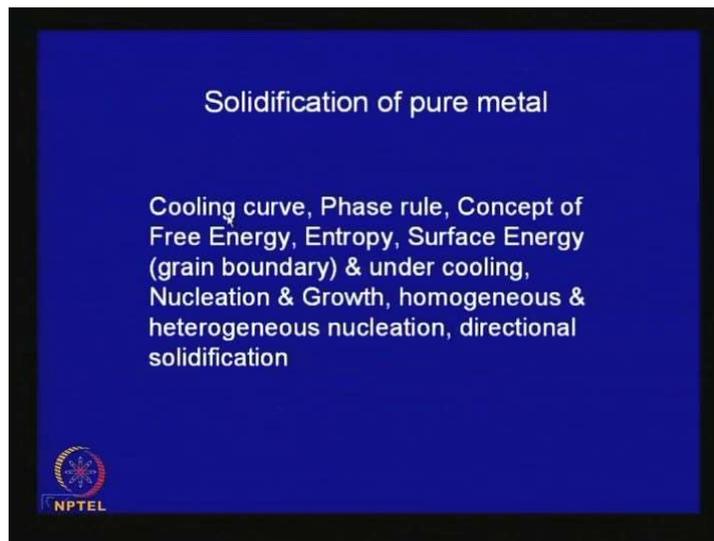


Principles of Physical Metallurgy
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Lecture No. # 07
Solidification of Pure Metal

Good morning. Today we shall begin a new chapter. This is on solidification of pure metal. Metal is mostly used in its solid state and its structure depends on how it has solidified during the process of solidification.

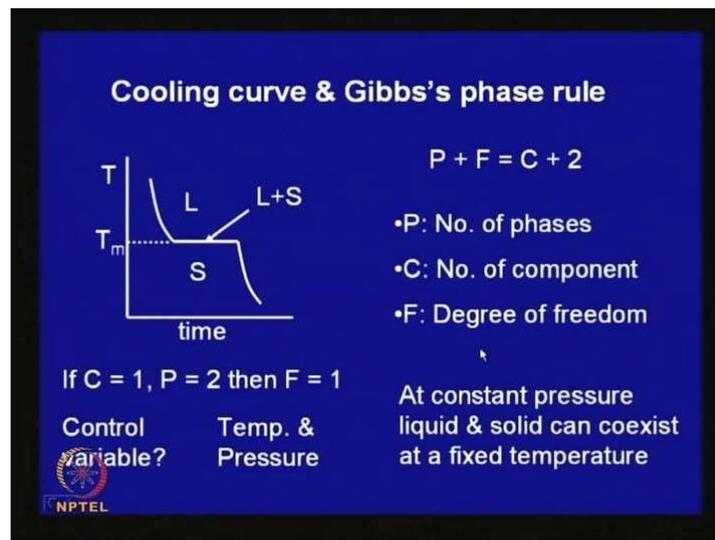
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So, we shall look at it in little detail and under this, we will cover the nature of cooling curve, we have already talked about it during thermal analysis. During the process of solidification, it will pass through a state, when both liquid and solid will be coexisting, and phase rule states; defines, how many phases or what are the variables, which can control this. We will also introduce concept of free energy, entropy, and surface energy. They are very important concepts to understand the process of solidification. We will also explain: why for solidification to proceed some amount of under cooling is necessary and the process of solidification is a time dependent process. There are two steps and these are called nucleation: when a certain number of very small nuclei of solid will form in the liquid.

We will look at energetics of nucleation and there after nucleation, there is a time dependent growth process: Former; nucleation: this is probabilistic / stochastic in nature, whereas this is deterministic. It will follow certain growth rules. We will make a distinction between homogeneous and heterogeneous nucleation, what they are and then we will also look at the constraints which are imposed on liquid metal during solidification and why the solidification proceeds in a particular direction. And this has been used to solve or to get particular desired properties and textures in materials.

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Now, let us look at the cooling curve of a pure metal, how does it look. Say at a particular temperature above it is melting point, it is liquid. Structure of liquid is quite different from that of solid. We have seen that solids are crystalline. Atoms in solids they are arranged in a regular periodic fashion. Solids are incompressible its bulk modulus is very high. In comparison to this, liquids flow easily, whereas solid: it does not flow, unless you apply certain stress it does not flow, whereas liquid will flow on its own and it can take the shape of the container where you keep it. That is not so in case of a solid.

This is primarily because atoms are not as closely packed as in solid, secondly the atoms are mobile and you can say that atoms are arranged in a disordered fashion, but there may be some amount of short range ordering. Using x-ray diffraction technique; the density of packing also has been estimated. Say: in case of solid, we have seen that coordination number; that maximum coordination number in metal that you can have is 12 in face

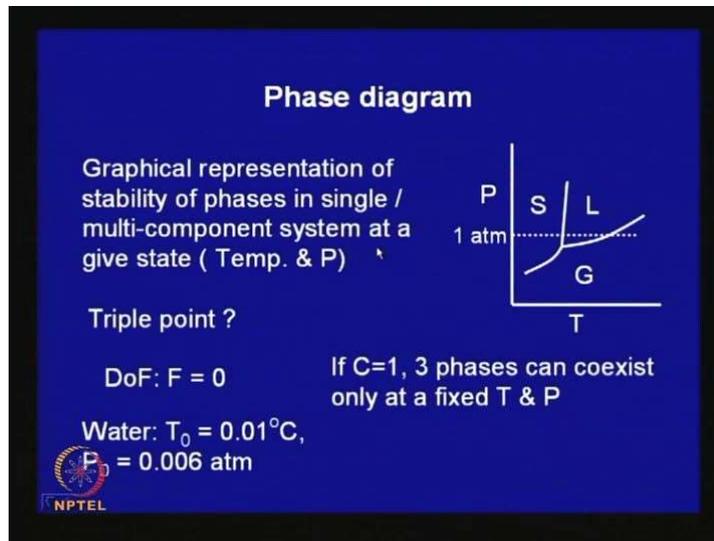
centered cubic, whereas same metal, which has in solid face centered cubic structure; if it gets converted to liquid possibly, you won't have that 12 as the coordination number. Coordination number, will be less than 12. But nevertheless; still it's quite high maybe 10, 11.

