Fundamentals of Surface Engineering: Mechanisms, Processes and Characterizations
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Lecture-33
Surface Modification Techniques: Carburizing and Cyaniding

Hello I welcome you all in this presentation related with the subject fundamentals of surface engineering and you know we are talking about the surface modification techniques and under this heading we have talked about the techniques where just surface metallurgy is changed and there is no change in chemical composition. At the same time we have also talked about the few techniques where the surface composition is modified intentionally to achieve the required set of the properties for improving tribological behaviour via resistance of the material.

So under this category there are various processes where the change in chemical composition and the surface is brought in by the various approaches and 1 category is the diffusion based approach where the suitable environment enriched with the particular element which is to be incorporated or which is to be added at the surface is created at high temperature. So that diffusion can help to modify the surface composition and form the compounds and phrases which will help to improve the surface properties.

And in this category we have talked about the carburizing process, in the carburizing process you know the carbon content at the surface is increased especially low carbon steels. So that higher carbon content at the surface can be used to have the martensitic transformation at the surface which internal will be leading to the higher hardness and improve the residual compressive stresses at the surface.

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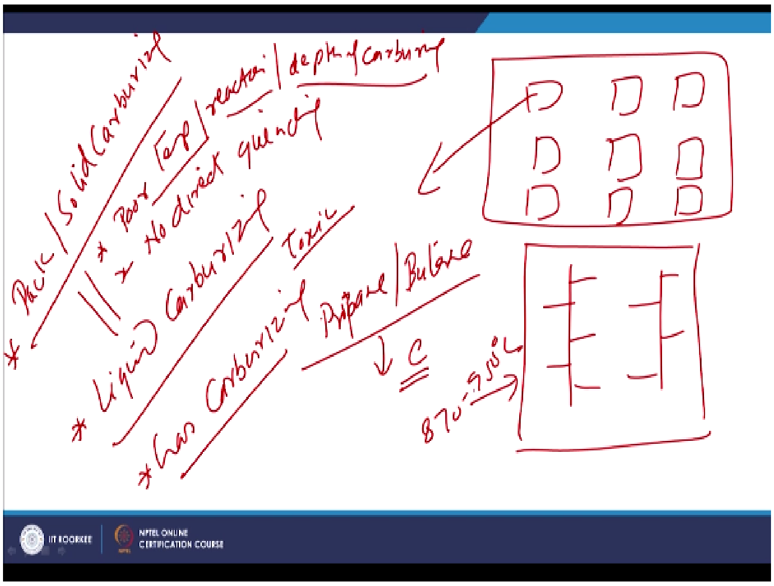

And combination of these characteristics help to increase the tensile strength increase the strength as well as the increase the wear resistance of the material. So under the carburizing process we have talked about the 2 methods of the carburizing and these are the pack or the solid carburizing where mixture of the charcoal is used and in that mixture of charcoal the components to be carburized are kept in the enclosed chamber at high temperature for sufficient time.

So the carbon diffuses into the surface of the component and that is how the carbon in which maintain the surface and subsurface layers take place and once the component is carburized it is subjected to the hardening treatment. So that the required high carbon martensite can be formed for improving the properties. But problem in this method was like poor control over the temperature during the carburizing and poor control over the reactions which were taking place.

And therefore we had the poor control over the depth of carburizing. So this was the 1 aspect and the second point associated with the pack carburizing was it did not permit because the nature of the process was such that it did not allow the direct quenching of the carburized component for the hardening purpose. So no direct quenching due to the inherent nature of the processes in the include chamber all the components carburized, so these components needs to be taken out properly.

And in meantime when they are taken out the temperature will get reduced direct hardening and quenching is not possible and these 2 deficiencies were effectively overcome in case of the liquid carburizing where molten salt bath is used. So that helps to have the better control over the temperature, better control over the reactions which are taking place into the good control with regard to the depth of the carburizing was there with the liquid carburizing.

