Heat Treatment and Surface Hardening (Part–1)

Professor Kallol Mondal
Professor Sandeep Sangal
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture Number 34

Avrami Kinetics - 3

So continuing with what we were discussing in the last lecture that is Avrami kinetics.

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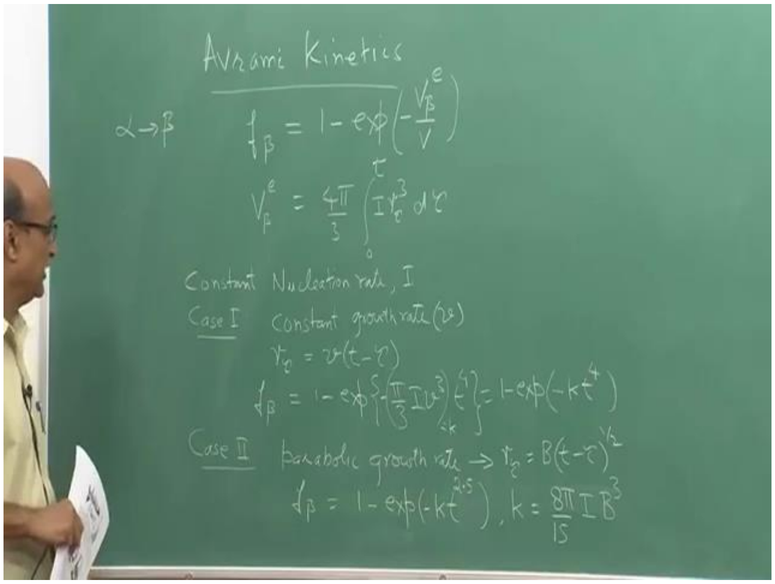

Avrami Kinetics

$\alpha \to \beta$

$$f_\beta = 1 - \exp\left(-\frac{V_\beta^e}{V}\right)$$

$$V_\beta^e = \frac{4\pi}{3}\int_0^t I r_\tau^3 \, d\tau$$

Constant Nucleation rate, I

Case I Constant growth rate (v)

$$r_\tau = v(t-\tau)$$

$$f_\beta = 1 - \exp\Big\{-\underbrace{\left(\frac{\pi}{3} I v^3\right)}_{=k} t^4\Big\} = 1 - \exp(-kt^4)$$

Case II parabolic growth rate $\rightarrow r_\tau = B(t-\tau)^{1/2}$

$$f_\beta = 1 - \exp(-kt^{2.5}), \quad k = \frac{8\pi}{15} I B^3$$

We had consider two cases but first let me just write down to basic relationships the fraction in alpha to beta transformation the fraction transformed is given by 1-exponential minus the extended volume V beta e divided by the volume of the system. And the extended volume of the transformed beta was written as 4 pi by 3 integral 0 to t, the nucleation rate times the radius of a nucleus nucleated at time tau cube d tau.

And the two cases we had discussed were cases where nucleation rate was a constant. So constant nucleation rate I and hence I can be taken out of the integral. And in case 1, one considered constant growth rate given by v and therefore the size of the nuclei which nucleated at time tau would be at any time t was written as the growth rate times the instant of time (t-tau).

Substitute substituting this radius into this integral taking this I out of the integral we can then integrate to get the extended volume and substitute the extended volume into the top equation and which gave us the fraction beta transformed as 1-exponential {- (pi by 3 Iv cube) t to power 4}. We can lump all of these quantities which are a constant in one parameter k and hence the relationship that was written turns out to be exponential (-kt to power 4).

Similarly Case 2 was (cons) considered and in the case of case 2, nucleation rate was parabolic no sorry nucleation rate was still kept constant. We have parabolic growth rate, that is growth rate is proportional to the square root of time and hence r tau in this case becomes a constant B times (t-tau to power half). From this one got the function for fraction of beta transformed as a function of time as 1-exponential (-kt to power 2.5 or 5 by 2).

Where k in that case was 8 pi by 15 the nucleation rate times the constant B cube. So what we find is that we have different exponents of time depending on what model of growth rate one chooses. And of course what model of growth rate one would choose would depend on the system whether you have interface control of diffusion control here as shown here.

Similarly one can look at couple of other cases here we had considered nucleation rate occurring throughout the transformation there is a possibility where you would have most of the nucleation getting completed in the very early stages of transformation. And that can happen when site saturation takes place. Site saturation means sites for nucleation get completely exhausted.

