Basics of Materials Engineering
Prof. Ratna Kumar Annabattula
Department of Mechanical Engineering
Indian Institute of Technology, Madras

Lecture - 66
Martensite Transformation, C-C-T Diagram

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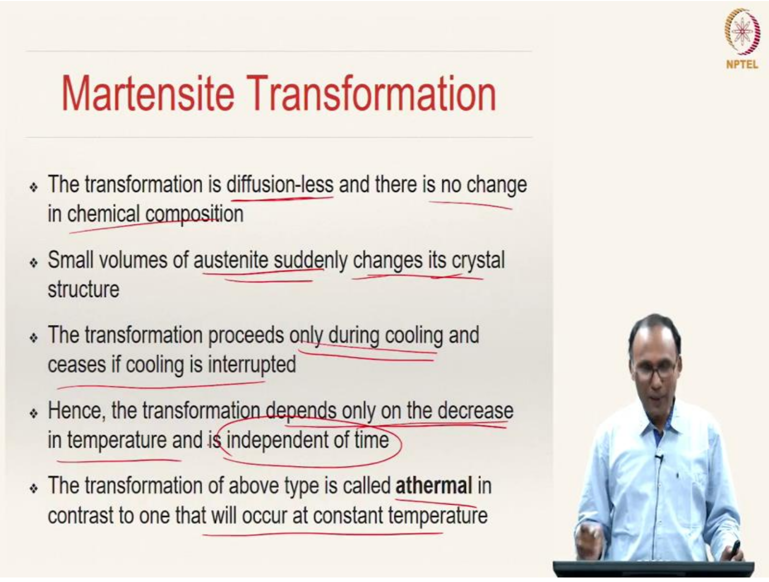

Welcome back. In the last class, we have looked at different transformation products from austenite. Transformation of austenite to pearlite occurs above the nose and austenite to bainite below the nose. Under rapid cooling, we have seen that austenite would transform to martensite.

We have stopped the discussion at this particular slide, where we were discussing the martensite transformation. As we have already mentioned, the transformation of austenite to martensite is a diffusion less transformation. Hence, there is no change in chemical composition.

Under rapid cooling, small volumes of austenite suddenly change their crystal structure. The transformation proceeds only during cooling and ceases if cooling is interrupted.

That means, if you stop reducing the temperature beyond martensite start temperature, further transformation of austenite to martensite will not happen.

Hence, the transformation depends only on the decrease in temperature and is independent of time. At a given temperature, however, long you keep, the transformation will not happen because the martensite transformation is only a temperature dependent transformation. It always happens at a constant temperature and it happens readily; there is no time involved there.

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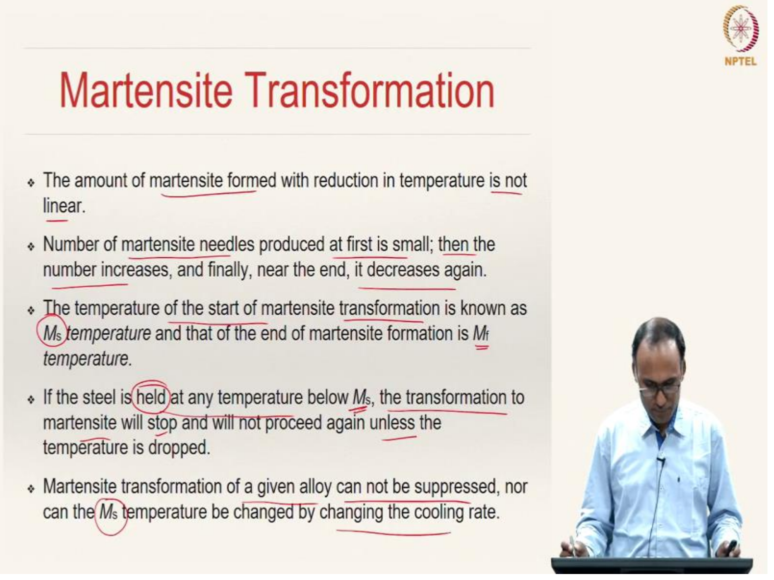

The amount of martensite transformed with reduction in temperature is not a linear function. If you are reducing the temperature from martensite start temperature below, the amount of transformation from austenite to martensite does not scale linearly with the temperature reduction. The number of martensite needles produced at first is small and then, the number increases and finally, near the end it decreases.

It is like an S-shaped curve, where initially you have a small amount of transformation of austenite to martensite and at medium temperatures in between, the transformation rate will be more.

At temperatures very close to martensite start temperature, the martensite needles produced are very low. In the middle range, i.e., in between martensite start to martensite finish temperature, you will have reasonably steep increase in number of martensite needles and finally, it decreases again.

The temperature of the start of martensite transformation is known as M_s or martensite start temperature and the temperature at which martensite transformation finishes; that means, when austenite transforms to martensite completely, then it is called martensite finish temperature.

If steel is held at any temperature below M_s, then the transformation to martensite will stop. If you are holding at that particular temperature, the transformation will not proceed unless the temperature is dropped. The martensite transformation of a given alloy usually cannot be suppressed. If the cooling rate is high, if you are hitting the martensite start temperature, it will transform from austenite to martensite.

Neither can the transformation be suppressed nor can the temperature M_s be changed. The martensite start temperature cannot be changed by the cooling rate. It only depends on the alloy composition. For a given alloy composition, martensite start temperature and martensite finish temperature are fixed.

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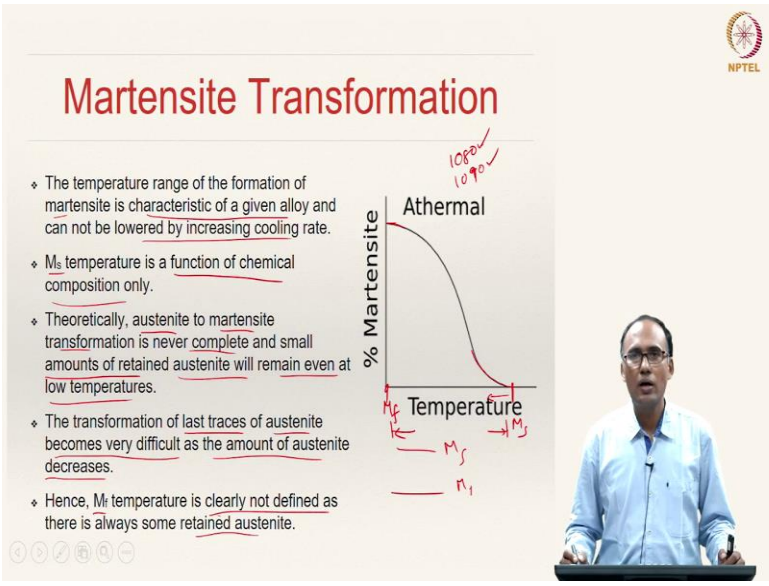

As you are reducing the temperature, initially the martensite transformation will be less and as you are further reducing the temperature, the martensite transformation picks up and again in the end it slows down.

This is sort of your martensite start temperature and this is probably martensite finish temperature. So, this range during which the martensite transformation happens from austenite is a characteristic of a given alloy and it cannot be lowered by increasing the cooling rate.

