Thermo-mechanical and Thermo Chemical processes
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Module No # 08
Lecture No # 36
Gaseous Nitriding of Pure Iron and Iron Based Alloys

Greetings to everyone. So, today we will continue discussing about the gaseous nitriding. So, in the last lecture, we have come to the understanding that why it is possible to perform gaseous nitriding using ammonia hydrogen mixture rather than with pure N_2.

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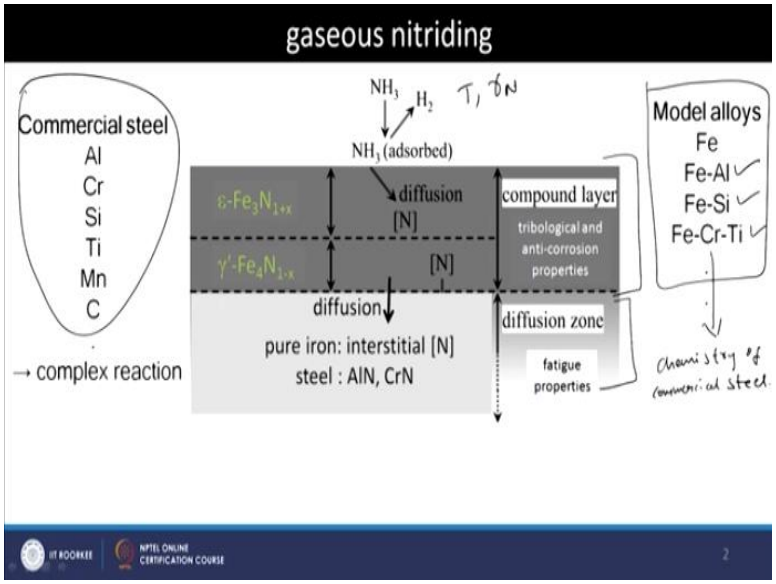

gaseous nitriding

Commercial steel
Al
Cr
Si
Ti
Mn
C

→ complex reaction

NH_3 H_2 T, γ_N

NH_3 (adsorbed)

ε-Fe_3N_{1+x}

diffusion [N]

γ'-Fe_4N_{1-x}

[N]

diffusion

pure iron: interstitial [N]
steel : AlN, CrN

compound layer
tribological and anti-corrosion properties

diffusion zone
fatigue properties

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

Chemistry of commercial steel.

And then we have also come to the situation where how actually the microstructure evolves as the nitriding process continues. So, in this slide what is shown is the schematic microstructure. So, we discussed about its features in the last class, so to cover quickly, so, we have an outer layer that is called the compound layer or often it is called as white layer, because when you do the metallographic preparation of the nitrided specimen cross sections and when you etch it with nital and take it into the light microscope, all these iron nitrides appear white because they actually does not get etch and they just simply reflect back all the light. So, that is it is also known as a white layer in the especially in industry.

And then other layer which is the diffusion zone, we discussed about that also what kind of properties can be obtainable from that and then we said that if we have a commercial steel, as you see that here (refer to above figure), the commercial steel will have several elements inside, these are all have been added to give a bulk property which is essential for the component.

So, now, when we doing nitriding for a commercial steel, this is becomes a very complicated situation, because the nitrogen is diffusing inwardly into the sample and we have to understand how these nitrogen actually interacts with all the elements in the solid individually or collectively and that is what actually leads to the overall nitriding response. So, in this context, today, we will at least we try to understand what happens in nitriding of a relatively simple alloys.

So, the most simplest would be the pure iron so, in this lecture, we look at what actually happens when we nitride the pure iron and then we go on to understand actually the other alloys such as when we add a aluminum into the iron or silicon or you know that we can also club the elements and like this we can build on to the chemistry of commercial steel.

So, this kind of understanding helps in optimizing the chemistry of the steel as well as the nitriding parameters that is the temperature and nitriding potential r_n in the outer atmosphere.