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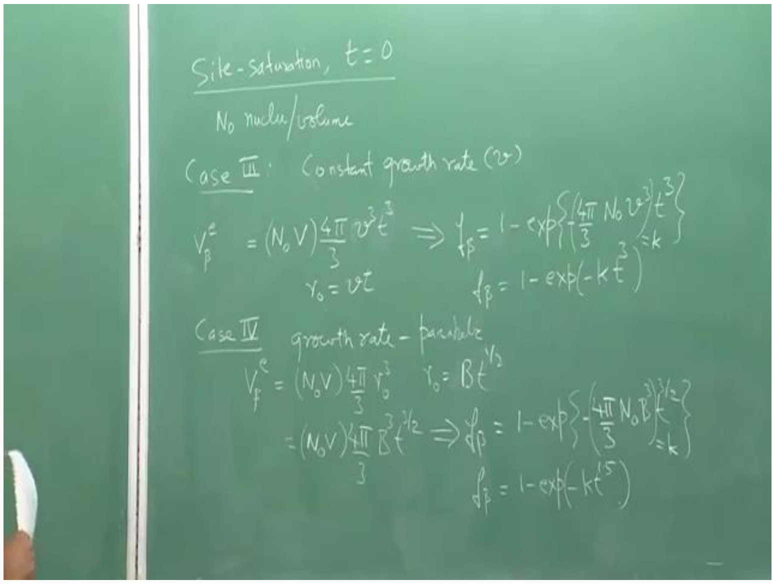

Site-saturation, $t = 0$

N_0 nuclei/volume

Case III: Constant growth rate (v)

$$V_\beta^e = (N_0 V)\frac{4\pi}{3} v^3 t^3 \Rightarrow f_\beta = 1 - \exp\left\{-\underbrace{\left(\frac{4\pi}{3} N_0 v^3\right)}_{=k} t^3\right\}$$

$$r_0 = v\tau \qquad f_\beta = 1 - \exp(-k t^3)$$

Case IV growth rate - parabolic

$$V_\beta^e = (N_0 V)\frac{4\pi}{3} r_0^3 \qquad r_0 = B t^{1/2}$$

$$= (N_0 V)\frac{4\pi}{3} B^3 t^{3/2} \Rightarrow f_\beta = 1 - \exp\left\{-\underbrace{\left(\frac{4\pi}{3} N_0 B^3\right)}_{=k} t^{3/2}\right\}$$

$$f_\beta = 1 - \exp(-k t^{1.5})$$

So let us take am extreme case where site saturation takes place at basically at the start of the transformation or time t equal to 0. And let us say that we have N0 nuclei per unit volume present at time t is equal to 0 and beyond this time there is no more nucleation is going to take place. Hence all growth would take place for only those nuclei essentially which formed right at the start of the transformation.

In this case the extended volume would then become (dep) or rather the extended volume would would have to take this into account that there is no (nuclei) nucleation occurring beyond time t is equal to 0. But we still have to choose what growth model to take for example suppose we consider a third case where we assume a constant growth. So constant growth rate v since all the nuclei are formed at time t is equal to 0.

Volume of all any nucleus at any time t would simply be 4 pi by 3, 4 pi by 3 r0 cube, where r0 is essentially the the (())(07:56) zero is designating all the nuclei which formed at time t equal to 0. The total extended volume would then this volume of 1 nuclei multiplied by the total nuclei present in the system and volume of the system we have been taking as V and we have N0 nuclei per unit volume therefore the total number of nuclei present at the start of the transformation is N0 times V multiplied by volume of each nucleus.

This then becomes simply the extended volume, we substitute this extended volume into this exponential relationship to get fraction beta transformed as 1-exponential -4 pi by 3 N0 and inside here is r0 cube and this r0 cube can be replaced by r0 is simply the growth rate times t. And hence r0 cube can be replaced by v cube t cube. So in this expression then f beta is equal to 1-exponential {(4 pi by 3 N0 v cube) t cube}.

Here again you will see that one can take these terms in the circular brackets as a constant k. And this time we have fraction beta transformed as 1-expoential (-kt cube). Here is now the exponent of time in this case is 3 as compared to the previous two cases where we had an exponent of time of 2.5 and exponent of time of 4. Let us consider one final case as well and of course one can look at other cases as well but here in this lecture I will just take one more case where the growth rate is (parabol) parabolic.

Now the extended volume would simply be (N0V) times 4 pi by 3 rnot cube and r0 would be written as (vt) to power half. So it is following square root of time or rather this should not be v at all we can just put it by some constant B t to power half. Substituting this in r0 one will get (N0V) 4 pi by 3 B cube t to power 3 by 2. And from this now the fraction beta transformed at any instant of time t is given by f beta 1-exponential {-(4 pi by 3 N0 B cube) t to power 3 by 2}.

