Nanostructure and Nanomaterials: Characterization and Properties

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Lecture - 04
Introduction to Nanomaterials (C1)

Next we consider the defect which is twin and the associates in face the effect which **is** the twin boundary. Like before we can now think of a twin, either based on a geometrical entity which is the usual kind of a definition or we can think of a twin in terms of a physical property.

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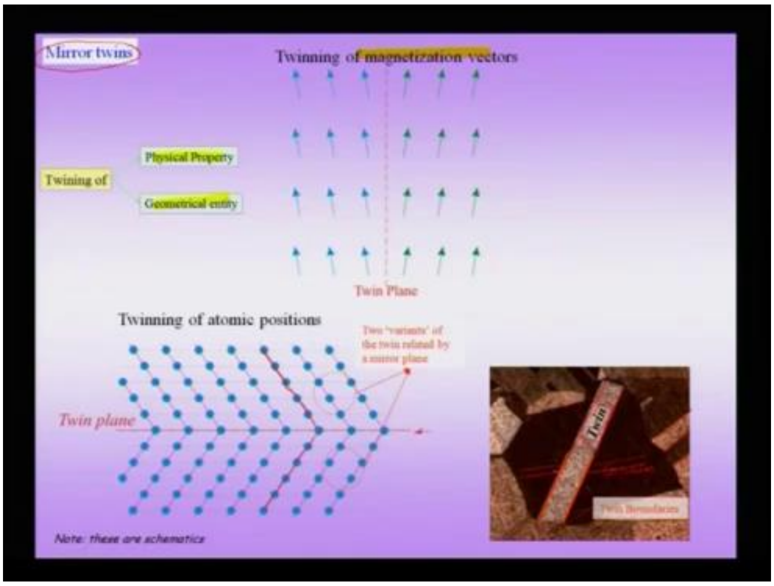

Mirror twins

Twinning of magnetization vectors

Twinning of
- Physical Property
- Geometrical entity

Twinning of atomic positions

Two 'variants' of the twin related by a mirror plane

Note: these are schematics

There are examples on this slide which show you both this kinds of twins. The one on the top is twining with respect to the magnetization vectors, and let me out at this stage that these are schematics. In real systems the actual orientation of these spun vectors could be slightly different and that depends on the specific system under consideration or for instance even the property under consideration.

The figure on the bottom shows the right bottom first shows twin as seen at an optical microscope. The sample here is actually annealed copper and in annealed copper you find these straight lines, which can be seen here for instance these lines which are marked in red. Here these 2 lines which can be taught which are actually the twin boundaries. So, let me extend this straight line to show you where the twin boundaries are.

As you can see their signature is that, they are extremely straight. There are the twin boundaries right here in the same picture, this are the twin boundary, this twin boundaries reside within a grain. Now, what happens at this twin boundary, at the twin boundaries you can see that the atomic planes are reflected and since we are here talking about the reflection therefore, these twins are called the mirror twins as the slide title shows you.

These are the mirror twins and on one side of this mirror plane which I am marking with an arrow, you can see that atoms atomic planes go in this orientation. On the other side you can see that they are reflected by the twin boundary which acts like a mirror plane. This kind of a twin boundary of course, is called a coherent twin boundary, but at this stage we will not go into the details of what is a difference between a coherent twin and an incoherent twin. The important note here is that that twin itself the twin region itself is a volume defect.

If you talk about this defect with respect to the remaining of the grain. So, this is my grain and in this grain the twin boundary introduces a misorientation of the plane. The second twin boundary restores the orientation of the plane and if I have had to look at my atomic planes and we are drawing some schematics here. They will be on the same orientation across the twin boundary. This implies that the twin interface which is otherwise call the twin boundary, is one of the atomically sharp interfaces as compared to a grain boundary or other kind of interfaces typically which are somewhat defused.

Now, a twin need not only be a mirror twin, there are other kinds of twins which are possible and just to site such an example, there is one here which is called a rotation twin.

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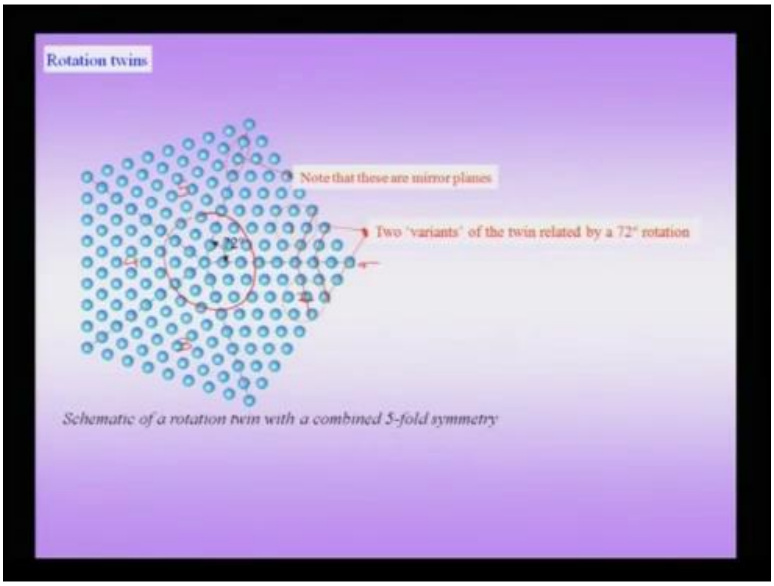

Rotation twins

Note that these are mirror planes

Two 'variants' of the twin related by a 72° rotation

Schematic of a rotation twin with a combined 5-fold symmetry

In a rotation twin, there are many variants and for instance this is one variant. There is a second variant right here, there is a third variant and the fourth variant and the fifth variant. Put together you can see that on an average these are misoriented by an angle of about 72 degrees. Of course, it is not accurately 70 degrees in real systems, but its approximately 72 degrees.

I can go from region one to region 2 by a rotation of 72 degrees and therefore, this is called a rotation twin. In other words a mirror twin is associated with reflection symmetry, the rotation twin with a rotation symmetry. The general principle in this area is that, the mirror twin mirror boundary or the twin boundary or the symmetry operation in considering cannot be the inherence symmetry operation of the crystal, if it were so then it will be a single crystal and they will not be 2 variants.

Of course, when I am talking about variant one and two, I can also think of this boundary between the 2 which I am marking with an arrow as sort of a mirror twin as well. So, you can see that this can also be thought of as a reflection of twins, but on the whole this is a rotation twin. Importance of this rotation twin this context is that, suppose one way to perform a diffraction experiment, say in a transmission electron microscope by putting as selected area diffraction of purchase in region in compassing this phi twins.

Then the person would see a symmetry higher than that available for a single variant. In other words this twined configuration mimics a symmetry which is higher than that of available for the crystal. So, in this case you will observe a phi fold symmetry which as you know is disallowed in crystals.

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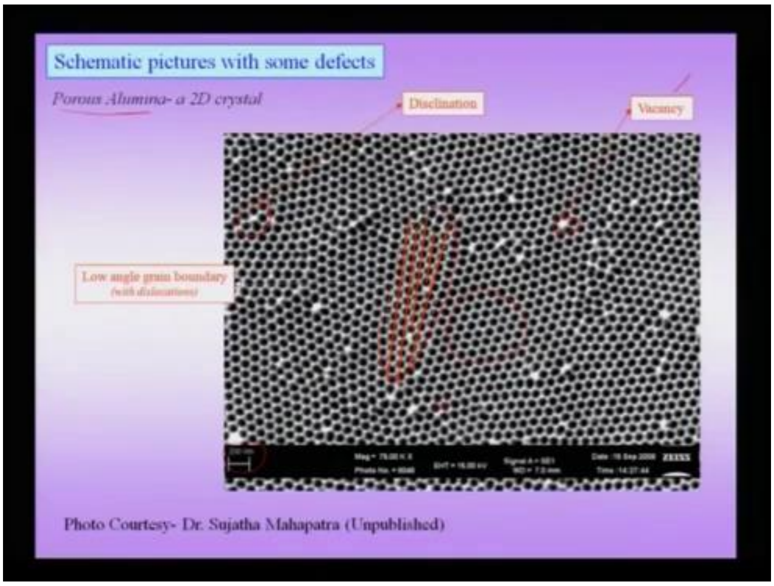

Schematic pictures with some defects

Porous Alumina- a 2D crystal

Photo Courtesy- Dr. Sujatha Mahapatra (Unpublished)

So, let us have a look of a totally different kind of a schematic or let us put it this way, a different kind of understanding of a real crystal and this actually happens to be the from the nano world. This is an example of a porous alumina which can be thought of as a 2 dimensional crystal. This 2 dimensional crystal has crystalline regions and this is not a single crystal.

So, there are crystalline regions, but you can see that a region like this is nicely single crystalline. So, this is some sort of a poly crystalline alumina, but what is the motive here the motives are this force along with the region in claw, in compassing this. Therefore, I can think of a motive which is a pour plus a material which is actually decorating the 2 dimensional artist. If I try to identify defects in such a material, then I can think of region like his as a vacancy as marked here.

So, this is not a vacancy where in atom has gone missing, this is not a vacancy where in a set ions have gone missing, but this is a vacancy in a 2 dimensional crystal, when the motive is actually some pour along with some alumina. So, this is a totally different kind of an example. If you look at the dimensions of these pours they are in the scale of nano metre as the scale bar on the left bottom of the micrograph shows.

So, this is a nice example of a nanomaterial and we will come back to it when we start to classify nanomaterials and try to understand them better, but this happens to be a nice example. You can see that even in this nanomaterial we can think of a region as if it were a low angle grain boundary. This low angle grain boundary as shown here has an extra half plate. In other word it is a dislocation in a certain different region.

You can also visualise certain kind of a defect, where in instead of having this region having can be also thought of as a disclamation. Therefore, we can visualise many defects even in crystals which are not the conventional crystals or there crystals in a different land scale all together. So, let us briefly revise the various defects, a collage of which we had construct before. So, we had said that there can be 0 dimensional defects like the interstitial the substitutional atoms.

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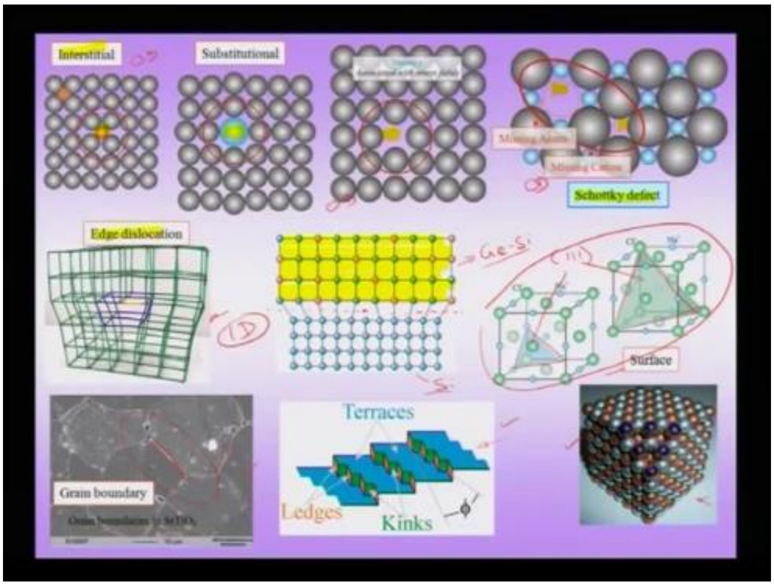

The vacancy or the short key defect we can have one dimensional defects like the dislocation. We construct 2 kinds of dislocation one which is localised to interface as shown in the example of the G S i 1 S i. So, this interfacial dislocation is called the interfacial misfit dislocation and is actually playing a structural role and therefore, can be classified as a structural dislocation.

The other inhabitable defect we said was a surface in a crystal and we considered one important kind of a surface, which is polar in nature which I am encircling here. We also briefly talked about this, but we will consider little more detail, that the surface may have further defects which are called kinks and ledges. Therefore, the surface itself may have a complicated structure, unlike a very simple structure which normally we consider.

The grain boundary is another important structural unit and it is the boundary which is between 2 grains in a polycrystalline material. We even noted that at some times the grain boundary can be pretty straight.

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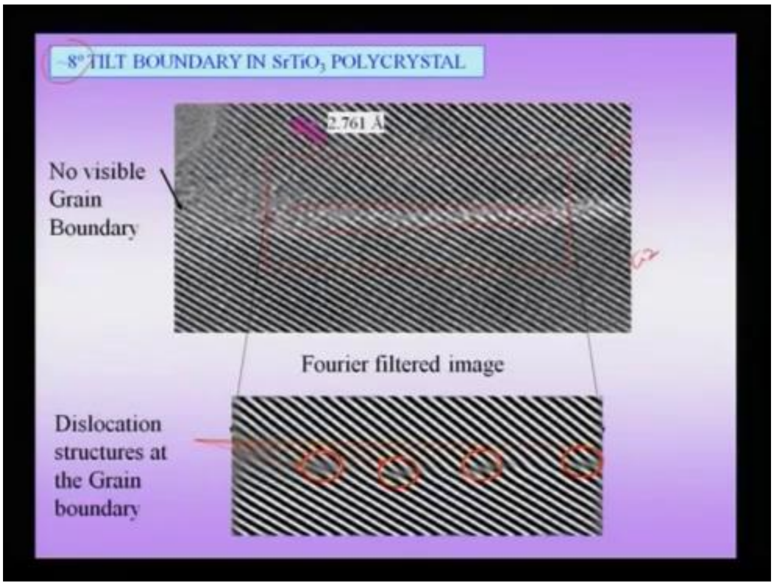

~8° TILT BOUNDARY IN SrTiO$_3$ POLYCRYSTAL

No visible Grain Boundary

Fourier filtered image

Dislocation structures at the Grain boundary

We also took a very specific example of another kind of a structural dislocation, which accommodates the misfit the tilt misfit between 2 grains which have a small tilt misfit and this is called the low angle grain boundary, which can be thought of as an array of dislocations, according to a model which is called a readshok remodel of a low angle grain boundary. We also talked about mirror twins and we notice that the twin boundary is a 2 dimensional defect, while the twin region itself can be thought of as a 3 dimensional defect residing typically within a grain, as an example of a copper which we saw right here.

