# **Phase Diagrams in Material Science Engineering Prof. Krishanu Biswas Department of Material Science and Engineering Indian Institute of Technology, Kanpur**

# **Lecture - 37 Cast Iron – II**

In the last class I discussed with you about the iron carbide phase diagram and iron graphite phase diagram. So, let us move on before actually we discussed about the cast iron, what is actually the effect of silicon? I have been telling you that we need silicon in cast iron to promote the formation of graphite. Silicon actually reduces the nucleation potential of graphite formation. What is that mean, if you want to nucleate something from a liquid or solid you have the phase which is to be formed or the product phase, it needs to cross a nucleation barrier and this barrier is mainly because of the interfacial energies between the two phases.

Suppose, if I want to form graphite on the liquid the interfacial energy between the liquid and graphite that dictates the barrier, height of the barrier actually just like a bump on the road if you want to cross a bump you have to push it give a little bit more energies same thing happens for the nucleation of graphite. Now, silicon reduces that height so that means, what silicon helps in nucleating graphite very easily that is the idea. Now, that is what he said eutectoid eutectic of graphite occurs at 1140 degree, 54 degree Celsius temperature as compared to eutectic reaction happening at eutectic reaction for the other thing happening at 1147 degree temperature and this eutectic reaction is written here.

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The carbon concentration 4.3 or 4.26, better write 4.26 because that is what it show 4.26 percent carbon going to gamma of 2.14. These are wrong actually I am correcting it on graphite. Now, eutectic graphite reaction is competing these reaction is basically competes with the eutectic reaction of Fe3C at 1143 degree Celsius temperature what is that? That is basically this gamma plus Fe3C; these two reactions are competing with each other.

In cast iron, that is what I written here a silicon is used to control the formation of graphite phase I told you just now few minutes back the eutectic reaction does not occur at 1144 not 1148 not 4.35 percent because of the addition of silicon it will actually you know eutectic reaction leads to formation of graphite. So, if you want to have nuclear graphite you need silicon that is what I have been telling you.



Now, to explain that I am showing you something new which you have not seen or probably, they are not in the books. It better to plot you know a phase diagram which is called pseudo ternary phase diagram anyway. We will discuss ternary, but pseudo ternary, this is again temperature versus composition axis not there is no third axis, but only two axis, two dimensional plot iron with 2 percent silicon and carbon concentration because that is what happen 2 percent silicon is similarly present in cast iron what you see here is this. This is the gamma plus liquid plus graphite gamma plus graphite eutectic reaction here and this is the alpha plus gamma plus graphite.

This is the eutectoid reaction here you see. So, everything gets modified even these point which is normally 0.02 percent of carbon is about 0.05 percent carbon correct and this is what is your alpha plus graphite this is not your pearlite, pearlite alpha plus cementite this is alpha plus graphite and i will show you what will happen if alpha plus graphite this is not a pearlite.

So, you can see here this has been calculated and also experimentally verified. This diagram tells you, if you had silicon and then carbon concentration increases in this alloys the phase formation will happen like this way see you do not see any duct of cementite in this diagram, what you see here everywhere cementite is replaced by graphite.

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# **The Effect of Silicon** The Si is converted to an equivalent carbon and the desired total carbon content is about 4.3 wt% C. This is expressed as: Carbon Equivalent (C.E.) = %C +  $\frac{\%Si}{3}$  = 4.3 This equation is taken from the ranges of carbon and Si in ferrous alloys for different types of cast irons.

So, in a nutshell silicon can be converted because that is silicon 2 percent carbon with silicon. So, iron 2 percent silicon with carbon phase diagram. It is a pseudo binary phase diagram pseudo means why pseudo because there are three components iron silicon carbon, but you are plotting like a two dimensional plot in a binary phase diagram that is why it is called pseudo binary phase diagram.

Therefore, what you do we just convert silicon equivalent to carbon and the carbon contents about. So, that prevents 4.3, how it is done? Well as you know silicon has stronger effect on graphite formation. So, therefore, carbon equivalent is nothing, but percentage carbon plus silicon divided by three. So, if you want to form eutectic mixture you must have 4.3 percent carbon. So, I can actually, if I have a cast iron certain amount of carbon I can decide, what is the amount of silicon required? So, that I can get into 4.3 percent carbon that is what I want you to take a message out of this. So, that is what is known as carbon. This is equation is taken from the range of carbon and silicon in ferrous alloy for different types of cast iron this is valid for almost all the cast iron.



