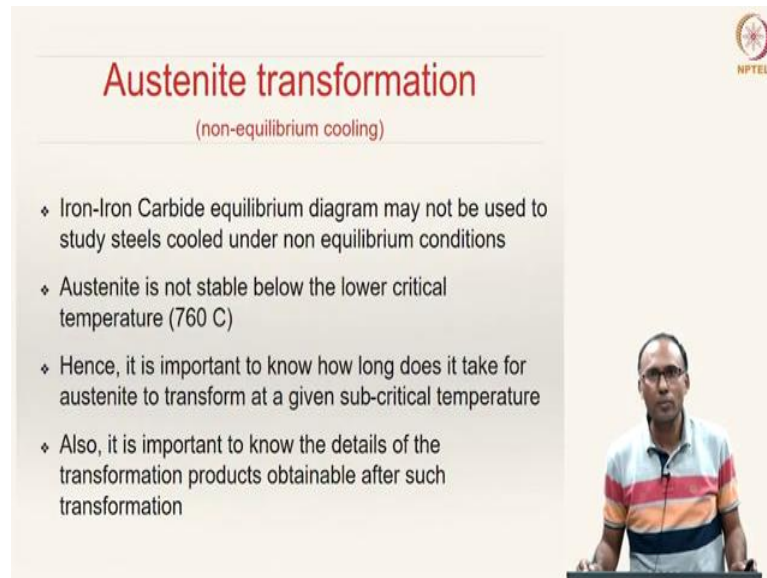


Basics of Materials Engineering
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Lecture - 65
Isothermal Transformation Diagram

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Austenite transformation
(non-equilibrium cooling)

- ❖ Iron-Iron Carbide equilibrium diagram may not be used to study steels cooled under non equilibrium conditions
- ❖ Austenite is not stable below the lower critical temperature (760 C)
- ❖ Hence, it is important to know how long does it take for austenite to transform at a given sub-critical temperature
- ❖ Also, it is important to know the details of the transformation products obtainable after such transformation

The slide includes an NPTEL logo in the top right corner and a video inset in the bottom right corner showing Prof. Ratna Kumar Annabattula at a podium.

Welcome back. In the last class, we have looked at the nucleation and growth during transformation either from liquid state to solid state or within solid phase. When there is a phase transformation, we have discussed the details of nucleation, how nucleation happens, and what are the parameters that govern the nucleation and the nucleation rate and also followed by growth and the overall transformation rate.

In this class, we will primarily focus our attention to a specific material system called steel. We will discuss the solid-state transformation from austenite to the room temperature phase, particularly for plain carbon steels, ferrite and cementite. The transformation of austenite to pearlite is something that we are going to look at.

The iron-iron carbide equilibrium diagram cannot be used to study steels which are cooled under non-equilibrium conditions as it is applicable only under equilibrium conditions.


That means, if you are cooling at a faster rate, you cannot right away use iron-iron carbide equilibrium diagram in order to understand the micro structures, right? We know that

austenite is not stable below the critical temperature 760°C . When you are cooling down at a faster rate, you should know how much time it is going to take. It is important to know how long does it take for austenite to transform at a given sub critical temperature.

Above 760°C , it is stable. If you are cooling it down to a temperature below 760°C , say 500°C , then, how long does it take for austenite to transform to its product phase. It is also important to know the details of the transformation products.


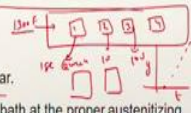
Firstly, the time it takes, and when it transforms from parent phase to product phase, what will be the constituents of your product phase? These are important to know.

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Isothermal Transformation Diagram

- ◆ The austenite transformation may be understood through isothermal transformation diagram
- ◆ How to produce such a diagram?
 - ◆ **Step 1:** Prepare several samples cut from the same bar.
 - ◆ **Step 2:** Place the samples in a furnace or molten salt bath at the proper austenitizing temperature for long time for transformation to complete austenite.
 - ◆ For 1080 steel it is 1425°F
 - ◆ **Step 3:** Place the samples in a molten salt bath which is held at constant subcritical temperature (below A_1), say 1300°F .
 - ◆ **Step 4:** After varying time intervals in the salt bath, each sample is quenched in cold water or iced brine.
 - ◆ **Step 5:** After cooling, each sample's hardness and microstructure are studied.
 - ◆ **Step 6:** The above steps are repeated at different subcritical temperatures until sufficient points are determined to plot the curves on the diagram.



