Structure of Materials

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Lecture - 40

Chapter - 08

Phase Transformations

The thing left is that we have to understand.

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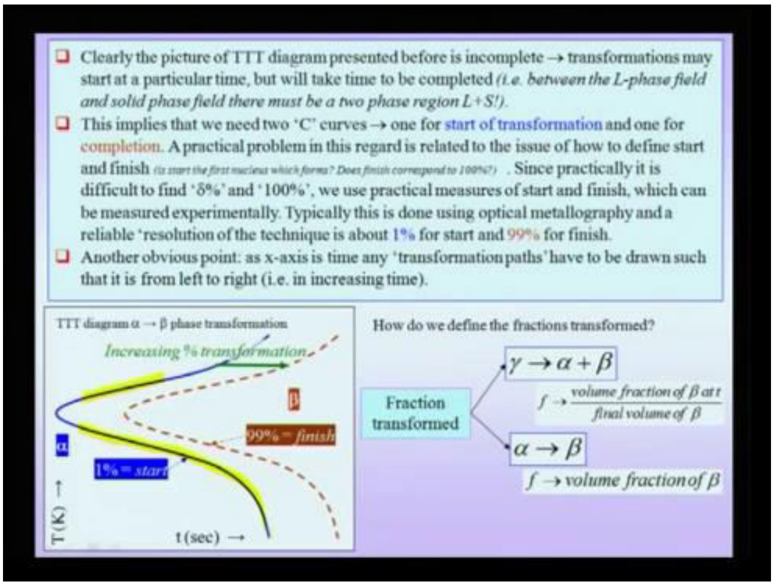

- Clearly the picture of TTT diagram presented before is incomplete → transformations may start at a particular time, but will take time to be completed *(i.e. between the L-phase field and solid phase field there must be a two phase region L+S!)*.
- This implies that we need two 'C' curves → one for start of transformation and one for completion. A practical problem in this regard is related to the issue of how to define start and finish *(is start the first nucleus which forms? Does finish correspond to 100%?)* . Since practically it is difficult to find 'δ%' and '100%', we use practical measures of start and finish, which can be measured experimentally. Typically this is done using optical metallography and a reliable 'resolution of the technique is about 1% for start and 99% for finish.
- Another obvious point: as x-axis is time any 'transformation paths' have to be drawn such that it is from left to right (i.e. in increasing time).

How do we define the fractions transformed?

Fraction transformed

- $\gamma \to \alpha + \beta$
  - $f \to \frac{\text{volume fraction of } \beta \text{ at } t}{\text{final volume of } \beta}$
- $\alpha \to \beta$
  - $f \to \text{volume fraction of } \beta$

How can we actually compute the function of the transformation rate, as a function of the under cooling or the temperature.

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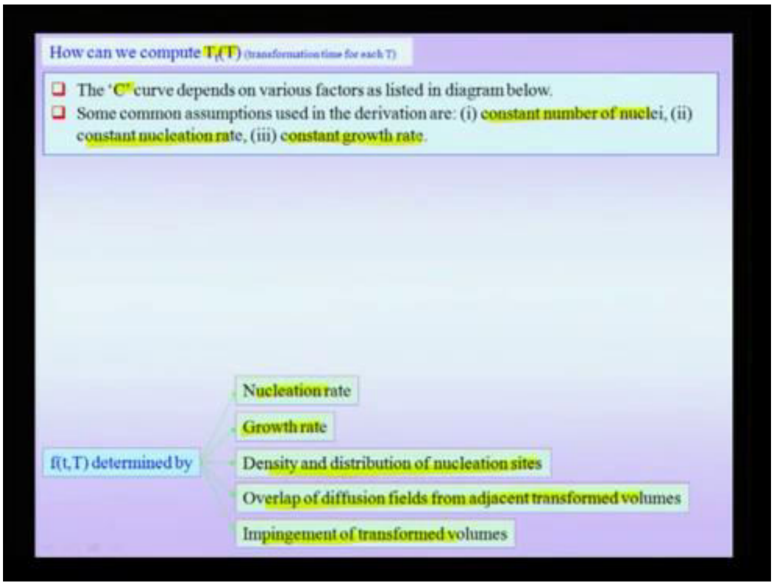

How can we compute $T_f(T)$ (transformation time for each T)

- ❑ The 'C' curve depends on various factors as listed in diagram below.
- ❑ Some common assumptions used in the derivation are: (i) constant number of nuclei, (ii) constant nucleation rate, (iii) constant growth rate.

f(t, T) determined by

- Nucleation rate
- Growth rate
- Density and distribution of nucleation sites
- Overlap of diffusion fields from adjacent transformed volumes
- Impingement of transformed volumes

That means I would like to know my subscript T as a function of temperature and this I would like to know, for instance once I know for each temperature, I can compute this. Now, the C curve which we have seen before, because ((Refer Time: 01:02)) this curve as the shape of a C, it is often referred to as a C curve which is seen here, depends on various factors. It obviously depends on the nucleation rate, it depends on the growth rate it depends on the density and distribution of nucleation sites.

That means, I now need to know what we call as the details of the microstructure, you may need to know how the diffusion fields overlap from adjacent transformed volumes. Then finally, we need to know how the impingement of transformed volumes take place, in other words this is a complicated function to calculate and therefore, I need to work under certain assumptions. So, that I can simplify my derivation and common assumptions are we use a certain constant number of nuclear that means, we take the nucleation rate out of the equation.

But, instead we work with a constant number of nuclei in the volume of material, which is to be transformed of course, we can also work with constant nucleation rate assumption and further, we can use a constant growth rate assumption. A combination of these assumptions can also to be used to simplify our overall understanding at the derivation process.

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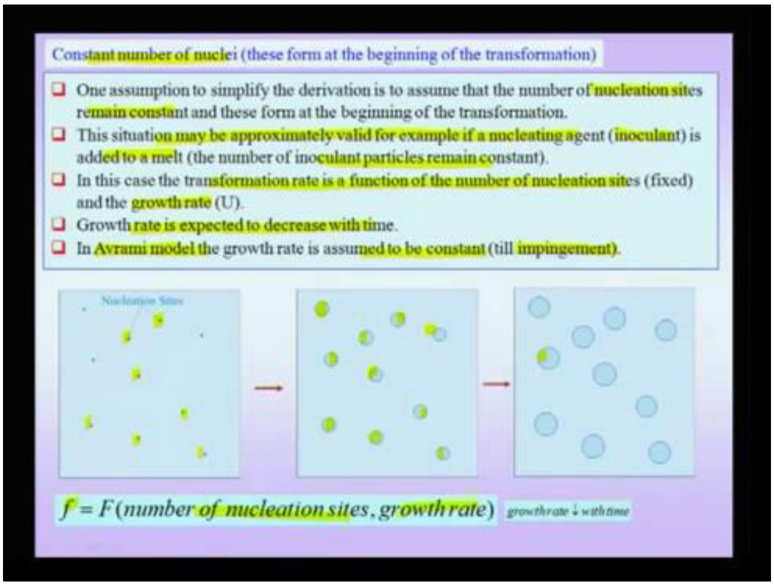

Constant number of nuclei (these form at the beginning of the transformation)

- One assumption to simplify the derivation is to assume that the number of nucleation sites remain constant and these form at the beginning of the transformation.
- This situation may be approximately valid for example if a nucleating agent (inoculant) is added to a melt (the number of inoculant particles remain constant).
- In this case the transformation rate is a function of the number of nucleation sites (fixed) and the growth rate (U).
- Growth rate is expected to decrease with time.
- In Avrami model the growth rate is assumed to be constant (till impingement).

$f = F(\text{number of nucleation sites}, \text{growth rate})$ growth rate ↓ with time

Let us start with the first of these, which is assuming that the number of nuclei are constant, here we will not do the detailed derivation, but we will see talk about the assumptions. And of course, the final form of the function which is based on the assumptions, so we assume that there are number of nucleation sites are fixed and this remain constant. That means, we are not adding any more nucleation sites as the transformation is proceeding.

And additionally we also will have to assume that this constant number of nucleation sites are used up are exhausted almost at the beginning of the transformation. This situation may be approximately valid for example, if a nucleating agent which is sometimes called an inoculants also, is added to the melt or a transforming volume. Melt of course, is an example which is true for any kind of transforming volume that means, if I have a transforming volume and I add a certain nucleating agent.

Obviously, the number of particles I am adding is going to be fixed and therefore, I can assume that the number of nucleon nucleation sites are constant. And this number does not change with time assuming that, we are not adding any more of those inoculant particles, in this case the transformation rate is the function of the number of nucleation sites which is fixed and the growth rate. That means, now the thing I need to worry about is the growth rate and this growth rate is typically expected to decrease with time.

But, further in certain models like the Avrami model, we can assume that the growth rate is assumed to be constant with time. Of course finally, when the transformation volume goes to 0, I mean the untransformed volume goes to 0 which happens when the impingement of the particles takes place. This implies that the growth rate is going to finally, of course sees to grow when the transmission rate is going to 0, but till impingement we can assume that the growth rate is constant.

So, in other words the first of these simplifying assumptions is that, that I have a fixed number of nucleation sites as shown in the figure, these are represented by these blue dots. And start of the transformation I would assume that these nucleation sites are almost very quick after the start of the transformation are exhausted. And these transformed volumes continued to grow, and this growth rate is though expected to be decreasing with time, if I assume that this growth rate itself is a constant.

Then I get what is called the Avrami model and I can derive the transformation rate as a function of the under cooling. So, this is one of the models and in this case clearly, the transformation rate the function is the function number of nucleation site and the growth rate.

