Thermo-mechanical and Thermo Chemical processes

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Module No # 08
Lecture No # 39
Alloying Element Nitride Precipitation during Nitriding of Iron based Alloys

Greetings to everyone. I welcome you all to this lecture on thermochemical surface treatments. So, if we recap what we have covered in the last lectures, we have seen that the in the gaseous nitriding, if you have a particular alloying element in the steel, which you are subjecting to the gaseous nitriding treatment. Then depending on the character of this alloying element and its interaction with nitrogen, we can expect different types of growth pattern of nitride layer.

So, we have seen that first for iron nitride layers when they want to grow, how the presence of alloying elements would interfere with the growth of iron nitride layers. In that context we have seen if we have an easy nitride forming elements and a difficult nitride forming elements how that would influence the morphology.

And after that we have seen if we try to grow the austenite i.e. an iron nitrogen austenite on the sample surface and the presence of alloying elements how they would modify the way the austenite wants to nucleate and grow. So, now, we will look in this lecture the details of only alloying element interaction within the ferrite matrix. That means it is a purely ferritic state, the matrix remains the ferrite.

And only the alloying elements would try to interact with the nitrogen, which is coming inwardly and then try to form the nitride layers. So, in this context, we have seen that from Lehrer diagram depending on the temperature and the applied nitriding potential, we can actually tune the whether we are allowing other iron nitrogen phases to develop or not.

So, in most of the next lectures, we apply the nitriding conditions such that it will remain in a ferritic state.

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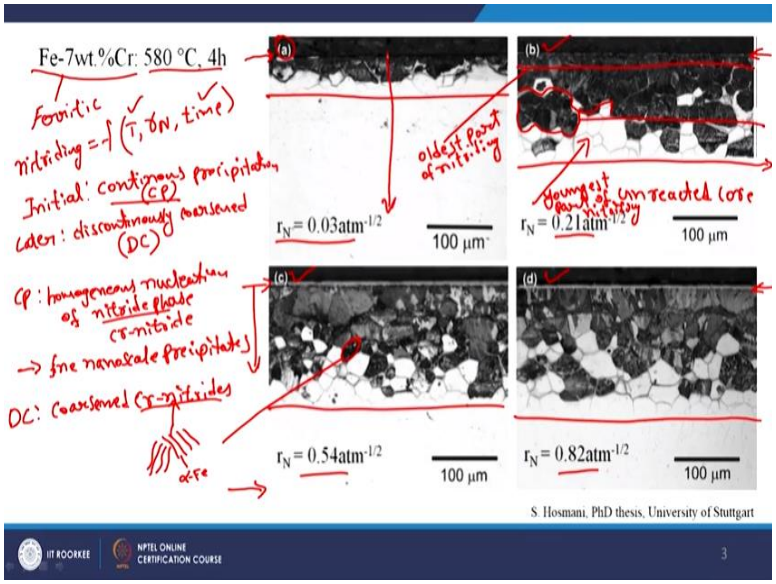

Fe-7wt.%Cr: 580 °C, 4h

Ferritic

nitriding = f (T, r_N, time)

Initial: continuous precipitation (CP)

Later: discontinuously coarsened (DC)

CP: homogeneous nucleation of nitride phase Cr-nitride

→ fine nanoscale precipitates

DC: coarsened Cr-nitrides

S. Hosmani, PhD thesis, University of Stuttgart

So, in that for example, if we take an iron chromium so, what is shown in this slide (refer to above figure) it is a binary iron 7 wt. % chromium alloy. Remember that this is actually with this amount of chromium, this is fully ferritic and then we know that the nitriding parameters which are actually a function of temperature, r_n that is a nitriding potential and the time.

We know that these are the three parameters. Now, to understand the way the different parameters influence we need to keep the other things constant. In this case temperature and the time has been kept constant. You see that it is 580°C and 4 hours. Now, what you see here, these a, b, c, d are the light optical micrographs taken from the cross-section of the nitrided sample.

So, what you are seeing here on the top, all these arrows indicate that is the surface of the sample. That is a sample surface and you are going into the sample that is from the surface into the depth somewhere you will have the core of the sample.

Now, what is the difference between a, b, c and d, as we said we are varying only the nitriding potential. So, in these cases, nitriding potential is 0.03, 0.21, 0.54 and 0.82 (refer to above figure). The first thing is you see that the layer thickness, let us say that what do you mean by layer. For example, I would say that where you see the visibility of the grain boundaries until that depth that this is the nitride layer thickness. The thickness of this layer would be about 100 or 120 µm.

And you see that this layer thickness is increasing with increasing nitriding potential. So, that means that by increasing the nitriding potential, the nitriding potential increase in the atmosphere implies that we are having actually the increased amount of ammonia in the gas mixture. So, we have a high ammonia hydrogen gas mixture, in that percentage of ammonia is being increased from this a, b, c and d.