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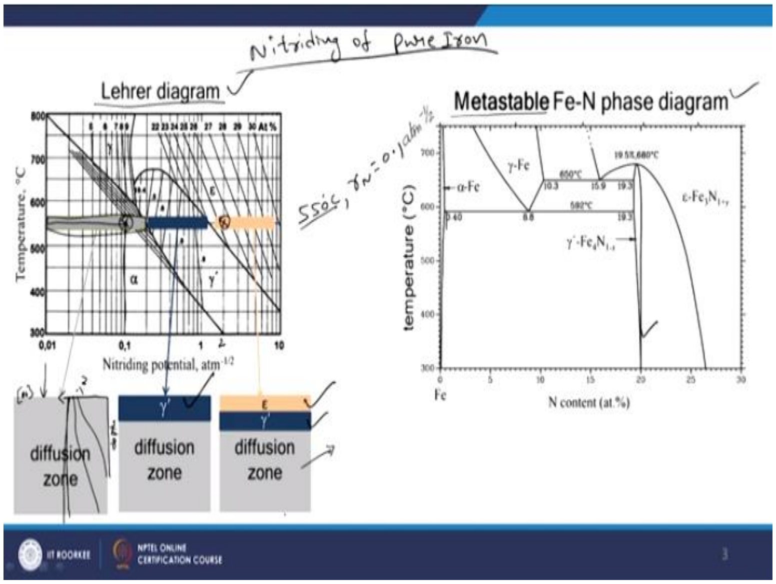

So, now when we look at nitriding of pure iron so, then the diagram of this (refer to above figure) iron nitrogen phase diagram, this we have discussed already why it is called metastable and this will be of more direct relevance. Because as you see that in this diagram is only valid for iron and nitrogen alloys whereas, actual commercial steels we cannot use this kind of a diagram.

And now, we have also seen this Lehrer diagram. This is also actually only for this is done for when we try to nitride pure iron, that is why these two diagrams can give direct comparison of the obtained results for nitriding of pure iron and then we can understand thermodynamics of nitriding of pure iron utilizing these diagrams.

So, we have understood that in the last lecture, if you apply the nitriding conditions within this α field of the Lehrer diagram that means, we are sticking to this region of BCC iron. A very small window and then we have this other region of γ' where we can produce the γ' iron nitride on the sample surface. Now, we try to understand actually what happens when we are nitriding with nitriding conditions.

That means, for example at 550 °C let us say with a nitriding potential with r_n of 0.1 that means, we are using this situation as for the nitriding this (refer to above figure) point. Now, we know that from this thermodynamically it will not be able to form the immediate nitrides which we expect is the γ' iron nitride that is this compound in this iron nitrogen phase diagram.

So, now, when we do that what happens actually for example, we have a sample and then the nitriding atmosphere supplies the nitrogen into it that means, we provide the nitrogen into it and then it starts to dissolve. And initially, if you look at actually how the concentration is changing, so, if I am plotting here (refer to above figure) the concentration how it will be changing, then it will be something like that, and then if you keep it for enough time, so, slowly this will be saturating, and then you end up with a saturation level of nitrogen content.

So, now, this nitrogen content once it reaches throughout the sample, that means, throughout the thickness of the sample then we know that the sample has saturated. So, what I am showing here with this curve, is the nitrogen content as a function of depth below the surface. So, this axis I am plotting percentage of nitrogen and this is the depth below the surface and this is what we expect that this will get saturated.

This is the first you know the when we do the nitriding of pure iron that is what it happens here. Now, at the same temperature of 550 °C by changing the nitriding potential to different values as you can see that you can change it from 0.01, 0.02 then what exactly we can change is the amount of nitrogen that is this level that is the equilibrium saturation level of nitrogen, which have BCC iron can take up at this temperature we can vary systematically.

That means, we see that there is a maximum solubility of nitrogen in the BCC iron is here it is given as 0.4 atomic percent. Now if I want to produce a BCC iron with 0.2 atomic percent nitrogen that is possible by appropriately choosing the nitriding potential at the given temperature. So, this is the very nice feature of gaseous nitriding we can thoroughly control the thermodynamics of the process.

That means, we can produce all the phases of the iron nitrogen phases diagram as pure phases by starting from the pure iron. Now, let us move to if we use the nitriding conditions, which allow the formation of let us say the iron nitride. That means now, I take a nitriding potential, let us say the nitriding potential of 2 at the same temperature.

Now, you know that you will be able to form ε iron nitride that is at the surface, γ' immediately below that, followed by the diffusion zone. This is where you have a dissolved nitrogen content. So, now actually how such a process runs. So, that is what we will see initially we know that as the nitrogen enters into the solid it gets dissolved right.