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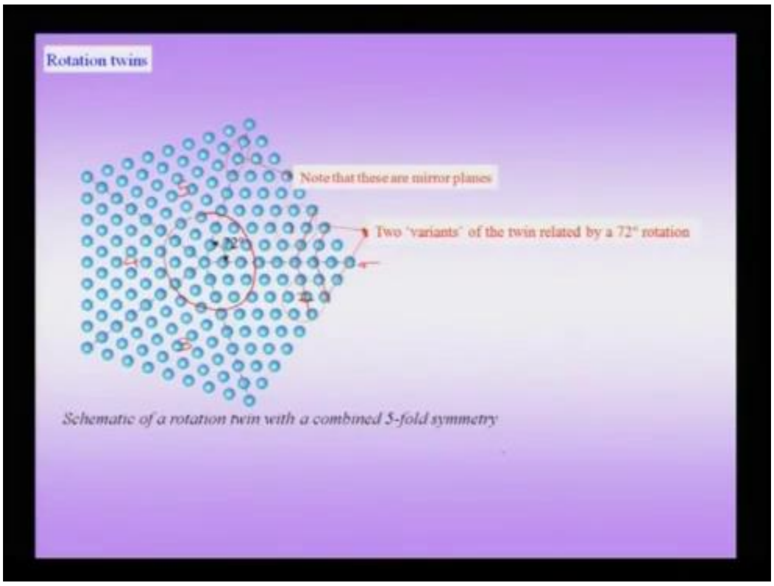

Rotation twins

Note that these are mirror planes

Two 'variants' of the twin related by a 72° rotation

Schematic of a rotation twin with a combined 5-fold symmetry

We can also thing of rotation twins and please note the important point that the rotation twin can actually mimic certain symmetry which is disallowed normally within the single crystal, which we normally consider. We also noted that when a defect becomes part of the crystal structure itself, like for instance a vacancy getting ordered or for instance its staking for getting ordered. Then the symmetry not only that it can be thought of as a defect in the original parent structure, but it becomes part of the structure itself.

Therefore, we get a new crystal structure all together which may have a different unit cell and also a different kind of a symmetry translation and other kind of symmetry is possible. Therefore, defects can not only dictate the properties, but they can at a fundamental level, even all the crystal structure and that is why defects are very important. Next, let us take up an example, wherein we are talking about interaction of 2 kinds of defects.

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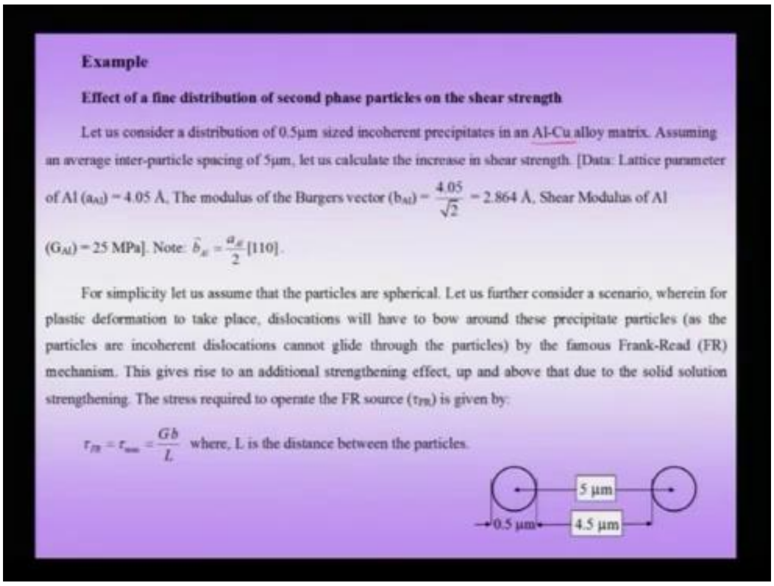

Example

Effect of a fine distribution of second phase particles on the shear strength

Let us consider a distribution of 0.5µm sized incoherent precipitates in an Al-Cu alloy matrix. Assuming an average inter-particle spacing of 5µm, let us calculate the increase in shear strength. [Data: Lattice parameter of Al (a_{Al}) = 4.05 Å, The modulus of the Burgers vector (b_{Al}) = $\frac{4.05}{\sqrt{2}}$ = 2.864 Å, Shear Modulus of Al (G_{Al}) = 25 MPa]. Note: $\vec{b}_{Al} = \frac{a_{Al}}{2}[110]$.

For simplicity let us assume that the particles are spherical. Let us further consider a scenario, wherein for plastic deformation to take place, dislocations will have to bow around these precipitate particles (as the particles are incoherent dislocations cannot glide through the particles) by the famous Frank-Read (FR) mechanism. This gives rise to an additional strengthening effect, up and above that due to the solid solution strengthening. The stress required to operate the FR source (τ_{FR}) is given by:

$\tau_{FR} = \tau_{max} = \frac{Gb}{L}$ where, L is the distance between the particles.

Here this interaction of 2 kinds of defects serves as an engineering application to in fact strengthen the material. Suppose, I take an aluminium crystal, an aluminium as an FCC lattice, wherein aluminium ion sits in it this kind of a crystal typically is very ductile, but on the other hand is very week. Therefore, it is not suitable directly as a structural application.

Such a crystal can be strengthen by adding an alloying element like in the case here. You can make an aluminium copper solid solution. The solid solution of copper and aluminium actually serves as to strengthen the parent crystal, but further to that, we can have further strengthening by actually precipitating certain precipitates in the aluminium copper system.

We had briefly considered how we do what is called a (( )) treatment followed by an aging treatment. Wherein we actually precipitate certain fine distribution of precipitates, which gives us an enhance strength. What is the origin of this strength, it is we had noted that what is weakening the crystal is actually the presence of dislocation.

Suppose, I had a single crystal without any dislocations and we the strength of the crystal would be or the order of gigapascal the shear strength, but in the presence of dislocations the crystal is severely weaken by a couple of orders, few orders of magnitude. Now, we have a much weaker crystal in the presence of a dislocation or a large number of dislocation as the usually the case is. Now, if I want to strengthen the dislocation crystal back again I have to strategy set my disposal. Let me briefly write down those 2 strategies.

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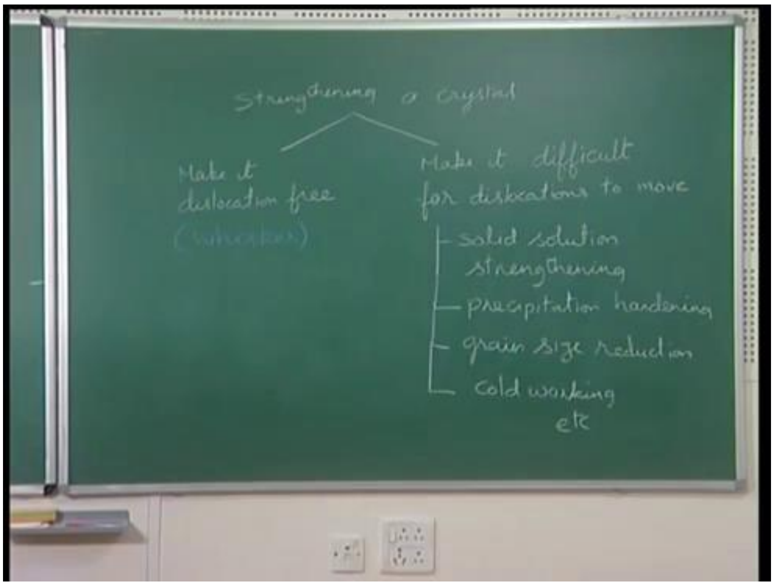

So, there are 2 strategies available for me to strengthen the crystal, which has weaken by the presence of dislocation. Either I can make it totally dislocation free, to obtain something known as a whisker. Whiskers has been produced is a small this cylindrical specimens which is totally dislocation free. Such as material or actually have an in hand strength, but the problem with this strategy is that, under actual service such a whisker may actually nucleate a dislocation.

First of all it is very difficult to produce these whiskers which are totally dislocation free, but in service again dislocation we nucleate thus weakening the crystal. Therefore, this is in most cases not a viable option to actually strengthen a crystal. So, what is the better option or the usual engineering option, is to make a difficult for dislocations to move. In this respect we have many strategies available, how do to make it.

We can do something known as a solid solution strengthening. We can do precipitation hardening. Some of the strategies we typically used for increasing the strength of a weaken material is to use solid solution hardening which in some sense actually increases inherent latex friction for the dislocation to move. We can use precipitation hardening.

In other words you put a fine distribution of precipitates which can impeach the motion of the dislocations. You can actually do what is called a hallpetch hardening, in which case you decrease the grain size and the grain boundaries act as impairments to the motion of dislocations, we just thus increasing your strength. We can do cold walking and this cold walking essentially increases your dislocation density. Thus, you have an increased in the strength of the material.

Of course, it is a curious question that, actually dislocations are weakening then how an increase in dislocation density can lead to a strengthening effect. This is because when you think of a single dislocation moving in a forest of other dislocations. There are interactions between these dislocations and these interaction lead to increase in dislocation dense.

In other words in increase in density and therefore, you have an increased strength. We are going to solve this example, for the case wherein we are precipitating certain second phase into the matrix, which is going to give us strengthening. The case we are specifically talking about here is the aluminium copper system.

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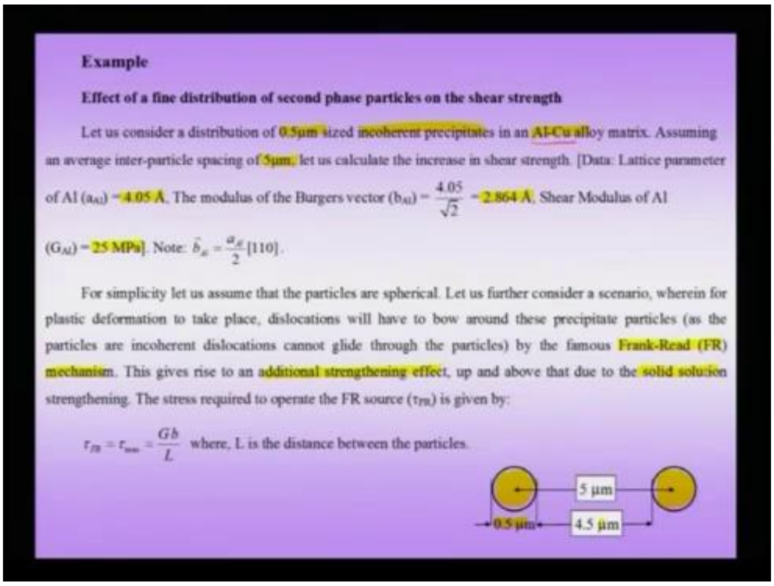

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In which a second phase precipitate has been put and we will make certain simplifying assumptions to understand how this distribution of precipitates actually gives rise to hardening. We will also dwell in to a little of regarding the mechanism which is actually giving rise to this hardening. When we go nanomaterials, we will see that some of these mechanisms can be effectively use and some of them will actually seems to exist when you nanomaterials.

That is why it is important what is one example in detail in regard to the hardening of a material, which is one of the important mechanical properties. Now, let us consider a fine distribution of precipitates for instance a 0.5 micron size. For now we will consider what are called incoherent precipitates. That means lattice planes are not continuous across from the precipitate to the matrix.

You will assume an average inter particles pacing a vote 5 microns which is shown in the figure below. So, the for now we will assume some spherical precipitates and we should note that in actually in the aluminium copper system, the precipitates may not be spherical are in fact are not spherical, but we just for understanding other concepts we will consider that. We will assume that the diameter of these particles are about 0.5 microns and the inter particle spacing is about 5 microns.

The distance from surface to surface, thus turns out to be a volt 4.5 microns or 4.5 micro meters. The lattice parameter of aluminium is about 4.05 angstroms and in the presence of a solid solution this will be alter, but we will for now assume that this is the lattice parameter we need to consider. The burgers vector in the FCC lattice is root 2 a by 2. In other words it is a by root 2 and for this case it will turn out to be about 2.86 angstroms.

The shear modulus of aluminium is 55 megapascals and we will now make a calculation as to how what is the increase in strength up and above the normal ((Refer Time: 18:37)) strength or the normal shear strength of the material. Now, what is going to give rise to the hardening in this case. The hardening is going to come from a fact that when the dislocation moves, there are precipitates and these precipitates being in coherent therefore, the dislocation cannot actually glide through the precipitate.

In fact it will bow around the precipitate by a mechanism known as the frank read mechanism. For now we will assume that, the entire plastic deformation is being detected by this process. In other words we will not consider other kind competing processes in this system. We will try to find out what is the additional strengthening affect up and above that do to the solid solutions strengthening and for that we need to know what is a shear required to operate a frank read source.

This stress required to operate a frank read source is given by this formula which is given by Tau frank read which is the maximum of the stress which we required to actually operate a frank read mechanism. In the coming slides I will show you what is this frank read mechanism and how it actually works, but the Tau max is given for now by the formula G b by L, where G is the shear modulus in a material b is the burgers vector and L is the distance between the particles which happens to be 4.5 microns.

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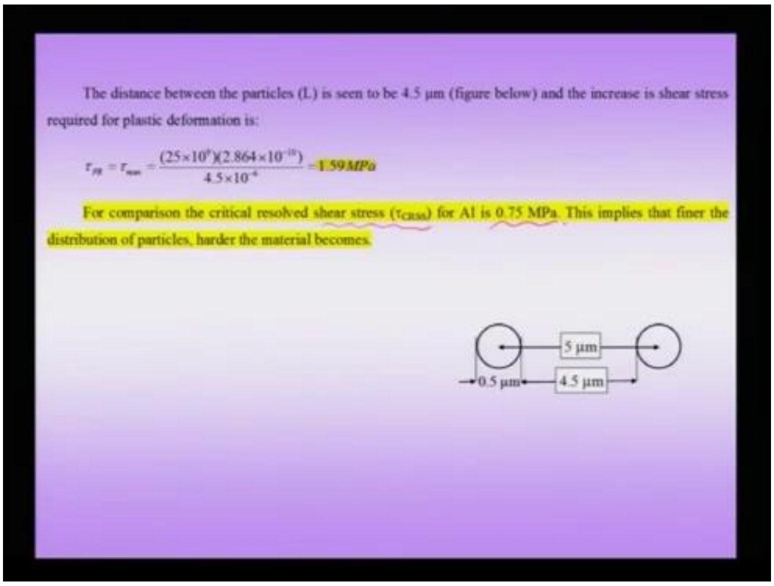

The distance between the particles (L) is seen to be 4.5 μm (figure below) and the increase is shear stress required for plastic deformation is:

$$\tau_{FR} = \tau_{max} = \frac{(25\times10^{9})(2.864\times10^{-10})}{4.5\times10^{-6}} = 1.59 MPa$$

For comparison the critical resolved shear stress (τ_{CRSS}) for Al is 0.75 MPa. This implies that finer the distribution of particles, harder the material becomes.

So, I have all my parameters in place, if you plug it into this formula and calculate my tau max, it turns out to be about 1.59 megapascals. Now, I need to compare this number with the critical resolve shear stress or what is known as the tau shear assess, tau shear is very similar to the pearl stress, which we had talked about before. The only difference being tau shear asses is usually experimentally determined while pearl stress is theoretically determined.

The second thing is that the tau shear asses or the critical resolved stress is usually at some finite temperature, like it could be the room temperature as the example considered here. So, we are talking about their resolved shear stress which needs to act on the slip plane to activate slip. That is called the critical resolved shear stress. Critical resolved shear stress like as I told you the pearl stress is an inherent material property at the atomic level or the slip plain level.