It does not depend on the cooling rate and as we have already mentioned, the temperature M_s is a function of chemical composition only. If you are talking about 1080 steel and 1090 steel, their martensite start temperatures and finish temperatures are fixed. This one will have a specific martensite start temperature; this one will have another specific martensite start temperature.

So, the martensite start temperature depends only on the chemical composition, not on the cooling rate. Theoretically, austenite to martensite transformation is never complete; that means, you will not have 100 percent austenite transforming to martensite.

Theoretically, it is never complete and small amounts of austenite will remain even at low temperatures. Whenever we are referring to completion of the austenite to martensite transformation, it is not necessarily 100 percent, probably 99 percent. So, remaining 1 percent is retained as austenite.

The transformation of last traces of austenite becomes very difficult, as the amount of austenite decreases. Hence, the M_f temperature, the martensite finish temperature is not clearly defined as there is always some retained austenite in the product.

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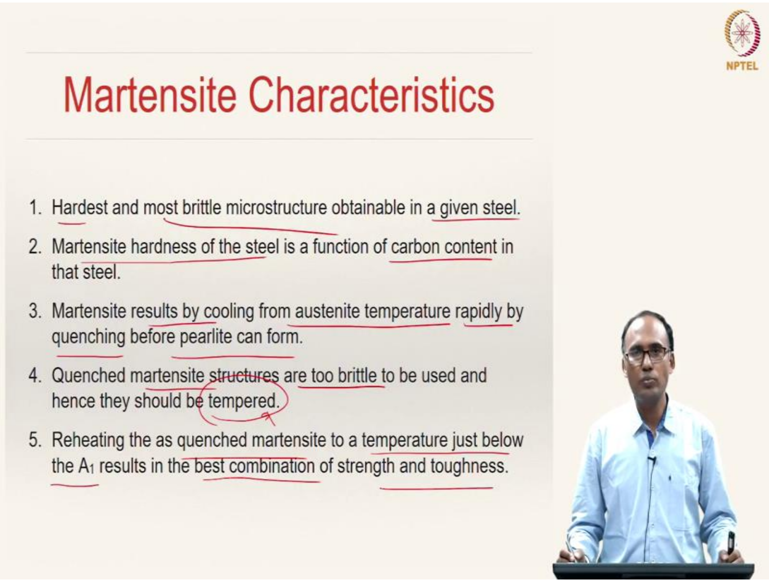

Martensite is the hardest and the most brittle microstructure that is obtainable in a given steel. So, for a given steel alloy, the martensite microstructure is the hardest and brittle microstructure that one can obtain. The hardness of martensite is a function of carbon content in the steel.

We know that, as you increase the carbon content, you will increase the hardness and brittleness. Similarly, the amount of hardness is also a function of carbon content. So, the martensite results by cooling from austenite temperature rapidly by quenching before pearlite can form. So, how do you get it?

Before pearlite can form, you quench it. Quenching means rapid cooling. You rapidly cool austenite such that no pearlite is formed and you bring the temperature all the way down to martensite start temperature; that is when your austenite transforms to martensite.

The quenched martensite structures are too brittle because of the rapid cooling rate and the microstructure development. Hence, they cannot be used for applications right away, unless they are tempered.

All the martensite microstructures should be undergoing another heat treatment process called tempering. Only the tempered martensite will offer some additional strength and toughness; otherwise, in its quenched form, martensite is extremely brittle to be used for any technological applications.

Reheating the as-quenched martensite to a temperature just below A_1; that means, lower critical temperature results in a best combination of strength and toughness. So, you need to do another heat treatment process after obtaining quenched martensite.

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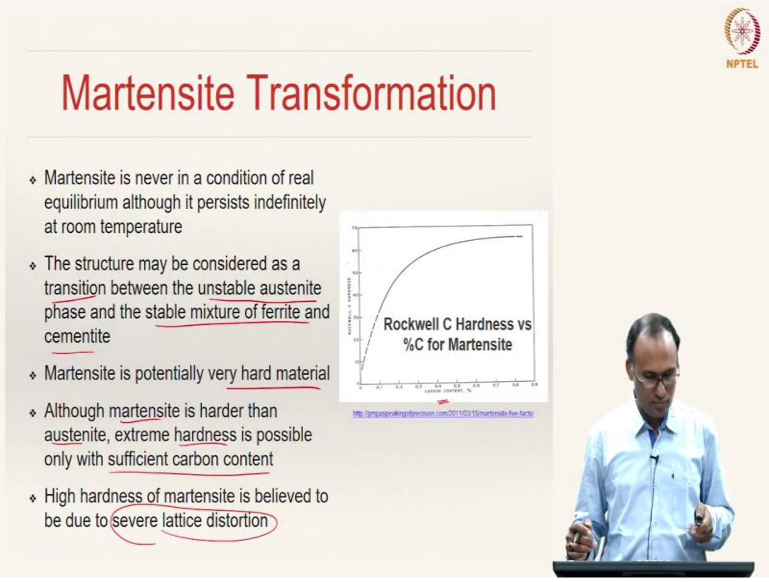

The martensite hardness as a function of carbon content is shown in this figure. As the carbon content increases, the martensite hardness increases. Of course, beyond certain value of carbon content, the martensite hardness levels off.

Martensite is never usually in a condition of real equilibrium - it is a non-equilibrium phase, although it persist indefinitely at room temperature. In that sense, the structure or the martensite structure can be considered as a transition between unstable austenite phase and stable mixture of ferrite and cementite.

It is some phase in between unstable austenite and a stable pearlite microstructure and as we have discussed, it is a potentially very hard material. Although martensite is harder than austenite, extreme hardness is possible only with sufficient carbon content. If you do not have enough carbon content, you may not have a good enough hardness. Another reason why the martensite shows extreme hardness is because of the severe lattice distortion caused by the trapped carbon atoms in the lattice.

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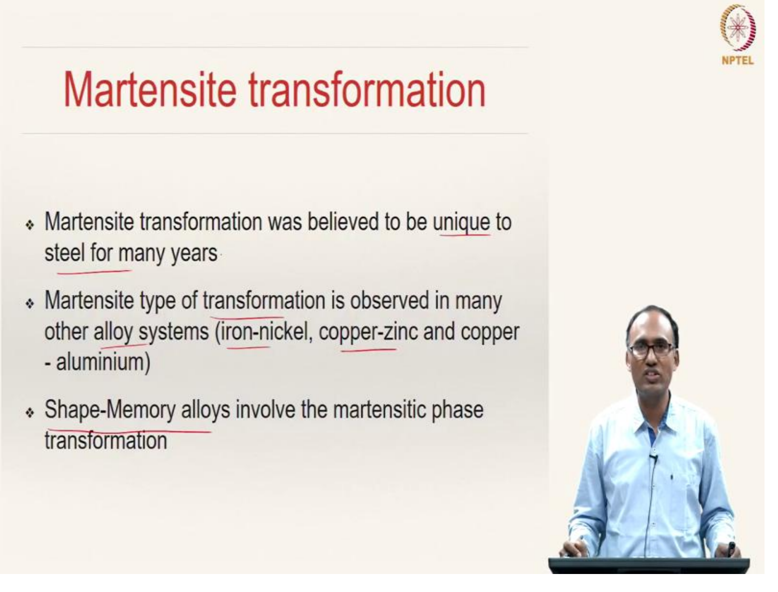

For several years, the transformation of austenite to martensite under rapid cooling was believed to be unique for steel. People thought this is a special phenomenon in steels.

