Material Science
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Lecture No 23
Phase Transformations (Contd.)

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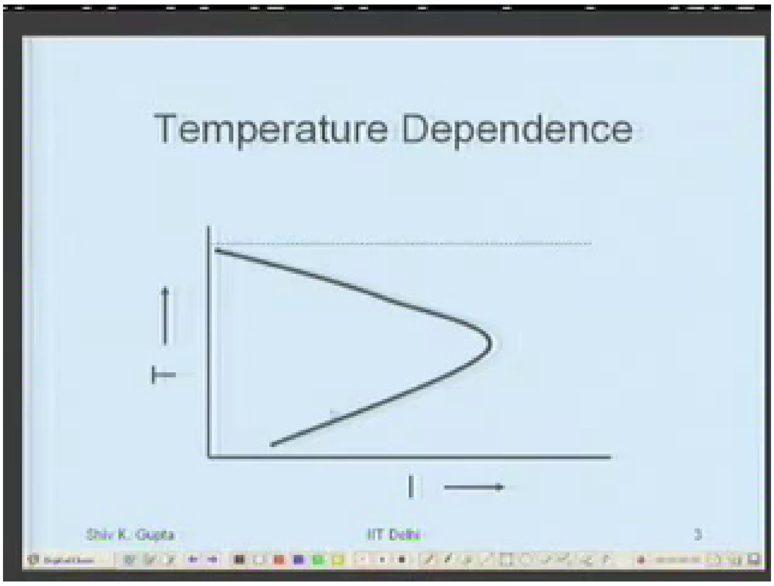

Temperature Dependence

Well in the last class we were talking about the nucleation process and we had looked at the homogenous nucleation, the rate of homogenous nucleation was seen as this the equilibrium temperature that is where it is 0 and this rate increases with decrease in temperature passes through a maximum and then goes again to 0 at 0 kelvin. So this is the homogenous nucleation rate that is what we saw.

You can see this as compared to the Arrhenius relationship where the rate keeps on increase with increasing temperature, the story is not so. Rate is increasing with the increasing temperature in the lower branch and then when it reaches a maximum beyond that it is decreasing with increasing temperature, and at equilibrium temperature the rate of transformation or rate of nucleation is 0, right.

The transformation may not begin at the equilibrium temperature and you would notice that it is because of the rate equation, the activation energy has delta f star and delta Hd, the diffusion across the interface is delta Hd and delta f star is the critical free energy or the free energy of the critical nucleus and this is the function of temperature because of the free energy change involved and the interface which is formed and that is what is causing this two the decreasing with decreasing temperature, here as the temperature is decreasing the rate is increasing rather initially because the driving force become more and more and more available, right.

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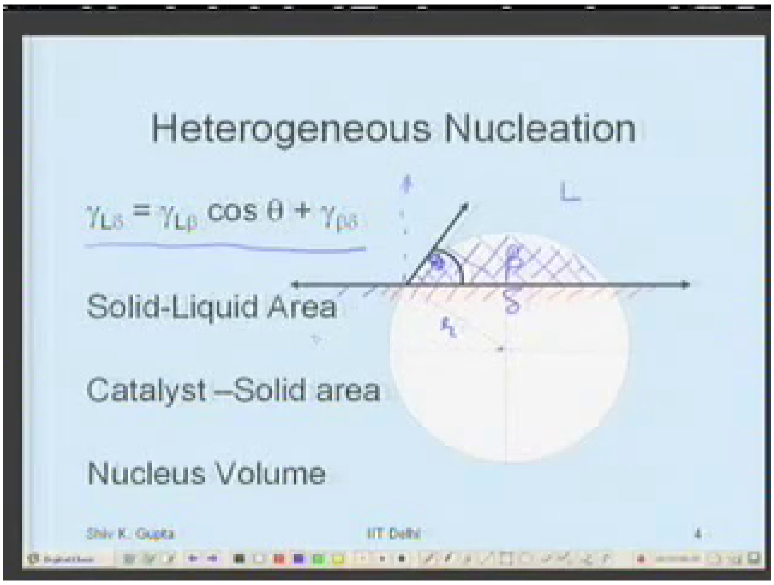

Heterogeneous Nucleation

$\gamma_{L\delta} = \gamma_{L\beta} \cos\theta + \gamma_{\beta\delta}$

Solid-Liquid Area

Catalyst –Solid area

Nucleus Volume

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Now we shall very quickly go over the heterogeneous nucleation, I consider the process of heterogeneous nucleation. Let us say this is the ball of the container and on that container ball a small particle forms of beta phase which is here as a small spherical cap, it is not a spherical particle but it is a small spherical cap. So this spherical cap here is the interface between the liquid and the beta. While I have another interface here between and the wall of the container let me call it as delta.

Between beta and delta there is an interface created but before this interface was created there was something here, what was there, interface between liquid and delta, this is the container, I poured the liquid in it, the solid particle forms, it is replacing there liquid delta interface and creating a beta delta interface and that is what in heterogeneous nucleation usually… Beta delta interface has a very very low energy that is helpful and here at this point the surface tension between liquid and beta is acting in that direction.

Now let us say this angle is theta and this is the surface tension acting between liquid and delta and it is here between beta and delta so that has been balanced here in x direction but the component of this force in the y direction has been left unbalanced. It will remain unbalanced that is to be taken care of by the wall which is rigid, container wall is solid and is rigid, it has to take care of this force onto it, that means it undergo the elastic deformation.

So that is unbalanced but the x direction when you balance this is the relationship, we can work out because this is liquid beta is this one, cos theta in that direction is a component, gamma beta and delta is also added in that direction and then it is balancing the gamma, liquid and delta. As far as the interface is concerned I have to take care of this beta liquid interface which is newly formed interface like it was forming in the homogenous nucleation.

But also I am forming a catalyst or the delta, the wall of the container and the beta phase interface but the same area I am removing of the interface between liquid and delta. Something which is being removed liquid and delta, and place of that I am forming beta and delta, that is what going to help us and the volume of this nucleus is going to be, only this cap which is small volume, it is not the whole sphere, I made the whole sphere with the center and that is called the particle, while you can work these areas out, you can make the balance, I am not going to do that.

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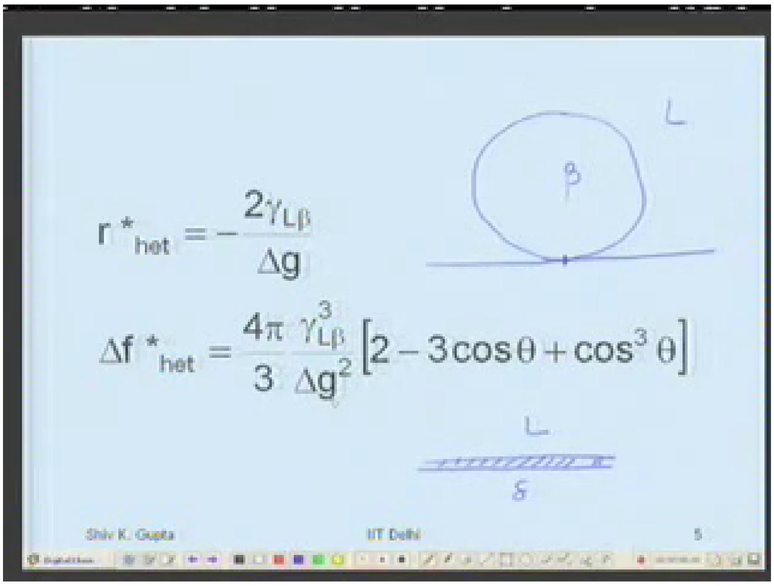

$$r^*_{het} = -\frac{2\gamma_{L\beta}}{\Delta g}$$

$$\Delta f^*_{het} = \frac{4\pi}{3}\frac{\gamma^3_{L\beta}}{\Delta g^2}\left[2-3\cos\theta+\cos^3\theta\right]$$

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But what happens is with the result of this we get this r star heterogeneous, this minus 2 gamma liquid beta that is an interfacial energy of liquid and beta and delta g. What was it for homogenous nucleation, was it different. Gamma is there so the interface between liquid and beta, so that is what it is, 2 gamma by delta g you found out there, this is the same and not different. But the volume of the cap is not smaller now, it is not whole sphere, and then when you work over the delta f star, accordingly instead of 16 pi by 3 gamma cube by delta g square it comes out 4 pi by 3, gamma cube at delta g square. And other factor of 4 is replaced by this square bracket, 2 minus 3 cost theta plus cos cube theta.