Unlike a gross macroscopic property like the eel stress which is an average of this over and entire system or entire material. Now, if you take this critical resolved shear stress value for aluminium, it turns out to be having a value of 0.75 megapascal and I can clearly see that by adding these incoherent precipitates I obtain a strengthening affect above this 0.75 to value of 1.5 9 megapascals.

Now, if I go to look at this formula, it tells me that the L is sitting in the denominator. So, how do I increase my strength, either I have a material with a larger value of b and larger value of G which are not under our control because we considered as vector specific systems.

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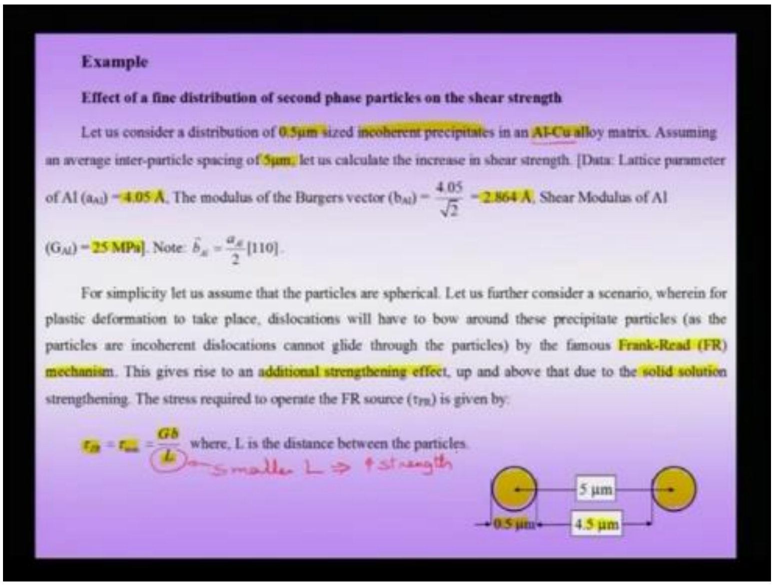

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smaller L ⇒ ↑ strength

The second possibility is to actually however smaller value of L because as I told out at the atom at the slip plane level, if I am able to in peat the motion of dislocations then automatically the strength of the material is going to increase because this is what is actually weakening the crystal. The motion of dislocations leaving the crystal is what is weakening the crystal. Now, that means if I am able to distribute the precipitates in a very fine manner by actually decreasing L, which is sitting in the denominator of this formula.

Then I am going to have an increased strength. In fact this is the whole strategy behind what is called precipitation hardening in a precipitation hardening system like aluminium copper. Though I had mention this before maybe briefly I will talk about the steps involved in this mechanism.

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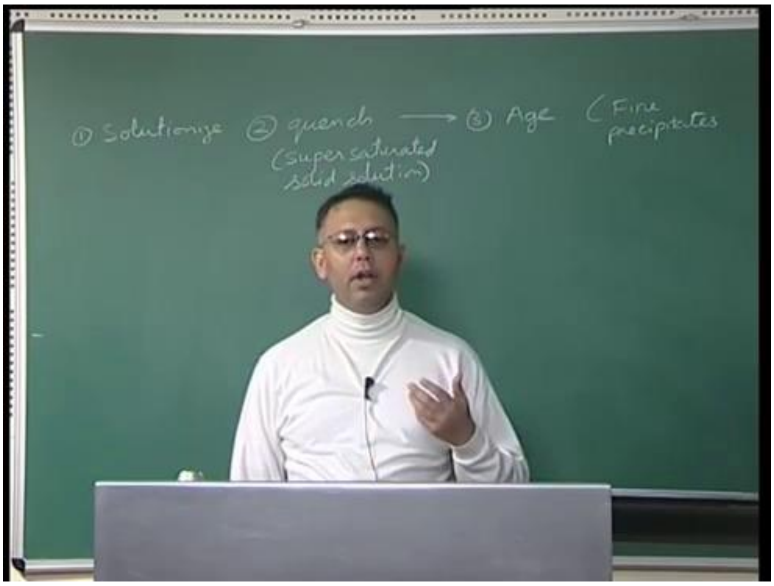

The step one is to solutionize, the step two is to quench and the quench substance produces a super saturated solid solution. After quenching aged to produce fine precipitates. Of course, one may ask this system why do I have to adopt such a complicated procedure of three steps, solutionising, quenching, ageing to produce instead of actually slowly cooling the system because any how at room temperature the theta phase, the amount of solubility is very less for a copper and aluminium.

Therefore, automatically the theta phase would precipitate out. The answer lies in a fact that if I do a slow cooling then actually the system would be growth dominant and nucleation restricted. In other words when you slowly cool, you will have a few nuclei which will grow large. Therefore, I will have a very close precipitate that means the theta paces which would be produced would have a micro structure something like this. So, this is a slow cooled system and we are already considered a micro structure like this before. So, this will mean slow cool, these are we.

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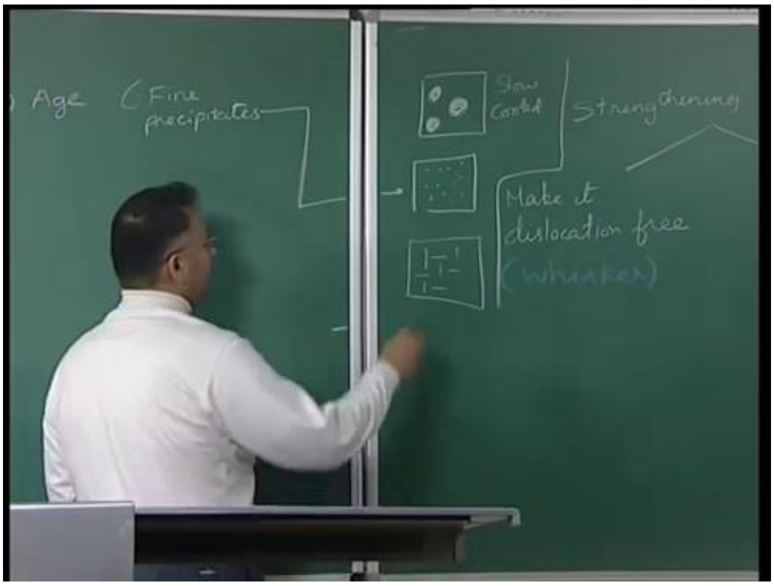

Suppose, I consider a system which has gone through this kind of a treatment which will have a one distribution plus pace. Of course, the mod for here the precipitated will be not be what I am showing here, this is just a crude schematic. In fact if you look at them transition electron micrograph that G d G p is own separate stage, they will look something like, this they will have them more for G like anyway, that is the detail

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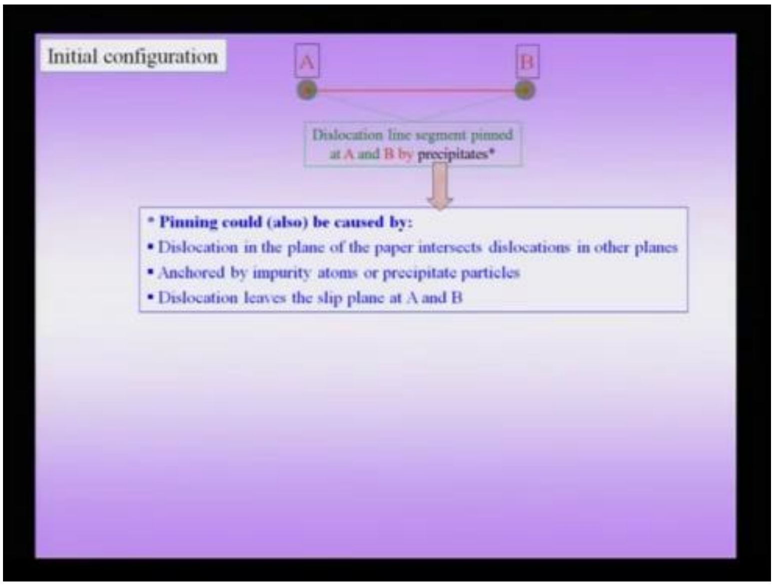

Initial configuration

Dislocation line segment pinned at A and B by precipitates*

*** Pinning could (also) be caused by:**

- Dislocation in the plane of the paper intersects dislocations in other planes
- Anchored by impurity atoms or precipitate particles
- Dislocation leaves the slip plane at A and B

The important thing is that there will be a fine distribution of precipitates and the reason is ampliclear now. As to what this fine distribution of precipitates can do in terms of the strength additional strength which I obtain. Now, we have talked about this frank read source. Let us understand what is the implication of having a source like a frank read source and p what are the other competing mechanisms, which are possible because at the heart of this strengthening is this double ended frank read source, which has been shown here in the fight hand side.

Now, in the double ended frank read source the.starting.is that we having a dislocation, which is moving on its slip plane. On the slip plan there are these incoherent precipitate particles which handle the motion of the dislocation. So, let us consider configuration like this. Therefore, these are my precipitates and this is my dislocation line segment. For now we will understand that this dislocation line segment has been pinned at these 2 points.

In other words wherever the precipitate is it cannot move. There are other sources opinion possible like for instance at points a and b, actually the dislocation may leave the slip plane or there could be other kind impediments to the motion of the dislocation, but for now we are considering precipitates which are sitting there. For now they are incoherent precipitates. In an aging schematic like this let me have a solutionising, quenching and an aging.

This kind of incoherent precipitates are produced either by aging at higher temperature or aging for a long time at a lower temperature. Now, what happens what is the sequence of events in increasing stress when you actually try to press this dislocation against this 2 pinned points. So, let us think about it the system. So, you have 2 variables in this system.

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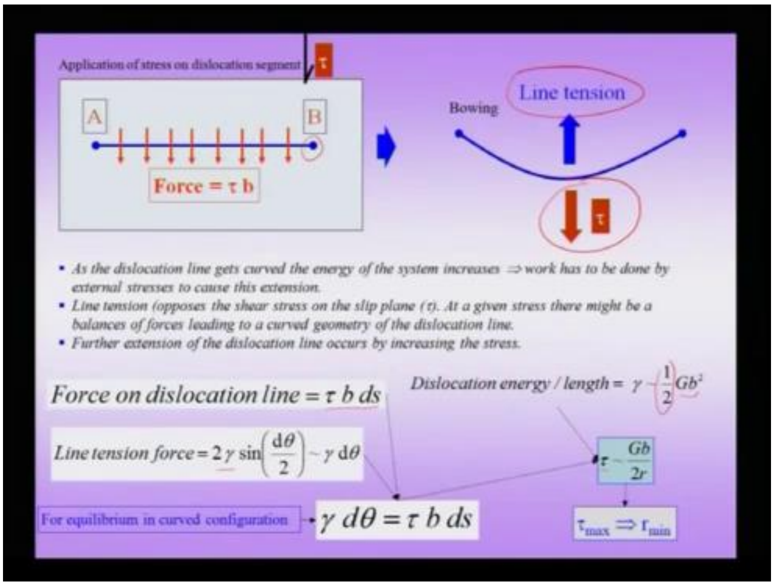

- As the dislocation line gets curved the energy of the system increases ⇒ work has to be done by external stresses to cause this extension.
- Line tension (opposes the shear stress on the slip plane (τ). At a given stress there might be a balances of forces leading to a curved geometry of the dislocation line.
- Further extension of the dislocation line occurs by increasing the stress.

Force on dislocation line $= \tau\, b\, ds$

Dislocation energy / length $= \gamma \sim \frac{1}{2} G b^2$

Line tension force $= 2\gamma \sin\left(\frac{d\theta}{2}\right) \sim \gamma\, d\theta$

$\tau \sim \frac{Gb}{2r}$

For equilibrium in curved configuration → $\gamma\, d\theta = \tau\, b\, ds$

$\tau_{max} \Rightarrow r_{min}$

One is an external applied shear stress which translates you externally applied shear force which translates into a shear stress at the level of the slip plane. On the other hand if the dislocation line is not straight, then you have a line tension which is trying to make the dislocation straight. Therefore, there are 2 competing forces and if these forces are the level of the dislocation are equal, then the dislocation will be in a stable configuration.

Now, this is my initial configuration, wherein the dislocation has been pinned at points c and b. Please do not look at this reason carefully because this is just a schematic there will be more it is not actually on the precipitate, but it will be stuck around the precipitate or slightly aware from it. Now, on application of the shear stress at the dislocation line level there will be a source is tau b which is acting on this. This is coming from the externally applied shear force in a material.

As you increase this externally applied force the dislocation would tend to get into a curved geometry. The force on the dislocation line can be written as tau b, b S b S being the unit length along the dislocation line. The dislocation energy per unit length is proportional G b square and approximately it half G b square, where in we have actually ignored something known as a core energy of the dislocation.

The line tension force which is actually trying to contract the dislocation line can be written as 2 gamma sin d theta by 2. If you look at the next picture. So, d theta being along the radius of what you might call the dislocation line, the angle it obtains. Therefore, this is approximately equal to gamma d theta. For equilibrium in a curved configuration we need to have gamma d theta is equal tau b s, which gives us by putting all these equations together. We get the formula which we had used in the case in the case of finding these strengthening effect of the precipitates, which is tau with which is given by 2 G b by 2 r.

Obviously, when r is the maximum, you get the r is the minimum you get the maximum in tau max. Let us see when this actually you have the maxima in the shear stress which it needs to be shear force which needs to be applied. So, in this figure you can see that you have configuration one which is a starting configuration, the configuration 2 3 4 and 5.

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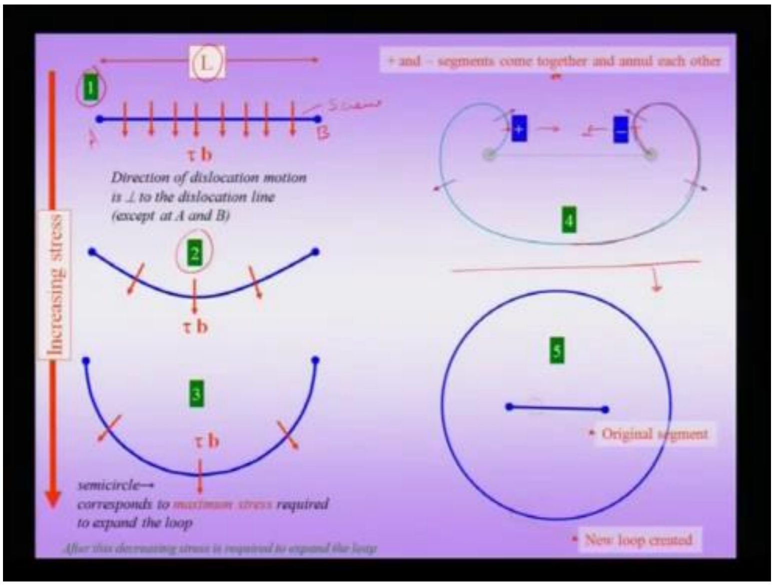

+ and − segments come together and annul each other

Direction of dislocation motion is ⊥ to the dislocation line (except at A and B)

semicircle→ corresponds to maximum stress required to expand the loop

After this decreasing stress is required to expand the loop

- Original segment
- New loop created

So, we start with a pining point at a distance of length L which is shown here. We increase external shear stress and therefore, in under the presence of this shear stress the dislocation length increases and also it gets into S curved configuration. On further increasing of shear stress, we see that it can actually get into a semi-circular configuration. This semi-circular configuration is important because still we obtain a semi-circular configuration the stress has to be increased and beyond that point.

