Phase Transformation in Materials
Prof. Krishanu Biswas
Department of Material Science & Engineering
Indian Institute of Technology, Kanpur

Lecture - 29
Dendritic Solidification

We have been discussing about the different types of growth modes, during solid to liquid transformations. Just recap of the discussion which you had in the last class. You know solid liquid interface can be of 2 different types.

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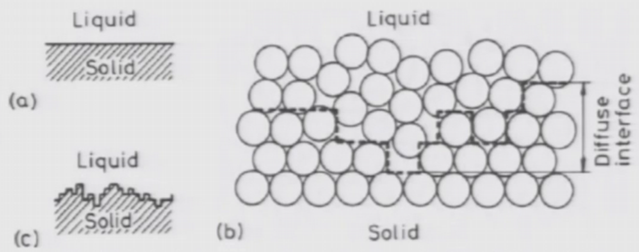

Fig. 3.63 Solid/liquid interfaces: (a) atomically smooth, (b) and (c) atomically rough, or diffuse interfaces. (After M.C. Flemings, *Solidification Processing*, McGraw-Hill, New York, 1974.)

The one which can be atomically smooth, the other one which can be atomically rough depending on the type of interface, the growth modes will be changing right.

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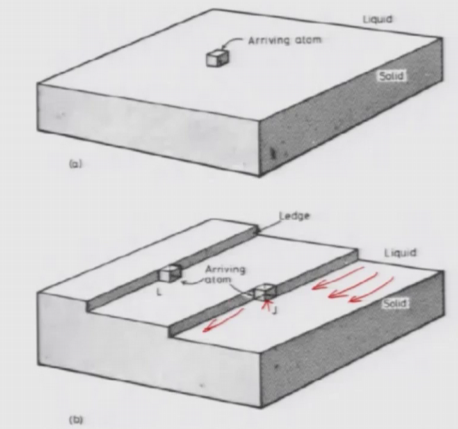

Fig. 4.11 Atomically smooth solid/liquid interfaces with atoms represented by cubes. (a) Addition of a single atom onto a flat interface increases the number of 'broken bonds' by four. (b) Addition to a ledge (L) only increases the number of broken bonds by two, whereas at a jog in a ledge (J) there is no increase.

In case of you know rough interface, where the interface is jaggered, what you need is basically a step or ledge or a kink on the ledge for the growth to proceed and this is very routinely happen in the case of biggest metalloids like silicon, germanium. So, this kind of growth is basically known as step wise growth. As you see here, there is a ledge on the surface, this ledge basically forms because of the surface nucleation and which I have discussed in the last class and then this ledge can also bent and form and kink.

And because of this kinks, an atoms from the liquid can arrive nicely and sit on this position known as J, mark as J here and then make the further progress of this step in this direction, slowly, steps will move like this and so, the one layer of the solid will be convert, liquid will be converted into one layer solid and then further goes things happens.

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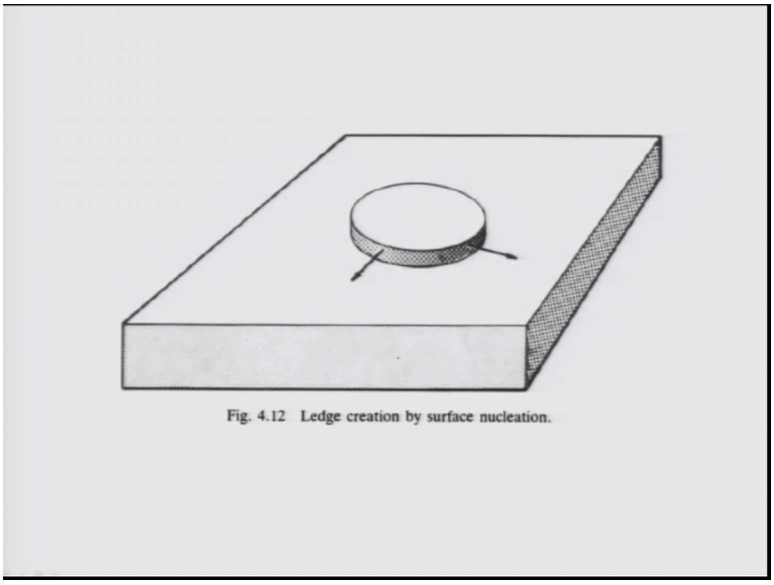

Fig. 4.12 Ledge creation by surface nucleation.

And surface nucleation is the main mechanism for the ledge creation. Ledges are created because of this surface nucleation. Surfaces which are basically kind of a very rough in this way, so there can actually have such a nucleation happening and that this can lead to promotion of this step.

