Phase Diagrams in Materials Science Engineering
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Lecture - 09
Solidification of Isomorphous Alloys

So, we are going to continue our discussion on the Isomorphous systems. In the last class I told you the basic features of the binary Isomorphous systems, and today, we are going to continue on the same thing. Just to give a recap of the whole thing. If you add one element to other, we form a binary alloy.

In the system like two components, we have three variables to be considered; the first is the temperature, second one is the pressure, and the third one is the completion of one of the components, because composition of the other component can be easily obtained. So, therefore, the Isomorphous a binary phase diagrams, will have three different axis pressure, temperature, and composition, and as you know it is not easy to deal with the three dimensional space diagrams, in a phase diagrams like binary systems. So, therefore, you always take a section, and the section is always taken at one atmospheric pressure. Once you do that, that is what I discussed in the last class let me just tell you again. So, three dimensional section to look like this.

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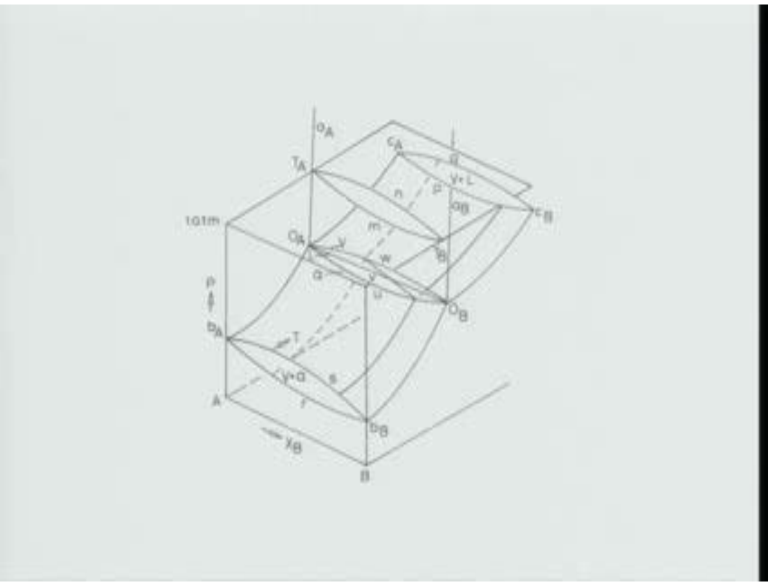

We have composition axis on the x, pressure section on the z, and temperature axis on the y, and it tells you whole phase diagram in terms of liquid plus solid, liquid plus vapor, and vapor plus solid equilibrium. So, therefore, it is very difficult to work on such a three dimensional diagram, and to make it simpler we take a section at one atmospheric pressure, and that is done here.

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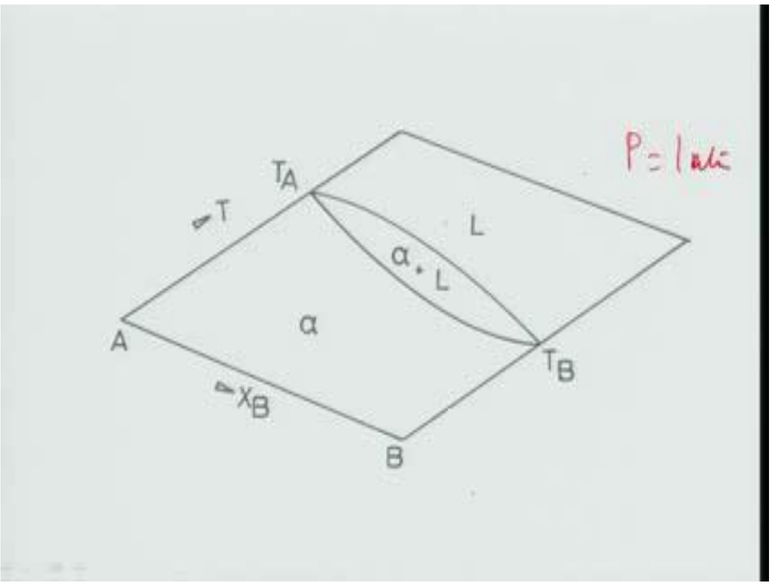

So, if I take a section at a pressure one atmosphere then it is becomes p equal to one atmosphere. Then it becomes a two dimensional section, because we have taken a section at one atmospheric pressure, so it becomes a two dimensional section, and the two dimensional section, you have a x axis remains as a temperature x compositional axis of component b that is the x b x b is the more fraction of b, and y axis is basically now temperature axis. So, z axis is comparably done, and in a simplest possible phase diagram what it is known as isomorphous phase diagrams. We have three zones one is liquid, which is demarked by l, other one is alpha demarked by solid, and in between this two you have a lens supervision known as liquid plus solid or alpha plus liquid. Solid is alpha phase here. So, that is how actually the phase diagram develops. Now, I have given you many derivation of these different type of solid solutions.