Student: The energy is again per unit volume.

Professor: Yes.

Student: Which volume?

Professor: Volume which is transformed, there is a cap over there, volume of the liquid which is transformed to the solid, it is only the cap volume, I cannot talk of the total volume, that is only to give you the radius and other things you can work out, right. Alright.

So this we have seen now with the help of this angle theta and try to understand what is the situation now theta is 180 degrees, what shall my drawing be when theta is 180 degrees, and just a point contact. Point contact means zero area of contact, no surface removed, no new surface formed between beta and delta, no liquid delta interface removed, it is just like homogenous nucleation and it should become homogenous nucleation if theta is 180 degrees.

To that cos theta is minus 1 so 2 plus 3 and cost theta would cube theta would also be minus 1, 2 plus 3 minus 1 become 4 and 4 into 4 become 16, this is the same thing as homogenous nucleation. 16 pi by 3 gamma cube by delta g square that is what you worked out. Now when theta is 0 degrees then what happens? A thin film of beta forms all over the wall of the container.

So this is the thin film, right and that is what form. And put theta equals to 0. This becomes 2 minus 3 plus 1 which is 0, square bracket becomes 0, delta f star is 0, you want these therefore if heterogeneous nucleation has to speed up my nucleation process then theta should be as close to 0 as possible.

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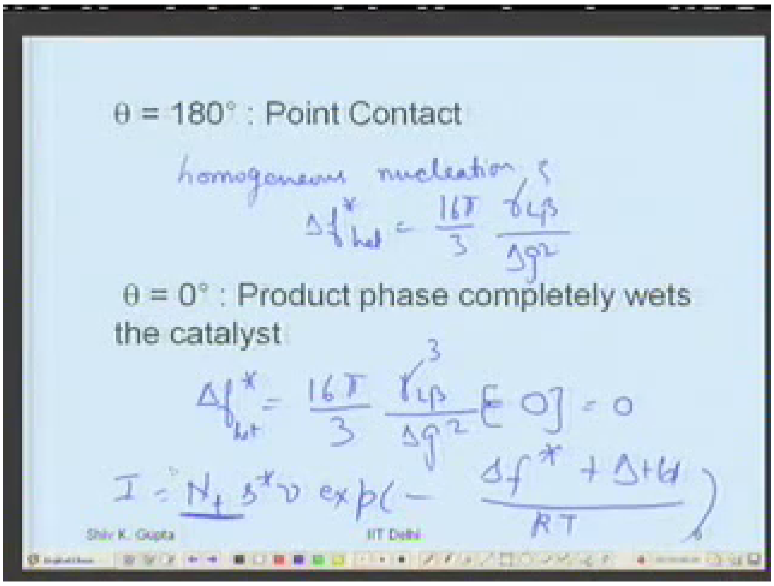

θ = 180° : Point Contact

homogeneous nucleation

$$\Delta f^*_{het} = \frac{16\pi}{3}\frac{\gamma_{L\beta}}{\Delta g^2}$$

θ = 0° : Product phase completely wets the catalyst

$$\Delta f^*_{het} = \frac{16\pi}{3}\frac{\gamma_{L\beta}^3}{\Delta g^2}[0] = 0$$

$$I = \underline{N_t} s^* \nu \exp\left(-\frac{\Delta f^* + \Delta H_d}{RT}\right)$$

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This is the point contact, homogeneous nucleation, gamma is between liquid and beta and this is 0 because this angle is there. In this case it is going to be same and that is what we try to do when we want to do the heterogeneous nucleation. Unfortunately when delta f star is becoming 0 or small it is the number of nucleation sites Nt, it is reducing down and look at the nucleation down.

I have written for nucleation rate Nt, s star Nu exponential of minus. When this is becoming small or closer to 0 places where nucleation can take place is reducing in numbers with our preferred sites. Look at the whole volume of the liquid and the volume available close to the wall of the container is a very small volume. So number of place the nucleation can take place as we are going down while this affects the (())(12:32) or as a magnitude, this is reduced by 16 order of magnitude.

So I am not getting very fast process but this tells us how the nucleation can be affected by if you have heterogeneous nucleation events provided the interface between beta and delta as a 0 energy then the theta is 0 otherwise theta is not 0. There is a meaning of that, the interface matches on the two sides.

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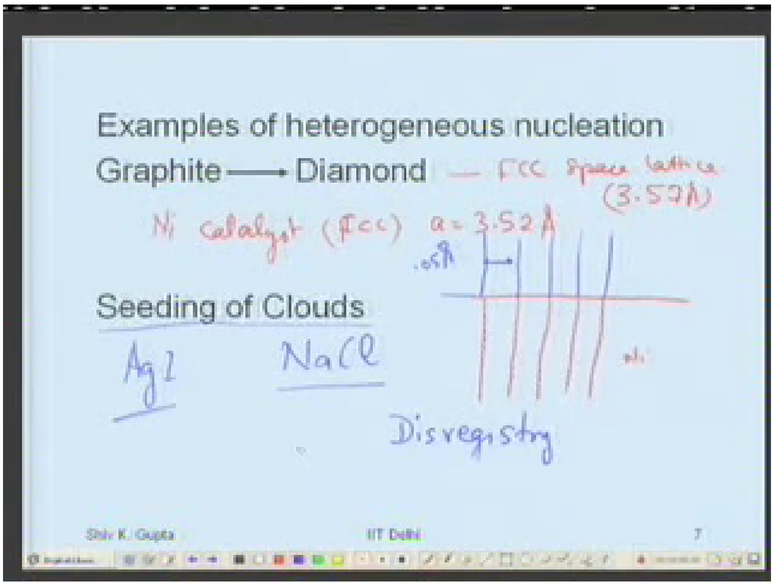

Examples of heterogeneous nucleation

Graphite ⟶ Diamond — FCC space lattice (3.57Å)

Ni catalyst (FCC) a = 3.52 Å

Seeding of Clouds

AgI NaCl

Disregistry

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The examples of two heterogeneous nucleations, very interesting to engineers, one is we convert graphite to diamonds, industrial diamonds are produced like that, you need to have very high temperatures and high pressures for this and what we use, we use nickel as a catalyst. Nickel is FCC, its lattice parameter is 3.52 Angstrom. Diamond is a diamond cubic structure but diamond is also FCC space lattice and its lattice parameter is 3.57 Angstrom.

If I look at crystallographic planes in nickel and what is going to form in diamond, within 1 or 2 atomic diameter distances near the interface there are some small strain, 0.05 Angstrom, it is a very small strain, it is not 0. The interface is not 0 in interfacial energy, theta is not 0 but close to 0 and that is what help us in producing over these planes, the planes of diamonds, okay the same way.

