Defects in Materials
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Lecture - 33
Interfaces – 01

Welcome you all to this course and defections in material. Today we will have discussion on interfaces in material, even if we consider any material as perfect, even if it is a single crystal one defect which cannot be avoided is the surface. Why do we consider surface as a defect because at the surface, if you look at that material at any material that is the surface is a discontinuity that is the if you look at a atoms inside the sample, where the number of identical atom positions which are available if you look at the surface some bonds are broken. That means, that when a surface is created a material without a surface and with the surface there is some energy which is required to generate the surface because some bonds have to be broken. So, this is an excess energy which is required correct.

And this energy which is required are the energy which is available to the surface or the surface energy is called as the surface energy that is per unit area, this is what we uses gamma; the surface energy; that means, there if you have a sample that sample could be made vapor to solid or liquid to solid or it could be this type of interfaces of could be between solid and solid as well. Most of the materials which we use; the solid to solid interfaces which is very important that will come to later, but essentially does not matter what is the method by which we are making a solid sample.

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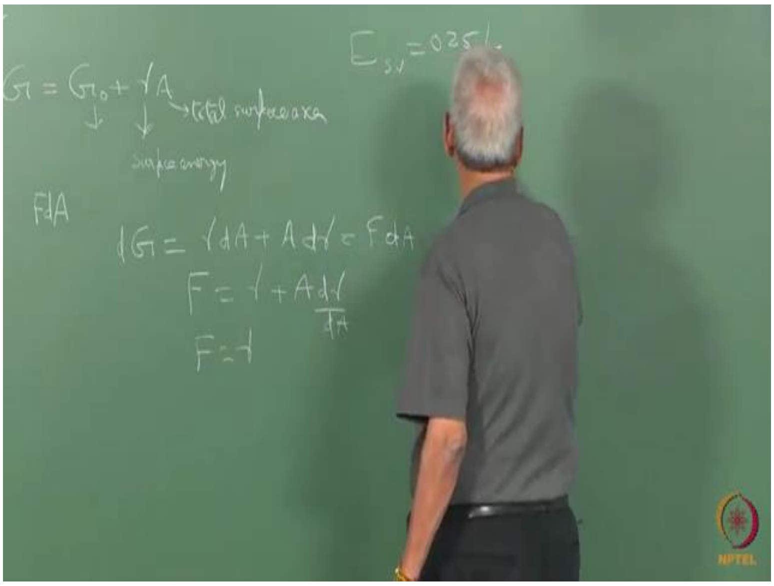

An interface is invariably created even in a single crystal. So, that interface will be there. So, what will be the free energy of that sample if we consider? That free energy will be the total free energy depends upon G 0 plus gamma into A; A is the total surface area gamma is there surface energy; G is the bulk chemical free energy if you look at this expression.

How can we calculate this surface energy? If there any experimental way in which it could be measured one can think of a way in which a thought experiment which we can do, it is you take a wire of a sample you apply we some load try to pull it then when we do there is going to be an increase in area which is going to take place. So, the total energy which we are putting into that sample is F into suppose, d A is the F into d A becomes the total energy increase. If this energy is just sufficient, assume that to balance the new surface which is being created it is not doing anything else rather than just to balance that surface energy. So, to create the surface some require some free energy. So, how we can calculate it if take this differentiate, this will be equal to gamma into d A, A into d gamma. This is the change in it is just balancing this then we can write this to be equal to F into d A correct or you can write F can be equal to gamma plus A into d gamma by d A, this is how this expression.

So, this is nothing, but the force and gamma is the surface energy this is the rate at which the surface energy changes multiplied by the area this although force will be varying.

Suppose we assume that it is from the liquid to in a liquid if we consider it then what is going to happen is it may be liquid the surface energy is independent of the area correct. So, this term will turn out to be 0. So, this will become F will be equal to gamma then in this case we can consider this as a surface tension, the force will it is a surface tension and surface energy the same can be used. But in the case of solid samples we cannot assume that they are the same because when we take a sample the liquid film and try to increase its area quickly the atom molecules rearranged themselves. So, that the surface created in a material solid material if you try to pull it and the atoms are to rearranged on the surface it may be taking a finite time.

