Phase Diagrams in Material Science Engineering
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Lecture – 25
Solid state reaction

So, in the last class I said that we are going to start a new topic on solid state reactions, but before I do that, I think it is important that I clarify you few things. Hopefully you remember that in this, about few classes ago, I discussed about the intermetallic or intermediate compounds. And I drawn your attentions to different types of compounds which formed and their formation metallurgy and many other things, but I just like to point it out (Refer Time: 00:48) that synthetic reaction also, you have intermediate phase; like this one here.

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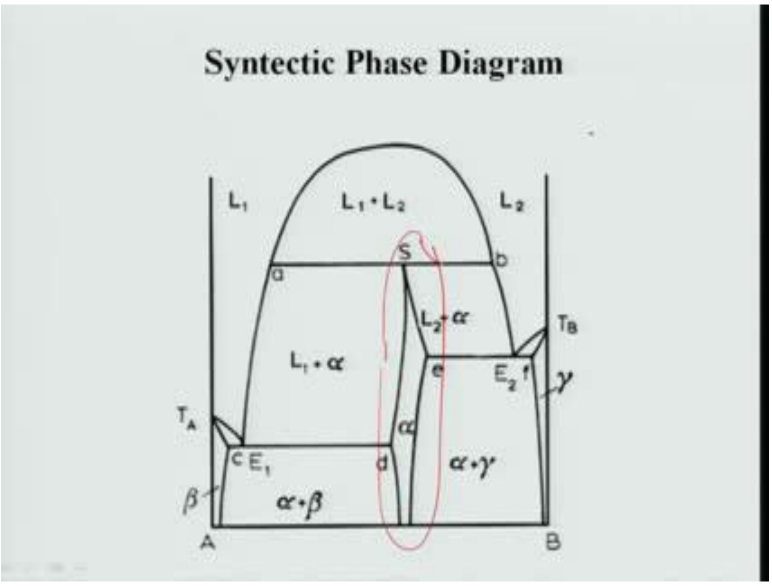

In the phase diagram showing you; alpha phase which forms between synthetic reaction is an intermediate phase, and these phase also satisfy those rules and regulations I told you about the intermediate phases previously.

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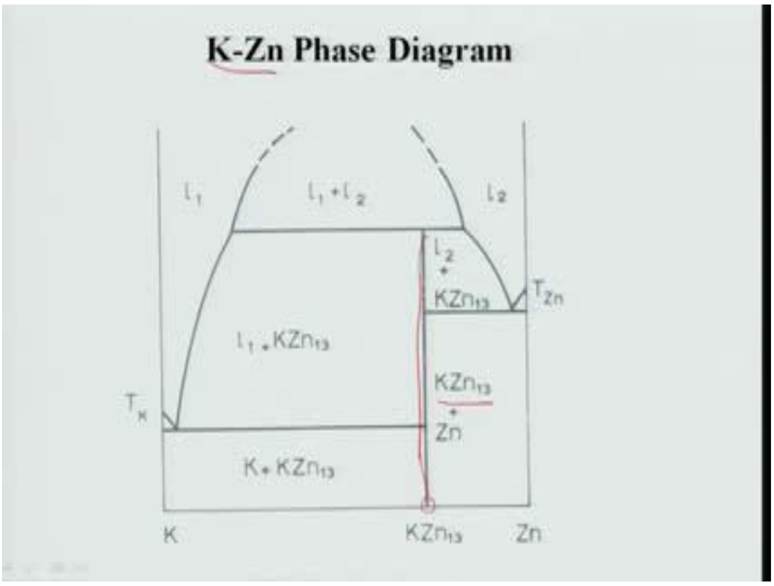

So, to just to give you an example the real phase diagram; like here it is potassium zinc, you can see here that there is a phase from known as k z n thirteen, and this phase is an intermediate phase which is forming a certain concentration of zinc and the potassium. So, this is also intermediate type of phase. In fact, this is similar to that of phase which forms in (Refer Time: 01:34) reaction.

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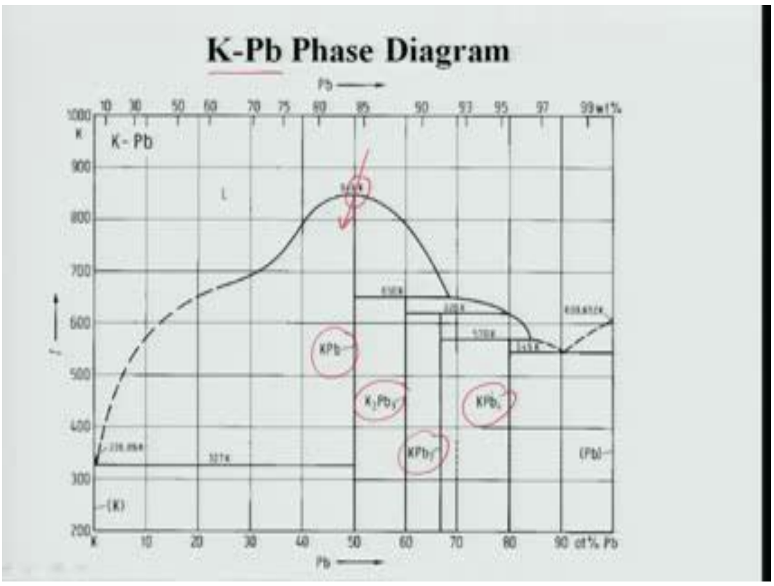

Similarly, for the potassium (Refer Time: 01:40) phase diagram, there are many intermediate type of phase forms due to synthetic reactions. The one which is important here is, the congruent type; like k b k p b which directly comes from the liquid without any reaction or without any synthetic reaction the (Refer Time: 01:59) phases is which forms, like this 1 k 2 p b 3 k p b 2 k p b four, they all different types of intermediate phases and they are also comes under that category, just to enlighten you on this matter.

You do not really appreciate this phases, because they are not really used in applications, but for the sake of (Refer Time: 02:22) of understanding we must know, that synthetic reaction also leads to (Refer Time: 02:27) of intermediate phases. So, now, before I go back in the solid state reaction, another thing I have to, I want to finish, or I have to talk to you about that, is about the dendrites, and I talked to you about dendrites many times, but I never discussed with it, but I thought it is important for you to know about dendrites and their morphologies. You know dendrites are (Refer Time: 02:55) its solidified structures.