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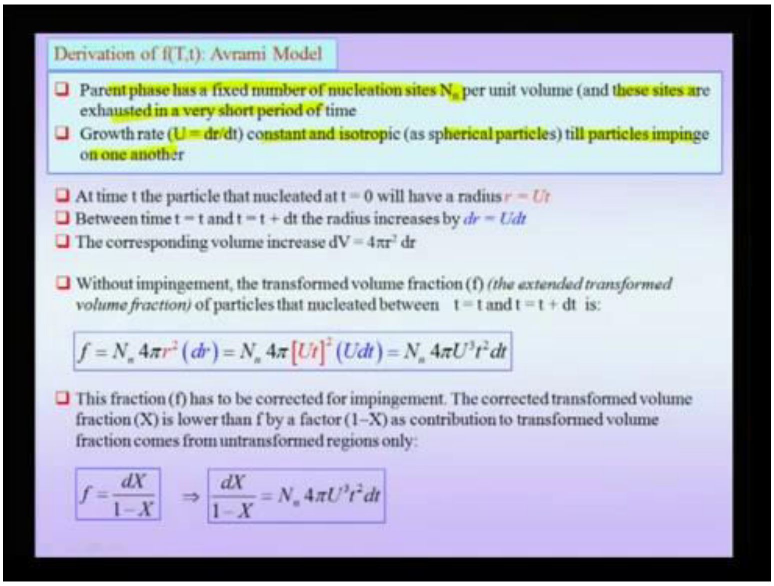

Derivation of f(T,t): Avrami Model

- Parent phase has a fixed number of nucleation sites N_n per unit volume (and these sites are exhausted in a very short period of time
- Growth rate ($U = dr/dt$) constant and isotropic (as spherical particles) till particles impinge on one another

- At time t the particle that nucleated at t = 0 will have a radius $r = Ut$
- Between time t = t and t = t + dt the radius increases by $dr = Udt$
- The corresponding volume increase $dV = 4\pi r^2\, dr$

- Without impingement, the transformed volume fraction (f) *(the extended transformed volume fraction)* of particles that nucleated between t = t and t = t + dt is:

$$\boxed{f = N_n 4\pi r^2 (dr) = N_n 4\pi [Ut]^2 (Udt) = N_n 4\pi U^3 t^2 dt}$$

- This fraction (f) has to be corrected for impingement. The corrected transformed volume fraction (X) is lower than f by a factor (1–X) as contribution to transformed volume fraction comes from untransformed regions only:

$$\boxed{f = \frac{dX}{1-X}} \Rightarrow \boxed{\frac{dX}{1-X} = N_n 4\pi U^3 t^2 dt}$$

Now, if we will not go into the details of the derivation of the Avrami model, but let us just see what are the assumptions involved like we saw before, that the parent phase has fixed number of nucleation sites, which can be written as N subscript 10 per unit volume.

And these sites are exhausted in a very short period of time the growth rate which is d r by d t is constant an isotropic that means, that any point of time I would have spherical particles.

These transformed volume say for instance, suppose I am talking about a solidification of a melt, I am assuming that they are they will have spherical crystalline phases which are present in the melt. And this growth rate is constant till the particles impinge on one another or the crystallites impinge on one another.

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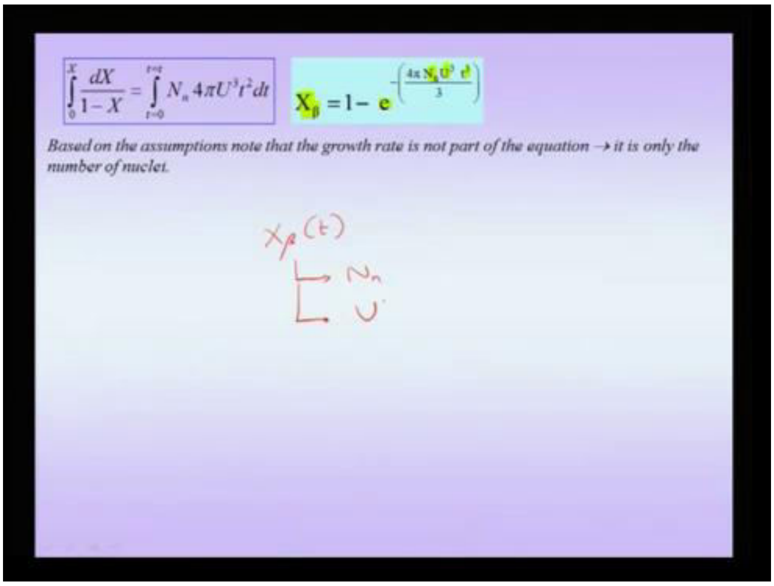

$$\int_0^X \frac{dX}{1-X} = \int_{t=0}^{t=t} N_n 4\pi U^3 t^2 dt \qquad X_\beta = 1 - e^{-\left(\frac{4\pi N_n U^3 t^3}{3}\right)}$$

Based on the assumptions note that the growth rate is not part of the equation → it is only the number of nuclei.

$X_\beta(t)$

$\hookrightarrow N_n$

$\hookrightarrow U$

So, using these assumptions I can derive what you call the transformation rate function or in other words, I can derive the fraction of beta which is transformed of course, beta is the product phase which is coming from the parent phase. And I can see that this function goes as 1 minus exponential minus 4 pi N n is of course, the number of nucleation sites and U is the growth rate and it is a function of time.

Therefore, now I have a function of x beta which is now, I am calculating x beta as a function of time and obviously, this x beta is also a function of a number of nucleation sites; and the growth rate which is assumed to be constant with time. So, I can get a function like this which is now based on the model, which is known as the Avrami model.

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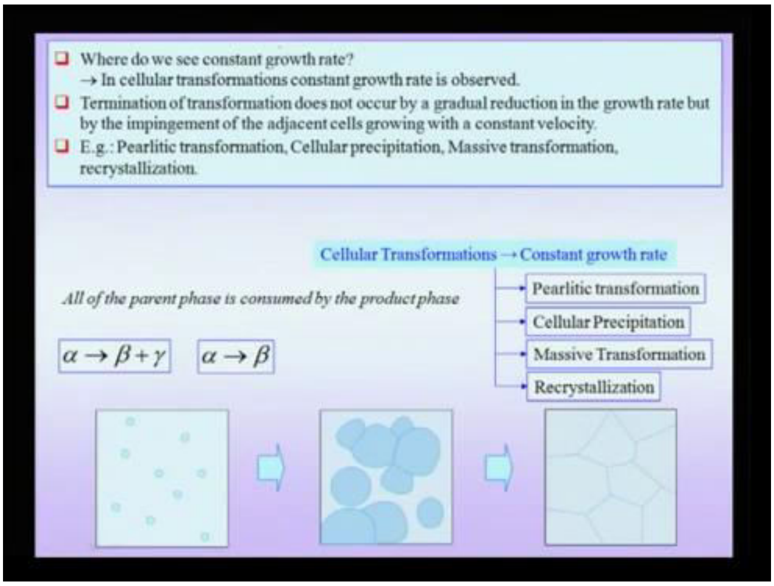

- Where do we see constant growth rate?
  → In cellular transformations constant growth rate is observed.
- Termination of transformation does not occur by a gradual reduction in the growth rate but by the impingement of the adjacent cells growing with a constant velocity.
- E.g.: Pearlitic transformation, Cellular precipitation, Massive transformation, recrystallization.

Cellular Transformations → Constant growth rate

- Pearlitic transformation
- Cellular Precipitation
- Massive Transformation
- Recrystallization

All of the parent phase is consumed by the product phase

$\alpha \to \beta+\gamma$ $\alpha \to \beta$

Similar to the Avrami model I can use other set of assumptions to derive, what we call the x beta function, but before we go to that let us see, where do we see a constant growth rate kind of a phenomena. This is typically seen in cellular transformations, wherein the constant growth rate is observed, termination of transformation does not occur by gradual reduction in growth rate, but by the impingement of adjacent cells growing with a constant velocity.

So, this is as close to the Avrami model we get, wherein the growth rate is constant, examples of such kind of cellular transformations are, wherein you observe constant growth rate are pearlitic transformations, cellular precipitation, massive transformations and recrystallization. Though we are not going into details of each one of these processes her, but it is important to note that, here we have a certain number of nuclei which are growing.

But, and the growth rate remains constant with time till of course, two particles impinge on one other that means, suppose I have an impingement of course, growth ceases. But, till such impingement occurs I would assume that the growth is isotropic and it is constant with time, the U growth rate is constant and isotropic. So, this is the assumption based in Avrami model, but this as we can see from many transformations, which come very close to this kind of an assumptions that the Avrami model is not so bad to explain.

Many such transformation phenomena like pearlitic transformations, cellular precipitation, massive transformation and recrystallization. Now, the other assumptions which I can use is not a constant number of nucleation sites, but a constant nucleation rate. In constant nucleation rate ((Refer Time: 08:10)) I land up with a model known as the Johnson-Mehl model, which is one of common models of phase transformations or kinetics of phase transformation.

And in this case, the transformation rate is the function of both the nucleation rate and the growth rate, so I assume that the nucleation rate is playing a role in the phase transformation that means, the number of nucleation sites is not fixed, but the nucleation rate is fixed. And further we have to see the dependence on the growth rate, the growth rate as expected would decrease with time.

But, further suppose we make an assumption that not only the nucleation rate is fixed, but the growth rate is also fixed or constant there we get the Johnson-Mehl model. So, I have a situation here that a scenario, wherein I have a certain nucleation rate that means, let me go to the board and try to understand the situation.

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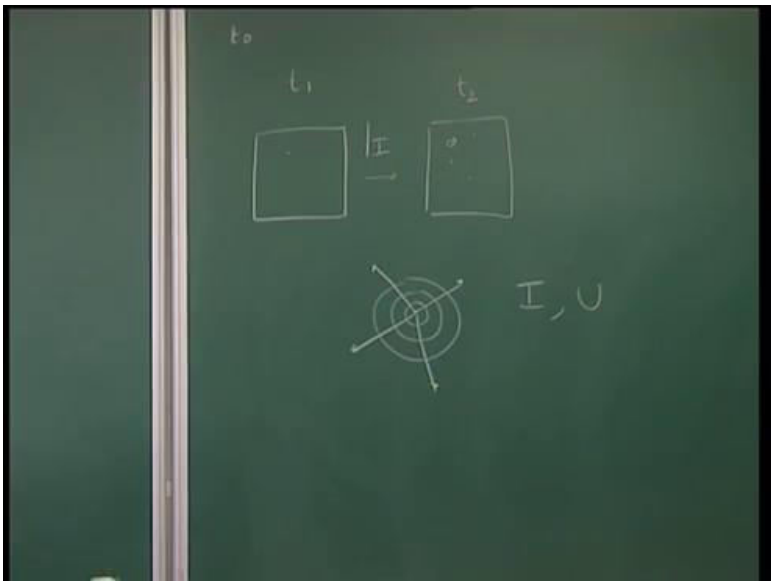

So, at a time t 1 I have a picture that there is an volume in which there are no nuclear, now say transformation starts at a certain time, say this is t 0 that, there are no nucleation rates and t 1 is where the nucleation starts and there is one nuclei forming. But, with time the rate is constant that means, the I is constant, I have a constant nucleation rate and therefore, I would have a particles forming at time t 2 I may have a few nucleation sites.