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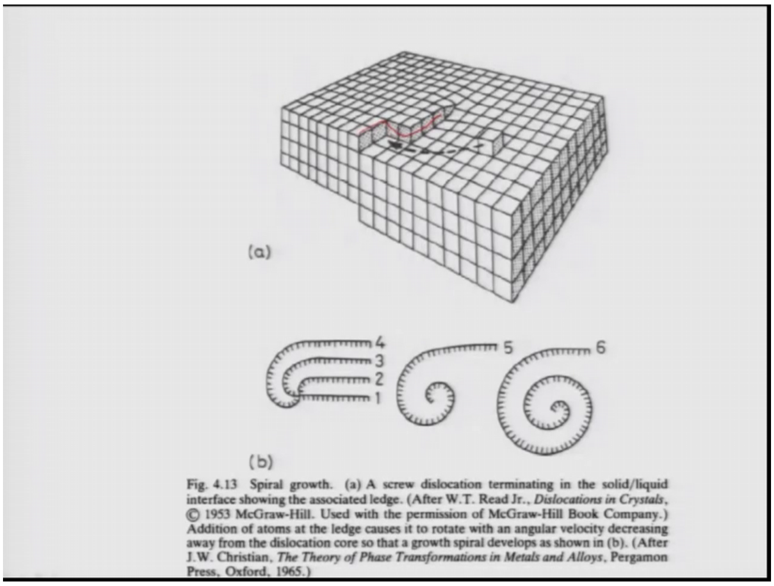

Fig. 4.13 Spiral growth. (a) A screw dislocation terminating in the solid/liquid interface showing the associated ledge. (After W.T. Read Jr., *Dislocations in Crystals*, © 1953 McGraw-Hill. Used with the permission of McGraw-Hill Book Company.) Addition of atoms at the ledge causes it to rotate with an angular velocity decreasing away from the dislocation core so that a growth spiral develops as shown in (b). (After J.W. Christian, *The Theory of Phase Transformations in Metals and Alloys*, Pergamon Press, Oxford, 1965.)

Well, step on this surface can also be create by screw dislocations. A screw dislocations is shown on this surface, as you clearly see, this is step where which is bent. So, because the atoms can go and sit there the screw dislocations start rotating itself to keep this positions intact and this is normally happens in the screw dislocations. Suppose, you have edge dislocations, that edge dislocations will be slowly converted into a dislocation free structure. But, where screw, it is not possible, because of its nature of bents and this can lead to the further growth of the phases. Further growth of the system is in the positive directions.

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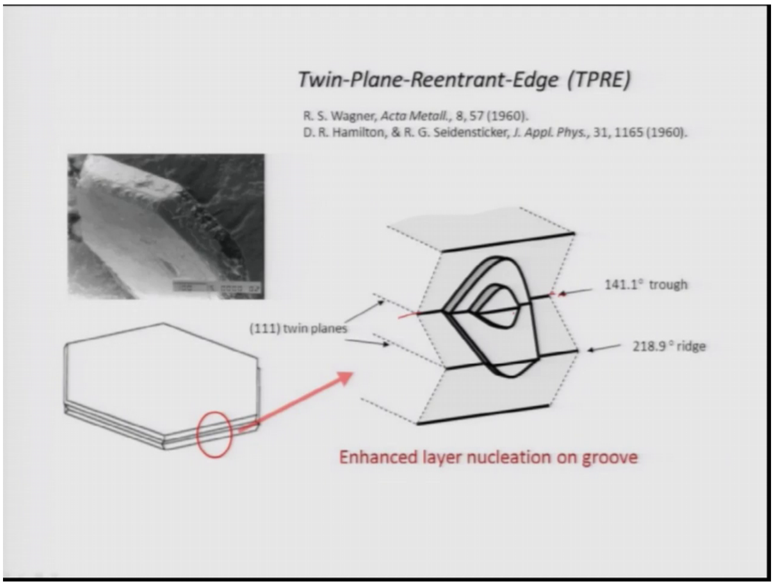

You can also have a new mechanism or it is already there, what is known as Twin Plane Reentrant Edge or T P R E. This is proposed by professor Wagner, long back and later on substantiated by D. R. Hamilton and R. G. Seidensticker in 1960s actually. What you can have is, basically, you can have a twin formation on the surface and when these 2 twin planes meet, they create a reentrant edge and this reentrant is shown here, this is a reentrant edge you can see here.

Basically, there are 2 ridges here, which are actually 218.9 degrees and these 2 ridges when they meet together they form a reentrant angle and this reentrant angle is at an angle of 141.1 degrees. Enhance liquation on this edge, on this groove actually, not edge, groove easily possible when the liquid atoms come and sit there and join the solid. These are the actual pictures which can happen in case of silicon; silicon crystals are basically like that and therefore, there are varieties of ways, such a kind of growth mechanism possible like dislocation mediated or twin mediated or even by 2 towards the surface nucleation.