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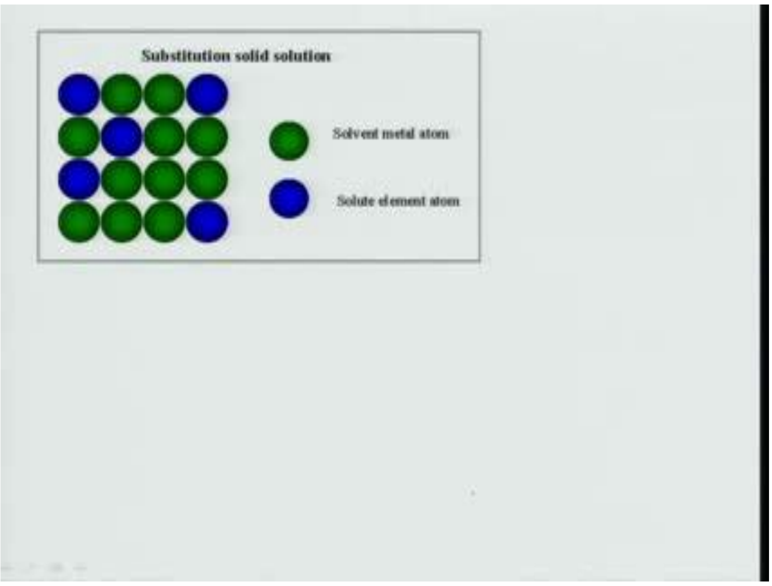

Substitution solid solution

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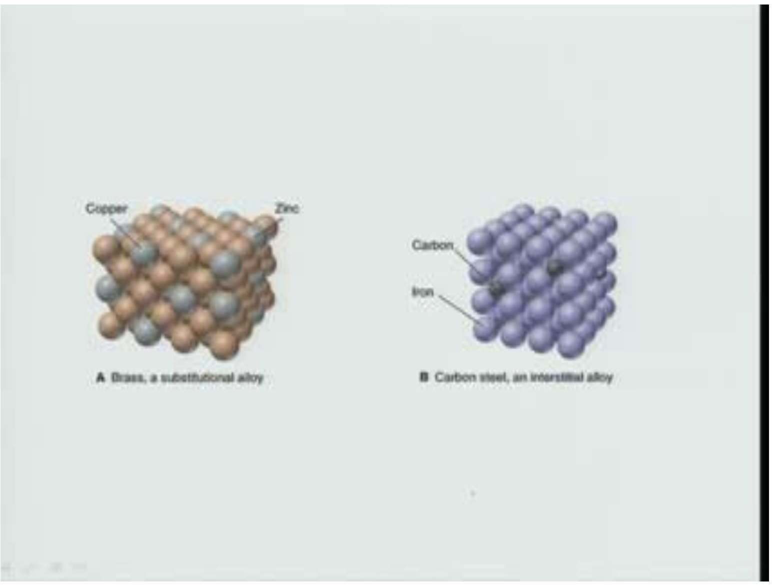

A Brass, a substitutional alloy

B Carbon steel, an interstitial alloy

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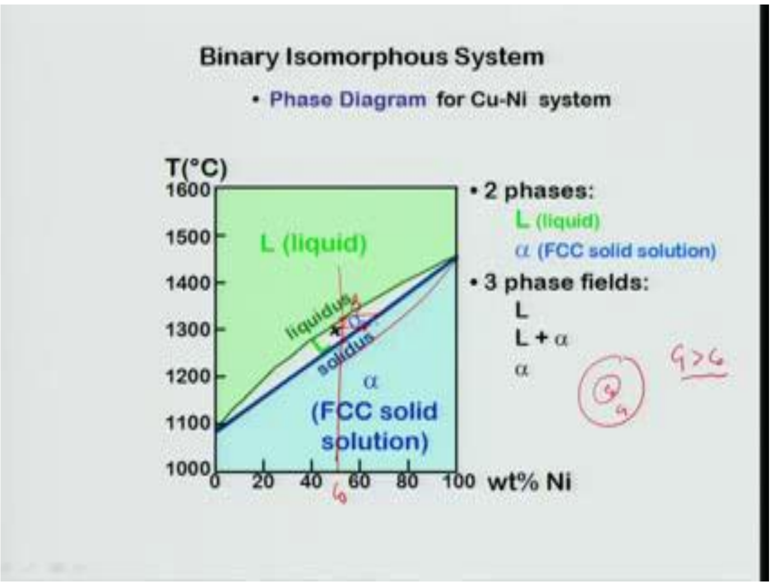