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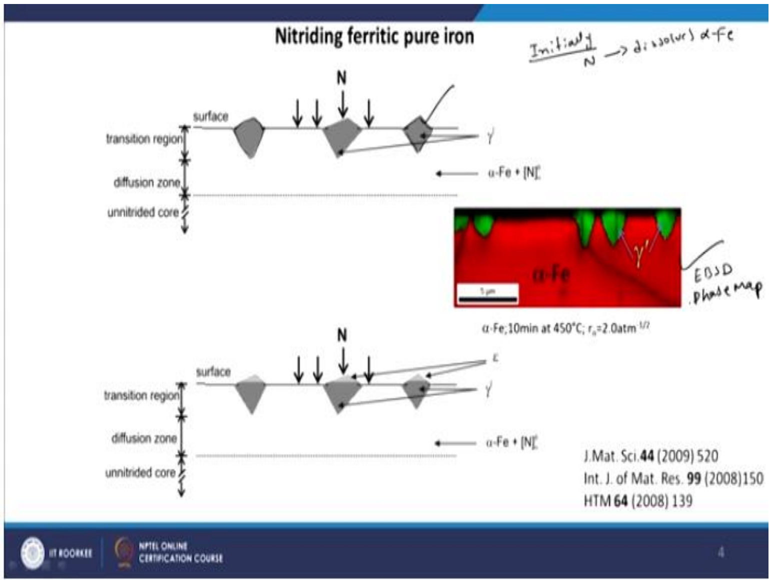

Nitriding ferritic pure iron

Initially N → dissolves α-Fe

EBSD phase map

α-Fe;10min at 450°C; r_n=2.0atm $^{-1/2}$

J.Mat. Sci. **44** (2009) 520
Int. J. of Mat. Res. **99** (2008)150
HTM **64** (2008) 139

As we look at as a function of time initially nitrogen dissolves into α iron, that is BCC iron and once at the given temperature we surpass the solubility limit of the ferrite matrix, then actually you start to from the iron nitride nucleation at the surface. You can read from the phase diagram what is the solubility limit of the ferrite matrix at a given temperature.

This is what is shown here schematically (refer to above figure). This is the sample surface and you have placed the nitriding atmosphere here, that is applying nitrogen and this nitrogen dissolves into the BCC iron and after some time it surpasses the solubility limit and the nucleation of this iron nitrides starts here. So, when this iron nitride nucleation happens on the isolated places on the surface, you see that there will be a some surface relief at that location that comes because of the volume misfit between the iron nitride and BCC iron.

For example, if you have a Fe_4N nitride and if you are producing it from pure iron, there is a volume increase of about 20%. So, that is what actually leads to this kind of a situation. Now, the applied nitriding potentially is high enough to allow also the ε iron nitride then it starts to nucleate on top of the nitride nuclei. This is the γ′ nuclei as it is shown (refer to above figure), on top of that you start to produce that ε iron nitride nuclei.

So, that is how actually this starts and what is shown here (refer to above figure), this one, which you see as the relative red colored matrix with green colored features, this is a EBSD phase map like light microscopy, we use to distinguish the different phases, one can use the electron backscatter diffraction. I will not go into the details of this technique, but by which we can also identify the phases based on their crystal structure.

So, that is how one can actually see that this is the γ′ Fe_4N phase and this red color is meant for the iron matrix. This is the schematic and this is what is the real microstructure (refer to above figure). So, now if you prolong the nitriding, you have started the nucleation sites.

