Surface Engineering for Corrosion and Wear Resistance Application
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Lecture – 28
Liquid and Salt Bath Nitriding

Welcome to the 28th lecture of Surface Engineering. We have been discussing nitriding as an alternative to carburizing.

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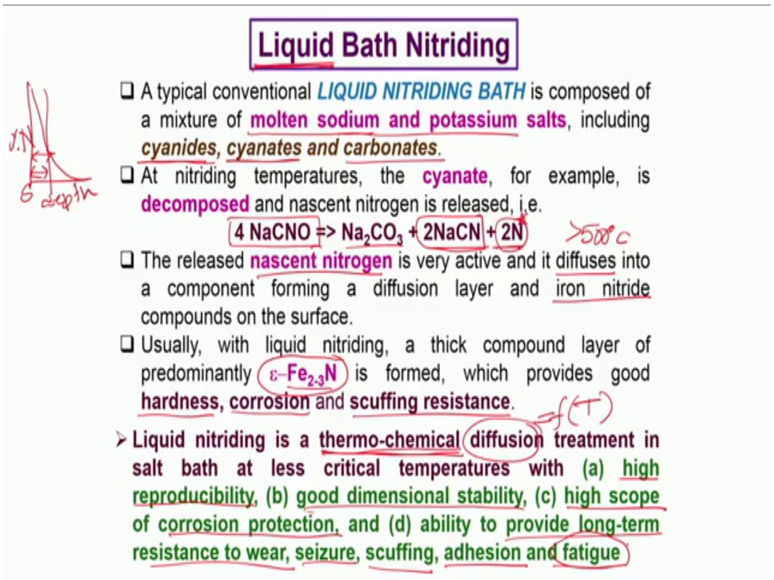

Liquid Bath Nitriding

- ☐ A typical conventional ***LIQUID NITRIDING BATH*** is composed of a mixture of **molten sodium and potassium salts**, including ***cyanides, cyanates and carbonates***.
- ☐ At nitriding temperatures, the **cyanate**, for example, is **decomposed** and nascent nitrogen is released, i.e.

$$4\,NaCNO \Rightarrow Na_2CO_3 + 2NaCN + 2N$$

>500°C

- ☐ The released **nascent nitrogen** is very active and it diffuses into a component forming a diffusion layer and iron nitride compounds on the surface.
- ☐ Usually, with liquid nitriding, a thick compound layer of predominantly $\varepsilon\text{-}Fe_{2\text{-}3}N$ is formed, which provides good **hardness, corrosion** and **scuffing resistance**.
- ➢ **Liquid nitriding is a thermo-chemical diffusion treatment in salt bath at less critical temperatures with (a) high reproducibility, (b) good dimensional stability, (c) high scope of corrosion protection, and (d) ability to provide long-term resistance to wear, seizure, scuffing, adhesion and fatigue**

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So, where the strategy is based on introducing nitrogen to the surface, but unlike in carburizing nitrogen does go to the interstitial positions, locations, but forms compounds. So, the strengthening primarily comes the strengthening usually arises from the ability to form very hard compounds, interstitial compounds various types of nitrides.

So, today we yesterday I mean the previous lecture we discuss about gas nitriding having nitrogen in the gaseous atmosphere. And today we are going to discuss Liquid Bath Nitriding. So, we essentially have an aqueous bath and in a salt bath which we have it in the molten state and then immerse the work piece into the bath. And then allow the nitrogen to be liberated from the salts and then get adsorbed and then gradually diffuse into the bulk of the solid from the surface.

So, as I said we deal with molten salts molten sodium and potassium salts and they are usually cyanides in some cases cyanides and carbonates. So, carbonates is more like an activator, but cyanide is the main source of nitrogen in many cases we do not deal with cyanide directly because it is highly toxics extremely toxic we deal with cyanides. And for example, sodium cyanide at the temperature where we do the nitriding process.

So, typically around or about 500 degrees centigrade this is where the cyanate decomposes into sodium carbonate and most importantly the sodium cyanide. So, this sodium cyanide actually is very important because, in the process we get nitrogen liberated. And so the bath that is why the bath is called cyanide bath and cyanide itself can actually react with oxygen or other gaseous substances in the bath dissolved in the bath and then liberate further nitrogen.

