Basics of Materials Engineering
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Lecture - 62
Phase Diagram (Iron-Iron Carbide Phase Diagram)

Let us now look at iron-iron carbide equilibrium diagram, because it is a very important system for us as mechanical engineers. We will be dealing a lot with steel in general and hence, it is important to understand this particular phase diagram.

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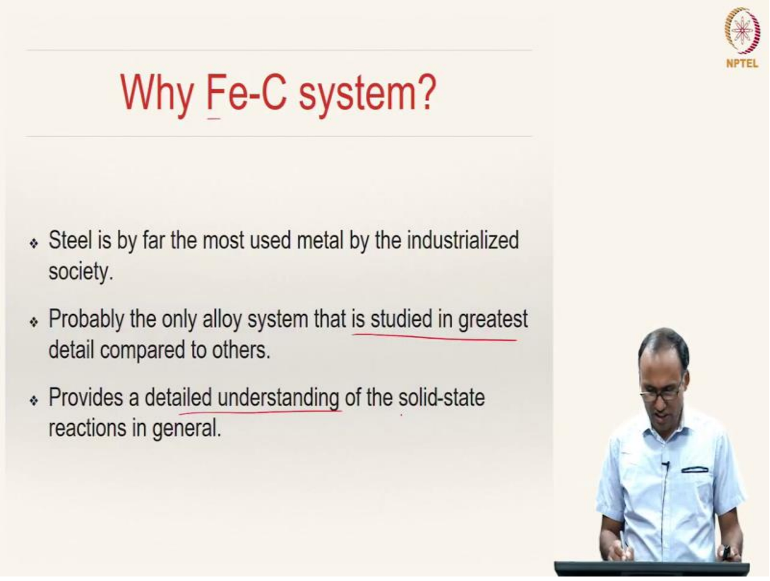

Why Fe-C system?

- Steel is by far the most used metal by the industrialized society.
- Probably the only alloy system that is studied in greatest detail compared to others.
- Provides a detailed understanding of the solid-state reactions in general.

Why are we studying iron-carbon system? Because steel is by far the most used metal by the industrialized society. And probably the only alloy system that is studied in greatest detail compared to any other alloy system. You know a lot about this particular alloy system and this iron-carbon phase diagram provides us a detailed understanding of the solid-state reactions in general.

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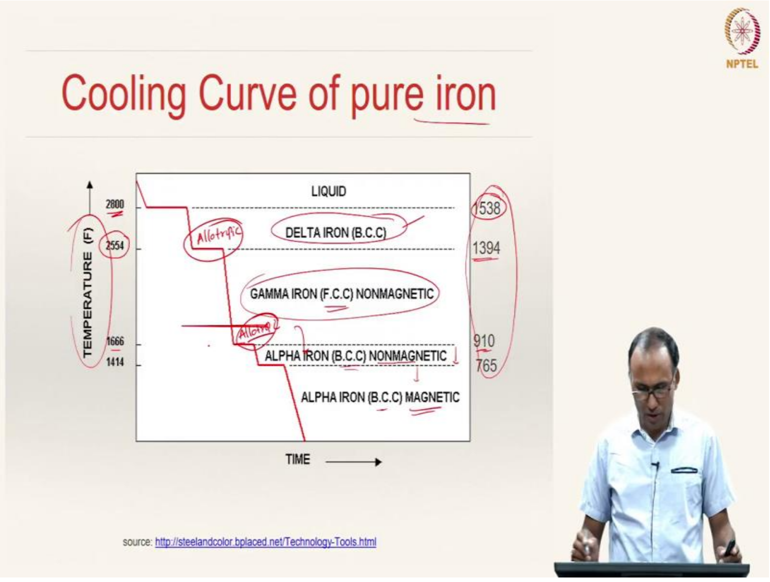

Cooling Curve of pure iron

source: http://steelandcolor.bplaced.net/Technology-Tools.html

This is how the cooling curve of pure iron looks like. The temperature is shown in degree Fahrenheit; on this side, it is shown in degree Celsius. Pure iron is in the liquid state above 1538° C or 2800° F, which is the melting temperature of steel. When you cool it down, at 2800° C, the liquid transforms to solid state.

At this position, it is called δ iron, which has BCC crystal structure. At about 2554° F, or about 1400° C, the δ iron undergoes an allotropic transformation (a solid-state transformation) and converts to γ iron, which is FCC (Face Centered Cubic structure).

Here, you have an allotropic transformation and then, until 910° C or 1670° F, the γ iron is stable. At that temperature, about 900° C, another allotropic transformation takes place and then, the γ iron transforms to α iron. And then, α iron is going to be non-magnetic to begin with until 765° C and below 765° C, it develops magnetic properties.

However, the crystal structure will still be BCC. So, for pure iron as we have discussed, we have two allotropic changes when it is cooling down, one from δ iron to γ iron, another one from γ iron to α iron.

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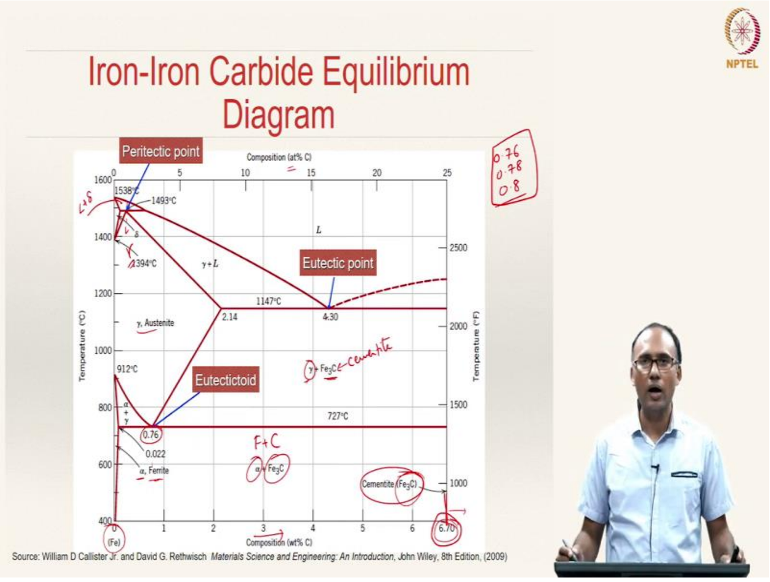

Iron-Iron Carbide Equilibrium Diagram

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

So, this is the typical iron-iron carbide equilibrium diagram. It is not iron-carbon equilibrium diagram that we are showing here, it is a portion of iron-carbon equilibrium diagram. As we have discussed in our Type IV alloys, whenever you had an intermediate solid solution or intermediate phase, you can see that portion as an independent phase diagram.

Same is the case here. Actually, here we are seeing on the left-hand side, you have iron and this is the composition of carbon in weight percentage (on the top it is in atom percentage). 6.7% carbon here, you will have a special intermediate compound that is called cementite Fe_3C.

Hence, in between, you can see this as an independent phase diagram, like as we have discussed in the Type IV alloys. Carbon can actually in the form of graphite, go up to 100%, but we are only interested in the iron-iron carbide diagram. We will not use any iron-carbon alloy beyond this carbon percentage as that is going to be extremely brittle.

For this phase diagram, on the left-hand side you have iron, on the right-hand side you have Fe_3C. Let us identify some important points. This is eutectic point - liquid is transforming to solids - γ which is also called austenite, i.e., γ iron or austenite and this is Fe_3C. Another name for Fe_3C is cementite.

γ is called austenite; α phase is called ferrite. This is the eutectic point and that is the eutectoid point, where austenite transforms to ferrite and cementite - I will also call F + C. This is the peritectic point, where liquid + solid transforms to another solid.

This is our δ region. This two-phase region - liquid + δ upon cooling will give you γ. So, that is the peritectic reaction point. It is important that we remember the compositions and the temperatures of these reaction points.

In several text books, this number 0.76 can vary; in this book it is written as 0.76; in some text books it is written as 0.78, 0.8. So, there may be slight variation, but it is about 0.8. This percentage of carbon is about 0.8 and that is what is called eutectoid compound or eutectoid alloy.

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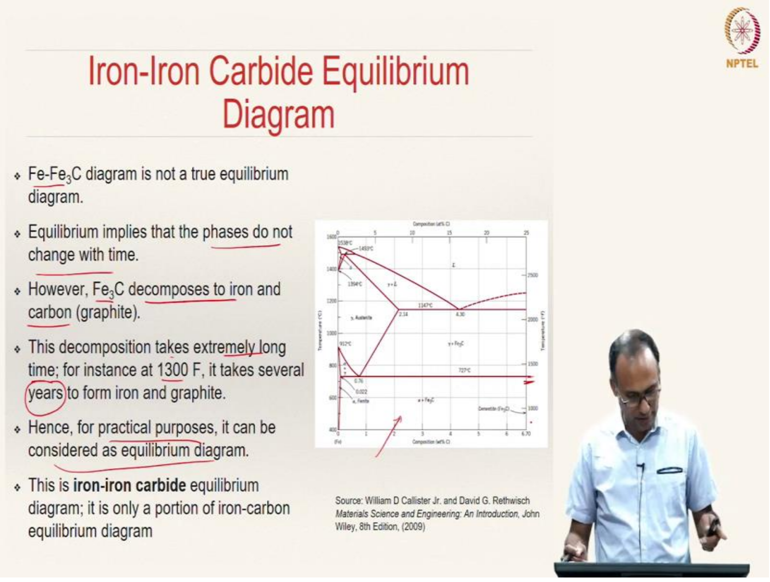

Iron-Iron Carbide Equilibrium Diagram

- Fe-Fe_3C diagram is not a true equilibrium diagram.
- Equilibrium implies that the phases do not change with time.
- However, Fe_3C decomposes to iron and carbon (graphite).
- This decomposition takes extremely long time; for instance at 1300 F, it takes several years to form iron and graphite.
- Hence, for practical purposes, it can be considered as equilibrium diagram.
- This is **iron-iron carbide** equilibrium diagram; it is only a portion of iron-carbon equilibrium diagram

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

Please note that Fe-Fe_3C diagram is not a true equilibrium diagram. Why? Whenever we are saying equilibrium, it implies that the phases do not change with time. That means the phases that we are talking about should not change with time, if it is a true equilibrium diagram.

