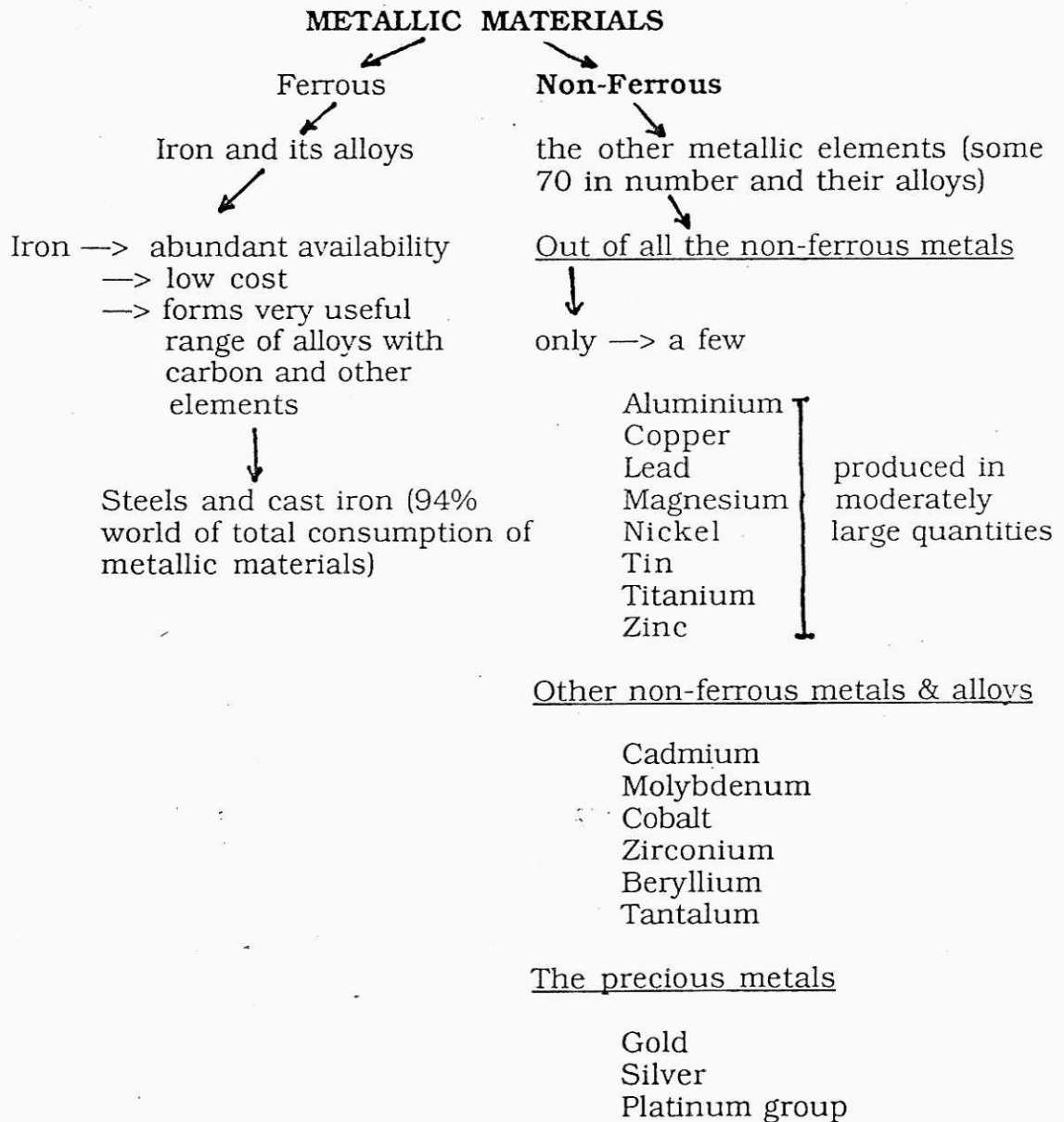


PHYSICAL METALLURGY OF SOME IMPORTANT NON-FERROUS METALS AND ALLOYS

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It is the purpose of this lecture to discuss some of the important non-ferrous metals and alloys from the aspect of physical metallurgy. Particular emphasis is placed on their commercial importance. Portions of tentative equilibrium diagrams are presented for a number of non-ferrous alloys. Numerous photomicrographs have been used to illustrate typical structures. For complete understanding, the reader is requested to consult the references given at the end of the notes.



I. COPPER AND COPPER ALLOYS

Copper → one of the oldest metals known to man

Pure Copper → Properties

Melting point	1083°C
Crystal structure	face centered cubic
Density	$8.93 \times 10^3 \text{ kg/m}^3$
Young's modulus, E	122.5 GPa
Tensile strength	220 MPa
Electrical resistivity	$1.67 \times 10^{-8} \Omega \text{ m}$ at 20°C
Corrosion resistance	Very good

- * High electrical conductivity,
- * High thermal conductivity,
- * Good corrosion resistance,
 - * Good machinability,
 - * Good strength,
 - * Ease of fabrication
 - * Non-magnetic
- * Has a pleasing colour
 - * Pure copper is red
- * Zinc additions produce a yellow colour
- * Nickel addition produce a silver colour
 - * Can be welded, soldered, brazed
- * Is easily finished by plating or lacquering

Applications → Pure copper → extensively used for →

- o Sheet, for architectural cladding
- o Tubes, for heat exchangers and domestic installations
- o Cables; wires → for electrical windings
- o electrical contacts
- o wide variety of other parts that are required to pass electrical current → i.e. electrical conductors

99.9% Cu
0.02 to 0.05% oxygen

→ This is electrolytic tough-pitch copper (ETP)

combined with copper as the compound cuprous oxide (Cu_2O)

or
oxygen-free high conductivity copper (OFHC)

As cast, copper oxide and copper form an interdendritic eutectic mixture (Fig.1).

After working and annealing, the interdendritic network is destroyed and the strength is improved (Fig.2).



