

## UNIT II

**Extractive Metallurgy:** Hydro, pyro and electro metallurgy, refining of metals. Powder Metallurgy: methods of production of metal powder, mixing of metal powders, compaction of powders - applications. Extraction process of Iron: manufacture of pig iron, blast furnace operations, chemistry of reactions. Manufacture of cast iron, varieties of cast iron, effect of impurities. Production of steel, Bessemer process, open-hearth process, L D methods. Classification of steel, effect of impurities. Heat treatment process: annealing, hardening, tempering, normalizing and gas carburizing. Fe- Carbon phase diagram.

### Metallurgy

The extraction of metals from their ores, heat treatments and the production of alloys.

### Production of metals

- Mining
- Concentration
- Metal extraction

### Mining

*Five main types of mining:*

- Open cast mining
- Underground mining
- Open pit mining
- Dredging
- Solution mining

### Ore concentration

Also called **ore dressing**, the aim is to increase

The amount of metal in each tonne of ore. The

Ore is crushed then ground and concentrated,

The following methods may be used:

- Gravity concentration
- Flotation
- Magnetic separation
- Amalgamation

### Metal extraction

*The process of extracting metals from concentrates:*

**Pyrometallurgy** – furnace heat is used with a reducing agent (iron uses coke) and a flux to produce metal and slag waste.

**Hydrometallurgy** – leaching dissolves ore in a solvent and then electrolysis is used to separate the metal.

**Thermo-electrometallurgy**- Aluminium can be extracted from salt or mineral mixtures by electrolysis. It uses a lot of electricity making it an expensive process. Blister copper is refined by electrolysis.

### **Extraction Metallurgy Part 2: Case studies**

- Copper – Pyrometallurgy route and environmental concerns. The hydrometallurgical alternative.
- Hydrometallurgical processes – ion exchange processes, solvent extraction, and bacterial leaching.
- Iron – Pyrometallurgy and the blast furnace.
- Silicon – The electric arc furnace. Purification by the Czochralski process.
- Aluminium – Electrolytic reduction.
- The siderophiles – The extraction of Au and the Pt group metals and their purification.

**Pyrometallurgy of copper Reminder:** Pyrometallurgy is the use of heat to reduce the mineral to the free metal, and usually involves 4 main steps:

- 1.Calcination:** thermal decomposition of the ore with associated elimination of a volatile product.
- 2.Roasting:** a metallurgical treatment involving gas- solids reactions at elevated temperatures.
- 3.Smelting:** a melting process which separates the chemical reaction products into 2 or more layers.
- 4.Refining:** treatment of a crude metal product to improve its purity.

Cu ore usually associated with sulphide minerals.

Most common source of Cu ore is the mineral chalcopyrite ( $\text{CuFeS}_2$ ), which accounts for 50% of Cu production.

Other important ores include:

chalcocite [ $\text{Cu}_2\text{S}$ ],

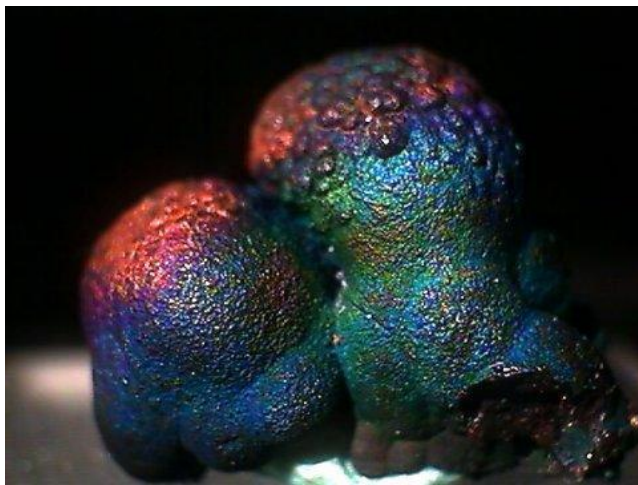
Malachite [ $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ],

Azurite [ $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ],

bornite ( $3\text{Cu}_2\text{S} \cdot \text{FeS}_3$ ),

covellite ( $\text{CuS}$ ).



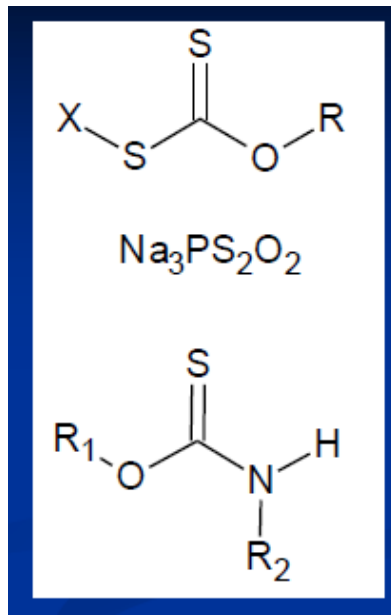
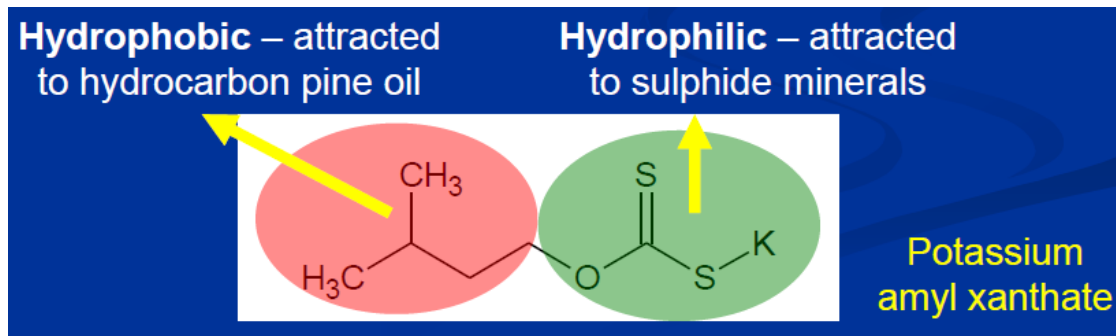


**1. Concentration** Only ~0.7% of the extracted ore contains Cu

Finely crushed ore concentrated by the froth-flotation process:

- Copper ore slurry mixed with: Lime water – to give basic pH Pine oil – to make bubbles An alcohol – to strengthen bubbles A chemical collector

Chemical collectors such as xanthates (salts & esters of xanthic acid), dithiophosphates, or thionocarbamates make the ore surface hydrophobic.



Raising the pH causes the polar ends to ionize more, thereby preferentially sticking to chalcopyrite ( $\text{CuFeS}_2$ ) and leaving pyrite ( $\text{FeS}_2$ ) alone.

Air is bubbled through the suspension.

Finely divided hydrophobic ore particles latch on to the air bubbles and travel to the surface where a froth is formed.

