Thermominusmechanical and Thermo Chemical processes
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Module No # 07
Lecture No # 35
Thermodynamic of Gaseous Nitriding- II

Greetings to everyone. So, we were discussing in the last class about gaseous nitriding starting from the thermodynamics of gaseous mixtures. And if we place a solid sample inside a gaseous mixture maintained at a constant temperature and pressure, what will be the equilibrium? So then in that context, we have seen that when we use the N_2 gas that is a molecular nitrogen gas has a source of nitrogen to introduce nitrogen into the solid samples then we looked at on the thermodynamics you know the of that particular situation.

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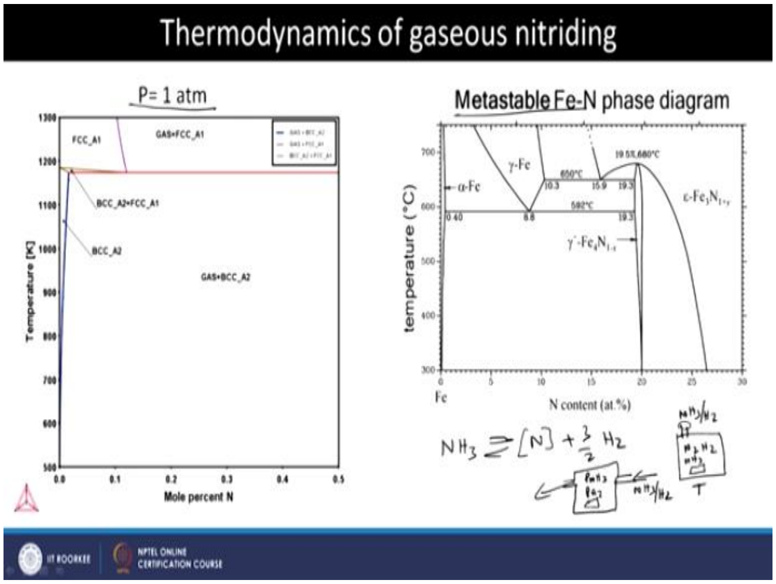

Thermodynamics of gaseous nitriding

$$NH_3 \rightleftharpoons [N] + \frac{3}{2} H_2$$

Then we have seen that from the phase diagram that, so, if you do the one atmospheric pressure of N_2 has been imposed on the sample surface and which you do that at different temperatures, then what we see is that, we get a very small amount of nitrogen dissolvable in the BCC iron that is the ferrite right. This is the region where maximum solubility is given by this line (refer to above figure).

And we do not see that any other iron nitrogen compounds which are known as from the meta stable iron nitrogen phase diagram, where we see that you have these two iron nitrates and also the amount of nitrogen which is dissolved in the ferrite is much higher than what we get from the N_2 gas. Now, we want to see that how these kind of iron nitrides can be realizable by using instead of N_2 gas if we use ammonia gas for nitrogen source.

So now let us look at into the thermodynamics of it how that can be realizable? So, for quickly recapitulating.

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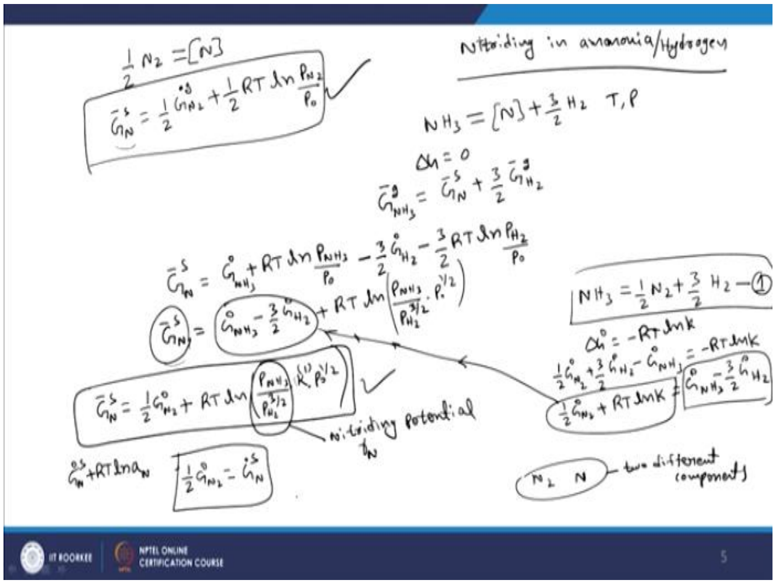

