Surface Engineering for Corrosion and Wear Resistance Application

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Lecture – 26

Liquid Carburizing and Gas Carburizing

Welcome to the 26th lecture of Surface Engineering. In the last lecture, we discussed carburizing as a strategy for improving wear resistance or surface dependent mechanical properties and compared to the mechanically driven processes like shock peening or shot peening and so on. Here the process was based on thermo chemical approach whereby we changed the composition of the near surface region and then also carried out thermal treatment so, that carbon could diffuse. The whole objective was to enrich the surface with carbon; the beginning material usually is a mild steel less than 0.2 0.3 percent weight percent carbon.

So, we enriched the surface with carbon to take it to close to eutectoid temperature a eutectoid composition so, somewhere around point certainly more than 0.4. So, typically I would say 0.6 to 0.8 percent carbon sometimes even higher and then we carry out certain heat treatment processes, but that we have not discussed so far. In pack carburizing or solid state carburizing as the name suggests, though everything is done in the solid state and only due to the chemical reaction within the furnace or the atmosphere, gaseous pre casters form.

And these are essentially through dissociation of sodium carbonate leading to formation of carbon dioxide, reacting with carbon or grapha and available charcoal activated charcoal and forms carbon monoxide which in contact with the hot iron piece or solid steel surface deposits carbon and this carbon in the form of activated or nascent form gets adsorbed and then subsequently absorbed or diffused into the material. So, that is the overall process in the solid state.

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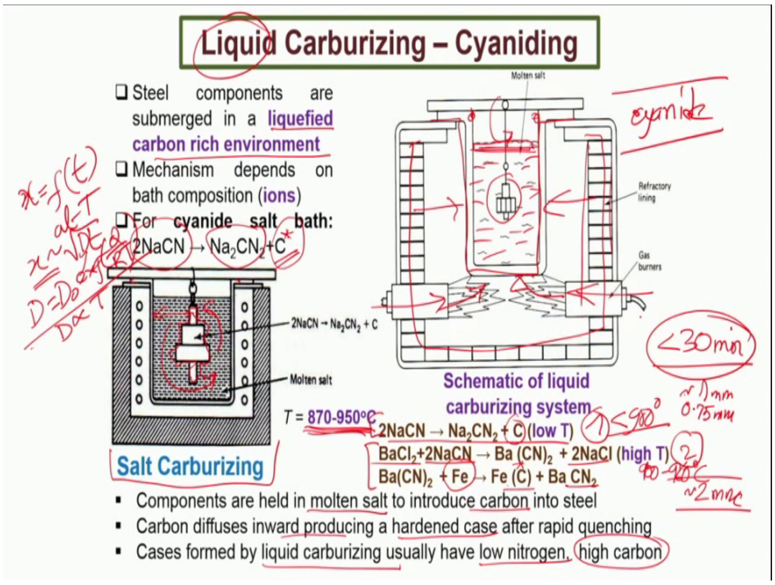

Liquid Carburizing – Cyaniding

- ☐ Steel components are submerged in a **liquefied carbon rich environment**
- ☐ Mechanism depends on bath composition (**ions**)
- ☐ **For cyanide salt bath:** $2NaCN \rightarrow Na_2CN_2 + C$

Salt Carburizing

Schematic of liquid carburizing system

T = 870-950°C

$2NaCN \rightarrow Na_2CN_2 + C$ (low T)

$BaCl_2 + 2NaCN \rightarrow Ba(CN)_2 + 2NaCl$ (high T)

$Ba(CN)_2 + Fe \rightarrow Fe(C) + BaCN_2$

- Components are held in molten salt to introduce carbon into steel
- Carbon diffuses inward producing a hardened case after rapid quenching
- Cases formed by liquid carburizing usually have low nitrogen, high carbon

Now, we are going to discuss liquid carburizing sometimes which is also called cyaniding and subsequently will also discuss a similar process of carburizing in the gaseous state. So, the basic difference bit from what we discussed earlier is the fact that we are talking about the process which is a liquid state processing not the solid sample, but the medium. So, we have a liquefied carbon rich environment and that is typically sodium cyanide and the sodium cyanide actually.