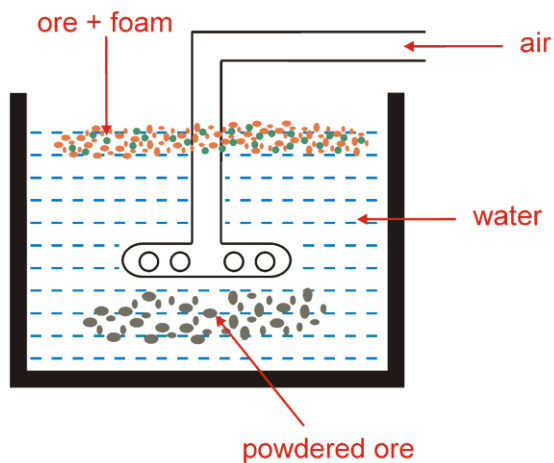
The froth containing the Cu ore is skimmed off and reprocessed.

In this manner, the ore is concentrated to an eventual value of over 28% Cu.

The remaining material (sand particles & other impurities) sink to the bottom & is discarded or reprocessed to extract other elements.



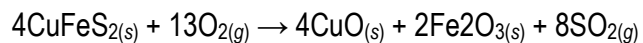
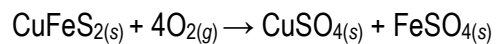
### Froth-flotation



## 2. Roasting

Involves partial oxidation of the sulphide mineral with air at between 500C and 700C.

For chalcopryrite, the main reactions are:



Reactions are exothermic, roasting is an autogenous process requiring little or no additional fuel.

NB, not all the sulphides are oxidised, only around 1/3. Rest remain as sulphide minerals.

The gases produced contain around 5 – 15% SO<sub>2</sub>, which is used for sulphuric acid production.

Objectives of roasting: 1) Remove part of the sulphur. 2) Convert iron sulphides into iron oxide and iron sulphate to facilitate removal during smelting. 3) To pre-heat the concentrate to reduce amount of energy needed by the smelter.

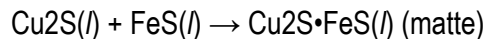
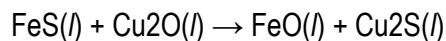
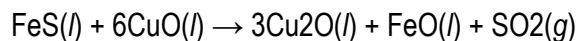
### 3. Smelting

Smelting consists of melting the roasted concentrate to form 2 molten phases: 1) a sulphide “matte”, which contains the iron-copper sulphide mixture. 2) an oxide slag, which is insoluble in the matte, and contains iron oxides, silicates, and other impurities.

Smelting is carried out at around 1200C, usually with a silica flux to make the slag more fluid.

The matte layer sinks to the bottom, and the slag layer floats on top of the matte & is tapped off & disposed of.

The main reaction is the reduction of copper oxides (formed during roasting) back into copper sulphide to ensure that they migrate into the matte phase:



### 4. Conversion

After smelting, matte contains from between 30 to 80% Cu in the form of copper sulphide.

The sulphur is removed by selective oxidation of the matte with O<sub>2</sub> to produce SO<sub>2</sub> from S, but leave Cu metal.

Converting is carried out in two stages: 1) an iron removal stage, and 2) a copper-making stage.

#### Iron removal

A silica flux is added to keep the slag (see below) molten.

Air is blown into the converter to oxidize the iron sulphide according to the following reaction:  $2\text{Cu}_2\text{S} \cdot \text{FeS}(l) + 3\text{O}_2(g) + \text{SiO}_2(l) \rightarrow 2\text{FeO} \cdot \text{SiO}_2(l) + 2\text{SO}_2(g) + \text{Cu}_2\text{S}(l)$

Si added to help form FeO slag.

The oxidized Fe and Si form a slag (insoluble in matte) that is skimmed off & disposed off.

#### Copper making

The sulphur in the Cu<sub>2</sub>S can now be oxidized to leave behind metallic copper according to the following reaction:  $\text{Cu}_2\text{S}(l) + \text{O}_2(g) \rightarrow 2\text{Cu}(l) + \text{SO}_2(g)$

Pyrometallurgy of copper 4. Conversion (*cont.*) The end product is around 98.5% pure & is known as blister copper because of the broken surface created by the escape of SO<sub>2</sub> gas.



## 5. Refining

Almost all copper is refined by electrolysis.

The anodes (cast from blister copper) are placed into an aqueous CuSO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> solution.

Thin sheets of highly pure Cu serve as the cathodes.

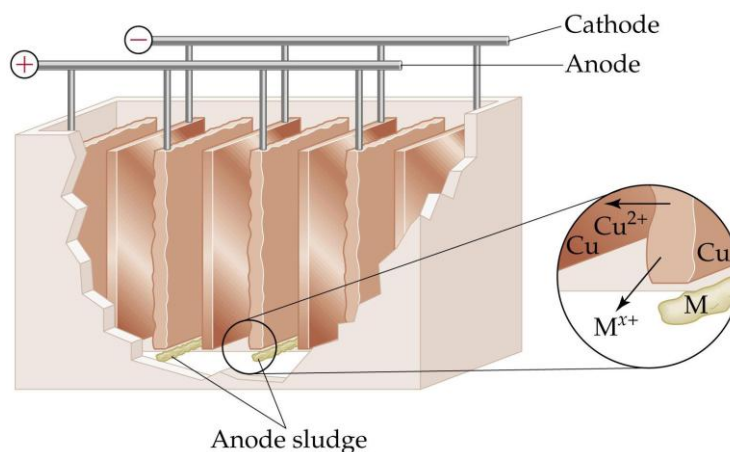
Application of a suitable voltage causes oxidation of Cu metal at the anode.

Cu<sup>2+</sup> ions migrate through the electrolyte to the cathode, where Cu metal plates out.

Metallic impurities more active than Cu are oxidized at the anode, but don't plate out at the cathode.

Less active metals are not oxidized at the anode, but collect at the bottom of the cell as a sludge.

The redox reactions are:  $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$   $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$   $E_{\text{red}} = -0.83\text{V}$



## Environmental impact

Large amount of gases produced present air pollution problems, in particular SO<sub>2</sub> gas acid rain.

Dust produced contains heavy metals such as mercury, lead, cadmium, zinc health problems.

Waste water contaminated with: Insoluble substances, mostly waste sludge (finely ground rock). Soluble substances (heavy metals, sulphates). Chemicals from flotation process.

### Typical Air Emissions

*(milligrams per normal cubic meter)*

<i>Parameter</i>	<i>Maximum value</i>
Sulfur dioxide	1,000
Arsenic	0.5
Cadmium	0.05
Copper	1
Lead	0.2
Mercury	0.05
Particulates, smelter	20
Particulates, other sources	50

### Hydrometallurgy of copper

#### Advantages

Much more environmentally friendly than pyrometallurgy.

Compared to pyrometallurgy, only a fraction of the gases liberated into the atmosphere.