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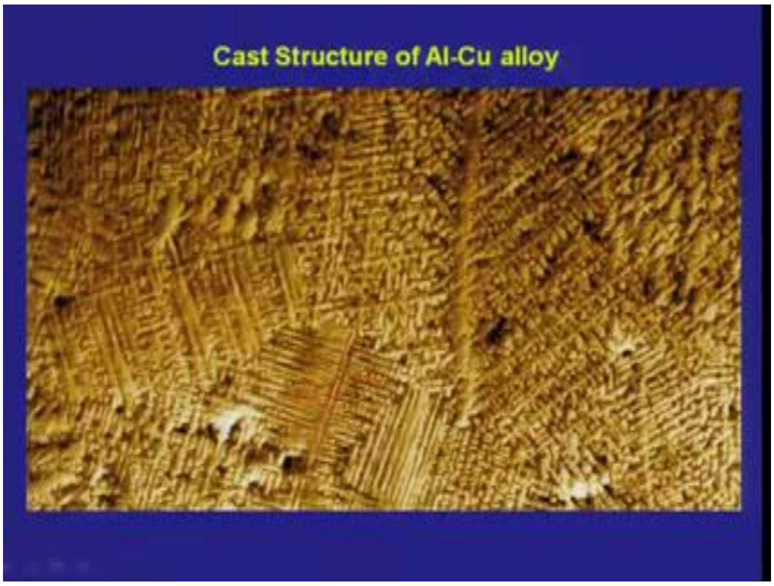

If you look at any solidified product dendrites are part of it, you cannot avoid them. So, it is better to understand that. It took almost forty to fifty years in the last century to understand the formation of dendrites, and they are you know they are mechanism formation, there problems and also how to use them in the cast structures. So, I am not going to discuss all these things, but I am going to tell you how they appear, what is their morphological formation and also how do they are normally formed. So, let us take a very simple task aluminium copper alloy, which is shown here aluminium copper alloy let us take that, and you know this aluminium copper alloy is a (Refer Time: 03:40) type, it is used in a aerospace industry.

So, you can see here there are lots of you know structures in the micro structures, and this is I want to tell you that, this is a very long structure it is about a 7 millimeter (Refer Time: 03:54) 5 millimeter is the length and breadth of this picture, and within that you can see there are tree like structure this is one you can see the branches are like this. There is another one which is here; there is a trunk branches are going like this and many others. There is another one here. Each of these are known as dendrites in two dimensions, you see they are (Refer Time: 04:17) like a tree like structure. Actually dendrite comes, what come from Dendron in the Greek (Refer Time: 04:22) a literature, and it means tree. So, anything which is like a tree like structure in a solidified product or micro structure is known as dendrite. And dendrites as I have said it has basically it looks like a pine tree or tree, and it has side branches coming out from the main branch. To give you better idea, suppose this is cast steam a (Refer Time: 04:46) steam structure.

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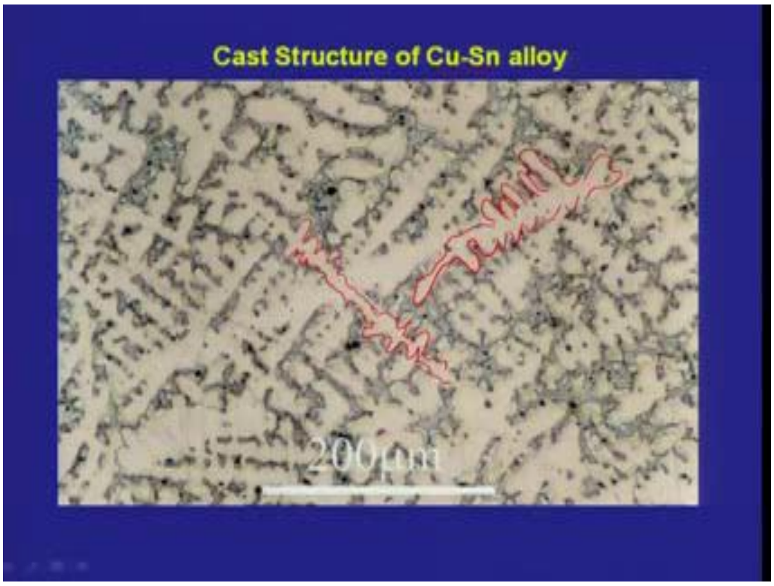

You will see this (Refer Time: 04:49) when you are working with solidified product. Here you see dendrites are not very clearly visible, but you can see the skeleton of dendrites; like here I can show you this is the dendrite, you can see this is the skeleton of a dendrite I am drawing like this, skeleton of a dendrite going. So, therefore, and there are many others. There is another one here skeleton of a dendrite, and the second (Refer Time: 05:15) phase which is formed around this skeleton of the dendrite, are can be seen as a black in copper tin or bronze kind of structure. So, there are many such, I am not drawing it.

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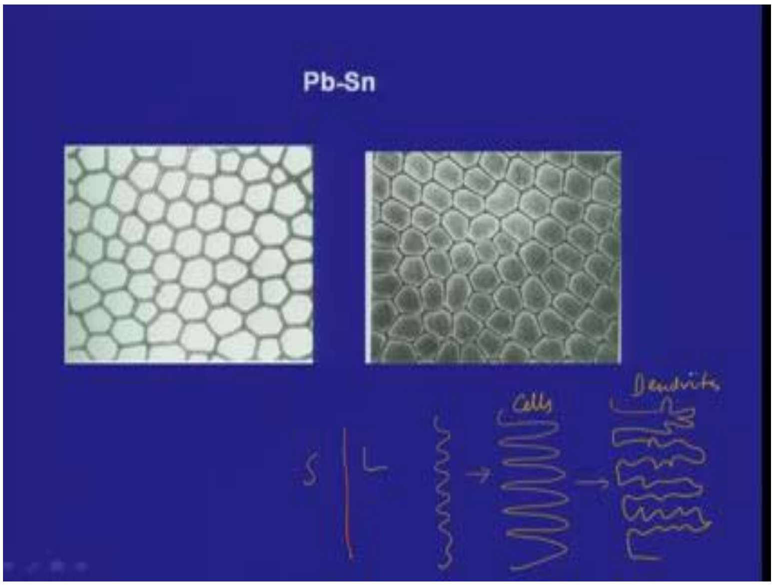

So, the fact dendrites actually are a fall out of cells. So, let me just tell you, say suppose you take a solid liquid interface which is kind of a, you know flat one solid and liquid interface, and suppose solid is go in the liquid, and at certain conditions which is dictated by this interface, and also the applied condition for the solidification during casting, this one this interface can become better, and form this kind of structures, and these are known as perturbations.

