Iron Making and Steel Making
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Module – 06
Lecture – 26
History of Steelmaking

This is the first lecture in steelmaking and I will first give a brief history of the steelmaking.

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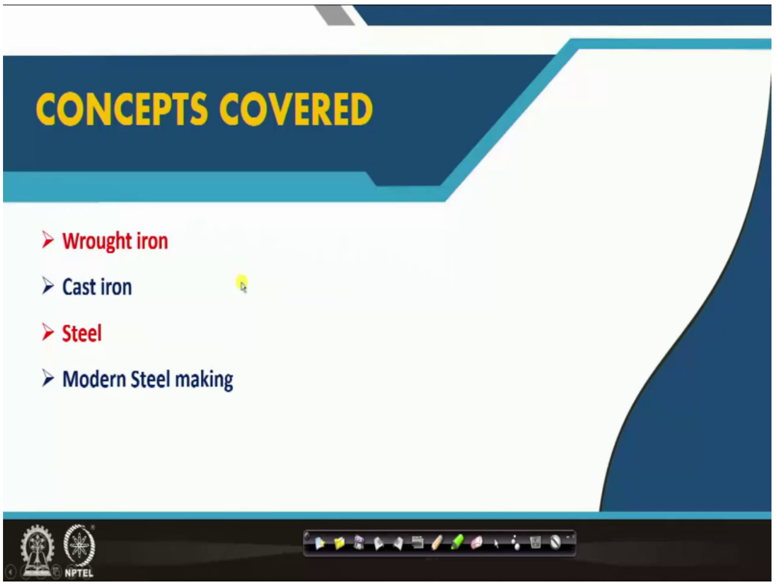

Topics to be covered are mentioned in the slide above.

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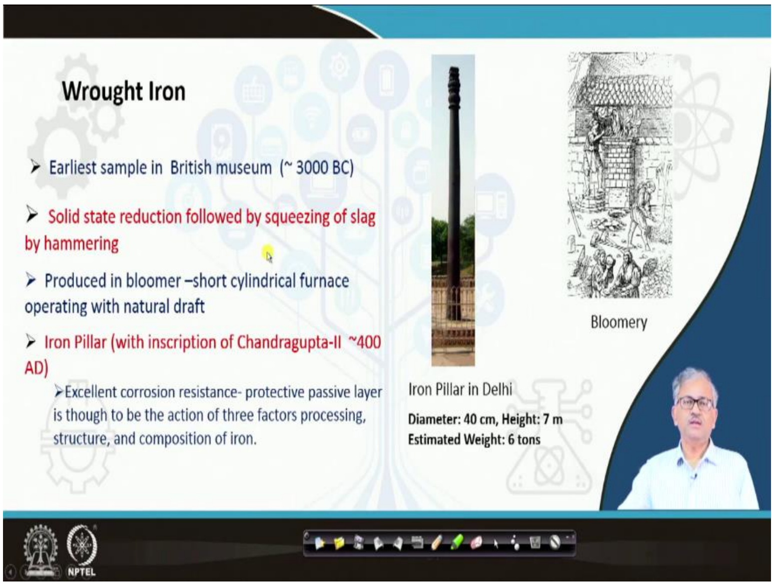

Ancient form of manufactured iron was called the wrought iron, which derived its name from the phrase "worked iron"; in hindi it is called "Pitoa iron". Wrought iron was produced by heating iron in presence of carbonaceous material in semi-solid state and subsequently hammered to squeeze out the softened slag partially. The final product was almost pure iron with traces of impurities like carbon and phosphorus, mixed up with retained slag, called the wrought iron. Story goes like that in ancient time wrough iron was accidentally discovered while human were backing animal like mice in an earthen oven. Later on people produced wrought iron in a proper oven, called the bloomery (Figure 26.1). What happens during the process is that iron ore get reduced in presence of carbon at temperature (~1100^{o}C) much below the melting temperature of iron. Such temperature could be achieved in cylindrical oven operated with cold air flow under natural draft in the bloomery. At this temperature the ore gangue and ash of carbonaceous material form softened slag, which could partially be squeezed out under hammering. Earliest sample of wrought iron could be found in British museum, dates back to 3000BC.