Again we can put lump all of these parameters as a constant k and one will get f beta equals 1-exponential (-kt to power 1.5). So in these 4 cases that we have considered we have got different exponents for t 1.5, all the way to 4. So there is whole range of exponents we get and we can try other combinations of nucleation rate and growth rate for example sometimes nucleation rate could be consider itself as an exponential function of time.

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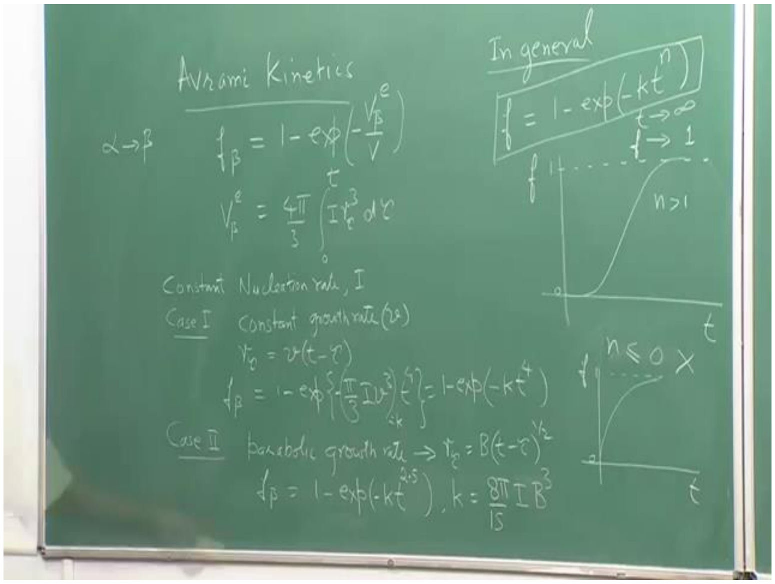

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$$f_\beta = 1 - \exp(-kt^{2.5}),\ k = \frac{8\pi}{15} I B^3$$

In general

$$\boxed{f = 1 - \exp(-kt^n)}$$

$t \to \infty$

$f \to 1$

So which could also be plugged in and one would get a somewhat different relationship. So in general then, so in general the Avrami relationship could be written as f is equal to 1-exponential (-kt to power n). Now what kind of a function is this if I plot this as f versus t, then of course the fraction transformed f will (cha) vary between 0 and 1. So this function is going to basically vary between 0 and 1 as time increases from 0.

And one would get a curve a typical curve like this which is also call the sigmoidal curve. In fact this is the same kind of curve we had got right when we had started discussing the kinetics of phase transformation and I had shown you simulation, which ofcourse did not assume any of those equations but the simulation gave me the same kind of sigmoidal curve. And in fact in that simulation if you fit it that curve one would get different value of n depending on what growth model one has taken and what nucleation model one has taken.

Another thing about this function to note is that at t is equal to 0, the fraction transformed is 0 as expected. And as t tends to infinity the fraction transformed tends to 1. And then this function can be examined for different values of n, so for example you will get a shape like this for n greater than 1.

So this is a shape corresponding to n greater than 1. What happens for let us say n less than or equal to 0, if I take n less than or equal to 0. This function for n is equal to 0 this function would be a constant. So it will have some constant value which essentially appears to be in that whatever has transformed has transformed at t is equal to 0 and then it remains fix.

So that is kind of absurd so you cannot have value in the Avrami parameter n to be 0 or in fact if n become less than 0 then this function would have a decreasing value that again will not make any sense. That without any transformation the fraction transformed is reducing hence for n less than or equal to 0, this relationship has no meaning. Between n greater than 0 and less than 1 this function looks like a continuously decreasing rate of transformation.

But will still go from 0 to 1. Here for n greater than 1 there is a kind of in incubation period before which any measurable transformation takes place then the transformation rate keeps increasing until it reach a point where the transformation rate will start to reduce again and as you can see towards the end the transformation rate becomes very slow. It can be explained on the basis that initially very few nuclei are present and hence the rate is slow and then large number of nucleation is occurred by this time.

And they are all growing, so the rate is going up but towards the end now fraction of untransformed material has become less and hence the number of nuclei that are new nuclei that are forming also reduced and therefore your transformation rate slows down. With these few comments I will basically look at this relationship and see how I can apply.