Nitriding in ammonia/Hydrogen

$\frac{1}{2}N_2 = [N]$

$\bar{G}_N^s = \frac{1}{2}G_{N_2}^{0g} + \frac{1}{2}RT\ln\frac{P_{N_2}}{P_0}$ ✓

$NH_3 = [N] + \frac{3}{2}H_2$ T, P

$\Delta G = 0$

$\bar{G}_{NH_3}^g = \bar{G}_N^s + \frac{3}{2}\bar{G}_{H_2}^g$

$\bar{G}_N^s = G_{NH_3}^0 + RT\ln\frac{P_{NH_3}}{P_0} - \frac{3}{2}G_{H_2}^0 - \frac{3}{2}RT\ln\frac{P_{H_2}}{P_0}$

$\bar{G}_N^s = \left(G_{NH_3}^0 - \frac{3}{2}G_{H_2}^0\right) + RT\ln\left(\frac{P_{NH_3}}{P_{H_2}^{3/2}}\cdot P_0^{1/2}\right)$

$\bar{G}_N^s = \frac{1}{2}G_{N_2}^0 + RT\ln\left(\frac{P_{NH_3}}{P_{H_2}^{3/2}}K^{(1)}P_0^{1/2}\right)$ ✓

nitriding potential r_N

$G_N^{0s} + RT\ln a_N$

$\frac{1}{2}G_{N_2}^0 = G_N^s$

$NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$ — ①

$\Delta G^0 = -RT\ln K$

$\frac{1}{2}G_{N_2}^0 + \frac{3}{2}G_{H_2}^0 - G_{NH_3}^0 = -RT\ln K$

$\frac{1}{2}G_{N_2}^0 + RT\ln K = G_{NH_3}^0 - \frac{3}{2}G_{H_2}^0$

N_2 N — two different components

When we use the N_2 gas giving rise to nitrogen dissolved and then when we wrote these are actually chemical potential of nitrogen in the solid that is $\bar{G}_N^S$ is given as

$$\bar{G}_N^S = \frac{1}{2}G_{N_2}^{0\,g} + \frac{1}{2}RTln\frac{P_{N_2}}{P_0}$$

This is how we have seen that the chemical potential of nitrogen in the solid can only be controlled or changed by changing the pressure of N_2 at a given temperature.

That is we have seen. Now, if we use for the nitriding in ammonia hydrogen gas mixture. So, how can we understand now that $\bar{G}_N^S$values can be now tuned in a different way, that is the strategy we have in finding it from the ammonia hydrogen gas whether that can offer as a high values of chemical potential of nitrogen, which we can impose on the solid. So, the reaction when we use ammonia hydrogen gas mixture can be seen as NH_3 giving rise to N dissolved with hydrogen all hydrogen being produced as H_2 gas.

$NH_3 = [N] + \frac{3}{2} H_2$.

So, here we are able to dissolve, if we start with one mole of ammonia gas, we are able to dissolve one mole of nitrogen into that and by having a $\frac{3}{2} H_2$. Now, what does this situation implies that, at a given temperature and the total pressure, if we can maintain these values of the partial pressures of hydrogen and ammonia in the gas mixture, that means we fill in $\frac{3}{2} H_2$ and NH_3 in this ratio. And if we can retain that, then that will impose certain amount of nitrogen into the solid.

Now here, like in the case of N_2 gas, how we can write the chemical potential of nitrogen? So for that again, we will start with $\Delta G = 0$ at equilibrium for this reaction. Now, we can write that this will be chemical potential of NH_3 gas.

$$\bar{G}_{NH_3}^{g} = \bar{G}_N^S + \frac{3}{2}\bar{G}_{H_2}^{g}$$

this is all gaseous states.

Now, this is what actually if you rearrange that then we can write

$\bar{G}_N^S = G_{NH_3}^0 + RTln\frac{P_{NH_3}}{P_0} - \frac{3}{2}\bar{G}_{H_2}^{g}$

This $\frac{3}{2}\bar{G}_{H_2}^{g}$ quantity equal to

$$\frac{3}{2}G_{H_2}^0 + \frac{3}{2}RTln\frac{P_{H_2}}{P_0}$$

Then upon rearranging, you get

$$\bar{G}_N^S = G_{NH_3}^0 - \frac{3}{2}G_{H_2}^0 + RTln\left(\frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}}P_0^{\frac{1}{2}}\right)$$

So, this is how we can write.

