Fundamentals of Materials Processing (Part–1)
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Lecture Number 19
Zone Refining (Continued)

So we will continue our derivation for the relation for zone refining.

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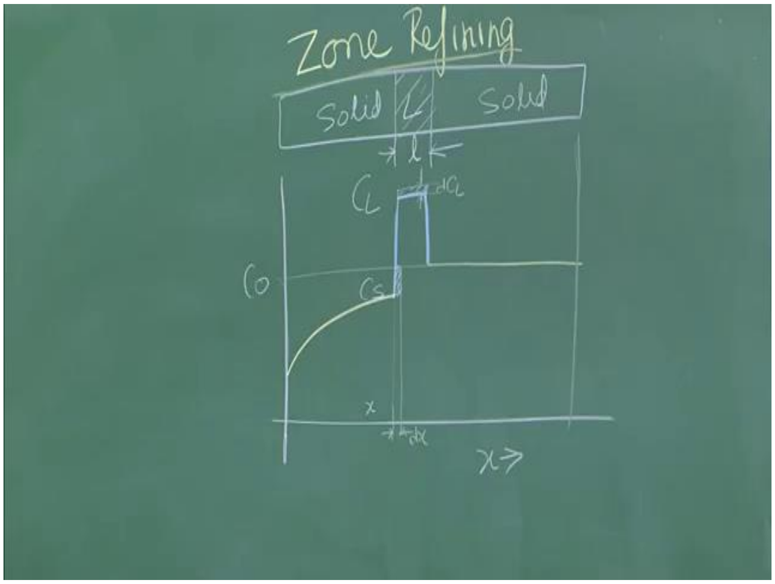

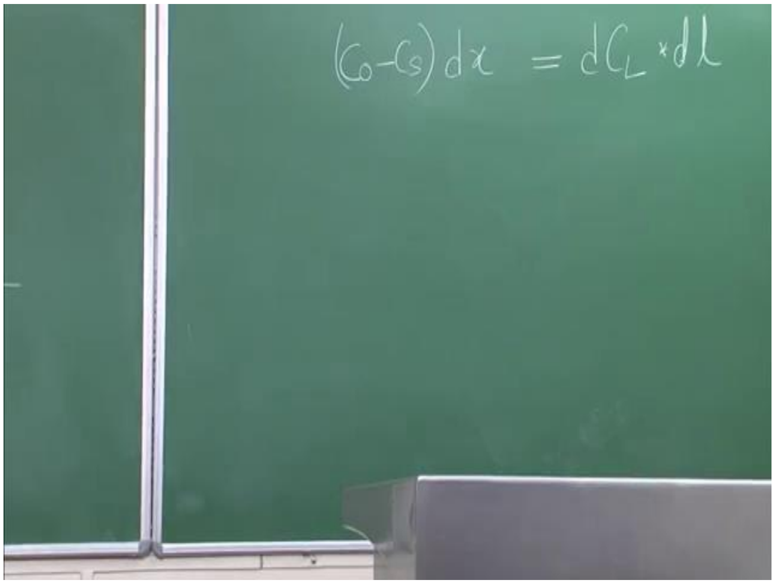

So here is the plot that we were discussing last time, and this was with respect to zone refining. So we saw that this is, we said this is a, we are assuming that this is the concentration of a crystal that is shown over here. And then in zone refining, you are using the fact that the solute that forms during solidification has concentration less than that of the liquid. And so taking that concept further, what we do is solidification in a very limited zone; so this length we are looking at is only L. So this is a (different) zone which is in liquid state. L stands for the length here, and here this upper case L that I am writing is for the liquid state, this is solid state, ad this is also in solid state.

So originally this solid overall had a concentration C0 like I have said here. And, when we do the solidification, then this, there is a curvature somewhere over here, curvature mean there is a distribution, redistribution of the solutes, and the solute concentration has come down. So somewhere over here, let us say this is, this has this concentration, which we can say CS, and taking the interface equilibrium, the corresponding concentration of liquid is CL.

