Thermo-mechanical and Thermo Chemical processes
Prof. Sai Ramadu Meka
Department of Metallurgical and Materials Engineering
Indian Institute of Technology – Roorkee

Module No # 08
Lecture No # 37
Gaseous Nitriding of Iron Based Alloys

Greetings to everyone and welcome to today's lecture in this series of lectures on gaseous nitriding. So, in the last lecture we have discussed about the how actually the different alloying elements may change the way iron nitrides wants to grow when you are nitriding an alloy of iron having some element inside its lattice in a dissolved state.

That means we have a BCC iron with some element, then how actually that can grow that is where actually we discussed about how we can treat different alloying elements as you know the easy and difficult nitride formers.

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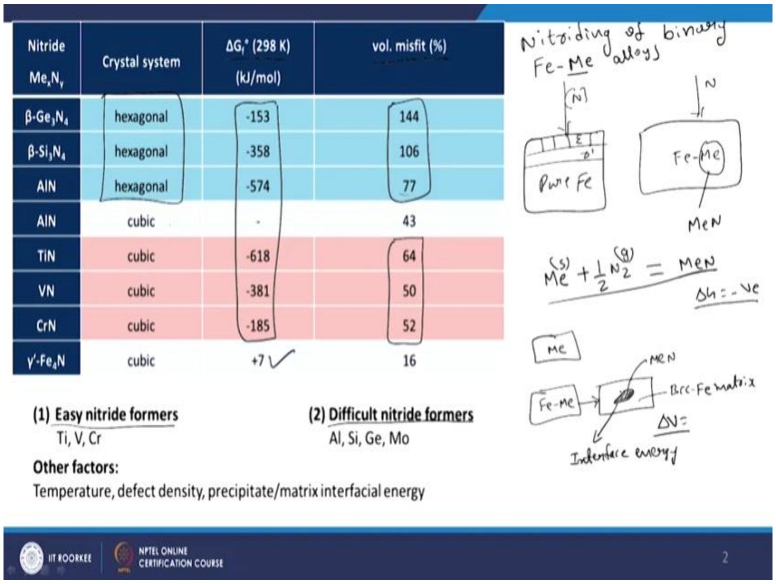

Nitride Me_xN_y	Crystal system	ΔG_f° (298 K) (kJ/mol)	vol. misfit (%)
β-Ge_3N_4	hexagonal	-153	144
β-Si_3N_4	hexagonal	-358	106
AlN	hexagonal	-574	77
AlN	cubic	-	43
TiN	cubic	-618	64
VN	cubic	-381	50
CrN	cubic	-185	52
γ'-Fe_4N	cubic	+7 ✓	16

(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, that is what we have done. This (refer to above figure) is the slides from the previous lecture, we have distinguishing the elements as difficult nitride formers and easy nitride formers that we have done based on the standard Gibbs energy change associated with the formation of these nitrides. According to such reaction and the difficulty for precipitation is associated with the volume misfit between when Me is dissolved in the solid and if it converts to MeN, there is a change in the volume and that involves actually you need to create a volume space also to develop these nitrides and that involves some difficulties.

So, that is the quantification for we can see it in the form of volume misfit. So, now we will see how actually the different alloys behaved in the actual condition. So, firstly we let us look at the easy nitride formers.

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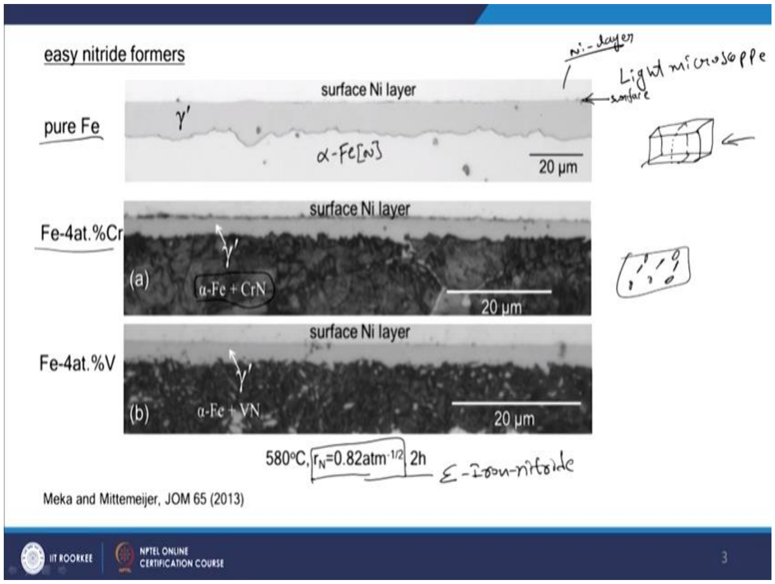