So, the configuration would be somewhat like this that, this is the chamber which is to be sealed and this portion needs to be very properly sealed. In fact, sometimes as a precautionary measure, the top layer also is covered with the charcoal so, that whatever dissociates from sodium cyanide does not go into the atmosphere its a highly toxic gas.

So, this is basically a salt bath in which the sample is immersed or dipped inside and obviously, the liquid covers the surface of the solid or the sample object from all sides and the this is usually suspended from the top or there could be also a provision of rotating this so, that there is some amount of percolation or agitation within the bath. But normally this is good enough to just heat it from the bottom so, that the salt is in the molten state. So, the salt is in the molten state and in this molten or liquid state the sample is dipped.

Now so, these are essentially flames or burners through which we heat up. The whole chamber is actually enclosed in an furnace with a certain amount of refractory lining so, that the heat is radiated back onto the vessel containing the salt bath. So, the bath is actually maintained always in liquid state. Usually whenever we deal with salt bath processes these kind of activities never completely ceases; in other words you rarely once you have molten the salt you generally would not like to allow it to come to room temperature because every time you do that there is a lot of dissociation that takes place and in the process the composition can change significantly.

So, once on we always maintain in the molten state, but obviously, the temperature can be decreased, but not necessarily we always maintained this kind of an reaction temperature we reduce it to maybe just a few hundred degrees maybe 300 400 degree centigrade, where the salt will still be in the molten state. Now usually in all kinds of salt bath furnaces or salt bath we actually use multiple salts so, that they form a eutectic, but in case of liquid carburizing particularly the sign aiding process, its a single salt which is heated to approximately there are two versions actually like one is this load so, called a low temperature variety, the other one is the high temperature variety.

Typically this low temperature variety would mean you are heating certainly less than 900 degrees centigrade typically about 800 to 850 860 degrees centigrade whereas the high temperature variety would be anywhere between 900 to about 960 degree centigrade. Now in the low temperature variety which actually is slightly slower process what we see in terms of chemical reaction is the sodium cyanide, that dissociates into lower salt which is disodium cyanamide and in the process we see liberation of activated or nascent carbon.

So, this nascent carbon like in the previous case if this is the work piece that we are talking about, then this is the work piece which actually is covered with this nascent carbon which gets adsorbed to the surface. So, this is initially just a chemi absorption process and then subsequently because of high temperature environment we are maintaining which is an isothermal temperature.

So, carbon diffuses inside the material up to a certain depth and that we have discussed already in the previous lecture that this diffusion depth the so, called x of the diffusion that is a function of time of course at a given temperature T. So, approximately we use an empirical relationship wherein we know that this is the depth with which we expect for the diffusion of carbon and this D in turn is a temperature dependent term which basically is derived from this kind of an Arrhenius relationship, which simply says that D is proportional to temperature.

So, there are certain definite advantages. The first advantage is that the test piece the work piece that is being carburized is covered by the solution from all sides. So, the entire surface the entire surface area the contour of the work piece is treated at the same time and hence the diffusion depth of carbon is very uniform throughout, no matter what the shape and complexity of the geometry is.

Number 2 is, in all solid state processes for example, pack carburizing, there will always be some pressure of oxygen or some presence of oxygen within the atmosphere within the furnace atmosphere. So, even if it is present in very low partial pressure, little amount of oxygen presence at least initially can cause formation of some thin oxide layer onto the surface of metal which is steel basically.

Iron has very high affinity for oxygen at high temperature. So, it can always form a very thin layer of oxide and that does create problems if this oxide layer is not so thin or happens to be little adherent. So, it is for this reason we actually back in when we do solid state carburizing, we have to back with sufficient amount of graphite or activated charcoal which should take care of the oxygen present in the atmosphere and then convert this into carbon dioxide.

In case of liquid state processing that kind of a difficulty or worry does not arise, because this is immersed in a molten bath of salt with very little scope of oxygen ingress from outside. First of all this is closed this is sealed here and moreover there is very little bit solubility of oxygen in this molten bath. In order to hasten the process accelerate the process sometimes some amount of agitation is a created by way of mechanical stirrer or rotating the sample and so on. But that is not always needed because the bath is already in a molten state and there is a natural convection because somewhat there will always be a temperature gradient from the surface to the sample. So, there will be a natural convection which will take care of a good amount of circulation.

