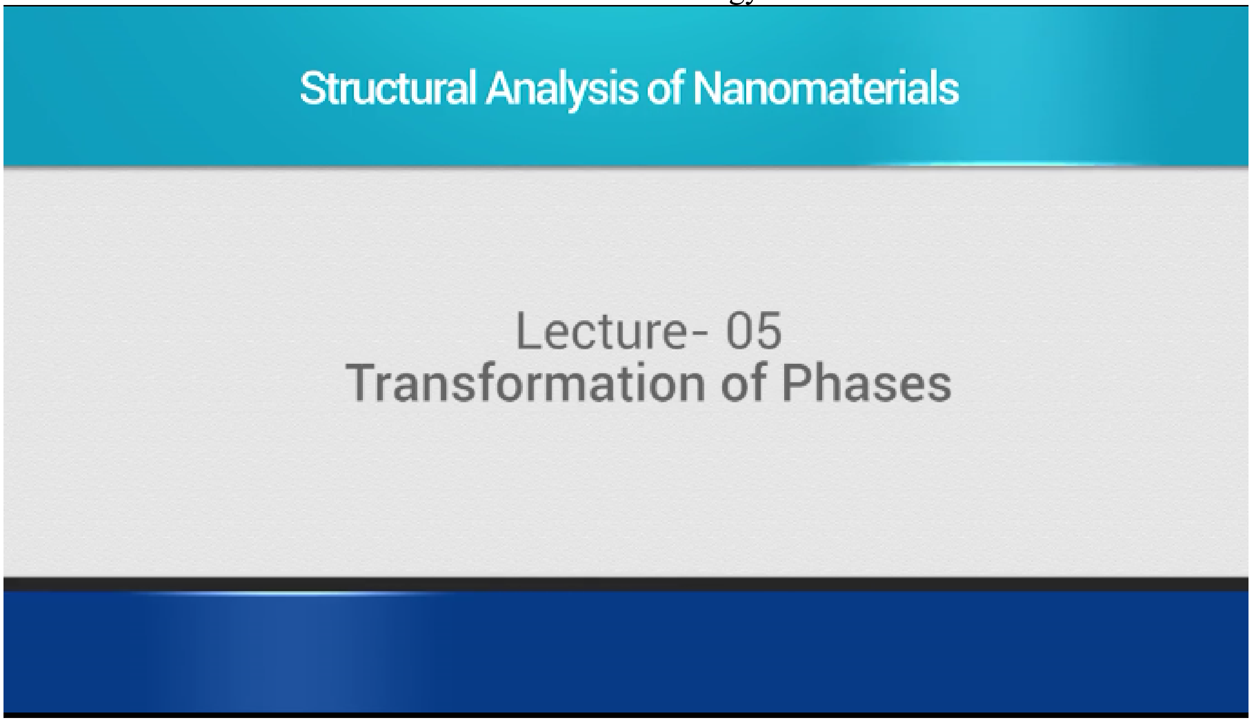
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
NPTEL
NPTEL ONLINE CERTIFICATION COURSE
Structural Analysis of Nanomaterials
LECTURE – 05
Transformation of Phases
With
Dr. Kaushik Pal
Department of Mechanical & Industrial Engineering
Indian Institute of Technology Roorkee



Structural Analysis of Nanomaterials

Lecture- 05
Transformation of Phases

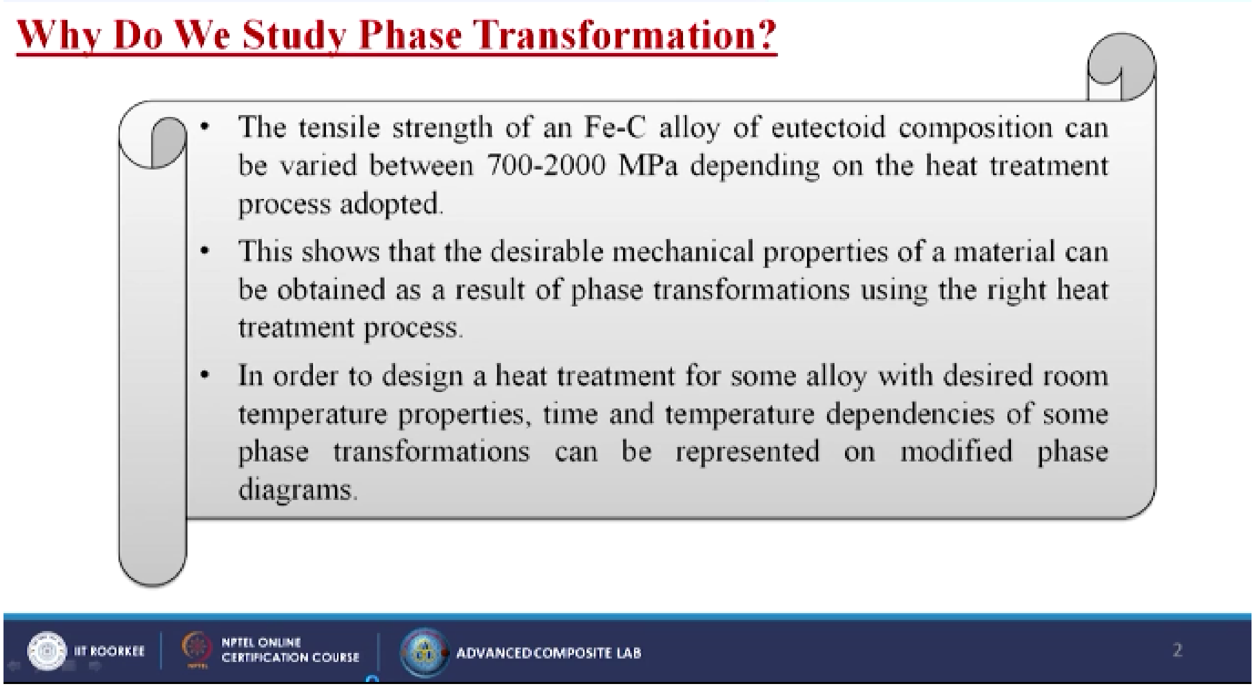
With

Dr. Kaushik Pal

Department of Mechanical & Industrial Engineering
Indian Institute of Technology Roorkee

Hello, today actually we are going to discuss about the transformation of phases, if you remember in our last two lectures we have discussed about the phase, about the phase diagram and then how we are getting the different materials at different temperature.

So in this particular course we are going to discuss about the phase transformations means we are going to change the material phases from one phase to another, so that we can get the better properties in terms of mechanical properties or maybe the thermal properties or maybe the electrical properties, sometimes it is required for us from the material scientist point of view that to change the material properties for gaining the materials in a wider applications.

