Structure of Materials
Prof. Anandh Subramaniam
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 36
Chapter - 07
Phase Diagrams

Next let us solve an example, considering the lead in eutectic system.

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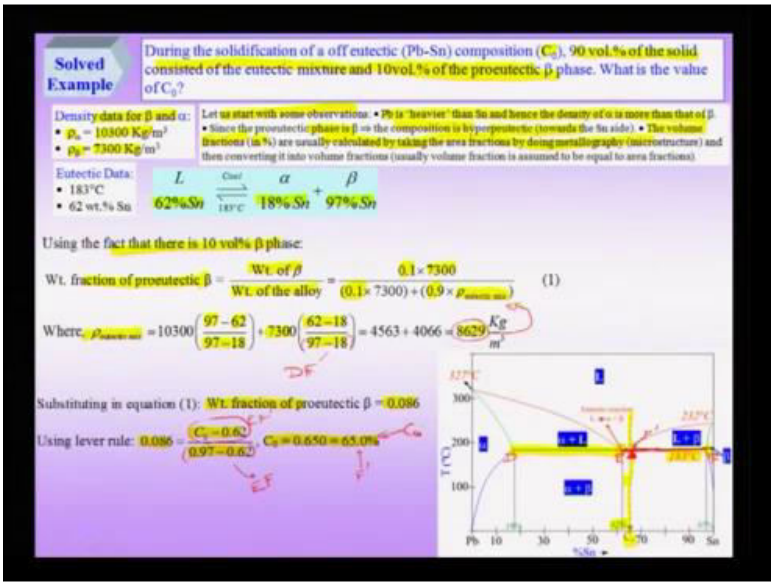

Solved Example

During the solidification of a off eutectic (Pb-Sn) composition (C_0), 90 vol.% of the solid consisted of the eutectic mixture and 10vol.% of the proeutectic β phase. What is the value of C_0?

Density data for β and α:
- $\rho_\alpha = 10300\ Kg/m^3$
- $\rho_\beta = 7300\ Kg/m^3$

Let us start with some observations. • Pb is "heavier" than Sn and hence the density of α is more than that of β. • Since the proeutectic phase is β ⇒ the composition is hyperpeutectic (towards the Sn side). • The volume fractions (in %) are usually calculated by taking the area fractions by doing metallography (microstructure) and then converting it into volume fractions (usually volume fraction is assumed to be equal to area fractions)

Eutectic Data:
- 183°C
- 62 wt.% Sn

$$\underset{62\%Sn}{L} \underset{183°C}{\overset{Cool}{\rightleftharpoons}} \underset{18\%Sn}{\alpha} + \underset{97\%Sn}{\beta}$$

Using the fact that there is 10 vol% β phase:

$$\text{Wt. fraction of proeutectic } \beta = \frac{\text{Wt. of } \beta}{\text{Wt. of the alloy}} = \frac{0.1\times 7300}{(0.1\times 7300)+(0.9\times \rho_{eutectic\ mix})} \qquad (1)$$

$$\text{Where, } \rho_{eutectic\ mix} = 10300\left(\frac{97-62}{97-18}\right)+7300\left(\frac{62-18}{97-18}\right) = 4563+4066 = 8629\frac{Kg}{m^3}$$

DF

Substituting in equation (1): Wt. fraction of proeutectic β = 0.086

$$\text{Using lever rule: } 0.086 = \frac{C_0-0.62}{0.97-0.62},\ C_0 = 0.650 = 65.0\%$$

EF

C_0

Let us assume that, we are solidifying a composition C 0 and we want to find out the C 0, given the fact that, 90 percent of the volume fraction of the solid consisted of the eutectic mixture and about 10 percent of the volume fraction, the pro-eutectic beta phase. The given fact that, the phase is a pro-eutectic beta phase, we can clearly see that, the composition C 0 has to the lie to the right of the eutectic composition, which is 62 percent of tin.

Let us make this and certain other observations that, lead is heavier than tin and hence, the density of alpha is more than that of the beta phase, the two terminals are solids solutions. Since the pro-eutectic phase is beta, the composition which we want to find out is on the hyper eutectic side. The volume fractions in of course, volume percent are usually calculated taking into account the area fractions doing a metallography or a microstructure analysis.

Then, converting these volume fractions, these area fractions you calculate, into volume fractions. In other words, first I would do a metallographic study and say, suppose I have a microstructure ((Refer Time: 01:44)), in which I have a two phase mixture, in which there is one phase which is the shaded phase and the other phase say for instance, this is the my alpha phase and this is the beta phase. I can make an assumption that, these area fractions are equal to the volume fractions and from these volume fractions, I can further calculate the weight fractions.

Now, the density data given for beta and alpha are, the density of alpha is 10300 kilogram per meter cube, beta is 7300 kilogram per meter cube. And we know that, the eutectic composition is 62 percent of tin and the eutectic reaction takes place at 183 degrees Celsius. The liquid of course, is 62 percent tin, the alpha is 18 percent tin and the beta is 97 percent tin, which are these two compositions in the diagram. Now, we are interested in finding, what we call the C 0, now how would such a microstructure of course, look ((Refer Time: 02:45)).

We already had a look at that, suppose I am solidifying, I would first have some pro-eutectic phase and in this diagram of course, instead of alpha, the pro-eutectic phase is beta and then of course, I have an eutectic mixture, which surrounds it. And the fraction of this pro-eutectic phase is 10 percent as given in the question, we are trying to solve. Using the fact that, there is 10 percent, volume percent of the beta phase, the weight for fraction of the pro-eutectic beta is the weight of the beta divided by the weight of the alloy.

So, we convert the percentages, which is 10 percent of volume percentage of beta phase, which is the pro-eutectic beta phase into fractions in 0.1. The density of this beta phase is 7300 then, further I divide this by the weight of the alloy, which consists of the pro-eutectic beta phase and an eutectic mixture. So, for now, I do not know the density of the pro-eutectic mixture and I multiply this by 0.9 into rho of the eutectic mixture. Therefore, I have to now calculate the rho eutectic mixture, which we know from the lever rule and now I am talking about points D and E we had taken into account, D and f, and E being of course, the eutectic in between.

I use these percentages, which is 97 percent of tin in the beta phase, 62 percent is the eutectic composition and 97 minus 18 is of course, the whole length of the lever plus

7300 is the density of the beta phase, 62 minus 80, which is this number. This length of the arm of the lever divided by 97 minus 18, which equal to the full length of the lever this is equal to D f. Therefore, I can calculate the density of the eutectic mixture to be 8629 kilogram per meter cube.

Now, since I have the density of the eutectic mixture, I can now substitute it back into this equation 1 here and therefore, I can get the fraction of the pro-eutectic beta, which is what I am trying to calculate here to be 0.086. This is the weight fraction of the pro-eutectic beta phase and that means, I have converted now my volume fraction or volume percentage into 0.86 weight percent. Now, I can use the lever rule again, assuming of course, the fulcrum of the lever to be at the mean composition C 0 here, so these are now a new lever, this is my fulcrum for the new lever here.

And now, my arm of the lever, the lever extends from point E to point F and this is my new fulcrum F prime. Therefore, I can use a lever rule to calculate 0.086 is equal to C 0 minus 0.62, which is the smaller arm of the lever divided by 0.97 minus 0.62, which is the entire length of the lever starting from E to F. So therefore, I can write down that, this numerator is the smaller arm of the lever E F prime and this is the larger arm of the lever the denominator, which is nothing but, E F.

From this, I can calculate the mean composition C 0, because thus to be 65 percent, therefore C 0 is just to the right of the point E and therefore, this is the point corresponding to F prime, otherwise this is the composition C 0. Therefore, repeatedly applying the lever rule and using some simple definitions like the fact that, the mass per unit volume is density and that the data, which I get from metallography is actually volume percent.

And I need to convert into weight percent before I can use the lever rule, because the phase diagram all the quantities are given in weight percent and therefore, using the simple formulae of conversion, I can now calculate the mean composition taking at my metallographic data. So, this kind of a procedure is routinely applied, to now know what is the composition, if I know my fractions. Or of course, if you know the fractions using the phase diagram, I can conversely calculate the fraction of the pro-eutectic phase and the eutectic mixture.