But, this first nucleus which form for instance here, it would have grow and now I assume that the nucleation rate that means, number of nuclei forming per unit time, per unit volume is constant, further also the growth rate is constant. That means, that if a particle which is forming it is growing, then this rate at which it grows is going to be constant with time. So, this not only is the growth rate constant, I will assume it is isotropic, therefore my I is constant and my U is constant in the derivation of the Johnson-Mehl model.

So, my picture would look something like, I am seeing here ((Refer Time: 10:16)) in the slide, wherein I see that there is a certain nucleation rate, and these nuclei continue to grow with time. But, there are further new nuclei which may form for instance, you may have a new nuclei forming here at a later period of time, further with this nuclei may go, by the times another nuclei may form somewhere else. And finally, though in reality we may observe a reduction in growth rate with time, if I make an assumption that the growth rate is also constant, then I land up with the Johnson-Mehl model.

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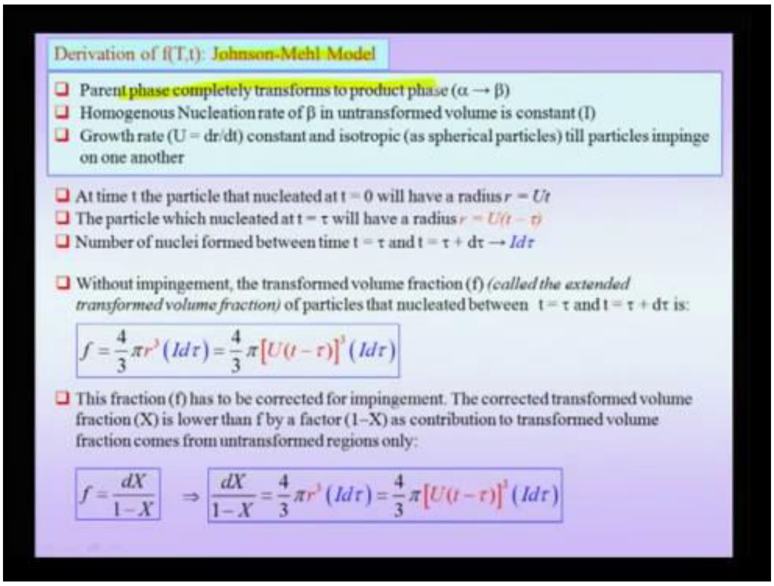

Derivation of f(T,t): Johnson-Mehl Model

- ☐ Parent phase completely transforms to product phase (α → β)
- ☐ Homogenous Nucleation rate of β in untransformed volume is constant (I)
- ☐ Growth rate (U = dr/dt) constant and isotropic (as spherical particles) till particles impinge on one another

- ☐ At time t the particle that nucleated at t = 0 will have a radius $r = Ut$
- ☐ The particle which nucleated at t = τ will have a radius $r = U(t - \tau)$
- ☐ Number of nuclei formed between time t = τ and t = τ + dτ → $Id\tau$

- ☐ Without impingement, the transformed volume fraction (f) *(called the extended transformed volume fraction)* of particles that nucleated between t = τ and t = τ + dτ is:

$$\boxed{f = \frac{4}{3}\pi r^3 (Id\tau) = \frac{4}{3}\pi [U(t-\tau)]^3 (Id\tau)}$$

- ☐ This fraction (f) has to be corrected for impingement. The corrected transformed volume fraction (X) is lower than f by a factor (1–X) as contribution to transformed volume fraction comes from untransformed regions only:

$$\boxed{f = \frac{dX}{1-X}} \Rightarrow \boxed{\frac{dX}{1-X} = \frac{4}{3}\pi r^3 (Id\tau) = \frac{4}{3}\pi [U(t-\tau)]^3 (Id\tau)}$$

So, let us jump to we will skip the derivation and we will ah once again of course, revisit the assumptions, but we will get to the final function. So, the parent phase completely transforms the product phase, this is the assumption number 1, homogenous nucleation rate of beta in untransformed volume is constant that means, the I is constant. The growth rate which is d r by d t is constant an isotropic and growth will cease when particles impinge on one another.

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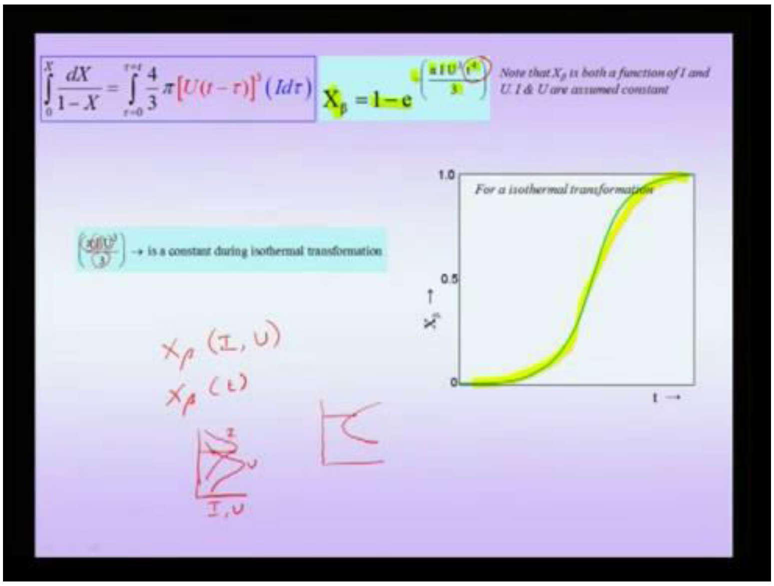

$$\int_0^X \frac{dX}{1-X} = \int_{\tau=0}^{\tau=t} \frac{4}{3}\pi[U(t-\tau)]^3 (Id\tau)$$

$$X_\beta = 1 - e^{-\left(\frac{\pi I U^3 t^4}{3}\right)}$$

Note that X_β is both a function of I and U. I & U are assumed constant

$\left(\frac{\pi I U^3}{3}\right)$ → is a constant during isothermal transformation

Therefore, I can land up with an x beta function which we have seen before, is now x beta is 1 minus exponential of pi I U cube t power 4 by 3, so we have encountered this function before. And we already plotted that x beta function looks like the standard sig modal growth curve, now in this case x beta as we have seen depends on the transformed volume x beta. Now, depends on both the nucleation rate the and the growth rate and I have now my function of x beta as function of time.

And this is the function and it has a fourth order dependence with time, now if I am talking about an isothermal transformation that means, I am at a constant temperature monitoring the transformation. Then, I can notice that the terms in the exponent which are the pi I and U cube are all constant and therefore, this term is constant. Now, if I go back to my previous case of isothermal transformation diagram, I am notice that my transformation rate for a give under cooling remains the nucleation rate and growth rate, both would be two separate curves, but the values would be constant.

Therefore, I can assume that of course, this is the time and if I am talking about the rates I know that I have a nucleation rate curve and I have my growth rate curve, and I can assume now that my nucleation rate or the growth rate for a given under cooling or a given temperature are both constant. So, this is my nucleation rate curve, this is my growth rate curve and both have a certain fixed value at a constant temperature, therefore based on assumptions I can derive the x beta function.

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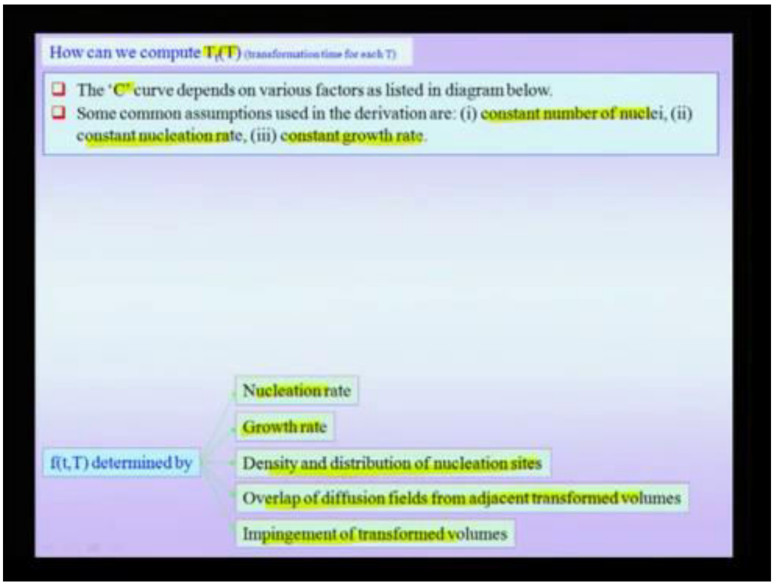

How can we compute $T_f(T)$ (transformation time for each T)

- ☐ The 'C' curve depends on various factors as listed in diagram below.
- ☐ Some common assumptions used in the derivation are: (i) constant number of nuclei, (ii) constant nucleation rate, (iii) constant growth rate.

f(t, T) determined by

- Nucleation rate
- Growth rate
- Density and distribution of nucleation sites
- Overlap of diffusion fields from adjacent transformed volumes
- Impingement of transformed volumes

So, let us go through this section since we went in a little haste on all these matters, I would like to know my ((Refer Time: 13:3)) TTT diagram that means, I would like to derive my TTT diagram. And do for doing this diagram I need to know my transformation time as a function of the under cooling that means, I need to know that for a given temperature on under cooling, what is my transformation time.

So, if I know this function, then I can plot my what I can see here as the T, subscript T as a function of time, now to do this derivation I need to make some assumptions, because this function is actually complicated by the fact that it depends on many factors, two of each are very obvious the growth rate and the nucleation rate. Further, it depends on the density and distribution of nucleation sites, for instance we could be talking about a heterogeneous nucleation, a homogenous nucleation or a combination of homogenous and heterogeneous nucleation.