Fig.1 : Copper-copper oxide eutectic in cast tough-pitch copper.
Lightly etched with sodium dichromate

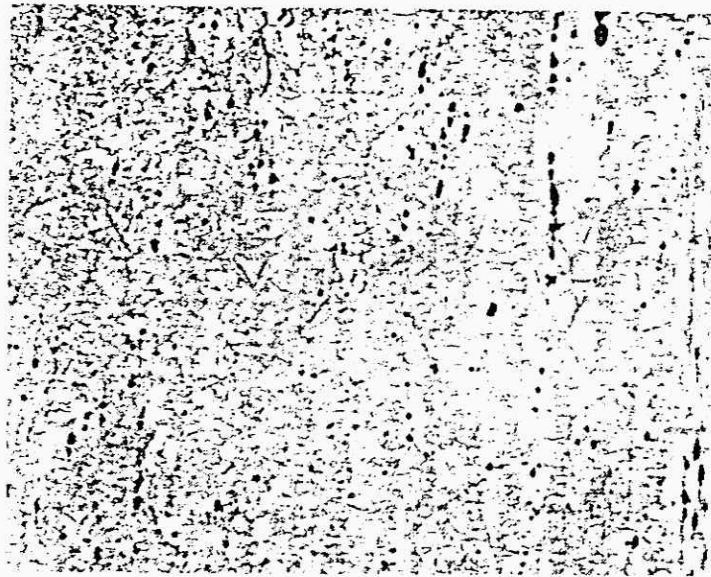


Fig.2: Particles of copper oxide (black spots) in wrought
tough-pitch copper. Lightly etched in ammonium
hydroxide and hydrogen peroxide

Types of Copper

Arsenical copper
about 0.3% arsenic

Free-cutting copper
0.6% tellurium

Silver-bearing copper
7 to 30 oz per ton

Copper may be alloyed with a number of elements to provide a range of useful alloys.

Most important commercial copper alloys

1. **Brasses** - alloys of copper and zinc
 - A. Alpha brasses - alloys containing up to 36% zinc
 - i) Yellow alpha brasses - 20 to 36% zinc
 - ii) Red brasses - 5 to 20% zinc
 - B. Alpha plus beta brasses - 54 to 62% copper
2. **Bronzes** - up to 12% of alloying element
 - A Tin bronzes
 - B Silicon bronzes
 - C Aluminium bronzes
 - D Beryllium bronzes
3. Cupronickels - alloys of copper and nickel
4. Nickel silvers - alloys of copper, nickel, and zinc.

Designations system for copper-base alloys

Wrought alloys

100xx	-	159xx	Commercially pure Cu
160xx	-	199xx	Nearly pure Cu but age hardenable due to Cd, Be or Cr
		2xxxx	Cu-Zn (brass)
		3xxxx	Cu-Zn-Pb (leaded brass)
		4xxxx	Cu-Zn-Sn (tin bronze)
		5xxxx	Cu-Sn and Cu-Sn-Pb (phosphor bronze)
		6xxxx	Cu-Al (aluminium bronze)
		7xxxx	Cu-Ni (cupronickel), Cu-Ni-Zn (nickel silver)

Cast alloys

800xx	-	811xx	Commercially pure Cu
813xx	-	828xx	95-99% Cu
833xx	-	899xx	Cu-Zn alloys containing Sn, Pb, Mn, or Si
		9xxxx	Other copper alloys, including tin bronze, aluminium bronze, cupronickel and nickel silver

Brasses - general

- * Commercially important alloys of copper and zinc
- * Have composition up to 40% Zn
- * Addition of zinc to copper increases in strength because zinc enters into solid solution in the copper.
- * Unusual feature : ductility also increases with dissolved zinc content, reaches a maximum ductility value at a zinc content of 30%
- * Zinc is cheaper than copper, so brasses are more economical than pure copper.
- * Brasses are widely used in a variety of applications
- * where electrical conductivity is important, pure Cu is used.

Copper - zinc phase diagram (Fig.3)

- * This portion of binary alloy phase diagram is applicable to commercial alloys (from 0 to 40%). Zinc melts at 419°C and copper at 1083°C
- * The solubility of zinc in the alpha (α) solid solution increases from 32.5% at 903°C to about 39% at 400°C.
- * Since copper is fcc, the α solid solution is fcc.
- * β phase is bcc, changes from random to ordered structure in the region of 454°C to 468°C as indicated by the broken line on the diagram.
- * This β^1 is still bcc but Cu atoms at the corners and the zinc atoms at the centers of the unit cubes.
- * On cooling in this temperature range, the bcc β phase, with Cu and Zinc atoms randomly dispersed at lattice points, changes continuous to the ordered structure β^1 .
- * But ordering takes place in certain solid solution alloys at specific composition ranges.
- * The ordering reaction is so rapid that it cannot be retarded or prevented by quenching.

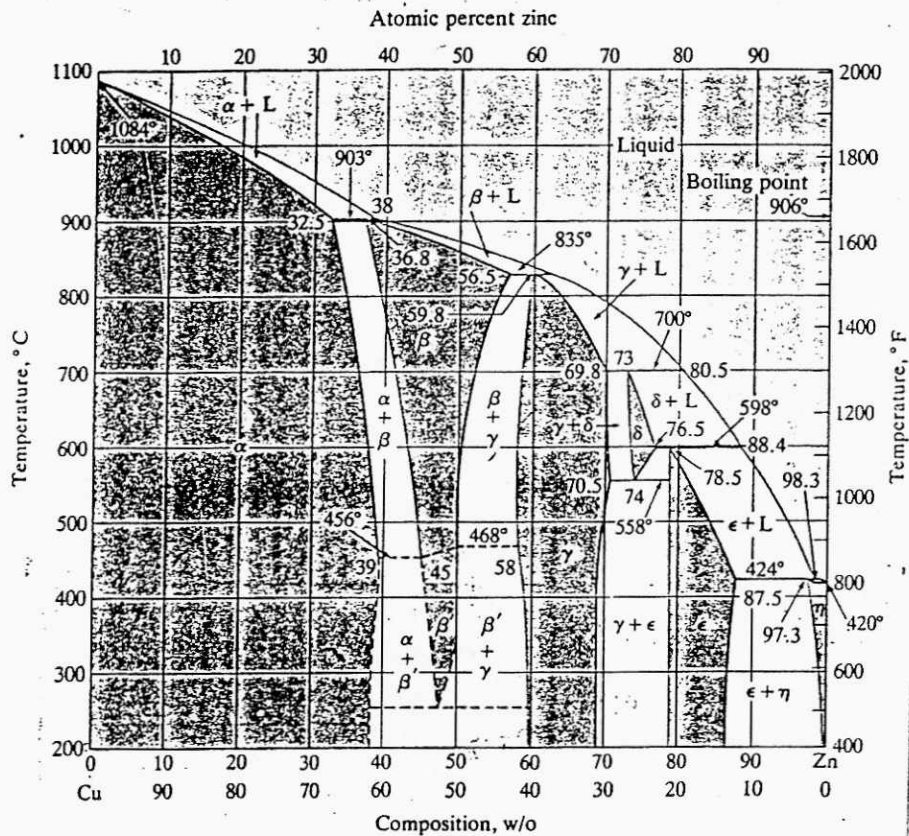


Fig.3 : Copper-zinc phase diagram

Commercial Brasses

α Brasses

* for cold working

$\alpha + \beta$ Brasses

* for hot working

Yellow α Brasses

- * Contain 20 to 36% zinc
- * Good strength & high ductility
- * Common practice : Stress relief anneal after cold working to prevent season cracking/stress corrosion cracking.
- * This is because of high residual stresses left in the brass as a result