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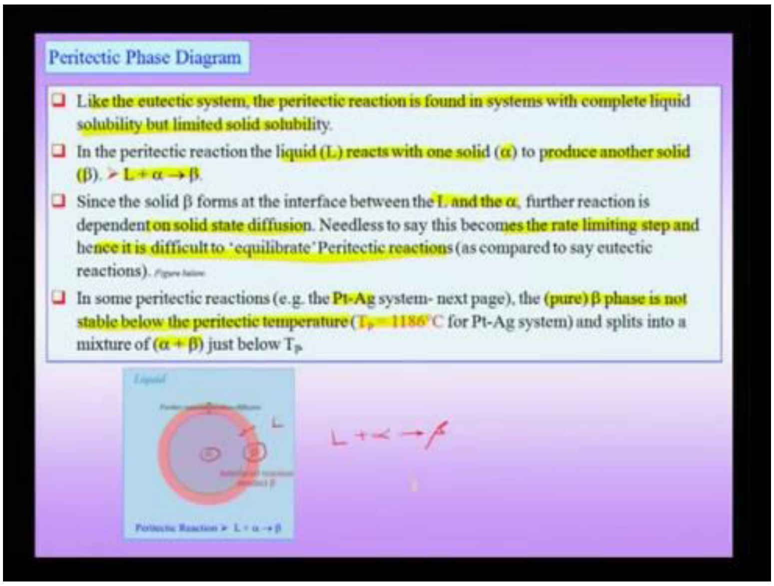

Peritectic Phase Diagram

- Like the eutectic system, the peritectic reaction is found in systems with complete liquid solubility but limited solid solubility.
- In the peritectic reaction the liquid (L) reacts with one solid (α) to produce another solid (β). ➢ $L + \alpha \rightarrow \beta$.
- Since the solid β forms at the interface between the L and the α, further reaction is dependent on solid state diffusion. Needless to say this becomes the rate limiting step and hence it is difficult to 'equilibrate' Peritectic reactions (as compared to say eutectic reactions). Figure below
- In some peritectic reactions (e.g. the Pt-Ag system- next page), the (pure) β phase is not stable below the peritectic temperature (T_p = 1186°C for Pt-Ag system) and splits into a mixture of ($\alpha + \beta$) just below T_p.

$L + \alpha \rightarrow \beta$

Let us move to a different type of a phase diagram next, which is known as the peritectic phase diagram. Like the eutectic system, the peritectic reaction is found in systems complete liquid solubility, but limited solid solubility and typically, for those elements whose melting point have is very very different. In the peritectic reaction, the liquid reacts with one solid alpha to produce another solid beta. So of course, crudely I can write down this peritectic reaction to be liquid plus alpha giving rise to beta.

Since the solid beta forms at the interface between liquid and alpha, further reaction is dependent on solid state diffusion, needless to say this becomes a rate limiting step. And hence, it is difficult to equilibrate peritectic reactions, because when we are drawing phase diagrams, we want to be as close to equilibrium as possible. This is easy to achieve in the case of eutectic systems, but because of the involvement of solid state diffusion, it becomes difficult in the peritectic reaction.

Illustrate to understand this using the schematic here below that, I have a liquid and I have an alpha here, this liquid reacts with this alpha to produce the interfacial reaction product, which is beta here. Now, since beta is a solid phase, if further reaction has to take place and this beta actually separates in three dimensions, the alpha and the liquid. That means, there is no contact between alpha and liquid and this implies, there has to be some diffusion involved.

And this solid state diffusion becomes a rate limiting step and therefore, if I am studying a peritectic system, I have to give sufficient time so that, I attain equilibrium. And we will be considering at least couple of peritectic kind of a systems, one of them which is we will consider in the next page is the lead platinum silver system. And in this case, the pure beta phase is not stable below the peritectic temperature and we will of course, describe this more when we come to the next slide.

And this peritectic temperature happens to be about 1186 degrees Celsius and therefore, just below the peritectic temperature, the beta phase splits into a mixture of alpha plus beta. So, this is point note worthy that, even though I am having liquid plus a giving beta, the beta immediately splits below the eutectic temperature into alpha plus beta, but still I cannot write this reaction as liquid plus alpha giving alpha plus beta, I should write this reaction as liquid plus alpha giving beta.

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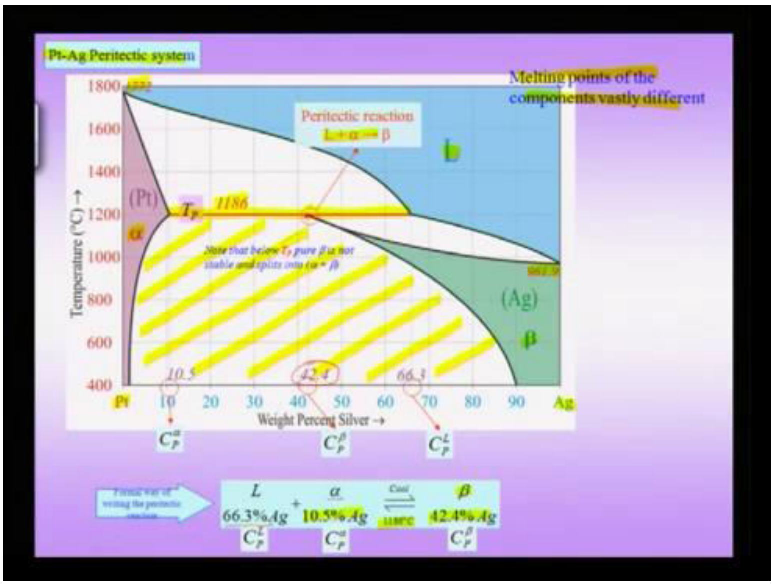

Pt-Ag Peritectic system

Melting points of the components vastly different

Peritectic reaction

$L + \alpha \rightarrow \beta$

Note that below T_P pure β is not stable and splits into $(\alpha + \beta)$

Formal way of writing the peritectic reaction

$$\underset{C_P^L}{\overset{L}{66.3\%Ag}} + \underset{C_P^{\alpha}}{\overset{\alpha}{10.5\%Ag}} \underset{1186^{\circ}C}{\overset{Cool}{\rightleftharpoons}} \underset{C_P^{\beta}}{\overset{\beta}{42.4\%Ag}}$$

So, let us take this example of the platinum silver peritectic system and I note that, the melting point of platinum is 1772, which is much above silver, which is 961 degree Celsius. In the peritectic reaction of course, I have the horizontal line, which is the temperature at which the peritectic reaction takes place and this is 1186 degrees Celsius, the de-peritectic. At the two ends of this red line, the tie line or this red line, where there is a three phase equilibria, you have the alpha phase and the liquid phase, this alpha reacts with this liquid to produce beta phase at this point.

So, this is where the beta phase is produces the composition of the beta, which happens to be 42.4 percent of silver. So, liquid with 66 percent of silver reacts with alpha with 10.5 percent of silver to give the beta phase with 42 percent of silver at a temperature of 1186. But, as evident from the phase diagram, just below this temperature T peritectic 1186 degrees Celsius, you see actually the phase field, which I am going to highlight now, this phase field is an alpha plus beta phase field.

So, just if suppose, I am talking about a temperature just below the peritectic temperature, what is stable is an alpha plus beta mixture and not just the pure beta, which was produced during the peritectic reaction. And therefore, if I were to slowly cool this system, I would find that, even for a peritectic composition, which is 42.4 percent of silver, I would note that, just as I am cooling below the 1186 degrees Celsius, I would get an alpha plus beta mixture, though this is not the original product of the peritectic reaction.

So, we can see that, this is an example of a peritectic system, this is a new kind of a reaction, wherein one liquid with a solid produces an interfacial beta, which is the peritectic system. And all the single phase fields in this diagram have been marked in different colors, the liquid phase above the alpha phase and the beta phase. Like we did for the eutectic system, I can also consider now for instance, slow cooling of various compositions and try to figure out, what will be the resulting product.