And now other features what we see in these micrographs is at the close to the surface you have a dark appearing region and below that you have the bright appearing ferrite grains. So, what are these differences? As we know that if we look as a function of nitriding time, this top surface region of the sample is the oldest part of nitriding. This is unreacted core (refer to above figure). This region which are appearing brighter, these kinds of regions is the youngest part of nitriding. So, now what it shows is that initially something actually is developing as a function of nitriding, that is called as initial precipitation and we have a so-called continuous precipitation region. These all bright appearing i.e. this youngest part that initially what develops is called continuous precipitation layer. And then what you see as a later developing i.e. this kind of regions the oldest part is called as a later developing that is discontinuously coarsen region.

This is called as a CP(continuous precipitation) with abbreviation, this is usually termed as a DC(discontinuous coarsening). You have this continuously precipitating layer development initially and then later some other reaction starts i.e. the discontinuous coarsening and that is what leading to this dark appearing regions after etching. Now what is the difference between this continuous precipitation and discontinuous precipitation?

So, as one can see that initially when your nitrogen is entering into the sample what develops is a very continuous precipitation this implies of a homogeneous nucleation of nitride phase. This is usually always known as for example, in this case nitride phase can be thought as chromium nitride. So, that means actually you have a homogeneous nucleation means the rate at which the nucleation of this nitride happens is same everywhere in the material.

That means, it homogeneously develops as a very fine, the precipitates are in this case would be very fine nano-scale precipitates. Now, if you look at that discontinuous coarsen regions i.e. the dark appearing regions, which we see close to the surface, we have coarsened chromium nitrides.

So, if we look closely into these dark regions by using a high-resolution microscopy like a scanning electron microscopy or a transmission electron microscopy, we would see something like a lamellar structure.

If we look in a very high magnification you see the development of something comparable to a pearlitic microstructure. You have this (refer to above figure) white one the ferrite, and the red one the chromium nitrides. Like this alternate lamellar will be developing here. This is the way the microstructure evolves, if we have a chromium-alloyed sample. Now, we are already seeing that these are already the coarsened chromium nitrides.

And we will see what is the problem with this kind of discontinuous coarsening reaction. In the next slides now, we look actually the how the nitrogen profile evolves that means, from the surface to inside we want to see how the nitrogen concentration is changing as a function of depth because that is where we will know the kinetics of the process.

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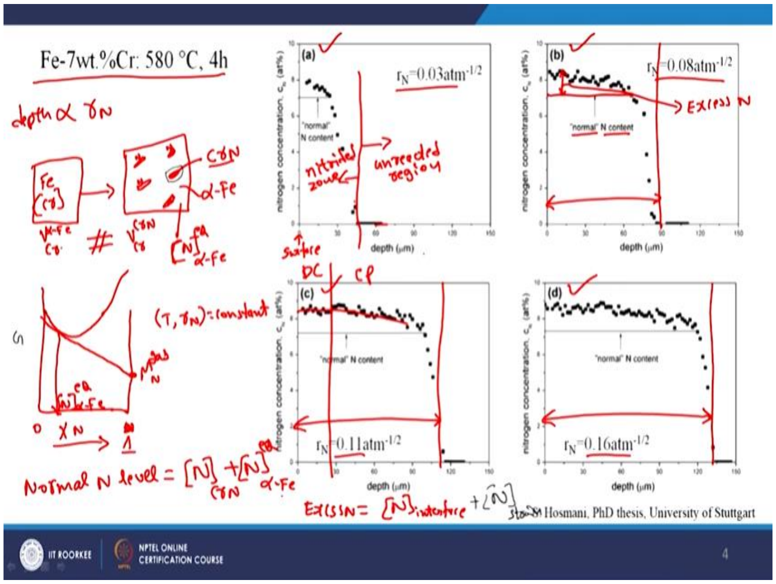
Fe-7wt.%Cr: 580 °C, 4h

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So, what are shown in this slide (refer to above figure) is again the same iron 7 wt. % chromium here you have a, b, c, d and these 3 and 4 are for the different nitriding potentials as one can see here the increase in nitriding potential and then you see the development of this measured nitrogen concentration as a function of depth. So, this zero depth implies this is the surface of the sample.

And then you are going into the sample. You see that the nitrogen concentration is close to about 8 at. % and then going down and then you see that it is rather zero in the core. If you remark here (refer to above figure), this side of the region is the unreacted region, and this side is the nitride zone.

So, again you see the same as what we have seen from the light optical micrographs, the thickness of this nitrided region i.e. this depth is also increasing with increasing nitriding potential. And we will see why this is happening later, but what we see is that, the nitriding depth is proportional to the nitriding potential. You see that there is a, some sort of proportionality between the nitriding depth and the nitriding potential.

