

Materials Science and Engineering
Dr. Vivek Pancholi
Department of Metallurgical & Materials Engineering
Indian Institute of Technology, Roorkee

Lecture - 16
Equilibrium and non-equilibrium cooling

Hello friends you might have seen a big change now the way we are delivering the lecture I am not moving now too much and I will be whatever I have to use to write on the board I will be writing on a pad now. And that will be coming on your screen ok; so, slight change from the earlier lectures ok, but I think it is not going to affect our learning process.

So, in the previous lectures we were on trying to understand the phase diagrams ok. So, now, we and we will we said or we discussed this that we are discussing the equilibrium phase diagram. That means, the process is; so, slow and it is reversible that we can always trace back our step back and we will be doing the things slowly ok. So, that we allow the system to come into equilibrium at each stage and that is what we say about the equilibrium phase diagram.

However in the practice the conditions are not in under equilibrium conditions ok; we deviate from this equilibrium condition because we have to do things fast our productivity is going to be affected; if I do not do the process in a in with a higher kinetics ok.

So, today we will like to discuss that in equilibrium condition; if we do a certain transformation or if I do it in non equilibrium condition how it is going to affect the microstructure of the material? Because that is ultimately is what decides properties for us as we have already discussed earlier also and that we should understand before going any further ok.

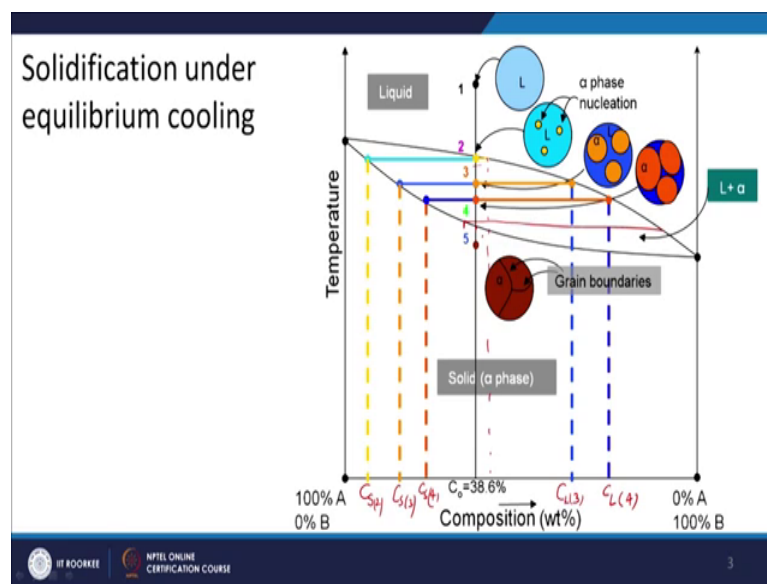
So, today's lecture will is on equilibrium and non equilibrium cooling and to elucidate the whole process ok, we will we will take the simple phase diagram and one of the simplest phase diagram is isomorphous phase diagram where we know that both the components are fully miscible in each other ok. So, there is no solubility limit I can add

for example, copper nickel system, I can add copper in any amount or nickel in any amount without any problem.

So, we will take that system and equilibrium and non equilibrium cooling we will discuss in that context ok. So, what is the equilibrium condition? If we want to do phase transformation under equilibrium condition that we have already discussed that we allow or give enough time for redistribution of alloying element to reach the equilibrium phase composition at the particular temperature ok.

So, at each temperature you are allowing enough time for phase or for components to raise distribute between the two equilibrium phases. So, that you reach a equilibrium condition ok. So, that is what is what do we mean under equilibrium condition.

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So, one example here lot of colors on this slide and this is solidification under equilibrium condition and yes you can notice that we are using here isomorphous phase diagram ok. So, my A is completely soluble in B for all the composition in liquid phase my A is soluble in B or B is soluble in a for all the composition in solid phase also ok; so, these are called isomorphous phase diagram

So, here I; I we will take one alloy with a composition is given here C naught 38.6 percent and at 0.1 the we have heated the alloy and we have brought the alloy into completely liquid phase ok. So, at 0.1 it is completely liquid and what is the condition of

the system at that particular point is depicted in this particular circle here. And we are showing here the liquid as a blue color and with a composition given by this C naught ok. So, at this point the liquid phase has composition of 38.6 percent and the whole see this whole volume is liquid.

