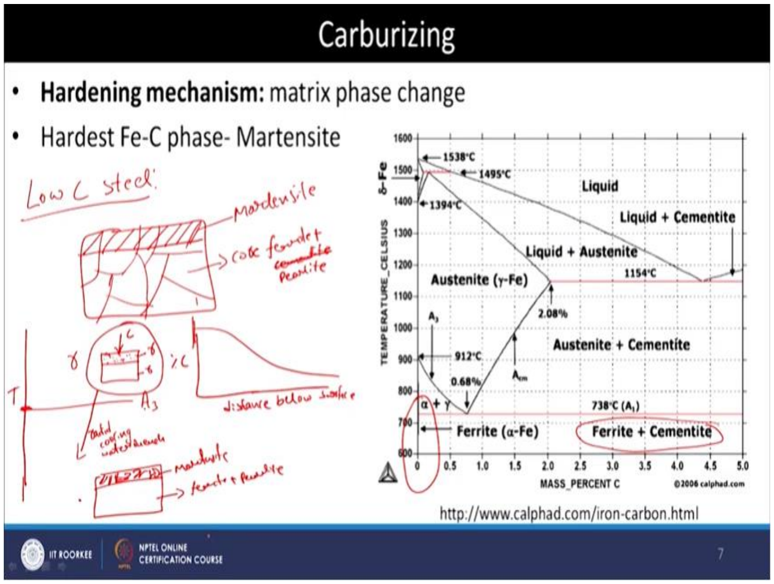
Thermo-mechanical and Thermochemical processes
Prof. Sai Ramadu Meka
Department of Metallurgical and Materials Engineering
Indian Institute of Technology – Roorkee

Module No # 07
Lecture No # 32
Overview of Themo-chemical Treaments (Contd.)

Greetings to all, so in this lecture we will be discussing about one process of thermochemical treatment which is called carburizing. It means, we are trying to introduce carbon into the surface regions of the workpiece. We discussed in the last lecture, the three possible ways we can harden the surface region material of a component one is by the precipitation hardening,

(Refer Slide Time: 00:57)



Carburizing

- **Hardening mechanism:** matrix phase change
- Hardest Fe-C phase- Martensite

http://www.calphad.com/iron-carbon.html

other one is by the solid solution strengthening and by changing the phase of the existing material surface. That means like, it was initially a tempered martensite which is martensite with precipitated carbides. Now, we will change that with the purely martensite. We know that in the iron carbon system, the martensite is the hardest phase.

So, that is why we would like to have the martensite at the surface of the components which provides a good wear resistance. So, how we can do this process? Let us look at first the iron carbon phase diagram (refer to above figure). So, here what you see is the different phase fields of the iron carbon phase diagram where you have the high temperature austenite field right, then you have a eutectoid reaction it is called A1 temperature at 738 ◦C and this is the function of mass percent of carbon and this is the temperature axis. So, for a given temperature and the amount of mass fraction of carbon, we can actually know what phases are expected to be at the equilibrium condition. That means, we heat very slowly and cool very slowly.

So, now, if you look at the temperature below 738˚C, it shows only very small solubility for the ferritic iron. That means, it has a very small solubility, the moment you add a carbon beyond a very small limit, then you form actually the two phase mixture of ferrite + cementite. Whereas, the if you go to this (refer to above figure) condition of the austenite right which can take a lot of carbon into it.

So, it is like at 1154˚C you see that it can take up about 2.08 weight % of carbon maximum amount it can be taken up in the solid solution. That means, it will be a FCC iron lattice having carbon atoms in the interstitial sites. So, now, for example, you have the low carbon steel component having certain microstructure, it will be largely ferrite plus a small amount of pearlite.

So now if we want to do the carburizing then objective is to have if suppose this is the surface region (refer to above figure), we want to have this to be martensite, whereas the core will be just like a ferrite + cementite or you can say that ferrite + pearlite. So, this is the kind of situation we want to have after the carburization treatment. So, how can we achieve that? Now, the issue is, we know that a lot of carbon can dissolve in the austenitic phase.