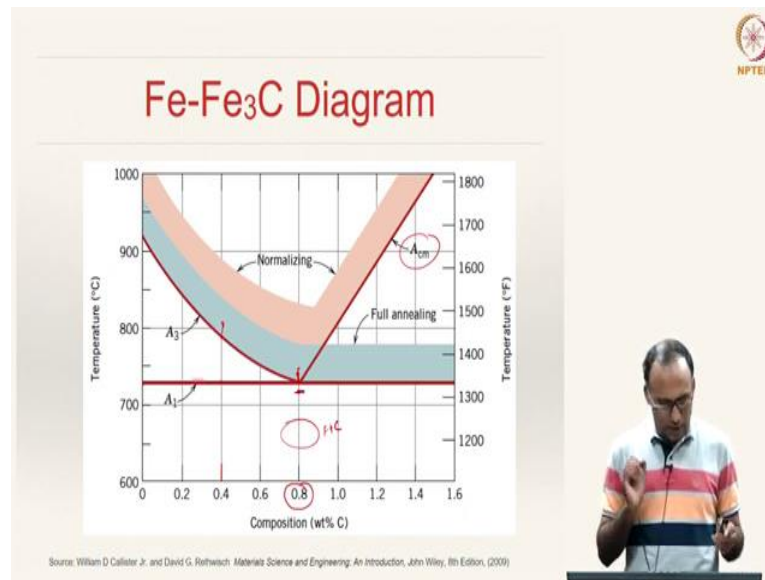
The above information that we are seeking i.e., the time taken and the product phases is something that can be obtained from this diagram called isothermal transformation diagram.

The austenite transformation may be understood through this isothermal transformation diagram. So, how do we generate such a diagram? The process is pretty simple although it is laborious. You take a plain carbon steel ingot and prepare several samples which are cut from the same bar.

The number of samples depend upon number of data points that you need. Cut it from the same ingot in order to ensure that the ingot has same kind of initial microstructure and initial concentration of individual components.

If it all there are some inclusions, they are also uniformly distributed, if you are getting it from the same ingot. This ensures the same operating conditions for the ingot. That is step 1 - you cut several samples. In step 2, place the samples in a furnace or molten salt bath at proper austenitizing temperature.

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What do we mean by austenitizing temperature? For instance, in this portion of iron-iron carbide equilibrium diagram, let us say you have a eutectoid steel at 0.8% carbon. If you are heating the parent phase from below 760° C to above 760° C, then pearlite i.e., ferrite + cementite, can be transformed to austenite completely.

If you are at 0.4% carbon, then the austenite transformation begins here and ends here. Only above this temperature you have complete austenite. Depending upon the composition and hence your temperature at which austenite transformation finishes is going to be different, right. Depending upon the composition of your alloy, place the samples at proper austenitizing temperature for sufficiently long time for transformation to complete austenite.

You know that the room temperature microstructure for an iron-carbon alloy is ferrite and cementite. This ferrite and cementite microstructure will completely transform into austenite or some other microstructure. For steels, because the carbon content is less than 2%, it will completely transform to austenite.

Once you have transformed the entire parent phase to austenite phase, now place the samples in a molten salt bath which is held at constant sub critical temperature below A_1 . This is our A_1 below which austenite is not stable. This is A_3 , above which austenite is stable.

Between A_1 and A_3 , austenite starts transforming to product phase or vice versa depending upon whether you are cooling or heating; that is for hypoeutectoid steels. For hypereutectoid steels, above A_{cm} , austenite is stable. So, you need to keep the samples at a constant sub critical temperature - at any temperature where you want to understand the phase transformation. Let us say below 1300°F which is somewhere here.

If you are taking 1080 steel, first you heat it up to certain temperature above 700°C and then bring it here and then at that temperature, keep it in a furnace. You take the sample after completely austenitizing and keep it there; that means, you are waiting there for sufficiently long time.

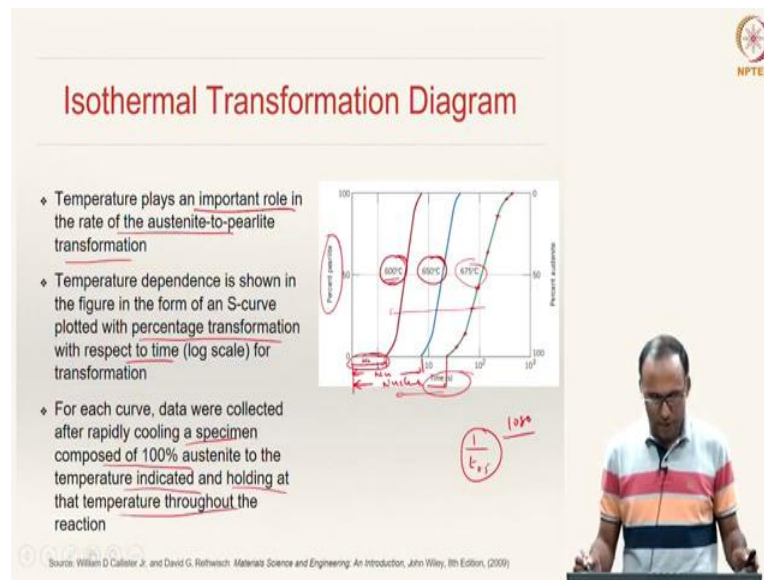
You keep all the samples in the 1300°F furnace and after varying intervals of time, each sample is quenched in cold water or iced brine.