So, if the experiment is being done is very slow that time which it takes experiment is done in a fasting, but the time it takes for rearrangement to be in such cases the surface tension of the surface force need not be the same as the surface energy is it clear that is because this term is not going to be equal to 0 because there are viscous forces are going to be there is highly viscous the sample is. If you wanted to find out the surface energy a fact suppose A; a specific surface what is the way in which theoretically we can try to find out in a very simple way is essentially see how many bonds have to be broken to generate that surface correct.

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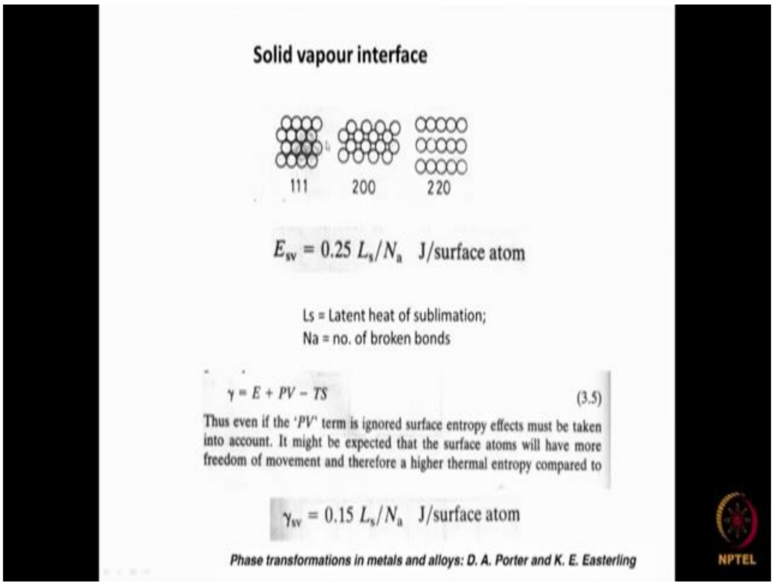

Solid vapour interface

$$E_{sv} = 0.25\, L_s/N_a \quad \text{J/surface atom}$$

Ls = Latent heat of sublimation;
Na = no. of broken bonds

$$\gamma = E + PV - TS \qquad (3.5)$$

Thus even if the '*PV*' term is ignored surface entropy effects must be taken into account. It might be expected that the surface atoms will have more freedom of movement and therefore a higher thermal entropy compared to

$$\gamma_{sv} = 0.15\, L_s/N_a \quad \text{J/surface atom}$$

Phase transformations in metals and alloys: D. A. Porter and K. E. Easterling

Here in this particular case, in the fcc like there are 3 types of surfaces which are being considered that is with the low index plane 111, 100 or 110 type of surfaces 111 in fcc is the close packed surface. In this case if an atom is sitting at for this atom if we consider it the nearest neighbors which should have been there if another layer is there on top of it would have been 1, 2, 3, atom positions it would have occupied.

So, these 3 types of bonds have been broken compared to 12 coordination which is going to be there correct with respect to an atom if you contain a close packed direction that are 12 are there out of which 3 are getting broken.

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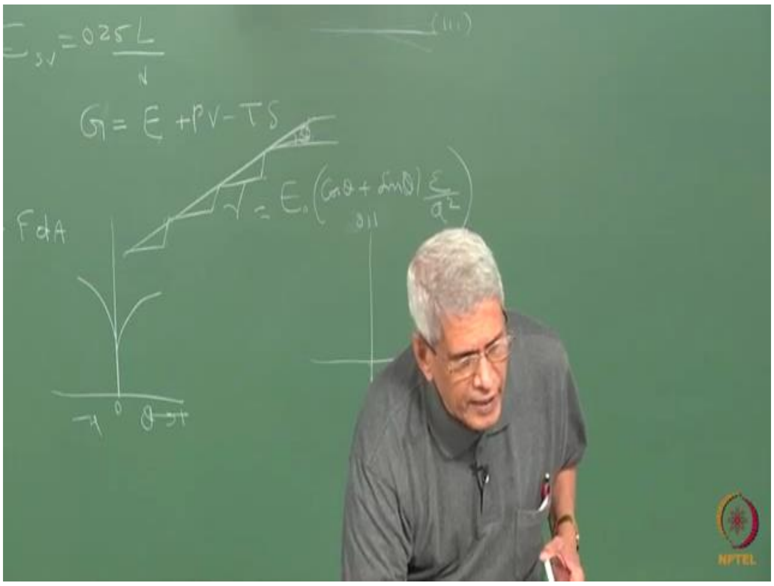