Binary Isomorphous System

- Phase Diagram for Cu-Ni system

- 2 phases:
  - L (liquid)
  - α (FCC solid solution)
- 3 phase fields:
  - L
  - L + α
  - α

Or substitution solid solution, interstitial solid solution. And then finally, I have shown you this slide where, I talked about how to use this phase diagrams. So, let us taken very simple way, the copper nickel phase diagram. I want to discuss with you, because copper nickel is an important, industrial important systems, and this is the first phase diagram where two models from a isomorphous type of system. As you can see here l stands for liquid, alpha stands for solid, and in between we have a lens of a region known as alpha plus l or l plus alpha whatever it is. The top curve is known as liquidus, bottom one known as solidus. So, there are two phases liquid and solid which are simple solutions, and there are three phase fields; here, one is liquid, another one is alpha, another one is third one is liquid plus alpha.

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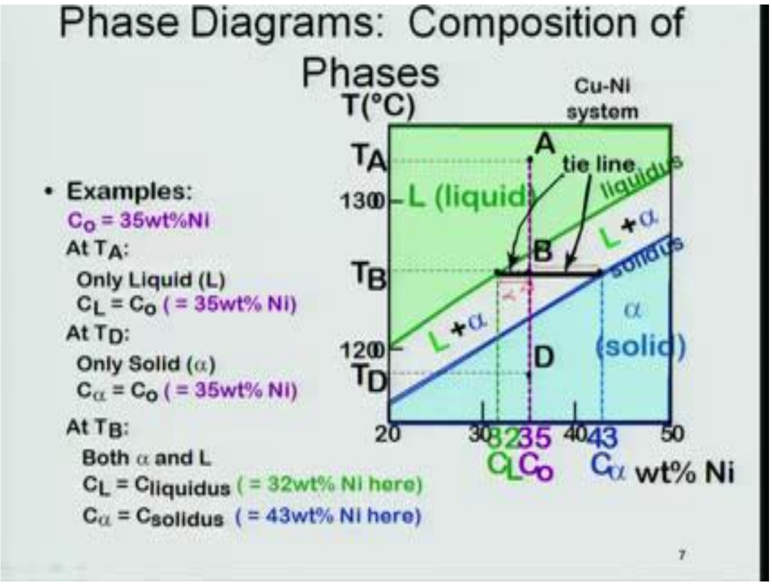

Phase Diagrams: Composition of Phases

- Examples:

C_o = 35wt%Ni

At T_A:

Only Liquid (L)

$C_L = C_o$ (= 35wt% Ni)

At T_D:

Only Solid (α)

$C_\alpha = C_o$ (= 35wt% Ni)

At T_B:

Both α and L

$C_L = C_{liquidus}$ (= 32wt% Ni here)

$C_\alpha = C_{solidus}$ (= 43wt% Ni here)

Now, here in this class what I am going to discuss with you is that, how to discuss the solidification of alloys in the systems. So, obviously to know that we should know how to apply the lever rule, and this again I have discussed in the last class. Lever rule is very simple; suppose I have to calculate the amount of phases liquid and alpha in the two phase field, inside the lens of the region, what I do is that I draw a horizontal line parallel to the x axis, or compression axis at the particular temperature t b, and this line is drawn here like a black one, connecting the liquid and solid phases, or liquidus to solidus. So, therefore, this is tie line you can consider, because it ties this liquidus and solidus, and in this line the one end of the line actually connects the liquid to the other end as a solid alpha.

So, if I consider that as a liver with falcon at the composition at which you want to the calculation. So, the solid phase is given by this arm, thus is alpha is given by this arm divided by total arm of the lever and the liquid is given by this arm divided by the total length of the lever. Thus, how actually calculate the amount of phases. Same thing is done in this slide if I consider composition to alloy to be 38 percent of nickel, and to draw this tag line at a temperature t b is between 1200 and 1300 degree Celsius. Then you can see here that c l is equal to basically, the composition or liquid is equal to 32 weight percent and c alpha is basically, 43 weight percent here. You can see here this is what it two points it cuts. So, if you use the lever rule you can calculate the volume pressure this phase very easily that is it given here.

