# Basics of Materials Engineering

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

## Lecture - 67
## Martensite Transformation, C-C-T Diagram

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Welcome back. In the last class we have looked at the isothermal transformation diagrams and continuous isothermal transformation diagrams and the continuous cooling curves. At that time, we have said we will also discuss about the heat treatment. In this course, we shall study two important types of heat treatments.

Here, I have given a definition of heat treatment taken from Materials Handbook. Heat treatment is a combination of heating and cooling operations, timed and applied to a metal or an alloy in the solid state in a way that will produce desired properties.

The purpose of heat treatment is to obtain certain desired properties. In order to do so, you have to apply a predetermined set of heating and cooling cycles and that is how you would obtain the desired properties.

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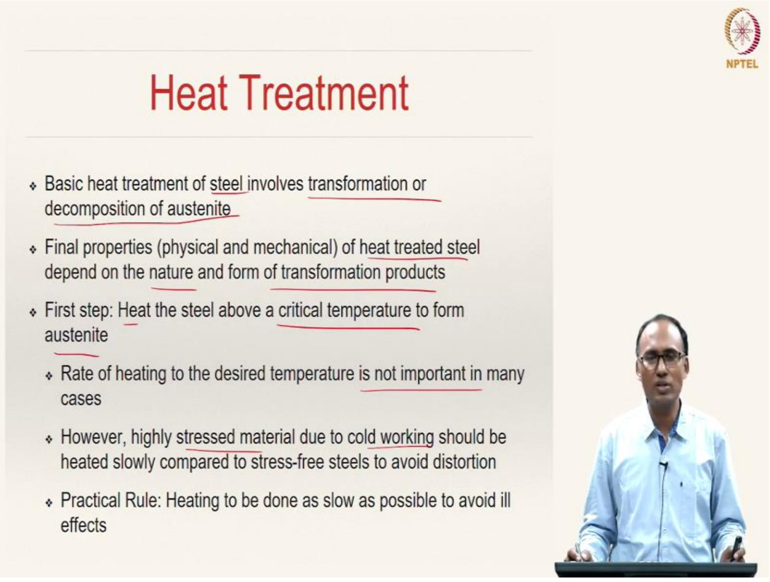


In this class, we will primarily be discussing about the heat treatment of steels. The basic heat treatment of steel involves transformation or decomposition of austenite - that is the basis of heat treatment. The final physical and mechanical properties of heat-treated steel depend on the nature and form of transformation products, like we have already discussed.

Whether it is happening at high temperature or medium temperature or very low temperature, accordingly you will have the hardness of the material changing and the microstructure of the material changing. The first step in the heat treatment process is to heat the steel above a critical temperature to form austenite.

Depending upon the alloy composition, you need to heat it to a certain temperature above which austenite is stable. There, the entire microstructure is completely transformed to austenite. The rate of heating to the desired temperature is actually not an important criterion. So, you can actually heat it as fast as you can.

However, if the material is already pre-stressed, if it is highly stressed due to some cold working that is done before, then we might want to heat it at a comparatively slow rate in order to avoid any distortion to the system.

The guideline is that heating needs to be done as slow as possible to avoid any ill effects. But the heating rate is not as stringent a condition to be maintained as compared to the cooling rate in order to get a particular microstructure. So, the key is that you need to transform the entire microstructure to austenite.

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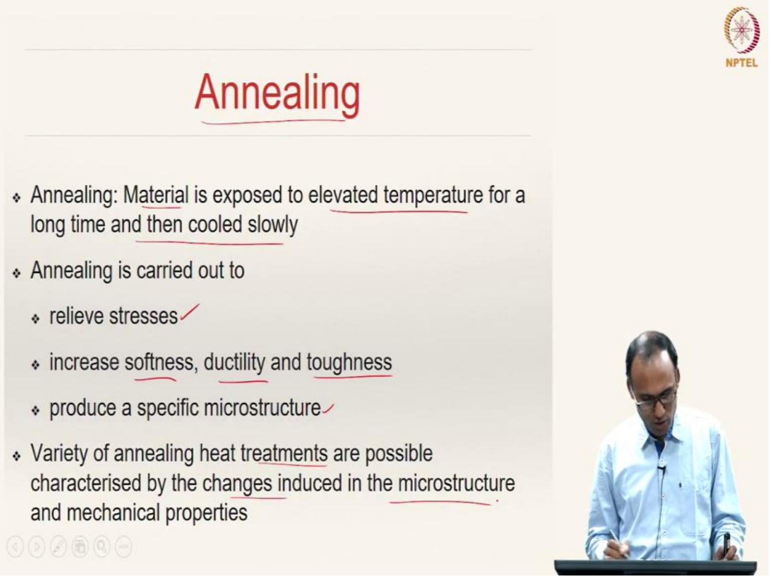


All the other phases have to be transformed to austenite phase. Let us first look at an important heat treatment process called annealing. In annealing, the material or an alloy of steel is exposed to elevated temperature for a long time and then cooled down slowly.

You expose a material to a higher temperature for long time and then cool it down slowly. So, the purpose of annealing is usually to relieve any internal stresses in the material and increase softness, ductility and toughness of the material and produce a specific microstructure. A variety of annealing heat treatments are possible characterized by the changes induced in the microstructure and mechanical properties.