So, if you know what is the bond energy, but each type of a bond then we can find, what is going to be the surface energy correct that is what essentially is given by this formula this is E, this is solid to vapor N where N is the number of a bonds which are broken bonds so; that means, that depending upon the L is the latent heat of sublimation for the atom to sublime from the surface which we assume it to be a constant for the material. So, that needs that depending upon the number of bonds to be broken which is going to change depending upon the nature of the surface the surface energy will change. Close packed plane will have the lower surface energy, is this clear? Then this energy which we talk about is that surface energy this surface energy is not the same at the free energy of the surface the free energy will be; we write plus P V minus T S, correct we solved writing.

So, if P V is constant then essentially E is the suffering T S. So, T S is where that entropy term comes into the picture in the case of a surplus the entropy term because lots of bonds are getting broken atoms will be moved from their positions. So, the contribution of entropy is going to be high and that is going to change from surface to surface and in addition to it lot of defects could be produced on the surface. So, when we try to calculate what is going to be there free energy of the surface that can vary from surface to surface here in this table what is being given is the surface energy which has been calculated close to melting point for different type of samples and the cases which we have considered.

So, far what we have done we have looked that close pack planes are low index planes which we have considered it and when we look at surfaces 2 things which we have to consider one not only the energy of the surface and another is the structure of the surface the structure part of it we will come later. But now we are essentially trying to concentrate on the energy of the surface suppose we wanted to find out what is going to be the surface energy it is a high index plane that is we are so far we have considered with respect to 111 which you are considered these type of surfaces we looked at it, but we can look at any surface which we can take any cut section can be a surface it could be a high index plane.

So, how do you find out the surface energy from values which are known for low index plane the method which is adopted this is what is called as a broken bond model where you look at this surface.

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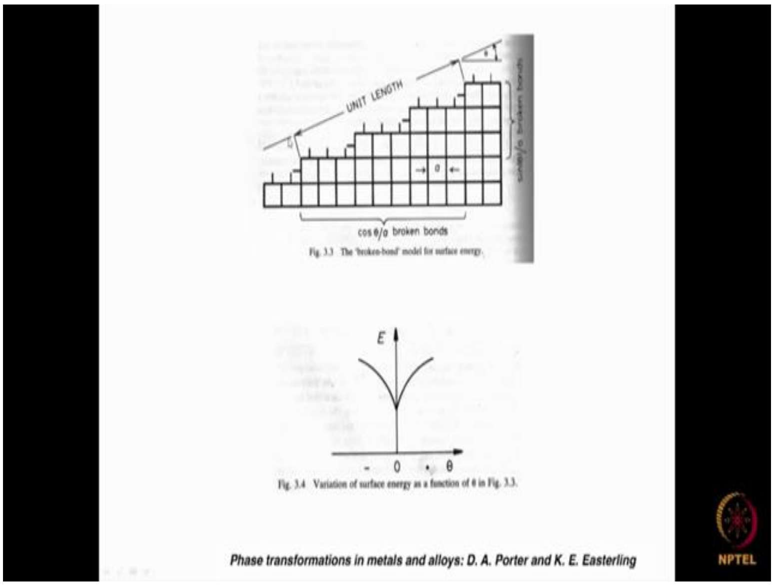

Fig. 3.3 The 'broken-bond' model for surface energy.

Fig. 3.4 Variation of surface energy as a function of θ in Fig. 3.3.