And when, the liquid cools, the plot temperature-time, it can be a smooth curve like this, and this will be primarily determined by the temperature of the metal and the surrounding. And usually this follows Newton's law of cooling. And that is why I have put it like this, and when it reaches freezing point: that is the time, if some amount of solid forms then the two phases will coexist for certain length of time, liquid and solid. And during the solidification process, it will release heat also and you will find that here, for some time that cooling just stops. It maintains a constant temperature until solidification process is complete. Once this is completed, then again, the temperature keeps dropping.

Now, Gibbs's phase rule gives us a simple relationship between the number of phases that can coexist at a given condition: experimental condition. Normally by experimental condition: we mean say the temperature is one and maybe the pressure at which you are doing the experiment. Usually for most practical applications, this pressure will be one atmosphere. So, you have two control variables: temperature and pressure and Gibbs's phase rule states it like this: $P + F = C + 2$, where P is the number of phases, C is number of components. Now, in case of a pure metal the component: that's just 1 metal, so number of component is 1 and F represents degree of freedom. Basically, it is number of control variable that you have. Basically here, the control variables are temperature and pressure.

Now in this case, when during the process of freezing, you have two phases liquid and solid coexisting in that case, number of phases are two and then if you substitute here, you get degree of freedom is 1. And in fact, this 1 degree of freedom means it is the pressure. So, this temperature: freezing point or the melting point is fixed for any metal is fixed at a given pressure. If you change pressure, of course, this melting point can change. So, at a constant pressure liquid and solid can coexist at a fixed temperature. So, this is the outcome, I mean, this is the prediction or what Gibbs phase rule states and this is applicable to even multi component systems.

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Now, what is the phase diagram? Basically, phase diagram is a graphical representation of the stability of phases in a single or multi component systems at a given state and a state is defined in terms of control variable. Say, usually only two of these; out of temperature, pressure and volume, only two you can control and for most practical purposes, we can control temperature and pressure. Now, let us look at how this stability of a single component system depends on pressure and temperature. And this is shown over here. This axis represents pressure. This is temperature and you can have a pure metal, say: you can have 3 different states: liquid, solid and gas.

And this pressure temperature diagram gives us the regime in which the solid, liquid or gas is stable, which is shown here like this. There are 3 important lines and this line represents the equilibrium between solid and gas. There is a possibility, the solid can be transformed entirely to gas without going through this liquid route. Similarly, you have this line, which represents the equilibrium between solid and liquid and this line represents the two-phase equilibrium between 2 phases: liquid and gas and suppose 1 atmosphere line intersects here. In that case this is the freezing point of the metal and this is the boiling point of the metal. This particular point is a critical point, which represents equilibrium between all 3 so; that means, under this condition all the 3 phases solid, liquid and gas can coexist. So, for this particular case, if you try to apply phase rule you find for the triple point the degree of freedom is 0. So, for any material any pure material, say water this is a fixed point and this is written over here. This $T_0 = 0.01^\circ\text{C}$ and pressure at that point is 0.006 atmosphere. (No audio from 11:20 to 11:28)

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Gibbs's Free Energy (G)

A thermodynamic parameter representing stability of a phase.

$$G = H - TS$$
$$dG = V dP - S dT$$

Liquid = Solid

$$dG_{lq} = V_{lq} dP - S_{lq} dT$$
$$dG_s = V_s dP - S_s dT$$

H: molar enthalpy
S: molar entropy

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Now, let me introduce the concept of Gibbs free energy, if we put an analogy, this is some kind of potential. Say like energy, you know, or let us say electricity flows from higher potential to lower potential. Similarly, any transformation when it takes place; it will take place in a direction: from a higher potential energy to a lower potential energy. And Gibbs free energy you can say it is an analogy; it is something similar to chemical potential. And we know that, from second law of thermodynamics that although the entire amount of mechanical work can be converted totally to heat, but it is impossible to convert totally the heat into mechanical work.

So that means, in a system there is always a part of the energy, which is not accessible, which you cannot transform. And Gibbs free energy: it is a thermodynamic parameter. You can see that it determines stability of a phase. Any phase, which has a lower free energy will be more stable and this is defined as G is the Gibbs free energy, it is H means, it is molar enthalpy, minus T is the temperature in degree Kelvin times a term called entropy (S). The entropy is a measure of disorder and if you multiply this entropy by the temperature, this gives a measure of energy which cannot be converted. It is locked. Whatever is left is the free energy $G = H - TS$.

And we use this expression; whenever, there is a reaction taking place at a constant atmosphere and for most practical experiments or processes, the atmospheric pressure is constant. And usually it is 1 atmosphere pressure. There is a differential way of

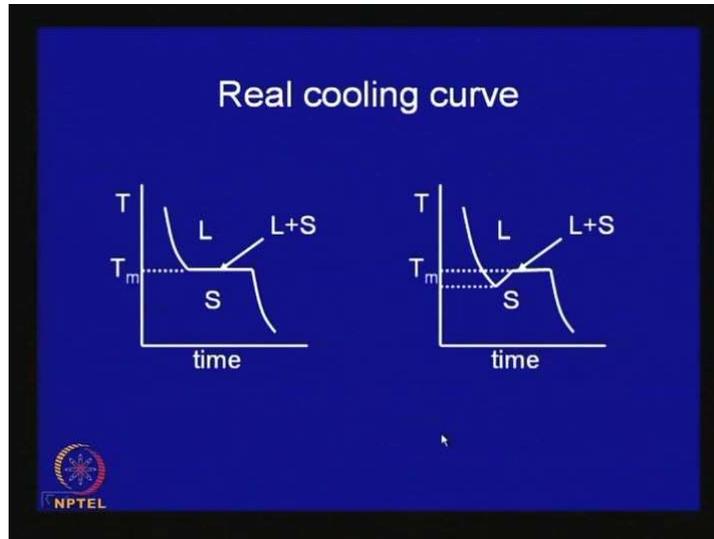
representing this. And this is simple thermodynamic principles. You can convert it and write in differential form that is dG . You can convert it from enthalpy and entropy to pressure and temperature, because these are the easily controllable variables. Then it comes out that the incremental increase in free energy: $dG = VdP - SdT$.

Now, let us look at the process of solidification. We are concerned with the stability; relative stability of two phases: one is solid, another is liquid. And if you try to plot, this is solid not entropy here: this line represents the free energy as function of temperature for solid and this line represents free energy of liquid as function of temperature. Now, let us look at it at high temperature: which has lower free energy? It is liquid. So, at higher temperature liquid is more stable and these two lines intersect here. So, this is the freezing point or melting point below this: (no audio from 15:19 to 15:22) below this solid is more stable because it has lower free energy.