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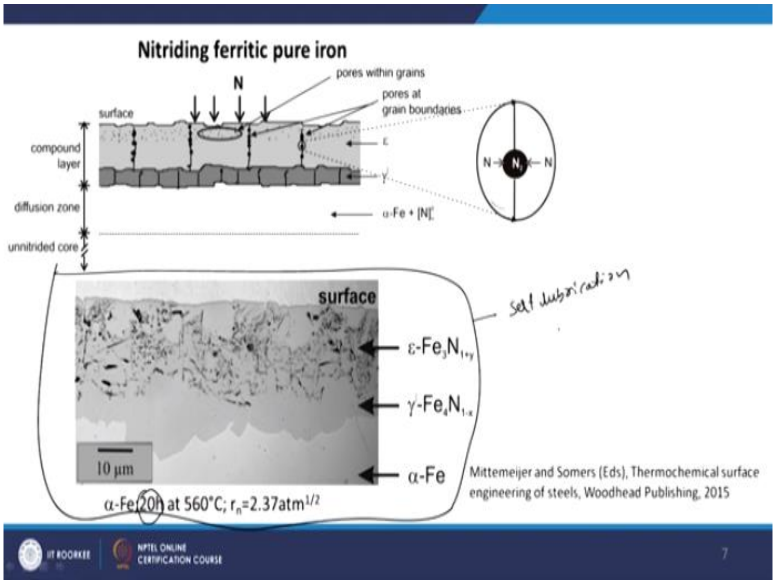

Nitriding ferritic pure iron

α-Fe 20h at 560°C; r_n=2.37$atm^{1/2}$

Self lubrication

Mittemeijer and Somers (Eds), Thermochemical surface engineering of steels, Woodhead Publishing, 2015

And then when we prolong the right riding, then slowly you form a closed layer of γ′ as one can see here (refer to above figure) and then on top of that you form a closed layer of ε iron nitride. And below that you have a diffusion zone that is nothing but BCC iron matrix with dissolved nitrogen. Whenever N is shown within the square bracket and with the phase of α or you know whatever the phase that means this is a about a dissolved nitrogen in that solid phase.

So, this is the schematic (refer to above figure), what is shown on the top and the actual micro structure is shown below for a particular condition of nitriding. So, as one can see that you have a top surface having a ε iron nitride and below that γ′ iron nitride. These are the grain boundaries, these lines of this compound layer, this is a grain boundary in the ε iron nitrate layer, these are shown schematically here with these lines (refer to above figure).

And then the way these layers grow is they try to grow like a column and then keeping the grain boundaries more or less perpendicular to the sample surface. This is the sample surface and you see that grain boundaries are running more or less perpendicular to the sample surface that is because the nucleation happens and they try to grow inwardly and with laterally bringing the grain boundary which is more or less normal to the sample surface.

You see here, this sample has been nitrided for 5 hours at 550 °C using this nitriding potential 2.37. So, if you look into the Lehrer diagram 2.37 means we are somewhere here (refer to above figure). That is why we are forming ε, γ′ and α as schematically shown here, that is what exactly we are seeing in the microstructure. So, now we have discussed in earlier lectures that, the phase diagram what we see for iron nitrogen with indication of all the iron nitrides that is γ′ and ε is a metastable phase diagram. And why we call it as a metastable phase diagram?

Because, it has always a tendency to produce N_2 gas by dissociating these iron nitrides and then actually you will not end up with any iron nitride.

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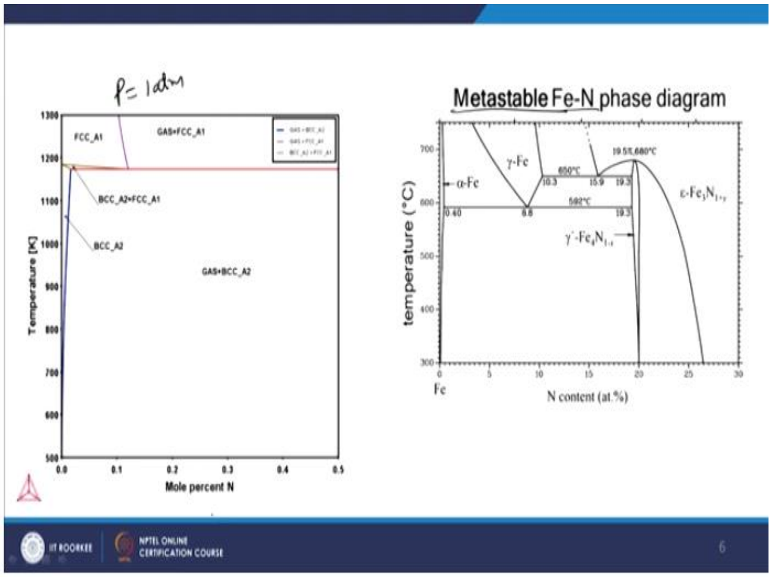

Metastable Fe-N phase diagram

We will end up with only a BCC iron with a small amount of nitrogen solubility as shown here (refer to above figure). So, this is a phase diagram when we allow the ultimate equilibrium to be established, it starts formation of N_2 gas. Whereas here in this diagram, we are not allowing the equilibrium to be established that means, we are not allowing the N_2 gas formation and then we end up with this kind of iron nitrides.