So, now in the previous slide we have seen that close to the surface you have something called the continuously precipitated regions, like say CP region and discontinuously coarsened region. So, if we superimpose the microstructure you see that close to the surface you always have discontinuously coarsen region, and you see that nitrogen concentration is not really changed from continuous precipitation to discontinuous coarsening region.

If that was the case we would have seen the some difference here. but that situation we see in some alloying elements that I will discuss in the next slide. So, now I want to draw your attention to another feature which is shown in all these a, b, c, d pictures. You see one level is indicated, this (refer to above figure) line and it is called as normal nitrogen content.
What is the meaning of this? We know that for example, in the case of 7 wt. % chromium, in case of iron and chromium being atomic weights are quite close, this is almost equal to also atomic percent. So, what do we expect as a level of nitrogen by under some assumptions i.e. the normally expected nitrogen? Initially we have a sample this (refer to above figure) as iron and chromium in the dissolved state and it is ferritic.

Now, let us say that after the nitriding, we assume that complete precipitation of chromium as its nitride for example, CrN. Suppose these are all now the chromium nitride and then you have this CrN is embedded in the α iron. This is the ferritic matrix that is a α iron (refer to above figure).

And now you can count actually what is the total amount of nitrogen associated with the CrN that would be same as the amount of chromium if you assume that all the chromium as precipitated out as CrN. So now the remaining α iron also will dissolve some amount of nitrogen. This matrix will dissolve some amount of dissolved nitrogen. I show it with a square bracket with indication of α iron (refer to above figure) that means it is a nitrogen which is dissolved in α iron.

How do we know this amount? In this case, we have applied some temperature, in this case 580℃ and a constant nitriding potential. So, we have seen in our first lecture that temperature and nitriding potential will set the equilibrium level of nitrogen which can be dissolved in pure iron that means a fully ferretic iron.

So, that we have seen with the help of the condition can be imposed from the thermodynamics. As if we look if you plot the Gibbs energy of α iron and as a function of nitrogen content, for example X_N and then it will be going from some concentrations and somewhere here you have 100% nitrogen axis (refer to above figure), and now you have some trend for the Gibbs energy curve.

This is the 100% nitrogen axis here, $X_N = 1$ and it in zero, this is a pure iron here. We know that the chemical potential of nitrogen in the gas atmosphere can be kept constant by fixing the temperature and nitriding potential. Now if we have a T, r_n , both kept constant. That means we are fixing the chemical potential μ_n in the gas phase (refer to above figure).

Now, for the chemical equilibrium between two phases, in this case gas and the solid, we impose that the chemical potential of nitrogen should be same, that can be read with a tangent. Placing a tangent to this Gibbs energy curve, with this as an intercept as this one is constant. And wherever you see this (refer to above figure), where it makes the tangency with the Gibbs energy curve that is so called equilibrium.

So, this is the nitrogen quantity expected in α iron at equilibrium. So, this can be obtained individually by doing experiments with the pure iron samples. So how it this can be done, you take a very thin foil of pure iron and you start to nitride it at a constant temperature and constant nitriding potential condition and then you keep tracking the amount of nitrogen taken up.

So that can be done very accurately by just taking the weight of the sample as a function of time. And then the weight starts to increase and then it comes to saturation level that implies no more nitrogen is being taken, that is what is the equilibrium level of nitrogen, which can be taken up by the solid at the given temperature and nitriding potential.

So, knowing the amount of chromium, you know the nitrogen bonded with CrN and the sum of these two is called normal nitrogen level. The content is given as nitrogen bonded with nitride particles as CrN and this depends on the amount of chromium. That amount plus nitrogen which is dissolved in the α iron matrix that is in equilibrium with the outer atmosphere.

Now you see the observed nitrogen content. This (refer to above figure) is the measure nitrogen content and this is the level expected under assumptions of some kind of a situation. The gap between this normal level and this level is called this gap is called excess nitrogen. So, why this excess nitrogen comes? I will now explain that.

What we can think of the reasons for this excess nitrogen? One region we can think of is when you form these chromium nitride precipitates in the ferrite matrix; you have interface between the ferrite matrix and the nitride particle. Nitrogen can adsorb at these interfaces.

Now that can be an additional nitrogen that one can consider. So that can be written as excess nitrogen can be due to N interface (refer to above figure) that means it is absorbed at the ferrite matrix and nitride particle interface. And then the other quantity which we can think is, we have said the N equilibrium level of the α iron that we are getting it from the experiments on pure iron, that will be the matrix of pure iron will be only fully ferrite, but in our actual samples of this kind of alloys when you form these nitride particles, there will be misfit strains between the particles and the matrix. Because the chromium when it is in the dissolved state in the ferrite, there is a certain volume occupied by chromium in the dissolved state in α iron.