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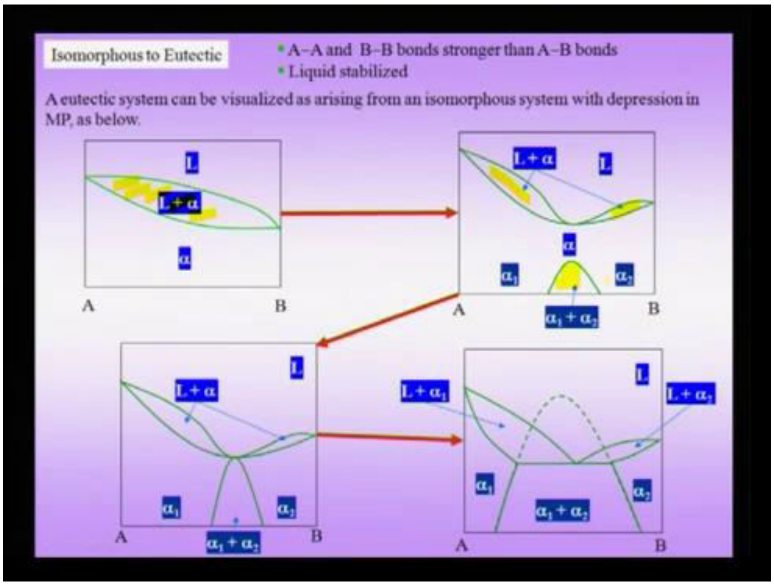

Isomorphous to Eutectic

- A–A and B–B bonds stronger than A–B bonds
- Liquid stabilized

A eutectic system can be visualized as arising from an isomorphous system with depression in MP, as below.

But, we will skip that for now and we will try to understand, how we can think of the peritectic system evolving from an isomorphous system. We did this for the eutectic system sometime back, in which case we consider an isomorphous system, it is typical double lens kind of a system here. And we said that, there is a variation to this, wherein I have a depression in the freezing point and which also implies a phase separation at low temperatures. And then, I considered the eutectic system as a limiting case of this kind of a, what you might call a depression freezing point with an phase separation system.

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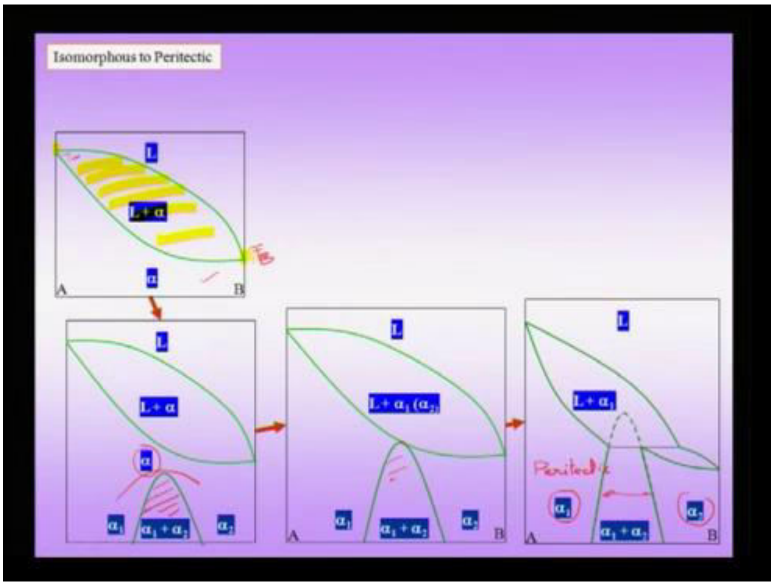

Isomorphous to Peritectic

Now, similarly for the peritectic, I can again visualize the double lens isomorphous system, but now with the melting points of A and B, very very different. So, I can see that, this is the melting point of A and this is the melting point of B and they are vastly different. Now, as I again pointed out, this is not a single phase diagram, many of these systems may actually not be present, but we can think visualize this in terms of an mental constraint.

So, from this simple system, I can think of a phase separation system and the two phase field being here at low temperatures. Then, I can think of a limiting possibility, where the two phase mixture doom actually touches my isomorphous double lens and finally, I can think of a limiting case, where I have an peritectic system. So, this is my peritectic system, so this was my original, the dotted line shows the original double lens construction.

And here is my the two phases, which originally came out, the alpha 1 plus alpha 2 phases, which were present here as continuous solid solution, but now they have been separated by this two phase field. And there is no region, where I can go continuously from the alpha 1 to the alpha 2 phase, which is in fact, the alpha phase which at high temperatures. So, thus I can visualize a series of constructs to go from the isomorphous system to the peritectic system.

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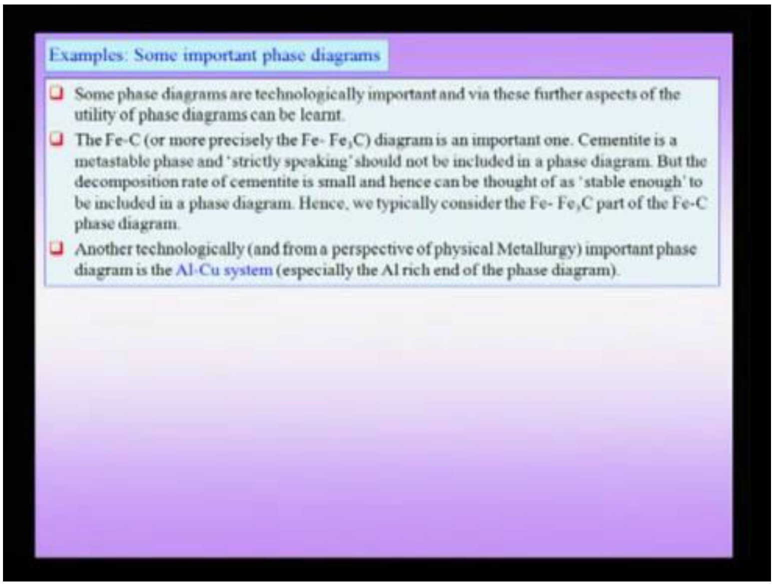

Examples: Some important phase diagrams

- Some phase diagrams are technologically important and via these further aspects of the utility of phase diagrams can be learnt.
- The Fe-C (or more precisely the Fe- Fe_3C) diagram is an important one. Cementite is a metastable phase and 'strictly speaking' should not be included in a phase diagram. But the decomposition rate of cementite is small and hence can be thought of as 'stable enough' to be included in a phase diagram. Hence, we typically consider the Fe- Fe_3C part of the Fe-C phase diagram.
- Another technologically (and from a perspective of physical Metallurgy) important phase diagram is the Al-Cu system (especially the Al rich end of the phase diagram).

We are not talking in detail about many more of those phase diagrams, we talked about like for instance syntactic system or the monotactic system, but we will consider some important examples of phase diagrams. And the most important of these of course, we will talk about is, what is known as the iron carbon diagram or truly speaking, the iron cementite phase diagram. In this context of course, I had pointed out cementite is actually a meta stable phase and if left sufficiently long enough, you would expect that the iron, the cementite would break into iron and carbide.

But, we shall tolerate cementite part of the phase diagram and we will consider the, what you might call the iron rich side of the iron carbon phase diagram, which is technologically very very important. Now, another technologically important phase diagram is the aluminum copper system, which we shall consider in the next chapter when we talk about phase transformations.

And in this aluminum copper system, we are specially interested in the aluminum rich kind of the phase diagram. And this is aluminum copper system, is not only technologically important, but it is a rich system from understanding perspective of physical metallurgy and the various processes, which take place when I try to engineer my alloy in the aluminum copper system with typically with an 4 percent copper content.

