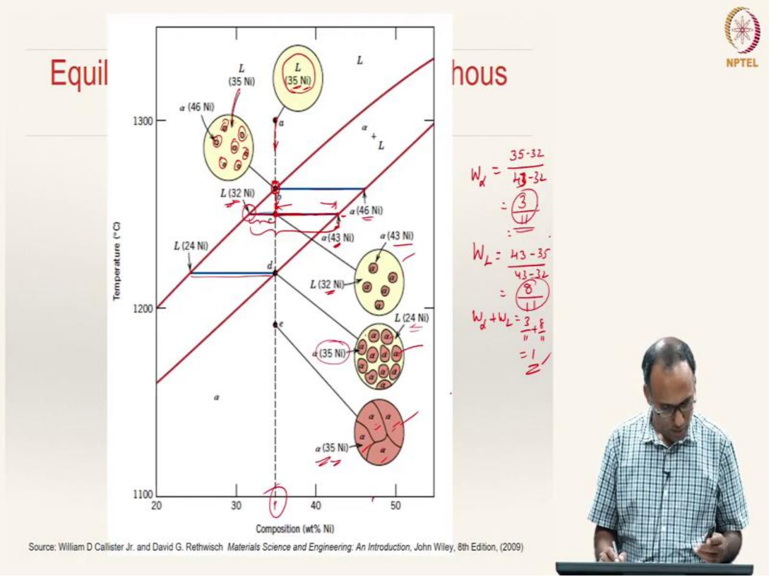
Basics of Materials Engineering
Prof. Ratna Kumar Annabattula
Department of Mechanical Engineering
Indian Institute of Technology, Madras

Lecture – 57
Phase Diagrams
(Type 1: Isomorphous Alloys, Microstructure evolution in Equilibrium and Noon equilibrium cooling)

(Refer Slide Time: 00:14)



$W_\alpha = \frac{35-32}{43-32} = \boxed{\frac{3}{11}}$

$W_L = \frac{43-35}{43-32} = \boxed{\frac{8}{11}}$

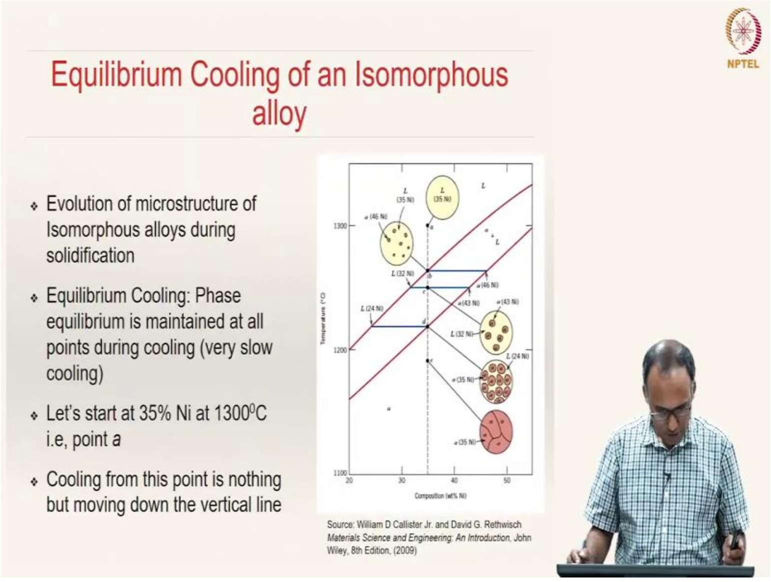
$W_\alpha + W_L = \frac{3}{11} + \frac{8}{11} = 1$

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

Let us now look at the equilibrium cooling of an isomorphous alloy. What do we mean by equilibrium cooling? When we are cooling down an alloy from a liquid state to a solid state, we are giving sufficient time for the process to follow the equilibrium path, i.e., cooling is done at a very slow rate.