Now to find the relation for what will the plot look like, the new concentration plot will look like, what we will do is use a similar concept that we used for deriving Shell’s equation; so this is the solute; let us say this is the additional amount of liquid that is solidifying. So this is the distance dx that has solidified, and therefore this amount of solute will get taken away from here; because you see the solute concentration was at this point earlier, and then after solidification, it will reach here.

So this is the solute concentration, or this is the total amount, not solute concentration, the total amount of solute that will be moved away. And where will it go? The liquid concentration will increase by a delta amount that is dCL. So this liquid concentration has increased. So we will use his fact to set up the equation. So let us write down how the equation should look like.

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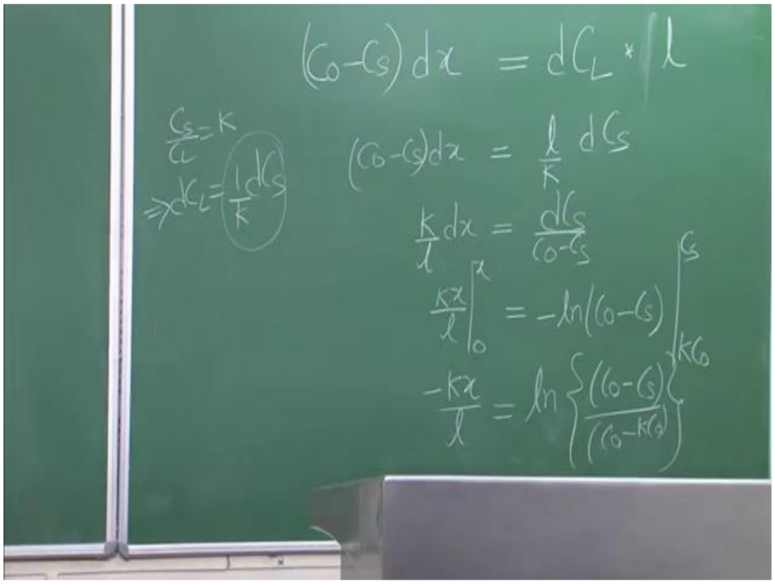

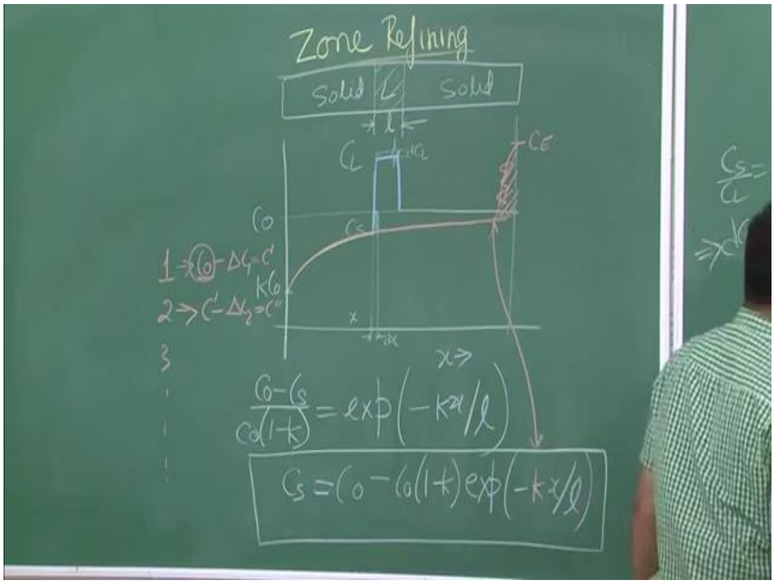

CS is a variable, CL is a variable, but they are related. So C0 minus CS times dx is this total amount of solute, and on the right side we RHS, we have dCL into (DL) into, not DL actually, it is L; dCL into L. So this is the dCL region, and this is the L region. So now we have a equation over here, and what we will do is we will also invoke the relation that CS by CL is equal to K implies dCL is equal to 1 over K dCS. And we will put replace dCL by this quantity 1 over dCS; so we will have a equation like this; or you can make it L over K dCS.