Emissions of solid particles comparatively non-existent.

#### Disadvantages

Large amount of water used, greater potential for contamination.

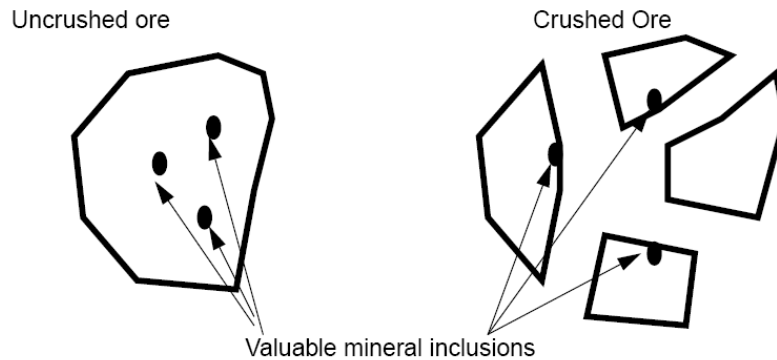
Waste waters contain soluble metal compounds, chelating compounds & organic solvents.

The following steps are involved:

- 1.Ore preparation
- 2.Leaching
- 3.Solution purification
- 4.Metal recovery

#### 1. Ore preparation

Ore undergoes some degree of comminution (crushing & pulverisation) to expose the Cu oxides & sulphides to leaching solution.



Amount of comminution depends on quality of ore: Higher grade ore – more comminution. Lower grade ore – less comminution. (Why??)

If possible, ore is pre-concentrated; reject ore that contains very little Cu.

### 1. Leaching

**Definition** : The dissolution of a mineral in a solvent, while leaving the gangue (rock or mineral matter of no value) behind as undissolved solids.

Cu is normally leached by one of three methods:

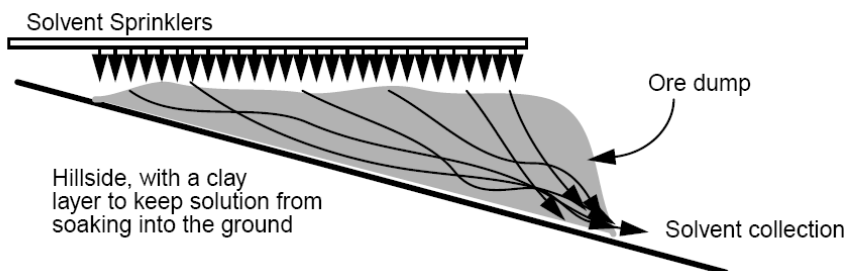
(a) Dump leaching (b) Heap leaching (c) Bacterial leaching

Leaching solution trickled over a dump.

Runoff solution collected & the Cu recovered from it.

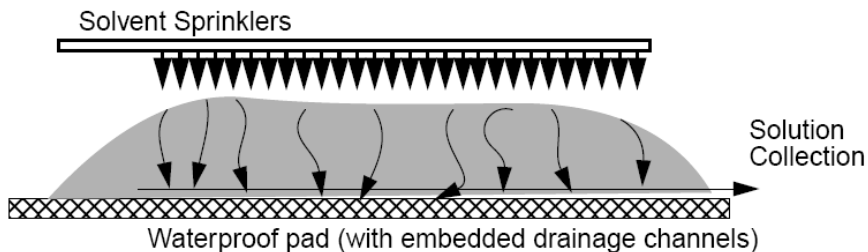
A slow process that takes months or years to complete.

Typically only around 60% of the Cu in the dump is recovered.



Similar to dump leaching except ore not simply dumped on a hillside, but is crushed to gravel size & piled onto an artificial pad.

After leaching (6 months to 1 year) gangue is removed from pad, disposed of & replaced with fresh ore.

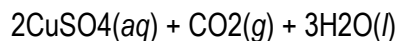
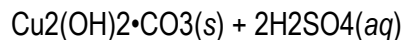


**Leaching reactions** Nature of ore determines if leaching is non-oxidative or oxidative. **Non-oxidative leaching:** No change in oxidation state. e.g.

(1) dissolution of copper sulphate by water:



(2) dissolution of alkaline materials by acid:



**Oxidative leaching:** Many ores only soluble once oxidised. e.g. covellite ( $\text{CuS}$ ) much more soluble if oxidised to  $\text{CuSO}_4$   $\text{CuS}(s) + \text{O}_2(g) \rightarrow \text{CuSO}_4(aq)$

**EXERCISE : work out which species is oxidised, and which is reduced, and write out the balanced half reactions for each.**

SOLUTION:  $\text{CuS}$   $\text{Cu} = +2$ ,  $\text{S} = -2$   $\text{O}_2$   $\text{O} = 0$

$\text{CuSO}_4$   $\text{Cu} = +2$ ,  $\text{O}_4 = -8$ ,  $\text{S} = +6$

$\text{S}^{-2} \rightarrow \text{S}^{+6} + 8e^-$  (oxidation)  $2\text{O}_2 + 8e^- \rightarrow 4\text{O}^{2-}$  (reduction)

Several bacteria, especially *Thiobacilli*, are able to solubilise metal minerals by oxidising ferrous to ferric iron, as well as elemental sulphur, sulphide, and other sulphur compounds to sulphate or sulphuric acid.

20 to 25% of copper produced in the USA, and 5% of the world's copper is obtained by bacterial leaching.

Very slow process; takes years for good recovery

But low investment and operating costs.

### ***Thiobacilli***

Are acidotolerant; some grow at pH's as low as 0.5

Are tolerant against heavy metal toxicity.

Are chemolithoautotrophs (C source is  $\text{CO}_2$  & energy derived from chemical transformation of inorganic matter).

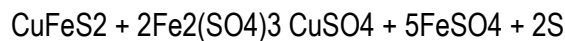
**Mechanisms** Generalised reaction :  $\text{M(II)S} + 2\text{O}_2 \rightarrow \text{M}^{2+} + \text{SO}_4^{2-}$

Two mechanisms: (a) indirect mechanism involving the ferric-ferrous cycle, and (b) direct mechanism involving physical contact of the organism with the sulphide mineral.

