Surface Engineering for Corrosion and Wear Resistance Application
Prof. Indranil Manna
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

Lecture – 27
Gas Nitriding

Welcome to the 27th lecture of a Surface Engineering course. We have in the last few lectures; we have discussed one specific approach of a thermo chemical surface modification or surface engineering of steel. Primarily, which is based on introduction of carbon enriching the surface with carbon from mild steel level of about 0.2 percent carbon to all the way to 0.6 0.8 percent carbon. And this typical case depth was in those cases anything from a less than a millimeter few hundred micrometers to of almost as high as 5 or 6 millimetre.

The entire strategy is based on the principle of enriching carbon. So, that on subsequent heat treatment when martensite is formed, that martensite will have sufficient hardness and very and offer adequate wear resistance. Surface hardening or improving the mechanical properties onto the surface both in terms of a hardness, wear resistance, frictional coefficient, erosion resistance and several other mechanical interaction processes.

To improve upon the steel component, there is another strategy which is a in some respect actually, offers even higher hardness or higher mechanical properties. And actually also makes the surface fairly passive against corrosive attack, but has certain other limitations which is why carburizing is very widely used ah. So, the technique that I am referring to is based on introduction of nitrogen instead of carbon.

(Refer Slide Time: 02:07)

So, today we are going to discuss a nitriding of steel and in particular Gas Nitriding. So, first of all as I said nitriding essentially means we are going to enrich the surface of steel with the nitrogen and obviously, nitrogen is one of those four elements which are fairly small to be able to find a place in the interstitials of alpha iron or a BCC iron. For example, we all know that a hydrogen, carbon, nitrogen and oxygen are the elements which easily can be accumulated in the interstitials

So, this technique is all about introducing nitrogen in the interstitials of steel at the surface up to a certain depth this is a diffusion control process thermally activated so, it is usually conducted at elevated temperature. Now there is a subtle difference and in fact, a very significant difference between the approach based on carbon and approach based on nitrogen. So, when we actually introduce nitrogen, nitrogen actually chemically reacts and forms a series of inter metallic compounds and they are called nitrides.

So, the entire process of nitriding it is based not on solid solution strengthening and subsequently formation of a supersaturated solid solution. But here of course, nitrogen gets dissolved up to a certain extent, but principally the entire process is based on formation of a series of nitrides. So, the nitride it case actually is harder than even tool steels or carburized steels so, in that respect actually you derive greater advantage, but we will realize that this is not always an advantage that we want.

This treatment typically is done in the ferretic range so; that means, we are talking about in terms of the again the eutectoid part of the iron carbon diagram, we are talking about the temperature range which is below the eutectoid temperature. So, this is A 1 and we are talking about a typical treatment range which will be ideally say about 480-90 to about 550 or so typically in this temperature range.

Now, this is important for us to make a distinction, why we choose the ferretic range and not austenitic range in case of carburizing. We were very clear that we would always like to go to single phase gamma region, because gamma offers you to accommodate carbon to the tune of almost 2 percent. Whereas, we know very well that in ferritic range in ferritic zone, the maximum solubility of carbon is 0.0 to 5. But of course, it can accommodate slightly a almost a similar amount of nitrogen or maybe even a little less, then why do we prefer nitriding to be conducted in the ferritic zone.

This is primarily because the strengthening mechanism is not as I said just a few minutes ago, the strengthening mechanism is not based on formation of solute super saturation, but it is based on formation of compounds the nitrides. So, solubility is not the criterion what is even more important in this case is the ability to diffuse.

So, since diffusion is faster in the BCC iron, we would prefer to conduct the all the treatments in the ferritic range, though the solubility is lower we are aware of that. Now, if steel contains allowing elements like a aluminium, chromium, molybdenum, vanadium these are titanium. So, these are the elements which actually are known to be strong nitride formers. So, we would prefer to do it either in plain carbon steel or alloy steels containing one of these alloying elements.

The temperature I just now mentioned would be typically about a close to 500 to 550 in the ferritic zone. And the most important reaction which is the key for nitriding is dissociation of ammonia into a nascent nitrogen and hydrogen. Though I mentioned only about ammonia, I must also clarify that typically nitriding gas mixture will always contain hydrogen along with the ammonia.