So, this was for the pressure of one atmosphere that means, we are imposing a N_2 gas of one atmosphere and then what phases we get. So, as we know that any metastable phases have a tendency to go to the equilibrium phases right, but it is a matter of time, we agree that is what exactly happens with these nitrides.

If we prolong the nitriding time, that means we continue to nitride the sample like if you take a relatively thick sample of iron, let us say about 5 millimeter thick, and if you keep on nitriding these iron nitride starts to grow from the surface then they start to thicken and now as you continue, the oldest iron nitrides because they are also at a temperature of nitriding, they can exercise all kinetic mechanisms to go to the more equilibrium state that means, they want to precipitate out N_2 gas molecules.

So, this is what exactly happens, you see that here (refer to above microstructure figure), what you shown, the microstructure is that without any pores like in this. First let us focus on this schematic in the top. So, what shown here is that you have a thicker layer of this ε and γ' and along the grain boundaries of this ε iron nitride, you start to see this formation of N_2 gas filled pores.

That means the nitrogen atoms go there and form N_2 molecule and this N_2 molecules as a gas phase starts to build up a pressure and that leads to such a situation as shown schematically here (refer to above microstructure figure). The recombination of nitrogen atoms leading to the formation of N_2. And you see that this process also has a barrier for nucleation. For example, if the N_2 gas has to form within the grain of iron nitride, then it is not easy because it requires a more driving force.

So, we can see from the basic thermodynamics what actually the driving force means, so, we will not go into the details of that, but you know that easy sites of this precipitation for N_2 gas is the grain boundaries and at the surface, then later they also start to become nitride. So, this is a schematic microstructure what you see here, below here this is the real microstructure, after prolonged nitriding (refer to above microstructure figure).

So, in the previous slide, what we have seen the microstructure after 5 hours of nitriding now, you see that this is for after 20 hours of nitiding under identical conditions (refer to above microstructure figure). So, you start to see that now all these pores like what you see as open grain boundaries I could call it so, these are all actually the porous regions within the iron nitrate layer. So, now, when it comes to the practical applications, whether these porous layers are you know the beneficial or not that they are usually detrimental for the mechanical property point of view.

First of all these iron nitride layers are very hard that means they are also brittle, they have a very good wear resistance. But with the porosity, they easily start to break away when in the any of the impact loads. So, but only some applications where this porosity in the iron nitride layers will be useful like if you want to have a self-lubrication situation for example, if you have a moving part which requires a lubrication if you have a porous layer of this kind of iron nitrides, the lubricating oil can go into the pores and then starts to wet the walls while it is coming down and then this can do continuously.

So, that kind of very selected applications where this porosity can be even engineered. This is all about nitriding of pure iron with nitriding conditions, such that we allow the formation of iron nitrides and how the process runs. So, now if we look at that actual steels will contain now other alloying elements added into this right.

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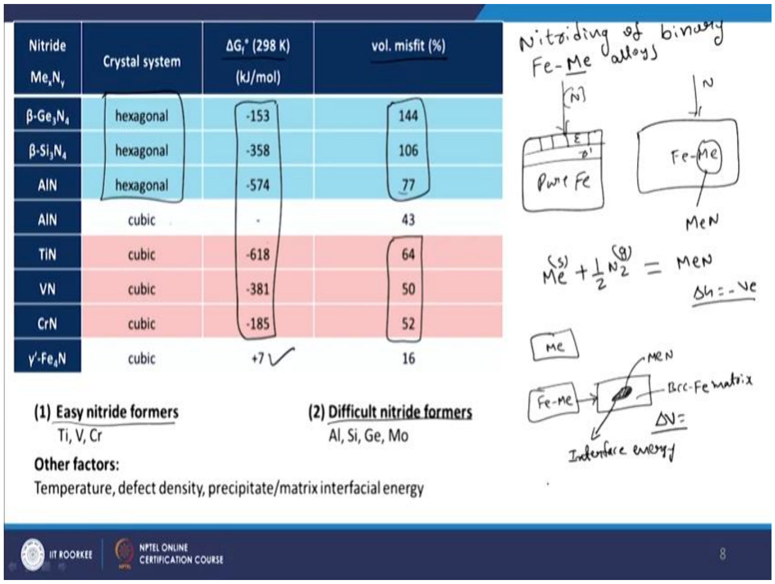