This perturbations can be a compositional fluctuations or temperature fluctuation (Refer Time: 06:12) phase, which is very usual in the solidified product. When something that is solidified, it is very common that there will be a fluctuation of temperature and solid concentrations are (Refer Time: 06:23) phase, and these actually are perturbations of that this are like a sign wave. Now if you allow them the sign waves to grow under certain conditions, then they can become big, and form what is known as cells.

And this is what I have shown here is a picture lead tin cells; the hexagonal cells which can be formed. So, now, if you allow them to go further, they can actually form side branches, and become dendrites; like this I have drawn. So, these are cells, and these are all dendrites. How this transition happens, and what is the mechanisms for it, this is very complex to very big story, not complex understood properly still, very big story which I cannot discuss in this lecture, but what I can tell you that this is the way most where dendrites formed in the solidified products. There are many such theories which are there, but most importantly the theory which I told you just now is the accepted theory and that is how it is forms. Now, this is what I have shown you here, this has been proved by experiments like using organics, like calcium tetrabromide which is transparent light.

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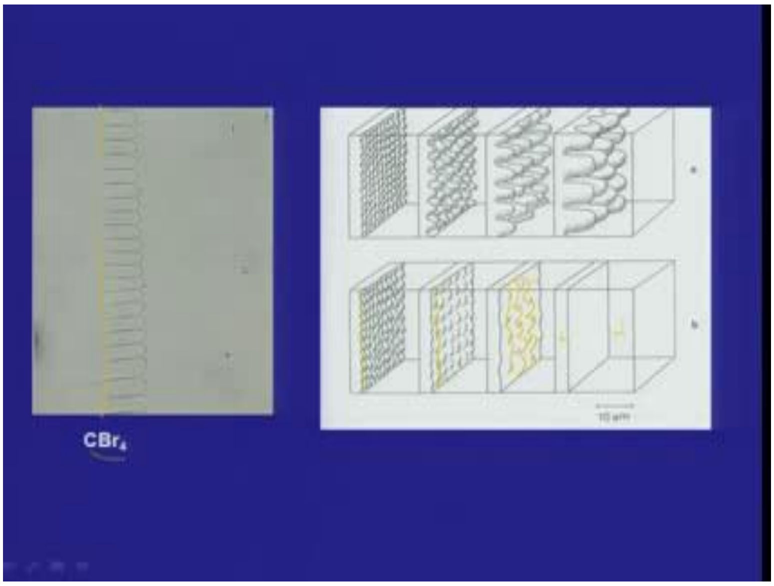

You can take this calcium tetrabromide and (Refer Time: 07:45) using optical microscope, but you will find this kind of cells formation like this. The important factor which you understand is that the interface which is there as a flat one here, has broken down and become like a cell. This is actually shown here you see here this is what your solid liquid interface, this is a solid, this is liquid.

Now you can see here this perturbation has formed, this is (Refer Time: 08:08) perturbation like this, like this, like this, or like this, or like this, and then this perturbation sorry I have drawn other way. So, this is should be written this way let me just draw it properly. This is like this actually which is signed wave. So, it follows a perturbation, and then you can see here this has grown, this has grown, this has grown, this has grown, this has grown, this has grown like this. So, then it finally, it has became a big cell. So, these are actually the mechanisms dendrite formations are described and discussed.

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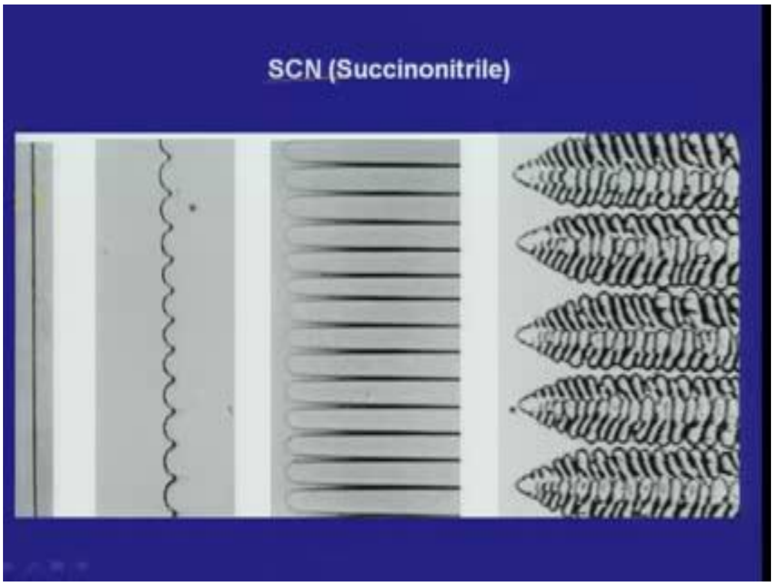

Similarly, I am taking an example on form the literature from the work of prof (Refer Time: 08:56) in U S A for there we use (Refer Time: 08:58) which is also a transparent organic compound, and you can see this is a solid liquid interface is your flat, then the same a perturbation forms like (Refer Time: 09:08) wave and finally, cells forms, now cells you can from dendrites.

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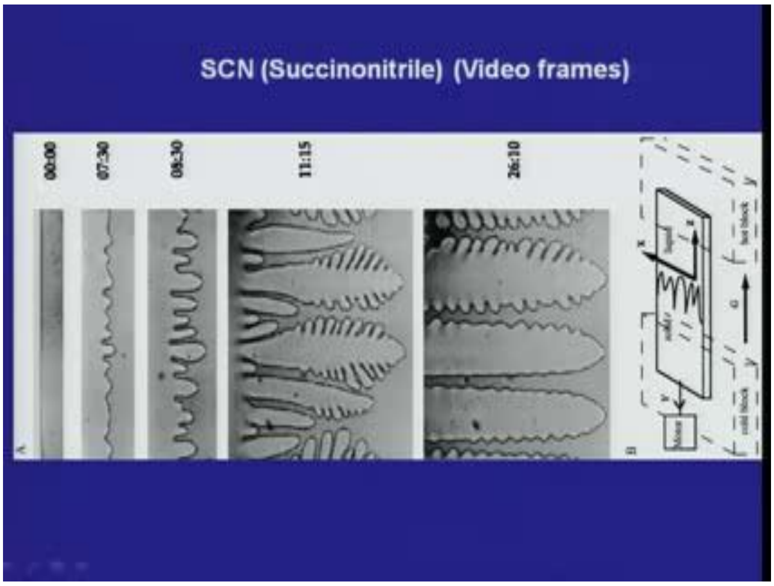

So, therefore, these dendrites are actually a very simple you know ubiquitous morphology which is present in all solidified products. Similarly from the video frames which has been done by again Prof Trivedi and his co workers. You can see that how it is simple experiment we can explain the formation of dendrites very easily, as the interface is broken down into dendrites.