Suppose I what I had experimental data and I wanted to fit this relationship to experimental data. Then how do I fit this equation to experimental data in order to determine k and n. And what is the purpose of that is that I have an experiment I do an experiment in which I am I have measured fraction transformed as a function of time. I fit that data into this expression and try to find n and k.

And interestingly the value of n would give me a clue as to what kind of a mechanism that may be operative. For example if I get value of n close to 4, this tends to suggest that I have a constant nucleation rate constant growth rate. If I had a value of n equal to 1.5 or close to that then this may suggest that site saturation is taking place and the growth rate may be parabolic.

But we cannot make this conclusion unambiguously because there may be other processes that may be operating which may also lead to similar values of n. But this only would give us a clue as to what kind of mechanism of transformation that may be taking place and one will have to generate more evidences from other kinds of experiments in order to finally make a conclusion as to the mechanism of phase transformation.

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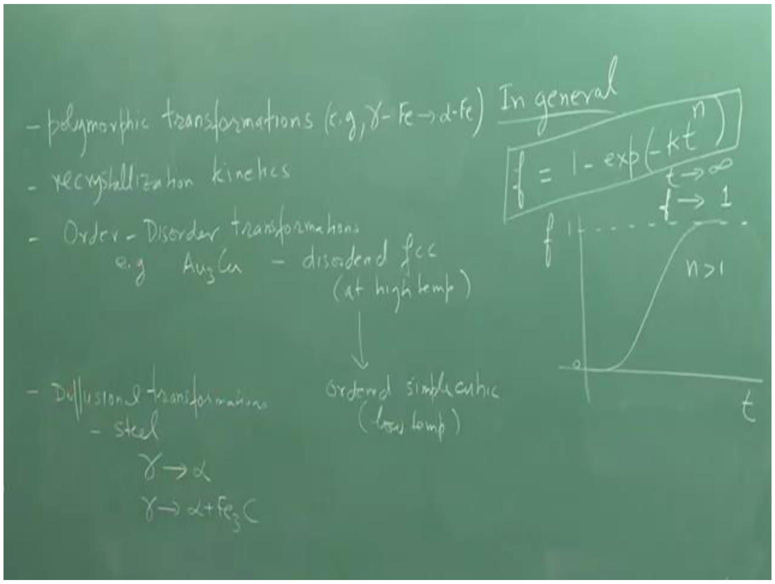

- polymorphic transformations (e.g, γ- Fe $\rightarrow$ α-Fe)
- recrystallization kinetics
- Order - Disorder transformations
  e.g Au_3Cu - disordered fcc (at high temp) $\downarrow$ ordered simple cubic (low temp)
- Diffusional transformations
  - steel
    $\gamma \rightarrow \alpha$
    $\gamma \rightarrow \alpha + Fe_3C$

In general

$$\boxed{f = 1 - \exp(-kt^n)}$$

$t \rightarrow \infty$
$f \rightarrow 1$

So let us look at this equation and how we can apply it. To what kind of systems first of all we can apply this Avrami relationship well this Avrami relationship can be applied to very large number of systems. It could be applied to polymorphic transformations. It could be applied to recrystallization kinetics. It could be applied to some order disorder transformations.

Polymorphic transformation for example could be iron in the face centered cubic state gamma iron transforming to alpha iron or the body centered cubic iron. Recrystallization kinetic we deform a material and we anneal it so there is recovery recrystallization in grain growth so one can look at the kinetics of those using this relationship, order disorder transformation an example of that could be a gold copper alloy.

For example there are other order disorder transformation as well, so for example this particular alloy (go) gold copper AU3CU at high temperature this is disordered face centered cubic this is at high temperature. This undergoes a transformation on lowering the temperature to ordered simple cubic. This is at low temperature.

Disordered FCC implies basically that it is an face centered cubic structure where gold or the copper atoms can be at any of the lattice points whether it is a face centered cubic or whether it is a face centered lattice point or a corner lattice point of the cubic unit cell. But when it transforms to this ordered simple cubic then copper atoms are at the corners of a cube and gold atoms reside at the phase centers of the cube.

So even this can be analyzed with the Avrami relationship, then you can have diffusional transformations. None of these actually require long range diffusion, so when I talk about diffusion transformation I am implying long range diffusion. In the case of diffusional transformation we can look at steel or the iron carbon system. In the iron carbon system gamma can austenite can transform to ferrite, austenite can transform to pearlite lamellar of ferrite and cementite one can look at these transformations in the light of the Avrami relationship.