But on the other hand for the atomically smooth surfaces where there are this diffuse interface; that means, there is huge layer between the solid and liquid. Atoms actually can easily sit on the surface and grow and that kind of growth is known as continuous growth. And this growth, which is basically by twin or the dislocations or by surface nucleation is basically known as step wise growth.

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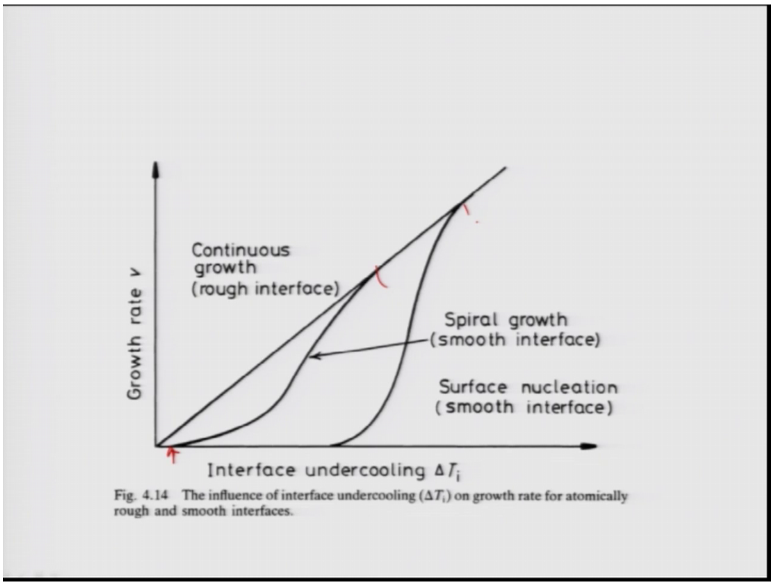

So, now we can actually is possible to calculate the growth rate and all this growth rate will be function of undercooling. I am not doing the whole mathematics here, it is there in the book or you can actually consult each of this case. I have done for the continuous growth as shown you this is directly proportional to delta T. So, therefore, the growth rate v as is basically a straight line for the continuous growth.

And for this spiral and the surface nucleation dominated growth they are not directly proportional to delta T, but they are proportional to some functions of delta T and they are basically exponential function there to see as you seen from the nature. So, basically the growth rate by surface nucleation is very slow at the initially. It requires a larger undercooling, that is because it need surface nucleation and nucleation require to create new surface to each generated. And that is why you need more driving force and the more diving force means more amount of undercooling. On the other hand spiral growth, which is, basically because of the screw dislocations is, does not require much undercooling, you can see this undercooling curve is respectively low. So, and it starts of and it goes and then finally, it is at high undercooling. Thus, this growth can be all the actually go there will be same as like continuous growth, that is what you see here and there. This is the basically very important plot, in the sense that, at low undercooling continuous growth rate will be the maximum, but high undercooling, all the growth rate is will be similar same.

In the intermediate undercoolings, normally the spiral growth will be go that will be higher than the surface nucleation growth rate. So, depending on the amount of undercooling (Refer Time: 06:21) the systems, the growth rate for these systems can vary, it can system can choose depend on undercooling which growth more to be adopted. So, that is fine that is about the different growths.

But, what is the growth morphology; you know solidification means what, as the liquid solidifies to a solid or forms a solid there is a latent heat evolution of the interface. Now, because of this latent heat evolution, because latent heat is getting released, that will heat atmospheric conducted away or it may be convicted away by the liquid or the solid, solid to the liquid. Depending on the how the heat transfer happens, the interface morphology can change and we are going to discuss for the case of a pure metal, what happens to pure metal when these kind of situation arises.

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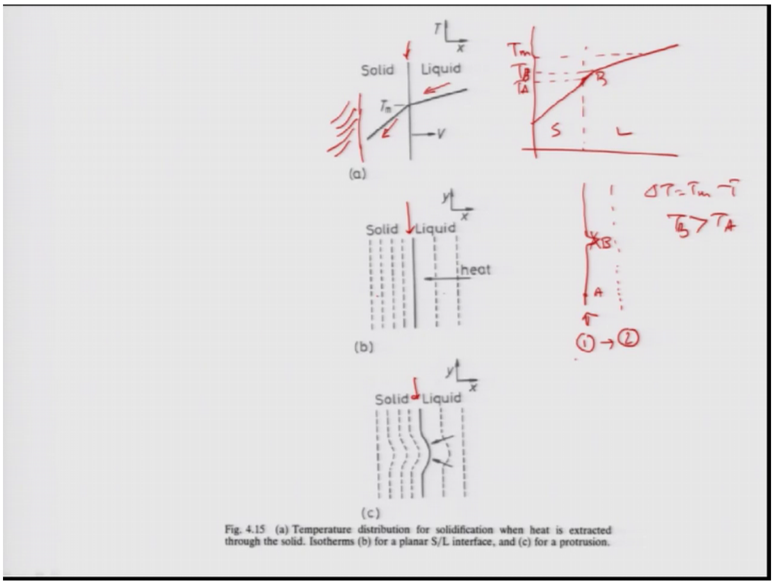