Now let us put K over L on this side times dx is equal to dCS by C0 minus CS. Now when we integrate it, this becomes Kx by L in a range; we will describe the range, and this becomes minus ln C0 minus CS, and the range. So what are the range? X moves from 0 to some value x. So this x goes from 0 to x. And in the same period, what happens to CS? It moves from KC0, you remember the first solid that forms is of concentration KC0; so it moves from concentration KC0 to some concentration CS.

Then we can take the minus sign over here; and I will not write any more over there, I will write the final equation that we should get over here, which will be. So, starting from this equation, if you solve it and using the limits that distance goes from 0 to x, concentration of CS goes from KC0 to CS; this is the equation you will get or to simplify it further or to put it, put CS on the LHS, you will get CS equal to C0 minus. Now what do you see over here? We see that CS is equal to C0 minus some quantity; everything here is positive.

So the concentration of the solid part is less than C0; but it cannot of course happen throughout the length; but this equation from what we see, we see that it will happen throughout the length. That is because we have excluded the final transient zone. So let me to describe it, let me draw it, draw the plot in red. So, let us say this is during the process; after the process how would this plot look like? This would look like something like this. It is all less than C0; so see this is the concentration of solid starting from x equal to 0 to some value of x; and if we go by this relation, it should keep going below C0.

But, at some particular point, the concentration of the liquid will no more be C0, or it will or basically there will not be enough liquid, and all the solutes will have reached that particular concentration. So, it will start to solidify over here; and this would probably be concentration CE. So we are not talking of discs part in this equation; so this equation is limited only upto this point. So whenever we write a equation, you should also be aware of what are the limits, upto which it is being used and in this case this equation is being used only upto this point. And we can clearly see that the concentration of solid, the resolidified solid is lower than that of the original concentration.

Now this is just for one pass. Now let us say you get some another concentration or average concentration from this, which is obviously less than C0. So next time you do it, you will get concentration even lower than that. So that way if you keep doing one pass, you reach C0 minus some delta C1 equal to C prime. Second pass you may reach C prime minus delta C2 equal to C double prime, and so on. So you see, if you keep increasing the number of passes, your concentration is decreasing far below the C0 value, and this is how you get the refinement or purification of the metal that you are using.

And the K value that we have used over here is if you, this over here we have assumed that it is complete diffusion, and there is no convection; but what we can also do is we can have some amount of convection in which case we will have to use the K effective value. And remember one thing that I did not explicitly mention about the K effective, but let me put it over here.

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When you are growing a single crystal of limited length, then we know that, for only diffusion; when only diffusion is (())(09:46) in place in the liquid, this is how the concentration profile looks like for the solid; and if you keep increasing the amount of convection, what happens to this plot; that should where the K effective becomes very useful which I did not explicitly mention earlier, but let me show it now. I am drawing this Z kind of or this zigzag to show that the concentration increases sharply over there, and probably it is out of scale. If you increase the, if the K effective is even different, you may get something like this.

You may see that something, I am just putting some of the, of the tip of the tongue some values; these are not meant to be taken literally, these are just to give you an idea what may, what means when we are changing from complete diffusion to some amount of convection. So, let us say the K value, the actual K value was 0 point 3; when you have, very high amount of convection, the

K prime may reach equal to, K equal to 0 point 3. So if you depending on what is the K effective value, you may get different different kind of distribution or the solute concentration plot.

So this is again you can see one more thing from here regarding zone refinement, that when your original distribution is like this, and if you use the same condition, your new concentration will become smaller and smaller. So for example, this one was KC0, this is K prime C0 for this K prime C0, and your concentration gets the solute concentration in the solid becomes lower and lower. So that is all of the ‘plane front solidification’ in single phase alloy. Now what we will do is we will quickly take look at one example to get a better feel for this.