So, this kind of a process at low temperature essentially as I said requires or involves decision of sodium cyanide into dye sodium cyanide and this kind of a dissociation also liberates this nascent carbon and this nascent carbon will actually as I said will diffusing to the material. Temperature is tip its lightly lower comparatively; on the other hand if we actually want.

So, typical depth of penetration here would be about a millimeter all at times may be less than a millimeter may be 0.75 millimeter and but the time required for this kind of a process is very small its less than 30 minute. Compared if you compare this with the pack carburizing process typically the to get about 1 or 2 millimeter you require easily something like 8 to 10 hours compared to that this is a very rapid process also the penetration of carbon is not only quicker, but also is more uniform.

Now, if you actually want to instead of just a millimeter or 0.7, 0.8 millimeter if you want to go somewhat like about 2 millimeter or more, you would go for slightly a higher temperature which is about 950 960 degree centigrade and then this the sodium and cyanide bath that we use is actually mixed with barium chloride. So, in this process the barium chloride reacts and creates a barium cyanamide and also liberates the sodium chloride.

In fact, some amount of sodium chloride or potassium chloride salts are always added as additional compounds which actually prevent unnecessary chemical reactions from outside. So, they remain morals neutral, but with the addition of barium chloride barium actually displaces the sodium cation and forms that barium cyanamide and then barium cyanamide actually in turn now reacts with the heated steel or iron and dissociates and liberates carbon.

So, this the dissociation of BaCN 2 to BsCN 2 not the cyanide radical dissociates into cyanamide radical and as a result it liberals carbon and this carbon is in activated state or nascent state. So, the same process happens that carbon goes to the surface gets adsorbed and then subsequently absorbed by way of diffusion. So, in this kind of a salt carburizing or so called cyaniding process what we have already understood is that we have molten salt bath and the components are dipped or immersed inside and that is how we introduce carbon into the steel surface.

The carbon diffuses inward and enrichment of carbon produces the so called hardened case and in fact, sometimes this sample this immersed specimen after liquid carburizing can be directly lifted and immersed or quenched into coolant and there is no separate heat treatment needed in that case.

So, that is how we create an hardened case and whatever we produce by liquid carburizing usually the target is carbon enrichment, but sometimes nitrogen also goes inside the solid sample. Now if you actually happen to a follow a processor or create as a situation whereby both carbon and nitrogen goes into solution, then you actually end up producing what is known as carbonitrides and this carbonitrides actually create a much harder case.

As it is this kind of a process creates a slightly harder case than pack carburized surfaces, but with introduction of nitrogen the hardness on the surface is even higher and that actually is both good and bad news. The good news is that you have higher hardness so, you can expect better wear resistance at least empirically.

But on the other hand if you make the surface too hard then there is no chance of further machining or any other shaping processes as a follower. So, by and large liquid carburizing is an advantageous process. The biggest disadvantage is the fact that we are dealing with cyanide and we all are aware that cyanide is an extremely toxic compound even accidentally if the operator happens to inhale vapor of cyanide, that certainly can cause very little action.

So, we have to be extremely careful and even disposal of these molten salt or treating or refurbishing recharging all these are fairly hazardous processes. So, that is something which is why despite the fact that it is a very fast kinetically quick process still liquid carburizing or cyaniding its not a very popular process adopted very widely in the industry. In fact, its usually done only for very limited components and in only by few companies only a few companies.