Heterogeneous nucleation with multiple kind of sites operating like for instance, grain boundaries, excess vacancies or triple junctions and each one of them may have a certain role to play in the overall transformation. Further, I need to worry about the overlap of the diffusion fields from adjacent transformed volumes; and I also need to know how this impingement of transformed volumes, actually leads to the stop of the transformation.

Now, the very fact that it depends on so many of these functions, makes my overall derivation complicated, therefore I can work under certain assumptions, for instance I can assume that either the number of nuclei is constant. That means, for instance when I add some heterogeneous nucleating agent to a for instance the solidification of a melt, then the number of nucleation sites is fixed and these are exhausted typically in a very short time. Or I can assume that the nucleation rate is constant or I can assume that the growth rate is constant, or I may use a combination of these kind of assumptions ((Refer Time: 15:05)).

If I assume that the number of nuclei is constant and further assume that the growth rate is constant and isotropic, then I land up with what is known as the Avrami model of phase transformation. And in the Avrami model ((Refer Time: 15:17)) I can get an x beta function, which is a function of the number of nucleation sites and it is also a function of the growth rate, and the dependence of x beta on time is a t cube kind of a dependence.

On the other hand, suppose I assume that my nucleation rate is constant and my growth rate is also constant, then I land up with the Johnson-Mehl model wherein of course, my final x beta function depends on the nucleation rate and growth rate. But, the time dependence is now t power 4 and in real life of course, we do see examples of constant growth rate and constant number of nuclei. Especially in transformations like pearlitic transformations, cellular transformations, massive transformation and recrystallization which very close to what is assumed under the Avrami model assumptions.

Now, therefore, even though the underlying physics is very complicated, there are ways of simplifying underlying physics, so that we can get some tangible functions, which we can plot. And under the Johnson-Mehl equation we get x beta if we plot as a function of time, we get the classic sig modal growth curve. As we pointed out before, it is observe under many many circumstances not only in phase transformations, but certain other economic scenarios and certain other areas of sociology and science.

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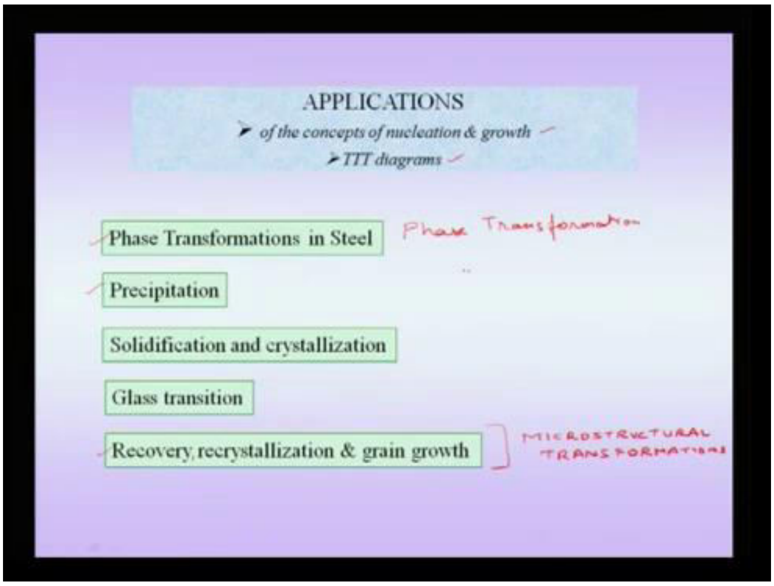

APPLICATIONS

- of the concepts of nucleation & growth
- TTT diagrams

Phase Transformations in Steel

Phase Transformation

Precipitation

Solidification and crystallization

Glass transition

Recovery, recrystallization & grain growth

MICROSTRUCTURAL TRANSFORMATIONS

Now, we have understood some basic aspects regarding what we might call the nucleation, the growth and what we might call phase transformations of which have the first order characteristic. Now, let us jump to some applications to see how we can apply these nucleation and growth concepts, and how we can apply the concept of the TTT diagrams in understanding microstructures, and designing heat treatments.

So, in this context of course, we will study phase transformations in steel, we will try to see some examples of precipitation and we will also perhaps consider one important micro structural transformation, which is recovery recrystallization and grain growth. Where actually we do not have phase transformation, but what we may have is micro structural transformation, so these for instance involve phase transformation and so it has precipitation.

But, and of course, any phase transformation also will lead to a change in microstructure as we know, but in the bottom case the recovery recrystallization and grain growth, we actually observe what we call micro structural transformations.

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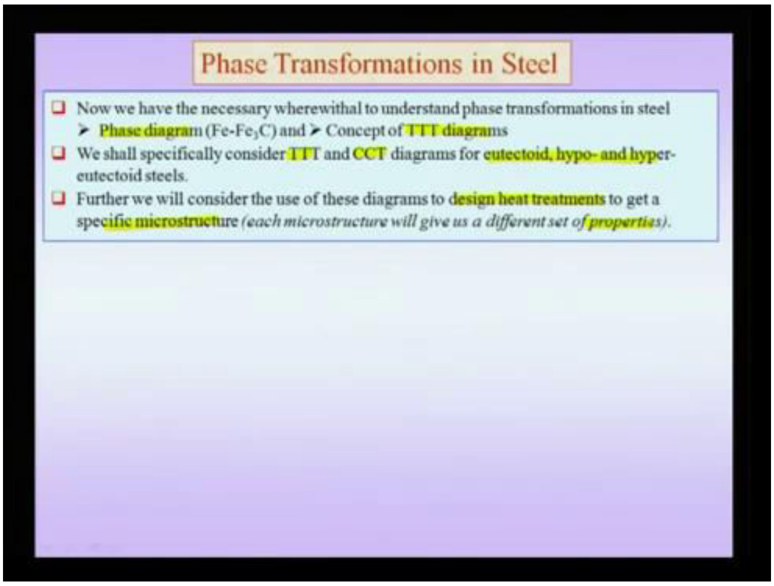

Phase Transformations in Steel

- ❑ Now we have the necessary wherewithal to understand phase transformations in steel
  - ➢ Phase diagram (Fe-Fe_3C) and ➢ Concept of TTT diagrams
- ❑ We shall specifically consider TTT and CCT diagrams for eutectoid, hypo- and hyper-eutectoid steels.
- ❑ Further we will consider the use of these diagrams to design heat treatments to get a specific microstructure *(each microstructure will give us a different set of properties).*

So, Let us start with phase transformations in steel and for understanding all the concepts we have the basics in place, for instance we already seen the iron, cementite phase diagram. And we also have the concept of TTT diagrams with us which both of which we can put together to understand phase transformations in steel. We will try to see some two kinds of diagrams one which is called TTT diagrams, and the other which is called the continuous cooling transformation diagrams.

And we will consider these for eutectoid and hypo and hyper eutectoid steels and most importantly, we will use these diagrams to design heat treatments to get a specific microstructure. And the reason for designing these heat treatments to get a specific microstructure is obviously, to engineer my properties that means, I have a microstructure depending property; and I would like to engineer this property without changing for instance the composition.

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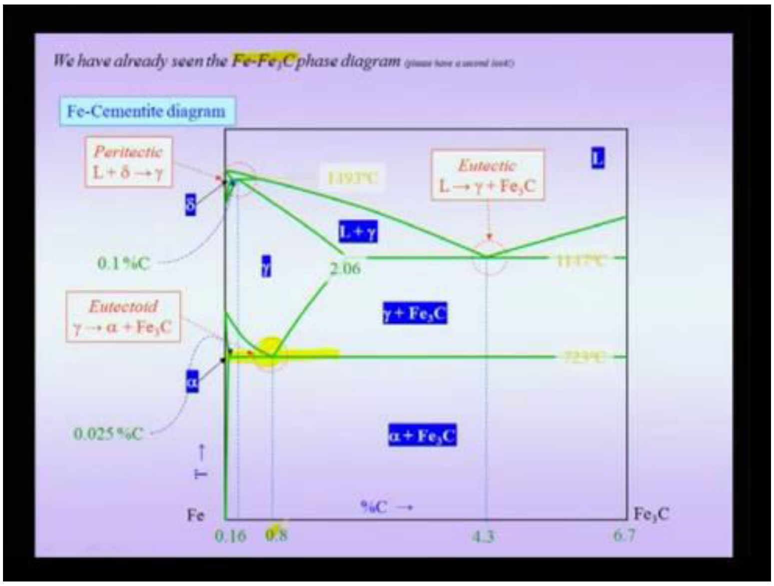

We have already seen the ***Fe-Fe$_3$C*** *phase diagram* (please have a second look)

So, we already seen the iron cementite phase diagram and we have noted that the interesting region of this phase diagram is close to the iron rich end of the phase diagram, typically less than about 2 percent of carbon. And this is where my eutectoid transformation lies and we will specifically worry about compositions, which are close to 0.8 percent carbon or around it like, for instance 0.6 percent carbon or 1 percent carbon.

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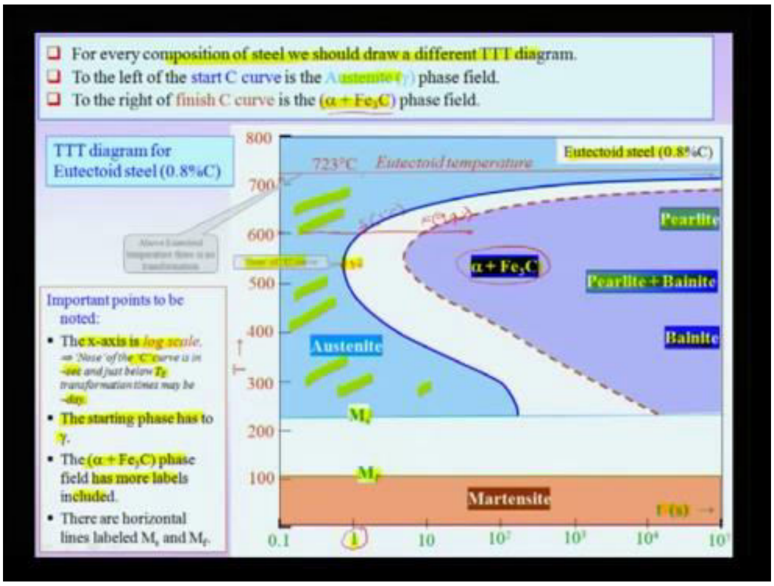

- ☐ For every composition of steel we should draw a different TTT diagram.
- ☐ To the left of the start C curve is the Austenite (γ) phase field.
- ☐ To the right of finish C curve is the (α + Fe$_3$C) phase field.