From a practical perspective, this may not be feasible. However, equilibrium cooling of an isomorphous alloys is an interesting thing to study, so that we can understand how the microstructures evolve. Compared to such an idealistic equilibrium cooling, what happens in a realistic scenario is also something that we will look at.

(Refer Slide Time: 01:02)



Equilibrium Cooling of an Isomorphous alloy

- Evolution of microstructure of Isomorphous alloys during solidification
- Equilibrium Cooling: Phase equilibrium is maintained at all points during cooling (very slow cooling)
- Let's start at 35% Ni at 1300^{0}C i.e, point *a*
- Cooling from this point is nothing but moving down the vertical line

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

Let us look at this system. Consider an alloy 35% nickel which is in liquid solution at point a which we are trying to cool. When we are cooling it down, until point b -- just above point b it is liquid solution, on this line you will start having two-phase region; that means, when you are just reaching the point b, small nucleus of solid solution start forming.

You can see these are all small nuclei of solid forming; you are already in the two-phase region now. Since you are in the two-phase region, you should draw a tie line and identify the compositions of the liquid and solid phases. Because you are in the very beginning, the liquid phase composition will be almost same as the original composition, i.e., 35% nickel - that is what it is shown.

Whatever initial solid that is formed is very rich in nickel, that is 46% nickel. If you draw a vertical line, that corresponds to 46% percent nickel. So, you entered the two-phase region. What happens if you further cool it down? When you are further cooling it down, let us look at point c, you are still in two-phase region and then you draw a tie line.

Let us now look at the compositions of liquid and solid. This line hits the liquidus at this position, which corresponds to 32% nickel. So, what is happening? Initially liquid was 35% nickel and then by the time it reaches here, the liquid became lean in nickel; that means, nickel composition in liquid is reducing. So, it became 32% nickel and the solid has also reduced to 43% nickel from 46%.

Now, you know what is the liquid composition and the solid composition. What happens to the weight fraction of solid and liquid? The weight fraction of α is,

$$\mathrm{W}_\alpha = \frac{35-32}{43-32} = \frac{3}{11}$$

The weight fraction of liquid is,

$$\mathrm{W}_\mathrm{L} = \frac{43-35}{43-32} = \frac{8}{11}$$

We should always have $\mathrm{W}_\alpha + \mathrm{W}_\mathrm{L} = 1$. You can see now if you look at position b, the distance from the fulcrum point to the liquidus is 0; that actually represents the weight fractions of the solid. So, the weight fraction of solid is almost 0. By the time you come to c, the weight fraction of the solid has increased.

That is what is expected to happen, because you are starting from a liquid state, when you are cooling down - all the liquid has to slowly transform to the solid. Here, the solid solution has a composition of 43% nickel and the liquid solution has a composition of 32% nickel. That is how you represent the microstructure. So, the yellow color represents liquid and saffron or orange color represents the solid solution.

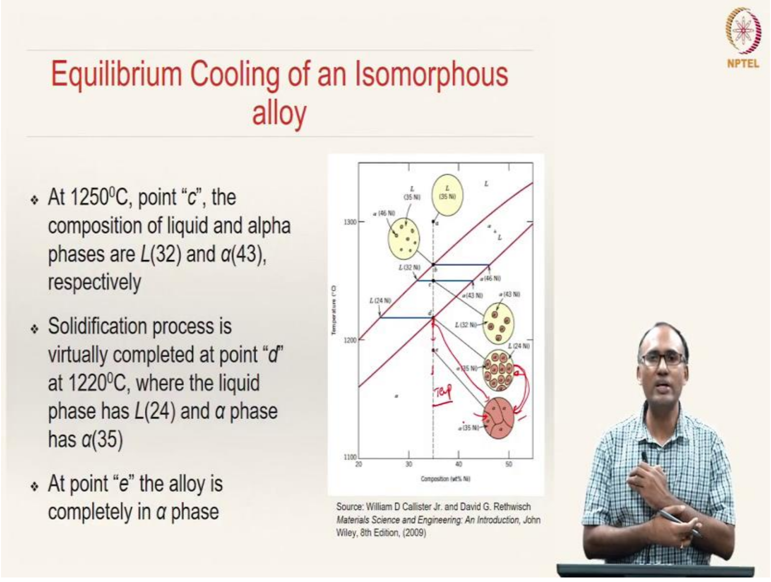
If you further cool it down, just above the solidus line, again you are in the two-phase region and then you can see that it hits the liquidus at 24% nickel and the solidus is hit at 35% nickel. At this particular configuration what is the weight fraction of the solid?