easy nitride formers

580°C, $\boxed{r_N=0.82 atm^{-1/2}}$ 2h

Meka and Mittemeijer, JOM 65 (2013)

So, what is shown here in this slide (refer to above figure) is the light optical micrographs that means, these are all recorded from light microscope. So, these are all actually the cross sectional microstructures that means, you have a sample of certain thickness and when we do the nitriding and then make a sectioning like that and we are trying to see this section. That means on the edges we see the surface.

So, that is how actually you can see that suppose for example here this is the surface of the sample and what you see on the top is a nickel layer. So, this nickel layer was not there before, but this nickel layer was deposited after the nitriding just to protect these edges. For example, we all discussed that these iron nitrides are very brittle. So, if I do not have a support here, when I am preparing the for the metallographic preparation, these nitrides can break away

So that is why actually this nickel layer was electrodeposited. That is actually to the to protect the edges so it has nothing to do with the nitriding it is only for the convenience of doing a better metallographic sample. Then we record those microstructures and that is what is shown here (refer to above figure). And this is for the pure iron the top one and the below one is when you do the nitriding of iron 4% chromium. And next one is iron 4 at. % vanadium. So, as you see that we have treated chromium and vanadium as easy nitride formers based on their Gibbs energies of formation and the volume misfit associated with their nucleation in the ferrite matrix. So, what you see in the case of a pure iron that is the top most this picture, you have a growth of the iron nitride layer, this is the iron nitride layer γ'.

That means, if you look at this nitriding potential what is chosen, at 580 and 0.82 if you look into the Lehrer diagram, they fall into the γ' region of the Lehrer diagram that means, at these conditions ε iron nitride cannot develop. That is why we have only γ' iron nitride. And now in the below this iron nitride layer what we have is a α iron with dissolved nitrogen in it.

Now you see that it grows like a layer. That means it starts the nucleation at some isolated locations and they grow laterally and form a continuous layer. Now if you look at for the alloy iron chromium then you see the again here it is the iron nitride layer at top surface and below that you see now some dark etched region. It is appearing darker as compared same region below the iron nitriding pure iron.

This appears darker because now it has a chromium and now this is not a pure α iron matrix. It is actually the α iron matrix with chromium nitride precipitates inside. You have a α iron matrix with the development of chromium nitride precipitates. And now actually when you do the etching of such a microstructure because of this chromium nitride and α iron have a very distinct reactivity with your etchant so, it creates a large roughness and that leads to actually the very dark contrast for this.

Like the way pearlite looks when you look in the optical microscope. Now, what you see here is that here we have a chromium nitride in the α iron, on top of that you have a γ' iron nitride. And similarly, for the iron vanadium we see the very similar situation. So, what we understand is that the morphology of the layer which is growing actually starts like a layer as it was the case for pure iron and then it continues to grow. While below the iron nitride layer you have this diffusion zone having also these nitrides of elements that has chromium and vanadium.

Because they are treated as easy nitride formers so, they have already developed in the diffusion zone. Now, what happens if you do the nitriding of you know that when you do the prolonged nitriding of pure iron, we start to form the N_2 gas porosity that means, we start to precipitate N_2 gas that we discussed in one of our lecture.