And after the precipitation, then volume occupied by chromium in the chromium nitride, this will be different, these two are not equal. Because of this misfit, you introduce a strain fields around the particles. So, we will have a misfit strain field around the particles. These are like the ferrite matrix is strained in the immediate surroundings of the particles.

Because of that strain you change the Gibbs energy of your matrix i.e. the ferrite phase. This is what we have shown here (refer to above figure). This is a Gibbs energy for a strain free iron nitrogen ferrite. Now due to the strain fields we will change this curve because of that your common tangent now will intersect at a different location and that would lead to the increased level of nitrogen that is called as a N strain.

Now these two quantities can actually contribute as excess nitrogen and this N interface that depends on the volume fraction of nitrides and the size of the nitrides. So, that would decide actually the overall interfacial area and that’s why the amount of nitrogen. So, how to obtain quantitatively because what you can measure from these kinds of measurement is the total nitrogen.

And here we are talking about four types of nitrogen which we can think of should be present and this is the total amount all these quantities can be present. And this can be extractable all these quantitatively from the so-called nitrogen absorption isotherms. We will not be discussing that in this lecture.

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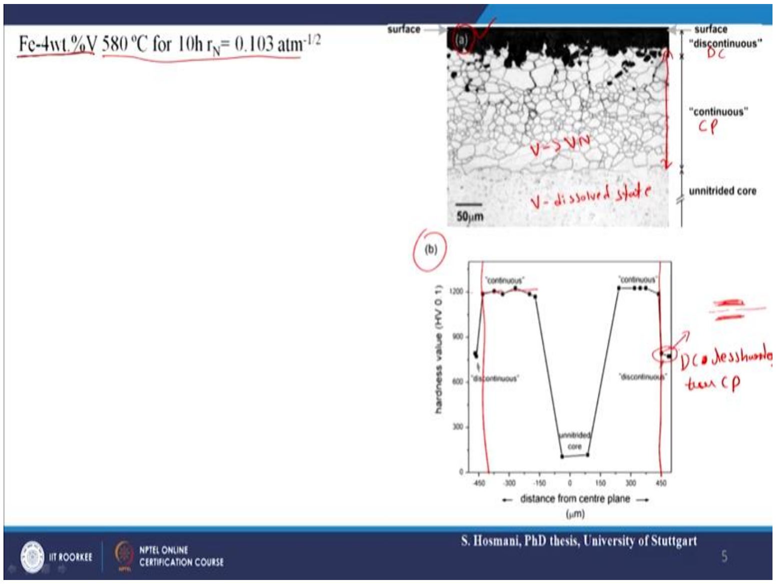

Fe-4wt.%V 580 °C for 10h r_N= 0.103 atm$^{-1/2}$

S. Hosmani, PhD thesis, University of Stuttgart

If you look for example, iron vanadium now. We are now switching to a different element that is iron vanadium. Again the temperature, time and the nitriding potential applied in this samples as this shown here (refer to above figure) and what you see here, is the light optical micrograph the cross sectional micrograph.

Similar to iron chromium you also see that there is a CP region and a DC region close to the surface and you have a unnitrided or a unreacted core that is here (refer to above figure). You see that you will be able to distinguish these regions, you see that when you do the etching with natal, this unnitrided core in that region we are unable to reveal the ferrite matrix grain boundaries.

Whereas in the nitrided region we are able to reveal that. That is because in this unreacted core vanadium is present in dissolved state. So, that will actually modify the way your etching reaction happens whereas, in this nitrided region vanadium is precipitated, vanadium has become vanadium nitride for example, that is where actually this etching reaction is different that allows nicely distinguishing these regions.

Now if you look at this picture (b) this is below this light micrograph, is the what is the level of hardness as a function of distance away from the center of the sample. For example, this is the surface of the sample and you are going into the center you can interpret like that or this is the center of the sample I can go to the positive side and negative side to reach the surface (refer to above figure).

So, you see that the surface hardness that is this region or this region (refer to above figure) because this sample is a thin plate having the two surfaces. So, if you have a cross section like that (refer to above figure), this is a center plane and here you have a DC region on the both sides and below that you have a continuously precipitated region.

And important point to note here is this discontinuous regions less harder than CP, the discontinuously coarsen region shows less hardness than CP. You see that here, this continuous precipitated region has about 1200 HV level of hardness in this region and in this region close to the surface where we have a discontinuous coarsening there is a drastic drop in the hardness level.

So, that is what actually shows that in this region already there is a coarsening of the precipitates, discontinuous coarsening. So, because of coarsening of the precipitates their precipitation hardening effect has reduced so, that is leading to the decreased hardness.