This is the point and from that point, this is the distance to the liquidus line. So, it is almost 100%, just above this line.

So, you have several solid solutions and some amount of liquid is remaining. Whatever α that is remaining, that has already got 35% nickel and remaining liquid has got 24% nickel. The moment you come here, you are in the single-phase region, all liquid has gone - everything is now alpha with 35% nickel. It should come back to 35% nickel because that is what is the alloy composition with which we have started off.

This is how the microstructure evolves. You have a liquid state and when you are cooling it down gradually, you are forming grains of alpha. It is possible that several nuclei might form within the liquid and each one of them grows independently until they meet each other and then form final grains like this.

(Refer Slide Time: 08:42)



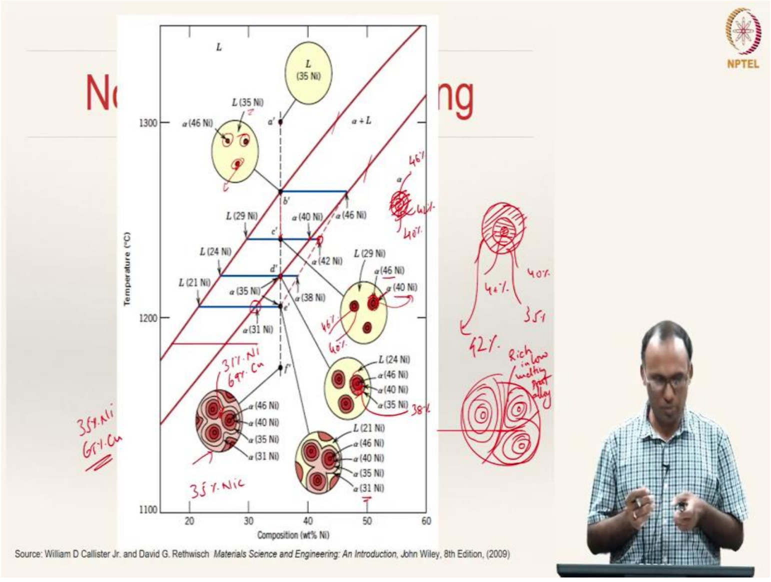
Equilibrium Cooling of an Isomorphous alloy

- At 1250^{0}C, point "*c*", the composition of liquid and alpha phases are *L*(32) and *α*(43), respectively
- Solidification process is virtually completed at point "*d*" at 1220^{0}C, where the liquid phase has *L*(24) and *α* phase has *α*(35)
- At point "*e*" the alloy is completely in *α* phase

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

So, we have discussed that alloy is completely in α phase at point e.

(Refer Slide Time: 08:47)



Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

Let us now look at what happens when perform cooling in a non-equilibrium manner. What is the meaning of that? Please understand one important point here - when we are talking about being just above d in terms of temperature - just on the two-phase region, you have some α and some liquid, right? But then, just below that, not only up to e, even here, the microstructure will be same. As you are completely coming down, the microstructure does not change. All that changes is the temperature.

Does that mean that from this state to this state, it changes all of a sudden? No. There is a sufficiently long amount of time that is spent in order for the system to go from this state to this state. We are simply not showing the time in this phase diagram. There is no time in this phase diagram.

