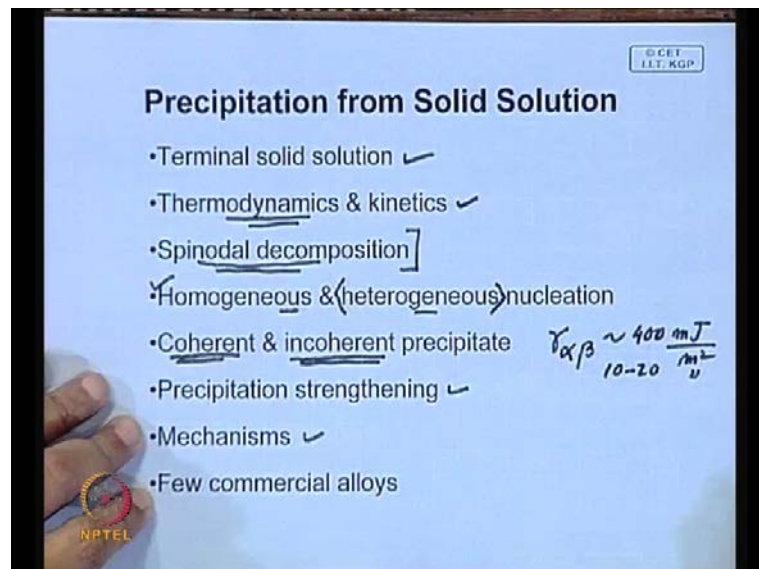


Principles of Physical Metallurgy
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Module No # 01
Lecture No # 30
Precipitation for Solid Solution (Contd.)

Good morning, we continue with our lecture on precipitation from solid solution and main purpose or objective of this topic is to illustrate or is to show you how by controlling processing we can get an optimum distribution of precipitate which will give you stable and high strength or desired properties.

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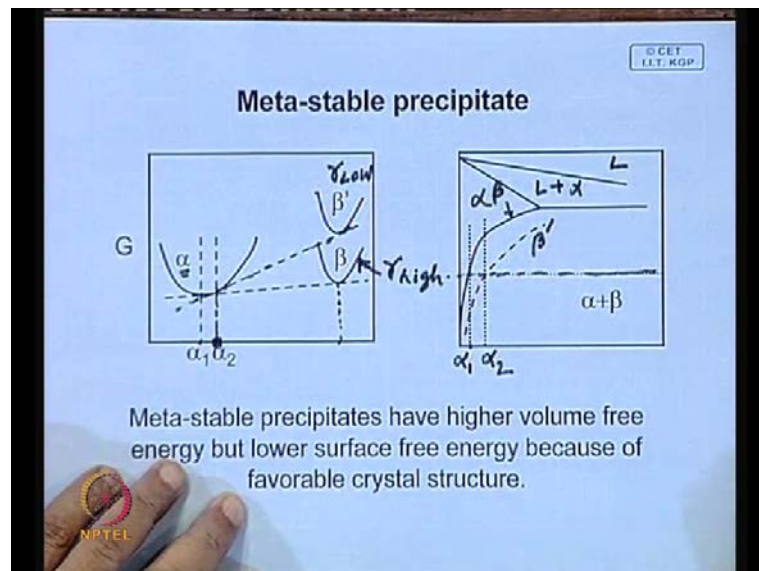


Now last class, we looked at few of these, we learnt about terminal solid solution. We learn that any terminal solid solution, when it is quenched from the single phase region and it is in the super saturated state and if it is edge there is a process of precipitation. We looked at the thermodynamics of the process of precipitation. We also talked about the energy barrier which has to be overcome so that precipitation process can take place or continue. So, that means we talked about that of kinetics of precipitation. We talked

about the homogeneous and heterogeneous precipitation and how they can be control, and we learnt that to get a good uniform distribution of precipitate in the matrix you have to somehow promote homogeneous nucleation rather (()) heterogeneous nucleation.

We talked about different types of precipitate, like coherent precipitate where the surface energy is extremely low, but it may have some amount of coherent, coherency (()) associated with it. On the other hand, normal precipitate we are we know about they are incoherent and all incoherent precipitate has high surface energy that means if in a matrix alpha, that alpha beta precipitate there will be an alpha beta boundary and this is of the order of quite high may be 300 or 400 or milli joule per meter square. Whereas, coherent precipitate this surface energy will be extremely low it could be 10 20 milli joule per meter square and you can also have some intermediate precipitate in between which has any coherent precipitate, and today we will look at precipitation hardening, the mechanism of precipitate hardening and we will talk about few commercial alloy and we will know about spinodal decomposition. This is also a technique to get in certain alloy system. We can get a precipitation can take place by a process where you are likely to get uniform precipitate in the matrix.

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Now, last class we introduce the concept of that meta-stable precipitate. This is the beta say, suppose this is the solid solution which is that super saturated alpha. So, say suppose we have this is the free energy composition diagram for the phase alpha, which is the matrix, and this is the free energy composition diagram for the precipitate phase beta,

and we know under equilibrium you can say this is the composition alpha 1 will be in equilibrium with beta, but this has a high surface energy. Therefore, kinetically I mean you need to provide some amount of activation. otherwise, I mean this process is difficult that process, it is not kinetically favourable, you have to give some amount of under cooling or some amount of super saturation only then precipitation can take place. Whereas, if you have a meta-stable precipitate, a coherent precipitate say something which we shown here.

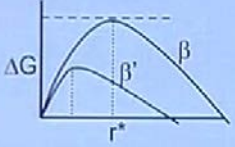
So, thermo dynamically it is little unstable so it has higher free energy but look at what happens. Here, if this is a here you know this has low gamma, gamma is low, this is incoherent that stable precipitate, gamma is high. Now, one this low gamma you know it is preferred because it will have a low activation hill to overcome so this is more likely to form with lower degree of super saturation, but when it forms look at what is the composition of alpha with which it will remain in equilibrium. You see you draw a common tangent that it means, so this is the composition of b in alpha which can be in equilibrium with this particular meta-stable precipitate. So, what it means say if you say that this free energy composition diagram corresponds to this phase diagram this is liquid, this is liquid plus alpha, this is alpha and we are considering let us see at this, **this** is the temperature at which we have drawn this free energy composition diagram. Now, this is alpha 1, this is alpha 2.

So, that means so this is the **solvest** line for the stable precipitate beta this is the **solvest** line for meta-stable precipitate or coherent precipitate the beta prime. So, similar thing and many phases we may find not just one this process of precipitation can take place to a number of meta-stable, meta-stable precipitates. So, in **in** short what we can say meta stable precipitate have higher volume free energy, they are that way they are unstable, but lower surface energy because of favourable crystal structure and that means very little perfect coherency or very little lattice mismatch.