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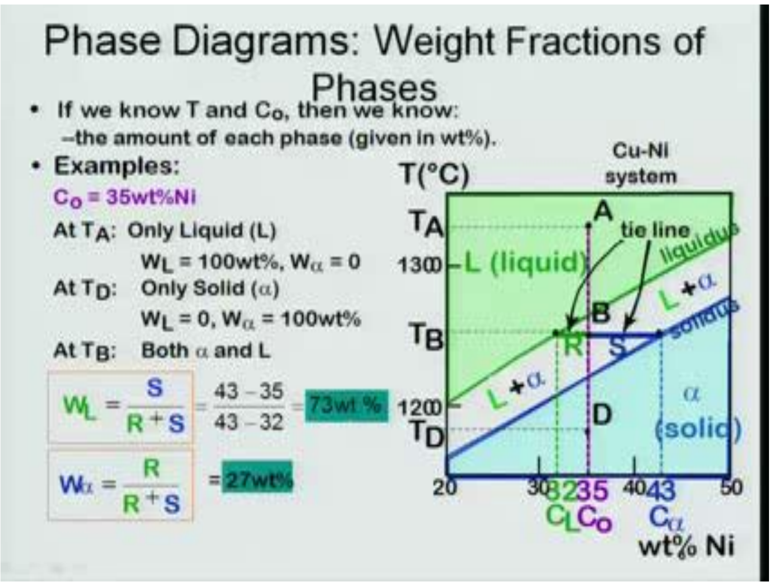

Phase Diagrams: Weight Fractions of Phases

- If we know T and C_o, then we know:
  - the amount of each phase (given in wt%).
- Examples:

C_o = 35wt%Ni

At T_A: Only Liquid (L)

W_L = 100wt%, W_α = 0

At T_D: Only Solid (α)

W_L = 0, W_α = 100wt%

At T_B: Both α and L

$$W_L = \frac{S}{R+S} = \frac{43-35}{43-32} = 73\text{wt \%}$$

$$W_\alpha = \frac{R}{R+S} = 27\text{wt\%}$$

volume fraction that is all given by r divide by r plus s. So, r divided by r plus s is 27 weight percent, and the volume percent of liquid is given by s by r plus s it is equal to 73 percent. So, these are the basic thing you need to know; when you want to discuss solidification to alloys. So, we will just go head.

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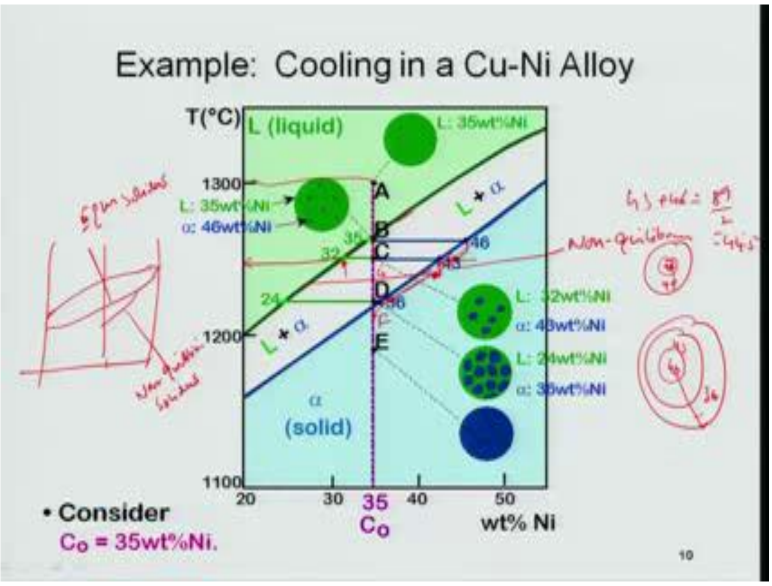

Example: Cooling in a Cu-Ni Alloy

- Consider
  C_o = 35wt%Ni.