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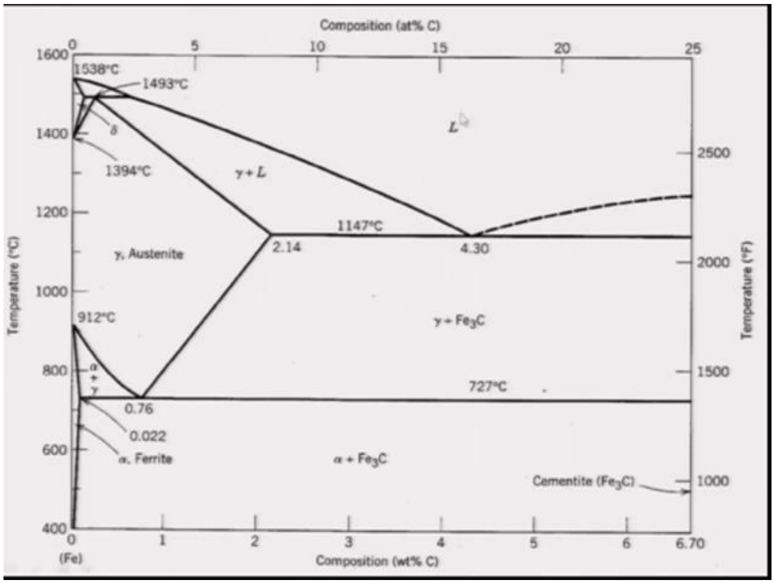

So just to quickly understand the diffusional transformation of austenite to ferrite and austenite to pearlite you can see the iron carbon phase diagram here and if I (che) choose a steel with the hypoeutectoid composition so less than 0.8 percent or 0.76 percent carbon then the kind of microstructure I will get as I start to cool down from austenite region into this ferrite plus austenite, ferrite will start to transform in a diffusional manner.

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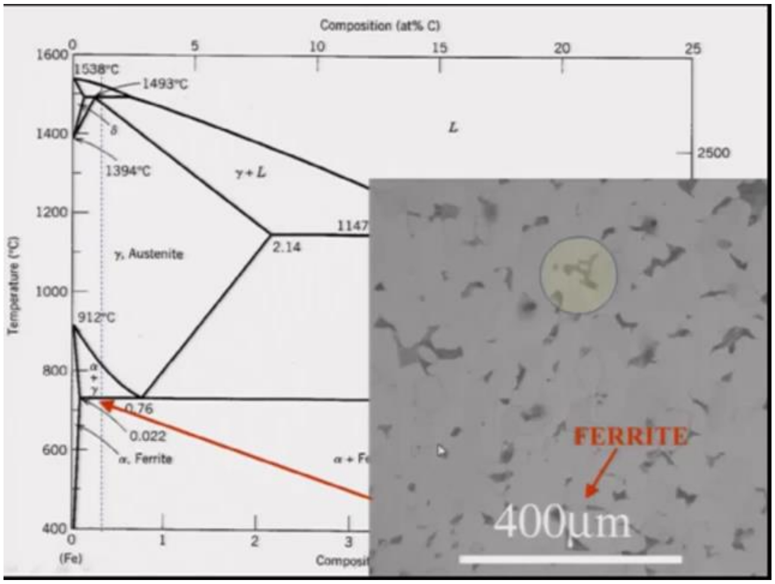

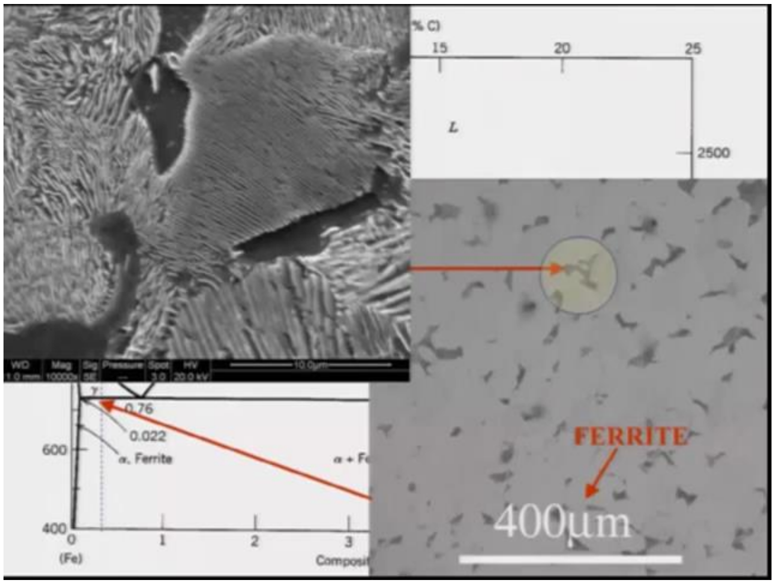

And that finally (go) going below the eutectoid line the remaining austenite transforms to pearlite and this is what is displayed in the microstructure here. So there are pearlite islands in an (aust) in a ferrite matrix and you can more clearly see the structure in a scanning electron (micro) microscopy image and the pearlite can be even more clearly seen in an atomic force microscope image here, where the lamellar of ferrite and cementite are very clearly visible.