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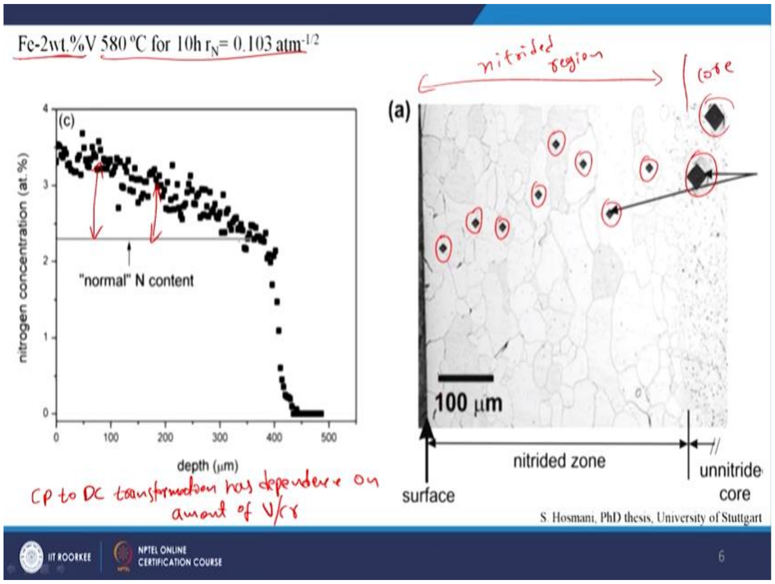

Fe-2wt.%V 580 °C for 10h $r_N = 0.103\ atm^{-1/2}$

nitrided region

core

CP to DC transformation has dependence on amount of V/Cr

S. Hosmani, PhD thesis, University of Stuttgart

So, now if we move on to the comparison with the similar situation like in iron chromium. Now in this case it is iron 2 wt. % vanadium and these are the nitriding conditions. What you see is also there is a so called excess nitrogen (refer to above figure). This is the normal nitrogen level and this is the excess nitrogen level and we will do in tutorials how to calculate normal nitrogen content.

And what you see here (refer to above figure) is, these are all the hardness indents, which are now quite small as compared to these ones. Larger the size that means it is a less harder. This is the core and this is the nitrided region (refer to above figure). As we have seen in the previous slide with 4 wt. % vanadium under the same nitriding conditions you see that 580°C, 10 hours and r_n of 0.1, we have seen this appearance of this discontinuously coarsen regions. That is where we have a lesser hardness.

This is not the case for the same conditions when you have only 2 wt. % vanadium. You see that there is no discontinuously coarsen regions visible at the surface. This is the surface and you are going into the sample and you see only continuously precipitated region (refer to above figure).

That means CP to DC transformation has dependence on amount of vanadium or chromium. As we have seen in the previous slide, because the discontinuous coarsening decreases the hardness drastically, so we would like to avoid this discontinuously coarsened region coming at the surface because our whole intention is to get highest hardness to the surface.

So, that is where actually, it is important to optimize the chemistry and conditions such that we will have the highest hardness at the surface.

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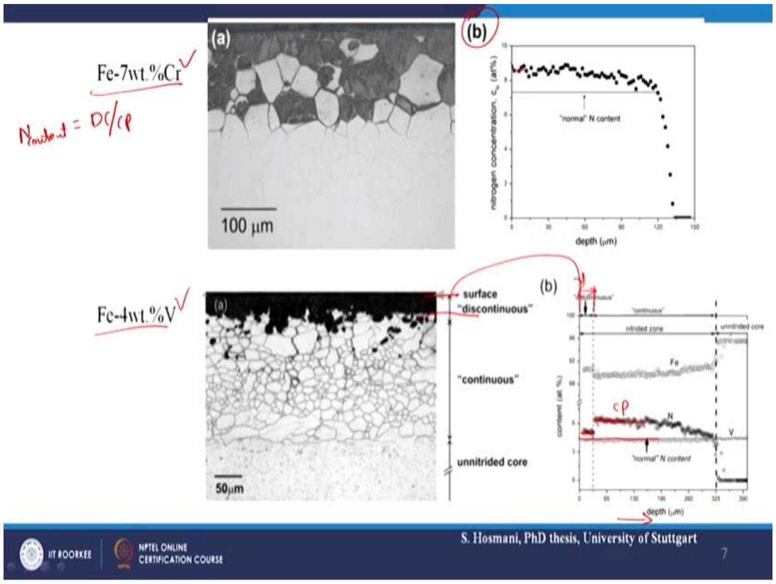

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There is one difference between iron chromium and iron vanadium. In both the cases depending on the amount of chromium or vanadium, you have a discontinuously coarsened regions i.e. these are dark appearing reasons (refer to above figure), but if you look in the case of iron chromium the nitrogen content is same in the DC and CP regions.