And now you we have started cooling from this condition and we have come to a condition where which is pointed by a ah number here is 2. So, a 2 we want to understand that what is the condition of our alloy; so, 2 as we discussed earlier also I will draw a tie line tie line is a line which is parallel to the composition axis or you can say it is a isotherm at a constant temperature we have that. And if I want to know that what will be the composition of the solid phase here that tie line wherever it is cutting the solidus line that will give the composition of the solid phase which is given here.

So, see this is the composition at stage 2 here which I am showing in a in bracket ok. So, this is the composition of solid at 0.2; similarly you can see that it is cutting the liquidus line at some point here ok. So, I can again plot a line from there wherever it is cutting here that will be the composition of liquid at 0.2.

We can also find out what will be the fractions ok; so, this particular armed line divided by the total lever the lever arm we will give you the fraction of solid and this blue arm length divided by the total arm length we will give you the fraction of liquid.

So, as you can see that this is a bigger arm length. So, I should have more liquid here and because this is solidification has just started you have just two three nuclei of solid which is formed in the liquid. So, the fraction of liquid is higher the friction of solid is lower composition of solid is much lower than the overall composition which you took at this stage ok. And composition of liquid is higher than what we the alloy we have initially designed.

Now, after that we have come to the 0.3 here now again I can draw a tie line. So, the composition of solid at 0.3 will be given here. So, I can again write C S in brackets 3 this will be the composition of solid at 0.3 ok. Again I can go and see where this tie line is cutting the liquidus line that will give me the composition of liquid at 0.3.

Again you can see that my solid here still has a lower composition than the liquid ah liquid has a higher composition than the overall composition C naught and solid as a

lower composition than the overall composition C_{naught} . But since we are doing it at a very slow rate ok; I am giving enough time as you can see the first solid which form was having much lower concentration of B the solidus stage 3 which is formed as a composition higher than the what we got a 2; that means, I need now more solute atom from the system to enrich the solid phase here and to have a equilibrium composition ok; I have to give enough time for to redistribution of the solute within the whole solid.

Liquid again as you can see earlier the liquid composition was very close to the overall composition, but now the liquid composition is increased ok. Because my solute is rejecting the solute my solid is rejecting the solute in the liquid phase and that is why the composition of liquid is increasing, you can say that I can again find out the fraction here.

So, these arm length divided by the total arm length will give me the fraction of solid; this arm length divided by the total will give me the fraction of liquid. So, now liquid and solid are almost of equal fraction weight fraction similarly at point 4; we can see again I can find out the composition of solid at 0.4 and here the composition liquid at 0.4 and again we can find out the fraction and when we come to the point some point here.

Now, the liquid which was increasing getting higher and higher solute content you can see that slowly the liquid the solid will come to this composition ok. And the last liquid which will form it will give all the solute to the solid and we have to give enough time to this solid to redistribute the all the alloying elements ok. As you can see if I draw very close to some point here a tie line like this ; you can see that now my composition of solid is approaching the composition of the overall composition C_{naught} and my liquid has is having very high solute content.

So, this solute content has to be redistributed in the whole of the solid when it reaches this point at the where the overall composition is cutting the solidus line ok. So, all the solute has to be taken into the solid it has to be redistributed and the ultimately at 0.5; I will get a fully solid phase of these are different orientations. So, you have grain boundary in between ok; so, these three for nucleating they join together now they cannot grow already it is solid, this is solid, this is solid.