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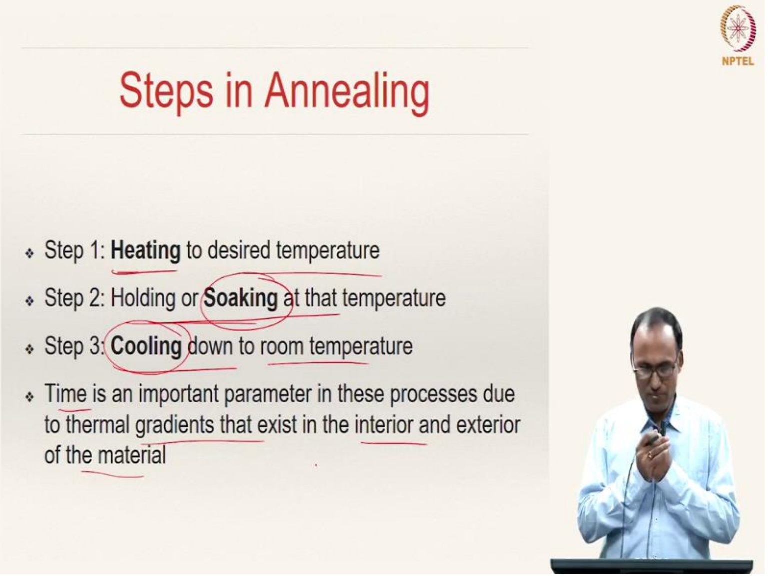


What are the different steps in annealing? Any heat treatment process in general has three important steps. The first step is to heat the specimen to the desired temperature and then holding the specimen at that temperature which is also called soaking.

Soaking the specimen at that temperature is done for a sufficiently long time so that transformation can occur; for instance, if you are heating eutectoid steel from room temperature, you have to increase the temperature above 760° C, where austenite is stable.

Then, all the pearlite phase will transform to austenite - you have to give sufficient time. So, holding at that particular temperature, whichever temperature you are heating it up to and then after the transformation has happened, you have to cool down the specimen.

You have to cool it down to room temperature at a different rate. Depending upon the type of heat treatment process, this cooling rate will be determined. In this entire process, time is a critical parameter. It is an important parameter in these processes due to thermal gradients that exist in the interior and exterior of the material.

When you are cooling it down, the exterior of the material cools down very rapidly, but the interior takes some time to dissipate the heat. Hence, you need to be very careful in order not to induce any stresses because of the thermal gradient within the material from the core to the surface.

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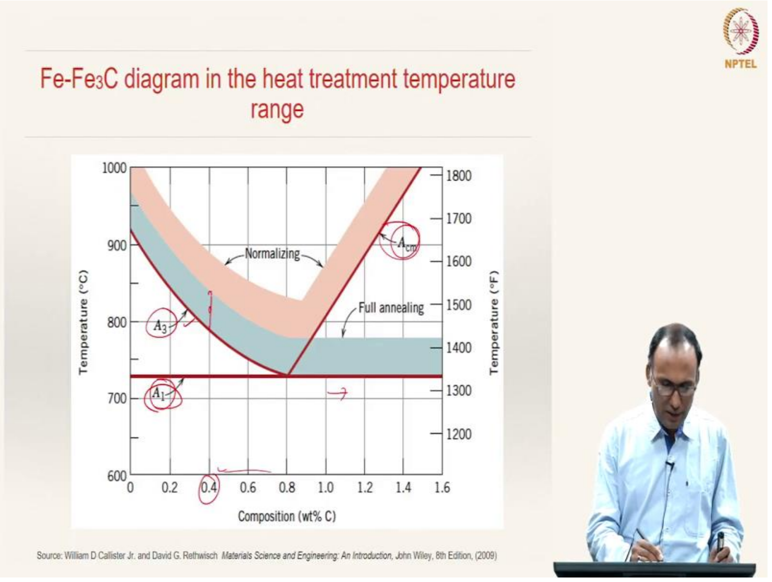


Let us look at this iron-iron carbide equilibrium diagram in the heat treatment temperature range. $A_1$ line here is what we call lower critical temperature about $760°$ C and $A_3$ line is the upper critical temperature above which the complete transformation to austenite takes place for different compositions. On the hypereutectoid steel side, you have $A_{cm}$, which is the upper critical temperature above which complete austenite will be present.

When we are saying lower critical temperature, we are essentially meaning this $A_1$ and upper critical temperature for hypoeutectoid steels will be $A_3$, for hypereutectoid steels will be $A_{cm}$. Depending upon the composition, this temperature is going to change. That is why you need to know the composition and then you need to find out the desired temperature.

In full annealing, you have to heat the material in the appropriate temperature range. For instance, 0.4 percent carbon, you need to heat up to here within this zone so that all the ferrite and cementite phases are transformed to austenite.