In fact, the amount of hydrogen is much higher than nitrogen typically, a gas mixture would have anything like 80 20 or even maybe 90 or 95 percent by volume of hydrogen. So, more amount of hydrogen because hydrogen actually creates the situation whereby the surface oxide gets reduced easily and nitrogen it can move in. In fact, there is also a

school of thought which believes that actually hydrogen helps in creation of a thin plasma which actually removes all the scale or oxides.

So, here is a process where we can actually achieve extremely high hardness much higher. So, typically in terms of a Vicker; the Vickers number it will be anything like 950 to 1000 Vickers number and in terms of a Rockwell RC we are talking about easily something like 70 or even 75 HRC, it is so very high hardness. The depth could be the 0.1 to 0.6 millimeter maybe close to a millimeter.

An applications actually cover a very wide range of component based on steel the gear components, the valves, the cutters or various kinds of slicing equipments, sprockets, boring tools, pump devices then fuel injection pump parts, nozzles various kinds of applications and in fact, is very widely used not only for ferritic steel, but also austenitic stainless steel.

(Refer Slide Time: 08:44)
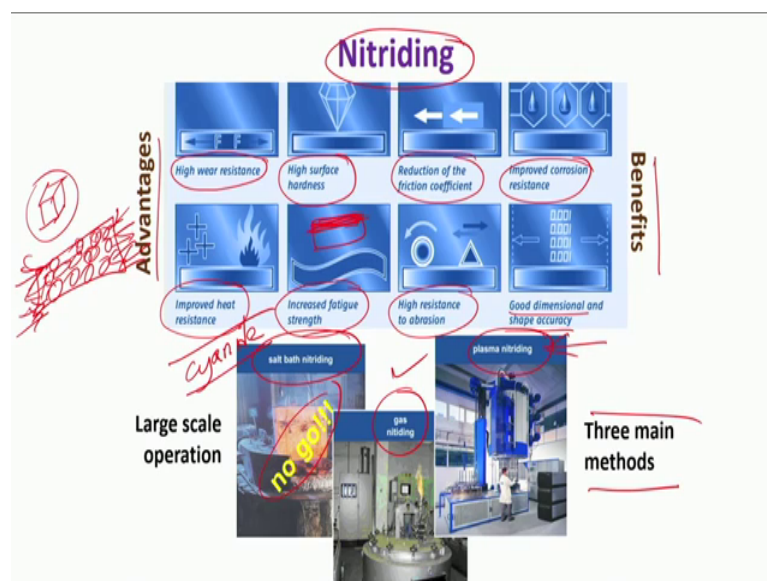
There are plenty of advantages; so, when we talk of nitriding, we are talking about a large number of advantages and benefits. For example, we of course, derive high wear resistance, very high surface hardness harder than what you can achieve through martensitic hardening, the coefficient of friction is a reduced to a very significant extent. So, that the surface is very smooth and it does not offer much of wear, we also make the surface fairly passive and the corrosion resistance is improved than native steel.

So, steel which otherwise is known to rust very easily after nitriding will actually maintain their shining surface to allow for a much longer period. It also reflects heat incident a heat wave is reflected because of a very smooth surface and also the compounds that we have on the surface these nitride compounds, actually are heat resistant. And they have fairly high melting temperature, much higher than iron itself. There is also an argument that though there is no super saturation, no formation of martensite which actually causes expansion of the matrix and creation of residual compressive stress.

Even in nitriding those such kind of mechanisms does not exist; mechanisms do not exist yet formation of so on the case if we actually have a rich nitride layer these nitrided nitride compounds actually have a higher lattice parameter. So, in the matrix which is a BCC iron, if you in the matrix if you produce now nitride at phases which actually are having a larger lattice parameter than so, if this is the kind of a BCC unit cell you are talking about.

Typical hexagonal unit cell of these one of these nitrides would be bigger than this. And if it is bigger than this and when these are actually precipitates form, they tend to deform or create plastic strain and the reaction to that will mean that on the surface you actually end up creating residual compressive stresses or forces which are acting towards each other. This is an advantage obviously, because of very high hardness and lowering of friction coefficient, the abrasion resistance is improved and we also maintain very good dimensional and shape accuracy, because the coefficient of thermal expansion of these nitrided layer is fairly low.