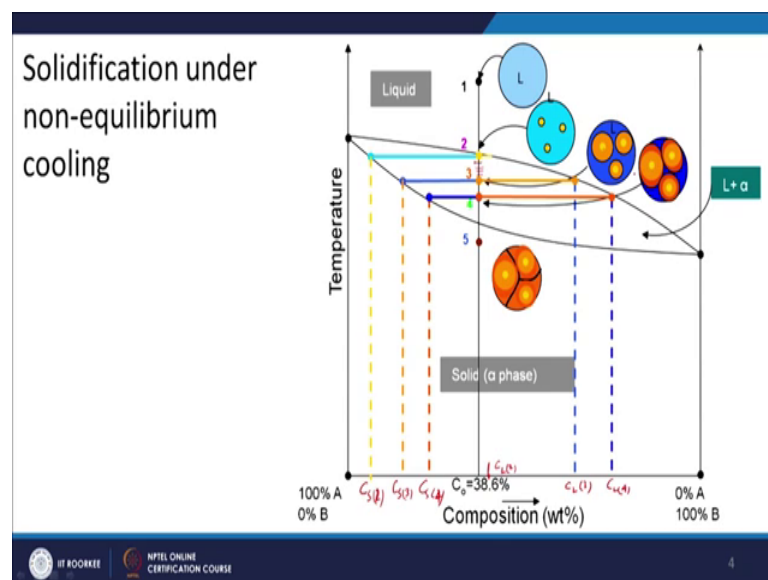
So, wherever they are joining you will have some kind of a boundary and this boundary then we may not be able to call it as a grain boundary at the stage at this stage, but there

is some boundary between the three different grains ok. And that will be at 0.5 and all the solute have now been redistributed according to the composition overall composition C naught ok.

So, you can see a different stages the solute had different solute content ok. So, equilibrium cooling means we are giving enough time for this solute to redistribute throughout the volume of that particular phase. So, this is how we do in when we do for a under equilibrium condition

Now we will see what will happen if I am doing it under a non equilibrium condition ok. So, again we have taken a same phase diagram isomorphous phase diagram and again I am taking the same 38.6 percent composition scene of my alloy.

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Now, I am heating the alloy up to the 0.1 and ah; so, of course, this will be in liquid state at this point ok; the whole volume is under liquid condition ok. Now we started cooling from 0.1 ; so, as soon as it cuts the liquidus line there will be some solid which started forming.

So, we are looking just below the liquidus line at a 0.2 ok; again I can draw a tie line here and I will show that you have the composition C_s here at 0.2 and you have some composition of liquid here which will be very close to the overall composition this will be C_l at 0.2.

Now, these are some solid which has nucleated in the liquid phase of course, fraction also you can get now we come to the stage 3 here. Now you understand that we are doing it at much faster pace I am now giving enough time for a solute to redistribute. So, what happens because of that when I go from 0.2 to 0.3 earlier if you remember I can show you the previous slide my the overall composition I depicted with having the same color throughout the solid phase and same color in the liquid phase.

But now I am showing you that whatever the solid formed at the stage 2; it is still having the same composition what it had at 0.2 ok. And the after that whatever solid has formed over the initial stage that has a different composition which is shown by an orange color. So, you have a condition here where the solid initially whatever composition it had is still in the same color and over above that at stage 3; it is a now different color.

Of course because for the discussion purposes we are defining different points here ok, but in reality it will be a continuous cooling which is going on. So, at each stage you will have composition given by at that stage. So, you can see that I can also divide these stages in multiple. So, between 2 and 3 also you should have gradient of colors here ; if you want to show the variation of solute in terms of color. Actually it should not be too discrete the discrete colors, but it should be a continuous variation in color ; that means, it should be a continuous variation in the solute concentration.

So, now you understand that you might have noticed that we are trying to show that you will have different solute concentration at different point. So, what at what time the solidification of that particular layer has taken place ok, you can see it like that that it is remembering that at that this solid was transformed at this stage that memory is still there ; you can understand it from that point of view and liquid also of course, we are rejecting some solid.

So, it will be enriched with the solute that is how we have shown with a different color here then I will come to 0.4; now again you can say at 0.4 I am showing it with a darker orange color here ok. So, the composition at stage 2 whatever we had this is the composition at stage 3 whatever we had and this is the composition at stage 4.

So, I can tried that that C S at the stage 3, C S at stage 4 this is liquid at 3 and this is liquid at 4 ok. So, this is how the composition variation is now there kind of imprinted in

the solid ok. So, now you can also understand that now the solute here is having much lower concentration than this darker yellow and then the orange one ok.