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Meta-stable precipitates: activation hill



$\gamma_{\alpha\beta}$ 500
 $\gamma_{\alpha\beta'}$ 30-40 \uparrow Low
 $\dot{n} \propto \exp\left(-\frac{\Delta G^*}{RT}\right)$

Meta stable ppt has lower surface energy: $\gamma_{\alpha\beta} < \gamma_{\alpha\beta'}$
 Therefore its has lower activation hill its nucleation is kinetically more favorable than stable precipitate.

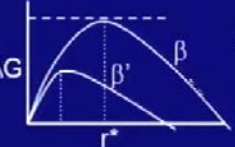
$\alpha' \rightarrow \alpha_1 + \beta' \rightarrow \alpha_2 + \beta$

NPTEL

Now, if you look at we did derive last class that expression for that activation **hill** and which you will see here,

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Meta-stable precipitates: activation hill



$r^* = -\frac{2\gamma_{\alpha\beta}}{(\Delta G_v + E_c)}$ & $\Delta G^* = \frac{16\pi\gamma_{\alpha\beta}^3}{3(\Delta G_v + E_c)^2}$
 $|\Delta G_v| < E_c$ & $\Delta G_v < 0$

Meta stable ppt has lower surface energy: $\gamma_{\alpha\beta} < \gamma_{\alpha\beta'}$
 Therefore its has lower activation hill its nucleation is kinetically more favorable than stable precipitate.

$\alpha' \rightarrow \alpha_1 + \beta' \rightarrow \alpha_2 + \beta$

NPTEL

If you go back that for in the case of precipitation process. If you consider recall your earlier lecture, we calculated this activation hill, and this activation hill is inversely proportional to the square of the sum that is volume free energy plus the coherency (()) energy also plays an important role. Now, look at it say suppose if you have a meta-

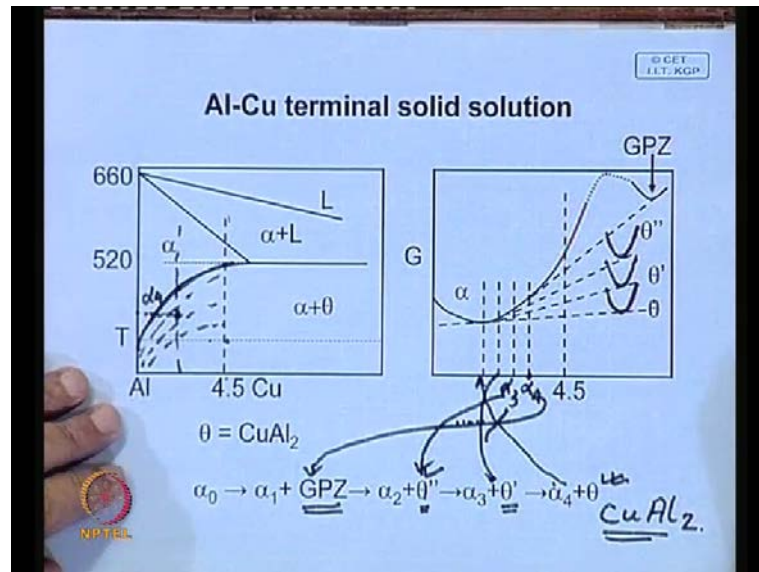
stable precipitate, what is going to change meta-stable precipitate, will have low surface energy so that means gamma alpha beta this is low.

So, that means if gamma alpha beta is a normal precipitate of the order of 500 or 400 milli joule gamma alpha beta prime, may be of the order of 30 40. So, in that you show what you get immediately. You see that your activation that critical nucleus size. This becomes smaller, this is small. So, this becomes smaller and also that activation hill which it has to overcome, this also this term will dominate, so this also will be lower. So, what is shown over here that means meta-stable (()) you know it has less activation that height of that activation hill is lower, therefore it is will be kinetically favourable because if you recall it your earlier that rate of nucleation or process or you can say this is proportional to the exponential that activation hill ΔG^* over $R T$.

So, the number of nuclear that forms you know if this is low and you can easily see from here that you have more number of nuclei or rate of nucleation will be high and therefore, meta-stable precipitate, since it has lower surface energy, it has lower activation hill its nucleation is kinetically more favourable than stable precipitate, and that is why this is the way precipitation takes place in any super saturated solid solution. So, here we have written one, but in many alloy system there may be in multiple intermediate meta-stable phases.

Now, aluminium copper system has been most extensively studied. In the, in this particular alloy system the process of precipitation has been extensively studied.

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So, let us if you refer to this, it is shown here say this is the super saturated solid solution that free energy diagram and here you have number of intermediate stages. Initial precipitate that forms it is just a form of cluster of copper atom. In certain aluminium that lattice say some places, you have number of copper atom will form a cluster and which is fully coherent, but it is unstable no doubt free energy volume free energy is much higher but, it is perfectly coherent. So, with this if you can draw a common tangent to this phase. So, this is the composition which it will be equilibrium. So, this is let us say, say this, this is say alpha o. Similarly, there is another, if does not go through just one stage there are multiple number are depending on the composition, you can have multiple number of precipitate, in intermediate precipitate.

First precipitate which is cluster of copper atom this is known as (()) zone or G P zone. Next, precipitate is theta double prime. Which is the, which is shown here. It is (()) which is shown by this free energy composition diagram, next is theta prime. So, these are all coherent and finally, this is the stable precipitate theta, which is the final precipitate and this is actually is C u A L 2. Now, when this precipitate form this precipitate they are this is just the cluster of copper atom, but when this structure will be very similar, copper also collection of copper atom also will have phase centred cubic structure, aluminium has a phase centred cubic structure. So, this also will but, it is a very thin just a cluster of few copper atom in aluminium lattice.

Next, is theta 2 it has a definite crystal structure will come to know about it and certain direction, it is lattice will be exactly parameter may be exactly similar to that of aluminium. So, that will be the preferred plane on which this precipitate will form. This also has a little different structure than theta double prime and finally, so it is it goes on changing and you can see this has the highest solute content. Next is alpha 3. This is, alpha 4 is G P zone, this is alpha 3. So, this is this one and this is, you can say I think this is alpha 4. So, what we can say this is the (()) curve for theta that is that alpha 4. This represents the alpha 3 line will be somewhere like this, then alpha 2, then alpha 1.

Therefore, depending on the temperature and where you are ageing say if you are this is the composition of the alloy and you are ageing at this temperature it will pass through all these intermediate steps, but if it is say somewhere alloy content is here and you are ageing it at this temperature, in this case only precipitate which is possible is theta prime and theta.


So, that means the sequence of precipitation process will depend not only on the composition, but also at the temperature at which you give the ageing treatment.