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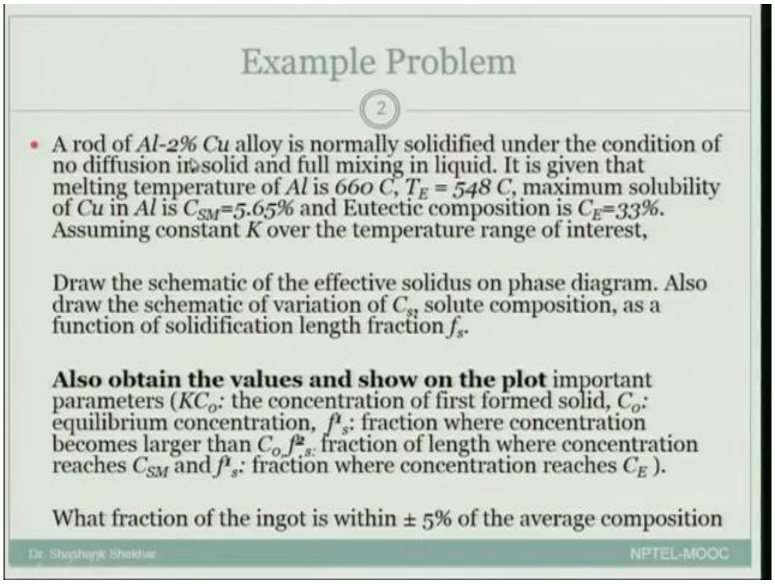

Example Problem

②

- A rod of *Al-2% Cu* alloy is normally solidified under the condition of no diffusion in solid and full mixing in liquid. It is given that melting temperature of *Al* is *660 C*, $T_E = 548$ *C*, maximum solubility of *Cu* in *Al* is $C_{SM}=5.65\%$ and Eutectic composition is $C_E=33\%$. Assuming constant *K* over the temperature range of interest,

  Draw the schematic of the effective solidus on phase diagram. Also draw the schematic of variation of C_s, solute composition, as a function of solidification length fraction f_s.

  Also obtain the values and show on the plot important parameters (KC_o: the concentration of first formed solid, C_o: equilibrium concentration, f^1_s: fraction where concentration becomes larger than C_o, f^2_s: fraction of length where concentration reaches C_{SM} and f^3_s: fraction where concentration reaches C_E).

  What fraction of the ingot is within ± 5% of the average composition

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So let us go to the slide, and what you see over here is a problem that is given with respect to ‘plane front solidification’. What it says is that a rod of aluminium 2 percent copper; meaning aluminium is the main content, copper is your (concen) the added ingredient, so basically on the left side you will have aluminium, and you have added 2 percent copper alloy in is normally solidified under condition of no diffusion in solid, and full mixing in liquid. It is given that melting temperature of aluminium is 660 degrees celsius, TE is equal to 548 C, maximum solubility of copper in aluminium is given, and eutectic composition is given.

So what you are given is that there is no diffusion in solid, and full mixing in liquid. So no diffusion in solid is something that we have always been considering, and the second condition it says is that full mixing in liquid, meaning there is no concentration gradient in the liquid. So let us to get a feel of it, let us draw how this plot should look like.

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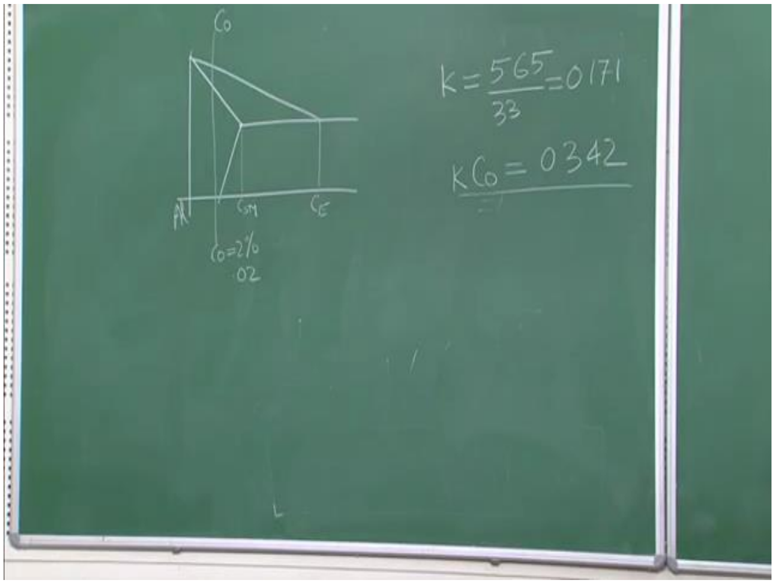