But cyanate having cyanate is actually what is normally practiced, because it liberates nitrogen and nitrogen in nascent form. So, this nascent nitrogen is very active can easily or immediately can get adsorbed to the surface and then diffuses into the bulk from the surface. So, we obviously create a diffusion profile which is somewhat like this. So, this is depth and this is the surface and this is the percentage nitrogen we are talking about. So, within a very shallow depth from the surface we have reasonable amount of nitrogen and a few almost 6 7 or even 10 percent of nitrogen at a very thin layer. But certainly up to a certain depth of few millimeter or less than a millimeter we have at least a one or more percentage of nitrogen.

So, when nitrogen diffuses as I mentioned it forms the iron nitrides. In fact, there are several types of nitrides that are formed, but the most important and the most prevalent one which actually provides a very high hardness and wear resistance is the epsilon nitride which is a not pure line compound not a fixed stoichiometric compound can have a composition with the varying amount of nitrogen in it.

And then this kind of a compound layer forms it actually produces so called white layer on to the surface which is effective in providing very high hardness, reasonably good corrosion resistance or passivity and also scuffing resistance for any amount of relative motion between solid surfaces. So, as I have been saying in the last few lectures that, the beat carburizing or nitriding or any of the variance of these processes these are essentially thermo chemical processes. So, we need both temperature and change in composition in the surface and it is a diffusive process.

So, obviously a temperature dependent process so diffusion means it is a function of temperature. And the difference with previous processes that we have discussed so far is the fact that here we are dealing with a liquid bath or nyquist bath. Actually it is a molten to be more precise is a molten salt bath. Temperature is a somewhere around 500 as I said 500 to 550 or maybe 480 to 550 around that temperature. And because of this exposure for it could be in the limit the minimum could be about an hour, less than hour 30 minutes or so, but usually about a few hours maybe 5 6 hours at the most depending on what level of thickness of the nitrided layer we desire.

So, what are the tradeoffs, what are the advantages or benefits we derive? We derive high reproducibility very precise, very good dimension and stability this is one very important first of all we are heat treating at 550 at the most. So, even if we quench after this less scope of distortion and even when we heat to 500 or so there is expansion, but not a very large scale expansion. So, the finished components can be directly subjected to nitriding, because of this good dimensional stability.

We have high scope of corrosion protection because these nitrides are extremely cathodic in nature. So, when you expose to various kinds of oxidizing atmosphere in aqueous or in atmospheric condition the aggressive ions even including the halides they do not necessarily immediately can attack because of the protection given by these nitrides. So, we actually the biggest advantage is that we create those nitride, series of nitrides which can provide very long term resistance to wear.

So, they do not allow easy degradation or loss of material from the surface prevent seizure, two surfaces do not allow the mating surface to form cold welding and then cease the motion very little scope of scuffing because the hard surface does not allow scooping of material from the surface. And it also provides as I said resistance against any kind of adhesion because this surface being very hard and nonreactive does not allow diffusion to take place transient or a long term with another mating surface.

And the another very very important fact is that though there is no direct phase transition involved, but there is new phase formation which are these nitrides and because of the formation of the nitrides we do get fairly good amount of residual compressive stress developed onto the surface because of which the fatigue strength also improves. So, there are multiple benefits.

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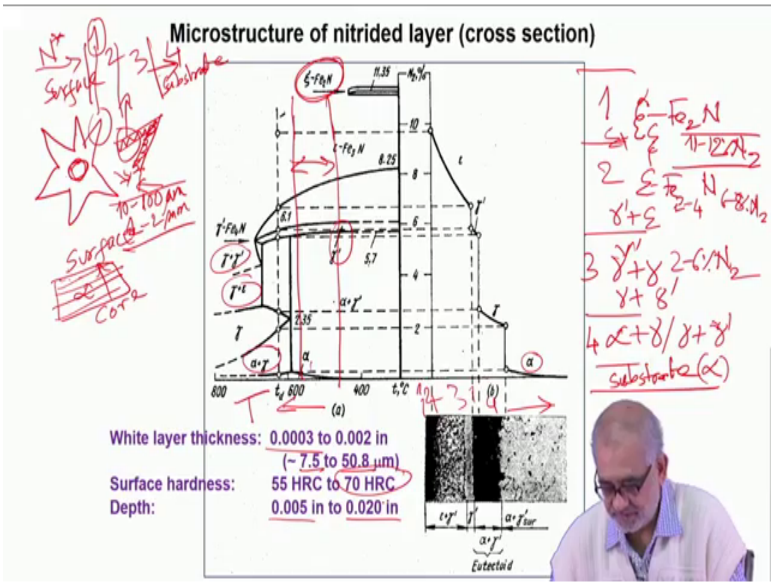