Again we are going to discuss 2 cases; first case is basically for a solid liquid transformation, in which the temperature gradient is the positive in the liquid and the solid, but it is there is a interface between the solid and liquid. Remember, heat transport it depends on the temperature gradient, developed in the system. So, because of the difference of temperature from one place to other, the temperature gradients do develop in the system. Let us suppose, we have a solid, liquid, you can see this is solid, this is liquid and as the liquid solidifies and forms a solid latent heat it is released at the interface.

Therefore, if the situation is such that, the liquid has been poured into a mold and the mold was at room temperature and liquid was in very high temperature, because of this solid forming at that mold wall, the heat will be transported to the mold wall and such a case liquid will be always at a higher temperature then the solid and plus the heat is getting transported through the mold wall. So, therefore, the temperature gradient develop from the liquid to interface, interface to the solid.

And this interface is shown as a line here, you can see here or you can see here, you can see here, these are line. Now, as you see here, because temperature gradient is high, the temperature gradient is positive rather in the liquid, so what will happen, because of that the heat will transport from the liquid to the interface and the interface to the solid and to the solid to the mold wall, this is the mold wall suppose. That is how the heat transport will happen because of the temperature nature of the temperature gradients created.

Now in under such a situation you know if I suppose if I have a small protrusion created on the surface what will happen then well as you can see suppose if I draw the draw this picture here and this is my interface this is solid this is liquid, temperature gradient is having like this there is a temperature gradient liquid in the solid and let us suppose this point is mark as a B and suppose I mark this point as A and this is my interface, now you know I can clearly see that B will be at a higher temperature, this is point B, if I mark it here. So, B temperature is T B, I marked it here T B and A which is on the interface itself is temperature is T A, I have marked there and the melting temperature is given some over there this is T m.

Now, this is the temperature profile because there is a there is a protrusion created on the surface, this is what the temperature profile, now what will happen; you can clearly see the temperature of B is higher than temperature of point A; that means, the total undercooling, undercooling is nothing but, delta T is nothing, but T m minus the temperature T and for the B is basically T m minus T B about a it is T m minus T a and a is lower than T b. So, therefore, undercooling at A is higher than undercooling as B and because the temperature of B is higher because T B is higher than T A and undercooling is low. So, therefore, the even if this protrusion is forming there it will go away why because it will not field you know undercooled more than these flat interface. So, because it is not feeling undercool more than this flat interface, it will not able to grow, because, growth is dependence on amount of undercooling available, of the undercooling available to point B is lower than undercooling available point A, so, therefore, A will go faster and that is why this interface will become given as a flat even is grows from position A 1 to position 2.

And in this process any protrusion which is forming on the surface will be melted away. So, this one will vanish, this thing will vanish, as the system moves from one position to position 2 and this is exactly what happens, when you have a positive temperature gradient the liquid this situation is very common in welding. Suppose, you are using a heat source to make the weld pool, is may be lesser or it may be anything else electron beam or gas or a arc.

So, because, we are using a heat source on the top, on the joining positions, so, therefore, the temperature gradient on the liquid will higher. It is very simple, because, you have heat source is placed on the joined pool, so, therefore, the heat is provided on the surface as, because of the temperature from the bottom of the pool to top of the pool will be positive, temperature gradient will be positive and the same situation arise and because of these in all this welding or you know situations, temperature gradient is positive in the liquid and interface do move like a flat one or continuous growth happens.

Interface will not be forming such a kind of protrusion on the surface that is very clearly observed even in experimental conditions and this is why positive temperature gradient will induce continuous growth or the growth of the flat interface, across solid liquid interface region will be happening like a continuous manner and this will never be able to form any protrusion on the surface. On the other hand, the situation will be completely different; if I have negative temperature gradient the liquid, this situation is more prevalent in industrial conditions. Suppose, I have a mold, which is little bit heated up, it may not be at room temperature; it slightly higher the heated up and we pour a liquid hot metal actually into this mold and because temperature in the liquid you know in the mold wall is little higher. So, because of that, any solid from the mold wall, will be at a temperature, higher than the liquid temperature obviously, when the solid forms in a mold wall, a little latent heat will be released.