So we are given some C0, that C0 is 2 percent copper; so here you have aluminium, C0 is equal to 2 percent copper. You are given CSM, you are given CE. Now if you are given CSM and CE, you should be able to find K, which is the partition ratio. So we can get K equal to CSM by CE, which is 33, so it comes to 0 point 171. And, we also know C0; so C0 is 2 percent, so let us put it in fraction, so it becomes point 02, or if you put it or if you want to just use fraction percentage, that is also okay. So here we will be using percentage; so it becomes 0 point 171 into 2 is equal to 0 point 342.

So your KC0 value is this. And now let us look at what are the things that we need to find. So let us get back to the slide. Now these are the conditions that we are given, so we have plotted it, and now we have a feel of it. Now let us look at what the questions asks us to do. Draw the schematic of the effective solidus on phase diagram. Well we have already done that. Also draw the schematic of variation of CS, solute composition as a function of solidification length fraction fs. So this (was), this part is also easy.

Now what it asks, next part is the more important; also obtain the values and show on the plot important parameters, KC0, the concentration of first formed solid is C0, the equilibrium concentration, and there are different fractions it wants. f1s, fraction where concentration becomes larger than C0; f2s, where fraction of length becomes, where concentration reaches CSM and it should be f3s, fraction where concentration reaches CE. So, we need to find fractions, and put it on the concentration versus length plot.

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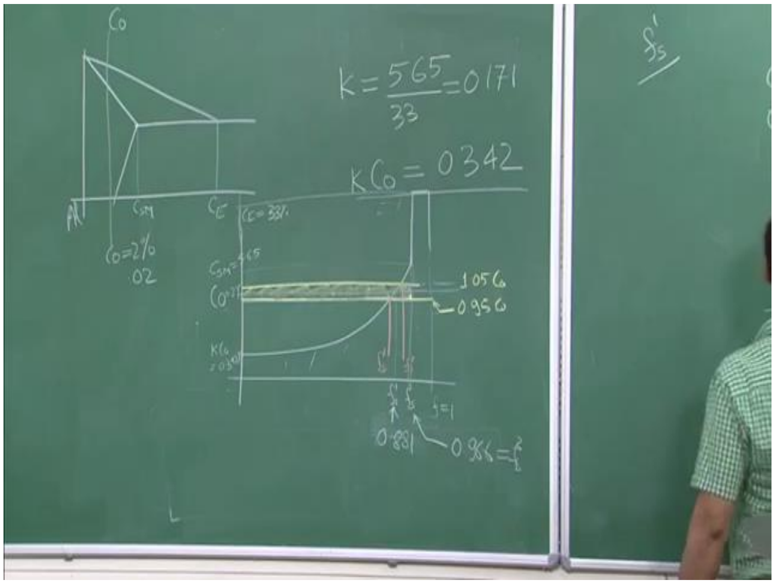

So we will, this is how, first we will draw just in a schematic way how it should look like. This is; so this is fraction f equal to 1. C0 we know is equal to 2 percent; this is KC0, which is equal to 0 point 342 percent. This is where what has been described as fs1. This is the point, this is fs1 because it is at this point that the concentration of solute increases beyond C0. fs2 is the point where it reaches CSM. So this is CSM, which was given as 5 point 65. So we have to find a concentration for this. Then we have to also find the concentration where it reaches CE. So this is CE equal to 33 percent. So the fraction corresponding to this is fs3.