However, after several years of studying various other alloys, the martensite transformation was observed in many other alloy systems such as iron-nickel, copper-zinc, copper-aluminum, nickel-titanium and so on. A special class of materials called shape-memory alloys involve the martensite phase transformation, wherein, there is a diffusion-less transformation. Hence, they sort of give very interesting properties, where they can remember their shapes.

If you apply certain deformation to a shape-memory alloy at room temperature, and then if you supply additional heat energy, the material goes back to its original configuration. Even if you impart plastic deformation, it goes back to its original shape.

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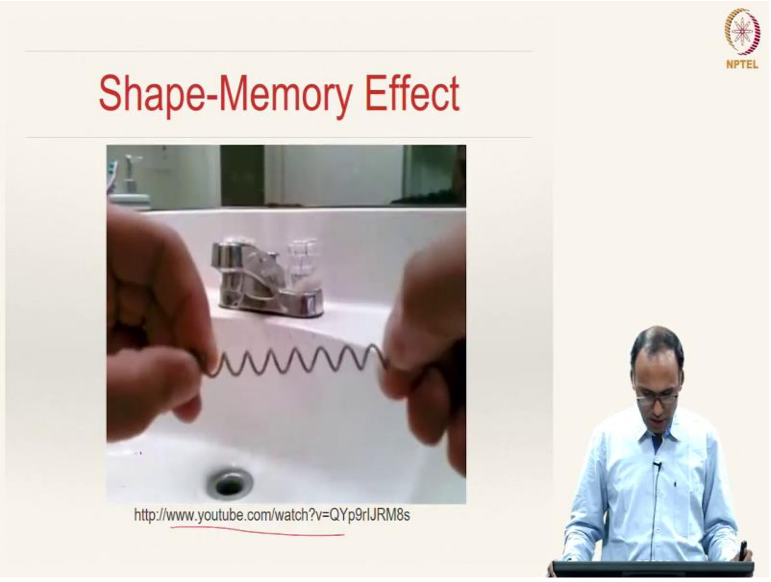

Here I am showing you a video which describes the shape-memory effect of a nitinol alloy; a spring made of nitinol alloy. You can view at this YouTube link. Here we can see that the spring which is a shape-memory alloy made of nitinol is being deformed plastically i.e., a permanent deformation is applied.

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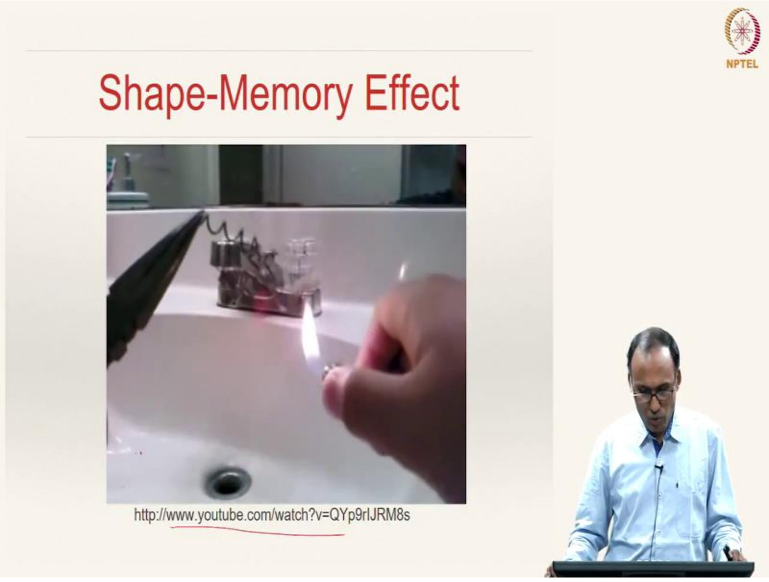

You give a very complex deformation and a rather large deformation; the strains are also large as you can see here. When heat energy is provided, it undergoes a phase transformation and goes back to its original configuration.

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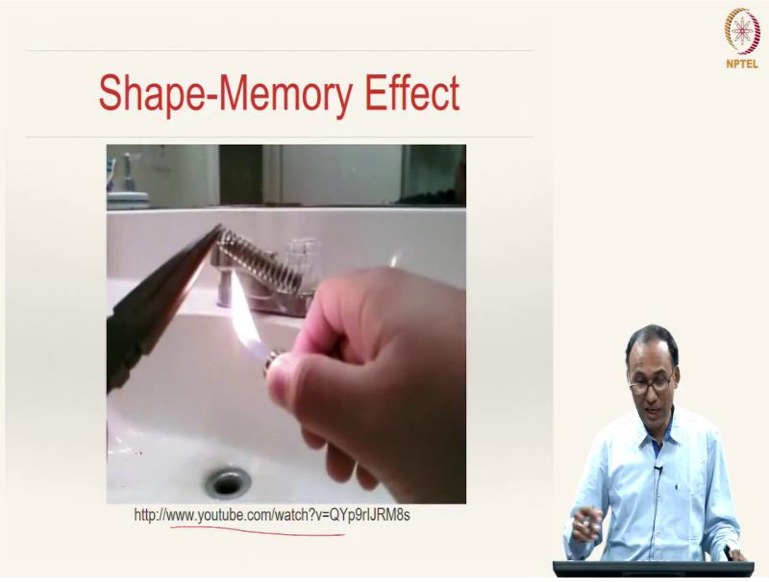

You can see that with the supply of heat energy, there is some transformation happening and then, the entire spring is regaining its original shape. It is not elastic deformation that is getting regained, even if it is plastically deformed to another state with very complex deformation, you are able to regain the shape.

Nowadays, these materials are called smart materials and they have several applications, particularly in medical industry, aerospace industry and so on. I encourage you to go through certain literature that is available on shape-memory effect in several textbooks or the online resources.

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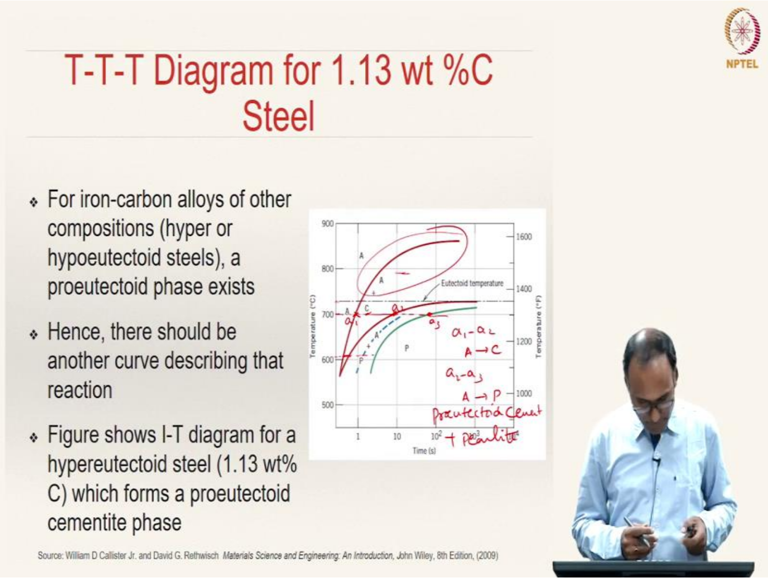

We have seen the Time-Temperature-Transformation diagram or isothermal transformation diagram for eutectoid steel. However, how does such a Time-Temperature-Transformation diagram look like for a non-eutectoid steel i.e., either hyper eutectoid steel or hypo eutectoid steel. Here, we are showing the T-T-T diagram for 1.13 weight percent carbon steel, which is hypereutectoid steel.

