Thermo-mechanical and Thermo Chemical processes

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Module No # 08
Lecture No # 40
Kinetics of Gaseous Nitriding

Greetings to everyone. So, in today's lecture of this thermochemical surface treatments, we will discuss about the kinetics of the growth of nitride layers when we are doing nitriding with the conditions such that it does not allow formation of any other iron nitrogen phases. That means, the matrix remains ferritic. So, only the alloying elements which are present in the ferritic matrix will interact with the inwardly diffusing nitrogen and that is what leads to the development of the nitrided layer.

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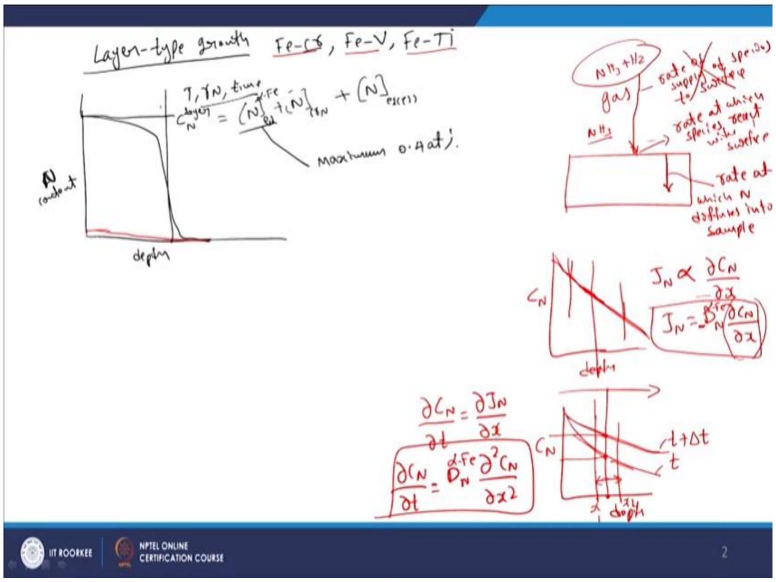

Layer-type growth Fe-Cr, Fe-V, Fe-Ti

T, r_N, time

$C_N^{layer} = [N]^{\alpha\text{-}Fe}_{dil} + [N]_{rN} + [N]_{excess}$

Maximum 0.4 at%

$J_N \propto \frac{\partial C_N}{\partial x}$

$J_N = -D_N^{\alpha\text{-}Fe}\frac{\partial C_N}{\partial x}$

$\frac{\partial C_N}{\partial t} = \frac{\partial J_N}{\partial x}$

$\frac{\partial C_N}{\partial t} = D_N^{\alpha\text{-}Fe}\frac{\partial^2 C_N}{\partial x^2}$

So, in the previous lecture, we have seen the layer type growth of nitrided region. I call it as a layer type growth, because we do not have any defined compound which is growing like iron nitrides rather than layer growth. So, we have in that situation for example, iron-chromium, iron-vanadium and we have not discussed, but it is known that iron-titanium will also behave similarly.

So, you see that if you look at as a function of depth, for example, this is the nitrogen content as a function of depth we see something like this (refer to above figure). So, where you have unreacted core and you have a nitriding front growing up. Now, it has its own kinetics of growth this layer. So, we are interested in now to understand the growth rate of these layers.

For example, as a function of time for a given temperature and nitriding potential or if we are changing the temperature by keeping the nitriding potential and the time constant, how the temperature actually changes the growth of these layers. We have seen that these parameters does influence the growth rate in the previous lecture. So, now, to define some quantities, let us say that this level (refer to above figure) is the concentration of nitrogen as a layer.

I use the term layer so this level I would define it as a CN layer. This is actually the total nitrogen level that has actually the different contributions as a dissolved nitrogen, which we have discussed and the nitrogen which is bonded with the nitrides, if we take the chromium for example, the nitride bonded with chromium-nitride.

And we have discussed also N excess, I will not go into the details of that, but we can say that all this together we have a CN layer. If you look at what is this level of the CN equilibrium α iron, this amount is maximum 0.4 at. %. That means if we see in this total nitrogen profile, if we try to look at what are the way this will be there that will be rather small, so you will have maybe something like that (refer to above figure) and this is the only nitrogen which is participating in the diffusion process. Because this nitrogen which is bonded with the nitrides is actually the sort of frozen nitrogen. So that nitrogen will not participate in the diffusional process. Now, to understand the kinetics of the nitriding process, several reaction rate steps needs to be considered.