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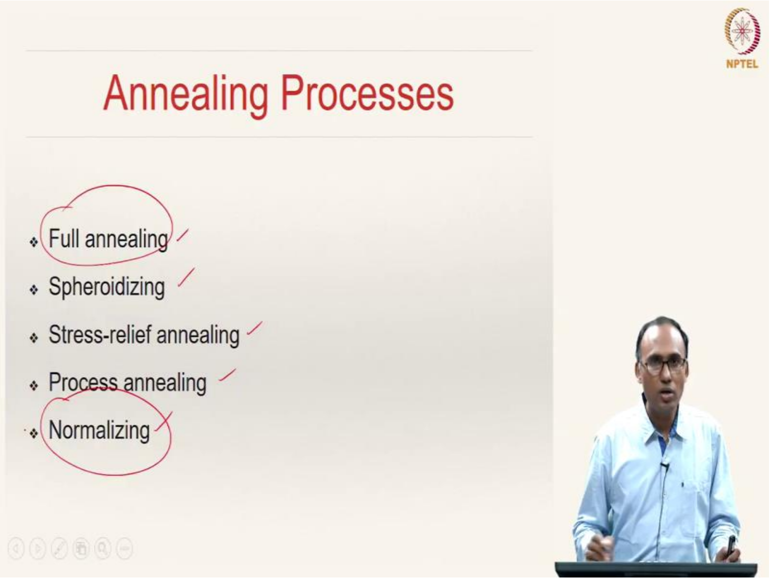


There are five different kinds of annealing processes that we are talking about; full annealing, spheroidizing, stress-relief annealing, process annealing and normalizing. In this class, we will mainly focus on these two processes; full annealing and normalizing.

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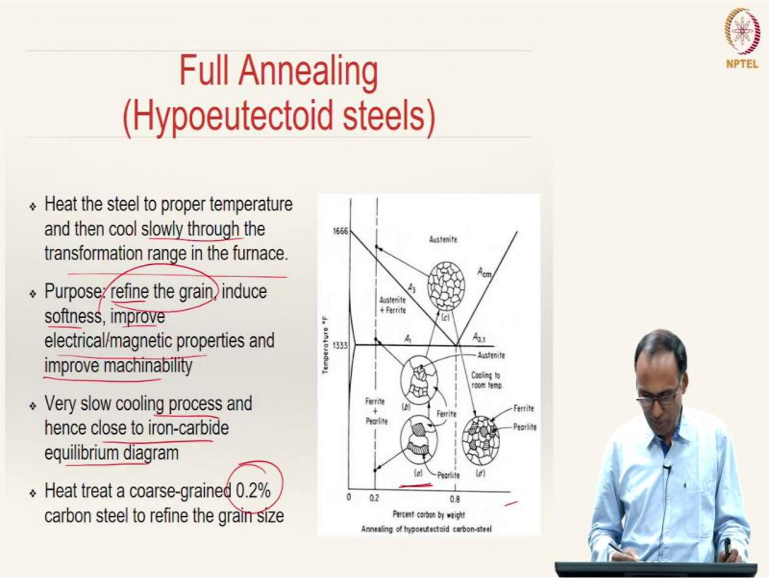


Let us look at how do we go about doing full annealing for hypoeutectoid steels. Here again, we are showing the iron carbide diagram in the heat treatment zone. This is weight percentage of carbon. Let us say that we have a steel to begin with, which is having a microstructure as shown in figure $a$ here.

Heat the steel to proper temperature and then cool slowly through the transformation range in the furnace - that is the total process that we need to do. The purpose of full annealing is to refine the grain, induce softness, improve electrical or magnetic properties and machinability. It is a very slow cooling process that one needs to do and hence close to iron-iron carbide equilibrium diagram.

Because when we are cooling it down, we have to do in an extremely slow manner and hence the microstructure evolution can be very close to what would happen in iron carbide equilibrium diagram. Here we are taking the case of a 0.2 percent carbon steel to refine the grain size.

Initially you have a coarse-grained 0.2 percent carbon steel and we would like to refine the grain size - that is the objective.

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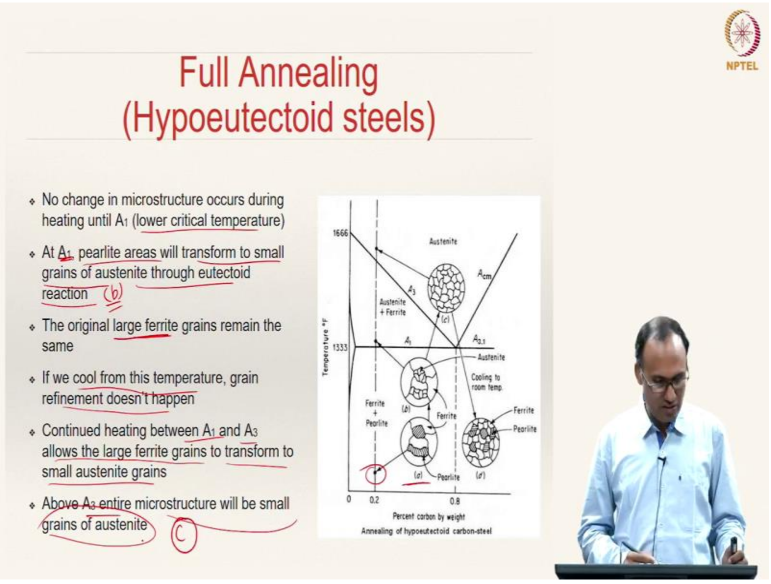


Let us see how do we go about doing that. So, when we are heating the material as we show in figure $a$ here, when you are heating it up from the initial position somewhere at the room temperature, until we heat it up to the temperature $A_1$, which is the lower critical temperature, no change in the microstructure will happen.

