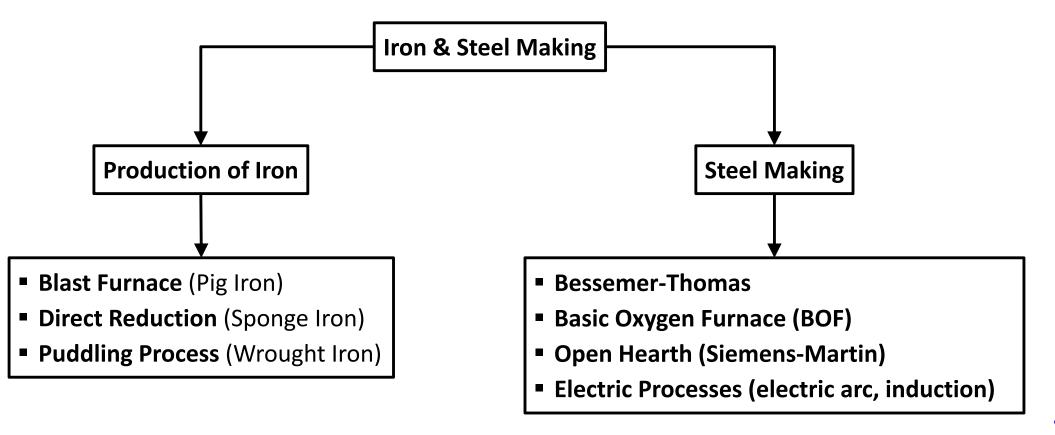


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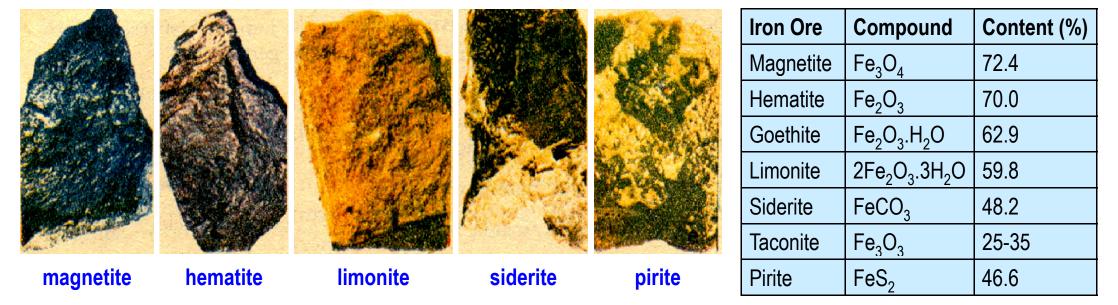


- > Ferrous metals (steels and cast irons) are the most widely used engineering materials.
- A variety of structures and properties can be obtained from steels (to some extent from cast irons) by changing carbon content, adding alloying elements, heat treatments, or processing.
- In this chapter, the objective is to understand making of iron & steel and to familiarize with the constituents of ferrous metals in order to facilitate the study of their physical metallurgy.





- Iron is the fourth most plentiful element in earth's crust.
- Iron ores are almost never found in their native or metallic state. Instead, they are found all over the world in the form of various compounds (mainly oxides).
- Depending on the type, iron content of the ore ranges from 25% up to 70%. Until recently, ores containing less than 30% iron were not considered viable. However, a shortage in iron supply has changed the scenario, and taconite is now readily mined for iron.



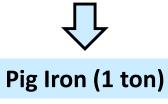
- Ores are removed by open-pit mining (instead of costly and hazardous underground mining). Then, they are separated from the worthless material (gangue) and refined to produce iron.
- ➤ The procedure is: mining ► concentration ► purification ► reduction ► refining

