Advanced Materials and Processes

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Lecture – 16
Shape Memory Alloys

Welcome to NPTEL; myself, Dr. Jayanta Das from Department of Metallurgical and Materials Engineering, IIT, Kharagpur. I will be teaching you Advanced Materials and Process. So, today we will start a new topic on Advanced Material which is Shape Memory Alloys. The Shape Memory Alloys, the term itself says that the material remembers its shape. So, there is a large group of shape memory materials. Here, the materials means it could be alloys and such kind of shape memory behaviour has been also observed in polymer or ceramic system also.

However, these alloys and the shape memory behavior are very much well linked and are useful for many different types of engineering applications. Therefore, it is of our interest to discuss these advanced materials. The shape memory behavior in an alloy can be achieved due to phase transition which is controlled by temperature and stress.

Since, phase transformation is involved in this process; therefore, we must recapitulate the phase transformation in materials. In this particular subject in case of different metals and alloys, we should try to learn and try to think about how phase transformations are linked with the shape memory behavior. So, today we will try to focus more on the phase transformation in metals and alloys.

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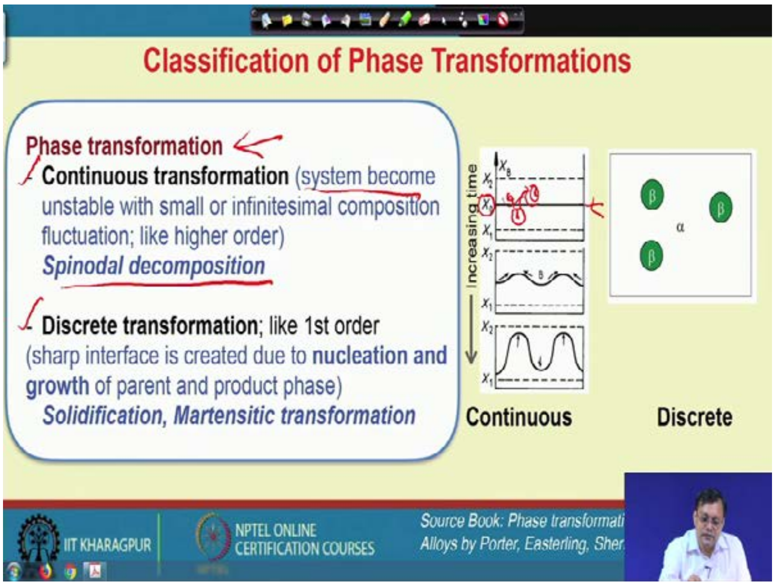

Classification of Phase Transformations

Phase transformation

- **Continuous transformation** (system become unstable with small or infinitesimal composition fluctuation; like higher order)
  Spinodal decomposition
- **Discrete transformation**; like 1st order (sharp interface is created due to **nucleation and growth** of parent and product phase)
  Solidification, Martensitic transformation

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Source Book: Phase transformati
Alloys by Porter, Easterling, Sher

The Phase transformation usually classified into two major categories; the first one is called as Continuous transformation and the second one is the Discrete transformation. The continuous transformation here means that the system becomes unstable with a very small composition fluctuation like higher order phase transition. The example if I tell you, you will understand it is a spinodal decomposition. You must have heard the spinodal decomposition in your undergraduate days. However, we will again discuss the same and some other topics also will be discussed.

So, in case of a spinodal decomposition, we have a solid solution which has an average composition of X_0 and if we introduce a very little composition fluctuation, here, a composition fluctuation means if we have to deplete solute in an area, then definitely there will be enrichment in other place locally because the atom will move to the nearby site and in such a case, there will be a localized fluctuation of composition in the system.

The localized fluctuation in the composition in the system will decrease the free energy of the system; means system always go in favor of making the composition fluctuation. It also says in other way that there is no activation energy for such kind of process.

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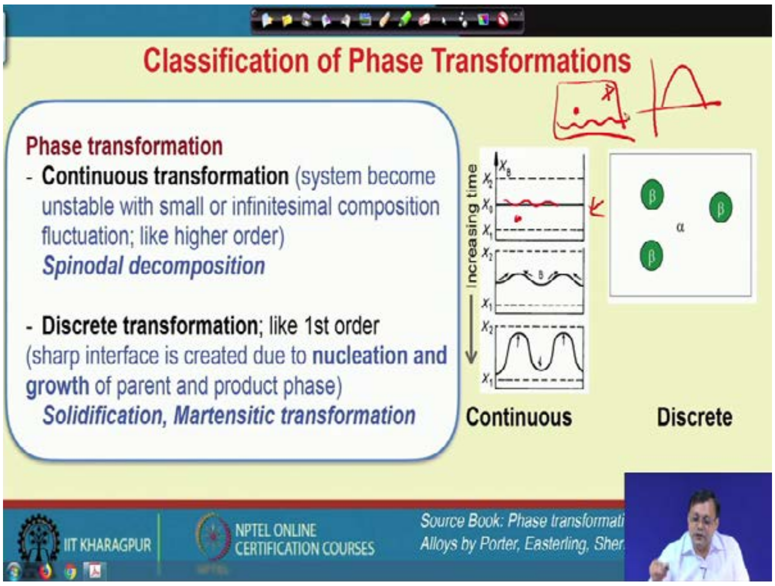

