Structure of Materials

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Lecture - 37
Phase Transformations

We move on to the next chapter, which is on phase transformations in the truer sense this itself is an entire course by itself.

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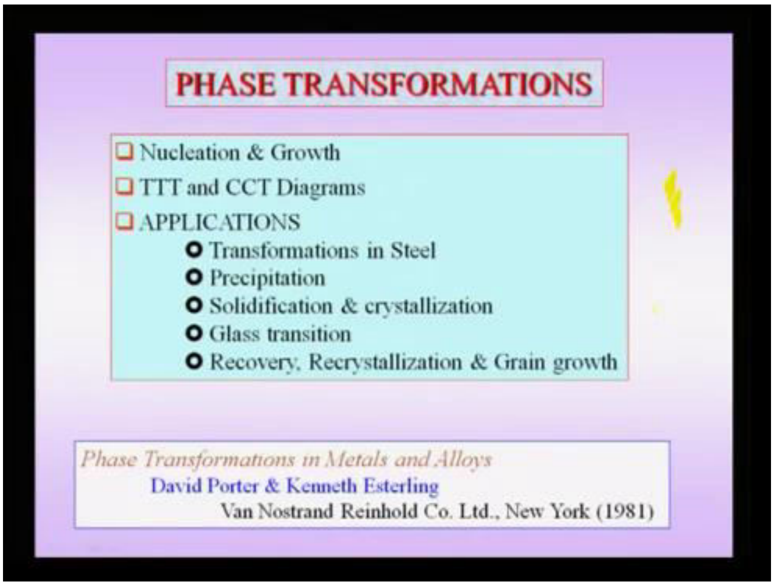

PHASE TRANSFORMATIONS

- ☐ Nucleation & Growth
- ☐ TTT and CCT Diagrams
- ☐ APPLICATIONS
  - ○ Transformations in Steel
  - ○ Precipitation
  - ○ Solidification & crystallization
  - ○ Glass transition
  - ○ Recovery, Recrystallization & Grain growth

Phase Transformations in Metals and Alloys
David Porter & Kenneth Esterling
Van Nostrand Reinhold Co. Ltd., New York (1981)

But, here we will consider some of the salient and important features of phase transformations, especially we will talk about the phenomena of nucleation and growth. We will talk about two kinds of diagrams, which are the TTT and CCT diagrams which are invaluable tools for a material scientist, then we will talk about certain applications of phase transformations, in transformation of steal and certain other phenomenon. The book by Porter and Esterling is a standard text for this subject and has served, the materials community for quite some time as an important resource for phase transformations.

Before, we start this chapter, let us do a very simple experiment, an experiment which you would have seen many times before, but let us try to understand it from a different perspective, from the perspective of phase transformations. So, do the simple experiment I have here with me an aerated drink here ((Refer Time: 01:29)) and so I have a glass here and what I am trying to do is of course, I am trying to take this aerated drink and [FL].

So, and I just fill this aerated drink into this bottle, when I open the bottle there was some sound and the gas escaped, a little bit of the gas. But, now what I am doing, I am taking this aerated drink and let me assume that I am poring this into the glass, I observe something, that slowly bubbles evolve you can see, that if you observe the glass closely slowly bubbles are evolving. And the gas which was dissolved in this aerated drink is slowly evolving out, this gas was originally put into this aerated drink at high pressures.

And now when this liquid which has dissolved gas in it, is exposed to atmospheric pressure which is lower than the pressure at which, the gas was incorporated and this gas is of course, carbon dioxide. Now, I see that the bubbles are slowly evolving, further what I will try to do is that and if somebody observes carefully, some of these bubbles tend to form on the walls of the glass, they do not form uniformly all over, but they preferentially form along the walls of the glass.

A similar phenomena you would have noticed, when you say for instance pour, wine or bear into a glass, where in you would observe that these bubbles tend to form at some points preferentially, especially at the liquid glass interface. Now, I have salt here with me and suppose I take a pinch of this common salt and put it into this liquid, you can observe what happens, you see there is vigorous bubbling taking place. And if I had this you can see even, now that this bubbling going on and if I had like this glass full of this liquid.

In fact, this liquid will tend to pour over, if I put this salt into it, so you can clearly see that my putting salt into it, has somehow invigorated the process of the evolution of bubbles, in other words by putting salt I am able to evolve more gas that means, now this liquid will tend to come down to its equilibrium concentration of the dissolved gas. So, this is an important simple, but important experiment in understanding, the phenomenon of phase transformations.

So, number 1 we observe that the gas was put into this aerated drink at a higher pressure, when I brought this to atmospheric pressure, this liquid by pouring it into a glass here at one instant all the gas does not escape, this is surprising. Because, at atmospheric pressure the solubility of carbon dioxide in this liquid is much lower therefore, the excess carbon dioxide should evolve and come out. But, that does not happen it starts to happen at a slow rate, typically by bubbles nucleating along the walls of the glass in at the liquid glass interface.

But, we are putting salt which I did before you can see that, suddenly this process is invigorated and you have again you can see that the process, if start the more bubbles tend to form, when I put pour of salt into it and gas is evolved at a brisker phase. And therefore, the solution tends towards its equilibrium concentration of carbon dioxide at atmospheric pressure and that is an important point to note.

So, I have an experiment in which I have an high pressure gas, put into a liquid and then I have an under pressurization, when I open this liquid and put it into atmospheric pressure and further I see that, this bubble evolution can be enhanced by putting a medium like salt. So, let us return to the main chapter and we will keep this experiment in mind and we will try to return to it, at an appropriate point to understand the phenomena involved as to why, that the gas does not escape immediately on opening the all the gas does not escape, on in opening the container and it slowly evolves with time and how does this salt help in this process of gas evolution.

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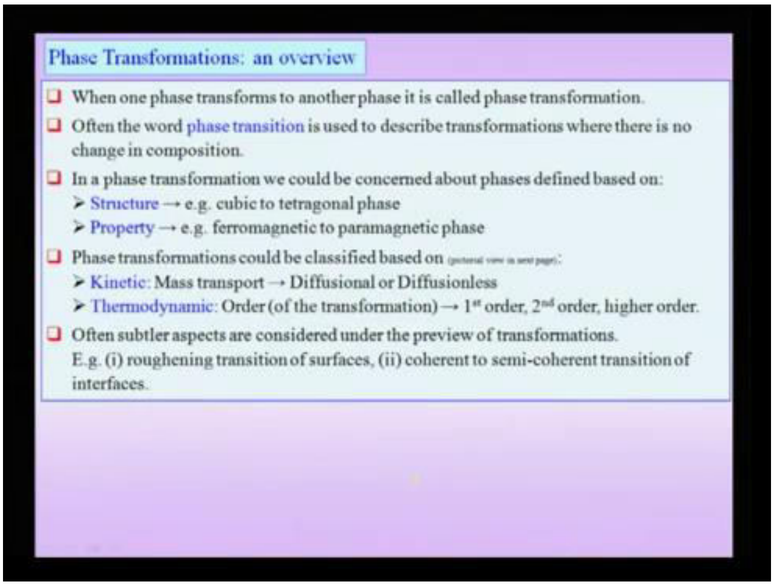

Phase Transformations: an overview

- When one phase transforms to another phase it is called phase transformation.
- Often the word phase transition is used to describe transformations where there is no change in composition.
- In a phase transformation we could be concerned about phases defined based on:
  - Structure → e.g. cubic to tetragonal phase
  - Property → e.g. ferromagnetic to paramagnetic phase
- Phase transformations could be classified based on (pictorial view in next page):
  - Kinetic: Mass transport → Diffusional or Diffusionless
  - Thermodynamic: Order (of the transformation) → 1st order, 2nd order, higher order.
- Often subtler aspects are considered under the preview of transformations. E.g. (i) roughening transition of surfaces, (ii) coherent to semi-coherent transition of interfaces.