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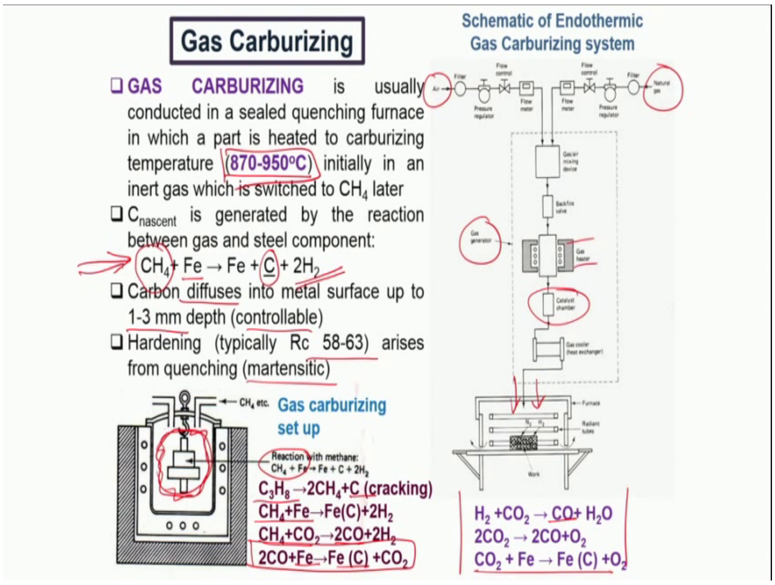

Gas Carburizing

- ☐ GAS CARBURIZING is usually conducted in a sealed quenching furnace in which a part is heated to carburizing temperature (870-950°C) initially in an inert gas which is switched to CH_4 later
- ☐ $C_{nascent}$ is generated by the reaction between gas and steel component: $CH_4 + Fe \rightarrow Fe + C + 2H_2$
- ☐ Carbon diffuses into metal surface up to 1-3 mm depth (controllable)
- ☐ Hardening (typically Rc 58-63) arises from quenching (martensitic)

Gas carburizing set up

$C_3H_8 \rightarrow 2CH_4 + C$ (cracking)

$CH_4 + Fe \rightarrow Fe(C) + 2H_2$

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$

$2CO + Fe \rightarrow Fe(C) + CO_2$

Schematic of Endothermic Gas Carburizing system

$H_2 + CO_2 \rightarrow CO + H_2O$

$2CO_2 \rightarrow 2CO + O_2$

$CO_2 + Fe \rightarrow Fe(C) + O_2$

Compared to that gas carburizing is another process where the intention is the same that we want to enrich the surface of a solid component with carbon to the tune of a certainly more than 0.4 weight percent easily something like 0.6 0.8 weight percent carbon. The temperature of treatment is 870 950 degree centigrade this is somewhat similar to what we experienced in case of pack carburizing.

Pack carburizing actually can be done even at a slightly higher temperature, but since we are dealing with the fluid here. So, the temperature is 950 is good enough for temperature for carrying out this kind of a treatment. The main distinction point of distinction apart from the state of the medium which is gaseous in this case, the main difference arises from the fact that we are essentially dealing with a single carbon containing gaseous compound methane.

So, its methane which actually in this chamber of gas carburizing chamber actually dissociates in contact with though its a saturated hydrocarbon, but it actually undergoes decision in contact with hot metal. Hot metal means heated solid steel surface and liberates nascent carbon and this nascent carbon actually is the species which actually diffuses into the material as deep as few millimeters and this can be very easily controlled because everything is in gaseous state.

So, precise control of temperature, time of exposure and certain things can be easily controlled. Also the presence of hydrogen is helpful because it does not allow any undue oxidation to take place. So, we do get fairly high hardness Rc in the Rockwell c scale measuring all the way up to 63 hardness which is fairly high hardness and that is purely because we after the follow up heat treatment we expect the microstructure to be predominantly martensitic.

So, mostly it is methane based process, but you can also use higher hydrocarbons may be ethane or propane and so on. So, for example, C 3 H 8 can dissociate gets dissociated at high temperature. So, we get again nascent liberation of nascent carbon otherwise this is the usual process. There is also a possibility of converting some of these carbon if there is some amount of carbon dioxide present in the chamber it can actually react and form carbon monoxide and once carbon monoxide forms again in contact with the hot steel surface it can liberate carbon this is exactly the kind of reaction that we see in case of pack carburizing.

Similar thing can happen over here also but that is not the main path through which you introduce carbon. So, unlike the previous case where we had a liquid bath, here we have a fluid bath of course, but this is gaseous surrounds the whole surface we have the same advantage of carburizing from all sides and uniformly there is no need of any agitation or percolation because the gaseous medium will have a natural convection.

