

Chapter 4

Extraction of Iron

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Chemical Engineering Department
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Outline

- *How do we extract iron from its mineral ores like the iron oxide ores?*
- *The raw materials needed?*
- *The chemistry of the blast furnace.*
- *Why convert iron into steel?*
- *How do we convert it into steel?*

Introduction

- *Iron (Fe) is the 26th element on the periodic table and has been used by humans for over 5000 years.*
- *It is one of the most abundant metals on Earth, making up to 5.6% of the Earth's crust and nearly all of the Earth's core.*
- *Iron has played a key role in humanity's history, as those who could manipulate it to craft weapons, tools, and other materials gained economic and political power.*
- *In modern society, iron is the most important of all metals, as it is used to craft different types of steel which is used in a diverse array of applications.*
- *Steel is used to make paperclips, skyscrapers, and everything in between.*

Introduction

- *Iron is also an important element in plant and animal life.*
- *In plants it plays a role in the creation of chlorophyll, and in humans it plays a crucial role in the vascular system.*
- *Iron makes up 95% of all metal tonnage produced worldwide, with over 500 million tonnes of new iron and 300 million tonnes of recycled iron being output each year.*
- *This output of iron is possible due to the enormous reserves of iron on earth, exceeding 100 billion tonnes.*

Iron Ores

- *There are a variety of iron ores such as:*
 1. *Limonite*
 2. *Hematite*
 3. *Magnetite*
- *These ores are rich in the element iron and mined extensively to produce iron and steel.*
- *These minerals, in addition to iron, contain other elements.*



Limonite



Magnetite



Hematite

Raw Materials for Iron Production



Magnetite



Limestone



Coal

Production Steps

➤ *The process of the extraction of iron is carried out by the following steps:*

1. Concentration of ore

In this metallurgical operation, the ore is concentrated by removing impurities like soil etc.

The process involves the crushing and washing of ore.

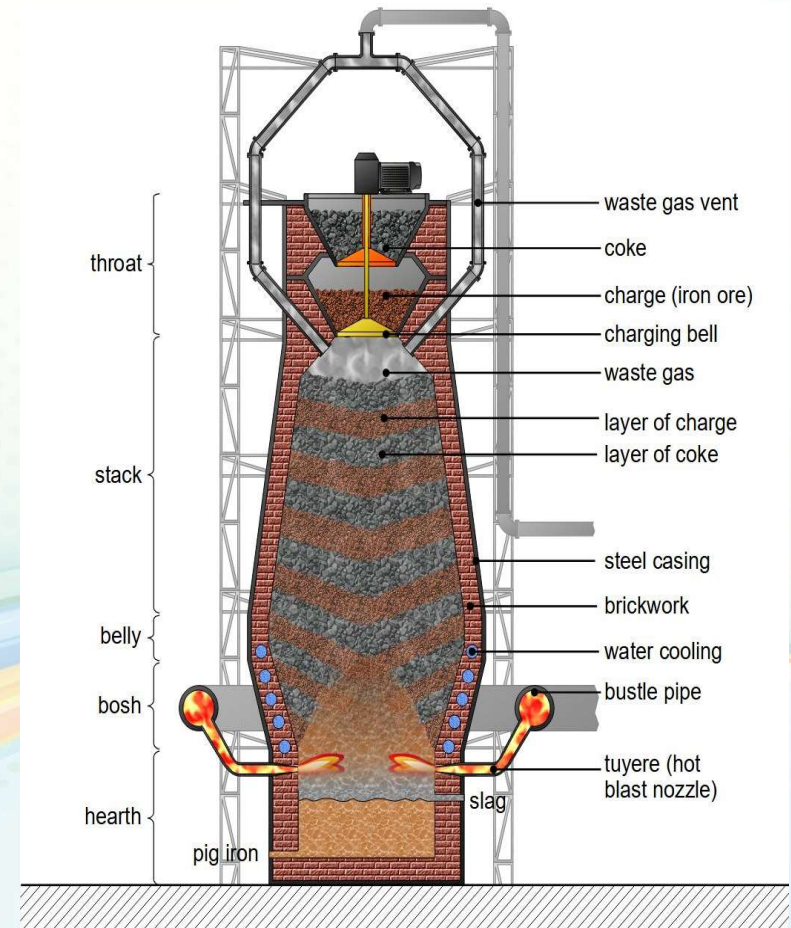
2. Calcination or Roasting of ore

The concentrated ore is now heated in the presence of air. The process of roasting is performed to remove moisture, CO_2 , impurities of sulphur, arsenic.

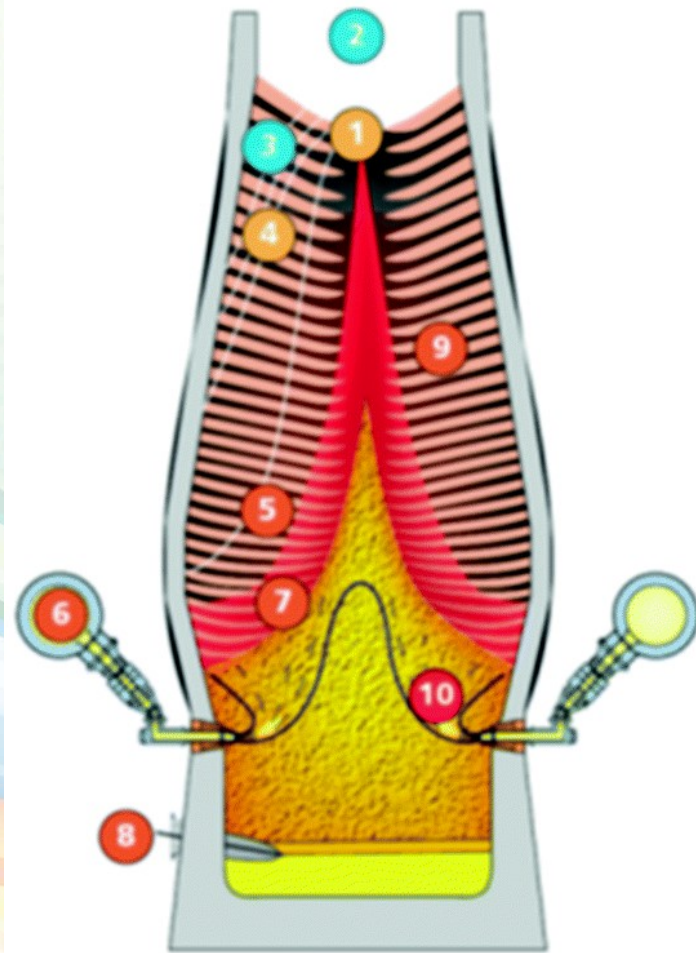
Ferrous oxide is also oxidized to ferric oxide.

3. Reduction of ore

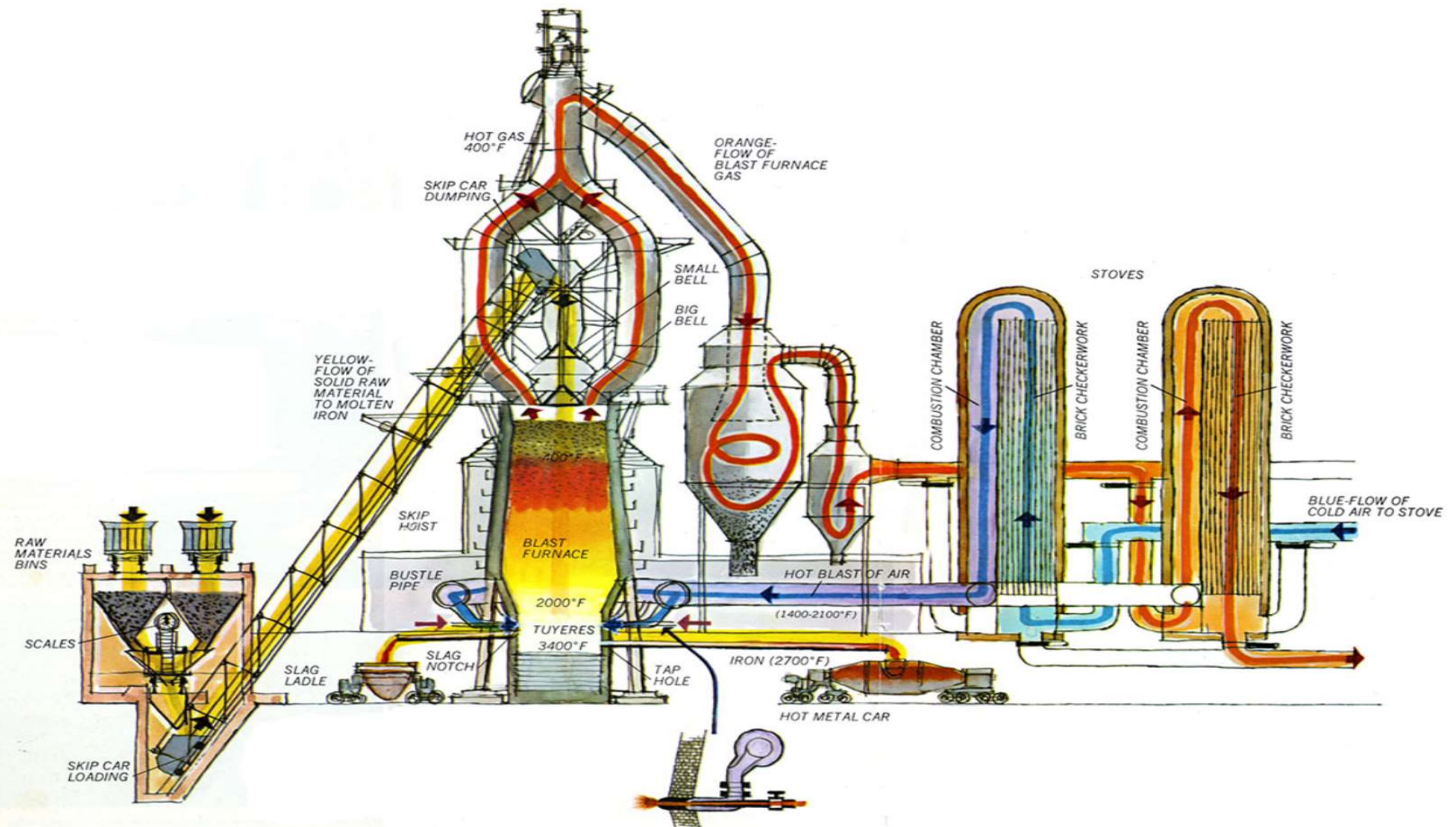
- The process of reduction is carried out in a blast furnace.
- The blast furnace is a cylindrical tower like structure about 25 m to 35 m high.
- It has an outer shell of steel.
- Inside of furnace is lined with fire bricks.
- The top of the furnace is closed by a cup- cone feeder