So, you can visualize the process of transformation as a chemical reaction like this: liquid = solid. They can coexist at this freezing point. Both can coexist at the freezing point at that time. If we can use this expression: you can write two separate expressions; one for liquid and other for solid and you could equate the two. (No audio from 15:56 to 16:05) So, essentially, what is happening? Does solidification begin immediately, when T falls; it comes below the freezing point? At freezing point: this is 0. But what happens when a solid nucleus: a nucleus of a solid forms? New surface is created. And to create the surface you have to apply certain amount of energy. Where does it come from? What is the driving force?

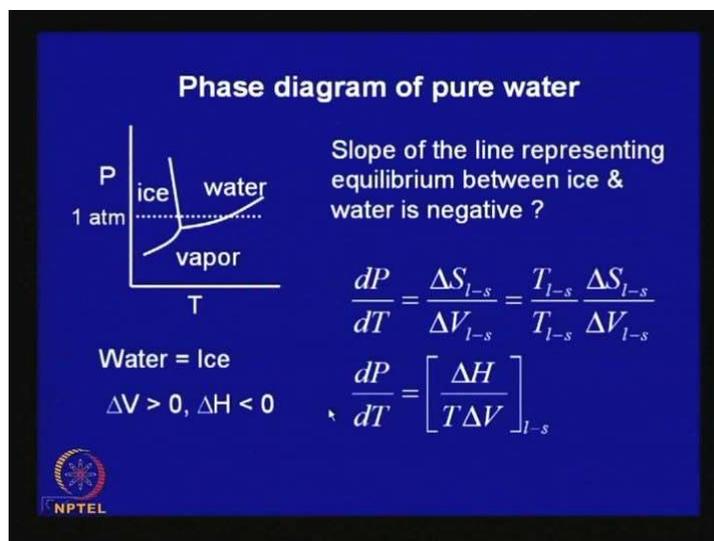
So; that means, that energy has to be supplied, and this can come from this chemical potential. And this is possible, only if you go down. I mean under cool a bit. Cool the system to a little lower temperature. Then you have: the solid has less energy: lower free energy than the liquid. So, there is a net energy for transformation; you know there is a net available energy which is used up in creating new surface. So, for the solidification to proceed, you need some amount of under cooling.

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And this is shown over here. Ideal curve we had initially shown. But here even if you leave it indefinitely at this temperature solidification will not begin, unless you have enough energy to create new surface; that is the surface, that is: solid liquid surface is created. So, this is shown over here. And once the solidification begins that latent heat will raise the temperature back to the freezing point or melting temperature. And here, both liquid and solid will coexist until entire amount of liquid is transformed into solid and thereafter, it will follow the normal Newton's law of cooling.

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Now, we had shown this phase diagram for a pure metal or a pure material. Let us look at the case of water as it freezes. There are 3 phases involved ice, water and vapor. Now, here

look at this slope. What is it? See most cases, this slope is positive. Whenever the transformation is associated with increase in volume. Say ice to vapor, liquid water to steam or vapor, it is accompanied by an increase in volume. So, the slope of this line, whether it is here, here they are positive. Now, what happens in this case? It is possible to go to: use the concept of free energy to derive a relationship, which will define, which will say, what is the effect of pressure on the freezing point of water or for any metal.

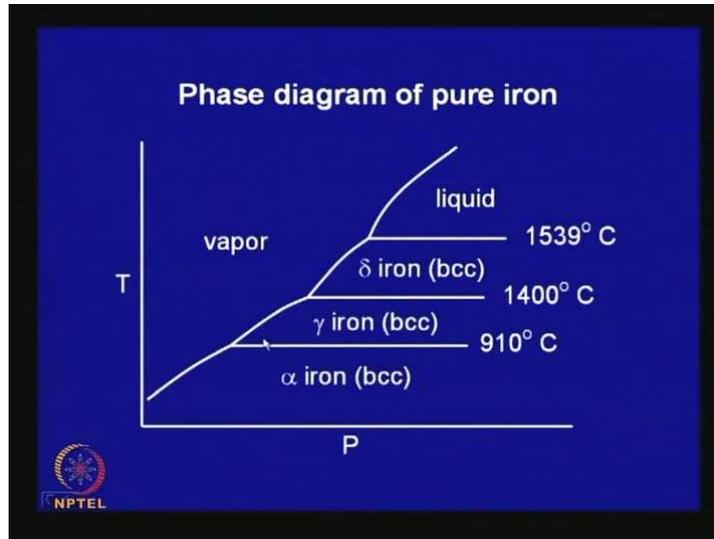
And this is shown over here, if we equate, say if we go back, if we equate the two and because both are equal at freezing point. So, if you can equate the two and a little bit of algebraic simplification, you will be able to show that this is equal to; $\frac{dP}{dT} = \frac{\Delta S_{l-s}}{\Delta V_{l-s}}$ and

you can multiply both numerator and denominator by the freezing temperature, melting point in degree Kelvin that is T : $\frac{dP}{dT} = \frac{T_{l-s}}{T_{l-s}} \frac{\Delta S_{l-s}}{\Delta V_{l-s}}$. And this is energy, which is enthalpy.

That is; you can say, this is the latent heat of transformation: $\frac{dP}{dT} = \left[\frac{\Delta H}{T\Delta V} \right]_{l-s}$

Now, in case of this reaction water to ice, here when from water you get ice you have to extract heat. So; that means enthalpy is negative and we also know that this is, when ice forms, there is an associated expansion, volume expansion. So, $\Delta V > 0$. Therefore, this is positive, this is negative, this slope is negative. So, in any such cases, wherever there is reverse (positive) change in volume, then the slope will be negative.