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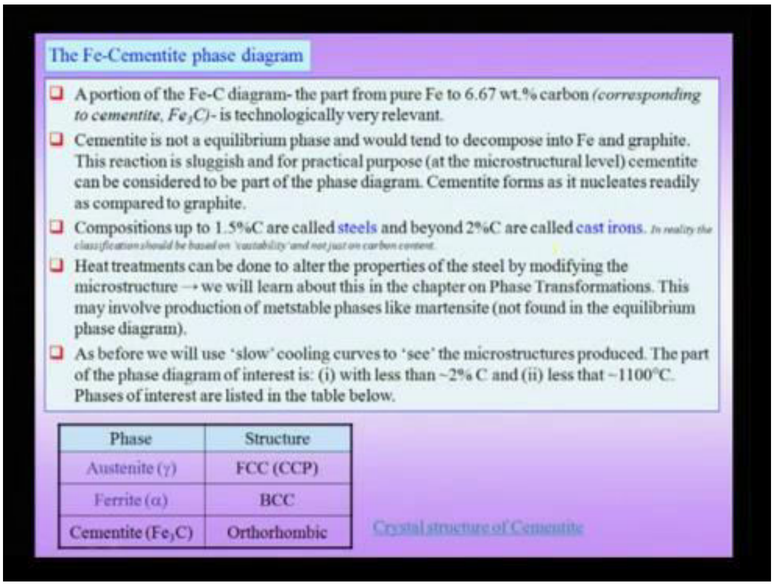

The Fe-Cementite phase diagram

- A portion of the Fe-C diagram- the part from pure Fe to 6.67 wt.% carbon *(corresponding to cementite, Fe_3C)*- is technologically very relevant.
- Cementite is not a equilibrium phase and would tend to decompose into Fe and graphite. This reaction is sluggish and for practical purpose (at the microstructural level) cementite can be considered to be part of the phase diagram. Cementite forms as it nucleates readily as compared to graphite.
- Compositions up to 1.5%C are called steels and beyond 2%C are called cast irons. *In reality the classification should be based on 'castability' and not just on carbon content.*
- Heat treatments can be done to alter the properties of the steel by modifying the microstructure → we will learn about this in the chapter on Phase Transformations. This may involve production of metstable phases like martensite (not found in the equilibrium phase diagram).
- As before we will use 'slow' cooling curves to 'see' the microstructures produced. The part of the phase diagram of interest is: (i) with less than ~2% C and (ii) less that ~1100°C. Phases of interest are listed in the table below.

Phase	Structure
Austenite (γ)	FCC (CCP)
Ferrite (α)	BCC
Cementite (Fe_3C)	Orthorhombic

Crystal structure of Cementite

So, let us now go on to the iron cementite phase diagram, which is a very very important phase diagram and this of course, this is technologically important, but many of the aspects we have been talking about phase diagrams, will become clear when I use this as an illustrative example. And this iron cementite, the carbon percentage corresponding to cementite is 6.67 weight percent. Of course, in atomic percent, carbon is just one fourth, one fourth of course, this means it is 25 percent, but in weight percent, carbon being a light element is only 6.67 percent.

As I pointed out, cementite is not an equilibrium phase and would tend to decompose into iron and graphite, but this reaction is very sluggish and for all practical purposes at the micro structural level, I can think of cementite to be a part of the phase diagram. Now, cementite when you are cooling from the melt, cementite readily forms as a nucleus readily as compared to graphite and therefore, the phase which forms typically when I cool is the cementite phase.

Typically of course, this is not a hard and fast rule, the compositions with low carbon are called steels and those with high carbon are called cast irons. Of course, in reality, the castability is the true criteria for the classification of steels and cast irons and not the carbon content. The important point of course, which we will come to in lot of details in the next chapter is the fact that, heat treatments can be done to alter the properties of steel by modifying the microstructure.

In other words, I can carry out microstructure engineering and we will do a lot of this microstructure engineering in the chapter on phase transformations and try to understand, how we can alter the properties, given a fixed composition. That means, if somebody comes and ask me what is the yield strength of 0.8 percent carbon steel, there is no such number. The micro structure it depends on the processing route and therefore, yield strength being in microstructure sensitive property, it would depend on my processing and the microstructure.

And we will also consider later on when we talk about phase transmission, meta stable phases like martensite, which are not part of the phase diagram and therefore, we will not be considering it in this chapter. And as before, we will be using, what we call slow cooling curves to see, how certain microstructures are produced. And the part of the phase diagram iron is, which we are interested is the one with less than 2 percent carbon and at a temperature less than about 1100 degrees Celsius.

The important phases which we will consider in the iron cementite phase diagram is the austenite phase gamma, which is a cubic closes packed structure. It is interstitial solid solution of carbon in iron and we already noted that, the carbon goes into the octahedral void. The second one is a ferrite, which is a terminal solid solution and this is the room temperature structure of iron, the BCC. Again the carbon going into the smaller octahedral void and of course, an intermediate compound Fe 3 C cementite, which is an orthorhombic phase that means, it is got lower symmetry and typically, the cementite is very brittle.

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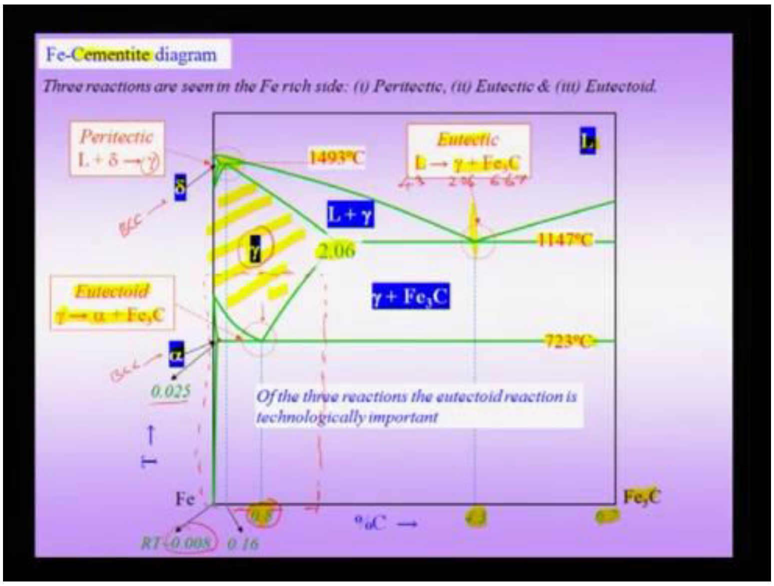

Fe-Cementite diagram

Three reactions are seen in the Fe rich side: (i) Peritectic, (ii) Eutectic & (iii) Eutectoid.

Of the three reactions the eutectoid reaction is technologically important

Now, let us focus on the iron cementite diagram, keeping our focus on the part of the phase diagram, which is what we might call the iron rich side and extending upto about 6.67 percent of carbon, which corresponds to the compound Fe 3 C of course, which is of course, an interstitial compound. If you look at this phase diagram, there are three important reactions we need to note, at high temperatures is what we call the peritectic reaction.

And we will try to understand the difference between this peritectic reaction and the one we considered before for the platinum silver system. At a lower temperature of 1147 degrees Celsius, we have the eutectic reaction and at even lower temperature the 723 degrees Celsius, we have the eutectoid reactions. And as I pointed out, when I consider the overview of phase diagrams, I told you that, the eutectoid reaction is a solid state analog of the eutectic reaction.

In the eutectic reaction, we have a liquid which gives rise to gamma and Fe 3 C two solid products, but in the eutectoid reaction, starting phase itself is a solid, the gamma phase and it gives two products, the alpha and Fe 3 C on the eutectoid reaction. This eutectoid reaction and the 723 degrees Celsius is the truly important part of the phase diagram that means, if I want to dealing at the important part of the phase diagram, I can think of it extending in this box.

So, important part of the phase diagram is the one, which is close to 723 degrees Celsius and above, and wherein the eutectoid reaction takes place now. So, as I pointed out, the three important reactions at high temperatures at 1493 degrees Celsius, we have the peritectic reaction, wherein the delta phase reacts with the liquid phase to give the gamma phase. We have already noted that, the gamma phase is the FCC structure, the delta phase came to the alpha phase is a BCC structure.

So therefore, a two BCC structures, the low temperature one which is a BCC and the high temperature one which is a BCC and this is something, which I had pointed out when we consider the iron unary phase diagram. That, normally the room temperature structure of most cases are the low temperature structure is the close packed structure and as you heat, you have the open structure. In the case of iron, there is a contribution to the energy, the Gibbs free energy from the magnetic contribution and therefore, it is happens that, you have at room temperature a open structure.

But then, after that, it transforms to the gamma phase which is a close packed structure and but at even higher temperatures, it again forms an open structure. So therefore, gamma to delta transformation is what you commonly expect, what you do not expect is the existence of a BCC phase at lower temperatures. So, in this peritectic reaction which is here, you notice that, unlike the case of the platinum silver system in this peritectic reaction, you note that, even below the peritectic temperature, the single phase beta which is the product of the peritectic reaction is stable.