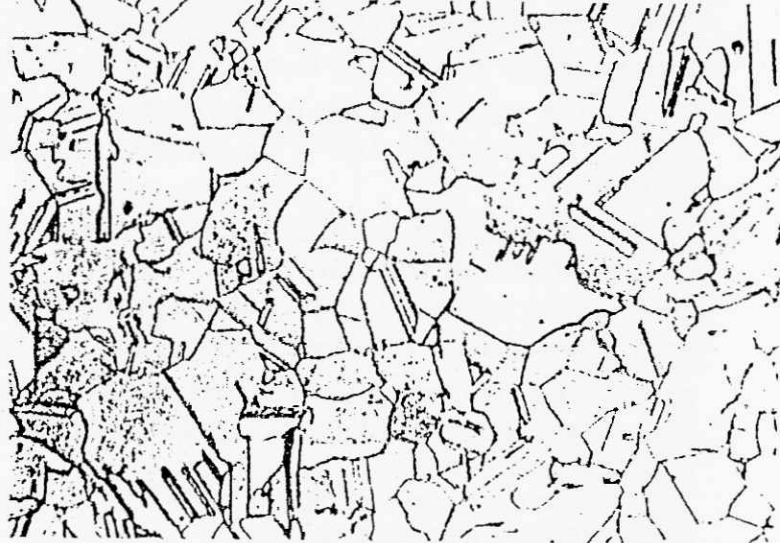


Fig.4 : Micrograph of cold worked and annealed deoxidized copper. Some of the equiaxed crystals show pronounced annealing twins. α Brass and other α -phase copper alloys have a similar microstructure

- * Yellow α brasses are also subject to a pitting corrosion, called **Dezincification**. When brass is in contact with sea water or fresh waters that have a high content of oxygen and carbon dioxide.

Dezincification : Dissolution of the alloy and a subsequent deposition of porous nonadherent copper. Action of this kind, unless stopped, will eventually penetrate the cross section of the metal and lead to leakage through the porous copper layer. Small amounts of tin/antimony minimize dezincification in yellow brasses.



Fig. 5 : Stress-corrosion cracking in α brass (cartridge brass)

- * Most widely used yellow α brasses : Cartridge brass, **70 Cu - 30 Zn**
- * Used for the manufacture of cartridge and shell cases because of its high ductility (Refer Fig. 5).

Red Brass

- * Contain between 5 and 20% zinc
- * better corrosion resistance than yellow brasses
- * not susceptible to season cracking or dezincification

For example, * Gilding metal \rightarrow 95 Cu - 5 Zn \rightarrow used for coins, medals tokens, emblems.

- * Commercial bronze \rightarrow 90 Cu - 10 Zn \rightarrow costume jewelry, lipstick cases, marine hardware, screws, rivets
- * Red brass \rightarrow 85 Cu - 15 Zn \rightarrow electrical circuit, sockets, heat-exchanger tubes
- * Low brass \rightarrow 80 Cu - 20 Zn \rightarrow ornamental metal work, thermostat bellows, musical instruments.

$\alpha + \beta$ Brass

- * Contain from 54 to 62% copper, remaining zinc
- * Consider Fig.3, these alloys consist of two phases α and β^1
- * β^1 is harder and more brittle at room temperature than α
- * That's why, these alloys are more difficult to cold-work than the α brasses
- * At elevated temperatures, the β phase becomes very plastic
- * Therefore, heat-treat into the single phase β , region then they have excellent hot-working properties

Most widely used $\alpha + \beta^1$ brass : **Muntz metal** (60 Cu - 40 Zn)

- * High strength & excellent hot-working properties.

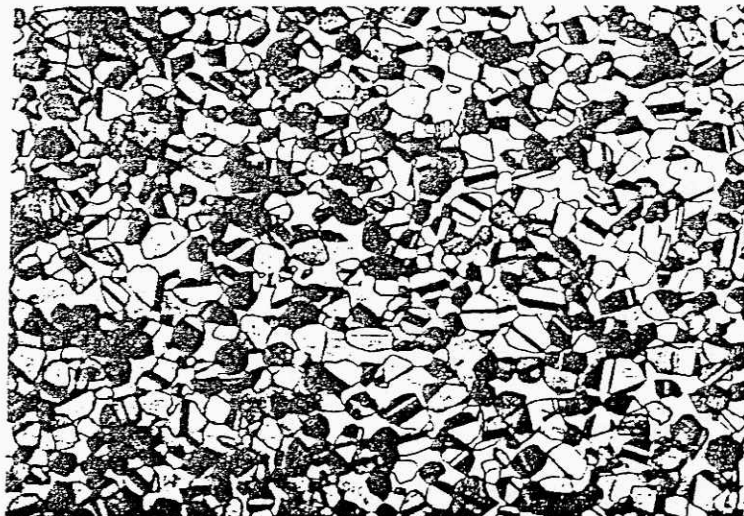


Fig.6: Two-phase structure of annealed muntz metal. Light area is β . Dark area is α . Etched in ammonium hydroxide and hydrogen peroxide

- * Rapid cooling from the β region may suppress the precipitation of most of the α phase. The quench preserved most of the β , but some α has formed, particularly at the grain boundaries.
- * Subsequent reheating to a low temperature will allow more of the α to come out of the supersaturated solid solution. Therefore it is possible to heat treat this alloy.

Uses : in the sheet form \rightarrow for ship sheathing, condenser heads, perforated metal, architectural work, valve stems, brazing rods, condenser tubes.

- * If we add 0.40 to 0.80% Pb to Muntz metal, machinability will be improved.

Naval Brass : also known as "tobin bronze" 60 Cu - 39.25 Zn - 0.75 Sn

- * High resistance to salt-water corrosion

Uses : Condenser plate, welding rod, piston rods, propeller shafts, valve stems.

Note : The structures of high-tensile brasses are generally $(\alpha + \beta)$, but may sometimes be wholly β . Used in the form of castings and hot worked products.