Just above d to just below d, it could be several hours which is not being shown in this phase diagram. When we are saying that we are just above d, we are looking at a time which is reached in equilibrium state. So, this is an equilibrium configuration. From that equilibrium configuration, if you reduce the temperature at a very slow rate just below d, and after sufficiently long time you would have got structure like that.

It is simply that we are not showing the time factor here in this phase diagram. We will talk about the time in the next module when we are discussing heat treatment of steels. Here, when we are talking about binary phase diagrams, we are not showing time explicitly. When we are drawing these microstructures, the assumption is that the cooling is done in an equilibrium manner - meaning, we have done the cooling at a sufficiently slow rate.

What happens if you do non-equilibrium cooling i.e., if your cooling rate is not as slow as what we have shown here; that means, the systems did not reach their equilibrium configuration. If the cooling rate is high, the systems do not reach their equilibrium configuration. What happens if you have such a such kind of cooling rate and what will that lead to the changes in microstructure? So, this picture represents the evolution of the microstructure for non-equilibrium cooling.

Here, the two red solid lines represent the solidus and liquidus line for equilibrium cooling and we are assuming that in the liquid state, the equilibrium exists and only in the solid state, there is no equilibrium. The cooling is done in a non-equilibrium manner only in the solid state, but not in the liquid state. That is a reasonable assumption because in the liquid state, you are doing at very high temperature.

The assumption that the equilibrium exists in the liquid state is a reasonable one, but in the solid state you need sufficiently long time for solid state diffusion to take place. So, it is a time-dependent process and hence cooling rapidly is going to be detrimental or going to change certain things when we are looking at solidification in the solid region.

Hence, there is no change in the liquidus line. However, during non-equilibrium cooling, the non-equilibrium cooling solidus line is represented by this dashed line. The microstructure should evolve according to this new solidus line.

Now, we have the same 35% nickel alloy; when we are cooling down up to point b nothing changes because the liquidus line did not change. Again, small nuclei of solid α form and the composition of α will be about 46% and composition of liquid will still be 35%.

Let us now say we are cooling down to c'. If you have drawn the equilibrium cooling, it should have got 40% nickel. Because we have done it in a non-equilibrium fashion, the tie line hits the solidus line at 42% nickel. Please keep in mind that this is 46% nickel and here you should have got 42% nickel, because you are cooling at faster rate.

Because you are cooling at a faster rate, the solid-state diffusion does not have enough time. What should happen? Initially you have got 46% nickel formed here; by the time you come here this 46% percent nickel should actually change to 42%, right? But, if you do not give sufficient time, there is no possibility for diffusion to take place from the solid state to the neighboring liquid state or the neighboring solid that is there.

As a result, the outer most layer will have 40% nickel corresponding to this and the inner most layer will have 46% percent nickel. On an average this entire solid has 42% nickel which is consistent with previous case. However, this 42% nickel composition is not uniform.

This phase is a non-homogeneous phase, because at the center you have 40 percent nickel, at outer phase you have 46 percent nickel (**correction**: at the center you have 46 percent nickel, at outer phase you have 40 percent nickel).

If you further cool it down to d', again, normally you should have 38% nickel. May be the center size that is having 46% nickel is reducing, but the next core will have 40% and the next one will have 35% nickel. However, effectively this entire thing together will have 38% nickel.

So, the phase is not homogeneous from center to the boundary; the solid grains are forming as shown, with different percentages of nickel. So, this is 46% nickel and this is 40% nickel and this is 35% nickel. Together, if you take the average of all these things, it will be 42 percent nickel.