Temperature Distribution



1	Centre Coke	600–900 °C
2	Top Gas	110 °C
3	Evaporation of water	100 °C
4	Reactions start	500–600 °C
5	Start of softening front	1000–1200 °C
6	Hot blast	1050 °C
7	End of cohesive zone	~1400 °C
8	Hot metal	1500 °C
9	Granular zone	
10	Raceway Flame	2100–2300 °C



What happens in the Blast Furnace?

- *The purpose of a Blast Furnace is to reduce the concentrated ore chemically to its liquid metal state.*
- *A blast furnace is a gigantic, steel stack lined with refractory brick where the concentrated iron ore, coke, and limestone are dumped from the top, and a blast of hot air is blown into the bottom.*
- *All the three ingredients are crushed into small round pieces and mixed and put on a hopper which controls the input.*
- *Hot air is blown from the bottom and coke is burned to yield temperatures up to about 1900 °C*

- *Burning coke provides the majority of the heat required for this process.*
- *At such high temperatures, coke reacts with the oxygen in the hot air to form carbon monoxide (CO).*
- *The CO and heat now move upwards and meet the raw material running down from the top.*
- *The temperature in the upper parts of the Blast Furnace is considerably lower than the 1900 °C at the bottom.*
- *In this part, Haematite (Fe_2O_3) and Magnetite (Fe_3O_4) are reduced to Ferrous Oxide (FeO).*

Details of the Process

- Iron ore is used to make iron and steel.
- Iron is produced in a blast furnace by reducing iron oxides with carbon.
- It is the carbon monoxide that removes the oxygen from the iron oxides – hence carbon monoxide is known as a reducing agent.
- Iron oxide ore is mined in many parts of the world.
- Examples of rich or high-quality ores are hematite Fe_2O_3 and magnetite Fe_3O_4 .
- A solid mixture of magnetite/hematite ore, coke and limestone is continuously fed into the top of the blast furnace.

Displacement Reaction

- Because its position in the reactivity series of metals, iron can be extracted using carbon in a blast furnace because iron is below carbon (iron is less reactive than carbon).
- Therefore, iron can be displaced from its oxides, by heating with the theoretically '**more reactive**' carbon in a sort of displacement reaction.

Metals		Reactivity
Potassium		Reacts with water
Sodium		
Lithium		
Barium		
Strontium		
Calcium		Reacts with acids
Magnesium		
Aluminium		
Carbon		
Manganese		
Zinc		
Chromium		
Iron		
Cadmium		
Cobalt		
Nickel		Included for comparison
Tin		
Lead		Highly unreactive
Hydrogen		
Antimony		
Bismuth		
Copper		
Mercury		
Silver		
Gold		
Platinum		

The Double Role of Coke

➤ The double role and function of coke (carbon) in the process of iron extraction is:

1. Coke function as a fuel:

- ✓ The coke is ignited at the base and hot air blown in to burn the coke (carbon) to form carbon dioxide in an oxidation reaction (C gains O).
- ✓ The heat energy is needed from this very exothermic reaction to raise the temperature of the blast furnace to over 1000 °C to affect the ore reduction.
- ✓ A preheated blast of air at 1500 °C, is blown into the furnace under pressure near to the bottom.

➤ The blast oxidizes carbon to CO₂:



2. Coke function as a reducing agent:

- ✓ At high temperatures the carbon dioxide formed, reacts with more coke (carbon) to form carbon monoxide.



- ✓ Carbon dioxide, CO_2 , is reduced by oxygen loss to the carbon, and the carbon is oxidized by oxygen, O gain, to carbon monoxide.
- ✓ CO is the molecule that removes the oxygen from the iron oxide ore.
- ✓ Reduction is a process of oxygen loss (or electron gain) and oxidation is a process of oxygen gain (or electron loss).
- ✓ The Fe_2O_3 loses its oxygen O (reduction), or Fe_3^+ gains three electrons to form Fe.

- ✓ CO is known as the reducing agent because it is the oxygen (O) remover and gets oxidized to carbon dioxide in the process (CO gains oxygen).
- ✓ This frees the iron, which is molten at the high blast furnace temperature, and trickles down to the base of the blast furnace and run off.
- ✓ An example of the main reduction reaction is:

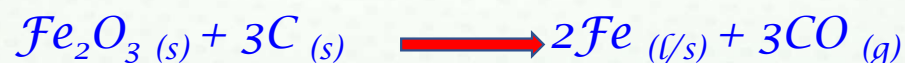
iron (III) oxide + carbon monoxide \longrightarrow iron + carbon dioxide



- ✓ Iron is initially formed as a liquid and then obviously solidifies on cooling.
- ✓ Note that the oxidation and reduction always go together.

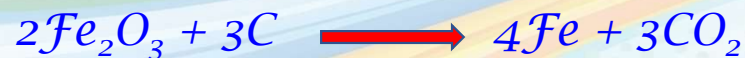
- ✓ Other possible iron ore reduction reactions are direct reduction of the iron oxide by carbon itself.

Iron (III) oxide + carbon \longrightarrow iron + carbon monoxide



or

iron(III) oxide + carbon \longrightarrow iron + carbon dioxide



For Magnetite:

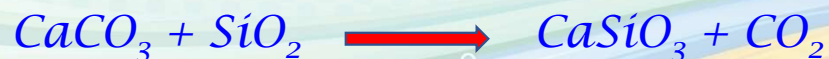


Or



The Role of Limestone

- The original ore contains acidic mineral impurities such as silica (SiO_2 , silicon dioxide).
- These react with the calcium carbonate (limestone) to form a molten slag, the main ingredient being calcium silicate.
- There are two ways to show the formation of the waste slag, which is mainly calcium silicate.



- This reaction is a sort of displacement reaction. The less volatile high melting/boiling silicon dioxide (silica) displaces the more volatile gaseous carbon dioxide.

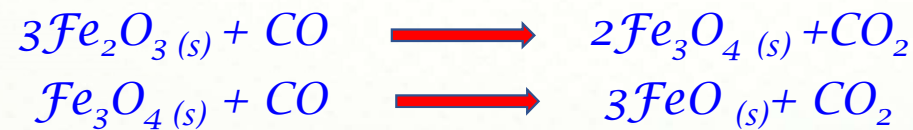
- However, this is sometimes shown in two stages reaction:



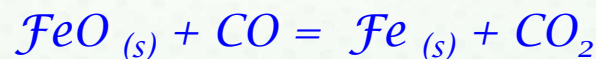
- The 1st reaction is the thermal decomposition of calcium carbonate into calcium oxide and carbon dioxide, and the reaction needs a high temperature of over 900 °C.
- The 2nd reaction is the combination of the basic calcium oxide and the acidic silicon dioxide to form calcium silicate.

Chemical Reactions in the Blast Furnace

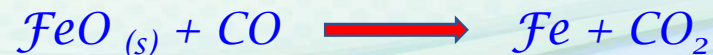
- **Zone 1** (< 950 °C), upper zone of stack, reduction of Fe_2O_3 , Fe_3O_4 takes place:



- **Zone 2** (950-1000 °C), chemical reserve zone, FeO is in equilibrium with gaseous phase:

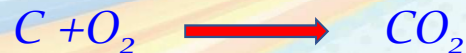


- **Zone 3** (950 < T < 1050 °C), the reduction of FeO by rising CO gas takes place:



- **Zone 4** (> 1000-1050 °C), direct reduction of FeO by carbon takes place.

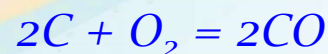
- Reaction in raceway zone:



Followed by



Overall



Slag

- The molten slag forms a layer above the denser molten iron, and they can be both separately, and regularly, drained away.
- The iron is cooled and cast into pig iron ingots OR transferred directly to a steel producing furnace.



Waste Gases and Dust

- The waste gases and dust from the blast furnace must be appropriately treated to avoid polluting the environment.
- The highly toxic carbon monoxide can be burnt to provide a source of heat energy, and in the exothermic reaction it is converted into relatively harmless carbon dioxide :



- Acidic gases like Sulphur dioxide from Sulphide ores, can be removed by scrubbing through an alkali solution such as calcium hydroxide solution ('limewater') where it is neutralized and oxidized to harmless calcium sulphate.