So, let us start with a overview of phase transformations, when one phase transforms to the other we call it an phase transformation, often the phase transformation is used to describe transformations, where in there is no change in composition. And we will take up a few examples of these also in the coming slides that means, phase transformation is a super set, phase transition is a subset of these phase transformations, where in there is no change in the composition and one phase transforms to the other.

For examples suppose I have a paramagnetic phase of or ferromagnetic phase of iron and I heat this iron, it turns into a paramagnetic phase and in this process there is no change in the composition. Suppose I am talking about a liquid, a pure iron in this molten form and I cool this, this will transform into a solid iron, typically a polycrystalline iron and this does not involve any change in compositions. So, such kind of phase transformations, are also referred to as phase transitions.

And we have already noted, that when we talking about phases, the phases can be defined either based on the geometry or a physical property. And similarly the phase transformation could be about based on the structure in which, case for example, I have a cubic to tetragonal phase transformation or it could be based on a property like the 1 I just considered, which is ferromagnetic to paramagnetic phase in other words a broad classification of phase transformations could be based on, if the phase transformation involves as change in structure does not involve a change in property.

And of course, I could always have a combination of both that means, I could have a transformation in which I have a change in the property that means, I have a change in the property and a change in the structure like for instance, in tin the white form of tin and the gray form of tin, not only a structure will be different. But, their bonding itself is different and therefore, the property changes, when I have this transformation.

And further, we could have other classifications of phase transformations and this, could be based on kinetic aspects or it could be based on thermo dynamic aspects. In this chapter of course, we will only consider a brief overview of some of these aspects and we will leave the reader to more advance courses, on phase transformations to well deeper into some of these concepts based on kinetic aspects, which essentially means I am talking about mass transport, phase transports can be called diffusional or diffusion less transformations.

Our essential focus on in this chapter will be on diffusional transformations, though we will consider a little bit of diffusion less transformations as well. Based on thermodynamic aspects, we can classify phase transformations using a term called the order of a transformation. And we can classify a phase transformations as first order, second order or higher order transformations.

And often even subtler aspects of transformations come under the preview of phase transformations, though strictly speaking these are not phase transformation. But, they are transformations of a subtler kind like for instance, we can talk about roughening transition of surfaces, coherent to semi-coherent transition of interfaces etcetera, like suppose I take a aluminum copper system, which we will consider later in this chapter.

And I start heating this system, I first of all I take it to high temperatures solutionize that means, all the copper is form present in the form of an solid solution in aluminum, then I quench this solid solution to retain, a solid solution a super saturated solid solution at room temperature. Then, I slowly heat it to a lower temperature then I would see that, initially I will form coherent precipitate, which on growth will become semi coherent and then finally, they will become incoherent.

These kind of interface chain characteristics, can also be brought into the preview of transformations, though that is of a subtler kind therefore, to review this slide you have a broad subject of phase transformations. And of course, I will make a comment here that we will go to even a super set of this of phase transformations and that will be in one of the coming slides.

And a subset of these phase transformation is something known as phase transitions, where there is no change in composition involved. I could be defining a phase transformation based on a structure like cubic to tetragonal phase, a property like a ferroelectric to a Para electric phase or a combination of these, I could classify my phase transformations based on kinetic aspects or thermodynamic aspects.

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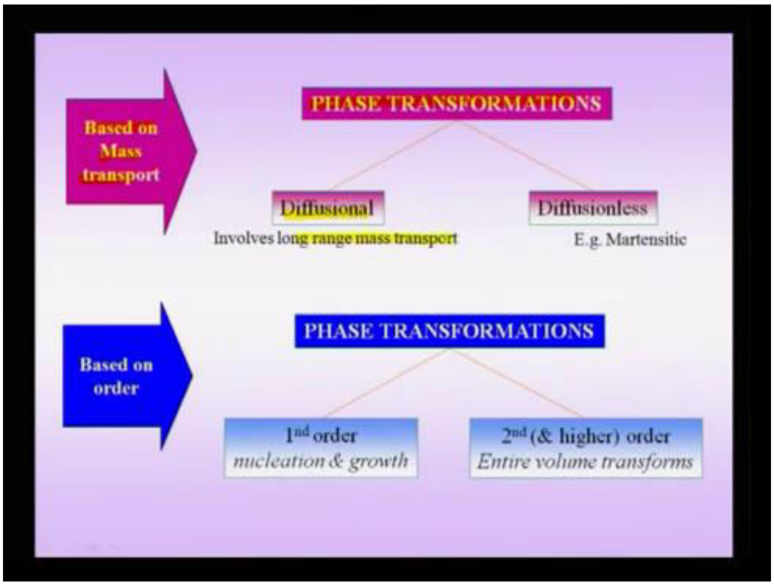

Based on Mass transport

PHASE TRANSFORMATIONS

Diffusional

Involves long range mass transport

Diffusionless

E.g. Martensitic

Based on order

PHASE TRANSFORMATIONS

1st order
nucleation & growth

2nd (& higher) order
Entire volume transforms

So, this slide brings out some of these in a pictorial form, that based on mass transport I can classify phase transformation as diffusional and when I mean diffusional, I am typically talking about long range mass transport or diffusional, diffusion less. For instance, we will consider in this chapter a particular kind of diffusion less transformation known as the Martensitic transformation, further thermodynamically based on order, we can classify phase transformations as first order.

Which involves a concept known as nucleation and growth, we will dwell into this concept of nucleation and growth in lot of detail in the context of transformations like solidification, an alpha to beta phase transformations etcetera. And typically you can also classify based on order, phase transformations to be second order or even higher order, typically if second and higher order transformations are club together, though in principle you could talk about second order and third order etcetera.

And as I pointed out if the if a first order phase transformation involves nucleation and growth, a second and higher order transformation the entire volume transforms simultaneously. And this is a characteristic and an example of this could be the order disorder transformation. So, if as I pointed out even phase transformations in some sense is a restricted or a subset of is a set, of a some super set which can be defined which will consider in this slide of transformations of materials.