Similarly, phosphorus also has effect which you normally ignored phosphorus actually is a more important element. I know very interesting element in cast iron and so you know phosphorus is added to cast iron many times to formation of graphite. So, again if you have phosphorus, you can also have a carbon equivalent carbon equivalent carbon percentage plus silicon plus phosphorus divided by 3, you see the equation very clearly. So, basically if you have a cast iron with silicon and phosphorus iron carbon and you want to have a 4.3 percent carbon, equivalent carbon then this is the formula I have to use determine to determine basically silicon and phosphorus content you need to have to get 4.3. So, that is the effect of silicon, I have discussed for last 5-10 minutes last class and this class.

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Now, let us discuss about the different cast iron. You know cast irons I have described here, five types. First one I have discussed is grey iron or grey cast iron where carbon is present as a graphite, but flakes then you have a white cast iron while carbon is present, as a carbides the often alloyed third one is known as, this is second one this is white iron why it is called white, it will clear when I discuss about white iron and third one is a ductile iron in which you have again cast graphite as a second phase not carbide and graphite has a shape of nodule or spheroid, third one a fourth one is the malleable iron malleable cast iron. Basically, a cast iron in which you have a carbon presence in graphite and the fifth one is basically alloy. If you have a alloying elements and then this what will happen.



Now let us first discuss about white iron. We will spend little bit time white iron for almost of the time will spent on graphite or the or the grey iron and graphite iron and malleable iron, white iron you have these are the features you have mostly less than one percent silicon weight percent silicon is brittle and hard very brittle due to presence of this cementite not used for any application except to make malleable iron.

This is the source material for malleable iron, you have to understand that. So, what is it because it contains primary cementite that is why you break it these are the primary cementites white things you see here, these are the white things cementites. So, this was gamma earlier and this is cementite which is the eutectic reaction product if you have less silicon into the alloy and this gamma later on transformed into pearlite; obviously, because gamma is not stable from room temperature that is what you see pearlite in each of this.

Here again same thing, these are the cementite. This is pearlite you say cannot see inside because these was not stably that is what you see when the pearlite namely inside it because it contain cementite. If you break it little bit the surface look like void that is why it is called white iron that is the main reason why you called white iron and because it is brittle, it is not used for any application whatever except for making malleable iron.

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Now, you know white iron can be both, you say eutectic alloy 4.26 percent or 4.3 percent carbon. So, you can have hypo eutectic or hyper eutectic, but if you have a hypo eutectic what will happen you have a hypo eutectic alloy will have primary gamma; obviously, let me go back to the phase diagram, yes if you have a hypo eutectic alloy here. So, you will have primary gamma forming please you go back to my eutectic you know phase diagram discussions from these temperature these temperature you will form primary gamma and then finally, eutectic reaction will happen lead to the formation of cementite and gamma.

As you see here, these are the primary gamma black regions why very simple they are the dendrites they are form like a gamma forms a dendrites from the liquid and they have become black, why because gamma is transformed into pearlite at the moment it transformed into pearlite, it will look like black because inter laminar spacing is. So, fine and if you highly it look like black whereas, these are the regions of the eutectic transformation as you see here the white things are cementite and black things are graphite your or gamma and that gamma again has transformed into pearlite. So, therefore, you have two types of gamma, this is the primary gamma which has form primary gamma which has form directly from the liquid before the eutectic reaction happens and this gamma is basically this is called eutectic gamma. It has transformed into pearlite again this is also transform into pearlite again this is what you see here.

So, either way you form pearlite either way it form pearlite and these pearlite is basically forming because transformations that is why you see them black and this is called hypo what will happen in hyper, yes you have understood quietly hyper, you will have primary cementite c blocks of cementite primary cementites greens hyper is on the other out other side right side of the eutectic.

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So, primary cementite plus eutectic and eutectic is this cementite plus gamma and gamma is again transformed into pearlite because gamma is not stable. This is very important I go back again where hyper eutectic alloys what will have hyper eutectic alloys you have primary gamma plus eutectic gamma plus cementite, you have no primary cementite. So, this is not so brittle infact because it has primary gamma gamma is a you know gamma is a more ductile than that, but on the other hand if you have hyper eutectic then you have primary cementite and this primary cementites have blocks of cementites in the slides you see white areas and they are very, very brittle that is why they are never used even though molecular iron also used the other one the hypo that is about the white iron.