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Precipitates in Al-4.5 Cu alloy

GP zones	coherent	disk	Cu cluster
θ''	coherent	disk	Tetragonal a=4.04 c=7.68
θ'	Partially coherent	plates	Tetragonal a=4.04 c=5.80
θ	Incoherent		Tetragonal a=6.07 c=4.87

Al: FCC a=4.04 Angstrom

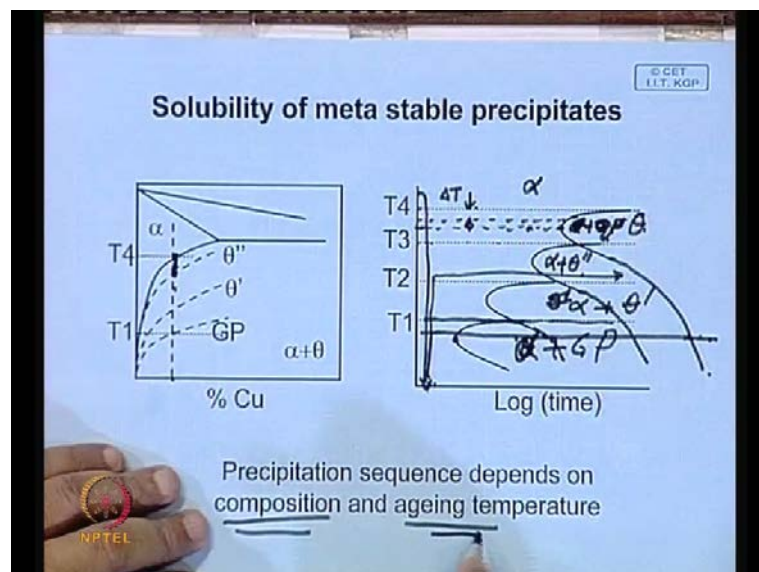


Now, this if you look at the table which gives the lattice parameter of the different phase, we talked about, and may be you can look at the computer that, here it will be clear which are listed G P zones, the type of precipitate is coherent and its shape is that of a disk and it is just a copper cluster. So, why it is because in one direction only the lattice

parameter they will be matching the other direction, and in the one plane only so if it tries to go perpendicular to the plane it loses coherency.

Therefore, it will be restricted to shape will be most of the cases, this **or** thin plates, theta double prime it is coherent, this has a tetragonal structure, the lattice parameter are listed here. These are the values given in **angstrom**. Theta prime this is partially coherent, here this is also tetragonal, these are lattice parameter and incoherent precipitate is tetragonal, and these are the lattice parameter and if you look at the lattice parameter of pure aluminium which is 4.04 **angstrom**. You find from between this and this is no chance of forming any coherent precipitate. I mean this will be totally incoherent, that if you look at this and let us say theta prime there is a slight **and** in this particular that is that cube plane that is 1 0 0 plane, it can form on 1 0 0 plane because lattice parameter they are perfectly matching, but if it tries to go along the c direction, there will be lattice mismatch. So, which you will cause to higher amount of strain. So, similarly here also similar **thing** is happening.

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Now, this is the diagram we just talked about, this is the solubility of meta-stable precipitate. This will depend as you know which are shown over here. This is the **(())** curve for stable precipitate the theta, this is the **(())** curve for theta double prime, this is **(())** theta prime and this is the G P zone, and suppose, and let us see, let us see, look at that if you **etch** this how will that process of precipitation take place. It process a precipitation is will be a time dependent process. So, rate of nucleation will depend on

the magnitude of under cooling. So, what mean if you look at over here you see that means, if you are keeping this is the alloy let us say as the particular composition and we are **have kept it the** temperature T_4 . T_4 means here, so here you can see this is, on the line on the **(())** curve. So, even if you keep it for infinite length of time there will not be any precipitate. So, this axis is a temperature and here we are trying to plot the time it takes for the precipitation to start.

So, in this particular phase here there is no super cooling **it** takes continuously it will remain in the state of alpha, but when you come down here there is a degree of super cooling, higher this degree of super cooling higher is the driving force. Therefore, nucleation becomes favourable and the kinetics will be determine that movement of atom to form the precipitate, the atom this **mean** you need to move the atom, you have to give the time, you have to give time for the atoms to move that is a copper atom to move in aluminium lattice, and this is a process of diffusion and diffusion. We know higher the temperature higher the rate of the diffusion.

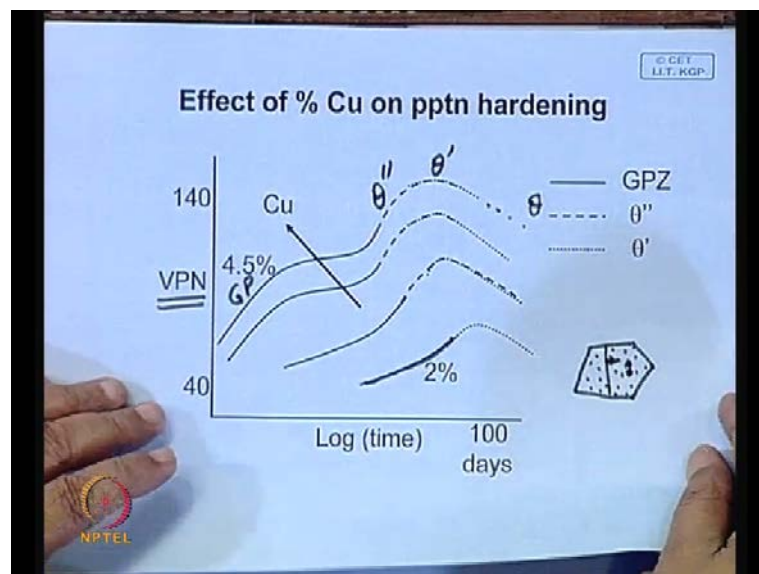
Therefore, as you go down **diffusion rate** decreases diffusion becomes slower and there is an optimum condition. Here, so the two things they are they vary in opposite to a that is rate of nucleation is faster, higher the super cooling and rate of diffusion becomes slower, if the temperature becomes slower. Therefore, there will be an optimum case where you will have the maximum rate of precipitate formation. So, this is the case where the precipitate forms in the shortest possible time. So, here which is the precipitate, here you have G P zone. So, you will have alpha plus G P zone. Similarly, this precipitate second precipitate theta double prime will try to form, when this **(())** line is crossed. So, this is the **(())** line, so **(())** will have a c shape nature, and this is theta prime and this is theta.

So, that means if you want to give a proper solution hardening treatment what you need to do you have to heat it above the **(())** say somewhere here, first you quench. So, if you quench you can get fast rate of cooling you must avoid this **(())**. So, rate of cooling will be faster than this point, particular point, and after that you will heat it, you will take it heat it and **age it** at a particular temperature. If you do it here you will get theta double prime if you **age** it here, say **say** suppose it if you age it. So, normal **ageing** so I think you need to make a correction, this is the G P zone actually so I think here you will have

alpha plus G P zone this is, so T 1 is the temperature, if you age it below T 1 you will have alpha plus G P zone you (()) about it, this is the alpha plus beta prime.