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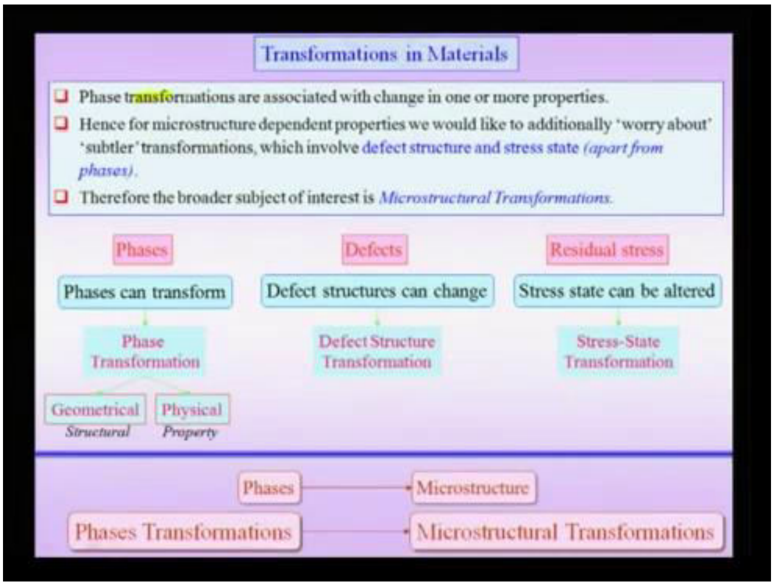

Transformations in Materials

- ❑ Phase transformations are associated with change in one or more properties.
- ❑ Hence for microstructure dependent properties we would like to additionally 'worry about' 'subtler' transformations, which involve defect structure and stress state *(apart from phases)*.
- ❑ Therefore the broader subject of interest is *Microstructural Transformations*.

Phase transformations are associated with change in one or more properties of a this is the reason, that we are studying phase transformation that we want to engineer the properties. And if therefore, microstructure dependant properties, we would additionally like to think about and we would also worry, how as to how the defect structure and the stress state change apart from the phases, in other words I need not only worry about the phase transformation.

But, I have to worry about how the defect structure changes and how the stress state in the material changes, when in an earlier chapter we had considered that residual surface stresses, in glass toughens the glass. And similarly suppose I want to harden aluminum, I can cold work the aluminum, so that my defect structure that means, my dislocation density increases and therefore, the material becomes hard.

But, suppose now I un heal this aluminum it will lose its hardness, because much of this dislocation should be unrelated and therefore, I would have a lower hardness or a lower strength. Therefore, from a property prospective when I am talking about transformations in materials, I need to worry about the defect structure, the stress state and also the phases and their distribution. And this implies that I have to deal with a broader subject known as micro structural transformations.

Because, I we have defined microstructure functionally to be phases, defects, residual stress and their distributions therefore, in a diagrammatic form let us consider, that phases can transform and this we call phase transformation. We can have defect structures can change that implies that means, I told you the dislocation density can change the vacancy concentration can change. We could have more of twins being introduced by deformation and which can get unhealed and therefore, I can have apart from phase transformation, I can additionally have what we call a defect structure transformation.

And the third component of microstructure, the residual stress and therefore, the stress state can be altered and this stress state, could be thermal residual stresses or it could even be residual stresses coming from defects like dislocations and therefore, I can have a stress state transformations. And so putting the picture together I can have phase transformation, I can have defect structure transformation and I can have stress state transformation.

Are in one phrase I can talk about, apart from phase giving rise to a microstructure I can talk about, a phase transformation going to a super set called the micro structural transformations. So, in this chapter not only we will be talking about phase transformations, we will also briefly consider what you call micro structural transformations. And we will worry about treatments like unhealing, we will worry about treatments like re-crystallization wherein the microstructure transforms.

So, this is an important slide in which we have, now use the concept of a microstructure and therefore, evolved a super set to phase transformations, which is called the micro structural transformations.

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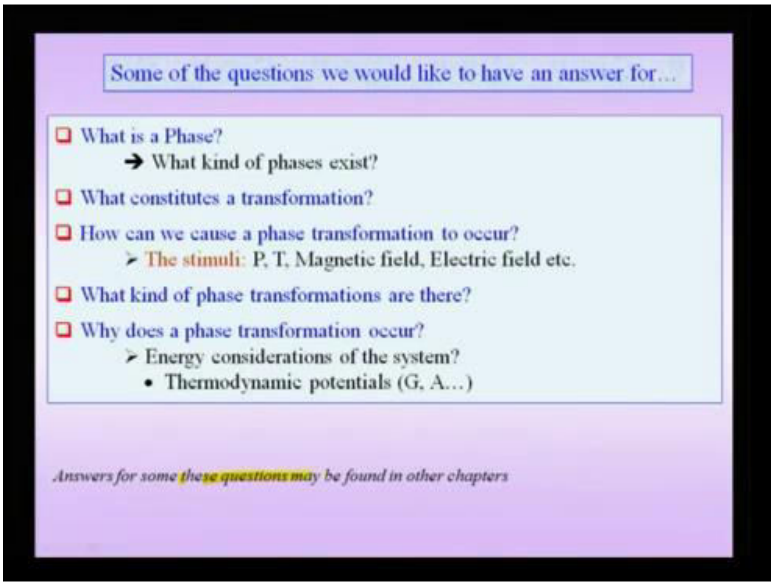

Some of the questions we would like to have an answer for…

- ☐ What is a Phase?
  - ➔ What kind of phases exist?
- ☐ What constitutes a transformation?
- ☐ How can we cause a phase transformation to occur?
  - ➢ The stimuli: P, T, Magnetic field, Electric field etc.
- ☐ What kind of phase transformations are there?
- ☐ Why does a phase transformation occur?
  - ➢ Energy considerations of the system?
    - Thermodynamic potentials (G, A…)

Answers for some these questions may be found in other chapters

And at the end of this chapter, we would like to have the answers for some of these questions of course, some of these answers to some of the other questions, may some of these questions, may be found in other places and other chapters. But, we will try to understand some of these try to search for some of the answers, for some of these questions, for the first question. of course, is that we have what is the phase and what kind of phases exist.

We have already dealt with it in the previous chapter, but we will again revisit this concept then of course, I will ask a question that what constitutes a transformation. And how can we cause a phase transformation to take place that means, can I heat the substance, can I put it in the magnetic field or can I pressurize the system. And we have already seen, when draw the drew the iron pressure temperature unary diagram, that both pressure and temperature can cause phase transformation.

But, additionally we have to note that other factors like electric fields and magnetic fields can also transformation, though we will not consider these aspects in detail here. Of course again we will ask the question, that what kind of phase transformations are there that we need to consider. And why does the phase transformation take place that means, what is the energy considerations on the system, that causes phase transformation to take place.

And are there any barriers to this phase transformation, what is the relevant thermodynamic potentials which we need to consider and we have already noted, that if you are working at constant temperature and pressure. It is the Gibbs free energy which is the relevant thermodynamic potential, which we need to consider when we are talking about phase transformations that means, that systems will tend to go downhill in Gibbs free energy.

And therefore, if there is a lowering of Gibbs free energy possible by a phase transformation, then the system will go will transform. But, however, we have to remember that Gibbs free energy can only tell us that, if there is a tendency for a phase transformation to occur, it is the kinetics which will tell us that if actually the phase transformation will take place.

In other words thermodynamics may warrant, but may kinetics may prohibit and a classic example given is the windowpane glass, for instance which is present in many places in this room, that the windowpane glass is a meta stable state and by crystallization the Gibbs free energy of that can reduce. But, the kinetics is, so frozen at room temperature that this glass can exist for a few 100 years without much change in its crystallization.