Important points to be noted:

- The x-axis is *log scale*.
  - ⇒ *'Nose' of the 'C' curve is in ~sec and just below T_E transformation times may be ~day.*
- The starting phase has to γ.
- The (α + Fe$_3$C) phase field has more labels included.
- There are horizontal lines labeled M_s and M_f.

Now, the important point to note is that, for every composition of steel we should draw a different TTT diagram that means, that I cannot use a TTT diagram drawn for instance

0.8 percent carbon, for a 0.4 percent carbon steel. And in drawing all these diagrams, we have to of course, remember that my starting phase is my gamma phase, which is my austenite. And this phase is finally, of course on cooling transforming to alpha plus F e 3 C, so I am starting with this gamma phase field here.

I am heating my alloy above this these two lines and finally, cooling or holding isothermally below the, what we might call the a one line or the eutectoid line 723 degrees Celsius. Maybe if I am using an eutectoid composition I will hold it here, or if I am using an hypo-eutectoid I may hold it somewhere here, or an hyper-eutectoid I may hold it here. So, I will cool below the or hold it below the eutectoid temperature to cause transformations, and the final products of this transformations will be alpha plus F e 3 C in all these cases.

Now, the way these alpha and F e 3 C is distributed we have seen, even in the case of phase diagrams is very very different and these different micro constants or microstructures are given specific names. So, here is the diagram for 0.8 percent or eutectoid steel, so in this diagram of course, we have the gamma phase field which is shown in light blue color on the left hand side, which I am shading now. Or the austenite phase field, and on the right hand side is my transform product, which is alpha plus F e 3 C.

So, in all such cases I am starting with gamma isothermally holding it, for instance suppose I may instantaneously quench to 600 degrees Celsius, I will isothermally hold to cause a transformation to alpha plus F e 3 C. As usual I have my start line, where the transformation starts and a finish line where the transformation finishes. And we have already seen that this start and finish, typically I had defined based on practical considerations to say for instance B 1 percent which is my start.

And for instance this could be 99 percent which is my finish, now the important points to be noted in this diagram which I will go one by one slowly is that, the x axis for this diagram is in log scale. That means, the time which is in seconds, starts from 1 second which is where the nose of the TTT diagram lies, so this part can I label as my nose, so that is where my nose lies close to 1 second.

But, suppose I am talking about a transformation time at a temperature slightly below the eutectoid temperature, for instance about say 15 degrees Celsius, then the transformation time could be even in terms of days. That means, it take a very long time to transform and the transformation time may go into days that means, I am talking about a time scale starting from seconds to going even perhaps up 2 days.

And that is means that the x axis in log scale and for a plain carbon steel this nose of the seeker, which is I am marked in N is of the order of seconds. And as I pointed out just below T E or at very low temperature the transformations times could be of the order of days. The starting phase in all these diagrams has to be gamma, so I am heating about the eutectoid temperature, because now I am talking about a eutectoid carbon steel, 0.8 percent carbon steel right here ((Refer Time: 23:10)) in the phase diagram, this is my composition.

And therefore, for this I heat above 723 degree Celsius to obtain a pure gamma phase, which is my starting phase, the alpha plus F e 3 phase field has more labels included and we should pay close attention to these labels. And these labels are pearlite, bainite and sometimes a combination of pearlite plus bainite, in addition this diagram also have certain other labels which are like labeled as M s and M f to which we will pay attention, and try to understand what are these labels in the context of this eutectoid steel.

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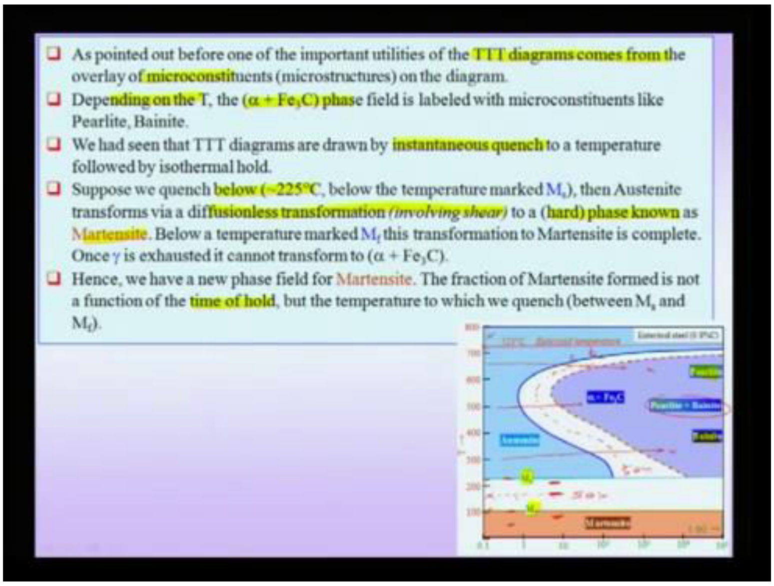

- ☐ As pointed out before one of the important utilities of the TTT diagrams comes from the overlay of microconstituents (microstructures) on the diagram.
- ☐ Depending on the T, the (α + Fe_3C) phase field is labeled with microconstituents like Pearlite, Bainite.
- ☐ We had seen that TTT diagrams are drawn by instantaneous quench to a temperature followed by isothermal hold.
- ☐ Suppose we quench below (~225°C, below the temperature marked M_s), then Austenite transforms via a diffusionless transformation *(involving shear)* to a (hard) phase known as Martensite. Below a temperature marked M_f this transformation to Martensite is complete. Once γ is exhausted it cannot transform to (α + Fe_3C).
- ☐ Hence, we have a new phase field for Martensite. The fraction of Martensite formed is not a function of the time of hold, but the temperature to which we quench (between M_s and M_f).

Now, we have pointed out before that even in the case of phase diagram, sometime to enhance the utility we overlay microstructures or slowly cooled microstructures, on phase diagrams. But, one of the important utilities of the TTT diagram happens to be, that we actually overlay microstructures on the diagram. Depending on the temperature at which the transformation is taking place, noting fully well that we are talking about an isothermal transformation diagram.

The alpha plus F e 3 is phase field, we can form micro constituents like pearlite, if I am transforming at a high temperature that means, I am causing a transformation would take place about 650 degrees Celsius. On the other hand, suppose I am allowing my transformation would take place at 300 degrees Celsius, I would get bainite, we should note that pearlite and bainite both are a combination of alpha plus F e 3 C as dictated by the phase diagram.

On the other hand, suppose I am cooling close to the nose of the TTT diagram, wherein my transformation times are very small of the order of seconds or tens of seconds. Then I land up with a combination of both pearlite and bainite in my final microstructure, as before we have to always make sure that, we are talking about an instantaneous quench and followed by an isothermal hold. And only lines which are going from left to right can be drawn on these diagrams, now as I pointed out there are additional labels.

And of course, we will come back to what is this pearlitic microstructure, how does it form and how is it different from bainite all these things we will address very soon. But, we will try to understand these labels which is M s and M f now, but even before this of course, we already know. But, it is worth emphasizing again that if I hold above the eutectoid temperature or even at the eutectoid temperature we know that phase transformation cannot take place.

That means, we can infinitely hold at 723 degrees Celsius and I will have no phase transformation. Now, these labels m s and m f like for instance, suppose I take my steel and quench it to a temperature which is say for instance here ((Refer time: 26:00)) that means, I bring my temperature down to a below for in a region between M s and M f. Now, this will not lead to the formation of the usual products, which we see in the phase diagram which is alpha plus F e 3 C, but instead we will actually see what is called an diffusion less transformation.

A transformation which involves actually shear for to take place and we produce actually in the case of a steel a hard phase known as Martensite, so instead of isothermally holding at a temperature above M s. Suppose, I go instantaneously to a temperature below M s and of course, I can even go below M f in that case, I would obtain a phase which is a product of a diffusionless transformation which involves shear. And this phase happens to be very hard and because, this phase is very hard, it is very important technological applications.

And this one of the reasons that steel is an important material, because of this very transformation and this phase Martensite is not produced by the conventional mechanisms life long range diffusion, so that is to be noted, so it is involve shear. And suppose I quench below this temperature M f, M s stands for Martensite start, M f stands for Martensite finish M f. And suppose I quench between these two temperatures, then I will land up with a certain fraction of Martensite, say for instance this is could be the 50 percent Martensite line.

Like for instance previously, we could even note for instance I could draw a dotted line in between the start and finish lines for alpha plus F e 3 C and these line for instance could be a 50 percent transformation line. But, the difference between these kind of diffusional transformation and Martensitic transformation is that, the percentage or the fraction of Martensite which forms is not a function of the time I hold, unlike in diffusional transformation.

It depends on the time, for instance suppose I hold it for say for instance in this diagram, hold it for at this 650 degree Celsius I hold it for this amount of time, then I get t 1, I will get a certain fraction, I hold it even larger to t 2 I will get a certain fraction and so forth. And if I hold it even longer say for instance about 1000 seconds, then I will land up with completely a pearlitic microstructure, but in the case of Martensite it does not depend on the time.

But, it depends on the temperature hold or the temperature to which we quench, suppose I quench to a temperature which is just below the M s line, then I may obtain a small volume fraction of Martensite. And the remaining of course, should be the untransformed gamma, suppose I quench to a say the 50 percent line, I will get 50 percent Martensite and suppose I quench below this M f line, then I will have a complete Martensite in my microstructure.

So, now we have introduced a new kind of phase transformation, a diffusionless phase transformation involving shear. And we are talking about a important phase known as a

Martensitic phase, which is not produced by the usual mechanism of long range diffusion, or in usual mechanism even in long range diffusion. But, now it depends on the temperature of the quench and therefore, if I quench to a temperature, which is between M s and M f, then I will get a certain fraction of Martensite, but if I quench below that, then I will land up with fully with Martensite.

And now while we talked about this formation of Martensite, we said that we need to quench of course, and we are quenching so that we are now avoiding what we may call the diffusional transformations which lead to pearlite or bainite. Now, strictly speaking though we said that the assumption involved is that we have an instantaneous quench, but any finite cooling should not be over lead on an truly speaking a TTT diagram.