**Mechanisms: Indirect** First step: ferrous sulphate is converted into ferric sulphate by the action of *Acidithiobacillus ferrooxidans*: (c) Bacterial leaching  $4\text{FeSO}_4 + \text{O}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$  **CLASS EXERCISE : work out which is ferric- and which is ferrous sulphate, and write out the balanced half reactions for each.**  $\text{FeSO}_4$   $\text{SO}_4^{2-}$   $\text{Fe}^{2+}$  (ferrous)  $2\text{Fe}_2(\text{SO}_4)_3$   $3 \text{SO}_4^{2-}$  = -6, but 2 Fe  $\text{Fe}^{3+}$  (ferric)

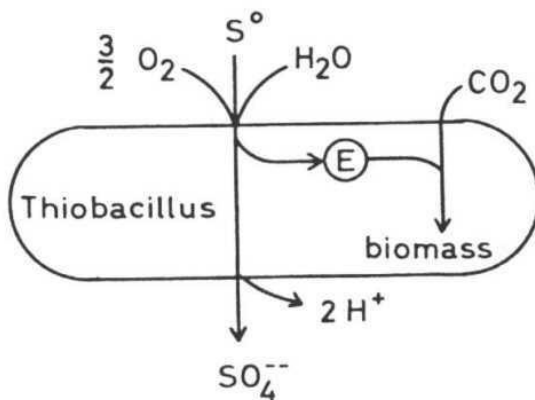
**Mechanisms: Indirect** (c) Bacterial leaching  $4\text{Fe}^{2+} + 4\text{Fe}^{3+} + 4\text{e}^-$  (oxidation)  $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$  (reduction)  
Ferric sulphate is a strong oxidising agent capable of dissolving a range of sulphide minerals.

In the case of chalcopyrite:



**Mechanisms: Indirect** (c) Bacterial leaching

The elemental S produced by the indirect method can be converted to  $\text{H}_2\text{SO}_4$  by *Acidithiobacillus ferrooxidans*:



The  $\text{H}_2\text{SO}_4$  helps maintain the pH at levels favourable for bacterial growth.

**Mechanisms: Direct** (c) Bacterial leaching

Bacteria actually adheres to the mineral surface prior to enzymatic attack.

The mineral is oxidised with oxygen to sulphate and metal cations without any detectable intermediate occurring.

In the case of covellite:



**Compared to other extraction techniques:** (c) Bacterial leaching

Traditional methods expensive (i.e. roasting + smelting) & require high concentrations of Cu in ore.

Bacteria can effectively deal with low [Cu] as they simply ignore surrounding waste materials.

Up to 90% extraction efficiency.

**Compared to other extraction techniques:** (c) Bacterial leaching

*Economical:* Simpler, cheaper, less infrastructure.

*More environmentally friendly;* no SO<sub>2</sub> emissions, less landscape damage.

**ADVANTAGES:**

*Economical:* Very slow compared to smelting; less profit. Delay in cash flow for new plants.

*Environmental;* Toxic chemicals sometimes produced. H<sub>2</sub>SO<sub>4</sub> pollution. Precipitation of heavy ions (Fe, Zn, As) – pollution.

Leaching reactions not perfectly selective other elements in solution as well, not just Cu. These need to be removed.

After leaching, Cu in solution can be very dilute. need a way to concentrate it.

Both of these are generally done using ion exchange processes, the two most common being ion exchange chromatography, and solvent extraction.

## 2. Solution Purification

### **Ion exchange chromatography**

**DEFINITION:** a solution containing a mixture of metal ions is contacted with a resin that is insoluble in the metal-ion solution.

Ion-exchange resin consists of an inert solid phase to which labile functional groups are chemically bonded.

Functional groups can either be acidic (H<sup>+</sup>) or basic (OH<sup>−</sup>) groups that exchange with cations (M<sup>+</sup>) or anions (M<sup>−</sup>), respectively.

The ion-exchange process is reversible.

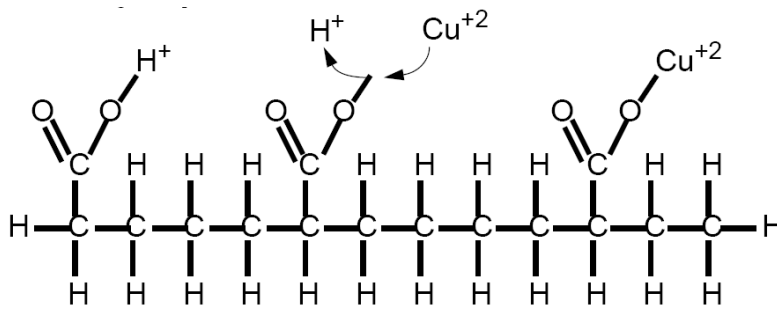
### **Ion exchange chromatography: Theory**

Analyte molecules retained on a column (stationary phase) based on coulombic (ionic) interactions.

Stationary phase has ionic functional groups (R-X) that interact with analyte ions of opposite charge.

Two types: cation exchange chromatography:  $\text{R-X-C}^+ + \text{M}^+\text{B}^- \rightarrow \text{R-X-M}^+ + \text{C}^+\text{B}^-$  anion exchange chromatography:  $\text{R-X-A}^- + \text{M}^+\text{B}^- \rightarrow \text{R-X-B}^- + \text{M}^+\text{A}^-$

### Cu Ion exchange chromatography



Carboxyl groups exchange the ion it currently holds (H<sup>+</sup>) for a Cu<sup>2+</sup> ion.

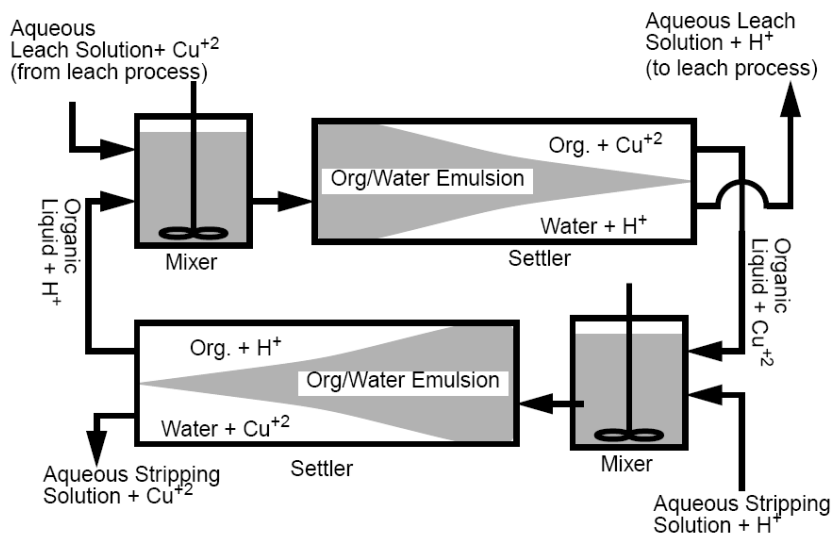
The Cu<sup>2+</sup> is later released by contacting it with a stripping solution (very high H<sup>+</sup> conc.).

### Solvent extraction

**DEFINITION:** a method to separate compounds based on their relative solubilities in 2 different immiscible liquids.

In industry, this is usually set up as a continuous process.

### Solvent extraction



### 4. Metal Recovery:

At this point, the metal needs to be recovered from solution in the solid form.

This is either achieved chemically, or electrochemically.