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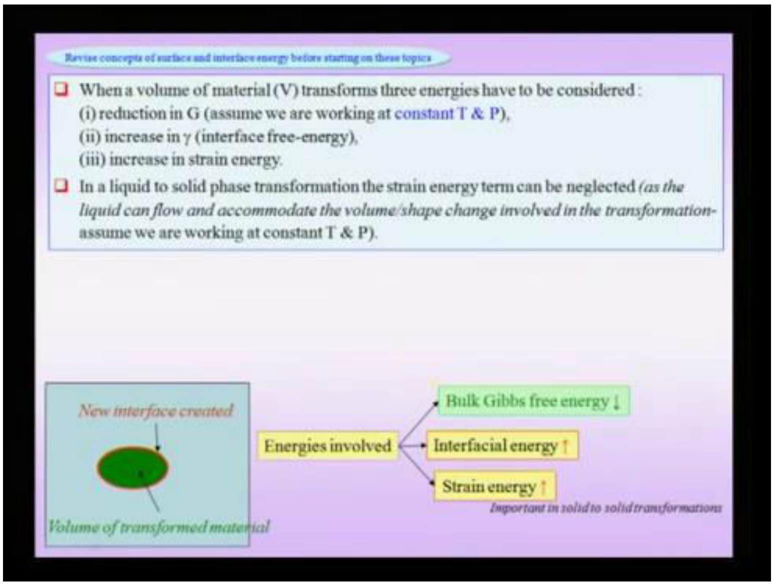


Revise concepts of surface and interface energy before starting on these topics

- ☐ When a volume of material (V) transforms three energies have to be considered:
  (i) reduction in G (assume we are working at constant T & P),
  (ii) increase in γ (interface free-energy),
  (iii) increase in strain energy.
- ☐ In a liquid to solid phase transformation the strain energy term can be neglected *(as the liquid can flow and accommodate the volume/shape change involved in the transformation-* assume we are working at constant T & P).

New interface created

Volume of transformed material

Energies involved

Bulk Gibbs free energy ↓

Interfacial energy ↑

Strain energy ↑

Important in solid to solid transformations

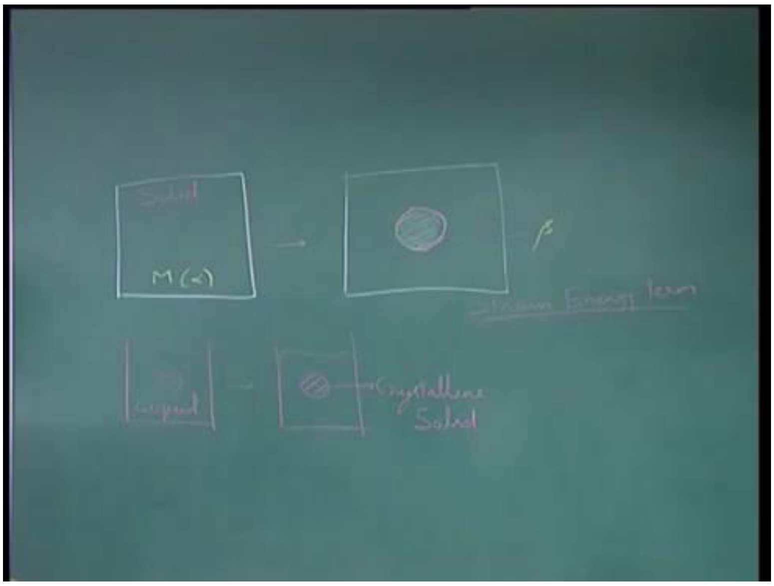
And we need to worry a little bit before, we understand this whole the some of the aspects of this chapter. And one of those important aspects is that we need to revise the concept of a surface, the concepts of an interface and the concepts of surface tension and surface energy. And we will do, so we will do that very soon, but before that we will talk about ask the questions, that suppose I have a volume of material v like for instance in the diagram below, I have here a region which is marked in green, which is I will shade now.

So, this region is suppose I consider a volume of material v, which is transforming then what is the change in the energies I need to talk about. Of course, if I am assuming that this volume wants to transform that means, at constant temperature and pressure the Gibbs free energy must reduce. But when this uniform phase which is present, suddenly throughout this little volume of green material that means, originally I had a matrix which is shaded in blue here.

So, this is my matrix and in this uniform matrix I suddenly had have, now a green phase this implies that an interface has been created, which is marked in red between the matrix and the new phase, which I can call for instance second phase. And therefore, there is an increase in the interfacial energy, that automatically brings us to the point I just mentioned, that I need to understand what is this interface energy, what is the origin of this interface energy.

And of course, one of the interfaces which is easiest to understand is the free surface, so I can equivalently try to understand, that what is the free surface and what is the origin of the surface energy. And how is this surface energy link to the equivalent concept or a related concept known as surface tension. And if I am talking about a solid to solid phase transformation then additionally, I need to worry about what is called an increase in the strain energy.

Now, to understand these aspects let us draw this diagram, once more schematically on the board, (Refer Slide Time: 19:41):



so I have an uniform volume of material, which again called a matrix. And in this volume of a material suddenly I assume that there is a second phase present, suppose this second phase it is a blue phase. But, the appearance of this blue phase two things have happened number 1, I would assume that the volume or the Gibbs free energy of a localized region is reducing.

Because, of the presence of this blue phase which I will again once more highlight in yellow color, so this is my phase which has been created. But, and this implies two things first of all of course, I told you the first thing the Gibbs free energy would be reduced corresponding to the volume of material created. But, additionally an interface is created between the two phases, suppose I am talking about a matrix m here in which this phase is coming out this blue phase, which I can call the beta phase.

And this matrix I can call the alpha phase, then I have an increase in interfacial energy, because of the presence of this one additional term comes, because suppose I am in this case suppose this I am talking about not a solid to solid phase transformation. Suppose I am talking about a liquid to solid phase transformation that means, I have a liquid bath in which I have the formation of a solid phase, then this solid phase assuming it is a crystal will have a lower volume with respect to originally, the volume occupied by this liquid there.

But, then since the I am working at constant temperature and pressure and the volume is left free to expand or contract therefore, there will be no strain energy, associated with this system, because of the formation of this little amount of solid a crystal. So, this is my liquid, but suppose I am talking about a solid to solid phase transformation, so this is a solid alpha in which a beta phase is coming, I would have an additional term which is the strain energy term.

And we will try to understand all these energies in little more detail as we go along, so the energy involves in involved in general are the Gibbs free energy reduction, which is actually what is trying the phase transformation. An increase in interfacial energy, which tends to oppose, your phase transformation and an increase in strain energy, which becomes important in solid to solid phase transformation. In other words if I am talking about a constant pressure system and I am talking about a liquid to solid phase transformation, usually the strain energy term can be neglected.

And this is, because as we know liquid can flow and accommodate the volume and shape change involved in a phase transformation. And, but on the other hand if I talking about a solid to solid phase transformation or even a formation of a liquid pocket, within a solid then often this may lead to certain strain in the material. And therefore, in a solid to solid phase transformation, I cannot ignore the strain energy term, so let us try to understand the strain energy term.

