Thermo-mechanical and Thermo Chemical processes

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Module No # 08
Lecture No # 38
Duplex and Dual Phase Microstructures through Nitriding

Greetings to everyone. So, I welcome you to this new lecture on gaseous nitriding of iron based alloys. So, in the last lecture, we have discussed about the influence of different alloying elements which are added into the steel on how they influence the growth of iron nitride layers.

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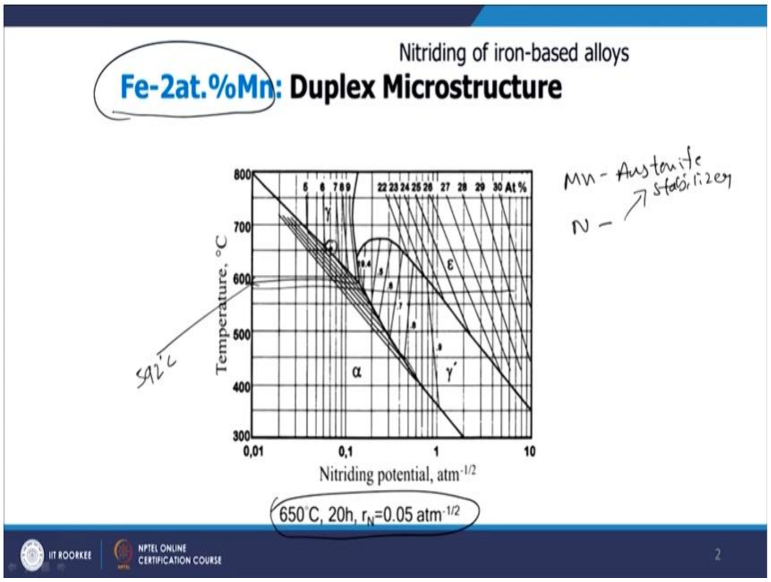

Nitriding of iron-based alloys

Fe-2at.%Mn: Duplex Microstructure

650°C, 20h, r_N=0.05 atm$^{-1/2}$

So, as one can see, we have discussed about this (refer to above figure) Lehrer diagram, if we are carrying the nitriding experiments in this (refer to above figure) region of phase diagram. So, that is where we have either γ′ or ε iron nitride can develop. So, we stayed below this temperature this about 592°C, that is the eutectoid the temperature of iron nitrogen system. That means, we are not allowing any austenite to nucleate in those treatments.

So, we discussed in the overview lecture that carburizing is always carried in the austenitic region, because of the reasons that it can take up huge amount of carbon and that can lead to development of martensite when we quench it. However, there are also examples where nitriding can also be used in the austenitic state and that is what we will be discussing in today's lecture.

The model system which we will be discussing is about iron with 2 at. % manganese. So, this alloy is such that it remains ferretic at the nitriding conditions. So, now, we look at the nitriding conditions at 650 °C and with a nitriding potential of 0.05 so, that will be at this point here (refer to above figure). So, we are just into the γ region of the Lehrer diagram. So, it is expected that we should allow the growth of austenite.

So, one can see in this case, we are taking manganese which is known to be an austenite stabilizer and we know that nitrogen is also austenite stabilizer. So, that means, this Lehrer diagram is known to be applicable truly only for pure iron, but now being the manganese having austenite stabilizing effect so, we expect this phase borders to be shifting towards lower nitriding potential.

That means, this point what we have chosen could be already into the γ region when it comes to the iron manganese alloy.

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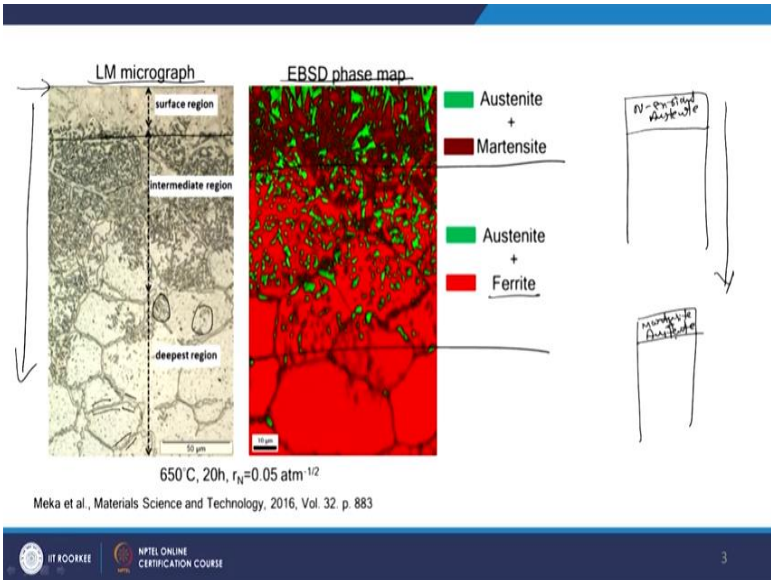