Because it is hypoeutectoid steel, above $A_1$, pearlite is not stable; that means, the eutectoid mixture of pearlite and cementite starts transforming. All the pearlite will transform to small grains of austenite through eutectoid reaction as shown in figure $b$.

Figure $b$ represents such a microstructure. However, the original large ferrite grains remain the same. The ferrite grains are remaining the same, but only the pearlite is transforming to fine austenite grains, i.e., if we cool from this temperature, grain refinement does not happen.

So, you need to continue the heating between $A_1$ and $A_3$, thereby allowing the larger ferrite grains to transform to small austenite grains. All the ferrite would transform to small grains of austenite. Above $A_3$ line, entire microstructure will be small grains of austenite.

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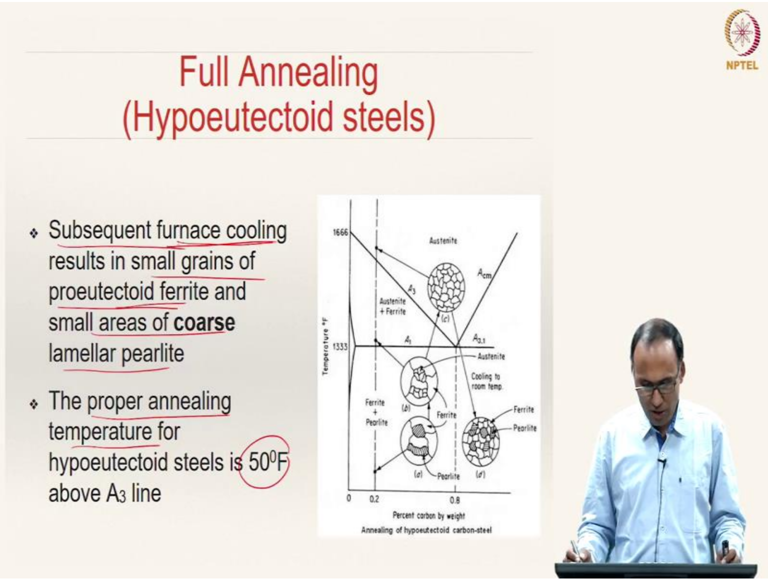


Figure c here shows the small grains of austenite. Furnace cooling means you are keeping the specimen in a furnace and gradually reducing the temperature of the furnace so that the cooling is extremely slow.

Subsequent furnace cooling results in small grains of proeutectoid ferrite and small areas of coarse lamellar pearlite - eutectoid reaction takes place and the remaining austenite would be transforming to alternate layers of ferrite and cementite. Hence, the final microstructure will have small grains of proeutectoid ferrite and small areas of coarse lamellar pearlite.

Up to what temperature we need to heat the specimen? If the temperature is increased by typically 50° F above the $A_3$ line, all the ferrite and cementite would have transformed to austenite.

From that fine microstructure if you cool down in furnace, then each of these austenite grains would be transforming to proeutectoid ferrite and fine microstructure of pearlite.

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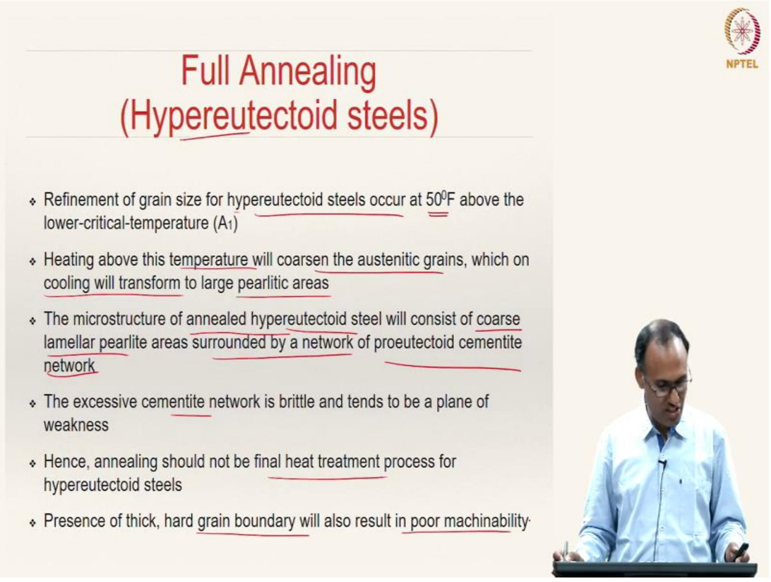


How do we go about doing full annealing for hypereutectoid steels? So, the refinement of grain size for hypereutectoid steels occurs at about $50°$ F above the lower critical temperature, right? So, how do we go about it? Heating above this temperature will coarsen the austenite grains, which on cooling will transform to large pearlitic areas.