Now we have according to the question we have drawn the schematic for the phase diagram; we have drawn the schematic for the concentration profile. What we need to do now is just find values of fs1, fs2 and fs3. So let us start with fs1. What is the equation that we will use over here? We will use the Shell’s equation; because it is the Shell’s equation that is valid when you have no solid diffusion and complete homogenization in liquid. So let us write the equation which is.

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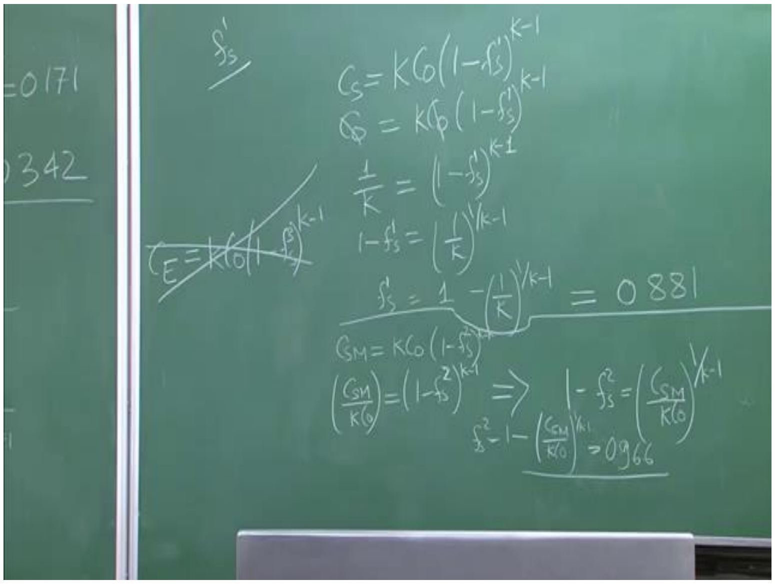


f_s'

$C_S = KC_0(1-f_s')^{K-1}$

$C_0 = KC_0(1-f_s')^{K-1}$

$\frac{1}{K} = (1-f_s')^{K-1}$

$1-f_s' = \left(\frac{1}{K}\right)^{1/K-1}$

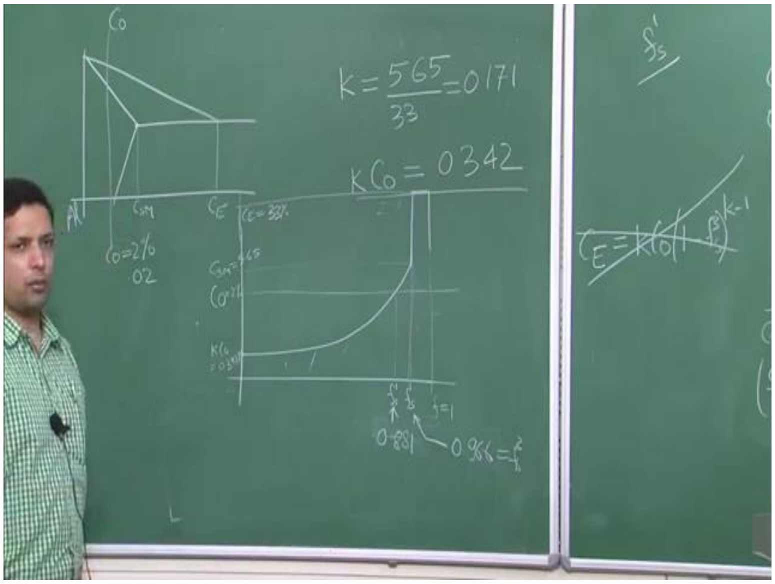
$f_s' = 1 - \left(\frac{1}{K}\right)^{1/K-1} = 0.881$