Typical Applications

- 1) For the manufacture of ships' screws and marine fittings
- 2) In the brazing alloys.

Important : No commercial alloys are made containing more than 50% zinc, as above this value, the presence of γ phase in the structure would embrittle the alloy.

BRONZES

- * originally they are copper-tin alloys
- * Now, any copper alloy contains up to $\sim 12\%$ principal alloying element (except Cu-Zn alloys).
- * Commercial bronzes are primarily alloys of Cu and tin, aluminum, silicon or beryllium.

Bronzes

Tin bronzes	Silicon bronzes	Aluminium bronzes	Beryllium bronzes	Cupronickels	Nickel silicon
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1. Tin bronzes :

- * Generally referred to as phosphor bronzes because phosphorus is always present as a deoxidizer in casting
- * Tin between 1 and 11%

* Phosphorus between 0.01 and 0.5%

Refer Fig.7 →

1. The β phase, within the limits shown, forms as the result of a peritectic reaction between α and melt of 25% tin at 798°C
2. β is bcc and transforms eutectoidally at 586°C to $\alpha + \gamma$, γ is also bcc
3. Now, γ undergoes a eutectoid transformation at 520°C to α and δ ($\text{Cu}_{31}\text{Sn}_8$) → new two-phase constituent ($\alpha + \delta$)
4. Again, δ phase by eutectoid reaction at 350°C to ($\alpha + \epsilon$)
5. The solvus line on the diagram below 520°C indicates a decrease in the solubility of tin as the α phase cools. These changes are so sluggish, so they may be disregarded. So, for all practical purposes, the reaction $\delta \rightarrow \alpha + \epsilon$, may be considered non-existent.

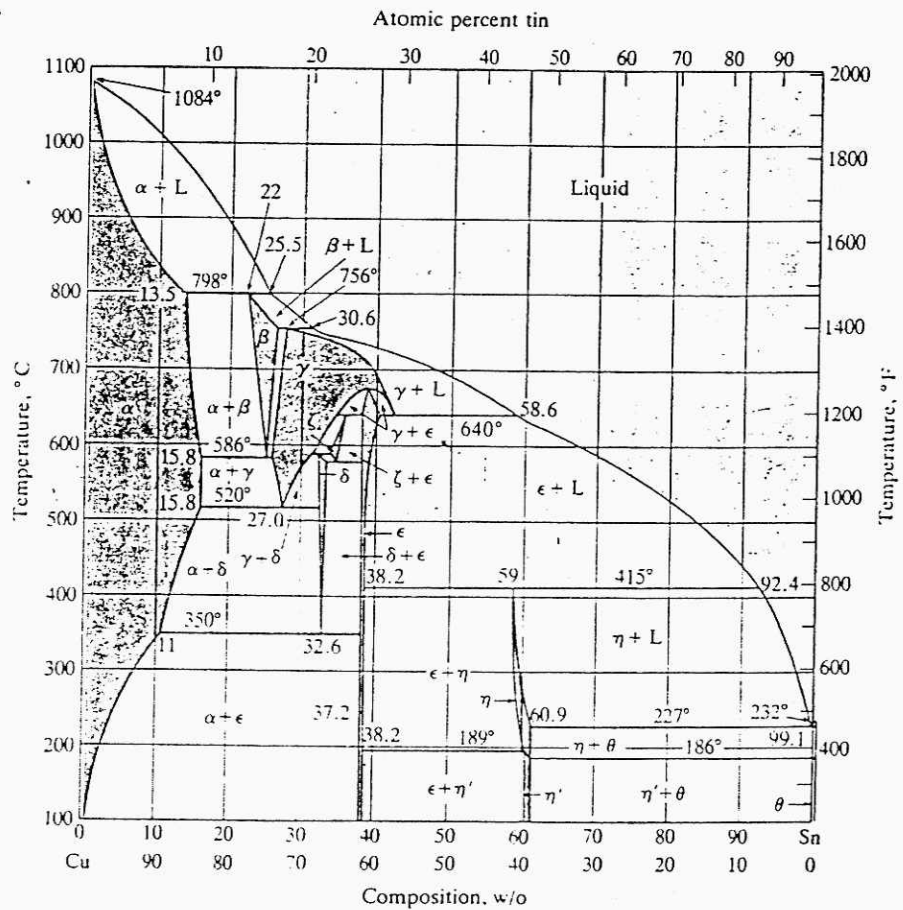


Fig.7 : Copper-tin alloy system

Properties : High strength, toughness, high corrosion resistance, low coefficient of friction. freedom from season cracking

Applications : Diaphragms, bellows, lock washers, cotton pins, bushings, clutch disks, springs

2. Silicon Bronzes

Commercial silicon bronzes, generally contain < 5% Si are SINGLE PHASE ALLOYS (α). α is fcc. So these alloys are **not hardenable** by heat treatment.

Properties :

1. Silicon bronzes are the strongest of the work-hardenable copper alloys.
2. Mechanical properties comparable to those of mild steel & corrosion resistance comparable to that of copper.

Applications: Tanks, pressure vessels, marine construction, hydraulic pressure lines

3. Aluminum Bronzes

- * Most commercial aluminium bronzes → contain 4 to 11% Al

Single phase Al-bronzes

- Properties :**
1. Good cold working properties
 2. Good strength combined with corrosion resistance to atmospheric and water attack

Uses : Condenser tubes, corrosion-resistant vessels, nuts, bolts, for protecting sheathing in marine applications.

Two-phase Al-bronzes :

1. They can be heat-treated to obtain structures similar to those in steel.
2. Cold-working properties are not good
3. $\alpha + \beta$, Al-bronzes are quench hardenable water quenched from 815 - 870°C and Tempered at 370 - 590°C to increase strength and hardness
4. 10.7% Al bronze quenched (β) → martensite β
5. On furnace cooling from above the eutectoid temperature, β will transform to a lamellar structure resembling pearlite in steel.

Uses : Heat treated ones; gears, propeller hubs, blades, pump parts, bearings, bushings, nonsparking tools, drawing and forming dies.