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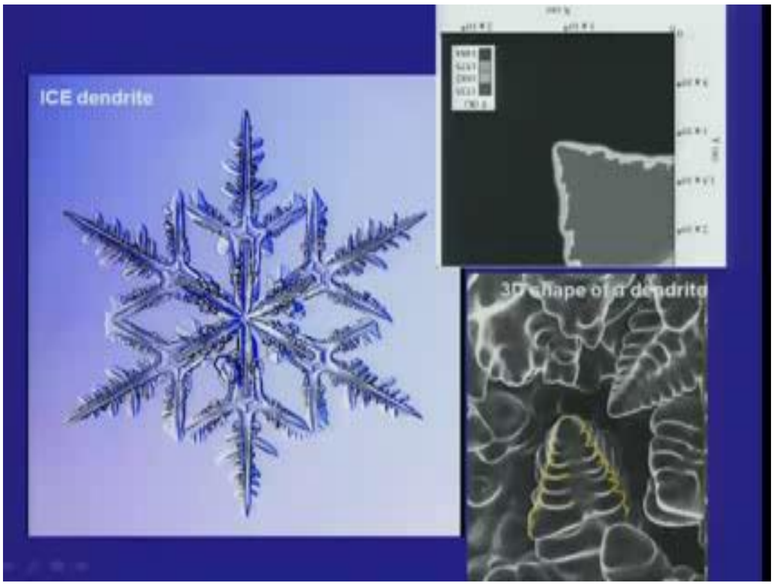

And this has been the case for long time, and you know long back (Refer Time: 09:41) even has seen this dendrites in a ice or water systems, and this is a typical ice dendrites; tree like structure branched, and you know this dendrites actually are hexagonal ice. So, therefore, they have a typical hexagonal pattern, you can see here. And you can actually do experiments in such way then metals also you can get out (Refer Time: 10:03) shape of a dendrite tip. You can see this is what is the wave, fluctuation wave, whatever you can way say the sinusoidal wave which has grown as a dendrite like this way, a several couple of (Refer Time: 10:15) present here, and this is the contour map of temperatures for these dendrite temperature flux very low inside, and high inside, is a liquid, is a solid. So, therefore, happens and this is (Refer Time: 10:28) crystal dendrites.

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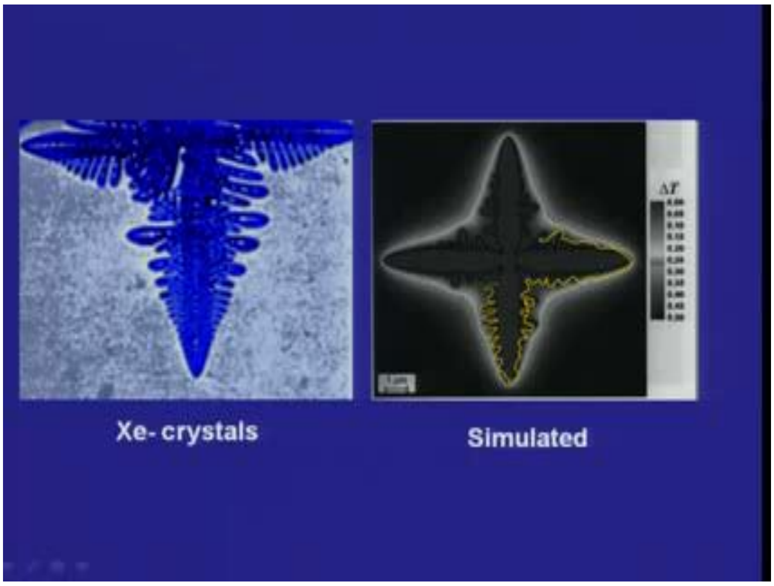

You will see that how the dendrites are grown is. It is exactly similar like metallic dendrites. And one (Refer Time: 10:34) simulate now with using these theories to show that these are the dendrites you can see inside the density pattern is engraved, very clearly. I am just following the things, so you can do that. So, this is a two dimensional picture that is why you can step hold for dendrites verti dimensional.

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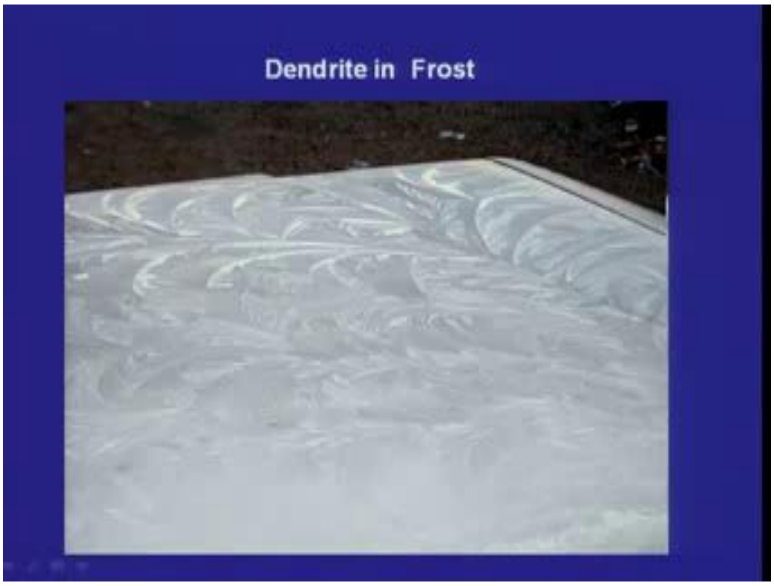

Even you can see dendrites in frost in the cool countries, the frost forms on the wind panes or the wind shields of the car, can have distendity morphology, because this frost is nothing, but consisting of the ice crystals, and ice crystals will be have a dendrity like structure.

