Principles of Physical Mertallurgy
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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 it is solid state, and it is structure depends on how it has solidified during the process of solidification.

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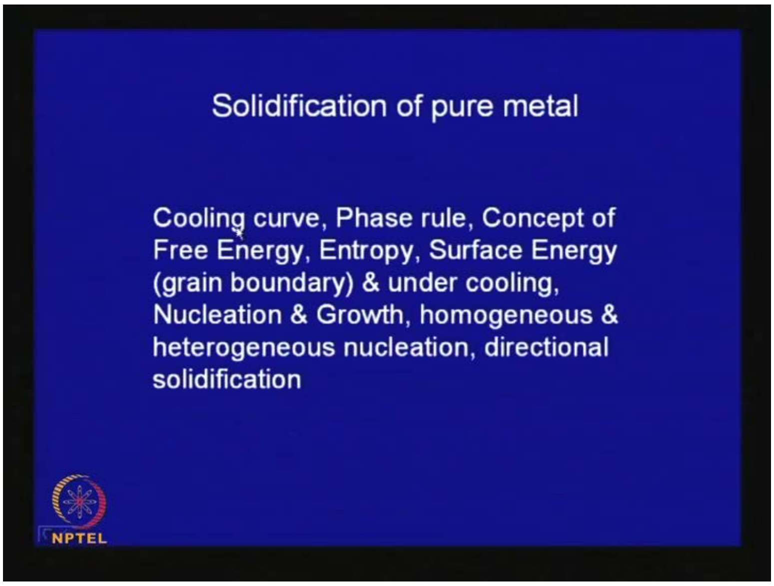

Solidification of pure metal

Cooling curve, Phase rule, Concept of Free Energy, Entropy, Surface Energy (grain boundary) & under cooling, Nucleation & Growth, homogeneous & heterogeneous nucleation, directional solidification

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 and during thermal analysis, and during the process of solidification, it will pass through a (( )) state, when both liquid and solid will be coexisting, and phase rule states a 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 concept 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 it energetics of nucleation and there after nucleation, there is a time dependent growth process form a, this is probabilistic as stochastic in nature, whereas this is a 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 use to solve to get particular desired properties and textures in materials.

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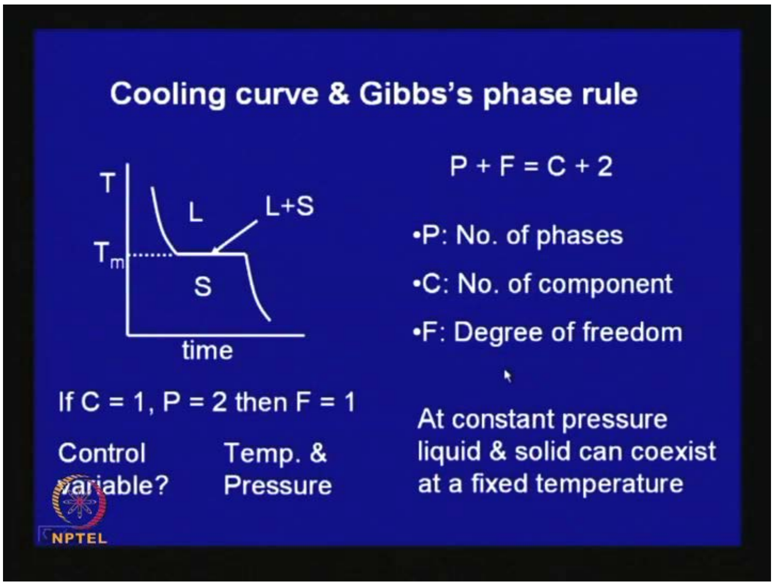

Cooling curve & Gibbs's phase rule

$P + F = C + 2$

- P: No. of phases
- C: No. of component
- F: Degree of freedom

If C = 1, P = 2 then F = 1

Control variable? Temp. & Pressure

At constant pressure liquid & solid can coexist at a fixed temperature

Now, let us look at the cooling curve of a pure metal, how does it look, set 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 it is 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 of it is own. And it can take the shape of the container where you keep that is not so, in case of a solid.

This is primarily because atoms are not as closely pack as in solid, secondly the atoms are mobile and and you can see that atoms are arranged in a disordered fashion, but there may be some amount of short range ordering using extra diffraction technique. The density of packing also has been estimated, say in case of solid, we have seen that coordination number at maximum coordination number in metal that you can have is 12 in phase centered cubic, whereas same metal, which is in has as in solid phase centered cubic structure. If it gets converted to liquid possibly, you would not have that 12 has the coordination number coordination number will be less than 12, but nevertheless till quite high may be 10, 11.

And when this liquid cools, say it will cool and as and this plot temperature, it can be a smooth curve like this, and this will be primarily determine by the temperature of the metal, and the surrounding and usually this follows a Newton's loss 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, and 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, and normally experimental condition, we mean say the temperature is 1, and may be and the pressure and at which you are doing the experiment, and usually for most practical applications, this pressure will be one atmosphere. So, you have two control variable temperature and pressure, and Gibbs's phase rule states it is like this P plus F equal to C plus 2, where P is the number of phases, C is a number of component. Now, in case of a pure metal the component that just 1 metal, so number of component is 1 and F represents degree of freedom. So, 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 a state as as states and this is applicable to even multi component system.

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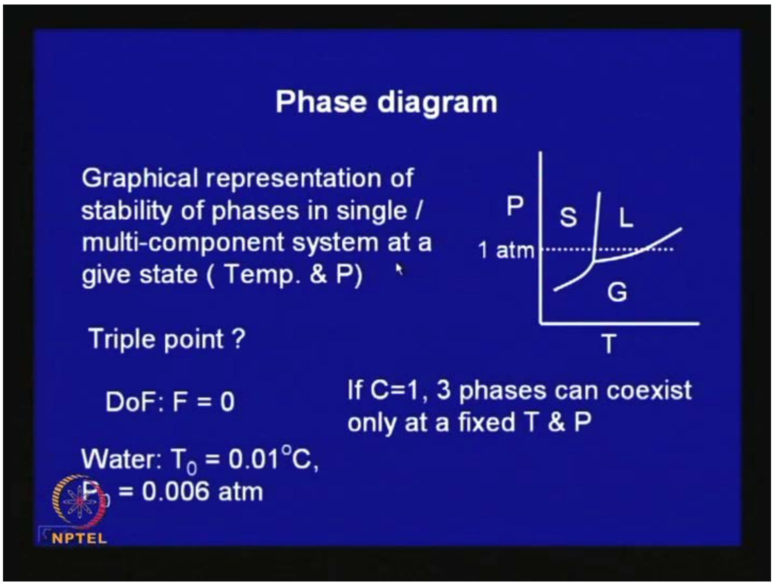

Phase diagram

Graphical representation of stability of phases in single / multi-component system at a give state (Temp. & P)

Triple point ?