Now, say after one second, you take the first sample out and quench it, and look at the microstructure; then you will be able to see how the amount of product phase present after 1 second; that means 1 second time is given for austenite to transform. Take the second sample after 10 seconds, again repeat the above process; then you will know the fraction of the product phase. Take the third sample after 100 seconds repeat the process – this needs to be done for several samples.

Then, you will be able to plot y , i.e., the transformed product as a function of time. After cooling, the hardness and microstructure of each sample are studied.

The above step is repeated for all the samples as we have discussed. So, now, this is at 1300°F . You do another set of samples at 1200°F and as many subcritical temperatures as you want in order to understand the complete transformation from 760°C or 1400°F .

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Let us say your sub critical temperature is 675° C. At 675° C, you have certain samples. For them, you have measured the percentage pearlite because austenite transformed to pearlite; for instance, consider 1080 steel.

1080 steel will undergo eutectoid reaction and hence it has to transform to alternate layers of ferrite and cementite, and hence you will have pearlite.

This is the nucleation stage at 675° C. And these are the nucleation stages for 650° C and 600° C. So, this is the time that is taken for nucleation. You can see that as you are reducing the temperature of the phase transformation, the nucleation time is also reducing, as we have already discussed.

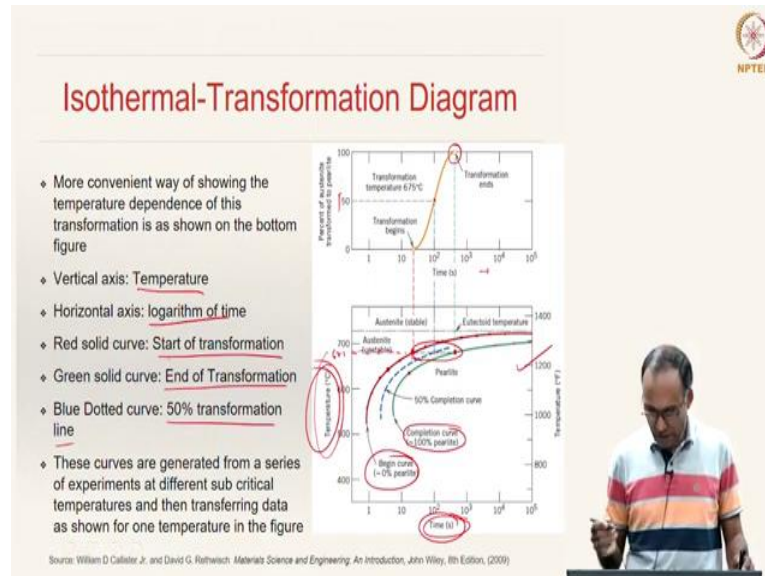
Farther away from the critical temperature at which the transformation is supposed to happen, the degree of under cooling is large, nucleation happens readily.

Then you have growth; you have plotted growth of all the samples. Corresponding to say 20 samples, you will get 20 points on that. Then, if you repeat the same experiment at 650° C and 600° C, you get curves like this.

Temperature plays an important role in the rate of the austenite to pearlite transformation. We have defined rate as $1/t_{0.5}$. So, the temperature dependence is clearly shown in this figure as an S curve, plotted with percentage of transformation with respect to time. Time is always on log scale because the times are going to be pretty large.

For each curve, we have collected the data after rapidly cooling a specimen composed of 100% austenite to the temperature indicated and holding at the temperature throughout the reaction.

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If you take one such curves, let us say at transformation temperature 675° C. There is a more convenient way of showing -- this shows you the percentage of austenite transformed to pearlite as a function of time.

There is a better way or more convenient way of showing these rather than showing different curves at different temperatures. You take this curve at 675° C; on the bottom we are plotting temperature vs time.