Phase transformations in metals and alloys: D. A. Porter and K. E. Easterling

Here this is the simple cubes which are joined together the bonds are broken at different places what we are considering it is essentially any surface which we can consider it a random surface could be considered as creating some steps on the sample surface right that is supposed the surface which is going to be there low index one is the one which has got the minimum free energy. So, that is the one we should try to have.

So, which steps if we try to create surface like this the average if you look at each of the surface this will be a low index only some step is being created. That means, that closer to a step some bond breaking will be the number of bonds are broken will be slightly different, using this number of bonds which are broken we can try to calculate what is going to be the surface energy in terms of the close packed plane, that in terms of with respect to this surface what is the angle theta which it does just a minute this is equal to the surface energy of any surface which we can consider it this is with respect to a low index plane. So, depending upon the angle which makes the step which is created this plus this is a low index this is essentially a simple geometry with which it can be calculated.

So, epsilon is the number of bonds which are there a is the lattice parameter separation if you do that then what is going to happen if that with respect to the surface, we consider it like this which is essentially a close packed surface assume that it is a 111 in fcc then if you take any surface which makes an angle inclined with respect to this surface the energy as a function of theta if we consider it has to increase whether the theta is positive or negative that is what essentially is given their theta. This is positive side and this is negative side this is how the energy is going to change. So, with a minimum which is they are corresponding to where the theta is 0; that means, that with respect to the low index plane with respective fcc 11 is the closest pack plane and then we have 20 100 plane 220 planes are also going to be there they will have energy which is slightly higher; that means, that when we go away from close packed plane the energy of the surface is going to increase.

So, if we try to plot with respect to an origin if we choose or it could be a 2 dimensional or it could be a 3 dimensional figure also if you consider as a function of theta with respect to suppose we have 100 could be here, here it could be a 110 type of a plane, 111 may come in between this is we are considered 2 dimensional figure and this will be a; the purple normality, it is going to be a 110 type of a plane this will be essentially 111, this is 011, this plane could the direction could be 011 bar. This is the one with respect to which we are looking at it then what is going to happen if that we will be getting a plot which we called as a gamma plot gamma plot is nothing, but trying to find out various surfaces if a material can have what will be the how will be the energy be changing the vector from origin to the surface that is from here to here; any direction if you take it that gives the energy the minimum of the energy occurs along some close packed directions, correct.

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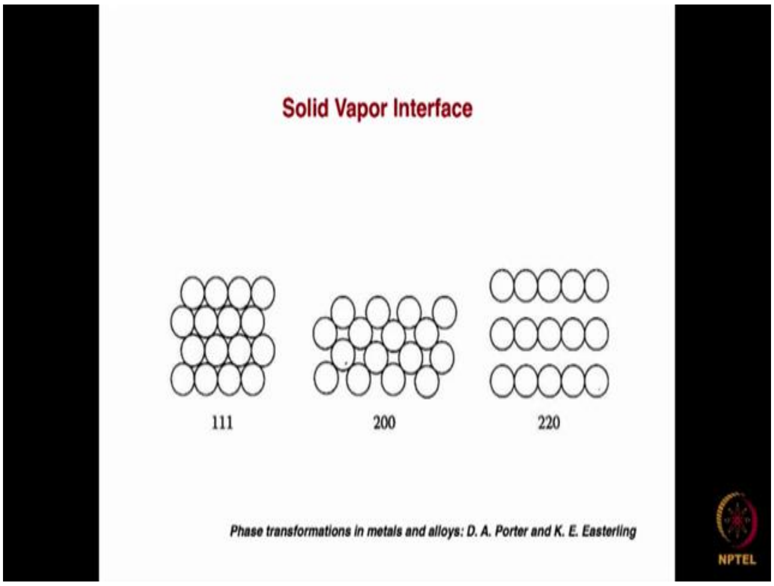

Solid Vapor Interface

Phase transformations in metals and alloys: D. A. Porter and K. E. Easterling

So, this is how a gamma plot looks at it; that means that on different directions we will have different (Refer Time: 18:52). From this surface we can get some lot of information about the morphology which a material can have.