Actually the system goes down heel in stress as from configuration 3 to configuration 4, where in actually the system, you do not have to apply extra shear stress, but the system itself goes down heel in stress. It takes the dislocation takes a very convoluted appearance as you can see here, in the form of a certain kind of a curve.

Now, when you look at a curve like this, an initially suppose i was talking about a pure screw dislocation. Suppose, this segment was our screw then this segments would constitute positive and negative edge segments. As we know that positive and negative edge segments will actually attract themselves. Therefore, they will tend to count together as this loop expands further. In the end you would notice that.

So, this stare segment will tend to come towards this segment in an expanded configuration. In the end you will see that the positive and negative segments and null each other. Finally we are left with one circular loop and the original segment what we started off with. So, what the implication of such a mechanism? The implications are twofold, number one that actually the dislocation density has increased because originally we had a dislocation length, which is between points a and b. Suppose I have to label these points a and b, but now we have an additional dislocation loop, which is sitting around these 2 precipitates.

The second implication is that, suppose I were to drive want to operate the same source again. In other words suppose I start with a new dislocation line which is approaching my loop. Then to operate the same source I need because now this this dislocation loop is actually going to repel my oncoming loop or oncoming dislocation line. Therefore, I need to apply additional stresses to operate the same or actually to try to move the dislocation, which is coming in.

Therefore, this will automatically lead to a strengthening effect. Since I have done work on this system to actually produce this extra dislocation length. This means that the systems actually going to harden as I am going to do the deformation. So, let us summarise the frank read mechanism.

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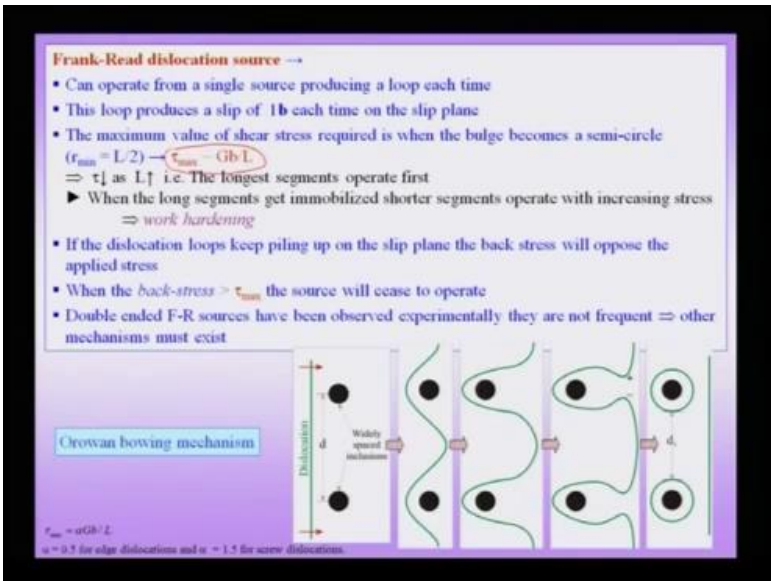

Frank-Read dislocation source →

- Can operate from a single source producing a loop each time
- This loop produces a slip of 1**b** each time on the slip plane
- The maximum value of shear stress required is when the bulge becomes a semi-circle ($r_{min} = L/2$) → $\tau_{max} = Gb/L$

  ⇒ τ↓ as L↑ i.e. The longest segments operate first

  ► When the long segments get immobilized shorter segments operate with increasing stress ⇒ *work hardening*
- If the dislocation loops keep piling up on the slip plane the back stress will oppose the applied stress
- When the *back-stress* > τ_{max} the source will cease to operate
- Double ended F-R sources have been observed experimentally they are not frequent ⇒ other mechanisms must exist

Orowan bowing mechanism

$\tau_{max} = \alpha Gb/L$

$\alpha = 0.5$ for edge dislocations and $\alpha = 1.5$ for screw dislocations

The frank read mechanism can operate a single resource without depletion can keep one operating to produce more loops each time. The loop produces a slip of one b on the slip plane each time it operates. The maximum stress co responses semi-circle configuration and at that configuration the stress required is tau max which is given by G b by let us all order a G b by L.

If I have various spinning segments in a material, like for instance a dislocation various dislocations maybe pinned at various precipitates, which are at not at a constant distance l, but different lengths, then the ones with the largest distance will operate first and the ones with which are separated by this smallest distance will actually operate later. Since, with time I am going to exhaust all my longer segments and I will only left with shorter segments which I need to operate this will tell me, that there is work hardening.

In other words I need to apply higher and higher stress to actually deform the material plastically. Now, when the back stress is greater than tau max the applied or the applied or the applied force which translates into shear stress at the slip plane level, the source will see to operate.

Once of course, beside point which we need to note here is that typically in normal experiments. They are found that double ended frank read sources are not that common, but it is one of the possible mechanisms by which actually you can have 2 fold things. One is increase in dislocation density and the second being and increased stress required for further deformation which is otherwise called work hardening. In this whole analysis, we are assuming that a single mechanism which is double ended frank read source mechanism is operating, but we could have other competing mechanisms like the Orowan Boeing mechanism or certain other mechanism of plastic deformation, which may be competing which the mechanism I am considering.

Like for instance in the figure below the mechanism shown is the Orowan Boeing mechanism. For now I have ignored these other mechanism which are competing with the frank read mechanism or the frank read source mechanism for plastic deformation. Therefore, I made many other simplifying assumptions, but the heart of this whole analysis lies a fact, that you have defects. These defects may interact with each other.

These defects may grow in density that means as we saw that the dislocation density increasing. I need to know a lot of details about these defects like for instance is a boundary of this precipitate with the matrix coherent, is it semi coherent, is it incoherent because if the precipitate happen to be coherent and the dislocation actually glide through the precipitate. You will not be operating a frank read mechanism.

Therefore, all these details I need to know about the defect structure in a material. It is this evolving scenario of defect interactions which is actually giving rise to many other properties like in the case we considered the ell of the material.

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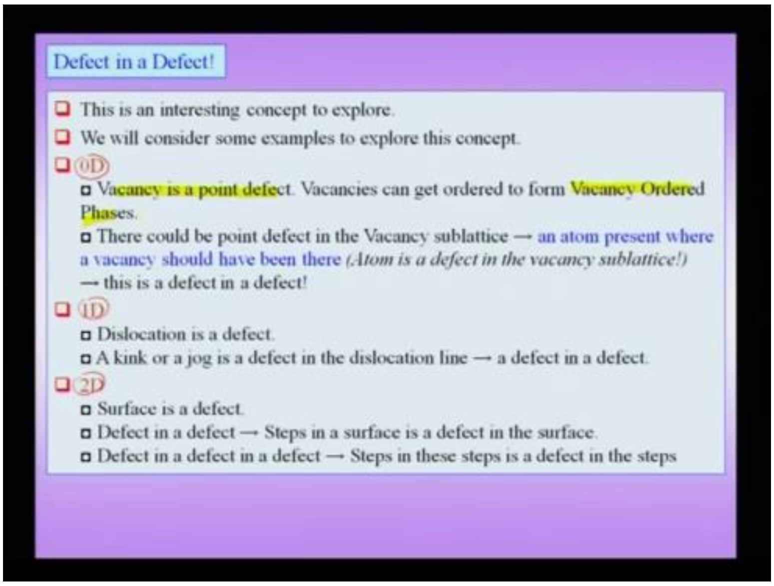

Defect in a Defect!

- This is an interesting concept to explore.
- We will consider some examples to explore this concept.
- 0D
  - Vacancy is a point defect. Vacancies can get ordered to form Vacancy Ordered Phases.
  - There could be point defect in the Vacancy sublattice → an atom present where a vacancy should have been there *(Atom is a defect in the vacancy sublattice!)* → this is a defect in a defect!
- 1D
  - Dislocation is a defect.
  - A kink or a jog is a defect in the dislocation line → a defect in a defect.
- 2D
  - Surface is a defect.
  - Defect in a defect → Steps in a surface is a defect in the surface.
  - Defect in a defect in a defect → Steps in these steps is a defect in the steps

Before we leave the concept of the effects and the details regarding a defect structure. Let us explore couple of interesting viewpoints which is the concept of a defect in a defect, the concept of a defect association and what we might call hierarchy of defects. Now, often these are not found in elementary text books, but these are very important viewpoints when we want to understand the properties of a material.

Now, to explore this concept, let us consider this defect in a defect concept in 0 dimension in one dimension and in 2 dimensions. Now, these are just examples we are considering here, but on the in the detail these are subjects of study in themselves. Now, we have noted that vacancy is a point defect in a material in a crystal. Vacancies can get ordered to form vacancy ordered faces. Now, once you have a sun lattice which being occupied only by vacancies.

Therefore, I have a vacancy ordered system, in which one of the sub lattices is actually occupied purely by vacancies. Then there could be a scenario in which the vacancy the vacant sub lattice side could actually an atom could be present. Now, is this is a vacancy sub lattice the presence of an atom in this sub lattice is actually a defect. What is the defect here, it is an atom. So, in the vacancy sub lattice, an atom is a defect. Therefore, this is a defect in a defect concept because vacancy is a defect in a material the atom in the vacancy sub lattice is a defect in the vacancy ordered sub lattice.

Therefore, this is a concept which is awake defect of the concept of a defect in a defect. This is of course, in 0 dimensions, of course, we will come back to this point later wherein we talk about the hierarchy of defects, but for now we will take it, that when somebody says there is a vacancy, we should not always think of it as a missing atom.

As the interesting example points out in the vacancy sub lattice the presence of an atom is actually a vacancy, in some sense of understanding of the word. Let us now consider a dislocation. Now, a dislocation is a defect in a perfect crystal. Now, we can have a kink or a jog in a dislocation line which is a defect in the dislocation line. A kink or a jog is not a defect directly or easier way to understand it is not by thinking of it as a defect in the crystal, but thinking of it as a defect in the dislocation line.

Therefore, a kink is a dis defect in the dislocation line, a dislocation line is a defect in the crystal. Therefore, a kink or a jog is a defect in the defect. Now, what is a kink or a jog, let me see if I got a figure here for instance this shows you that.

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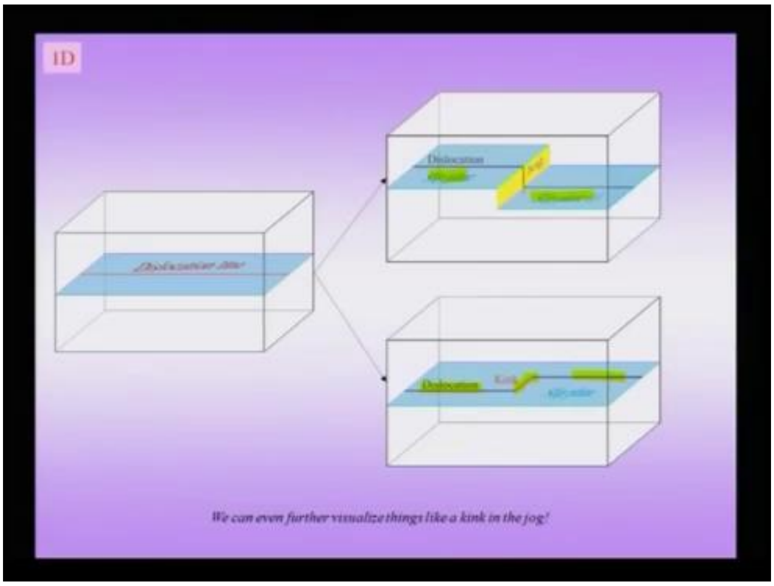

We can even further visualize things like a kink in the jog!

Therefore, this is now a jog and this jog takes the dislocation from one slip plane for instance the one which is above here, to another slip plane and in the process serves as a defect in a defect. The kink which does not take the dislocation line outer the slip plane in fact a single slip plane can be thought of as you can see here, as a bend in the dislocation line segment. It is a bend in the line dislocation line and therefore, this kink is a defect in the straight dislocation, which is what we want to consider here. Suppose, I am looking at this segment.

This is saved dislocation line, the straight dislocation line in a kink without taking the dislocation outside the slip plane actually produces an additional length segment. In other words it also cost energy to the crystal to put kinks into the material. Actually kinks and jogs can be produced by intersection of this dislocations and this itself can serve us a mechanism by which the material hardens.

Therefore, I can think of a kink and a jog as a defect in a dislocation line which is a defect in the crystal. In 2 d surfaces I can think of a surface as a defect in the perfect crystal.

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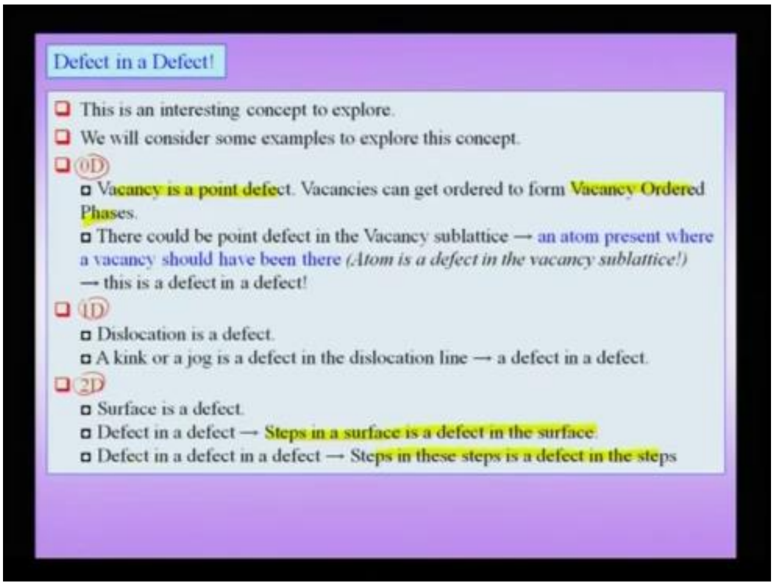

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- ②D
  - Surface is a defect.
  - Defect in a defect → Steps in a surface is a defect in the surface.
  - Defect in a defect in a defect → Steps in these steps is a defect in the steps

In fact it is a termination to a perfect crystal. In other words I take a single crystal I make or an infinite crystal in, make a cut then I produce 2 surfaces and on the surface of the bonds are broken. In fact the surface may undergo other kind of transformations like relaxation and reconstruction on and it will not merely be the termination of the bulk. That may not be the scenario, but here we are talking about, how we can think of defects in this surface. Steps on a surface is a defect in the surface and steps in these steps can be thought as a defect in those steps. Let me now show you a figure which can actually simplify the point. So, I have a surface which I have pointed out is a cut in an infinite crystal.