Now the chemical potential of nitrogen in the solid. This quantity $\bar{G}_N^S$ is now related to the standard Gibbs energies of the ammonia and hydrogen and more importantly on the ratio of the partial pressure of ammonia by $P_{H_2}^{\frac{3}{2}}$.

So, now, to have a comparison with the nitriding in the N_2 gas where we wrote the chemical potential of nitrogen in the solid in this fashion (refer to above figure), to get some comparison. If we can also bring in N_2 which is not at all there in this reaction then we can actually relate this two. That can be done by the following way.

If you look at the, the ammonia dissociation, we wrote that as

$$NH_3 = \frac{1}{2} N_2 + \frac{3}{2} H_2. \qquad \ldots\ldots 1$$

So when we write the, ΔG if we relate this to the ΔG^0 of this reaction is

$$\Delta G^0 = -RTlnk$$

This is what we know. And now this ΔG^0 is given as the

$$\frac{1}{2}G^0_{N_2} + \frac{3}{2}G^0_{H_2} - G^0_{NH_3}$$

So the value of this quantity that is given as

$$\frac{1}{2}G^0_{N_2} + \frac{3}{2}G^0_{H_2} - G^0_{NH_3} = -RTlnk$$

So now if we rearrange these terms, then you see that

$$\frac{1}{2}G^0_{N_2} + RTlnk = G^0_{NH_3} - \frac{3}{2}G^0_{H_2}$$

So this is the quantity $G^0_{NH_3} - \frac{3}{2}G^0_{H_2}$, one can substitute this $\frac{1}{2}G^0_{N_2} + RTlnk$ quantity into this $G^0_{NH_3} - \frac{3}{2}G^0_{H_2}$

Then we can write this equation a

$$\bar{G}^S_N = \frac{1}{2}G^0_{N_2} + RTln\left(\frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}}\right)(K^{(1)})$$

$K^{(1)}$ is of $NH_3 = \frac{1}{2} N_2 + \frac{3}{2} H_2$ reaction.

. So, that is what actually comes into the picture

$$\bar{G}^S_N = \frac{1}{2}G^0_{N_2} + RTlnk\left(\frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}}K^{(1)}P_0^{\frac{1}{2}}\right)$$

Now if we look at this reaction

$$\bar{G}_N^S = \frac{1}{2}G_{N_2}^0 + RTlnk\left(\frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}}K^{(1)}P_0^{\frac{1}{2}}\right)$$

and this reaction

$$\bar{G}_N^S = \frac{1}{2}G_{N_2}^{0\ g} + \frac{1}{2}RTln\frac{P_{N_2}}{P_0}.$$

In both the cases, here we are getting some chemical potential of nitrogen in the solid when we use N_2 gas as a nitriding medium that is related to the partial pressure of N_2.

And now here in the case of ammonia hydrogen gas what we see is that interestingly now, we got the same sort of reference state value for here too and this has got also the this ratio $\frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}}$. Now, by changing this ratio and because the value of this K is very high, as you look at this (refer to above figure) one, ΔG^0 is for this reaction will be very high.

So, that means, we are able to impose the large magnitude of this quantity by maintaining some ratio of partial pressure of ammonia to hydrogen and then we are able to impose certain amount of nitriding potential in the solid. Now, the thing is that we here now by controlling this ratio of partial pressure of ammonia and hydrogen we control chemical potential of nitrogen in the solid. So, this$\frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}}$ quantity, this partial pressure of ammonia and hydrogen is called nitriding potential.

Usually with r_n. So, this has been now defined as a another quantity. Here this $\frac{P_{N_2}}{P_0}$ nitriding potential that is the potential of the atmosphere in order to nitride your solid sample is represented here by the pressure of N_2 and here that is represented by the ratio of this partial pressure of $\frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}}$. So, this is now at a given temperature, we are not given pressure we know that these two quantities $K^{(1)}P_0^{\frac{1}{2}}$ are constant, because this is the equilibrium constant of the reaction 1 and that remains constant.