650°C, 20h, r_N=0.05 atm$^{-1/2}$

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So, now, what kind of microstructure it will lead to develop when we nitride such an alloy. That means, we have a 2 wt. % manganese. What is shown in this slide (refer to above figure) is, this is a light optical micrograph and what you see here is the surface of the sample and what you are seeing is as a function of depth, how the microstructure starts to develop (refer to above figure).

So, you can see that this is the deepest region that is the youngest part of the nitriding and you see some features growing along the ferrite grain boundaries. One can see that there is some phase growing along the ferrite grain boundaries and as you move towards the surface that means, as the nitriding continues as we move to the close to the surface that becomes oldest part of the nitriding you start to see that the features also start to develop within the ferrite grains.

And as you come even closer than this density within the grains increases, and when you come to the surface, you see that you have a closed layer that means a fully one type of a phase and with some sort of a two-phase region below that. So, one can say that you have a surface region, intermediate region and deepest region to distinguish these features. Now, as we have started the experiments in such a way that we expect the growth of austenite and to see whether what kind of phases are present.

What you see on this right side is the electron backscatter diffraction phase map (refer to above figure). So, this is a technique in which we will be able to distinguish the phases based on their crystal structure. So, I would not go into the details of the technique, but what you see in this picture is the different phases which have been discerned based on their crystal structure, you have the austenite that is what is shown with this green color.

And you have a martensite that is shown with this relatively dark red color and this bright red color belongs to the ferrite. So now what you see here is in this region you have a austenite + martensite microstructure and below that you have a ferrite + austenite (refer to above figure). So, such a kind of a region. And along the grain boundaries what we are seeing in the deepest region in the light microscope that is actually the austenite growing along the ferrite matrix grain boundaries.

So, this microstructure is rather very different if you look at under identical conditions if we nitride the pure iron and then what we expect is as a function of depth in the microstructure a layer of nitrogen enriched austenite which a very clear demarcation between a nitrated region and a un-nitrated core and this (refer to above figure) nitrogen enriched austenite upon quenching can partly become martensite.

So, at the max what we expect is a martensite + austenite layer at the surface. So, we do not see this kind of evolution of a duplex microstructure where the very fine austenite particles are growing within the ferrite matrix. So now why such a microstructure evolves when we have austenite stabilizing element.

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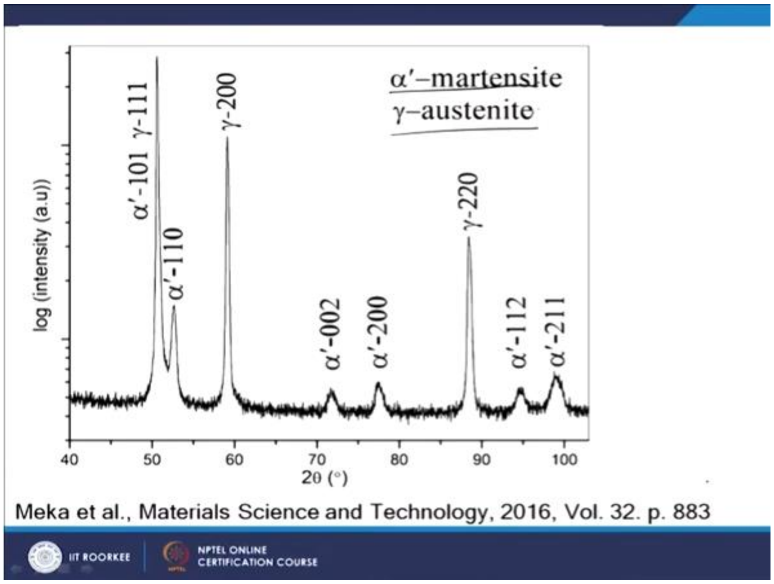

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So, before we discuss that if we look at what exactly is present at the surface region, we have a EBSD phase map where we are able to discern what is presented the surface. So, we know that it is austenite + martensite and the same thing we can see also with a X-ray diffraction (refer to above figure) what is plotted is a the X-ray intensity as a function of the Bragg angle or a diffraction angle.