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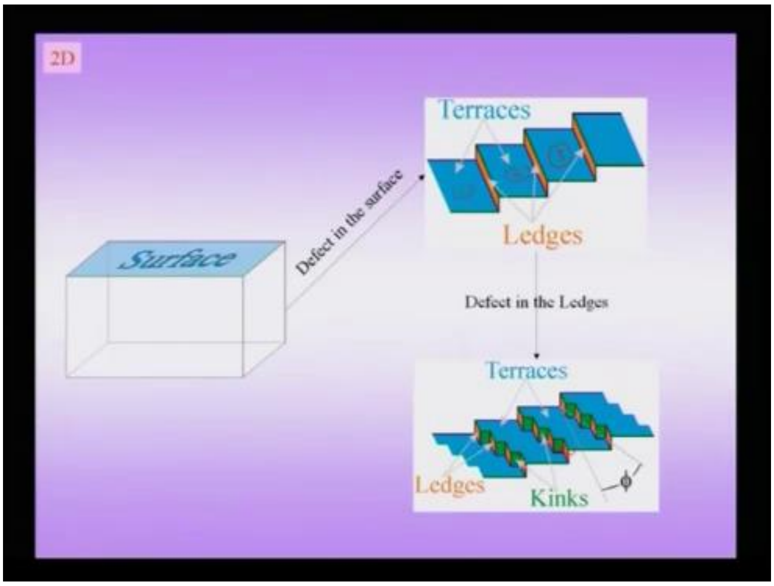

I also pointed out that this need not be have a structure which is just the termination of the bulk. In other words it may undergo relaxation or reconstruction. Typically though we talk about a 2 dimensional surface to be a 2 dimensional defect this is as I pointed out when I talked about defects. That this is in some senses geometrical viewing of the structure. In reality the surface can be thought of as a few atomic layers starting from the true geometrical surface. In other words the extent of the surface where atomic bonding has been disturbed the bulk lattice parameter has been changed, what actually be a few atomic diameters from the true geometrical surface.

Now, in this surface I could have these steps which are called ledges. Of course, this ledges and terraces, the terraces have been label blue and the ledges have been coloured orange and this ledges and terraces can be thought of as a defect to in the surface. Further we can have a breakup of these ledges into these kinks. So, you can see that if I am climbing a staircase then I can think of myself going from the step 1 to step 2 to step 3 via these ledges.

Now, within a single ledge I can think of going from this 1 to 2 to 3, this to the orange to the grain to the orange to the grain via series of steps which are kinks in the ledge. Therefore, I have here defect in a defect. A kink is a defect in the ledge, the ledge is a defect in the surface, the surface is a defect in the crystal. So, this is an alternate viewpoint which makes it very interesting to study some of these defects. So, let me briefly summarise the concept of a defect in a defect. I may have a defect belonging to one dimensions 0 dimension or 2 dimension.

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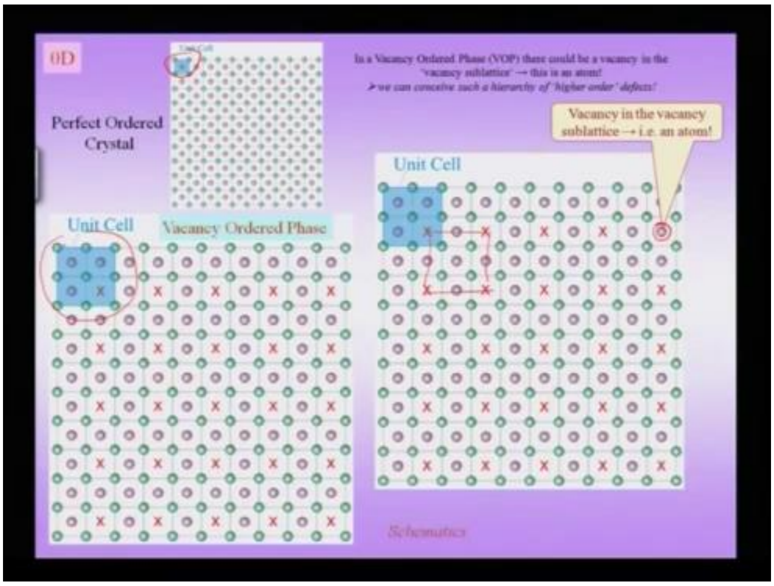

0D

In a Vacancy Ordered Phase (VOP) there could be a vacancy in the 'vacancy sublattice' → this is an atom!

➢ we can conceive such a hierarchy of 'higher order' defects!

Vacancy in the vacancy sublattice → i.e. an atom!

In the case of the 0 dimensional defect we considered the vacancy ordered face. For instance in this figure I see a vacancy sub lattice which is formed by these crosses. So, I have this vacancy sub lattice. Now, in the vacancy sub lattice I may have a missing vacancy, like in this case here where a cross should above be and actually there is an atom sitting there. Therefore, this is a defect in the vacancy sub lattice and vacancy itself is a defect in the perfect crystal or perfect crystalline order. It would have caution here we had already pointed out this aspect that, actually in a vacancy ordered face, the vacancy is sometimes not are more precisely not thought of as a defect, but belonging to the part of the crystal structure itself.

If I talk about the original unit cell, which is smaller unit cell for the vacancy ordered phase we actually have a larger unit cell, which goes on to give you the entire vacancy ordered phase crystal structure, but nevertheless this is an interesting viewpoint which you can keep in mind.

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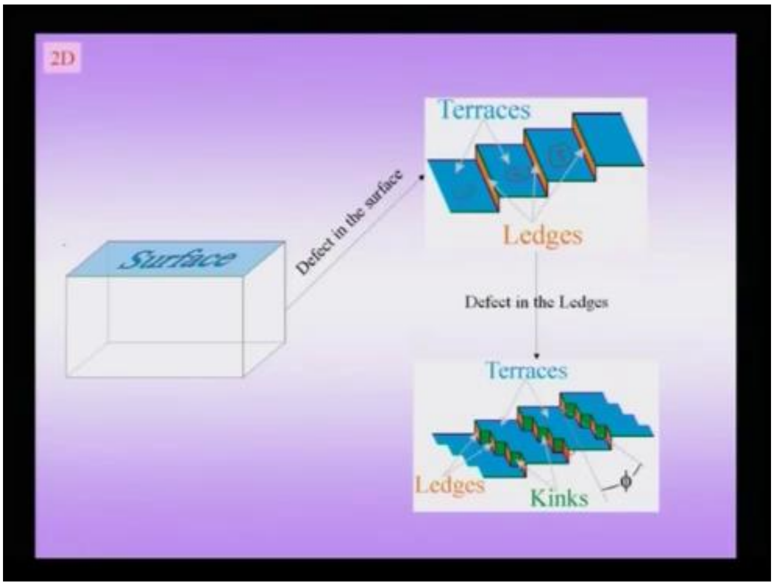

Same case we had talked about jogs and kinks in a dislocation line and also ledges kinks ledges and surface the kinks and ledges on a perfect surface, which itself is a defect in the perfect crystal. Next interesting viewpoint which we are considering is a concept of hierarchy of defects.

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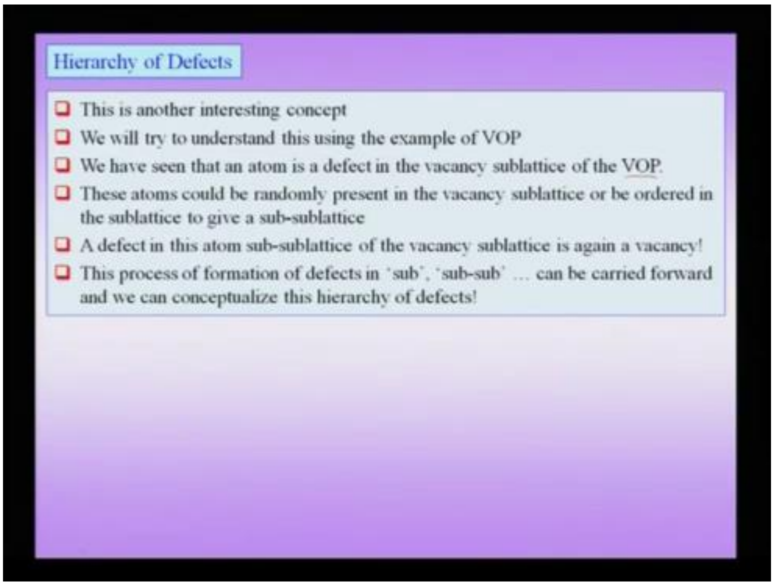

Hierarchy of Defects

- ❑ This is another interesting concept
- ❑ We will try to understand this using the example of VOP
- ❑ We have seen that an atom is a defect in the vacancy sublattice of the VOP.
- ❑ These atoms could be randomly present in the vacancy sublattice or be ordered in the sublattice to give a sub-sublattice
- ❑ A defect in this atom sub-sublattice of the vacancy sublattice is again a vacancy!
- ❑ This process of formation of defects in 'sub', 'sub-sub' … can be carried forward and we can conceptualize this hierarchy of defects!

Now, again we will use the concept of a vacancy ordered phase to understand what is meant by hierarchy of defects. Though in term practical sense some of these maybe actually rare that you may actually have some of these hierarchy of defects. From a point of view the nanomaterials this is going to become important because in a totally different context we will actually consider what is called hierarchical structures.

Now, where is this hierarchy of defects coming from. We already seen that a vacancy can get ordered in a vacancy ordered phase. Now, we have seen that a presence of an atom is actually a defect in the vacancy ordered sub lattice. Now, these atoms in the vacancy ordered sub lattice may themselves get ordered. Therefore, you can have think of an atom sub lattice in the vacancy sub lattice, which is present actually in the crystal.

Therefore, now we can think of 2 levels of sub lattices one sub lattice wherein the vacancies are ordered and a sub lattice within the vacancy ordered sub lattice, wherein atoms are ordered. Therefore, this is in some sense a hierarchy of defects. So, we have 2 orders of hierarchy of defects and this is pointed out though may be intellectual exercise, but there is an interesting exercise to understand, what you might call the defects not only are present as defects, they can get ordered, but can even have an hierarchy amongst themselves.

Let us take up the next topic which is exceptionally or extremely important, is the concept of association of defects. We already considered one example of clear cut example of interaction of defects. That interaction of defects was the interaction of a dislocation line with a precipitate in the crystal. Now, in this example we are talking about association of defects.

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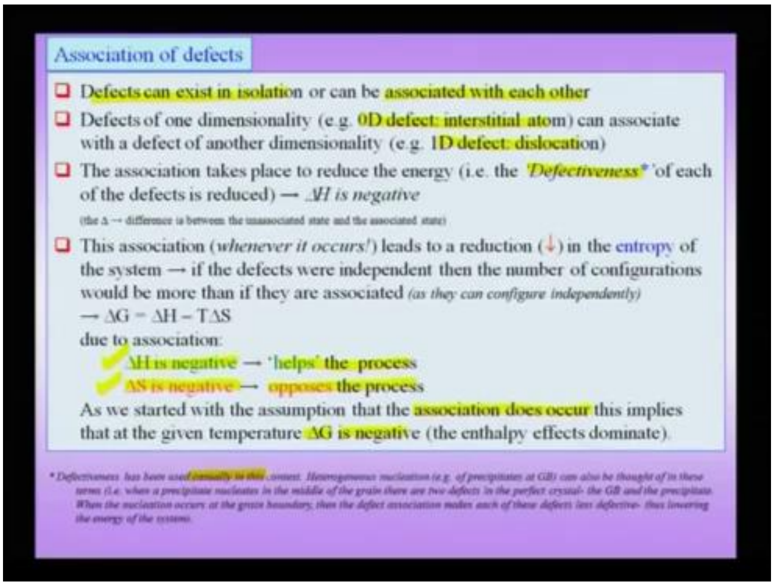

Association of defects

- ☐ Defects can exist in isolation or can be associated with each other
- ☐ Defects of one dimensionality (e.g. 0D defect: interstitial atom) can associate with a defect of another dimensionality (e.g. 1D defect: dislocation)
- ☐ The association takes place to reduce the energy (i.e. the *'Defectiveness*'* of each of the defects is reduced) → *ΔH is negative*
  (the Δ → difference is between the unassociated state and the associated state)
- ☐ This association (*whenever it occurs!*) leads to a reduction (↓) in the entropy of the system → if the defects were independent then the number of configurations would be more than if they are associated *(as they can configure independently)*
  → $\Delta G = \Delta H - T\Delta S$
  due to association:
  ✓ ΔH is negative → 'helps' the process
  ✓ ΔS is negative → opposes the process
  As we started with the assumption that the association does occur this implies that at the given temperature ΔG is negative (the enthalpy effects dominate).

** Defectiveness has been used casually in this context. Heterogeneous nucleation (e.g. of precipitates at GB) can also be thought of in these terms (i.e. when a precipitate nucleates in the middle of the grain there are two defects in the perfect crystal- the GB and the precipitate. When the nucleation occurs at the grain boundary, then the defect association makes each of these defects less defective- thus lowering the energy of the system.*

Defects can exist in isolation or they can be associated with each other. As a ((Refer Time: 45:57)) the important point, such a defect association can actually drastically alter the properties of a material. Now the important thing is that the defect of one dimensionality for instance a 0 dimensional defect like an interstation atom can associate with a defect of a different dimensionality. Like for instance a one dimensional defect like a dislocation. Of course, there could be association with of defects of the same dimensionality.

For instance a vacancy could also get associated with another vacancy. Now, what is the reason that such an association should take place. The reason is that, the enthalpy of the system may reduce when such an association takes place. In other words the enthalpy delta h, change an enthalpy is negative. In other words this change in enthalpy is helping the process.

Now, we are considering those kind of associations only for now herein the enthalpy happens to be negative. That is we are assuring that the association actually thus occur and therefore, this is helping our process to take place. Now, what will happen if, such an association occurs. There will be a negative delta s, in other words the entropy change will try to oppose our process.

Now, I am assuming a distorting itself, that the certain association for instance association of an interstational atom with a dislocation is taking place. So, what is the criteria I would use to actually see the feasibility of the association. I had actually used delta G as my criteria at constant temperature and pressure and I am assuming that the delta G is negative. What I am trying to do now is, further analyse this delta G in terms of a delta H and a delta S and I am seeing actually, that the delta H in this association is trying to help the process to take place, while the delta S is negative actually tries to oppose the process.

So, let us see why this happens, in a little more detail. Now, why should delta H be negative, we have seen that whenever there is a defect I can think of it being associated with a certain kind of defectiveness. Of course, I am using defectiveness in a rather what you might call a casual sense, but we all have an understanding of what is meant by defectiveness.