Now, that I given a perspective of that. Suppose if I want to study a solidification of the alloy composition, which is given by 35 percent of nickel. Obviously, I start from the pure liquid; pure liquid means, when everything is liquid. As I know above the liquidus the whole alloy will be the liquid state and below the solidus whole alloy is in solid state. Now, let us follow from the high temperature, low temperature what actually happens along this vertical line which are done at 35 weight percent of nickel. So, at point a, it is fully liquid, and I am going to follow the solidification in equilibrium manner. What is meant by equilibrium manner. It means if sufficient time base system, so that it remains in the equilibrium state, equilibrium conditions. There is no such change which we can happen as time dependent.

Equilibrium means it is one state which is the final state at any time, at any temperature. So, which is specifically a system is kept a long time, so that the composition temperature (Refer Time: 07:44) is homogenized. So, at a point a, which crossed 1300 degree Celsius temperature as you have seen here 1300 Celsius temperature. it is a completely liquid state, because it is above a liquidus. So, above liquidus everything will be liquid.

Now as you cool down from a to b, b is just slightly below the liquidus to temperature, as you see, this is rather point b is nucleus of the solid alpha is going to happen. Obviously liquidation should have happened at a point exactly on the liquidus (Refer Time: 08:20) on the liquidus; that is exactly on this curve, this curve, but it did not happen, because of the nucleus and kinetics, because as you form solid of the liquid you (Refer Time: 08:31) interface between solid and liquid, and energy correspond to that, it must be provided by the system. So, that energy can be provided by the system is finite positive energy.

So, as you know of the melting temperatures or the liquidus temperature, the give energy difference between solid and liquid phases zero. So, therefore, there is no available energy to the system, which can be spent to create the interface between solid and liquid, and that is why we need to cool down below the liquidus to form solid alpha. So, that is what I have joined here.

So, I put the point b, I put a point b here and that point actually corresponding to the temperature little below the liquidus at which the solid alpha can you create and we have given the solid alpha composition of 46 percent of nickel, and the (Refer Time: 09:25) the composition of 35 percent nickel, (Refer Time: 09:29) 35 percent of nickel because there is very little amount of solid alpha as formed. Nuclei which will be form on the liquid it will be very small size. So, therefore, the volume fraction, amount of the phase is very small. So, liquid will be almost at the same composition at which you started. Now component b to c as you cool it down what is going to happen.

We can clearly see if I go down from b to c solid to form a composition which is given by this point 43 percent of nickel and the liquidus composition 32 percent nickel these two curves are used the tie lines are actually falling on will give you this compositions of solid and liquid as I told you earlier. So; that means, the initial solid which is formed which is a composition of 46 percent nickel, but at point c at this at lower temperature than pure b, a solid actually form another composition b 43 percent.

So, there is a compositional difference between these two solid which is formed. So, between from point b to point c, the micro structural or feature wise these nuclei which is falling in the liquid will grow, become bigger, but as they grow the composition is changing as per the phase diagram. So, therefore, that must be adjusted, that must be adjusted properly in the sense that we are doing this experiment equilibrium condition. So, that is why the composition will be adjusted between this solid alpha which is formed in the liquid.

So, that the whole solid is homogeneous composition. There will be no composition variation in the solid when you cool it down from b to c. This is a very important point we must remember, you should not forget, because of the change in temperature composition of solid forming, high temperature given by point c as lower solid content, or lower nickel content then at point b, but this must be adjusted at an un equilibrium conditions by compositional change. So, that is possible, because liquid as a large pool of nickel, a liquid can provide a nickel to solid. Now, this will keep on happening as you cool it down from point c to point d, d is the point which is just sitting above the solidus, and as you see here if you come down from c to d, the composition of nickel has decreased from 43 to 36 percent, because the point d is lying at a much lower temperature.

Similarly, composition of this liquid will be given by this point which is at 43, 25 percentage. So, therefore, if I solidify an alloy from point b to point d, the solid composition will keep on changing, at any temperature; that is given by this solidus curve. So, these must be adjusted in such a way that composition of solid is forming any temperature, will be of any form composition, and as you understand this is only possible; the diffusion of the solid which is forming at any temperature with the solid which is previously formed, is possible all is you can keep at the temperature for a long time. Why; because you have to keep time for diffusion to happen, is like this, at point b I form a solid its composition is 46 percent. Now, at point c i form a solid its composition is 43 percent; nickel. So, now, because these two solid has different compositions. In fact, solid inside has a higher (Refer Time: 13:20) outside, you need diffusion to happen from inside to outside; otherwise the whole thing will not be able to form a composition.