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Because for making any nuclei of a second phase particle, or let us say if I have a parent phase and I want to introduce a product phase into it; then there will be an activation energy barrier, which is controlled by the surface area, the volume. But in this case, where a very small composition fluctuation always make the system stable, because there is a net decrease of the free energy of the system. And so this spinodal decomposition is a type of continuous transformation. So, in this particular diagram, you can see that X_0 is the average composition of a solid solution and the solute atoms are segregated in some localized region like here and here.

So, let us say that solute B atoms are present in solvent A. So, that basically means B atoms segregated locally and there is always a net decrease of the free energy by changing a small composition fluctuation. And finally, if we try to make a higher and higher fluctuation and it always stabilizes the system. Now, in case of a discrete transformation which is often like a first order transformation is characterized by a discontinuity in the enthalpy curve. So, you have seen those things in the in the earlier lectures.

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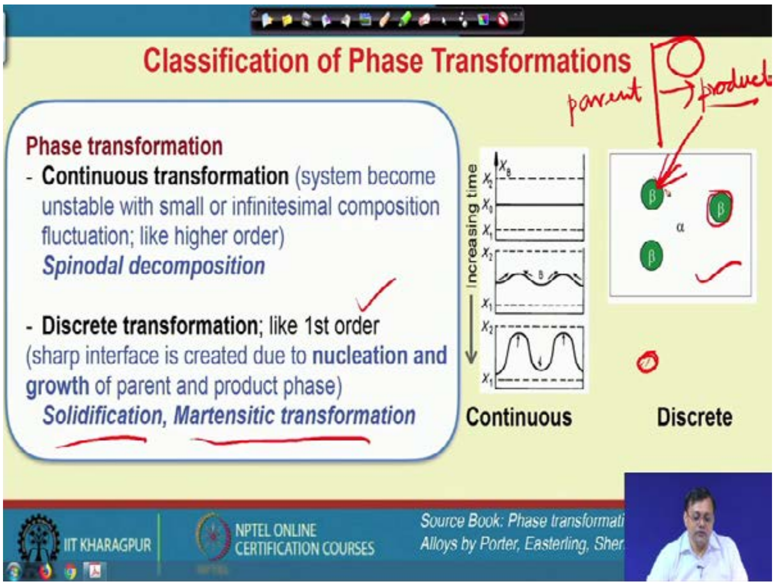

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So here, when there is a parent and product phase coexist, there is a sharp interface in between parent and product phase. So, to form a product, we have to go through a nucleation and growth type of processes. If a nuclei has to form in a matrix, then there is a need of an interface and this is a first order transformation. The common example of such discrete transformation is solidification.

Here, we already know that if we take a liquid and the solid nuclei has to appear. First a particular cluster of atoms will appear in liquid and if they have a greater size than the critical size of a nuclei, then only the cluster will be stabilize and there is a need to decrease the free energy of the system and we need to overcome the activation barrier for such a case.

Also a martensitic transformation is also a first order transformation. Here, the transformation goes through a nucleation of the martensite plate and its growth in the austenite matrix phase. So, this is also a discrete transformation. So, an example is shown here schematically I have shown that I have α-matrix and here is a β-phase which is the product phase, and there is an interface between α/β phases; there is a sharp interface between them. So, these are the two major types of phase transformations.

However, we can also classify phase transformation by considering several other aspects. What I want to mean that we can consider about the order of the transformation. So, here we can classify a phase transformation in terms of whether they are first order transformations or there is a second order.

Second order means that there is no discontinuity in the free energy curve. So, like a glass transition, I earlier talked about what is a second order transformation. So, in the enthalpy versus temperature plot you will not get sharp discontinuity. Also, since when a product has to form in parent matrix, the atomic rearrangements has to be made. Here, the atom can rearrange themselves by a simple shear and transforms into the product phase from a parent matrix or parent lattice or the atoms can move like a civilian motion. A civilian motion in a street, you can see that each and every person is going into different directions.