Microstructure of nitrided layer (cross section)

White layer thickness: 0.0003 to 0.002 in (~ 7.5 to 50.8 µm)

Surface hardness: 55 HRC to 70 HRC

Depth: 0.005 in to 0.020 in

Now, at this moment we need to spend a couple of minutes on understanding: what is the microstructural evolution. So, if let us say we are talking about a particular component say reasonably complex shape of a gear and. So, what is important is that we retain the core we retain the core as it is.

So, that it can maintain reasonably software microstructure or software aggregate so that the toughness of the core is regained. But at the same time if you look at this tip we actually expect this tip to develop some amount of very hard layer and the typical thickness of this layer would be somewhat not very high maybe few may be 10 to 100 micrometer and in the in some cases it can be even 1 to 2 millimeter. So, in order to develop this we expect these hard nitrides to form, but if you further zoom on to this.

You actually we will see a gradation. If this is the surface and this is towards the core then we will have a thin layer we have a slightly thicker layer and the more thicker layer and then the substrate. So, in this gradation of let us say 1 2 3 4 regions we will have different levels of nitrogen penetration; obviously, the surface which is exposed to the aqueous bath. So, this is where nitrogen comes in so obviously, the concentration of nitrogen in the first layer that we discuss will have the highest concentration.

So, let us say this is the so called first layer and this is where we expect formation of these zeta compounds. So, this zeta is basically F e 2 N and here you require as high as about 11 to 12 percent of nitrogen. So, this is very high nitrogen and this layer if at all it forms it actually is never a single monolithic layer these are only dispersed compounds. So, this zeta F e 2 N is essentially only available in the form of dispersion or a very thin layer at the surface. But most importantly what we have built is the layer below which is the so called epsilon nitride.

And this epsilon nitride I have already mentioned is typically layer which is it can be F e 3 N and F e 3.5 N or something. So, essentially this is composite layer and this is a compound layer and this compound layer would require anything above 6 to 8 percent of nitrogen. Then we will have gamma the third layer which will be predominantly gamma prime and so this gamma prime essentially requires nitrogen content which can be anywhere between c 2 to 6 percent and then below this will have the alpha layer and then we have the unaffected or unchanged substrate.

Now, when I say alpha I mean actually not alpha alone maybe alpha and gamma and maybe at times gamma plus gamma prime or gamma plus. So, this is essentially this can be gamma plus gamma prime. Then we will have when I say epsilon we actually mean starting all the way from gamma prime to epsilon and then finally, this is epsilon plus zeta. So, we always have gradation of microstructure. So, this is the substrate and then the substrate essentially will be alpha.

So, we have then alpha and gamma. So, we are talking about formation of alpha. So, this is the pure alpha region this is the two phase alpha plus gamma region, then comes formation of gamma. And in fact, a pure gamma prime is here which is an interstitial compound, but in between we have regions which will have either gamma plus gamma prime or gamma plus epsilon these are high temperature varieties. So, essentially if you are referring. So, this is the temperature axis this is how temperature is changing.

So, typically the temperature band of treatment of nitriding would be around this so this is the temperature band. And in this is the kind of phase aggregates that we are discussing. So alpha, then alpha plus gamma, then alpha plus gamma prime, then gamma prime, then gamma prime plus epsilon, then some amount of epsilon predominantly 95 percent epsilon. And then in very rare cases we have where we have done the treatment at slightly higher temperature and exposed from longer period of time there is possibility of seeing some dispersion of the zeta nitrides.

So, we see combination of these nitrides. So, after the required level of exposure we started with all ferritic matrix with some amount of dissolved nitrogen in it. Then we end up creating all kinds of nitrides layer wise, but these layers are not 100 percent not monolithic of a single compound they are all mixed compounds. And the volume fraction of these compounds actually vary to higher and higher level as we go from bottom or core of the component. So, this is the core to the surface.