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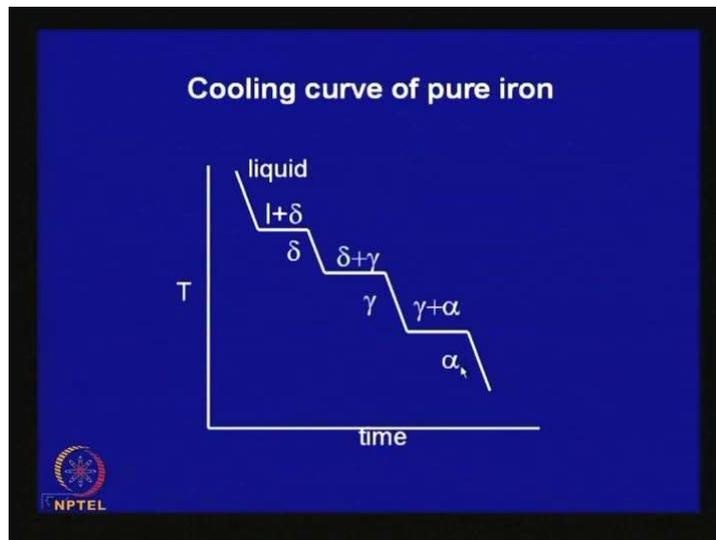
Now, let us look at this. Extend this concept to a very commonly used metal that is iron; commonly used metallic material is definitely steel, which is an alloy of iron and carbon. And let us look at the phase diagram of pure iron. Now pure iron can exist in solid state, can have different crystal structures. For example, at low temperature its crystal structure is body centered cubic; whereas at intermediate temperature; it's crystal structure is face centered cubic and before melting again it gets transformed into a body centered cubic structure. Therefore, in this particular case, we expect there are several, not just 3 phases, several phases are possible, at least two additional phases are possible.

And how does this equilibrium line will be represented in the phase diagram, which is shown here in this. I have just reversed it, basically, you can do it anyway. I put the temperature here. As an engineer very often, it is easy to visualize it like this. We will as we go to later parts, we look at multi component system, we will always represent temperature along y axis and here, this axis represents pressure. Now at higher temperature this is the region, which is gas phase or vapor phase of iron, and depending on the temperature it can exist as I said at a low temperature, it's a bcc form of iron, and it is commonly known as alpha iron.

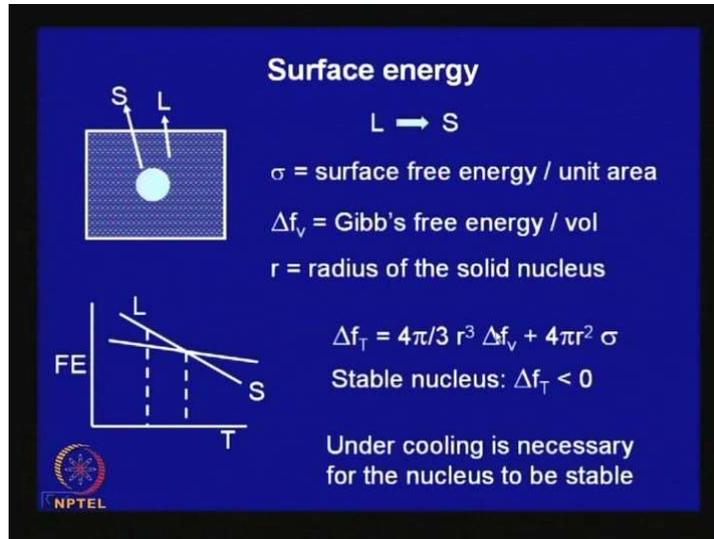
At intermediate temperature between 910 to 1400; iron has a crystal structure, iron's crystal structure is body centered cubic at 1400, it again transforms, sorry, I think there is a mistake here, please correct, this is face centered cubic and again here it gets transformed into a body centered cubic, and finally, at the melting point 1539, there it transforms into liquid. So, you have 2 additional lines, although I have drawn it exactly as perfect horizontal.

There will be some amount pressure effect depending on the volume change, which are associated, I leave it to you to find out. See here, when a BCC changes to FCC, there is an increase in volume.

So, decrease in volume, FCC is more close-packed, there is a decrease in volume. So, by heating you have a decrease in volume, and try to find out, what will be the slope, it will be positive or negative. Similarly, here, later on it again transforms from FCC to BCC, so this will be associated with expansion, this is here, there is contraction here, that is expansion, and here; obviously, from solid to liquid that is expansion, but nevertheless this volume change is very small, so therefore, even if there is some definite finite slope, it will be very small. (Refer Slide Time: 24:53)



And from this it is easy to draw the cooling curve. Cooling curve will look like this. You will have, say, one step here, when the liquid transforms to delta, again there will be, this is a solid-state transformation, here the two phases at this temperature; delta and gamma can coexist. Then again at 910 gamma and alpha, the transformation gamma to alpha, FCC to BCC transformation is taking place, here also, this is a fixed temperature where both these phases can coexist. (No audio from 25:31 to 25:36) (Refer Slide Time: 25:32)

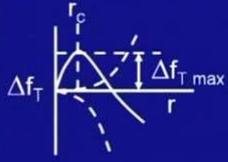


Now, let us look at the concept of surface energy: what was mentioned: that for solidification to proceed some amount of under-cooling is a must. Now, is it possible to make some rough estimate, what is the order of the under cooling? And how does it depend on the magnitude of surface energy? This is shown pictorially over here. Suppose in a liquid a nucleus of solid forms. We have for simplicity, we have assumed, that it has a shape of a sphere, a spherical nucleus, later on, we will see this is the most stable shape because the sphere has the minimum energy.

And this is a situation, this solid you know, this type of nucleation it is called homogeneous nucleation, there is no substrate, it is forming inside the liquid and suppose it has a radius 'r'. Then a new area is created, an area, surface area is equal to that of a sphere: $4\pi r^2$. Now if σ is the surface energy per unit area, then we can say that energy = $4\pi r^2 \sigma$. This is the energy which need to be supplied for making this nucleus stable. And this will come from the transformation of the chemical free energy that's Gibb's free energy. And pictorially it is shown here. Say this the melting point: here definitely no nucleation; no nucleus is stable, but if you under cool here, you have a driving force. This is the difference in free energy.