This is only possible only for you keep this whole system at point c for long time, to equilibrate, and similarly, from point c to point d. So, at point e the whole thing will be completely solid, because point e sitting must lower than the solidus curve. So, at point e will have a complete solid forming, and this solid will have uniform composition of 35 percent of nickel in all grains of the solid, and the solidification will be completed. So, I hope by this discussion you have understood how you can solidify an alloy from liquid state to solid state and equilibrium conditions.

But you know, you cannot have equilibrium conditions under real situations; why; because real situation you cannot keep the sample at a particular temperature for a (Refer Time: 14:29) long time does not possible. In industrial scale time is the money. So, therefore, you cannot keep the sample at a temperature suppose at point c or point d for sufficiently long time for it to create, and thus things will change. So, that is why I will discuss you the next what will happen if you solidify the alloy under non equilibrium conditions.

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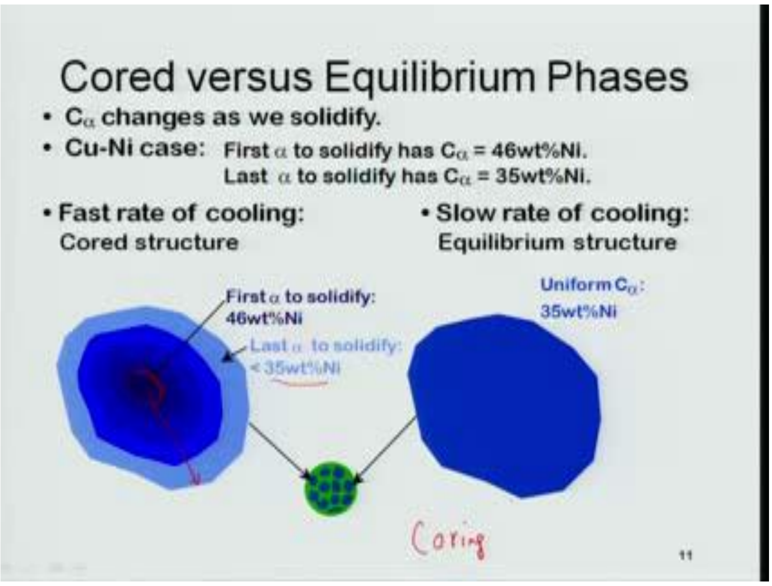

Cored versus Equilibrium Phases

- C_α changes as we solidify.
- Cu-Ni case: First α to solidify has C_α = 46wt%Ni.
  Last α to solidify has C_α = 35wt%Ni.

- Fast rate of cooling:
  Cored structure
- Slow rate of cooling:
  Equilibrium structure

First α to solidify: 46wt%Ni

Last α to solidify: < 35wt%Ni

Uniform C_α: 35wt%Ni

Coring

What is that? if I solidify a alloy in such a way that, I do not keep sufficient time at different point like b c d. So, what will happen that is very simple. This is shown here as I said the first solid is formed inside core, will have a composition of 46 percent nickel, but the last solid (Refer Time: 15:18) formed here composition of less than 35 percent of nickel. So, in between also there many (Refer Time: 15:25) form, as you see in the slide here. as you come from b to c, c to d what is happening, b will have 46 percent nickel, c will have 43 percent nickel, d will have 36 percent nickel. So, you are creating a gradient from a (Refer Time: 15:44) of a solid in which nickel concentration is varying from 46 percent to 36 percent or even less.

So, that is why actually solid which will form and non equilibrium conditions will have this compositional gradient in the solid, and this composition gradient will create further problem, what the problem it will create, because it is a compositional gradient, the solid will be of non- uniform composition from center to the periphery, and because of the non- uniform composition properties will be non- uniform and this is not good, and this kind of situation in the literatures is known as core.

This is known as coring actually c o r i n g why it is known as coring, because you form compositional variations from the core to periphery; that is why it is known as coring, and this is a very typical feature in any industrial practiced alloys. You cannot avoid it is very difficult. So, all the solidified products industry, because of time constraint or practical limitations will have core microstructures, and this core micro structures must be removed, people who apply this alloys for some applications. So, by this lecture, you are able to understand how the core micros structure will form. This is mainly because of the non- equilibrium nature of solidification process, in which the system is forming solid, whose composition is varies from center core to periphery, and this variations is going to create compositional modulations or variations.