Suppose we assume that a crystal is being grown from the melt it takes some depending upon the surface energy which is available that is going to control the rate at which the surface will also grow, with respect to that if you try to take it we get some faceted surface right. The faceted surface can always occur suppose we take a lot of a material take it to a or a ball of a sample, take very close to a melting point and keep it for a long time the atom should rearranged on the surface and it given shape faceted shape we should take or if a sample, if you take it there is a void is there quite often whenever voids are there in the sample especially it has been seen in radiation damage in the samples are irradiated lot of vacancy which produce the agglomerate together and form of void generally the void assumes a faceted shape. Whereas, if it is a gas which is they are inside that applies a uniform pressure it never takes a faceted shape it takes as spherical shape this is used as one of the indication to tell that (Refer Time: 20:27); that means, that internally now, it tries to take a shape void. So, that the surface energies total surface energy is minimum correct, this is what them.

This we can do it using what is called as a wolf plane that is if we draw a vector from here to this surface draw a plane normal to this vector that is the one surface which the material can occur that represents the surface and this point represents the energy corresponds to it because here the coordinates if you see these are all the directions which are crystallographic directions which are chosen correct. Any plane normal to this vector will give that is will give that plane. So, if we; to this vector, if you draw a plane normal a perpendicular to it that will represent the plane 110 plane that is essentially what it is being shown.

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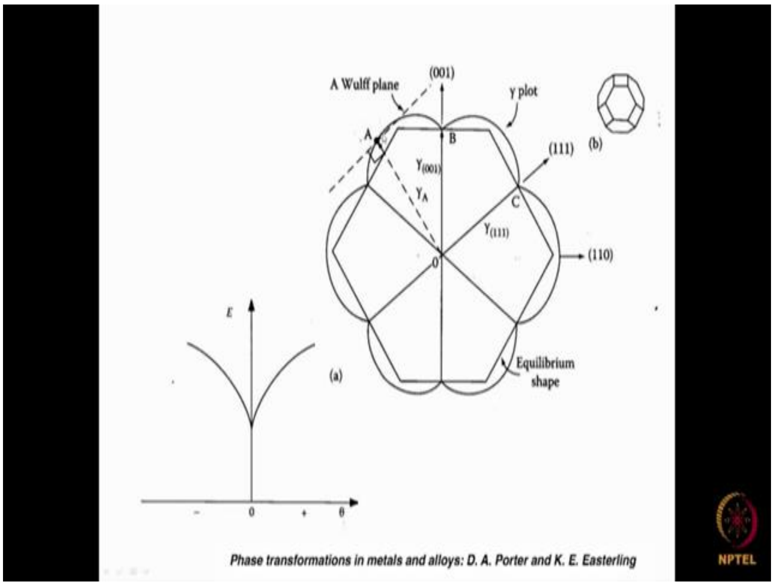

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So, if we take the regions which correspond to this minimum that locus these are all the and if we try to join all of them together the surface which it includes that surface is the one which it will choose to form the crystal when it forms the crystal this is the morphology it will it will adopt. Essentially what we can do it is that from here there are so many points are there every point I can take and find out which will be the normal to this vector that gives the plane which it is there when you take inclusive of all this one the one which joints together, the minimum if you say that with respect to area this is the one which it would will be giving raise to others should be outside of it. That means, that if you know the surface energy are the minimum in surface energy which is occurring and different planes the morphology which the crystal can have is going to change that will be determined by the relative energy difference between the surfaces.

Here this is a specific case for an fcc which is being considered right. For all the samples we are going to get a surface of similar type only this is going to give the equilibrium shape if a void which forms this should have this type of a shape this is the 3 dimensional one that is essentially the surfaces which it is has got 100 as well as 111 type of surfaces which are there correct. The normal, if you see this is corresponding to 111 plane, this is 001 plane and what is going to be the surface area which it will come? The ratio between the surface area if we take it of the crystal which has formed, it is equal to the ratio between the surface energies for those 2 planes.