DoF: F = 0

If C=1, 3 phases can coexist only at a fixed T & P

Water: $T_0 = 0.01^\circ C$, $P_0 = 0.006$ atm

Now, what is the phase diagram, basically phase diagram is a graphical representation of the stability of phases in a single or multi component system at a given state, and a state is defined in terms of control variable. So, unusually only two of this set out of temperature, pressure and volume, only two you can control, so and for most practical purposes, we can control temperature and pressure. Now, let us look at the how this stability of a single component system depends on pressure and temperature, and this is shown over here, this access represent pressure this is temperature, and you can have a pure metal, say it can you can have 3 different state 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 these lines represent the equilibrium between solid and gas, there is the possibility, the solid can be transformed entirely to gas without going through this liquid route. Similarly, you have this line, which represents the line in which which represents the equilibrium between solid and liquid, and this line represents the two phase equilibrium between 2 phases liquid and gas, and say 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. So, in and 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 a particular for this particular case, if you try and 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 which is written over here, this T naught is equal to point almost 0.01 degree centigrade, and pressure that point is 0.006 atmosphere. (No audio from 11:20 to11:28)

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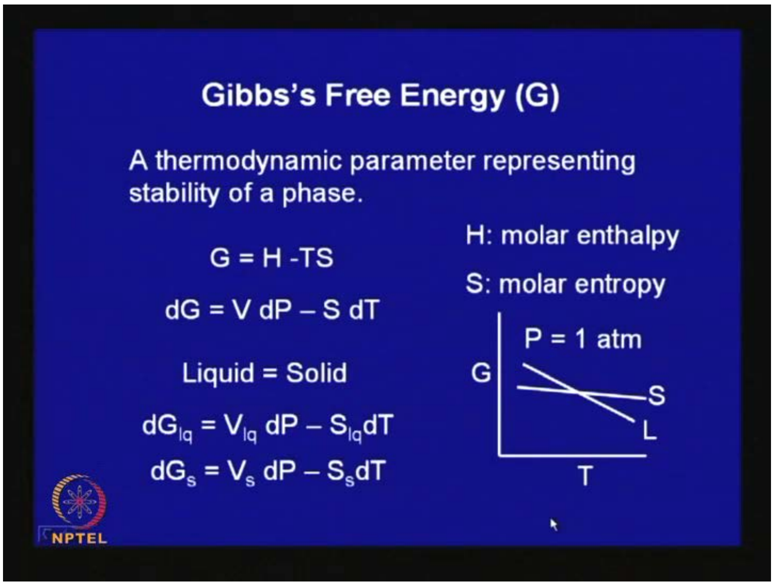

Gibbs's Free Energy (G)

A thermodynamic parameter representing stability of a phase.

$G = H - TS$

$dG = V\,dP - S\,dT$

Liquid = Solid

$dG_{lq} = V_{lq}\,dP - S_{lq}dT$

$dG_s = V_s\,dP - S_sdT$

H: molar enthalpy

S: molar entropy

Now, let me introduce a concept of Gibbs free energy, this if we put an analogy, this is some kind of potential say like energy, you know you can or let us say electricity flows from higher potential to lower potential. Similarly, any transformation when it takes place the will it takes 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 all though 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 a 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 hence it is molar enthalpy minus, T is the temperature in degree Kelvin times a term called entropy. 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 not over is the free energy is G is enthalpy minus T d T times entropy.

And we use this expression (( )) whenever there is a reaction taking place at a constant atmosphere, and for most practical experiments or processes, the atmosphere atmospheric pressure is constant, and usually it is 1 atmosphere pressure, that is a differential way of representing this. And this is a simple thermodynamic principles, it you can convert it, and write in differential form that is dG, and you can convert it in terms of from enthalpy and entropy to pressure and temperature, because these are the easily controllable variable. Then it comes out the dG incremental increase and free energy is equal to V plus incremental a times incremental pressure minus S dT.

Now, let us look at the process of solidification, we are concern with the stability relative stability of two phases one is solid; another is liquid, and if you try, so this is a something 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, higher temperature liquid is more stable, and these 2 lines intersect here, so this is the phasing point of 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 to solid, and 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 right two separate expression, one for liquid; and other for solid. And if you equate the two. (No audio from 15:56 to 16:05) So, essentially, what is happening is does solidification begins immediately, when it fall comes below the freezing point, at freezing point this is 0, but what happens, when a solid nucleus, a nucleus of a solid forms a 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, it cool it the system to a little lower temperature, then you have the solid has less energy free energy then the liquid. So, there is a net energy transform you know there is a net available energy is there, which is used up in creating new surface, so for the solidification to precede, you need some amount of under cooling

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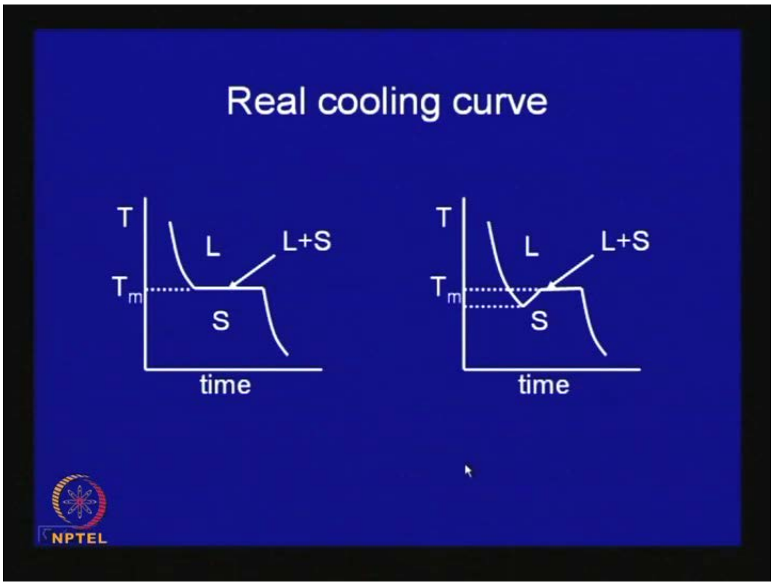