And let us say that Δf_v , this is the free energy per unit volume, which it can provide and this times the volume of the sphere, this is the net energy, which this chemical reaction can provide and for the nucleus to be stable in this transformation this energy should be negative and which is a possibility. So; that means, this clearly shows thermodynamically that under cooling is necessary for the nucleus to be stable. (Refer Slide Time: 28:18)

Critical nucleus

$$\Delta f_T = 4\pi/3 r^3 \Delta f_v + 4\pi r^2 \sigma = a r^3 + b r^2$$


$$\frac{d\Delta f_T}{dr} = 4\pi r^2 \Delta f_v + 8\pi r \sigma = 0$$

$$r_c = -\frac{2\sigma}{\Delta f_v} \quad \Delta f_{T \max} = \frac{16\pi}{3} \frac{\sigma^3}{\Delta f_v^2}$$

Higher super cooling? ↗

Smaller critical radius,
lower activation hump



Now, let us look at; and try to find out what is the concept of critical nucleus size. Now this is the expression for the total energy: that is of transformation and this is a strong function of the dimension of the nucleus. So, this part is proportional to r^3 and the second part is proportional to r^2 which is shown here. This is the surface energy: increases like this, whereas, this free energy per unit volume, it decreases and since the power is cube, it decreases much more rapidly. So, there is a possibility that total: if you find out, if you add this and this; this will show a behavior like this.

And what we say that, if this energy hump, there is peak energy, if this can be crossed then what happens that if the nucleus radius increases the energy will keep dropping. So, therefore, this process will be spontaneous. So, for that nucleus to be stable and grow spontaneously, this energy hump must be exceeded and this can easily be found out by finding at what size of the nucleus, this free energy change is maximum. So, you differentiate it with respect to 'r' and then equate it to 0. In that case you get the critical nucleus size to be $= -\frac{2\sigma}{\Delta f_v}$ and you can substitute this back into this, you get what is the magnitude of this energy hump.

So, this shows that higher the super cooling the smaller is the critical nucleus size and also higher the super cooling the height of this energy hump is lower. So, in a way, you can see that, if the super cooling is more the reaction will be much more spontaneous, it can take place easily. Therefore, to get a finer grain size in the solidified material, you have to cool it fast so that there is a higher degree of under cooling and the critical nucleus size is small.

Other extreme if you want to grow a single crystal, a very large crystal, then you have to use, you have to form, I mean, a very low and controlled super-cooling; so that the critical size is large and then it is possible to grow large single crystal.

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Homogeneous nucleation rate

$$\dot{n} = \frac{kT}{h} \exp\left(-\frac{E}{kT}\right)$$

$$E = \frac{16\pi}{3} \frac{\sigma^3}{\Delta f_v^2} V^2 = \frac{16\pi}{3} \frac{\sigma^3 V^2}{\Delta G^2}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H}{T_0}$$

$$\Delta G = \Delta H \left(\frac{T_0 - T}{T_0}\right)$$

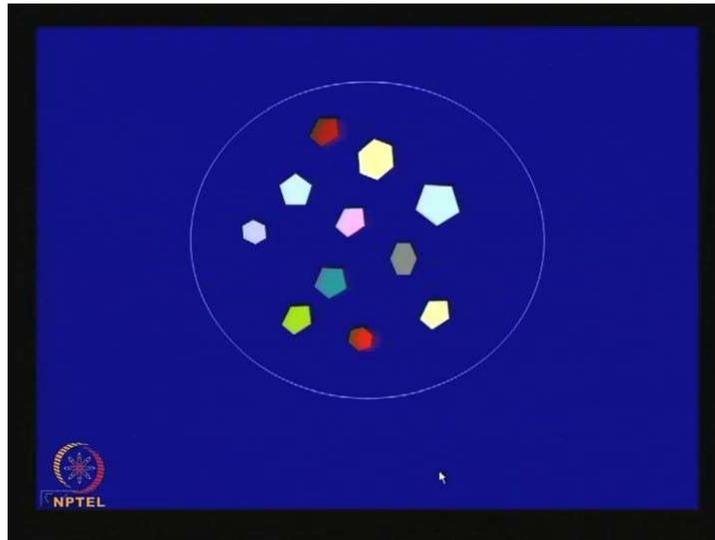
Lower the activation hill higher is the nucleation rate.



Now, it is also possible to extend this concept to find out the rate of nucleation and how that homogeneous nucleation; here the nucleus that has formed, it has formed within the liquid not on any surface. Therefore, this type of nucleation, we say it is a homogeneous nucleation. Nucleation rate; it is easily, I mean, you can use this, that reaction rate theory, rate at which that nucleation takes place, this is a frequency term, which is kT , it is the Boltzmann energy you divide by Plank's constant. This is the frequency factor and this is the total frequency factor, but successful frequency of formation of number of nuclei, out of this, this is the total number of attempts being made.

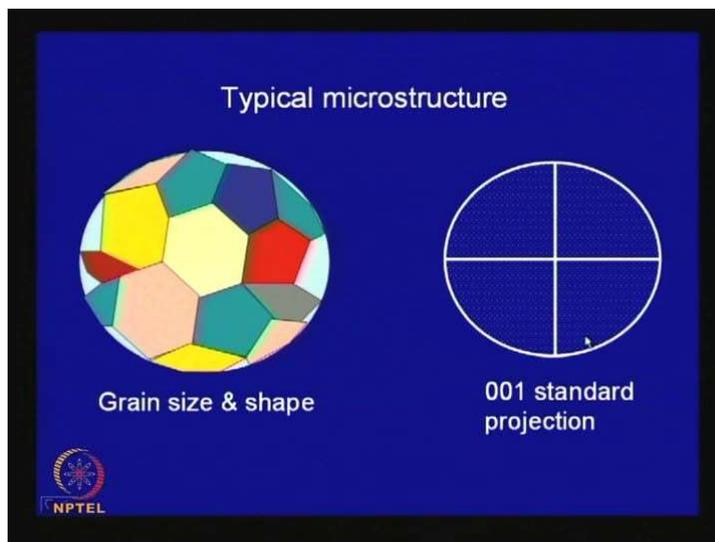
How many of these are becoming stable that will depend on whether this can exceed or overcome the energy hump. This is given by Boltzmann statistics, you see that E is the energy of transformation over kT . So, here this energy of transformation; you go back to the previous, what you can? See you can substitute this over there. So, in this expression, all these are in molar quantity, so what you do, to find out this energy, you multiply the numerator and denominator by V^2 , which is the molar volume, and then you get this. This is the molar free energy of transformation, and so, basically you can see that more clearly, say, that lower the activation hill, higher is the nucleation rate and finer is the structure.

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Now apart from it, say, this pictorially shows some nucleus formed, but this is a concurrent process; nucleation and growth, both take place simultaneously, and this will keep growing.