Next, is alpha plus theta, this is theta here because between if you are ageing here the only precipitate which can form is theta. If you come down then only theta double prime will form. Therefore, if you are ageing somewhere here, so what happens first the G P zone will form then it will cross this line you will have theta prime forming, then this line, then this. So, last precipitate you form will be theta. So, the thing is you remember that means this sequence of precipitation will depend on composition of the alloy as well as the ageing temperature.

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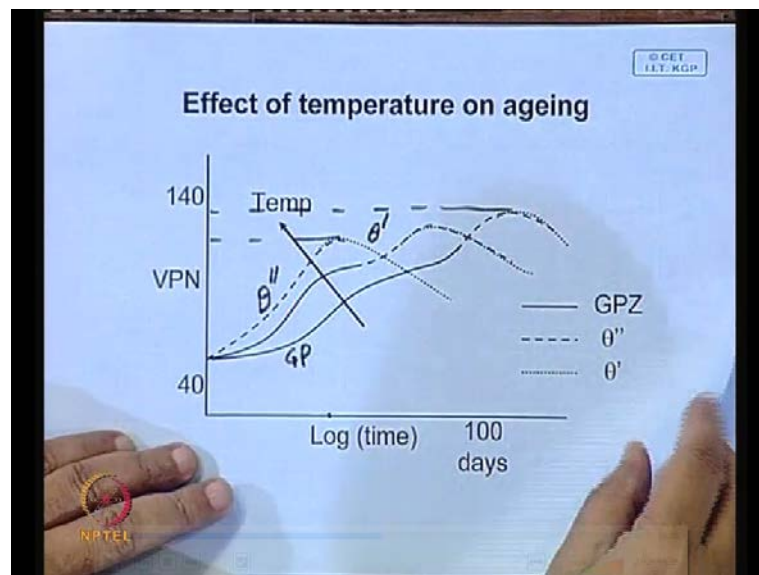
Now, when this process of precipitation takes place you have different types of precipitate forming in the matrix, and obviously when this precipitate form in the matrix what it will do, it will make, it would process of deformation more difficult because we have learnt that metals deform by movement of dislocation. So, this precipitate gives in the matrix, if you have the matrix, you have precipitate the dislocation which is there. It will be difficult for it to move or cross this precipitate.

We will see how it is, how this takes place later. So, that means when this precipitate form you will have some additional (()) and this is shown by this a and this can be followed by measuring the hardness and if you measure hardness, usually the hardness is measure in weakest pyramid number and which is shown over here. So, if that alloy has

a 2 percent you possibly find that here, that alloy composition is such if you go back to the previous diagram you will see that possibly you will have G P zone and after that you will have this is theta prime.

So similarly, but if you have 4.5 percent copper possibly, you will see this is the where you will have G P zone this is theta double prime, then theta prime and subsequently when it over ages this side it will become theta, and you will find that effect of composition, **composition** has a significant effect on the extent of hardening. If you increase copper actually you are increasing volume fraction of precipitate. So, if the volume fraction increasing and secondly you can also control, if you have a more particles and the particles are small the distance between the particles also will be small. So, that will provide as a more effective barrier to dislocation movement.

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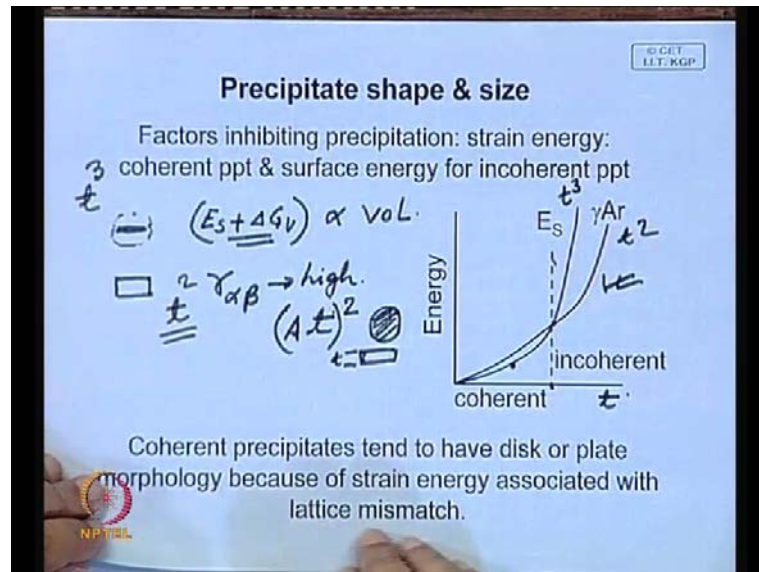


So, that means the extent of hardening will depend on the chemical composition that alloy content and as well as it will also depend on the time of **ageing**. It will also depend on the temperature of ageing so if you age at a higher temperature you have less number of precipitates, you know. Say, suppose if the highest temperature over here which is shown then there is no chance of G P zone formation. G P formation takes place at a lower temperature its **(())**.

So, this temperature is higher than G P zone **(())**. So, here you do not see G P zone whereas, here you have G P zone. So, here you will have theta double prime, then theta

prime and you will also see, if you increase the that higher temperature, higher the temperature, the **peak** also of hardness comes down and it is again at a **quicker**, it is attained at a shorter time. So, that means process of precipitation is faster. So, here it will be difficult to control the precipitation process. Therefore, to get good amount of **strength** the lower ageing temperature will be preferable.

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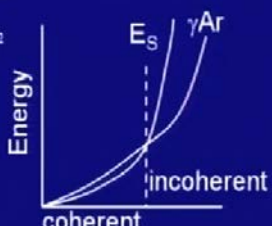
Now, a point about you know that whenever a precipitate forms actually it is whenever you precipitate form say here, even if it is coherent then it is strain **feel** associated with it around that. Therefore, and this strain, that means there will be a strain energy apart from that volume free energy, and this will be proportional to the volume of the precipitate and secondly, opposing factor is whenever, now this precipitate forms, a incoherent precipitate forms this is incoherent precipitate, this has high gamma, this is high.

So, in one case this is high, another case this is high. Now, we know that means this volume actually will be proportional to the dimension. Basically, the dimension if we say the thickness it is possible to show that volume will be proportional to this. Whereas, surface area will be proportional to the thickness square of the thickness. So, in fact it is possible to show a simple calculation which is shown on that computer screen.