### Basic Steps In Powder Metallurgy

Powder Production

Blending or Mixing

Compaction

Sintering

Finishing

### **Powder Production**

Atomization the most common

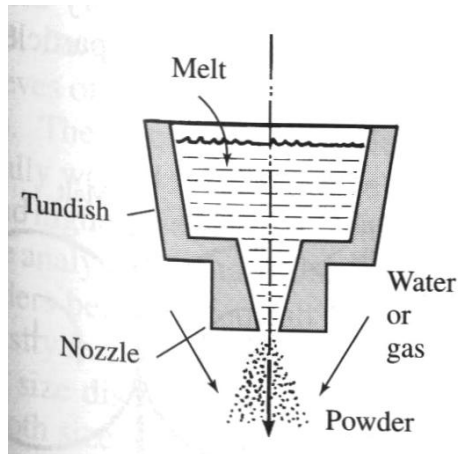
Others

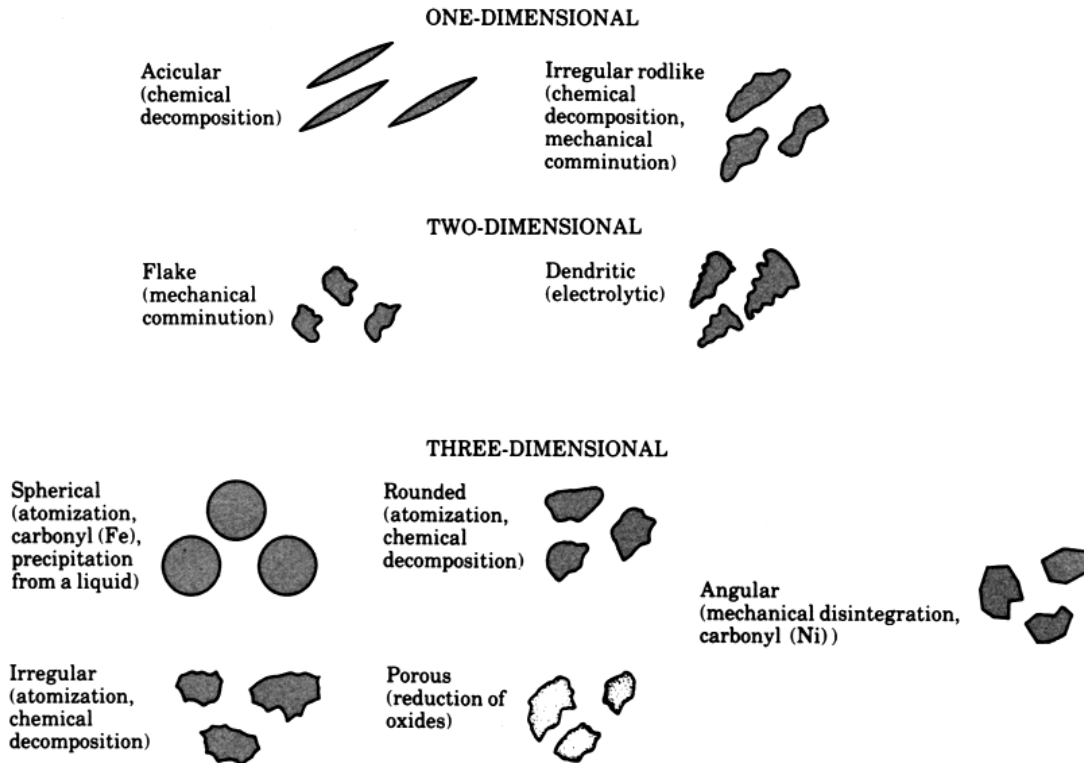
Chemical reduction of oxides

Electrolytic deposition

Different shapes produced

Will affect compaction process significantly



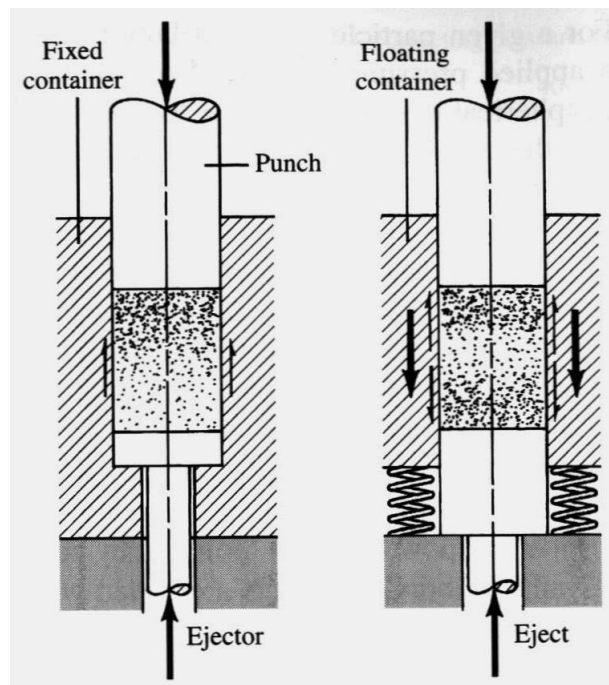
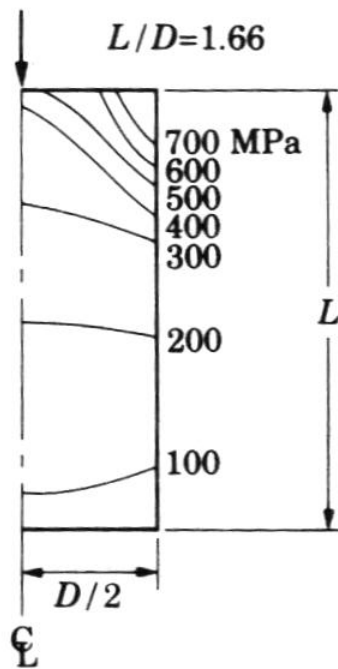
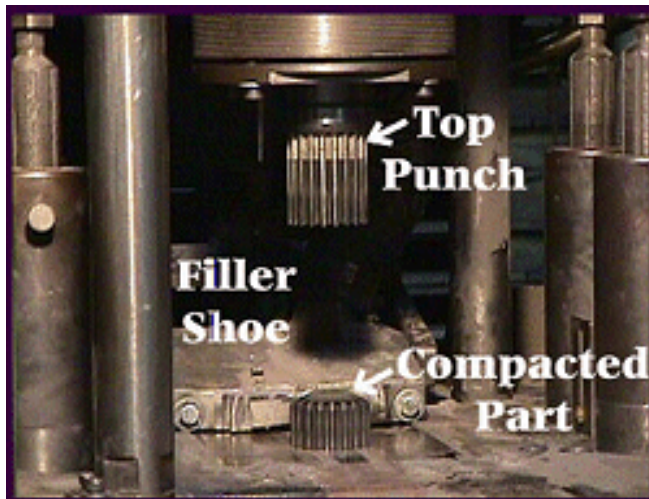