Figure 26.1: Bloomery in the ancient time

One brightest example of wrought iron today is the iron pillar that exists in Delhi, and the inscription on the iron pillar says that it was made by Chandragupta II during Maurya dynasty at around 400 AD. So, this pillar is more than 1500 years old; but you cannot find any rusting - that is the most interesting thing. The excellent corrosion resistance is attributed to a very passive protective layer over the surface. Several modern research has gone through and the presence of hydrated phosphate has been traced over the surface and supposed to provide the corrosion protection. It is to be noted wrought contained impurities like phosphorus (which could not be removed in absence of lime as is done in BOF steelmaking today), which could have produced the outer layer of hydrated phosphate by weathering. Besides intermixing of iron and slag is also attributed to such corrosion resistance. It is to be noted that wrought iron contained very low carbon (0.1 to 0.3) due to limited diffusivity of carbon in iron in the solid state. And such low carbon in iron made the product malleable and suitable for hammering and forging. Iron pillar is also supposed to be made through forging of wrought iron.

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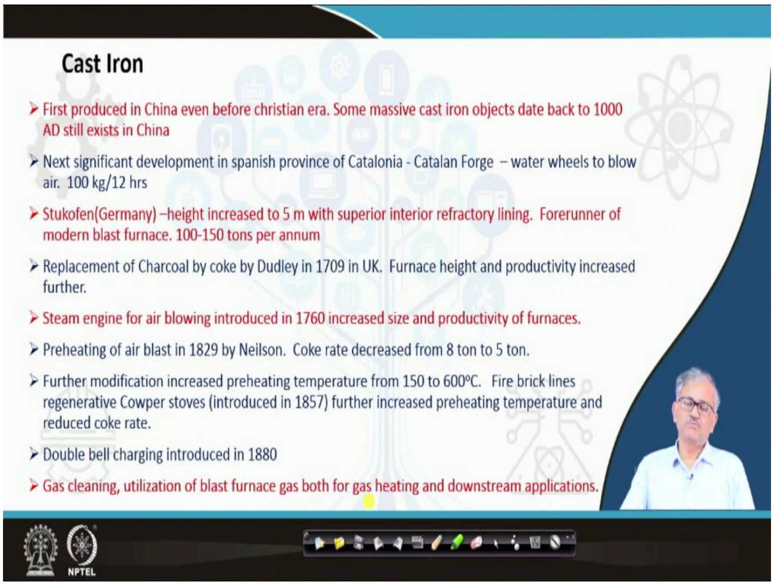

Cast iron came much later. As the name suggests that iron that is cast from its liquid state, called the cast iron. So, for producing cast iron, iron in liquid state is essential. In ancient time, major problem was the oven temperature. Carburized wrought iron could be melted at 1200^{o}C and above. Liquidus of iron could be further lowered in Fe-C-P system (unlike today's steel phosphorus was prevalent in ancient iron). Attaining 1200^{o}C was possible using forced draft of air (using air bellows) that enhance the carbon burning rate. Presence of big cast iron products is traced in Chinese museum dates back to 1000 AD.

And, next significant development came after these technology moved towards Europe; Catalan Forge was such a development where water wheels were used to blow the air to the oven to produce cast iron in the Spanish province of Catalonia. Catalan forge were able to produce cast iron at the rate 100 kg per 12 hours. So, it was significantly increase.

And, then came the Stukofen in Germany, which is considered as the forerunner of today's blast furnace. It had interior superior refractory lining to restrict the heat lost to the atmosphere and it used to produce 100 to 150 tons per annum. So, quite large amount at that time.

And, then all these furnaces used to run by wood charcoal, which was subsequently replaced by the coke by Dudley (UK) in 1709, i.e., the early 18th century. This lead to the increase in the height of the furnace with much stronger material inside the furnace.