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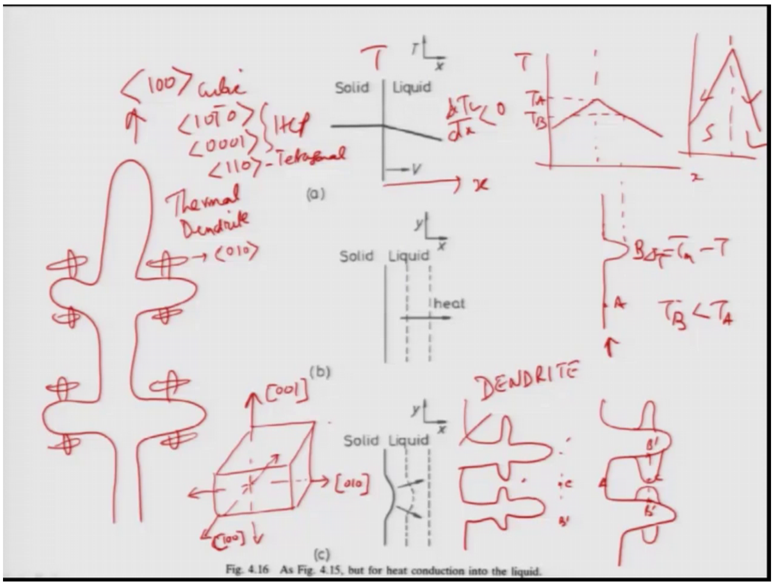

And the latent heat is transported to the liquid, because of this negative temperature gradient; the solid will grow much faster in the liquid, as compared to the one which have seen in the last case. So, none the less, even if such a situation arises in the liquid, when the temperature get into the liquid, you can see this is the distance x, that is what is shown as temperature T, so therefore, you can see the slope of this curve is negative.

As the slope of the curve is negative, what will happen to the same situation, which I have drawn there; let us draw it here, let us suppose I have a flat interface and there is a protrusion created there and I am drawing the interface here and the temperature getting in the solid is positive, but temperature get in the liquid is negative and this is temperature, this is distance x and let us suppose that, this is point B and this is point A, the point B is on the protrusion, point A is on the interface.

So point B and point A, point B temperature is where, point B is here, point B temperature is some, point A is temperature is this one T A and point B temperature will be somewhere there, this is point B, we control the point B there, this way, what you see here, very clearly, because of negative temperature get into the liquid, the point B, temperature T B is less than T A and therefore, the point B is undercooled more than the point A, because undercooling is again define as T A minus T. Now as T B is lower than T A, total undercooling delta T is higher on point B than A. As B is getting undercool more than A, so B will have more driving force to grow. So, therefore, the protrusion which was formed on the interface, as so here will grow and this protrusion will lead to the breakup of the interface.

Interface which was flat in a earlier case when temperature get into the liquid is positive, will now break up and form this kind of large protrusions on the surface. Remember this protrusions can easily form like this; suppose, if I draw a simple picture, I have suppose 2 protrusions created and this is point B, this is also point B, let us suppose these are point B prime, B prime and this is point A and if I draw a vertical line and this is suppose point c now what will happen, you clearly see, that at point C the liquid is, you know more undercool than point B.

That is obvious, because the point B is basically sitting on the solid surface, because this is already a solid and because this solid is solid any further growth of this solid, will lead to revolution of the latent heat. And this latent heat whatever getting evolved here, because with solidification happening further, will heat up the liquid nearby point B. So, therefore, C which is far away from point B prime, here you can see here, these 2 are the point B prime which are far away from these 2 positions will be more undercooled and because it is more undercooled, so what will happen, it is very easy to form another you know let me try to firstly, so, what I have done is, like this, I have drawn 2 protrusions and I have drawn 2 points, B prime and B prime here and then I have drawn here point C this is point A.

So, as point C is basically getting undercooled more than the point B prime to B prime; see obviously, A is at a higher temperature, so, the question of A does not arise. Just to show I have drawn A, because of these higher undercooling and point B, point C sorry compare to point B prime, the protrusion will be forming like this and growing. It can be grown like that. Finally, what happens, if I actually have to draw the whole picture, so, it will be like a tree like structure will form and this tree like structure which forms on interface are known as dendrites. Dendrite is basically a word originated from a Greek word known as Dendron and Dendron means tree.