So, in this case of course, the beta is gamma, because now it is the FCC structure and it is stable. To understand this, let us go to the board ((Refer Time: 22:36)), so you have the temperature axis and this of course, the percentage carbon axis and I have my peritectic system here. Now, this is my delta just my BCC structure, there is a liquid phase field here, so this is liquid plus delta structure and here is my gamma phase field. And if I now consider the two terminal points, this is my peritectic temperature, so the peritectic reaction is...

Of course, the formal way of writing these reactions we already seen before that, we should use a double ended arrow and we should write the compositions, etcetera. But, for simplicity we will write it this way and therefore, the composition of gamma, which is produced is here. But, even below this composition, we note that the gamma phase is stable and continues to be stable. So, unlike the case of the platinum silver system, where the beta phase was not stable below the peritectic temperature.

In this case, even if you go down below the peritectic temperature, the gamma phase is stable and continues to be stable till you encounter the eutectoid reaction, where the gamma phase transforms. So, this is my peritectic reaction, which occurs at high temperatures in the iron cementite phase diagram. Coming back to the slides, therefore this is my high temperature peritectic reaction, which produces the gamma phase and this gamma phase field is the one, which is I am going to shade now.

So, at high temperatures I got the gamma phase and at lower temperatures, since gamma phase transforms by the eutectoid reaction into the alpha and Fe 3 phases. The important point to note of course is that, the alpha phase has very low solubility of carbon in it, unlike the gamma phase which can dissolve upto 2 percent carbon at a temperature of about 1147 degrees Celsius. And this solubility of carbon in BCC iron keeps falling, so it is maximum at the eutectoid temperature of 723 degrees Celsius of about 0.025 percent and it keeps falling till it reaches at room temperature of 0.008 percent.

That means, the solubility of carbon in alpha iron, the BCC form of iron is extremely small at room temperature. Therefore, most of the carbon is present in the form of cementite when you slowly cool a eutectoid composition, which is at 0.8 percent carbon. This eutectoid composition is to be noted, because repeatedly we will encounter this composition, the eutectoid composition which is 0.8 percent carbon. The eutectic reaction occurring at a high temperature, which produces a combination of gamma and cementite is not technologically that important.

But, we have to note that, suppose I were cooling an alloy with 4.3 percent carbon then, this 4.3 percent carbon alloy will produce a mixture of 2.06 percent carbon and 6.67 percent carbon cementite, so this will be their terminal compositions. So, my gamma will have 2.06 percent, my cementite will be 6.67 percent, if I am cooling a liquid of 4.3 percent carbon. We will future focus all our attentions on this dotted rectangle, which I had marked before, which is my low temperature iron rich side of the phase diagram.

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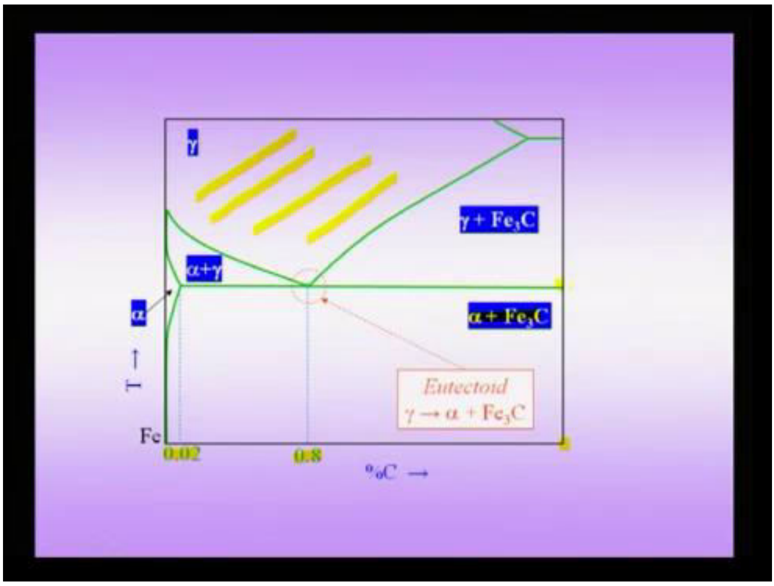

So, this is the iron rich side of the phase diagram, I have the gamma phase field above and this is my gamma phase field, which I am shading now and by the eutectoid reaction, the gamma produces an alpha plus Fe 3 C mixture. Now, there are important things of course, to be as I pointed out to be noted, though alpha the BCC form is not that ductile as the gamma form, which is more ductile, still it even the alpha is much more ductile compared to the Fe 3 C.

And we will note important features that, when you cool an eutectoid mixture, even though Fe 3 C is a, what you might call a highly brittle phase, because the morphology in which this Fe 3 C comes out, the overall alloy is not very brittle. So, these are some important things we will note, so I have my eutectoid reaction, in which 0.8 percent carbon steel gives 0.02 percent carbon alpha and 6.67 percent carbon Fe 3 C. So, this is my important point of the phase diagram, where you have the eutectoid reaction.

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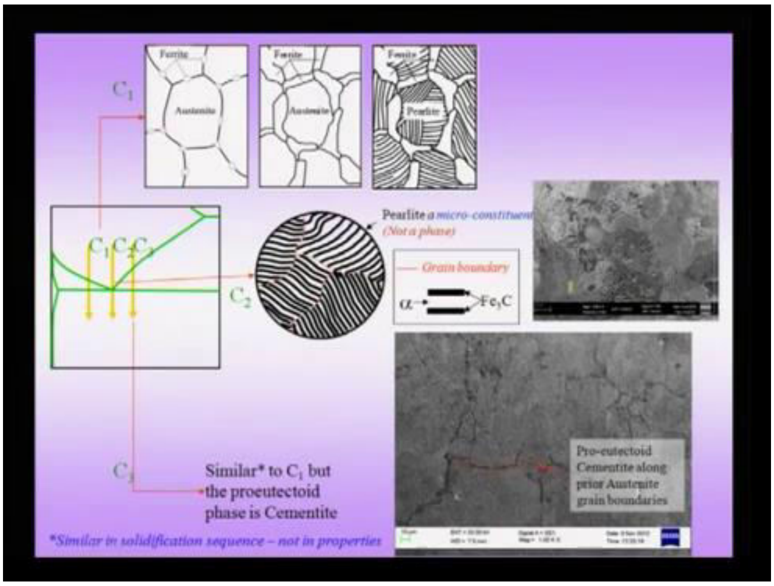

Pearlite a micro-constituent (Not a phase)

Similar* to C_1 but the proeutectoid phase is Cementite

Pro-eutectoid Cementite along prior Austenite grain boundaries

*Similar in solidification sequence – not in properties

Now, let us consider that, what would happen if I take three compositions and slowly cool, one composition which is the eutectic composition, which has been marked as C 2. The second composition is a hypoeutectic composition, hypo implying that the carbon content is lower than that for the eutectoid composition that means, a composition something like 0.6 or 0.7 or 0.5 percent carbon. And additionally, we will consider the slow cooling often hypereutectic eutectoid composition, the hypereutectoid means carbon percentage more than 0.8 like 1 percent or 1.1 percent of carbon.

Now, what happens of course, at high temperature, my starting point for the slow cooling is the gamma phase field that means, I start with the gamma phase and I slowly cool along this C 2 curve. When I do so, of course, I start with a polycrystalline gamma and these are of course, the grain boundaries of the polycrystalline gamma. Now, as I cool and as I cross my eutectoid temperature, I would notice that, actually a mixture of alpha and Fe 3 C come out simultaneously, this is very very similar to the eutectic reaction, where we had an alpha plus beta coming out for the liquid.

But, in this case, you have an alpha plus Fe 3 C coming on from the solid mixture and this produces a microstructure, which looks something as shown here. Therefore, you have a alternating lamella of alpha and Fe 3 C and in of course, the two dimensional section, these would look like bands of alpha and Fe 3 C. If you look at a scanning electron micrograph, you would notice again the same thing that, I have these two phase mixture, which is now there are bands of alpha and there are bands of Fe 3 C.

Of course, if I look at a picture like this, I would notice that, the spacing between the alpha and Fe 3 C that is, the periodicity looks very different in different regions. For instance, the periodicity is very close here, if you go to region like this, the periodicity is even more and this here is even more and this is because of the fact that, even though I have an alpha and Fe 3 C mixture.