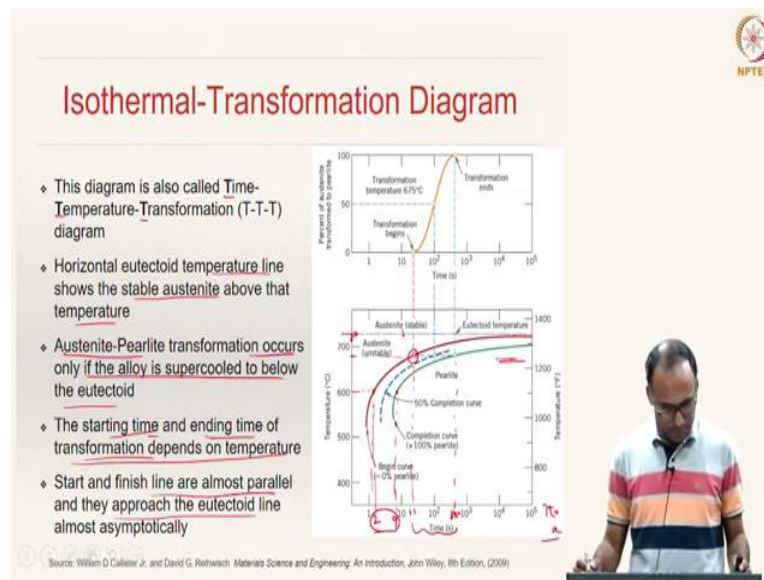
The transformation begins at this time. You drop a vertical and then, this is the time corresponding to start of transformation and this is the time corresponding to end of transformation. At 650° C, the transformation begins at an early stage and also finishes early.

Now, you obtain all the points representing the transformation begin time, at different temperatures. Connect all of them, then you will get this transformation begin curve, i.e., 0% pearlite. Similarly, for different temperatures obtain the time at which transformation finishes - connecting all those points gives the transformation completion curve or 100% pearlite.

It is also customary to show the 50% completion line. This diagram is what we call isothermal transformation diagram or Time-Temperature-Transformation diagram or TTT diagram.

Here, the vertical axis is temperature, horizontal axis is time in logarithmic scale. The red curve represents the start of transformation, the green solid curve represents the end of transformation, and the blue dotted curve represents 50% transformation line. As we have discussed, these are generated from a series of experiments at different subcritical temperatures and then transferring data as shown for one temperature in the figure.

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In the Time-Temperature-Transformation diagram or TTT diagram, here you can see this is the critical temperature, called as the eutectoid temperature above which austenite is stable below which actually austenite is not stable.

When you are cooling here, we are doing non-equilibrium cooling because austenite is not stable here. The horizontal eutectoid temperature line shows the stable austenite above that temperature. And below that, the austenite-pearlite transformation occurs. It occurs only if the alloy is super cooled to below eutectoid.

The transformation otherwise will not occur, at this temperature it will not occur. You have to cool it below the eutectoid, only then the transformation begins. This red curve is asymptotically reaching the eutectoid temperature; it may not touch eutectoid temperature


at all. You need to do some under cooling in order to start austenite to pearlite transformation.

For this particular curve, this is the starting time that is about 11 seconds and it has ended at about, 800 seconds. So, the total time for this transformation is about 790 seconds. The starting time and ending time of transformation depends on the temperature.

If you take at 600° C, this is the starting time that is the ending time. How much time it takes? At 600° C, the transformation start time is about 2 seconds, the end time is about 9 seconds, i.e., it only takes 7 seconds for complete transformation. Whereas, at a higher temperature, it takes much longer time.

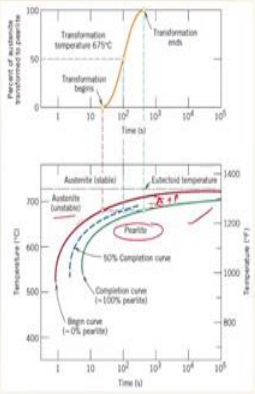
Hence, the starting time and ending time of transformation depends on the temperature at which we are doing the transformation. As we have already seen here, the start line and finish line are almost parallel and they approach the eutectoid line, almost asymptotically.

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Isothermal-Transformation Diagram

- ◆ To the left of the transformation start curve only austenite (unstable) is present
- ◆ To the right of transformation finish line only pearlite is present
- ◆ In between, the austenite is transforming to pearlite and hence both the constituents will be present
- ◆ The above diagram is only applicable for eutectoid plain carbon steel
- ◆ The diagram will change if we change the composition



Source: William D Callister, Jr. and David G. Rethwisch: Materials Science and Engineering: An Introduction, John Wiley, 8th Edition, (2000)