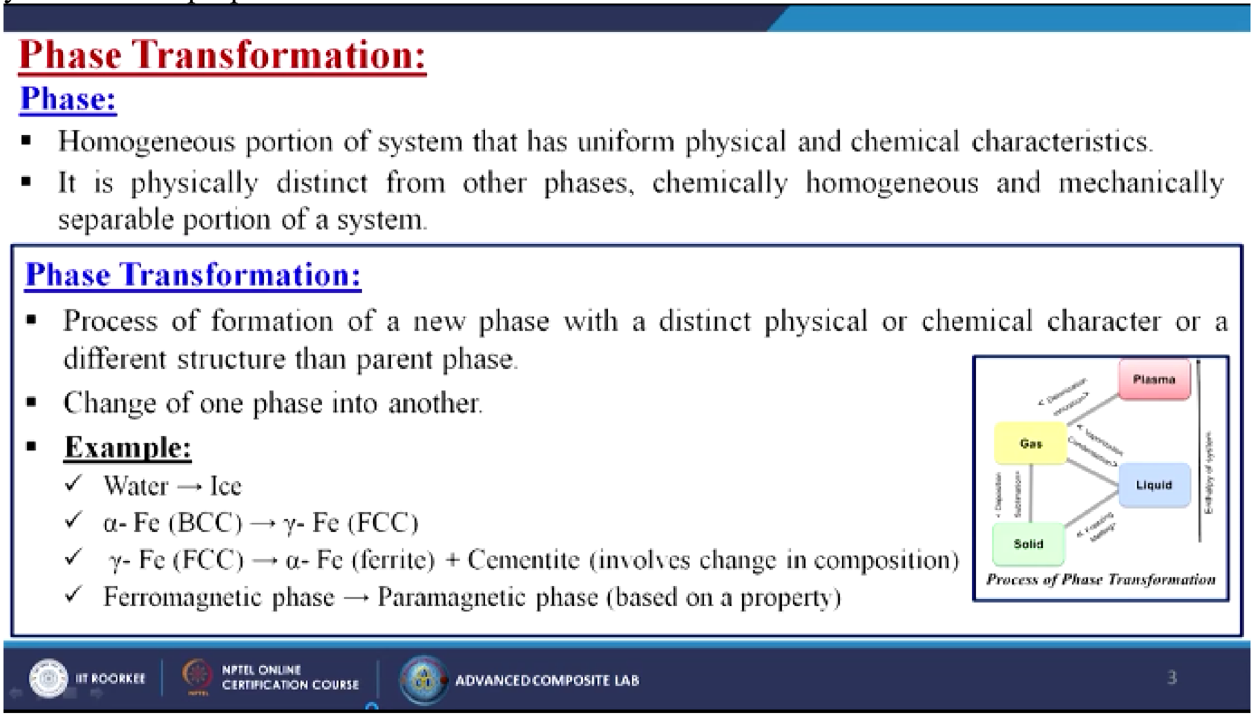


Why Do We Study Phase Transformation?

- The tensile strength of an Fe-C alloy of eutectoid composition can be varied between 700-2000 MPa depending on the heat treatment process adopted.
- This shows that the desirable mechanical properties of a material can be obtained as a result of phase transformations using the right heat treatment process.
- In order to design a heat treatment for some alloy with desired room temperature properties, time and temperature dependencies of some phase transformations can be represented on modified phase diagrams.

So first we are going to discuss that why we need to study about the phase transformations, say suppose I am giving you one small example, so the tensile strength of an iron carbon alloy of eutectoid compositions and be varied between 700 to 2000 megapascal depending on the heat treatment process adopted, so that means suppose I am having one materials, I am supplying the heat to that materials and the material is changing or maybe its segregating from one phase to another phase and it is giving you the better mechanical properties, the source that desirable mechanical properties of materials can be obtained as a result of phase transformations using the right heat treatment process, yes off course it should be the proper, it doesn't means that every time I can give some heat or maybe I can cool down the materials and the material will give that desired properties no, there is some specific conditions and it varies from materials to materials physical properties that it can show the better properties.

In order to design a heat treatment for some alloy with desired room temperature properties, time and temperature dependencies of some phase transformations can be represented on modified phase diagram, yes of course the material which we are preparing day to day in our labs or maybe in the industry, so just to increase certain kind of properties, we can do the heat treatment process of that particular materials, but we have to know the phase transformations of that materials that at what temperature, at what pressure the material will behave or maybe it can give you the better properties.



Phase Transformation:

Phase:

- Homogeneous portion of system that has uniform physical and chemical characteristics.
- It is physically distinct from other phases, chemically homogeneous and mechanically separable portion of a system.

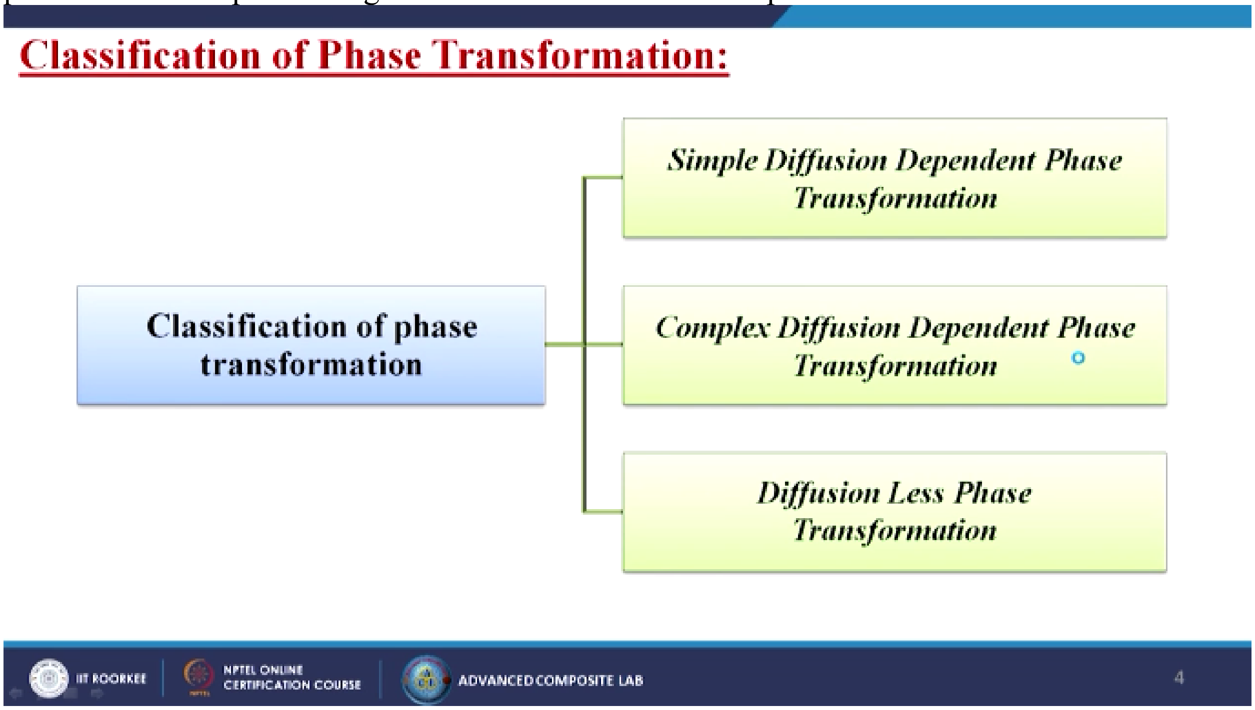
Phase Transformation:

- Process of formation of a new phase with a distinct physical or chemical character or a different structure than parent phase.
- Change of one phase into another.
- **Example:**
  - ✓ Water → Ice
  - ✓ α- Fe (BCC) → γ- Fe (FCC)
  - ✓ γ- Fe (FCC) → α- Fe (ferrite) + Cementite (involves change in composition)
  - ✓ Ferromagnetic phase → Paramagnetic phase (based on a property)

Process of Phase Transformation

So first, before going to start let us know what is phase? So phase is the homogeneous portions of system that has uniform physical and chemical characteristics, it is physically distinct from other phases, chemically homogeneous because the material throughout the whole area or maybe the whole volume it will show you the same properties, and mechanically separable portions of a system.

Now what is phase transformations? Process of formation of a new phase with a distinct physical or chemical character of a different structure then parent phase, change of one phase into the another say simple we are changing the phase from one, maybe from solid to liquid, or maybe sometimes it may happen from liquid to solid or maybe sometimes it may happen from solid to solid or maybe liquid to liquid, so there are so many types or maybe so many steps are available by which we can change the properties of the material. So suppose if I give an example, say suppose from water to ice, simple from liquid to solid we are changing its phases, alpha, iron, BCC to gamma iron FCC structure or maybe from gamma iron FCC to alpha, iron, ferrite + cementite which involves changing in compositions, some ferromagnetic phase to paramagnetic phase based on a property, so sometimes we can change the magnetic properties of that materials also, and this is the things which I also discussed in our last lecture that suppose if I go directly from the solid to liquid, so I'll go through the melting and from liquid to solid I'll come through the freezing process. Liquid to gas I'll go to the vaporization process and from gas to liquid it will be the condensation process, if I go to solid to gas directly, it is called the sublimation process and if it is from gas to solid it is called the deposition process, and if I go for the gas to plasma which is generally we are thinking that it is the four state matter or maybe fourth state of any kind of materials, so direct if I go, want to go from gas to plasma it is called the ionization process and from plasma to gas it is called the deionization process.

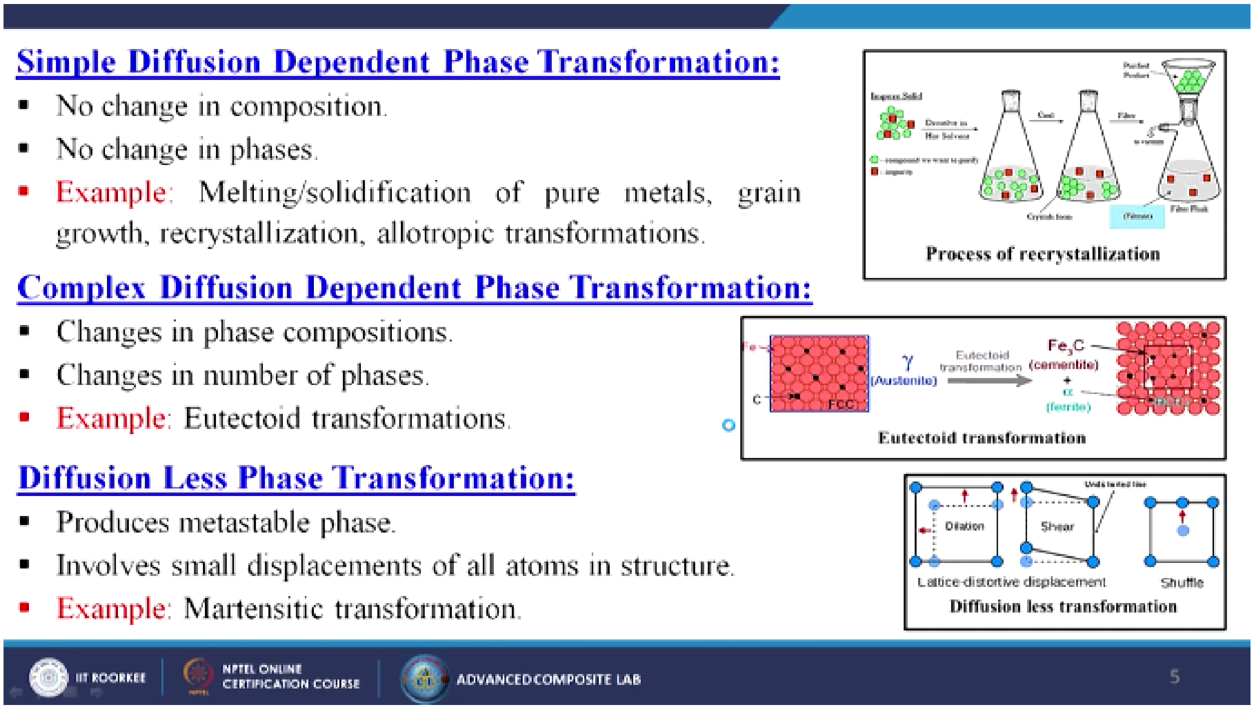


Classification of Phase Transformation:

Classification of phase transformation

- ***Simple Diffusion Dependent Phase Transformation***
- ***Complex Diffusion Dependent Phase Transformation***
- ***Diffusion Less Phase Transformation***

So now we have to discuss about the classifications of the phase transformations, so it is divided into three parts, first one is called the simple diffusion dependent phase transformations, second one is called the complex diffusion dependent phase transformations, and third one is called the diffusion less phase transformations.



Simple Diffusion Dependent Phase Transformation:

- No change in composition.
- No change in phases.
- Example: Melting/solidification of pure metals, grain growth, recrystallization, allotropic transformations.

Process of recrystallization

Complex Diffusion Dependent Phase Transformation:

- Changes in phase compositions.
- Changes in number of phases.
- Example: Eutectoid transformations.