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Precipitate shape & size

Factors inhibiting precipitation: strain energy:
coherent ppt & surface energy for incoherent ppt

$$E_s = \frac{1}{1-\nu} \bar{V} \bar{E} \delta^2 = \frac{3}{2} \left\{ \pi (At)^2 t \right\} \bar{E} \delta^2$$
$$\gamma Area = \gamma \left\{ 2\pi (At)^2 + 2\pi At^2 \right\}$$
$$t_{crit} = \frac{4}{3} \frac{\gamma}{E \delta^2} \left[1 + \frac{1}{A} \right]$$


Coherent precipitates tend to have disk or plate morphology because of strain energy associated with lattice mismatch.

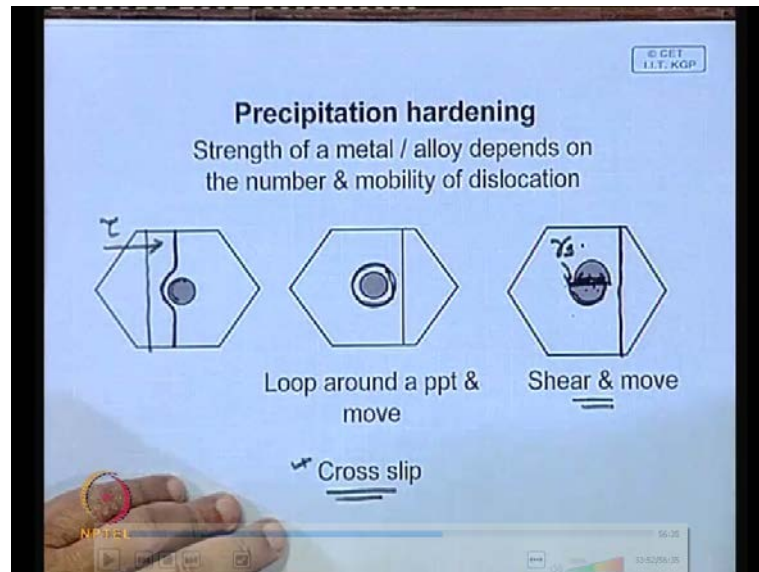
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If you look at, that how do you calculate this strain energy. Strain energy where will depend on, will be proportional to the volume the modulus, volume at the precipitate modulus and the lattice mismatch. Delta represents lattice mismatch and therefore, and nu is the poissonal ratio, which is usually around 0.3 so we **we** can make some approximate calculation. That means this volume will be equal to if you assume it to be disk, say in a disc and if you assume that there is a shape factor A, so this **this** you assume this may not be perfectly circle.

So there may be a shape factor, so it is proportional to this area of the disk is proportional to this square of t and then to get volume, you have to multiply by their thickness, this thickness is t. So, you get this will be equal to t q whereas, the area of the same disk, if you try we can find out the area of the **top** surface and area of the cylindrical surface. If you can find out then you get the surface energy and if you equate the 2, so this gives a switch over, you know and you can find out by equating the 2 there is a critical thickness, where both this and this are equal, and what does this mean.

So, look at a over here if you plot this energy and this is t, so this **varies as** t q, this **varies as** t square. So, t q because t dimension is quite small, so initially here the precipitate, **preferred** precipitate will be coherent, but when it goes causes this critical point, in that case incoherent precipitate will be more preferred. So, that means there is a critical dimension, as the precipitate tries to go, you know it will that lattice mismatch will increase and finally, it will be replaced by incoherent precipitate.

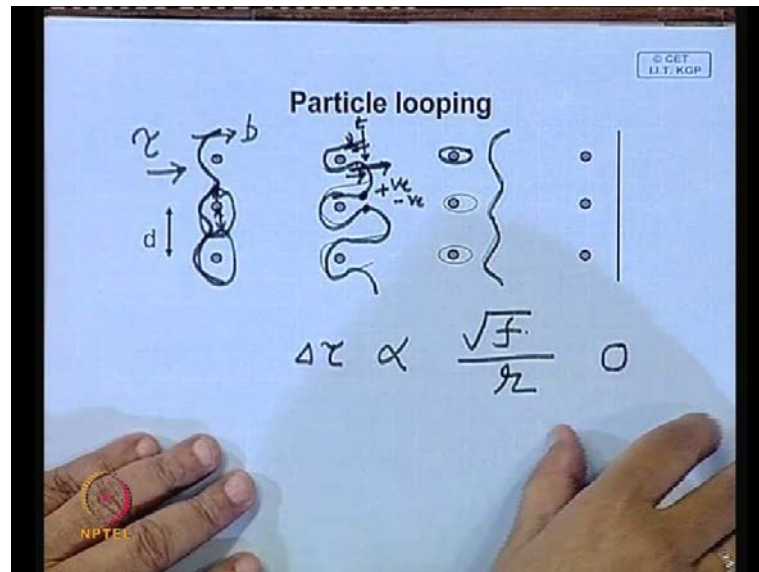
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Now, let us look at the process of hardening. What we say that strength of a metal it depends on its ability to move its dislocation and the lattice. Now, suppose here this is a grain this is a precipitate and you have a dislocation, if it is somewhere here it will be straight and when you apply τ plus τ the dislocation you push it and now this opposes the dislocation movement. So, here when it comes near it becomes bent and after that one possibility is, it can cause this and leave behind a trail.

So, one mechanism of this dislocation movement in a particle and a precipitate containing alloy is the looping around a precipitate loop and move, this is one. Another possible way will be if this is the precipitate, we apply stress and the stress here is sufficient to fracture the precipitate or shear the precipitate. In that case this is how the precipitate has been sheared and this moves here. So, what happens after shearing some additional area is being created, additional area where it will have some surface energy is being created. Secondly, if the precipitate has some order structure, that order is disturbed and this, so that means to **fracture** you need some additional or to move to slip of shear the precipitate, you need a sufficient amount of stress, for this to happen. So, this is **the other** mechanism. There is also a possible mechanism **cross slip** that we will not consider here. I think these two **we feel** is most important to explain or understand the process of precipitation hardening.

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And now same thing is shown in little detail here. If you have a distribution of precipitation the matrix and you have a dislocation which has bent over here, like this. You, when you apply this will happen, when you apply τ tau. Now, you increase this stress it will bent for the and it can move something like this, around this and look at if you have a **assign** at dislocation direction t. So, this is the direction of the dislocation and it has a τ vector say suppose you say this is the τ vector b.

So, there will be cases here, you know. So, in this case dislocation direction is like this τ vector is like this, whereas over here the dislocation direction is τ vector is this, dislocation direction is this. So, that mean nature of the dislocation keep changing, you know, and it is quite happen likely to happen, say one case it will be a positive dislocation, this may be a negative dislocation. So, **ultimately** they will try to join and then when they join what happens, the loop is left behind and this dislocation moves and later on it becomes straight and with this assumption it is possible to work out the relation magnitude of the additional the shear stress which you need.