- *Any contaminated water must be purged of harmful chemicals before being released into a river or recycled via water treatment plant.*
- *The waste slag is used for road construction or filling in quarries which can then be landscaped.*
- *Iron from a blast furnace is ok for very hard cast iron objects BUT is too brittle for many applications due to too high carbon content from the coke.*
- *The presence of carbon within the structure of iron is considered as impurities.*
- *These impurities are favorable up to certain percentage.*
- *The carbon atoms are smaller in size compared to iron atoms and hence they make interstitial impurities.*

Impurities within Structures

➤ Schematic representation of different point defects:

1) *Vacancy:*

- Unoccupied lattice site
- Formed at time of crystallization

2) *Self-interstitial:*

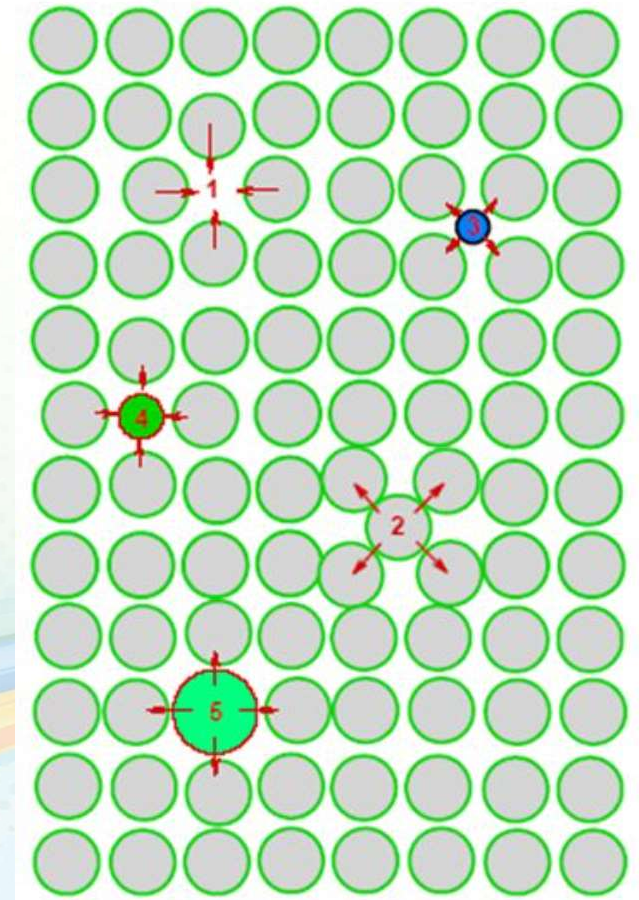
- Occupies normal lattice site,

3) *Interstitial impurity:*

- Occupies position between lattice sites-
- Alloying element, e.g., C in Fe

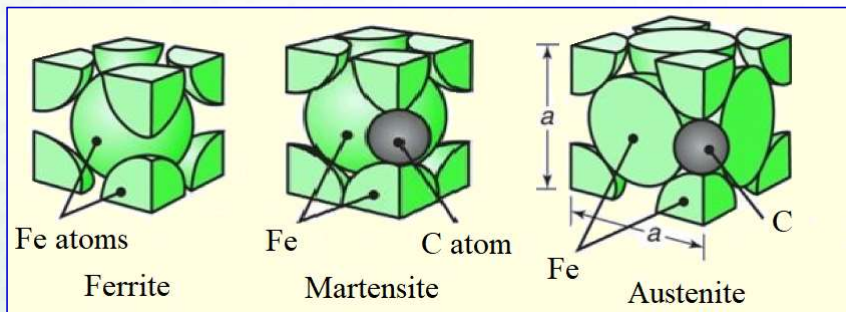
4&5) *Substitutional impurities*

➤ The arrows represent the local stresses introduced by the point defects



Atomic radius:
C : 0.071 nm and Fe 0.124 nm

5- Iron-Carbon (Fe-C) Phase Diagram

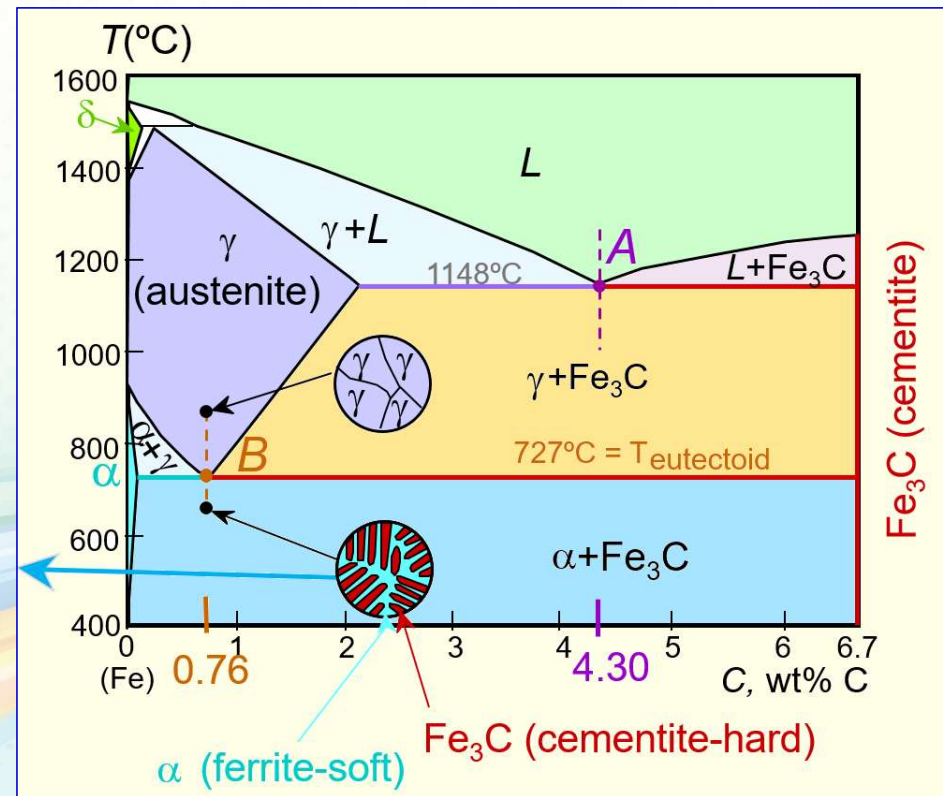
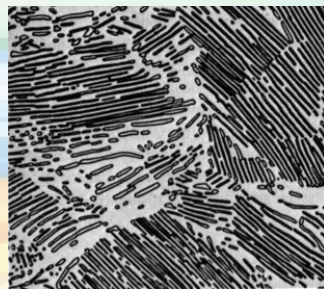


➤ Two important points

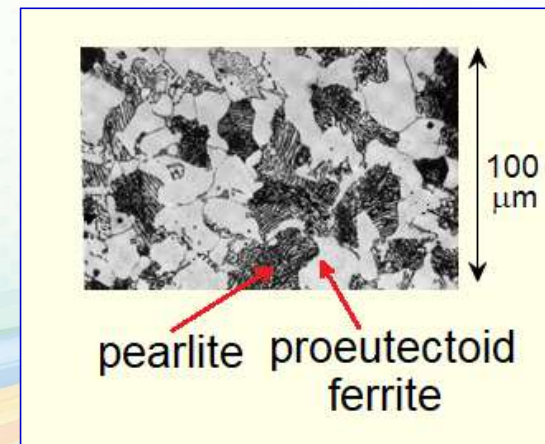
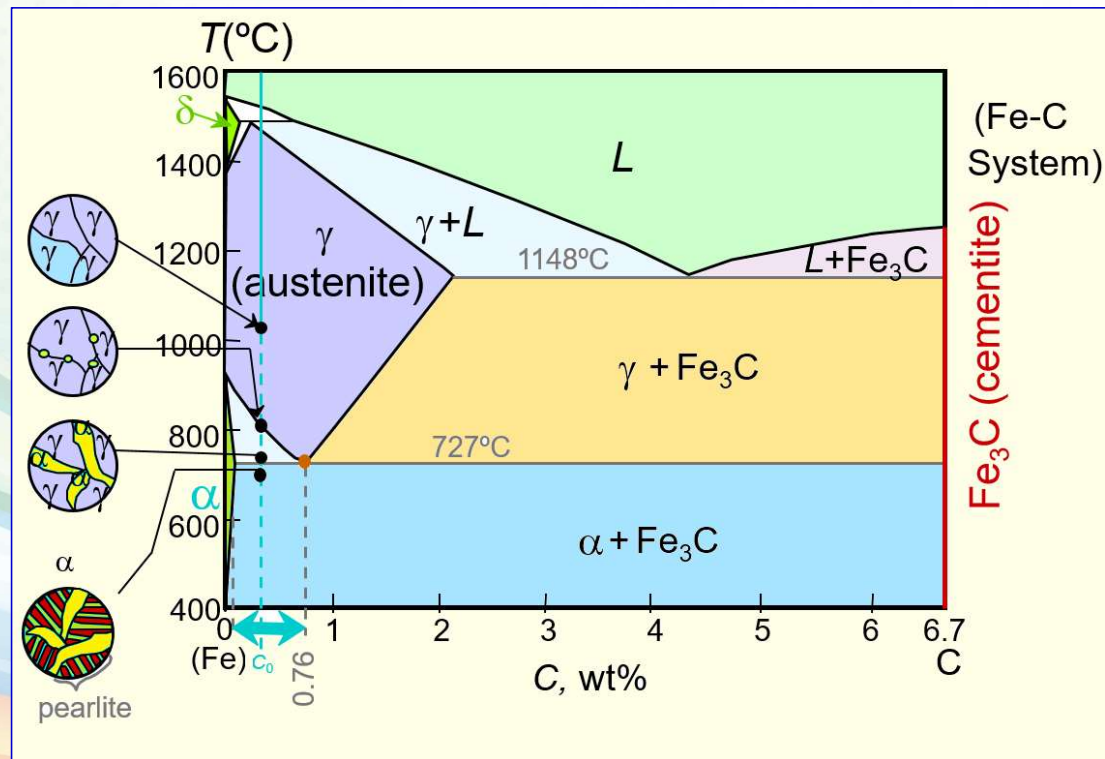
- ✓ **Eutectic (A):** $L \rightarrow \gamma + Fe_3C$
- ✓ **Eutectoid (B):** $\gamma \rightarrow \alpha + Fe_3C$