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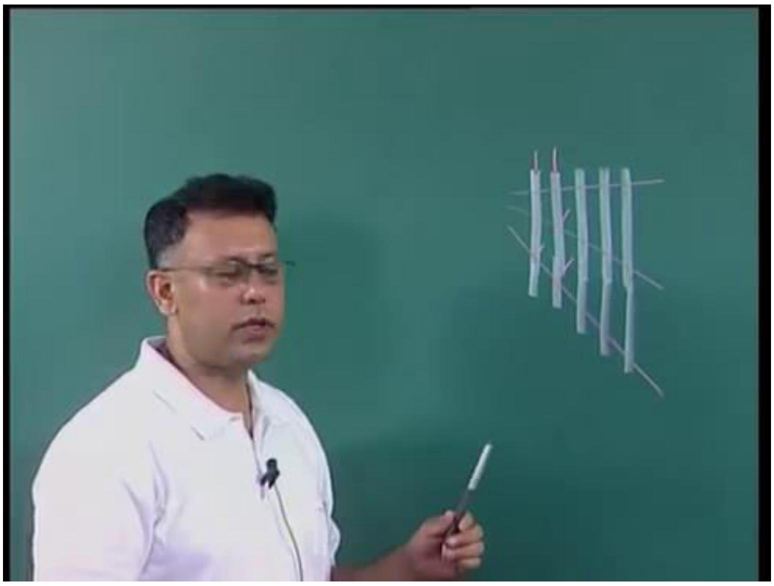

For instance, suppose I consider this to be the alpha and Fe 3 C mixture and these are my lamella of alpha and Fe 3 C, a lamellar microstructure. Suppose, I am making a metallographic section, assuming that the lamella are approximately of constant spacing, though they will never be equal and this lamellar spacing also depends on the cooling rate. But for now, we will assume that, this periodicity or the lattice parameter of this kind of a alternating lamella is constant.

But, suppose I am taking three sections, one section like this and one section like this and let another section at even higher steeper angle then, I would notice that, in the first case, this will be my spacing, the second case my spacing would have increased, in the third case my spacing would have even further increased. So, often when you are trying to interpret microstructures, we have to be in careful that, what we are seeing is a two dimensional section through a three dimensional microstructure.

And thus implies that, even though if I am starting off with a constant spacing lamella, I would observe different spacings in my microstructure. So, such a micro constituent is called pearlite, which consists of alternating lamella of alpha and Fe 3 C. The next chapter of course, when we talk about phase transformation, we will see that, how such a what you might call alternate laminar microstructure arises. But for now, we will just observe that, we obtain a microstructure, which consists of a micro constituent, which is named as pearlite, which consists of alternating lamella of alpha and Fe 3 C.

Now, suppose I choose and this polite unlike pure cementite has actually higher ductility and we will be doing some tests in the next chapter to understand this. But, the fact that, now my brittle phase is inter dispersed in the lamellar fashion between the semi ductile or some much better ductility alpha phase. The ductility of the overall micro constituent increases and therefore, my ductility of the microstructure, which is pearlitic microstructure increases ((Refer Time: 32:09)).

Now, suppose I am cooling an hypo-eutectoid composition C 1 and I am starting with an uniform phase field gamma then, I would again have my grain boundaries, which are now my austenite grain boundaries present. And when I slowly cool this, first I cross my temperature here, wherein I start to precipitate my, so this is my alpha phase, wherein I start to precipitate my alpha phase, the ferrite phase. Now, this ferrite phase like the pro-eutectic phase, this is the solid state analog of that, therefore this is the pro-eutectoid alpha phase.

So, I would precipitate my pro-eutectoid alpha phase in this temperature regime starting from here to here. So, in this regime, I would have my pro-eutectoid alpha phase coming out and typically, because as we shall note in the next chapter that, this phase transformation occurs by a process known as nucleation and especially, by a process known as heterogeneous nucleation. In heterogeneous nucleation, grain boundaries and other defects in the material act like nucleation centers.

That means, that the precipitation starts not somewhere, typically is not somewhere in austenite, which could also occur of course, but typically preferentially occurs along these grain boundaries. Therefore, I have got all my phases forming along the grain boundaries and as I cool from, say a temperature T 1 to a temperature T eutectoid, I would notice that more and more of this pro-eutectoid alpha will come out. And slowly by the formation of these nuclei and their growth, I would notice that, the prior austenite grain boundary region would practically be coated by these pro-eutectoid alpha phase.

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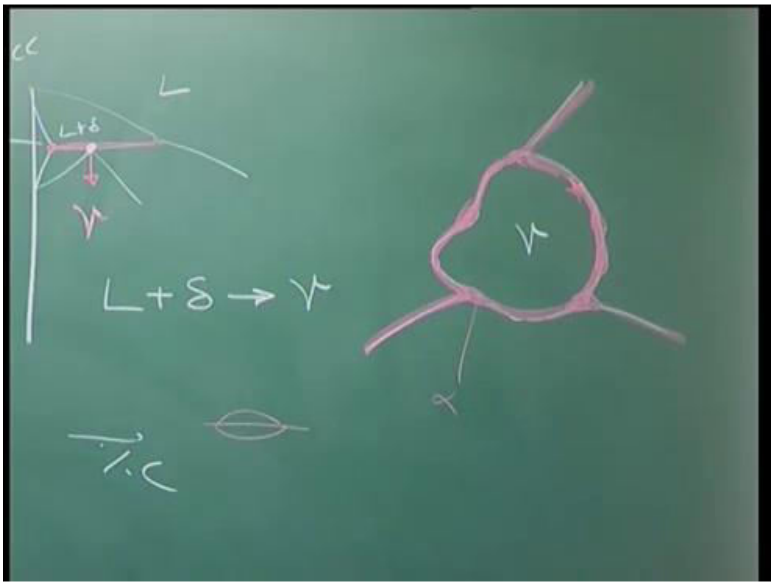

So, let me draw that schematically now, once more let us see the zoomed in picture, so I have my prior austenite grain boundaries here. And first initially, a small pro-eutectoid alpha may form here and at a later instant, because some of may form here and here and typically, the structure of these would be something like a double lens construction. And at a later instance, some more would precipitate out, here by this times the previous ones would have grown a little bit.

So, as you lower the temperature and as more and more of this pro-eutectoid alpha comes out, so this is my prior austenite phase gamma and this is my pro-eutectoid alpha, slowly what happens is that, the grain boundaries sort of gets coated with this. I am using a crude term coated, what it means is that, the precipitation process takes place in such a way that, I have most of this pro-eutectoid alpha coming out along the prior austenite grain boundaries and I would have microstructure, which looks something like this.

Now, coming back to the slides ((Refer Time: 35:43)), this is the region which I had marked with these hashes. So, I have all my pro-eutectoid alpha coming out along my prior austenite grain boundaries. Now, when I cross this temperature T eutectic, the remaining gamma would transform, now this remaining gamma as we had noted before, would have travelled along this line and reached a composition, which is now my eutectoid composition, which I call C e.

So, it would have reached a eutectoid composition or a composition similar to C 2 and therefore, this composition is ready for the eutectoid transformation. And therefore, I would also obtain a two phase mixture of alpha and Fe 3 C, which would come out in the remaining part that means, I would now have my pearlitic phase coming out here. So, the final microstructure would consists of the pro-eutectoid alpha, which is now present as almost like a continuous layer along the prior austenite grain boundaries and a eutectoid mixture of alpha and Fe 3 C.

Now, the important point of course is that, which we had noted before that, even though I am starting off from a composition like C 1, which is an hypo-eutectoid composition, the fact that now the first alpha which is coming out would be along this horizontal line and would be in equilibrium with this gamma. The alpha composition will travel along this line, the gamma composition will travel along this line, the diagram is getting clouded. So, I will draw it here ((Refer Time: 37:28)).

So, I am solidifying a composition which is C 1, which is off eutectoid, I would note that the first alpha which comes out would be here and the alpha composition would travel along this line and the eutectoid composition would travel along this line. And that means, when I am at the eutectoid temperature T eutectoid, I would notice that, the composition is actually C eutectoid and this composition will undergo the eutectoid transformation.