Upon cooling, the microstructure that we would expect based on our study on phase diagrams is that you will have a pro eutectoid cementite. Austenite first transforms to pro eutectoid cementite above the lower critical temperature and once it reaches A_1, it starts transforming to eutectoid mixture of ferrite and cementite.

You have a pro eutectoid cementite phase and a pearlite phase. You have an additional curve which represents your pro eutectoid cementite phase. So, if you are at eutectoid temperature and above that you will have transformation to pro eutectoid cementite phase.

That is why this region is A + C that is cementite. Once you are below the eutectoid temperature, then you will have transformation from the remaining austenite, i.e., whatever austenite is remaining. Some amount of austenite is transformed to cementite and remaining austenite would transform to eutectoid mixture ferrite and cementite, that is pearlite.

Basically, if you are cooling down to $700°$ C and then, you are waiting here, you see that between point A_1 and A_2, austenite is transforming to cementite and between A_2 to A_3 austenite transforms to pearlite and after A_3, the microstructure has pro eutectoid cementite plus pearlite.

This additional curve represents the pro eutectoid transformation as we have already discussed and here, we will know the time taken for austenite to transform for a given alloy -- this is 1.13 weight per carbon. So, you can see that if you rapidly cool it down, the amount of pro eutectoid phase reduces.

At higher temperature, the amount of pro eutectoid phase is more and at lower temperature, the fraction of pro eutectoid phase is going to be less. Most of it will be converted to pearlite. By looking at this, you can design the cooling cycle in such a way that you can get the desired amount of pro eutectoid cementite in the microstructure.

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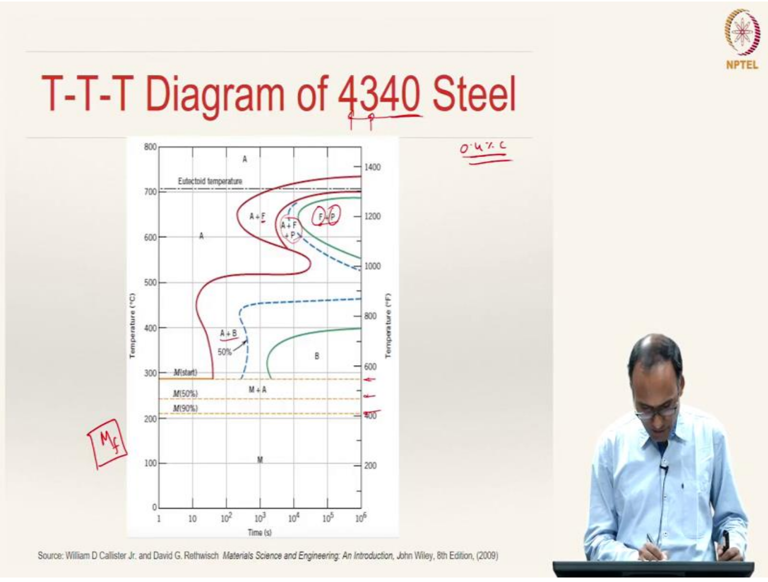

This is the Time-Temperature-Transformation diagram for a 4340 steel. So, here 4 represents the alloy steel type, 3 percent represents the predominant alloy in composition and 40 represents 0.4 percent carbon.

For this particular alloy, you see that the Time-Temperature-Transformation diagram looks much more complicated. Here you have austenite - because it is 0.4 percent carbon, you will have pro eutectoid ferrite phase. So, that is why you have austenite plus ferrite.

And then, you will have austenite + ferrite + pearlite and then, pearlite + ferrite. Ferrite + pearlite is because of pro eutectoid ferrite and the remaining pearlite. Here, you will see that austenite is transforming to bainite below the nose.

Nevertheless, you will have again, there is martensite start temperature, 50 percent martensite transformation and also 90 percent. Nowhere have we seen M_f because as we have discussed martensite finish temperature line is very difficult to identify, because there is always going to be some amount of austenite that is going to be retained.

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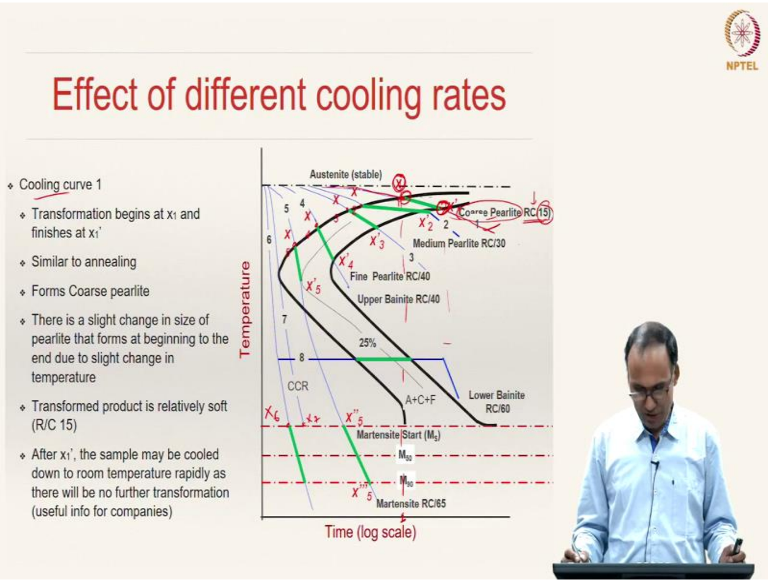

There will not be 100 percent martensite line; it is very difficult to identify such lines. Usually, most of the T-T-T diagrams will show 90 percent martensite. Let us now look at the effect of different cooling rates and the resultant microstructures of the eutectoid alloys. We are paying attention to eutectoid alloys - so that is 0.8 percent carbon.

Here we have 8 different cooling curves and will see what sort of a microstructure one would get for each of these cooling curves. So, here this is cooling curve 1 and from cooling curve 1 to 8, we have increase in cooling rate.

This is X_1, X_2, X_3, X_4, X_5; this is X_6 and this is X_7. Let us look at what is going to happen in this system. For instance, let us look at cooling curve 1. We have shown in between on that line, a green hatched line, which represents the transformation progress scenario.

Here, X_1 is very slow cooling rate and you can see that the transformation does not begin until the time corresponding to X_1 is reached.

The transformation begins at X_1 and ends at $X_1{}'$. We can see that, here, the transformation is happening at very high temperatures. At high temperatures, the nucleation rate is low, but the diffusion rate is high. Since the nucleation rate is low, the number of nuclei formed are few and as a result, the microstructure will be coarse.