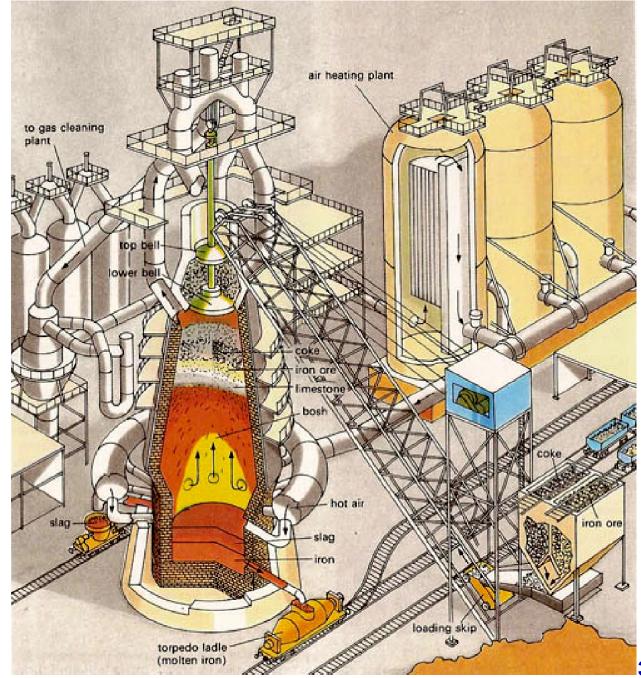


- Pig iron is produced in the blast furnace (a refractory lined chamber of 11 m wide and 40 m high).
- Three raw materials (iron ore, coke, limestone) are put into furnace, and molten iron with slag is produced.

Raw Materials (7 tons)

- iron ore (2 tons)
- coke (1 ton)
- Iimestone (0.5 tons)
- various gases (3.5 tons)
 - carbon monoxide (CO)
 - hydrogen (H₂)
 - carbon dioxide (CO₂)
 - water (H₂O)
 - nitrogen (N₂)
 - oxygen (O₂)

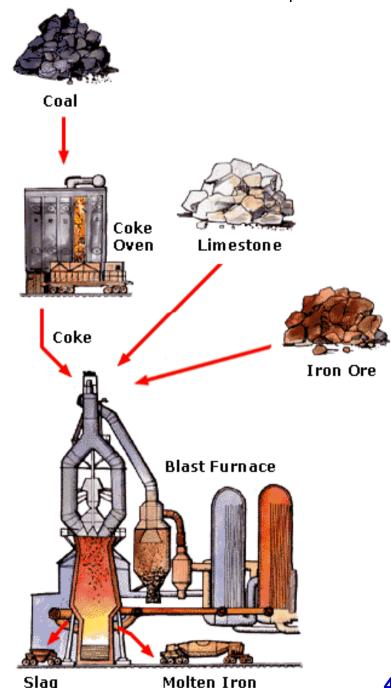






► Iron ores are pelletized & sintered before use in furnace.

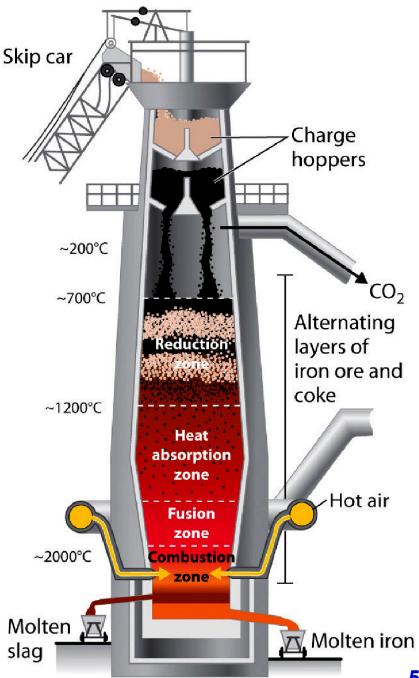
- > Limestone (kirec taşı) is a rock having high proportions of calcium carbonate (CaCO₃). It is used as a flux to react with and remove impurities in molten iron as slag.
- > This waste slag is lighter than iron in weight, so it floats on top of iron and helps protect the iron from oxidation.
- It is drawn off periodically, and hauled away in slag cars.
- Coke (kok kömürü) is obtained after burning certain soft coals without air in a coke oven.
- ➤ It is hard, brittle, porous material having 85-90% carbon together with some ash, sulphur, and phosphorous.
- Coke serves two functions in the reduction process:
 - It is a fuel supplying heat for the chemical reactions
 - It produces CO to reduce the iron ore





In blast furnace, iron ore is reduced by combining it with coke. In other words, oxygen is removed from iron ore and combined with carbon. Thus, metallic iron is released from its oxides.