And these can only be removed by further heat treatments; that is known as annealing. So, if I take this solid piece, heated up to high temperatures, above solidus temperature for sufficiently long time (Refer Time: 17:41) atoms will happen, from center to periphery and this can be annealed out. So, this is as I shown here, this is a fast rate of cooling, which is normally the fastest things in the industry, will have a core micro structure, compared to the slow rate of cooling in which the uniform compositional possible, and this is equivalent to equilibrium structure, but it is not possible to follow the slow rate of cooling, in the actual at practical application. So, that is why you will have lot of this coring happening in the micro structures. Let me just show you few pictures.

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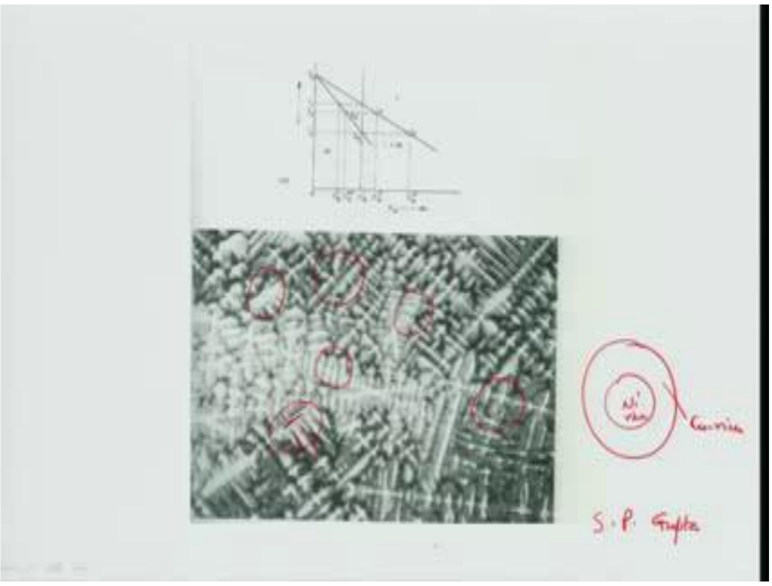

Let us take this one, this is a basically, a picture taken in our laboratories, and taken from the book of professor S.P. Gupta. he himself has gathered copper nickel alloy. As you had seen here this is a typical dendritic microstructures. We will discuss why dendrite form later, but this is a typical dendritic microstructures, but if I clearly look at one dendrite, suppose if I look at this dendrites, you can see center is very light, but the periphery are dark.

Normally, we (Refer Time: 18:53) samples in metal graphically by using certain polishing and then powered by etching. So, if you etch it, the basically etching means of using certain such a kind of I do not know chemical etchants to remove certain things in the micro structure. Like in copper nickel alloy you use (Refer Time: 19:11) etchant. So, what will do (Refer Time: 19:13) will react with copper, it remove the regions were copper is present, and if I remove those regions the regions will form micro dents, and that will optical microscopically they will look as dark. So, here we can see that the dendritic core here, reach in nickel; that is what you have seen in the earlier picture. On the other hand dendritic (Refer Time: 19:33) in copper or otherwise lean in nickel.

Therefore, initially what are the solidus from the center of the dendrites, there nickel rich a periphery has copper rich or nickel (Refer Time: 19:49) and that is the mainly that known a coring, and that is what I exactly I discussed. So, in all this dendrites to see here anywhere you take, you can clearly see the core micro structures, and this is bad news for the applications, why because you have any non- uniform composition (Refer Time: 20:09) properties and cannot be applied. So, therefore, this particular samples needs to be annealed heat treated. Now, before I conclude this lecture, let me, this is one side picture of copper nickel alloy.

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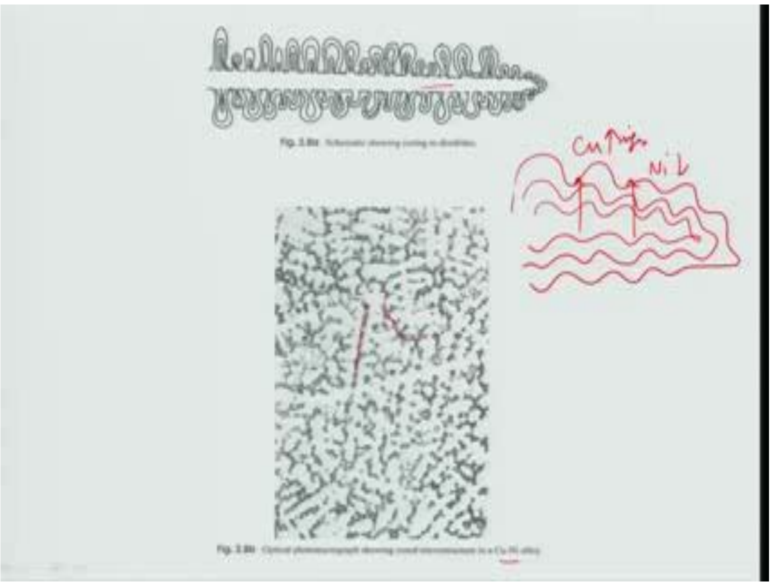