Real cooling curve

And this is shown over here, actual ideal curve we had initially shown, but here even if you leave it in definitely 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 (( )) will raise the temperature back to the freezing point a 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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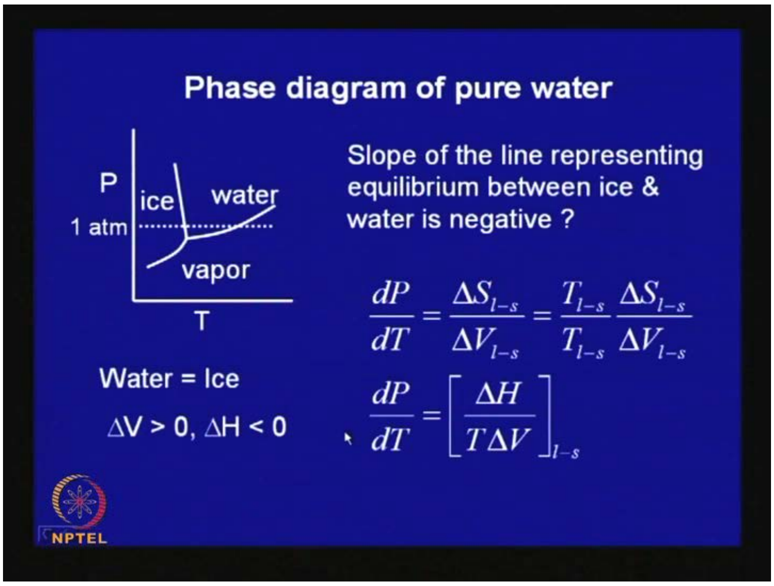

Phase diagram of pure water

Slope of the line representing equilibrium between ice & water is negative ?

Water = Ice

$\Delta V > 0, \Delta H < 0$

$$\frac{dP}{dT} = \frac{\Delta S_{l-s}}{\Delta V_{l-s}} = \frac{T_{l-s}}{T_{l-s}}\frac{\Delta S_{l-s}}{\Delta V_{l-s}}$$

$$\frac{dP}{dT} = \left[\frac{\Delta H}{T\Delta V}\right]_{l-s}$$

Now, we had shown this phase diagram for a pure metal and or a pure material, and let us look at the case of water, it freezes there are 3 phases involve ice, water and vapor. Now, here look at this slope 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 this concept of free energy to derive the relationship, which will define which will see, 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 little bit of algebraic simplification, you will be able to show that this is equal to delta dP dT equal to delta S that is change in entropy, which change in volume. And you can multiply both numerator and denominator by the freezing temperature melting point, and degree Kelvin that is T T T. And this is an energy, which is enthalpy that is the enthalpy that is you can say this is the latent heat of transformation.

Now, in case of this reaction water to ice, here when this 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 it is associate that is an associated expansion volume expansion. So, delta V is greater than 0, so therefore this is positive, this is negative, this slope is negative. So, any cases such cases, wherever that is a reverse transformation change in volume, then the slope will be negative.

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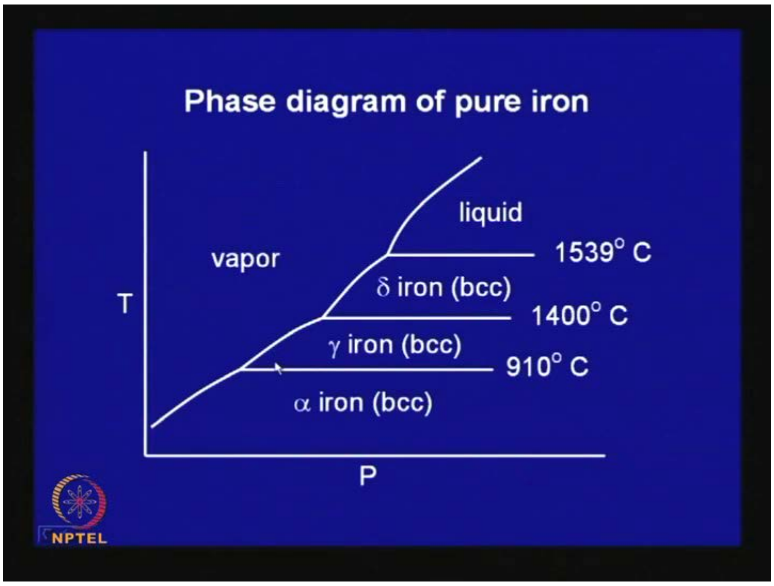

Phase diagram of pure iron

Now, let us look at this extend this concept to a very commonly use metal that is iron a commonly metal metallic material definitely steal, which is an alloy of iron and carbon. And let us look at the phase diagram of pure iron, now pure iron has can exist in solid state in can have different crystal structures. For example, at low temperature it is crystal structure is body centered cubic; whereas at intermediate temperature is crystal structure is face centered cubic, and before melting again it gets transform into a body centered cubic structure. So therefore, in this particular case, we expect there are several not not just 3 phases, there are more than 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, and this I have just reversed it basically as you can do it anyway. So, I put the temperature as an engineer very often it is easy to visualized like this. We will as we gone later part, 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 is 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 a crystal structure is body centered cubic at 1400. It again transforms sorry, I think there is the 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 is a it transforms in to liquid. So, you have 2 additional lines although have drawn it exactly is a perfect (( )). There will be some amount pressure depending on the volume change, which are as 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 much more close pack there is a decrease in volume. So, by heating you have a decrease in volume, and try to find out, what will with the slope it will be positive or negative. Similarly, here some later on it again transforms from fcc to bcc, so this will be associated with expansion, this is here, there is a contraction here, that is expansion, and here; obviously, from solid to liquid that is expansion, but nevertheless this volume changes very small, so therefore, have that even if there is a some definite finite slope, it will be very slope will be very small.