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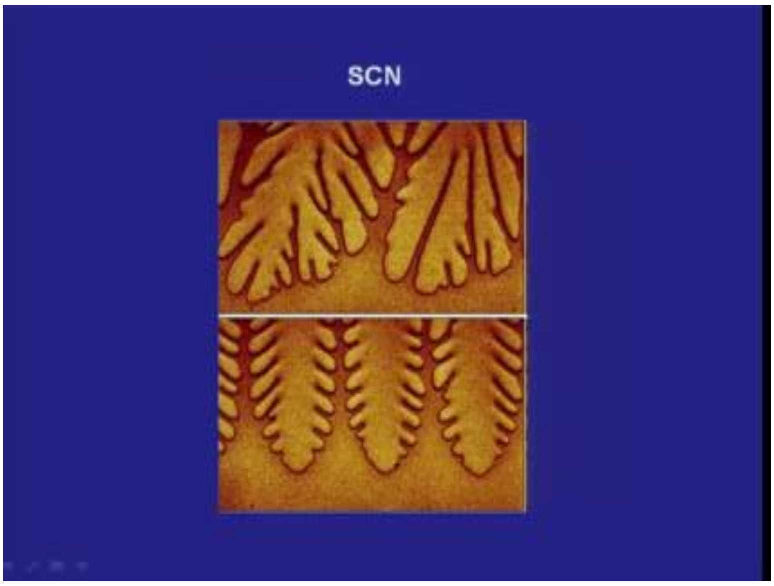

Well this is exactly the same picture I shown you for a (Refer Time: 11:15) I am showing you again. So, that you get impressed upon this is a very common form of the pattern which is observed in the solidified products.

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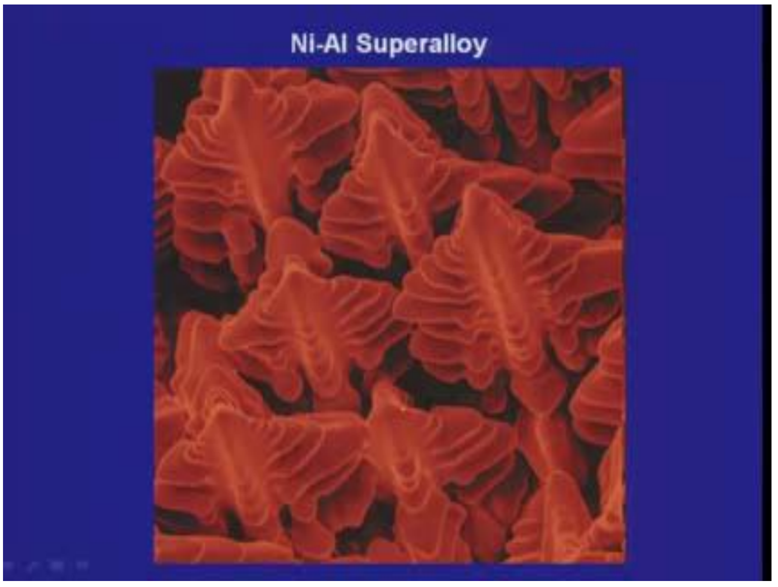

Super alloy this is the word taken from b tech and babu, which has been published in long back, in a wild like structures super alloys nickel aluminium, nickel three aluminium. We can see the dendrites three dimensionally very clearly, they are a classic structure which has been seen; super alloys dendrites, and this is reported in literature long back.

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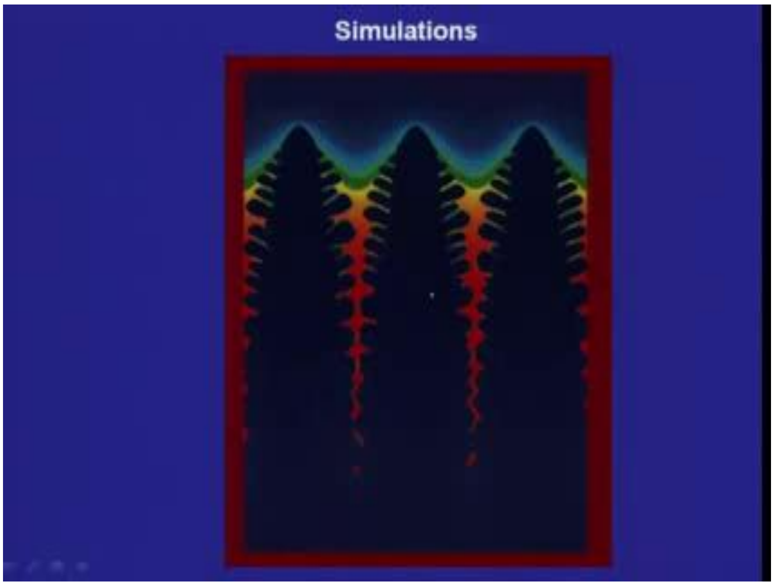

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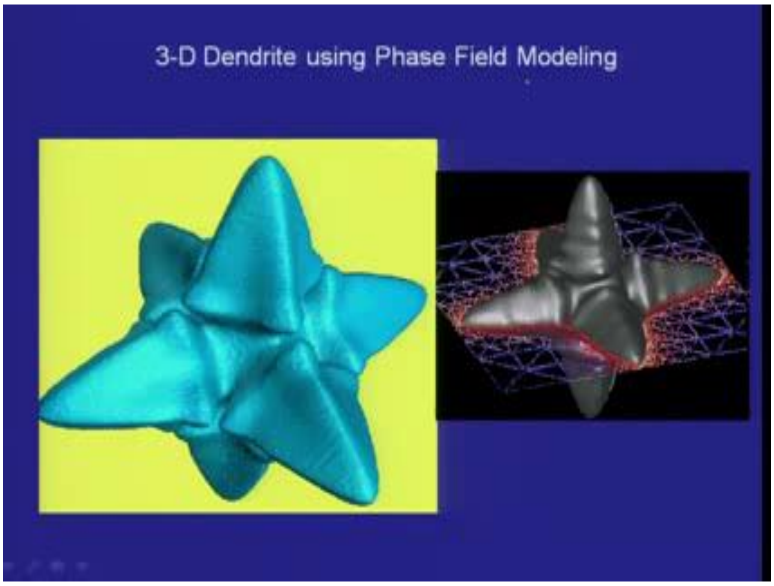

Simulations are also done. Three dimensionally they are looking like this. I am just showing you three and dimensional dendrites of a simulated one, three dimensionally they look like this kind of structures, and where you can actually see the six fold dendrite going along with 61 o directions of a cubic crystals, and which is done using phase field modeling by Allen karma and his group.