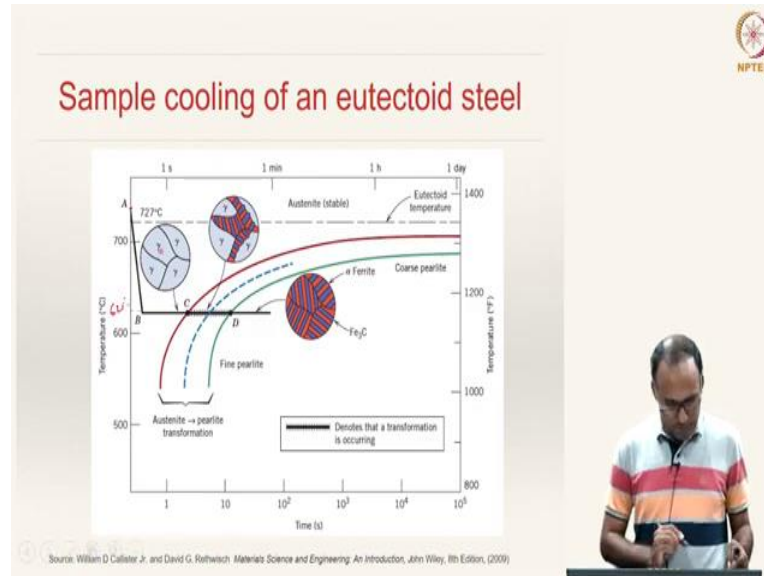


To the left of the transformation start line, austenite is unstable and to the right of the transformation end line, only pearlite is present. Pearlite is stable at this temperature. In between austenite starts transforming to pearlite - in some sense it is a two-phase region.

Hence, both constituents will be present, and this diagram that we have seen here, is only a part of the diagram. You will see the full diagram in the next slides. This diagram is only applicable for eutectoid plain carbon steels. If you are changing the alloy composition and

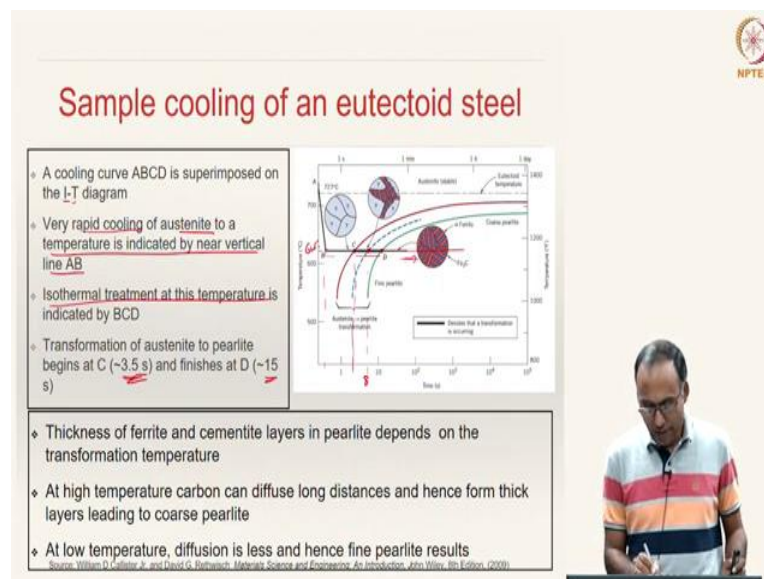
if it is not a plain carbon steel, the diagram will change. So, for a given composition we are drawing this diagram.

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Let us look at a sample cooling of a eutectoid steel. Let us say we are cooling it down here. Initially at 727° C, everything is austenite and you are rapidly cooling down to say 625° C.

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The line ABCD is superimposed on the TTT/isothermal transformation diagram. AB represents very rapid cooling of austenite to a temperature below. So, that is about 625° C

- line AB shows that. Line BCD is basically isothermal treatment at this temperature. That means, at that temperature you are holding the specimen. From point B to C, i.e., from this time to this time which is about 3.5 seconds, nothing will happen – it is the nucleation time.

The hatching represents progress of transformation. The transformation begins at C at about 3.5 seconds and ends at D at about 15 seconds. At 3.5 seconds austenite starts transforming to pearlite. Now you are at say 8 seconds.

By the time you reach 8 seconds, 50% austenite would have transformed to pearlite. If you look at the micro structure here, you will see 50% pearlite and 50% austenite. But if you see the micro structure here, all the austenite would have transformed to pearlite.

What happens if you continue to wait? You are holding at that temperature and it is not necessary to wait, because the transformation has already finished here. So, this isothermal transformation diagram gives you an understanding of how much time you need to wait when you are transforming a product at a given temperature.

If you have this information, you can actually save lot of energy cost. Because if you do not know the temperature in order to be safe, you will keep it for a sufficiently long time, but if you know that at 625° C, if it is a 1080 steel, then that transformation finishes by 15 seconds. All the austenite would have transformed to pearlite. So, you really do not need to wait for sufficiently long time there.

The red region here represents ferrite and the blue region represents cementite. Here, we can see the alternate layers of ferrite and cementite as it is a eutectoid mixture of ferrite and cementite.