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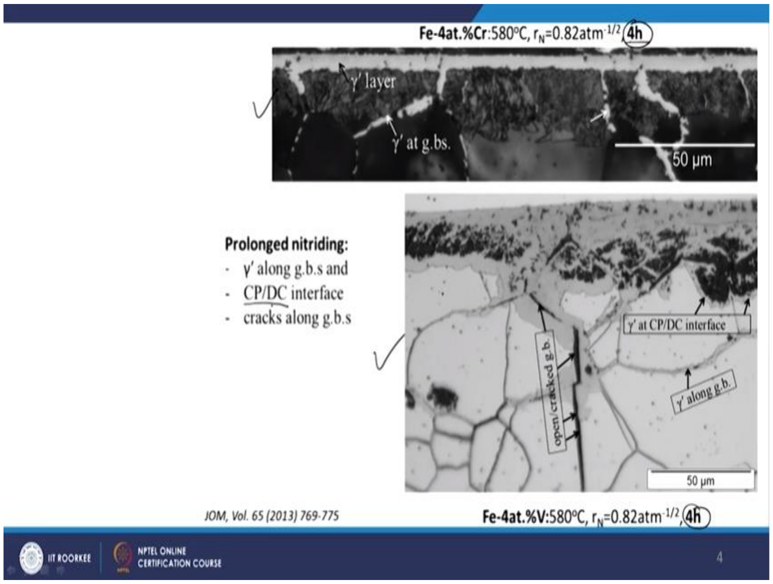

Fe-4at.%Cr:580°C, r_N=0.82atm$^{-1/2}$ 4h

Prolonged nitriding:
- γ′ along g.b.s and
- CP/DC interface
- cracks along g.b.s

JOM, Vol. 65 (2013) 769-775

Fe-4at.%V:580°C, r_N=0.82atm$^{-1/2}$ 4h

So, now what happens when you prolong the nitriding of these alloys, for example here (refer to above figure) if you take the same iron 4 at. % chromium alloy, now it is for the nitrided for 4 hours. You see that in this (refer to previous figure) picture they are nitrided for 2 hours, this iron chromium alloy and now, we have increased the time to 4 hours, you see that now, we have increased the time.

And now you see that of course, you have a layer on the surface this γ′ nitride layer, this is appearing white, but now you also see that there is some extensions of this layer as you know the threads into the sample. This is all actually the γ′ iron nitride forming at the original grain boundaries of the ferrite matrix. These are all actually the initial grain boundaries of the ferrite matrix there also you see the growth of this iron nitrides.

So, now this is for the iron chromium. Similarly, if you look for the iron vanadium this is also now nitrided for 4 hours, a very similar situation one can see sometimes it appears that it is also forming at the interfaces. This is the surface here we have a nickel layer and then here also like it is all extending along the grain boundaries of the ferrite matrix and sometime you see that some grain boundaries are even opened up. This grain boundary is really opened up like you know the crack.

So, that is actually now similar to the iron nitrides when we they start to form porosity and this is expected because of the formation of the N_2 gas porosity along the grain boundaries. Now, another aspect which I will discuss in a later lecture in more detail, but if you compare with the iron chromium sample here with this iron vanadium, what you see is, here you have a nitride layer and then a dark region.

And then you have again a bright region which is appearing like iron nitride layer and then below that you have something which is appearing as a white region right for etching. That means it is rather smooth surface after etching. So, this comes because of so called continuous precipitation and discontinuous coarsening. The CP means continuous precipitation and DC means discontinuous coarsening. These two can be treated as continuous precipitation means it is like a homogeneous nucleation and discontinuous coarsening is treated as a heterogeneous nucleation.

So, we will talk about that later, but time being we will only stick to the way iron nitrides are growing because these features come for the diffusion zone when you do not have even the iron nitride layer these phenomena can be well understood. So, this is the situation with the easy nitride formers. In summary, they develop as layers like in pure iron but upon prolonged nitriding, they tried to penetrate through the grain boundaries and develop as layers along the grain boundaries of the ferrite matrix and later they start to open up as cracks.