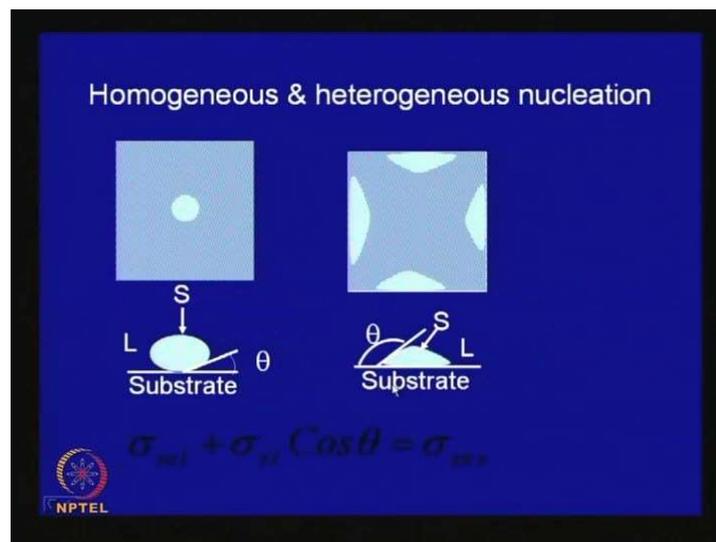
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And then finally, when each grain, if meets another grain, so this growth in this direction is inhibited and what finally, you will get, a number of grains and each grain may have different orientation, and which is shown by different color and this is a typical microstructure of a solid pure metal. You will have several grains. They are all differently

oriented, and looking at the microstructure, an important parameter that you can find out is the grain size, the diameter of the grain, size, shape. You can also try to find out, what is the average number of boundary per grain, and average number as we will go down at the end of the lecture, you will see, I leave this as an exercise that, if you look at microstructure this will be some number between 5 and 6.

And now you can extend this orientation of this grain, if you try to represent on a standard projection, what will happen? Say, let us try to put orientation of cube axes of each of these grains. Where they will be located? Now, if it is a single grain say, we can say that 1 cube axis is here, 001 is here, 100 is here, 001 is here, but you have several of these. For the second one it may not be at these 3 points, but may be somewhere; here, here, here. Similarly, for this it will be at a different place. So, on the whole what you can see that these cube poles, they will be uniformly distributed as shown here with red dots, I am sorry, these dots are too fine. I should have made it little bigger. So, basically, they will be uniformly distributed, whereas, if there is a preferred orientation, somehow you can control the solidification, that is, it is forming almost directionally solidified structure then it's possible that all cube may be located here, along this; along this; along this. So, you will have more density of such poles in these areas, whereas these portions will be vacant. There will be no dots; no poles; points over here. (Refer Slide Time: 36:16)

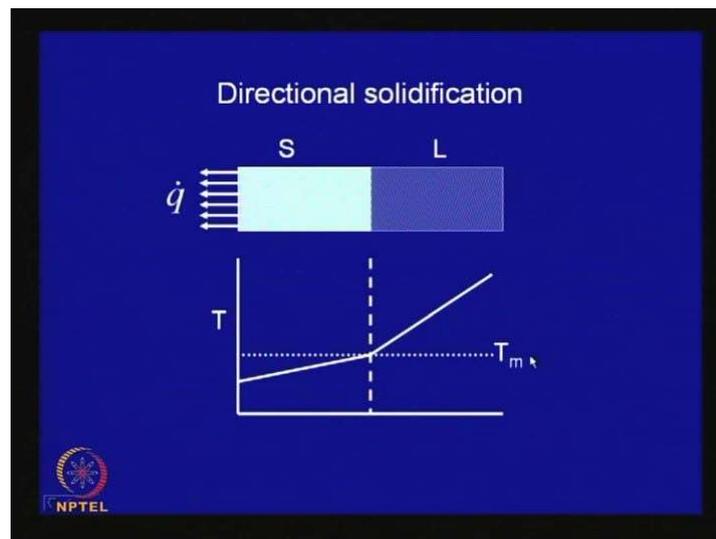


Now, let us look at heterogeneous and homogeneous nucleation, now in case of this heterogeneous and homogeneous, we talked about this homogeneous nucleation. In this case, the nucleus shape is spherical, it takes place within the liquid, and there is a distinct

interface between solid and liquid, and there is no substrate here. Suppose we put a substrate then depending on the nature of the substrate if solid forms, you will have surface energy interactions. So, surface energy; as we said that σ is the surface energy between liquid and solid. Say, suppose here, this is the solid and surrounding is the liquid. So, this is σ and this subtends an angle with respect to the substrate; θ .

Now, similarly there will be a separate surface energy between substrate and solid, also substrate and liquid. And in fact, if you can resolve this, these forces should balance that is $\sigma \cos(\theta)$ plus this surface energy between this substrate and liquid. This should be equal to the surface energy between the substrate and solid, because the solid: it is forming here, which is acting in the opposite direction. Usually, whenever you have this kind of shape, that angle, in that case, you can say that, the liquid wets this substrate and here a stable nucleus can form. So, it will depend on the surface; it will be determined by the surface energy or particularly this contact angle.

And if it is wet-able then the substrate is a favorable site for nucleation of solid and this is schematically shown. Say homogeneous nucleation, here, I have tried to show. There is no wall, no interface. So, within the liquid, which is in fact, very difficult to reproduce to carry out this experiment, whereas here if you allow the metal to solidify in a container. So, there is interface; solid interface available here, and nucleation will start from this end; all these interfaces. So; that means, heterogeneous nucleation needs less chemical potential, the driving force for heterogeneous nucleation will be low, but it will depend on whether you have a favorable substrate or not. (Refer Slide Time: 39:26)