- Charge is raised to hoppers via skip cars on inclined rails, and raw materials enter furnace through hoppers until the entire furnace is filled with charge.
- Cross-section of the furnace increases towards bosh region. Charge is compressed at lower-bosh region due to smaller cross-section, and this compression supports the weight of the material above.
- Air is blown in through tuyeres at bottom of furnace. Before this, it is preheated to 600-800 °C (in stoves of refractory bricks) in order to increase the efficiency of production. To reduce erosion, the shell of furnace is water cooled.



C: coke (85-90% carbon with impurities) raw Fe_2O_3 : iron(III) oxide (ferric oxide – hematite) materials → hot gases Fe_3O_4 : iron(II,III) oxide (magnetite) **5** around 900 °C FeO : iron(II) oxide (ferrous oxide) CaCO₃: limestone (calcium carbonate) limestone decomposes into lime: CaO: lime (calcium oxide) $CaCO_3 \rightarrow CaO + CO_2$ 200 °C CaSiO₃: slag (calcium silicate) moisture loss lime combines with silica to form slag: SiO₂: silica in iron $CaO + SiO_2 \rightarrow CaSiO_3$ 700 °C **2** after 700 °C lime also removes sulphur from iron: reduction $CaO + FeS + C \rightarrow Fe + CaS + CO$ iron(III) oxide is reduced to iron(II,III) oxide: $3 \operatorname{Fe_2O_3} + \operatorname{CO} \rightarrow 2 \operatorname{Fe_3O_4} + \operatorname{CO_2}$ 1200 °C **4** before 1200 °C heat absorption **B** around 850 °C iron(II) oxide is reduced to iron: 1600 °C · iron (II,III) oxide is reduced to iron(II) oxide: $FeO + C \rightarrow Fe + CO$ fusion $Fe_3O_4 + CO \rightarrow 3 FeO + CO_2$ 2000 °C carbon dioxide is re-reduced: — hot air combustion $C + CO_2 \rightarrow 2 CO$ around 1650 °C coke unites with oxygen of hot air: Int. $2C + O_2 \rightarrow 2CO$ slag

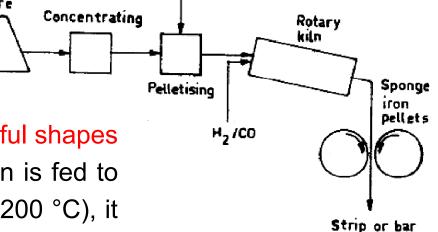
Production of Pig Iron

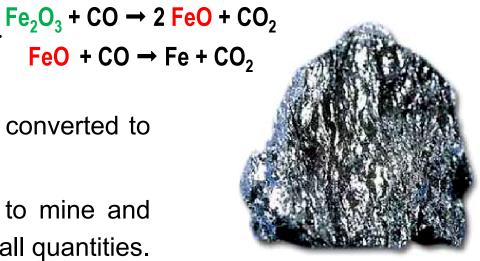
molten iron

- Molten iron (at the bottom of blast furnace) contains carbon (3.0-4.5%), silicon (4%), and manganese (up to 1%) as well as some other unwanted impurities (such as sulphur and phosphorous). These are later removed to some extent during steel making process.
- Production of pig iron is an intermediate stage in the manufacture of steel. The iron is tapped at intervals and collected in a transfer car which is insulated to keep the iron hot. Then, it is moved to the steel furnace and added to the charge of steel scrap with limestone.
- Sometimes, the iron is not made into steel. Instead, it is poured directly into moulds. Before the introduction of pig casting machines, the iron was poured into open sand moulds consisting of a groove or through with many small moulds on each side (reminding one of sow and pigs), hence the name is pig iron. Iron pigs are melted in cast iron foundries and in steel mills.

- ► Iron from ore can be directly reduced to produce sponge iron in a solid state reduction at 750 °C using natural gas or some other reductant.
- > This iron has a spongy appearance, and it can be converted to steel using an electric process.
- > Solid state, low temp. reaction makes it possible to mine and produce this iron from very remote areas in very small quantities.
- Considerable research has gone into development of this technology, and small-size steel plants were constructed (such as HyL, Midrex, SL/RN, Accar).
- Recent development is converting sponge iron into useful shapes by **sintering & pressing**. Sponge from direct reduction is fed to a large-dia rotary kiln. After gaseous reduction (1100-1200 °C), it is passed into small-gap rolls to have 80% reduction in thickness.
- > The products have similar mechanical properties of conventional low carbon steel, but the structure is guite different.