So, if I say this is the temperature axis and this is where actually the A_3 temperature. This is the temperature above which everything will be austenite. A_3 temperature is here. It will be single phase γ. And then we take this sample to this region and then we introduce the carbon into the surface region (refer to above figure).

Then what happens, if you go from the surface, the percentage of carbon as a function of distance below surface, we generate something like this (refer to above figure). But if you see the microstructure of entire sample that means the surface region having the carbon enriched region and core region having less amount of carbon, both are austenite right.

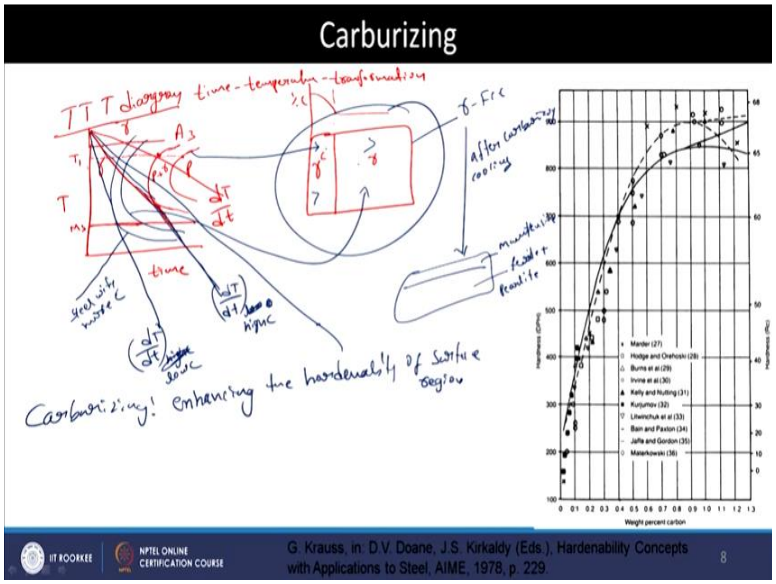
At this condition both regions have γ phase, γ is for the austenite. But the amount of carbon is different, that means the surface region γ has got a higher carbon than the γ region which is below the surface. So, when you take such a composite sample and cool rapidly, that means after quenching, let us say that water quenching. So, then you get actually the surface region having a martensite with the underlying layer being ferrite + pearlite. Now we know that when you heat up the sample to austenitic region entire sample will be of austenite, right from the surface to the center of the sample.

But when you cool it down by rapidly only the surface region which is enriched with carbon is able to get the martensite. Why is it so? We all are aware of hardenability of the steel. We have a definition for hardness which is a material property. Hardenability is the ability of the material to able to form martensite when it is cooled.

So, how easily in order to form martensite we need to do a non-equilibrium cooling. That means you should cool the austenite to room temperature at a very rapid rate. More rapid we need to cool that means it is more difficult to form martensite that means it has a low hardenability as compared to when you can cool slowly and get the hardness that means it has a high hardenability.

So, in order to understand we need to understand the so called TTT diagram or the CCT diagram.

(Refer Slide Time: 08:51)



Carburizing

G. Krauss, in: D.V. Doane, J.S. Kirkaldy (Eds.), Hardenability Concepts with Applications to Steel, AIME, 1978, p. 229.

For example, you know, the TTT diagram where the three T stands for time, temperature, transformation. So what this diagrams provides, is you have a temperature as a function of time and then you can mark the temperature for example, this (refer to above figure) can be A_3 temperature and then you have a timescale. Then there are the fields where you get the different phases for example the C curves can be seen and this is γ, this diagram tells us that.

How you can construct such a diagram you take a steel sample, take it to the austenitic region that means the above A_3 and rapidly cool it down to let us say temperature T_1 (refer to above figure) and you hold it at this temperature and suppose if it is a eutectoid steel then when it will start to form the pearlite, that time will be given by that this is a pearlite start and then if I keep it there, then the amount of pearlite will be keep increasing and when it will be fully pearlite, is the pearlite complete (refer to above figure).