Before you come what is the consequence of this one of the consequence is if a crystal forms an fcc crystal, it can have 100 surface and 111 surface as with which it can form. If you take a polycrystalline material and which has been heavily deformed we anneal it at high temperatures it tries to form a grain, what is the shape the grain can have, this is the type of a shape the grain can observes him because it forms with surfaces grain boundaries which are something equivalent to similar to surfaces with which it forms. Ultimate shape which it can have will be of this type with flat surfaces, this will come to later that is why another way in which we can consider it see if we try to join grains of these shapes along surfaces we will be having a polycrystalline material.

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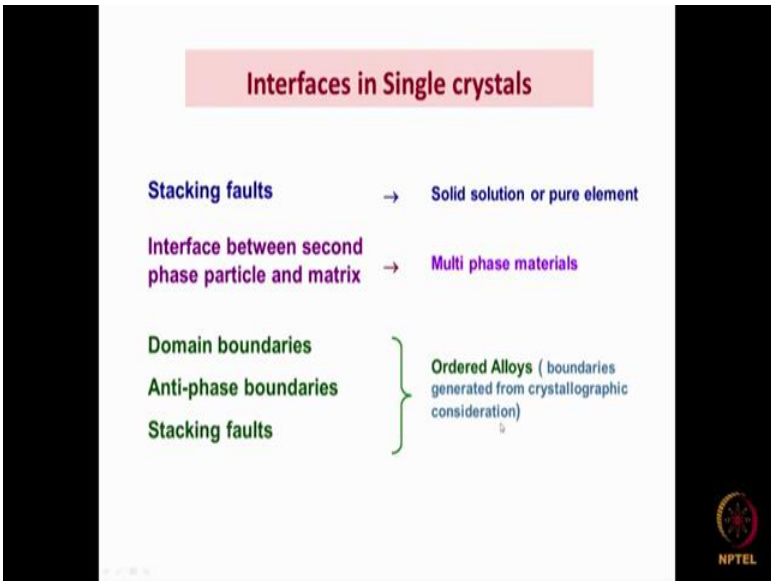

Interfaces in Single crystals

Stacking faults → Solid solution or pure element

Interface between second phase particle and matrix → Multi phase materials

Domain boundaries
Anti-phase boundaries
Stacking faults
} Ordered Alloys (boundaries generated from crystallographic consideration)

Other is; so, we have so far we have talked about the type of surfaces this is with respect to energy which we have considered what is the equilibrium shape when a crystal is grown from a melt or it is from a vapor if you are depositing and trying to form what is the type of surfaces which the grains are the single crystal which can have. And this we are considering consider on the basis of a broken bond model this is called as that is the surface energies essentially decided by how many bonds have to be broken correct.

One important consequence which happens is there if we look here, we have considered the this is all continuously increasing or coming to a 0, another one is it has to be the same way, it is possible that there are some regions are some other direction for which maybe you assume this to be in this particular direction the interface is such that the number of grounds to be broken is less compared to other regions there could be small cusps could be occurring at different points correct. That means, that whenever we have different types of interfaces which form grain boundary is formed as a function of angle theta if you try to calculate miss orientation, depending upon the type of nature of the boundaries which we will come to later we will address it in the next class that there could be some minimum in energies which could be seen that comes from directly from this gamma plot.

This gamma plot is one important one to understand not only the equilibrium shapes it will take how the energy of the surfaces are different surfaces are changing that information also we get it. Before we go further let us look at what all types of interfaces which we can have in a material suppose we take a single crystal of a material one interface which it is always going to have this surface. In addition to it suppose the material have at low stacking fault energy stacking faults could be produced in the material and the stacking fault to create the stacking fault.

Some energy is required the surface energy will be there that is because the fault itself can be considered as nuclei of another crystal; that means, another crystal is formed within this. So, on interface is created. So, that interface energy comes into the picture which we call it as stacking fault energy, correct and quite often the material need not be a single element not a single element, it is possible that they are alloys in alloys also the alloy in addition their fault energy reduces in addition to it in many alloys at different temperature the concentration of the solute that are the super saturation of the solute is there some pressures. So, precipitation occurs whenever a precipitate forms there is an interface between the precipitate and the matrix and this interface also depending upon the type of a interfaces which we look consider between the second phase that is suppose a precipitate which forms like this.