So, this is like a civilian; whereas, if you think about a movement of the military, where there is a group of people who are making equal footing to a particular direction. So, there is basically no relative movement between the 2 persons or 2 soldiers, which is like a military type of transformation. So, a military type of transformation does not need the diffusion of atoms. So, such transformation is called as a diffusion-less transformation; whereas, in case of a solidification, we need diffusion of atom and partitioning between the elements are required. In case of a solidification or let us say in a steel if there is a eutectoid transformation and so on, then the diffusion of atoms is required. .

So, the phase transformation, we can also classify in terms of whether the atomic movements are diffusional or diffusion-less; whether there is any relative movement between the atoms or not. However, whenever there is a discrete transformation as I said it goes through a nucleation and growth process, then this nucleation could be also two different type, where a nucleation could be occurred homogenously all over the places in the parent phase. So, like a container less solidification.

So, in a container less solidification, the nuclei we will appear all over the liquid in different places and then they will grow and fill up. In that particular case, we may get a more homogenous microstructure. But if we chill or if we cast a cast iron or let us say aluminum alloys in a cast iron block mold, then we will see that three different layers are appeared near the mold surface. Because the solidification has initiated at the mold wall by forming a chilled layer.

So, there the cooling rate is faster at the mold wall and it acts as a heterogeneous site for nucleation. And therefore, the nucleation start from the surface of the mold wall and it require less activation energy; where homogenous nucleation require higher activation energy because you have to create a surface and creation of surface required extra or excess energy. However, in case of heterogeneous nucleation the surface is already there only some atom has to move and it requires less activation energy.

So, heterogeneous nucleation is mostly favored. So, if you like to solidify a liquid in the mold, then heterogeneous nucleation will start at the interface between the mold wall and the liquid. However, the growth of a product phase could be also interface controlled or diffusion controlled growth. So, let us say a product phase if it has to grow in a parent matrix, then diffusion of atom may be required.

So, growth may be controlled without diffusion and if we consider a martensitic type of transformation, where there is no long range diffusion is required; then the only the interface moves. Interface moves means and it completely covered the whole parent phase, it become an interface control and there are many other example of such cases. So, we can also classify and identify a phase transformation process by considering these particular aspects.

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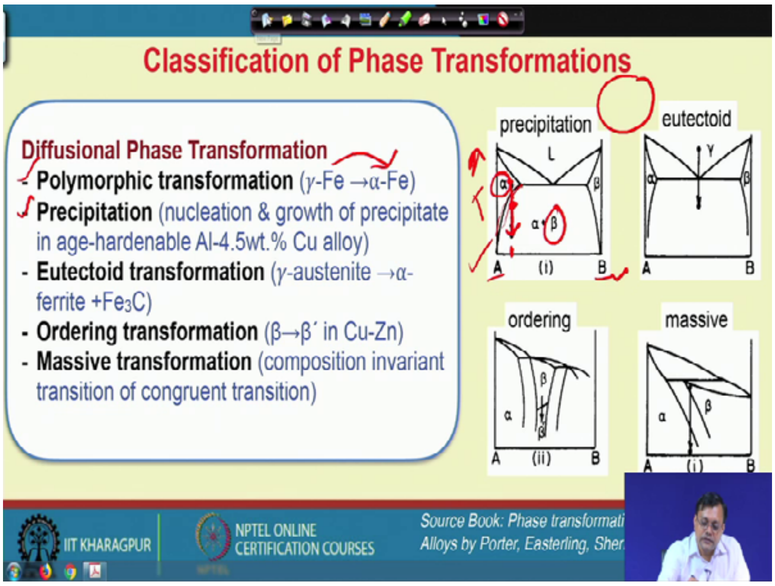

Classification of Phase Transformations

Diffusional Phase Transformation

- **Polymorphic transformation** (γ-Fe $\rightarrow \alpha$-Fe)
- **Precipitation** (nucleation & growth of precipitate in age-hardenable Al-4.5wt.% Cu alloy)
- **Eutectoid transformation** (γ-austenite $\rightarrow \alpha$-ferrite +Fe_3C)
- **Ordering transformation** ($\beta \rightarrow \beta'$ in Cu-Zn)
- **Massive transformation** (composition invariant transition of congruent transition)

Source Book: Phase transformati
Alloys by Porter, Easterling, Sher

Now, let us discuss a diffusional phase transformation. A diffusional phase transformation means that long range atomic diffusion is required to initiate this phase transformation and to complete the phase transformation. One is the initiation which is the nucleation and also the growth. So, mostly there are so far five different types of diffusional phase transformation has been observed. So, this 5 types are Polymorphic transformation. Here, you can take a pure metal the first example is a pure Iron.