Nitride Me_xN_y	Crystal system	ΔG_f° (298 K) (kJ/mol)	vol. misfit (%)
β-Ge_3N_4	hexagonal	-153	144
β-Si_3N_4	hexagonal	-358	106
AlN	hexagonal	-574	77
AlN	cubic	-	43
TiN	cubic	-618	64
VN	cubic	-381	50
CrN	cubic	-185	52
γ'-Fe_4N	cubic	+7 ✓	16

(1) Easy nitride formers
Ti, V, Cr

(2) Difficult nitride formers
Al, Si, Ge, Mo

Other factors:
Temperature, defect density, precipitate/matrix interfacial energy

Nitriding of binary Fe-Me alloys

$$\overset{(s)}{Me} + \frac{1}{2}\overset{(g)}{N_2} = MeN$$

$\Delta h = -ve$

So, now we will look at that aspects. We do not have now pure iron we are looking at nitriding of binary Fe-Me alloys. This Me means other alloying element which can be know the chromium or aluminum and all other that alloying elements. Now how this kind of alloys will behave during nitriding because of the presence of this additional element what will happen to the growth of the this iron nitride layers.

So, in this context we are only focusing at the iron nitrides which are actually wants to grow on the surface of iron. That means, if you have a pure iron and let us say you have a Fe-Me alloy and when we start to do nitriding of this both of them you know that in this case of the pure iron, here we know the way the iron nitrides can grow as you know the ε and γ' layers. That is what we have seen.

And now because of this element Me what happens to the growth of the iron nitride layers in this kind of situation. So, for that before we go further, now can we distinguish different types of Me elements in the context of nitriding of Fe-Me alloys. So that means can we give some way the classification we have several elements which you can put so, how we can distinguish them as different kind of nitrides.

So, then in that context we want to have a demarcation as easy nitride formers and difficult nitride formers. That means elements which has Me which can easily form their own nitrides. That means suppose if I have Me then how easily it can form Me N nitrides for example. So, it is not always 1:1 stoichiometry as you see that silicon nitride and germanium nitride, they have a difference stoichiometry.

And then you have can group other kind of elements which are difficult nitride formats, that implies they do form their own nitrides like MeN but their formation is relatively difficult. So now to what kind of characteristics we can consider without having any experimental knowledge about these things? So, one is that how easily a MeN nitride forms that depends on we can look at from the if I have a Me metal, if I make it to react with the nitrogen gas, then this Me^{S} is a solid then it forms MeN suppose.

$$\mathrm{Me}^{S} + \frac{1}{2}\mathrm{N}_2^{g} = \mathrm{MeN}$$

Now, what is that Gibbs energy change associated with that reaction. For the considered nitrides, we are saying that difficult nitride formers and easy nitride formers that means, they all tend to form nitride have negative Gibbs energy, but the more the negative that means they have a more tendency or a stronger affinity to nitrogen that means they can be treated as easy nitride formers.

But now what we are seeing in this

$$\mathrm{Me}^{s} + \frac{1}{2}\mathrm{N}_2^{g} = \mathrm{MeN}$$

reaction is about, if I have a Me metal and then if I put that Me metal reacting with a molecular N_2 gas of one atmospheric pressure how it can form the nitride. But the situation which we are considering is Me is not present as a you know the metal but it is present as an element which is dissolved in iron matrix. It is not that we have a pure Me but we have a Fe-Me alloy. Now Me is present in a iron matrix right.

We are considering only the solutions between iron and nitrogen, that means we are considering the chemistry of Fe-Me alloys within which Me can dissolve into the iron lattice. Now in this situation when the Me is present in a solid, now in this if Me wants to precipitate upon reaction then this is have to form as a particle of MeN in BCC iron matrix. Now because something has to develop in a constraint matrix, that means you have a surrounding solid in which you need to create a space to form these nitrides. So, this leads to a certain difficulty for nitride formation. So now these two parameters, larger the negative value of Gibbs free energy, that is easy to form. Now, here the difficulty depends on what kind of volume misfit happens, what kind of volume change occurs when Me precipitate as MeN in BCC iron.