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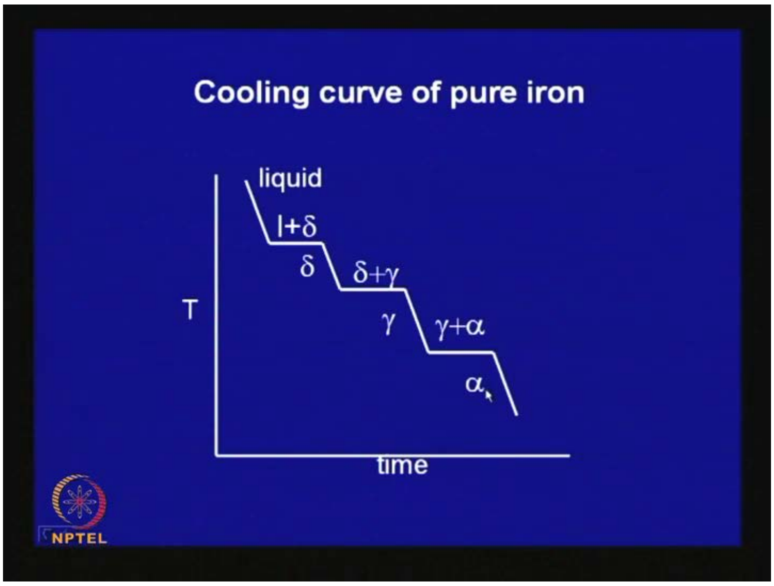

Cooling curve of pure iron

And from this is easily to it easy to drop the cooling curve cooling curve will look like this you will have. So, one step here, when the liquid transforms to delta again there will be this is the 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 the fixed temperature were both these phases can coexist. (No audio from 25:31 to 25:36)

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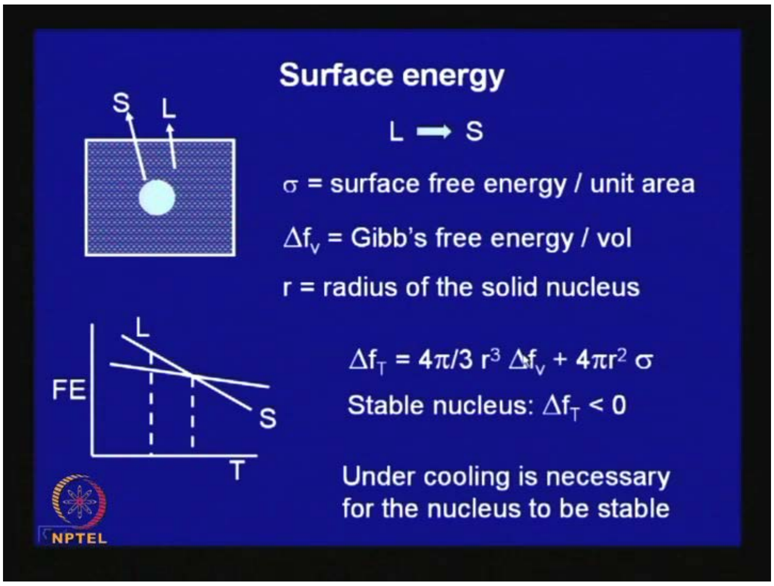

Surface energy

L → S

σ = surface free energy / unit area

Δf_V = Gibb's free energy / vol

r = radius of the solid nucleus

$\Delta f_T = 4\pi/3\, r^3\, \Delta f_V + 4\pi r^2 \sigma$

Stable nucleus: $\Delta f_T < 0$

Under cooling is necessary
for the nucleus to be stable

Now, let us look at the concept of surface energy, what was mention 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, and this is (( )) shown pictorial over here suppose in a liquid in nucleus of solid forms. We have for simplicity, we have assume that it has a shape of is free as farcical nucleus later on, we will see this is the most stable phase because this will have free has the minimum energy.

And this is the situation is 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. Then a new area is created an area surface area is equal to of it is fear 4 phi r square. Now if it is sigma is the surface energy per unit area, then we can see that energy that is 4 phi r square time 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 Gibb's free energy, and pictorial it is shown here, said this the melting point, and here definitely no nucleation no no nucleus is stable, but if you under cool here, you have this is the difference in free energy.

And let us see that delta f v this is the free energy per unit volume, which is we can provide, and this times the volume of the fear this is the net energy, which this chemical reaction can provide, and for stable nucleus to be stable 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.

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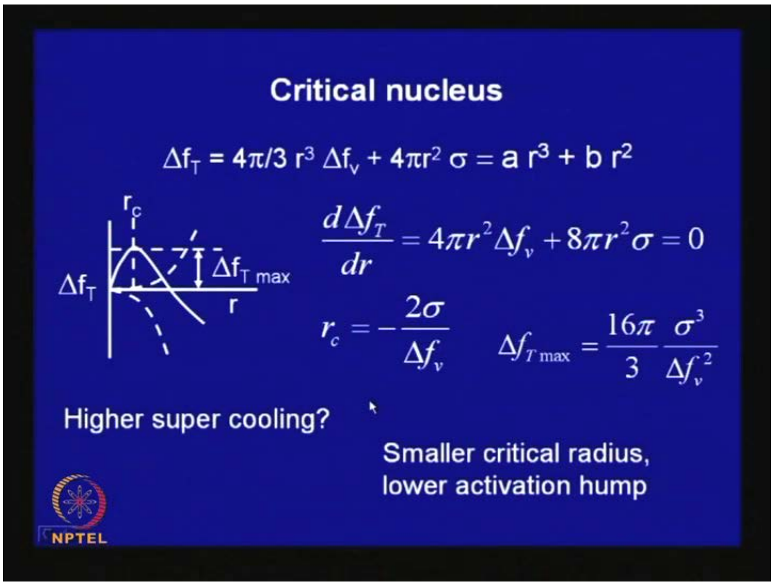

Critical nucleus

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

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

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

Higher super cooling?