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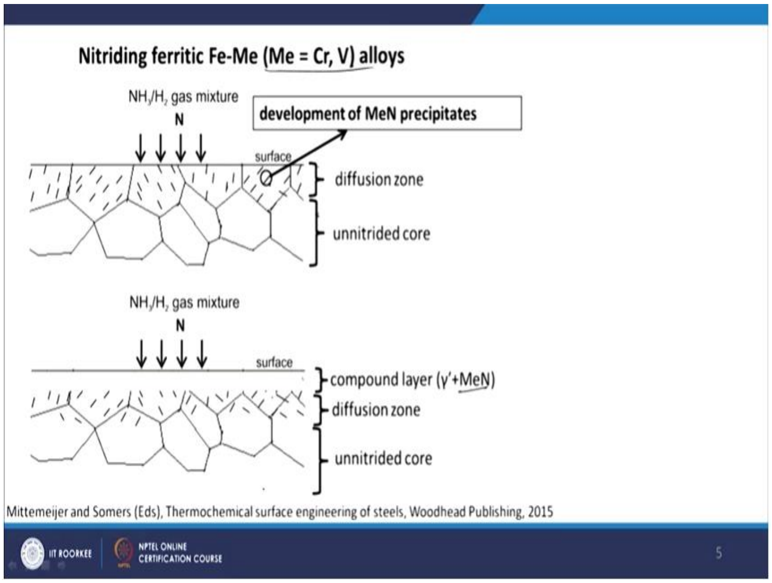

Nitriding ferritic Fe-Me (Me = Cr, V) alloys

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

So, now how do we understand this? By here in this slide (refer to above figure) we are showing schematically how the process runs in the case of this easy nitride formers. So, so the nitrogen diffuses inwardly from you know it is supplied from the dissociation of ammonia and this is defuses inwardly and because these nitrides can easily develop you start to form their alloying element nitrides.

These are all actually schematically illustrating for example the chromium nitrides developing. So now what happens is that initially nitrogen diffuses in and now we know that in pure iron there is some amount of nitrogen which can be dissolved. But now in the presence of these elements like chromium this level can be different. And now once you surpass that level you start to develop these nitrides.

Now this inwardly coming nitrogen gets consumed as long as you have the alloying element like chromium or vanadium and because they will continue to absorb the nitrogen from the matrix to form these nitrides. Now, once all the alloying element at the surface has precipitated out as nitrides of their elements, then you start to grow the iron nitride layer on top.

Now, this iron nitride layer actually grows now not on a pure iron, it is forming from a ferrite with nitrides. That means this growing iron nitride layer is a composite nitride layer which is a γ' matrix with these nitrides inside and this is the difference between the iron nitride layer in this alloy and the pure iron. In the case of pure iron this iron nitride layer will be purely iron nitride, but now it is an iron nitride matrix with these nitrides.

So, this is how we can understand the process. Now, let us look at other class of alloys that is elements which are difficult nitride formers. So, something very interesting one can see.

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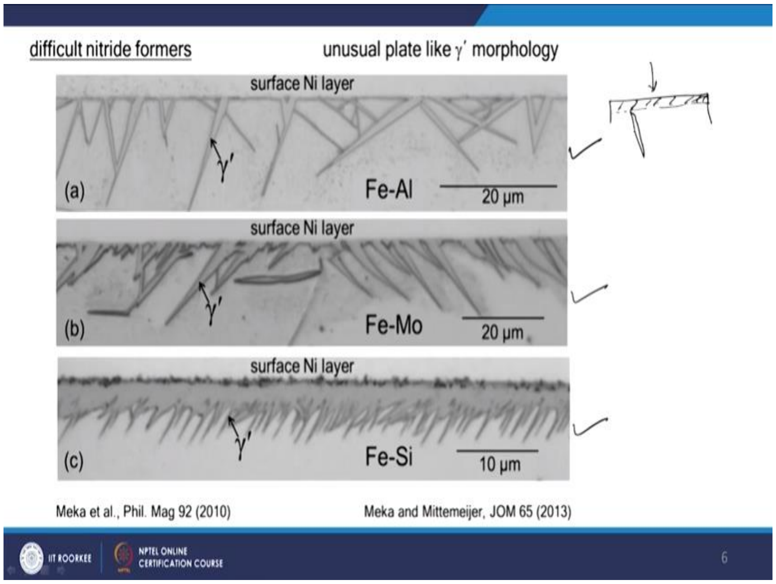

difficult nitride formers

unusual plate like γ′ morphology

Meka et al., Phil. Mag 92 (2010)