So, you do not want to heat it above that temperature. The microstructure of annealed hypereutectoid steel will consist of coarse lamellar pearlite areas surrounded by a network of proeutectoid cementite. The excessive cementite network is extremely brittle and hence that happens to be a plane of weakness.

Hence, annealing should not be the final heat treatment process for hypereutectoid steels. Hypoeutectoid steels can have annealing as their final heat treatment process, but for hypereutectoid steels, it is not a good idea due to the presence of a continuous cementite network.

This continuous cementite network has to be broken to enhance, for instance the machinability of the steel. If you have a continuous cementite network, it offers extreme resistance for the tool to cut through and that is not going to be useful. Moreover, it is going to be extremely brittle as well. The presence of thick hard grain boundary will also result in poor machinability.

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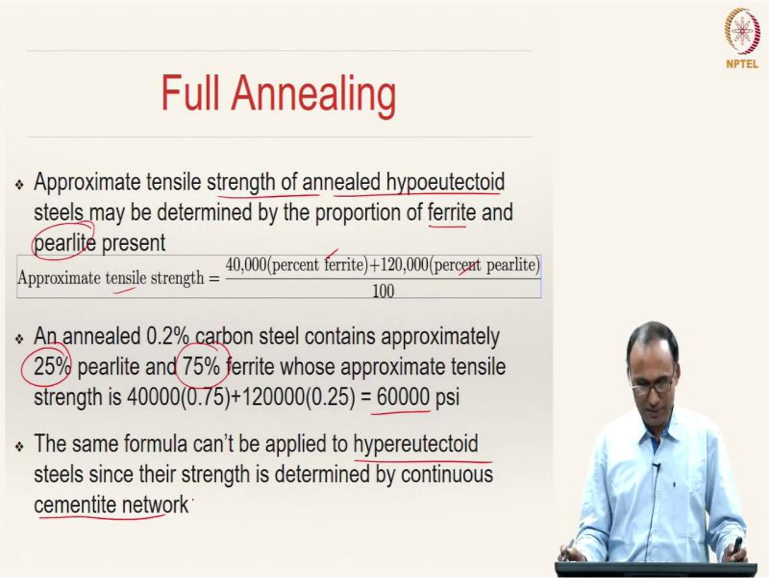


Hence, full annealing cannot be the final heat treatment process for hypereutectoid steels. So, now, we have seen the heat treatment process called annealing for hypoeutectoid steels.

The approximate tensile strength of annealed hypoeutectoid steels maybe determined by using this formula, by knowing the proper proportion of ferrite and pearlite.

$$\text{Approximate tensile strength} = \frac{40000 \times \text{ percent ferrite} + 120000 \times \text{ percent pearlite}}{100}$$

For 0.2 percent carbon steel, we can see that about 25 pearlite and 75 ferrite. The approximate tensile strength is going to be about 60000 psi for 0.2 percent hypoeutectoid steel. So, it is going to be stronger than your ferrite. However, the same formula cannot be applied for hypereutectoid steels as the strength is determined by the continuous cementite network and not by either ferrite and cementite.

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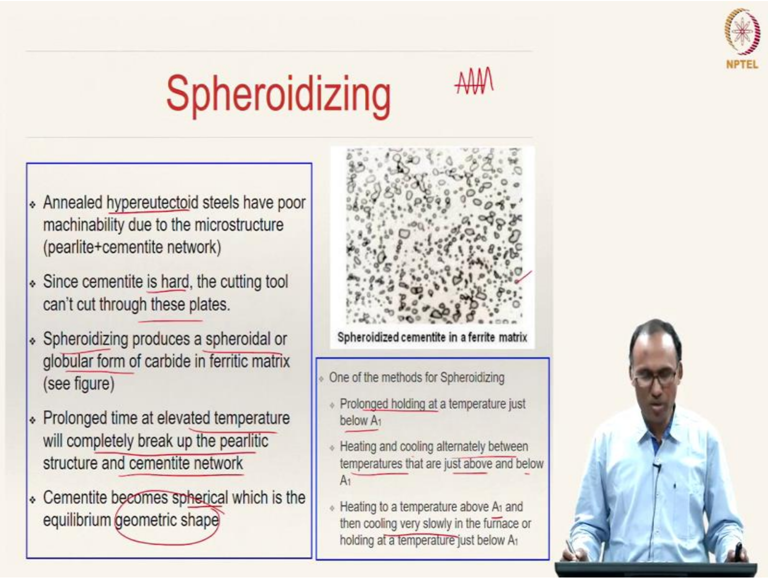


As we have discussed, the annealed hypereutectoid steels have poor machinability due to the microstructure, because you have a pearlite plus thick cementite network - continuous cementite network. Since the cementite is brittle and hard, the cutting tool will not be able to cut through these plates. So, that will be not be useful for good machinability.

There is another process called spheroidizing which produces a spheroidal or globular form of carbide in ferrite matrix. If you see this figure, the cementite looks like a globular form; that means, the cementite network is broken and that results in another equilibrium shape that is a spherical shape.