N content is same for DC and CP. But here in this case of iron vanadium, if you look here in the composition profiles you look at the nitrogen concentration as a function of depth, you see that there is a decreased level of nitrogen. This is the discontinuously coarsened region close to the surface (refer to above figure). So, in both the cases you see decreased darkness, but in case of iron vanadium you see also the decreased level of nitrogen.

And that can be due to the excess nitrogen somehow reduced here after discontinuous coarsening because we see that it is still above the normal level, this is the normally expected level (refer to above figure) and after discontinuous coarsening it is lesser as compared to in a continuous precipitation region. This entire region is continuous precipitation. But it is still higher that means excess nitrogen capacity has reduced here.

And that can be understood based on the coarsening of the precipitates. When you have a precipitate coarsening, it will reduce the overall precipitate matrix interfacial area and that will reduce the amount of nitrogen which can be taken up. Now, in the over view lecture, we have also said that thermochemical surface engineering treatments have to be tuned not only to get the highest hardness to the surface, but also to get a desirable residual stress state, often we need compressive residual stress states.

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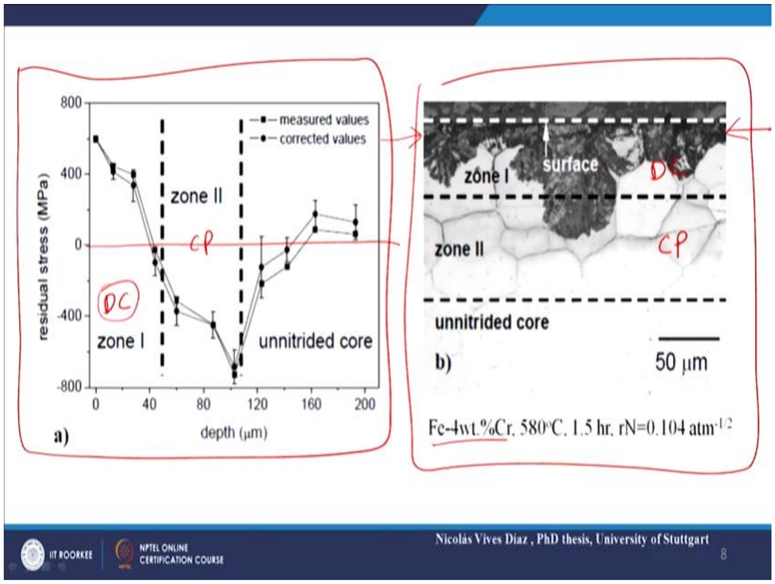

Fe-4wt.%Cr, 580°C, 1.5 hr, rN=0.104 atm$^{-1/2}$

Nicolás Vives Díaz , PhD thesis, University of Stuttgart

So, now, if you see in this picture (refer to above figure) what shown here is this is the light optical micrograph of iron 4 wt. % chromium with has the nitriding conditions and this is the white dashed line is the surface of the sample and you have this DC region i.e. a zone 1, and the zone 2 is CP region. And now if we look at what is shown here in this side (refer to above figure) is the residual stress level at a different depth below the sample.

If you look actually the residual stress if we start to measure as a function of depth that can be done with a diffraction technique, which we will not go into the details, then you see that in the zone 1 that is actually the DC and this is the CP and this is the unreacted core. You see that the stress level is zero in the core and what you see is that in the DC region, you have the tensile residual stress.

This is the surface of the sample right and here you have generated now the tensile residual stress and the CP region has a compressive is residual stress. You see that now by development of this discontinuously coarsened regions not only reduces the hardness, but also introduces the tensile residual stresses which are not at all favorable for a good fatigue resistance.

Because all the cracks start to initiate and travel into the sample from the surface so, we always would like to have compressive stresses at the surface. So, that way, this is also very important to keep in mind that it is not only the hardness level what we are trying to optimize also the residual stress level also needs to be optimized simultaneously. Now, what we have seen is about the situations in which this chromium and vanadium where the element actually is precipitating quite quickly and we were farming actually a sort of a layers of nitrided region.