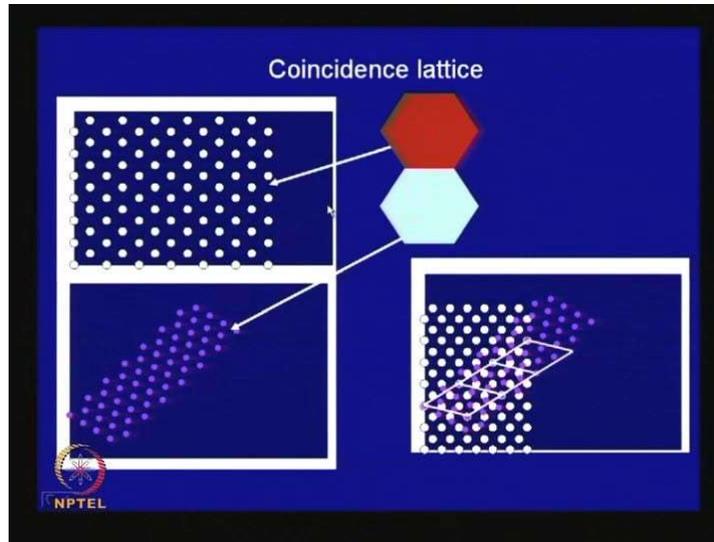


Now, a few points about the directional; concept of directional solidification, when you allow a metal to solidify in a container, so, the external cooling setup will determine how the structure or evolution of structure takes place in this solid. And this is schematically shown here in this diagram. You have a container. Let us say, we can extract heat from one surface only, so this is the solid; part of the solid, which has formed. This is the liquid, and heat can flow only along this, and as we know that, when solidification takes place heat has to be extracted.

Now in this particular case, this side that heat can flow, only if there is a favorable temperature gradient. Like in the solid, here at the solid liquid interface the temperature is the melting point, here this is the temperature. Outside, you can control the temperature, here, this is at your control, and you can control the heat extraction rate. So, this temperature gradient will determine that heat extraction rate. Therefore the movement of the solid liquid interface will depend on how fast you can; that heat can be extracted and flow through this growing solid layer and since that end in this case in the liquid basically is the melting point, basically this liquid some amount of heat, when it comes out, if it goes here, so, basically what you will find that temperature within the liquid, it goes up.

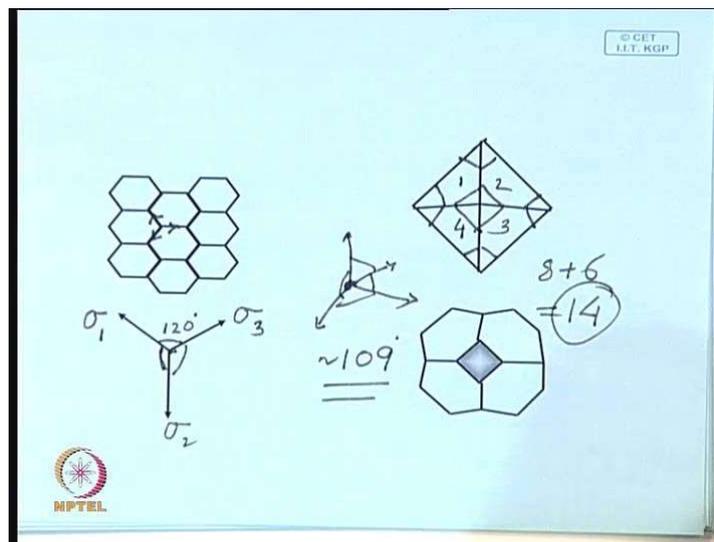
So, if this kind of temperature gradient is maintained in that case this, and we have seen that solid liquid surface has a definite surface energy and it will always try to remain in the minimum state of energy. So therefore, it is going to be straight, so basically it is a stable interface, a planar front, which will move in this direction and this, in fact, because the heat is being extracted directionally, crystal will grow in this direction. By this it is possible to grow (even single) by controlling this directional solidification, it is possible to grow single crystals.

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Now, let us look at the structure of this metal in a little more detail. Let us look at that how the grains, when you arrange, in what way do they pack, what is their shape and what is the role of surface energy.

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Now, let us look at a 2D structure, two-dimensional grain structure, say suppose we draw like this, hexagon. Say; by constructing these hexagons you can fill up this space. Now point is you can fill up this space by arranging square also: but which will represent a proper microstructure? Now here, we have seen this boundary has some energy associated, each of these boundaries has some energy associated, which is called surface tension. So, there has to be an equilibrium between the energy or surface tension which is shown here.

This is the grain one, σ . I am putting it as σ because it is pure metal and the surface energy of pure metal, let us say they are same.

So, if it is same then this angle has to be 120° . (no audio from 43:47 to 43:54) So, therefore, it is not that the grain surface energy of the crystal on every surface is same, but the difference in the surface energy with respect to the orientation; the magnitude of this difference possibly is very small, so therefore whenever you look at it in a 2D structure; simplest experiment to do is with soap bubble. If you take a ring put it in a soap water take it out; you will find that soap bubble, which forms that is a 2D structure, they all will be like regular hexagons and it maintains this equilibrium.

So, depending on, if these grain boundary energies are little different; σ_1 , σ_2 , σ_3 . Then these will be slightly different, but these angles still will maintain, I mean, that equilibrium will still be maintained. Say, it may be slightly less; this angle, this may be slightly more, but the forces must balance. Now what happens in case of a 3-dimensional structure, because in metals the grains are arranged at random and the packing: when you start packing, it should fill up this space. Now the best way to; I mean, people have done lot of experiments and making models; try to fill up and the best way to fill up space is; look at this octahedron. So, which has eight faces which is shown here.

So, on the top surface 1, 2, 3, 4, so this is four surfaces, four at the bottom, but this if you try to pack you will not able to fill up the space. Now there are two criteria, one is the space filling and second is the equilibrium of surface energy or surface tension equilibrium must be maintained. Now, when these surfaces they meet. There will be a grain boundary and now in 3D say it's quite likely that many places, you will have one this, one this, one this, so there will be four lines like if you try to recollect that carbon bond structure and the four bonds. If all these energies are nearly equal the angles have to be equal and I think we said that this angle is around 109° or so. To maintain, I mean, both these; it should be a shape of the grain; it should be such that it should fill up the space, at the same time, wherever these grains are meeting each other; there will be these lines formed, and you will have this; wherever these four lines are meeting; they should be at an angle around this. To satisfy this condition, it has been found that the nearest it can do, is a truncated octahedron, so this is the octahedron: truncate it like this. Similarly, this, you truncate then you get a shape, say, something like this, I mean, tried to show it here. And this will have how many

faces? Eight and then it has one, two, three, four, five, six corners. So, six more faces will be added, so 8 plus 6, so, it will have 14 faces.

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The slide, titled "2D ARRAY", contains a diagram of a space-filling arrangement of polygons. The polygons are labeled with numbers 1 through 15. The diagram shows a central polygon (labeled 4) surrounded by other polygons (labeled 5, 6, 5, 5, 5, 5, 5, 5, 5, 5, 5, 5, 5, 5, 5). The polygons are arranged in a way that they touch each other at their edges and corners.