Eutectoid transformation

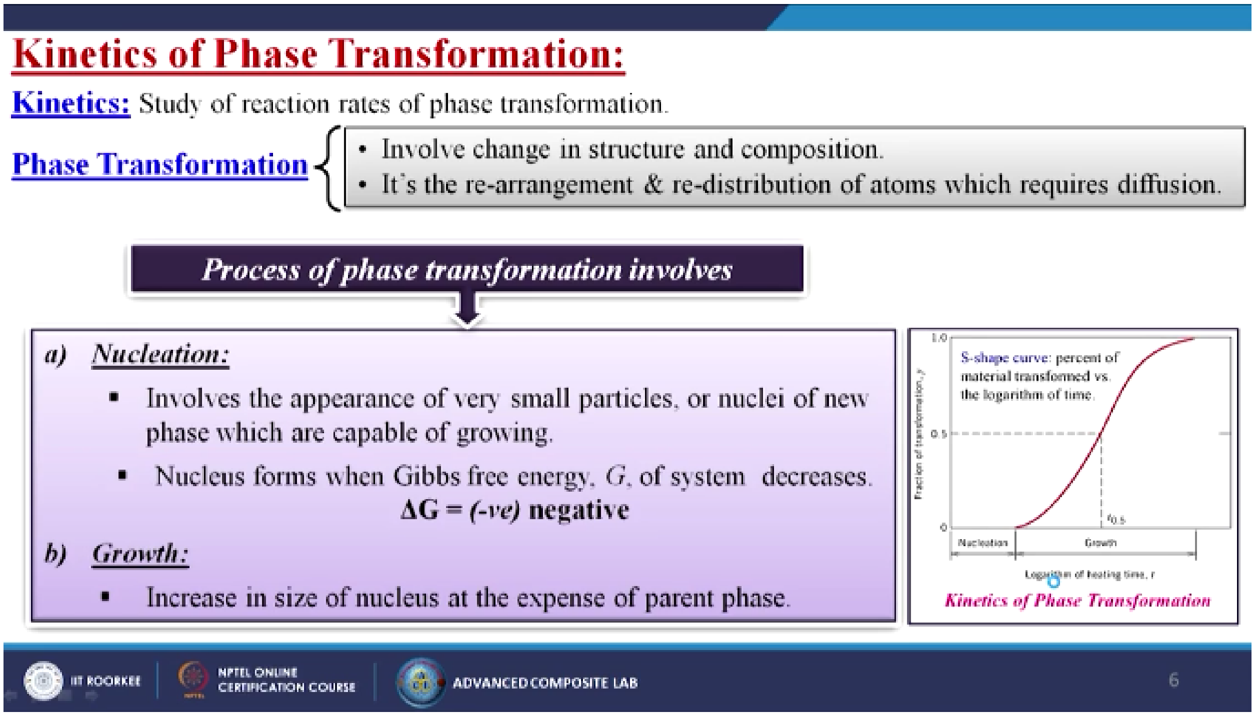
Diffusion Less Phase Transformation:

- Produces metastable phase.
- Involves small displacements of all atoms in structure.
- Example: Martensitic transformation.

Diffusion less transformation

So what is simple diffusion dependent phase transformations, so in that case no change in compositions, no change in phases. Example, melting and solidification of pure metals, grain growth, recrystallization, allotropic transformations, say suppose I'm having any solid metals, in that metals some impurities are there, so what I am going to do? Either I'll dissolve into some solvent or maybe I can heat it and then simple from that I'll remove the impurity, so in this case you can see that from by the sol-gel methods we are dissolving in some hot solvent and then after filtering just we are removing the filtrate or maybe the impurities from that particular material.

Next is called the complex diffusion dependent phase transformations, where there is no change in phase compositions only changes in number of phases, example the eutectoid transformation, say suppose I am having the gamma austenite and I am doing the eutectoid transformations over there, so I am getting 2 types of phases over there, one is called the cementite which is nothing but the Fe3C, another one is called the alpha ferrite, and you can distinctly see the crystal structure of this two phases are different, then we are going to discuss about the diffusion less phase transformations which produces the metastable phase involves small displacement of all atoms in structure, example martensitic transformations, in this image you can understand that the atom they are going to shipped or maybe they are going to change their places and due to that some shuffling is taking place, some distortion is taking place in this particular point and some are the undistorted atoms, so like this way the diffusion less phase transformations is taking place.



Kinetics of Phase Transformation:

Kinetics: Study of reaction rates of phase transformation.

Phase Transformation
- Involve change in structure and composition.
- It's the re-arrangement & re-distribution of atoms which requires diffusion.

Process of phase transformation involves

a) ***Nucleation:***
- Involves the appearance of very small particles, or nuclei of new phase which are capable of growing.
- Nucleus forms when Gibbs free energy, G, of system decreases. $\Delta G = (-ve)$ **negative**

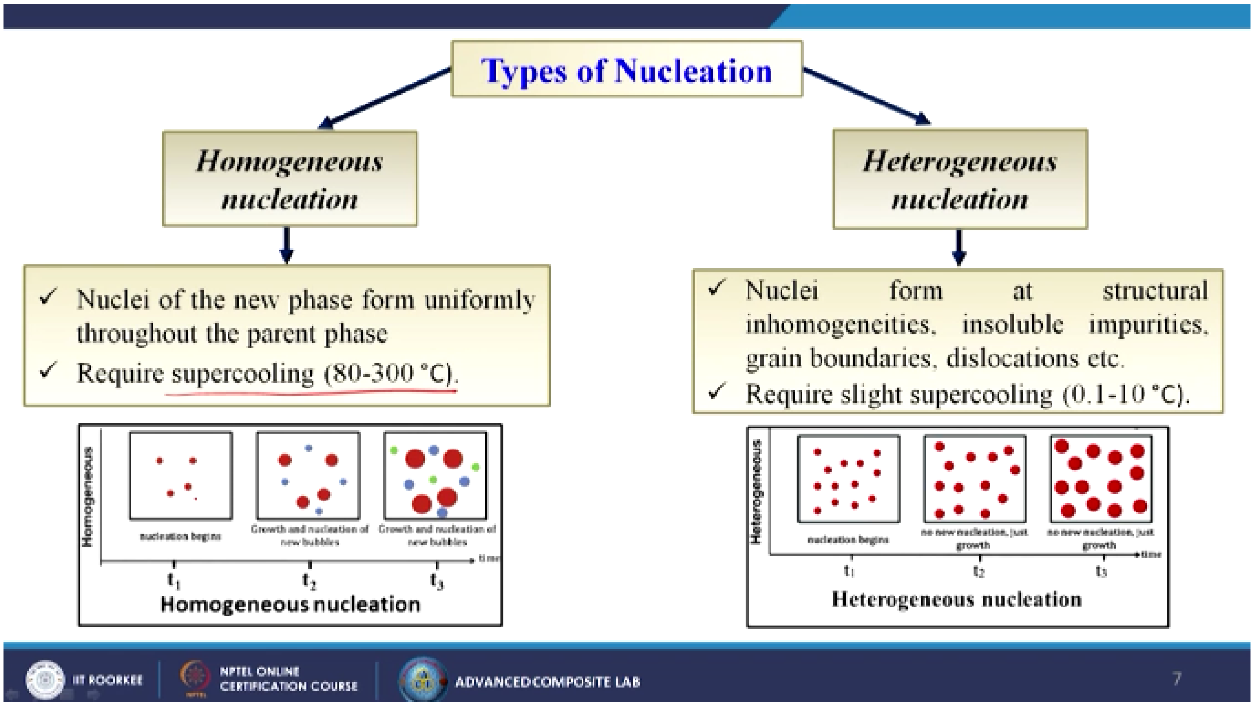
b) ***Growth:***
- Increase in size of nucleus at the expense of parent phase.