Meka and Mittemeijer, JOM 65 (2013)

So, what you shown in this slide (refer to above figure) is, these are again the light optical micrographs, this is for a nitride iron aluminum alloy, iron molybdenum alloy and iron silicon alloy. What you see is, now from the surface iron nitrides are not growing as a layer before as one can see here they are growing rather like a needle or a plate like into the matrix. These are all iron nitrides which are growing into the matrix.

And a very similar observation you see for molybdenum as well as for the silicon. So, we have now a very drastic difference in the way iron nitride is growing during nitriding. So, in the case of other alloys it grows like a layer, but here it is growing like a very unusual shape. So, this is very difficult to conceive why such a growth of iron nitride occurs. So, one can think, why in this kind of alloys actually.

Because if we have a sample which is receiving nitrogen, so, you expect highest amount of nitrogen be realized at the surface you expect the iron nitride to grow like a layer. But now, something is growing something like that, that implies there is some other mechanism must be operating.

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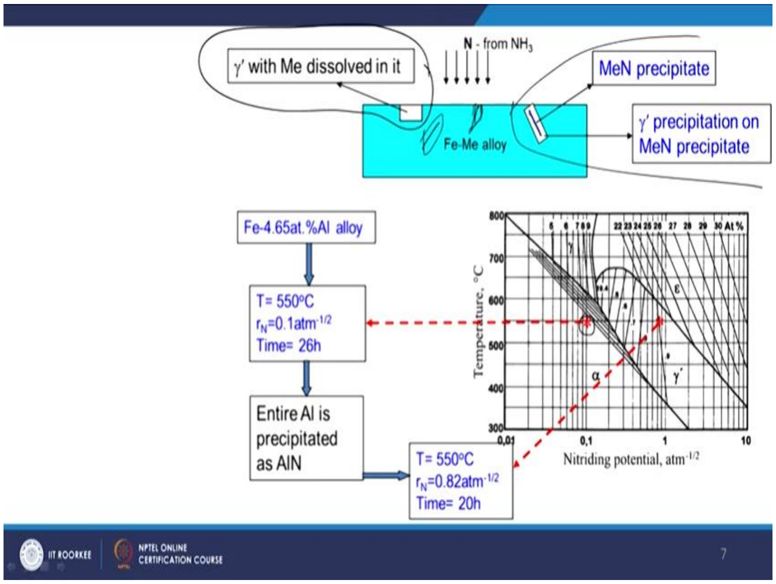

γ' with Me dissolved in it

N - from NH_3

MeN precipitate

γ' precipitation on MeN precipitate

Fe-Me alloy

Fe-4.65at.%Al alloy

T= 550°C
r_N=0.1atm$^{-1/2}$
Time= 26h

Entire Al is precipitated as AlN

T= 550°C
r_N=0.82atm$^{-1/2}$
Time= 20h

So, how one can think of what kind of mechanisms can be operating? Remember we are nitriding a Fe-Me alloy and that is receiving the nitrogen by diffusion. Now, you can imagine two situations, one situation once it reaches to some concentration you form γ' iron nitride with Me also dissolved in the iron nitride. That means you have iron nitride lattice in that some atoms of iron can be substituted by this element of the alloy.

This is the one scenario. If this happens, then it can simply grow as a layer. Other possibility which we are considering initially forms MeN nitride as a platelet because you have a small amount of Me, so, you will have actually precipitates of MeN and now this MeN precipitate which has developed can act as a nucleation site for the iron nitride.