Result:

Pearlite = alternating layers of α and Fe_3C phases



Hypoeutectoid Steel



Hypoeutectoid Steel

Hypoeutectoid Steel

- Just above the eutectoid line

$$W_{\delta} = \frac{s}{r + s}$$

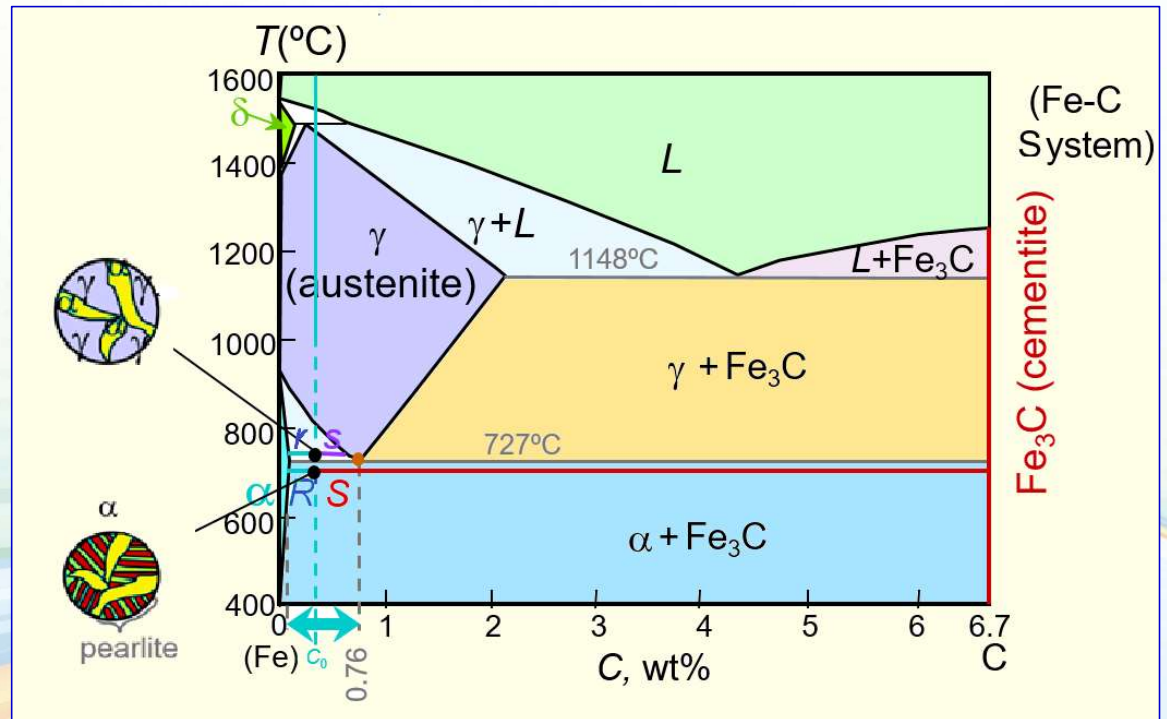
$$W_{\gamma} = (1 - W_{\delta})$$

- Just below the eutectoid line

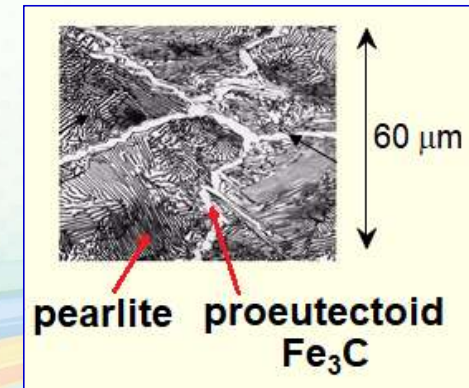
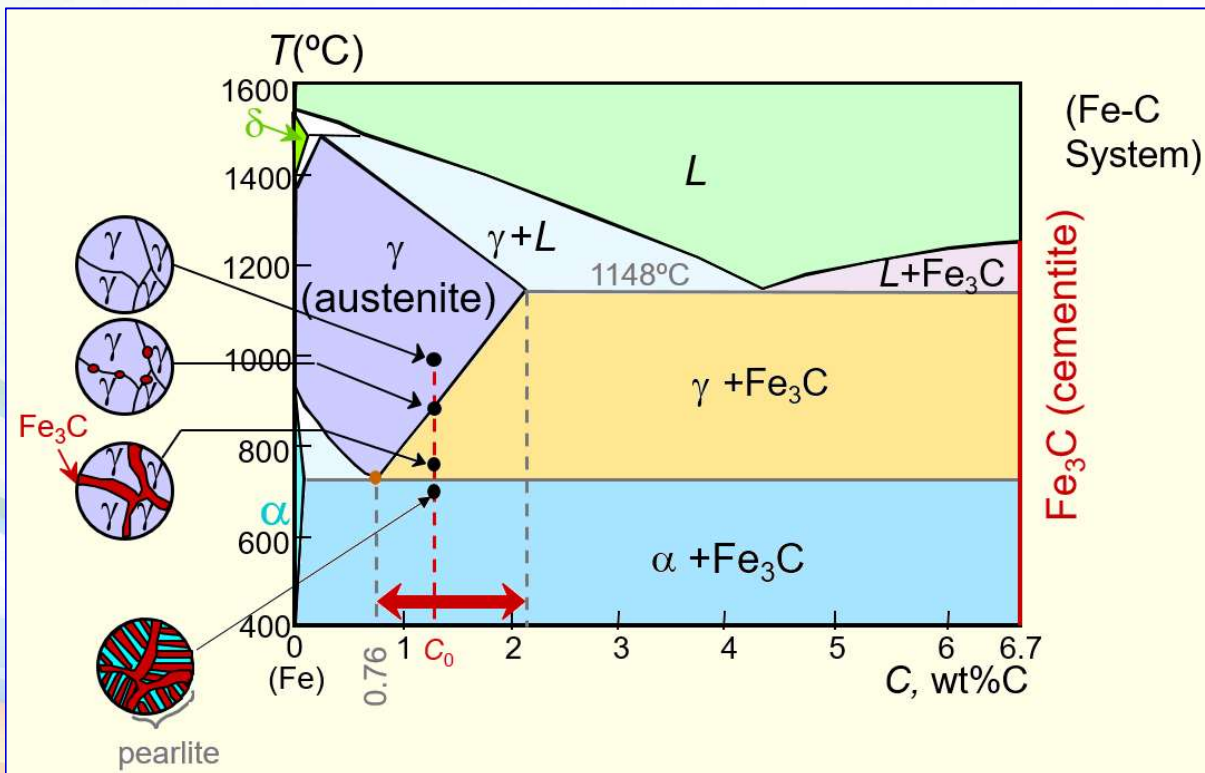
$$W_{\text{pearlite}} = W_{\gamma}$$

