Surface Engineering for Corrosion and Wear Resistance Application

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Lecture - 25
Case Carburizing

So, welcome to the 25th lecture of Surface Engineering. At the moment we are discussing in the last couple of lectures about various approaches possible for hardening the surface primarily of steel. We started discussion with various mechanical deformation aided processes like shot pinning or shock pinning or laser shock pinning, wherein the entire process was only based on certain deformation or plastic zone induced onto the surface.

Then we talked about flame or induction hardening where we used thermal activation heating through one of the two either of the two possible ways of heating flame or induction. In both the cases, one thing was in common though one was mechanical the other one was thermal process, but one thing was common the surface chemistry we did not change.

So, essentially they were surface hardening processes without changing the composition of the surface. Now, we are going to discuss another set of surface hardening exercises which essentially is not just which is certainly not mechanical which is thermal, but to be more precise which is thermo-chemical in nature for obtaining the desired aim.

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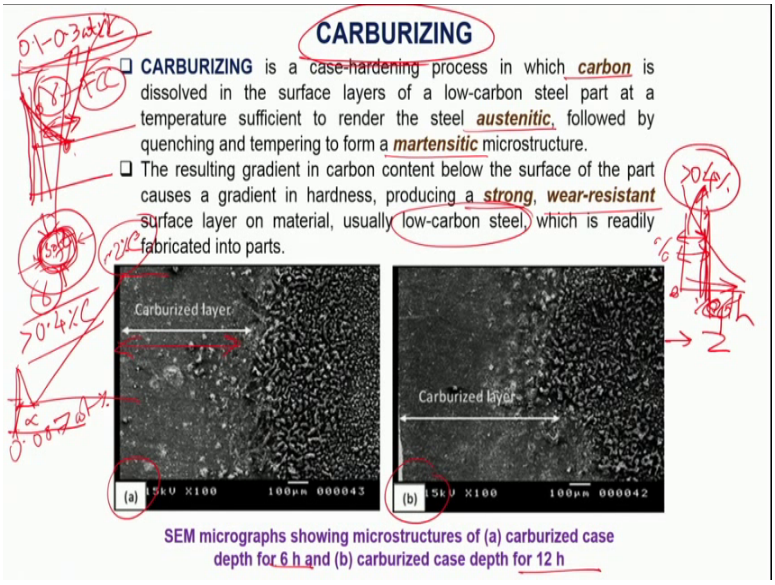

CARBURIZING

- CARBURIZING is a ~~case-hardening~~ process in which carbon is dissolved in the surface layers of a low-carbon steel part at a temperature sufficient to render the steel austenitic, followed by quenching and tempering to form a martensitic microstructure.
- The resulting gradient in carbon content below the surface of the part causes a gradient in hardness, producing a strong, wear-resistant surface layer on material, usually low-carbon steel, which is readily fabricated into parts.

SEM micrographs showing microstructures of (a) carburized case depth for 6 h and (b) carburized case depth for 12 h

So, this process is called carburizing and here in we actually if you recall in the previous lecture we said the steel that we generally use will have should have a minimum content of about 0.4 percent carbon, 0.3 to 0.6 or 0.8. Typically, more than 0.4 weight percent carbon in the steel ah, because we do not change the chemistry and that is the minimum amount of carbon. We need to be able to convert the surface into martensite and that martensite should develop adequate strength or hardness and in order to get that you require a minimum amount of 0.4 percent carbon.

Compared to that, if you now look at this carburizing process as I said this is a thermo chemical process. So, here again if you refer to the steel part of the phase diagram, iron cementite diagram then this is the eutectoid point usually this kind of treatment is applied to mild steel; low carbon steel. So, now we are talking about a range which typically would be about 0.1 to at the most 0.3 weight percent carbon.

So, purposely we are choosing a stock which has lower carbon. So, that the component that we are going to treat will actually have a core which will be not only ferritic or ferrito pearlitic, but because of low carbon will actually be much more softer and eventually provide higher toughness for the entire component. So, this portion we purposely want to remain as soft and that is why we require a carbon content which should be sort of in this range. But, in order to get requisite hardness or optimal hardness of martensite at the surface, we already know that you require carbon content which is certainly more than 0.8 0.4 percent carbon.