That means it provides like a template and then on top of that you are growing now the iron nitride, so γ' precipitation on MeN precipitate. Now we can imagine that if such a situation is happening because of the nitrides then we expect to see the needle or a plate like growth of the iron nitrides. Because these alloying element nitrides may be growing here and there and then on top of them you can always grow the iron nitride.

Now out of these two, what is actually operating one can find out. How one can do that? Now, you take the iron aluminum alloy and you first nitride that in the conditions where you do not form iron nitride. Now what you are doing is if I make already all the Me as nitrides, they are no longer present as dissolved Me that is what you can do by nitriding, in this condition then you converted all the sample aluminum into aluminum nitride.

That means, you have a ferrite matrix with aluminum nitride precipitates no more dissolved Me is present. This is a sample having BCC matrix with aluminum nitride and take it to this condition where now you try to grow the iron nitrides. That means if I already create them, then what way the growth of iron nitrides can happen? So, such a strategy can be employed in order to find out.

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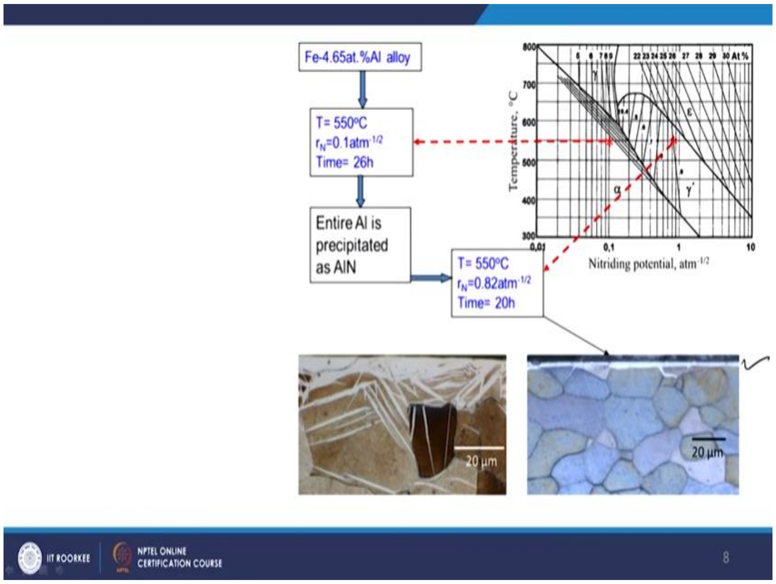

Fe-4.65at.%Al alloy

T= 550°C
r_N=0.1atm$^{-1/2}$
Time= 26h

Entire Al is precipitated as AlN

T= 550°C
r_N=0.82atm$^{-1/2}$
Time= 20h

So, that is what is actually done and the outcome is when you do like this double nitriding that means you nitride first in the ferrite region and then nitride here in the γ' region the same sample what you are seeing is the microstructure are having again like a layer type growth of iron nitride. This is what we have seen in the case of pure iron also. Now it is not showing, but whereas if you do directly the nitriding we saw like this kind of unusual plate like growth of γ' iron nitride.

So, with this we can say that it is actually the dissolved aluminum which is making such a situation if aluminum can form as aluminum nitride. In this sample what we did was, we have already created the aluminum nitride in the matrix. That means no more dissolved aluminum is present. In that situation the growth of iron nitride is normal like a layer. But in this situation, the aluminum is not made to precipitate as aluminum nitride and that means it is in a dissolved state that is interfering with the way iron nitride can grow and that is what actually leading to this unusual development of the phases. So, now, how actually, we can understand this phenomenon is. Now if we need to see whether iron nitride in this case is developing before the aluminum precipitates as aluminum nitride or not when we are nitriding in this condition. Now, when the nitrogen is coming into the sample, it is forming a first aluminum nitride or the iron nitride that is not known.