Smaller critical radius,
lower activation hump

Now, let us look at an try and 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 cube, and the second part is propositional to r square, and which is shown here, this is the surface energy increases like this, where as this free energy per unit volume is decreases and since the power is cube with decreases much more rapidly. So, there is a possibility that total if you find out, if you add this and this this will show it behavior like this.

And what we see that, if this energy hump there is peak energy, if this can we cross then what happens that if the nucleus radius increases the energy will Gibb’s dropping. So, therefore, this process will be spontaneous, so, for that (( )) nuclear to be stable and grows spontaneously. This energy hump must be exceeded and this can easily be found out by finding at what size of the nucleus, this is this free energy changes maximum. So, you differentiate does with respect to are, so and then equate it it 0 and that case you get the critical nucleus ice to be twice sigma over delta f v that is free energy per unit volume, 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 this 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 and, so therefore, to get a fine a 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 control super cooling.

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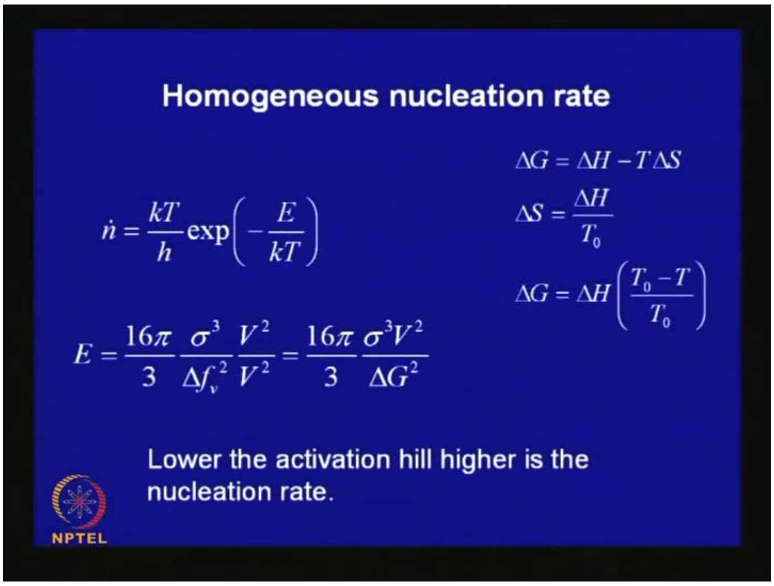

Homogeneous nucleation rate

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

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

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

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

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

Lower the activation hill higher is the nucleation rate.

So, that the critical size is large, and then then it is possible to grow large single crystal. Now, it is also possible to extend this concept to find out the rate of nucleation, and how that homogeneous nucleation here that nucleus that has form it has form do within the liquid not on any surface. So therefore, this type of nucleation, we say it is a homogeneous nucleation, and nucleation rate it easily am in you can use this that reaction rate, theory rate at reach that nucleation takes place. This is a frequency term, which is you kT is the (( )) that energy you divide by blanks constant this the frequency factor, and this is the total frequency factor, but successful frequency of formation of number of nuclei out of this is the total number of attains being made.

This is the how many of this are becoming stable that will depend on whether this can cover (( )) exceed are overcome the energy hump, this is given by that Boltzmann statistics, you say 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 this are in molar quantity, so what you do to find out this energy, you multiply the numerator and denominator V square, which is the molar volume, and then new get this is the molar free energy of transformation, and so, basically you can see that, it more clearly says that lower the activation hill, higher is the nucleation rate and fine a is a structure.

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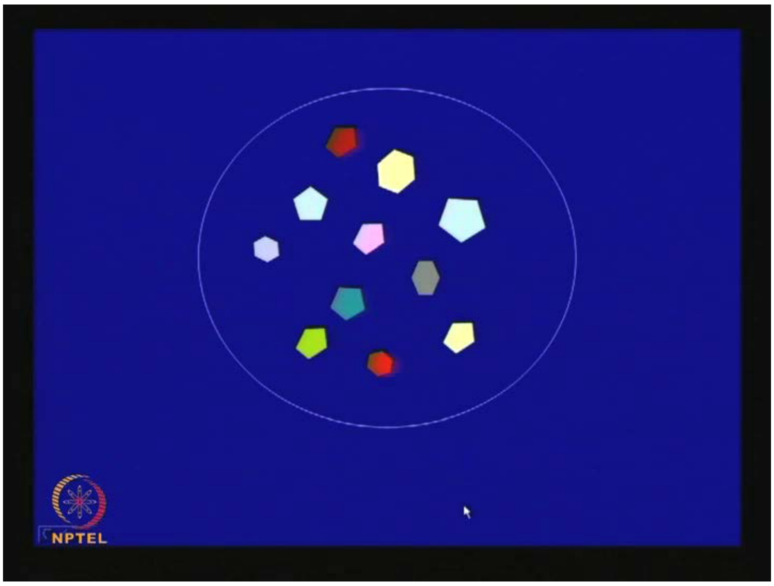

Now apart from say this pictorial issues some nucleuses form, but this is a concurrent process nucleation and growth both take place simultaneously, and this will keep growing.