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Particle looping

$$\Delta\tau = \frac{T}{bR_{\min}} = \frac{0.5Gb^2}{b\left(\frac{d}{2}\right)} \ln\left(\frac{d}{2r_0}\right) = \frac{Gb}{d} \ln\left(\frac{d}{2r_0}\right)$$

$$\frac{1}{d} = \frac{1}{r} \sqrt{\frac{3f}{2\pi}}$$

$$\Delta\tau = \frac{Gb}{r} \sqrt{\frac{3f}{2\pi}} \ln\left(\frac{d}{2r_0}\right)$$

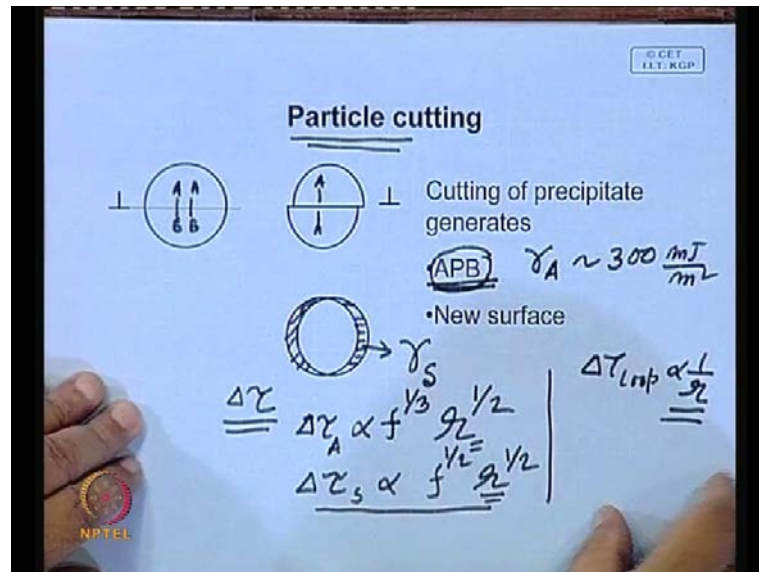
$$\Delta\tau \propto \frac{\sqrt{f}}{r}$$

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And if you remember your earlier lecture that additional shear stress which you would apply. You know that radius of curvature it depends on, that is a function of that shear stress that you apply and this is given by this is the line tension, line tension T over $(\)$ vector v and this is the radius of curvature. Now, the minimum radius of curvature it is possible to calculate and we have done it earlier and if you substitute this, an expression for T is usually roughly proportional to $0.5 G b^2 \ln$. This is, we can take, this is actually d over, this d is this $(\)$ precipitate $(\)$. So, what we can say that dislocation the effective the strain field of the dislocation is half of this.

So, this is $(\)$ we say that this is the area that dislocation, the strain energy of the dislocation is located within this area. So therefore, here you substitute d and also it is possible to relate d with the volume fraction and radius of the particle, and this is a simple $(\)$ derivation which I leave it as an exercise. It is possible to show, that if you have uniform particle of radius r distributed in a unit volume and the volume fraction of precipitated v it is possible to show that the distance between the particle will be given by this. So, if you substitute over here you get this expression. So, in short what it shows that this additional the strengthening which you are getting is proportional to the volume fraction, root of volume fraction of precipitate over the size of the precipitate or radius of the precipitate which is quite important and we will use it later.

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In the same way it is possible to do similar calculation for particle cutting. You go into the detail of the process of calculation, but here two things happen. When the precipitate is sheared, here if there is a, this is a order precipitate. so you have bond A B type bond here, **here** you see, here you see, so if you slip it, you may find say then, if you slip it, you may find this, is a this also becomes.

So, that means that order gets disturbed and this that means, this will have an additional energy and this is called anti phase domain boundary and there is some anti phase domain boundary energy associated with it, and this is anti phase domain boundary energy can even be quite large, it could be around 300 milli joule per meter square. Whereas, coherent precipitate, we have seen may be one tenth of this and secondly, whenever this process shear takes place, you have new surface created. This is the additional surface created. So, this will have another energy, the surface energy.

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Particle cutting



Cutting of precipitate generates

- APB
- New surface

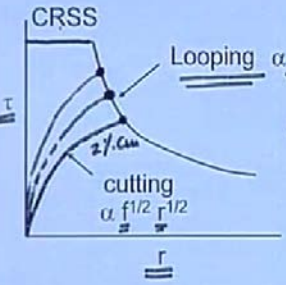
$$APB: \Delta\tau \propto f^{1/3} r^{1/2}$$

$$\gamma_s: \Delta\tau \propto f^{1/2} r^{1/2}$$


So, this will need for this to happen, you have to apply some amount of additional shear stress and how can you, what is the nature of this relationship which is shown here. If you calculate it with a little rigorous calculation with anti phase domain boundary you get this also essentially what it shows that, it remains f to the power $\left(\frac{1}{3}\right)$ one third, r to the power r , this is $\Delta\tau$, this is what anti phase domain boundary and this is for that new surface created. So, that means this increases as the particle grows, whereas looping, for looping $\Delta\tau$ loop, this is inverse loop proportional to r . So, this is quite important and we will look at that implication of this, which is shown here.

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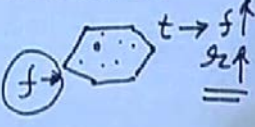

Particle looping vs cutting



Smaller precipitate: cutting more likely

Initial stage: small coherent particles form & f keeps increasing till its limiting value. Strength increases due to both f & r

Once f reaches its limit particles coarsen & become large enough to allow looping

So, this is a plot of the shear stress and this is the particle size. Now, this is the ideal strength of the crystal, this is the critical resolved shear stress. So, this is the limit that you can have. Now, here this line plots that looping stress, which is proportional to \sqrt{f} over r , it is inversely proportional to r , therefore r decreases this goes up. Whereas, when you have just ageing has started, you do not have any precipitate. So, initially what happens some amount of precipitate will form and this will follow this plot. So, this is the precipitation stage or the ageing process. So, this volume fraction as well as r keeps on increasing. So, this is for a particular alloy composition, say may be this is for, let us say 2 percent copper, if you increase more copper, where you will have more volume fraction, in that case this may follow a plot like this.

So, what it shows actual process of precipitation is, as the precipitate forms and grows in the lattice, say suppose this is a $(())$ two things happening, you have a precipitate forming and this precipitate also will grow. You have another precipitate forming and this also keep growing. So, with time two things increases, f increases as well as the precipitate also increases and this defines the limit, that is the maximum strength that you can have in the alloy system.

So, this in a way you can say, that this defines that maximum strength that you can get in a precipitation harder than alloy. So, this you can do primarily by controlling, I mean you want to increase it further, you have to increase the $(())$ and thereafter when the maximum, but there is limit to work f can attain. So, there is an equilibrium limit and when this limiting value has reached, you can say that you have reached over here, and after that what is, what can happen. When that limiting size that equilibrium amount of precipitate has formed and you are still ageing, you have thermal activation, there the precipitate can grow and when it grows again a precipitate coarse strength is draw, that is following this path.