And that is how we do the seeding of clouds also to cause rain, clouds are tiny particles or water which are there in the atmosphere, upper atmosphere, there if you sprinkle silver iodide or sodium chloride where the planes match with those of the crystalline planes or crystal planes of eyes, these water droplets, the slice as ice and more and more droplets joint them to make it a big crystal of ice.

This big crystal of ice when it becomes heavy drops due to gravity. When it drops due to gravity it has a friction with the atmosphere and heats up again to become the water droplet and it causes rain. So what I am doing is I am trying to convert the water which is at minus 43 degree centigrade, the upper atmosphere which cover to ice and covert that to ice I am using these crystals where the planes match with those of ice crystals and therefore the matching of the interface takes place with some small strains of course and then the crystal of ice conformed.

That is heterogeneous nucleation we are doing. I will give you more examples of heterogeneous nucleation as we proceed. So interest is to have planes which are matching thing, distance between the planes are matching, so strain is as small as possible, this strain here is also called disregistry, smaller the disregistry small will be the strain and small will be the angle of contact which we can also call it as waiting angle.

If the product completely gets (())(17:30) my catalyst that means it perfectly matches and it can do so if the crystal which is growing from the liquid and the catalyst is the same crystal then the (())(17:43) planes will match perfectly. If let us say I am growing a silicon single crystal for making a chip from a silicon malt I take a seed which is (())(17:55) silicon crystal, I can make it touch with the liquid and slowly pull it out and the same planes will keep growing, the same crystal will grow and the interfacial energy would be 0. This interface will be quite… There will be no interface.

Student: (())(18:21).

Professor: It is heterogeneous but I have put external source, the whole thing is taking place only at that place. Okay. Solid which is forming the catalyst provides an interface with 0 energy, right.

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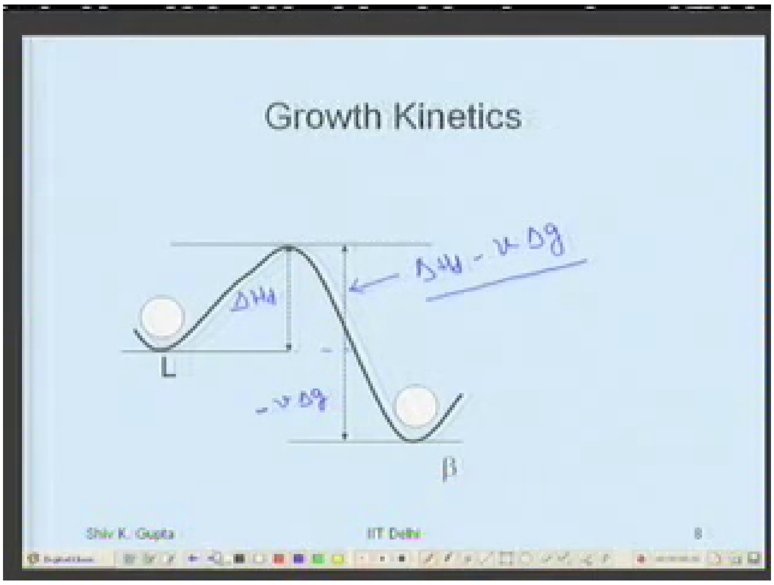

Growth Kinetics

Well with this, the kinetics for nucleation whether it is homogeneous or heterogeneous it is going to be a, delta f star is going to behave in the same fashion with temperature and the dependence temperature dependence is what is showed you. Now once the particle has become satiable, the critical nucleus, I have added one more atom to it, it has gone greater than R star and therefore it has become super critical, now it can only grow in size and lower its energy.

Now here I will show you the energy, atom which is in the liquid here as at some level of energy, then it has to cross the interface and reach or acquire an energy equal to delta Hd this level if it can then goes down to the other side with the crystalline solid but this difference is not reaching the same level, lower level because delta g is lower. So this value, this difference, from here to there will be let us say volume transformed because of one atom is small v times delta g, but delta g is a negative sign so I will put a minus sign.

So this height from the energy of beta through this activation energy level is going to be delta Hd minus v delta g, this is the plus terms because delta g is a negative term. So this height is more and this height is less. Why I am showing us this, when an atom from the liquid close to the interface is trying to jump into the crystalline solid, those atoms in the crystalline solid which are close to the interface can also try to jump back to the liquid.

The one which is in the liquid trying to jump back to the solid, I call it a forward jump and it is going to lower the energy of the system but the one which is in the solid crystalline solid wants to jump into the liquid, it can also jump that is going to increase the energy, right. In other words what I am trying to say is if you look the probability of this atom can acquire delta Hd energy and go to the other side is much more than this atom acquiring energy delta Hd minus v delta g and going to other side to become a liquid.

In other words more of these atoms from the liquid will be going to beta and less of these will be going from beta to the liquid. We will be then transform the atoms from liquid to the beta and that is why I am calling it growth, all the time beta particle is going to grow in size and volume, so let us look at the rate of jump of these atoms from the liquid into the beta cross the interface.

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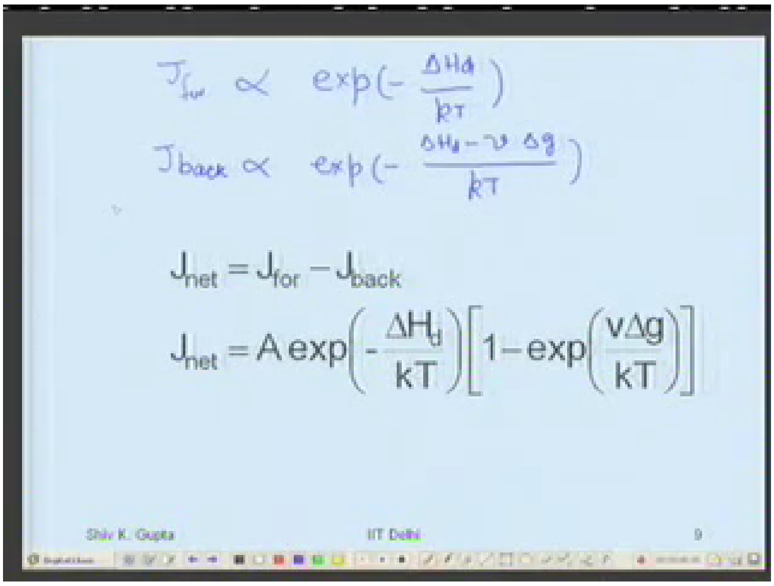

$$J_{for} \propto \exp\left(-\frac{\Delta H_d}{kT}\right)$$

$$J_{back} \propto \exp\left(-\frac{\Delta H_d - v\Delta g}{kT}\right)$$

$$J_{net} = J_{for} - J_{back}$$

$$J_{net} = A\exp\left(-\frac{\Delta H_d}{kT}\right)\left[1-\exp\left(\frac{v\Delta g}{kT}\right)\right]$$

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That is call it forward jump and it is going to proportional to exponential of minus delta Hd by kt, the probability that atom can acquire this energy delta Hd. Similarly, the atoms which are in the solid can jump into the liquid, I call it as backward jump which will be proportional to exponential of minus the height is delta Hd minus v delta g upon.

I make a simpler estimate of the estimate and say the proportionality constant for both of them is the same and then the net number of atoms going from liquid to solid to show the growth would be net rate of forward jump minus net rate of backward jump, that is it. Net rate of jump will be there, let the proportionate constant is A, is A times exponential of minus delta Hd by kt is forward, A times exponential of minus delta Hd minus v delta g by kt is backward. I subtracted backward from the forward and I get the net.

And I can take exponential of minus delta Hd by kt, it is common and proportionality constant is also (())(23:29), this gives me 1 and this gives me exponential of minus and minus becomes plus, v delta g by kt. So this is the net rate of jump for atom from liquid to the solid.