So, now, we need to enrich the surface with carbon. The process of carburizing essentially is a technique by which we can enrich the surface with carbon by solid state diffusion. So, we do not take the stock to temperature above melting temperature, it is entirely a solid state process. Now we again need to go to a temperature which has to be higher than the AC 3 temperature, why is it so? Because we want the entire microstructure of the steel to be austenite and why austenite because, austenite we all know is FCC Face Centered Cubic structure and the maximum carbon solubility or the limit of carbons solubility.

In austenite is much higher is highest in all the possible solid phases of steel and that would be typically if I draw it a fresh then this is the steel portion, we are talking about and this is the eutectic isotherm beginning. So, this is the portion which is approximately 2 percent carbon; so, you can pack in as high as up to 2 percent of carbon in the interstitials of austenite, not in ferrite. In ferrite, the maximum solubility is only 0.025 percent and that too at the eutectoid temperature. At room temperature of course, we have nearly 0; at room temperature phase is ferrite and ferrite typically the room temperature solubility will be very very low typically let us say 0.007 weight percent.

So, in order to pack maximum possible amount of carbon, we need to go to austenite and we cannot afford to do that exercise in the ferritic zone; so, that is why first of all we choose low carbon stock. So, that the core remains inherently soft and eventually provide the required toughness, but on the other hand the surface should be enriched in carbon, and for that reason the surface we want up to a certain depth to go to austenitic range.

So, that during diffusion solid state diffusion it can acquire carbon which can be usually we target somewhere in this range up to about say somewhere around 0.4 to point maybe 8 or maybe up to about 1 percent carbon. So, typically in this range; but, one can go theoretically to as high as 2 percent carbon.

So, the process is the same as I said enriching the surface with carbon, we heat and then take the surface up to a control depth to austenite and then subsequently we employ separate heat treatment to convert the carbon enrich surface to go to austenitic range and then subsequently be quench to martensite. What we get in turn is a strong wear resistant surface and the stock to begin with will be ideally a low carbon steel which is used for various manufacturing processes.

Now, when you do carburizing, then with time actually how the depth of carbon penetration changes so, this is a is up to 6 hours and b is up to 12 hours. So, by employing another 6 more hours you can increase the depth of carbon penetration typically, from about let us say 3 400 micrometer to almost close to a millimeter.

So, the carbon penetration from the surface so, if this is percentage carbon and if this is depth z, so this is the surface and this is towards the interior the carbon diffusion profile will be like this. So, up to a certain depth the our idea is that if this is the desired depth. So, within this desired depth region one should have at least the minimum amount of carbon. So, this cutoff point is typically about 0.4 percent carbon, and this is the depth from the surface which has would have acquired the required amount of carbon which can be more than 0.4 percent carbon.

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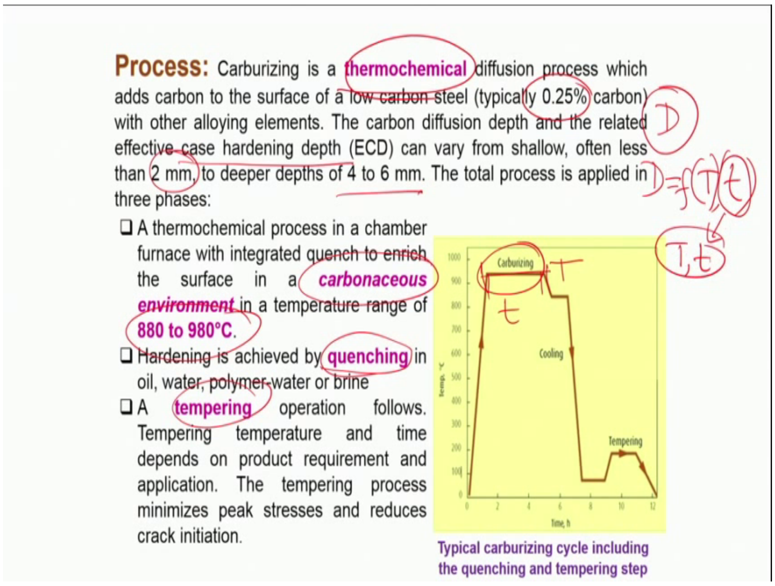