So, this is where actually you have a pearlite and austenite and then here you end up with fully pearlite steel (refer to above figure). So, now some line will be there that is called as a martensite start temperature line that means if you can reach this point, we can produce the martensite.

Now for example in carburizing, we have a sample at the surface region the carbon content will be more and core region have less carbon content. So, this (refer to above figure) is also γ enriched with carbon, this is also γ which is having less carbon. Now, if we want to produce the martensite in this particular steel, from this state we need to cool it by at least this rate (refer to above figure).

This should be the minimum cooling rate. This is actually the DT/ Dt, cooling rate is slope of this line. This is the minimum cooling rate at which you can get the martensite. If you are going smaller than this then you will enter into this region (refer to above figure) where you produce actually the pearlite, you will not get the martensite.

However, these diagrams have a dependence on the steel chemistry. For example, I have another steel having a more carbon than what has been shown previously. Now because it is being shifted towards right. These curves are for the high carbon and these curves are for the low carbon. So, I hope it is clear to you that when you have more amount of carbon these curves will shift away from the temperature axis that means shift towards right offering.

Now when this region and this region (refer to above figure), have been cooled at the same rate and for example, that rate is given by in between. Now, this region is unable to produce the martensite, because it has got its CCT curve here. So, now when I cool with this rate, for example in between, then this region is unable to produce martensite, but this region is able to produce a martensite (refer to above figure).

So, by carburizing we are enhancing the hardenability of surface region. So, after adding the carbon because it has improved the hardenability, by cooling it you are able to produce the martensite at the surface. This is what actually happens in a low carbon steel where you have a core which is softer and by adding carbon into the steel, we are able to enhance the surface hardness by producing martensite.

Now, on this right here, in this plot (refer to above figure) it is shown that how the hardness of the martensite changes with the amount of carbon on x-axis as a weight percent of carbon. Here it is a Rockwell C scale; it is a diamond pyramid a hardness number. This is another means to look at the hardness. You see that initially it has got a very small increase in the hardness but if you want to have a significant rise in the hardness, you need to have the martensite with more carbon.

For example, our aim is to get about 60 RC for the surface then we should have at least about 0.48 weight percent carbon. So, that is where we need to have a martensite which is also having a decent amount of carbon inside. Our objective is not to get any martensite, a low carbon martensite will not have enough hardness what is we are looking for. So, that is where we want to actually realize that high carbon content to the surface.

This provides two things one is that it improves the hardenability and at the same time when it forms the martensite that will also have a higher hardness. So, these are the things one can realize from the carburizing. So, in this case actually we see that one issue, when we do the carburizing now the entire component has to be heated up to the austenitic region. That means when we do carburizing entire sample is taken to the temperature where it is γ that is FCC.

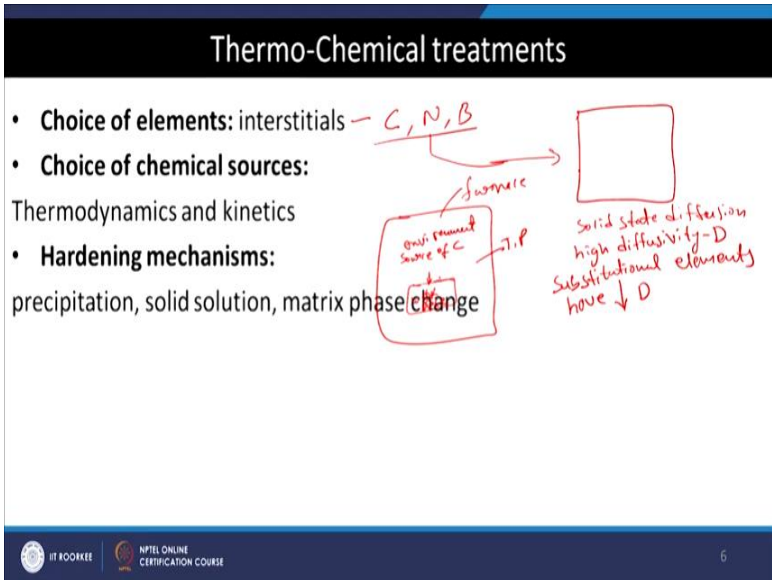
And now when we are cooling it after carburizing, we are making the sample surface to be martensite and the subsurface be ferrite + pearlite. So due to this because FCC being a much close packed structure as compared to BCC ferrite or the body centered tetragonal martensite, so there will be a volume increase when we cool the sample after the carburization. You imagine that you have a big component, let us say a very big gear. And we do the carburizing by heating up this entire big gear to the austenizing temperature. And we know that we need to cool it rapidly in order to produce the martensite at the surface and when we do that entire sample tries to change its phase and there will be a large distortion.