The end product here is going to be coarse pearlite and besides each and every microstructure, we also written the Rockwell hardness on Rockwell scale C. Here you can see that Rockwell hardness is 15 and as you are coming down, the hardness increases because you are increasing the cooling rate.

Here you have coarse pearlite. Note that here when you are cooling down, you are not waiting at constant temperature, you are continuing to reduce. The austenite that has transformed to pearlite here is happening at higher temperature, compared to the transformation of austenite to pearlite at this location.

That means, the temperature is lower compared to here, which means the pearlite microstructure is also going to have a gradation. It is coarse pearlite overall; but again, within that, you will have the grains of austenite transforming to pearlite here will have a larger size compared to the grains of austenite transforming to pearlite here.

There will be a slight change in the size of pearlite that is forming in the beginning and in the end. After $X_1{}'$, you do not need to continue to cool at the same rate because all the transformation has happened; now, you can rapidly cool it down.

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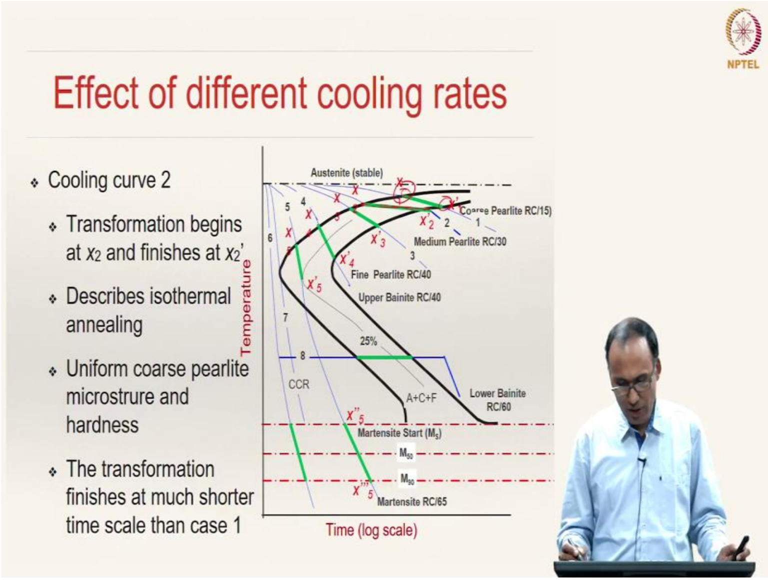

This information is extremely useful for industry because you know until what time you need to wait for complete transformation of austenite to pearlite. After the transformation has happened, you can cool down at a much faster rate because you do not have any non-equilibrium phases staying there anymore.

Further cooling down will only reduce the temperature of the component. Let us look at cooling curve 2; this is X_2 and this is X_2'. The transformation begins at X_2 and ends at X_2'. This sort of represents isothermal transformation; that means, you are actually at constant temperature.

You are holding this specimen at that temperature and then, you can see that because it is at constant temperature, the pearlite grain size that you are getting will be uniform throughout. However, the size of the grain will be smaller than what has been produced in this region, because the temperature here is lower.

So, you will have a uniform grain size and the size of the grain will be little smaller than this coarse pearlite. It is somewhere between these two sizes -- this size and that size. The transformation finishes at X_2', after which you can cool down rapidly.

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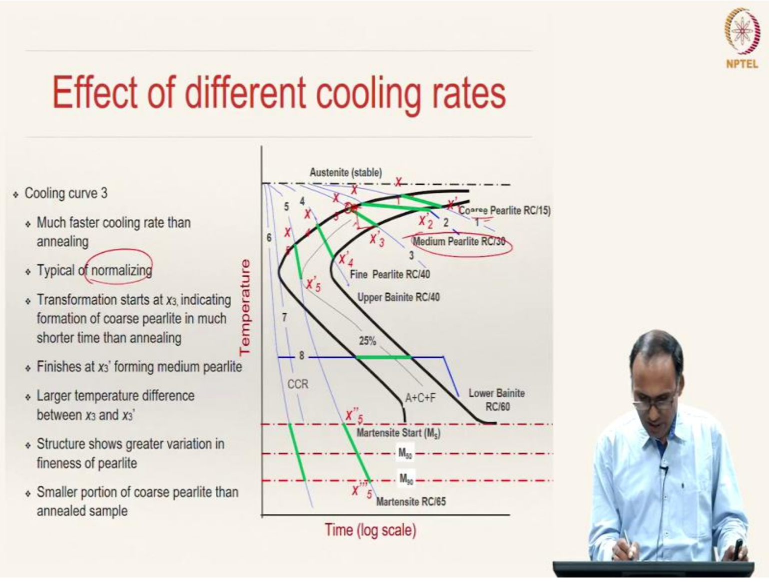

Let us look at X_3. This is a much faster cooling rate and there is the range about which your cooling is larger compared to first $X_1 - X_1'$ range. A faster cooling rate of this range is typical of a heat treatment process called normalizing. We will see what is normalizing. Normalizing uses a higher rate of cooling, whereas, the first one i.e., $X_1 - X_1'$ sort of represents the annealing process.

The transformation begins at X_3 and ends at X_3'. The microstructure of the pearlite is medium pearlite because it is going to be finer than coarse pearlite; that is why it is called medium pearlite. In this case also, you will have a size variation from the pearlite that is formed in the beginning to the end. There will be a greater variation in fineness compared to $X_1 - X_1'$, because there is a larger temperature gradient.

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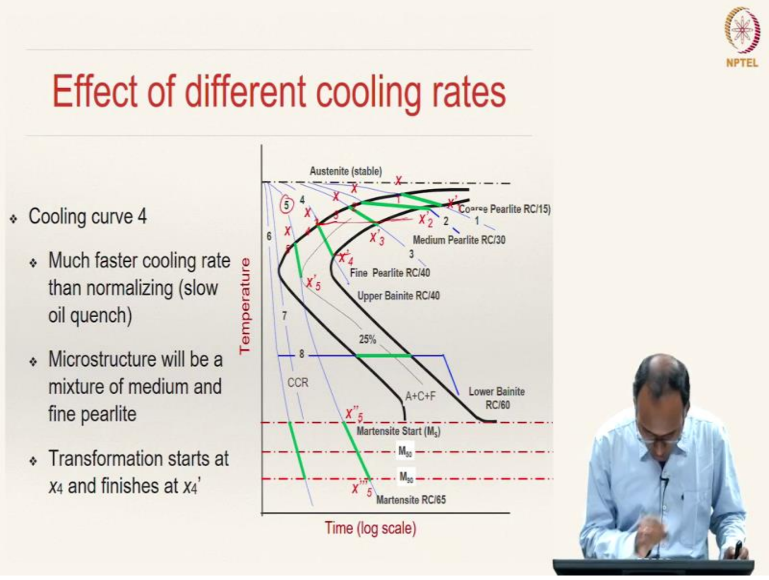

Let us look at curve 4, which has a much higher cooling rate. You can see that this is very close to slow quenching - it is not quenching, but it is not very slow cooling rate. It also has a cooling rate much faster than normalizing. Again, the microstructure will be starting from medium pearlite. In this region, you have medium pearlite; in this region, you have fine pearlite. So, the microstructure will have a medium pearlite to fine pearlite variation.