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The slide is titled "Over ageing: particle coarsening". It contains the following content:

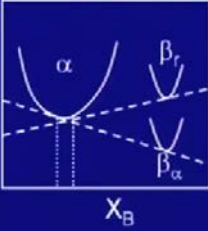
- Equation: $r^3 \propto kt$
- Equation: $k \propto D \gamma X_e$
- Text: γ (circled)
- Text: Low γ : Nimonic
- Text: Low X_e : TD Nickel (W)
- Text: Low D: Low alloy steel
- Phase diagram: A graph showing a parabola for phase α and a dashed line for phase β . The diagram is labeled with α , β , α_1 , α_2 , and X_B .
- Schematic: A circular precipitate with arrows indicating diffusion. It is labeled with α_2 and α_1 .

So, this is the mechanism of strengthening and this is over ageing which is shown over here, actually this over ageing takes place when this precipitate **grows** because if you have a one precipitate another large precipitate. So, they will have different thermodynamic stability. The smaller precipitate are thermodynamically unstable they have **higher** free energy. These are coarse precipitate which is thermodynamically more stable they have lower energy. Now, if you draw back you can see, this precipitate here that concentration, **if** this is alpha 1 composition, this is alpha 2. Now, here smaller precipitate here, you have concentration is alpha 2, here concentration in alpha 1 and alpha 2 is greater than alpha 1.

So, there is a concentration gradient, so this will diffuse and finally, this will disappear, this will **grow**.

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Over ageing: particle coarsening

$$r^3 - r_o^3 = kt$$
$$k \propto D\gamma X_e$$


Low γ : Nimonic
Low X_e : TD Nickel (W)
Low D: Low alloy steel

NPTEL

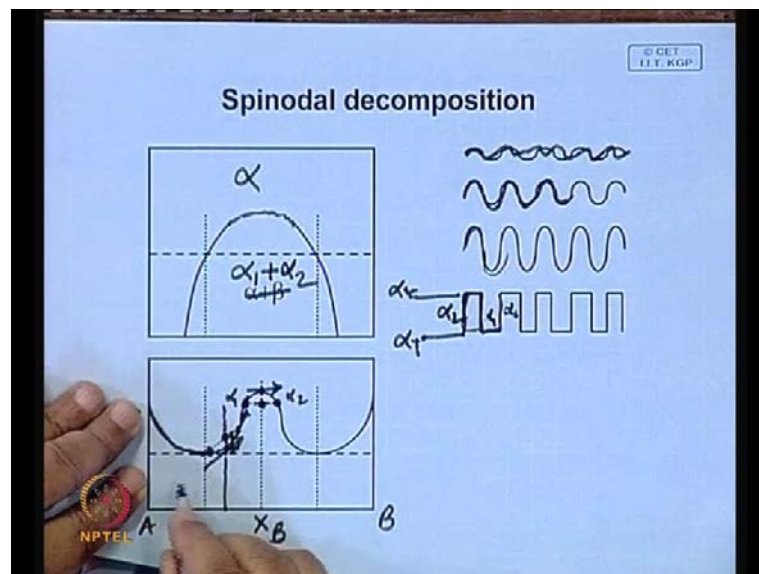
So, this is the process called **(())** and it is possible to show that the process of **lightening** follows a kinetics something like this. **This** is the radius of the precipitate, this is original initial precipitate size. So, that means the r cube is actually proportional to a constant times t and k this is the rate constant, this is proportional to, so definitely the diffusivity will play one important role. Second, is the surface energy when the, they are growing in that case **net** surface energy diffuses. So, surface energy is also a driving force and another important driving force is the amount of **soluble** you have, a solubility that you have, that equilibrium solubility limit then you have larger you can then, **then** if this is large that is there can be a large difference that concentration variant can be there.

Now, you think in order to design precipitation **(())** alloy and to improve its strength so particularly precipitation **(())** alloy they have lot of application they are applied even at a high temperature alloys, and there if you want to improve that high temperature strength it is subjected to high temperature exposure. Therefore, at high temperature when it is in service you have to reduce k, how can you reduce k. There are three ways; you can play with bring down the diffusivity, bring down gamma, bring down the solubility limit. So, this is the and if you look at some of the common high temperature alloy, the nimonic, **nimonic** you have a gamma, gamma **prime** matrix gamma prime precipitate, and this gamma gamma prime precipitate they are perfectly coherent, so they have very low surface energy.

So, that is why they are high temperature stability is very high. So, this is a very popular high temperature alloy. Another example for a low X E (()) solubility is very low in matrix. So, if you have this thodium oxide nickel. So, in nickel matrix if you have thodium oxide disperse, then you can say the solubility of thodium the oxide in nickel will be very low, Therefore, this thodia particle will be a perfect. I mean they will be stable precipitate which will respect the movement of this location. Same thing can happen thodia disperse tungsten.

Another is low alloy steel is very often used for high temperature application boiler tubes or steam turbine blades and here so if it is a plane carbon steel, the carbon diffusivity is very high. Therefore, the carbide will coarsened. Now, you can bring down the coarsening rate of carbide by adding some alloy element which goes into carbide. So, strong carbide formers, if you add you can decrease that coarsening rate of precipitate and increase the high temperature stability of low alloy steel.

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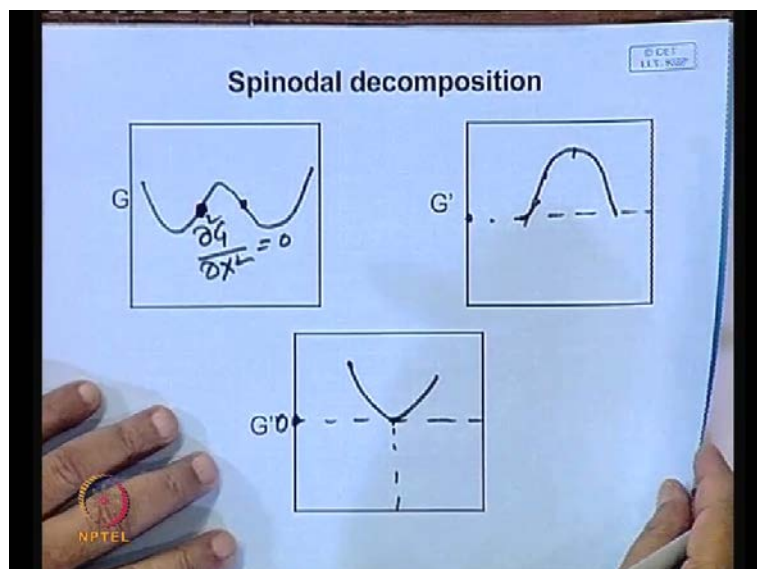
Now, a quick look with another method of precipitation which is called spinodal decomposition. It does not take place in all alloys, it typically takes place in alloys where you have visibility gap. So, something like this, see visibility gap like this, if you have alpha and here is a region it breaks down into two solid solution below a particular temperature. So, in this case if you look at these free energy composition diagram this is X B this is B this has this type of a plot. Now, here if you look at an alloy over here and suppose and let us say that whether a small fluctuation, any alloy the atoms are

not stationary the atoms keep moving, the solute atom will keep moving. So, at any instant the concentration at a particular point can change.