Process: Carburizing is a **thermochemical** diffusion process which adds carbon to the surface of a low carbon steel (typically 0.25% carbon) with other alloying elements. The carbon diffusion depth and the related effective case hardening depth (ECD) can vary from shallow, often less than 2 mm, to deeper depths of 4 to 6 mm. The total process is applied in three phases:

- ❑ A thermochemical process in a chamber furnace with integrated quench to enrich the surface in a ***carbonaceous environment*** in a temperature range of **880 to 980°C.**
- ❑ Hardening is achieved by **quenching** in oil, water, polymer-water or brine
- ❑ A **tempering** operation follows. Tempering temperature and time depends on product requirement and application. The tempering process minimizes peak stresses and reduces crack initiation.

D

$D = f(T, t)$

T, t

Typical carburizing cycle including the quenching and tempering step

So, as I said this is a thermo chemical process diffusion control, we start with a low carbon steel and which may have other alloying elements. But we actually produce carbon penetration up to a certain depth, which can be a millimeter or certainly less than 1 or 2 millimeters, but if needed we can go even up to 6 millimeter so, the effective case depth can be as high as 6 millimeter.

So, in order to introduce carbon to the surface, we need carbon containing or carbonaceous environment and expose the material to somewhere around 880 to 1000 degree centigrade. Because that is the temperature range where everything is austenite and solubility of carbon in austenitic stage is higher. All carburizing treatment is to be followed up with a separate heat treatment called quenching process, but an even tempering process, but that we will discuss some other time. So, what is important for us is to know that we are exposing to a fairly high temperature above 900 and so and hold for a certain period of time.

So, both temperature of heating and the time of holding both are very important. Because the whole thing is diffusion controlled and we know diffusivity is a function of both temperature and not time, but the diffusivity is a function of temperature. But, time also for a given at a given temperature time and temperature overall will determine what is the depth of carbon penetration.

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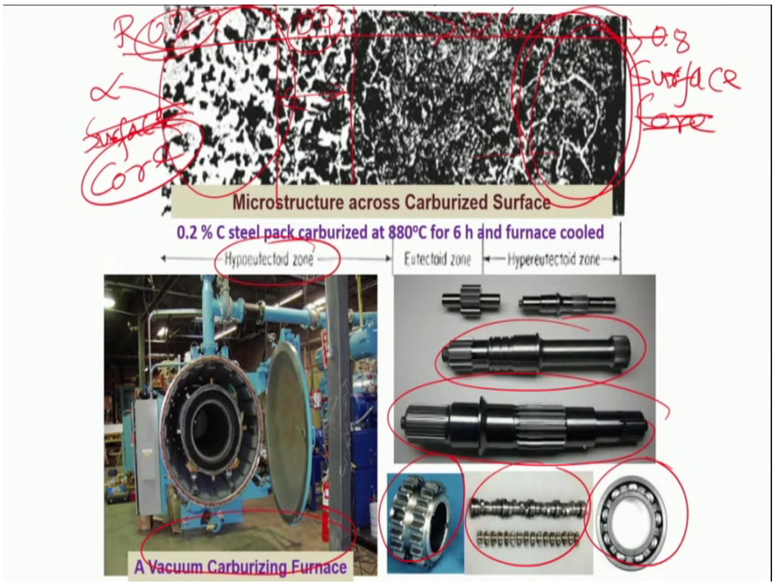

Microstructure across Carburized Surface

0.2 % C steel pack carburized at 880°C for 6 h and furnace cooled

Hypoeutectoid zone | Eutectoid zone | Hypereutectoid zone

A Vacuum Carburizing Furnace

So, if this is the surface after carburizing and this is towards the core so, this kind of a gradation of microstructure we see. So, typically this is where we have much larger carbon this is where we have carbon content which is in between and this is where the carbon content reduces and we actually can get I am sorry I made a mistake here this is the core region and this is the surface region. So, this is the so called hypereutectoid zone and this is the hypoeutectic eutectoid zone low carbon.