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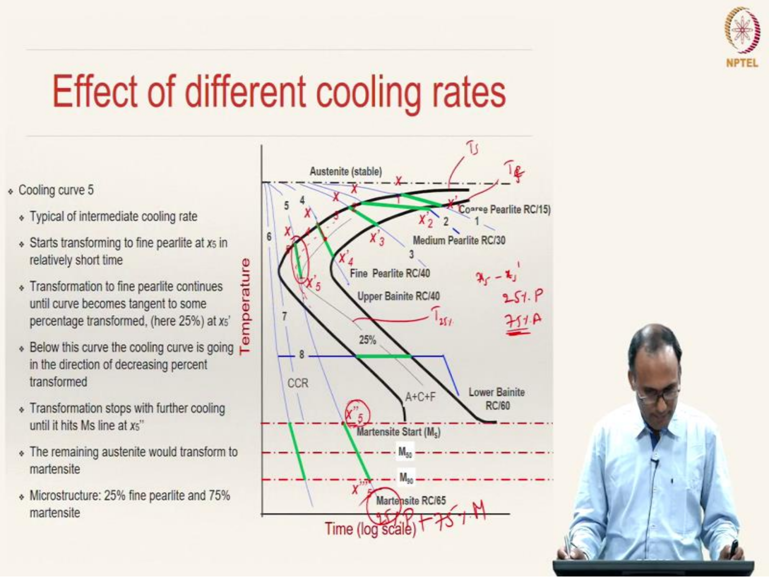

The cooling curve 5 is very interesting. It is a typical of an intermediate cooling rate. You can clearly see this is the transformation start and this is transformation end line or finish line and this is transformation 25 percent.

When you are cooling down along this region for instance X_4, by the time it reaches here, you have only 25 percent of your austenite transformed to pearlite. Now, if you come here on the X_5 line, it is becoming tangent to this curve.

Suppose if you are seeing here, what will be the transformation? That will be less than 25 percent; that means, the moment this cooling curve becomes tangent to one of the transformation fraction lines, that is when the transformation stops. Because below that the transformation is actually less than 25 percent; that means, there cannot be any transformation happening and that is the reason why you do not have this green line extending throughout this region; only in this region, the green line is present.

That means, the transformation happens only from here to here. By the time it reaches here, for $X_5 - X_5'$, you have 25 percent pearlite and remaining 75 percent is austenite. On continuing the cooling process at the same rate, you do not have further transformation and then, you are hitting martensite start temperature at X_5''.

The moment you are hitting martensite start temperature at X_5'', that is when the remaining 75 percent austenite will start transforming to martensite. In this case, let us assume this is the martensite finish temperature.

Then, the remaining 75 percent austenite would have transformed to martensite. So, here the microstructure will be 25 percent pearlite + 75 percent martensite.

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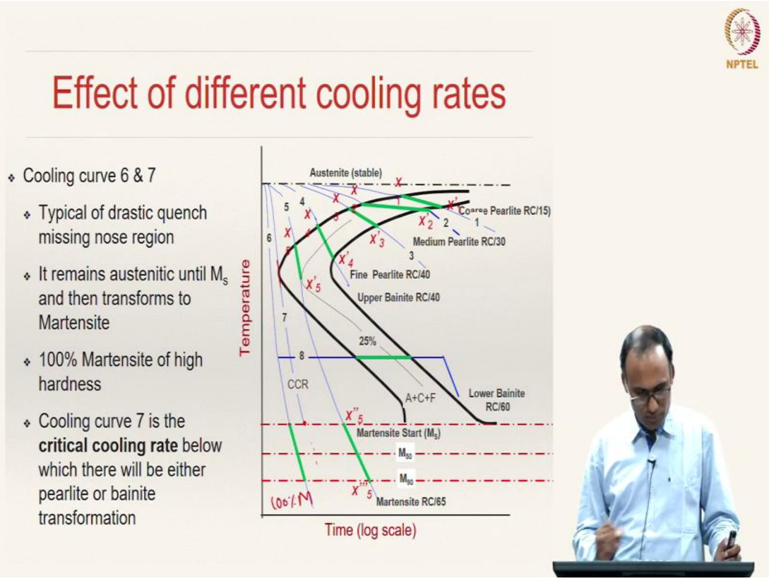

Let us look at X_7 first before going to X_6. It is tangent to the transformation start line; that means, it is never going into the two-phase region and no transformation of austenite to pearlite can take place. This rate of cooling is called as critical cooling rate.

Below this cooling rate, only austenite to pearlite or bainite transformation takes place, and above this cooling rate, austenite will not transform to pearlite or bainite; it will directly transform to martensite. So, you can see this cooling curve 7 ends here actually. If it is ending here, what happens? At this temperature, you have stopped; that means, you are not further reducing the temperature.

All the microstructure will be only of austenite because you have not reduced the temperature further. The martensite transformation requires a further reduction in the temperature. If you do not reduce the temperature, even if you wait there for sufficiently long time, no transformation takes place.

Now, look at 6. Here it is continuing to cool down; that is when all austenite is transforming to martensite. The microstructure will be 100 percent martensite.

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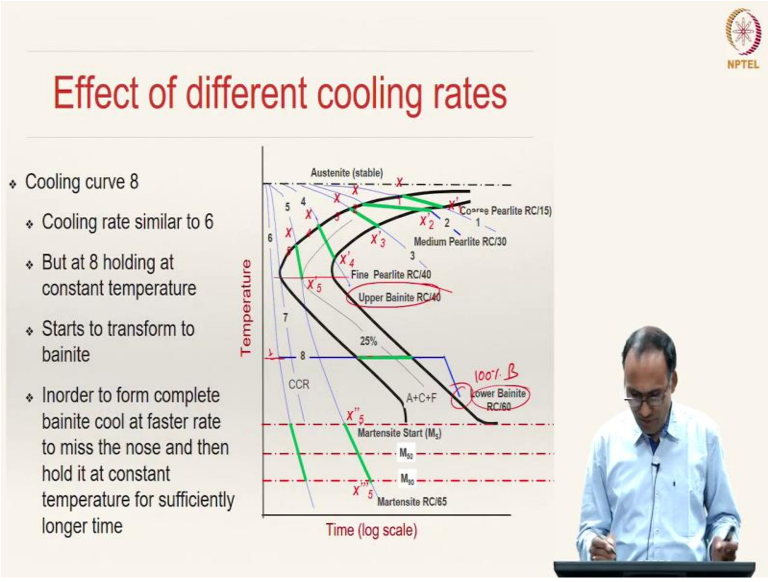

Let us look at cooling curve 8. How does this look like? So, you can see here, it is a very high cooling rate, but you are not continuing to cooling down, you are holding at this temperature. This temperature is your below the nose. The moment you are coming below the nose, all the austenite will have to transform to bainite.

That is why you see that this is all transforming to bainite. So, the microstructure here will be 100 percent bainite. Very close to nose will be upper bainite, far away from the nose will be lower bainite. So, it is somewhere close to lower bainite.