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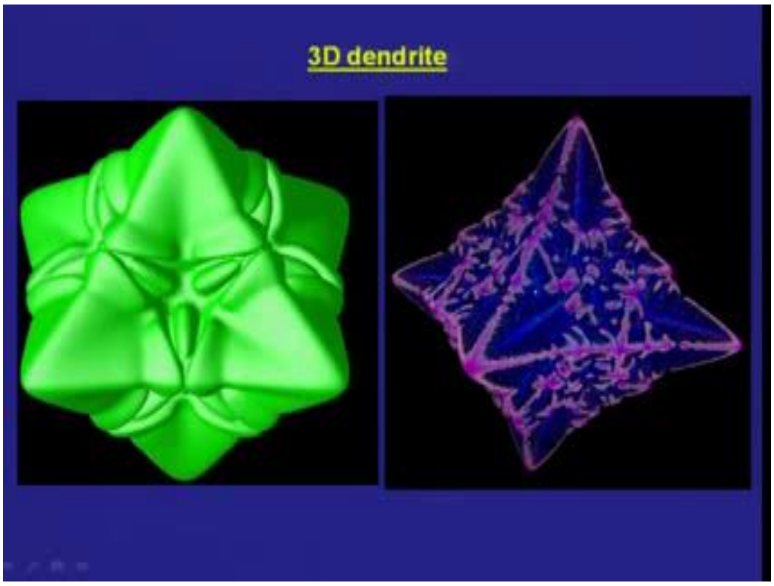

And one can actually even do better you can do this, you know for the composition profile on the dendrites, you can see here the dendrites are grown in such a way that even the compositions can be mapped, and this is the typical temp temperature profile of the three dendrites, again simulations done by Allen karma.

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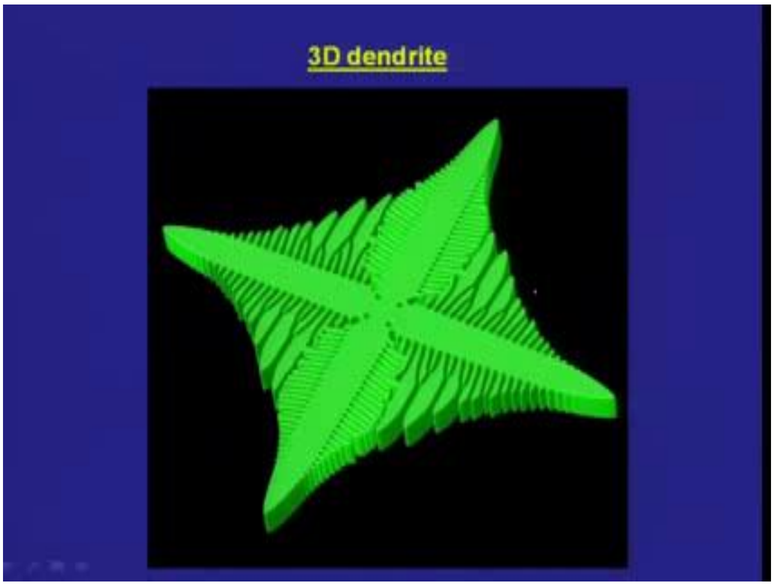

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And long back Glicksman I should not forget his name; that is why I wanted to show you, also has done classic experiments, to using the optical camera and to show how a dendrite grows. This is actually a collage of different pictures, taken at different time scale, and here you can see the clearly that this collage is so. This is what the first time skill, second time skill, third time skill, fourth, fifth, sixth. You can see here that initially there are no side branches and then the side branches has grown, and become full grown dendrites. So, I will just skip these things.

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Just to show you this part, that this is the three parallel dendrites growing in a direction solidified micro structure, and many times I am using, but you may not understand, but you must know, that this is a typical things which form in the solidified product, I have shown you for eutectic hyper eutectic hyper eutectic alloys, but I never shown you in detailed manner. So, I am just telling you that these are actually present in every solidified product, you cannot avoid them. So, they forms the way I told you, and they are represents in the different structures. So let me just stop it here for the gendertic growth discussions, and now just I gave you a little bit idea about the different caste structures. I now go back to the solid state reactions, which I where suppose to teach you today.

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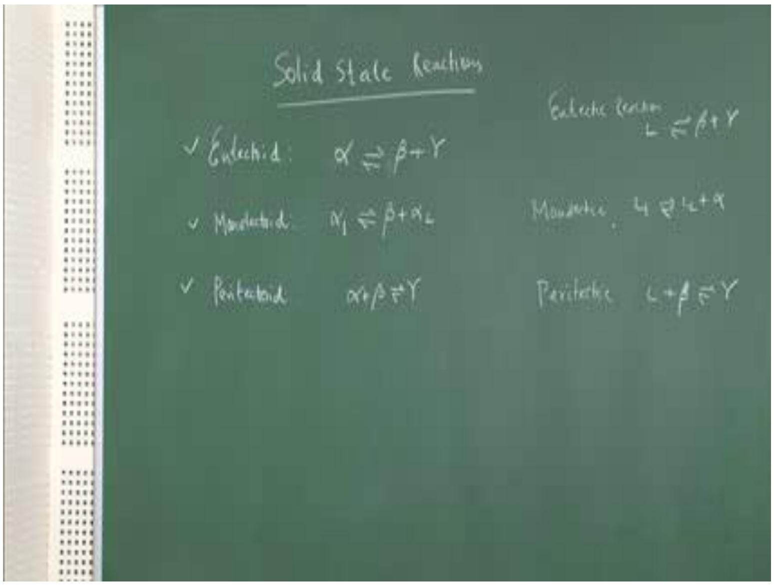

So, you know there are three solid state reactions which where we need to discuss today, this just I first go back to the board and discuss with you. So, I have discussed written the three reactions in solid state; the first one is known as eutectoid reaction, which is what we spent lot of time on that, this eutectoid reactions are (Refer Time: 14:19) present in the iron carbon system, and it controls the iron carbon system micro structure and properties.

And this reaction actually goes like this, is solid phase alpha, transforms to solid phases beta plus gamma; that is how it happens. see it is exactly like eutectic reactions, which I will write, but in eutectic reaction you have one liquid on liquid phase transform into two solid phases, but here this l is replaced by or rather let me write it (Refer Time: 14:55) common way and then you will understand here liquid going to beta plus gamma. So, here l is replaced by alpha or alpha is a solid state not a liquid that is what is the difference between these two. So, if you understand this reaction nicely you can understand this reaction also. Difference is that here, liquid is transform into solid phases, but they in this case a solid phase is transferred into two other different types of solid phases. The next one is important reaction, it is monotectoid reaction. I have discussed with monotectoid reactions; let me write down again if you have not forgotten; monotectic reaction is what l 1 into l 2 plus solid alpha.

So, liquid l 1 transformed to another liquid l 2 plus alpha. Similarly in the in this monotectoid solid state version of these alpha 1 transferred to beta plus alpha 2. What is difference between this alpha 1 and alpha 2. They are similar crystal structure a same crystal structure, rather compositions are only different. Here also l 1 l 2 they are all 2 both are liquids that is no difference, the compositions of these two liquids are different. Similarly alpha and alpha 2 compositions are only different crystal structure remain same; that is the second reaction which you are going to discuss. Third reaction which is important for us to discuss, is the peritectoid reactions.