$\cancel{C_E = KC_0(1-f_s^3)^{K-1}}$

$C_{SM} = KC_0(1-f_s^2)^{K-1}$

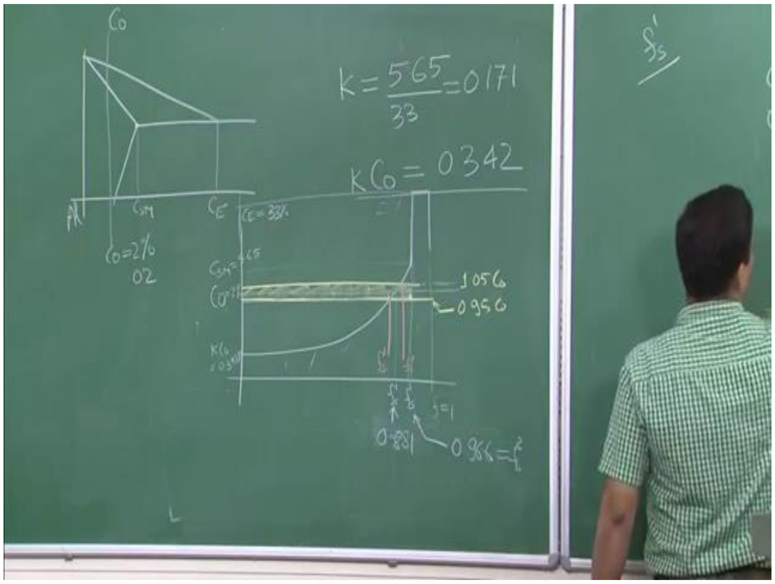
$\left(\frac{C_{SM}}{KC_0}\right) = (1-f_s^2)^{K-1} \Rightarrow 1-f_s^2 = \left(\frac{C_{SM}}{KC_0}\right)^{1/K-1}$

$f_s^2 = 1-\left(\frac{C_{SM}}{KC_0}\right)^{1/K-1} = 0.966$



$k = \frac{5.65}{33} = 0.171$

$KC_0 = 0.342$



What we need here is fs. We know CS for that particular fs, and other values are constant. So for fs1, what is CS? For fs1, CS is equal to C0. So we will put CS equal to C0; so we are trying to find fs1 over here; so this is C0. And therefore, you can take, this becomes 1 over K. So you have to just put in the values, this is, and to be consistent let me put fs1 over here. So this, these are the fs1 values, and when you put in the K values, you would get 0 point 881. So this is fs1. Now next what we wanted is fs2, the point where concentration reaches CSM. What is CSM? CSM is given as 5 point 65 percent.

So we will use again the same equation. Now instead of CS equal to C0, we will put CS equal to CSM which is 5 point 65; so we will put like this. This is fs2. So do not get confused that this is square, it is just a fs2, superscript 2 represents the second fraction that we are trying to calculate here. So I will write over here. Now when you put the values, you would see that fs2 would come out equal to point 966. So we have fs1, we have fs2, and these are the values. Now what about fs3? So do you think what we should also do the same thing. Now if we want to get the concentration fs3 for CSM should be put it like CE equal to KC0. Is would that be the right way?

Well, we said earlier; there is a limit up to which this Shell's equation can be applied, and what is that limit? That limit is this point, the CSM value; because rest of it at that particular point in liquid state, and the point at that point in time, or the point in temperature when the solid reaches this concentration, the liquid reaches this concentration. So both of them solidify simultaneously, and therefore, what you see or the fraction at which you see CSM, it is the same fraction at which the liquid solidifies, and therefore fs2 would be equal to fs3 and this equation is not valid for the, for finding the fraction at which concentration reaches CE.

And therefore, this equation or this plot, we can just simply now write the values; fs1 is point 881, fs2 is point 966 and fs is equal to fs3. So these are the different values of fs and we have also solved it completely and we have found all the fractions that were needed. Now there is a still another part in the question which says “what fraction of the ingot is within plus minus 5 percent of the average concentration?” Which means, we have to find what is the delta fs that lies. If this is C0; let me use a different chalk for this to emphasize. So we can say this is point 95 C0, and this is 1 point 05 C0.

So this question, this part of the question is saying, “what fraction of the overall solid lies within this composition?” Because overall composition was C0; so we want to know if some delta amount of fraction is lying within that C0 fraction, and what is that, what is that delta amount of the length of the fraction. So, here is your C0, and this is the solute concentration, which is continuously changing. Therefore what we need to find here is, this fs and this fs. Let us call it fs prime, and let us call it fs double prime. And, what is the concentration at fs prime? The concentration at fs prime is point 95 C0; the concentration at fs double prime is 1 point 05 C0.