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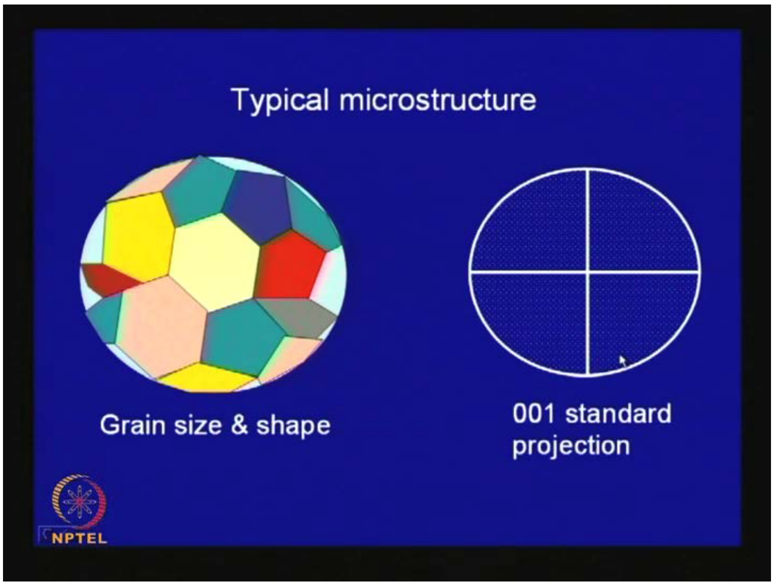
Typical microstructure

Grain size & shape

001 standard projection

And then finally, when each grain it meets another grain, so this growth and 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 there all differently oriented, and what looking at the microstructure in important parameter that you can find out is the grain size the diameter of the grain size shape. You can also try and find out, what is the average number of boundary number of boundary per unit per grain, and average number as we will go down at the end of the lecture.

You will see alive 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 and represent on a standard projection, what will happen say let us try to put is orientation that cube axis of each of this grains, where they will be locate it. Now if it is a single grain say, we can say that 1 cube axis is here, 0 0 1 is here, 1 0 0 is here, 0 1 1 0 0 1 is here, but you have several of this for the second one it may not be a at least 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 will said dots, I am sorry this dots are too fine as should may did little bolder. So, basically they will be uniformly distributed, where as if there is a preferred orientation somehow you can control solidification, that is it is forming almost it directionally solidified structure then possible that all cube may be located here, along this along this along this, so you will have more density of such poles, and these radius, whereas this portions will be vacant their (( )) no dots no poles pointed over here.

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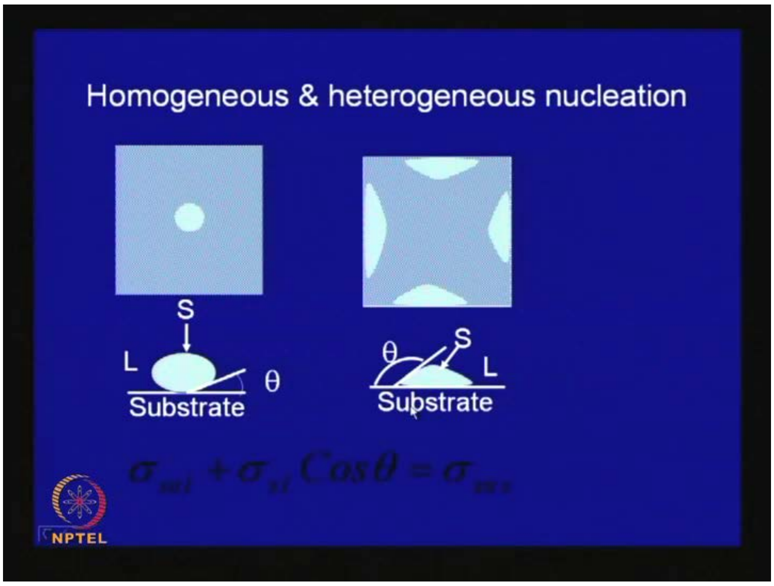

Homogeneous & heterogeneous nucleation

$$\sigma_{ml} + \sigma_{sl} Cos\theta = \sigma_{ms}$$

Now, let us look at this heterogeneous and homogeneous nucleation, now in case, of this heterogeneous and homogeneous, we talked about this homogeneous nucleation and this case, the nucleus shape is spherical, it takes place within the liquid, and there is distinct interface between solid and liquid, and there is no substrate here, suppose we put a substrate then on the pending on the nature of the substrate. If a solid forms you will have the surface energy interactions, so surface energy (( )) this has we said that sigma is the surface energy between liquid and liquid and solid, so supposed here, this is the solid and surrounding is the liquid. So, this is sigma and this sub stains an angle with respect to the substrate theta.

Now, if you and similarly there will be a separate surface energy between substrate and solid substrate and solid also substrate and liquid, and in fact, if you can resolve this this 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 of solid it is forming here, which is up acting opposite direction unusually, whenever you have this kind of shape that angle. In that case, you can see that this solid this liquid this substrate and here a stable nucleus can form, so it will depend on the surface it will be determine by the surface energy are particularly this contact angles.

And if it is vacable than the substrate is a favorable sight for nucleation of solid, and this is schematically shown say homogeneous nucleation here (( )) to show that is no wall no interface. So, within the liquid, which is in fact, very difficult today produce in a (( )) to carry out this experiment, whereas here you 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 this interfaces so this. So; that means, heterogeneous nucleation needs less chemical potential the difference that driving force for heterogeneous nucleation, we will low, but it will depend on whether you have a favorable substrate or not.

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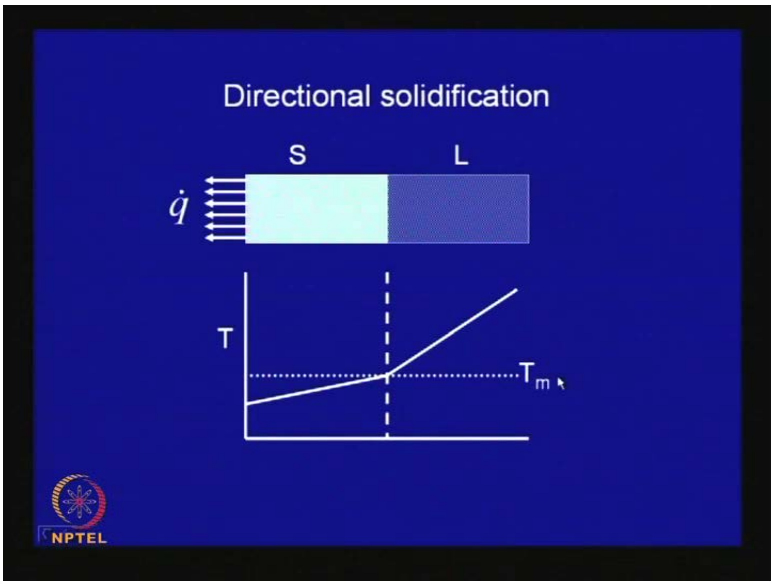

Directional solidification

Now, if 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 the how the structure or evolution of structure takes place in this solid, and this is schematically shown here in this diagram, so you have a container a let us say, we can extract heat from one surface only, so this is the solid part of the solid, which was formed this is the liquid, and heat can flow only along this, and has we know that, when solidification takes place heat has to be extract it.