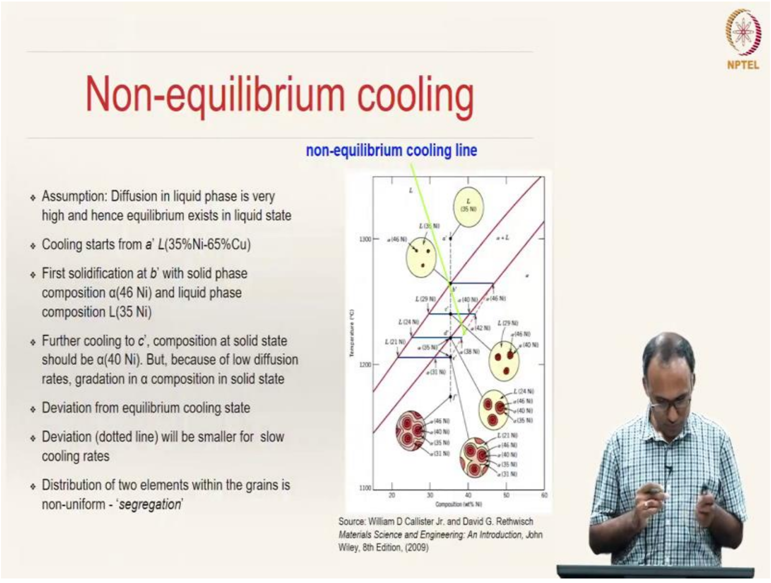
Normally if you are doing equilibrium cooling, you would have finished your solidification at this point d'. But because we are doing non-equilibrium cooling, the solidification does not end at say $1220°$ C, but it happens at a much lower temperature, approximately at $1200°$ C. You need to come up to e' and there you will have 31% nickel - you would have been on the solid state. But effectively you will have 35% nickel and hence you will have outer most layer having 31% nickel corresponding to that.

The microstructural outcome of this non-equilibrium cooling is that you will have a cored structure of your solid phase. The cored structure is again in a way that the outer most layers are rich in low melting point alloy.

Here, normally this should have been 35% percent nickel - on an average it will be still 35 percent nickel, but in here you also have regions of α which have lower percentage -- particularly this one has 31% nickel (69% copper) as opposed to 35% nickel (65% copper).

That means, you have the low melting alloy getting segregated near the boundary between two particles. So, such a cored structure is an outcome of non-equilibrium cooling. This process is called segregation.

(Refer Slide Time: 19:31)

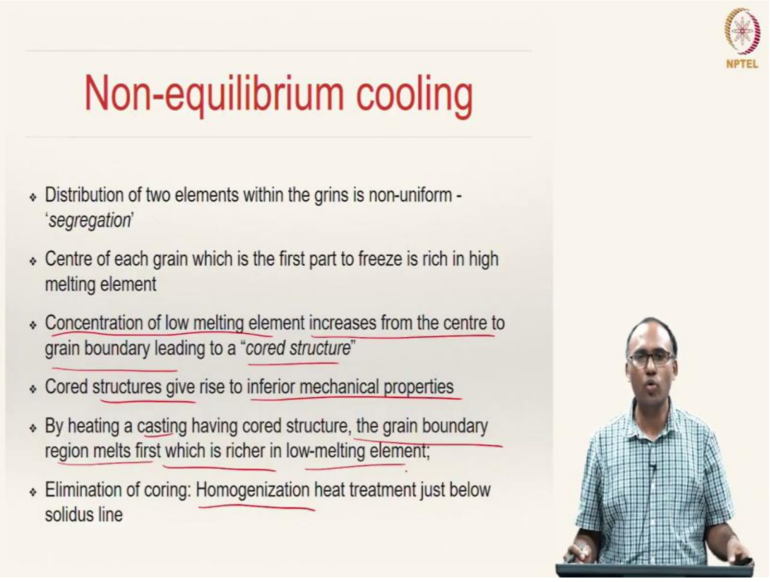


Non-equilibrium cooling

- Assumption: Diffusion in liquid phase is very high and hence equilibrium exists in liquid state
- Cooling starts from *a'* *L*(35%Ni-65%Cu)
- First solidification at *b'* with solid phase composition α(46 Ni) and liquid phase composition L(35 Ni)
- Further cooling to *c'*, composition at solid state should be α(40 Ni). But, because of low diffusion rates, gradation in α composition in solid state
- Deviation from equilibrium cooling state
- Deviation (dotted line) will be smaller for slow cooling rates
- Distribution of two elements within the grains is non-uniform - '*segregation*'