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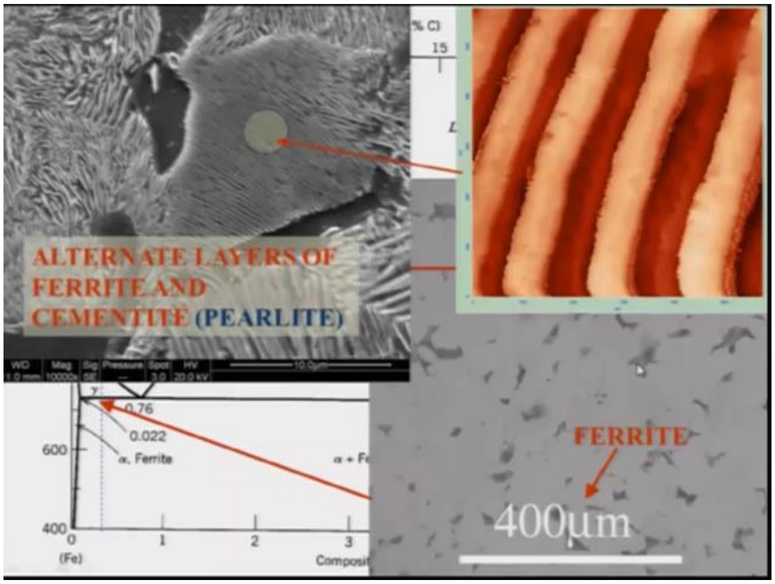

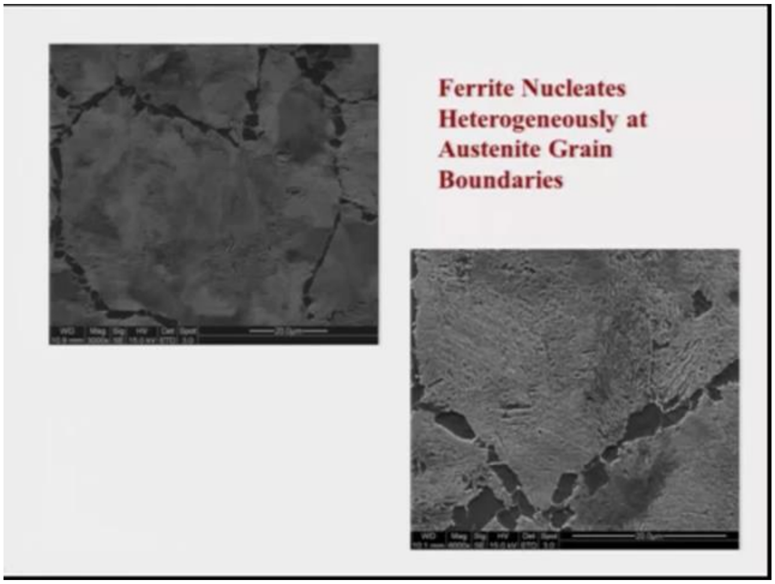

Ferrite Nucleates Heterogeneously at Austenite Grain Boundaries

So whether it is austenite to ferrite transformation one can study this it is a diffusion transformation one can study it from the perspective of the Avrami relationship and determine what the parameters n and k are experimentally as we will soon see how in these micrograss one can also see that the ferrite these dark regions all around and inside here is pearlite so all these ferrite is actually heterogeneously nucleated onto the austenite grain boundary.

So austenite grain boundary are the sites for nucleation and it could so happen at least in some systems that you may end up getting site saturation.