However, the cementite or Fe_3C decomposes to iron and carbon over time - but this time can be very long. Eventually, it will decompose and hence strictly speaking, we cannot call this iron-iron carbide equilibrium diagram as true equilibrium diagram. However, as I mentioned that decomposition takes extremely long time, several years.

For instance, at 1300° F, it takes several years to form iron and graphite. Cementite takes several years to form iron and graphite. At low temperatures, it will take even longer time. And hence, for practical purposes, it can be considered as an equilibrium diagram.

Please note that this diagram that we are looking at is iron-iron carbide equilibrium diagram; that means, it is a portion of iron-carbon diagram; but it is not complete iron-carbon equilibrium diagram.

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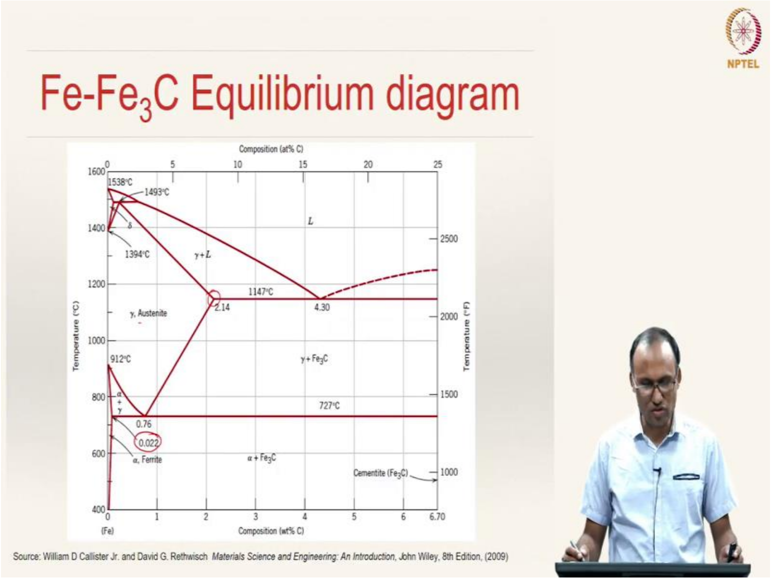

Fe-Fe_3C Equilibrium diagram

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

All of you should be able to draw this diagram and identify what the compositions and the solubility. For instance, if you see this α iron/ferrite has maximum solubility of 0.022 weight percentage of carbon here and γ iron has 2.14% weight solubility of carbon in iron. So, the solubility limits are something that you should remember. You should be able to draw this diagram completely at the end of this course.

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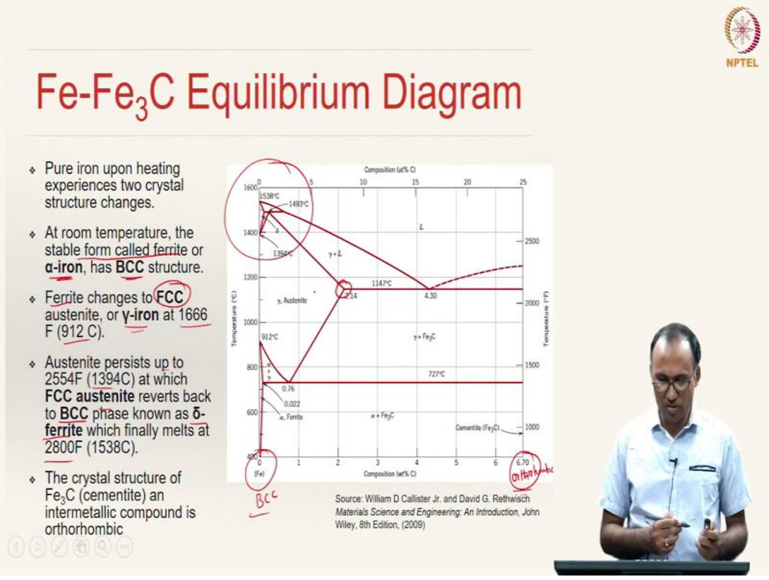

Fe-Fe_3C Equilibrium Diagram

- Pure iron upon heating experiences two crystal structure changes.
- At room temperature, the stable form called ferrite or α-iron, has BCC structure.
- Ferrite changes to FCC austenite, or γ-iron at 1666 F (912 C).
- Austenite persists up to 2554F (1394C) at which **FCC austenite** reverts back to **BCC** phase known as **δ-ferrite** which finally melts at 2800F (1538C).
- The crystal structure of Fe_3C (cementite) an intermetallic compound is orthorhombic

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

Pure iron upon heating, experiences two crystal structure changes as we have seen; one from δ iron to γ iron and then, from γ iron to α iron. At room temperature, the stable form is called ferrite or α iron which has BCC structure. When you are heating it up, the ferrite changes to FCC structure and it is called austenite or γ iron at about $1666°$ F or $912°$ C.

Austenite remains stable up to $1394°$ C or approximately $1400°$ at which FCC austenite reverts back to BCC phase. But this BCC phase is known as δ ferrite, which finally melts at $2800°$ F. So, we have seen two phase transformations α iron to γ iron and γ iron to δ iron.

The crystal structure of iron at room temperature is BCC and what is the crystal structure of Fe_3C? The crystal structure of Fe_3C, which is an intermetallic compound is orthorhombic. As we have already discussed, the size of the carbon atom is relatively smaller compared to the size of iron atom and secondly, their crystal structures are not the same.

Even if you see Fe and Fe_3C, they have different crystal structures and hence, they will only form an interstitial solid solution.

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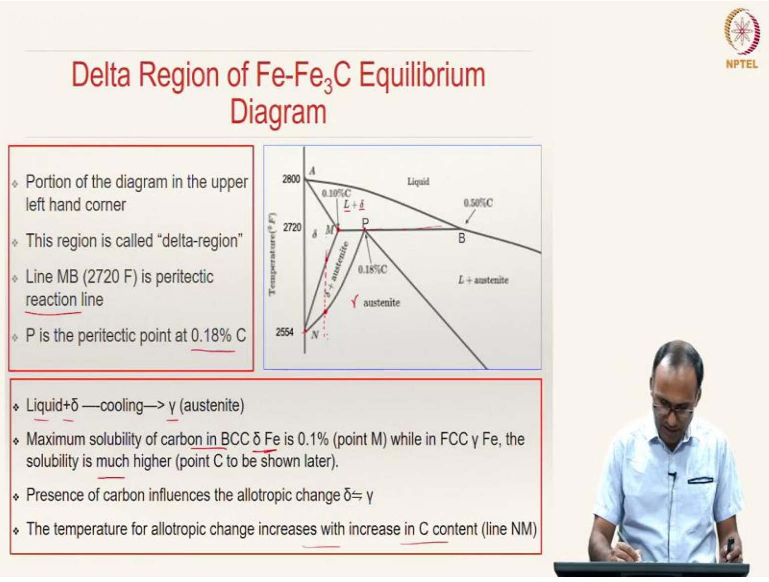

Delta Region of Fe-Fe_3C Equilibrium Diagram

- Portion of the diagram in the upper left hand corner
- This region is called "delta-region"
- Line MB (2720 F) is peritectic reaction line
- P is the peritectic point at 0.18% C

- Liquid+δ —cooling—> γ (austenite)
- Maximum solubility of carbon in BCC δ Fe is 0.1% (point M) while in FCC γ Fe, the solubility is much higher (point C to be shown later).
- Presence of carbon influences the allotropic change δ⇋ γ
- The temperature for allotropic change increases with increase in C content (line NM)

So, now, let us look at each of these important regions in Fe - Fe_3C diagram. This region is called δ region, where the δ iron is stable and is the upper left-hand portion of the phase diagram. We are zooming in this region and trying to see what is happening there.

MPB is the peritectic line. The peritectic reaction takes place along that line. Line MB is called peritectic reaction line and P is the peritectic point at 0.18% carbon. The peritectic alloy has 0.18% carbon.

What is the reaction that is taking place at point P? Liquid + δ transforming to austenite or γ iron - liquid plus δ upon cooling gives γ. The maximum solubility of carbon in BCC δ iron is about 0.1%.

You cannot have more than 0.1% carbon in BCC δ iron at point M, while in FCC, the solubility is much higher. In FCC, the solubility is 2.14% as compared to 0.1% in the BCC δ iron. So, the temperature for these allotropic changes increases with increase in carbon content.

So, we can see that, here pure iron converts from γ iron to δ iron at 2554°C. But, if you are at higher temperatures, for instance, higher carbon contents somewhere here, then the complete transformation to δ iron - it starts here and it ends here.

So, austenite starts transforming to δ iron here and ends transforming to δ iron here. That means, it happens at a higher temperature than for the system which has lower carbon contents.

The temperature for allotropic change increases with increase in carbon content; that is described by this line NM.