How do we go about doing that? We have to have a prolonged time at elevated temperature or the system will completely break up the pearlitic structure and cementite network. And, the cementite becomes spherical which is the equilibrium geometric shape.

You have to heat it to a certain level where the cementite network and pearlite network completely breaks. And, then you will have the spheroidal form of the cementite network that is formed which will be easier when you are going to do machining on these components.

One of the methods for spheroidizing is that you have to keep the prolonged holding at temperature just below $A_1$; that means, lower critical temperature. And then, you just cycle through $A_1$, the heating and cooling alternatively between temperatures that are just above and below $A_1$. So, if it is your $A_1$ temperature, you will be cycling like that.

Heating it to a temperature above $A_1$ and then cooling very slowly in the furnace or holding at a temperature just below $A_1$ allows us to break the cementite network, and convert it into this globular form which will enhance the machinability of hypereutectoid steels.

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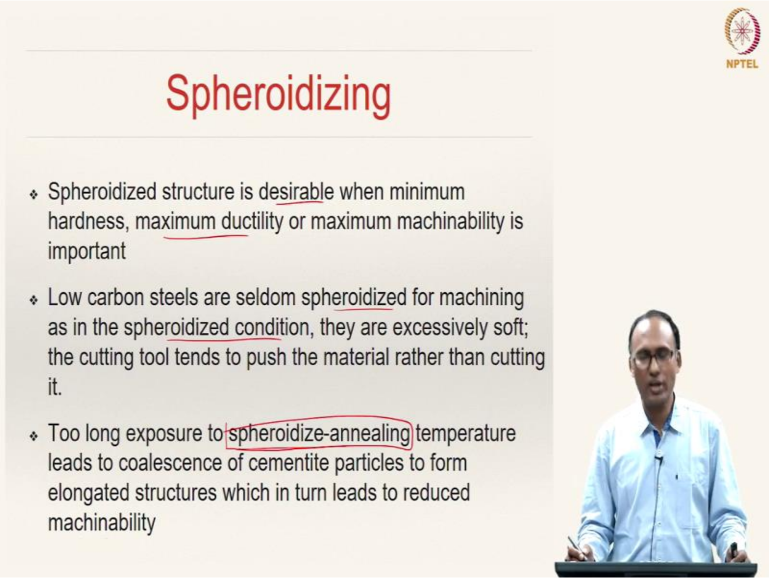


The spheroidized structure is desirable when minimum hardness, maximum ductility or maximum machinability are important. We know that low carbon steels are usually not spheroidized for machining as in the spheroidized condition, they are very soft. Hence that will not be good for the cutting tool; because the cutting tool will push the material rather than cut.

Additionally, care should be taken, as too long exposure to spheroidize-annealing temperature causes the already formed spheres of cementite to coalesce and form an elongated network throughout the phase.

So, that is why it is important to know how much time one needs to keep the specimen at spheroidized annealing temperature. Too long exposure will again create a continuous cementite network which is not desirable.

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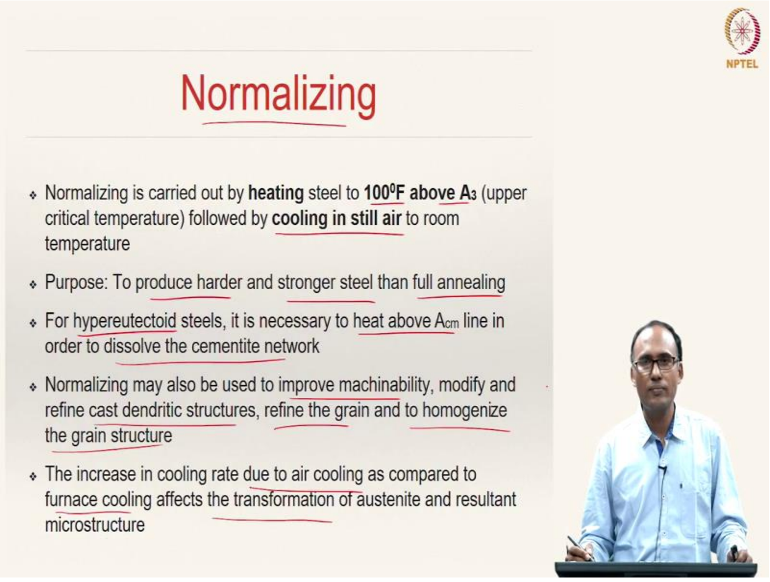


The next heat treatment process is normalizing. Normalizing is carried out by heating the steel above $A_3$ at about $100°$, followed by cooling in still air; so, when we are cooling in still air compared to annealing, it is a much faster rate.

Annealing cooling is done in the furnace whereas, for normalizing usually it is done in still air. It is not very rapid cooling, but it is a medium cooling rate. The purpose of doing annealing is to produce harder and stronger steel than full annealing, because full annealing is going to provide soft steel.

If you want to have steel which is going to be little bit harder than the steel produced by annealing, then people use normalizing. For hypereutectoid steels, it is necessary to heat above $A_{\text{cm}}$ line in order to dissolve the cementite network.