$$W_{\alpha} = \frac{S}{R + S}$$

$$W_{\text{Fe}_3\text{C}} = (1 - W_{\alpha})$$



Hypereutectoid Steel



Hypereutectoid Steel

Hypereutectoid Steel

- Just above the eutectoid line

$$W_{\gamma} = \frac{x}{v + x}$$

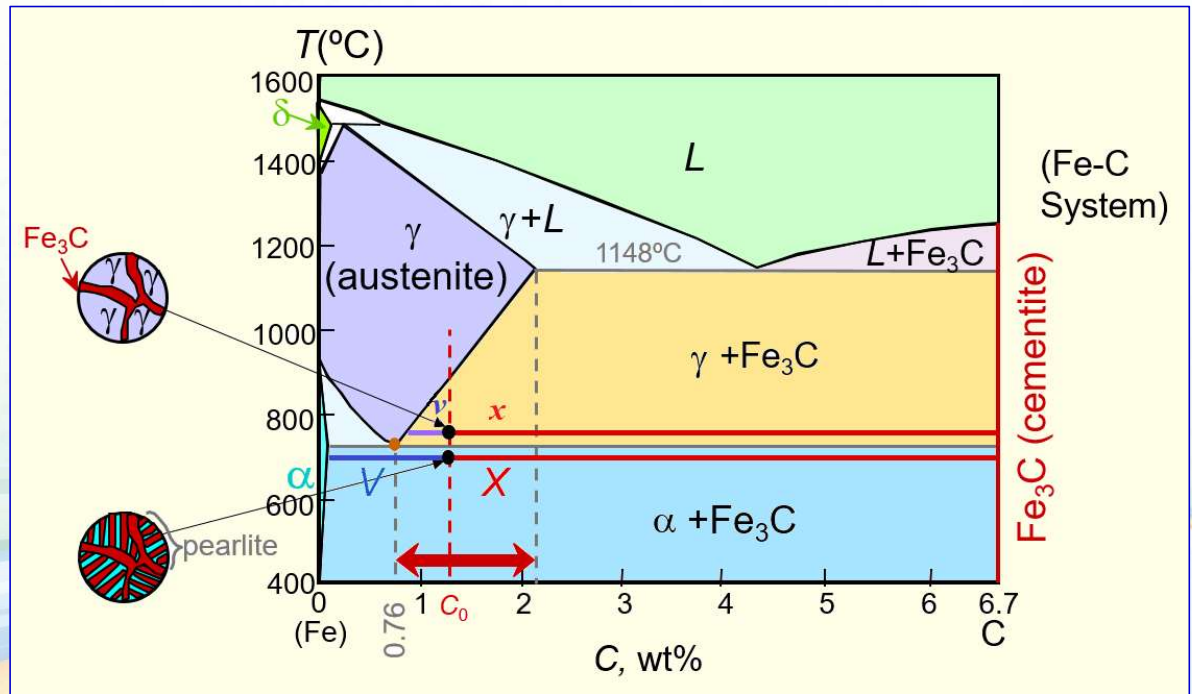
$$W_{Fe_3C} = (1 - W_{\gamma})$$

- Just below the eutectoid line

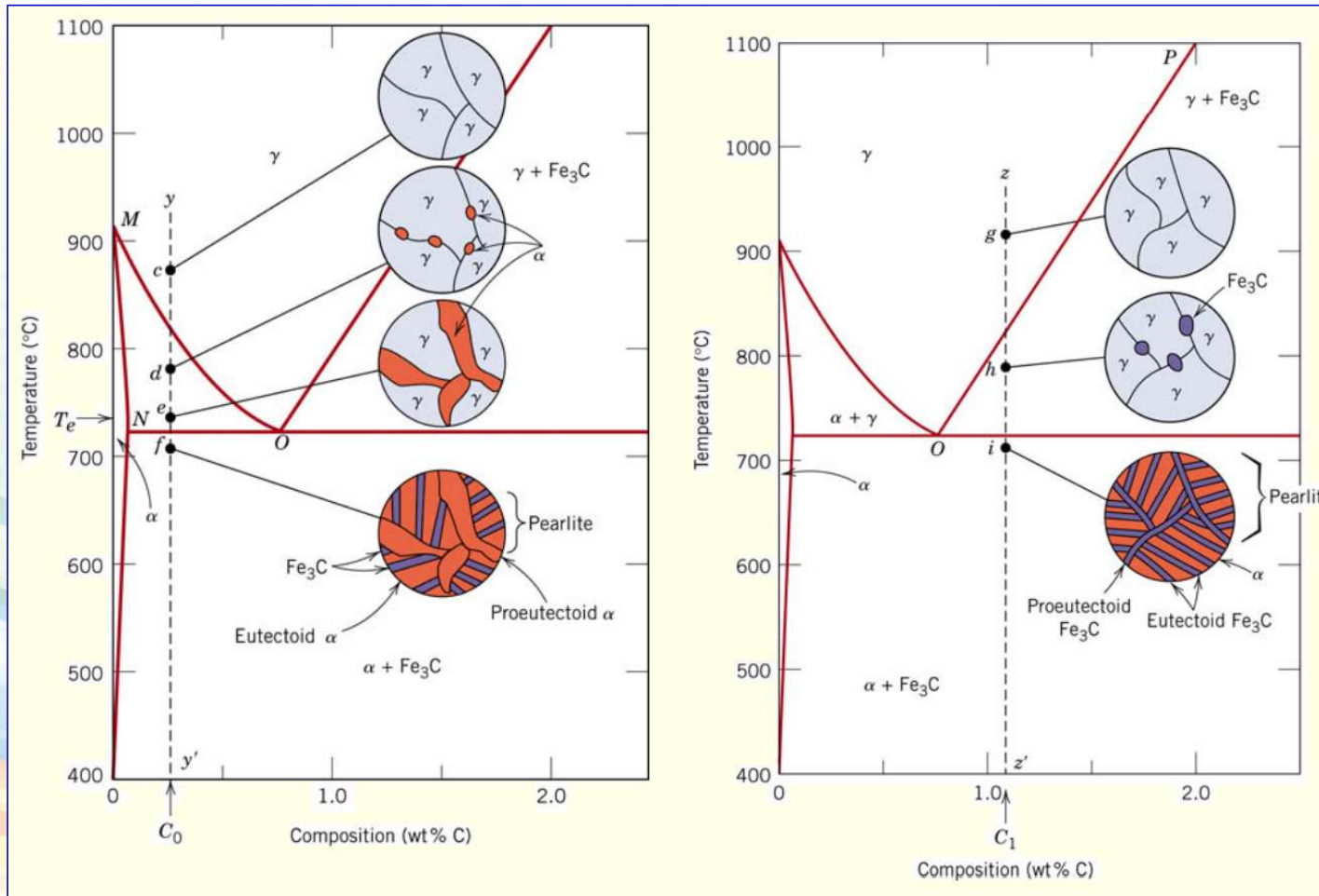
$$W_{pearlite} = W_{\gamma}$$

$$W_{\alpha} = \frac{X}{V + X}$$

$$W_{Fe_3C} = (1 - W_{\alpha})$$



Hypoeutectoid & Hypereutectoid



Phases in Fe-Fe₃C Phase Diagram

1. α -ferrite - solid solution of C in BCC Fe

- ✓ Stable form of iron at room temperature.*
- ✓ The maximum solubility of C is 0.022 wt%*
- ✓ Transforms to FCC γ -austenite at 912 °C*

2. γ -austenite - solid solution of C in FCC Fe

- ✓ The maximum solubility of C is 2.14 wt %.*
- ✓ Transforms to BCC δ -ferrite at 1395 °C*
- ✓ Is not stable below the eutectic temperature (727 ° C) unless cooled rapidly*

3. **δ -ferrite** solid solution of C in BCC Fe

- ✓ The same structure as α -ferrite
- ✓ Stable only at high T, above 1394 °C
- ✓ Melts at 1538 °C

4. **Fe_3C** (iron carbide or cementite)

- ✓ This intermetallic compound is metastable, it remains as a compound indefinitely at room T, but decomposes (very slowly, within several years) into α -Fe and C (graphite) at 650 – 700 °C

5. Fe-C liquid solution

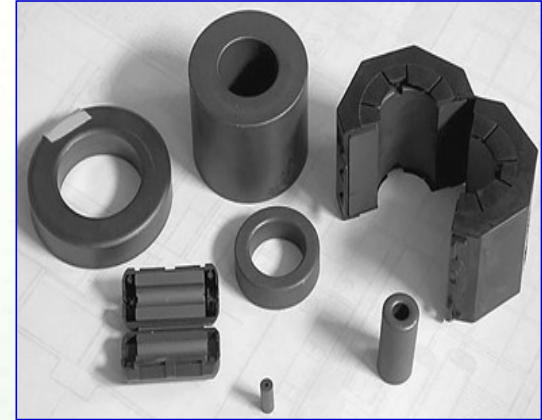
A few comments on Fe-Fe₃C system

- *C is an interstitial impurity in Fe. It forms a solid solution with α , γ , δ phases of iron.*
- *Maximum solubility in BCC α -ferrite is limited (max. 0.022 wt % at 727 °C) - BCC has relatively small interstitial positions.*
- *Maximum solubility in FCC austenite is 2.14 wt % at 1147 °C - FCC has larger interstitial positions.*
- *Mechanical properties: Cementite is very hard and brittle - can strengthen steels.*
- *Mechanical properties also depend on the microstructure, that is, how ferrite and cementite are mixed.*
- *Magnetic properties: α -ferrite is magnetic below 768 °C, austenite is non-magnetic.*

Classification of Iron

➤ Three types of ferrous alloys:

1. **Iron:** less than 0.008 wt % C in α -ferrite at room T.
2. **Steels:** 0.008 - 2.14 wt % C (usually < 1 wt%) α -ferrite + Fe₃C at room T.
3. **Cast iron:** 2.14 - 6.7 wt % (usually < 4.5 wt 50 %).



Example:

For a 99.6 wt% Fe and 0.40 wt% C steel at a temperature just below the eutectoid, determine the following:

- a) The compositions of Fe_3C and ferrite (α).*
- b) The amount of cementite (in grams) that forms in 100 g of steel.*
- c) The amounts of pearlite and proeutectoid ferrite (α) in the 100 g.*

Solution

a) Using the RS tie line just below the eutectoid

$$C_a = 0.022 \text{ wt\% C}$$

$$C_{\text{Fe}_3\text{C}} = 6.70 \text{ wt\% C}$$

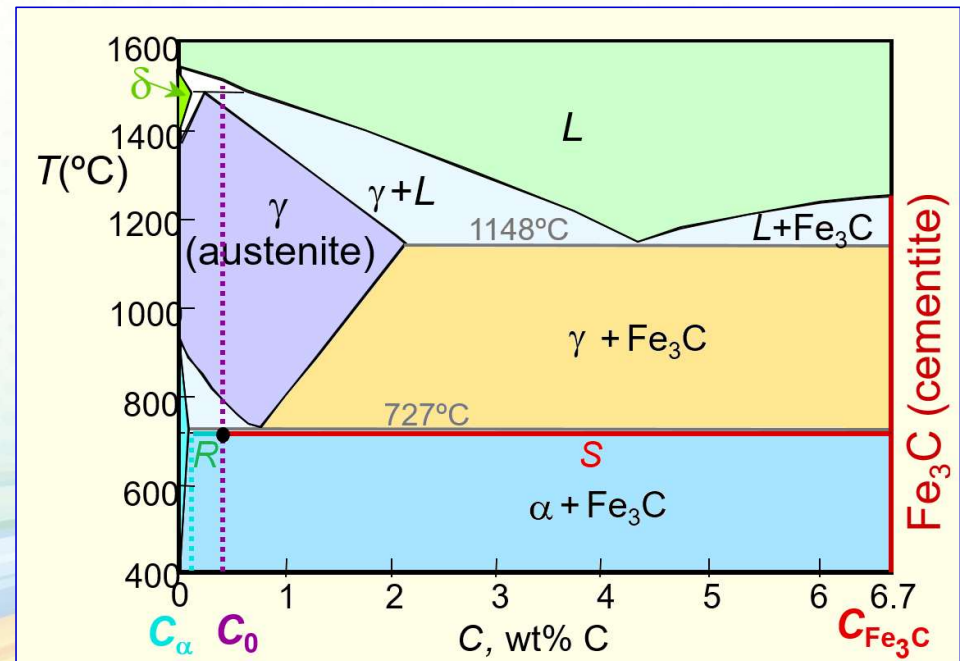
b) Using the lever rule with the tie line shown

$$\begin{aligned} W_{\text{Fe}_3\text{C}} &= \frac{R}{R+S} = \frac{C_L - C_\alpha}{C_{\text{Fe}_3\text{C}} - C_\alpha} \\ &= \frac{0.4 - 0.022}{6.7 - 0.022} = 0.057 \end{aligned}$$