So, what you are seeing this bright regions are the ferritic regions and these are pearlitic regions. So, this is a ferrito pearlitic core which is what we had at the beginning and this is the mixture of ferrite and this is a mixture of this is the region where you have introduced more amount of carbon; so, the volume fraction of area fractions of ferrite pearlite is changing. And so, let us say typically this would be in the range of if this is 0.2 percent carbon, this would be typically about 0.4 percent carbon and this may be more than 0.6 percent carbon. And this certainly is the hyper eutectoid range so; obviously, you are talking about a carbon range which is greater than 0.8 percent carbon.

So, we create compositional gradation and hence micro structural gradation after carburizing treatment. This is a vacuum carburizing furnace, typically used for carburizing, but gas carburizing not the pack carburizing that we are talking about. And these are the typical components which are used for which are subjected to such carburizing treatments. So, it can be a long shaft or camshaft or gear wheel or a ball bearing assembly and so on and so forth.

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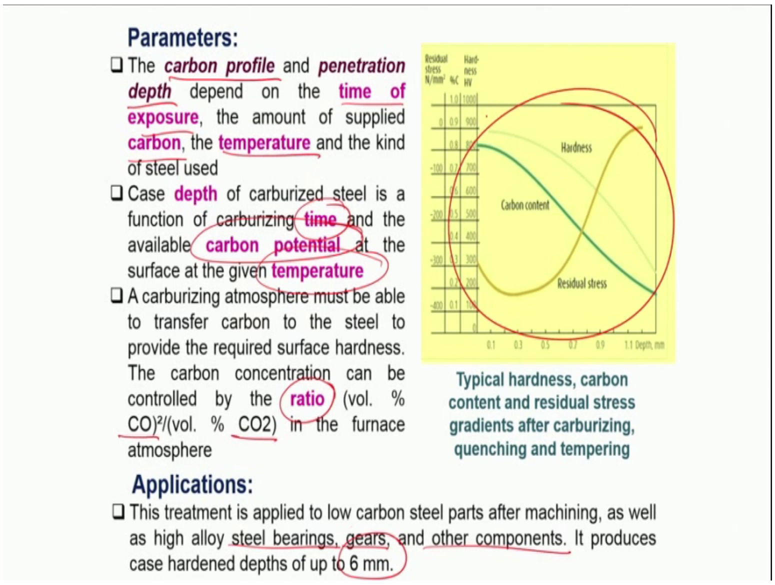

Parameters:

- ❑ The ***carbon profile*** and ***penetration depth*** depend on the **time of exposure**, the amount of supplied **carbon**, the **temperature** and the kind of steel used
- ❑ Case **depth** of carburized steel is a function of carburizing **time** and the available **carbon potential** at the surface at the given **temperature**
- ❑ A carburizing atmosphere must be able to transfer carbon to the steel to provide the required surface hardness. The carbon concentration can be controlled by the **ratio** (vol. % CO)²/(vol. % CO2) in the furnace atmosphere

Typical hardness, carbon content and residual stress gradients after carburizing, quenching and tempering

Applications:

- ❑ This treatment is applied to low carbon steel parts after machining, as well as high alloy steel bearings, gears, and other components. It produces case hardened depths of up to 6 mm.

So, the carbon profile and the penetration depth they will depend upon the time of exposure, the carbon activity in the environment which can be a solid or solid converted into gas and the temperature that we employed; Of course, the base composition of the steel is also important. So, we need to expose for a certain period of time to build the required amount of carbon potential and at and a isothermal temperature that we subject the stock too.

This process as I said is based upon creating a carbon riched environment and that will primarily depend upon the ratio of carbon monoxide to carbon dioxide. So, this gas mixture ratio determines what is the carbon activity in the furnace, what is going to dictate, what would be the depth of penetration of carbon into the surface. Typical applications as I already mentioned could be on the bearing assembly, the gears the cutting heads the shear blades even shafts or cams and so on and so forth. But, these are all to begin with they should have very low carbon so, mild steel 0.2 or so and the case depth can be to the maximum something like about 5 6 millimeter.