Now, let us examine whether this small change composition will be stable or unstable over here. So, here if you look at over here in that case, say suppose this is a small change in composition then the mixture will have this free energy. Whereas, the solution has, the **solid** solution has this free energy so this is **solid** solution has lower free energy more stable. So, here this type of fluctuation will **die** it cannot cannot grow. Whereas, if you look at somewhere here, **here** if there is a small fluctuation, so this is alpha 1 this is alpha 2 and the free energy of the mixture is this, free energy of the **solid** solution is this. So, that means here this fluctuation will be stable and **will grow**, something like this, say if this fluctuation is there, this is trying to go like this, it has grown and finally, it has form this precipitate.

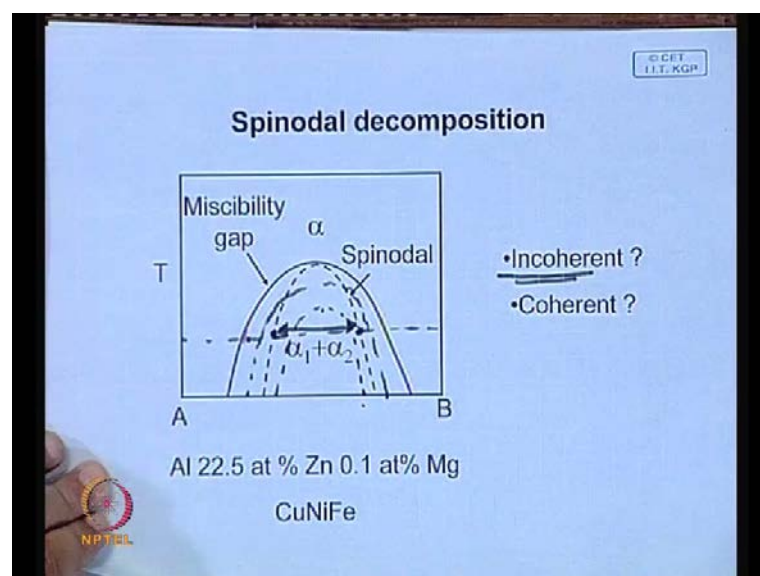
So, this is a suppose we say that this is alpha 2 this is alpha 1 this composition. This is alpha 2 this area so that way. So, this corresponds to one composition, this corresponds to alpha, so this corresponds to alpha 2, this lower one corresponds to alpha 1. So, what is the advantage of this precipitate, if such small fluctuations you can let it form into a precipitate, it will be a homogeneous precipitation. You will have uniform precipitate all through the **matrix** and you can easily show that the condition under which this take place. If you look at the slope of this curve, the slope here is increasing somewhere in **between** it becomes maximum again the slope comes down.

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So, if you try to do it you will find that somewhere the slope of this, if you define this is the slope, you know, somewhere the slope is let us say, here is 0 and then somewhere slope will become maximum and come down. If you differentiate it again you will find you will again get, this is 0. So, again you will get this slope is increasing and then decreasing. It has a high slope, but later on it decreases somewhere here. So, there is a composition where you can say there is an **inflection** point say if this is the type of a free energy composition diagram, say this is the case, here you can say the double differential **(())** this will be 0 this is where **inflection** point and this point is called spinodal.

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So, what you have if you have an alloy system, this is a spinodal. this is the solvest curve and here you have this two type of precipitation. It is possible to show this is the spinodal point at a particular temperature. So, within this you can have small fluctuation stable. So, within this you can have homogeneous precipitation uniform distribution of precipitation. Here, it will be a normal nucleation **(())**. This is the case we are considering where the precipitate is incoherent, if the precipitate is coherent we can **extend** this solvest curve of coherent precipitate will be somewhere here. Similarly, for coherent precipitate you will have a different spinodal. So, main advantage of this is, a spinodal decomposition is possible in many alloy which is listed here.

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A few age harden-able alloy system

Aluminum	Al-Ag	Zones $\rightarrow \gamma'$	γ : Ag_2Al
	Al-Zn-Mg	Zones $\rightarrow \text{M}'$	M: MgZn_2
	Al-Mg-Si	Zones $\rightarrow \beta'$	β : Mg_2Si
	Al-Cu	GP $\rightarrow \theta'' \rightarrow \theta'$	Q: CuAl_2
	Al-Mg-Cu	Zones $\rightarrow \text{S}'$	S: Al_2CuMg
Copper	Cu-Be	Zones $\rightarrow \gamma'$	γ : CuBe
	Cu-Co	Zones $\rightarrow \beta$	β
Nickel	Ni-Cr-Ti-Al	γ' (cubes)	G: $\text{Ni}_3\text{Ti/Al}$




And next, if you look at this slide it gives a few common age harden-able alloys which are listed and each of these this we talked about in detail, but similar sequence of this precipitation is followed in everywhere it goes through zone, some coherent precipitate finally, incoherent precipitate and these are listed here; some of the aluminium base alloy, some common copper base alloy, and a nickel base alloy, and it is possible I mean this list by no means is **comprehensive**, there are many other alloy systems.

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Summary

- All terminal supersaturated SS where coherent precipitates form can be age hardened
- Fine precipitates with spacing $< 1\mu\text{m}$
- Suppress heterogeneous precipitation (low γ & E_s)
- Strength = F (particle size, volume fraction)
- Effect of composition & ageing temp & time
- Mechanism: looping & particle cutting
- Over ageing: loss of strength due to particle coarsening



So, to sum up what we looked at, that what we understood all terminal super saturated solid solution where coherent precipitates form can be given, can be age hardening and the fine precipitates, you need very fine precipitate to get precipitation hardening and this magnitude of that spacing is of the order of one micron and to get a good precipitation hardening, we have to suppress heterogeneous precipitation which is possible when gamma is low and there is some amount of coherency strength. The strength is a function of particle size and volume fraction. We looked at effect of composition, ageing temperature and time and the process of hardening. We looked at the mechanism of hardening, that is looping, dislocation looping and particle cutting. We also looked at over ageing which leads to loss of strength due to particle coarsening thank you and next class we will take up another topic. Thank you.