Then came the steam engine (1760) to blow air that increased coke burning rate and increased the size and productivity of the furnace. Subsequently, came the preheating of the air blast in 1829 by the Neilson. Sensible heat supplied through preheated air blast supplemented the heat supplied by the coke partially and reduced coke rate and increased productivity. And, then further modification increased preheating temperature from 150 to 600 degree centigrade. And, finally regenerative Cowper stove equipped with fire brick lining came in 1857, which increased the preheating temperature further; and today we have the capacity to preheat the air to 1200°C.

Double bell charging was introduced in 1880 that reduced the pollution of atmosphere by eliminating off gas release through the charging stream. Subsequently, gas cleaning system was introduced to separate dust particles and utilize the cleaned gas for heating Cowper stoves and other downstream application.

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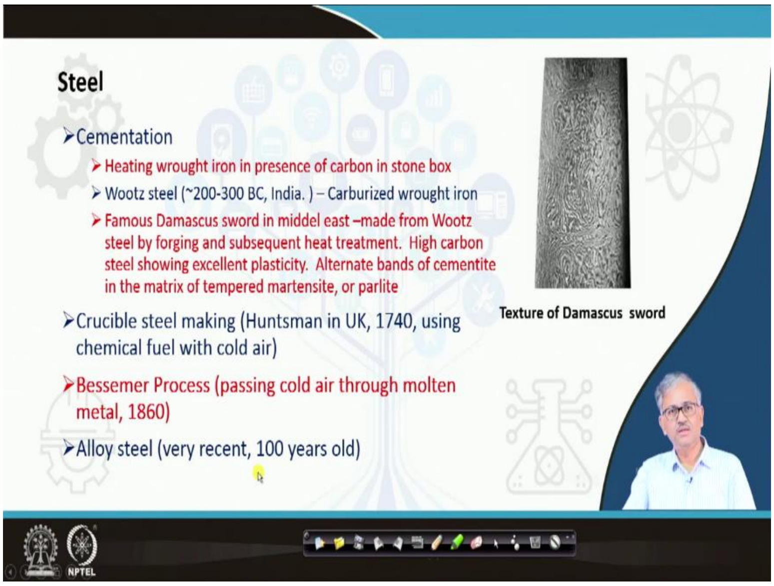

Now, let us see the developments in steel. Wrought iron was very malleable due to very low carbon. Therefore, wrought iron was carburized to produce steel of sufficient strength, called the cementation process. In cementation process, wrought iron was heated in presence of carbon in stone box that is called a cementation process. So, it is a reverse steelmaking. First you produce a pure iron and then you incorporate the carbon into it (Unlike today, where we first produce hot metal with lot of carbon, this is subsequently reduced during steelmaking).

Wootz steel is an example of ancient steel in India that was produced through cementation process. It was available in India in Tamilnadu; the name Wootz has been derived from the word ukku in Tamil, called the fire. So, Wootz steel was a very famous and the most advanced material during 200 to 300 BC in India. Wootz steel reigned for around 1000 years as the only the advanced material in the world.

The famous Damascus sword available in the middle-east was made from the Wootz steel, which was in demand and exported to various parts of the world at that time. Wootz steel hammered to give the shape of the sword and subsequently heat treated to produce the high quality sword. The sword had alternate layer of cementite in the matrix of tempered martensite or pearlite. The wood grain texture of Damascus sword (Figure 26.2) was unique.

Figure 26.2: Wood grain microstructure of Damascus sword

So far steel was produced in solid state and as a result carbon composition was not uniform (carbon percentage decreases from surface to the core). So producing steel in liquid state was felt to homogenously mix carbon in the iron to derive the uniform properties across the cross section. And, it was Benjamin Huntsman in UK, who could melt steel in crucible in 1740, called the crucible steel making. He used chemical fuel and combusted the fuel by cold air to produce temperature around 1400^{o}C and was able to melt the carburized wrought iron in a crucible in a very small scale. Crucible process dominated Europe and north America till Henry Bessemer in UK developed the famous Bessemer process, which heralded the advent of steel production on a mass scale.