This we have noted for the case previously for the eutectic transformation, now corresponding to this, I could also consider a composition which is hyper eutectoid, which is a like a composition C 3 here. For the composition C 3, what happens is that, this situation is very very similar to C 1, but instead of obtaining my pro-eutectoid alpha phase, I would obtain a pro-eutectoid cementite phase. In terms of properties of course, this could be very different, but let us come to that in a moment.

So, when I slowly cool an alloy like C 3, for a temperature regime between a temperature which is marked here for instance, I mark this T 3 and the T eutectoid I would obtain the pro-eutectoid cementite phase. Now, this is the gamma plus cementite phase field and therefore, I would obtain a gamma plus cementite. And therefore, I would obtain Fe 3 C coming out and like before, this Fe 3 C comes out along the prior austenite grain model, so this can be seen here, this is now my Fe 3 C coming out at the prior austenite grain boundaries.

Now, when I cross my eutectoid temperature, the remaining mixture of course, from the fact that, there is very little of the pro-eutectoid phase in the micrograph shown here. It is clear that the C 3 composition chosen for this particular here for this C 3 is very very close, it is tending towards my eutectoid composition, C eutectoid. So, that is very clear, but in general of course, I would obtain a pro-eutectoid cementite followed by the eutectoid recreation. That means, in the remaining microstructure, I would actually obtain my eutectoid transformation, which is my pearlite which is here, so all this is pearlite, though it is not very well resolved in this micrographs.

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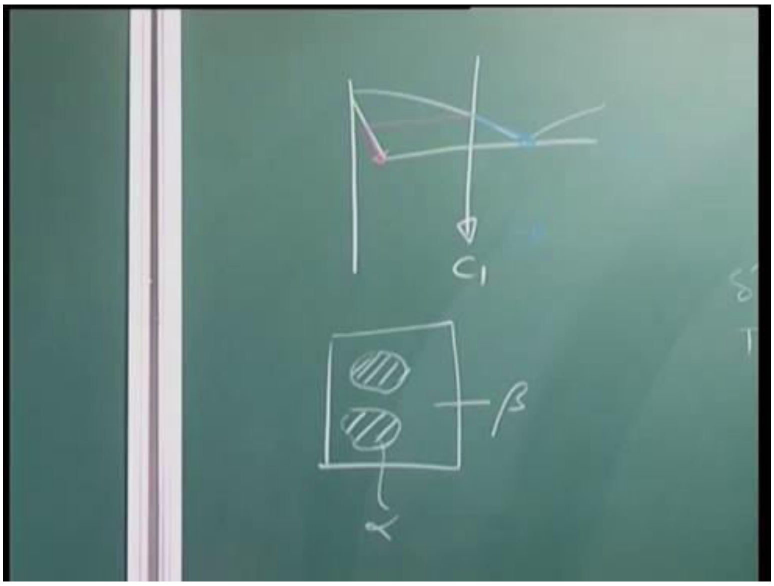

But, we can see that, in the next micrograph, where I have a zoomed in version, where I have my pro-eutectoid cementite along the prior austenite grain boundaries. And then of course, I have an eutectoid mixture consisting of alpha and Fe 3 C in the remaining part, so this is my pearlite coming out. So, this is an SEM micrograph of an hyper-eutectoid composition, which is close to about 1 percent carbon ((Refer Time: 40:32)).

So, for a composition like C 3, what happens is that, I have of course, precipitation below T 3 of the pro-eutectoid phase. The composition of the gamma will move along this line towards eutectoid composition C eutectoid and finally, of course at my eutectoid temperature, I would have the eutectoid transformation giving rise to a pearlitic microstructure. So, let us have a zoomed in view of this micro constituent called pearlite and of course, this is we have already seen is for 1 percent carbon steel or close to 1 percent carbon steel.

The above micrograph is the one we considered with 0.8 percent carbon which means that, have a complete eutectoid transformation and there is no pro-eutectoid phase. And this also highlights the point, which I mentioned that, the lamellar spacing here seems to be very large. In this case, I am cutting my lamellar at a very steep angle and here the lamellar spacing is small that means, I am cutting my lamellar almost perpendicular to the lamellar construction.

So, these are some typical micrographs obtained for steels consisting of carbon percentage around the eutectoid carbon percentage of 0.8 percent carbon.

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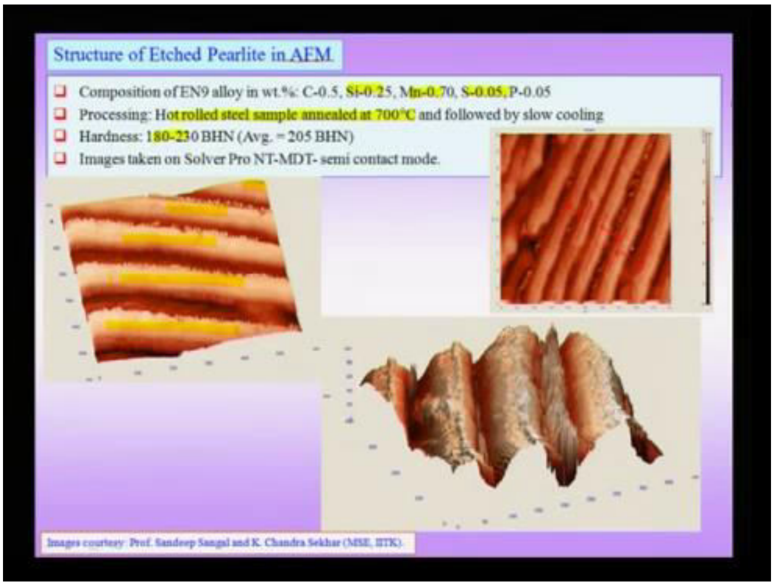

Structure of Etched Pearlite in AFM

- ☐ Composition of EN9 alloy in wt.%: C-0.5, Si-0.25, Mn-0.70, S-0.05, P-0.05
- ☐ Processing: Hot rolled steel sample annealed at 700°C and followed by slow cooling
- ☐ Hardness: 180-230 BHN (Avg. = 205 BHN)
- ☐ Images taken on Solver Pro NT-MDT- semi contact mode.

Images courtesy: Prof. Sandeep Sangal and K. Chandra Sekhar (MSE, IITK).

Now, these are again pictures of the pearlitic structure, but now steam in what we call an atomic force microscope. And this is the surface morphology, which is revealed and this is of course, not plain carbon steel, this is other elements like silicon, manganese and other of course, trace elements, phosphorus and sulfur. And this particular alloy has been hot rolled at 700 degrees followed by slow cooling and this gives rise to a hardness of the range of about 180 BHN.

But, the important point to note is now, I can clearly see in three dimensions or a three dimension looking image of these lamellar structure of pearlite. So, you can see that, I have in an AFM, which is now the AFM gives a surface topography at a very high resolution and therefore, I can see in all these picture, this lamellar morphology. And from this of course, I can measure my lamellar spacing and this lamellar spacing can further be correlated with the cooling rate.

So, this is a nice AFM picture, the previous picture were all taking in a scanning electron microscope and this is an atomic force microscope, which is giving me the lamellar morphology of pearlite.