You can see that this is the schematic picture of the dendrites which is core center with lot of nickel, periphery have lot of copper, and you can see here the way it is done is like this this is the center dendrite, and periphery like this done, and drive taken for your help and finally, this you (Refer Time: 20:41) the layers in, every temperature you draw you find layers for center of periphery the copper concentration is increasing, and nickel concentration is decreasing. So, copper concentration increase, and nickel concentration decrease from center to periphery. So, nickel will decrease; that is what happening, because of coring this is a (Refer Time: 21:02) up to the micro (Refer Time: 21:04) where you can see the these are the copper rich regions, and which is this looks like dark, and this white regions are copper lean regions which are nickel rich regions (Refer Time: 21:16). Now, when you people actually modify this phase diagram which I will do here. You can modify this phase diagrams. So, how you can modify this phase diagram.

Suppose this is my alloy compositions c zero, and I know that solidification will take place in this manner, molecular manner. So, you can actually see the phase diagram will be looking like this why that is because a very simplest thing you have to understand, if is not clear I will discuss with you in the next class.

Again is very simple that this solidus is forming; suppose a fast solid is just form at b which has composition of suppose c 0 then second solidus composition c1 and c1 is lesser than c0. So, the average composition of solid will lie between c1and c0. So, that is why if you draw this tie line, which will not form on solidus. It will fall between this two points. So, that this point will like this, this is for point b, let me just go back there. So, the average composition of solid between b and c will be falling between b and c 46 and 43 and that must be lying somewhere here, between 43- 46is basically 44 something like that 43 plus 46 is how much is 9 8.

So, 44.5, but temperature is same as this tie line. So, that is why this point will be somewhere there, and if you do this for every tie line like that. So, you will get a (Refer Time: 22:58) like this, like this, and this is what I have drawn this is known as non-equilibrium (Refer Time: 23:07). So, because of this non equilibrium (Refer Time: 23:10) extension, certification will be at our point; suppose f which is lower than point d, or lower than liquidus temperature. So, a non- equilibrium condition solidification will never finish at the solidus temperature, it will get over add a temperature given by point l. I hope I am clear little bit. So, let me just again draw this thing and show you. Let me again draw and show you or again tell you how it is possible, a little bit erasing part will help you. So, what I am saying is that, from point b to point c, I have two different solid forming 43 and,46 percentage.

So, average composition of solid at point c is given by basically, I was just calculating using (Refer Time: 24:02) mass of the solid which form at point b and point c, but anyway for the sake of understanding let us assume that thing (Refer Time: 24:11) similar at point b and point c; therefore, average composition will given by average of these two 46 and 43 and that is 44.5 percent, and that 44.5 percent line point will be falling somewhere there. Now, that my alloy system is at point temperature corresponds to point c, this is what this is. So, therefore, if I have to get this point what I will do. I extended this vertical line horizontal line this way and draw a vertical from this 44.5, point to this now, this is my new equilibrium point, or non- equilibrium point at temperature given by point c. Similarly at point suppose at g this is by my line. So, this will be given by this point similarly, at point d this will be given here.

So, I can join this points and get a line which will be, then with in a at point f. So, that is in all the book we will find this is what it will be drawn I will just going to draw it again to for you this is my temperature this is a composition. So, this this whole thing will be falling like this. This is the non- equilibrium non equilibrium solidus line, solidus (Refer Time: 25:29) and the equilibrium one is this one, this is the equilibrium solidus.

I hope this I made convince that the solidification of the this kind of isomorphous alloys is not so simple, this rather its it depends on how fast you cool how fast you solidify. And normal situation solidification will be happen in non- equilibrium manner, and this is will to core micro structure, and by this we can actually change the phase diagram.

In the next class I will discuss with you how actually we can, what are the conditions for ismorphous phase diagrams, and how you can change the phase diagrams and move into eutectic systems.