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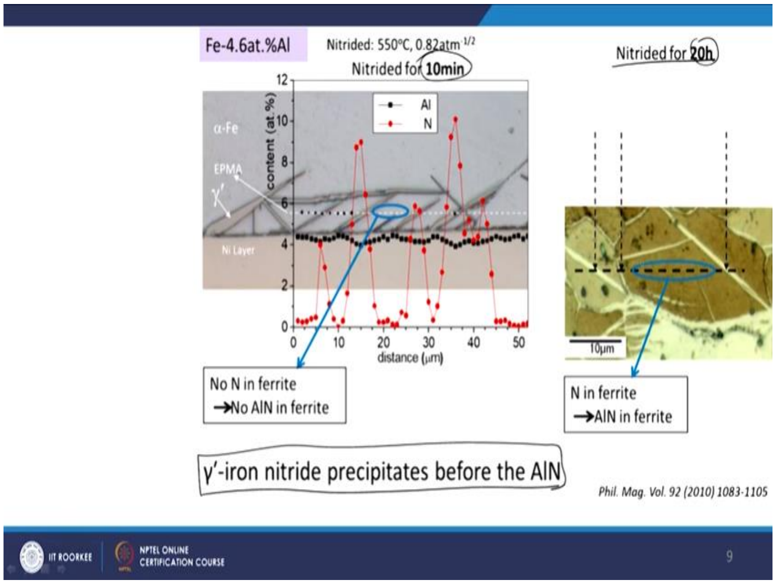
Fe-4.6at.%Al

Nitrided: 550°C, 0.82atm $^{1/2}$

Nitrided for 10min

Nitrided for 20h

No N in ferrite
→No AlN in ferrite

N in ferrite
→AlN in ferrite

γ'-iron nitride precipitates before the AlN

Phil. Mag. Vol. 92 (2010) 1083-1105

So that one can see by doing a very short time nitriding experiments like in this (refer to above figure) case it is done for only 10 minutes of nitriding. Then you see the growth of this iron nitride needles and now one can find out whether this is the ferrite matrix in between these iron nitride needles. Now, we want to see whether aluminum nitride has developed in this region or not, then you can do, this wide dashed line what you see is here, this is where one can make the one made an electron probe microanalysis measurement.

That means, at every point, you are trying to find out what is the composition of the material. Like these points and that has been plotted here, with this that what is the amount of aluminum and the nitrogen which is coming up. Now, you see that when you are hitting this kind of iron nitride for your analysis you see there is a peak in the nitrogen content. When you are in the matrix in between the nitrides you see that it has almost negligible amount of nitrogen. That means here there is no aluminum nitride precipitation.

So, this implies that γ` iron nitride precipitates before the aluminum nitride precipitation. That means, nitrogen in the dissolved state is making actually the different character for the growth of iron nitride. Now, how we can see that if we nitride it for longer time, for example, 20 hours and then you make the same EPMA measurements like a line and now this is the iron nitride and this is the ferrite matrix in between and now here one sees that there is a lot of nitrogen being absorbed here that is not shown here (refer to above figure). As compared to here it is negligible here one saw like lot of nitrogen that means that at a later stage, aluminum nitride precipitate. That means initially iron nitrides grow and later aluminum nitride precipitate. This is where the role of the dissolved aluminum is actually coming into picture in the influencing the way iron nitride is growing. And now in when you see that things are growing not like a layer like a plates.

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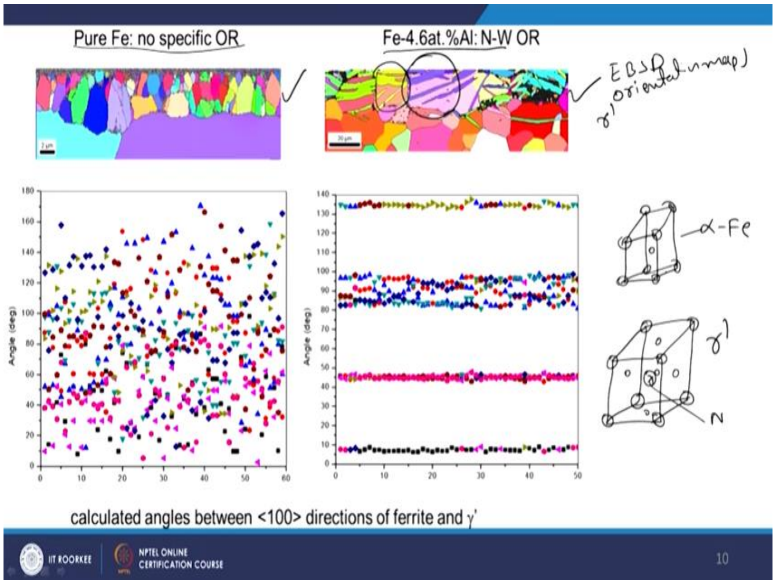