In case of pure iron, if we go above 910 °C, then we will get γ-Fe. γ-Fe is the pure iron which is as a crystal structure of face centered cubic FCC. And now, if we cool it down; then the γ-Fe will transform into α-Fe and this transformation requires nucleation of α-Fein the γ-Fe boundaries. The solid-solid transformation during heating, the growth of those γ-Fe nuclei will occur.

α-Fe nuclei will appear during cooling of γ-Fe. So, this is a polymorphic transformation; where there is no compositional change. Now in case of a second type of diffusional phase transformation which is called as a Precipitation process. So, in a precipitation also it is also controlled by nucleation and growth of the precipitate. Like as an example I show you here, the aluminum-copper phase diagram. So, this is just a schematic diagram and here A and B, these are two different component of the system and they have a eutectic reaction in the phase diagram and they have a very low slope of this solvus line.

This is a solvus line and here we can simply chose such a composition and heat it up. This is the temperature axis and go up to here, then we will get a single phase α and now, if we quench it, then we can get a supersaturated solid solution or we cool slowly then β phase will be precipitated in α-matrix

What I want to mean that during cooling from α, so let us assume that this is the microstructure of α which is kept at this temperature. And so β will nucleate here, nucleation of β will occur and then β will grow. So, this is the precipitation phenomena because from one solid phase we are getting another solid phase which is precipitating in the matrix from the parent phase. So, this is a precipitation phenomenon and similar phenomena observed in an age-hardenable aluminum-copper system. The third type of diffusional phase transformation is the eutectoid transformation.

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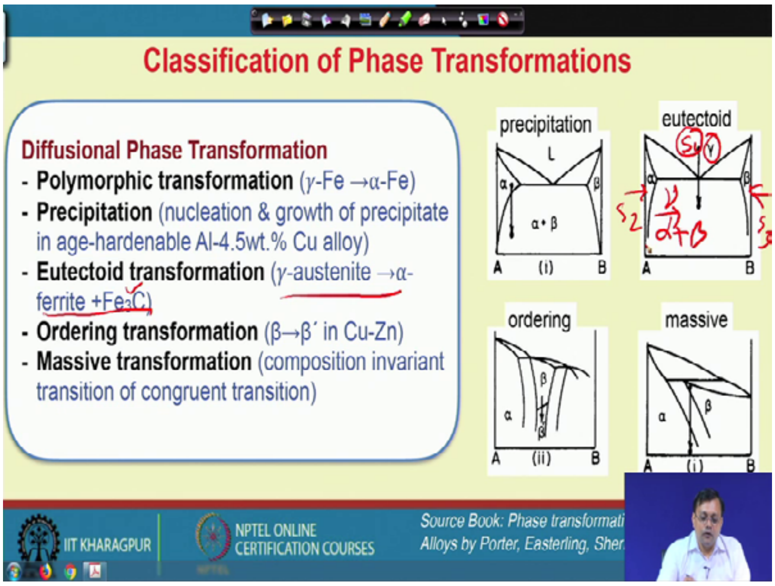

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In a eutectoid transformation, it is a solid-solid transformation means this is in a solid phase which is solid 1; where we will get basically two different solids. So, S_2 and S_3 from S_1 so, here it is γ to α and β. This is just a schematic we have shown and a specific example of such transformation is the γ-austenite that transform into α-ferrite to and cementite. Cementite is a metastable phase also and this eutectoid transformation we all know.

So, here let us say α and β, which will evolve from γ. Now there is also another diffusional phase transformation that is ordering. In ordering phenomena, the diffusion of atoms is not very long-range. However, a diffusion is required, but not like the diffusion that occure during solidification. So, here β to β' transformation an example in copper-zinc system. So, here you see if we choose a composition near to 50-50 of copper and zinc, copper-zinc type a system is shown here.

So, here from β, we will get an ordered phase which is β'. So, this dash actually represent that it is an ordered structure. So, a specific type of atoms means let us say the zinc atoms occupy some specific site in a FCC lattice or some other kind of structures. So, this is called as an Ordered transformation. However, the last type of transformation that is called a Massive transformation. So, the massive transformation, here the important feature of such transformation is a composition invariant transition. So, like there is no compositional change during transformation. Here, you may think that since there is no compositional change then there is no need of a diffusional transformation but it is not like that.