At the same time it also allowed the direct quenching but like the toxic gases emission of the toxic gases was one of the issues and the process becomes dirty when it will be using the liquid or the molten salt bath, at the same time it also use the sodium cyanide which is poison. So it is harmful for the operators and we need very good control over the ventilation related aspects. Third method was the gas carburizing.

In case of the gas carburizing we have seen some of the things like the propane and the butane kind of the gases are used and these gases provide the required carbon for diffusion to take place. So the mixture of the gases that is mixture of the gases are passed in the chamber where the components to be carburized have been kept under good temperature control is maintained for this purpose in the range of the temperature of the 870 to 950 degree centigrade.

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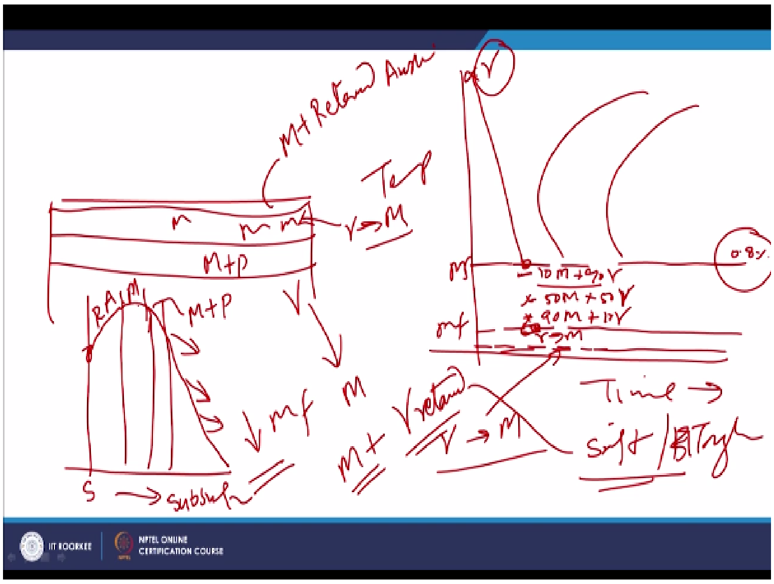

And these gases are passed in so through the decomposition of these gases carbon is made available and this carbon will be getting diffuse into the components. So some of the chemical reactions which are involved in production of the carbon required for diffusion to take place on the surface of the component includes like this C3 H8, this will be decomposing into the Methane CH4.

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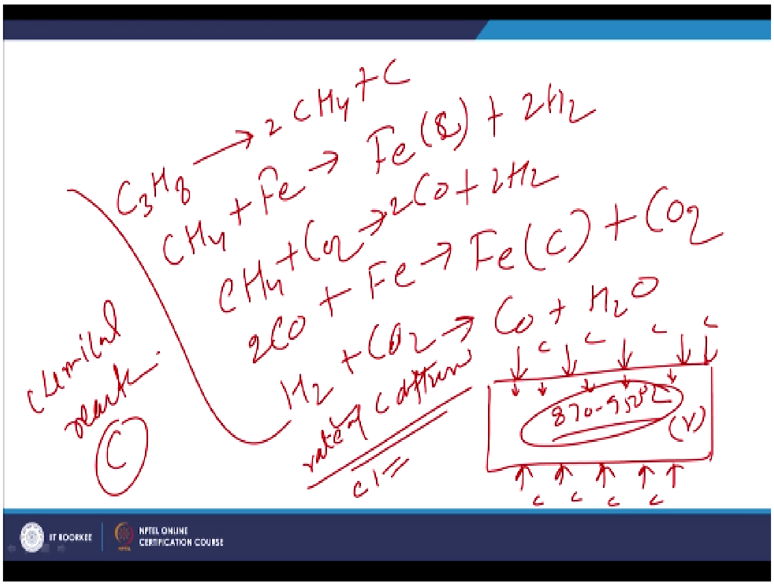

And producing the carbon and this CH4 interacting with the iron to produce iron with carbon and hydrogen is also produced and this CH4 reacts with CO2 to form carbon monoxide+hydrogen and the CO also reacts with the means interacts with the iron to form the iron+carbon leading to the carbon dioxide and some of the reactions like hydrogen interacting with Co2 leading to the formation of Co and H2O.