Kinetics of Phase Transformation

Now what are the actual kinetic of phase transformations? So generally the kinetics is the study of reaction rates of phase transformations, so phase transformations generally it involves in change in structure and compositions of any kind of materials, it's the rearrangement and redistribution of atoms which requires the diffusion process, so process of phase transformations involves two things, one is called the nucleations, another one is called the growth.

Nucleation means the it is the initial stage, so first the material with nucleate it will start to be born and then after that, that will become bigger and bigger, so it's like a humans birth type of things, so suppose I am having the embryo then it will be little bit bigger so it's like a baby, so nucleation is taking place and then from that baby to the mature person that means the growth is taking place, so nucleation involves the appearance of very small particles or nuclei of a new phase which are capable of growing, so that means it is the small things in which it is going to grow.

Nucleus forms when Gibbs free energy G of system decreases, del G is called, here is the negative. Now growth, growth is the increase in size of nucleus at the expense of parent phases, so now it has been born and now it will become bigger and bigger, so here this is known as the nucleations, and then after that the growth has started tremendously and this is the graph of fraction, of transformations versus logarithmic of heating time.



Types of Nucleation

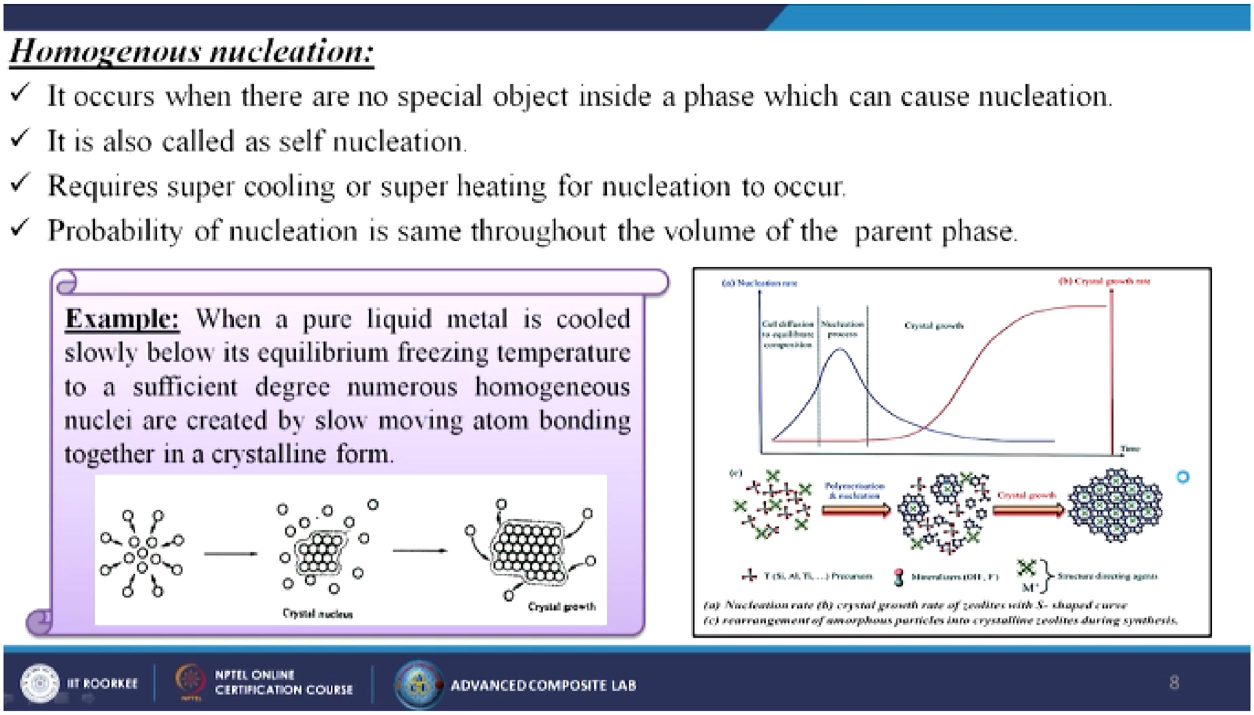
Homogeneous nucleation

- ✓ Nuclei of the new phase form uniformly throughout the parent phase
- ✓ Require supercooling (80-300 °C).

Heterogeneous nucleation

- ✓ Nuclei form at structural inhomogeneities, insoluble impurities, grain boundaries, dislocations etc.
- ✓ Require slight supercooling (0.1-10 °C).

Now there are two types of nucleations, one is called the homogeneous nucleations, another one is called the heterogeneous nucleations, what is homogeneous nucleations? First, I'll tell you the theory, nuclei of the new phase form uniformly throughout the parent phase require super cooling of 80 to 300 degree centigrade, from this image you can understand that at time T1 that nucleations begins, means small, small particles or maybe the atoms has been formed, and then after that growth at nucleations, so whatever has formed earlier that is becoming bigger and bigger and also some new phases or maybe the new atoms are still forming, so like this way it is called the homogeneous, so at last growth and nucleations of the new bubbles is going at higher time also, and when we are talking about the heterogeneous, heterogeneous means nuclei form at structural inhomogeneities, insoluble impurities, grain boundaries and the dislocations, require slight super cooling it's 0.1 to 10 degree centigrade, so in this particular case nucleus have started, no new nucleation will be there in future, so only the growth will be taking place of that existing nucleations, so no new nucleations just growth is taking place and at the higher time also the same thing is happening.



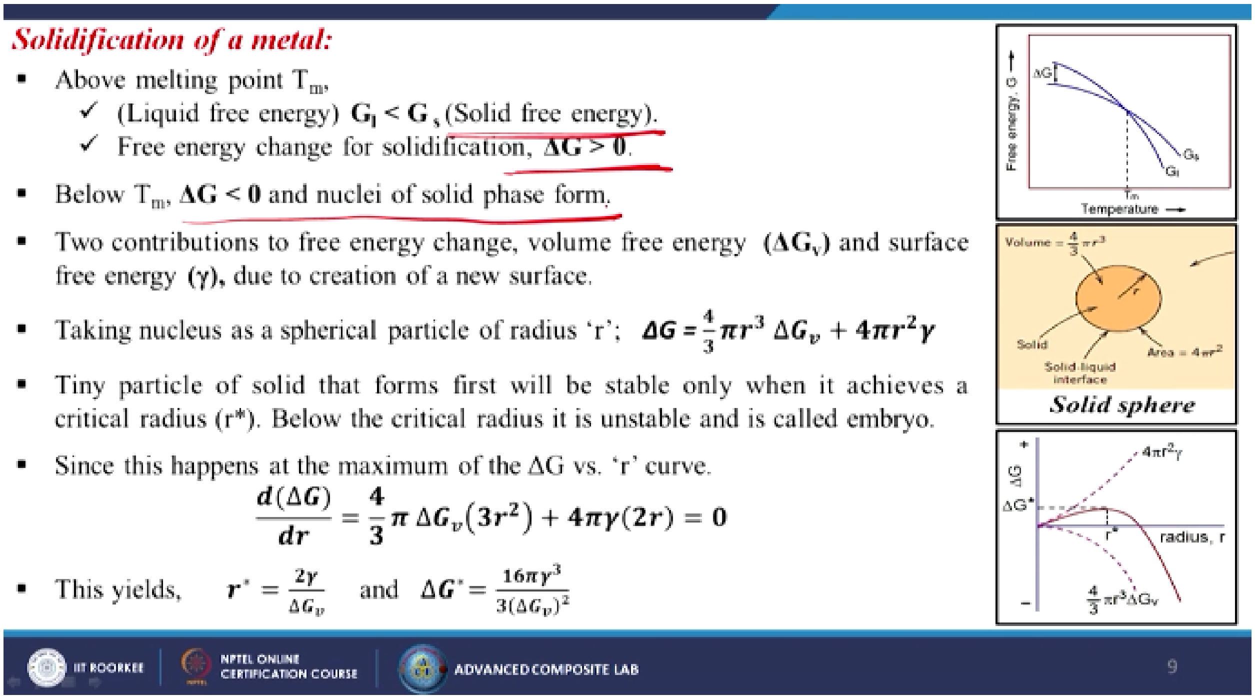
Homogenous nucleation:

- ✓ It occurs when there are no special object inside a phase which can cause nucleation.
- ✓ It is also called as self nucleation.
- ✓ Requires super cooling or super heating for nucleation to occur.
- ✓ Probability of nucleation is same throughout the volume of the parent phase.

Example: When a pure liquid metal is cooled slowly below its equilibrium freezing temperature to a sufficient degree numerous homogeneous nuclei are created by slow moving atom bonding together in a crystalline form.

(a) Nucleation rate (b) crystal growth rate of zeolites with S- shaped curve
(c) rearrangement of amorphous particles into crystalline zeolites during synthesis.

Now we are going to details for the homogeneous nucleations, it occurs when there are no special object inside the phase which can cause the nucleations, it is also called as the self-nucleations, requires super cooling or super heating for nucleation to occur, so super cooling and super heating is required, probability of nucleation is same throughout the volume of the parent phase, what is the example? When a pure liquid metal is cooled slowly because it's equilibrium freezing temperature to a sufficient degree numerous homogeneous nuclei are created by slowly moving atom bonding together in a crystalline form, so in this particular case what happened? So crystal nucleus is forming and then after crystal growth is taking place, but still some new atoms are creating or maybe the bubbles are creating, so this is the examples of the homogeneous nucleations.



Solidification of a metal:

- Above melting point T_m,
  - ✓ (Liquid free energy) $G_l < G_s$ (Solid free energy).
  - ✓ Free energy change for solidification, $\Delta G > 0$.
- Below T_m, $\Delta G < 0$ and nuclei of solid phase form.
- Two contributions to free energy change, volume free energy (ΔG_v) and surface free energy (γ), due to creation of a new surface.
- Taking nucleus as a spherical particle of radius 'r'; $\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$
- Tiny particle of solid that forms first will be stable only when it achieves a critical radius (r*). Below the critical radius it is unstable and is called embryo.
- Since this happens at the maximum of the ΔG vs. 'r' curve.

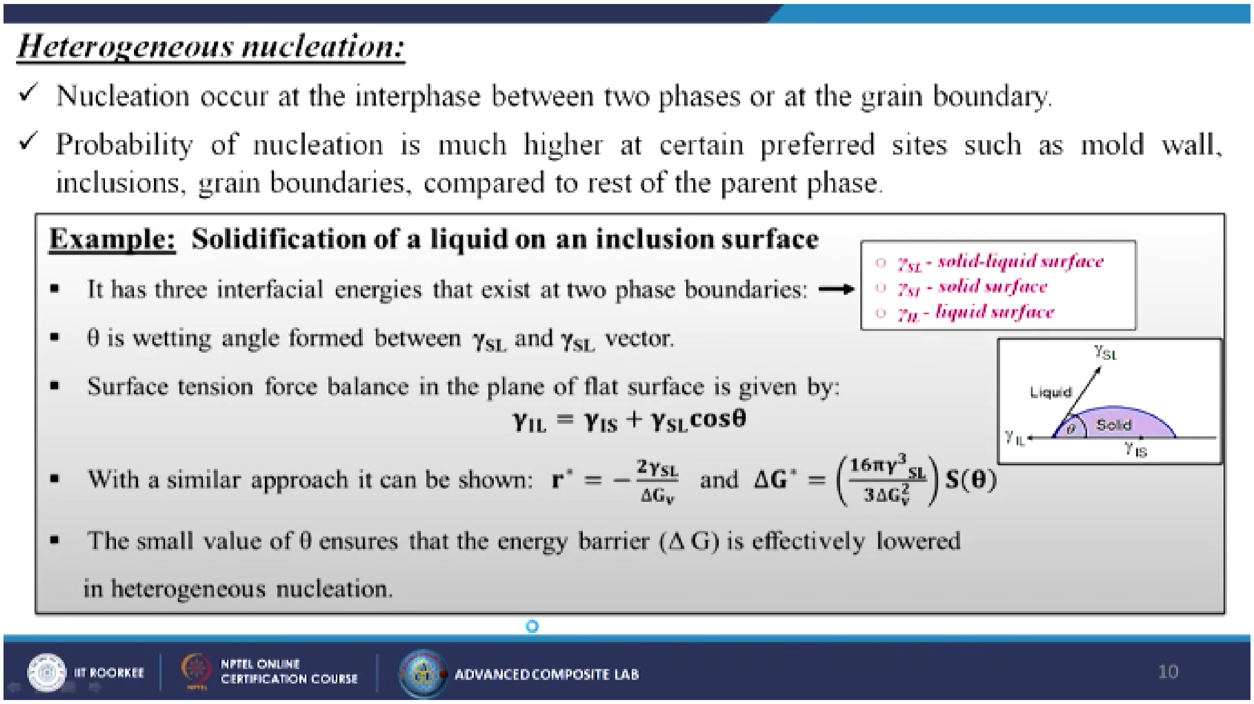
$$\frac{d(\Delta G)}{dr} = \frac{4}{3}\pi \Delta G_v(3r^2) + 4\pi\gamma(2r) = 0$$

- This yields, $r^* = \frac{2\gamma}{\Delta G_v}$ and $\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$

Solid sphere

Now we are going to discuss about the solidifications of a metal, so above melting point like Tm generally we are giving the notations for the melting temperature, liquid free energy Gl is less than Gs so which is called the solid free energy Gs, so free energy change for solidification del G is greater than 0, so below melting temperature del G is less than 0 and nuclei of the solid phase form means it starting, two contributions to free energy change, volume free energy that is del Gv and surface free energy that is gamma due to creation of a new surface. Taking nucleus as a spherical particle of radius R, so in this particular case this is the formation is taking place, nucleation has started, so suppose this is the atom and we are taking its radius as a R, so this is the solid liquid interface and the rest of the area is the liquid one, so del G = 4/3 pi R cube del Gv + 4 pi R square gamma, tiny particle of solid that forms first will be stable only when it achieves a critical radius R prime, below the critical radius it is unstable and it is called the embryo, that means it has been started and then this radius is not stable, after certain time it will achieve the stable radius or maybe the stable shape or maybe the size.