So, nitriding actually can be achieved through one of these three approaches salt bath nitriding, but this is kind of a no go it is because they deal with the cyanide bath. So, because of the need to deal with cyanide it is all about nitriding is generally avoided, gas nitriding is very popular and even more popular and effective is plasma nitriding. So; obviously, today we are discussing gas nitriding and we will soon discuss also this plasma nitriding. So, these are the three methods of a large scale nitriding operations.

(Refer Slide Time: 12:14)
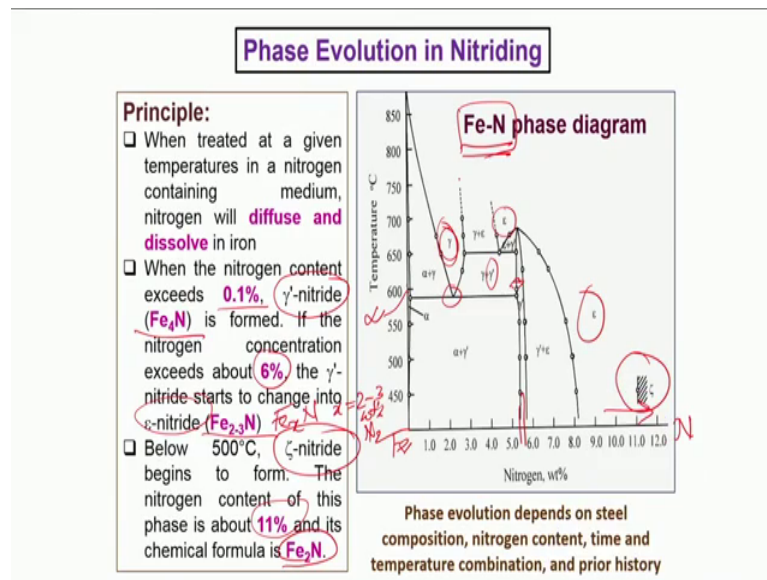
Before we go into the actual process, probably it is important that we take a look at the iron nitrogen diagram, not iron carbon diagram or iron cementite diagram. So, when we talk of iron nitrogen that phase diagram would look very similar. So, actually ah, but then I mean on the pure nitrogen side, you actually will have the same allotropic transformations right from the liquid state. So, liquid followed by gamma iron which is BCC, then sorry liquid to delta iron which is BCC with a larger lattice parameter.

So, delta iron transforms to gamma iron which is FCC then gamma iron again transforms back to BCC form which is beta iron para magnetic and then beta again will transform to alpha iron. So, all these allotropic transitions are possible in pure iron, there is no problem with that, but on the other side what we have is nitrogen. In fact, this diagram is not complete, its sort of incomplete because the phases that may form beyond about 11 12 percent of nitrogen is not easily to determine. So, essentially the phase diagram beyond 11 or 12 percent is and they were shown.

And in fact, this particular zeta nitride is actually so hard and so brittle that you cannot form any other higher nitride beyond this. And the entire phase aggregate beyond about 8 percent is already a fairly strong nitride which is an epsilon nitride. So, we do see an eutectoid transformation here, we have a very little amount of formation existence of a ferrite here alpha and then we have the FCC variety austenite and then we have a series

of interstitial compounds which is a gamma which is which can be epsilon, which can be gamma prime.

So, gamma prime typically forms at around so, this is an congruent compound which has a certain solubility range not a line compound, but this congruent compound actually is one of the very hard phase and then we have even harder phases like epsilon carbide or zeta carbides and so on. So, the as we go to higher and higher nitrogen containing region so, these nitrides actually also get richer and richer in nitrogen.

So, the first interstitial compound that we can think of is this gamma prime which is typically expressed in terms of Fe_4N stoichiometry and so, any time we cross nitrogen contained to more than 0.1 percent up to about 6 percent. We continue to form these gamma prime phase and beyond 6 percent we go into the enter into another regime where we form epsilon nitrides which is typically Fe 2 point Fe_xN and this x can be anything like 2 to 3. So, as I said this is not a line compound, not a fixed stoichiometry, but a variable stoichiometric compound and x can be anything between 2 to 3 weight percent of nitrogen.