So these are the some of the chemical reactions through which the carbon is produced and carbon is made available at the surface of the component to be carburized. So the rate at which the carbon mean is being made available through the flow of the gases which will be a facilitating this chemical reactions. So the flow of these gases will be ensuring that required carbon is available at the surface.

But the carbon under the environmental conditions in which the component are kept of a certain of a certain temperature range like 870 to 950 degree centigrade, at this temperature this carbon due to the concentration gradient outside and at the surface and between the component the carbon will be getting defused within the steel component at a certain rate. So the rate of carbon diffusion to the steel component.

This will be a particular rate as per the temperature conditions and the kind of the metal systems obviously austenitic state. So but the rate at which carbon is being made available at the surface that should be equal to the rate at which carbon is getting diffused. So this kind of the balance has to be maintained.

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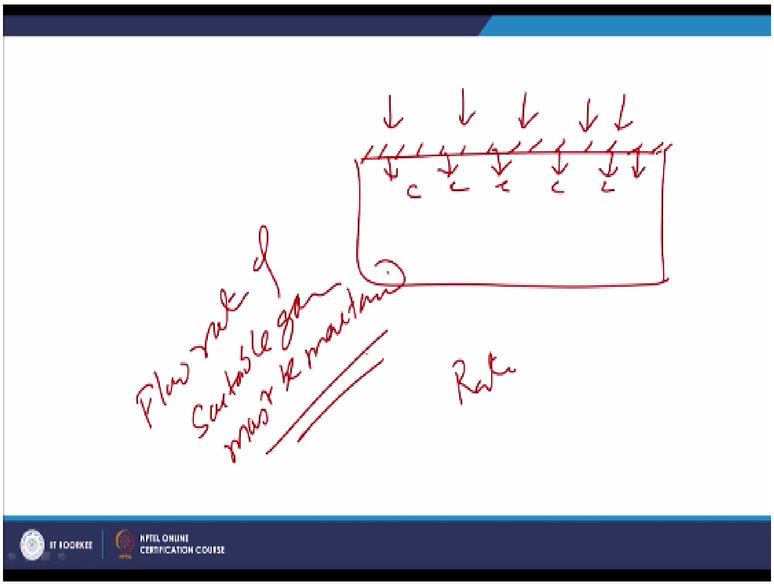

So whatever the rate at which the carbon is getting diffused into the steel at the same rate it should be made available, else the deposition of the carbon at the surface will start and this will hinder or adversely affect the process as a whole and suit formation also starts like a carbon layer, I will start forming over the surface of the steel components. So the rate at which carbon is being made available through the chemical reactions that must be equal to the rate at which carbon is getting diffused into the steel components.

So this is one of the thing which is to be kept in mind during the gas carburizing and therefore the low rate of the suitable gas mixture being used for carburizing purpose that must be maintained properly, else it will be adversely affecting the carburizing process as a whole and there is another variant of the carburizing which is called vacuum carburizing.