So, finally, we can actually create a very large tree like structure, like this, is a tree. It looks like a tree, you can actually create sub branches of the tree or even more further sub branches like this, in the same way what I discussed just now. And this is what is known as a typical dendrite in a solid, when the liquid transforms to the solid; obviously, we are discussing a pure metal. So, there only think which is important here is a transport of heat because there is no alloy, there is no solute. So, therefore, thus is very clear that the which are which will be forming because of the solidification, pure metal will be basically the growth of that will be dictated by the type of temperature gradient, which develops in the liquid.

If the temperature gradient is positive in the liquid, no dendrite tree like structure will form; even if they form, they will melt back or they will be vanishing from the system. But only when the temperature in the liquid is negative, please remember this word temperature in the liquid is negative; that means, the sign of the term del T by del x that is what is your temperature gradient right del T by del x or d T by d x in one dimensional case.

When this is negative in the liquid, this is liquid, then only the dendrites can form and dendrites will form because of the mechanism which I told you just now. So, such dendrites actually known as thermal dendrites because they are forming because of the heat transport, they are known as a thermal dendrite. Their growth basically depends on how fast we can transport the heat, that is the basically the important aspect. Now, this fast or slow transport of the heat will depend upon how long the temperature gradient. The temperature gradient is very high, then the heat transport will be faster as you know, because this specifically given by the Fourier’s law. The heat transport of the flux depends on the temperature gradient, just like a diffusion equation.

So, therefore, the higher the slope of this curve on the liquid, the faster is the heat transport, remember from the liquid to the interface to the solid. Again, if I want more heat transport from the solid to the mold wall I need a very high temperature gradient. Therefore, if I draw such a kind of curve like this; this is where the temperature gradient are much higher in the both, in the liquid and the solid. So, therefore, because of that the heat transport will be very fast both in the liquid and solid and this will lead to faster growth on dendrites; and that is what is done in the rapid solidification. Rapid solidification systems like when spinning or even atomization or thermal spray, this exactly what happens the temperature gradients are negative in the liquid and temperature gradient values this absolute values are very high and because of that heat transport is also very high.

Remember these dendrites do grow along certain crystallographic of directions. They do not grow any odd directions. Normally, for the cubic crystal, this crystallographic directions are 1 0 0. There is a many reasons for that, we will not discuss in details about why they grow along 1 0 0 directions, but the crystallographically, you know low index directions is what is has been found which along dendrites grow for the cubic, this is for the cubic; for hexagonal is basically 1 0 1 bar 0 or 0 0 0 1 these are the 2 growth directions which has been found for H C P crystal. Another hand 1 1 0 is found in tetragonal crystal. So, for every crystal structure there is well defined growth directions, normally observed when the dendrites grow. Therefore, if this is 1 1 o direction, so this will be pertaining to that, this one, this will be 0 1 o.

So, in a 3D, that is what you seen in 3 d structure, there will be 6 arms of dendrites and because in a cubic crystal there is 6 1 0 0 directions. That is very clear, if you draw a simple cubic unit cells there are 6 1 0 0 directions; this is 0 0 1, this is basically 1 0 0 and this is 0 1 0. So, I can always have 6 directions like this, you can clearly see the 6 directions, 1 2 3 4 5 6. That is why you always see the 6 arms of dendrites in the real 3 dimensional sets.

Before going into that, let me first show how things happens. This is taken from Reed-Hill, Physical Metallurgy Principles, is very interesting book.

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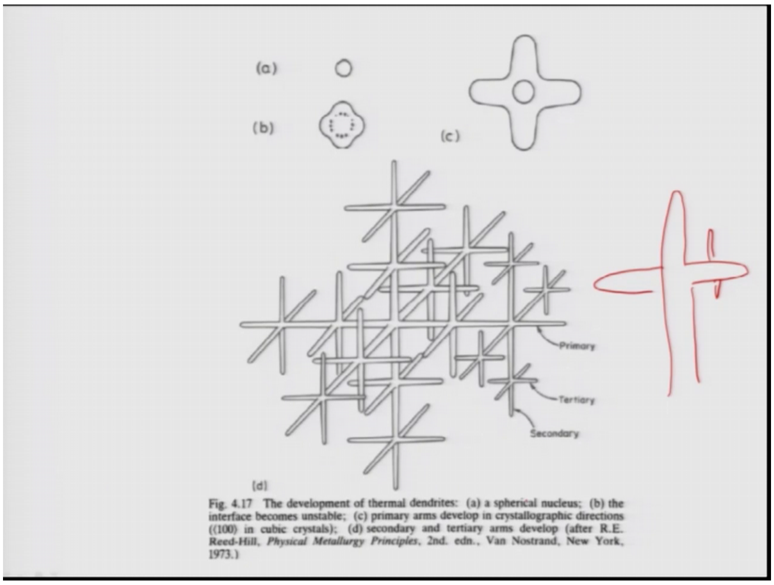

You can see here, this is a typical tree like digenetic structure in a solid and this arm is known as primary, because this is what again I draw, this is known as primary, this is known as secondary, I am drawing only one part and you can also have a tertiary; primary, secondary, tertiary, you can see here, shown there. So, they all under 90 degree angle each other in cubic crystal because 10 0 directions are at 90 degrees with each other. That is why and this is observed in a real situations.