So, if in the total volume if I see the solute content must be much lower than what we saw in case of the equilibrium condition. Here the whole volume had the same solute content which is very close to the my overall composition for the whole volume, but in the this stage now you have variations. So, if you see the average composition its concentration in the solid phase it will be much lower than what is given by the equilibrium phase diagram ok.

So, in this case in non equilibrium case you can understand that the equilibrium phase diagram itself should shift towards the left side in the solid phase. And now when the our whole solidification is ended you will see that it has a lot of with the solute gradient is there in each of the grain ok. And that will bring out variation in the solute concentration and of course, the properties will also change depending upon where you are measuring the a particular property ok. So, every lot of things changes because of that.

So, this is the problem with non equilibrium cooling which is actually we do in practice. So, you can understand that when we do solidification in alloys where we have big ingots the ingots can be size of this room very long. And then a big diameters are there and that you are doing this solidification. So, at different location of this ingot; you will see that there are there is large variation in the solute content and that is not a good condition for a for our material ok.

So, now to get rid of this problem we have some treatments ok. So, first let me introduce you to the term which we call as solidification coring.

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Solidification coring

During non-equilibrium cooling (fast cooling) the time is not enough for distribution of alloying elements. Since temperature is continuously decreasing, subsequent transformation of liquid to α phase takes place with composition which is higher in solute content. This results in segregation of alloying elements.

To solve this problem all cast structures are first subjected to homogenization.

Homogenization is heating of material to high temperatures (below solidus in present case) so that diffusion of elements becomes faster. We know that diffusion will take place from higher concentration to lower concentration. We can give enough time to approach uniform composition within some limit through out the sample.

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The solidification coring is the during non equilibrium cooling that is fast cooling the time is not enough for distribution of alloying elements. Since temperature is continuously decreasing subsequent transformation of liquid to alpha phase takes place with composition which is higher in solute content this results in segregation of alloying elements ok.

So, you can understand that there will be a large variation in the solute content you are alloying elements and that is not a good condition. To solve this problem all cast structures are first subjected to a process called homogenization. Now, there is always a ah kind of a solution for any problem ok. So, we have a problem here that when you do this ah solidification at a faster rate you have problem of what we call as solidification coring there will be a difference in the difference in the composition at different places ok

But there are processes which we can use to bring down this variation and this is one of the process which we use is called homogenization. So, it is the it is the word suggests it is to homogenize the and the composition throughout the ingot or throughout the solid structure ok. And now if you recollect one of the process which we can use here is what we understand or what we discuss is in the topic where we talked about diffusion.

So, we will take help of diffusion process here because you can see that there is a large variation in the concentration at different places. So, solute will diffuse from high

concentration regions towards the lower concentration regions and thereby you will have a homogeneous concentration throughout the solid. So, this homogenization process is basically a diffusion process where you have this large variation can be ah can be brought down by having the homogenization process.

So, as we when understand the diffusion process itself is a time and temperature dependent process. So, homogenization should be a process where we take our material in the solid phase itself to a higher temperature ok. So, by taking it to higher temperature; one thing is my diffusion becomes faster my atoms will be ready to move from one place to another place. If it is a substitutional alloying condition or alloy ok; that means, the alloying element occupy a substitutional position at high temperature you also have higher equilibrium vacancy concentration ok.

So, that gives you my alloying element to move it gives a additional site for my alloying element to move. So, my diffusion process is faster I am getting more vacancies to move the alloying element ok. So, homogenization is a process which has to be done at high temperature time of course, is going to be a factor here for how much time we have to expose.

Of course, again in engineering practices my time is also important because if I am heating for a material for a certain time it requires energy for that much time my one particular equipment will give be occupied ok. So, both time and temperature have to be played together to get a optimum time for homogenization.

So, homogenization is heating of material to high temperatures of course, below solidus in present case. So, the diffusion of elements become faster we know that diffusion will takes place from higher concentration to lower concentration, we can give enough time to approach uniform composition within some limit throughout the sample ok. So, we do not have to have a it you can say I an ideal homogenized condition where so, that at every place if you measure the solute content it has to be same ok.

You have to define a limit that up to this much variation, I can accept the alloy ok. Once you have defined that you will get a get a reasonable time a within which you can do homogenization process to get a uniform composition throughout the sample ok. So, with that we will stop this lecture here.

Thank you.