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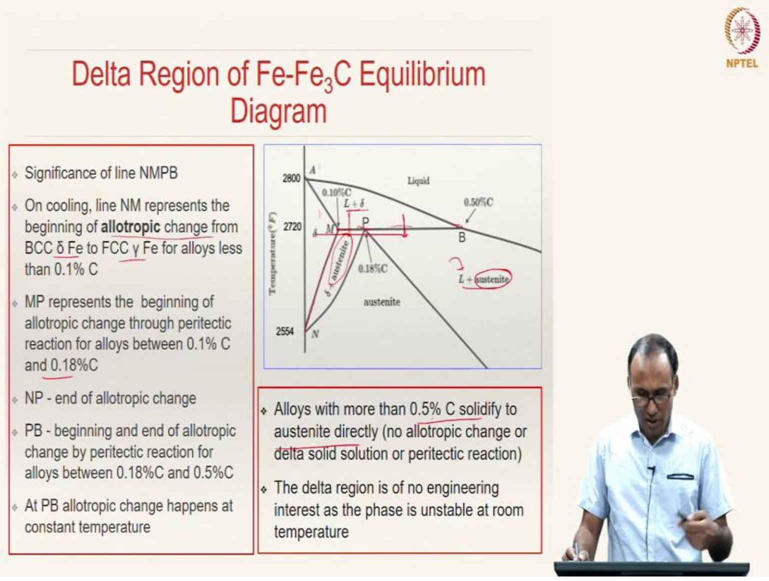

Delta Region of Fe-Fe_3C Equilibrium Diagram

- Significance of line NMPB
- On cooling, line NM represents the beginning of **allotropic** change from BCC δ Fe to FCC γ Fe for alloys less than 0.1% C
- MP represents the beginning of allotropic change through peritectic reaction for alloys between 0.1% C and 0.18%C
- NP - end of allotropic change
- PB - beginning and end of allotropic change by peritectic reaction for alloys between 0.18%C and 0.5%C
- At PB allotropic change happens at constant temperature

- Alloys with more than 0.5% C solidify to austenite directly (no allotropic change or delta solid solution or peritectic reaction)
- The delta region is of no engineering interest as the phase is unstable at room temperature

What is the significance of line NMPB? When you are cooling down, the line NM represents the beginning of allotropic change and the line NP sort of represents the end of allotropic change -- so, beginning of allotropic change from BCC δ iron to FCC γ iron for alloys less than 0.1% carbon.

This is the allotropic change starting point for alloys less than 0.1% carbon. And MP, this portion, represents the beginning of allotropic change -- δ transforms to austenite through peritectic reaction.

Liquid + δ is transforming to austenite through peritectic reaction for alloys between 0.1% and 0.18%. NP of course, represents the end of an allotropic change and the line PB is beginning and end of allotropic change, because below that -- here you have liquid plus δ, then liquid plus austenite.

Some amount of liquid plus δ would be converted to austenite and some amount of liquid remains. So, this is the beginning and end of allotropic change. Here the allotropic change happens at constant temperature; whereas, left to P, allotropic change happens over a range of temperatures. And for alloys with more than 0.5% carbon, you do not see the formation of δ iron.

The δ iron is not necessarily always a stable phase, because it depends on the carbon content. If the carbon content is greater than 0.5%, you will not have δ phase at all. So, 0.5% carbon solidifies directly to austenite; they will not go through allotropic change.

The δ iron is only stable in the portion where the carbon content is less than 0.5%. However, the δ region is usually of not great engineering significance, because this phase is unstable at room temperature. For plain carbon steel, it is not stable at room temperature and hence, not so much attention is usually paid to δ phase.

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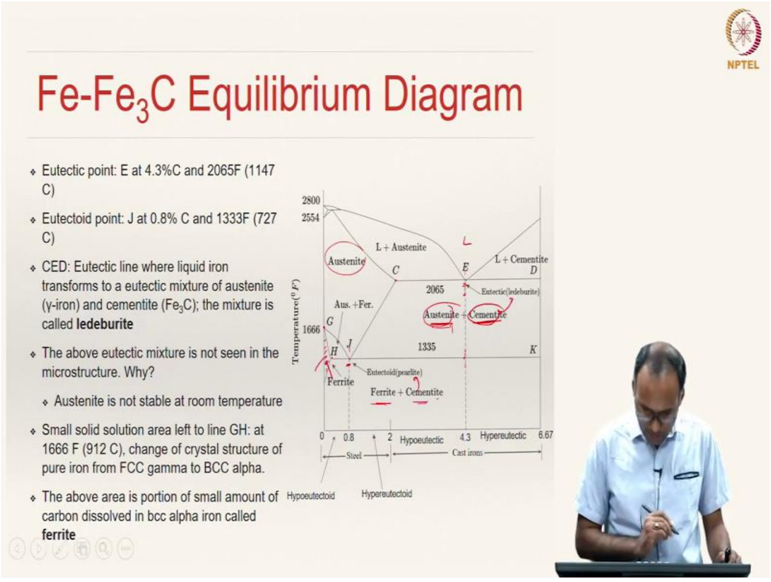

Fe-Fe_3C Equilibrium Diagram

- Eutectic point: E at 4.3%C and 2065F (1147 C)
- Eutectoid point: J at 0.8% C and 1333F (727 C)
- CED: Eutectic line where liquid iron transforms to a eutectic mixture of austenite (γ-iron) and cementite (Fe_3C); the mixture is called **ledeburite**
- The above eutectic mixture is not seen in the microstructure. Why?
  - Austenite is not stable at room temperature
- Small solid solution area left to line GH: at 1666 F (912 C), change of crystal structure of pure iron from FCC gamma to BCC alpha.
- The above area is portion of small amount of carbon dissolved in bcc alpha iron called **ferrite**

We have redrawn this iron-carbon equilibrium diagram. E is the eutectic point; J is the eutectoid point and C represents the maximum solubility of carbon in austenite and other two-phase regions are represented.

The liquid when it is going through eutectic reaction, will form austenite and cementite. The eutectic mixture of austenite and cementite is having a special name called ledeburite.

Similarly, at eutectoid reaction, austenite is transforming to ferrite and cementite. So, this will be eutectoid mixture of ferrite and cementite; that has a special name called pearlite. You have to remember these names. The line CED represents eutectic line which gives you the microstructure, ledeburite. The line HK represents the eutectoid reaction which gives the microstructure pearlite.

Usually in steels, the eutectic mixture is not seen, because even though you have formed the eutectic mixture of austenite and cementite - the ledeburite, at room temperature, it will again go through eutectoid reaction and eventually, you will only have ferrite and cementite because austenite is not stable below this temperature.

Small solid solution area left to GH at this position, you will have a change of crystal structure as we have discussed from γ to α and then, this is what is called ferrite which is BCC, having BCC microstructure.

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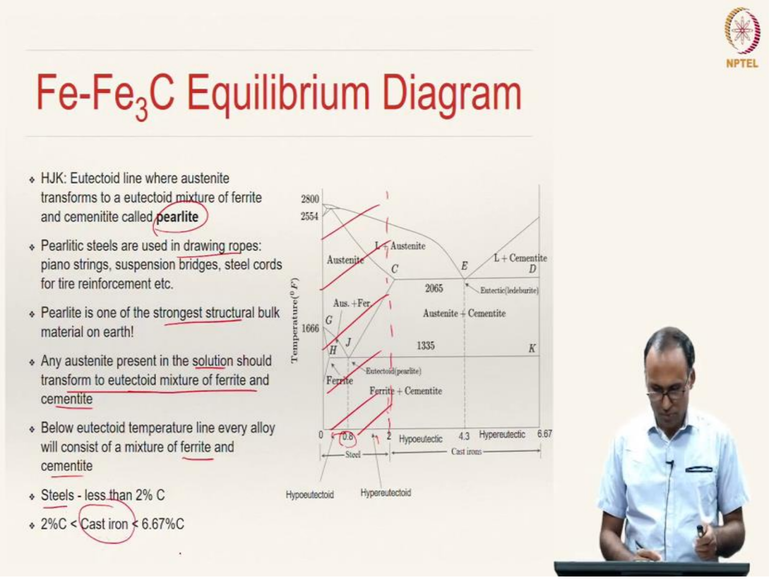

Fe-Fe_3C Equilibrium Diagram

- HJK: Eutectoid line where austenite transforms to a eutectoid mixture of ferrite and cemenitite called **pearlite**
- Pearlitic steels are used in drawing ropes: piano strings, suspension bridges, steel cords for tire reinforcement etc.
- Pearlite is one of the strongest structural bulk material on earth!
- Any austenite present in the solution should transform to eutectoid mixture of ferrite and cementite
- Below eutectoid temperature line every alloy will consist of a mixture of ferrite and cementite
- Steels - less than 2% C
- 2%C < Cast iron < 6.67%C

The line HJK, I have already mentioned is the eutectoid line; the mixture is called pearlite. Pearlitic steels are used usually in drawing process -- drawing ropes. The applications are piano strings, suspension bridges, steel cords and for tire reinforcement and so on.

Pearlite is one of the strongest structural bulk materials that is known to us. Any austenite present in the solution should transform to eutectoid mixture of ferrite and cementite, because austenite in not stable below 1335° F. And so, below eutectoid temperature line, every alloy comprises a mixture of ferrite and cementite.

Here, you see that the 0.8% carbon is the eutectoid composition, left to that it is called hypoeutectoid alloys and right to that, it is called hypereutectoid alloys. Usually, iron-carbon alloys which have a carbon percentage less than 2% are considered steels.

So, steel is an iron-carbon alloy with carbon less than 2%. Only alloys in this region can be classified as steels. If the percentage of carbon is greater than 2% and between 2% and 6.67%, they are called cast irons.