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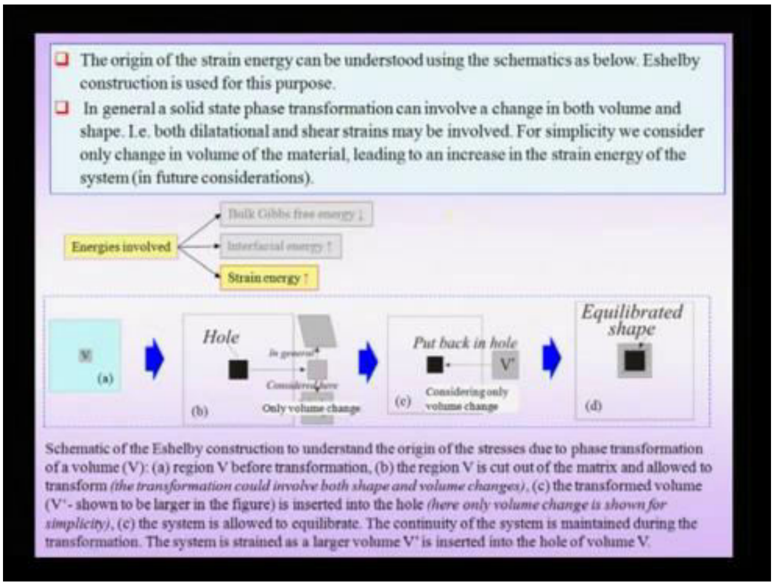

- ❑ The origin of the strain energy can be understood using the schematics as below. Eshelby construction is used for this purpose.
- ❑ In general a solid state phase transformation can involve a change in both volume and shape. I.e. both dilatational and shear strains may be involved. For simplicity we consider only change in volume of the material, leading to an increase in the strain energy of the system (in future considerations).

Schematic of the Eshelby construction to understand the origin of the stresses due to phase transformation of a volume (V): (a) region V before transformation, (b) the region V is cut out of the matrix and allowed to transform *(the transformation could involve both shape and volume changes)*, (c) the transformed volume (V'- shown to be larger in the figure) is inserted into the hole *(here only volume change is shown for simplicity)*, (c) the system is allowed to equilibrate. The continuity of the system is maintained during the transformation. The system is strained as a larger volume V' is inserted into the hole of volume V.

Before, we go on to understand the interfacial energy term typically we can understand this strain energy term by considering, what will is known as the Eshelby construction. And of course, I have to know that in general if I am talking about a phase transformation, the product phase may have a different volume and the different shape, as compared to the original matrix phase. And therefore, both dilatational and shear strains may be involved in a phase transformation, so therefore, if I am talking about a phase transformation I can write down.

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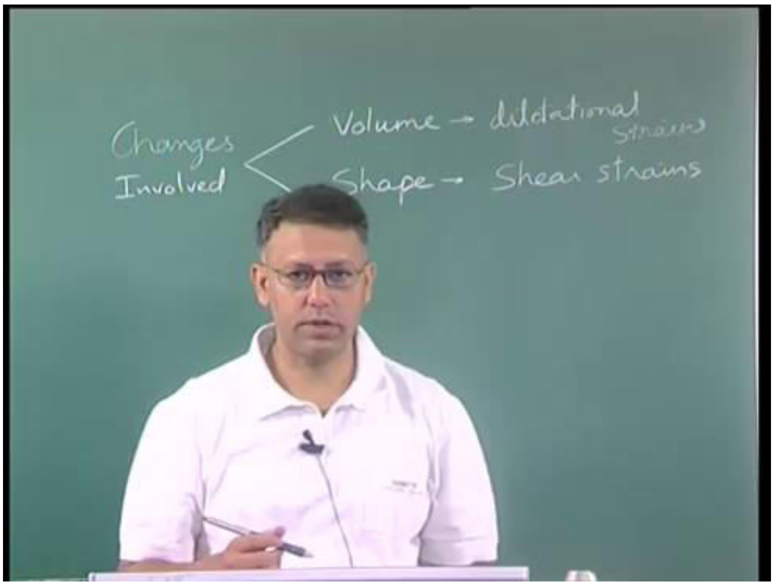

So, I have two kinds of strains involved the dilatational strains and the shear strains and both of these dilatational and shear strains, can give rise to corresponding strain energy which is stored in the material. And to understand this as I pointed out, I will do what is known as the Eshelby construction, so let us consider the figure here below in which there is a blue matrix phase, in which a volume v of material is ready to transform.

Of course, we already seen that we need some kind of a thermodynamic stimuli for this transformation to take place, example we could have for instance cool this, for instance suppose I am talking about an a alpha phase transforming into a beta phase or a gamma phase transforming, into an alpha phase. I could have cooled the system down below the transformation temperature, like for instance I could be talking about to the high temperature form of iron, which is gamma and I am cool the system, below its transformation temperature and therefore, it wants to transform to the alpha phase.

But this volume v of material assuming that it is ready to transform, what I do I do a material construct, in which I take this material of volume v out, allow to transform outside. And then I try to insert back this material, after transformation into this original hole which was created. So, this hole has a volume v, because now I have just pulled out this volume v of material, out of this matrix.

Now, what happens if I pull this out and allow the transformation to take place in general of course, I could have only a volume change as shown below that means, the volume after transformation could of course, be larger or smaller, in this schematic we have shown a larger volume here or this transformation could involve with change in shape, in which case of course, this volume of material would become change in shape. So, suppose I just have a shear strain involved, then this would be the new shape of this transformed volume.

So, I could have a new shape, but in general I could have a change in both shape and volume, since this aspect is important I will just go to the board and draw this all over again.

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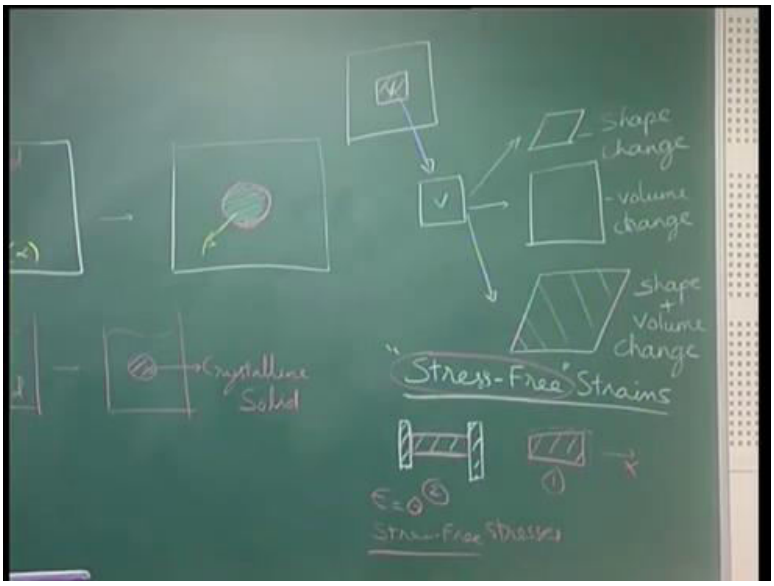

So, I have a volume v of material, which I have plugged out from the material from the inside of the matrix, I can have this volume v of material transforming just by pure shape change that means, I assume that the volume is constant I could have a pure volume increase that means, the shape is same or I could have a combination, where in I have a volume change and a shape change. So, I have a volume v of material and it is changing in shape for instance, in this case in this schematic it is a square, which became a rhombus or I could have a volume change in which case for instance I have considered a bigger volume here.

But, in principle it could also be a smaller volume or I could have a transformation in which I have a change both in the volume and the shape of the material. So, I have in general a possibility, that when the phase transformation takes place. Because, for instance this could involve for instance say change in crystal system itself and which means, that the system could go from a cubic phase for instance to a monoclinic phase, which could involve the change both in the shape and the volume of the material.