We just need to maintain the isothermal temperature desired isothermal temperature which would be somewhat like this. But the gas that we feed in actually in some cases comes either as purely from the gas bottles of methane bottles or we can also use hydrocarbon source for example, natural gas.

So, we can actually have a mixture of air and natural gas fit into a gas chamber and through certain arrangements inside which includes a gas heater because of which the gas dissociates and reacts and then goes to a catalyst chamber and then once we use a gas cooler or a heat exchanger, then we get the right proportion of methane or maybe methanone propanone and so on and that is what we feed in.

There is some amount of buffer gas also used for example, nitrogen and hydrogen which covers the surface and presence of hydrogen actually is beneficial, because it helps in removing whatever little oxide layer that might be present on to the work piece. So, the process would mean again the same thing that you if you have carbon dioxide present, there could be formation of carbon monoxide and then carbon monoxide or carbon dioxide can also lead to dissociation and deposition of carbon onto the surface. So, these are a parallel reaction possibilities not necessarily the main course of action, the main reaction is through exactly this process.

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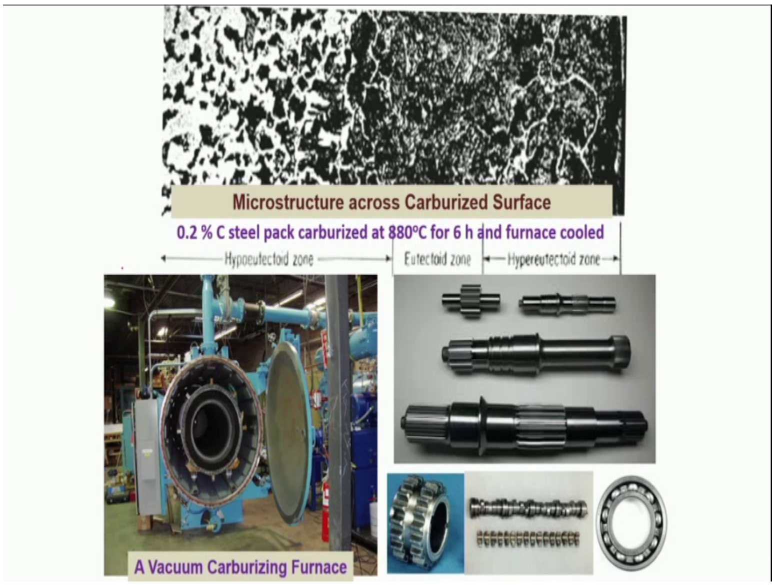

Microstructure across Carburized Surface

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

A Vacuum Carburizing Furnace

I decided to repeat this viewgraph so, that the concept is pretty clear. So, what we actually are what we expect in carburizing process like this is the following that. So, this is the surface area and. So, this surface area is this is the surface through which is exposed to this gaseous environment and this is the core of the sample. So, if we have a sample like this, this is how we are treating. So, this is the core.

So, if I take a section and just looking at half of it, then this is the core and this is the surface. So, this is the maximum carbon enrichment and this area is unaffected we just leave it without any kind of difference at all without any change in composition at all now. So, when we actually want to carry out this kind of carburizing treatment in gaseous environment, this is the kind of a furnace that we use which actually can allow you to evacuate and bring it to very low pressure.

So, something like you can reach ten raise to minus 5 millibar or minus 6 millibar, but then you have to backfill. So, you operate at maybe 10 raise to minus 2 or minus 3 millibar when you backfill with methane or other kind of desired gases and we already have discussed. So, these are standard these are very ideal specimens for gas carburizing or vacuum carburizing and so on.