Normalizing can also be used to improve machinability, modify and refine cast dendritic structures, refine the grain and also to homogenize the grain structure. These are the various purposes of normalizing. The influence of cooling rate due to air cooling as compared to furnace cooling affects the transformation of austenite and resultant microstructure.

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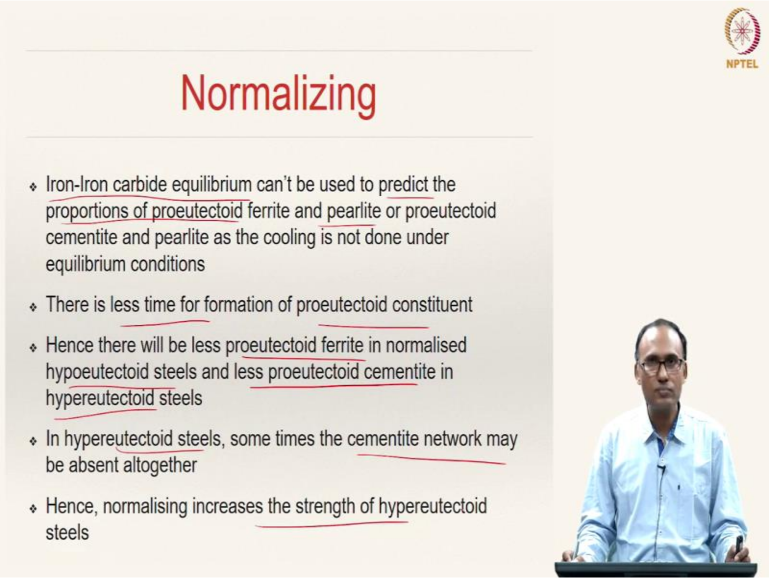


We know that normalizing is done at a faster cooling rate and hence we cannot use iron-iron carbide equilibrium diagram in order to predict the proportions of proeutectoid ferrite and pearlite, unlike for the annealing case.

Also, there is less time for formation of proeutectoid constituents, because you are cooling at a faster rate. Hence, usually under normalizing, you will have less proeutectoid ferrite in normalized hypoeutectoid steels and less proeutectoid cementite in hypereutectoid steels, due to the faster cooling rate.

Sometimes in hypereutectoid steels, it may be possible that the cementite network is altogether absent; it will only have alternate layers of ferrite and cementite. Hence, that is how normalizing increases the strength of hypereutectoid steels.

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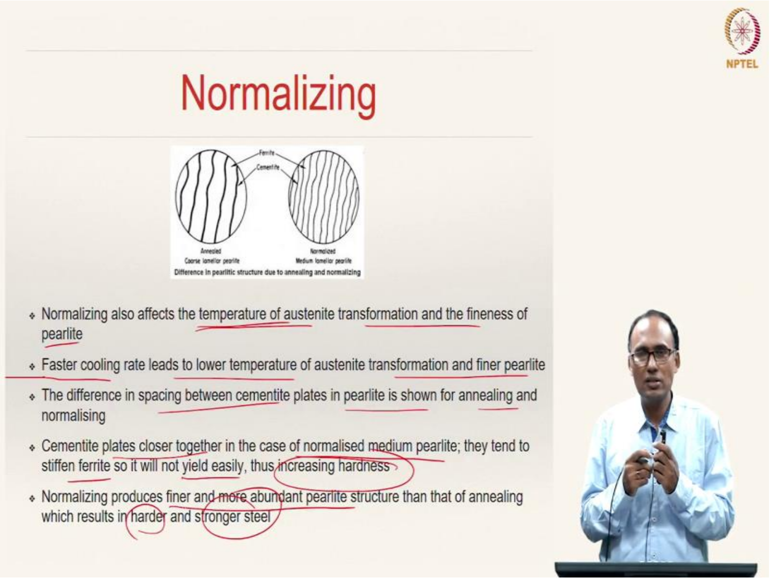


Here you can see the cartoon image showing the relative layer thicknesses of ferrite and cementite, in the case of annealed and normalized microstructures. So, normalizing also affects the temperature of austenite transformation and the fineness of pearlite because your -- it is sort of a continuous cooling scenario. And, hence your transformation start time is actually delayed.

As a result, the temperature is going to get affected. So, normalizing affects the temperature of austenite transformation and the fineness of pearlite. As we are cool faster, in the case of normalizing, it leads to lower temperature of austenite transformation and as a result you will get a finer pearlite.

At lower temperatures, you will have higher nucleation rate and hence more nuclei, less diffusion and hence, you will get finer pearlite. That is why you can see that the layer distance between ferrite and cementite is much less in the case of normalizing compared to annealing.

The difference in spacing between cementite plates in pearlite is shown for annealing and normalizing. The cementite plates are closer together in the case of normalized medium pearlite because of the finer microstructure and they tend to stiffen ferrite. So, it is not easy to yield such a material, thereby increasing the hardness of the system.

Normalizing produces finer and more abundant pearlite structure than that of annealing which will result in harder and stronger steel. The distance between two pearlite layers is less; as a result, the cementite layers offer more stiffness to the system.