And the next important step in this whole construction the Eshelby construction is the fact that this volume of material is not standing free, here of course, I have plugged this volume out of from this solids, we had only there a solid like this and I took a volume v of material plugged it out from the solid and then put it here. And I considered the transformation and this consideration this can be thought of as having, something known as stress free strains.

And this term stress free strains have needs to be understood a little more, suppose I had a metallic body and I pull it that means, that I am applying some force on the material, which translates into stress inside the body. And this stress leads to elongation which means strain, therefore, I have stress coupled with strain, but in certain situations like in the example of phase transformations, I could have something known as stress free strains and in certain other situations I could has strain free stresses.

So, let us take examples of these, what is stress free strain and what is strain free stresses, suppose I take two rigid walls and I put a body between the two. So, this is my rigid walls and I have a body between the two and this body I will just label in red, so this is my red body which is kept between the walls in an alternate scenario, I will just take a free standing body here of the same volume.

So, this is my free standing body, I will heat both these configurations, so this I say this is configuration 1 and this configuration 2, I heat both the systems. Because, of thermal of the heating this body will expand, but in the expanded state there will be strains that means, the body would have become longer, schematically I am showing it this way. And of course, should I increase in volume as well.

So, so this body would be expanded suppose I am interested in this direction x direction, so it will would have become longer in the x direction. But, there will be no stresses in the material that means, there are strains, but there are no stresses, so this is what we call stress free strains. Similarly, I took this volume of material v of free standing body and allowed it to transform, there are strains, there are shear strains and there are dilatational strains.

But, there are no stresses therefore, these thermal stresses are occurring into this phase transformation, thermal strains or like phase transformation strains which are stress free this of course, is true for a free standing body, which is heated. On the other hand suppose I have a body which is between two rigid walls and I heat it, in this case these rigid walls will not allow the body to expand that means, the strains will be 0.

But, because I am heating the body, the body will develop stresses, so this can be thought of as the opposite of stress free strains, which mean these are strain free stresses. So, these are strain free stresses and I have to remember, the strain I am talking about is the net strain, which is combination of the original strain it wants to expand counteracted by the rigid walls which is stopping them.

So, I can have stress free strains and strain free stresses and the 1 which is relevant to our construction now, is the stress free strains which can easily be understood by taking an analogy of a free standing body, which is heated. So, now the next step is that I have now with me a body, which is this which has change say for instance, now for simplify matters further I will assume that they just change in volume.

So, it is bigger though the generality will not be lost if consider shape change also, I have to consider body which is bigger in bigger in volume now. Now, this volume of material has to be inserted back into this original volume, which was taken from where it was taken out. Because, now actually this it is not standing free this is actually a part of them continuum, where in I have this matrix and this volume v and therefore, I have to make a material construct in which this volume v is inserted back into this.

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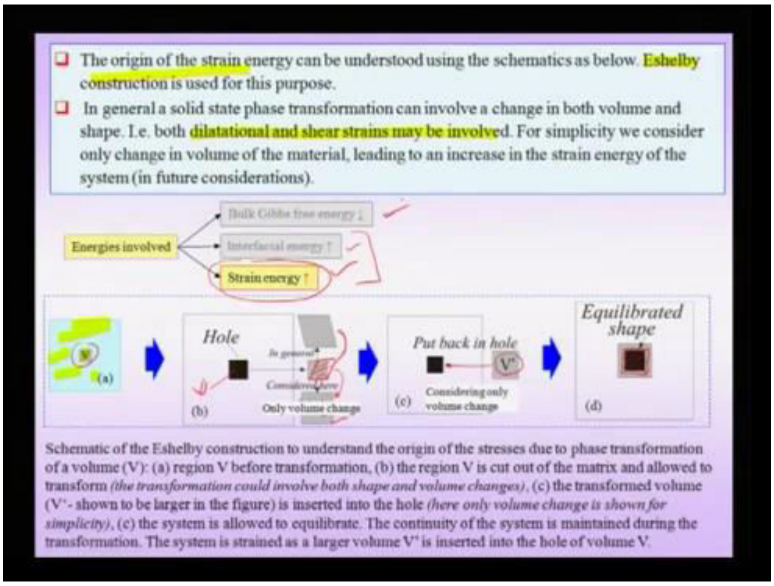

- ❑ The origin of the strain energy can be understood using the schematics as below. Eshelby construction is used for this purpose.
- ❑ In general a solid state phase transformation can involve a change in both volume and shape. I.e. both dilatational and shear strains may be involved. For simplicity we consider only change in volume of the material, leading to an increase in the strain energy of the system (in future considerations).

Energies involved
- Bulk Gibbs free energy ↓
- Interfacial energy ↑
- Strain energy ↑

Schematic of the Eshelby construction to understand the origin of the stresses due to phase transformation of a volume (V): (a) region V before transformation, (b) the region V is cut out of the matrix and allowed to transform *(the transformation could involve both shape and volume changes)*, (c) the transformed volume (V" - shown to be larger in the figure) is inserted into the hole *(here only volume change is shown for simplicity)*, (c) the system is allowed to equilibrate. The continuity of the system is maintained during the transformation. The system is strained as a larger volume V" is inserted into the hole of volume V.

So, in the process of doing, so let us see what happens, let us go back to the slide, so what I am doing here is that I have this volume v prime, which is now of the transform material. And I take this volume v prime and try to put it back into the original black hole, which was created when I took out this material. So, what would then be the tendency, that since this volume is larger as I have considered just in shape, just in size then this volume of material will tend to push the matrix outwards that means, this and the matrix will try to push this material inward.

Because, the matrix is not made of a 0 modulus material, it will also tend to push this whatever the transform material back and therefore, I will land up with an equilibrium configuration, which is shown by the dotted line here. So, the volume that the precipitate will occupy will not be the original volume, which was created as I showed in the board; that means, the larger volume there, it will not be the volume of the hole which was created, it will be something between the transformed free volume or the transform volume under free boundary conditions, these are the original hole which was created.

So, I will an equilibrium shape which is finally, the one which is marked in and obviously, the whole process involves strains the final net process and therefore, there will be strain energy associated with this whole process. And if I look at the stress state I will notice that the precipitate will be under compression, but the matrix will be under tension.

Because, if this is overall a free standing body then the next stress state has to be 0 therefore, all these strain energy which the system is paying will have to come from, somewhere the reduction on the Gibbs free energy which was originally present, in the absence of this strain energy, I would assume that the transformation can take place much more easily.

But, now because there is a strain energy term involved, the energy caused to the system is larger and therefore, the system has to pay a higher price, now not only in terms of the interfacial energy, which is interface energy which is created. But, also in terms of the strain energy which is coming from the phase transformation. So, therefore, to summarize this slide I can understand that strain energy can play an important role in solid to solid phase transformations, this strain energy the origin of the strain energy can be understood, by what we call the Eshelby construction.

Where in we take a volume of material pluck out a little portion of it allow it to transform, reinsert it into the original whole which was there, allow the system to equilibrate. And in the process understand the stress state of the system and the strain energy which comes from the transformation and these two terms as we have noted the interfacial energy and the strain energy oppose, our phase transformation while it is the bugs Gibbs free energy of the volume, which is transforming which is helping the process of the phase transformation.