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White iron therefore, white iron is nothing, but steel as the cast iron where there is no graphite. Please understand that you have only cementite as a phase. Now, the second one which is very, very important and widely used cast iron is also known as grey iron because all the lectures for the next you know 10-15 minutes I am going to discuss only on grey iron. Grey iron is basically iron, it is a basically cast iron family, it contains about 1.52 percent silicon and about 3.5 to 4.3 percent carbon where graphite is present you do not have cementite and graphite presence as a flakes, flakes means needles like that is like you know I may remember in a aluminium silicon I have discussed silicon comes as a fibre.

So, needles are actually like fibre only, but little thicker there actually needles there actually better to call them as flakes. You have seen flakes like take a tree leaves it looks like a flakes. So, what you have is superimposed on it basically they are actually superimposed they can be kish or normal type which will discuss later and they can be random or preferred orientation. You see here some of them are preferred these are preferred, but these are random long needle like these are preferred these are random matrix can be both pearlitic or ferrite. So, that depends upon what is the carbon concentration you have taken initially very simple.

So, suppose if I have eutectic reaction taking place. So, liquid going to gamma plus graphite and if I keep it at high temperature high means above the eutectic transformation temperature above a a one temperature for long time. So, what will happen graphite flakes will grow they will become thicker and thicker and if they grow they will take all the carbon out from the gamma. So, gamma gamma will be depleted of carbon. So, if the gamma has very low carbon less than or point zero five percentage carbon it will transform into alpha it will not transform into pearlite because do you want to perform pearlite you need to have carbon concentration more than this much right you see here remember that curve this is point zero five this is point zero eight. So, you need more than this amount of carbon that is what i required correct.

So, therefore, you can create either ferritic matrix or pearlatic matrix depending on the requirements on the other hand you have flakes you know this flakes of cast iron i have shown you nicely here.

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You see here some of them very, very sharp, some of them like wandering in the land. Some of you may be doing moving around. So, they are actually long moving, they are not and this is your pearlitic matrix you see that is why you see a contrast here this is because pearlites present.

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Well, we all know you all been thought you have also be saw graphite looks like a flake, but you know graphite is does not grow like a flake graphite rather grows like a cabbage basically graphite will goes like a needle it is like this. It is like a needle, now if I take cross section, I cut it off I see like this structure I see flakes that is what I see. So, therefore, it is like a cabbage like a structure you see here. It is started going like this then it gone like this like that you can draw now when you cut a sample you see what is the two dimensional section and this two dimensional section will have this kind of things flakes. So, they are not like flakes they are actually like a structure I shown you just now.

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And many times you will see this. This is what is shown here, this is actually you know EBST diagram electron backscatter diffraction as you see graphite. They are having same orientations as this ones, white ones the grey ones have different orientations that is because they are going in a different fibre and if you sketch it nicely you can see even graphite fibres mandering around in the matrix that is what is shown mandering around the matrix. So, basically its will be when I discuss. So, what basically means that graphite forms like a needle; it is a hexagonal crystal structure. So, it is easy for you to grow like a needle growing along the particle 0 1 directions and that is what is required that is what is seen in the actual microstructure.

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So, there are different morphologies also possible that is what I shown you. This is what is let us start with this is small and random this is what is known as Rosette. This is like a rose or rosette, this is random, but associated this is rosette, but very, very preferred and this is preferred. So, there are different flakes morphology possible these are all there in ASTM standard ASTM is what American society for testing a materials. So, this standard is there.

So, depending on these morphologies you can have different mechanical properties that is why as you understand graphite grows like a short fibre, long fibre paper oriented or this thing there are different morphologies.



This again I show. So, this is what I show you A is uniform flakes random orientation that is what is the first thing I showed, B one is rosette by the form by inoculation which will discuss later, C is what this is non-uniform flakes, non-uniform flakes random orientation there are uniform in thickness are biggest on biggest and you can also secondary graphite formation. It can be interdendritic curve before orientation. So, random orientation possible, D is interdendritic graphite, interdentrictic graphite means your last liquid last liquid which has present in the inter region will transform into graphite, but these three are the most important.