Now, the utility of the nitrided compound primarily depends upon how well these compounds are dispersed what is a volume fraction, what is the size and the morphology and so on. So, this is these are the typical zone. So, if I call this as first layer, then this is the second layer, then this is the third layer, the fourth layer and then we have the substrate. So, these depth wise we are talking about very very small layers can be anything like a few micrometers to few tens of a micrometer.

The hardness is certainly much higher than what we can achieve in case of carburizing because of the presence of these hard nitrides. And so they so this is the kind of depth that we aim to have and it depends on what material and what kind of service condition these components are exposed to.

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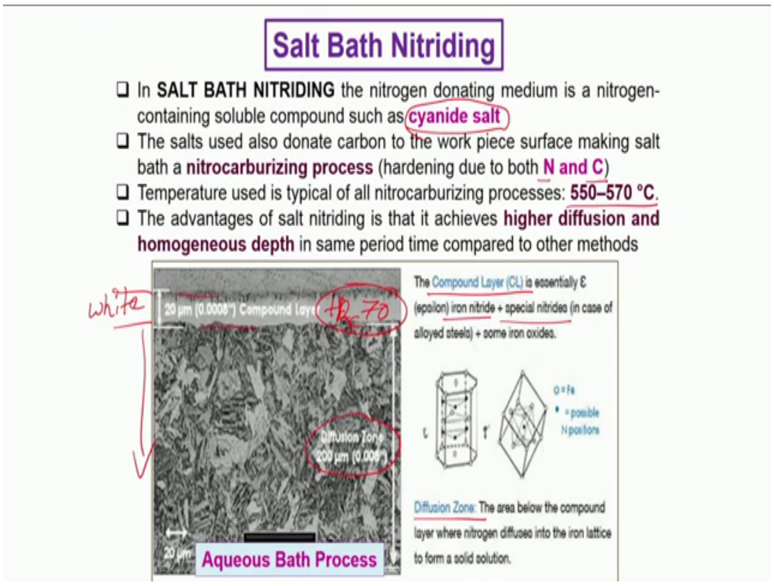

Salt Bath Nitriding

- ☐ In **SALT BATH NITRIDING** the nitrogen donating medium is a nitrogen-containing soluble compound such as **cyanide salt**
- ☐ The salts used also donate carbon to the work piece surface making salt bath a **nitrocarburizing process** (hardening due to both **N and C**)
- ☐ Temperature used is typical of all nitrocarburizing processes: **550–570 °C**.
- ☐ The advantages of salt nitriding is that it achieves **higher diffusion and homogeneous depth** in same period time compared to other methods

The Compound Layer (CL) is essentially ε (epsilon) iron nitride + special nitrides (in case of alloyed steels) + some iron oxides.

Diffusion Zone: The area below the compound layer where nitrogen diffuses into the iron lattice to form a solid solution.

So, typically when we talk of liquid nitriding then we use the cyanide as the precursor and when we stock of salt bath nitriding then we can directly use the sodium cyanide salt. And these sodium cyanide salts at that high temperature dissociate.

And then provide the ions and which further can dissociate and provide in some specific temperature and ph combination provide both nitrogen and carbon in the nascent form in the bath. So, temperature is slightly higher 550 to 570 whereas, normally gas nitriding you do at 480 to 550 or so less than 550 for salt bath nitriding. Because we need two things here dissociation of the cyanide salt we also need mobility of the ions and once these nascent form of nitrogen or carbon is deposited onto the surface liberated down to the surface then we need diffusion.

So, the formation of the compound layer which sometimes we call the white layer is what is responsible for this kind of very providing very hard surfaces. And they comprise both iron nitrides and in some cases some special nitrides in case the material is not plain carbon, but an alloy steel. For example, if you have we have already discussed if you have vanadium or titanium or molybdenum chromium all these elements have very high affinity for nitrogen. So, and the diffusion zone is the graded zone that we just discussed and few minutes ago. So, there you have a gradation.

In fact, the same thing these are real time microstructure. So, here we have a compound layer which is the so called white layer this is what we pension as white layer and then we have these various carbides and but this is also called the diffusion zone. That is because there is the there is a clear gradation of the microstructure the not only the amount of nitrogen varying as we go down in the depth, but also the kind of phases their identity and crystal structures they also vary. But this is a fairly very very hard layer.

In fact, this is extremely hard layer what we said just about if you maybe about 10 micrometer or even less with our with hardness as high as 70. But one thing we must remember that this entire process of either liquid bath or solid bath nitriding they are essentially aqueous bath or molten salt bath processes.