And, then alloy steel is a very recent phenomena; it maybe 100 years old and it is the early 20th century when alloy steel came into existance.

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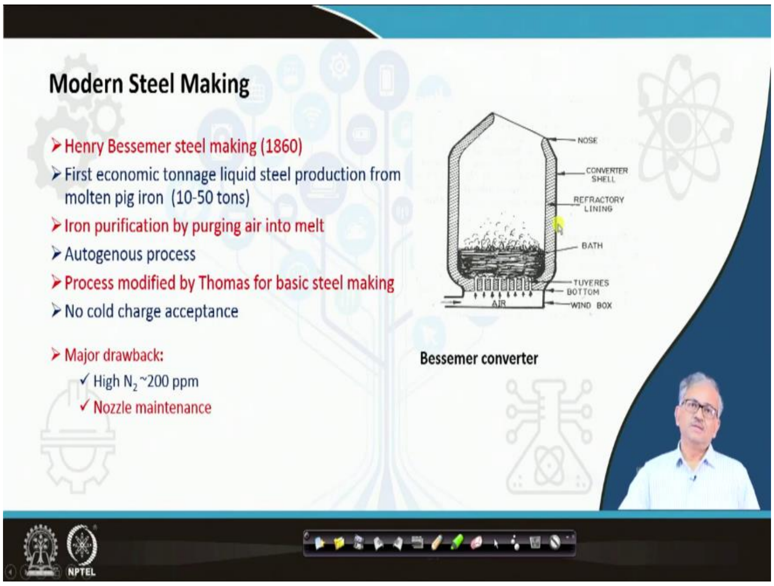

Modern steelmaking starts with the Bessemer steelmaking process. It is the first economic tonnage liquid steel production from the molten pig iron. Vessel had a capacity from 10 to 50 tons. By this time liquid pig iron were being produced through Stukofen but high temperature furnace for large scale refining of liquid pig iron was not available. Bessemer invented the autogenous refining furnace that was based on chemical heating by oxidation of impurities and attained 1600°C required to attain the liquidus of low carbon refined iron. Iron purification in Bessemer process was done by purging of air into the melt. Initially the Bessemer processes was limited to removal of impurities like carbon, silicon, manganese, called the acid process. Later on the processes was made basic by using basic slag and basic lining to remove phosphorus also, called the Thomas process. Heat generation by impurity oxidation was just sufficient to support the process and no extra addition of cold charge was possible. The schematics of the Bessemer furnace is given in the figure 26.3.

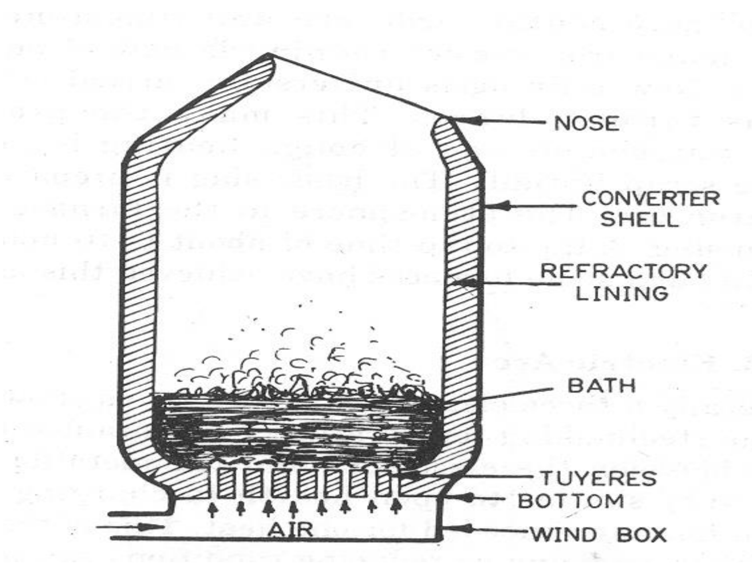

Figure 26.3: Schematics of Bessemer process

The bottom tuyere were later replaced by side tuyeres to avoid the wetting, flooding and blocking of the nozzle. The major drawback of this process was high nitrogen in steel as air was used directly as the source of oxygen. Nitrogen content was around 200 ppm that generated significant brittleness during cold working.