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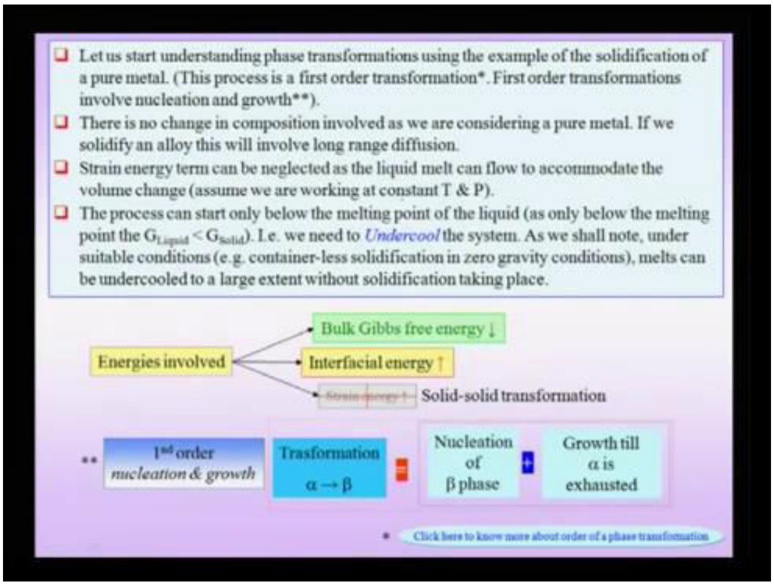

- ☐ Let us start understanding phase transformations using the example of the solidification of a pure metal. (This process is a first order transformation*. First order transformations involve nucleation and growth**).
- ☐ There is no change in composition involved as we are considering a pure metal. If we solidify an alloy this will involve long range diffusion.
- ☐ Strain energy term can be neglected as the liquid melt can flow to accommodate the volume change (assume we are working at constant T & P).
- ☐ The process can start only below the melting point of the liquid (as only below the melting point the $G_{Liquid} < G_{Solid}$). I.e. we need to *Undercool* the system. As we shall note, under suitable conditions (e.g. container-less solidification in zero gravity conditions), melts can be undercooled to a large extent without solidification taking place.

Energies involved

- Bulk Gibbs free energy ↓
- Interfacial energy ↑
- ~~Strain energy ↑~~ Solid-solid transformation

** 1st order *nucleation & growth*: Trasformation $\alpha \rightarrow \beta$ = Nucleation of β phase + Growth till α is exhausted

* Click here to know more about order of a phase transformation

Now, before we consider some examples of how this phase transformation, can take place and we will consider here detail of the first order phase transformations. We need to understand this other term which we had considered, which is the interfacial energy the origin of this interfacial energy what do we exactly mean by the interfacial energy. And that is will be the next thing we have to consider to understand the concept of interface energy, we will use the concept of surface energy.

Because, it is somewhat easier to understand and to understand surface energy, we will consider a small a neck doddle story, person a meets person k and asks person k why are you looking, so glum today. Person k says I suffered a loss of 4 cores of rupees in my business this year, that is why I am not looking very cheerful today, then he asks how did you suffer a loss of 4 core rupees this year, what wrong with your business. He, says last year I had a profit of 16 core rupees.

And this year I have a profit of only 12 core rupees, which means that I have suffered a loss of 4 core rupees, so the question to ask what is from this story is that did person k really suffer a loss of 4 core rupees. Because, at the end he still had a profit of 12 core, it was just 4 core with respect to the last year profits, which was 16 cores.

Similarly, we have to ask ourselves this is the important question of course, the story is here to tell you, the connection between this and the surface energy and that will become clear as we discussed more, the question we have to ask ourselves is surface energy or for that matter interface energy, truly an energy. And if it all yes in what sense can we considered to be an energy to understand these concepts.

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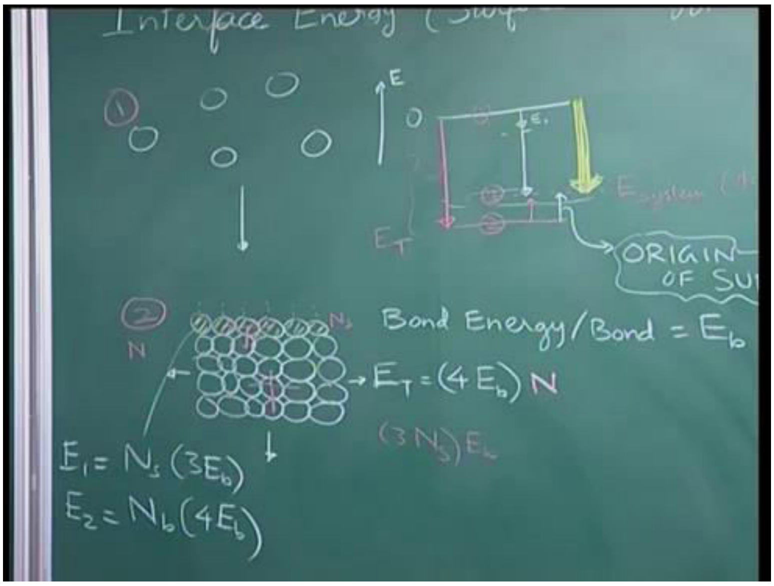

Let us consider and collection of atoms which are far apart that means, they are non interacting and therefore, I they are not bonded to each other. Now, I suppose I bring I do a mental, construct in which all these atoms are brought together and say I form a crystalline array. And since originally I talk about this original state, as some 0 state in energy, I can draw that 0 state in energy.

And on formation of a crystalline state, I assume that there is bonding between the atoms; that means, I assume suppose there are n atoms in this assemblage. And then I assume that each one of those atoms is bonded to its neighbors, so assume that in this crystalline array say I take an atom here, this atom is bonded to all its neighbors. Suppose the bond energy reduction per bond is e b, that means then given that e b is the bond energy reduction per bond, I can calculate the total reduction in or energy reduction in energy, when I form this crystalline array.

As, the because each atom is bonded to 4 atoms, I have total energy reduction suppose I call this total energy reduction e t is equal to 4 times into e b, into the number of atoms, in this assemblage, say for instance that number is n the total number. But, anybody who sees this experiment that means, now I have taken a non interacting set of atoms, whose energy state in this energy axis is 0, then I make a crystalline array out of this assemblage of atoms.

And in this crystalline array, now the reason for formation of this crystalline array is, that each atom can lower its energy by forming bonds, these bonds are shown in red color. And, because of this formation of bonds each atoms reduction per bond is e b that means, if its bonded to 4 neighbors, then I have a reduction of 4 e b per atom. And since there are total n atoms in this system, I will have a total deduction in energy as 4 e b into n.

Anybody clearly, watching my calculation can point out the error, that actually the surface atoms which are here are clearly not bonded to 4 other neighbors, they are just bonded to 3 other neighbors 1,2 and 3. So, there are 3 bonds 1,2 and 3 and therefore, and suppose this is an infinite array and now that means, it is infinite in this direction. But, this is my surface therefore, I will shade all the surface atoms.