We will come back to this discussion of this diagram later because in this discourse we are only talking about the carburizing and not the subsequent heat treatment. Once you have completed the heat treatment typically, but even after carburizing treatment this would be the carbon diffusion profile. And eventually, this is the kind of a hardness profile that you can generate and because of the martensitic transformation, you can also create residual compressive stress up to a certain depth below the surface.

So, this would be the range from the surface which will be developing residual compressive stress, but remember these kind of profile you can generate after the heat treatment that follows up carburizing treatment.

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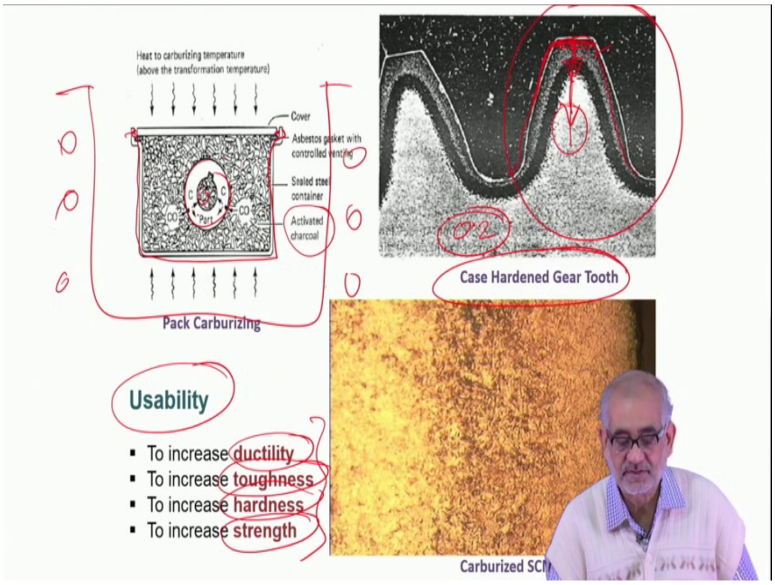

Pack Carburizing

Case Hardened Gear Tooth

Usability

- To increase ductility
- To increase toughness
- To increase hardness
- To increase strength

Carburized SC

So, this is the cross section of the tooth of a gear and this explains exactly what we are trying to do by way of these carburizing. Please remember, in case of induction hardening or flame hardening, you would have also got a very similar cross sectional profile, but the difference was that they are the steel the stock that we subjected to must have had already adequate amount of carbon.

So, the initial composition of the steel must be already having more than 0.4 percent carbon. But here we are dealing with a material which is having in the core to begin with only about 0.2 percent carbon, but the surface that we developed this bright region; white region that you are seeing as the contour line. This bright region is highly carbon enriched and is it can be actually close to eutectoid or even hyper eutectoid.

So, we see a compositional gradient from the surface towards the interior and this gradient gives you predominantly martensitic martins martensite plus pearlite and then subsequently ferritic pearlitic microstructure. So, that is kind of a desired scenario that we want to develop through this case hardening process. What we actually want to achieve is to not to sacrifice ductility, we want to retain ductility, we want to retain toughness, but we want to increase the hardness and strength of the surface. So, this is a tall order to have this kind of a combination.

How do we do it? So, in some cases this is called pack carburizing or even box carburizing, because you actually take a cast iron box like this, then this is your component and this is your component and you pack it with solid substances which are essentially graphite. And then calcium carbonate or barium carbonate or some other activators and we may have also certain other oxides. So, what is most important is this activated charcoal this is the main source of carbon, but please remember that if you use it we will come to that in the next very slides.

But let me just tell you that we need to seal up these portions here because we do not want fresh entry of air into it and we expose this whole thing inside the furnace. So, it goes inside the furnace and then we heat up to an isothermal condition which could be as I said anything from about close to 800 to 1000 degree depending on what the initial temperature the initial carbon content of the steel is.