Since this happens at the maximum of the del G versus R curve, so D upon del G/dr = 4/3 pi del Gv (3r square) + 4 pi gamma (2r) = 0, this yields R prime = 2 gamma/del Gv and del G prime = 16 pi gamma cube/3 del Gv square.



Heterogeneous nucleation:

- ✓ Nucleation occur at the interphase between two phases or at the grain boundary.
- ✓ Probability of nucleation is much higher at certain preferred sites such as mold wall, inclusions, grain boundaries, compared to rest of the parent phase.

Example: Solidification of a liquid on an inclusion surface

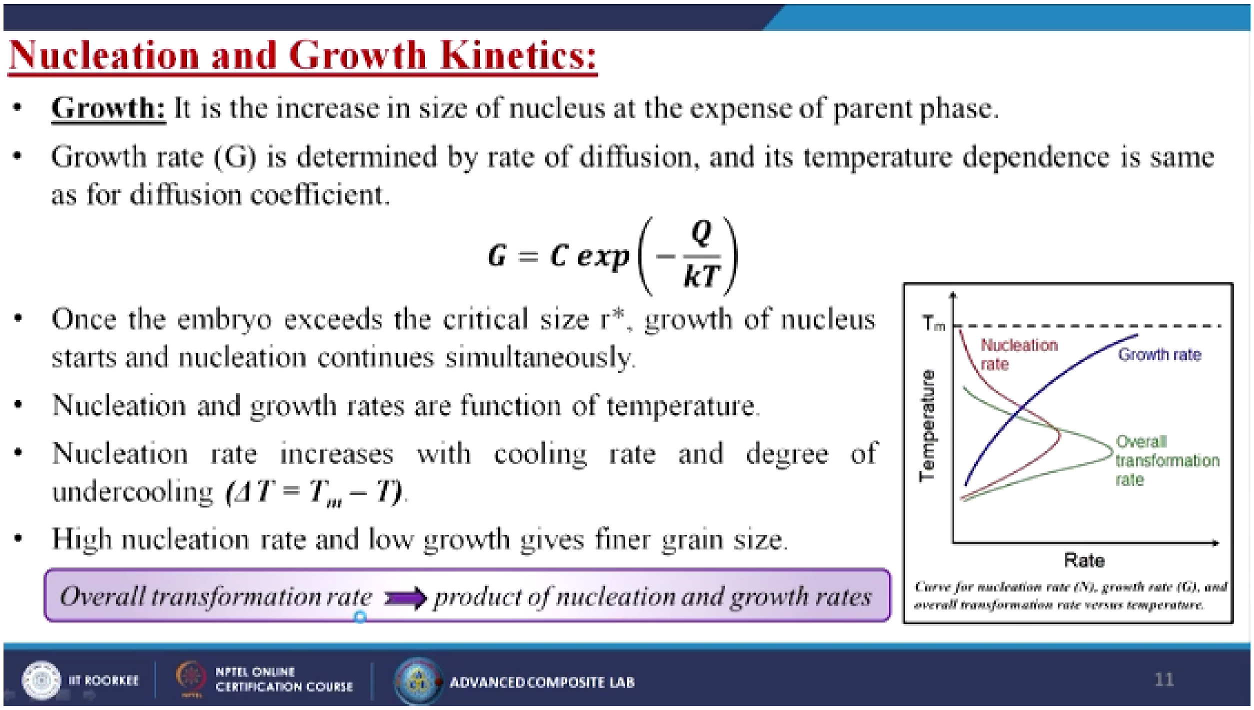
- It has three interfacial energies that exist at two phase boundaries: →
  - ○ γ_{SL} - *solid-liquid surface*
  - ○ γ_{SI} - *solid surface*
  - ○ γ_{IL} - *liquid surface*
- θ is wetting angle formed between γ_{SL} and γ_{SL} vector.
- Surface tension force balance in the plane of flat surface is given by:

$$\gamma_{IL} = \gamma_{IS} + \gamma_{SL}\cos\theta$$

- With a similar approach it can be shown: $r^* = -\frac{2\gamma_{SL}}{\Delta G_v}$ and $\Delta G^* = \left(\frac{16\pi\gamma^3{}_{SL}}{3\Delta G_v^2}\right)S(\theta)$
- The small value of θ ensures that the energy barrier (Δ G) is effectively lowered in heterogeneous nucleation.

So now we are going to discuss about the heterogeneous nucleations, so already I told that in the heterogeneous nucleations no new nucleation will be taking place, only whatever the nucleations has already been done in earlier the growth will be only taking place, so in this case nucleations occur at the interface between two phases or at the grain boundary, probability of nucleations is much higher at certain preferred sites such as mold wall, inclusions, grain boundaries, and compared to the rest of the parent phase, example solidification of a liquid on an inclusion surface, so suppose we are having that liquid and solid and then this surface is known as the gamma IS which is nothing but the solid surface, and gamma IL which is nothing but the liquid surface, and gamma SL which is called the solid and liquid surface is this one.

So now it has three interfacial energies that exists at two phases boundaries, theta is wetting angle formed between the gamma SL and gamma SL vector, so generally we are doing it by the contact angle measurement, so surface tension force balance in the plane of flat surface is given by gamma IL = gamma IS + gamma SL cos theta with a similar approach it can be shown that R prime = -2 gamma SL/del Gv, and del G prime = 16 pi gamma cube SL/3 delta Gv square into S theta, so the small value of theta ensures that energy barrier del G is effectively lowered in heterogeneous nucleations.