So here, one example of such Massive transformation shown here; so, if you have such kind of peritectic transformation where from β we will get actually α; However, please notice and take a note that there is no martensitic like transformation involved in this process. This is a complete diffusional phase transition from β to α. So, this is called as a Massive transformation; which involve diffusional movement of the atoms.

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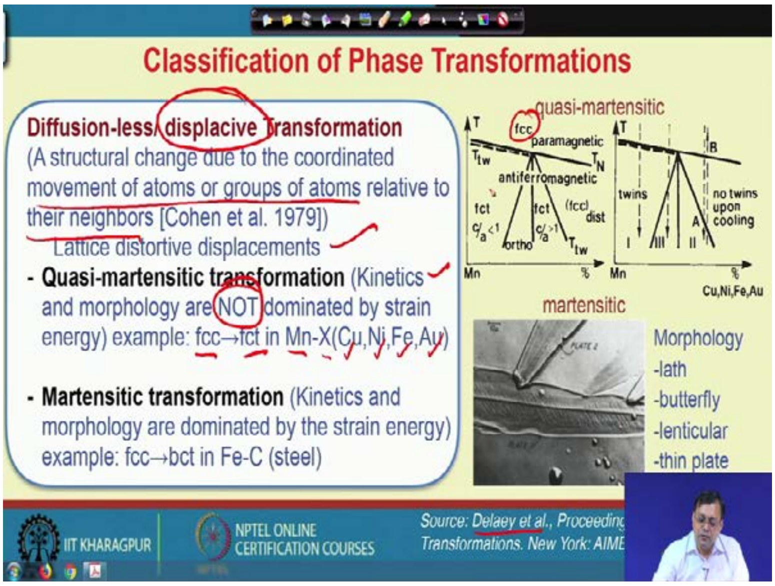

Classification of Phase Transformations

Diffusion-less/ displacive Transformation
(A structural change due to the coordinated movement of atoms or groups of atoms relative to their neighbors [Cohen et al. 1979])
Lattice distortive displacements

- **Quasi-martensitic transformation** (Kinetics and morphology are NOT dominated by strain energy) example: fcc→fct in Mn-X(Cu,Ni,Fe,Au)
- **Martensitic transformation** (Kinetics and morphology are dominated by the strain energy) example: fcc→bct in Fe-C (steel)

Source: Delaey et al., Proceeding
Transformations. New York: AIME

Now, let us discuss diffusion-less or military or another way we call it also a displacive transformation. So, in these particular case, a structural change occur due to a coordinated movement like military movement of the atoms or group of atoms and relative to its nearest neighbors.

So, the relative movement is almost 0. So, the diffusional, diffusion-less transformation or displacive transformation could be many different types and we will try to focus on these two type of transformation. One is martensitic transformation; another one is quasi-martensitic transformation. You may not have heard this quasi-martensitic earlier. However, the quasi-martensitic is a type of lattice distortive displacement; so this particularly means that there is a distortion in the lattice.

So, distortion in the lattice somehow means that in this particular case the kinetics and the morphology of the product phase is not dominated by the strain energy. There is a very classic example which was reported by Delaey et al quit long time ago in 1982 and he told that fcc to fct type of structure that evolve in manganese-X system. So, here X stands for copper, nickel, iron or let us say Gold.

So, this is a Quasi-martensitic transformation that occurs from a fcc phase to a fct type of structure. So, here a paramagnetic phase which show antiferromagnetic type of behavior. In that particular case, so here this is the temperature versus composition axis and you can see these are the sub-structures that are involved in this product phase.

Here, product phase is the face centered tetragonal and this is the parent phase is the face centered cubic. If we think about that how a fcc phase transform into face centered tetragonal, then we simply take a fcc lattice and stretch it into one direction may be in the Z axis or along the C axis.

Then, you will see that it is very easy to show how a fct structure can evolve in a fcc lattice. So, there is the limit of that composition beyond which that particular quasi martensitic transformation does not appear. And so these are mostly twin involve in this process; but you may also tell me sir, in case of martensitic transformation there is also twin is involve? Unfortunately, all martensitic transformation does not involve twinning. So, this is something new we will learn today.

So, let us continue with the martensitic type of transformation. In case of martensitic transformation, here be very specific that kinetics and morphology of the product phase are dominated by the strain energy which is alike a quasi-martensitic. So, in case of quasi-martensitic, it is not dominated where it is dominated by the strain energy.

So, it means that strain energy must be higher in case of martensitic transformation. So, we will slowly discuss what are they? So, and example is like FCC phase the transform into body centered tetragonal in case of a steel. It is iron carbon system. A very common example that you all know and I show you here one of the microstructure of such martensite.