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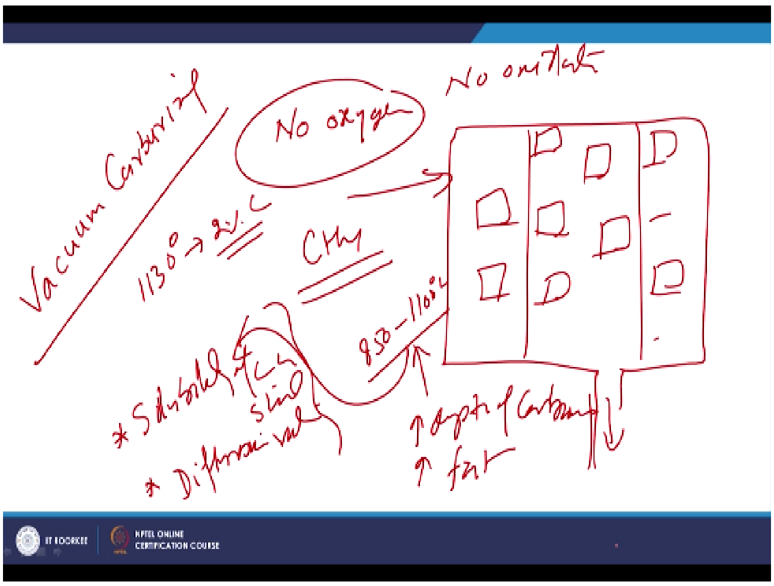

Vacuum carburizing is performed of course below the atmospheric pressure conditions. So there is no, so vacuum is created basically there is no oxygen in the chamber is like this so vacuum is created by taking out all the gases which are present and inside this chamber will be putting the component to be carburized, this racks and then it will be fair with the gases for carburizing purpose.

So the Methane is fed into this chamber which is kept at a quite high temperature like temperature range like in range of 850 to 1100 degree centigrade. So this temperature is much higher than what is normally used in the pack carburizing or the liquid carburizing. So and in the absence of the oxygen there is no oxidation tendency of the steel surface which can lead to the oxidation or the loss of alloying elements from the steel surface.

At the same time whatever the thermal decomposition of the Methane is taking place that will be making the carbon available for diffusion in the steel surface for carburizing purpose. So there 2 points are related with the high temperature conditions high temperature conditions increase the solubility of carbon in steel because with increase in temperature solubility of the carbon in the austenitic increases and decreases for plain carbon steel that is allowing 30 degree centigrade maximum 2% of the carbon can be dissolves.

So simply the increasing temperature there will be increasing solubility of the carbon in the austenitic state which is of course there in this particular case and then second one is that we know that increase in temperature also increases the diffusion rate. So because of this the high depth of carburizing is achieved and the processes fast.

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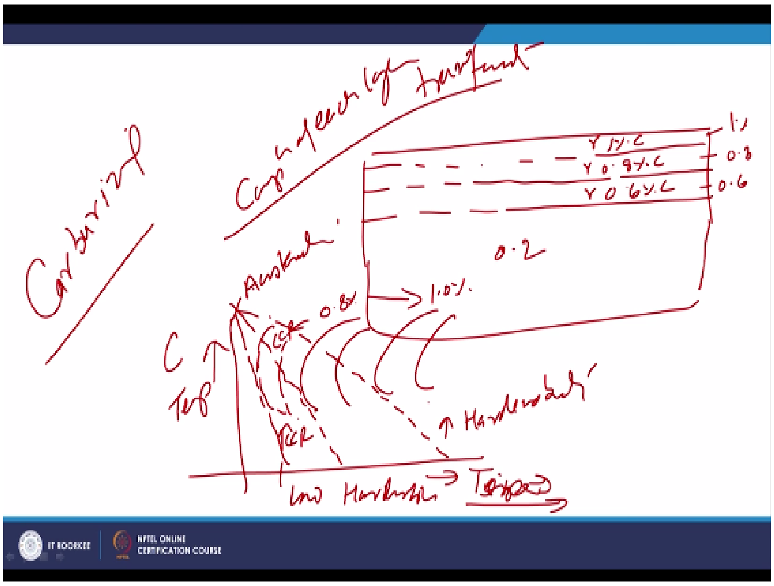

So it takes less time for the carburizing purpose and there is no oxidation of the steel component surface. Now another processor related with the let us see there is another aspect related with the carburizing what we have seen that in the carburizing how we are increasing the carbon content of the surface. So say the substrate is of 0.2% carbon steel and the surface layers will be enriched with the carbon maximum than somewhat lower and then somewhat lower carbon content.