Student: (())(23:48) v is the?

Professor: V is the volume changed, v delta g means delta g is per unit volume, v is not the vibrations, v is the lattice vibration frequency Nu, it is not v. It is a volume corresponding to one atom what is changed.

Now let us look at temperature dependence, near the melting point delta g is at the melting point, delta g is 0. When delta g is 0 exponential o f 0 is 1 minus 1, so net forwards jumps will be 0, no growth rate. Particle will not grow at all. As the temperature is lowered below the melting point I do the under cooling, delta g becomes less than 0 at this number exponential of certain negative number become a fracture, which is fraction is of course less than 1.

1 minus is small fraction, number becomes less, has become more since the rate has begin to increase. Net forward jump begin to increase as the temperature is lower but a situation would arise when this number becomes much-much smaller than 1, because this is a negative number, delta g is increasing in the minus science so this becomes less than less than 1. Then this 1 minus, this less than less than 1 is almost 1.

When it is almost 1it is this exponential term which takes over where delta Hd is not a function of the tm, it is constant. So then at that stage, as the temperature is further lowered the rate will begin to decrease. So like the nucleation rate growth rate also passed through a maximum at some temperature and then goes to 0 kelvin. However the temperature way the maximum growth rate occurs is closer to the melting point, closer to the equilibrium temperature as compared to the temperature where the maximum nucleation rate occurs.

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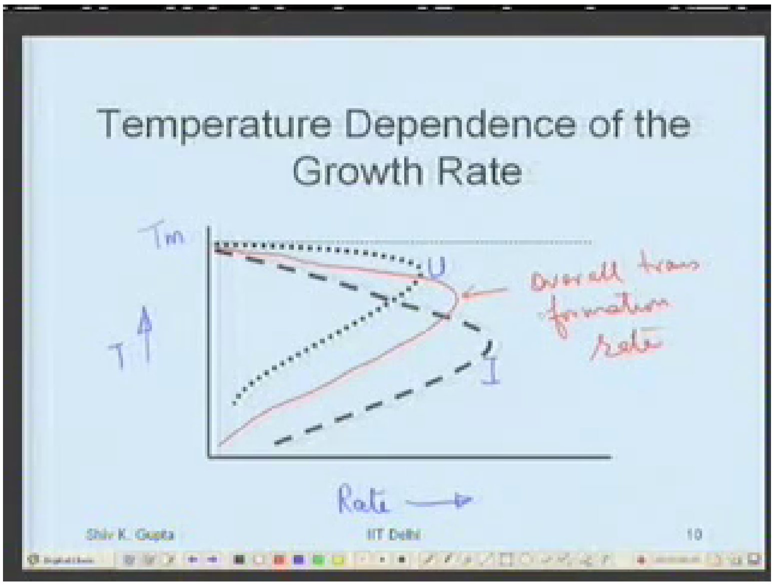

Temperature Dependence of the
Growth Rate

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So I show you this picture where again here I have the temperature on the y axis and the rate on the x axis, this is for the nucleation rate and I write the growth rate as U. So you see the maximum here for the growth rate is at a temperature which is higher than that where there maximum (())(26:41) nucleation rate occurs and this is because it is more diffusion dependent the growth.

Growth is more diffusion dependent so diffusion is more when the temperature is high, diffusivity is more therefore this is what it is happening close to the temperature of equilibrium, in this case solidification it is melting point, close to the melting point the growth rate is high and then as the temperature is lower the growth rate becomes less and less and nucleation rate passes the maximum like this.

Now if you look at the process of nucleation and growth, the mechanism of transformation, some particle nucleate initially, these particles begin to grow with time, while that is happening some other particles are nucleating in the volume. When the second stage particle nucleated, the first stage particles nucleated are growing, third stage particles nucleate, so process is continuous. Nucleation and growth go hand in hand.

So if I want to look at the overall transformation rate or kinetics it is going to be some kind of a product of the nucleation rate and the growth rate, right? So particle which is nucleated will be able to grow. Let us say for example here, rate of nucleation is very small but the rate of growth is very high, so particle which is nucleated will be able to grow to a bigger size but more particles nucleating will be less and less.

But if I am somewhere here nucleation rate is very high and growth rate is small, more and more particles will be nucleating but they will be growing to smaller sizes relatively and more and more still will be nucleating, and that is what is going to happen, so there is a some kind of overall transformation or overall volume changed will be some kind of a product to nucleation rate and growth rate. So that I can show as, this is overall transformation rate.

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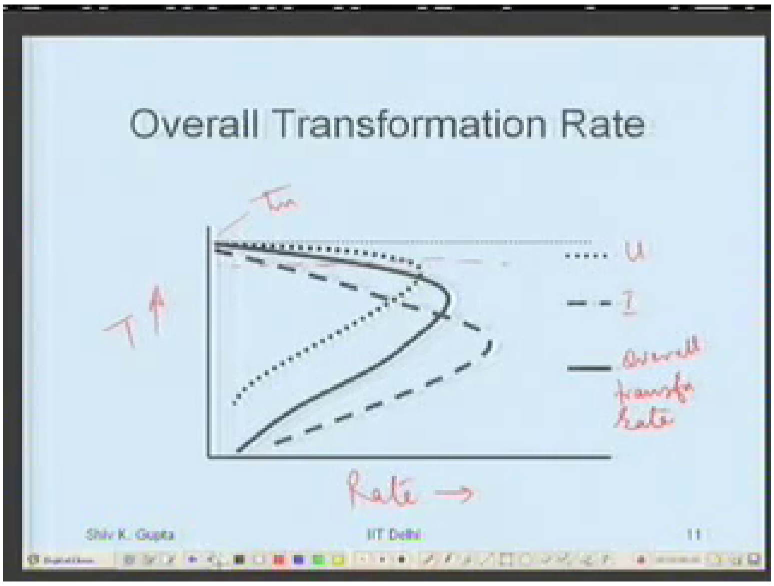

Overall Transformation Rate

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This is the temperature, that is the rate, that is the melting point, this is growth and this is nucleation and this is overall transformation. Now my problem is I have understood this that how this is going to happen. If I conduct an experiment is it possible for us to measure the rate for a process. What we can measure is only the extent of the volume which has transformed and the time taken for this transformation, at any point I cannot measure the rate directly.

So I can measure, what I can measure is, let us say I conduct an experiment at a particular temperature, I take the melt, take it to the temperature let us say 5 degrees below the melting point somewhere here and with time I can find out how much is the liquid solidified.

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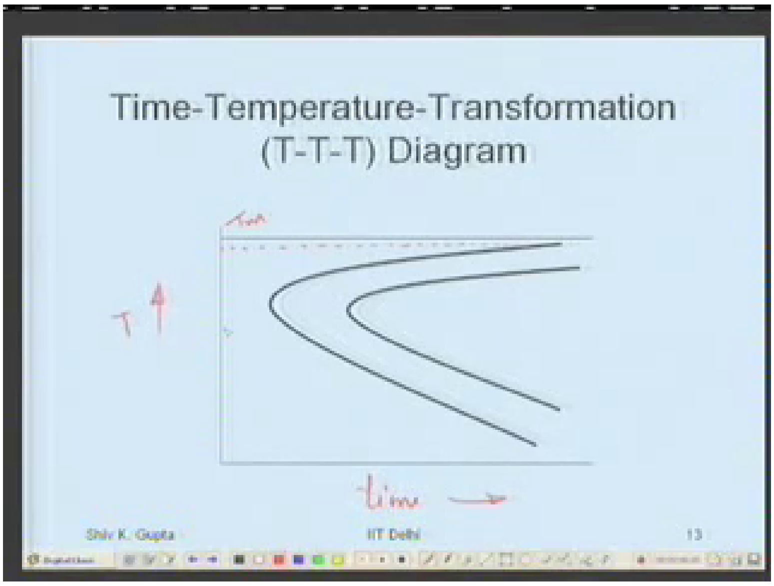

Time-Temperature-Transformation (T-T-T) Diagram

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So I plot here the temperature on this axis, time on this axis and the extent of transformation, let us say I have done the experiment, as I said some temperature below the melting point.