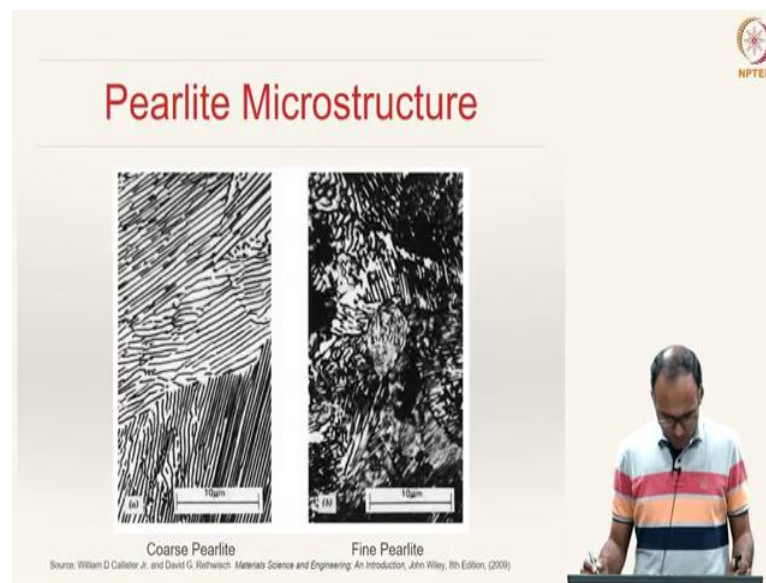
The thickness of ferrite and cementite layers in the pearlite depends on the transformation temperature. Whether ferrite will be thicker or cementite will be thicker, depends on the transformation temperature.

We know that at higher temperatures, carbon can diffuse long distances as the diffusion rate is very high, and hence, forms thick layers leading to coarse pearlite. At high temperatures, the nucleation rate is low, there are fewer nuclei, but transformation rate is higher.

And hence, you have a coarse grain microstructure. If you are doing this transformation at a high temperature, you will prepare coarse pearlite. At low temperatures, because the diffusion is low, and the number of nuclei is, the size of the grain will be small and hence at low temperatures you will form fine pearlite.

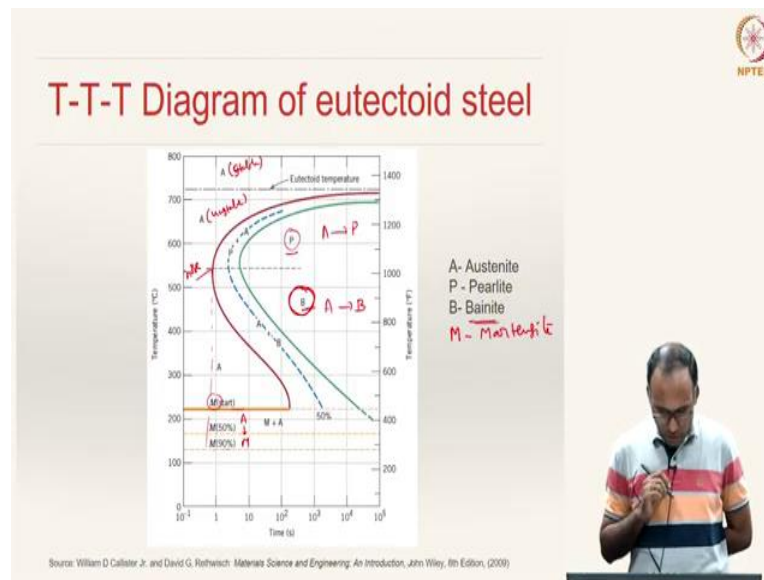
That is why here in this diagram, you can see at very high temperatures you have coarse pearlite, and at low temperatures you have fine pearlite.

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Under a microscope, this is how the microstructures of coarse pearlite and fine pearlite look like.

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The complete TTT diagram over all the temperature ranges, below the eutectoid temperature is shown in this figure. This is the TTT diagram of eutectoid steel again. You can see that you have a transformation begin line and the transformation end line. And you have a temperature at which the transformation rate is maximum, and hence the time taken is minimum.

This is what is called nose of your TTT diagram. Here, you know that this is A, it is stable and A here is unstable. A represents austenite and P represents pearlite. In the previous diagram we have only seen this part the top part. Now, we have drawn the complete one, and the microstructure below the nose is given a different name called bainite.

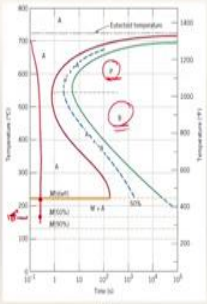
It is also a two-phase system containing ferrite and cementite. However, the microstructure will look little different compared to pearlite and hence it has got a different name called bainite. Above the nose you will have pearlite, below the nose you will have bainite. Above the nose, austenite always transforms to pearlite and below the nose austenite always transforms to bainite. M represents martensite.

At a very low temperatures, the orange lines here show martensite M; this is martensite start line, this is martensite 90% line, and somewhere far away you may have martensite finish line. At these very low temperatures, austenite starts transforming to martensite. In this region, austenite transforms to pearlite, here austenite transforms to bainite, here austenite transforms to martensite.