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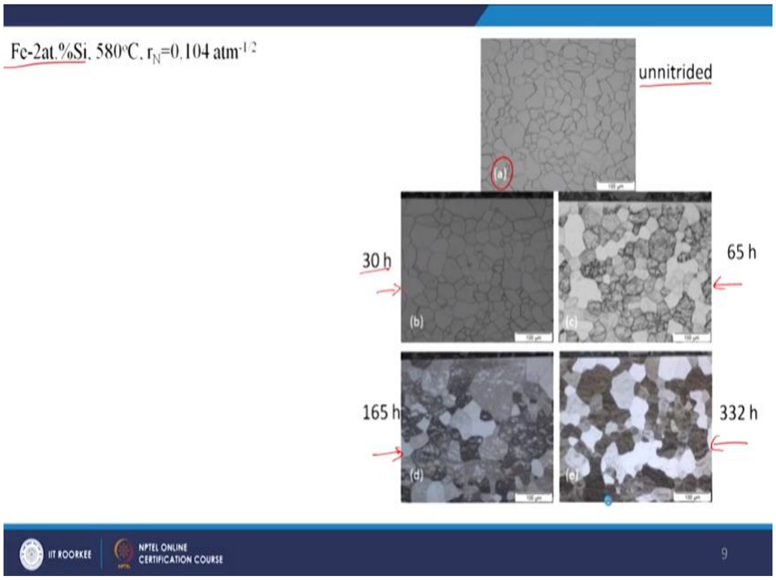

Fe-2at.%Si, 580°C, r_N=0.104 atm$^{-1/2}$

But now you have a different type of elements, for example here I will be picking up this iron silicon. So, if you add a silicon into the steel and then if you start to nitride what happens. Now I am showing these things because if you remember in the previous lectures, we have seen that chromium and vanadium show some character comparable with respect to the way iron nitrides tries to grow.

And the silicon and aluminum have shown a very different pattern. Now, the same situations same kind of contrast, we will able to see when we try to do the nitriding in the ferritic condition. So, what you see here is (refer to above figure), you have this a, b, c, d, e and these are the are light optical micrographs for these iron silicon samples. This is a unnitrided sample (a in above figure), just as a reference you know the microstructure.

Then this is after 30 hours of nitriding, this is after 65 hours, this is after 165 hours and this is after 332 hours. What you see is like in case of iron chromium and vanadium here you are not seeing any distinguishable regions as a function of depth, you know that there etching contrast and you see grain boundaries and you do not see grain boundaries, something like that.

You see homogeneous etching contrast. You see that here there is a change in the etching phenomena, but that looks similar throughout the depth and that is what you see also with increased time. So that implies that there is something happening but that is happening quite homogeneously.

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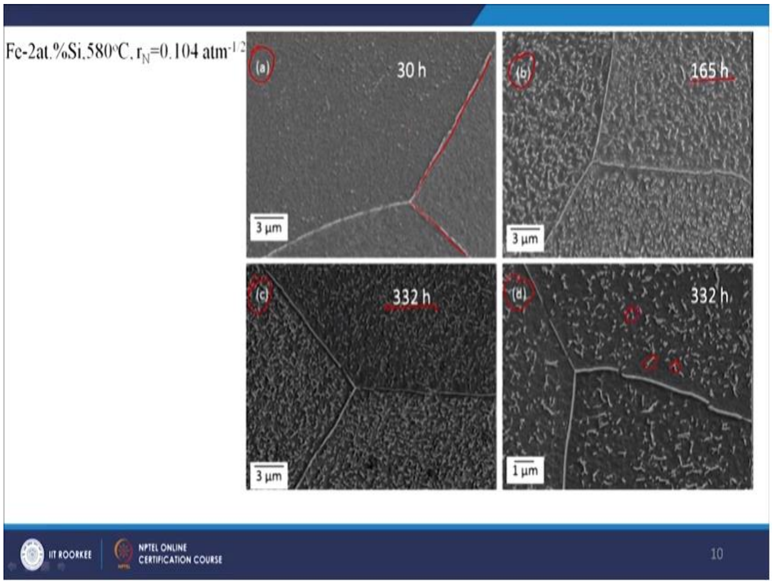

Fe-2at.%Si,580°C, r_N=0.104 atm$^{-1/2}$

If you look in more detail with scanning electron microscopy, what are shown here a, b, c, d are the scanning electron micrographs (refer to above figure). You see that after 30 hours you have some small precipitation are developing with something happening along the ferrite matrix grain boundary. And with increased time to 165 hours you see that now they start to develop more and after 332 hours you have more density and this is higher magnification picture of the 332 hours you see also something developing along grain boundaries.

And this kind of observations were not there for iron chromium and vanadium and here you see a distinguishable precipitate growing. So, if you look the hardness how the hardness is changing, if you remember for the iron chromium and vanadium there is a significantly high hardness to the nitrided region and sudden drop into the core of the sample.