### Blending or Mixing

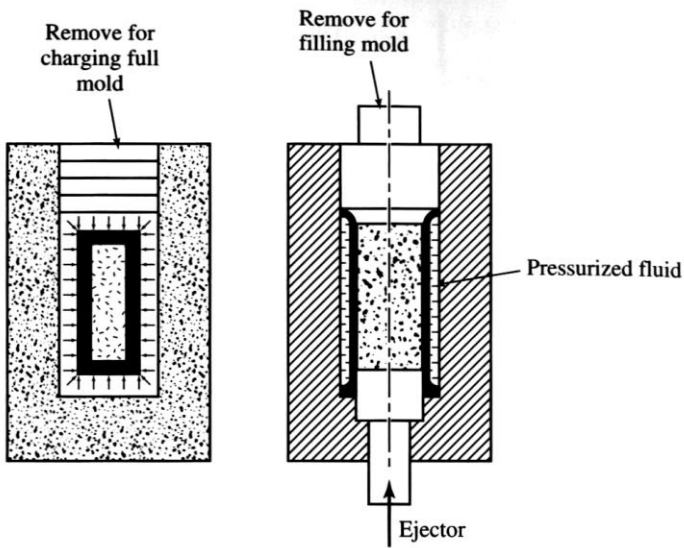
1. Can use master alloys, (most commonly) or elemental powders that are used to build up the alloys
  - a. Master alloys are with the normal alloy ingredients
2. Elemental or pre-alloyed metal powders are first mixed with lubricants or other alloy additions to produce a homogeneous mixture of ingredients
3. The initial mixing may be done by either the metal powder producer or the P/M parts manufacturer
4. When the particles are blended:
  - a. Desire to produce a homogenous blend
  - b. Over-mixing will work-harden the particles and produce variability in the sintering process

### Compaction

1. Usually gravity filled cavity at room temperature
2. Pressed at 60-100 ksi
3. Produces a "Green" compact
  - a. Size and shape of finished part (almost)
  - b. Not as strong as finished part – handling concern
4. Friction between particles is a major factor



Isostatic Pressing



1. Because of friction between particles
  - a. Apply pressure uniformly from all directions (in theory)
2. Wet bag (left)
3. Dry bag (right)

### Sintering

1. Parts are heated to ~80% of melting temperature
2. Transforms compacted mechanical bonds to much stronger metal bonds
3. Many parts are done at this stage. Some will require additional processing



1. Final part properties drastically affected
2. Fully sintered is not always the goal
  - a. Ie. Self lubricated bushings
3. Dimensions of part are affected

#### **Die Design for P/M**

1. Thin walls and projections create fragile tooling.
2. Holes in pressing direction can be round, square, D-shaped, keyed, splined or any straight-through shape.
3. Draft is generally not required.
4. Generous radii and fillets are desirable to extend tool life.
5. Chamfers, rather the radii, are necessary on part edges to prevent burring.
6. Flats are necessary on chamfers to eliminate feather-edges on tools, which break easily.

#### **Advantages of P/M**

1. Virtually unlimited choice of alloys, composites, and associated properties
  - a. Refractory materials are popular by this process
2. Controlled porosity for self lubrication or filtration uses
3. Can be very economical at large run sizes (100,000 parts)
4. Long term reliability through close control of dimensions and physical properties
5. Wide latitude of shape and design

6. Very good material utilization

**Disadvantages of P/M**

1. Limited in size capability due to large forces
2. Specialty machines
3. Need to control the environment – corrosion concern
4. Will not typically produce part as strong as wrought product. (Can repress items to overcome that)
5. Cost of die – typical to that of forging, except that design can be more – specialty
6. Less well known process

**Types of steels:** Below are given some applications. Details can be looked into references given at the end of the lecture. Broadly we have either plain carbon (carbon is the principle alloying element) or alloy (in addition to carbon there are other alloying elements like Nb, V, W, Cr, Ni etc) steel. Plain carbon steels are the following types:

The alloy steels are classified as low (less than 5 weight% alloying elements), medium (in between 5 to 10 weight percent alloying elements) and high alloy steels (more than 10 weight percent alloying elements).

**Effect of impurity elements on steel properties**

Carbon imparts strength to iron. It reduces ductility and impact strength. But presence of carbon allows heat treatment procedures. Sulphur segregates during solidification (segregation coefficient is 0.02). Sulphur causes hot shortness due to formation of FeS formed during solidification of steel. Sulphide inclusions lower weldability and corrosion resistance. Presence of sulphur may also lead to development of tear and cracks on reheating the steel.

Phosphorus segregates during solidification (segregation coefficient is 0.02). Presence of phosphorus impairs plastic properties. Silicon and manganese: Silicon reduces the drawing capacity of steel. Manganese is beneficial; it increases strength without affecting ductility and sharply reduces hot shortness. Gases: Nitrogen impairs plastic properties and increases embrittlement at lower temperatures. Hydrogen causes defects such as flakes, fish-scale fracture. Inclusions: Presence of inclusions at the grain boundary weakens intra-granular bonds. Inclusions also act as stress concentrators. Some type of inclusions is brittle. Tramp elements: Tramp elements like copper, zinc, tin, antimony etc create problems during reheating of steels because their melting points are much lower than steel reheat temperature.

## Heat Treatment

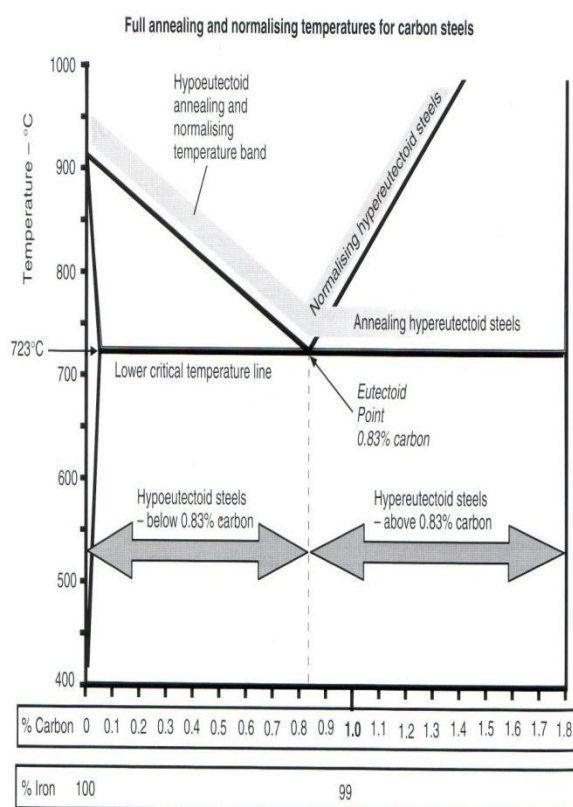
The amount of carbon present in plain carbon steel has a pronounced effect on the properties of a steel and on the selection of suitable heat treatments to attain certain desired properties. Below are some major types of heat treatment processes:

### Types

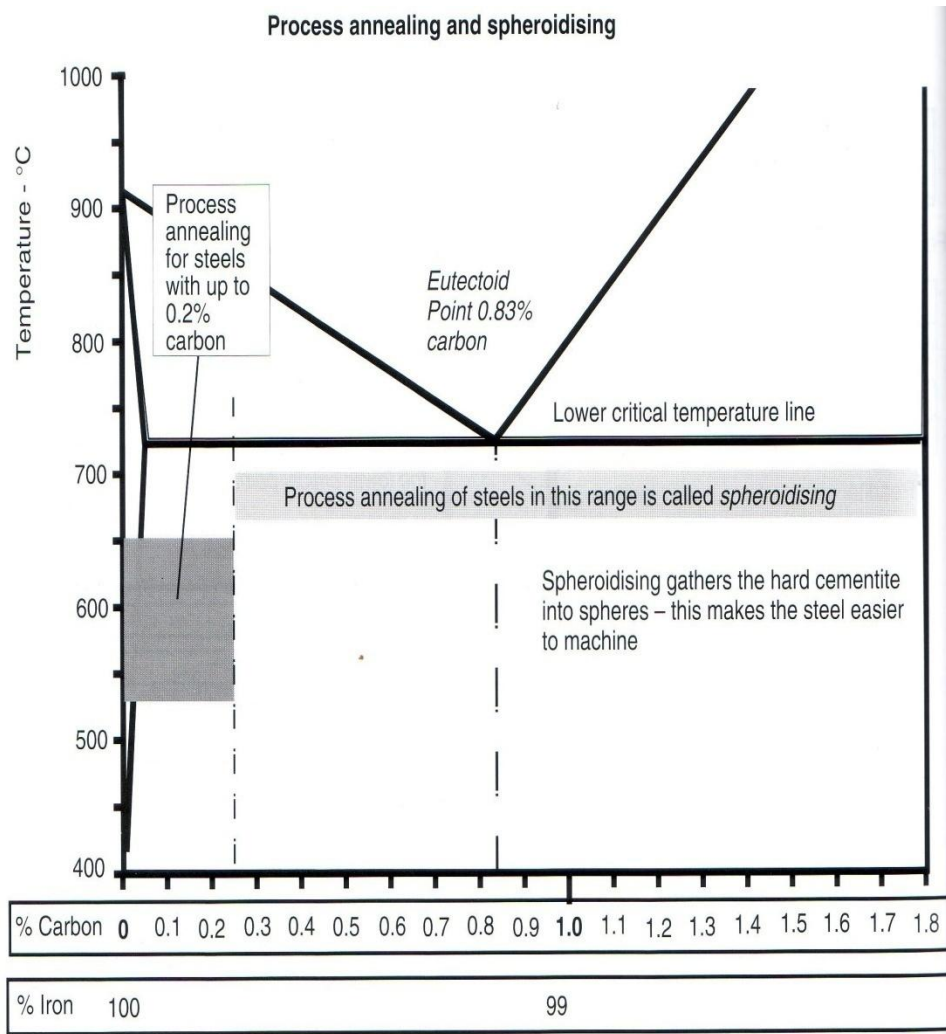
1. *Annealing*
2. *Normalizing*
3. *Hardening*
4. *Carburizing*
5. *Tempering*

### Annealing

1. Makes a metal as soft as possible
2. Hypoeutectoid steels (less than 0.83% carbon) are heated above upper critical temp., soaked and cooled slowly.
3. Hypereutectoid (above 0.83%) are heated above lower critical temp., soaked and allowed to cool slowly.



1. Process Annealing. Low carbon steels may harden through cold working. They can be heated to around 100 degrees below lower critical temp., soaked and allowed to cool in air.
2. Spheroidising. High carbon steels may be annealed just below the lower critical temp. to improve machinability.





1. **Normalising.** Internal stresses caused by rolling and rolling or forging are removed. Steels are heated above upper critical temp., soaked and cooled in air. The cooling rate is faster than annealing giving a smaller grain structure.
2. **Stress relieving.** The component is reheated and held at temperature for a period of time and cooled slowly.

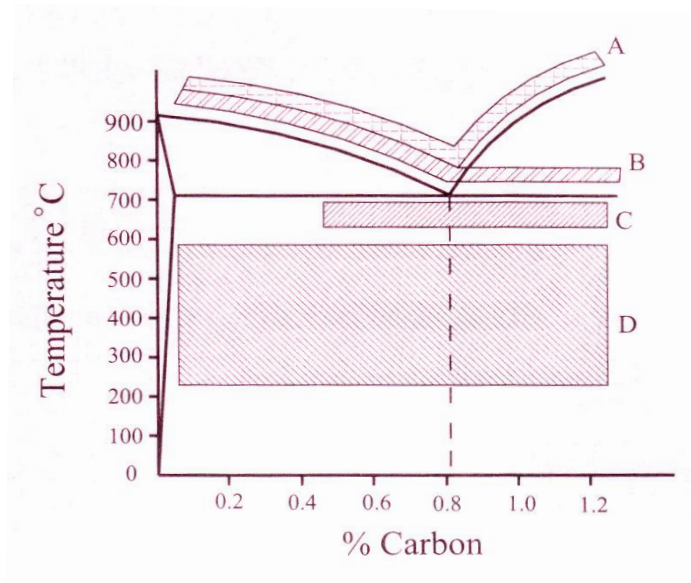
### Hardening

Medium and High carbon steels (0.4 – 1.2%) can be heated until red hot and then quenched in water producing a very hard and brittle metal. At 723 degrees, the BCC ferrite changes into Austenite with a FCC structure.

### Tempering

1. To remove some of the brittleness from hardened steels, tempering is used. The metal is heated to the range of 220-300 degrees and cooled.
2. Tempering colours are an indicator of temperature on polished metals. Colours range from yellow to brown to violet and blue.