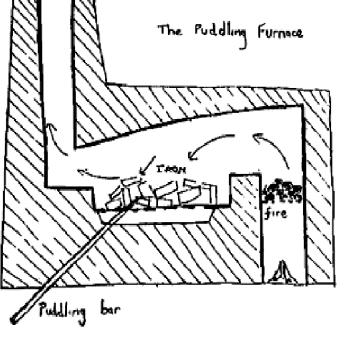
FeO + CO
$$\rightarrow$$
 Fe + CO₂







- In ancient times, before the advent of steel and pig iron, iron was produced by a direct process whereby the ore was heated in a forge to white heat to remove impurities. Charcoal fire in the forge was not hot enough to melt the iron, thus the result was a pasty mass of spongy iron that was then hammered to remove molten gangue or slag. Wrought iron is never cast; instead it is hammered, pressed, or forged.
- Wrought iron was used extensively before modern steel making processes (such as bars, plates, rails and structural shapes for bridges, boilers and many other applications). It has particularly been used where the parts are to be forged or welded.
- Wrought iron was made by puddling process: pig iron was melted in open hearth furnace. Iron oxide was added so that carbon and other impurities were removed by iron oxide slag. The mass of iron was removed and squeezed to remove the slag, but much of slag remained in the iron. The result was low-carbon, fibrous (due to trapped slag), soft iron.
- Today, Aston process is used: molten pig iron and steel are poured into open hearth furnace in a prepared slag. This cools the metal to a pasty mass, and it is squeezed in a hydraulic press. The slag is distributed in iron matrix as threads and fibers in rolling direction. This imparts excellent ductility to wrought iron. In addition, it has good machinability and corrosion resistance.







- Since pig iron contains too many impurities, it must be refined to produce steel or cast iron of various types. Steel is simply an alloy of iron with most of its impurities removed (containing 0.03 2% carbon, plus other alloying elements).
- Over 90% of steels is plain carbon steel (having less than 1% carbon with little manganese to control sulphur and other impurities). The rest is all other alloy steels.
- ► Major steel making processes (with their use in percentages):
 - 1. Bessemer-Thomas: 0% (not generally used today due to its product of inferior steel)
 - 2. Basic Oxygen Furnace (BOF): 60% (majority of steels are produced by this process)
 - 3. Open Hearth (Siemens-Martin): 15% (superior to Bessemer-Thomas)
 - 4. Electric Processes: 25% (for producing high quality & special purpose steels)
- > These processes are classified **depending upon the formation of slag**:
 - Acidic process: the slag with high silica
 - Basic process: the slag with high lime

Acidic Process

Non-metallic oxides oxidize iron into iron(II) oxide & iron(II,III) oxide which subsequently oxidizes C, Mn, Si (P is not oxidized as it would be reduced again in the presence of SiO₂):

 $2 \operatorname{Fe} + \operatorname{O}_{2} \rightarrow 2 \operatorname{FeO}$ $3 \operatorname{Fe} + 2 \operatorname{O}_{2} \rightarrow \operatorname{Fe_{3}O_{4}}$ $4 \operatorname{C} + \operatorname{Fe_{3}O_{4}} \rightarrow 4 \operatorname{CO} + 3 \operatorname{Fe}$ $C + \operatorname{FeO} \rightarrow \operatorname{CO} + \operatorname{Fe}$ $Mn + \operatorname{Fe_{3}O_{4}} \rightarrow MnO + 3 \operatorname{FeO}$ $Mn + \operatorname{FeO} \rightarrow MnO + \operatorname{Fe}$ $Si + 2 \operatorname{FeO} \rightarrow SiO_{2} + 6 \operatorname{FeO}$ $Si + 2 \operatorname{FeO} \rightarrow SiO_{2} + 2 \operatorname{Fe}$

Such oxides form slag which floats over molten steel protecting it from excessive oxidation:

> FeO + SiO₂ → FeO.SiO₂ 2 FeO + 3 SiO₂ → (FeO)₂.(SiO₂)₃ MnO + SiO₂ → MnO.SiO₂ 2 MnO + 3 SiO₂ → (MnO)₂.(SiO₂)₃

Refractory lining is acidic (silica) since it would otherwise react with the bath producing cracks.