And if you choose the reference pressure as constant, then at a given temperature, you can still vary the chemical potential of nitrogen by just changing this ratio. And being this as a large number. Now, this will be able to actually provide a large value of the chemical potential. Now, by comparison of these two relations

$$\bar{G}_N^S = \frac{1}{2}G_{N_2}^0 + RTlnk\left(\frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}}K^{(1)}P_0^{\frac{1}{2}}\right)$$

And

$$\bar{G}_N^S = \frac{1}{2}G_{N_2}^{0\,g} + \frac{1}{2}RTln\frac{P_{N_2}}{P_0}$$

If you write elaborate this chemical potential of nitrogen in the solid, this $\bar{G}_N^S$ can be written as

$$G_N^{0S} + RTlna_n$$

and the same can be done also for this chemical potential of nitrogen in the solid. And then what you see is that by comparison of these quantities, if I choose the reference state, this $\frac{1}{2}G_{N_2}^0$ is the reference state of the N$_2$ in the gaseous phase and this G_N^{0S} is for the solid state.

The molecular nitrogen N$_2$ and atomic nitrogen N are treated as two different components. So, now, because of that these N in the solid that implies actually if you take a what is the reference state for example, for chromium we take actually the pure chromium solid that is easy to visualize for somebody, but for the nitrogen, we can treat it as a atomic nitrogen solid that means there is an equilibrium with one atmospheric N$_2$ gas pressure. So, this way what we are saying

$$\frac{1}{2}G_{N_2}^0 = G_N^{0S}$$

So, this is what actually it implies and then we are relating the activity of nitrogen to this $\left(\frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}}K^{(1)}P_0^{\frac{1}{2}}\right)$ quantity. Now, one can also say that by controlling the nitriding potential, we can also modify the activity of nitrogen in the solid that is obvious because we are changing the chemical potential of nitrogen.

Now, if we look into the phase diagram, if we see that how we can now explain that we are able to produce the iron nitrides. Now, we want to see that how all these iron nitrides can come into picture. Now according to this reaction

$$NH_3 = [N] + \frac{3}{2} H_2$$

in order to have such a reaction in the actual practical situation by considering that ammonia is a very unstable molecule as we have seen that at a nitriding temperature this wants to always dissociate producing N_2 and H_2. So, the trick is, we have to maintain this ratio constant in the gas mixture.

How can we do that? For example, if I have a furnace then if I have my solid iron, and if I feed in actually the NH_3 and H_2 at some chemistry and if I close this and at some temperature, we know that this gas composition will continue to change and at one atmospheric pressure and we will end up with N_2, H_2 with a very small amount of NH_3 in the chamber. That means we are not maintaining this equilibrium what we are writing here (refer to above figure).

So, in order to have this equilibrium, we need to make sure that there is no N_2 formation happening upon dissociation of ammonia in the gas chamber. So, the fortunate thing is, ammonia is very unstable molecule, but its dissociation is rather slow, if we do not have a significant amount of catalytic surface, So, because of that, the slow nature of that instead of having a sealed atmosphere, if we maintain continuous flow of required NH_3, H_2 gas chemistry and then because of maintaining a constant flow and the slower dissociation of ammonia, we will be able to maintain this the partial pressure of NH_3 and H_2 in the gas chamber as expected from such reaction equilibrium.

When we do that, then only we can have practically the nitriding. If we do not do this continuous flow of the gas and then actually, we will not have any nitriding because our atmosphere will become N_2 and H_2 gas and that we know that N_2 gas will not be able to do significant nitriding. So, now by knowing this so-called nitriding potential, we can now look at that (refer to below figure).

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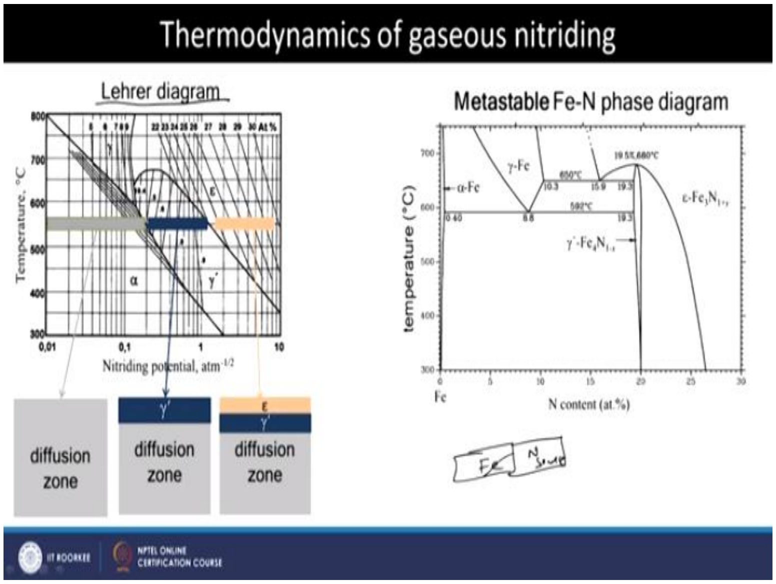