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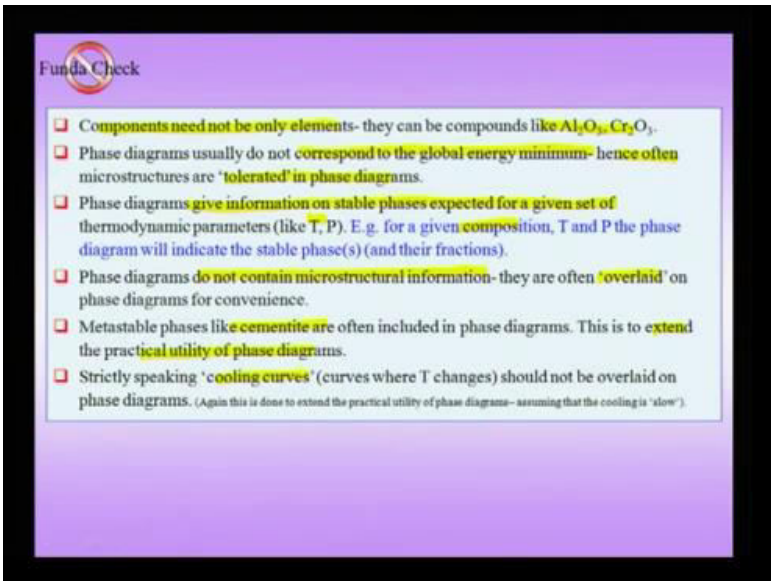

Funda Check

- ❑ Components need not be only elements- they can be compounds like Al_2O_3, Cr_2O_3.
- ❑ Phase diagrams usually do not correspond to the global energy minimum- hence often microstructures are 'tolerated' in phase diagrams.
- ❑ Phase diagrams give information on stable phases expected for a given set of thermodynamic parameters (like T, P). E.g. for a given composition, T and P the phase diagram will indicate the stable phase(s) (and their fractions).
- ❑ Phase diagrams do not contain microstructural information- they are often 'overlaid' on phase diagrams for convenience.
- ❑ Metastable phases like cementite are often included in phase diagrams. This is to extend the practical utility of phase diagrams.
- ❑ Strictly speaking 'cooling curves' (curves where T changes) should not be overlaid on phase diagrams. (Again this is done to extend the practical utility of phase diagrams– assuming that the cooling is 'slow').

So, let us make a few checks before we go further, we have already seen that, components need not be only elements, they can be compounds like alumina and chromia. Phase diagrams do not correspond to global energy minima and often, microstructures are tolerated in phase diagrams therefore. Phase diagrams give information on stable phases expected, for a given set of thermodynamic parameters like temperature, pressure and for a given composition.

Phase diagrams do not contain micro structural, but the overlay that and in the especially in the form of slow cooling curves that is, the microstructures obtained on slow cooling. Meta stable phases like cementite are included in phase diagram and this extends the practical utility of the phase diagrams. And further, I pointed out that, whenever we overlay cooling curves, we assume that the cooling rate is small.

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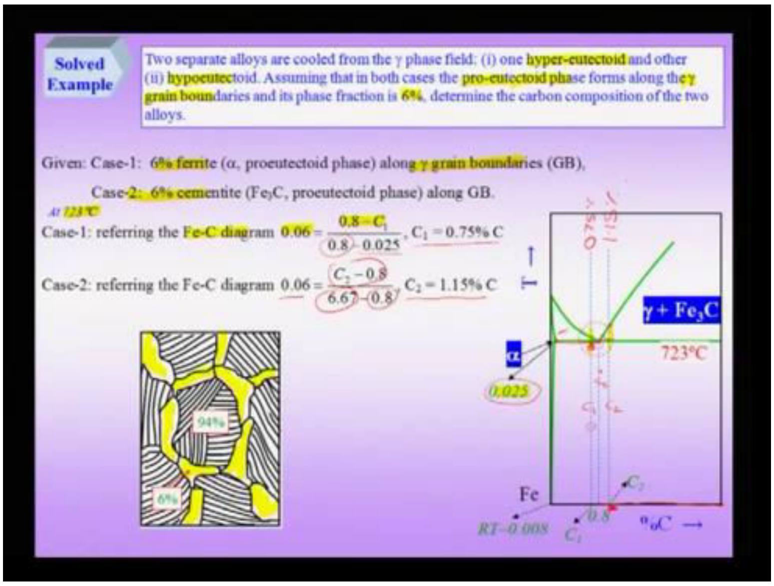

Solved Example

Two separate alloys are cooled from the γ phase field: (i) one hyper-eutectoid and other (ii) hypoeutectoid. Assuming that in both cases the pro-eutectoid phase forms along the γ grain boundaries and its phase fraction is 6%, determine the carbon composition of the two alloys.

Given: Case-1: 6% ferrite (α, proeutectoid phase) along γ grain boundaries (GB),

Case-2: 6% cementite (Fe_3C, proeutectoid phase) along GB.

At 723°C

Case-1: referring the Fe-C diagram $0.06 = \frac{0.8 - C_1}{0.8 - 0.025}$, $C_1 = 0.75\%$ C

Case-2: referring the Fe-C diagram $0.06 = \frac{C_2 - 0.8}{6.67 - 0.8}$, $C_2 = 1.15\%$ C

Now, further let us solve one more example, before we go on to the next chapter, the chapter on phase transformations. And in this case, we consist again take an alloy of steel and I consider two situations and that means, I have two separate alloys and I am slowly cooling these alloys from the gamma phase field. One alloy is an hyper-eutectoid alloy that means, it has carbon more than 0.8 percent. Another alloy is an hypo-eutectoid alloy, which has the carbon percentage lower than 0.8 percent, so this is an hypo-eutectoid alloy and this is an hyper-eutectoid alloy.

And I am trying to compare the microstructures obtained for these two cases and as an exercise, I assume that, the pro-eutectoid phase which forms and this obviously, we have noted forms along the gamma grain boundaries. We assume that, it is phase fraction is 6 percent, in one case of course and this is what I mean by the pro-eutectoid phase, which is present along the gamma grain boundaries. So, this yellow phase fraction I assumed is about 6 percent.

Now, in one case of course, this 6 percent would consists of the pro-eutectoid alpha for the composition to the left of the eutectoid composition in this case, I would obtain here. Of course, this solid during this range of solidification I would get an pro-eutectoid alpha and in the other case, I would obtain a pro-eutectoid cementite and I assume for now, that the phase fraction is 6 percent. What I would like to know is that, what is the carbon content of these two alloys given this fact that, the microstructure of course, looks similar, but of course, the actual phase present along the grain boundaries is different.

So, case 1 I am given that, 6 percent of ferrite is present along the gamma grain boundaries. Case 2, 6 percent of cementite is present along the gamma grain boundaries and I know my eutectoid reaction occurs at 723 degrees Celsius and I know the product alpha produced as 0.025 percent of carbon. So, referring to the iron carbon phase diagram, for case 1, 0.06 which is now the fraction of the pro-eutectoid phase, is 0.8 minus C 1.

C 1 being the composition, which I am trying to find out for this case, so this is my C 1 and this is the case of a C 2 and of course, this composition is C eutectic. So, 0.8 minus C 1 is divided by 0.8 minus 0.025, this is assuming that now I am putting my fulcrum of my lever here and this is the length of my lever. One end of the lever, there is the alpha phase, one end of the lever is the eutectoid composition. So, this is my 0.025 at one end here for the lever, at the other end of the lever is at the eutectoid composition 0.8 percent.

And since the fraction of the pro-eutectoid phase is proportional to 0.8 minus C 1, here this small arm of the lever and therefore, from this I can calculate my C 1 to be 0.75 percent carbon. Therefore, I can mark this carbon percentage, so I can now mark my carbon concentrations here and this is now my 0.75 percent. And now in case 2, similarly I can construct a lever, now the lever extends from 0.8 percent carbon here, to all the way up to the cementite composition here and the fulcrum of this lever is going to be here.

So, one end is at 0.8 percent carbon and the other end is at cementite composition, which is 6.67 percent carbon. Again I can write down my lever rule as 0.06, which is the pro-eutectoid phase composition is C 2 minus 0.8 divided by 6.67 minus 0.8, which gives me C 2 is equal to 1.15 percent carbon. Therefore, now my carbon percentage here is 1.15 percentage of carbon, therefore looking at, this is another example where looking at my microstructure, I can actually calculate the area fractions.

I can of course, convert my area fractions into volume fractions, typically assuming that the area fraction is equal to the volume fractions. And from the volume fractions, I can using the density of these phases, I can calculate the weight fractions and using the weight fractions and the lever rule, I shall be able to calculate the composition of... In some cases of course, if I do not know the overall composition, I can calculate the overall composition.

Of course, if I know the overall composition, I would like to know the phase fractions in equilibria, I can do that using the lever rule and the tie line construction. So, with that, we come to this end of not an extended chapter, but a brief chapter on phase diagrams. And as I pointed out, there are other technologically important phase diagram, there are other phase diagrams involving other kind of reactions like the monotactic and syntactic reactions.

But, we will not consider them here, instead we move on to the chapter on phase transformations, wherein we will consider typically that, how this phase transformations which we have been talking about. Say, for instance, the gamma phase giving the alpha plus Fe 3 C or the liquid plus alpha giving the beta phase, how do these phase transformation takes place we will consider in detail.