So say at the surface it is 1% below that it is 0.8. then it is 0.6 like that. So when the hardening is performed what we said what we see that the according to the composition of each layer the different transformation in each layer will be taking place. So here we have the austenite with the 1% carbonate here we have austenite with the 0.8% carbon, here we have austenite with the 0.6% carbon, since the carbon content affects the carbon content in the steel effects the trans hardenability.

And how that happens how that change is taking place that is what we can understand from the simple diagram like for 0.8 % carbon content this is the position of the nose and this affecting the critical cooling rate like this which in turn governs the hardenability. So this is critical cooling rate will be the carbon content is less than nose of the CCT continuous cooling diagram will be shifted towards the right.

And sorry it will shifted when the carbon content is high say for 1% nose of the curve is shifted towards the left and so the critical cooling rate is reduced. This increases the hardenability. So with the increase of carbon content the hardenability is increased. On the other if the carbon content is reduced like say for 0.6% carbon content then nose of the curve will be like this and in that case critical cooling rate will be increased.

So high critical cooling rate means the low hardenability, this is a simple the CCT diagram in x-axis we have a temperature and n axis as we have time and in y axis we have the temperature and this is the austenitic state where from the cooling is being done. So the temperature and the time and these lines are indicating the different cooling rates corresponding to the critical cooling conditions are required for transformation of complete transformation of austenite into the martensite.

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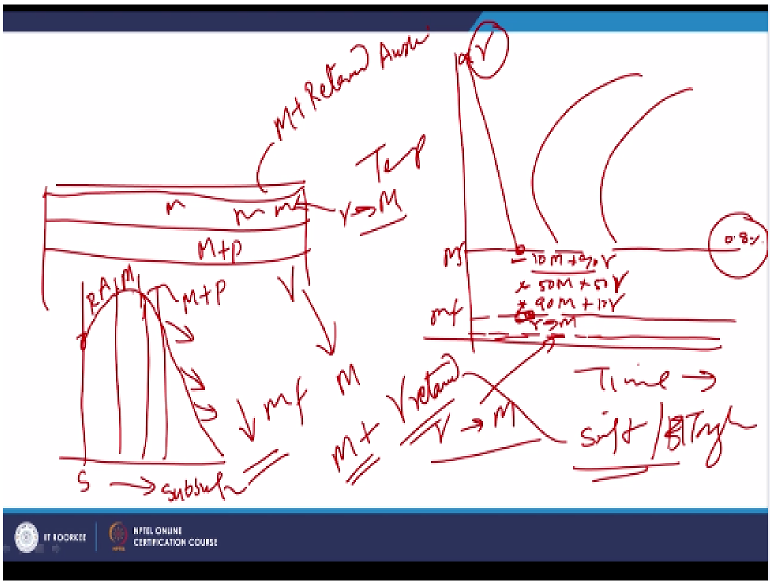

But apart from this there is one more aspect of the CCT diagram which is affected by the carbon content and that is like apart from these are the location of the martensite start and martensite finish lines is also affected. So if the in the CCT diagram if we see the time in the x-axis and temperature in y axis. So far 0.8% carbon this is the position of the MS line which is martensite start formation line.

And Ms line where martensite transformation completes on quenching at a particular temperature. So if we quench it at this temperature there will be 0 martensite formation of martensite transformation and below this certainly this is the temperature at which martensite transformation state and here that martensite transformation will complete. If we see if you quench then here we will get that 10% austenitic transforming into the martensite.

And balance it has 95% of the austenitic, it quench at this temperature maybe 50% martensite and 50% austenite for the lower temperature of the quenching may be 90% martensite+10% of the austenite. So if we are quenching below the NF temperature then only the 100% austenite to martensite transformation will be taken place and with increase of the carbon content.

So in this case for 0.8% carbon steel quenching below the NF temperature will be leading to the complete austenite to martensite transformation but when the temperature when the carbon content is increased further this temperature will be going down further and which will make the transformation of austenite to the martensite which make up the complete transformation of austenite into martensite will be difficult.