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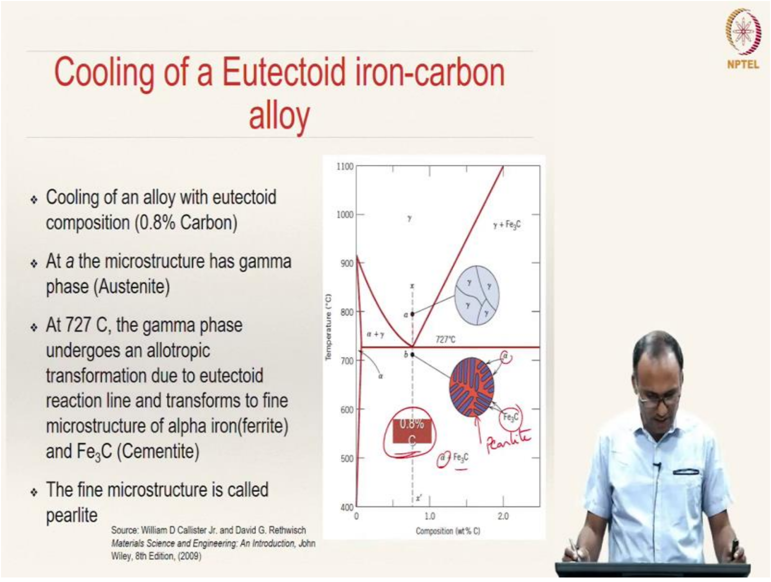

Cooling of a Eutectoid iron-carbon alloy

- Cooling of an alloy with eutectoid composition (0.8% Carbon)
- At *a* the microstructure has gamma phase (Austenite)
- At 727 C, the gamma phase undergoes an allotropic transformation due to eutectoid reaction line and transforms to fine microstructure of alpha iron(ferrite) and Fe_3C (Cementite)
- The fine microstructure is called pearlite

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

Let us now look at the microstructure evolution of a eutectoid iron-carbon alloy. Eutectoid percentage is about 0.8% carbon as we have discussed. It can be $0.76\% - 0.8\%$. But in this class, let us say it is 0.8% carbon.

At a it will be γ iron and the moment it reaches point b, it will go through eutectoid reaction; that means, the γ will transform to two solids α iron and Fe_3C. It will not give some generic microstructure, but it will have alternate layers of ferrite and cementite, like this.

The red region represents ferrite and the blue region represents cementite. There will be alternate layers of ferrite and cementite, just like the eutectic microstructure that we have discussed in the previous lectures. This fine microstructure is called pearlite. So, this is having a special name called pearlite; pearlite is a eutectoid mixture of ferrite and cementite.

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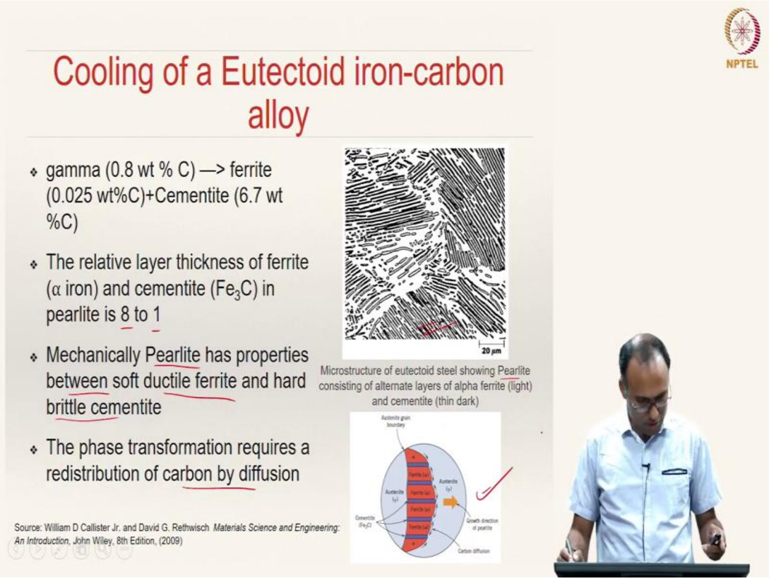

Cooling of a Eutectoid iron-carbon alloy

- gamma (0.8 wt % C) —> ferrite (0.025 wt%C)+Cementite (6.7 wt %C)
- The relative layer thickness of ferrite (α iron) and cementite (Fe_3C) in pearlite is 8 to 1
- Mechanically Pearlite has properties between soft ductile ferrite and hard brittle cementite
- The phase transformation requires a redistribution of carbon by diffusion

Microstructure of eutectoid steel showing Pearlite consisting of alternate layers of alpha ferrite (light) and cementite (thin dark)

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

Under the microscope, it looks something like this. This micrograph represents the microstructure of eutectoid steel. When we say eutectoid steel, that means, it is 0.8% carbon; steel with 0.8% carbon and then, that is called a pearlitic microstructure.

The relative layer thickness of ferrite and cementite in pearlite is about 8: 1. The layer thickness of ferrite is larger than the layer thickness of cementite. Mechanically, pearlite has properties between soft ductile ferrite and hard brittle cementite.

The phase transformation, as we have discussed, requires a redistribution of carbon by diffusion. As we have discussed in the case of eutectic reaction, why they have alternate layer formation rather than separate islands of this ferrite and cementite; that is because if you have alternate layers of ferrite and cementite, the requirement for atomic diffusion is less – that way, diffusion can happen only over short distances as we can see in this figure here.

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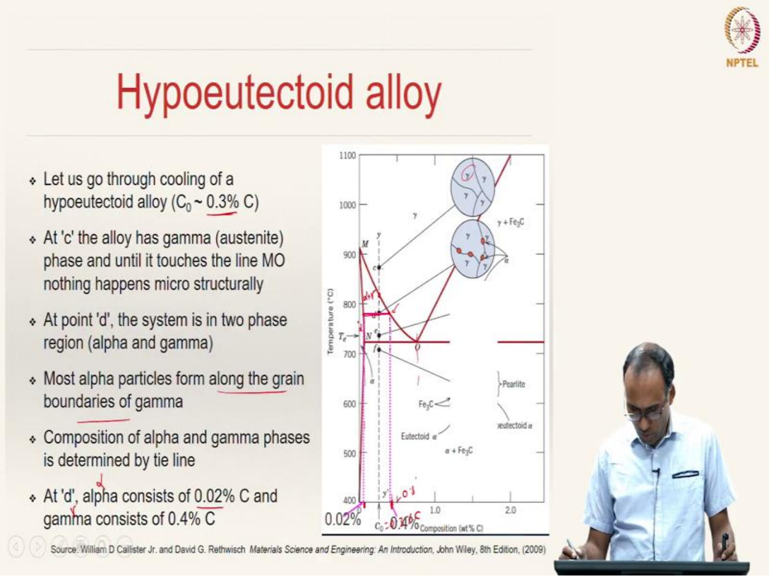

Hypoeutectoid alloy

- Let us go through cooling of a hypoeutectoid alloy (C_0 ~ 0.3% C)
- At 'c' the alloy has gamma (austenite) phase and until it touches the line MO nothing happens micro structurally
- At point 'd', the system is in two phase region (alpha and gamma)
- Most alpha particles form along the grain boundaries of gamma
- Composition of alpha and gamma phases is determined by tie line
- At 'd', alpha consists of 0.02% C and gamma consists of 0.4% C

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

All the alloy compositions left to eutectoid composition are called hypoeutectoid alloys; all the alloys right to the eutectoid compositions are called hypereutectoid alloy. Steels which have less than 0.8% carbon are called hypoeutectoid steels; steels which have carbon percentage greater than 0.8% carbon are called hypereutectoid steels.

Let us now look at the microstructure evolution in the case of a hypoeutectoid steel. This is our eutectoid composition. Let us go through the cooling of a hypoeutectoid alloy, whose composition $C_0 = 0.3\%$ carbon. At point C, you have γ iron (austenite) and as you are cooling down, until the temperature reaches this point nothing happens, everything will be γ; but as soon as it starts hitting this MO line, the transformation from γ to ferrite starts happening.

Because this is α, so this is a two-phase region, then you draw a tie line here and this is our γ phase and this is our α phase. You will have a two-phase region which is α plus γ, right? At point D, the system is in two-phase region α and γ and most α particles form along the grain boundaries of γ.

Here you can see γ and around the grain boundaries, you are forming the α particles. You can also find out the compositions of α and γ by drawing a tie line and draw the verticals and then, you will find out what is the composition of γ and if you draw the vertical here and then, you will know the what is the composition of α. When I say α, it is ferrite, when I say γ it is austenite.

We can see that at point D, the α is having a composition of 0.02% carbon and γ has about 0.4% carbon. You can also calculate the weight fractions using the lever rule.

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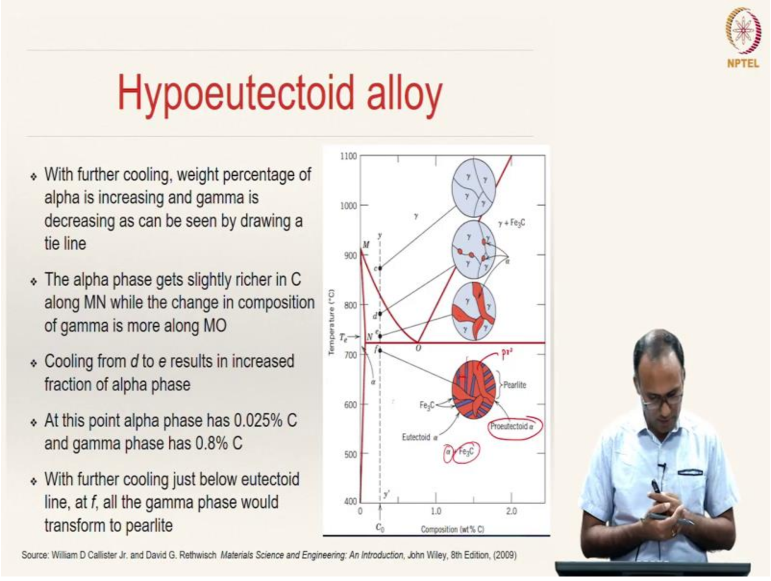

Hypoeutectoid alloy

- With further cooling, weight percentage of alpha is increasing and gamma is decreasing as can be seen by drawing a tie line
- The alpha phase gets slightly richer in C along MN while the change in composition of gamma is more along MO
- Cooling from *d* to *e* results in increased fraction of alpha phase
- At this point alpha phase has 0.025% C and gamma phase has 0.8% C
- With further cooling just below eutectoid line, at *f*, all the gamma phase would transform to pearlite

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

If you further cool it down, as you reach point e, the weight fraction of α ferrite increases - as you can see, the red portions represent our ferrite and the weight fractions of ferrite has increased. And the moment it hits the eutectoid line that is NO line, then the remaining γ would have to undergo the eutectoid reaction -- γ has to transform to eutectoid mixture of ferrite and cementite.