That means it wants to change and that can lead to a dimensional intolerance. Your gear has been manufactured with certain dimensions. Now due to the heat treatment which we are doing like my carburizing and then quenching we will introduce the dimensional changes. So, that requires again a machining and even a component can fail because of the stresses being generated from this transformation.

So, that is the one disadvantage of carburizing. And another problem is that, for example, you have a bulk microstructure that has been optimized by doing certain heat treatment and mechanical deformation, but now in the process of carburizing, you are killing all of it, it is like pressing reset button by heating the things to austenitic region. Whatever has been optimized, everything will come to the austenite now.

Now again it requires that we need to optimize the bulk property. So, that is also another disadvantages of carburizing, but it allows you to do very quickly because carbon sources are very. There are limitations for every process. So, keeping in mind these limitations now, we move to nitriding. So, whether this can be eliminated.

(Refer Slide Time: 21:38)



Thermo-Chemical treatments

- **Choice of elements:** interstitials – C, N, B
- **Choice of chemical sources:**

Thermodynamics and kinetics

- **Hardening mechanisms:**

precipitation, solid solution, matrix phase change

IIT ROORKEE | NPTEL ONLINE CERTIFICATION COURSE

So, the nitriding implies the hardening for the surface regions by the precipitation hardening mechanism. So, what is shown here (refer to above figure) is the metastable iron nitrogen phase diagram. It is metastable because here all these iron nitrides actually, are thermodynamically unstable.

The same holds for iron carbon phase diagram which is also metastable whenever we introduce cementite in that phase diagram. So, now here (refer to above figure) you see that this is only a portion of the iron nitrogen phase diagram because we have not gone to the 100% nitrogen axis. So, again you see here you have a ferritic phase that is only in this small region, this is the border for the ferritic iron, it has got a very low solubility.

You know that the eutectoid temperature of 592˚C it can only take up 0.4 atomic percent. This is given in atomic percent in 8% it will be somewhere around 0.1 right. So, and the moment you cross this nitrogen solubility limit you start to produce this γ prime iron nitride. So, that is what is expected to happen when you take a pure iron because this is an iron nitrogen phase diagram.

So, now actually, like carburizing in iron carbon phase diagram, here also γ iron has a large solubility for nitrogen right. So, like 10.3 atomic percent at the 650 ◦C. However, we do not want to go to this temperature because this is what we are doing in carburizing where we are able to produce a carbon enriched area that can produce martensite same thing can be done with nitrogen, you can produce iron nitrogen austenite, which is enriched with iron nitrogen and we cool it rapidly you produce an iron nitrogen martensite.

That is not the whole purpose because that can be already done by the carburizing. So how does this nitriding work? Because we do not want to have any phase transformation of the bulk of the material that means if I can do the treatment like below this temperature 592˚C, the face of the matrix will be simply the whatever is been fixed before, because there will be no transformations. Because for the iron carbon system, 738˚C is the eutectoid temperature whereas, for the iron nitrogen system, this eutectoid temperature is 592˚C. Because of this, if I do the nitriding at temperature less than 592 ◦C. So, the bulk microstructure of the steel will not change, because in order to change that we need to go to this (refer to above figure) temperature.