So means reduction in the martensitic finish temperature, martensitic finish temperature will make it difficult to completely transformed austenite into the martensite which means if the MF temperature has been reduced below the room temperature or in the sub 0 temperature conditions it has reached then the austenite to martensite transformation will be incomplete and in that case the structure will primarily have the transformed martensite.

And the martensite has been formed due to the transformation+the retained austenite, austenite which could not be transformed into the martensite and this retained austenite is soft it is tougher than the martensite and because of this now we will see from the carburizing point of view since at the surface we are having much higher carbon content while below the surfaces are having the lower carbon content.

So there is a possibility that the surface layer carbon is too much we may have the martensite+retained austenite while below the surface layers where the carbon content is like a round 0.78 we may have the complete austenite to martensite transformation. So this will be complete martensitic and below that uses the carbon content is for the lower, so we may have the martensite+pearlite kind of the phases.

And that is why what we get at the surface we may have some water hardness like this and then it will be increasing where complete austenite to martensite transformation of taking place and then again you will be decrease in. So this is the band where we have the retained austenite surface and this is the subsurface zone. This is the zone where we have the complete martensite transformation.

This is the zone where martensite+pearlite or other surfaces this side we have the increasing fraction of the surfaces is like pearlite or bainite but the zone where will have the martensite complete martensitic transformation. So this is the kind of the logic behind somewhat having somewhat lower hardness at the surface of the carbon content is too high and this is what is to be kept in mind when the carburizing is done.

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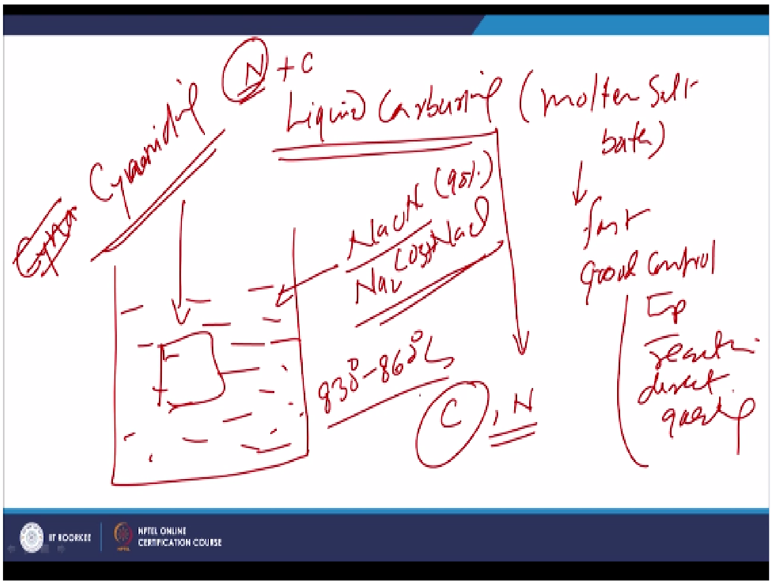

Another process is the cyaniding, cyaniding is similar to the liquid carburizing because it also uses the molten salt bath and because of this the processes fast with the good control over the control of temperature of reactions which will be taken place and the advantage of the direction quenching. So all these benefits are there with the cyaniding also and the kind of the mixture so the salt bath is created of the suitable constituents.

And it is kept at higher temperature 830 to 860 degree centigrade and this bath comprises sodium cyanide in a very huge amount maybe around 90% of the sodium cyanide and apart from that sodium carbonate and the sodium chloride is also used. So this will be forming the balance amount under the component to be a subject to the surface modification of the steel which will be submerged in this the bath for the required surface modifications to the chemical composition.

There is a difference with the carburizing and the cyaniding in the cyaniding process the surface modification is primarily brought in by the nitrogen edition at the surface and little bit modification is also contributed by the carbon addition or increasing carbon concentration at the surface layers. While reverse was true for the carburizing, in case of the liquid carburizing the primary change in the major change the change in properties were primary contributed by the highest carbon content.