But, if we go beyond then we may actually create or form another nitride which is the zeta nitride and this forms typically around 11 12 weight percent of nitrogen and the stoichiometry is expressed as Fe 2 and as I said beyond that is a domain which is not useful to any engineering applications and hence it is not even shown.
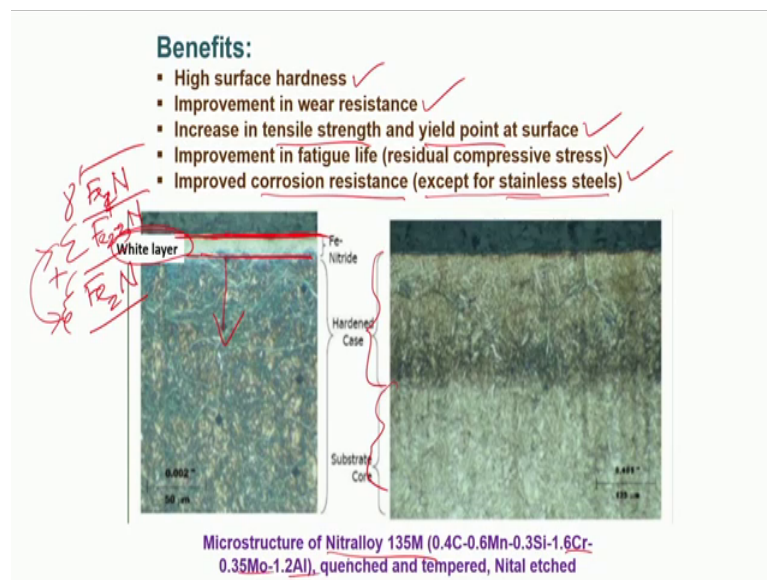
So, we must now reposition ourselves and move away from iron carbon and think in terms of iron nitrogen diagram and realize that there is very little solubility of nitrogen in alpha iron by the by we did make a brief mention while discussing about formation of various phases or micro structure evolution. In one of the lectures where in I did mention that alloying elements in iron or in steel can be divided into three categories. Ferrite stabilizers usually, the BCC elements are ferrite stabilizers, austenite stabilizers usually, the FCC elements are austenite stabilizers and a part of the BCC elements which have a very strong tendency of formation of carbides are called carbide formers.

We also have now another class of elements which we just discuss say for example, chromium, vanadium, the molybdenum or a titanium and many of these elements actually have a tendency of formation of nitrides; so, nitride forming. But nitrogen per say is itself a austenite stabilizer is an austenite stabilizer. So, that is the reason why if we

do not see large solubility of nitrogen in alpha iron whereas, we see a large solubility of nitrogen in either in the form of gamma or gamma prime or epsilon all these phases are nitrogen containing compounds. So, we do have solid solubility and the solubility is fairly large, but instead of that we may also have a good amount of a nitrogen containing compounds.

So, we understand that in a nitrogen containing system actually when we introduce nitrogen in steel, we actually tend to stabilize austenite and beyond the solubility limit we tend to form various compounds like all these gamma prime epsilon and zeta and so on and so forth.

(Refer Slide Time: 18:29)

Microstructure of Nitralloy 135M (0.4C-0.6Mn-0.3Si-1.6Cr-0.35Mo-1.2Al), quenched and tempered, Nital etched

Now, when we actually nitride we expect several benefits we did discussed in one of the previous slides, but let me just quickly repeat apart from very high surface hardness. We expect high wear resistance, we also expect a good increment in terms of both yield point and tensile strength, because of the larger lattice parameter of the phases that we form in the form of nitrides.

In the matrix, we expect expansion of lattice and as a result of the reaction to that tendency of expansion, we see a compressive residual stress on that surface and also a very I would say unique effect of a introduction of nitrogen the, because of which we create the nitrides and these nitrides actually are fairly corrosion resistance. So, we make the surface fairly passive.

But as I said that nitrogen also is an desirable alloying element for formation of nitrides on steel in stainless steel, but stainless steel itself is austenitic, but in the single phase. But when you introduce nitrogen, we do form certain nitrides for example, chromium nitrides that is not a good news for stainless steel because chromium nitrides is relatively cathodic compared to the rest of the metrics. So, then we introduced a possibility of a because of the creation of two phase microstructure in stainless steel by way of nitriding where we may have chromium nitrides and matrix which is austenitic.

So, in these two phase aggregate can actually create a galvanic cell because the nitrides happen to be a more cathodic than the metrics. So, it is not always very desirable to nitride stainless steel particularly when we are anticipating some level of corrosion. Now, we did mention the very important or very hard nitride phase as possible like gamma prime, then we talk of mentioned about epsilon and then we also talked about zeta nitrides and so on.