Bessemer vessel is called the forerunner of the modern Basic oxygen Furnaces, where air has been replaced by oxygen.

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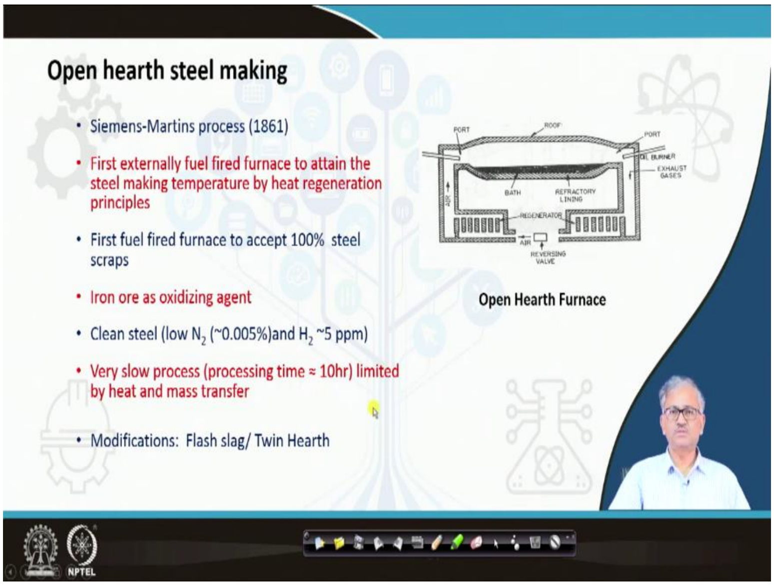

Since Bessemer process could not melt the cold charge, scraps generated from casting and forming processes were being piled up during that time. A furnace that could attain high temperature to melt steel scrap was not available. To fill-up this need open hearth furnace (OHF) came into existence (Figure 26.4). It is also called the Siemens –Martin process; because such furnace was developed by German born engineer Siemens and French engineer Martin took a license to produce steel.

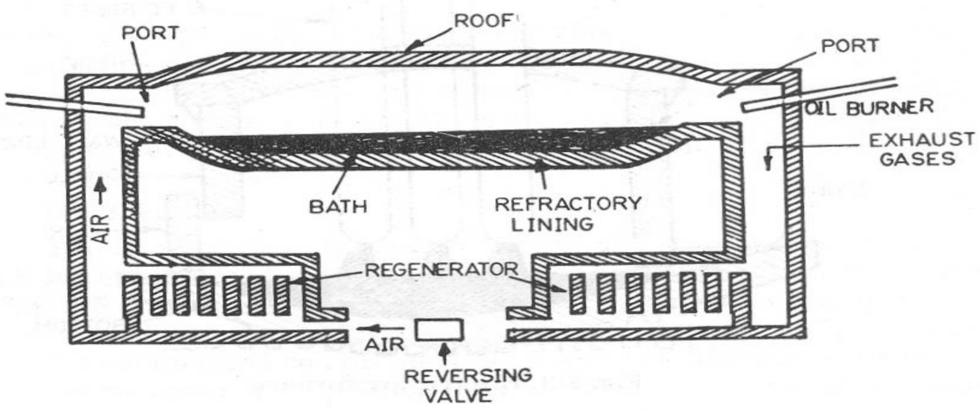

Figure 26.4 Schematics of Open Hearth Furnace (OHF) based on regenerative air preheating principles