What you see is the presence of martensite and austenite and in principle one can calculate the lattice parameters of this austenite and martensite and then estimate actually what should be the amount of nitrogen content. So, this I will give it as a tutorial problem where we will be able to utilize the available data and how lattice parameter changes as a function of nitrogen content for austenite and martensite and now from this measured data one would be able to use that to get the details.

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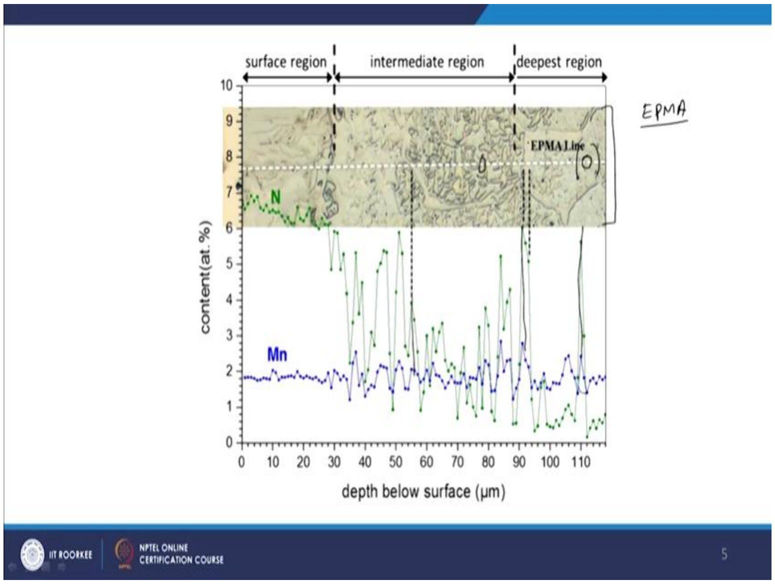

So, now, if we look at compositionally actually what is happening as a function of depth. So, what is shown in this slide (refer to above figure) is, you see here this is a light optical micrograph, and what you see here is the surface of the sample and we are seeing the cross section. So, that means, we are going into the sample along this wide dashed line along which actually the composition measurement has been carried out using a technique called electron probe micro analysis.

So, again we will not go into the details of the technique, but what you see is you have a surface region which we have discerned in the previous micrographs where we have a homogeneous contrast, you have a homogeneous nitrogen content and in this intermediate region, you see that there is a large fluctuations in the nitrogen content. And in the deepest region, you see the grain boundary phase that is austenite and you see the enrichment of nitrogen there.

And if you look more closely what is happening with the manganese content, again in the surface region you see that manganese content is homogeneous at the level expected based on the amount of manganese in the initial alloy. But later you see that wherever there is a manganese enrichment there is a nitrogen enrichment there is also a manganese enrichment, if you look at this point or if you look at this point (refer to above figure).

You see that there is an enrichment in both manganese and nitrogen and these enrichment regions coincide with the austenite particles in the microstructure. So, that means, initially you have a manganese which is homogeneously present in the ferrite matrix and as the nitrogen comes in, so, it tries to grow the austenite by partitioning the manganese.

So, it means manganese and nitrogen enrichment has to happen simultaneously in order to nucleate the austenite. So, you see that in this process, you always create a manganese depleted region around every austenite nuclei, and that is where actually a new austenite cannot grow. So, it leaves some space and then a new austenite grain grows. So, this is the mechanism which makes the development of this (refer to above figure) kind of a duplex microstructure.

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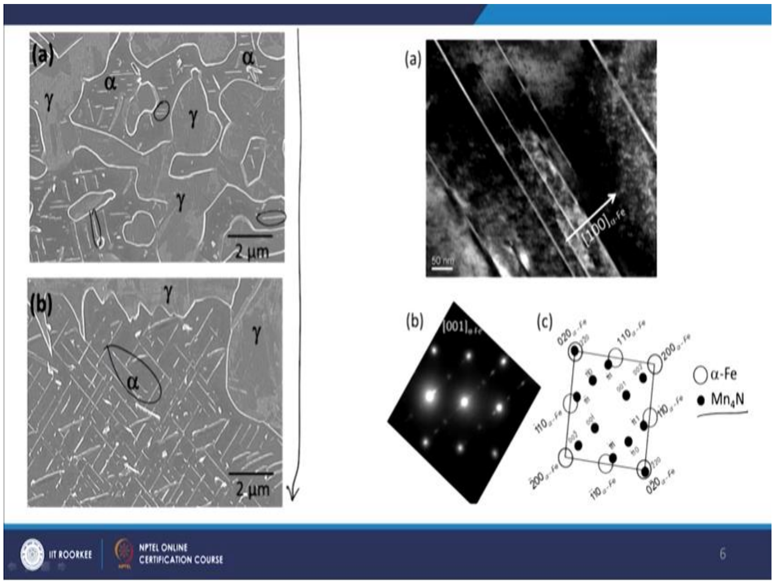