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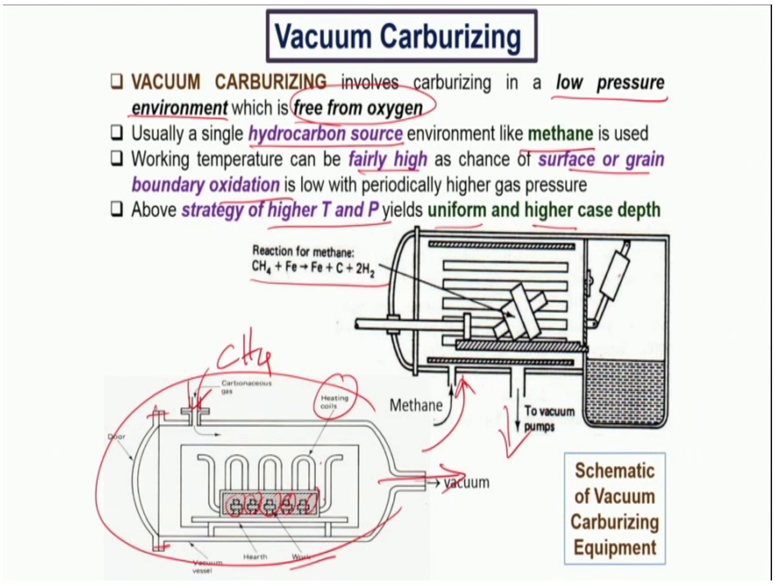

Vacuum Carburizing

- ☐ **VACUUM CARBURIZING** involves carburizing in a ***low pressure environment*** which is ***free from oxygen***
- ☐ Usually a single ***hydrocarbon source*** environment like **methane** is used
- ☐ Working temperature can be ***fairly high*** as chance of ***surface or grain boundary oxidation*** is low with periodically higher gas pressure
- ☐ Above ***strategy of higher T and P*** yields **uniform and higher case depth**

Reaction for methane:
$CH_4 + Fe \rightarrow Fe + C + 2H_2$

Schematic of Vacuum Carburizing Equipment

Another version of gas carburizing is when we actually do the operation under vacuum. Actually as I was just referring a few minutes back by vacuum what we mean is very low pressure environment and the main advantage is the fact that there is practically no presence of oxygen. Now oxygen actually is very detrimental because it always has a tendency of reacting with the steel surface hot steel surface and creation creating a thin oxide layer and this oxide layer actually forms at high temperature very easily. Once it forms it actually behaves as if it is kind of a barrier for other gaseous molecules or atoms or nascent carbon to diffuse further in.

So, we would like to avoid that by augments. So, just like gas carburizing here also the source of carbon will be a hydrocarbon typically methane as we did earlier. The temperature is usually high and the scope of surface oxidation is low as I just now said and we also change the gas pressure periodically and the temperature and pressure combination should be such that we are able to maintain very uniform and fairly high case depth.

So, this is the chamber, this is where we feeding the carbonaceous gas which could be methane and so, these are the heating coils, this is a work piece, these are the work piece and so these are the let us say tiny little work piece here and this whole chamber is evacuated. So, these doors are sealed here and this is how evacuate.

Whatever components you keep in you expose them to methane and the reacted gas actually comes out through this opening. So, by and large whether its a pack carburizing or gas carburizing or liquid carburizing, even vacuum carburizing the strategy is the same that we introduce nascent carbon onto the surface which can diffuse in and create a carbon rich layer.

And enrichment of carbon is required because of the reason that we discuss in one of the lectures on fundamentals that the martensite is the hardest solid solution provided we have sufficient amount of carbon. So, unless we have anything like 0.4 weight percent or more we do not necessarily can expect that martensite would give the very high hardness that it is known to provide something like Rc 63 64 65 at that range.

So, we deal we begin with low carbon stock 0.2 percent carbon so, that the core will maintain a ferrite pearlite or simply ferritic microstructure so, that it can absorb load it can provide high toughness and the surface actually will develop very high hardness. So, from the surface to the core we see a gradation of microstructure and hence gradation of hardness and other relevant mechanical properties and this is done by a so called thermo chemical process by way of introducing carbon onto the surface.

And very soon will discuss the subsequent heat treatment that is given and that would amply explain as to the creation of this graded microstructure also creates a challenge in terms of heat treatment of the stock after carburizing so, that we develop very high hardness and wear resistance on the surface, but maintain high toughness at the core.