In OHF, chemical fuel is combusted by preheated air to attain the high temperature 1600^oC to melt the steel. Air preheating was done through regenerative principles. In one cycle, the hot off gas from the furnace was allowed to pass through a checker brick works to exchange heat with the brick works. In the next cycle, the cold air was passed through the hot checker bricks to get preheated before it join the fuel for combustion in the furnace. Two brick structure were used and while one brick structure were on hot furnace gas and the other was on air. Through this regenerative principles the air was preheated utilizing the hot gas from the furnace. Due to preheating, the adiabatic flame temperature of the fuel combustion increased significantly to attain the steel making temperature. OHF was the first fuel fired furnace to melt the steel scrap using chemical fuel. Another unique feature of the furnace was the wide and shallow liquid bath to facilitate the heat transfer to the liquid bath from the furnace atmosphere. The wide hearth liquid surface was covered with a refractory-lined hood. The open hearth furnace derived its name from such open structure. Another feature of the furnace is called the carbon boil. Like top liquid-air interface, bottom refractory-liquid surface area was also large. During carbon oxidation CO bubbles are preferentially formed at the in the non-wetted pores of refractory and large

CO bubbles moves from bottom to the top, giving the bath appearance of a boil that enhances the mass transfer. Otherwise unlike Bessemer, there was no mechanical stirring of the bath.

The quality of the steel produced in OHF was very good. Unlike Bessemer, it did not contained nitrogen and hydrogen in absence of air purging. For scrap melting and refining was oaky with OHF. But later when hot metal from blast furnace also started to be fed in OHF along with scrap, then some modification were introduced. Since hot metal contained lots of impurities, slag load on OHF increased. Often de-slagging was required because slag thickness beyond a certain value limited the heat transfer to the bath. Therefore, external ladle desiliconization, flash slag practice came into existence. In flash slag practice, slag was continuously syphoned off when slag height exceeded a critical thickness of slag layer.

But the large refining time became a major drawback for this furnace. It took about 8-10 hrs for a heat. To improve the kinetics, the furnace was converted to twin hearth furnace. Here, the furnace was divided into two parts; one part was put on preheating and other part was on the melting and this increased the melting efficiency. Inspite of all these improvements, the furnace took atleast 6 hrs for a heat. Next generation of fast refining furnace, the basic oxygen furnace (BOF) took around 100 years to took over the OHF. The most popular version of BOF, the LD furnace, came around 1950.

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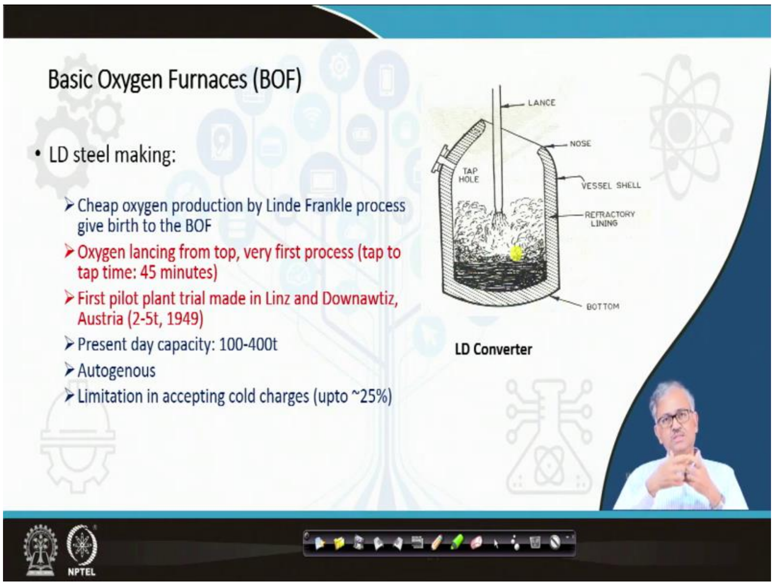

Cheap oxygen produced by Linde Frankle process give birth to the BOF process. First BOF process was the LD process, which derived its name after the name of the cities Linz and Donawitz in Austria where it was invented. In this process oxygen is struck over the liquid bath in supersonic speed that eventually leads to a gas-metal-slag emulsion formation where refining takes place in a very fast rate, not conceived before. Refining in LD takes place in 20 minutes and tap to tap time is only 45 minutes compared to 6 hrs in a most improved OHF. LD furnace started with 2 to 5 ton. Subsequently it has increased its capacity from 100 to 400 tons.