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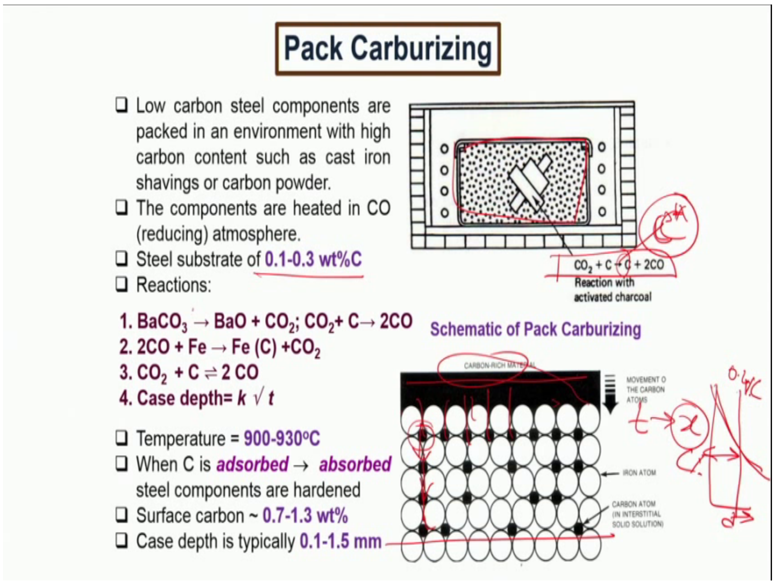

Pack Carburizing

- ☐ Low carbon steel components are packed in an environment with high carbon content such as cast iron shavings or carbon powder.
- ☐ The components are heated in CO (reducing) atmosphere.
- ☐ Steel substrate of 0.1-0.3 wt%C
- ☐ Reactions:

1. $BaCO_3 \rightarrow BaO + CO_2$; $CO_2 + C \rightarrow 2CO$
2. $2CO + Fe \rightarrow Fe(C) + CO_2$
3. $CO_2 + C \rightleftharpoons 2CO$
4. Case depth= $k\sqrt{t}$

- ☐ Temperature = 900-930°C
- ☐ When C is ***adsorbed*** → ***absorbed*** steel components are hardened
- ☐ Surface carbon ~ 0.7-1.3 wt%
- ☐ Case depth is typically 0.1-1.5 mm

So, in pack carburizing what is important again let me repeat is that we are beginning with low carbon stock, this is the kind of arrangement that this is the box which is packed with this particular let us say shaft and with packed with this carbonaceous materials. And the typical reaction which is responsible for carbon diffusion is like this where carbon reacts with carbon monoxide and deposits in the process. In the cooler region carbon onto the surface, but the difference is that this carbon is so called activated carbon.

So, this activated state is very important for carbon to diffuse in and schematically, if this is carbon enriched region then this is how the carbon atoms are able to penetrate to the surface and actually diffuse further down and reach up to a certain depth. So, they are not substituting an existing iron alpha iron atom, but they are going into the interstitious, but when one interstates one interstitial position is occupied it immediately creates a fair amount of strain field around. So, that the subsequent spots are not necessarily filled up immediately.

On the other hand depending upon the time that you allow, this time essentially determines to what depth you actually can expect carbon to diffuse in, we also have seen that the carbon diffusion profile decays with depth. So, as we go lower and lower the carbon content decreases; obviously, surface which is exposed to the carbon rich environment will actually have the maximum amount of carbon and the way below down inside you will have the least amount of carbon. So, this is how the carbon profile diffuse changes or decreases and we have already discussed that the typical case depth could be a few millimeter, maximum 6 millimeter and the cutoff point here should be 0.4 percent carbon.

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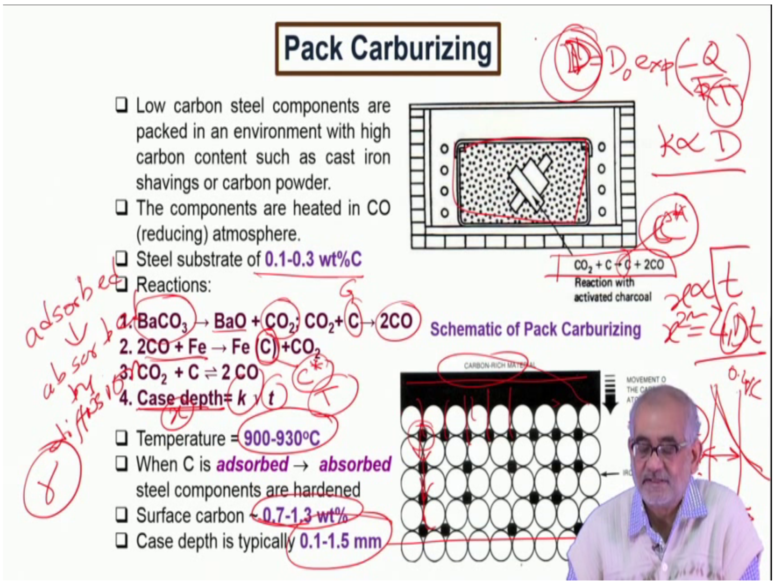