Beryllium Bronzes

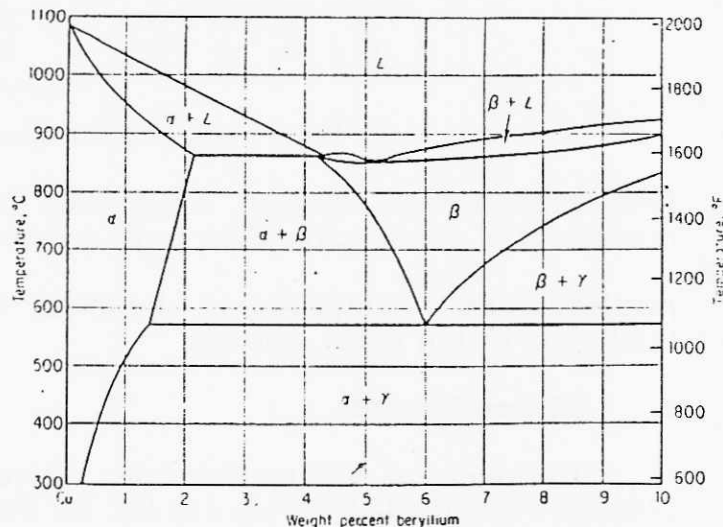


Fig.8 : Copper-rich portion of the copper-beryllium alloy system

1. The solubility of beryllium in the α solid solution decreases from 2.1% at 1590°F to less than 0.25% at room temperature.
2. This indicates the possibilities of **age-hardening**

For a given alloy \rightarrow two principal methods to increase strength & hardness : (1) **cold working**, (2) **heat-treatment**

For **non-ferrous alloys** \rightarrow heat treatment \rightarrow age hardening/precipitation hardening

Conditions : (1) Most metals show some solubility for each other in the solid state and therefore they form solid solutions. So, the **equilibrium diagram must show partial solid solubility**. (2) The slope of the solvus line must be such that there is greater solubility at a higher temperature than at a lower temperature i.e. **the solid solubility limit should decrease with decreasing temperature**.

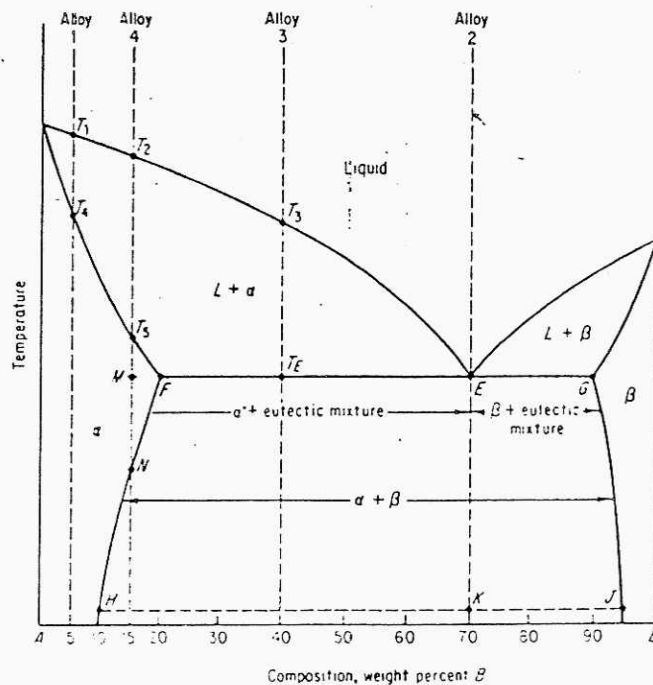


Fig.9: Phase diagram illustrating partial solid solubility

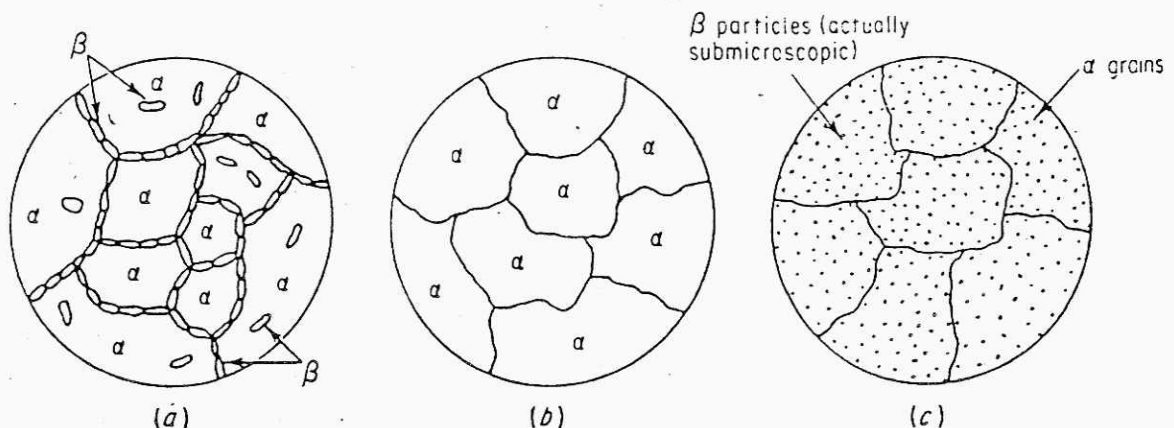


Fig.10 : Microstructure of an 85A-15 B alloy

Solution Treatment

- * Alloy 4 microstructure is shown in Fig.10(a)
- * This alloy is reheated to point M, then all the excess β will be dissolved and the structure will be a homogeneous α solid solution
- * Now, this alloy is rapidly cooled (quenched) to room temperature
- * A supersaturated solid solution (SSS) forms (with excess β trapped in solution). Now the microstructure looks like Fig.10(b).
- * The SSS is unstable and the excess solute will tend to come out of solution. The speed at which precipitation (by nucleation and growth process) occurs varies with temperature. This is called **Ageing**. This will lead to hardening.
- * The size of the precipitate becomes finer as the temperature at which precipitation occurs is lowered.
- * Extensive hardening of the alloy is associated with a critical dispersion of the precipitate.
- * If ageing is too far at any given temperature, coarsening of precipitates occur (the small ones tend to re-dissolve, and the large ones to grow still larger), the alloy becomes softer.