Then, you can see that eutectoid mixture of ferrite and cementite, here the blue one is cementite and the red one is ferrite. We know that the thickness of ferrite is larger than thickness of the cementite, as also seen here.

We can see this is our proeutectoid ferrite and the remaining is eutectoid mixture of ferrite and cementite; that is what is called pearlite. Again, this is a two-phase region because you have ferrite and cementite. By drawing a tie line, you will know the total compositions of ferrite and cementite.

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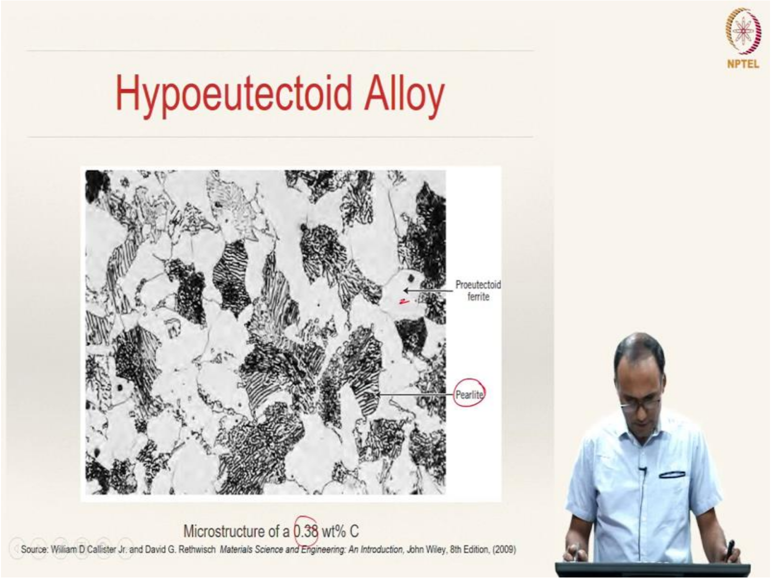

Hypoeutectoid Alloy

Microstructure of a 0.38 wt% C

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

This is the typical microstructure of a hypoeutectoid alloy of 0.38% carbon. You can see that this is proeutectoid ferrite and these are the alternate layers of ferrite and cementite called pearlite. You can see the eutectoid mixture of ferrite and cementite here.

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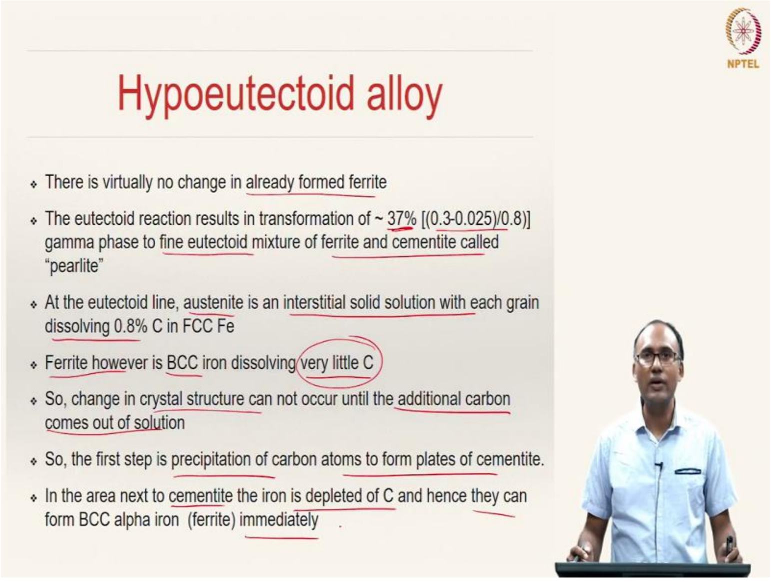

Hypoeutectoid alloy

- There is virtually no change in already formed ferrite
- The eutectoid reaction results in transformation of ~ 37% [(0.3-0.025)/0.8)] gamma phase to fine eutectoid mixture of ferrite and cementite called "pearlite"
- At the eutectoid line, austenite is an interstitial solid solution with each grain dissolving 0.8% C in FCC Fe
- Ferrite however is BCC iron dissolving very little C
- So, change in crystal structure can not occur until the additional carbon comes out of solution
- So, the first step is precipitation of carbon atoms to form plates of cementite.
- In the area next to cementite the iron is depleted of C and hence they can form BCC alpha iron (ferrite) immediately

With further cooling down, virtually there is no change in already formed ferrite. The eutectoid reaction results in the formation of about 37% (you can calculate the weight fractions from the tie line) of γ phase to fine eutectoid mixture of ferrite and cementite called pearlite - at the eutectoid line.

At the eutectoid line, austenite is an interstitial solid solution with each grain dissolving 0.8% carbon. At the eutectoid line, the austenite should be 0.8% carbon; that is what we call eutectoid composition. However, the ferrite is a BCC iron dissolving very little carbon.

You have austenite which is having 0.8% carbon and it transformed to ferrite and cementite which is FCC in structure. Ferrite is a BCC iron which dissolves very little carbon.

The change in crystal structure cannot occur until the additional carbon that is present in austenite comes out of the solution. You need to provide sufficient time for this additional carbon to come out, so that the α iron reaches its limited solubility.

The first step is the precipitation of carbon atoms to form plates of cementite, as we have already seen. In the area next to cementite, iron is depleted of carbon and hence, they can form BCC α iron immediately - that is how you will have alternate layers of ferrite and cementite.

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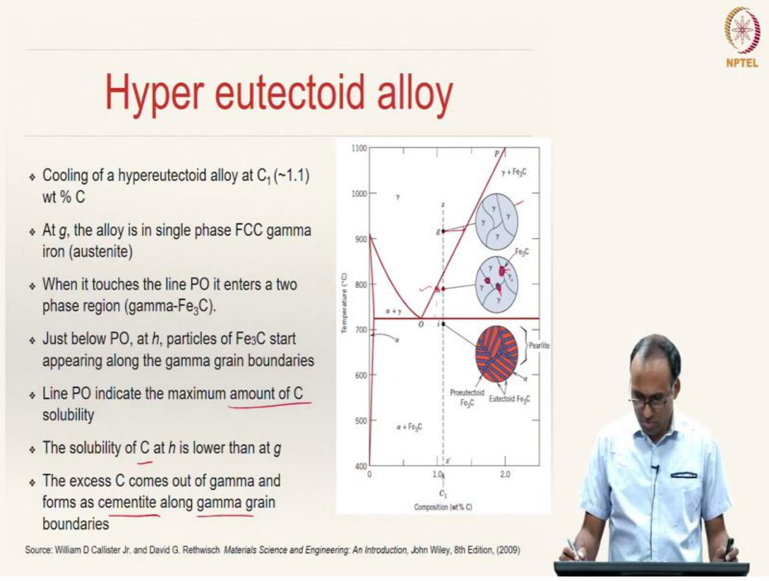

Hyper eutectoid alloy

- Cooling of a hypereutectoid alloy at C_1 (~1.1) wt % C
- At *g*, the alloy is in single phase FCC gamma iron (austenite)
- When it touches the line PO it enters a two phase region (gamma-Fe_3C).
- Just below PO, at *h*, particles of Fe_3C start appearing along the gamma grain boundaries
- Line PO indicate the maximum amount of C solubility
- The solubility of C at *h* is lower than at *g*
- The excess C comes out of gamma and forms as cementite along gamma grain boundaries

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

Let us now look at hypereutectoid steels. Here we have an alloy which has 1.1 weight percent carbon; again, at g, it is completely γ iron. As you are coming down, you will have proeutectoid phase of cementite, because in this region, if you draw a tie line, to the left you have γ and to the right you have Fe_3C. Hence, the proeutectoid phase will be of cementite not of ferrite, unlike in the other case.

For hypereutectoid alloys, the proeutectoid phase is cementite. For hypoeutectoid alloys, the proeutectoid phase is ferrite. When you are cooling it down and it touches the line PO, that is when it enters the two-phase region. Again, all the principles that we have adopted to calculate the compositions and the weight fractions in two-phase region in the discussion of phase diagrams can again be applied here.

Here, the line PO sort of represents the maximum amount of carbon solubility in γ. The solubility of carbon at h is lower than that at g. At g, you have this much solubility of carbon. So, you would have 1.1% carbon. By the time you come to h, the solubility of carbon at this position is -- in γ for instance, you have much less solubility.

This is the maximum solubility possible. So, what happens? The excess carbon comes out of γ. It cannot come as pure carbon, but it should come out as a solid solution. So, it comes out as Fe_3C. It comes out in the form of cementite along γ grain boundaries; that is what we see.

Why does it come out at grain boundaries? γ is already oversaturated and hence, it has to diffuse out additional carbon; that additional carbon comes and sits here as Fe_3C here; whereas, in hypoeutectoid steel it comes out as ferrite.