Peritectoid reaction is given by two solid phases reacting, or forming another solid phase. We know the peritectic reaction in liquid, this is l plus alpha given (Refer Time: 16:34) to solid phase beta. So, we are replaced this l or rather I will write otherwise we will get confuse. I replace l with. So, l plus beta going to gamma, I replace l with alpha. So, because solid state reaction will have all solid phases involved, now, if you look at eutectoid and peritectoid reactions, they are opposite to each other very clearly, but their formations and their the (Refer Time: 17:04) reaction mechanism occurs are not same, or not opposite rather I would say.

Although these two reaction looks like similar, but things are not opposite bulk of our discussion will happen about eutectoid reactions let me tell you, because we are going to discuss about I would say ten lectures on iron carbon systems. and in the next ten lectures I am going to concentrate on eutectoid reactions who the (Refer Time: 17:28) forms, and what are different ways we can control the quality micro structure steels, but lastly I will spend about one lecture on monotectoid reaction and one lecture on peritectoid reactions; that is what it is (Refer Time: 17:41) that for the whole thing will take about me about ten to twelve for thirteen lectures altogether for solid state reactions.

And I will also talk about some variations of these reactions. So, therefore, about fourteen lectures I will spend on solid state reactions altogether. So, now let me just go back to the phase diagrams, where this reactions happens, go back to the phase diagrams where the reactions actually takes place. So, as you see this is a classical example of the copper aluminium phase diagram, which I have shown here.

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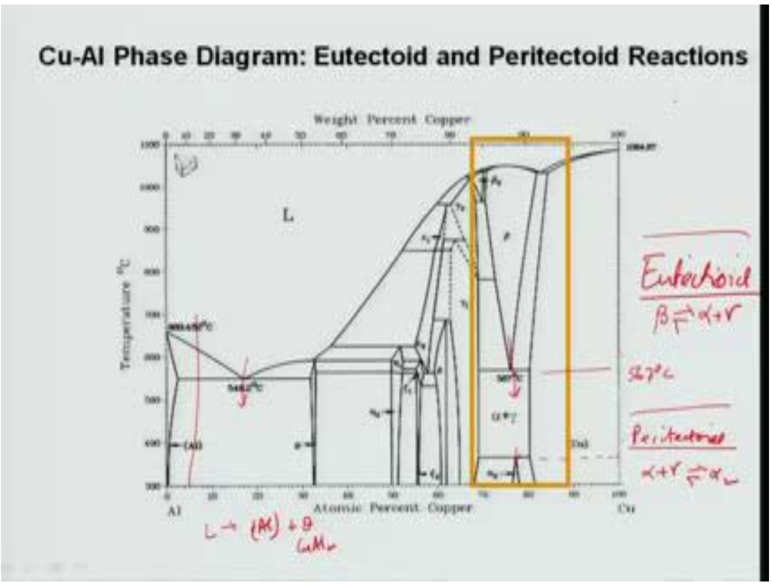

So, let me just tell you first the peritectoid reactions what is the peritectoid reaction I told you peritectoid reaction in nothing, but alpha or rather beta I can write down, 22 alpha plus gamma, this is the peritectoid reaction. Here you see this beta phase is transforming at 567 degree Celsius temperature, this is 567 degree Celsius temperature to alpha plus gamma, and this happens sorry this is not a peritectoid reaction, this is a eutectoid reactions, I am just making mistakes eutectoid reactions, you can see here the one phase beta eutectoid, one phase beta is transforming into two solid phases alpha plus gamma, at 567 degree Celsius temperature, and this happens at about 75 percentage of copper in aluminium copper alloy. I told you know aluminium copper alloy is very important for the aluminium (Refer Time: 19:27) why, because there is eutectic reaction here, you can clearly see this eutectic reaction is what, liquid going to alpha aluminium plus theta, and theta is c u a l 2.

This is very important alloy system for aerospace industry. It is about aluminium four or five atom percent of copper is (Refer Time: 19:50), and it is the bulk material for any aeroplane. So, and that is comes something around here; 1 2 3 4 5, something around here there. So, therefore, this in comparison to aluminium reach end, copper reach end has solid state reactions; one is this, second reaction is I am going to talk about this peritectoid reaction which is present here also, peritectoid a reaction which is present here also. And in this reaction what do you see. We see alpha plus gamma transforming into alpha 2, you can see clearly see here, and it happens about 350 degree Celsius temperatures. This is the peritectoid reactions which is present.

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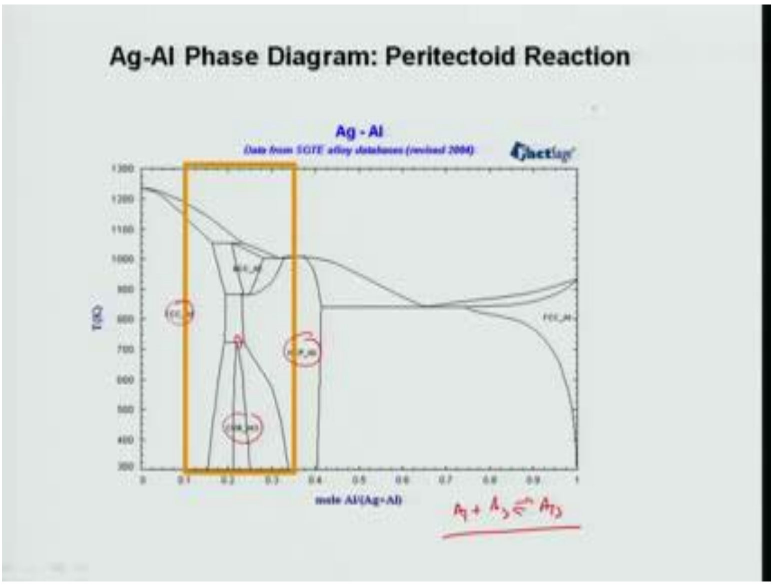

Now, let us me go to the next phase diagram which is the silver aluminium, and you can see here that this one this is a peritectoid reactions here. In fact, these two phases f c c f c c phase and (Refer Time: 21:02) phase reaction form a phase a thirteen. So; that means, a 1 plus a three giving rise to a thirteen; that is how it happens. a 1 is always cubic f c c type that is why it is called a 1, and a 3 is e c p type; that is why it is this. These are all types of structures, and cubic is your a thirteen structure. So, therefore, this is another example of peritectoid reaction.