So, until now we have only the microscopic features But now, if you look into the detail with a high resolution scanning electron microscopy or transmission electron microscopy, what is shown here (refer to above figure) is that these are the scanning electron micrographs. So, you see that there is a γ regions and there is a ferrite region in which the γ regions are growing.

And you see there are some very fine precipitates which are like a platelet kind of features and that you can be seen more pronouncedly, in the deeper region (refer to above figure). So, this is a grain boundary γ phase and within the ferrite grain in which we are unable to see anything in the light micrograph, but you see that there are some precipitates and if you look closely in the transmission electron microscopy to characterize what is the crystal structure of these precipitates.

Then after analyzing what we can see is that there is a presence of manganese nitride Mn_4N that is developing in the ferrite matrix with some crystallographic orientation relationship with the matrix. So, that we will not go into the details, but only you can see that now,in this bright field image, it is the TEM bright field image, you have these Mn_4N precipitate platelets and what this arrow indicates is along the normal to this arrow you have the 100 planes of your BCC ferrite matrix along which your nitride Mn_4N platelets are growing (refer to above figure).

So, with this we will be able to conclude that as a nitriding process runs initially you start to develop manganese nitrides in the ferrite matrix and followed by the growth of austenite.

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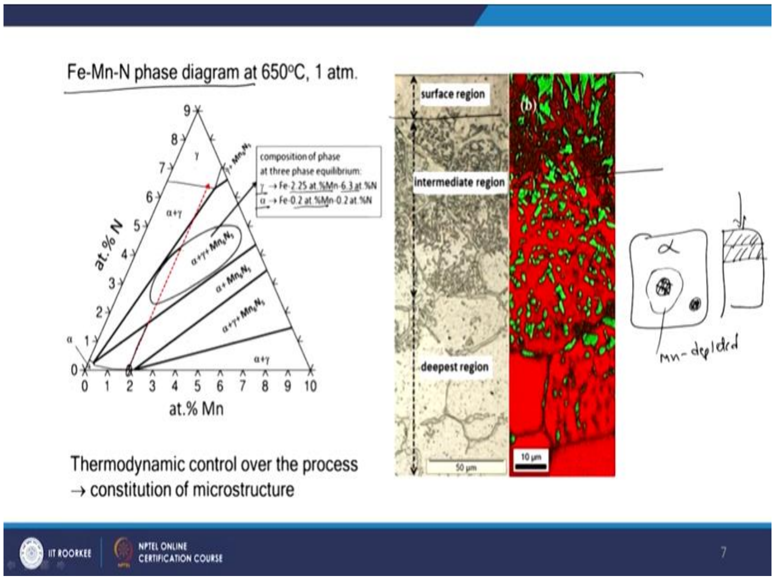

Fe-Mn-N phase diagram at 650°C, 1 atm.

composition of phase at three phase equilibrium:
γ → Fe-2.25 at.%Mn-6.3 at.%N
α → Fe-0.2 at.%Mn-0.2 at.%N

Thermodynamic control over the process
→ constitution of microstructure

Now, can we understand this development from the equilibrium thermodynamics, because these systems are simple as compared to the commercial steels. So, here we have a ternary system (refer to above figure) a binary iron manganese alloy and in which you start to add nitrogen into it that means you are developing a ternary alloy. So, what is shown in this slide is, it is an iron manganese nitrogen phase diagram at 650 °C and one atmospheric pressure.

So, we will not go into the details of the phase diagrams at this stage but I will definitely put one tutorial where you will be able to understand how to read the compositions in a ternary phase diagram. You have an iron-manganese binary on this side and you have an iron and nitrogen binary on this side and here you have a manganese and nitrogen binary (refer to above figure).