Basic Process

Metallic oxides oxidize impurities. Limestone is added as oxidizing agent unless oxygen is blown in the process (as in Bessemer process):

Steel Making

$$\begin{array}{c} CaCO_{3} \rightarrow CaO + CO_{2} \\ CO_{2} + Fe \rightarrow FeO + CO \\ C + FeO \rightarrow CO + Fe \\ Fe_{3}C + FeO \rightarrow CO + 4 Fe \end{array}$$

$$\begin{array}{c} Si + 2 FeO \rightarrow SiO_{2} + 2 FeO \\ Mn + FeO \rightarrow MnO + Fe \\ FeO \rightarrow CO + 4 Fe \end{array}$$

Slag forming reactions are as follows. <u>The third</u> <u>reaction</u> only takes place if slag is very basic and only slightly oxidizing (presence of Si reduces P, and it goes back to steel). In addition, S can be partially reduced in <u>the last reaction</u>.

> 2 FeO + 3 SiO₂ → (FeO)₂.(SiO₂)₃ MnO + SiO₂ → MnO.SiO₂ 2 Fe₃P + 8 FeO → (FeO)₃.P₂O₅ + 11 Fe CaO + FeS → CaS + FeO

Refractory lining is magnetite or dolomite.



- In both acidic and basic processes, the oxidizing agent is iron(II) oxide (FeO) although it is produced early in acidic process, and hence the time required for refining is shorter.
- Basic process has much more severe oxidizing condition, thus it is likely that some of FeO is present in steel which forms cellular structure around ferrite crystals reducing its strength.
- > Therefore, all being equal, acidic steel is probably more desirable.
- In most cases, too much carbon is burnt out during refining. Thereby, carbon content of steel is raised by adding ferromanganese (72-80% Mn, 6-8% C) or spiegeleisen (15-20% Mn, 4-6% C). They may be added during refining in acidic process whereas in basic process it is added in the ladle rest (which reduces phosphorous). Carburisers also act as deoxidizers.



- > The refined steel is produced through oxidation, and hence it may (in most cases it does) contain oxygen in the form of iron oxide and dissolved gas. This can be tackled by:
 - Deoxidation (killed steel)
 - Rimming (rimmed steel)

Killing

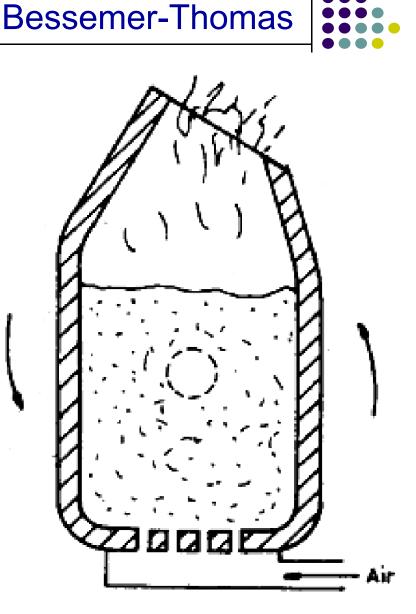
It is done by adding silicon (ferrosilicon) or aluminum, which form SiO₂ or Al₂O₃ by reacting with iron oxide or oxygen: $\begin{array}{c}
\text{Si} + 2 \text{ FeO} \rightarrow \text{SiO}_2 + 2 \text{ Fe} \\
2 \text{ Al} + 3 \text{ FeO} \rightarrow \text{Al}_2\text{O}_3 + 3 \text{ Fe}
\end{array}$

Rimming

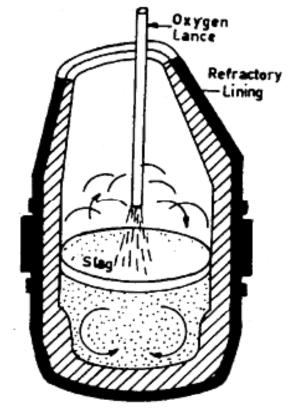
> Manganese is added in the form of ferromanganese which forms manganese iron oxide. During solidification, pure iron solidifies at the surface of the mold leaving the molten steel in the middle as enriched with carbon. Manganese iron oxide reacts with carbon to form CO.