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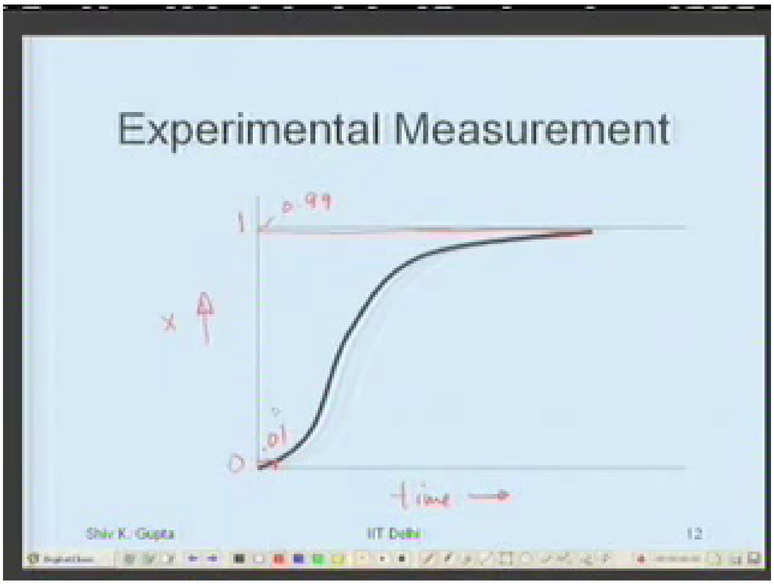

Experimental Measurement

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And that experiment looks like this, the action transform is 0 here, 1 here and that is the time. Normally if time taken is more we can plot (())(31:51) but this is the muddle kind of a curve, it initially start with slope process, the particles have to first nucleate and then only they begin to grow but some particles are nucleated, they are growing and some more are forming and it begins to accelerate, it begins to accelerate and then when it has filled more than 50% of the volume it again begins to slow down and it slows downs till the (())(32:16) is complete.

In an experiment when the transformation has begun I can say if I can observe some particles formed, I am looking at the microscope anything less than 5% is usually not observable but I can see through the other measurements like properties of electrical resistivity of the material, I may be able to see something like 0.2%, so below 0.2% I am not able to see anything, I am doing a crude experiment I can measure only 1%.

So till 1% material is transformed I don't see any change taking place and this is what I call incubation period. I cannot measure it in an experiment. Final experiment as I said 0.2% maybe you are able to measure. Similarly by the time you reach 99% because of your ability what to be able to distinguish rather 1% that is left over you will feel that it is 100% done.

So you measure the time for 1% transformation, you measure the time for 99% transformation and this is what I am showing here on this diagram that you are plotting here time taken for 1% transformation and then go on to find out the time taken for 99% transformation and thus will go on like this. Then you do the experiment as some other temperature.

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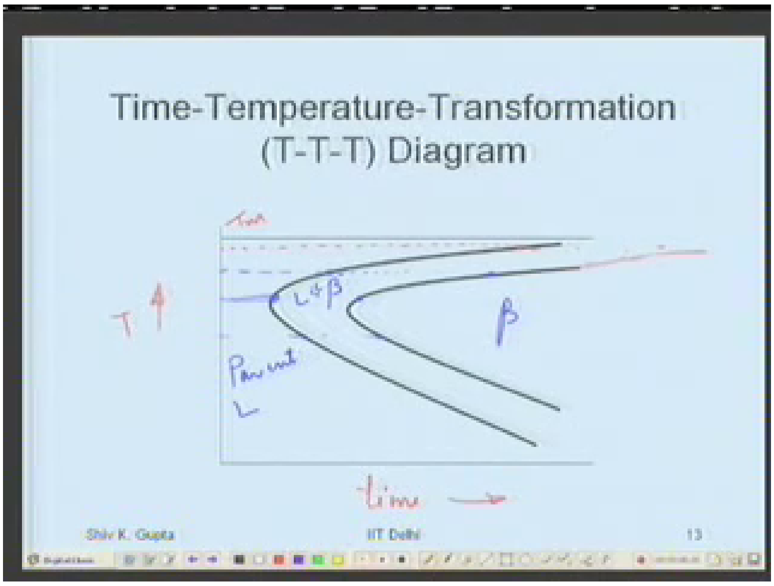

Time-Temperature-Transformation (T-T-T) Diagram

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Let us say this temperature when this is the incubation period at 1% transformation and that is the time for 99% transformation, at this temperature you can do this experiment.

Student: (())(34:31)

Professor: I am just telling you. First of all I have done the experiment to find out these points, for 1% and 99% transformation, I join them and I get this curve. This is the region of parent material; here no transformation has yet taken place which is in this case if liquid. When I crossed 99% it is almost 100% solid that is the solid region beta, this is the region in between where I have liquid and beta both existing together, right?

So I get a curve where the axis of time and temperature, and gives me the field transformation, so I call time temperature transformation diagram. And you would notice that in the previous diagram, again I remind you that.

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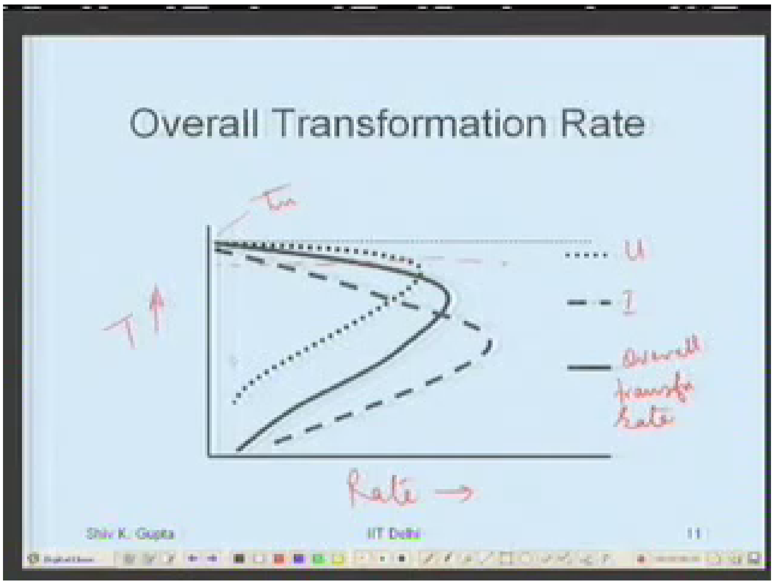

Overall Transformation Rate

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This is the rate of transformation, rate of transformation at the equilibrium temperature is 0, and it increases as the time our temperature is lower goes through a maximum, but here the time take will be the minimum for the process and then when it goes the rate again decreases and the time taken is more and more, that is what is shown clearly in this picture.