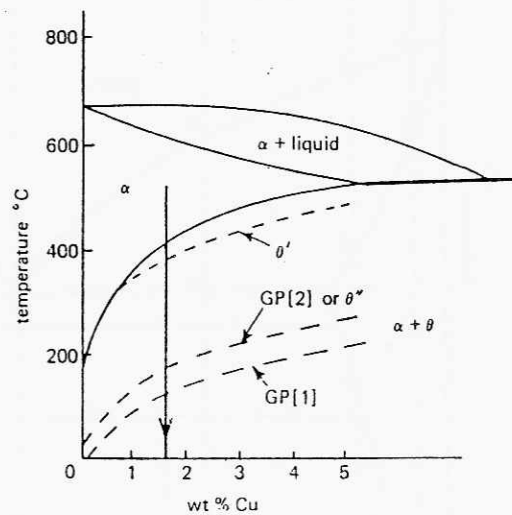


Fig. 11 : Al-rich Al-Cu binary diagram showing GP (1) θ'' and θ' solvus lines (dotted)

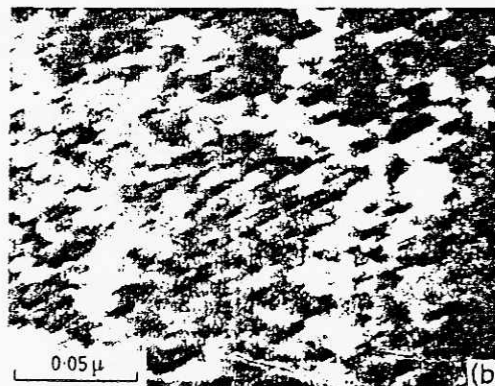


Fig.12 : TEM of Al-4% Cu aged 16 hrs. at 130°C showing GP(1) zones

5. Cupronickels :

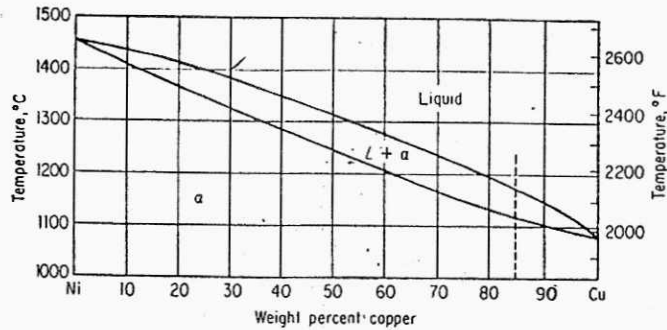


Fig.13 : Copper-nickel equilibrium diagram

1. It shows complete solubility (both at liquid & solid states)
2. That is why, all cupronickels are single-phase alloys
3. They are **not heat-treatable**
4. Their properties change only by **cold working**.

Properties : (1) High resistance to corrosion fatigue (2) High resistance to corrosive & erosive action of rapidly moving sea water.

Uses : Condenser, distiller, evaporator, heat exchanger tubes, nickel silvers → for naval vessels & coastal power plants.

6. Nickel Silvers

- * Essentially ternary alloys of copper (50-70%) nickel (5-30%) zinc (5-40%)

Properties : Excellent base metals for plating with chromium, nickel or silver.

Uses : Rivets, screws, zippers, costume jewelry, nameplates, radiodials.

Important etchants for coppers, brasses, bronzes, nickel silver, aluminum bronze

1. 20 ml NH_4OH , 0-20 ml H_2O , 8-20 ml H_2O_2
Immersion or swabbing 1 minute.
2. CrO_3 (saturated aqueous solution)
Immersion or swabbing
3. 10 g $(\text{NH}_4)_2 \text{S}_2\text{O}_8$ and 90 ml H_2O
Immersion : use cold or boiling
4. 5 g FeCl_3 , 100 ml ethanol, 5-30 ml HCl
Immersion or swabbing for 1 second to several minutes
5. 5 Parts HNO_3 , 5 parts acetic acid, 1 part H_3PO_4
Immersion
6. Equal parts of NH_4Cl and H_2O
Immersion

II. LEAD AND LEAD ALLOYS

Properties

- * Melting point : 327°C
- * Crystal structure: face centered cubic
- * Density : $11.34 \times 10^3 \text{ kg/m}^3$
- * E : 16.5 GPa
- * Electrical resistivity : $2.1 \times 10^{-7} \Omega \text{ m}$ at 20°C
- * corrosion resistance : very good
- * Heavy weight, High density, Softness, Malleability, Low melting point, Low strength, Lubricating property, Low electrical conductivity, High co-efficient of expansion, High corrosion resistance

Uses : In the manufacture of storage batteries, In the high-grade points as lead compounds, As a shielding material against β rays/r rays/nuclear waste (because of its high density), Because of its softness, for gaskets, Because of its flexibility, for cable sheathing, In chemical industry, because of its high corrosion resistance, As a roofing material, Bearing metals, Solders

Common Etchant : 3 Parts acetic acid, 4 parts nitric acid (conc), 16 parts distilled water.

Procedure : Use freshly prepared solution at 40-42°C

Immerse specimen for 4-30 min : clean with cotton in running water.

Lead-tin equilibrium diagram (Fig.14)

1. Alloy 1 contains 70% tin, is to the right of the eutectic composition. The microstructure consists of primary β dendrites (white) surrounded by the eutectic mixture (Fig.15a).
2. Alloy 2 is the eutectic composition : This is known as tinman's solder. Microstructure --> very fine mixture of α and β solid solutions Fig.15b. Back-scattered SEM. α is white, β is dark.

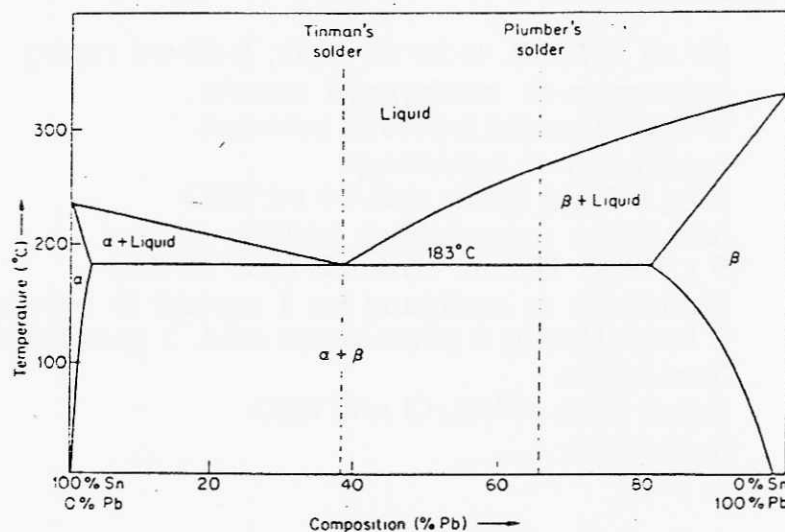


Fig.14 : Lead-tin equilibrium diagram

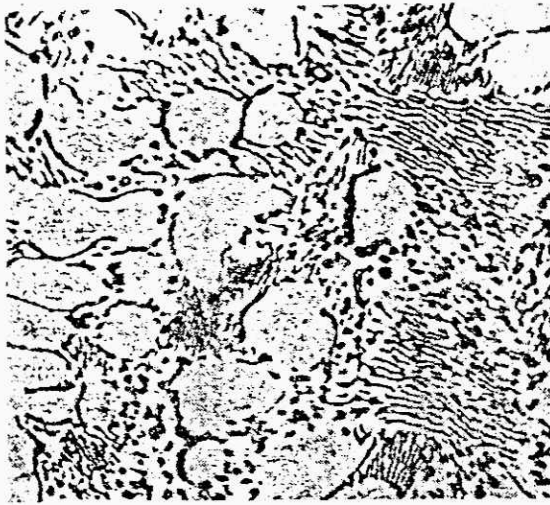


Fig.15(a)