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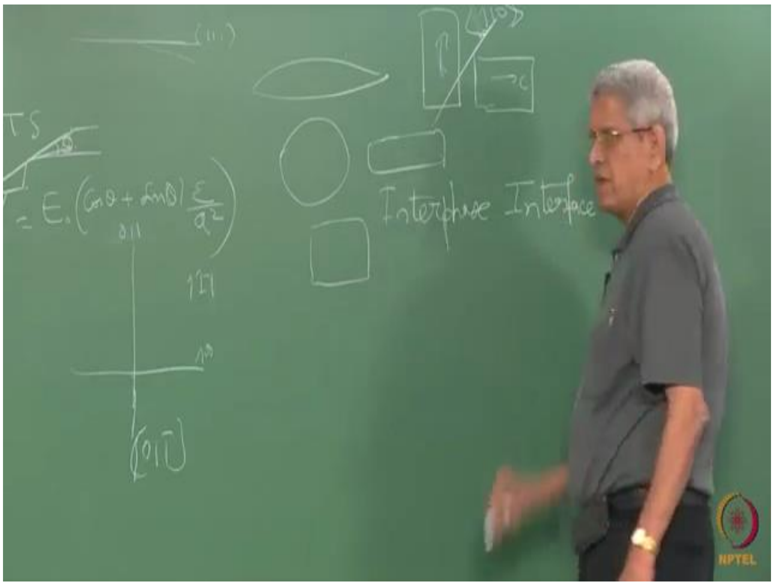

It can have with respect to this interface that can have some energy it can be a spherical one that is one, it could be a cuboidal shape it could be a plate shape then there are 2 types of interfaces are more than type of interface an each interface will have different interfacial energy just like what you as now in the broken one model we have looked at it. Because of this equilibrium shape what it will take is decided by the total free energy minimization that is what it is going to take place.

So, first an interface is created then what is the role of this interface there are many roles which this a interface play as far as the mechanical properties are concerned this interface can act as an obstacle to a moment of dislocations correct that is one. Then when we consider ordered alloys we said that ordered alloys especially when the crystal structure is non cubic there are different variants of the ordered phase can form in a single crystal of a material and when they come and join together the nuclei and interface will be created between them these are called as domain boundaries.

And in addition, if there are some anti phase domain boundaries are also created these 2 types that is one is called as a translational defect another is called as a rotational defect. The domain boundaries are called as rotational defects because if we consider a tetragonal lattice if one and another nuclei form these 2 when they form together the interface between them is this is between 110, type it can be here this is C axis in this is in this direction C axis is in this direction these has 2 types of domain. So, this boundary is called as a domain boundary. Another thing which we considered was that one variant is there another when there is a slight translational defect is there this which called as the anti phase boundaries both the types of defect are present these defects also can act as obstacle to the moment of dislocations.

So, what is the strength of these obstacles we will decide how much it contributes to hardening in the material? So, understanding these structures the nature of the difference these obstacles interfaces are very important, this is as for as single crystals are concerned. So, single crystals are concerned when surface is going to be there in addition to a surface the type of defects which can be produced in the material.

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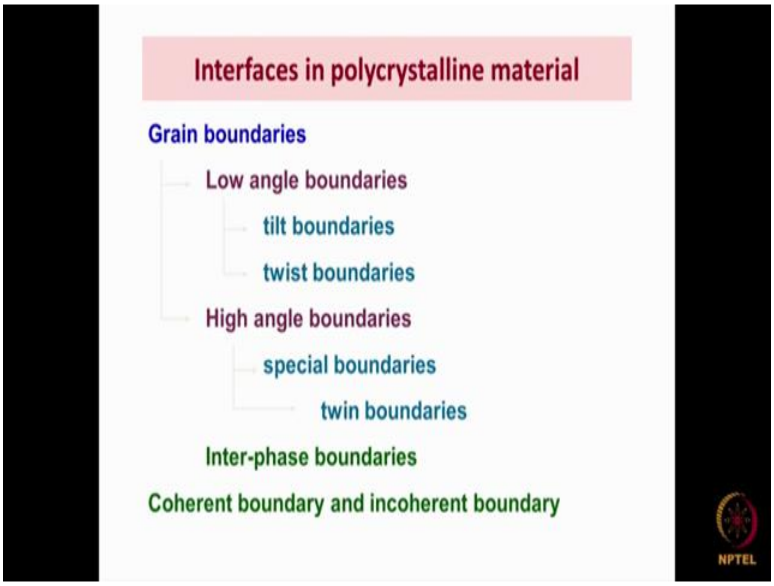