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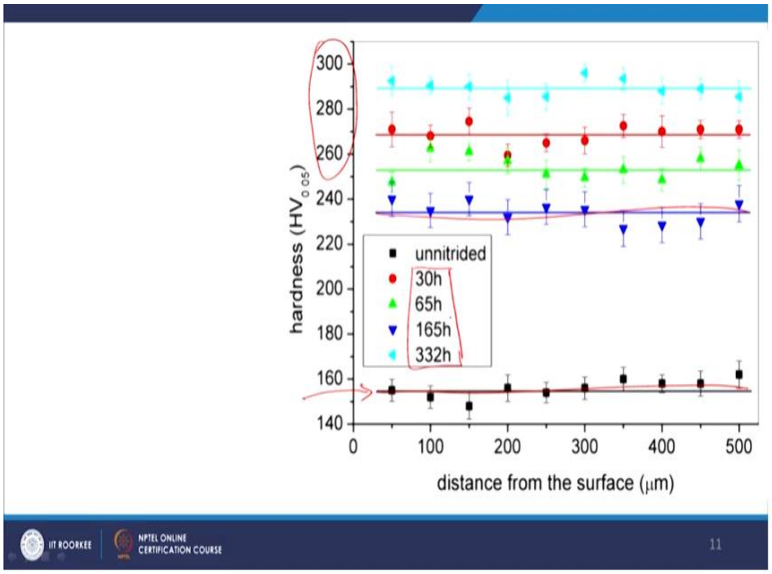

But here what you see is this (refer to above figure) is the hardness level as a function of depth in the sample. The level of hardness is quite same throughout the thickness of the sample. That means it is something like a bucket filling kind of effect and also the level of hardness if you see it is only a marginal increase as compared to a unnitrided. This the base level hardness as compared to that, you have only a small increase in the hardness.

That is understandable because we have seen in the previous slide, the precipitates are coarser and why they are Coarser because reaction is progressing very slowly. You look at these nitriding times, there way orders of magnitude higher nitriding times than in case of iron chromium or vanadium.

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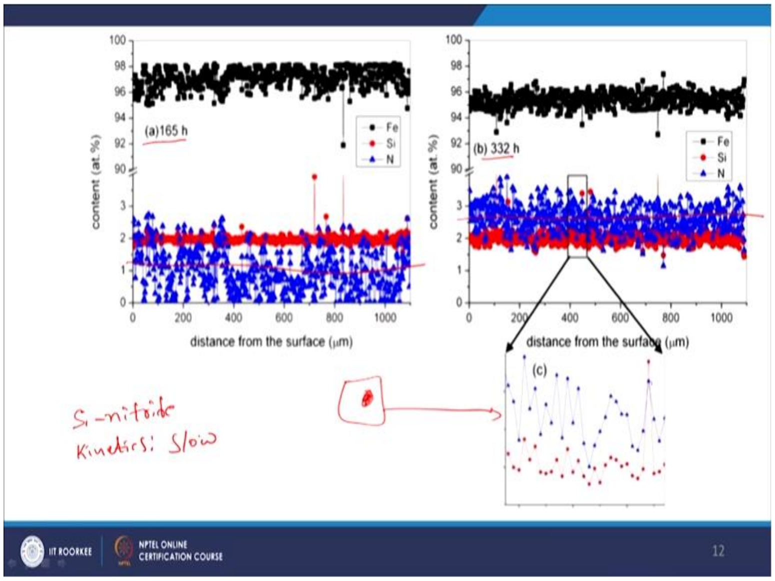

So, the same kind of results you can see also if you look at the concentration of nitrogen as a function of depth. This is after 165 hours (refer to above figure). You see if you look at this blue as a nitrogen concentration that homogeneous. There is a scatter that it is a you should not worry about it because you have a coarser particle of nitrate in the matrix.

Now, it is possible that when your electron probe hits the more the nitride particle there can be an increased peak in the nitrogen content and that is what you see that even after more time, if you look at this is the average level that has gone up here, but homogeneously. If you look closely as this analogy, if this is the nitride particle, then if there is a more nitrogen then we should also see more silicon. When there is the peak in the nitrogen content you also see peak in the silicon content.

So, in this case you are forming silicon nitride precipitates, but the kinetics are extremely slow. So, that is what we can see from this (refer to above figure). So, now we with this I would like to summarize this lecture. We have seen that the depending on the type of element for example, the chromium and vanadium kind of elements, which we know we have classified them earlier in the lecture as strong nitride formers, they try to interact very quickly with nitrogen and leading to a significant increase in the hardness and the hardness depth profile will be rather sharp.

You have a hardened region and a unreacted core which is soft that is usually desirable for the applications. Whereas, you have other class of elements for example, here we have discussed about silicon and the same holds with also sort of for aluminum.

You see that the precipitation is rather slow and this actually leads to very slow kinetics and a much smaller hardness because of larger size of the precipitates which evolve. With this I am at the end of this presentation, and we will meet for the next lecture with a discussion on how we can interpret the kinetics of nitriding from the way the layers are growing. Thank you.

Keywords – Iron, chromium, nitride, precipitation, hardness.