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# **Sizes of Graphite Flakes** · Rapid solidification results in finer graphite flakes. · But too rapid solidification will result in cementite unless there is a very high Si and C concentration. Graphite flakes are classified in sizes - like ASTM grain sizes - according to the maximum length observed at a magnification of 100x. No. 1 Longest flakes > 4 in (100 mm) No. 2 Longest flakes 2 - 4 in (50 - 100 mm) No. 3 Longest flakes 1 - 2 in (25 - 50 mm) No. 4 Longest flakes 0.5 - 1 in (12.5 - 25 mm) No. 5 Longest flakes (0.25 - 0.5 in (6.25 - 12.5) No. 6 Longest flakes (0.125 - 0.25 in (3.125 - 6.25) Etc.

Then there are different sizes of graphite flakes rapid solidification results in finer graphite flakes, but if you rapid too rapidly will have cementites that is because you can bypass this eutectic reaction unless there is a very high silicon and carbon concentration graphite flakes are classified by this see if it is you know longest flakes is more than four they are actually 100 nanometres there is called number one if longest flakes longest flakes means these are actually numbers 15 to 100 nanometres and then you have a longest flakes 20 to 50. There are three diff different types all are long only, but sizes are different categories number 1 to number 6, but these are all you need to remember depending on sizes.

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You see here this is a flakes number one very long little long then those heads small and this is fine. So, flux size six is finer size one is longer size two is thicker and size two three is also thicker, but little less longer and the size one and size one these are actually for you to know because if you want to create shapes and sizes or you want to characterize them after seeing this is what you should understand how does you solidify.



Well very simple first normally what happens. So, all these gray irons are hypoeutectic alloys; that means, they have composition less than eutectic composition less than 0.43 or 4.26 percent carbon 4.26 is better that is what happens when graphite is in iron. So, you have gamma firmly form on the liquid that is what is shown here gamma dendrites in the liquid and then and the eutectic transformation temperature you have see here this is for the gray this is for white. So, gray you then you have this gamma plus graphite as eutectic formation this dendrites are still here.

And finally, you have this gamma transforming into pearlites. So, basically these gamma which is present I showed you in the case of white iron will also be transformed into pearlite for this white iron you have gamma plus forming from the liquid, but eutectic reaction is different nucleation is lead to formation of gamma plus cementite and then finally, is gamma both in eutectic and the dendrite transformed into pearlite that is what happens solidification wise if you compare gray iron white iron a gray iron eutectic reaction is different.

So, I think I should stop here and just before I stop I like to tell you gray iron is very important material why because it is widely used in the automobile your engine block is made of gray iron, but you know gray iron is used in the engine block not only because it contains graphite, but it is very easy to cast because of presence of graphite flowability is very high. So, easily cast in different steps that is why the engine block i do not know whether you have seen it or not very complex steps can be easily cast using gray iron not only that because your graphite has needle present in this graph in this cast iron. So, what will happen graphite will as a very high thermal conductivity? So, needles will allow transfer of heat.

Because in a engine blocks you burn fuel you generate lot of heat that it needs to be conducted away. So, presence of graphite actually allows you to take the heat conducted away. So, graphite flakes because of directionality you can allows the transport of heat very fast that is why you want this graphite flakes to present in in the engine blocks and they have a very high castability very easy to cast that is why they are used and these are all the plus points you know very, very important plus points of the gray iron that is why gray iron is made up of you know gray iron is to make the gear box even gray iron is used to make engine blocks gear blocks many other box the housings in the in the automobiles, but problem is what because graphite is presence of flake and you know flake as a tip like any other thing it is a flake means it is a needle I do not know at the end of the needle you have very fine tip.

So, now if you have press stress applying some stress and because of the stress because it load not stress application of load and because of the fineness with tip what will happen the tip is fine. So, there will be what there will be lot of stress because of the fine tip area is very small. So, stress is nothing, but load divided by area because of high stress the crack forms there and it breaks. So, this is the problem one of the problem the important problem of gray iron and that is the actually creates you know you cannot use in many, many structural applications where the stress is quite high engine that is not the case. So, therefore, you can apply, but many other play parts are stress is very high where this flakes can create problem. So, that is why we need to modify the morphology of the flakes and that is what is done in iron you make them which will discuss in the next class.