Interfaces in polycrystalline material

Grain boundaries

- Low angle boundaries
  - tilt boundaries
  - twist boundaries
- High angle boundaries
  - special boundaries
    - twin boundaries

Inter-phase boundaries

Coherent boundary and incoherent boundary

Suppose we take a polycrystalline material, in a polycrystalline material each grain is like a single crystal, but oriented differently, the interface between them is the grain boundary. These interfaces there are a lot of classifications are there if the misorientation between these grains are small we call them as low angle boundaries, if the misorientations are high we call them as high angle boundaries.

Even on this low angle boundaries, depending upon the type of misorientation the classification which we use there are still boundaries are there as twist boundaries similarly on this high angle boundaries which we consider some of these boundaries could be considered as a type of special boundaries what are special boundaries suppose that boundary mismatch when the boundary come and meet even at high angle misorientation, it should be of a particular type of an interface which they create that it is like a low index plane if it comes between them. Then it can have very small that is a cusp in the minimum energy the energy could occur these are called as special boundaries this is what the CSR lambda type of boundaries which we call which we will come to later what is CSR lambda and all twin boundary is one simple examples.

If you take fcc twins from one to the other the angle between these boundaries is the misorientation between the unit cells it is going to be very high around close to 50 or that order, but the boundary where they meet it is 111 plane is an undistorted plane that is a perfect matching is there. So, if you look at the energy of that boundary, it is going to be extremely low understand. So, these are all types of special boundaries which we can have.

Then suppose it is a 2 phase mixture of a which forms the polycrystalline material then between the 2 different phases there could be an interface between them these are called as a inter phase interface, phase interface correct this is also another type of boundary. All these boundaries are special boundaries which are a going to act as obstacles to dislocation motion and understanding the nature of this boundaries is very important. These boundaries could be some boundaries could be coherent boundaries some boundaries could be incoherent boundaries this will talk about what all coherent and what are incoherent boundaries. Then another way at which these boundaries are considered is that like you look at the twin boundaries twin boundaries is one in an fcc 111 plane is the twin boundary plane there is no mismatch.

It is a perfect matching if there is a slight mismatch if you wanted to introduce. We can introduce a mismatch by introducing some dislocations into these boundaries any boundary could be considered as made up of introducing dislocations that is one model of a boundaries is a dislocation model. Depending upon the number of dislocations which we introduced to into the boundary, the misorientations can change that is one way to look at it. Another way to look at it what is the structure of the boundary itself in they come and meet it as one aspect which we can try to look at it. Then in both these cases whether we introduce dislocations or in the energy of the boundary is going to change how the energy of the boundary changes as a function of misorientation, that is you take one grain or a single crystal of a particular orientation you assume that the another grain which is forming has got a some misorientation you just go on changing the misorientation between both of them and try to find out how the energy is going to change of the boundary energy which will be changing that is one way to look at these boundaries.

Then what is the way in which the energy is going to change all these aspects we will look at it in the next class. Today what I had essentially try to do is give an introduction about the energy of the boundaries and about the different types of boundaries or interfaces which we can have in solid samples. As I have mentioned this is very much necessary to know about the nature of the boundaries because that is what is going to determine and also the strength of the boundary is important because that is control in a strengthening mechanisms in the material. What we will do is we will stop it here, in the next class we will look at the various types of boundary.