So, whether it is Fe 2 4 N Fe 4 N or Fe 2 to 3 N or Fe 2 N, whatever may be the actual nature of these nitrides. The first the topmost layer which will have the maximum concentration of nitrogen may actually contain combination of epsilon and zeta. So, when we have these high nitrides high nitrides formed onto the surface, the surface becomes completely passive and resistant to any amount of electrochemical etching by virtue of which we create or reveal a microstructure.

So, we tend to see a microstructure revealed underneath in the interior of the sample, but the surface layer does not etch at all and as a result it remains completely resistance resistant to any chemical attack. And hence it reflects any amount of light that is incident on it in other words when we polish edge and take it under the microscope optical microscope. We see complete reflection of light from the surface and as a result the entire surface appears very bright. So, that is why we call this layer as white layer or bright layer.

The white layer essentially means that we have combination of these nitrides and which are completely resistant to any chemical attack or electrochemical attack and hence we see a surface which is totally bright. But otherwise we actually typical hardened case will be like this which will have combination of nitrides and the core can still remain

unaffected. So, this is the microstructure coming from a particular alloy steel which contains various nitride forming elements.

(Refer Slide Time: 22:45)
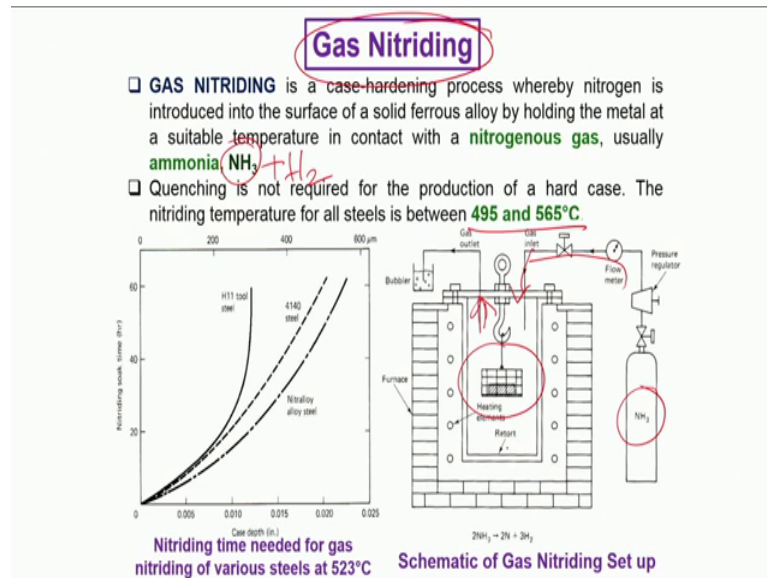
So, when we actually want to carry out an actual experiment of nitriding a gas nitriding is one of the most popular in effective methods. So, here we use ammonia as the precursor for introducing nitrogen as I mentioned right in the beginning in the nitriding furnace. The ammonia dissociates, in this typical temperature range around about 484-90 to about 550 degrees 565 degree centigrade and that is the optimal range where, diffusion coefficient is fairly high and you do not need to heat more than this. Because within a short distance nitrogen build up is fairly high to start forming the higher nitrides.

So, we have these ammonia as a main precursor, but as I mentioned that we never introduced only ammonia, we actually always mix it with hydrogen and then we feed in. So, this is the furnace and this is where the reaction takes place ammonia dissociates, it provides both nitrogen hydrogen and nitrogen. Actually gets further dissociated into atomic or nascent form and then gets same way like in case of carburizing, here also nitrogen is adsorbed and then absorbed into the interior by way of diffusion.

So, we use an either pre mixed or nitrogen ammonia bottle with hydrogen and then we feed in here. And we also so whatever is the gas that is exhaust or reacted output that moves out through this outlet. So, if you expose various kinds of steel say for example, H 11 tool steel, 4140 which is a chromoly steel or nitralloy steel which has large number of

nitride forming elements. What we see is that typically if you soak for a certain period of time at a given temperature let us say 500 degree centigrade.

So, for a certain period of time let us say reference time is a 20 hours. So, what we realize is that in 20 hours the case depth is a minimum in case of H 11 tool steel and is lot higher in case of nitralloy. That is purely because nitralloy contains composition wise lot of alloying elements like a chromium and vanadium and so on, with manganese and so on which actually forms large number of nitrides. So, the composition of the base steel is important for making the nitriding process very effective.