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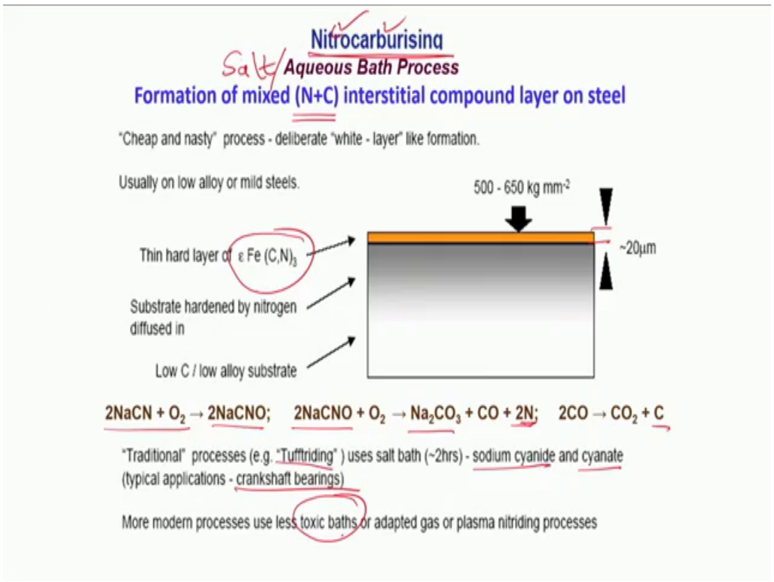

Nitrocarburising

Salt/*Aqueous Bath Process*

Formation of mixed (N+C) interstitial compound layer on steel

"Cheap and nasty" process - deliberate "white - layer" like formation.

Usually on low alloy or mild steels.

$2NaCN + O_2 \rightarrow 2NaCNO$; $2NaCNO + O_2 \rightarrow Na_2CO_3 + CO + 2N$; $2CO \rightarrow CO_2 + C$

"Traditional" processes (e.g. "Tufftriding") uses salt bath (~2hrs) - sodium cyanide and cyanate (typical applications - crankshaft bearings)

More modern processes use less toxic baths or adapted gas or plasma nitriding processes

So, what we were discussing that if we actually want to avoid direct use of cyanide then we actually would rather take cyanate, but essentially this is through an oxidative process, but not a very stable compound. So, at about 500 and above this cyanate actually will dissociate and then can form can actually get further oxidized and can form or liberate nitrogen in the nascent form and carbon also in the nascent form. But this very process is actually slightly different type of I would rather say more than aqueous bath their salt bath processes.

But the main idea here is that compared to the previous processes here we are taking advantage of the presence of both nitrogen and carbon. So, it is not the nitrides alone what we form is a mixed interstitial compound iron nitride, iron carbon nitrides and these because of the presence or the contribution of both nitrogen and carbon we call it nitrocarburizing. So, again the process is about the same the bulk of the substrate is left unaffected only a few micrometers from the maybe few tens of a micrometer of the surface actually develops this hard layer of a mixed or complex carbon nitrides.

Sometimes these processor are also called tough nitriding. I mean these are tread names used by various manufacturers and it also depends on what kind of precursor salts they are using. So, sodium cyanide and cyanate mixture of them these rotating parts they are very common to be exposed to such nitrocarburizing processes. We always should remember that we are dealing with an extremely toxic bath and even the gas that is emerges from the bath they actually need to be treated before they have discharged. So, the whole process has to be extremely conducted very very carefully.

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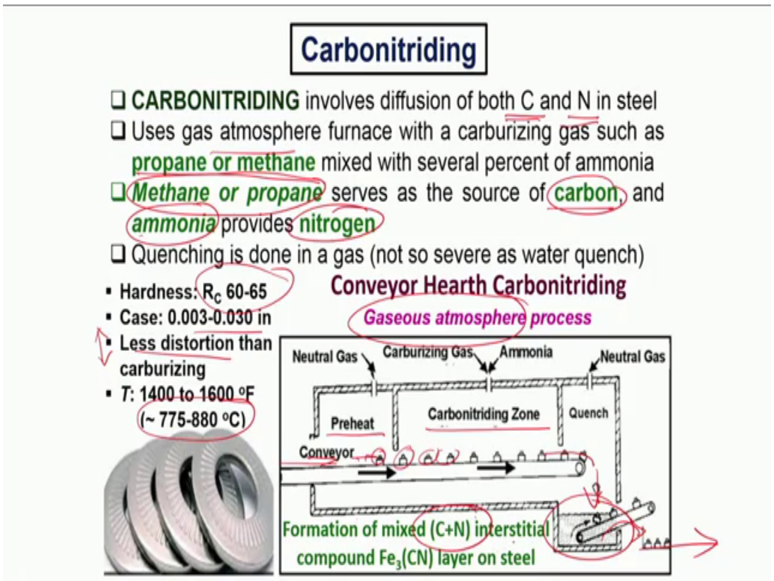