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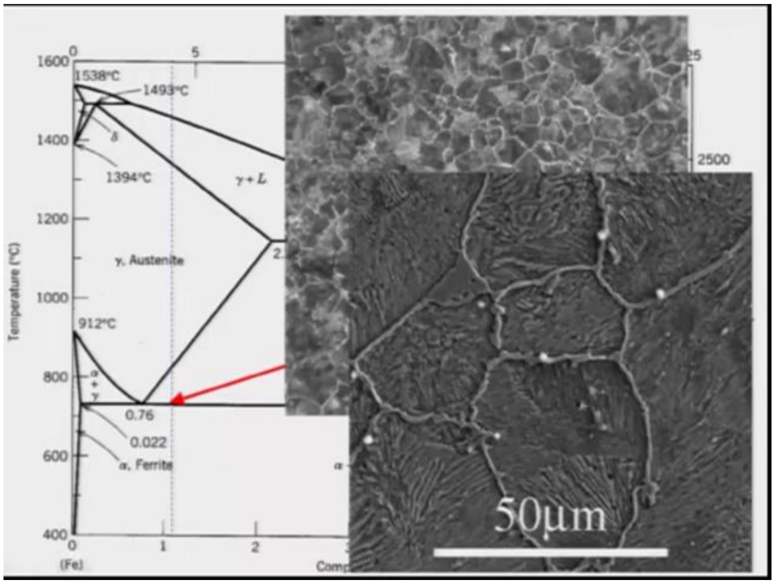

Similarly if I take a hypoeutectoid steel composition greater than the eutectoid 0.8 percent carbon then in this case the (mic) microstructure one would get would be cementite all along the austenite boundaries and pearlite developing in the rest of the region.

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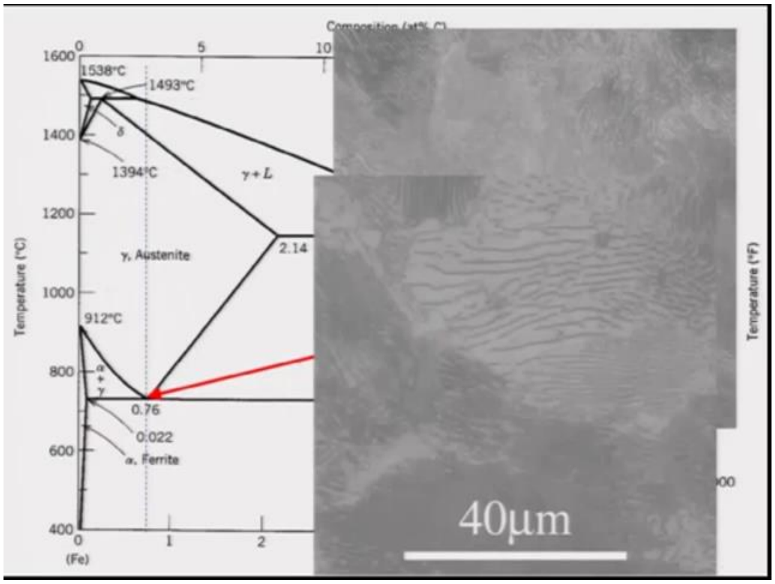

And finally of more interest to us right now is the eutectoid composition itself, where all of austenite transforms to pearlite through the eutectoid reaction gamma going to ferrite plus cementite and the microstructure one would get would be pearlite everywhere. At one can (de) design an experiment to experimentally investigate the kinetics of this particular transformation of austenite to pearlite.

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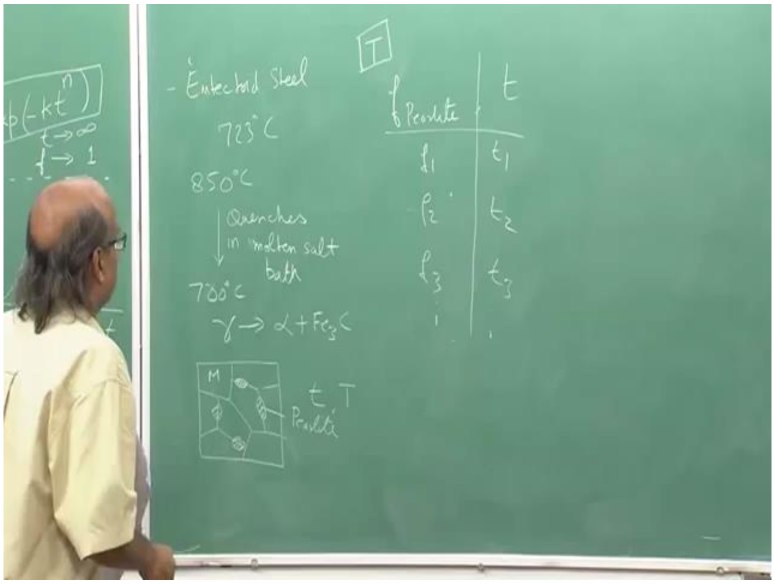

So we start with eutectoid steel heat it up into the austenitic region as per the phase diagram and then cool it just below the eutectoid temperature of 723 degrees centigrade to do this we have to do this very quickly. So let us say our steel was kept at 850 degree centigrade it has to be cooled rapidly to let us say 700 degree centigrade below the eutectoid temperature it could be 650 degree centigrade as well.