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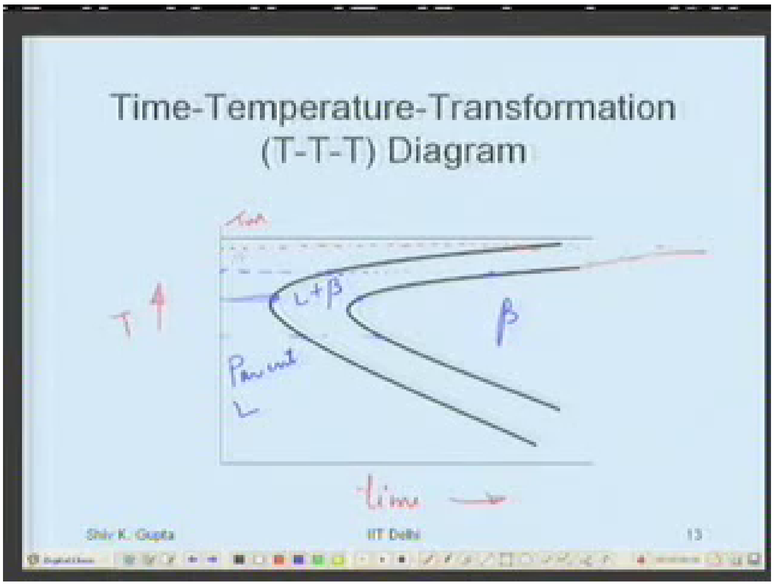

Time-Temperature-Transformation (T-T-T) Diagram

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At here the time taken is very large but at the maximum rate the time taken is the smallest, but again as the rate decreases time taken is more and more, so this is called the 1% transformation curve let us say, call the 99% transformation curve. So this is the untransformed region, this is the transformed region, this is the in between region, intermediate region where transformation is still on.

So this is how the rate is converted to time and you see where the rate is maximum time taken is the least, and the rate is zero time taken is infinity, as (())(36:47) to the melting line, this temperature axis and this constant temperature line is going (())(36:55) to that. It will not cut it, it will not cross it because the rate here is 0, time taken is infinite, so that is what is going parallel to that.

So such diagrams we create for all transformation, we study transformation, right and then we see how much is the time taken by the process, important time is the time we knows here, how much is this time. Usually this maybe from here to here, maybe 50 degrees, 100 degrees or 150 degrees, that is the kind of temperature range. If time is in microsecond I have to, if I am cooling the liquid from this temperature and a very fast cooling, I can avoid this and I can still retain the liquid, understand.

But it all depends upon this time whether I can bypass this time, am I able to do that or else I can do it slow cooling, I sure that transformation will go to completion if you are still fast, or slightly fast still it will go the completion.

But you want to stop the transformation you have to, this is called the critical time and this is also called as sea curve, the shape is that of the sea and the nose of the sea, if you can bypass this time you can suppress the transformation, all this depends upon the time scale and that is what we are going to see the next.

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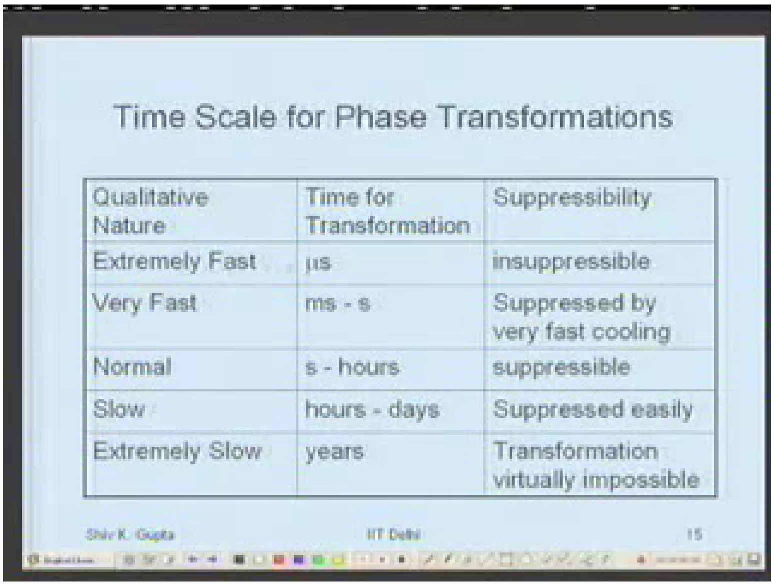

Time Scale for Phase Transformations

Qualitative Nature	Time for Transformation	Suppressibility
Extremely Fast	μs	insuppressible
Very Fast	ms - s	Suppressed by very fast cooling
Normal	s - hours	suppressible
Slow	hours - days	Suppressed easily
Extremely Slow	years	Transformation virtually impossible

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Well if the time taken by a process is in the range of microsecond, I have to cool down by about 50 degrees, the nose is about 50 degrees, and in the few micro seconds the rate of the cooling has to be a million degrees per second or so, if you want to suppress that, you cannot cool it that fast, it will cross this and the moment is crosses transformation begins, liquid goes to become solid.

So the time taken by a process in that sense extremely fast when it is in the range of microsecond and these processes are usually insuppressible, we cannot stop such a thing to happen, from happening, such a thing would happen, and lately we have developed, this late is also not so very late about 30 years or so now, the rate of cooling achieve in the range of 10,000 to 100,000 degrees per second, that is called splat cooling.

What is done is, the liquid is dropped from the top onto a water cool copper substrate, copper has a very good conductivity for taking away the heat, when it drops on the substrate which is given a shape like this, it spreads, forms a very thin fill, that droplets and thin films are in the thickness is smaller than a micro meter. So heat from the solid which forms is also taken away very quickly because thickness is very small and the rate of cooling achieved can be high and substrate is already made water cool.

So that is maintained at room temperature, such a thing is called splat cooling and some of the matters we have (())(41:02), we have been able to convert into liquid like structure what are called metallic glasses. Some of the magnetic materials are used in that form, in the form of thin ribbons which are produced by this splat cooling. So there we have avoided the crystalline structure formation, the crystalline structure at possible.

Then other process is called very fast, the time they take is between millisecond and second, in that range. This can be suppressed by very fast cooling, like the process is in the steel. You (())(41:42) transformation gamma going to form pearlite and that forms in this range. I can simply take the austenite which is above (())(41:53) temperature and quench it in water at temperature or oil at room temperature.

Suppress the formation of the pearlite and this pearlite will not form in the solid, all the carbon which is in austenite shall remain in solution, it will not segregate to form cementite but something else happens that we shall see in the next class. Then the processes which are normal processes, they take normally seconds to hours to take place, they can be easily suppressed. You don't have to do very fast cooling for that, they can be suppressed easily.

Then the processes which are slow they take hours to days, you can suppress no problem but the problem might be here that you want to accelerate the process. It is taking a few days and you want to cut down the industrial time, you would like to accelerate it. Can you accelerate it, you have to see that? And then the processes which are extremely slow take years, 15 – 30 years, like if you take a silicate glass, like window paints, if you want to make it a crystalline structure that of (())(43:12).

It may take 30 years, maybe so slow the process virtually not taking place, not becoming crystalline (())(43:12). So such processes take years and they are very slow, transformation is virtually impossible in such situations and we don't talk of even trying to accelerate that, these processes we may like to accelerate if possible.