So, this can be called as an semi infinite crystal in the semi infinite crystal, some of the atoms are sitting on the surface and these atoms do not saturate their bonds that means, there are some unsaturated bonds, which I will show by dotted lines. So, this surface atoms are only bonded to 3 other atoms that means, they have not lower their energy as much as I calculated.

So, what is this lowering of energy is that I come to a new state, so this is state 1 for instance I come to state 2 here, which is now the crystalline state and now this is my e t which is negative, because it is lowering in energy, because of the crystal formation. But, as we can clearly see I have over counted the bonds, the number of bonds, the surface atoms are not as well bonded as the interior atoms and therefore, I have to correct for these surface atoms.

And suppose this is the number of surface atoms is n surface, I have to correct for this surface energy and the net energy of the final system would be this e. So, this will be step 3, in step 3 I am correcting, so this is my step 1, here my step 1 of course, I start with here. Stage step 2 is my crystalline state, where in I did an over counting of the bands and to correct for the fact that there are some surface atoms.

And therefore, I have to correct for the fact, that these surface atoms n s are actually bonded only to 3 other neighbors and of course, I would account for the fact that there is a bond energy per bond of e b and of course, this is a crude what we call broken bond kind of a calculation in reality things are much more complicated. But, this is a nice illustrative example and therefore, I have to correct and land up things.

State 3, where in the true surface has been taken into account that means, we are not talking about a infinite crystal, but a semi infinite crystal wherein there is one surface. Of course, with bounded many more surfaces, it is a finite crystal then I have to correct for all the surfaces. But, the important thing to notice is that this is what is my surface energy, this correction I am doing is called the surface energy.

So, this is the origin of surface energy, in other words surface energy is not with respect to the 0 state the un bonded state or the non interacting state. But, the reference state for the surface energy is the fully bonded crystalline state, which is the state 2, it is actually the correction you make to the error of over counting an atom, all the atoms being bonded as if it is a full crystalline state.

So, this is my surface energy and as I pointed out in spite of the presence of the surface, if you look at the overall system there could be a reduction in the energy, as you go from the un bonded state to the state with the surface. So, there is this reduction energy is still possible, in other words the system with even a surface might have a lower energy as compared to the free state.

So, this correction is what is we call surface energy and in some sense, because it is reference state is the fully crystalline fully bonded state, it is a correction term and not an energy in itself in the sense of a starting with an non interaction collection of atoms. So, it is interesting to note this surface energy, as I said is a last not with respect to the non interacting state, it is not truly a loss it is a loss.

Because, of the fact that you over corrected the atoms of course, this calculation could have been performed in a different way, I could start with a non interacting set of atoms, then I could find out the number of atoms, which are sitting on the surface and call that n s and I know that these n s atoms are bonded to 3. So, I will write down as 3 e b, so I will get a step 1 deduction E 1, then I will locate the number of bulk atoms. And I will write it as n bulk and I know that these bulk atoms are bonded to 4 atom, 4 bonds.

Therefore, I will write my energy as E 2 and therefore, in two steps I can arrive at the final state which is the state 3 that means, that I consider my bulk atoms separate from these surface atoms, I do not land start from 1 and land up in 2. But, I land up at step 3 in two stages that means, I first lower for my surface atoms, which is a little small lowering E 1 then I lower for my bulk atoms.

And finally, land up in the final state which is this state which i am interested, so in two stages I can lower and in this case of course, the mystery of these surface energy would vanish. So, this is something which we need to we need to understand. But, this illustration should not confuse you, because this illustration is meant to truly understand the origin of surface energy.

But as we shall see the effects of the surface energy is very real, because the surface atoms, now are in comparison to a bulk atoms are purely bonded, they will always want to lower the surface area. And that means, atoms in the surface will warn to go towards each other and this will automatically result in surface tension. Because, now if I put out more atoms on the surface that means, that suppose I am talking about a liquid and there are more atoms on the surface, I am going to pay a higher price for these atoms which are not that well bonded.

Therefore, surface will want to close in on itself and therefore, this will result in real effects like surface tension and there are many more interesting phenomena, which are related to the surface tension and surface energy. And its role here in phase transformations definitely is of important consequence.

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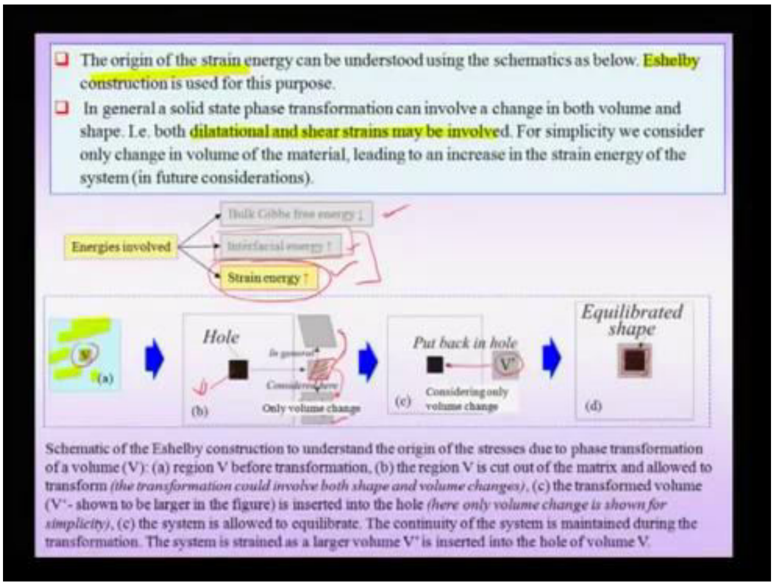

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Energies involved

- Bulk Gibbs free energy ↓
- Interfacial energy ↑
- Strain energy ↑

Schematic of the Eshelby construction to understand the origin of the stresses due to phase transformation of a volume (V): (a) region V before transformation, (b) the region V is cut out of the matrix and allowed to transform *(the transformation could involve both shape and volume changes)*, (c) the transformed volume (V'- shown to be larger in the figure) is inserted into the hole *(here only volume change is shown for simplicity)*, (c) the system is allowed to equilibrate. The continuity of the system is maintained during the transformation. The system is strained as a larger volume V' is inserted into the hole of volume V.

So, we have tried to understand three terms contribute to the formation of a for instance a phase transformation, one is the Gibbs free energy which helps you, the interfacial energy which we just understood, which tries to oppose you. Because, now the similar to the surface the interface atoms are poorly bonded with respect to either, the solid which is these inside solid either the matrix or the for instance the precipitate.

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So, suppose I have a system here with a precipitate beta, now the atom sitting on the interface here, are poorly bonded with respect to the beta or even with respect to the alpha. So, they have an higher energy state with respect to both of those crystals, we are talking about and therefore, interfacial energy also has the similar origin in terms of poor bonded less, though we have to remember interface energy there are material on both sides unlike a surface, where on one side we consider either vacuum or air at best.

So, the third and term is the strain energy which we have understood in detail, now to understand further phase transformations, let us take up the example of a solidification of a pure metal though this is a simple and illustrative example. We will see that this can make us understand some of the important issues inward and the most important of them, being the issue of nucleation.

And we will often find in literature terms like nucleation barrier that means, it seems like nucleation is going to stop this phase transformation from taking place, so we will understand these terms like nucleation barrier, under cooling and also something known as homogenous and heterogeneous nucleation.