It is also an autogenous process; and unlike Bessemer, it could produce heat much in excess to sustain the process. Such extra heat allows around 25% cold charge in the furnace.

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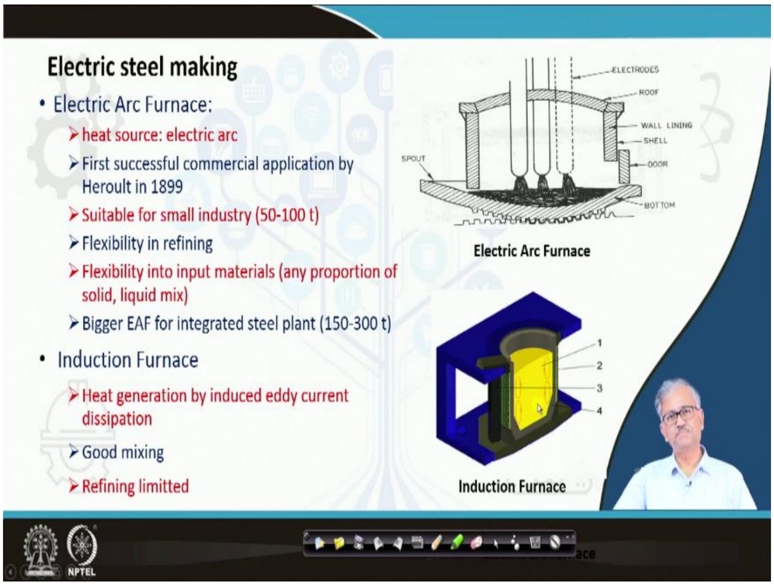
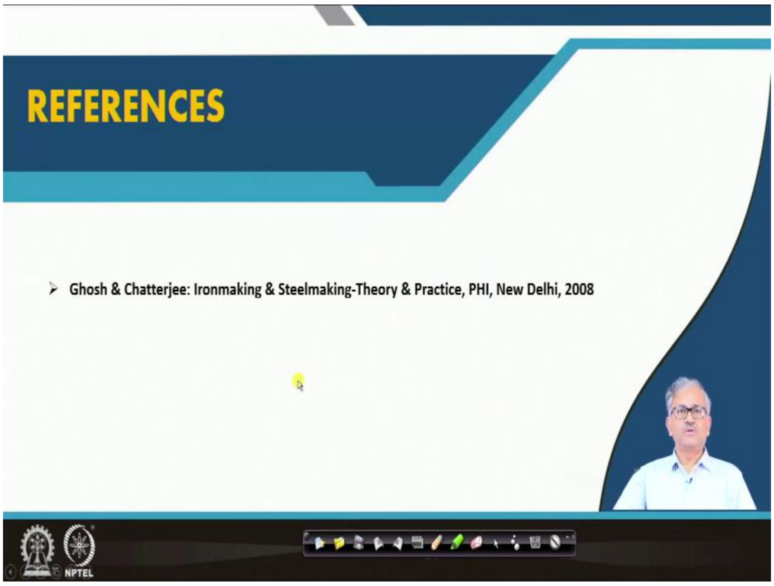


Electric steel making came into existence from early 20th century. Two types of electric heat sources are used: one is electric arc (electric arc furnace) and the other uses electrical induction in terms of eddy current in the charge (Induction furnace). First electric arc furnace was made by Frenchman Paul Heroult in 1907 and it was first commercialized in USA. EAF cater to the small scale industries to melt scrap and produce alloy steel in the capacities of 50 to 100 tons. Now-s-days bigger EAF are being designed for integrated steel plant also in the range of 150 to 300 ton.