For example, this is the sample and you have here the gas atmosphere and now the rate at which the molecules of the gas atmosphere that come to the surface of the sample is a rate of supply of species to surface. This can be thought of one rate and then at this surface you will have another rate controlling mechanism that could be rate at which species react with surface (refer to above figure).

And then we can see another thing, once the species are within the sample, you can have another thing i.e. the rate at which nitrogen defuses into sample. So, now it is important to know the rates of these steps and then we will we can figure out actually either one or the combination of the two or more of these rates could be rate determining in the overall growth of the nitrided region.

So, for example, this one rate of supply of species to surface we can neglect, if we are sufficiently making the flow of gas in the furnace atmosphere. So, this species coming to the surface can be assumed to be not a rate determining step. So, this we can neglect. Now the rate at which species react with the surface cannot be neglected or because it is the nitriding the rate at which the ammonia dissociates at the surface of iron having a finite rate. So, that is what actually allowing the practicability of nitriding because if this nitriding rate is very fast, then we will not be able to maintain the defined level of ammonia hydrogen gas mixture in the furnace. So, this gas is actually $NH_3 + H_2$ in the case of nitriding (refer to above figure).

Now, if the rate at which ammonia is dissociating is very faster as compared to the rate at which nitrogen can diffuse inwardly, then you will start to produce the hydrogen and nitrogen into the gas atmosphere. So, this has its own finite rate and then you have a certain rate at which the things are diffusing into the sample. Now, in order to understand this diffusional kinetics, let us just recapitulate the fixed diffusion equations.

For example, if you have a concentration having a certain profile like that (refer to above figure), and now for example, this is the diffusion direction and this is the depth along which diffusion is happening and now if you look at the specimen cross section, then flux would be for example, in this case (refer to above figure), the nitrogen leaving this cross section that would be proportional to the gradient in the composition that is the slope at that depth.

That is what actually the flux of species for example nitrogen, is proportional to the gradient in the nitrogen concentration as a function of depth at that depth.

$$J_N \;\alpha\; \frac{\partial C_N}{\partial X}$$

Then this proportionality constant is the diffusion coefficient of nitrogen.

$$J_N = D_N \frac{\partial C_N}{\partial X}$$

Now, if we assume that this concentration gradient is constant at different depths, that means you have a linear profile then the flux of nitrogen leaving at any section would be the same okay. The flux of nitrogen J_N would be the same that means you will not have any change in the level of this nitrogen as a function of time. That is why this is called steady state diffusion equation.

Because this will not be able to give you the raise in the composition as a function of time that is what happens usually in the real situations. So, that means, if you have a concentration profile at time t yeah, this is the concentration of nitrogen as a condition of depth. Now, at some other time $t + \Delta t$, you would expect it to be coming out like that. So, this is at, let us say $t + \Delta t$ (refer to above figure).

And now, if you take any constant depth now, this has gone up from this level to this level in a given time you know the Δt. Now if we want to know this, what is actually making this level to change, that should be only possible for this accumulation, if the flux entering this region should be more than the flux of nitrogen leaving from this region (refer to above figure).

So, that is only possible from this equation if your concentration gradient is different at these two points. That is the case here, if you see the diffusion profile comes here the gradient is more than here. So, the flux entering at this section let us say that this is x1 would be more than the flux leaving the section at x2 that is what lead to the calculation.

So, that is where you can get the expression for the Fick's second equation that is the way the concentration of nitrogen changing as a function of time at a given you know the depth would be given as this accumulation is because of change in the flux from the steady state diffusion equation within this ΔX range, that is the

$$\frac{\partial C_N}{\partial t} = - \frac{\partial J_N}{\partial X}$$

So, here you will see that there is a minus sign which I have not placed before because the diffusion happens again along the concentration gradient and this gradient is negative if you see as a function of depth.

So, whereas the net flux goes in the opposite direction that is where you will see the negative sign. Now, if you use the J_N as we see it here, then this is what we end up with the Fick's second equation. Now, if you treat the diffusivity of nitrogen is independent of composition then this is the how

$$\frac{\partial C_N}{\partial t} = D_N^{(\alpha Fe)} \frac{\partial^2 C_N}{\partial X^2}$$

we one can write the Fick’s second diffusion equation. Now, in order to precisely know the model the nitriding process, one need to solve the second Fick’s diffusion equation using appropriate initial and boundary conditions, which we will not be covering.

But we will be only covering the simplistic model which has been always used in understanding the nitriding kinetics in these kind of systems, by assuming a steady state diffusion of nitrogen into the sample. That is what I would explain now. So in that situation, because we know that the amount of dissolved nitrogen is very small as compared to the total nitrogen, so we can assume a linear concentration depth profile.