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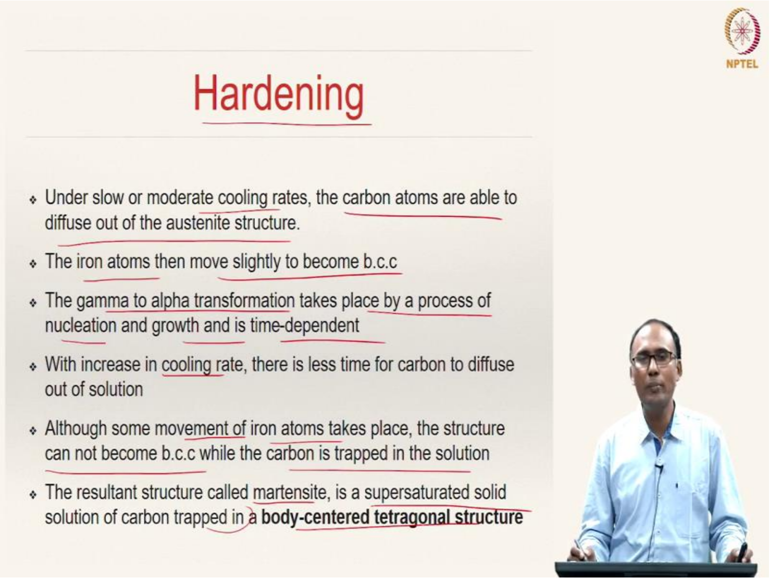


After studying annealing and normalizing, we will look at another process called hardening which we have already sort of discussed. Under slow or moderate cooling rates, we have seen that the carbon atoms are able to diffuse out of the austenite microstructure in order change its crystal structure from FCC to BCC; that means, the iron atoms move slightly to become BCC.

The $\gamma$ to $\alpha$ transformation takes place by a process of nucleation and growth and is time-dependent because, it has to happen through the phase transformation; that we have discussed, right?

The time is not enough for diffusion if you are cooling rapidly. Although some movement of iron atoms takes place, the structure cannot become BCC while the carbon is trapped in the solution, right? So, some of amount of carbon has to come out because ferrite has lower solubility of carbon.

That is the reason why the carbon is getting trapped and such a structure is called martensite which is a supersaturated solid solution of carbon trapped in body-centered tetragonal structure. That is why body-centered tetragonal structure is obtained instead of a body-centered cubic structure.

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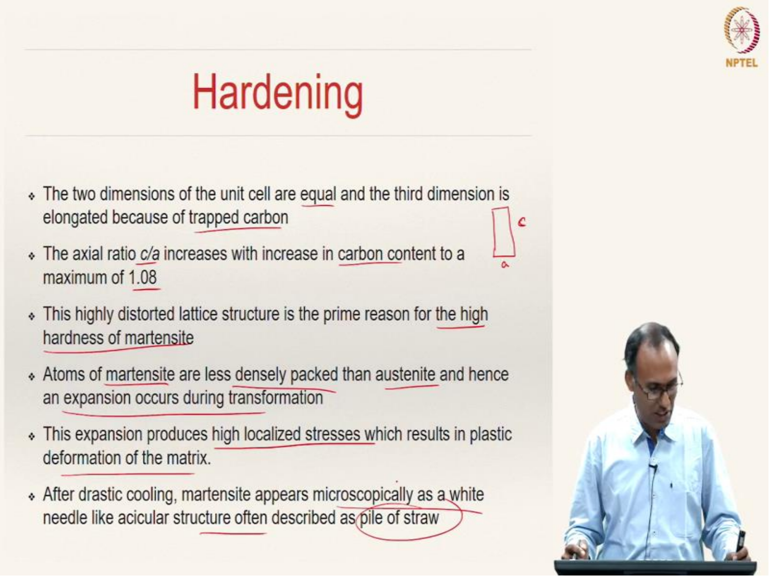


In the BCT structure, the two dimensions of the unit cell are equal and the third dimension is elongated because of the trapped carbon. If the third-dimension length is $c$ and the other two dimensions are $a$, then the axial $c/a$ ratio increases with increase in carbon content. As you are increasing the carbon content, the $c/a$ ratio increases - it gets elongated more and more with a maximum of 1.08.

So, that is causing the distortion to the lattice structure which is the primary reason for high hardness of the martensite. This lattice distortion caused due to the trapping carbon atoms is what is giving us high hardness to the microstructure. We know that atoms of martensite are less densely packed than austenite, because austenite is FCC and martensite is BCT.

Since they are less densely packed, some expansion occurs during transformation. This expansion produces high localized stresses which results in plastic deformation of the matrix. After drastic cooling, martensite appears microscopically as a white needle like acicular structure often described as a pile of straw.

We have already looked at hardening the martensite and how the martensite microstructure looks. With that, we are concluding this module on heat treatment of steels and thermal processing, where we have discussed the time temperature transformation diagrams and continuous cooling transformation diagrams.

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The material discussed in this module is based on the material available in these three textbooks; Sidney H Avner, Introduction to Physical Metallurgy, William D Callister's book on Materials Science and Engineering and Reed Hills textbook on Physical Metallurgy Principles. You can also see more information on this online resource. With that we are closing this module on heat treatment of steels.

Thank you very much.