It is the amount of strain for the lattice, amount of free volume that is introduced by the presence of a defect, amount of excess charge locally at least which is present in the defect etcetera or in the disruption to the perfect crystalline order, which the defect introduces. Now, when two defect come together then it could so happen that, this defectiveness is actually reduced. So, let me take up a schematic, to show this can happen. For instance I have a single vacancy in a crystal.

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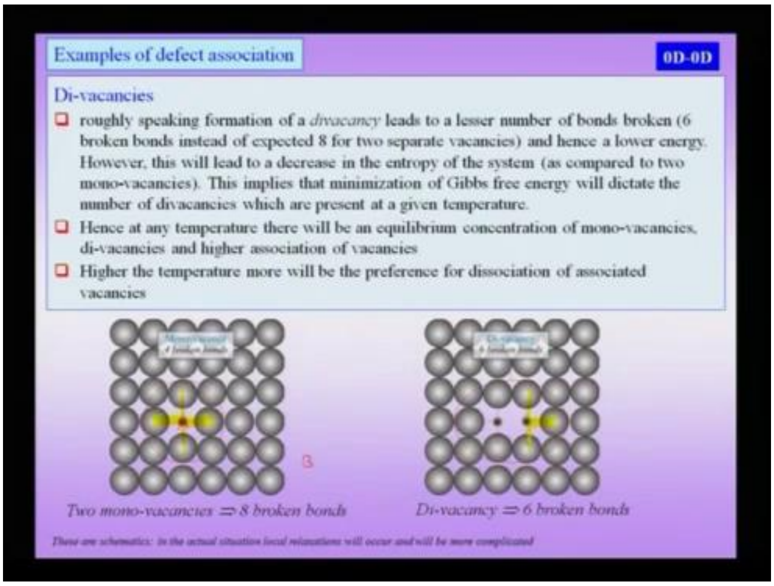

Examples of defect association

0D-0D

Di-vacancies

- roughly speaking formation of a *divacancy* leads to a lesser number of bonds broken (6 broken bonds instead of expected 8 for two separate vacancies) and hence a lower energy. However, this will lead to a decrease in the entropy of the system (as compared to two mono-vacancies). This implies that minimization of Gibbs free energy will dictate the number of divacancies which are present at a given temperature.
- Hence at any temperature there will be an equilibrium concentration of mono-vacancies, di-vacancies and higher association of vacancies
- Higher the temperature more will be the preference for dissociation of associated vacancies

Two mono-vacancies ⇒ 8 broken bonds

Di-vacancy ⇒ 6 broken bonds

These are schematics: in the actual situation local relaxations will occur and will be more complicated

This is responsible for of course, this I am showing here without the relaxation of atoms which would take place when the vacancy is present we crudely talk about 4 bonds being broken. Now, if there were 2 such vacancies located say at point a and point b for instance this could be point which have marked here and a point b somewhere else. Then I would have 8 broken bonds.

So, that means I am going to cost the crystal lot of energy. Now, suppose I talk about the formation of a die vacancy which means 2 vacancies located each to other, next to each other, then I would notice, that this is going to cost my only 1 2 3 and 3 at other sides 6 broken bonds. Therefore, clearly in many of these associations of defects there is an enthalpy benefit. Therefore, enthalpy is going to help me in the association of the defects.

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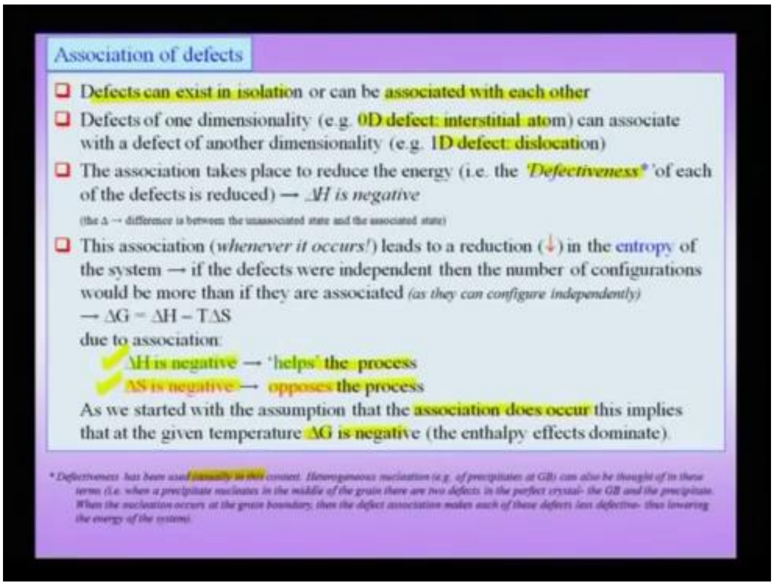

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Now, why should the entropy of the system come down when I have a defect association. This is because in the absence of the defect association, let me again go back to the example of these 2 vacancies here.

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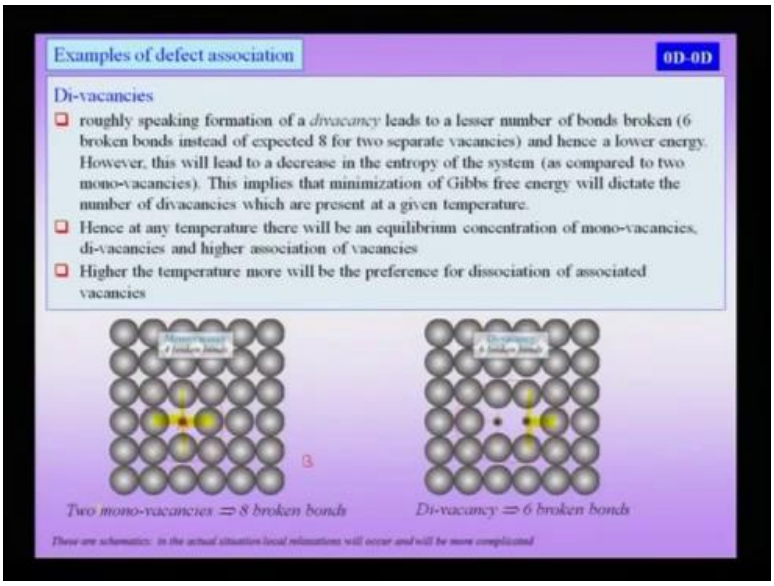

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Di-vacancy ⇒ 6 broken bonds

These are schematics: in the actual situation local relaxations will occur and will be more complicated

This vacancy could exist in one of the lattice crystal lattice positions and vacancy b again can be present in any one of the lattice positions except those adjacent to the place where a is located. Therefore, have lot of configurations at my disposal, 2 independent possible configurations in the entire mole of substance or larger. On the other hand when I have a die vacancy, this pair has to configure together. This is posing a severe constraint on the number of available configurations and we had already noted that S is equal k len omega.

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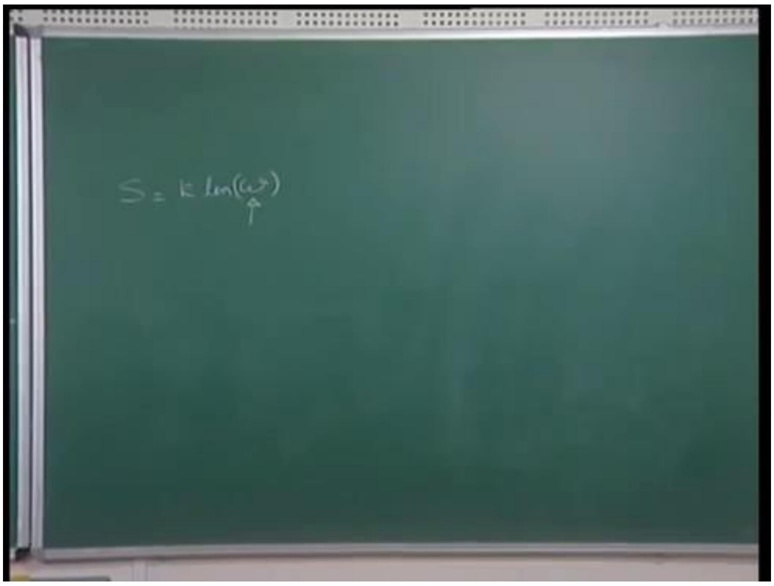

Since the number of available configurations is reduced a lot. This implies that my entropic benefit which is associated with this configurational entropy is reduced. Therefore, my delta S is going to oppose this process of defect association. Therefore, now given the fact I am already assuming that the defect association is thermodynamically feasible, it is in some sense can be thought of, that these are the 2 factors which go into it, but overall the delta G for the systemic negative.

Now, we have talked about the presence earlier. We talked about the presence of thermodynamically stable vacancies. Now, in when we introduce the concept of die vacancy the situation is little more complicated, which we will come to in a moment. Now, how do these association defect take place.

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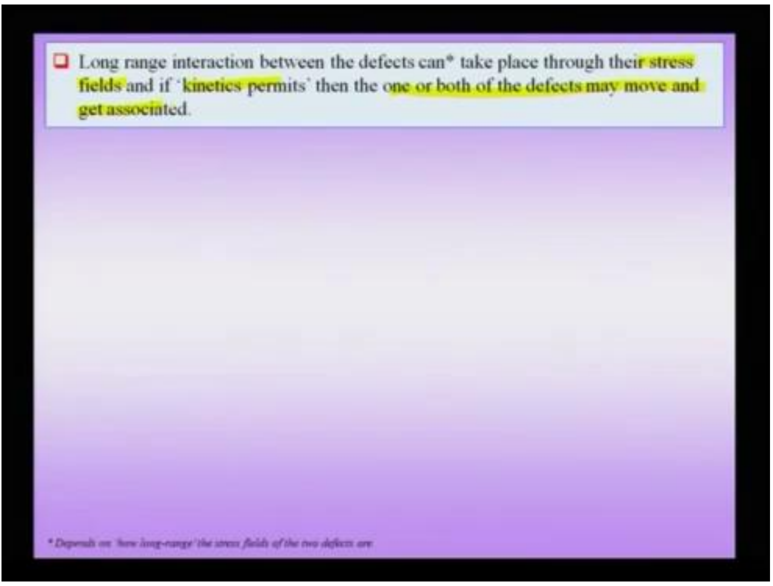

- ☐ Long range interaction between the defects can* take place through their stress fields and if 'kinetics permits' then the one or both of the defects may move and get associated.

* Depends on 'how long-range' the stress fields of the two defects are

The association of defects can take place, through the long range stress fields associated with these and if kinetic permits, then one or both of these defects may move and get associated. Now, that means that if these defects originally existed in isolated form and it is get interacting actually through a long range stress field. Like an example of one dislocation to another dislocation, then they actually attract each other.

If the kinetics permits, then they would come to close to each other and make it associated with one another, which is what we saw happened in the case of polygonization or the formation of a low angle grain boundary. We had originally constraint. So, let me re redraw that schematic for you. So, originally we had considered that in a bent crystal there are these statistically stored dislocations.

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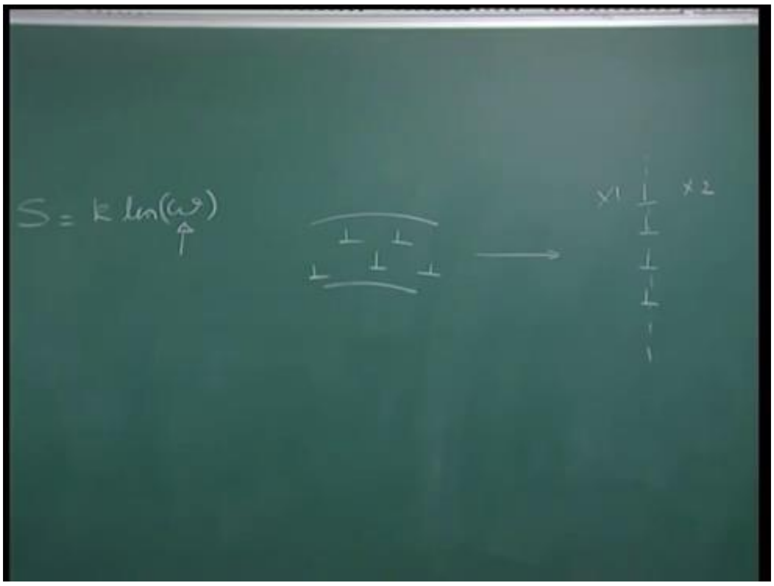

Then these dislocations may move in the presence of thermal activation to form a low angle grain boundary which is nothing but unary of dislocation. This is my low angle grain boundary and therefore, the crystal 1 and crystal 2 are disoriented. So, this is some sort of a sub grain boundary. Now, this is in some sense an extreme form of defect association, wherein all the dislocations were have been arranged one below the other.

They are associated one another to form a low angle grain boundary, but for such a kind of a motion to occur even they needs to be some kind of an activation which could be a thermal activation as in the case of the example of formation of the low angle grain boundary. Of course, I pointed out that the long range stress fields help in such a process to take place. Now, let us take these associations of defect one by one.

First we talk about the 0 dimensional 1, then we talk about a 0 dimensional 1, 1 dimension association and also a 0 dimensional 2 dimensional association.

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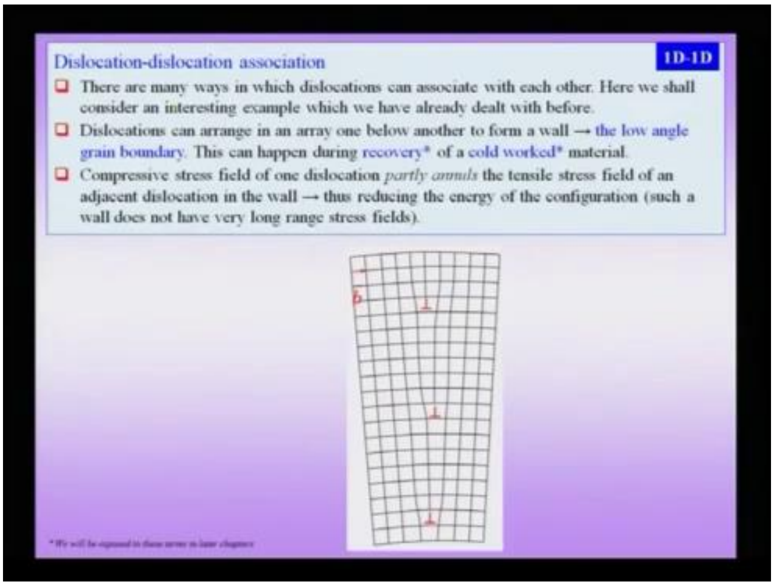

Dislocation-dislocation association

1D-1D

- There are many ways in which dislocations can associate with each other. Here we shall consider an interesting example which we have already dealt with before.
- Dislocations can arrange in an array one below another to form a wall → the low angle grain boundary. This can happen during recovery* of a cold worked* material.
- Compressive stress field of one dislocation *partly annuls* the tensile stress field of an adjacent dislocation in the wall → thus reducing the energy of the configuration (such a wall does not have very long range stress fields).