Amount of Fe_3C (eutectoid) in 100 g

$$= (100 \text{ g}) W_{\text{Fe}_3\text{C}} = (100 \text{ g})(0.057) = 5.7 \text{ g}$$

$$\text{Amount of total ferrite in 100 g} = 100 - 5.7 = 94.3 \text{ g}$$



c) Using the VX tie line just above the eutectoid and realizing that

$$C_o = 0.40 \text{ wt\% C}$$

$$C_\alpha = 0.022 \text{ wt\% C}$$

$$C_{\text{austenite}} = C_\gamma = 0.76 \text{ wt\% C}$$

$$W_{\text{Austenite}} = \frac{V}{V + X} = \frac{C_o - C_\alpha}{C_\gamma - C_\alpha}$$

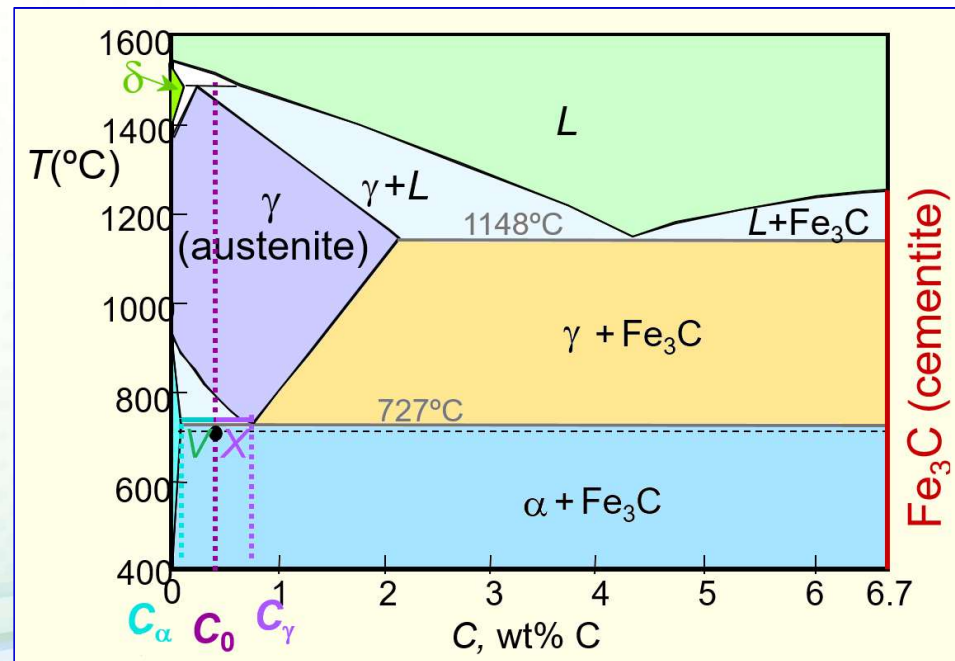
$$= \frac{0.4 - 0.022}{0.76 - 0.022} = 0.512$$

Amount of austenite in 100 g

$$= (100 \text{ g})(0.512) = 51.2 \text{ g}$$

Amount of proeutectoid ferrite in 100 g = 100 - 51.2 = 48.8 g

Then The amount of perlite ferrite (eutectoid) = 94.3 - 48.8 = 45.5 g



Why Steel

- Most metals in everyday use are alloys.
- Steel is an alloy because it is a mixture of a metal (iron) with other elements (carbon and perhaps other metals too).
- Iron is a good conductor of heat and can be bent or hammered into shape (malleable), quite strong physically - made stronger when alloyed with other materials.
- This makes iron useful as structural material and for making things that must allow heat to pass through easily and useful construction materials.



Cast Iron



Steel

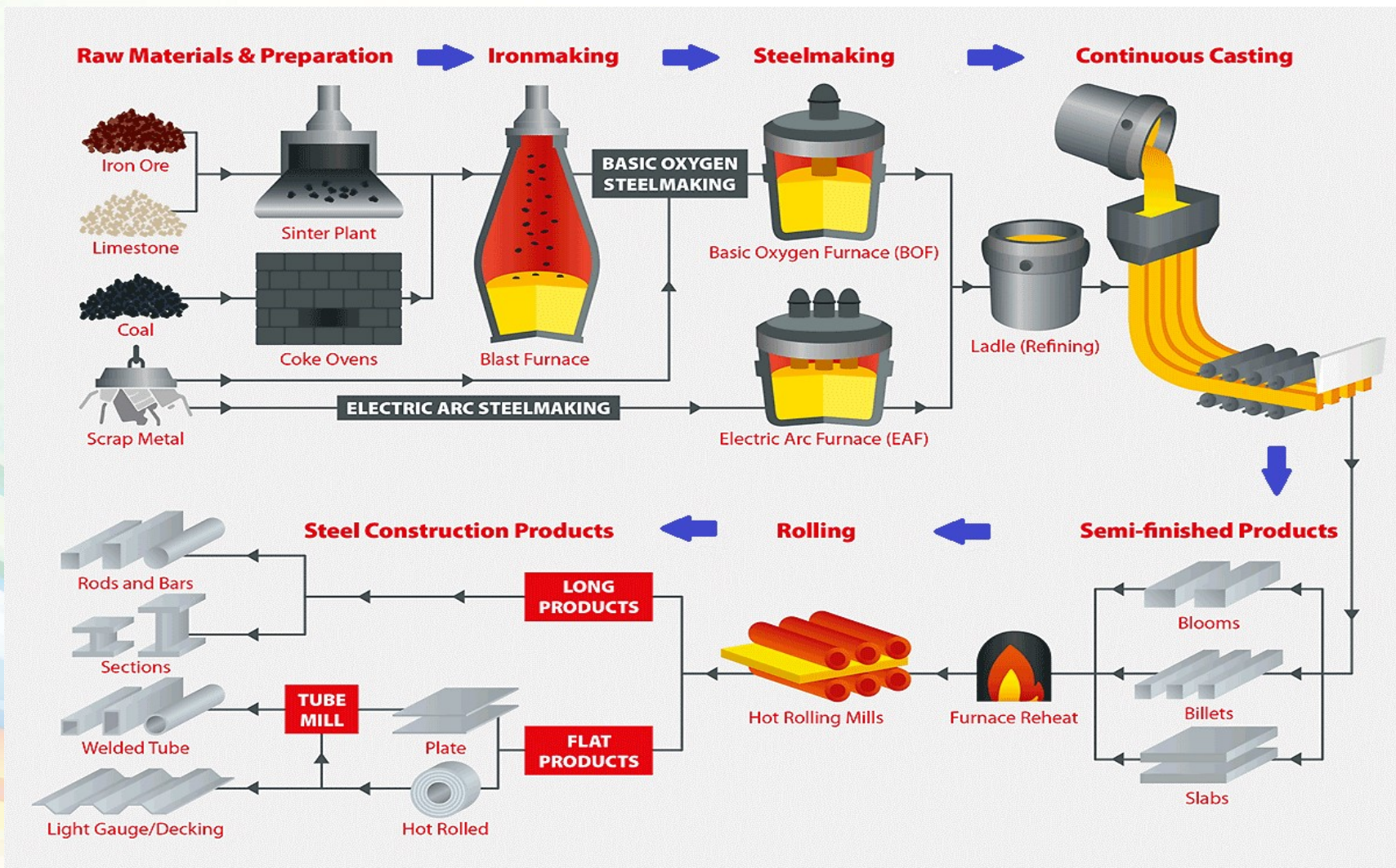
- *Iron from the blast furnace contains about ~96% iron with ~4% of impurities including carbon, silica and phosphorus.*
- *In this state the cast iron is too hard and too brittle for most purposes.*
- *Cast iron is hard and can be used directly for some purposes such as manhole covers because of its strength in compression and is very hard wearing.*
- *However, if all the impurities are removed, the resulting very pure iron is too soft for any useful purpose.*
- *Therefore, strong useful steel is made by controlling the amount of carbon and selected metals to produce an alloy mixture with the right physical properties fit for a particular application e.g., steel for car bodies, chrome stainless steel, extremely hard and tough tungsten-iron steel alloys etc.*

- *The real importance of alloys is that they can be designed to have properties for specific uses in terms of e.g., compression/tensile strength or corrosion reduction i.e., less susceptible to rusting.*
- *Low-carbon steels (0.1% carbon) are easily shaped for car bodies.*
- *High-carbon steels (1.5% carbon, often with other metals too) are hard wearing and inflexible and can be used for cutting tools, bridge construction.*
- *Stainless steels have chromium (and maybe nickel) added and are much resistant to corrosion (from oxygen/water) than iron or plain steel which readily rust.*
- *Objects made of iron or plain steel, particularly those exposed to the weather, regularly must be painted or coated with some other protective layer from the effects of water and oxygen.*

Main Process

- *Currently, the modern processes of making steel is categorized into two.*
- *Primary steelmaking which uses new iron commonly from blast furnace and Secondary steelmaking which uses steel scrap as the primary raw material.*
- *In primary steelmaking the method used is called basic oxygen steelmaking (BOS) wherein carbon-rich pig iron is made into steel.*
- *Most of the steel in the world is made using the BOS process.*
- *In secondary steelmaking, the equipment used is called electric arc furnace which is used for small amount and this mainly produces cast iron.*

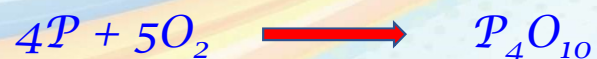
- *About 67% of the global crude steel total output is through the Basic Oxygen Furnace Steelmaking process and is recognized as the dominant steelmaking technology.*
- *Both molten pig iron and steel scrap are converted into steel with the oxidizing action of oxygen blown into the melt under a basic slag.*
- *A basic oxygen furnace yields high production with minimal labor involved and creates a finished product that is low in nitrogen.*
- *Because electric arc furnaces rely on mostly recycled materials to produce steel, the environmental factors alone are considered a major advantage.*



BOS Process

➤ The properties of iron can be altered by adding small quantities of other metals or carbon to make steel, one of the useful metal alloys in widespread use today.