So, here you do not go up to the 100 percent manganese or nitrogen, it is only portion of the iron manganese nitrogen phase diagram. So, we start with an alloy having about 2 at. % of manganese that is the initial alloy and you start to add nitrogen into that and then the alloy composition goes through this red dashed arrow (refer to above figure). As we increase the nitrogen content, this is how actually we travel in this composition space.

So, now, what information we can extract from this is, what kind of equilibrium products are expected to develop as the nitrogen content increases. So, one can see that initially it should it should form a ferrite matrix with one kind of a manganese nitride and as you cross further the nitrogen contain then it is expected to nucleate the γ phase. The ferrite with a austenite and this nitrides (refer to above figure).

And if we go further, we expect to see alpha + γ phase and then if you go further you form a fully austenitic phase. So, how we can discern these things in the actual microstructure is the base manganese content would be the deepest region in the microstructure. So, what you see here (refer to above figure) in the microstructure, somewhere in the deepest region you will have no nitrogen that means, that is where we are having the only the base material.

And now, as you add the nitrogen content, we are travelling up here. So, the nitrogen content goes up and now you come to the surface. In this way, we can see that in the deepest region, we have a ferrite with manganese nitride and then you start to see the development of this intermediate region where you have a austenite ferrite and having manganese nitrides in the ferrite matrix.

And then as you come closer to the surface, you start to see that you have a closed layer of austenite that means, it is a fully nitrogen austenite which develops and then what you are seeing as a martensite is coming because after the nitriding treatment these samples have been quenched into water. So, that is how actually one can see that you have a portion of the austenite as transformed to martensite.

So, this way we are able to generate the martensite-austenite, ferrite-austenite such duplex phase regions as a function of depth in the sample. This illustrates that by using the thermodynamic information that means by looking at the phase diagrams of the materials which we are actually doing the nitriding and by understanding what kind of phases are expected as we increase the nitrogen content we will be able to at least have a prediction on what kind of phases can develop.

So, with that, one would be able to actually design the chemistry of the base material in such a way that you can generate a unique microstructure. In this case having a small amount of manganese and if you go into this three-phase field, if you look here (refer to above figure), what is given here is the composition of austenite and ferrite. One can see that there is an enrichment of manganese in the austenite and nitrogen and the depletion of manganese in the ferrite matrix.

So, such equilibrium situation certainly demands that you have an isolated nucleation and growth of austenite particles in the ferrite matrix. The reason being you have a ferrite matrix and now if you grow the austenite as expected from this equilibrium, then actually you create a manganese depleted region around it. So, you will have a region where manganese is depleted. That is where you cannot have further growth of this austenite or the new nucleation of the austenite and then you have another place where austenite can nucleate.

So, this is the mechanism which makes the development of growth of austenite particles within the ferrite matrix otherwise, it has no reason to grow in this fashion. So, that is a difference with respect to a pure iron where it is only stabilizing the austenite, based on the nitrogen content. So, in case of a pure iron as the nitrogen enters, it will simply try to grow the austenite layer and this will continue to grow with time.

So, you will not see the austenite growing at a deeper region within the ferrite matrix. So, now actually, if it comes to the technological implications of such alloy design and carrying the experiments, this kind of microstructures having a finely dispersed austenite in a ferrite or a martensite matrix is known to have a unique combination of properties.

So, it will be able to offer a unique combination of strength and ductility and even these austenite particles upon deformation can transform to martensite and can lead give rise to so called transformation induced plasticity. So, this way, simple chemistry can create a very unique microstructures that can be having a very useful mechanical property.

So, what we have discussed is about if we have a situation where conditions are such that we are able to grow the austenite then what kind of alloy chemistry one can have in the base steel that can actually will dictate actually the kind of phases which can evolve with time. So, now by designing this chemistry and the nitriding conditions, that means the temperature and the nitriding potential and the base steel chemistry, this all together have to be optimized in order to generate useful microstructures.

So, with this, I am at the end of this lecture and then in the next lecture, we will discuss about the classical application of nitriding where it has been used only to produce the finely dispersed allowing element nitride particles in the ferrite matrix. Until now, what we have seen is when the nitrides tries to grow or austenite tries to grow, how these elements will influence in the absence of any other iron nitrogen phase is growing. So, how these alloying elements interact with the inwardly diffusing nitrogen and lead to the development of nitride particles that we will discuss in the next lecture thank you.

Keywords- Nitriding, austenite, nitride, nucleation, growth, microstructure.