(Refer Slide Time: 25:35)
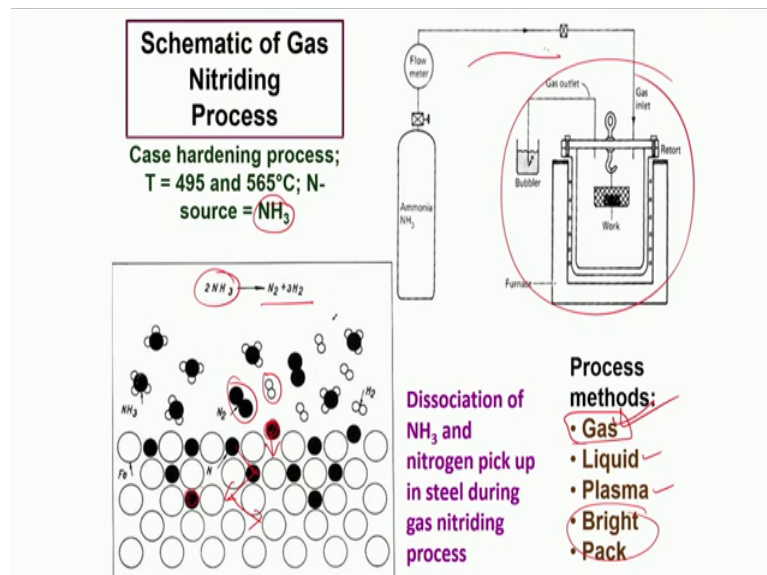
So, we must realize that though the source is a ammonia at high temperature should dissociate and provide nitrogen and hydrogen molecules, but the molecular form is not fit enough to enter into the lattice. So, they need to so, if you have an N 2 or H 2 molecule they actually need to further dissociate and reached the nascent state. So, that now this nitrogen atom is in a position to get adsorbed onto the surface layer and subsequently can actually diffuse likewise in this path.

It does not need to substitute or displace any existing lattice atom, it simply find its way to go into the lattice through the interstitial path. So, these are like interconnected channels through which the nitrogen atoms can move in, but we must realize that though this cartoon shows as if this nitrogen atom is smaller than the interstitial hole available. But actually in reality, it is the other way around the maximum hole diameter whatever

we can calculate. Geometrically is a fairly small at least the nitrogen atom would be easily 20 to 30 percent bigger in size than the available holes available the size of the hole.

So, we actually can carry out nitriding this is using gas, but we can also do in the liquid state or plasma state and also create the so called bright and packed nitriding processes. We are for the time being we are discussing gas nitriding and we will shortly afterwards we will discuss liquid or plasma nitriding. This is the typical chamber that we have already discussed and this is how we fill in the premix gas.

(Refer Slide Time: 27:31)
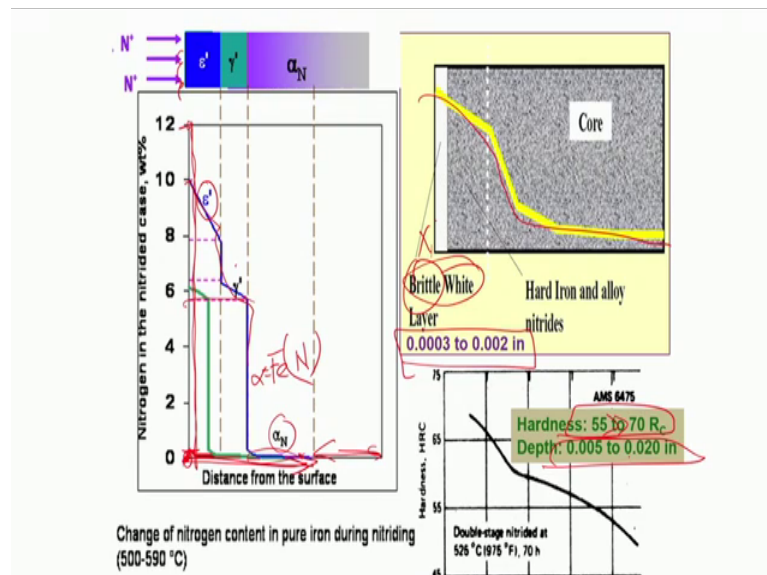
So, when we carry out these nitrding process as I said the topmost layer on the surface so, this is the distance from the surface so, this is the surface layer and this is towards the interior. And so the we expect epsilon or epsilon prime at the surface which is Fe 2 to 3 N higher nitride, in some cases we may have a very thin layer of even formation of zeta.