And little bit contribution was coming from them nitrogen addition, so there is a difference of the relative importance of the elements like carbon and nitrogen in these 2 processes in cyaniding it is the nitrogen that predominantly controls the surface modification and while in liquid carburizing it is the carbon that governs the properties and surface structure with regard to the surface modification.

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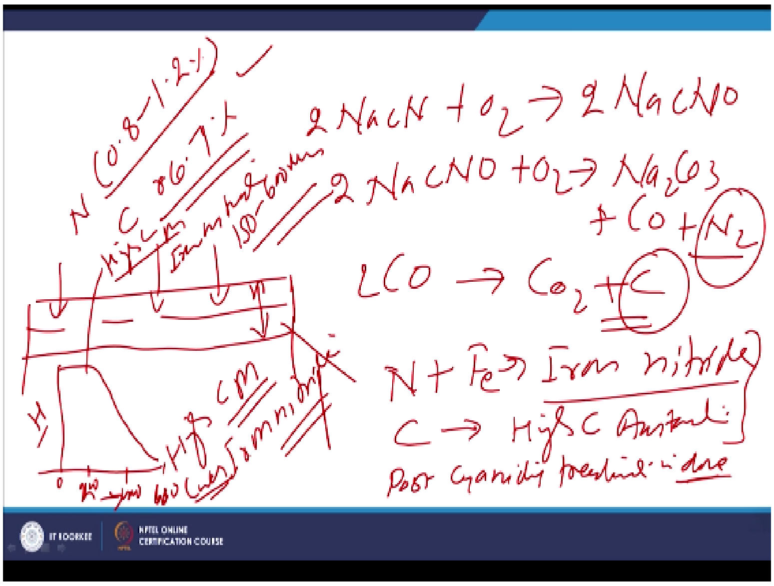

So during this process some of the chemical reactions which also take place and they will be making the carbon and nitrogen available for the chemical reactions, so the chemical reactions which are observed during the cyaniding process includes like twice of NAC and reacting with the oxygen to form twice NACNO and this will be further reacting with oxygen to form Na2CO3 Co+N2.

So this will be making available the nitrogen and then Co will be providing CO2+C. So this is how both carbon and nitrogen are being made available for enhancing the carbon as well as and nitrogen concentration on the steel surface. So the nitrogen concentration during the nitriding process is increased in the range of 0.8 to 1.2 % while carbon concentration at the surface layer is increased in the range of 0.6 to 0.7%.

So the both surface and subsurface layers will be having the carbon and nitrogen, so nitrogen will be a basically interacting with the iron from the iron nitride and which in turn will be increasing the hardness and the carbon will be leading to the formation of the high carbon austenite. So to get the beneficial effects of both these elements it is important that subsequent post cyaniding treatment is done.

So that we can get the high carbon martensite as well as we can get the iron nitrides for the required improvement in the surface properties, but like just for example these are the typical values of the carbon and nitrogen which are achieved after the cyaniding process and this the depth of surface modifications depending upon the temperature and time combination for which cyaniding is performed, it can range from like say 150 to 600 micrometre.

And accordingly we will see the kind of the variation like 0, 100 like 200, 400 and 600 and accordingly we will see the hardness will be varying like this. So significant increase in the hardness at the surface and near-surface layers is attributed to formation of this high carbon martensite as well as the iron nitrides. So this what you can see here this is the hardness and this is the subsurface layer and this units are micrometre.

Just for example I have given this idea now I will summarise this presentation, in this presentation basically I have talked about the 2 carburizing process and 1 cyaniding process, the carburizing process is like gas carburizing or vacuum carburizing both primarily will be increasing the carbon content and the surface layers for improving is surface properties while in case of the cyaniding process it is the enrichment of the carbon and nitrogen which helps to improve the surface properties, thank you for your attention.