Thermodynamics of gaseous nitriding

Suppose if you want to produce some phase diagram for example, iron and nitrogen. That means we need to have a means to add different amounts of nitrogen at a given temperature and then this controlling this temperature we will be able to produce these different phases of the iron nitrogen system. So, how we can do that? So, that actually you see that from the reaction equilibrium.

Now at a given temperature for example, we take 550˚C what is shown here is so, called a Lehrer diagram (refer to above figure). This is nothing but an activity diagram, where we are showing as a function of temperature, different values of nitriding potential, what are the equilibrium phases of the phase fields of the iron nitrogen system. Like here we see the different iron nitrogen phases, it is α iron with some amount of nitrogen and Fe_4N nitride and ε nitride.

And these all things can be stabilized at a given temperature by appropriately controlling the nitriding potential. That is what you see here (refer to above figure). Actually, if you maintain the temperature of 550˚C and if you maintain the nitriding potential within this region, then you will have simply BCC iron with dissolved nitrogen inside that means, we are within this (refer to above figure) region of the phase diagram, that is the phase field of the α iron.

And now if we use the nitriding potential which are falling in the region of this γ′, we are able to produce this γ′ iron nitride, this is iron nitrogen compound on the sample surface. Similarly, if you maintain the conditions of nitrogen potential at this temperature in this region, we will be able to produce this γ' and ε iron nitrides. It is another iron nitride it is a given as notion with ε.

So, now you see that always, if you form a diffusion couple between so called a rich in nitrogen source and the iron, what we expect is suppose if we have an iron solid with a nitrogen source. Depending on the level of this nitrogen source we start to generate the composition of nitrogen varying as a function of depth into the iron lattice. Now, at different nitrogen contains you expect to see the different phases of the iron nitrogen phase diagram as expected at that composition.

So, that is what exactly you see here (refer to above figure). Now, we are diffusing the nitrogen from ammonia hydrogen mixture having a high chemical potential. That is where actually we are able to produce these iron nitrides. As, we have seen that when we use only N_2 gas with a Gibbs energy curve of the iron nitrogen solid and iron nitrogen compounds which we have seen in the last class, one can actually go to high chemical potentials of nitrogen and stabilize this iron nitrides, but as we said before these iron nitrides are metastable. So, they always have a tendency to decompose into N_2 gas and iron that means if you produce them in leave them at the high temperature for longer time then they will start to decompose that is where you start to read the porous iron nitride layers.

So, with this I will now explain you what are all the microstructures we can expect when we do a nitriding of a steel. So, if we take a solid steel sample and if you place it in the ammonia hydrogen gas mixture and once you equilibrate it there then it starts to develop the different iron nitrogen phases.

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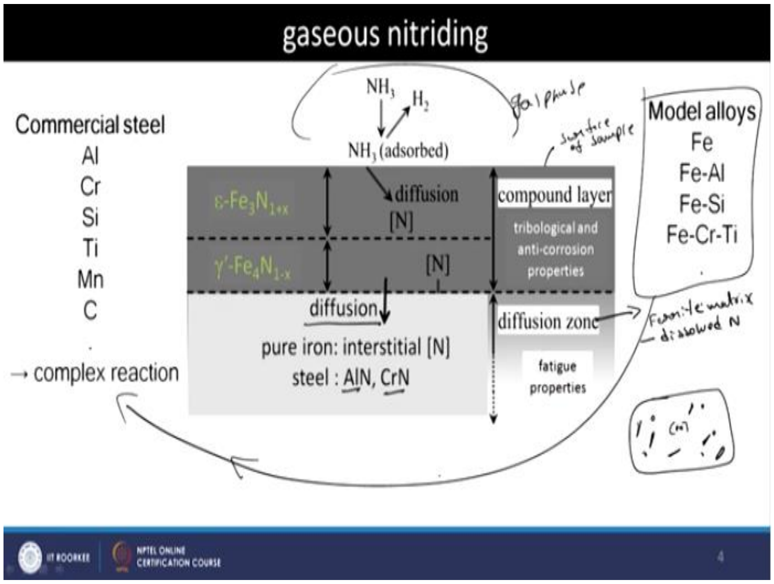

gaseous nitriding

Commercial steel
Al
Cr
Si
Ti
Mn
C
.
→ complex reaction

Model alloys
Fe
Fe-Al
Fe-Si
Fe-Cr-Ti
.