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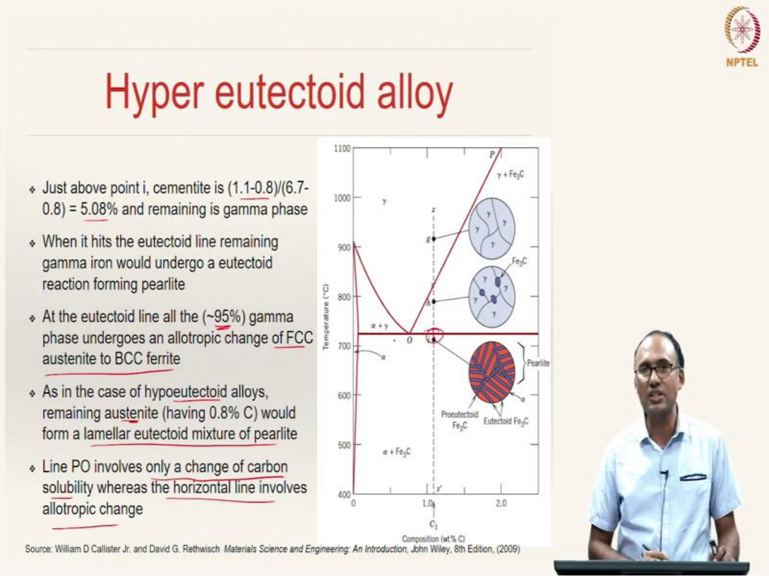

Hyper eutectoid alloy

- Just above point i, cementite is (1.1-0.8)/(6.7-0.8) = 5.08% and remaining is gamma phase
- When it hits the eutectoid line remaining gamma iron would undergo a eutectoid reaction forming pearlite
- At the eutectoid line all the (~95%) gamma phase undergoes an allotropic change of FCC austenite to BCC ferrite
- As in the case of hypoeutectoid alloys, remaining austenite (having 0.8% C) would form a lamellar eutectoid mixture of pearlite
- Line PO involves only a change of carbon solubility whereas the horizontal line involves allotropic change

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

Just about point i, cementite is about 5.08% (you can use the lever rule), and the remaining is γ. So, you have 5.08% of proeutectoid cementite or approximately 5% proeutectoid cementite is formed and remaining 95% is still γ.

What happens when it is crossing through this line at i? The remaining γ or austenite will have to transform to eutectoid mixture of ferrite and cementite. So, you will have 95% eutectoid mixture of ferrite and cementite or pearlite.

At the eutectoid line, all the 95% γ has to undergo an allotropic change of FCC austenite to BCC ferrite. As in the case of hypoeutectoid alloys, the remaining austenite would form a lamellar eutectoid mixture of ferrite and cementite; that is called pearlite.

Please note that there is a difference in terms of the activity that is happening across line PO and along the eutectoid line. Line PO involves only a change of carbon solubility -- that the carbon is only diffusing out; whereas, the horizontal line involves an allotropic change. Here, there is no allotropic change, but here there is an allotropic change that is taking place.

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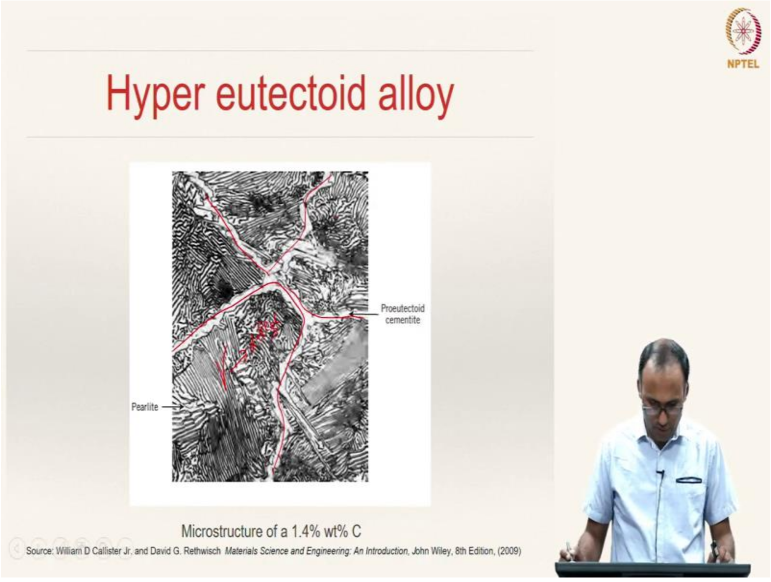
Hyper eutectoid alloy

Microstructure of a 1.4% wt% C

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

This is the typical microstructure of a hyper eutectoid alloy; wherein, you can see this white patch is the proeutectoid cementite network. These are γ that has converted to pearlite - α + Fe_3C; alternate layers of ferrite and cementite.

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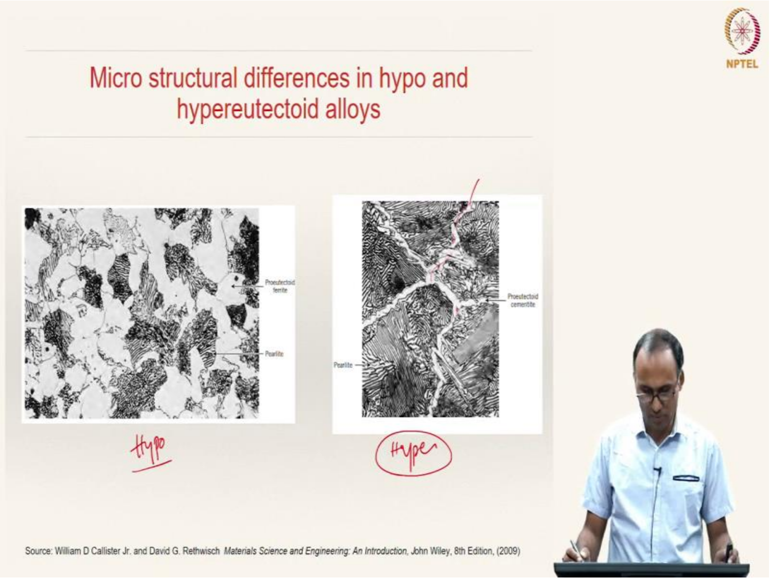

Micro structural differences in hypo and hypereutectoid alloys

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

This is how the microstructure looks like for a hypoeutectoid steel; this is the hypo eutectoid steel and this is the hyper eutectoid steel. In hyper eutectoid steel, you have a continuous network of cementite throughout the microstructure; whereas, here you proeutectoid ferrite and pearlite.

The microstructures are very different for hypoeutectoid steels and hypereutectoid steels. The cementite phase is brittle and hence, the presence of continuous cementite network as a pro eutectoid phase is something that one needs to be worried about as far as the mechanical properties of that system are concerned.

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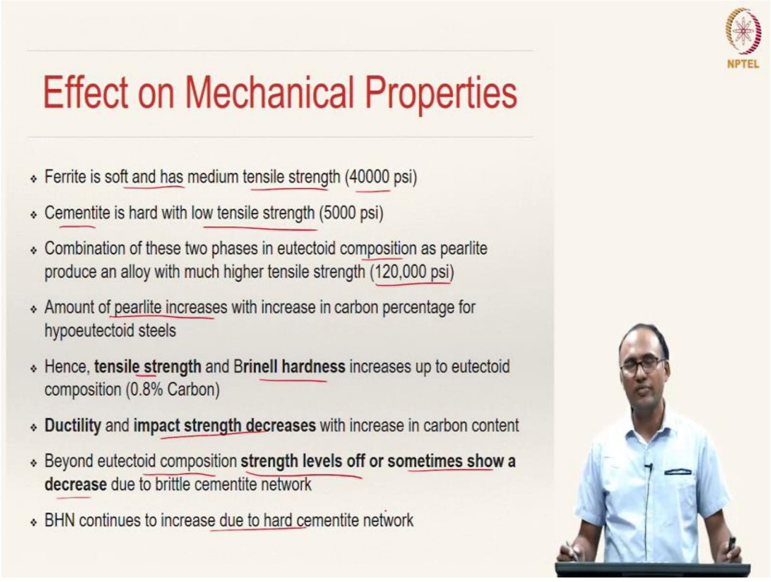

Effect on Mechanical Properties

- Ferrite is soft and has medium tensile strength (40000 psi)
- Cementite is hard with low tensile strength (5000 psi)
- Combination of these two phases in eutectoid composition as pearlite produce an alloy with much higher tensile strength (120,000 psi)
- Amount of pearlite increases with increase in carbon percentage for hypoeutectoid steels
- Hence, **tensile strength** and **Brinell hardness** increases up to eutectoid composition (0.8% Carbon)
- **Ductility** and **impact strength decreases** with increase in carbon content
- Beyond eutectoid composition **strength levels off or sometimes show a decrease** due to brittle cementite network
- BHN continues to increase due to hard cementite network

The ferrite is soft and has medium tensile strength about 40,000 psi and cementite is hard with low tensile strength about 5000 psi, and the combination of these two phases in eutectoid composition as pearlite produces a much higher tensile strength of about 120,000 psi.

As we increase the carbon percentage for hypo eutectoid steels, the amount of pearlite increases and hence, the tensile strength and Brinell hardness increases up to eutectoid composition. Ductility and impact strength decrease with increase in carbon content because carbon is going to increase the hardness of the system or brittleness of the system.

Beyond the eutectoid composition however, the strength levels off or sometimes show a decrease due to brittle cementite network. Hyper eutectoid steels are characterized by continuous brittle cementite network and that is going to limit the mechanical properties that one want to get obtained.

However, the Brinell hardness number or in general, hardness continuous to increase due to increase in the fraction of the hard cementite network.