So, now I want to only harden the surface region without changing the anything of the bulk that is the case, if I do the treatment at this low temperature. So, you have a component which has already fixed its internal microstructure, bulk microstructure. And now, I do not want to change anything of the bulk property that means, I should not heat it up to too high temperatures where transformations can happen. Now, because nitriding is a low temperature nothing will happen there. But now how the hardening will happen? You see that again the solubility of nitrogen in the ferritic iron is very low like the iron carbon, but one good thing about nitrogen is there are elements having huge chemical affinity to nitrogen for example, aluminum, titanium, vanadium.

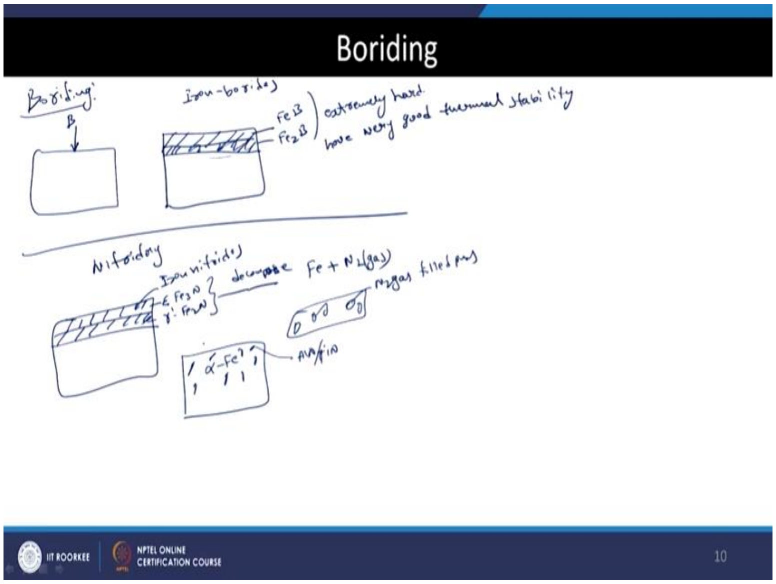
There are the elements which have a strong affinity to nitrogen to form for example, aluminum nitride or titanium nitride or vanadium nitride. So, this is the provision which makes nitriding possible. So that means if I have a steel, which has got some of these elements being alloyed inside, when I am introducing nitrogen, when this nitrogen diffuses in, a small amount can start to form these nitride precipitates.

This form a very nano sized precipitates of these nitrides. All these (refer to above figure) dots you can think of these nitrides will develop and that is where it leads to the precipitation hardening of this region. That means it will remain as a ferritic in the ferrite matrix, you are able to produce these nano sized nitrides and that will lead to the enhancement in the property. So, in this case after the nitriding you do not need to quench the sample because we not going to produce martensite, it is only ferrite.

So, that means you can cool slowly, so there will be less or no dimensional changes after the nitriding treatment. This way you see that the disadvantages of carburizing what we have seen can overcome, if you employ the nitriding treatment. So, this way we can actually optimize the process to give the surface hardness without changing the dimensions or the internal property of the core of the material.

So, this is where we are arriving a precipitation hardening. So, we have discussed another way to change the surface properties is to convert the surface region into a different compound of iron.

(Refer Slide Time: 28:38)



Boriding

For example, if you have a steel sample and the surface region of the steel sample being converted into a compound which is having a very hardened wear resistant so, that is where the this boriding treatment works. Boriding means we are trying to introduce boron into the surface regions of the material that will change the microstructure such that it will produce layers of iron borides at the surface (refer to above figure).

So, it forms so called FeB and Fe_2B layers and these layers are extremely hard and have a very good thermal stability. Thermal stability means when we heat up even up to 1000 ˚C, these layers will remain intact. That means you can even do the heat treatment to fix the internal microstructure.

Let us say that you produce this iron boride layer and then you can still do the heat treatment of the bulk. That means because you are able to go to the higher temperature. So, this is the disadvantage in case of nitriding. For example, you do the nitriding and then somehow you want to let say the change the microstructure of the entire bulk of the sample. That means, you need to heat up to the austenitic region and then cool it down and then you lose all the nitriding region because all the nitrogen will try to diffuse into the bulk of the sample.