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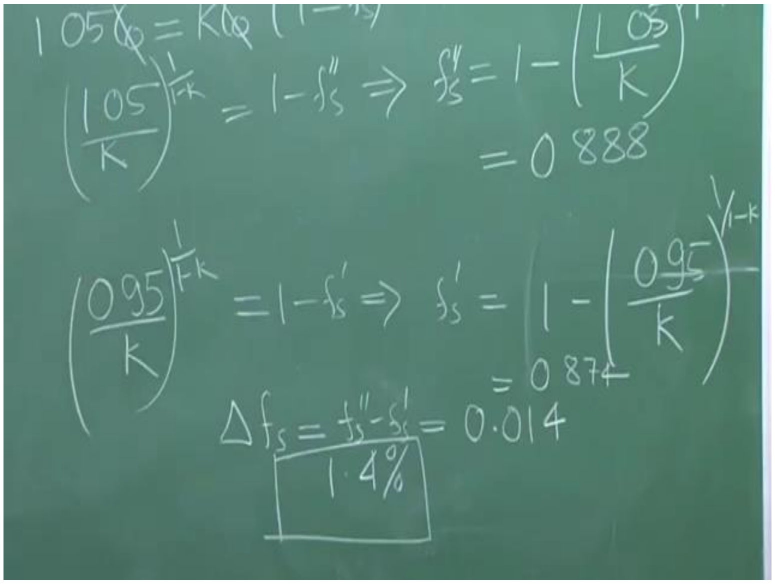

$$1\,05 C_0 = K C_0 (1-f_s)$$

$$\left(\frac{1\,05}{K}\right)^{\frac{1}{1-K}} = 1 - f_s'' \Rightarrow f_s'' = 1 - \left(\frac{1\,05}{K}\right) = 0\ 888$$

$$\left(\frac{0\,95}{K}\right)^{\frac{1}{1-K}} = 1 - f_s' \Rightarrow f_s' = 1 - \left(\frac{0\,95}{K}\right)^{1/1-K} = 0\ 874$$

$$\Delta f_s = f_s'' - f_s' = 0.014$$

$$\boxed{1.4\%}$$

So, let us again use Shell’s equation. So; this is fs prime, or sorry we have put 1 point 05; so it is fs double prime. So this is the relation to get you fs double prime, and you can get the value of fs double prime as. Now similarly, instead of 1 point 05, we could have put point 95; and we will get a value of point fs prime, which is equal to point 874. So the difference between these two is the fraction that lies within this. Fraction-wise, it is 0 point 014, which means 1 point 4 percent of the crystal that has solidified lies within plus minus 5 percent of the overall alloy composition C0.

So you see, it is a very very small fraction that lies within this C0 value. So this is a very interesting information that although the overall composition is C0, but the composition which lies within this plus minus 5 percent of the overall composition is a very small fraction; most of it lies outside. And in fact, most of it lies below it, and beyond this fs, the value that we found over here, point 966, you see values higher than CSM. So at that point, you are getting something like a eutectic.

So this is again another important aspect is, that point 966 is the value at which you reached point the CSM, or the solute concentration at the left most point of the liquidus, sorry left most point of the eutectic, and that is also the point where you reached, the liquid reached the eutectic; so around point 034 fraction of the solid has eutectic composition, which means that you have a very even in this very very small composition, you are able to reach the eutectic composition.

So, that is again to show that even though you may have a single phase alloy with very very minor concentration of the solute, you may still reach a eutectic composition and a two phase region. So with that we will end today’s lecture and we will come back into the next lecture with the second part, which is a cellular solidification. So this was all we had about the planar solidification in single phase alloy; now next we will get into cellular solidification of single phase alloys. We are still with the single phase alloys, but for the cellular solidification. See you in the next lecture.