Carbonitriding

- ☐ **CARBONITRIDING** involves diffusion of both C and N in steel
- ☐ Uses gas atmosphere furnace with a carburizing gas such as **propane or methane** mixed with several percent of ammonia
- ☐ ***Methane or propane*** serves as the source of **carbon**, and ***ammonia*** provides **nitrogen**
- ☐ Quenching is done in a gas (not so severe as water quench)

- **Hardness: R_C 60-65**
- **Case: 0.003-0.030 in**
- **Less distortion than carburizing**
- ***T*: 1400 to 1600 °F (~ 775-880 °C)**

Conveyor Hearth Carbonitriding

Gaseous atmosphere process

Formation of mixed (C+N) interstitial compound $Fe_3(CN)$ layer on steel

Another variant of a very similar process one might wonder as to what is this difference we are talking about the one time we say nitrocarburizing and now we are saying carbonitriding. But there must be a reason as to why we actually swap the preference between carbon and nitrogen. So, when we say nitrocarburizing we conduct the entire process at a temperature which is about 550, 570 or so. Certainly below the eutectoid temperature below the a one temperature.

So, that means the whole process is conducted with nitrogen as the principal target and when we say nitrogen as the principal target what we mean is that the strengthening will come from nitrides formation of nitrides. So, we actually end up forming nitride, but with a difference that those nitrides like we what we discussed in case of nitrocarburizing. Those nitrides would be interstitial compounds, but mixed or complex compounds not pure nitride, but carbon nitrogen together into the matrix.

Compared to that carbonitriding is a process which is akin to carburizing to some extent because we are exposing to a higher temperature. So, this is obviously above the eutectoid in one temperature and in all probability we are into the gamma phase. So, we actually have more solubility and because we have more solubility and also carbon happens to be faster diffusing than nitrogen. So, we will see you know in the in the process when we liberate both carbon and nitrogen carbon diffuses faster nitrogen is slightly sluggish because of two reasons one is the atomic diameter, but also another reason being that nitrogen is prone to formation of nitrides.

So, when the compounds are formed then; obviously, nitrogen further it does not diffuse further. So, you during the ingress of nitrogen into the matrix you progressively make different kinds of nitrides and hence the rate at which nitrogen goes inside is retarded. Carbon does not form such compound so carbon will always try to go through the channels the interstitial channels and then squeeze past and then go further inside and diffuse deeper inside.

So, other difference is that instead of salts is the gaseous process. So, essentially compared to the the previous aqueous or salt bath processes here is a technique which is essentially based on gaseous atmosphere. So, the gaseous atmosphere in the furnace will provide both carbon and nitrogen. The precursor is propane and methane and they in contact with certain catalysts will crack and then form both carbon. So, actually when you mix a methane and propane with ammonia.

So, this is the source for carbon and ammonia is the source for nitrogen. So, we actually are feeding a mixed gas and when we feed the mixed gas we actually form we take try to take advantage of both advantage of having this kind of hard nitrides and also super saturating the alpha iron with carbon which actually subsequently can be quenched and led to formation of martensite. So, but here the temperature is lower and because the presence of already existing nitrides the distortion is less key step may be a little lower, but the hardness that we achieve is higher.

So, this is how we actually treat we essentially that I mean the process is a continuous process unlike most of the other batch processes. So, through a convener a conveyor we actually feed the components. So, these are the engineering components which are being subjected to carbonitriding. So, we preheat and then we have carbonitriding zone which is a gaseous atmosphere having both some hydrocarbon and ammonia and they crack and then deposit carbon and nitrogen on the surfaces of these solid components steel.