1. Molten iron from the blast furnace is mixed with recycled scrap iron.
2. Then pure oxygen is passed into the mixture and the non-metal impurities such as silicon or phosphorus are then converted into acidic oxides [the BOS (basic oxygen steelmaking)].



3. Calcium carbonate (a base) is then added to remove the acidic oxide impurities (in an acid - base reaction). The salts produced by this reaction form a slag which can be tapped off separately.



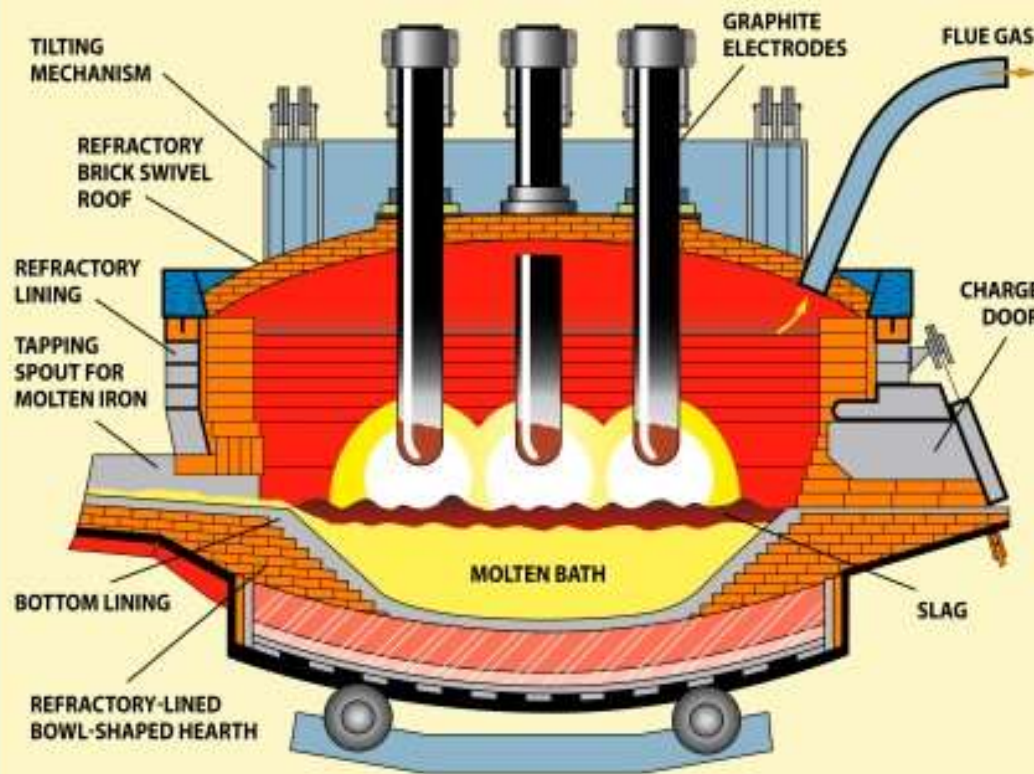
- These reactions produce pure iron.
- Calculated quantities of carbon and/or other metallic elements such as titanium, manganese or chromium are then added to make a wide range of steels with properties.
- Because of the high temperatures the mixture is stirred by bubbling in unreactive argon gas.

Electric Arc Furnace

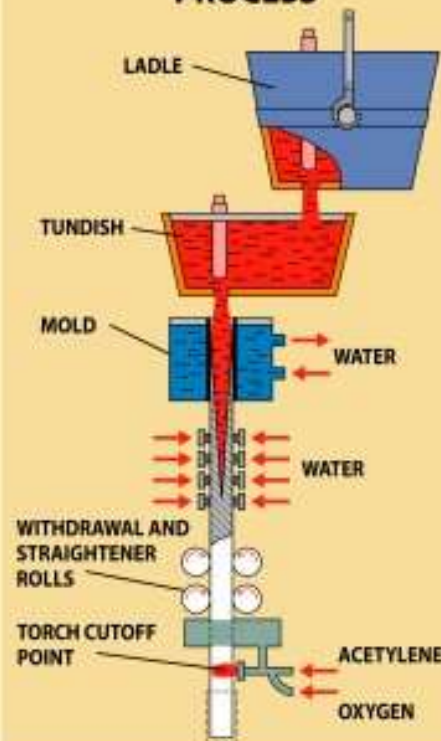
- *An electric arc furnace makes new steel from old steel scrap.*
- *It is a giant lidded steel kettle lined with heat-resistant ceramic refractory material.*
- *Its lid lifts for loading with scrap. The lid also holds the three graphite electrodes that create the electric arc to melt the scrap into new steel.*
- *After loading, the electrodes are lowered into the scrap and power fed to the furnace.*
- *Electricity arcs between the electrodes, creating the heat needed to melt the steel scrap. Fluxing compounds remove impurities.*

- *To obtain additional heat, steelmakers inject pulverized coal and oxygen to supplement the electrical heat.*
- *Roughly a third of the heat in electric arc furnaces comes from the injection of fuel and oxygen.*
- *An electric arc furnace provides precise control of the internal atmosphere and temperature. It emits almost no pollution.*