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$CO_2 + C \rightarrow C + 2CO$

Reaction with activated charcoal

Schematic of Pack Carburizing

$D = D_0 \exp\left(-\frac{Q}{RT}\right)$

$k \propto D$

$x \propto \sqrt{t}$

$x^2 = 4Dt$

adsorbed ↓ absorbed by diffusion

γ

C^*

0.4%C

Now what is that reaction that actually takes place inside, it is not the charcoal which is the one which actually starts the process. It is actually this activator barium carbonate which dissociates at 900 or 800 degree centigrade and dissociates into barium oxide and carbon dioxide. Carbon dioxide now reacts with activated charcoal or graphite and converts this carbon dioxide into carbon monoxide.

Carbon monoxide when it comes in contact with steel or iron at high temperature then it actually decomposes and dissociates to deposit activated carbon so, atomic carbon. Now, this is very important that this is in an activated state not in a molecular state, because unless it is in an activated state it cannot easily gets adsorbed and subsequently absorbed by diffusion. So, what is important is that the carbon at the surface is initially goes through initially gets adsorbed and then finally, get absorbed by diffusion.

So, we must have sufficient solubility for absorption and this is why exactly we always go to the austenitic range and then do not do it in the ferritic range. We already learned that austenite can give you can actually dissolve as much as up to point up to 2 weight percent of carbon. The temperature range would be that varies depending upon the stock that you are dealing with its initial composition and the depth to which you want to go and so on and so forth and then so, this is important here that the so called case depth that we are talking about will be a function of time and temperature.

So, at a given isothermal temperature the diffusion coefficient as we all know is a function of is proportional to the temperature. So, this is the factor which determines what is the effective diffusion coefficient and once we know the; so, this k basically is proportional to diffusion coefficient and for a given temperature since the D is fixed for a given temperature.

So, what we now need is to determine what is what should be the possible depth and this possible depth is actually proportional to the square of the temperature, because it derive it is derived from the relationship which is somewhat like this. So, these constant then obviously, the depth case depth essentially depends upon the square of time.

So, higher the time higher will be the depth of penetration, but I would like to reemphasize the fact that in order to enrich the surface with so high carbon and achieve a depth up to about 1.5 to 3, maximum 6 millimeter. We should have sufficient carbon potential in the environment and that is possible through this kind of a reaction where barium carbonate dissociates gives barium oxide and carbon dioxide.

Carbon dioxide reacts with activated charcoal creates carbon monoxide, carbon monoxide when it comes in contact with the hot surface of steel dissociates and deposits activated carbon. And this activated carbon now gets adsorbed and then subsequently absorbed into the stock by way of diffusion. And the depth of diffusion will be determined by the time the square root of time at a given isothermal temperature and diffusion will be dictated by the so called diffusion coefficient at that particular temperature.