Well, the reason behind this surface energy between solid and liquid which is the most important aspect, which play a role. In the solid crystals actually surface energies are anisotropic, the interface energy between solid and liquid basically anisotropic and because of that they preferential go along 10 0 directions. This is very important at that most of the crystals or the dendrites they grow is basically one over directions. Now I will show you some pictures before I go into the next class, just to show you some dendritic growth, dendrites, where next class will be waste on things, real pictures actually these are micro structures.

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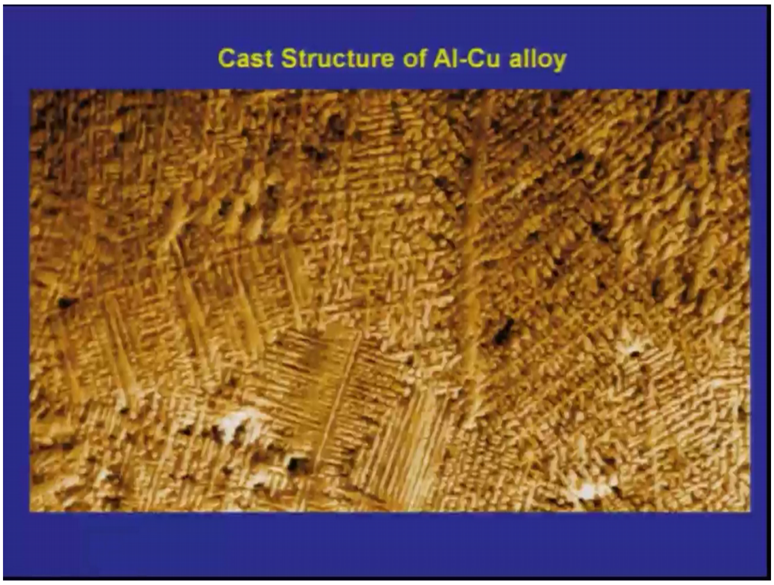

This is basically taken from a cast aluminum copper alloy, you can clearly see the different dendrites here, one here sorry one there is very clear can be seen, this is one, this is another one, many sets are there actually. So, cast actually consisting of lot of this dendrite. This is alloy although, because in pure metal, showing a dendrite is very difficult.

Basically, that way we show the microstructure by using a chent. Basically using some etching process; etching process means we use basically chemical etch, chemical, either acid or base something to react on the surface of these alloys or metals. You know in pure metals normally reaction will be uniform, but in alloy directions will be preferential. Some elements will reacts strongly than other and because of that it will leave the structure nicely revealed under opticalized micro structures. So, in a pure metal also dendrites do see, are seen, but they actually known as thermal dendrites that I told.

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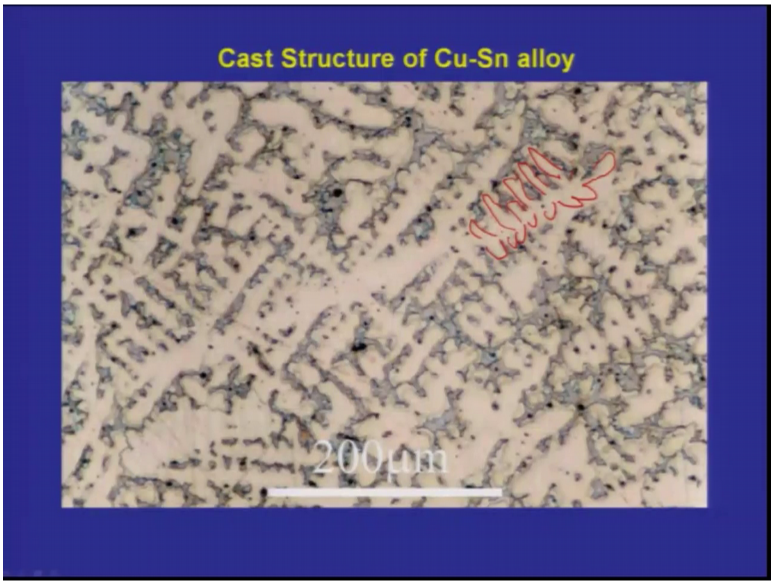

Like, this one basically copper tin which is a bronze, and as you see here, these are dendritic structures which are revealed. There is some other phase beta which is present as a (Refer Time: 26:09) basically dendritic phase and you can look at some of these places and see the dendritic structure developing, you can see here, this is what the dendrites, everywhere.