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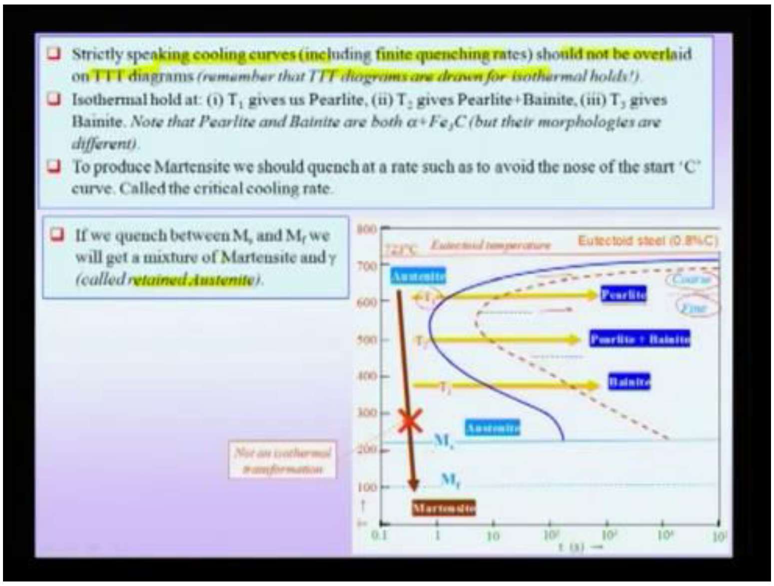

- ❑ Strictly speaking cooling curves (including finite quenching rates) should not be overlaid on TTT diagrams *(remember that TTT diagrams are drawn for isothermal holds!)*.
- ❑ Isothermal hold at: (i) T_1 gives us Pearlite, (ii) T_2 gives Pearlite+Bainite, (iii) T_3 gives Bainite. *Note that Pearlite and Bainite are both $\alpha + Fe_3C$ (but their morphologies are different).*
- ❑ To produce Martensite we should quench at a rate such as to avoid the nose of the start 'C' curve. Called the critical cooling rate.

- ❑ If we quench between M_s and M_f we will get a mixture of Martensite and γ *(called retained Austenite)*.

But then, we are extending the utility of a TTT diagram by including diffusionless transformations, like Martensite. Because, now even for an isothermal hold suppose I quench to a temperature like 200 degree Celsius, then I find that by this time I have started to form Martensite or I am forming Martensite in fraction of the original austenite actually transform to Martensite.

And the final product may consists of a mixture of Martensite and austenite, and this we austenite is called the retained austenite. But, before we do this extension of involving cooling curves or quenching curves on top of TTT diagrams, we should clearly note that strictly speaking cooling curves including finite quenching rates. Which means now like the way I would typically quench in an industrial scenario, wherein a sample in the lab should not be overlaid on TTT diagrams.

And this is because TTT diagrams are drawn for isothermal holds truly speaking, therefore for drawing cooling curves we are even quenching, very high quenching rates, we should use alternate diagrams which are known as CCT diagrams. But, often you would find that cooling curves or quenching curves are drawn on top of TTT diagrams also and now of course, we should understand what is the assumptions involved in such a process.

Now, we have already seen and we will reemphasize that, suppose I isothermally hold above the nose of the curve say at a temperature t 1, I will land up with a micro constant which is known as pearlite. And even there suppose, I hold on the upper side close to the eutectoid temperature, then I will obtain a coarse pearlite. And if I hold at lower temperature close to the nose of the curve, then I will obtain a fine pearlite.

The reason for this can be easily understood, we know that at higher temperatures it is nucleation rate is higher, but growth rate is sluggish. So, here of course, we should go back to our relative peaks of the nucleation rate and growth rate.

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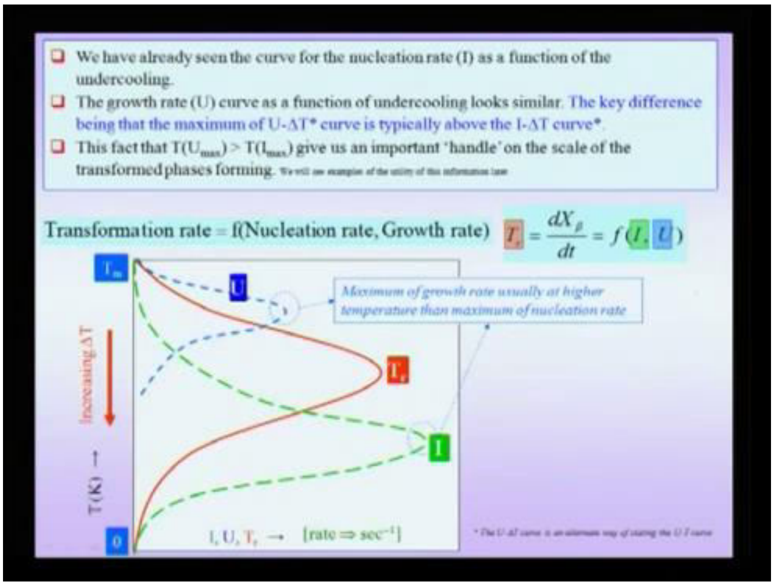

- We have already seen the curve for the nucleation rate (I) as a function of the undercooling.
- The growth rate (U) curve as a function of undercooling looks similar. The key difference being that the maximum of U-ΔT* curve is typically above the I-ΔT curve*.
- This fact that $T(U_{max}) > T(I_{max})$ give us an important 'handle' on the scale of the transformed phases forming.

Transformation rate = f(Nucleation rate, Growth rate) $T_t = \frac{dX_\beta}{dt} = f(I, U)$

Maximum of growth rate usually at higher temperature than maximum of nucleation rate

So, let us try to see the nucleation rate and growth rate curves, so we have noticed that if we are at a higher temperature, then you are closer to the maximum of the growth rate, but the nucleation rate is not very high. You can see that, suppose I draw curve line here I am at this under cooling, then I have a low nucleation rate, but a high growth rate, but I go down to a lower temperature, for instance somewhere here, then I obtain that the growth rate is small, but the nucleation rate is high.

So, lower the temperature I am expecting many more nuclei to form and this would be rather sluggish in growth, therefore I would get a fine scaled microstructure, this is precisely what we are seeing here. That if I have more number of nuclei forming at lower temperature, then I would get fine pearlite, while at wherein of course, the growth is limited, but at higher temperatures the growth is dominant and therefore, I would get a coarse pearlite. We will see a little more of this when we actually talk about the mechanism by which this pearlite forms very soon.

At a temperature t 2 I would obtain a mixture of pearlite and bainite, which is close to the nose of the curve and finally, at even lower temperatures I would obtain bainite. That means, if I want to form bainite by in an what you might call a somewhat of a real scenario, I need to quench below the nose of the curve and then, I need to isothermally hold. And we will of course, see that when we draw the CCT diagram that actually the bainitic wing is totally missing.

Now, the cooling rate with which I can actually miss the nose of the curve, and actually produce Martensite is called a critical cooling rate and if I want to produce complete Martensite. Of course, I have to quench not only at the critical cooling rate, but I have to quench to a temperature which is below the M f. And suppose M f happens to be below the room temperature for a certain composition, not for steel, not for eutectoid steel, but for certain alloy.

Then of course, if I only quench to room temperature the if the quenching medium is at room temperature, then I cannot get fully Martensite and I have to quench to, for instance in a liquid nitrogen bath or some kind of a cooled bath; so that I can get full amount of Martensite. So, again noting that though we are talking about isothermal transformation diagram, Martensitic transformation is not an isothermal transformation. But, typically you would notice that curves which show the formation of Martensite and temperatures M s and M f are overlaid on TTT diagram to extend it is utility.

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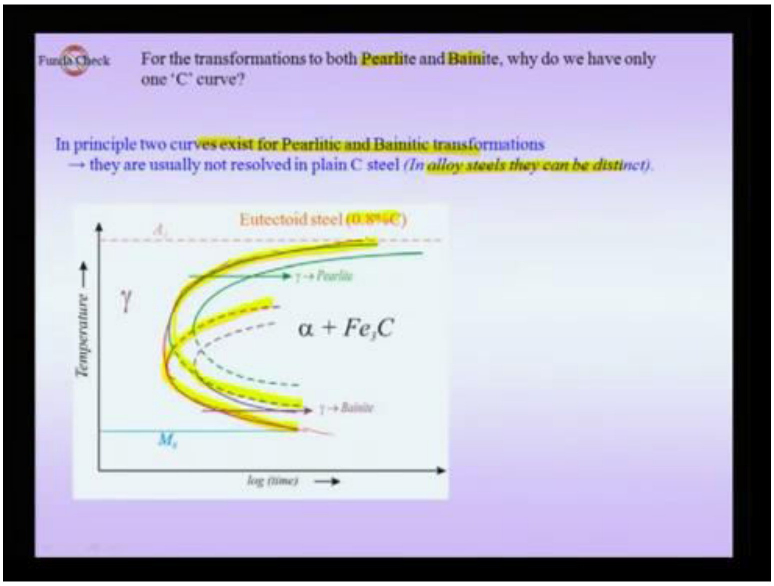

For the transformations to both Pearlite and Bainite, why do we have only one 'C' curve?

In principle two curves exist for Pearlitic and Bainitic transformations
→ they are usually not resolved in plain C steel *(In alloy steels they can be distinct).*

Now, one fundamental question which has been asked is that, we have two transformations, one to the micro constituent known as pearlite, other to the micro constituent known as bainite. Why do we have only one transformation curve that means, we have a start curve and a finish curve and one C curve for both pearlite and bainite, the answer to this is that in principle actually two curves exist for pearlitic and bainitic transformations.

And these are distinctly seen in alloy steels, but in the case of plain carbon steel, plain carbon steel implying that we have only carbon as the only allowing element in iron. And therefore, in this case of course, we are talking about a 0.8 person carbon steel, in this plain carbon steel we have the two C curves one of course, I could shown by the green curve, this green C curve assuming that it is for. The pearlitic transformation and correspondingly I can even draw C curve for the bainitic transformations, these sort of merge and in effect what we see for plain carbon steel is one master C curve which we have seen before.

So, a one master curve and these two individual components of this curve actually gets meshed up, but in when we when we see examples from alloy steels, we will see that there are two separate C curves. That means, I can actually talk about start of bainitic transformation and finish of the bainitic transformation separate from the, what you might call the pearlitic transformation.