So, that becomes a disadvantage of the nitriding treatment but in this (boriding) case because these boride layers are extremely hard and they have very good thermal stability. So, by having these layers produced, you can still do the heat treatments to the sample. So, this is another dedicated treatments people employ to produce a highly wear resistant and these are also known to have a good corrosion resistance layers on the steel surfaces.

In this case also because boron has a very negligible solubility in the iron. So, that it will not lead to much hardening by diffusion or dissolution in the matrix, but it will only produce these layers which are extremely hard. So, one may think that in nitriding, one can also produce layers of iron nitrides. So, there are two iron nitrides, it is called as a ε-Fe_3N and γ`-Fe_2N.

We will go into details of these structure and the properties of these nitrides when in detail we look into that. But the difference from the boriding is that if you look at the boriding and nitriding, in both the cases you are able to produce some compounds here, it is iron nitrides and iron borides. The difference is that these iron borides are quite stable as compared to these iron nitrides are metastable.

So, if I heat up the iron nitrides they simply decompose, they lead to decompose into Fe + N_2 gas. So, you end up with simply a porous material with nitrogen gas filled in the pores. So, that is where once you produce these iron nitrides, they are also hard but they have a very less thermal stability because they are thermodynamically unstable. So, you will not be able to have them as a porous free layer.

Whereas these iron borides are extremely stable. So, that is where actually this kind of compound layers can be produced with boriding and with good properties as compared to the iron nitrides. So, in the case of nitriding that is why mostly people wants only the no nitrogen compounds but a α-iron matrix with precipitates of alloying element nitrides. These are the nitrides of like aluminium nitride or chromium nitride or know the titanium nitride. This is the kind of hardening people wants.

Now, this is all you know the about a sort of a quick overview of these three categories of thermochemical treatments, carburizing where we are actually producing a martensitic layer on the surface of the steel by introducing carbon into the austenite and followed by its quenching.

This leads to carbon does two purposes, one is it will increase the amount of carbon that leads to the martensite forming will have a higher hardness and same time it is also improving the hardenability. With the cooling rate whatever you employ, it is easy to form martensite at the surface then into the core of your sample.

The other process which we have discussed is that because the carburizing has a disadvantages, that when you cool it down after the carburizing treatment, it involves the phase transformation of the entire sample that means, the bulk as well as the surface region right, that involves a transformation from a closed packed FCC γ phase into a much openly structured BCC or BCT phase.

So, this leads to your large volume misfits and you know the dimensional intolerance and localized the stresses creation, because we are rapidly cooling that can lead to the failure of a big sized components. Now, to overcome that, we need a treatment which can be done at a low temperature that means, where we will not change any phase of the iron carbon phases. Like if I have some ferrite it will remain as right it will not change to for example austenite.

So, that is the case with the nitriding you can do that nitriding at a below 585 or 592 ˚C. And if you contain elements, which have a strong chemical affinity to nitrogen, such as aluminum, titanium, and when you have these elements added into the steel, they will react with the nitrogen which is diffusing into the ferrite and form the nano sized nitride precipitates that leads to precipitation hardening.

So, whereas often you want to have a surface treatment which allows you to also do the further high temperature heat treatments of the steel that means whatever the phase you produce that the surface should be stable to go to higher temperatures. That is the case with the iron borides which you can be produced by treatment called boriding where we are introducing the boron into the surface regions which produces iron boride and that provides a very good wear resistance and they have a very good thermal stability.

So, it can be used even in the components operating at higher temperatures or it allows you to do the heat treatment. So, with this now, I want to conclude this lecture and in the coming lectures, we go into the details of the these three processes. So, like what are the thermodynamics of the source of carbon? What kind of atmospheres which are source of carbon can be used or atmospheres which are source of nitrogen or the atmospheres which are source or boron?

And how to deal with this thermodynamic state of those systems and then the kinetic path that how fast the process runs, how the reaction works atmosphere to the surface of the sample and then they should diffuse inwardly and how to deal with that kinetics of the processes? Once we covered those things, then you would be able to appreciate that what are the controlling parameters which needs to be kept in mind while engineering the property.