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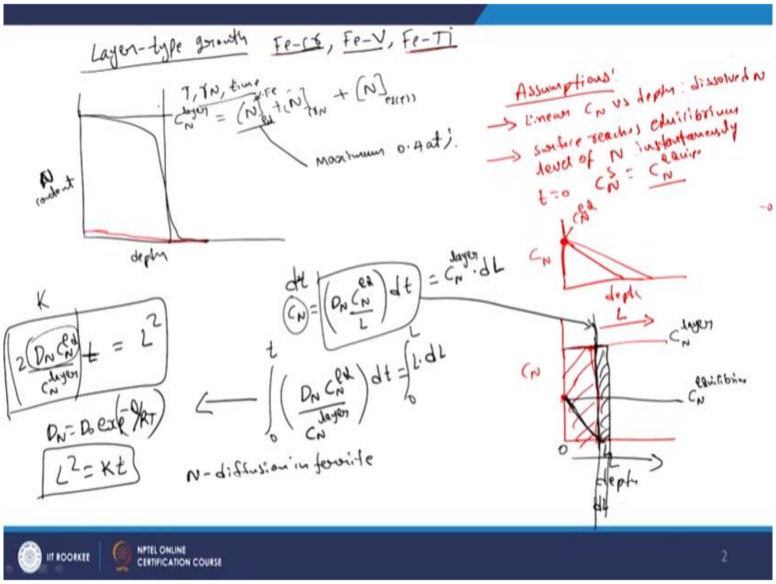

Layer-type growth Fe-Cr, Fe-V, Fe-Ti

T, γ_N, time

$C_N^{layer} = [N]_{\alpha\text{-Fe}}^{eq} + [N]_{\gamma'N} + [N]_{excess}$

Maximum 0.4 at%.

Assumptions:

→ Linear C_N vs depth : dissolved N

→ surface reaches equilibrium level of N instantaneously

$t = 0 \quad C_N^S = C_N^{equi}$

$dt \quad C_N = \left(D_N \frac{C_N^{eq}}{L}\right) dt = C_N^{layer} \cdot dL$

$\int_0^t \left(\frac{D_N C_N^{eq}}{C_N^{layer}}\right) dt = \int_0^L L \cdot dL$

$\boxed{2\left(\frac{D_N C_N^{eq}}{C_N^{layer}}\right) t = L^2}$ K

$D_N = D_0 \exp(-Q/RT)$

$\boxed{L^2 = Kt}$

N-diffusion in ferrite

So, in this simplistic model, there are certain assumptions which are made that is what lead to the simplicity of this model. These are the assumptions of this model which we will be considering (refer to above figure). There is a linear concentration versus depth for the dissolved nitrogen and this gradient will be present within that diffusion zone.

And the second assumption would be the surface reaches equilibrium level of nitrogen instantaneously. That means at t = 0 the concentration of nitrogen at the surface will be concentration of nitrogen expected for the equilibrium. We are talking about the dissolved nitrogen. So, this means your concentration profile will be like if you look at actually the assumption, if this is the concentration of nitrogen as a function of depth.

What we say is that this concentration is already reaches at time t = 0 as CN equilibrium (refer to above figure) and you have a linear profile into the sample. As a function of depth if we use the parameter L, so, you may be having different depths, but with respect to the same level you have a linear profile. So that is what is the assumption. And now, using these two assumptions, we can actually try to build the model.

For example, we have a nitride region growing let us say that at some stage this is a nitrided region with this level of nitrogen as the total level and you have a dissolved nitrogen profile which is going linearly like this. This is the C_N^{layer} that is the total nitrogen level and this is the C_N^{eq} that is the equilibrium level of dissolved nitrogen in the α iron and you have a linear profile.

For example, if I take a time step of dt and suppose if depth is represented as a parameter L that is increasing, here you have a zero for both X and Y-axis, then what is the amount of nitrogen that can be supplied or the flux of nitrogen for unit time at this depth L. That would be then C_N that one can get it from the first equation of the Fick's first equation that will be diffusivity of nitrogen times the gradient in composition.

In this case that gradient would be

$$\frac{C_N^{eq}}{L}$$

this is the slope of this concentration linear profile.

$$C_N = D_N \frac{C_N^{eq}}{L}$$

The concentration per unit area per unit time for a time step of dt will be

$$C_N = \left(D_N \frac{C_N^{eq}}{L}\right) dt \ ,$$

this is the level of concentration that will come at this depth, this C_N is the amount of nitrogen that comes at a time dt.