ELECTRIC ARC FURNACE STEELMAKING



CONTINUOUS CASTING PROCESS

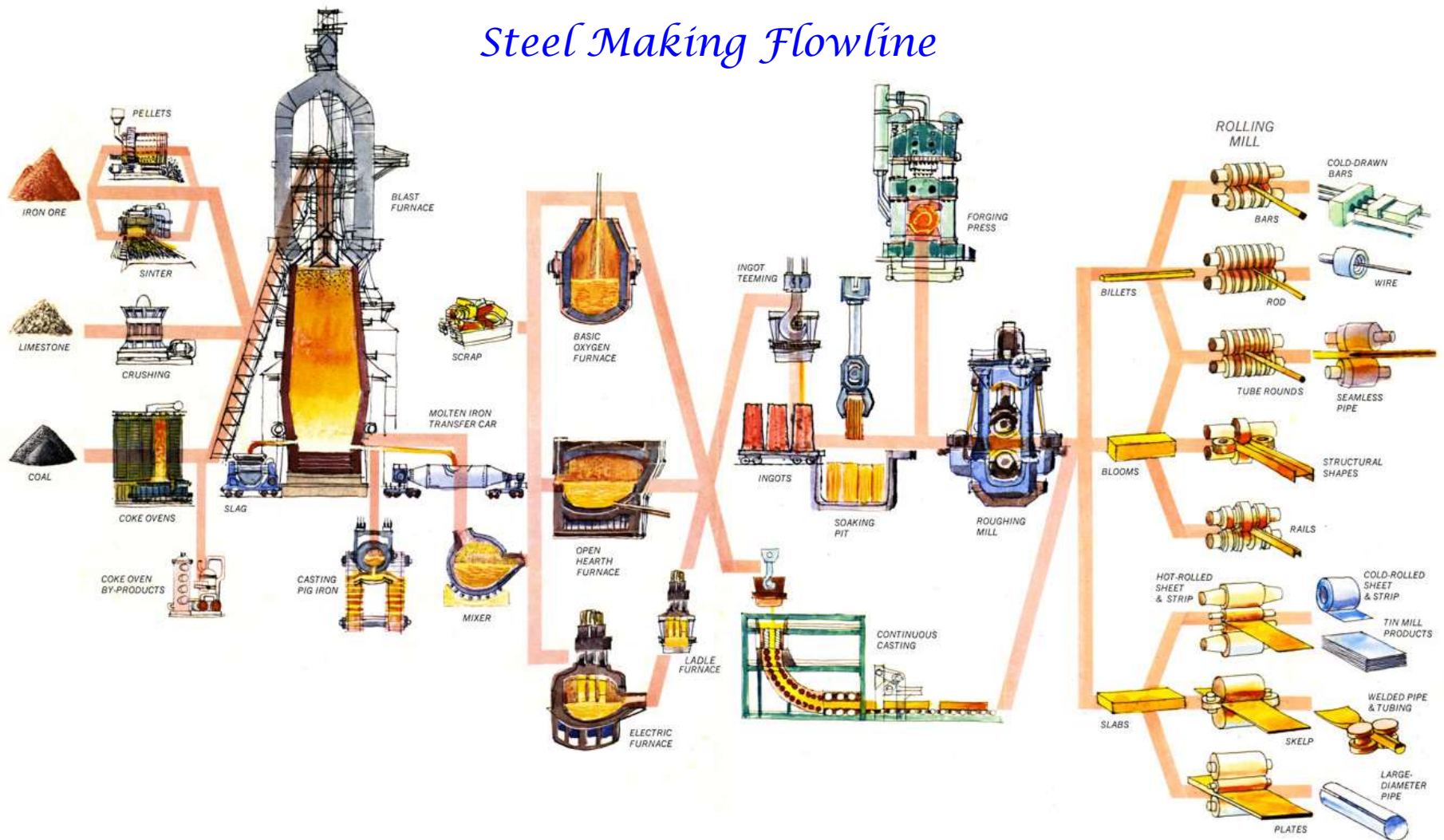


BOF Comparison with EAF

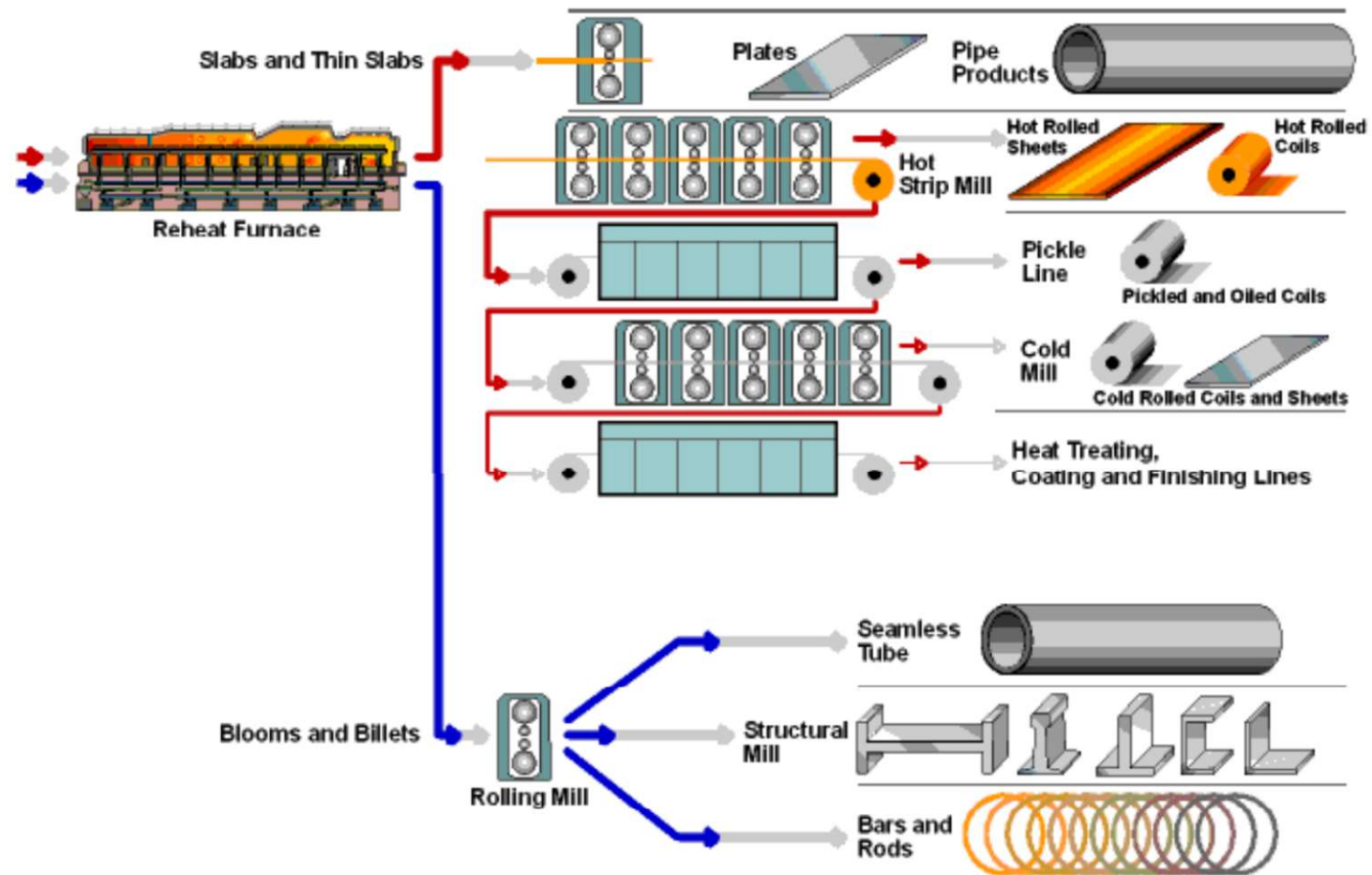
- *Blast furnace-basic oxygen furnace uses iron ore as its base raw material that accounts over just 50% of BOF steel costs, and electric arc furnace uses scrap as its base that represents around 75% of EAF steel cost.*
- *The Basic Oxygen Steelmaking process differs from the EAF is that BOF is self-sufficient in energy. The primary raw materials for the BOP are 70-80% liquid hot metal from the blast furnace and the steel scrap need to be balanced. These are charged into the Basic Oxygen Furnace (BOF) vessel.*
- *Oxygen (>99.5% pure) is “blown” into the BOF at supersonic velocities. It oxidizes the carbon and silicon contained in the hot metal liberating great quantities of heat which melts the scrap.*

- *A big difference between the two steelmaking processes however is in the capital investment costs involved.*
- *Whilst a typical integrated (i.e., BOF-route) steel mill today costs ~\$1100 per ton of installed capacity, a medium-size EAF-route mini-mill today costs under \$300 per ton in terms of the initial capital outlay*

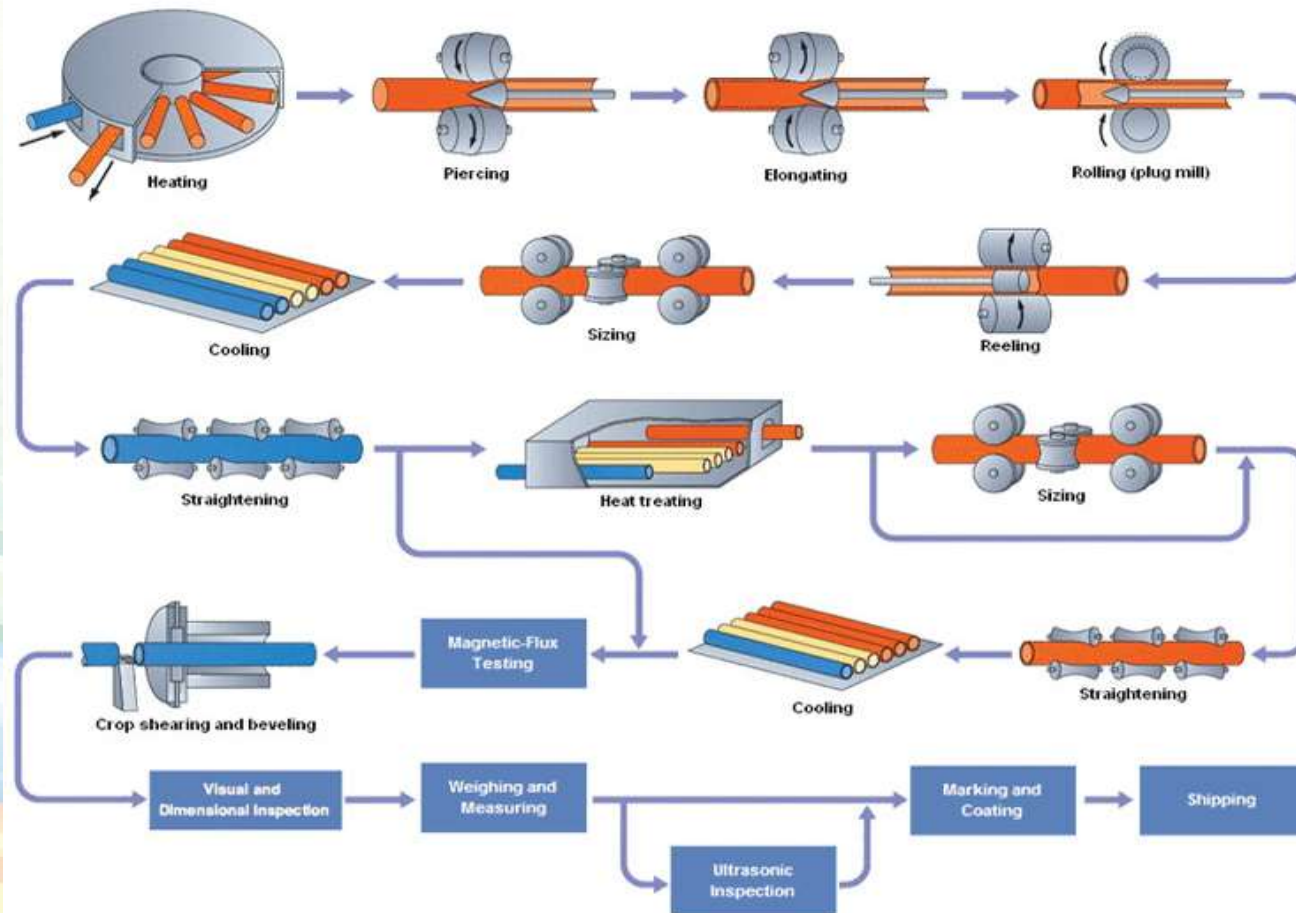
Steel Making Flowline



Steel Finishing Flowline



Hot rolling seamless steel pipe process flow



Economics of Recycling Scrap Steel

- Most steel consists of >25% recycled iron/steel and you do have the 'scrap' collection costs and problems with varying steel composition BUT you save enormously because there is no mining cost or overseas transport costs AND less junk lying around.
- Some companies send their own scrap to be mixed with the next batch of 'specialized' steel they order, this saves both companies money.
- About 42% of iron/steel in goods/components manufactured in iron/steel is recycled iron/steel, whether it be steel pans, car bodies, bridge girders, stainless steel cutlery etc.
- This makes good economics because recycling saves on several costs AND allows a mineral resource like iron's hematite or magnetite ore resources to last a lot longer.

- *Slower depletion of the Earth's mineral ore resources will make it last longer.*
- *Transport costs may be less.*
- *Mining costs are omitted – energy/machinery involved in digging out the ore, crushing it, transporting the ore.*
- *The cost of extracting the metal from its finite ore resource – chemicals needed (coke, limestone), constructing and running a blast furnace will be reduced as well.*
- *So, scrap metal merchants are doing a roaring trade now.*
- *The savings are partly reduced by the cost off collecting waste/scrap metal.*