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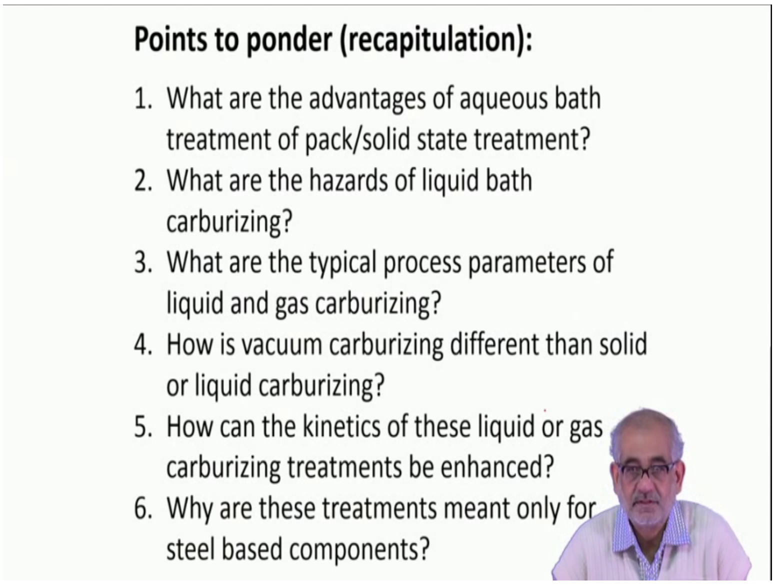

Points to ponder (recapitulation):

1. What are the advantages of aqueous bath treatment of pack/solid state treatment?
2. What are the hazards of liquid bath carburizing?
3. What are the typical process parameters of liquid and gas carburizing?
4. How is vacuum carburizing different than solid or liquid carburizing?
5. How can the kinetics of these liquid or gas carburizing treatments be enhanced?
6. Why are these treatments meant only for steel based components?

So, its time to summarize so, what we have generally discussed here is the relative advantages of the aqueous bath or liquid bath carburizing. Many advantages I mean including small time required, very uniformity of the microstructure and division depth developed and ease of operation and so on.

But the biggest disadvantage is that or the biggest hazard that we have to worry about is the adequate measures to be undertaken so, that cyanide gas or fume does not reach the atmosphere and is properly treated and taken care. So, the human the operator is working in the plant have to be properly protected and also adequate preventive measures are to be undertaken.

Then the process parameter wise since this is a diffusion control process all the processes except the initial shot peening kind of processes all the thermally activated processes are dependent on the diffusion coefficient, the temperature which in turn actually governs their level of diffusion coefficient and then at the isothermal condition what amount of time we give.

So, the combination of time and temperature is very crucial of course, the activity of carbon either in the solid back or in liquid bath salt bath or in the gaseous state that is equally that is also very very important independently should be control. The vacuum carburizing has the biggest advantage that you actually have the least scope of oxidation and the process actually can give you a slightly thicker carbonized layer. And but one thing I should have mentioned that in terms of the time for operation liquid carburizing takes the least time certainly less than an hour to create something like a millimeter and to create a similar millimeter case depth in case of pack carburizing you easily require 6 to 8 or 9 hours and the same in case of gaps gas carburizing could be even more 10 to 12 hours.

So, time of processing is larger in case of gas carburizing because the potential that you actually have carbon potential that you have in atmosphere is not adequate in case of gas in fact, gas carburizing needs a periodic recharging of the reactant gases. These treatments all the treatments that we have discussed so, far are all meant only for steel.

So, essentially whether its gas carburizing or liquid carburizing or pack carburizing everywhere we are dealing with steel. Now still I mean though it is mean for only one variety of metallic alloy still we do discuss at length these treatments because of very widespread applicability or need for application of these treatments for various components based on steel. And in manufacturing processes particularly wherever we deal with mechanical forces, steel is usually a very popular substrate for creating various kinds of engineering implements.

So, with this we end the discussion on carburizing related techniques, which is essentially to enrich the surface with carbon and then subsequently carry out some heat treatments to develop a wear resistant surface maintaining our tough core.

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Thank you very much.