So, this is the surface layer which is very very rich in a high nitrogen containing compounds and then gradually the amount of for example, epsilon decreases. So, we have epsilon then gamma prime then alpha nitrogen, this is alpha N means this is a alpha iron containing nitrogen so, interstitial solid solution of nitrogen in alpha iron.

And then of course, the matrix which remains unaffected so, this is solid solution range amount of nitrogen is very low, when we talk of gamma prime. Typically, the formation

can be anywhere from about 1 or 2 percent to about 6 percent to 8 percent and between 6 to 8 we do form epsilon and then beyond 8 or beyond 10 and 11 somewhere around 12 percent we form the eta nitrides.

So, as a result we create this bright or white layer appears very attractive in terms of hardness or mechanical property, but actually is quite detrimental because this is highly brittle. So, this brittle surface is actually no good for any further operation particularly machining or further shaping. In fact, this surface being so hard, then it actually interacts with another surface which probably is not as hard as this certainly cause causes damage to the other component or the other surface.

So, this is a typical hardness profile that we see what we it so, this is the nitrogen diffusion profile and this would be typically the hardness profile. And as I said the hardness can be as high as 70 R c or maybe even greater than this even greater than this. So, we are talking about the depth is very small, we are talking about a depth which is few tens of a micrometer maybe hundreds of a micrometer so, it is a less than millimeter for sure.

(Refer Slide Time: 30:03)

Points to ponder (recapitulation):

1. What is the difference in mechanism and strategy of surface hardening of steel in nitriding as compared to carburizing?
2. Why is nitriding temperature much lower that that for carburizing? Is any post-nitriding heat treatment required for hardening?
3. What is a white layer found in nitriding?
4. What are the main process parameters of gas nitriding?
5. What are the components usually subjected to nitriding?
6. Is nitriding useful to metals other than steel?

So, now let us try to summarize the discussion so far. So, in this lecture we actually invoked the possibility of using nitrogen as opposed to carbon as a means of a surface strengthening surface engineering. So, we introduce nitrogen with an intention not

necessarily to create martensite, but to create nitrides which are interstitial compounds of nitrogen in iron.

And these nitrides can be stoichiometric, can be off-stoichiometric or having interstitial compound or interstitial phase with a certain compositional range. They are very hard, they are very wear resistant, they are chemically inert and they reduce the friction coefficient, they give you all kinds of desirable properties on the surface of steel. So, apparently they are very very attractive, but I also mentioned that they can actually make the surface layer fairly brittle primarily because of the formation of the so called white layer.

So, formation of white layer particularly thick, white layer is undesirable, but you cannot avoid formation of some of this epsilon or even some cases the zeta nitrides. But, if they are dispersed in small volume fraction in alpha there is no problem, but if you have a monolith of epsilon or zeta then that surface can be completely very high hardness, but may not be usable at all in practical purpose.

So, as far as process parameter is concerned just like any other diffusion control process, here also the time, temperature, the activity of nitrogen in the atmosphere, surrounding atmosphere then the previous the condition of the surface and of course, the carbon content and composition of the material that we are subjecting to.

So, we generally prefer not only low carbon even interstitial free carbon or maybe a very low amount of carbon containing steel. Because otherwise if you already have sufficient amount of carbon present in the interstices, then solubility of nitrogen or penetration of nitrogen is even more retarded or the possibility even is lower. So, we discussed large number of components the valves, the springs, the sprocket not springs valves the sprockets the surgical instruments certain bearings and so on, they are subjected to nitriding.

And the useful thing is that while carburizing is a solely applicable to steel nitriding actually can be a very useful method of surface hardening not only to steel, but also other non-ferrous systems for example titanium. For example, even stainless steel or molybdenum or a titanium molybdenum, vanadium, manganese, base metals and alloys.

(Refer Slide Time: 33:07)

References

- Kenneth G. Budinski, Surface Engineering for wear Resistance,1988,Prentice Hall
- https://cdn.intechopen.com/pdfs-wm/39403.pdf

Thank you very much.