Pure Fe: no specific OR

Fe-4.6at.%Al: N-W OR

EBSD (orientation map)

γ'

calculated angles between <100> directions of ferrite and γ'

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What is shown in this slide (refer to above figure) is on top here these are the again the electron backscatter diffraction orientation maps and for the nitrided iron aluminum alloy and for pure iron. What is the meaning of orientation map here you see that you have all these plate like features are of iron nitride γ′ and these other you know the rather homogenous features are the original ferrite grain boundary.

So, with these different colors shows what is the orientation of, orientation means the crystallographic orientation, of the iron nitride and the BCC iron. This is a one grain of ferrite having some orientation that is reflected with this color one can see what is exactly this orientation and this is another grain and these are all iron nitride grains we having different orientations (refer to above figure).

These different colors mean you are seeing different plane of the iron nitride lattice on the surface. So, that is what one can think of. Now in these both cases, it is not only that they are actually unusual plate like and now whenever they are forming like this unusual plate like they are also developing always with a unique relationship with the orientation of the ferrite. Now you see in this grain, the ferrite orientation is given with one color and in that you have one colored that means one orientation of iron nitride and that changes here.

Because here now the orientation of the ferrite grain has changed, then this is coming up. This you do not see here you have one grain and in that actually all possible colors of iron nitride is shown that means, it is not bothered about what orientation of BCC iron grain is it is picking up randomly its orientation, whereas here it is picking with some relationship with the matrix that is a BCC iron.

So, that is what actually one can see, with this kind of analysis, we will not go into the details. Now, what we do is that both γ' and ferrite both are the cubic crystals system. One is of a you know the FCC based the cubic system another one is simple body center cubic. And now if you look at actually if you have a cubic structure.

For example, here (refer to above figure) I have a BCC iron and then I have a γ' that has got a FCC arrangement of iron atoms. And now, body center position is occupied by nitrogen. Now, if these two have always maintained some relation then either these planes of particularly this and this (refer to above figure) are parallel, that is what called a the crystallographic orientation relationship.

If, when the γ' is growing in α iron matrix without bothering about the way it should orient its crystal lattice with respect to α iron that means, there is no specific relationship between these two with respect to the way the crystals are oriented. That is what you see in case of pure iron. This shows that there is no specific orientation relationship that is reflected already here (refer to above figure).

But here you see that there is a specific orientation relationship between the two. Now, this already tells that whenever the things are developing with a specific relationship that means, that is the most possible or easy way to develop the γ' iron nitride with a defined relationship with the α iron matrix. That is why you see them as growing like plates.

If there is no relationship then it has no reason to grow like plates with the ferrite matrix. So, now that means, the growth of iron nitrides follow a certain crystallography of the BCC iron matrix that happens in the case of difficult nitride formers are present. That means, whenever these difficult nitride formers are present, then the nucleation of the γ' iron nitride seems to be not very easy.

That is why they look for what are the easy ways to nucleate by choosing a particular plane of the BCC iron matrix for their nucleation event that shows that there is some influence of the dissolved elements such as these difficult nitride formers in controlling the way the nucleation can happen. So, now, with this I will end this lecture and in the next lecture, we will look at what are the difficulties for the precipitation, what actually makes the speed at which an alloying element precipitates as it is nitride during nitriding will be controlled by the thermodynamics and the kinetic aspects of the process. Thank you.

Keywords- Nitriding, microstructure, crystallographic orientation.