Finally, of course, we will just revisit the example which we just now talked about which is a 1 dimensional 1 dimensional defect association. We will consider some more examples also. So, we had already seen that there is a specific reason why die vacancy should form. That is why and we had rationalized the formation of a die vacancy in terms of the enthalpy benefit which finally, translates into reduced energy in terms of the number of bonds broken.

We have also said that this actually now, puts a constraint on the number of configurations available for this system. Therefore, it is going to decrease by configuration an entropy which is going to oppose my formation of die vacancies. Therefore, if I have any particular temperature in mind, for instance I could be talking about 50 degree Celsius or 200 degree Celsius, I know that there is going to be a certain thermodynamic number of stable vacancies.

Now this number of vacancies not all of them would be completely associated, not all of them would be completely dissociated, but the point there will be an equilibrium number of mono vacancies, there will be a certain number die vacancies which are also present

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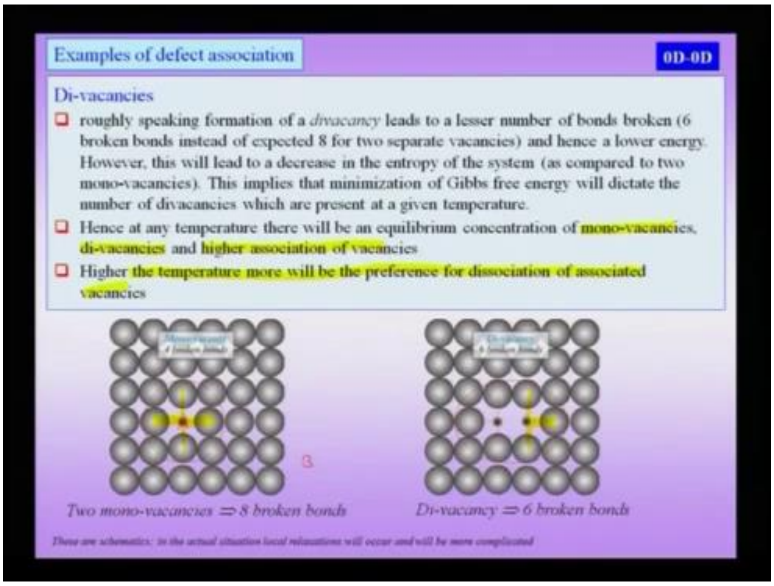

Examples of defect association

0D-0D

Di-vacancies

- roughly speaking formation of a *divacancy* leads to a lesser number of bonds broken (6 broken bonds instead of expected 8 for two separate vacancies) and hence a lower energy. However, this will lead to a decrease in the entropy of the system (as compared to two mono-vacancies). This implies that minimization of Gibbs free energy will dictate the number of divacancies which are present at a given temperature.
- Hence at any temperature there will be an equilibrium concentration of mono-vacancies, di-vacancies and higher association of vacancies
- Higher the temperature more will be the preference for dissociation of associated vacancies

Two mono-vacancies ⇒ 8 broken bonds

Di-vacancy ⇒ 6 broken bonds

These are schematics: in the actual situation local relaxations will occur and will be more complicated

Finally, they could also there is a possibility of higher vacancies also being present. In other words though my formation of die vacancy is going to help in terms of the enthalpy benefit, this is not the final story. At any given temperature I may have a certain equilibrium number of mono vacancies die vacancies and may be even higher custom vacancies, which can form.

Therefore, if I increase the temperature further, there will be more preference for dissociation of these associated vacancies and the reason is very obvious because the function which is going to dictate my stability.

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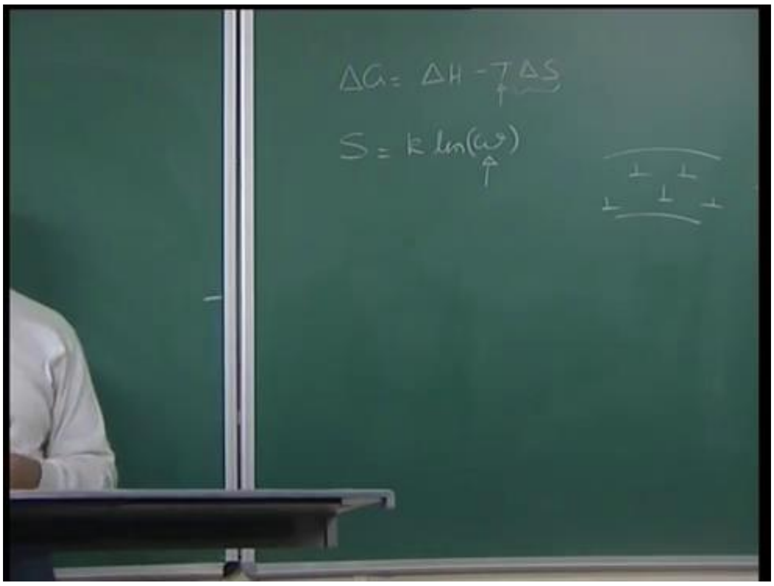

$$\Delta G = \Delta H - T\Delta S$$

$$S = k \ln(\omega)$$

So, the term which is going to dominate high temperature is the entropy atom because of the waving factor of temperature. Therefore at higher temperature you will have a tendency for these die vacancies to more and more dissociate. At lower temperature you may have more and more association of these die vacancies. As die vacancies are costly in terms of the entropy. Now, let us consider the next example, which is the association of a 0 dimensional defect like an interstitial solute atom with a one dimensional defect which is the dislocation.

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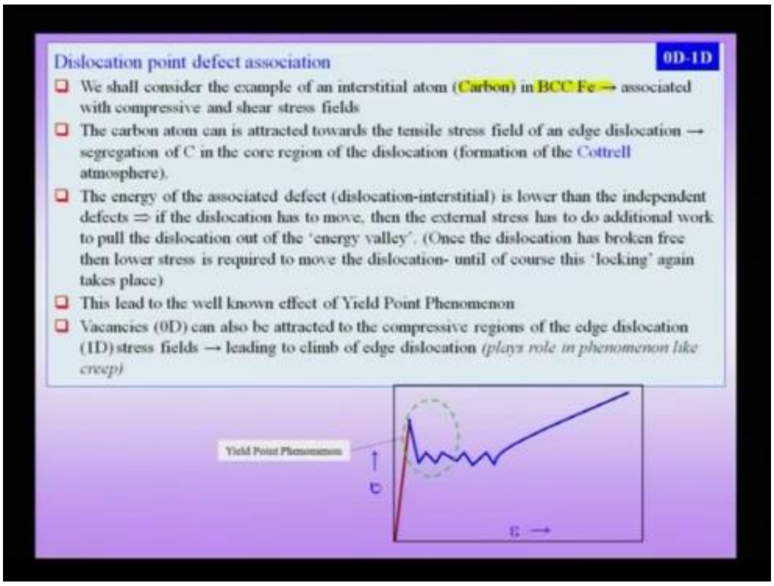

Dislocation point defect association

0D-1D

- We shall consider the example of an interstitial atom (Carbon) in BCC Fe → associated with compressive and shear stress fields
- The carbon atom can is attracted towards the tensile stress field of an edge dislocation → segregation of C in the core region of the dislocation (formation of the Cottrell atmosphere).
- The energy of the associated defect (dislocation-interstitial) is lower than the independent defects ⇒ if the dislocation has to move, then the external stress has to do additional work to pull the dislocation out of the 'energy valley'. (Once the dislocation has broken free then lower stress is required to move the dislocation- until of course this 'locking' again takes place)
- This lead to the well known effect of Yield Point Phenomenon
- Vacancies (0D) can also be attracted to the compressive regions of the edge dislocation (1D) stress fields → leading to climb of edge dislocation *(plays role in phenomenon like creep)*

The classic nice example of this is the presence of carbon solute in BCC iron which is otherwise called steel. Let us see what is the effect of this carbon solid solution and dislocations. At dislocation we as have noted is associated with a tensile feet and a compressive feet. Now, I am talking about an edged dislocation and an edged dislocation is associated with a compressive field wherever the extra half ((Refer Time: 57:04)) atom is dead.

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So, this is my extra half plane and this is where the compressive reasons are. The tensile regions that I am plotting sigma x x for now. These are is stressed cantors. So, as you go away and away. Then you will notice that this stress contores decrease in magnitude. So, this is higher stress contour this lower and lower as you go away from the core of the dislocation. Now, a vacancy also associated locally with a stress field.

It is associated with a tensile stress field and therefore, if a vacancy is present in the compressive region it will actually be attracted to this region. On the other hand interstitial atom is associated with the compressive stress field. Therefore, if I have an interstitial atom, it will be attracted to the tensile stress field of the dislocation. So, this is my extra half way.

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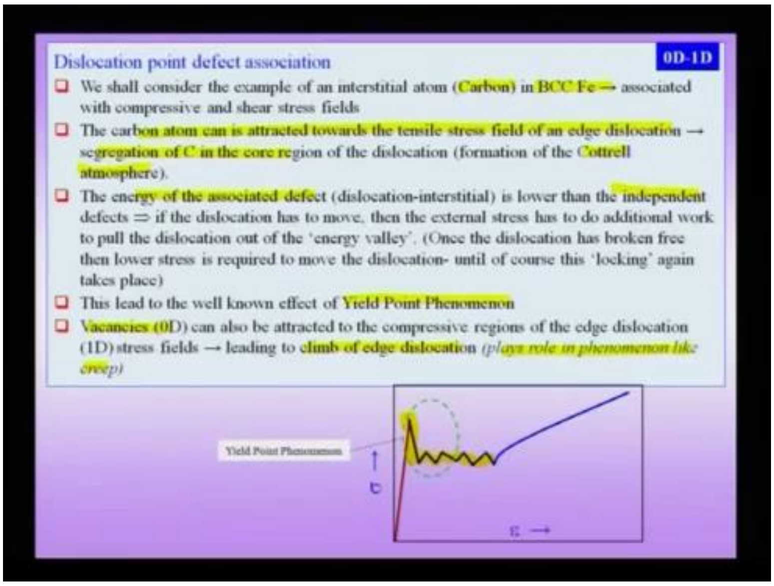

Dislocation point defect association

0D-1D

- We shall consider the example of an interstitial atom (Carbon) in BCC Fe → associated with compressive and shear stress fields
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- This lead to the well known effect of Yield Point Phenomenon
- Vacancies (0D) can also be attracted to the compressive regions of the edge dislocation (1D) stress fields → leading to climb of edge dislocation *(plays role in phenomenon like creep)*

The carbon atom is attracted towards a tensile stress field of the edged dislocation and can lead to a segregation of carbon at the core region of the edged dislocation. This selective segregation of the core of an edged dislocation is called the formation of the quarterly atmosphere. This is important consequences as shown in the figure below. The energy associate with the defect, the dislocation interstitial is lower than the independent defect like only a dislocation or only an isolated or far away interstitial.

Now, because of these as I am saying that because of this defect association, in the case the interstitial being associated with the core of the edged dislocation. The energy of the system decreases as this interstitial would partially annul the stress field of the dislocation or gives some relief to it. Therefore, when I apply external sheer stress, it has to pull the dislocation and that means I am applying external sheer force to cost plasticity which would imply in terms of these slip plane to move this dislocation of the slip plane.

This I have to do an additional work to move this dislocation away from this cortal atmosphere and the configuration of the dislocation with the interstitial carbon is a low energy configuration. Therefore, I need to apply additional force, additional sheer force to pull the dislocation out of this atmosphere of carbon and this is reflected in terms of the increased yield stress which you see in the stress strain diagram.

This is a nice schematic, in which you have a stress strain diagram in which you have the elastic region. You notice that you need to apply an additional stress till the dislocations can break free of the quartile atmosphere. Once it does so, than the ell stress drops and then of course, it oscillates till some more many of the other dislocations would do the same thing. This implies this whole yield point phenomena is related to the locking of the dislocation and locking I am using in a in the sense I told you of decreased energy state which is resulting from the association.

This resulting from the locking of the dislocation by the solute atmosphere. Therefore, the yield point phenomena, which is now a gross macroscopic phenomena seen in a normal uni actual tension test, is a product of this microscopic or atomic level segregation of carbon atoms at the core of the dislocations in a BCC iron crystal. Now, similar as I pointed out to the interstitials vacancies can also be attracted towards the compressive regions of an edges dislocation. This phenomena actually plays an important role in the climb of an edged dislocation.

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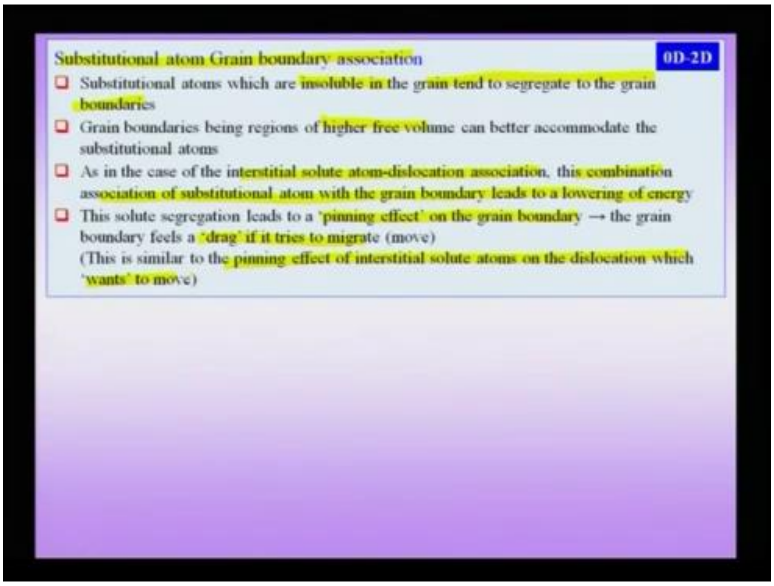

Substitutional atom Grain boundary association

0D-2D

- ☐ Substitutional atoms which are insoluble in the grain tend to segregate to the grain boundaries
- ☐ Grain boundaries being regions of higher free volume can better accommodate the substitutional atoms
- ☐ As in the case of the interstitial solute atom-dislocation association, this combination association of substitutional atom with the grain boundary leads to a lowering of energy
- ☐ This solute segregation leads to a 'pinning effect' on the grain boundary → the grain boundary feels a 'drag' if it tries to migrate (move)
  (This is similar to the pinning effect of interstitial solute atoms on the dislocation which 'wants' to move)

This would be very important when you are talking about high temperature loading of a material. So, this kind of a vacancy dislocation interaction can lead to what is called dislocation climb. Therefore, plays an important in the creep of materials. So, though this is looks like a very microscopic phenomena occurring at the atomic level, it has a gross macroscopic signature. Therefore, I cannot ignore defect association.