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 a solid liquid interface the temperature is the melting point, here this is the temperature outside, you can control the temperature, here this is at you control, and you can control the heat extraction rate. So, this temperature gradient will determine that it extraction rate and this, and therefore the movement of the solid liquid interface will depend on how fast you can that heat can be extract it, and flow through this growing solid layer, and since that and in this case in the liquid basically is a melting point, basically this liquid some amount of it, when it comes out if goosy as a 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 as 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 plainer 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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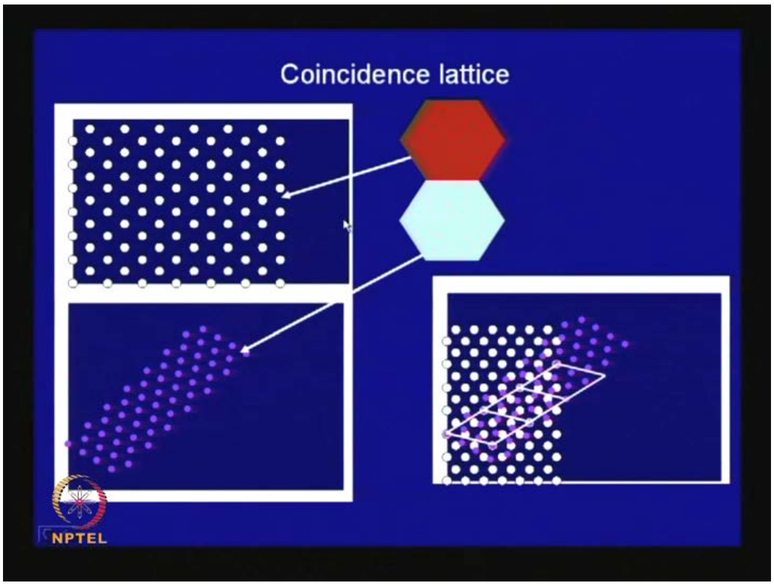

Coincidence lattice

Now, let us look at this structure of this metal structure a little more detail, let us look at that how the grains, when you arranged the what do the fair, what is the shape, and what is the role of surface energy.

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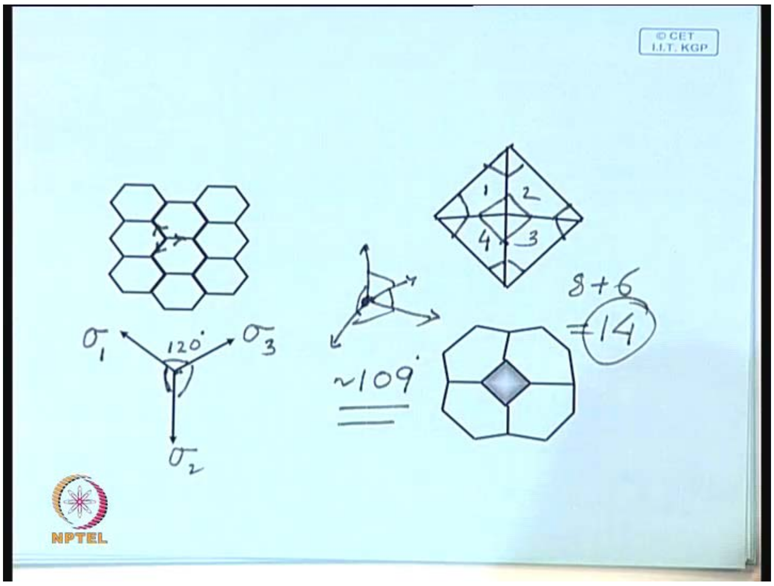

Now, let us look at a two d structure two dimensional grain structure, say suppose we draw like this say by constructing this hexagons you can fill up this space. Now point is you can fill up this space by arranging square also, but which will represent a proper microstructure. Now here, we have seen this boundary has some energy associated, each of this boundary has some energy associated, which is called surface tension. So, they has to be an equilibrium between the energy, which is shown here, this is the green one sigma sigma am putting it sigma because it is pure metal and the surface energy of pure metal it is let us see same.

So, if it is same then this angle has to be 120 degree. (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 on the surface energy with respect to the orientation. The magnitude of this difference possible is very small, so therefore whenever you look at it a two d structure simples experiment to do is with us, so babul if you take a ring put it in a soap water take it out; you will find that soap babul, which forms that is two d structure, there all will be like regular hexagons and it maintains thus equilibrium, so depending if this green boundary is an energy is are little different sigma 1, sigma 2, sigma 3.

Then this will be slightly different, but this angles still will maintain, I mean that equilibrium will still be maintain 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 three dimensional structure, because metals the greens are arranged at random, and that packing when you strap packing it should fill up this space. Now the best we to I mean people have done lot of experiments and making models try to fill up, and the best we to fill up spaces look at (( )) so, which has it phases which is shown here.

So, on the top surface 1, 2, 3, 4, so this is four surface, four at the bottom, but this if you try to pack you will not able to fill up this space. Now there are two criteria, one is the space filling and second is the equilibrium of that that surface energy of surface tension equilibrium must be maintained. Now, when this surfaces the meet they will be grain boundary, and now in three D said quite lightly that many places, you will have one this one this one this, so there we four points like a few and recollect that carbon that bond structure, and the four dimension.

If all this energy is an nearly equal the angles have to be equal, and I think we said that this angle is around 109 degree or something, so to maintain, I mean both these it should be a shape of the grain should be such that, it should fill up the spaces at the same time, wherever this grains are meeting each other. There will be this lines formed, and you will have this forever this 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 I mean at try to show it here. And this will have how many eat and then it has one, two, three, four, five, six corners. So, six more phases will be added, so 8 plus 6, so it will have 14 phases.