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

(Refer Slide Time: 19:35)



Non-equilibrium cooling

- Distribution of two elements within the grins is non-uniform - '*segregation*'
- Centre of each grain which is the first part to freeze is rich in high melting element
- Concentration of low melting element increases from the centre to grain boundary leading to a "*cored structure*"
- Cored structures give rise to inferior mechanical properties
- By heating a casting having cored structure, the grain boundary region melts first which is richer in low-melting element;
- Elimination of coring: Homogenization heat treatment just below solidus line

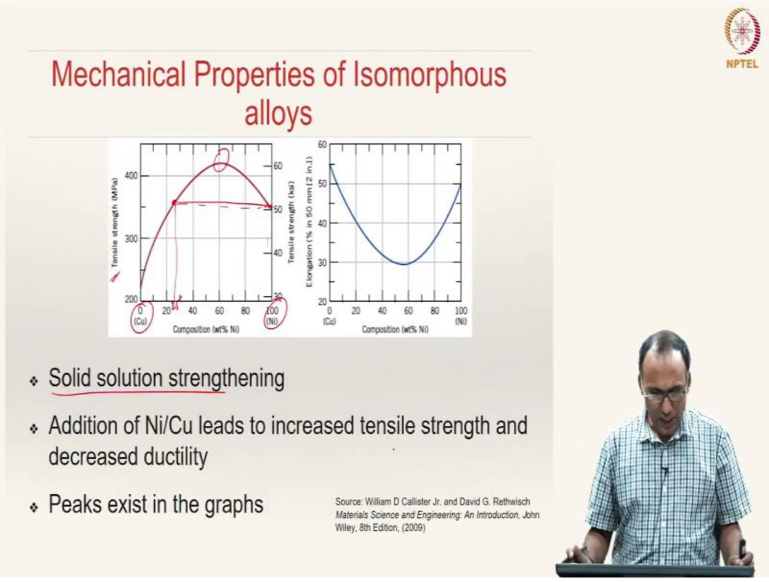
In other words, you have a higher concentration of low melting element increasing from the center of the particle to the grain boundary; that means, the boundary where two grains meet and such a structure is called cored structure. This core structure gives rise to inferior mechanical properties. Why? If you are heating a casting made out of such a system/such a cored structure, what might happen is the grain boundaries, which are rich in low melting alloy, might actually melt first.

Imagine using this component at high temperatures, the grain boundaries will melt. As a result, the material might actually give in; that means it might actually fail. So, the grain boundary region melts first which is richer in low melting element and that can be detrimental for actual service conditions.

However, in reality, we cannot do equilibrium cooling. Many times, we will only do non-equilibrium cooling. But, since we know that when we do non-equilibrium cooling, we will have this kind of cored structures, you need to do something to eliminate this coring.

Typically, at the end of the solidification process, all the alloys are usually subjected to certain kinds of heat treatments. Here, you call this as a homogenization type heat treatment, which has to be done in order to eliminate this core like structures.

(Refer Slide Time: 21:15)



Mechanical Properties of Isomorphous alloys

- Solid solution strengthening
- Addition of Ni/Cu leads to increased tensile strength and decreased ductility
- Peaks exist in the graphs

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

As we have discussed, alloying is done to enhance the mechanical properties, right? So, if you look at the tensile strength of copper-nickel system, you can see that the tensile strength of these alloys, particularly if you take about 60% nickel, it has the maximum tensile strength.

All the alloys from say 25% to almost 90%, are going to give you a higher tensile strength than both copper and nickel independently. This specific strengthening mechanism is called solid solution strengthening. So, addition of nickel and copper leads to increase in tensile strength and decrease in ductility.

With that, we will stop here and then we will look at some variations of Type I alloys and Type II alloys in the next class.

Thank you very much.