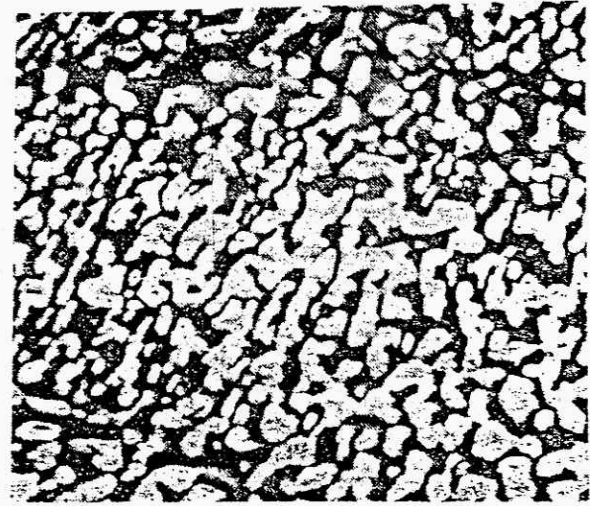


Fig.15(b)

Lead-base Babbitts or white metal alloys

- * Known as bearing materials
- * They should possess sufficient hardness and wear resistance so that it does not wear away during service but its hardness should be low relative to the shaft or journal in order to avoid wear or damage to the shaft, particularly during a start-up when, because of low oil pressure, there may be metal-to-metal contact.
- * The strength of the bearing material should be sufficient to sustain the load without deformation and yet possess considerable toughness to resist shock loading.
- * These requirements can be met by metallic alloys possessing a duplex structure with hard constituents to sustain the load embedded in a softer and tough matrix.
- * They are used in automotive connecting rods, main and camshaft bearings, diesel engine bearings, electric motor bearings.

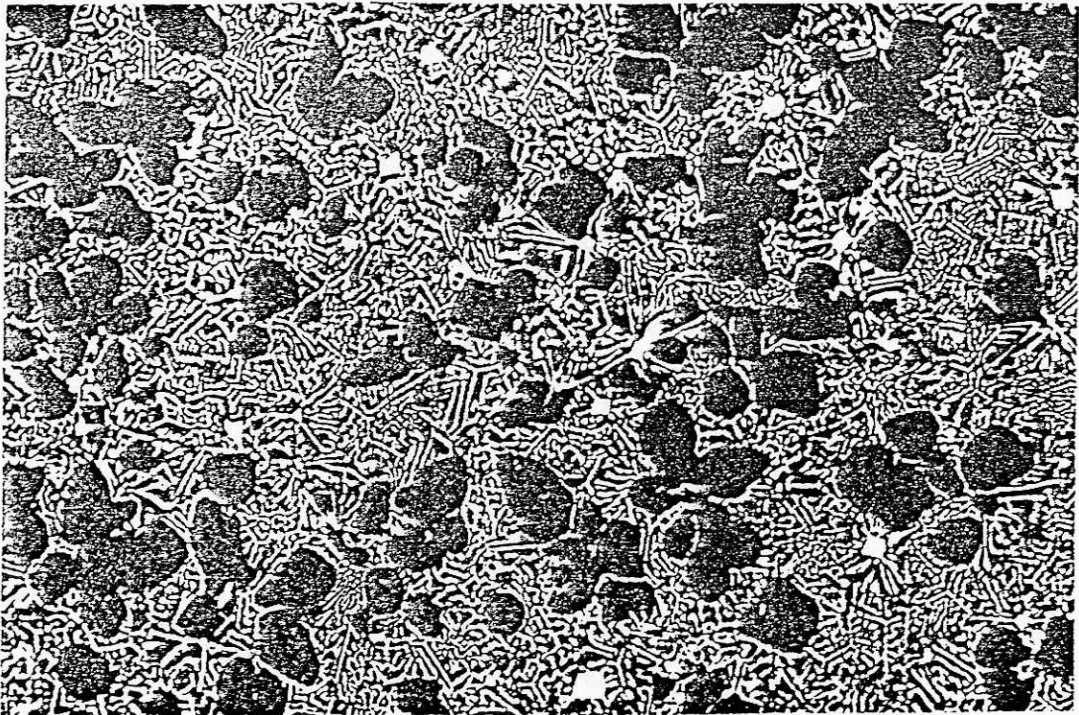


Fig. 16 : Lead-base babbitt (Pb-10 Sb-5 Sn-0.5 Cu)
Etchant : 15 ml acetic acid, 20 ml nitric acid, 80 ml water at 42°C

- * Features: (1) Dendritic grains of lead rich solid solution (black), (2) Primary cuboids of antimony-tin intermetallic phase (white), (3) matrix: ternary eutectic; (a) antimony-rich solid solution (white) (b) lead-rich solid solution (black) (c) antimony-tin phase (also white).

Tin and Tin Alloys

Properties

Melting point	:	232°C
Crystal structure	:	Body centered tetragonal
Density	:	$7.29 \times 10^3 \text{ kg/m}^3$
E, Young's modulus	:	40.8 GPa
Electrical resistivity	:	$1.15 \times 10^{-7} \Omega \text{ m}$ at 20°C
Corrosion resistance	:	Very good

Uses

1. Tin is an ideal metal for coating mild steel to make tin-plate for the manufacture of cans because tin is attractive in appearance, low melting point, good corrosion resistance and lack of toxicity. In the beginning, tin-plate was made by dipping sheets of mild steel into baths of molten tin. Now-a-days it is done by electrolysis.
2. Used in the manufacture of white metal bearings.
3. As an alloying element.
4. Earlier, tin foils were used for packaging, because of its high price, aluminium is being used now-a-days.