Handwritten text on the slide includes:

- $E: \text{Edge}$
- $P: \text{Polygon}$
- $C: \text{Corner}$
- $P - E + C = 1$
- $5 - 19 + C = 1$
- $C = 15$
- $P = 5$
- $E = 19$
- $C = ?$
- $P - E + C = 2$
- ↳ on surface of polyhedron

The slide also features a small logo in the bottom left corner that says "NPTEL" and a copyright notice in the top right corner that says "© CET I.I.T. KGP".

So, this kind of truncated octahedron, if you pack, which will nearly satisfy both this condition; that means, space filling and balancing of the surface energy. (no audio from 48:01 to 48:07) and it will be interesting to also look at this array a little carefully; the 2D array, if you try and fill up. And here is an example shown here, I have tried to put several polygons each touching each other, so this is a space filling two D diagram; space filling two D array. Now, some have 5 faces (edges); one has 6, another 4 over here. Now, when you pack them you generate number of edges, they meet each other. This is called grain boundary.

They meet each other, say this will have one crystal arrangement. Say here these planes are arranged like this, say here possibly those planes are arranged in a different way. So, if you move from one grain to another; the periodic array, you know, crystal structure is still same, but its orientation is different, the same planes are oriented differently. Now, you can count there are 3, I mean, when you do this packing, you also generate apart from edges, number of corners, where 3 or more than 3 grains meet like here, the 3 grains are meeting. Similarly, there may be places, here, there are 1, 2, 3, 4 grains are meeting, so you generate, in this figure you have a number of polygons that is P; you have a certain

number of edges E and you also have certain number of corners (C) and there is a relationship.

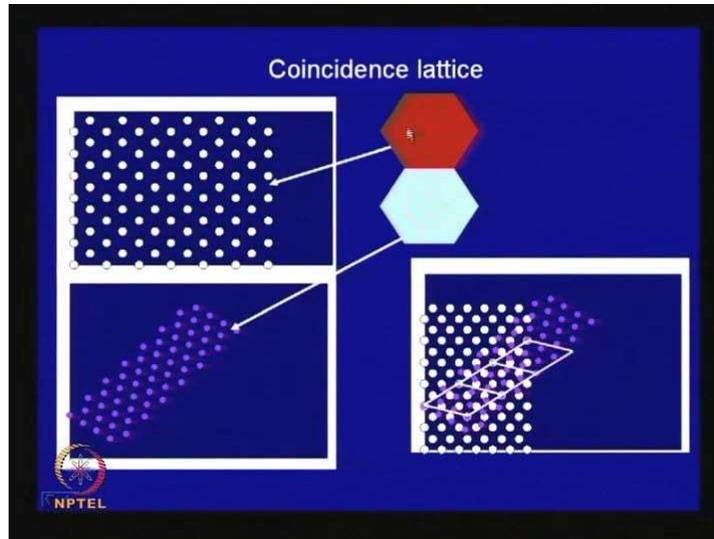
If this is a space filling, there is a relationship like this, which looks like or similar to that of Gibb's phase rule that is $P - E + C = 1$. So, this is true in a 2- dimensional case, 2D case. Now in this particular case you, try to count, now you have number of these grains; this is 1, 2, 3, 4, 5. So number of polygons (P) is 5, number of edges (E); I have tried to mark here 1, 2, 3, 4, 5, 6. So, you go on marking, so it comes out to be; the last one is 19, so this is 19. So, if you substitute here, what you get is: that $C = 15$, that means, you should have 15 corners. Now, you count the corner; this is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15. So, you get that 15 corners, so this is satisfied in a 2D array. And this rule is quite general.

In fact, there is an Euler law, which is valid on surface of polyhedron, like let us say truncated octahedron, we talked about. The truncated octahedron; also, you can apply this law $P - E + C = 2$, but this will be equal to 2, Here also, in this polyhedron also, you will have number of faces, corners, and edges. So, therefore, this can be applicable. It is a very general type of law; is very general, it can be applied to polyhedron also.

Now, let us talk about the grain boundary a little more. So, we said that here is one grain, here is another grain. So, what is the atomic arrangement along this interface called grain boundary. So, this is a boundary and I said that here crystal structure of this and this they are exactly same.

So, what you do? Say, suppose, we generate an array; the atomic array, how does it look? You can do it as an exercise, on a piece of paper, if you can take a transparent sheet and draw this atomic array at a regular interval; maybe; you take that close packed plane, you draw this close packed plane like atomic array one sheet and you repeat. You take a Xerox copy of that on another sheet. And now the transparent sheet, you put on that and try to rotate. Rotate through certain angle and that means, what you are doing? You are trying to visualize, what is the nature of array near the grain boundary. So, may be part of it, you say this; that means, you can. Can you generate this atomic array by rotating this grain? So, this kind of a planar arrangement, which is shown over here.

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It is called coincidence site lattice concept, I have drawn the same thing. This is one grain where these atoms are arranged like this, whereas in this grain, the atoms are arranged in this fashion, the same plane, but it is different, it's rotated. Now, what happens at the grain boundary? Near the grain boundary few layers 2 or 3 layer what happens? This is the layer, this is the one grain; this is the other grain, and you can say this is the grain boundary. If you extend the lattice, you will find that some of these points, they are coincident with these lattice points, which are marked over here.

So, this is a concept, which represents the type of the grain boundary. The nature of grain boundary, people try to see on the degree of rotation and the coincidence lattice type of relationship. So, this is, I mean, it is not that these atoms are occupying these places. You just superimposed and see what are the coincident lattice sites? And what you can? Find out this coincident lattice distance. This is significantly larger than this atomic distance. Like, in this particular case, you see that here, this is one atomic distance, so here, it covers the distance, this distance is 1, 2, 3.

So; that means, this coincident lattice dimension is 3 times the main lattice dimension, and by this it is possible to relate and find out the surface energy or the energy of the grain boundary. And this energy has a relationship between this angular rotation between the neighboring grains and that is how the grain boundary energies are classified and subsequently as we go down, you will find that, it is a very convenient way of classifying grain boundary. With this we conclude today's lecture and in fact, we have covered this

this topic fully. (no audio from 56:03 to 56:11) Next class, we will begin a new chapter.
Thank you very much.