So, let us consider some more examples of the defect association. We can think of substitution atoms which are segregating to the grain boundary. Substitutional atoms which are insoluble in the grain or have a low solubility in the grain as you want to put it, tend to segregate to the grain boundaries. Now, because grain boundaries associated with a certain amount of higher free volume and can better accommodate these substitutional atoms, which are otherwise have a very low solubility in the grain.

As in the case of an interstitial solute atom dislocation association, this combination of a substitutional atom in the grain boundary leads to a lowering of energy. Of course, when I am talking about energy here I am actually talking about the gifts, free energy of the system. Now, this has important consequences. This segregation actually mimic the grain boundary very weak, this segregation may actually lead to a precipitation at the grain boundary. This segregation may lead what you might call hot shortness or cold shortness when I am doing a plastic deformation.

Therefore, the materials properties could actually be drastically affected by the presence of this segregation of this solute to the grain boundary region. Further, suppose I am talking about a phenomena, like creep or any other phenomena like grain growth wherein I need to talk about the mobility of the grain boundaries. This presence of the solute actually has a pining effect on the grain boundary motion.

Now, if the grain boundary wants to move the solute atom has to move along with it because that is the low energy configuration. In other words, if that grain boundary tries to break free of the solute atoms there is a drag on the dislocation as it tries to migrate it. This is similar to the pinning effect of interstitial solute atoms on the dislocation, when it wants to move. This segregation of solute atoms to grain boundaries can actually very drastic effects.

One very drastic example of this I would like to site because it is a very exciting and drastic example, happens to be the case of segregation of gallium to the grain boundaries of aluminium. Actually one can do a nice experiment, one can take a thin aluminium foil sheet small strip of it and hang it by a small weight.

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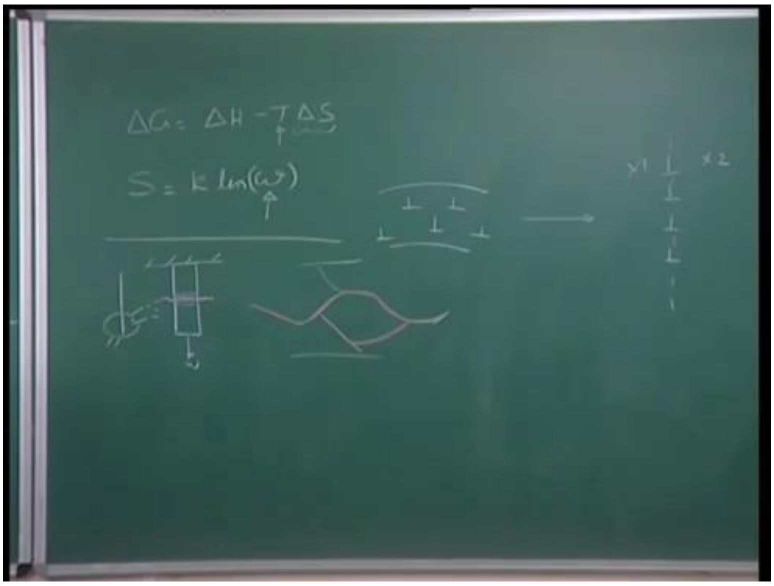

After doing so, you may you may want to edge away as small region of this to remove the oxide lie here in the aluminium foil. So, I am looking at this side if you look on edge on this would be a thin foil, this is a very thin foil. On this edge surface of course, I may want to heat this system by a for instance I had try on one of those things. So, that I give some hot air to the system to actually heat up and therefore, improve the kinetic.

So, there the kinetics of the process which I am going to do is going to be fast. Then I can drop a little bit of gallium on the edge of the surf or the pickle surface. Now, what happens when you put gallium onto this, impose gallium on this surface it that, suppose I am talking about now and the microscopic scale that this is my grain boundaries.

The gallium selectively defuses along the grain boundary because now it has got a very high diffusivity align the grain boundaries and a very poor solubility. When gallium segregation takes place at the grain boundary what can happen is that. So, this is of course, multilayer segregations I am showing here by red colour, then gallium being almost liquid like it the temperature we are talking here. The grain boundary de bonds and therefore, this material will fail by these 2 parts of the material actually separating out here. So, these 2 parts of the material will actually separate out.

So, this a very simple and nice experiment to do, but it had drastic consequences as you can see because of segregation of gallium which is taking place along the grain boundaries. Now, this is not we may think of as a very macro affect, but really micro affect along the grain boundaries.

Since, we have already talked a lot about this example of a defect association, I will briefly just summarise this example which we have dealt with in detail before that dislocations which are randomly present in a crystal can come together to form a low angle grain boundary as shown in this figure.

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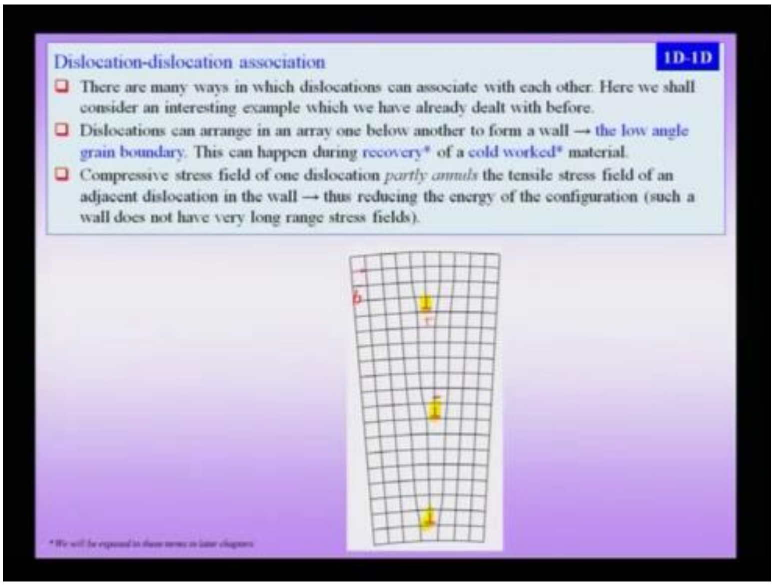

Dislocation-dislocation association

1D-1D

- There are many ways in which dislocations can associate with each other. Here we shall consider an interesting example which we have already dealt with before.
- Dislocations can arrange in an array one below another to form a wall → the low angle grain boundary. This can happen during recovery* of a cold worked* material.
- Compressive stress field of one dislocation *partly annuls* the tensile stress field of an adjacent dislocation in the wall → thus reducing the energy of the configuration (such a wall does not have very long range stress fields).

Which is this low angle grain boundary can be thought of as an array of dislocations and this array gives rise to a lowered energy state because the tensile region of this dislocation or let me. So, this is my tensile region of this dislocation partially and as a compressive region of this dislocation. Therefore, harden lower energies lower energy state. Such a low angle grain boundary does not have long range stress fields, unlike the case of an isolated edge dislocation. This is another interesting example, wherein I am talking about an association of a 1 D defect with a 2 D defect that means a dislocation as the example is with an interface.

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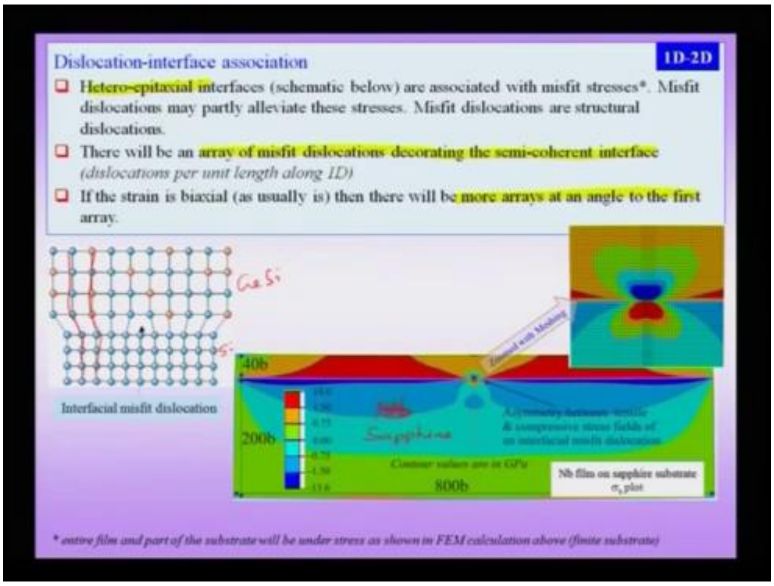

Dislocation-interface association

1D-2D

- ❑ Hetero-epitaxial interfaces (schematic below) are associated with misfit stresses*. Misfit dislocations may partly alleviate these stresses. Misfit dislocations are structural dislocations.
- ❑ There will be an array of misfit dislocations decorating the semi-coherent interface *(dislocations per unit length along 1D)*
- ❑ If the strain is biaxial (as usually is) then there will be more arrays at an angle to the first array.

** entire film and part of the substrate will be under stress as shown in FEM calculation above (finite substrate)*

The interface I am considering here is an epitextual interface between, for instance this is the in the example considered, this is my niobium substrate in which there is an epitextual layer which has been grown. When I mean epitextual layer it means that there is a one to one matching of atomic gross from the substrate to the film. Typically these are these epitextual films are grown in a very special manner by taking is like by molecular beam epitexture etcetera.

Now, this is also called the hetro epitextual interface because this sorry, this is a labelled wrongly, may I stand corrected. So, this is actually the niobium film which is on a sapphire substrate. So, the substrate and you can see as schematic of such a system on the left hand side. Now, typically in such systems what would happen when I grow the film a lot thick, then the misfit strait or the coherence stresses generated between the actual film and these substrate cannot hold the coherency.

You would actually observe misfit dislocation segments forming which or misfit dislocations forming which would lead to partial annulment of the coherency stresses. Now, this system can be thought of as an association of the hetro interface between the niobium and sapphire as this example is and a dislocation. Now, why do I need to think of it in that is because if I put a dislocation at any other position apart from the interface, the system will actually have a higher energy.

At the interface, it has typically unless of course, the model is difference between the substrate and the interface is a substrate and the film is too high which we are not considering here. Let us consider example where typically the modular of the 2 material are comparable. In that case you would note that the interface is the most stable position for the dislocation. It is localise to the interface and as we have pointed out before such a dislocation is actually a structural dislocation.

So, this is an example of an inter association of a 1 D defect with a 2 D defect. So, let me briefly summarise this once again. So, we have a substrate like sapphire in this case, a single crystalline substrate on which we epitextually grow a film and an amusing the word epitextual that means, there is an atomic matching or a lattice parameter which had very similar.

Therefore, the reason lattice pacing matching between the substrate and the film, but since they are not identical the lattice parameters or the relevant lens scale, there is some stresses which we may be call the misfit stresses or the epitextual stresses, but when the film grows thicker and thicker, the value of the stress becomes so much that it can no longer accommodate a completely coherent interface. That means an interface where atomic planes, if you see this is now a coherent atomically match plane.

This example itself can be thought of as G S i film on a silicon substrate. Now, it cannot maintain that kind of a coherency and at that stage, there is a formation of misfit dislocation segments. Of course, we are not going to the detail here, as to how this misfit segments form there are many mechanism by which they can form, but this interfacial misfit dislocation is localised to the interface and can be thought of as an association.

This whole system can be thought of as an association of at 1 DD defect with b a 2 D defect. Of course, there will be an array of such misfit dislocation decorating the semi coherent interface. With the word semi coherent implies there are misfit dislocations present. If I am talking about a film on a substrate, typically there will be a biaxial strain. Therefore, there will be more arrays at an angle to the first array of dislocations which you are seeing here, but the important energetic reason the whole process is that you can clearly see that you have a substrate which is typically compressive. A film which is tensile here and locally if you look around the dislocation, this leads to a partial stress relief.

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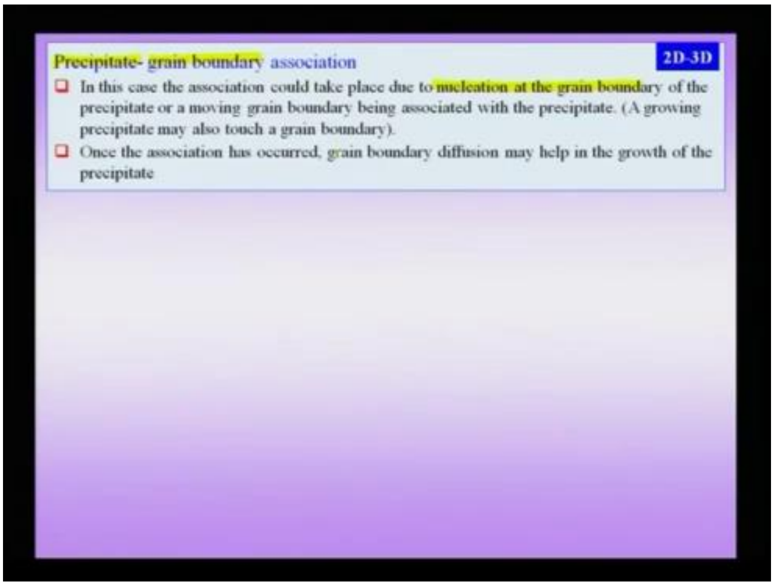

Precipitate- grain boundary association

2D-3D

- ☐ In this case the association could take place due to nucleation at the grain boundary of the precipitate or a moving grain boundary being associated with the precipitate. (A growing precipitate may also touch a grain boundary).
- ☐ Once the association has occurred, grain boundary diffusion may help in the growth of the precipitate

You can see that locally in fact the sign is reversed. The tensile region becomes compressive and this relaxation which the dislocation stress field gives to film stress field of course, the film stress field also interacts the dislocation stress fielding. This energetic relaxation is what is making the system feasible energetically. This would be nice configuration, which would evolve on growth of a film.

Now, let us talk about one last example of defect association. This is the example of a 2 D defect being associated with a 3 D defect. The 2 D defect we are talking about is a grain boundary and its association is really affect like a precipitate. Typically this takes place by the nucleation of a precipitate at the grain boundary. Now, the reason why such a nucleation takes place at a grain boundary, is grain boundary is a high energy region.

Therefore, serves as what you might call a preferred heterogeneous nucleation site for the formation of a precipitate. Now, once the precipitate has formed along the grain boundary, grain boundary diffusion itself can lead to the growth of this precipitate. Therefore, it actually helps in the process of this precipitate growing.

Further, if you have a precipitate at the grain boundary, it can have an effect which is similar to the effect of a solute pinning a grain boundary that means a precipitate can pin a grain boundary and can actually retard its migrations. So, I am talking about grain growth, the presence of the precipitate at the grain boundary can actually retard the migration.

Therefore, you can see that the properties at the microscopic level, which definitely reflex in them of the properties of the macroscopic level is altered severely when defect association takes place. Therefore, it is not only important for me to understand isolated defects, but their association in the scheme of the microscopic place and also the scheme of the macroscopic scale.