And as I explained before, suppose what you are seeing here in this picture (refer to above figure) is the cross section of a sample. That means if you have a plate of steel and now actually this plate after the treatment, you cut it and you are seeing this cross section. So, then we are able to see this is the surface there you will see the phase is expected for highest nitrogen content and then as a function of depth you start to see other phases which are expected at low nitrogen contents. That is what you see here (refer to above figure).

What you see here is at the top here is the nitriding atmosphere, this is all the gas phase. And this is the surface of the sample and then the ammonia dissociates here and supplies the nitrogen and that nitrogen diffuses inwardly and you will have a highest nitrogen content at the surface and that starts to decrease. So now if you see as a function of time, what evolves is initially a small amount of nitrogen goes into the solid then form so called this diffusion zone.

What is diffusion zone? Diffusion zone is nothing but you have a ferrite matrix with dissolved nitrogen, the nitrogen goes into the octahedral interstitial voids of the BCC iron lattice and that is what we call it as classically diffusion zone. Now, if you have a steel which has containing some elements, which have a strong affinity to nitrogen such as aluminum or chromium.

What is the meaning of strong affinity for nitrogen? For example, you have an iron and that requires certain level of nitrogen being dissolved in the lattice before we can form any iron nitrides. Similarly, for the others elements having a high affinity to nitrogen like aluminum or chromium, they will require a very small amount of nitrogen to be dissolved before they can form nitrides.

So, now if you have such elements they start to form their nitrides for example aluminum nitride or chromium nitride and that means you will have a BCC iron matrix with a dissolved nitrogen, you have a dissolved nitrogen atoms in the octahedral interstitial voids and if this contains the elements like aluminum you start to form the precipitates of these nitrides in the diffusion zone.

And now, the ferrite matrix containing dissolved nitrogen as well as the alloying elements nitride particles also called as diffusion zone in actual nitriding steel. Now on top of that, you have a high nitrogen content that implies that you can form the iron nitrides because the γ' iron nitrides request less nitrogen that forms after the diffusion zone saturates and then comes the ε iron nitride.

So, now, this is what actually the process which happens in a commercial steel. As you know that a commercial steel contains several elements, depending on the requirement of the bulk property of the component you will add several elements into the steel. That means, when you do the nitriding all these elements together with iron will try to interact with the inwardly diffusing nitrogen.

So, that means, we need to understand how these multi component steel responds to the inwardly diffusing nitrogen and then that is where we will be able to understand what exactly the kind of microstructure develops and with that, we will be able to understand what kind of properties these nitrided layers will have. For example, this diffusion zone where we have only the ferrite matrix with the know the nitride particles of alloying elements is like a composite, we have made actually a ferrite matrix with nano sized precipitates and this is known to have a very good fatigue property.

The reason being because we have a dissolved nitrogen and it actually brings the surface region to expand and that imposes macroscopic compressive residual stress that leads to the enhancement in the fatigue properties. Whereas, these iron nitride layers ε and γ' both together is called as a compound layer. These compounds have got a very good anticorrosion property.

That you will see that when you do etching of the polished surface of a nitrided steel, then you will see that these iron nitride layers does not react with the your etching reagent. So, that means that they are actually chemically more inert than your base steel. Because of that they also have a very good hardness. So, they lead to the improvement of the tribological and the anticorrosion properties.

So, now, in the next lecture, we will try to see what actually happens in a rather simple alloys how they respond to the nitriding for example, if you take a pure iron or iron aluminum alloy, so, that we can understand in the simple systems, how the system runs, and then one can actually obtain knowledge from such model alloys, can be transferred to a actual commercial steel, then we can actually obtain a precise understanding of the behavior of multicomponent steel during nitriding, so with this I am ending this lecture.

Keywords- Nitriding, Gibbs free energy, pressure, temperature.