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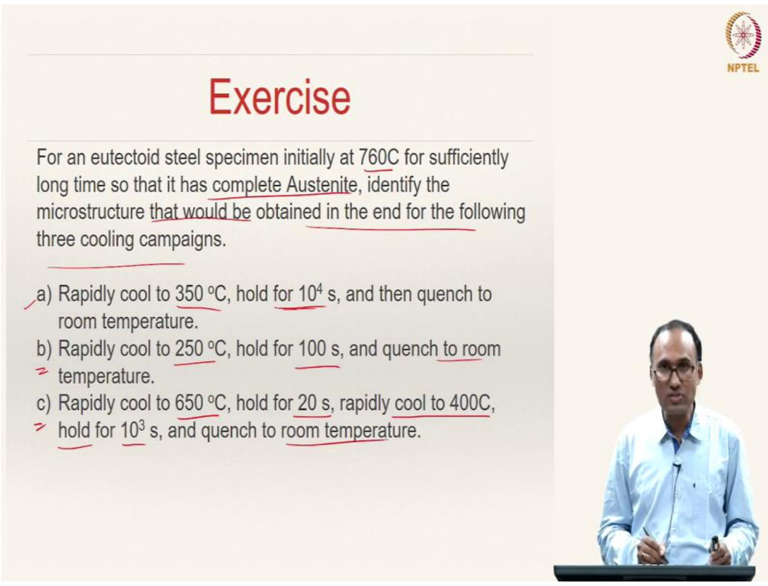

Let us now look at how this cooling curve works by solving this problem. For a eutectoid steel specimen, initially at $760°$ C, for sufficiently long time so that it has complete austenite -- it is completely austenetized.

If all the microstructure is austenite, now identify the microstructure that would be obtained in the end for the following three cooling campaigns. In the first case, we rapidly cool to $350°$ C, hold for 10^4 seconds and then, quench to room temperature. Let us look at each case one after the other.

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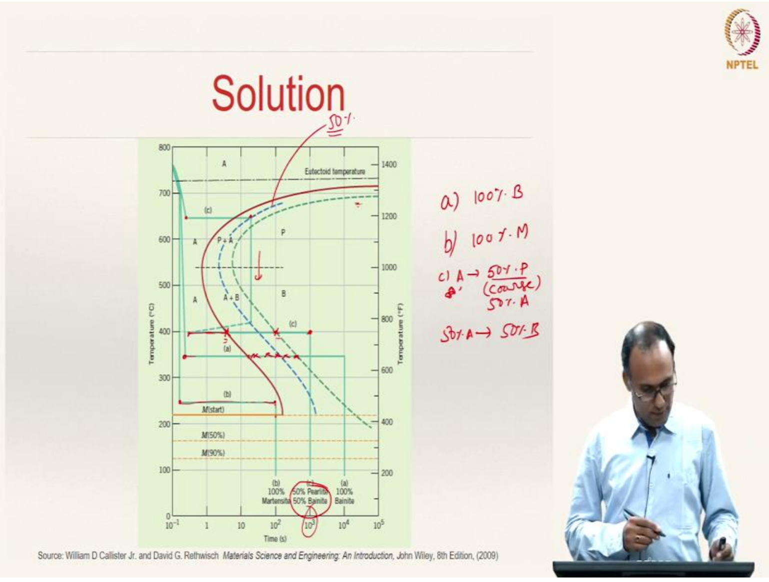

Here, you have these cooling lines drawn. Rapidly cool to $350°$ C -- that is this point and then, wait there for 10^4 seconds. So, you are actually missing the nose. Since you have missed the nose, it is above the martensite start temperature, so, bainite can form here.

During this process, by the time it comes here, austenite would have transformed to 100 percent bainite. The microstructure here will be 100 percent bainite. So, for the case (a), you will have 100 percent bainite. For case (b), rapidly cool to $250°$ C, hold for 100 seconds and then, quench to room temperature.

Rapidly cool to $250°$ C - that is $250°$ C and then, hold for 100 seconds; 100 seconds is this and then, I came below the nose and I am holding here for 100 seconds. Even after holding for 100 seconds, we did not hit the transformation start line - this red line and hence, no transformation of austenite to bainite takes place. But then, we are quenching it down.

Hence, what should happen here? All the austenite will be transforming to martensite. So, that will be 100 percent martensite. In the case (c), rapidly cool to 650° C, hold for 20 seconds and then, rapidly cool to 400° C and hold for 1000 seconds and then, quench to room temperature, right?

If nothing is written here, then it means it is 50 percent line. So, what happens here? Austenite is transforming to 50 percent pearlite. Is it fine pearlite or coarse pearlite? Here you have coarse pearlite.

So, it is 50 percent coarse pearlite. Now you are not allowing it to continue and you are suddenly cooling it down. Only 50 percent of it is converted to pearlite and you are continuing to cool down to 400° C and then, your time starts again, right? This dashed line is just to show that your time starts again and then, you are waiting for 1000 seconds.

Now by the time you are quenching, you are going below the nose here and hitting the transformation start line. So, the remaining 50 percent austenite will convert to the 50 percent bainite.

Here, all the remaining austenite is converting, i.e., 100 percent is converted. What is actually available? Out of the original composition, only 50 percent is available. So, that whole 50 percent is converted to bainite. So, you can see that the third one has 50 percent pearlite and 50 percent bainite.

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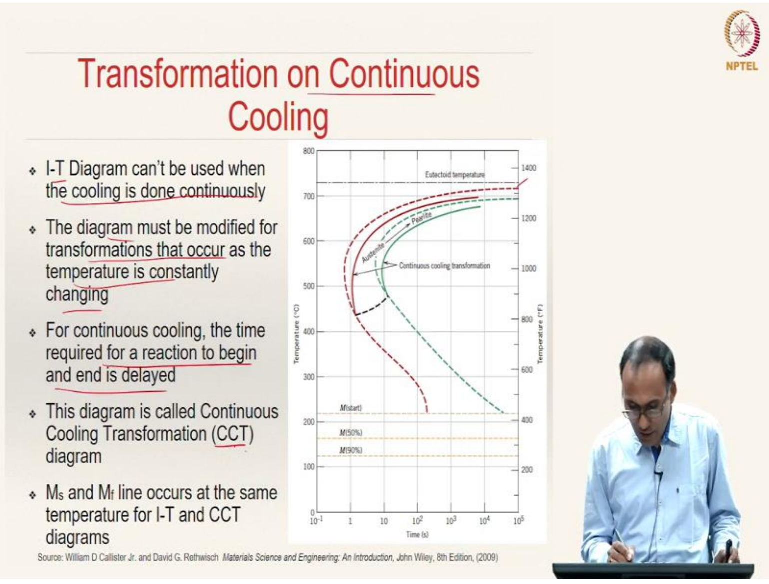

So, that is about the isothermal transformation. Let us now look at what happens when you are continuously cooling; because the continuous cooling is something would happen in the industry, not usually the isothermal transformation. So, that is why the continuous cooling is very important.

The transformation on continuous cooling is something that we would look at. The IT diagram or the isothermal transformation diagram cannot be used when cooling is done continuously. Hence, you need to modify the diagram for transformations that occur as the temperature is constantly changing.

The dashed lines represent the isothermal transformation diagrams. If you are doing continuous cooling, then the transformation start-time and the transformation end-times are going to increase as well as the temperatures are going to reduce.