So, that means, we are looking at if this volume misfit is very small, then it does not have to do any elastic work to create a space for its development. So, now these two parameters, one is the Gibbs energy of formation of the nitride, another factor what is the percentage of volume change, which happens when Fe-Me alloy converts to Fe and MeN kind of a two-phase mixture.

That is what these two parameters that is the volume misfit and the Gibbs energy change are shown here in this table (refer to above figure), this is the standard Gibbs energy change and this is the volume misfit, which happens when these nitrides developed in BCC ferrite matrix. And you see here the different several nitride forming elements are considered like germanium, silicon, aluminum, titanium, vanadium and chromium and also at the end you see also the iron nitride.

Now first of all, if you look at the iron nitride ΔG of formation is positive. That is because if you put the Fe in this Me place you can never produce the iron nitride that is why we call it as a metastable. And that for all other nitrides here, you see that ΔG is negative. You see that it is only for a comparison, these values have been computed at 298K, but in principle they should be taken for the actual nitriding temperatures and this is the volume misfit at room temperature. What is the amount of volume misfit you see that there is a distinctly varying volume misfit. Although the γ` nitride has a less volume misfit but it has a very small or a positive values of Gibbs energy. But here you have this kind of nitrides which have a cubic crystal system for their crystal lattice and these are titanium nitride, vanadium nitrate and chromium nitride.

They have a relatively lower misfit and also the decent amount of Gibbs energy formation of these nitrides and you have another group of nitrides which is a hexagonal crystal system. They have negative values of standard Gibbs energy of formation, but have a rather large volume misfit. So, now, you see here aluminum nitride is shown in both cubic and hexagonal modification because, it is absorbed that in during nitriding aluminum also tries to precipitate in a cubic crystal system structure with sodium chloride type structure.

So, that is why the value of for this nitride is not given here because it is metastable that will be a positive number, but in the given situations, what are these values that is not known. So, now with this two kind of nitrides, now the smaller the value of volume misfit and larger the negative value of the Gibbs energy makes that particular element as easy nitride formers.

So, now, whether these are only two factors, there are other factors also which we should in principle consider. For example, when we form a new phase of iron nitride, you are creating a new interface. Initially it is all one homogeneous alloy now you are creating this (refer to above figure) interface. So, the energy of this interface also plays a role in deciding whether particular element is easy nitride former or difficult nitride former.

So, we will not go into the details of this, but consideration of the interfacial energy also favors these nitrides i.e. titanium, vanadium and chromium nitride are known to form easily even in the context of interfacial energy consideration. So, now, let us see how this two class of materials actually behave while you try to do the nitriding. So, this I will continue in the next class.

So, to summarize what we have discussed in this lecture is we have tried to understand how actually the nitriding of a pure iron happens as a function of time for the given conditions of temperature and the nitriding potential. So, we have seen that these nitrides grow and due to their metastable nature, they try to also dissociate leading to the formation of N_2 gas, but because it requires certain time for these processes to run and this kind of N_2 gas porosity development happens when you do nitriding for prolonged times.

And then we have seen that now, when we want to understand if it is not pure iron, it has got some other elements dissolved in it. So, we are specifically considering the alloys in which other element is in a dissolved state. That means, we are, we are considering only the solution phases that means, it is still a BCC iron lattice with a dissolved another element, then how actually this kind of alloys will respond to nitriding in particular to the development of iron nitrides.

So, for that we have first seen that if we can understand how alloying elements can be grouped in the context of nitriding response, when they are present in the iron lattice, then we have seen them as we can group them as an easy nitride formers and difficult nitride formers. That means, we are considering the elements which forms nitrides because they have a negative values of Gibbs energies of formation, but they have a either a slow or a faster way of development of barriers for precipitation that has volume misfit which they have with the ferrite matrix. So, and with accordingly we have classified these elements. Now, in the next class, we will look at actually the actual behavior of these alloys when we have these kinds of elements in the system thank you.

Keywords- Gaseous Nitriding, pure iron, iron based alloys, metastable phase.