Induction furnace as the as the name suggest, heat is generated by the eddy current dissipation into the charge. It is clean, energy efficient and well-controllable melting process. Much refining could not be carried out in the induction furnace, because it is difficult to sustain a thick non-heat conducting slag at the top due to lack of heat generation. It is suitable for small scale industry to melt scrap and produce alloy steel. (Refer Slide Time: 36:12)



The major reference is Ghosh, Chatterjee. Besides, material from some web sources are also presented.

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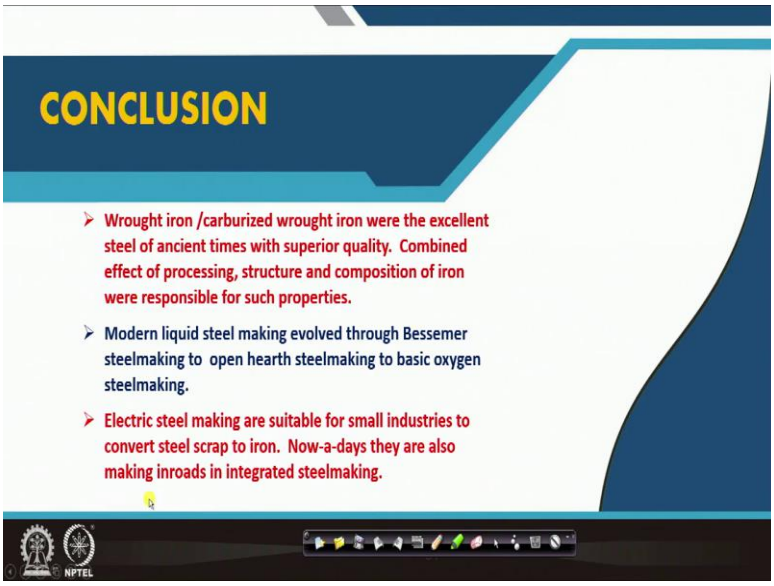

Modern iron making started with wrought iron that dates back to 3000BC. Iron pillar in India is a brightest example of wrought iron traced back to 400 AD in Maurya dynasty. Wrought iron was almost pure iron with intermixed slag. Impurities in wrought iron included traces of impurities like carbon (0.1 to 0.3 wt%), phosphorus. Presence of phosphorus might be one of the reason for non-rusting characteristics of iron pillar, which produced a hydrated phosphate passive layer over the surfaces protecting it against corrosion.

Cast iron came much later because it needed to produce liquid iron, which in turn required a furnace to produce temperature of 1200^{o}C and above. It was possible when device to inject air at higher speed was invented through air bellows. Big cast iron products are found in Chinese museum that dates back to 1000 AD.

Scale of production in cast iron increased progressively in the following order catalan forge>Stukofen>blast furnace. Initial production in BF production increased by introduction of coke replacing wood charcoal (Dudley, 1709), steam engine (1760) to enhance air blast rate and air preheating (Neil, 1829) and modern Cowper stoves(1857).

Ancient steel was produced by carburizing wrought iron, called the cementation process. Wootz steel, dates back to 300BC, was a brightest example of a product of cementation produce in ancient India. It was the most advanced material in the world and exported to various countries. Famous Damascus sword in middle-east was made of wootz steel.

First liquid steel was produced in crucible by Benjamin Huntsman in 1740, by coal fired furnace. First large scale steel making in tons was produced in Bessemer process (1860). First externally heated furnace to melt steel scrap was the seimens-martin process (1861), or the open hearth process. In this furnace chemical fuel was combusted by preheated air, using heat regenerative principles.

Electric steel making furnaces came into existence in 1907. It uses electrical arc to melt scrap and produce alloy steel in small scale in the range of 50 to 100 tons. Induction furnace is another version of electrical steel making where eddy current is generated in the charge to melt scrap.

Finally, the Basic oxygen furnace appeared in 1950 in Linz and Donawitz in Austria, called the LD furnace. It used supersonic oxygen jet to interact with liquid bath to make emulsion for superfast refining.