For a continuous cooling, the time required for reaction to begin and end are delayed. The diagram is called CCT diagram or Continuous Cooling Transformation diagram as opposed to T-T-T diagram. As we are doing continuous cooling, these two curves change; but the martensite start and martensite finish temperatures will not change because they do not depend on the cooling rate.

Because of this fact, for eutectoid steels, if you are doing continuous cooling, the transformation finishes above the nose region itself.

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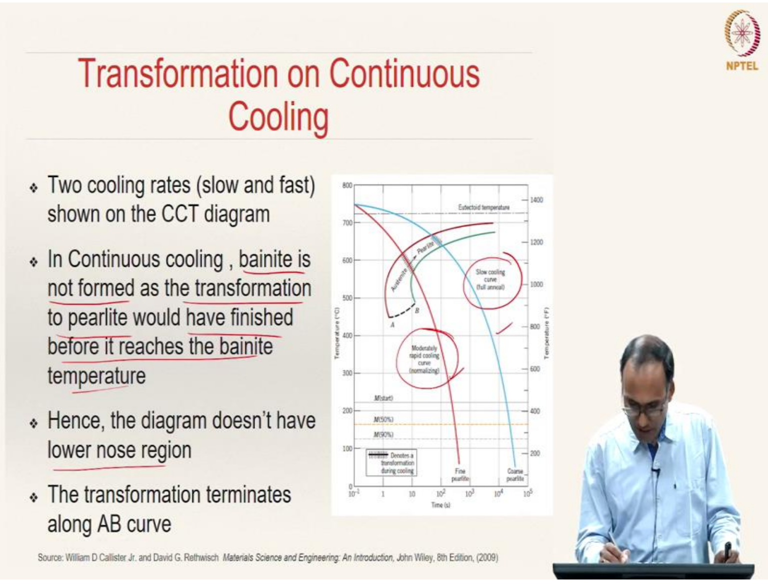

Here, you have two cooling rates; the blue curve represents a slower cooling rate compared to the red one. The blue curve is typical of full annealing heat treatment process that we will discuss at a later stage in this course. The red curve represents moderately rapid cooling which is typical of normalizing.

These are the two cooling rates. Since in the case of continuous cooling, bainite is usually not formed when you are dealing with eutectoid steels, as the transformation to pearlite would have finished before it reaches the bainite temperature. Because you are continuously cooling, you would always finish your transformation by the time you hit the nose.

By the time you hit the nose, all the austenite is already transformed to pearlite and hence, there is no possibility for transformation of bainite in the case of continuous cooling in eutectoid steels. So, that is why the diagram does not have lower nose region and the transformation terminates along the line AB.

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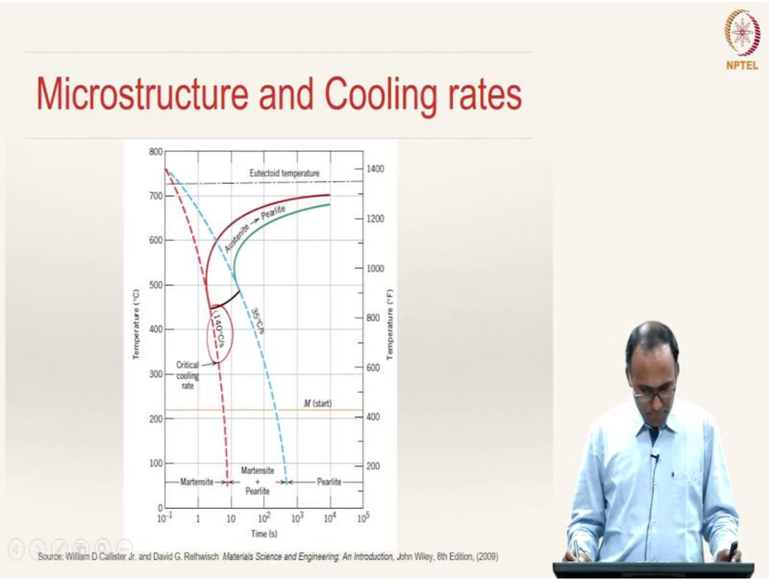

We know that the cooling rate is called critical cooling rate, when there is no transformation of austenite to pearlite; that means, it basically misses the nose. A cooling rate of 140° C/s represents the critical cooling rate.

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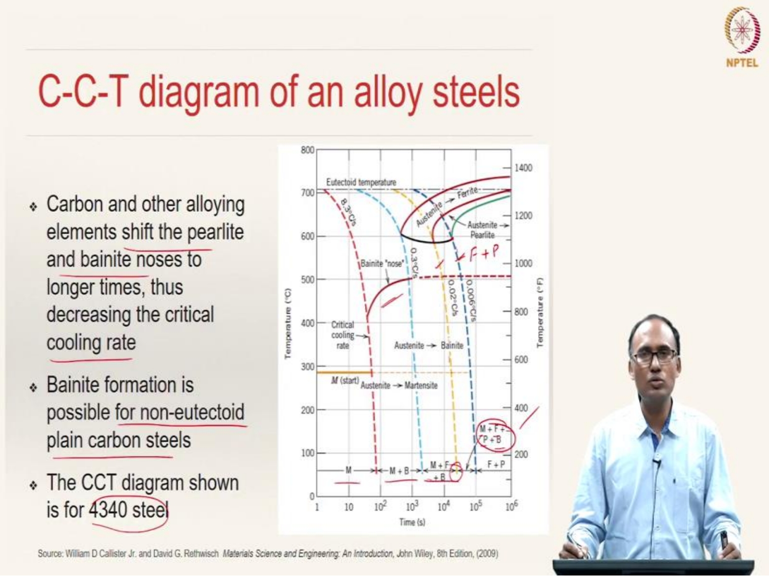

However, for an alloy steel which is more complex steel than a eutectoid steel, you can see the nose region. The bainite formation is possible for alloy steels, but not for eutectoid steel as we have seen before. Carbon and other alloying elements shift the pearlite and bainite noses to longer times thus, decreasing the critical cooling rate.

Bainite formation is possible for non-eutectoid plain carbon steels. Only for eutectoid steels, you see that it is not at all possible. So, this is the continuous cooling transformation diagram for 4340 steel, whereas we have seen the Time-Temperature-Transformation diagram for the same steel previously.

For different cooling rates, one would be able to find out the microstructure. Here, we have shown different cooling rates. For instance, if the cooling rate is between this blue line and the orange line, you will always form such a microstructure; martensite + ferrite + pearlite + bainite.

Because, you will have this austenite to pro eutectoid ferrite in this region. Here, by that time 100 percent transformation would have happened, so you will have pro eutectoid ferrite + pearlite.

Here, only the pro eutectoid phase is formed. So, the remaining material which would have transformed to a eutectoid mixture of ferrite and pearlite is not transforming and hence, some bainite transformation also has taken place in this region.

Then, if at all it is not hitting the bainite finish temperature, you will still have some martensite forming. That is why in each of these regions, you can see what is a possible microstructure that can be generated. So, with that we will close the discussion on the Time-Temperature-Transformation diagrams and continuous cooling transformation diagrams.

In the next class, we will look at heat treatment of steels and particularly, we will pay attention to two important heat treatment processes called Annealing and Normalizing. Thank you.