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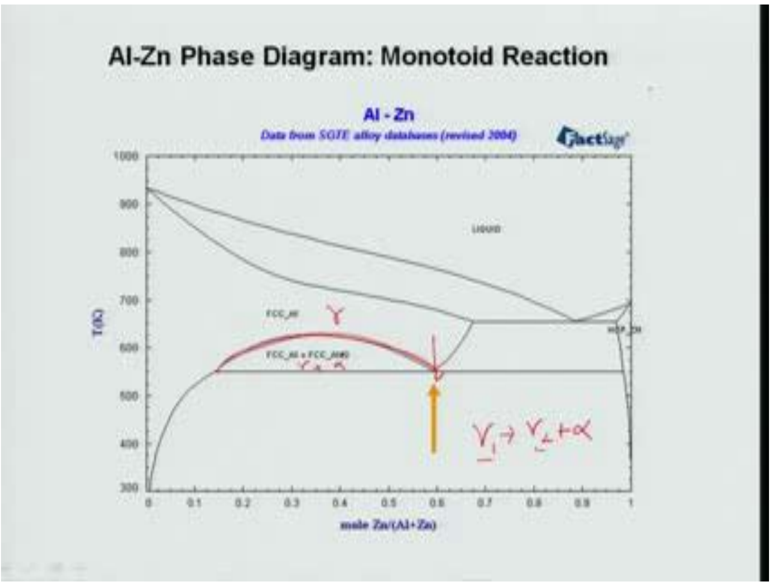

Let me just now give you monotectic reactions, which is seen in aluminium zinc system. you can see clearly see here this is f c c, suppose it is gamma, and this transform to two solid phases, basically this is not transform this is the dome similar to like monotectic reactions, this is like a dome like structure, similar to monotectic reaction, and with it that dome there is a phase (Refer Time: 21:54) happen between gamma and there is another phase called alpha let us suppose, and this is the monotectic reaction, monotectoid reaction, sorry monotectoid reaction where gamma 1 transforms to gamma 2 plus alpha. So, these two are actually same crystal structure composition are different. So, that is how actually the monotectoid reactions can be detected. The reason I am showing you this phase diagram is that, we must be able to detective particular reaction which is present in a diagram, otherwise what is the use of you know discussing this kind of reactions

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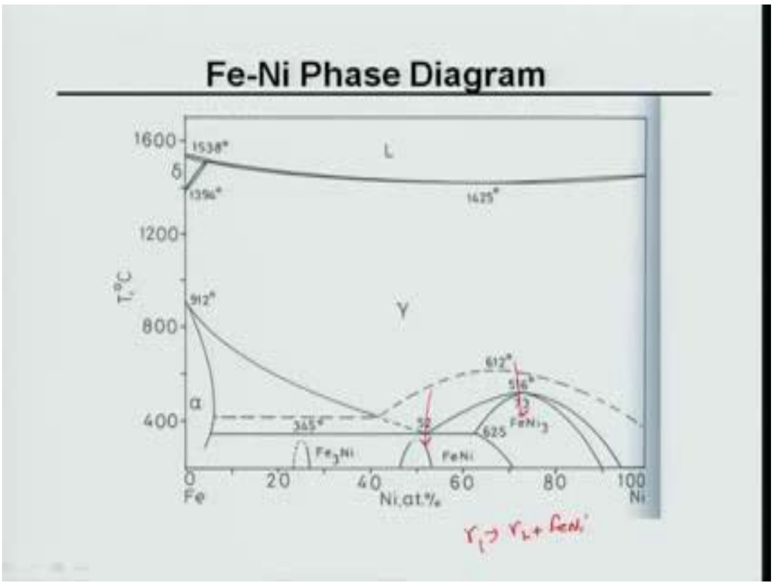

Another type of phase diagram which is very interesting, which I want to show you, is the iron nickel phase diagram. In iron nickel phase diagram is in solid state, so compounds like f e n I f e n I 3 f e 3 n i, but most importantly you can see here there is a monotectoid reaction here at about 52 percentage of these things. So, here gamma is transferred to gamma 1, transferring to gamma 2 plus f e n I that is possible. So, a similarly there is a phase separation here, but that is not the way monotectoid reaction happens; that is a different type of phase separations which, if I get time we will discuss later.

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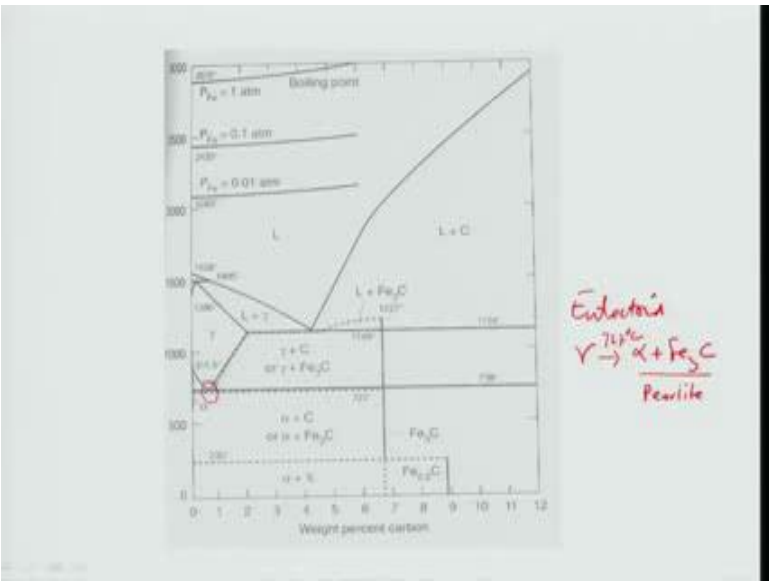

So, now, I just want go to the iron carbon phase diagrams which what we will discuss in next class in detail. Just to tell you that in iron carbon phase diagram there is an eutectoid reactions here, when which most of you have studied, or most of you have learnt, and this eutectoid reaction is what, in iron carbon phase diagram eutectoid reaction is very classic, it is known as gamma going to alpha plus f e 3 c, and this happens at about 727 degree Celsius temperature, and this is the this mixture alpha plus f e 3 c is known as pearlite (Refer Time: 23:55).

So, therefore, it is very clear that gamma transform to alpha plus f e 3 c in the, for the steels or composition of the, if iron carbon alloys which corresponds to steels and this reaction happens. So, for the next lecture, or most important aspect of understanding will be aspect, will understand this reaction and the phase formations, which we will do in the next lecture.