In order to do this rapid cooling one quenches the sample in a molten salt bath kept at the temperature of transformation whether 700 degree centigrade or 650 degree centigrade or 680 degree centigrade at whatever temperature one (wans) wants to investigate this particular transformation of austenite going to pearlite alpha plus Fe3C. So one will have to quench several samples each sample being kept at different times in the salt bath.

You keep it for certain amount of time in the salt bath and then quench it in water. The idea of that is that the remaining austenite the untransformed austenite is made to transform to marten site which is a metastable phase in the steel system. So then finally the microstructure one would get at some time t kept at some temperature capital T the initial austenite grain boundaries.

Suppose these are my initial austenite boundaries one will start to form pearlite at those boundaries. And rest of the untransformed austenite will be made to transform to marten site. So I will have marten site and pearlite, one will take this sample polish it put it under a microscope and then determine what is the volume fraction of pearlite that is there. That can be (deren) determine by standard stereological technique of for example point counting.

That you put a grid of points and count the number of points following inside pearlite that number divided by the total number of points I have superimposed would give me an estimate of the volume fraction of pearlite. So what I will have in the end is f pearlite versus time for some given transformation temperature t. So I will have f1 t1, f2 t2, fraction transform is f3 at time t3 and so on.

Now I take this data and then analyze it in terms of the Avrami relationship in order to find the parameters n and k.

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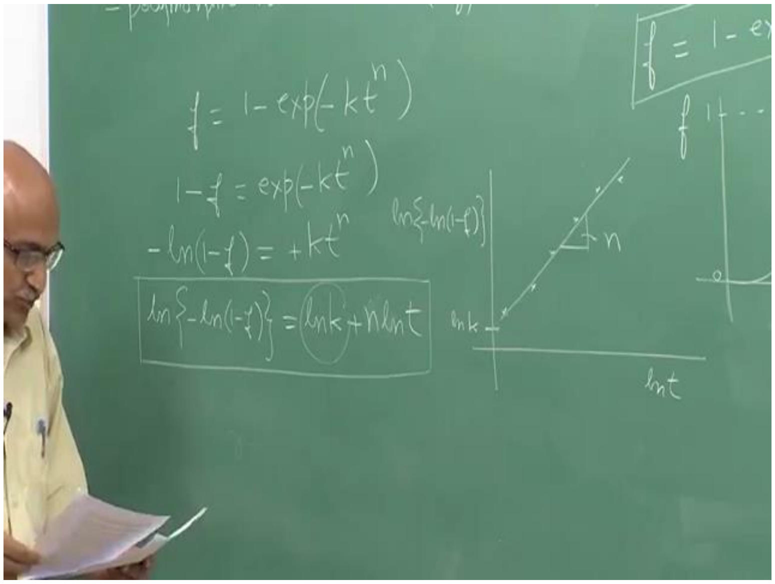

So what do I do, I take this relationship f is equal to 1-exponential (-kt to power n). I rearrange the terms write it as 1-f is equal to exponential (-kt to power n), take logs on both sides. So I will have natural log (1-f) equals –kt to power n. Now f is of course a fraction less than 1, so 1-f would be less than 1 so natural log of 1-f would be a negative number so what I do is I take this minus sign here and make this plus here.

So now what I have is positive values on both sides of this relationship. So I can take logs again, so natural log of minus natural log of 1-f would be equal to lnk + nlnt. What was the purpose of doing this well the purpose of this was to linearize the Avrami relation. Now the left hand side which is the function of two logs is a linear relationship with log t. So if I take that experimental data that I have and plot on the Y axis ln-ln (1-f) versus lnt, I (sh) if the data follows the Avrami relation then the experimental data points must roughly fall on a straight line.

I can put a best fit line through these data points, the slope of this line then would be from this linearized relation is simply n. And the intersection with the Y axis would give me l and k so. The intercept gives me log k, the slope gives me n. So this way from experimental data I can easily determine the parameters n and k. I will stop here in this lecture and in the next lecture we will take a very important topic where the Avrami from the Avrami relation how we can go to what is called as the time temperature transformation diagram, thank you.