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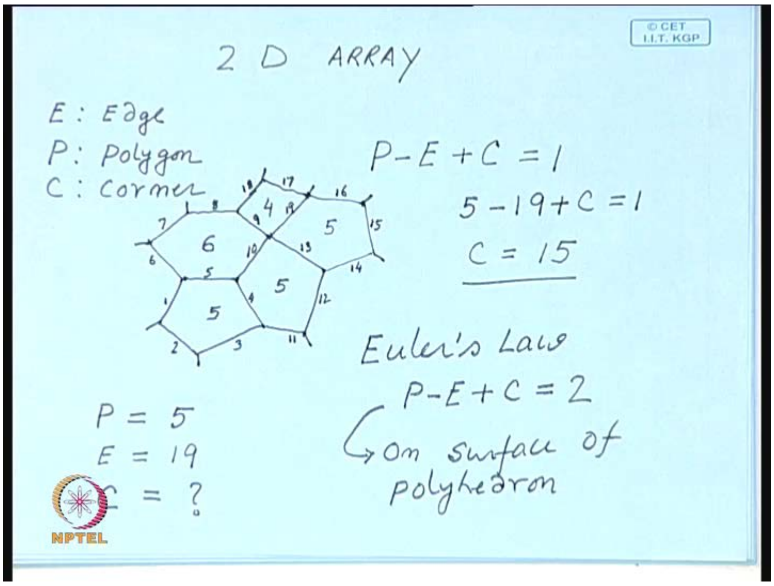

2 D ARRAY

E : Edge
P : Polygon
C : Corner

$P - E + C = 1$

$5 - 19 + C = 1$

$C = 15$

Euler's Law

$P - E + C = 2$

↳ On surface of polyhedron

$P = 5$
$E = 19$
$C = ?$

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

They meet each other said this will have one crystal arrangement say here this plaints are arranged like this, say here possibly that plaints 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 it is orientation is different, the same plaints are oriented differently. Now, you can count there are 3, I mean when you do this packing you also generate apart from ages number of corners, where 3 are more than 3 grains meet like here, the 3 grains are meeting. Similarly, they may be places here, there are 1, 2, 3, 4 grains are meeting, so you generate, so in this figure you have a number of polygon that is P; you have a certain number of ages E, and you also have certain number of corner and there is relationship.

If this is a space feeling there is a relationship like this, which is looks like similar to that Gibb's peace phase rule that is P minus E plus C equal to 1. So, this is in this is true in a two dimensional case two d case. Now in this particular case you try and count, now you have number of this screen this is 1, 2, 3, 4, 5. So number of polygon is 5, number of ages have try 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 is 15, so; that means, you should have 15 corner. Now, you count a corner this is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15. So, you get that 15 corner, so this is satisfied in a two D array, and this rule is quite general.

In fact, that 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 minus E plus C, but this will be equal to 2, Here also in this polyhedron also you will have number of phases, corner, and edges. So therefore, this can be applicable it is a very general this type of law is very general, it can be applied to polyhedron and 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 atomic arrangement along this interface called grain boundary, so this is the boundary and I said that here crystal structure of this on this there exactly seen.

So, what you do say suppose, we generate an array the atomic array, how does it lope, you can do it as an exercise an on a piece of paper, if it you can take a transparent sheet, and draw is atomic array at a regular interval may be you take that close pack plain, you draw this close pack plain like atomic array one sheet, and you repeat you take a xerox copy of that an another another sheet. And now on the transparent sheet, you put on that and try and rotate rotate through certain angle and; that means, what you are doing you trying to visualized, what is the nature of array near the grain boundary. So, may be part of it, you see this; that means, you can can you generate this atomic array by rotating this screen, so this kind of a plainer arrangement, which is shown over here.

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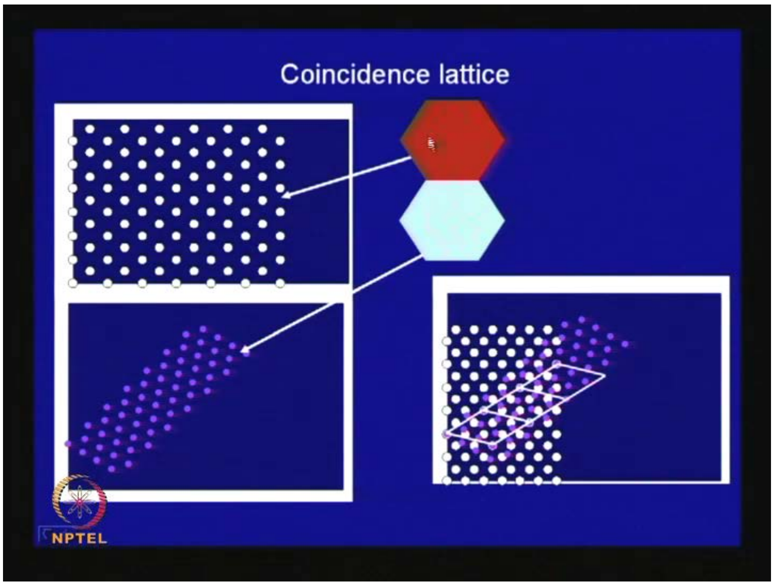

Coincidence lattice

It is called coincidence lattice concept, I have drawn the same thing this is one grain that this atoms arranged like this, whereas in this grain, the atoms are arrange in this fashion the same plain, but it is a different lattice rotate it. Now, what happens at the grain boundary near the grain boundary few layer 2 or 3 layer what happens, so this is the layer this is the one grain; this is the other grain, and you can this is the grain boundary. If you extend the lattice, you will find that some of these points, they are coincidence with the lattice with these lattice points, so which a 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 co incidence lattice type of relationship. So, this is I mean it is not that this atom of occupied this phase, you just super imposed and see what are the coincidence lattice sight, and what you can find out this coincidence lattice distance this is much 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 coincidence lattice dimension is 3 times that mean lattice dimension, and by this it is possible to relate and find out this surface energy all energy of the grain boundary, and this energy has a relationship between this angular rotation between to the neighboring grain, and that is how the grain boundary energy is a 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 fully this topic fully we have (no audio from 56:03 to 56:11) we have talk an next class, we will begin a new chapter thank you very much.