So, here this is a martensitic plate and this is let us say a parent austenite and this is a body centered tetragonal in FCC. So, these are all martensitic plate. So, this martensitic plate so far we have seen in the textbook that this could be lath type or plate type. However, there are also two other type of martensite morphology people have observed.

So, in total there are four different type of morphology observed. One is lath type; another one is the butterfly type; one is could be the lenticular type and another could be thin plate type. So, this morphology is very important and it also depends on how these structures evolve.

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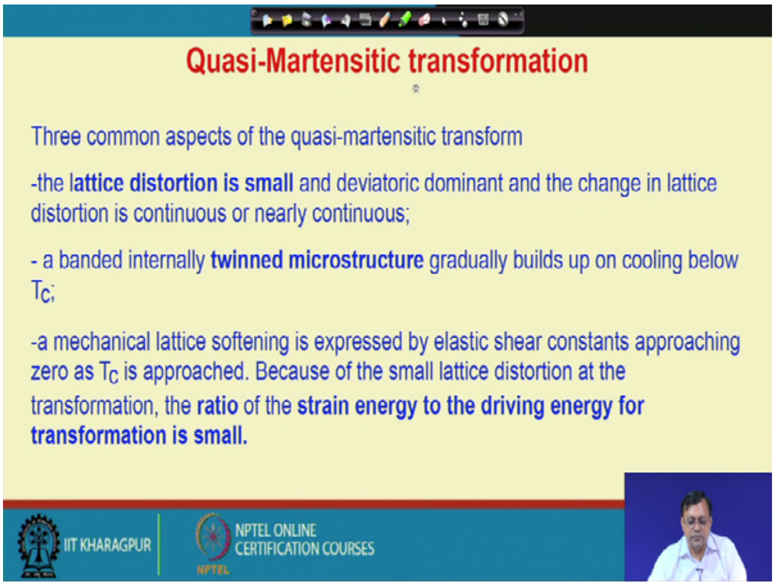

Quasi-Martensitic transformation

Three common aspects of the quasi-martensitic transform

-the **lattice distortion is small** and deviatoric dominant and the change in lattice distortion is continuous or nearly continuous;

- a banded internally **twinned microstructure** gradually builds up on cooling below T_C;

-a mechanical lattice softening is expressed by elastic shear constants approaching zero as T_C is approached. Because of the small lattice distortion at the transformation, the **ratio** of the **strain energy to the driving energy for transformation is small.**

So, let us try to summarize what is quasi martensitic transformation and what are the typical signature of such quasi martensitic transformation? So, 3 common aspect of such quasi martensitic transformation has been reported by Delaey et al. So, there should be a lattice distortion and this lattice distortion is very small and deviatoric dominant and the change in the lattice distortion is continuous or nearly continuous.

The second is that it may internally there could be twinned microstructure. So, here twin structure is the sub structure in the product phase; that gradually build up during cooling below the critical temperature. Here, since it is a magnetic and so on. So, we have seen and a mechanical lattice softening which occur by the elastic shear constant; when it is is approaching to Tc.

However, because of the small lattice distortion is involved, so, the ratio of the strain energy to the driving energy transformation is very small and that is the reason actually since this is lattice distortion small. So, the morphology is not dominated by that particular case.

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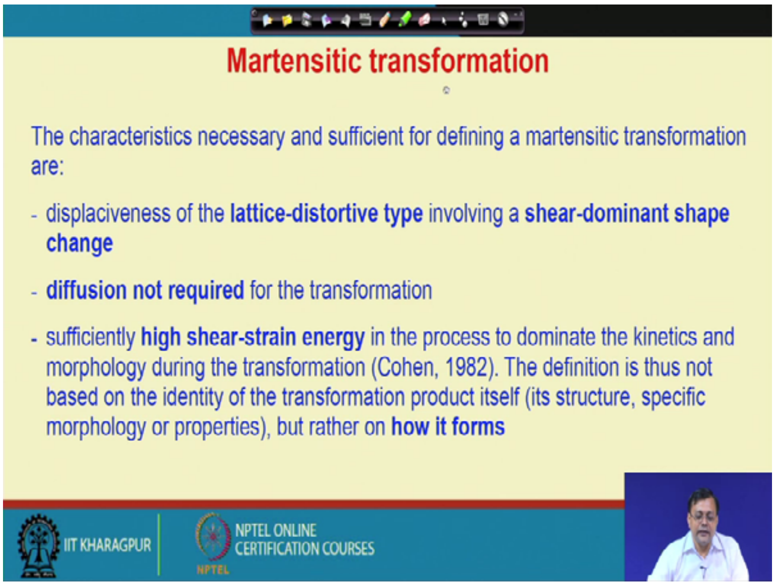