### Heat Treatments



A – Normalising

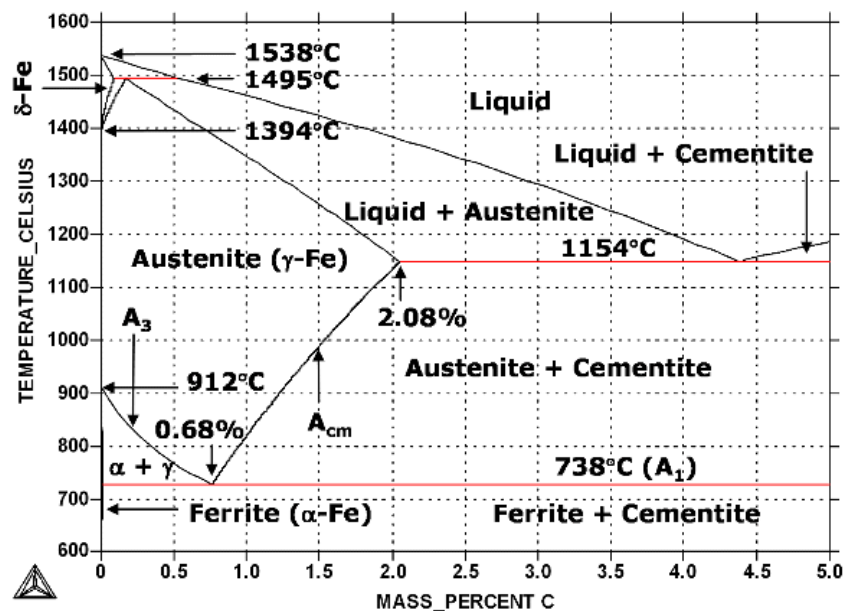
B – Annealing or Hardening

C – Spheroidising or Process Annealing

D - Tempering

### Phase Diagrams

Metastable Iron-Carbon (Fe-C) Phase Diagram



**Figure** The Fe-C phase diagram shows which phases are to be expected at metastable equilibrium for different combinations of carbon content and temperature.

At the low-carbon end of the metastable Fe-C phase diagram, we distinguish ferrite (alpha-iron), which can at most dissolve 0.028 wt. % C at 738 °C, and austenite (gamma-iron), which can dissolve 2.08 wt. % C at 1154 °C. The much larger phase field of gamma-iron (austenite) compared with that of alpha-iron (ferrite) indicates clearly the considerably greater solubility of carbon in gamma-iron (austenite), the maximum value being 2.08 wt. % at 1154 °C. The hardening of carbon steels, as well as many alloy steels, is based on this difference in the solubility of carbon in alpha-iron (ferrite) and gamma-iron (austenite).

At the carbon-rich side of the metastable Fe-C phase diagram we find cementite ( $\text{Fe}_3\text{C}$ ). Of less interest, except for highly alloyed steels, is the delta-ferrite at the highest temperatures.

The vast majority of steels rely on just two allotropes of iron

- (1) **Alpha-iron**, which is body-centered cubic (BCC) ferrite, and
- (2) **Gamma-iron**, which is face-centered cubic (FCC) austenite. At ambient pressure, BCC ferrite is stable from all temperatures up to 912 °C (the  $A_3$  point), when it transforms into FCC austenite. It reverts to ferrite at 1394 °C (the  $A_4$  point). This high-temperature ferrite is labeled
- (3) **Delta-iron**, even though its crystal structure is identical to that of alpha-ferrite. The delta-ferrite remains stable until it melts at 1538 °C.

Regions with mixtures of two phases (such as ferrite + cementite, austenite + cementite, and ferrite + austenite) are found between the single-phase fields. At the highest temperatures, the liquid phase field can be found, and below this are the two-phase fields (liquid + austenite, liquid + cementite, and liquid + delta-ferrite). In heat treating of steels, the liquid phase is always avoided.

The steel portion of the Fe-C phase diagram covers the range between 0 and 2.08 wt. % C. The cast iron portion of the Fe-C phase diagram covers the range between 2.08 and 6.67 wt. % C.

The steel portion of the Fe-C phase diagram can be subdivided into three regions: hypoeutectoid ( $0 < \text{wt. \% C} < 0.68 \text{ wt. \%}$ ), eutectoid ( $\text{C} = 0.68 \text{ wt. \%}$ ), and hypereutectoid ( $0.68 < \text{wt. \% C} < 2.08 \text{ wt. \%}$ ).

A very important phase change in the metastable Fe-C phase diagram occurs at 0.68 wt. % C. The transformation is eutectoid, and its product is called pearlite (ferrite + cementite):

gamma-iron (austenite)  $\rightarrow$  alpha-iron (ferrite) +  $\text{Fe}_3\text{C}$  (cementite).

Some important boundaries at single-phase fields have been given special names. These include:

**A<sub>1</sub>** — The so-called eutectoid temperature, which is the minimum temperature for austenite.

**A<sub>3</sub>** — The lower-temperature boundary of the austenite region at low carbon contents; i.e., the gamma / gamma + ferrite boundary.

**A<sub>cm</sub>** — The counterpart boundary for high-carbon contents; i.e., the gamma / gamma + Fe<sub>3</sub>C boundary. Sometimes the letters **c**, **e**, or **r** are included:

**A<sub>c</sub><sub>cm</sub>** — In hypereutectoid steel, the temperature at which the solution of cementite in austenite is completed during heating.

**A<sub>c</sub><sub>1</sub>** — The temperature at which austenite begins to form during heating, with the **c** being derived from the French *chauffant*.

**A<sub>c</sub><sub>3</sub>** — The temperature at which transformation of ferrite to austenite is completed during heating.

**A<sub>e</sub><sub>cm</sub>, A<sub>e</sub><sub>1</sub>, A<sub>e</sub><sub>3</sub>** — The temperatures of phase changes at equilibrium.

**A<sub>r</sub><sub>cm</sub>** — In hypereutectoid steel, the temperature at which precipitation of cementite starts during cooling, with the **r** being derived from the French *refroidissant*.

**A<sub>r</sub><sub>1</sub>** — The temperature at which transformation of austenite to ferrite or to ferrite plus cementite is completed during cooling.

**A<sub>r</sub><sub>3</sub>** — The temperature at which austenite begins to transform to ferrite during cooling.

**A<sub>r</sub><sub>4</sub>** — The temperature at which delta-ferrite transforms to austenite during cooling.

If alloying elements are added to an iron-carbon alloy (steel), the position of the A<sub>1</sub>, A<sub>3</sub>, and A<sub>cm</sub> boundaries, as well as the eutectoid composition, are changed. In general, the austenite-stabilizing elements (e.g., nickel, manganese, nitrogen, copper, etc) decrease the A<sub>1</sub> temperature, whereas the ferrite-stabilizing elements (e.g., chromium, silicon, aluminum, titanium, vanadium, niobium, molybdenum, tungsten, etc) increase the A<sub>1</sub> temperature.

The carbon content at which the minimum austenite temperature is attained is called the eutectoid carbon content (0.68 wt. % C in case of the metastable Fe-C phase diagram). The ferrite-cementite phase mixture of this composition formed during slow cooling has a characteristic appearance and is called pearlite and can be treated as a microstructural entity or microconstituent. It is an aggregate of alternating ferrite and cementite lamellae that coarsens (or "spheroidizes") into cementite particles dispersed within a ferrite matrix after extended holding at a temperature close to A<sub>1</sub>.

Finally, we have the martensite start temperature, M<sub>s</sub>, and the martensite finish temperature, M<sub>f</sub>:

**M<sub>s</sub>** — The highest temperature at which transformation of austenite to martensite starts during rapid cooling.

**M<sub>f</sub>** — The temperature at which martensite formation finishes during rapid cooling.