And in between the 2 denditic arm something else as formed as, it is little bit cumbersome to observe, but you can make it out by this way, that is what is dendrites is. So, many things are there.

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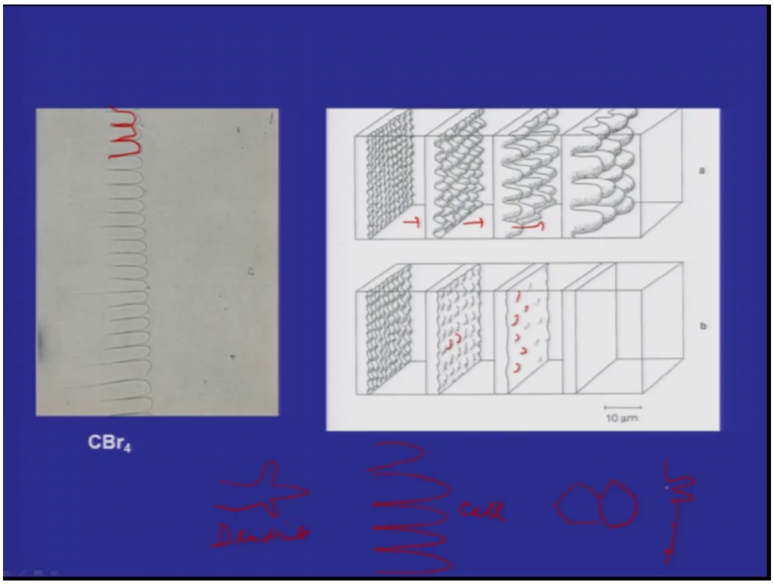

Now, we will go back then dendritic structure later, but to show you how evolution happens actually in dendrites initially the flat interface will be broken, you can see, this is the flat interface; some kind of protrusion are formed. And, this protrusions have grown off, and they are grown up bigger and bigger and finally, they form a structure and this is basically known as a cell, because cell is nothing, but a dendrite without any side arms. The moment you develop a side arms, it is called a dendrite, but the moment you do not develop a side arms it is called a cell. Basically, they looks like this is dendrite, this looks like a basically the honeycomb structure, that is what is shown here.

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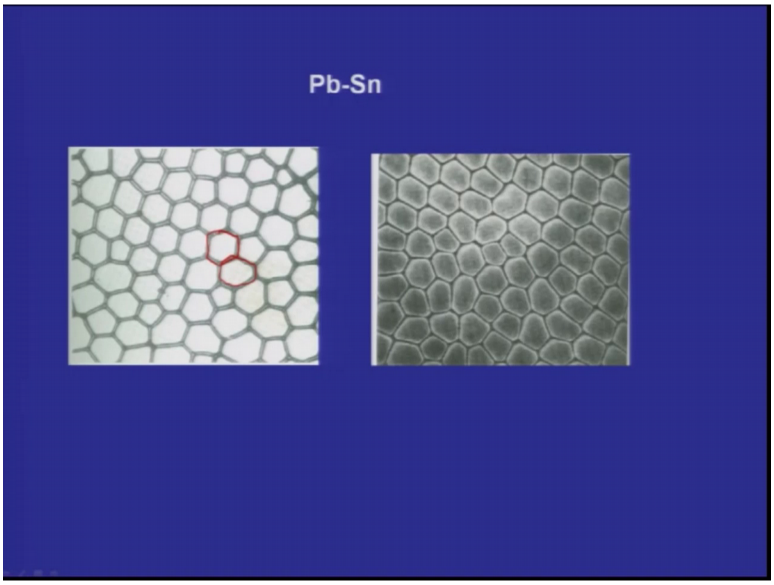

External cell in a tin alloy, you can see each of this external networks, out of the solid interface, let in a slow melting point solder or material basically, so, you can actually do that very easily.

So, the cells can be like one I drawn, this one or it can be like a external units, is possible to have that; but the origin of this cell is basically, because of these formation of these kind of a you know small perturbation which are basically there or basically on the surface you form a kind of a such a kind of things and these things then grow because of the diving force, high diving force available to then I just discussed just now.

So, the next lecture we are going to discuss what will happen to the, you know heat transport and how you can put it an mathematical form and also when you have alloy. Because, in case of alloy, if you have a solid which is also be ejected in the liquid and because of the ejection of the solid, you have a heat transport and solid transport both are present and this is going to be changing the whole situation differently than what you have seen just now.