Martensitic transformation

The characteristics necessary and sufficient for defining a martensitic transformation are:

- displaciveness of the **lattice-distortive type** involving a **shear-dominant shape change**
- **diffusion not required** for the transformation
- sufficiently **high shear-strain energy** in the process to dominate the kinetics and morphology during the transformation (Cohen, 1982). The definition is thus not based on the identity of the transformation product itself (its structure, specific morphology or properties), but rather on **how it forms**

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Whereas, in case of a martensitic transformation, there are some typical signatures; what we look at? Here, the displaciveness or the displacive transformation or the lattice distortive type; in that case we see a shear dominant shape change of the lattice. So, there is a definite shape change involved in the lattice and diffusion is not required at all, whereas, there could be a sufficiently high shear strain energy in the process which has also been reported by Cohen et all from very long time 1982. So, the definition of martensitic transformation is therefore, is not based on the identity of the transformation product.

So, if you looked at a product phase and if you find twin, then you will automatically say sir, this is a martensitic. It is not like that, but rather how the new product has formed in the microstructure, in the parent microstructure and that is the characteristic of a martensitic transformation. Initially, you may think things are not very clear, but as we progress you will see that we will understand what a really martensitic transformation means and there are many different tools which has been discovered till today which characterizes a typical martensitic transformation; and how are the typical signatures.

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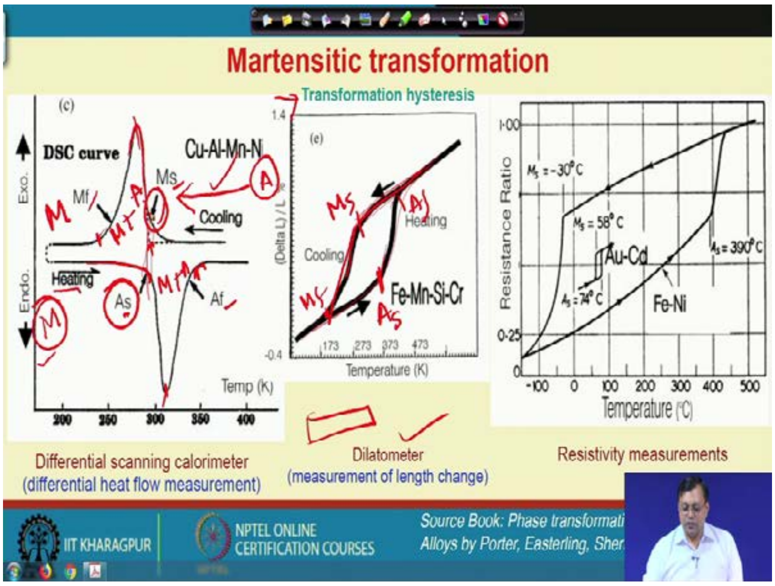

Martensitic transformation

Transformation hysteresis

Differential scanning calorimeter (differential heat flow measurement)

Dilatometer (measurement of length change)

Resistivity measurements

Source Book: Phase transformati
Alloys by Porter, Easterling, Sher

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A martensitics transformation is also often characterized by some sort of transformation hysteresis. So, there are 4 critical temperatures that characterizes a martensitic transformation. So, if you start with a martensite from room temperature or maybe we can start from austenite from a higher temperature. So, this austenite could be cooled and then, martensite will appear here.

So, this is the concept of the transformation which can be estimated through the tangents and then the transformation continues and then here is the end of the transformation. So, here all the phases here are the martensite and here martensite plus austenite and here it is the austenite. However, if you start with the martensite heating then it need some extra energy to transform.

So, here we call it as austenite start this suffix s stands for start and f stands for finish. So, here is also s stands for start and f , finish. So, here we have basically martensite plus austenite and here the all the martensite transforms into austenite. So, almost at the peak temperature, we can imagine or assume that 50 percent of the transformation from a martensite to austenite has completed or otherwise here. Very similar feature people have observed in case of a dilatometer.

In dilatometer, here the length changes or dimensional changes are measured. So, if you take a small rod of such martensite, then the very similar way you will see such kind of hysteresis where here is the austenite start and here is the austenite finish and here is the martensite start because of slope changes. So, here is the there is a plot which is linear and then the slope changes. So, the transformation has begun here. Here is also the slope changes that is why the transformation begin here. So, here this is actually M_f and the martensite finish and austenite start, there is always some sort of lag. You can see actually.