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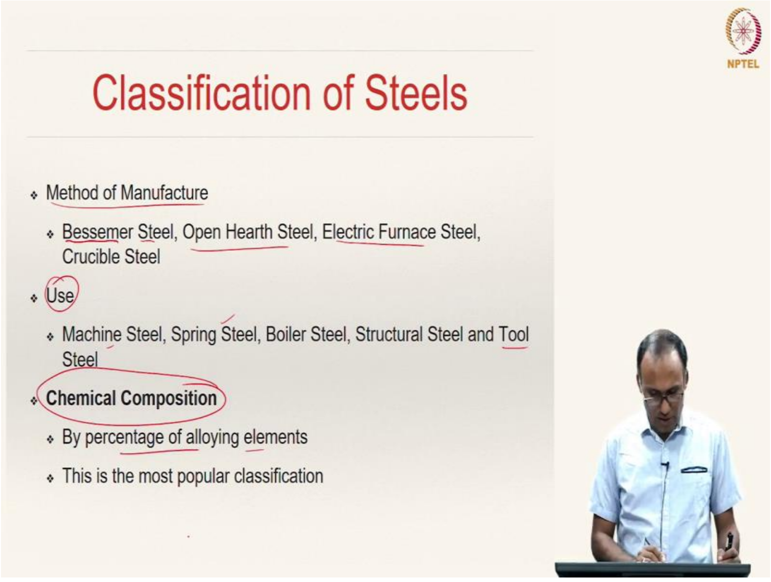

Classification of Steels

- Method of Manufacture
  - Bessemer Steel, Open Hearth Steel, Electric Furnace Steel, Crucible Steel
- Use
  - Machine Steel, Spring Steel, Boiler Steel, Structural Steel and Tool Steel
- **Chemical Composition**
  - By percentage of alloying elements
  - This is the most popular classification

Let us discuss the classification of steels. The steels can be classified based on the manufacturing process. Different types are Bessemer steel, open hearth steel, electric furnace steel or crucible steel. If Bessemer converter is used to make steel, such a steel is called Bessemer steel.

Sometimes, they can also be classified based on the usage such as machine steel, spring steel, boiler steel, structural steel and tool steel; if you are using for tools, cutting tools and so on, then such a steel is called as tool steel. However, the most popular classification is based on the chemical composition, which describes the percentage of alloying elements and that is most popular classification for the steels.

So, here in this class, we will discuss the classification for SAE steels -- Society of Automotive Engineers, have given some specifications for steel grades by their chemical composition.

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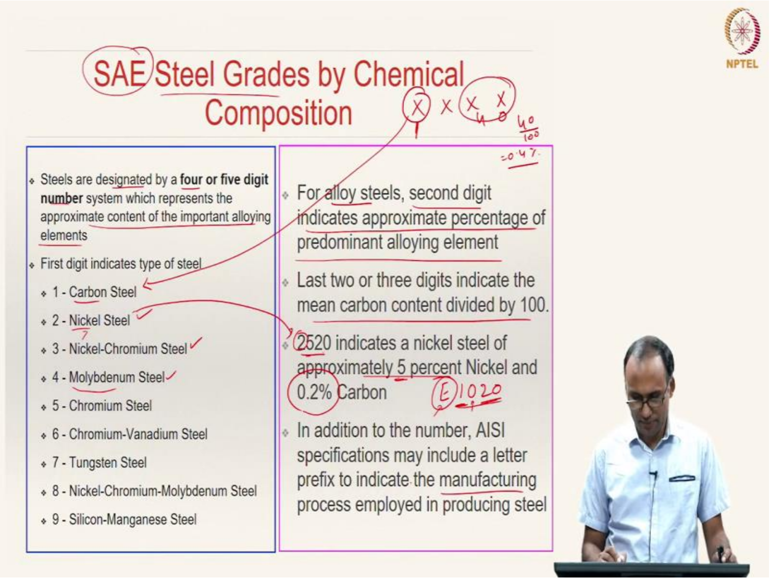

SAE Steel Grades by Chemical Composition

- Steels are designated by a **four or five digit number** system which represents the approximate content of the important alloying elements
- First digit indicates type of steel
  - 1 - Carbon Steel
  - 2 - Nickel Steel
  - 3 - Nickel-Chromium Steel
  - 4 - Molybdenum Steel
  - 5 - Chromium Steel
  - 6 - Chromium-Vanadium Steel
  - 7 - Tungsten Steel
  - 8 - Nickel-Chromium-Molybdenum Steel
  - 9 - Silicon-Manganese Steel

- For alloy steels, second digit indicates approximate percentage of predominant alloying element
- Last two or three digits indicate the mean carbon content divided by 100.
- 2520 indicates a nickel steel of approximately 5 percent Nickel and 0.2% Carbon
- In addition to the number, AISI specifications may include a letter prefix to indicate the manufacturing process employed in producing steel

Usually, according to the SAE designation, the steels are designated by 4- or 5-digit number system, which represents approximate content of the important alloying elements. Suppose you have 4 digits, this first digit represents that it is carbon steel.

The first digit indicates the type of steel. If it is 1, then that is a plain carbon steel and if it is 2, it is a nickel-based steel; if it is 3, nickel chromium steel; if it is 4, molybdenum steel. That means, primary alloying element is molybdenum; here primary alloying element is nickel and so on.

Here, carbon means there are no other alloying elements - plain carbon steel, except for some impurities, it is only a plain carbon steel. So, for alloy steels, the second digit indicates approximate percentage of the predominant alloying element. For instance, if you are talking about nickel steel, the second digit represents approximate percentage of the nickel percentage in that steel.

The last two digits or three digits, if it is a 5-index notation -- indicate the mean carbon content divided by 100. So, let us say if it is 40, then that means, 40 by 100 that is 0.4% carbon.

For instance, in 2520 steel, 2 means it is a nickel-based steel, approximately 5 percent nickel and 20 by 100, 0.2 percent carbon. 1020 steel is a plain carbon steel, there is no other alloying element and it is 0.2 percent carbon, that means, a hypoeutectoid steel. In addition to the number, sometimes the specification may also include a letter. For instance, if it is written E that means, it is electric furnace steel. So, to represent the method of manufacturing, there will be a letter that is usually used before that.

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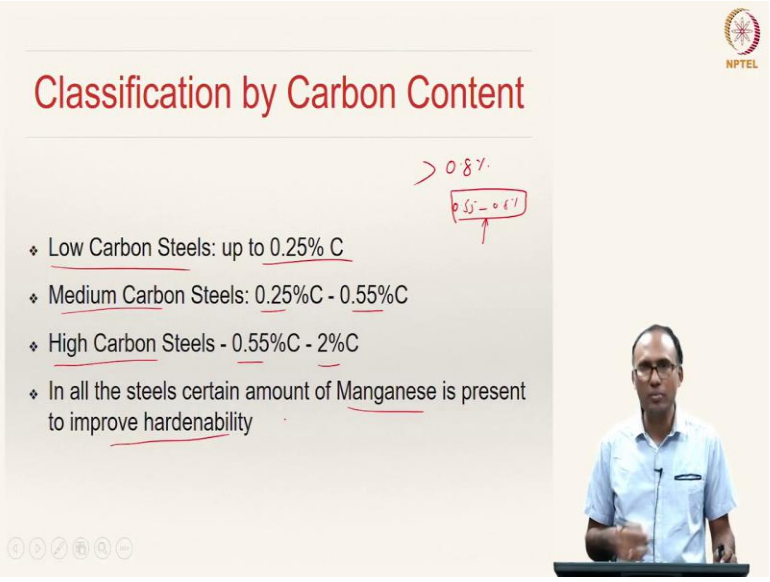

Classification by Carbon Content

> 0.8%

0.55 – 0.8%

- Low Carbon Steels: up to 0.25% C
- Medium Carbon Steels: 0.25%C - 0.55%C
- High Carbon Steels - 0.55%C - 2%C
- In all the steels certain amount of Manganese is present to improve hardenability

Again, the steels are classified based on the carbon content. If the carbon content is less than 0.25%, then such steels are called low carbon steels. If it is between 0.25% and 0.55%, then it is medium carbon steel and if it is between 0.55% and 2%, high carbon steel.

By that definition, all hyper eutectoid steels which are having carbon content greater than 0.8% are high carbon steels. Most of the hypo eutectoid steels are low carbon steels or medium carbon steels and some from 0.55% to 0.8% carbon, these of hypo eutectoid steels are high carbon steels. In all the steels, you always have certain amount of manganese because of the need for improving the hardenability of the steel; even for the plain carbon steel.

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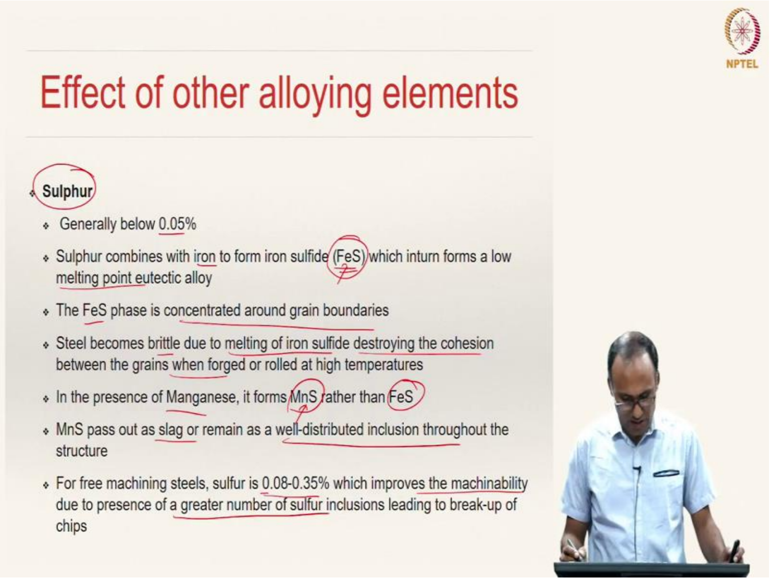

Effect of other alloying elements

- **Sulphur**
  - Generally below 0.05%
  - Sulphur combines with iron to form iron sulfide (FeS) which inturn forms a low melting point eutectic alloy
  - The FeS phase is concentrated around grain boundaries
  - Steel becomes brittle due to melting of iron sulfide destroying the cohesion between the grains when forged or rolled at high temperatures
  - In the presence of Manganese, it forms MnS rather than FeS
  - MnS pass out as slag or remain as a well-distributed inclusion throughout the structure
  - For free machining steels, sulfur is 0.08-0.35% which improves the machinability due to presence of a greater number of sulfur inclusions leading to break-up of chips

Now, let us look at effect of other elements on the properties of steels. So, first let us look at sulphur. Sulphur is generally maintained less than 0.05% steel. When present in steel, the sulphur combines with iron to form iron sulfide FeS, which in turn forms a low melting point eutectic alloy.