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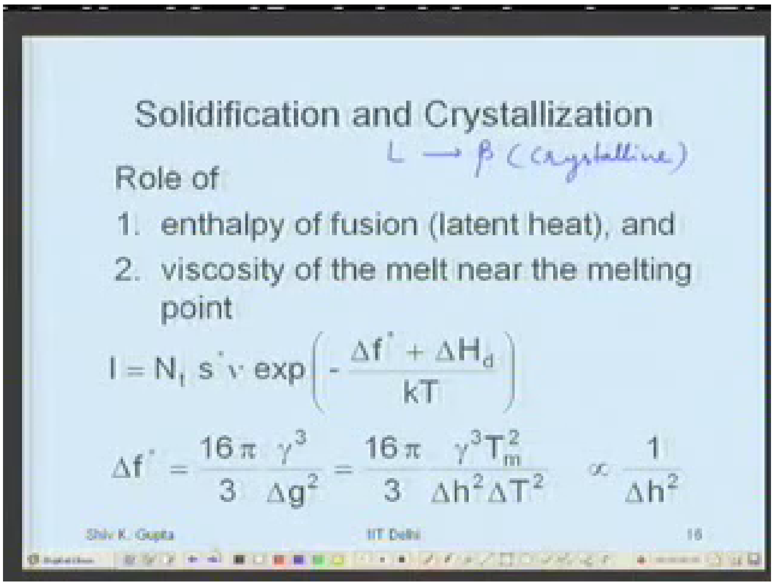

Solidification and Crystallization

$L \longrightarrow \beta$ (crystalline)

Role of

1. enthalpy of fusion (latent heat), and
2. viscosity of the melt near the melting point

$$I = N_t s^* \nu \exp\left(-\frac{\Delta f^* + \Delta H_d}{kT}\right)$$

$$\Delta f^* = \frac{16\pi}{3}\frac{\gamma^3}{\Delta g^2} = \frac{16\pi}{3}\frac{\gamma^3 T_m^2}{\Delta h^2 \Delta T^2} \propto \frac{1}{\Delta h^2}$$

Now continuing with the solidification process, solidification and crystallization, I mean the same thing, liquid is going to form a crystalline solid beta that is the transformation I am talking of, liquid remaining non crystalline solid is not crystallization of solidification that I call glass transition. We will talk about that later, but solidification crystallization is liquid is going to form solid, crystalline solid and this is the crystalline solid.

With the help of whatever nucleation rate I wrote, I would like to understand the role of the enthalpy of fusion that is called the latent heat of fusion and the viscosity of the melt near the melting point, these two things and then I will show you the difference between metals and glasses which you normally have. Rate of nucleation is Nt s start Nu exponential of minus delta f start plus delta Hd by kT and delta f star here in this term 16 pi by 3, gamma cube by delta g square.

If I had to consider to be homogeneous nucleation and delta g can be written as delta H, delta T by Tm, so it becomes 16 pi by 3, gamma cube Tm square by delta h square delta T square. In here delta f star is proportional or inversely proportional to the scale of delta H the latent heat fusion. Obviously you can see now that if delta h is high delta f star would be very small, if delta h star is low then delta f star would be high.

So in metals usually delta h is very high, so delta f star is small, in this expression if delta f star is small as compared to delta Hd nucleation rate would be high. Transformation rate would be high, that is one component is high, nucleation rate itself is high, overall transformation will be higher rate and crystallizing usually that is why the metals (())(46:14).

Second effect of the viscosity, viscosity is near the melting point when you talk about how the atoms translate with respect to neighbors, it could refer to a shuffling of atoms at the interface and shuffling of atoms if it is very rapid jumping across the interface would also be easier, and where viscosity is low and viscosity is high shuffling itself would be difficult and therefore jumping would be more difficult.

So therefore viscosity affect delta Hd, higher the viscosity higher is delta Hd, lower the viscosity lower is delta Hd, and if delta Hd is lower nucleation rate would be higher that is what happens in melt, delta f star is lower delta hT is also lower, the viscosity of the melt are smaller for metals, but in glasses viscosity is very high, so delta Hd is high, because delta Hd is high the rate is small, time taken is very very large.

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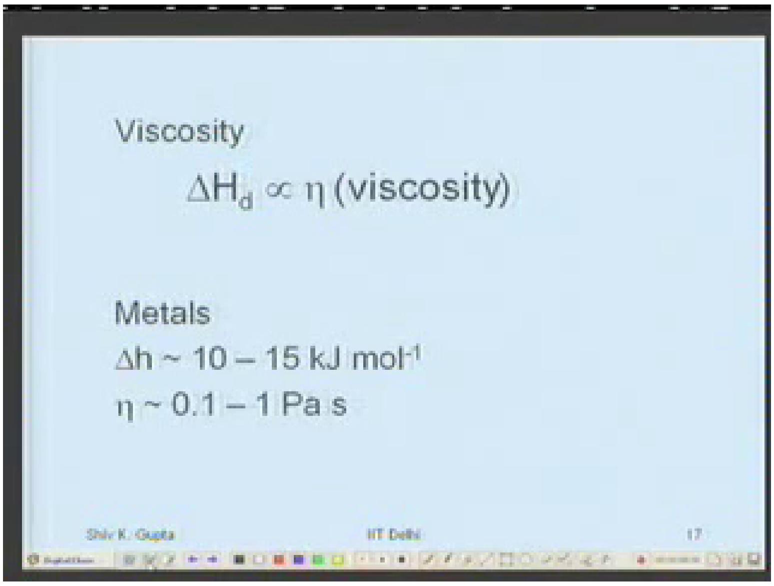

Viscosity

$\Delta H_d \propto \eta$ (viscosity)

Metals

$\Delta h \sim 10 - 15$ kJ mol^{-1}

$\eta \sim 0.1 - 1$ Pa s

So I have shown here this viscosity for metals and the latent heat of fusion rise in the range of 10 – 15 kJ per mole for metals and alloys and the viscosity is in the range of 0.121 Pascal second near the melting point therefore they normally crystallize because delta Hd is small, delta f star is small, both of them being small nucleation rate is high.

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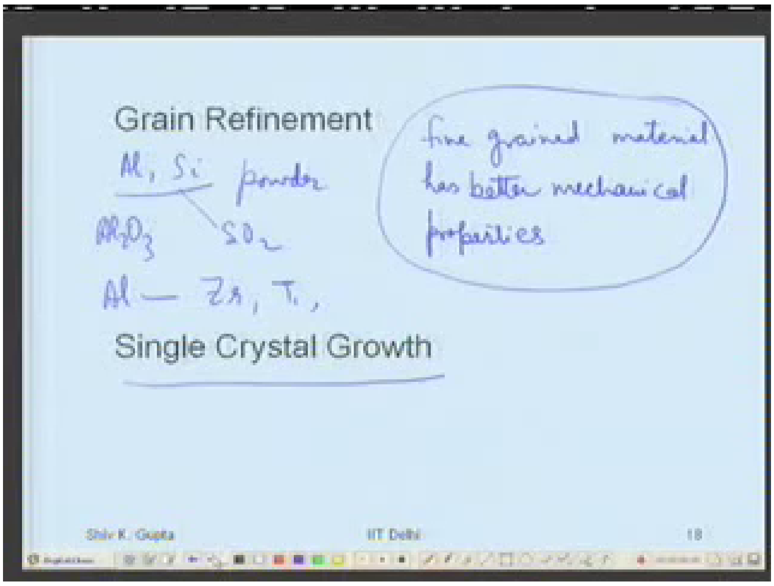

Grain Refinement

Al, Si powder

Al_2O_3 SO_2

Al — Zr, Ti,

Single Crystal Growth

fine grained material has better mechanical properties

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Problem in metals and alloys is one of growing single crystal, for engineer it is grain refined material problem. In here I shall make a statement today which I will be proving it later, a few weeks later I will prove that, if fine grained material which is going to solid, when I am talking about grain it must be solid, a polycrystalline solid has higher rather better mechanical properties. Okay! What I am saying is, fine grained material has better mechanical properties.

So if in steel, I want to develop fine grained steel so that strenehgth is high as mechanical behavior is better, what should I do with whatever you understand the solidification, how can I get fine grains in the given volume of the steel where I am solidifying this. I must have a large number of nucleation taking place. He asked me yesterday. So that each particle which is nucleated and trying to grow will start impinging with the neighbor quickly, I want large number of nucleation sites.

