper-nickel-zinc alloys (nickel silvers)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cast alloys</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C8xx</td>
<td>Cast coppers, cast high-copper alloys, the cast brasses of various types, cast manganese-bronze alloys, and cast copper-zinc-silicon alloys</td>
</tr>
<tr>
<td>C9xx</td>
<td>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</td>
</tr>
</tbody>
</table>

\(^1\)“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
   - 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

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% $\textit{Cu}$ with 0.045 $\textit{O}$ content.
- Used for the production of wire, rod plate and strip.
- $\textit{Oxygen}$ is almost insoluble in copper and forms $\textit{Cu}_2\textit{O}$ interdendritic eutectic upon solidification.
- Hot-working process breaks up this $\textit{Cu}_2\textit{O}$ network and appears as $\textit{particles}$ aligned in the working direction.
- Exposed to $\textit{H}_2$ at $T > 400^\circ\text{C}$ leads to pressure build up at grain boundaries, causing fracture. (hydrogen embrittlement)

\[
\text{Cu}_2\text{O} + \text{H}_2(\text{dissolved}) \rightarrow 2\text{Cu} + \text{H}_2\text{O}_{(steam)}
\]
**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$_2$O

- Hot worked microstructure also shows a *clear microstructure* and not affected by hydrogen embrittlement.
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 range of properties.

• **Sn, Al, Si, Mg, Ni, and Pb** are added elements, called ‘**alloy brasses**’.

• **Commercially used brasses** can be divided into two important groups:

  1) **α brasses (hypo-peritectic)** with α structure containing up to ~35% Zn.

  2) **α+β brasses (hyper-peritectic)** with α+β 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 $\alpha$ brasses

- **Microstructures** of the single-phase $\alpha$ brasses consist of $\alpha$ solid solution.

- **Annealing twins** observed in the $\alpha$ 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).

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

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

Increasing Zn content

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**Pure copper**
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**15% Zn**
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**37% Zn**
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**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.

- 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.

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**Microstructure of α+β brasses**

- **40% Zn addition** provides a complex structure of \( \alpha \) and \( \beta \) 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 $\beta'$ in $\alpha+\beta$ Cu-Zn alloys

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

1) **Rod-type $\alpha$ precipitate**

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

2) **Widmanstätten $\alpha$ precipitate**

   Nucleated uniformly throughout the $\beta$ grains and grew rapidly in the lengthwise below the $B_s$ temperature.

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**Section of Cu-Zn phase diagram**

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

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Microstructure of alloy brasses

Copper-Lead alloys (Leaded brasses)

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

- **Monotectic reaction** occurs at 955°C.

  \[
  \text{Liquid}_1(36\%\text{Pb}) \leftrightarrow \alpha(100\%\text{Cu}) + \text{Liquid}_2(87\%\text{Pb})
  \]

- **Eutectic reaction** occurs at 326°C.

  \[
  \text{Liquid}_2(99.94\%\text{Pb}) \leftrightarrow \alpha(100\%\text{Cu}) + \beta(99.99\%\text{Pb})
  \]
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 **α+β** 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**

<table>
<thead>
<tr>
<th>Colour change</th>
<th>Red</th>
<th>Gold</th>
<th>Green yellow</th>
</tr>
</thead>
</table>

- 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 α+β 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).

**Dezincification**

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

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

*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°C.

- Solid solubility limit of **Cu-Sn** is lower than that of **Cu-Zn**
- Upto about 11% **Sn**, precipitation of *ε phase* is found sluggish when cooled from above 350°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.

**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) up to 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.

![Cu-Al phase diagram](image)

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

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Cu-Al phase diagram

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**Microstructure and heat treatment of the complex aluminium bronzes**

- From *Cu-Al phase diagram*, the $\beta$ phase is introduced when the *Al content* is above 8% at $T > \sim 900^\circ C$. → complex microstructure.
- Above 9.5% *Al*, quenching from $\sim 900^\circ C$ gives almost $\beta'$ *martensites*, fig (a).
- Slowly cooled to 800 or 650$^\circ C$ and quenched gives less $\beta$ *martensites*, fig (b) and (c).
- Cooled to 500$^\circ C$ and quenched, the $\beta$ phase will decompose to form $\alpha + \gamma_2$, fig (d).

\[ \beta \leftrightarrow \alpha + \gamma_2 \] (aluminium bronze pearlite)

$\beta'$ martensite → strength, Ductility → brittle
Tempering of $\beta'$ martensite

- Good properties can be achieved by tempering $\beta'$ martensite at 450-600°C.
- Very fine $\alpha$ phase precipitates along crystallographic planes provide good strength and ductility.

![Tempering of $\beta'$ martensite at different temperatures in Cu-10%Al.](image)

(a) Soaked 1 h and quenching from 900°C.
(b) Tempered 1 h at 400°C.
(c) Tempered 1 h at 500°C.
(d) Tempered 1 h at 600°C.
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 $\beta$ 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**.

- **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°C.
- **Cu-Be alloys** with up to 2% **Be** are **precipitation hardenable** due to a rapid decrease in **Be** solubility.

- **Cu-Be alloys** can be **solution heat-treated** (at ~800°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.

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Cu-Be phase diagram

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**Precipitation sequence and microstructure**

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

\[
\text{SSSS} \rightarrow GP \text{ zones} \rightarrow \gamma' \rightarrow \gamma
\]

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

- Increasing **ageing temperature** (~380°C) produces **equilibrium ordered BCC \(\gamma\) phase CuBe** (eutectoid structure), *fig (b).* → **overageing** → **decreased hardness.**
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.
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.
- **α+β** 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
• www.cda.org.uk.