FeS is a low melting point eutectic alloy and FeS phase is usually concentrated around the grain boundaries. Steel sometimes becomes brittle due to melting of iron sulfide because it is a low melting eutectic phase and destroying the cohesion between the grains, when forged or rolled at high temperatures.

Hence, the sulphur presence in iron around iron atmosphere is not actually good. However, as we have discussed, plain carbon steel always will have some amount of manganese; however, in the presence of manganese, it prefers to form manganese sulfide rather than ferrous sulfide and the manganese sulfide has an advantage.

Manganese sulfide passes out as slag or remains as a well distributed inclusion throughout the structure, without causing the adverse effects that ferrous sulfide would cause. For free machining steels, sulphur is usually maintained at 0.08% to 0.35% which improves the machinability due to the presence of greater number of sulfur inclusions leading to break up of chips. It gives additional hardness and it allows us to break the chips better.

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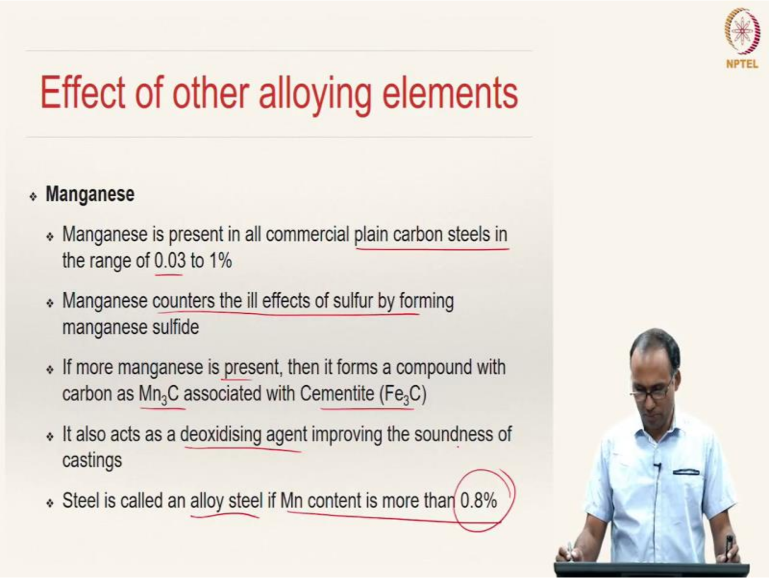

Effect of other alloying elements

- **Manganese**
  - Manganese is present in all commercial plain carbon steels in the range of 0.03 to 1%
  - Manganese counters the ill effects of sulfur by forming manganese sulfide
  - If more manganese is present, then it forms a compound with carbon as Mn_3C associated with Cementite (Fe_3C)
  - It also acts as a deoxidising agent improving the soundness of castings
  - Steel is called an alloy steel if Mn content is more than 0.8%

Manganese, as we have discussed is present in all commercial plain carbon steels in the range of 0.03% to 1%. One of the major advantages of manganese is that it counters the ill effects of sulfur by forming manganese sulfide.

However, if more manganese is present, it forms a compound with carbon as Mn_3C associated with cementite. Like Fe_3C is formed, similarly you will have Mn_3C. Also, manganese acts as a deoxidizing agent, improving the soundness of casting. It will get rid of some gases that are probably get trapped in the liquid state. Steel is called an alloy steel, if manganese content is more than 0.8%; otherwise, it is called plain carbon steel.

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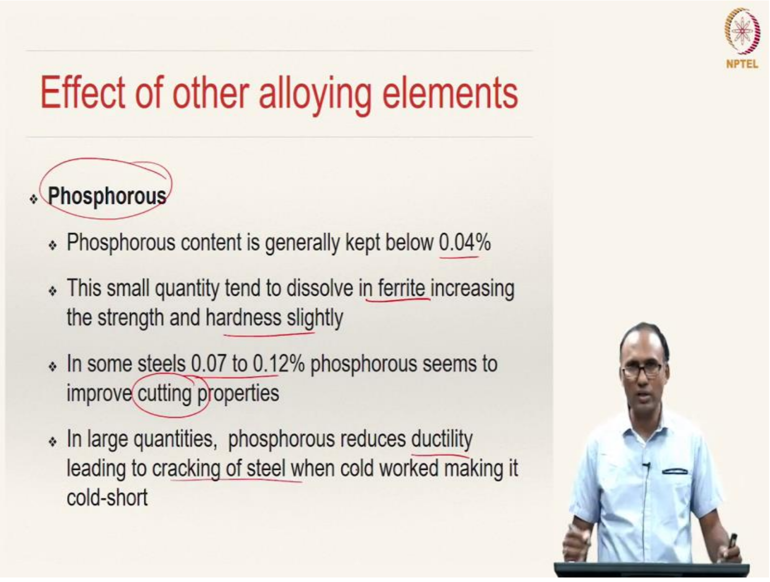
Effect of other alloying elements

- **Phosphorous**
  - Phosphorous content is generally kept below 0.04%
  - This small quantity tend to dissolve in ferrite increasing the strength and hardness slightly
  - In some steels 0.07 to 0.12% phosphorous seems to improve cutting properties
  - In large quantities, phosphorous reduces ductility leading to cracking of steel when cold worked making it cold-short

The next alloying element that we are interested in is phosphorous. Phosphorous content is usually kept less than 0.04%. This small quantity of phosphorous tends to dissolve in ferrite increasing the strength and hardness of the steel slightly. In some steels, you may have a higher percentage of phosphorous in order to improve the cutting properties.

However, if you have large quantities of phosphorous, it reduces the ductility leading to cracking of steels when cold worked making it cold short. So, you should not have too much of phosphorous in steels.

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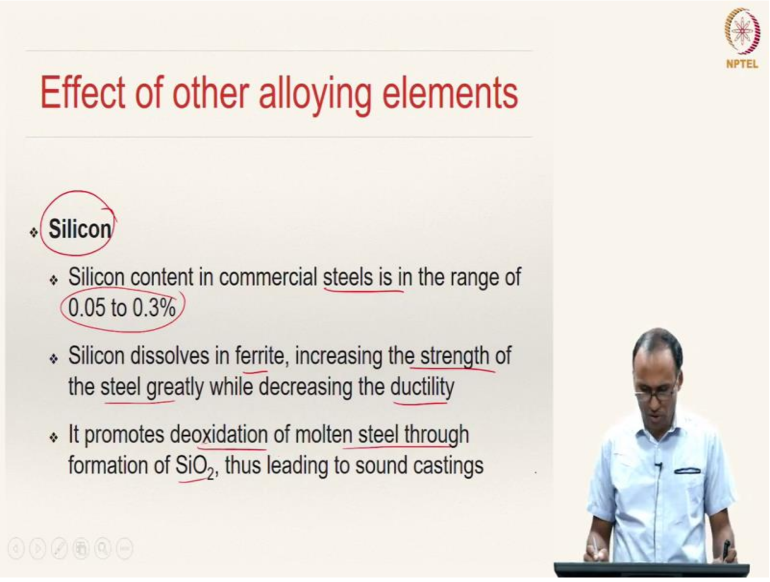
Effect of other alloying elements

- **Silicon**
  - Silicon content in commercial steels is in the range of 0.05 to 0.3%
  - Silicon dissolves in ferrite, increasing the strength of the steel greatly while decreasing the ductility
  - It promotes deoxidation of molten steel through formation of SiO_2, thus leading to sound castings

Another important alloying element is silicon. Silicon content in commercial steels is usually maintained less than 0.3%. It dissolves in ferrite increasing the strength of the steel greatly, while decreasing the ductility of the steel. Again, it also promotes the deoxidation of molten steel through formation of SiO_2, thus leading to sound castings.

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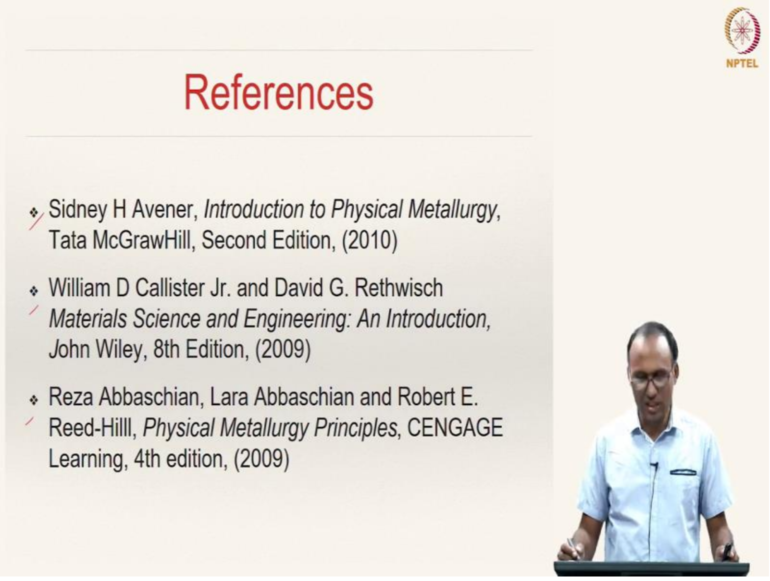

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- William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)
- Reza Abbaschian, Lara Abbaschian and Robert E. Reed-Hilll, *Physical Metallurgy Principles*, CENGAGE Learning, 4th edition, (2009)

So, with that we have finished our discussion on phase diagrams and then, spent reasonable amount of time understanding the phase diagram of iron-carbon system and we have also discussed the evolution of different microstructures for hypoeutectoid steels and hypereutectoid steels and effect of certain alloying elements. More details on phase diagrams and also iron-carbon system can be obtained or found from these three very useful sources. Sidney H Avner's Introduction to Physical Metallurgy; Callister's book on Material Science and Engineering and Reed-Hill's text book on Physical Metallurgy.

Thank you very much and we will start looking at heat treatment and thermal processing of steels in the next module.