This process uses pear-shaped converter (Bessemer Converter) with a capacity of 15-20 tons. It is filled with molten pig iron when it is in horizontal position. Pig iron is usually melted in a cupola before charging in the converter.

- The converter is turned to its vertical position, and compressed air (about 125 atm) is blown in through tuyeres which oxidizes all impurities to produce steel.
- The oxidation of carbon and silicon is an exothermic reaction (i.e. the heat keeps the steel molten). For low phosphorous iron, acidic process is used which takes about 10 minutes to oxidize the impurities.
- The quality of steel from this process is not very good, and hence this process is not commonly used.



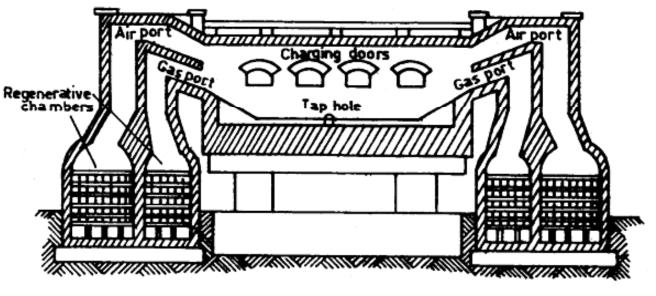
- Use of air in Bessemer process leads to high nitrogen steels, which is not desirable for certain applications. Basic oxygen process uses 98% pure oxygen instead of air. Basic oxygen converter resembles Bessemer converter, except that it is closed at the bottom.
- Molten metal in converter is refined by blowing pure oxygen at high pressures (higher than 800 atm) into the melt using water cooled lances. The agitation ensures uniform refining, and oxygen oxidizes the impurities and forming a slag.
- This is a basic process. It has the advantage of using 25% scrap as raw material to avoid excessive heat, and is faster than open hearth process (about 300 tons/hour).



Basic Oxygen

- The quality of steel is very good (due to low content of hydrogen and nitrogen). The further modification is to add lime powder into oxygen jets when using high phosphorous charge.
- > Lintz-Dowatz (L/D) process is commonly used for steel making.
- Kaldo and Rotor processes are the same as L/D, except that converter works in horizontal position instead of vertical. Largest proportion of steel is produced by these processes.

- In this process, steel is produced by heating molten pig iron, scrap, iron ore and other elements (such as ferrosilicon and flourspar to make slag viscous) in the furnace.
- It is superior to Bessemer process (not restricted to low phosphorous iron & uses steel scrap as charge).



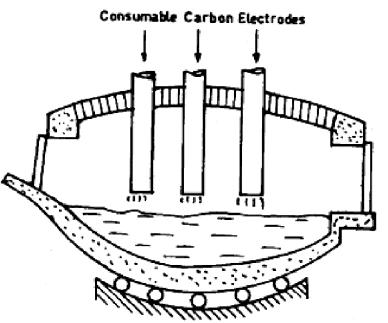
- Sufficiently high temperatures are obtained by using regenerative furnaces (the exhaust gases are used to heat up brick walls, which in turn supplies heat to the incoming gases).
- These furnaces produce 100-375 tons per heating of 8-10 hours. The flow of gases and air is alternated in every 15-20 minutes. Mostly basic process is used with limestone as flux.
- Although the quality of steel is good, limited amount of steel is produced by this process. Sometimes duplex process is used (acid Bessemer and basic open hearth are combined). Impurities (such as Mn and Si) are removed by Bessemer process followed by the removal of S and P in open hearth. However, duplex process is not very common.



- Electric steel making is employed when extremely high quality steel is required and electrical energy is cheap and plentiful. Alloy steels, tool steels, stainless steels and steel castings are produced by these processes.
- In such processes, pig iron and cold scrap are added as usual with other desired elements. The heat is provided by electrical energy in few ways. Atmosphere and temperature can be controlled precisely, and there is no excessive oxidation from furnace gases so that the steel composition can be manipulated accurately.