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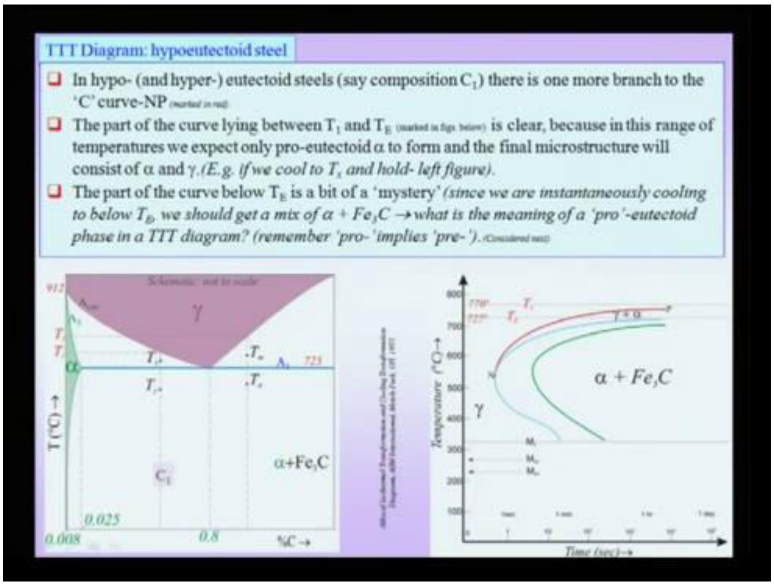

TTT Diagram: hypoeutectoid steel

- In hypo- (and hyper-) eutectoid steels (say composition C_1) there is one more branch to the 'C' curve-NP (marked in red)
- The part of the curve lying between T_1 and T_E (marked in figs. below) is clear, because in this range of temperatures we expect only pro-eutectoid α to form and the final microstructure will consist of α and γ. *(E.g. if we cool to T_x and hold- left figure).*
- The part of the curve below T_E is a bit of a 'mystery' *(since we are instantaneously cooling to below T_E, we should get a mix of α + Fe_3C → what is the meaning of a 'pro'-eutectoid phase in a TTT diagram? (remember 'pro-' implies 'pre-').* (Considered next)

Now, suppose I am not quenching an eutectoid steel, but I am talking about an hypo-eutectoid steel, the beginning of the TTT diagram, we had already pointed out that for every composition, we need to have a different TTT diagram. That means, I do not have a master TTT diagram which can be used for different compositions, that means if I am drawing a TTT diagram I need to take every composition and determine a separate set of C curves.

Now, for a composition which is hypo eutectoid like C 1 as the figure, there is one more branch to the C curve and this branch which is being labeled N p is shown in red, so I have my usual C curve which is present which is shown in B line this blue line to start, and the finish is red line. But, in addition to this I have this N t branch of the C curve, now if I am talking about a hypo-eutectoid composition, then I know that I have an intersection of this composition with the ACM line, which is my line above at say a temperature T 1.

So, this is my temperature T 1 which is shown here and I have my eutectoid temperature which is 723 degree Celsius, which I can label as T E and between these two temperatures, my final suppose I quench, I instantaneously to a temperature like T x as shown in this diagram, the phase diagram I quench to T x and I hold. So, my final product or the final transformed microstructure would consists of alpha and F e 3 C as dictated or alpha and gamma as dictated by this phase diagram.

So, say suppose I quench to a temperature between T 1 and T E which is now my temperature T x, so for instance my temperature T x, could be a temperature like this. So, I quench to T x, then what happens is that, that I would see the start of the transformation to alpha which we know is called the pro-eutectoid alpha. But, final my final product will have no F e 3 C I will land up with a combination of alpha and F e 3 C in that case, so this transformation is for gamma to alpha.

And the final microstructure would consists of alpha and F e 3 C, now suppose I quench to a temperature not T x, but below the eutectoid temperature which is now my T y for instance and my T y, for instance could be lying below the eutectoid point somewhere here, for instance this could be my T y, so this point is T y. Now, at a temperature T y, if I cause transformation, I would first observe the formation of the alpha phase that means, this part of the gamma will transform to alpha.

And finally, of course all the gamma we have an eutectoid transformation in the eutectoid transformation, I will have the gamma, remaining gamma transforming to alpha plus F e 3 C. Therefore, final product would be alpha plus F e 3 C, if I isothermally hold at a temperature T y, now the part of the curve below T e that means, for a temperature like T y is this part of curve, which I will mark once again. For instance, suppose this is my or suppose this part of the curve which starts from N and goes up to the point say for instance, I call this point P.

So, the part of the or maybe you call it B, for instance the part of the curve N b is actually a mystery and we will try to understand this, why is it a mystery in the next curve. Because, since we are instantaneously quenching and holding, since we are instantaneously quenching cooling to below T E, we should get a mixture of alpha and F e 3 C directly. Now, what is the meaning of a pro-eutectoid phase and when we talked about the pro-eutectoid phase, we told that the pro word here in this context, actually implies pre.

Why should we even get a branch which is the pro eutectoid alpha branch, that means if I am talking about holding to a certain time here, at temperature T here for instance in this case. Suppose, I hold to a temperature here, then I will land up with pro-eutectoid alpha at that means, I am holding from here to at this temperature here, then I land up with pro-eutectoid alpha. And the question we are asking is that I am at temperature T y instantaneously that means, I have instantaneously quench to T y, I am not slowly cooling to T y, if had slowly cool to T y, then for instance suppose we already seen how the slowly cooling curves look.

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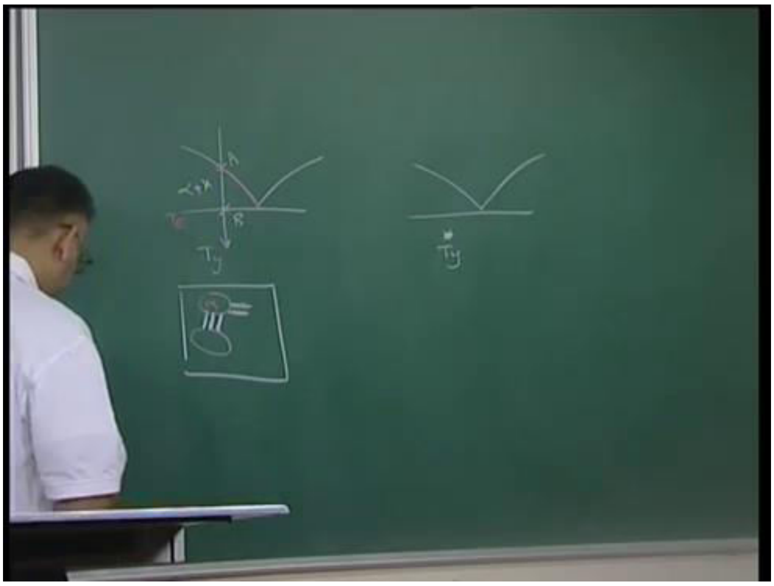

Since, my eutectoid line and suppose I slowly cooled to T y, then I would be crossing the alpha plus gamma phase field which will give me pro-eutectoid precipitation between points say A and B. And after B my composition of the gamma would have transferred along this direction and therefore, I would observe below this temperature T E, I would observe the eutectoid transformation. Therefore, final microstructure would consists of which we have seen before the pro-eutectoid alpha, followed by the eutectoid pearlitic transformation.

So, this is my final microstructure, so this is my pro-eutectoid alpha here, now in the current scenario, we are not slowly cooling, but what we are doing is that we are instantaneously quenching to this temperature T y. The question we are asking is that, since I did not slowly cool why should I get a pro-eutectoid phase, so we will try to understand this mystery coming slide. But, we shall note now that we have an additional arm to this diagram, so let me summarize this ((Refer Time: 42:46)) slide.

So, now I am doing trying to understand the isothermal transformation diagram, the TTT diagram for an hypo-eutectoid composition, for instance I could be talking about a point 6 percent carbon steel. Such a composition suppose I cool to a temperature between the point T 1 where the composition intersects the ACM curve and T E and an such a general point would be T x, then I will land up with a final microstructure that means, I am in this region.

And my final microstructure would consists of alpha plus gamma, my starting point is gamma part of it is transformed to alpha, I land up with alpha plus gamma, but suppose I am quenched to a point like T y which is below the eutectoid temperature. And I isothermally hold, then I have two kinds of events happening, one the formation of an alpha which for reasons which we are not explained so far, is something like a pro-eutectoid alpha. And finally, my final micro structure would consists of alpha plus F e 3 C as we would observe from the phase diagram.

So, apart from this aspect, the curve for the hypo-eutectoid steel looks very similar to the eutectoid steel and even in this case of course, if I quench directly to avoiding the nose of the diagram, I can produce Martensite as long as I am below the Martensite start line. And suppose, I quench to a temperature like about 250 degrees Celsius, I will land up with 50 percent of Martensite.

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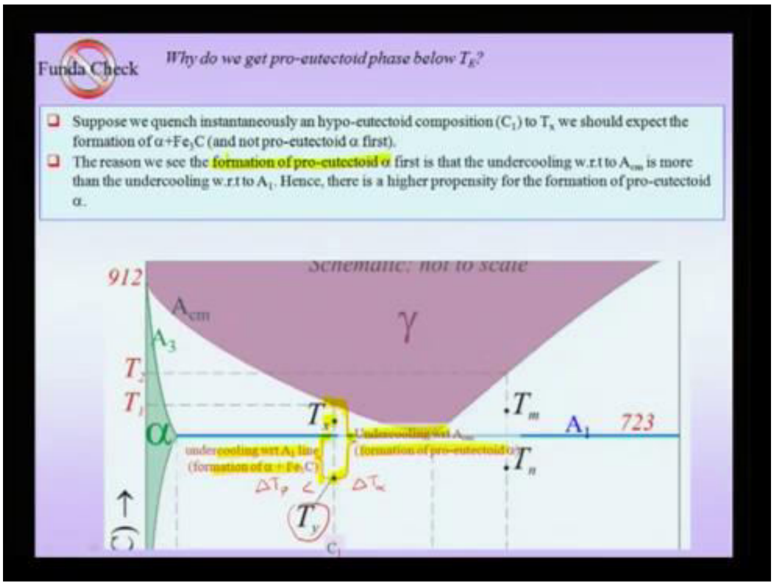
Funda Check

Why do we get pro-eutectoid phase below T_E?