Now, next is if we assume that all this nitrogen which has come at time step dt will be arranged as a layer, this $\left(D_N \frac{C_N^{eq}}{L}\right) dt$ entire amount we will be put as a thin layer however thin it is that depends on this amount, leads to increased in the depth by dL (refer to above figure). So, that means we have a nitrogen which is diffusing here and then you get some flux at the nitrided region N and this entire nitrogen will be now put into a layer.

So, what is the mechanism by which it will happen that we will not bother, as it is not rate determining. So, that will be going into a layer. So, now the level of this entire nitrogen in this hatched area i.e. the dL thickness nitrided layer will be C_N^{layer} ×dL. This amount will be equivalent

$$C_N = \left(D_N \frac{C_N^{eq}}{L}\right) dt = C_N^{layer} \cdot dL.$$

So now if we integrate this expression from the thickness from 0 to L, and the time from 0 to t, and then what we end up with the

$$\left(\frac{D_N C_N^{eq}}{C_N^{layer}}\right) \cdot dt = L \cdot dL$$

$$\int_0^t \left(\frac{D_N C_N^{eq}}{C_N^{layer}}\right) \cdot dt = \int_0^L L \cdot dL$$

we end up with

$$2\frac{D_N C_N^{eq}}{C_N^{layer}} t = L^2.$$

So, now, you see the relation between the thickness of the nitrided region with respect to the time and we know that its kinetics would depend on the temperature and the nitriding potential, the temperature effect is included in these two quantities, this C_N^{eq}, it depends on the temperature and the nitriding potential that we have discussed previously.

And similarly, the diffusivity of nitrogen it also has its own dependence on temperature

$$D_N = D_o \exp(-Q/RT)$$

as its own exponential dependence with a certain activation energy. Independently, we have the measurement of diffusivity of nitrogen in ferrite as well as independently the measurements on how the equilibrium level of dissolved nitrogen changes with the temperature and nitriding potential for a pure iron.

So, knowing this now, when we do the kinetic analysis, we should be able to get this quantity as the rate constant. So, if you put $2\frac{D_N C_N^{eq}}{C_N^{layer}}$ as a rate constant K, then you see that the kinetics are given by the parabolic rate constant with K as a rate constant

$$L^2 = Kt.$$

In this model we have made the assumptions that the kinetics are controlled by the nitrogen diffusion in ferrite. Ferrite is actually controlling the overall growth of the nitrided layers that is what is actually the assumption here, because here we are taking actually the only the diffusion of nitrogen, the moment that happens automatically the layer will start to grow right.

So, the rate-determining step is the nitrogen flux which is reaching at the end of the nitrided region. So, that is where actually one can do such analysis and such kind of analysis has clearly shown that is this model works quite satisfactorily for this kind of situation of like iron-chromium, iron-vanadium and iron-titanium.

So, in our tutorial, we will have actually one set of data where we have the layer growth kinetics data which has been measured for different temperatures. And then we will see actually how one can actually verify whether the model is working or not as we it is assumed. So, with this now, I am at the end of this lecture. As in the overview lecture, I have also remarked on doing dedicated nitriding treatments for the stainless steels.

So, that part we have actually not covered. So, but I will actually explain very briefly why it is very important to do a dedicated treatment of nitriding to harden the stainless steel surfaces. So, the stainless steels are having a significant amount of chromium that is what gives the stainless character for these steels. Unfortunately, this chromium has a strong affinity to both nitrogen and carbon.

So, if you if you try to do carburizing the there exist a huge thermodynamic driving force for the chromium to precipitate out as chromium carbides or chromium nitrides in case of nitriding. Both of these processes will remove the chromium from the solution and form chromium nitride or carbide precipitates. That way your matrix around the particles will lose its corrosion resistance.

So, we will reach the hardness levels, but at the cost of losing the corrosion resistance. So, the only way to harden these stainless steels is to do the nitriding or carburizing treatment in such a way that you will only allow the nitrogen to dissolve into the surface of the samples without forming any carbides or nitrides. So, that can be achieved with doing a low temperature treatment where the diffusivity of substitutional chromium is relatively much smaller as compared to the diffusivity of nitrogen.

So, in such kind of a situations, and if we impose a very high chemical potential of nitrogen in the gas atmosphere, that by that we are imposing actually large driving force for diffusion of nitrogen into the sample, then one can actually produce only so called nitrogen dissolved austenite layers on austenitic stainless steel surfaces. So, this is simply the effect of the solid solution hardening by the interstitially dissolved nitrogen.

So, that is actually a very dedicated treatment so, I could not cover that in this lecture series. So but somebody interested in that can read these references which I have cited in the previous lectures, the thermochemical surface treatments it is an edited book by Marcel Somers and Mittermeier. Thank you for your attention.