Electric Arc Furnace

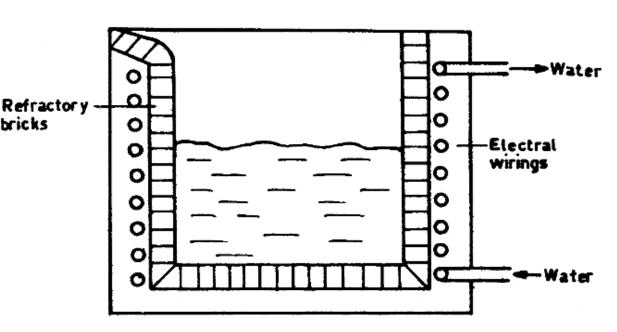
- Electricity from one electrode passes through an arc into the charge, and through another arc to other electrode.
- Usually a charge of graded-steel scrap is melted under basic slag (lime) to remove P. Second basic slag is used to remove S and to deoxidize the steel in the furnace.
- Capacity of furnaces may be 200 tons with production rate of 40 tons/hour and power of 50,000 KWh. Graphite electrodes (up to Ø760 mm, over 24 m long) are used. Operating potential is 40 V, and current exceeds 12,000 A.



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Induction Furnace

- A coil is wound around a crucible, and a high current in the coil heats the metal which forms the secondary of a transformer. Alternating current in the primary coil creates magnetic field and produces an eddy current in the metal.
- Penetration of eddy current depends upon the frequency, and a frequency of 500-2000 Hz is generally used.
- Capacity of furnaces usually ranges from few kilograms to 5 tons.
- High quality bearing and tool steels are produced by this process.
- Another method of heating the charge (which is sometimes used) is to make the charge a career of electricity. The charge is heated due to its electrical resistivity when electricity is passed through it (just like an electrical coil is heated when current is passed through it).







- > As a result of deoxidation and incomplete removal of impurities, the molten steel has either dissolved impurities (Mn, Si, P) and gases or suspended non-metallic inclusions.
- > These impurities remain in their positions through cooling and transformation to ferrite and pearlite structures. The dissolved impurities may strengthen ferrite or may react with other elements to form inclusions and other phases depending upon the nature of the impurity.
- > Manganese: promotes depth of hardening, but also liable to quench cracking. It may dissolve in ferrite to give solid solution strengthening; or it may form carbides, sulphites or manganese-silicate inclusions.
- > Silicon: present in most steels (usually less than 0.2%), and generally beneficial.
- > Sulphur: Should be kept in low amounts (< 0.05%). Exists as sulphide (MnS or FeS). FeS forms brittle, low melting point, yellowish brown film around solid steel crystals and causes the metal to split when forged. MnS is a dove grey colored inclusion which is only slightly soluble in iron and segregates into large globules irregularly distributed throughout steel.
- > It is plastic at high temperatures, and elongates into fibers during rolling without impairing mechanical properties. It may improve fatigue characteristics by enveloping brittle oxides. 19



- Phosphorous: has powerful tendency to segregate. The amount should be max. 0.05% (more than that is dangerous and should be avoided by keeping its content below 0.05%).
- ➤ It forms a compound which dissolves in iron up to 1.7%, but in the presence of 3.5% C its solubility is reduced to 0.3% and the excess forms a brittle eutectic found in cast irons.
- In rolled steels, areas containing high P are elongated into bands (ghost bands), which are characterized by the absence of pearlite (weak due to presence of P). In some specific cases, P is beneficial (e.g. in tin plates and for fire welding of spades).
- Dissolved carbon & nitrogen: cause strain aging after cold rolling in mild steels. They also affect the ductility as shown through impact tests.

Steel Finishing

- After steel making processes, the steel is poured into ingot moulds. These cast ingots are preheated (soaked) at 1200 °C. Then, they are formed into blooms, billets, and slabs.
- Billets Slabs Blooms > A bloom has square cross-section with min. size of 15 x 15 cm. ► A billet (smaller than bloom) has square cross-section from 4 cm up to the size of a bloom. > Slabs with rectangular sections Plates Structural shapes Rails Bars (min. 25 cm wide & 4 cm thick) are rolled from either ingot or bloom. The width is always 3 to 4 times Wire rods Skelp the thickness. Plates, skelp and Tube rounds Strip thin strips are rolled from slab. Wire Pipe and tubing > Other shapes are produced from slabs, blooms, and billets. Cold drawn bars Seamless pipe Tin plate Large diameter pipe