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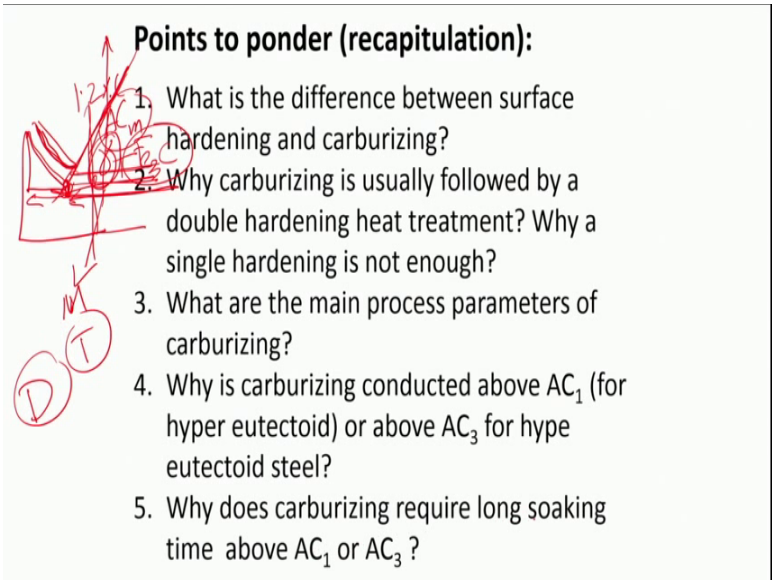

Points to ponder (recapitulation):

1. What is the difference between surface hardening and carburizing?
2. Why carburizing is usually followed by a double hardening heat treatment? Why a single hardening is not enough?
3. What are the main process parameters of carburizing?
4. Why is carburizing conducted above AC_1 (for hyper eutectoid) or above AC_3 for hype eutectoid steel?
5. Why does carburizing require long soaking time above AC_1 or AC_3 ?

So, now it is time to recapitulate what all we have discussed. So, as I said right at the beginning compared to shot pinning or shock pinning or laser pinning and so on this is different process, where we are taking not only the help of heating or thermal effect, but also we are changing the chemistry. So, this is a thermo chemical process compared to the other processes that we have discussed.

Then this whole technique is aimed at enriching the surface with carbon and we just heard that how do we do that we actually take charcoal, we take barium carbonate. We dissociate certain reactions take place in the vapor state and eventually carbon gets deposited in the activated form and that activated carbon diffuses inside.

The division profile is actually decaying from the surface highest at the surface and then gradually decreases the typical process parameters of course would be the activity of carbon that we create the temperature the time the surface condition and of course, the initial carbon content of the steel. We, this one important point that I need to address here, if we basically can divide the entire range of steel for all engineering applications in two main parts the so called hypoeutectoid and hyper eutectoid.

So, again if you refer to the steel part of the diagram then, so below the eutectoid point everything is called hypo eutectoid and above the eutectoid point in terms of completion is called hyper eutectoid. So, if we are dealing with hypo eutectoid, then this is the temperature band we target to achieve while treating hyper eutectoid steel we do not necessarily go above the AC m, Here we go above AC 3, but for hyper eutectoid we do not go above AC m. That is purely because the temperature here is fairly high, but already if the curve if the steel let us say is 1.2 percent carbon or 1.1 percent carbon.

Generally, these kind of steels are never subjected to carburizing treatment, but for whatever reason if you are doing anything with hyper eutectoid. You rather heat only above the eutectoid and not necessarily go above AC m, because above AC m you first have to go to very high temperature. There could be subsequent large thermal shock or thermal distortion during quenching more importantly, because of exposure to much higher temperature you actually can undergo undesirable amount of oxidation at high temperature.

But the most important thing is that when you go above the eutectoid temperature for hyper eutectoid steel, you already have 90 percent of the volume converted into austenite. If you applied lever rule for 1.2 percent carbon steel, you can easily see about 80 to 90 percent of the mike structure is already austenite and the remaining part will be cementite; cementite is a hard phase.

So, even if you retain 10 20 percent of cementite in the microstructure, it is not going to do harm rather it is going to provide you more hardness or more it is going to make the whole microstructure stronger. But your main intension is to convert austenite into martensite and if you already have 80 percent of the microstructure in austenitic state.

Even though you have heated only just above AC 1 and not above AC m, you better as well stay at the temperature range and be happy with 80 90 percent of austenite. Instead of trying to go all the way up above AC m and incur the disadvantages of spending more fuel, spending more money on heating exposing to more oxidation oxidative situation and also incur a greater amount of thermal shock while quenching.

So, and the time that we require for soaking will be primarily dictated by the diffusion coefficient and hence the temperature that we are referring too. So, that determines what amount of time we need for carburizing. So, that is all for the time being.

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Thank you very much.