However, these temperature are somewhat closure bit closer because transformation require some extra energy. So, in case of resistivity measurement very similar thing has been observed; some similar hysteresis we are talking about has been observed. So, in this particular case, we have noticed that the temperature and the resistance axis in case of Iron-Nickel system, the transformation begin here which is the austenite start and here is the austenite finish and here is the martensite start and here is the martensite finish. So, you can see there are several system which are not at all steel. So, copper, aluminium, manganese, nickel here is also with chromium here is iron nickel system and is the gold cadmium system.

So, martensitic transformation occurs in many different systems and those all system shows some hysteresis; whereas, somewhere the hysteresis could be small or hysteresis could be larger. So, these are a differential scanning calorimeter plot or dilatometer or let us say resistive measurement that shows such kind of feature.

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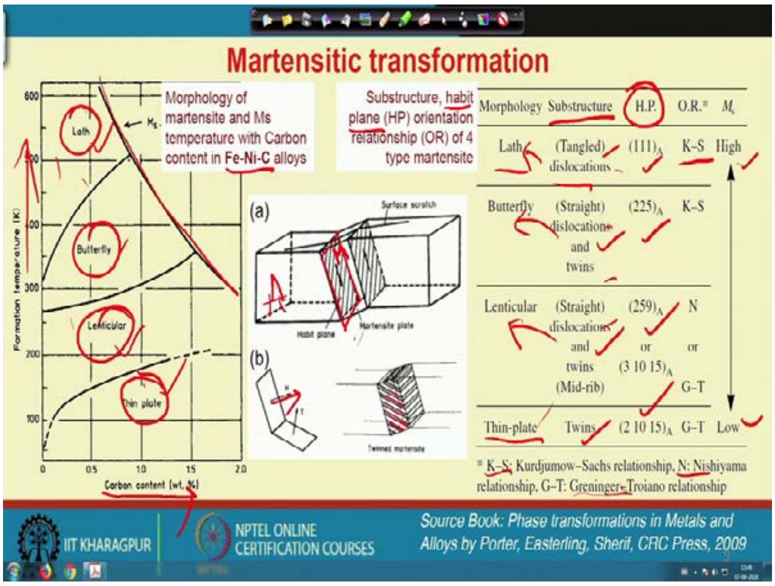

Martensitic transformation

Morphology of martensite and Ms temperature with Carbon content in Fe-Ni-C alloys

Substructure, habit plane (HP) orientation relationship (OR) of 4 type martensite

Morphology	Substructure	H.P.	O.R.*	M_s
Lath	(Tangled) dislocations	$(111)_A$	K–S	High
Butterfly	(Straight) dislocations and twins	$(225)_A$	K–S	
Lenticular	(Straight) dislocations and twins (Mid-rib)	$(259)_A$ or $(3\ 10\ 15)_A$	N or G–T	
Thin-plate	Twins	$(2\ 10\ 15)_A$	G–T	Low

* K–S: Kurdjumow–Sachs relationship, N: Nishiyama relationship, G–T: Greninger–Troiano relationship

Source Book: Phase transformations in Metals and Alloys by Porter, Easterling, Sherif, CRC Press, 2009

However, the morphology of the martensite could be also little different and in this particular slide, I show you that in case of Iron-Nickel-Carbon system, if we change carbon content and the transformation temperature if changes, the martensitic start temperature begin here; then we will get these four different morphology which I discussed with you just a few minutes ago with a lath, butterfly, lenticular or thin plate and these different morphology is involved with different kind of sub-structure.

So, a sub structure means; actually that like a tangled or let us say dislocation or dislocation and twin. So, not only twin can be involved in this process. So, in a lath we see only dislocations; whereas, in case of thin plate twin is only involve. Now, if we think about symmetrically that this is austenite and this is the product martensite, then this is the plane which is the interface between austenite and martensite which remain unrotated and undistorted is called as the habit plane.

So, the habit plane could be different in case of lath, butterfly, lenticular or let us say thin plate. So, this is the direction of the habit plane actually or this martensite could be with a sub structure of twin or dislocation. So, there are many different sub structure appears and the strain energy can change the morphology of the martensite from a lath to lenticular to thin plate and so on.

So, higher the temperature and the lower the temperature that has involved with this 4 type of transformation. So, you can see the orientation relationship or K-S relationship or let us say the Nishiyama type of relationship or let us say Greninger-type of relationship; there are many different relationships has been evolved and we can characterize this martensitic transformation with the product and so on.

So, in next class we will continue with this discussion to understand the phase transformation; how they are interlinked with the shape memory effect.

Thank you.