- Suppose we quench instantaneously an hypo-eutectoid composition (C_1) to T_x we should expect the formation of $\alpha + Fe_3C$ (and not pro-eutectoid α first).
- The reason we see the formation of pro-eutectoid α first is that the undercooling w.r.t to A_{cm} is more than the undercooling w.r.t to A_1. Hence, there is a higher propensity for the formation of pro-eutectoid α.

So, let us check why is that I get a pro-eutectoid phase, when clearly I am not slowly cooling now, so we are talking about two temperatures T x, wherein we do expect a phase, which is something like the pro-eutectoid alpha. And another temperature which is T y to which I am instantaneously quenching, the reason for formation of the pro-eutectoid alpha first is that, if I am talking about the formation of an phase the two competing things.

One is the formation of the alpha and the second is the formation of alpha plus F e 3 C simultaneously or nearly simultaneously which leads to the pearlitic microstructure. With respect to the alpha line, with respect to the or the ACM line, my under cooling is now given by this right which is that means, I have a larger under cooling with respect to the ACM curve. On the other hand, for the formation of alpha plus F e 3 C in the form of a pearlite my under cooling is this much.

So, I can clearly see that my under cooling for the case of I write down this is delta T ,for the formation of pearlite is smaller than delta T for the formation of alpha. Therefore, because of this large under cooling presented when I quench to a point like T y, alpha tends to form first and this alpha though is not the typical to be very strict. It is not the kind of thing which you obtain in slow cooling across from the gamma phase field to the alpha plus F e 3 C phase field for a composition like C 1, it is the under cooling which is causing the formation of the alpha first.

So, in some sense this is also a pro-eutectoid alpha, so now the mystery of the existence of this branch of the curve which is now between the N and B, which we have drawn N and B is gone. That why is that, that I am forming this pro-eutectoid alpha even though I am quenching directly to the alpha plus F e 3 C phase field.

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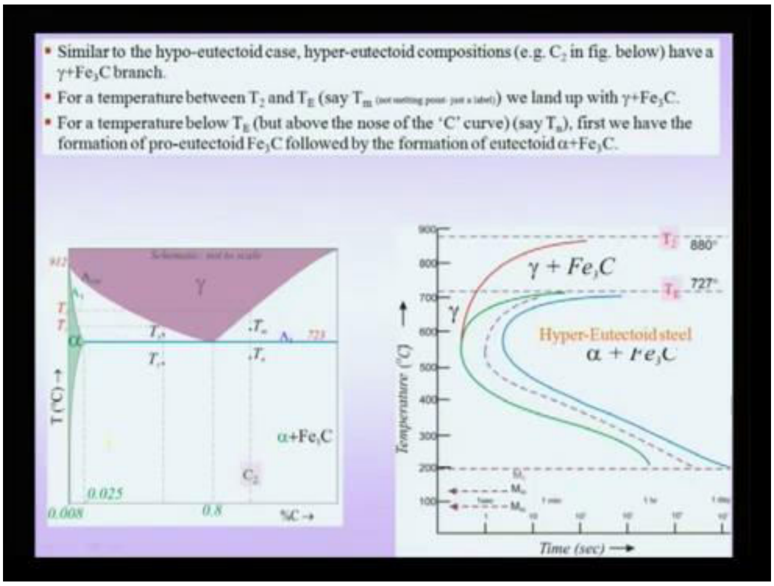


- Similar to the hypo-eutectoid case, hyper-eutectoid compositions (e.g. C_2 in fig. below) have a γ+Fe_3C branch.
- For a temperature between T_2 and T_E (say T_m (not melting point just a label)) we land up with γ+Fe_3C.
- For a temperature below T_E (but above the nose of the 'C' curve) (say T_n), first we have the formation of pro-eutectoid Fe_3C followed by the formation of eutectoid α+Fe_3C.

Now, the scenario for hyper-eutectoid steel is very very similar to the scenario for the hypo-eutectoid steel, now instead of a branch for alpha, which we saw in the case of the hypo-eutectoid steel. Now, we have a branch for F e 3 C, since we are at a hypo hyper-eutectoid composition like for instance, C 2. Now, for this composition suppose I quench to a temperature between T 2 which is here, and T eutectoid which is here, say for instance to a general temperature like T n.

Then between at T m, I would observe for instance this could be T m here, for T m I would first observe the formation of part of the that means, F e 3 C will form part of the F e 3 C will transform to gamma. And of course, the amount of F e 3 C which will form I can use calculating a tie line at this stage, so I know the composition. So, I can use a tie line to calculate the fractions of the alpha and F e 3 C putting the lever of course, at the fulcrum which is now my C 2 composition.

And then of course, the final microstructure would consist of alpha and F e 3 C, so this entire phase field to the right of this curve is an alpha and F e 3 C or gamma plus F e 3 C phase field, so right here. If I starting as usual is with gamma, but then I finally, land up with the gamma plus F e 3 C, now suppose I quench to a temperature like T n which is below the eutectoid temperature, but then not so low that I am crossing the nose of the curve.

That means, I am above the nose N, but below the eutectoid transformation temperature which is like 727 or 723 degrees Celsius, then for such a temperature I would obtain first. So, I am at this temperature like T n, I would first obtain the formation of the pro-eutectoid gamma, now fully understanding as for a pro-eutectoid F e 3 C fully understanding what does this word pro mean in the context of an isothermal transformation.

And we already seen this is caused by the under cooling effect that means, I have more under cooling with respect to T 2, then with respect to the eutectoid temperature, therefore first I have formed the gamma phase F e 3 C phase from the gamma phase. And finally, I will land up with a microstructure which consists of alpha and F e 3 C as dictated by the phase diagram, so the curves the diagrams for hyper and hypo-eutectoid steels are very very similar.

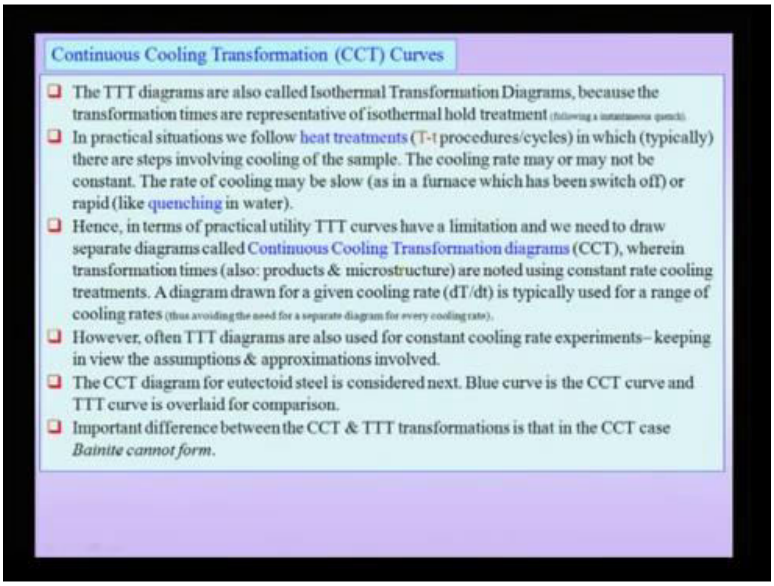
In both cases we have an additional arm to this C curves, and this additional arm as we can see is clearly not asymptotic to this eutectoid temperature, like for instance in the normal arm of course, is a asymptotic to the eutectoid temperature. But, this additional red arm is actually asymptotic to the temperature at which intersects the composition that means, this is asymptotic to a temperature like T 2 which is shown here. Therefore, now I have understood the TTT diagrams for eutectoid steel, which is here the hypo-eutectoid steel which is here ((Refer Time: 49:48)).

And the hyper-eutectoid steel in the process of understanding these diagrams I have also introduced certain transformations, which are actually not the equilibrium transformations which we would see on the phase diagram. But, deformation of a shear product or formation involving shear deformation which is the Martensite, we have also noted that this Martensite is technologically very important. Because, it is a very hard phase and we will see later that it actually happens to hard, but very brittle and therefore, we will have to do additional treatment to our steel to get the desired properties.

We have noted that the nose of the TTT diagram, is an important part of the TTT diagram which I need to avoid, if I want to form Martensite. And Martensite fraction depends not on the time I hold, but among the temperature to which I quench the lower the temperature more the fraction of the Martensite which forms. Further, we have noticed that by using these kind of diagrams, these additional quenching lines and I can extend the utility of my TTT diagrams.

We have also noted that ((Refer Time: 50:53)) in the case of alloy steels, this one common C curve which is shown for the pearlitic and bainitic transformations, actually spreads into two separate C curves. And in the case of the plain carbon steel these merge and therefore, we draw it as one single C curve of course, there are there always has to be two C curves in the sense that there is has to be one for the start and one for the finish. But, what we are talking about there no two separate set of C curves for the bainitic and pearlitic transformations, in the case of the eutectoid steel.

(Refer Slide Time 51:21)



Continuous Cooling Transformation (CCT) Curves

- The TTT diagrams are also called Isothermal Transformation Diagrams, because the transformation times are representative of isothermal hold treatment (following a instantaneous quench)
- In practical situations we follow heat treatments (T-t procedures/cycles) in which (typically) there are steps involving cooling of the sample. The cooling rate may or may not be constant. The rate of cooling may be slow (as in a furnace which has been switch off) or rapid (like quenching in water).
- Hence, in terms of practical utility TTT curves have a limitation and we need to draw separate diagrams called Continuous Cooling Transformation diagrams (CCT), wherein transformation times (also: products & microstructure) are noted using constant rate cooling treatments. A diagram drawn for a given cooling rate (dT/dt) is typically used for a range of cooling rates (thus avoiding the need for a separate diagram for every cooling rate).
- However, often TTT diagrams are also used for constant cooling rate experiments– keeping in view the assumptions & approximations involved.
- The CCT diagram for eutectoid steel is considered next. Blue curve is the CCT curve and TTT curve is overlaid for comparison.
- Important difference between the CCT & TTT transformations is that in the CCT case *Bainite cannot form*.

So, now we are ready to take up the topic of continuous cooling transformation curves.