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T-T-T Diagram of eutectoid steel

- ❖ Austenite transforms to another product called Bainite (feathery structure) at low temperatures while at high temperatures pearlite forms
- ❖ Austenite transforms to another phase called martensite (needle like structure) at much lower temperatures
- ❖ Austenite-to-Martensite transformation is diffusionless unlike A-P and A-B transformations
- ❖ Martensite is a non-equilibrium phase and hence does not appear in Iron-Iron Carbide equilibrium diagram



Source: William D Callister Jr. and David G. Rethwisch: Materials Science and Engineering: An Introduction, 8th Edition, (2009)



Austenite to martensite transformation is little different from austenite to pearlite or austenite to bainite transformation. The bainite microstructure is a feathery microstructure. If you look under microscope, when austenite transforms to bainite, you will see a feather like microstructure which happens at low temperatures, but at high temperatures, you will have pearlite.

As I mentioned austenite also transforms to another phase called martensite which is a needle like microstructure at much low temperatures. However, there is a difference between the transformation of austenite to pearlite or bainite and austenite to martensite.

Austenite to martensite transformation is a diffusion less transformation unlike austenite to pearlite and austenite to bainite transformation. There is no diffusion of atoms, whereas, in austenite to pearlite and austenite to bainite, there is a diffusion process required.

Martensite is actually a non-equilibrium phase, and hence does not appear in iron-iron carbide equilibrium diagram. Iron-iron carbide equilibrium diagram shows only the equilibrium phases.

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Little more about Bainite

- ♦ Bainite forms as needles or plates (depends on temperature)
- ♦ Bainite is composed of ferrite matrix and elongated particles of Fe₃C
- ♦ Pearlite forms above the nose and bainite forms below the nose
- ♦ Pearlitic and Bainitic transformations are competitive
- ♦ If some portion of an alloy transforms to pearlite/bainite, transformation to other microstructure is not possible unless it is re-austenitized.




Bainite forms as needles or plates depending upon the temperature at which austenite transforms to bainite. Bainite is composed of ferrite matrix and elongated particles of cementite.

We have discussed that pearlite forms above the nose and bainite forms below the nose. These two are competitive depending upon the temperature.

Once austenite transforms to pearlite, unless you bring it back to the austenitizing temperature, pearlite cannot transform to another any other product. Only this remaining austenite has possibility to transform to other products. However, already transformed products will not transform to anything else.


If some portion of an alloy transforms to pearlite or bainite, transformation to other microstructure is not possible unless it is re-austenitized. Once austenite transforms to pearlite, pearlite cannot transform to bainite; only austenite can transform to bainite or martensite.

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Spheroidite


- ❖ Spheroidite forms when a pearlitic/bainitic steel is heated and held at temperature below eutectoid for sufficiently long time
 - ❖ e.g., at 700c for 18-24 hours
- ❖ Fe_3C phase appears as sphere-like particles embedded in continuous ferrite matrix
- ❖ This transformation happens by additional carbon diffusion with no change in compositions or relative amounts of ferrite and cementite phases.



We will also look at something called spheroidite. Spheroidite forms when pearlite or bainitic steel is heated and held at temperatures below eutectoid for sufficiently long time. This is because, the cementite phase in this spheroidite microstructure looks like a sphere like particles embedded in continuous ferrite matrix; otherwise, the cementite network may be detrimental for the overall properties of the system.

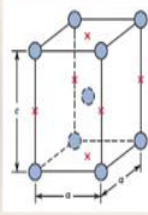
This transformation happens by additional carbon diffusion with no change in compositions or relative amounts of ferrite and cementite phases. It is only rediffusion of carbon such that the long cementite network is broken to make it into small spherical particles.

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Martensite

- ❖ Another transformation product like pearlite or bainite
- ❖ Forms when austenitized iron-carbon alloy is rapidly cooled
- ❖ Martensite is a nonequilibrium single phase structure
- ❖ Formed by diffusion-less transformation
- ❖ FCC austenite changes to BCT martensite



Source: William D Callister Jr. and David G. Rethwisch: Materials Science and Engineering: An Introduction, John Wiley, 8th Edition, (2009)



Let us now spend some time understanding martensite. Another transformation product which also looks very similar to bainite, is called martensite. Martensite forms when austenitized iron-carbon alloy is rapidly cooled. This is only possible when you are cooling it rapidly.

Martensite is a non-equilibrium single-phase microstructure and it is formed by diffusion less transformation. So, what happens when you are cooling it down suddenly at room temperature? Austenite is FCC; when you are cooling it down to room temperature, it has to change to BCC.

When the microstructure is changing from FCC to BCC, it will require sufficient amount of time. We know that the solubility of carbon in FCC is much larger about 2.14% compared to the solubility of carbon in ferrite.

At room temperature, we know the ferrite has a BCC crystal structure. The additional carbon that is present in the FCC lattice should come out; the carbon has to diffuse out of the FCC crystal lattice. But if you are cooling it down rapidly, there is not enough time for the carbon to diffuse out.