General Etchants

1. 2 ml HCl, 5 ml HNO₃, 93 ml methanol : Immersion
2. 5 ml HCl, 2g FeCl₃, 30 ml H₂O, 60 ml methanol or ethanol : Immersion
3. Picral (4g picric acid, 100 ml methanol or ethanol) : Immersion

Tin-base Babbitts

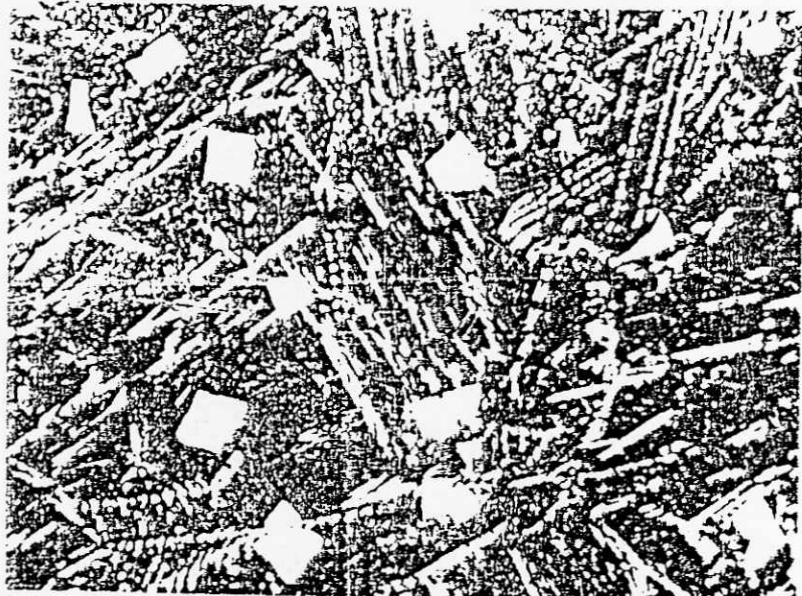


Fig.17 : Tin-base babbitt (80% Sn, 11% Sb, 6% Pb, 3% Cu). Showing cuboids of SbSn and network of Cu₆Sn₅ needles

1. Tin and antimony combine to form a very hard intermetallic compound, with the formula SbSn.
2. SbSn appear as cuboids
3. They appear in a soft matrix of ternary tin-lead-antimony eutectic
4. During the solidification of bearing metals, the hard SbSn cuboids solidify from the liquid first.
5. Since they are having low density, they come to the surface of the liquid metal.
6. To prevent the presence of SbSn cuboids (to some extent), copper (~ 3%) is added to the alloy.
7. Now, Cu₆Sn₅ (intermetallic compound) → which is hard, solidifies first
8. Cu₆Sn₅ looks like needle-shaped crystals
9. They form a continuous network throughout the melt.
10. This network largely prevents the SbSn cuboids from segregating to the surface of the melt when they begin to solidify.

IV. TITANIUM AND TITANIUM ALLOYS

Properties

Melting point	:	1660°C
Crystal structure	:	Close packed hexagonal(α) up to 880°C body centered cubic (β) above 880°C
Density	:	4. 54 x 10 ³ kg/m ³ (low density)
E, Young's modulus	:	106 GPa
Tensile strength	:	30 MPa (relatively high strength)
Corrosion resistance	:	Excellent (with respect to most acids, alkalies and chlorides)
*		Processing of titanium is difficult and costly
*		At very high temperatures (>700°C), titanium will readily dissolve oxygen, nitrogen and carbon, all of which cause embrittlement. (Small amounts will cause strengthening, with loss of ductility).

Commercially Pure Titanium : Lower strength, more corrosion resistant, less expensive than Ti alloys

Uses : Applications requiring high ductility for fabrication but little strength, such as : chemical process piping, valves and tanks, aircraft firewalls, compressor cases

Titanium Alloys

- * Addition of alloying elements to titanium will influence the $\alpha \rightarrow \beta$ transformation temperature.
- * α stabilizers/ β stabilizers (this happens because of the number of bonding electrons).
- * α stabilizers : aluminium and oxygen (most important)
 - they dissolve preferentially in the α phase
 - expand this field
 - raise the α/β transus
- * β stabilizers : molybdenum, vanadium
 - they depress the α/β transus and stabilize the β phase

- * Neutral element : Zirconium, tin and silicon
 - they do not have effect on either α or β phases

Alpha Alloys

- * The compositions of these alloys are balanced by high aluminium content so that the alloys are essentially one-phase alpha.
- * Because of the one-phase microstructure, weldability is very good.
- * Because of the aluminium, retention of strength at high temperature is obtained. **They cannot be strengthened by heat treatment (Ti-5 Al- 2.5 Sn).**

Applications :

Aircraft tail pipe assemblies, formed sheet components operating up to 900°F, missile fuel tanks and structural parts operating for short times up to 1100°F.

Alpha -Beta Alloys

- * Contain enough beta-stabilizing elements to cause the β phase to persist down to room temperature.
- * These alloys are stronger than α alloys.
- * **They can be further strengthened by heat treatment**
- * Quench from a temperature in the ($\alpha+\beta$) phase field and age at moderately at elevated temperature (homogeneous β solid solution is not formed here which is very common in age-hardening procedure).
- * Quenching suppresses the transformation of the elevated-temperature beta phase that would occur on slow cooling.
- * Aging at elevated temperatures causes precipitation of fine α . So, thin fine structure is stronger than $\alpha+\beta$ (coarse, annealed).
- * The most commonly used titanium alloy is Ti-6Al-4V ((α - β alloy). It is a general purpose alloy. Usually used in the annealed condition; i.e. solution-treated high in the ($\alpha+\beta$) phase field, quenched and aged or annealed at around 700°C. The resultant microstructure comprises equiaxed α -grains in a matrix of fully transformed β .



Fig.18 : Ti-6Al-4V (β treated, above the β transus), TEM photograph, shows plate like α grains (white), intergranular β (black).

Typical application of Ti-6 Al-4V

Aircraft gas turbine compressor blades and disks, forged airframe fittings, sheet metal airframe parts.

General Etchant : Kroll's reagent : 10 ml HF, 5 ml HNO₃, 85 ml H₂O
Immerse for 10 seconds.

Beta Alloys

- * **Can be strengthened by heat treatment**
- * Ti- 13V-11Cr-3Al
- * Structure consists of equiaxed grains of metastable β
- * Ageing leads to α precipitates in β grains

Uses : High strength fasteners, Aerospace components requiring high strength at moderate temperatures.

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