And, then subsequently when it comes out of the bath we actually directly quench into and a fluid bath where the high temperature of the hot materials get directly quenched and a part of it actually can be converted to martensite. And once the quenching is over then we take it out through the conveyor. So, we have both the formation of these mixed compounds and martensite.

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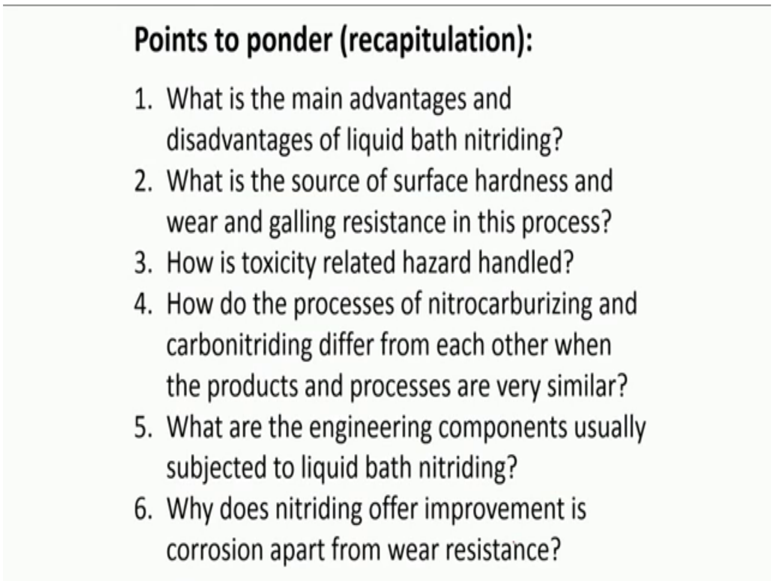

Points to ponder (recapitulation):

1. What is the main advantages and disadvantages of liquid bath nitriding?
2. What is the source of surface hardness and wear and galling resistance in this process?
3. How is toxicity related hazard handled?
4. How do the processes of nitrocarburizing and carbonitriding differ from each other when the products and processes are very similar?
5. What are the engineering components usually subjected to liquid bath nitriding?
6. Why does nitriding offer improvement is corrosion apart from wear resistance?

So, it is now time to summarize we need to really compare the processes of liquid bath nitriding cyaniding and so on and so forth. Hence, various salt bath processes and with gas nitriding or even with carburizing and see the relative advantages and disadvantages. The main source of a strengthening in case of nitriding we must remember is from the nitrides that we form.

Ah But in all these salt bath processes since we deal with extremely toxic compounds like sodium cyanide we have to be very very careful and always bear in mind that this is of the supreme interest or importance that the process is conducted with extreme we must take care of the safety before and should not create any possibility whereby the toxic gas or the bath can spill over. In nitrocarburizing and carbonitriding as I just explained a few minutes ago essentially takes the advantage of in case of nitrocarburizing its a closer to nitriding.

So, the strengthening comes from the nitrides and is conducted in salt bath or liquid bath whereas, carbon and at a slightly lower temperature below a one temperature. So, somewhere around 550 580 whereas, carbonitriding is a process where we again take advantage of both nitrogen and carbon, but we form not only in nitrides, but also some amount of martensite coming from the dissolution of carbon. So, in the carbonitriding process we conduct the experiments at higher temperatures about any anywhere around 800 or 750 to 800 degree centigrade which is in the.

So, we do have both alpha and gamma ferrite and cementite ferrite and austenite and austenite absorbs higher amount of nitrogen and carbon. So, we form both nitrides and martensite and be intric farabit of quenching and another important distinction is that this is done in gaseous atmosphere. So, some of the hydrocarbons like methane or propane provide the carbon and ammonia provides nitrogen. So, various engineering components the gears the shafts the cams the sprockets valves or various things actually exposed to all these nitriding processes and one of the important feature is that in the nitriding provides not only high hardness and wear resistance, less distortion and it also provides a highly passive layer. So, corrosion properties are also improved.

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References

- Kenneth G. Budinski, Surface Engineering for wear Resistance,1988,Prentice Hall
- http://www.ampht.com/carbonitriding.php

So, I think with this we come to the end of this particular discussion on a liquid salt bath nitriding and carbonitriding and nitrocarburizing; we will end the discussion on nitriding related subject with the next one on plasma nitriding.

Thank you very much.