As a result, instead of changing its crystal structure from FCC to BCC, the carbon gets trapped due to the less time available, and eventually it will have a body centered

tetragonal structure, as opposed to BCC structure. Martensite has this kind of a body centered tetragonal structure.

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Martensite Microstructure

Photomicrograph showing the martensitic microstructure. The needle shaped grains are the martensite phase, and the white regions are austenite that failed to transform during the rapid quench.

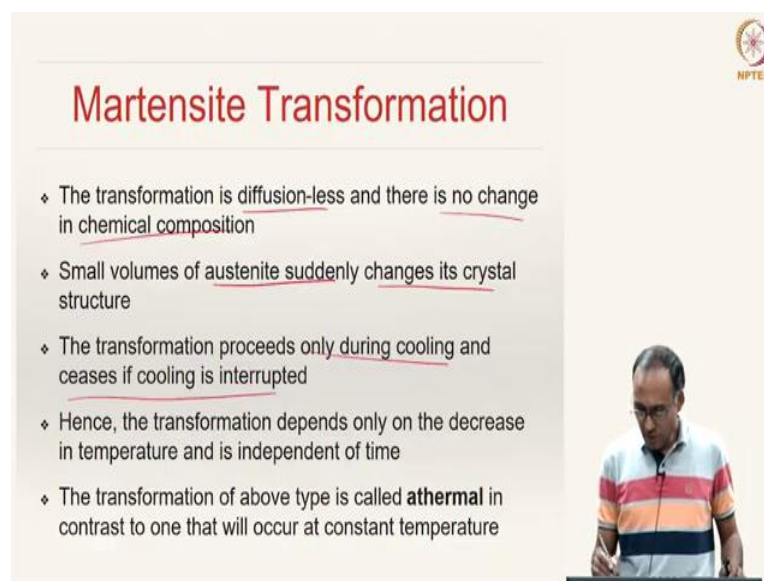
Source: Callister's book

Source: William D Callister Jr. and David G. Rethwisch: Materials Science and Engineering: An Introduction, John Wiley, 8th Edition, (2009)

The slide features a central photomicrograph of a metal microstructure with dark, needle-shaped regions (martensite) and lighter, irregular regions (austenite). To the right of the image is a small inset video of a presenter in a striped shirt.

If you look at the microstructure of martensite under microscope, it looks something like this; which is as we have discussed – it is a needle like microstructure. The white regions here are the austenite that failed to transform during rapid quench. So, that is retained austenite and the black ones are your needle like structure called martensite.

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Martensite Transformation

- ❖ The transformation is diffusion-less and there is no change in chemical composition
- ❖ Small volumes of austenite suddenly changes its crystal structure
- ❖ The transformation proceeds only during cooling and ceases if cooling is interrupted
- ❖ Hence, the transformation depends only on the decrease in temperature and is independent of time
- ❖ The transformation of above type is called **athermal** in contrast to one that will occur at constant temperature


The slide features a list of five bullet points describing the characteristics of martensite transformation. To the right of the text is a small inset video of a presenter in a striped shirt.

The transformation of martensite is diffusion less, and there is no change in chemical composition. Small volumes of austenite suddenly change their crystal structure because of the rapid cooling. The transformation proceeds only during cooling and ceases if cooling is interrupted; what is the meaning of that?

What happens on rapid cooling? Austenite starts transforming to martensite and if you are holding it at this temperature 175°C , then what happens? Even if you wait for sufficiently long time, austenite does not transform to martensite. It has already transformed to 50% martensite; it is only depending on temperature; it is not dependent on time.


Only with a further reduction in temperature, further transformation of austenite to martensite takes place. Otherwise, you will still have 50% martensite and 50% austenite. We will look at that in detail in the next class. So, the transformation proceeds only during cooling and ceases if the cooling is interrupted. Hence, the transformation depends only on the decrease in temperature and is independent of time. It is not a diffusional process and hence it is independent of time. This type of transformation is called athermal transformation, in contrast to one that will occur at constant temperature.

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Martensite Transformation

- ♦ The amount of martensite formed with reduction in temperature is not linear.
- ♦ Number of martensite needles produced at first is small; then the number increases, and finally, near the end, it decreases again.
- ♦ The temperature of the start of martensite transformation is known as *M_s temperature* and that of the end of martensite formation is *M_f temperature*.
- ♦ If the steel is held at any temperature below *M_s*, the transformation to martensite will stop and will not proceed again unless the temperature is dropped.
- ♦ Martensite transformation of a given alloy can not be suppressed, nor can the *M_s* temperature be changed by changing the cooling rate.



In the next class, we will discuss in detail about the martensite transformation. We will also talk about the effect of cooling rates on getting different kinds of microstructure for eutectoid steels. Thank you very much.