For that what we do is we add either fine aluminum powder or silicon powder through the (()) (50:14) and since they are light metals, we pour the molten steel after dropping a packet of aluminum silicon in it, so as this fine powder of aluminum and silicon, it is a powder form, as liquid metal is dropped, these aluminum particles and silicon particles began to rise in the metal but the liquid which we have poured from the convertor already has bubbling oxygen in it.

That oxygen which is bubbling combines with aluminum and silicon to form oxides of aluminum and oxide of silicon, and then these oxides have a melting point much higher than the molten steel temperature, that solid particles and act as heterogeneous nucleation sites.

Since you have added fine powder distribute it all over the liquid melt and they are all acting as heterogeneous nucleation sites, you get fine grained steel. So by the process all the oxygen get convert into this oxide and trapped.

When the steel is not solidifying there is no bubbles of oxygen left, no holes will form such as steel is called as killed steel, means all the oxygen is killed in this, okay. So that is you get fine grained steel but used to be like this. Similarly if you have produced aluminum, you should know how the aluminum is produced, you are using electrolytic baths and you are using the electrodes which are made of graphite or charcoal that is shorter (())(52:17) electrodes are filled with charcoal.

So in the molten aluminum some carbon from the electrodes is coming but carbon in aluminum is not at all soluble in the solid state, so what we use is we use some elements which are very strong carbide formers like we have added aluminum and silicon because I had oxygen here, good oxide formers, I make use of elements like for aluminum, zirconium, titanium and things like that which are strong carbide formers.

They form carbide because if whatever carbon is there in the aluminum melt and they form carbide which have higher melting point than aluminum, much higher melting point, they are solid and act as heterogeneous nucleation sites. I get fine aluminum grains in the polycrystalline aluminum solid which is forming. So that is how we do the grain refinement. This is for producing materials with better mechanical properties and selling them in the market.

But single crystals are used by scientist for working the laboratories, in here my problem is as I just described an example of few minutes back, I need one single nucleus to go and that is what I give an example, we use the same seed, let us say I am growing silicon single crystals and we put the silicon crystal itself as the seed and from the melt allow it to touch the melt of the seed so that it doesn’t melt by itself but because the surface tension the liquid gets pulled with it, it just pull it slowly out and the silicon crystals grows along with the same crystalline arrangement as that of the seed.

Okay, that is the problem of single crystal growth which is required at single crystal growing is not an easy task for that matter because you have to see that only one nucleus is the one which is growing.

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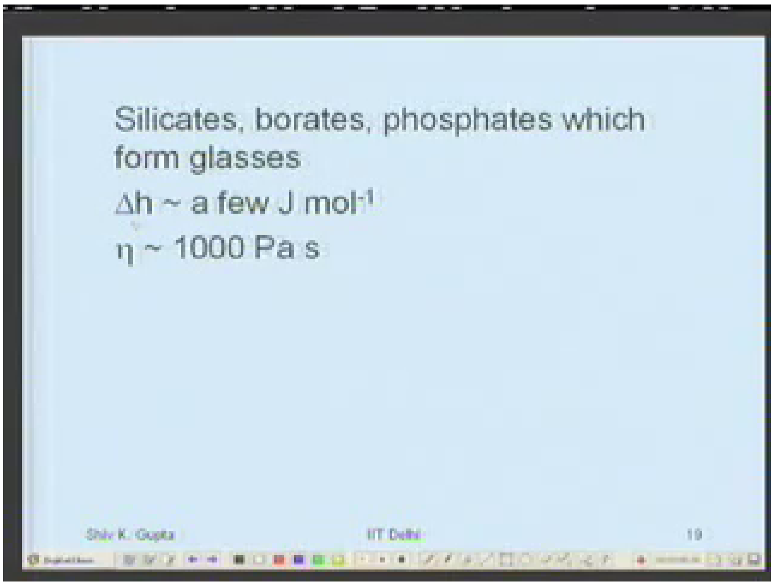

Silicates, borates, phosphates which form glasses

$\Delta h \sim$ a few J mol^{-1}

$\eta \sim 1000$ Pa s

Coming to silicates, borates, phosphates which form glasses usually, now you look at this latent heat of fusion is very small, it would be 2 – 3 joules per mole because what is this, the silicates, borates and phosphates or even for polymers between, polymer change are only secondly bonds so when they are melting, chain is translating to other chain, the secondary bonds which are broken, primary bonds are not broken so this energy is very small, latent heat of fusion.

Same is to about silicates, (())(55:08) network is broken at few places and that electrostatic bonds are formed there, delta h is very small. Eta that is the viscosity is very high, while in melts of the metals it is 0.121 Pascal second for glasses it is about 1000 Pascal second. I have a quite vicious therefore delta Hd is small and because of this delta f star, delta Hd is high and because of this delta f start is high. Both delta f star and delta Hd are high therefore nucleation rate is very very small that is why it takes very high time for crystallization of glasses, they don’t crystallize, they remain non-crystallize.

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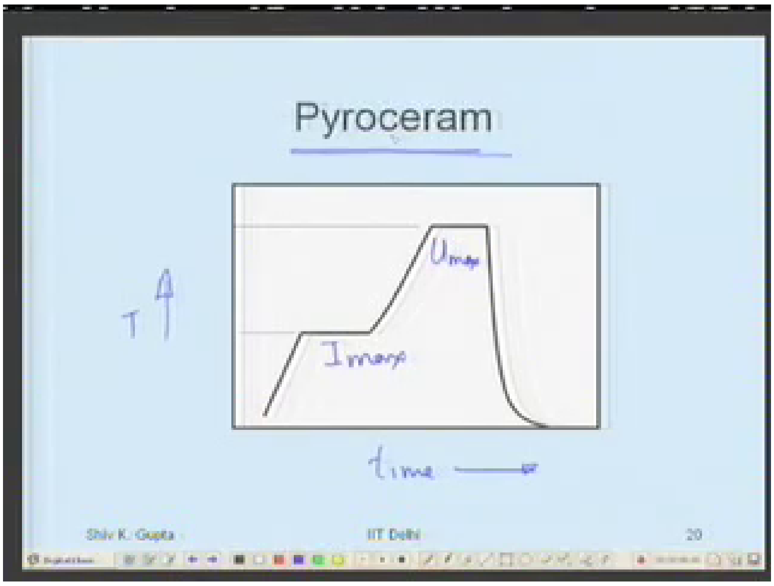

Pyroceram

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In here it is possible for me to crystallize them and those materials which are glasses or silicates crystallize are called pyrocerams, we exploit certain knowledge which we have gained. On this axis I have temperature, on this axis I have time. Time is not so relevant here. This material which is glassy form we add certain heterogeneous nucleation sites which are saleable in the molten state but may not be soluble in the liquid state and the soluble in the liquid state may not be soluble in the solid state.

So what we do is, we take such a glass to a temperature where the nucleation rate is the maximum, and keep it there maybe for a day, 2 days, 3 days so that it allows this nucleation to take place all over the volume of the glass in the solid state itself it is high because it is the solid state taken this and allow the two have the nucleation a high rate of nucleation is taking place. The whole volume is filled with the nuclei, I take it to a temperature where the growth is maximum and you know that the growth rate is maximum at a temperature high which closest the melting point.

Now whatever nuclei I had formed they will all be growing very fast, and the whole volume will get filled by crystalline grains such silicates are called pyroceram and they are such fine grained size that you can't even keep them on the flame, it won't crack, it will not break even though the conductivity is not very high, that is it materials, but they don't break, they have thermal shock resistance is developed in them and that is the material which are known by pyroceram they are available. That is how we can exploit were knowledge of nucleation growth. I will stop here and will start in the next class.