Nucleation and Growth Kinetics:

- **Growth:** It is the increase in size of nucleus at the expense of parent phase.
- Growth rate (G) is determined by rate of diffusion, and its temperature dependence is same as for diffusion coefficient.

$$G = C\,exp\left(-\frac{Q}{kT}\right)$$

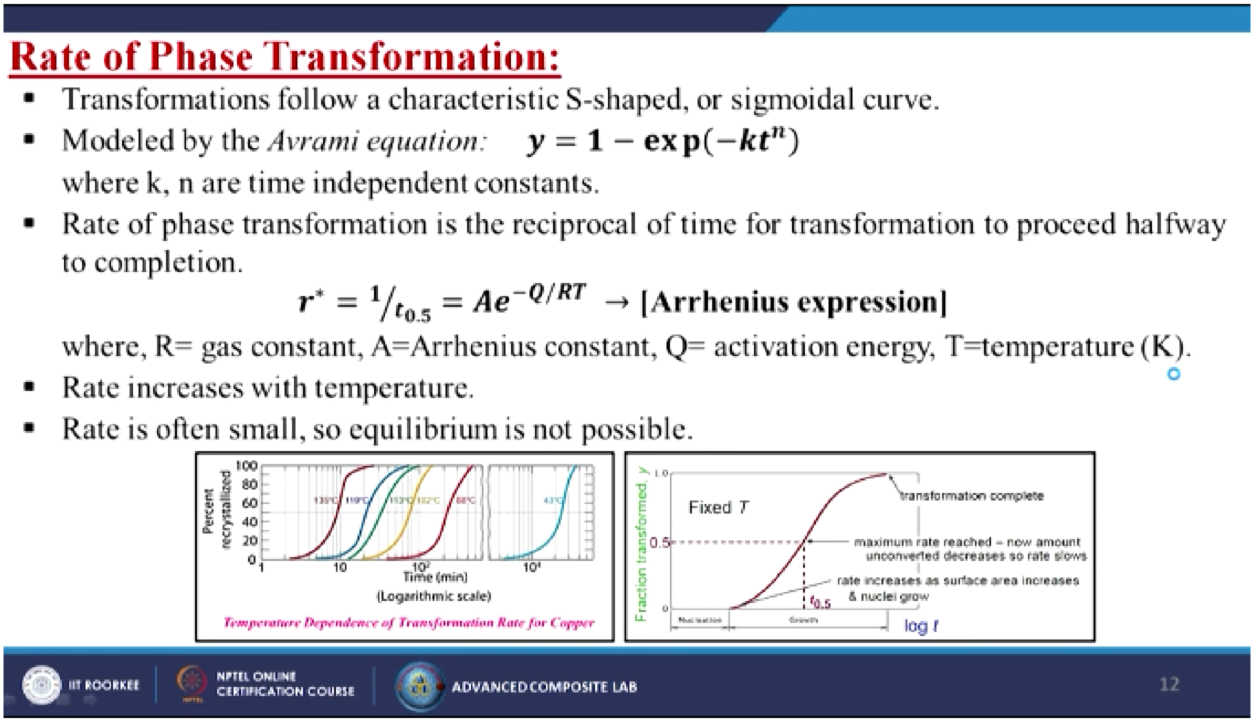
- Once the embryo exceeds the critical size r*, growth of nucleus starts and nucleation continues simultaneously.
- Nucleation and growth rates are function of temperature.
- Nucleation rate increases with cooling rate and degree of undercooling $(\Delta T = T_m - T)$.
- High nucleation rate and low growth gives finer grain size.

Overall transformation rate ➡ *product of nucleation and growth rates*

Curve for nucleation rate (N), growth rate (G), and overall transformation rate versus temperature.

So now nucleation and the growth kinetics, growth it is the increase in size of nucleus at the expense of parent phase, growth rate G is determined by the rate of diffusions and its temperature dependence is same as for diffusion coefficient, so G = C exponential (-Q/KT), once the embryo exceeds the critical size R prime which I have already told that critical diameter when it will cross growth of nucleus starts and nucleation continues simultaneously, nucleations and growth rates are function of temperature that means all the embryo is not going to be born, so it should first reach the critical diameter or maybe the critical radius and then after that the nucleation or maybe the grain growth will be taking place.

Nucleation rate increases with cooling rate and degree of under cooling that means del T = Tm – T, Tm is the melting temperature. High nucleation rate and low growth gives the finer grain size, so what is the consequence? Overall transformation rate means product of nucleations and the growth rates, so here is the graph that is temperature into the Y axis and the rate into the X axis and you can see that this is the nucleation rate, this is the growth and this is the melting temperature of that materials and this is the overall transformation rate which is nothing but the product of this nucleation rate and the growth rates.



Rate of Phase Transformation:

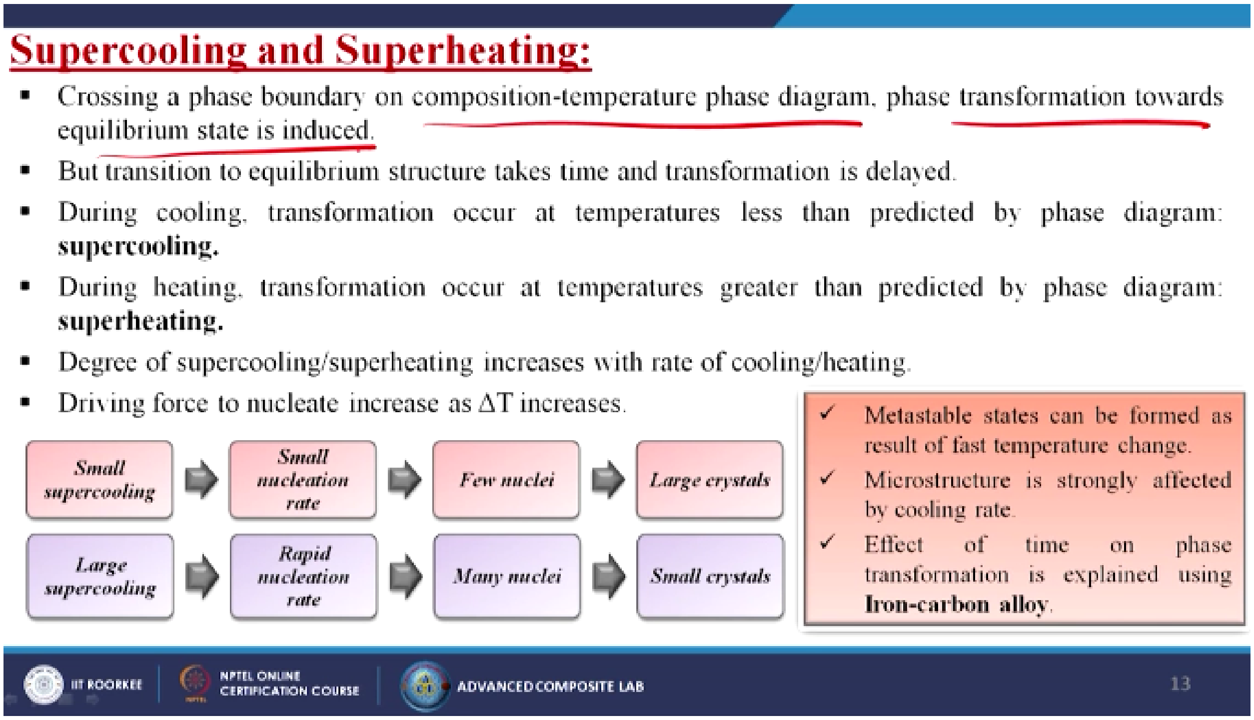
- Transformations follow a characteristic S-shaped, or sigmoidal curve.
- Modeled by the *Avrami equation:* $\mathbf{y = 1 - \exp(-kt^n)}$
  where k, n are time independent constants.
- Rate of phase transformation is the reciprocal of time for transformation to proceed halfway to completion.

$$r^* = {}^{1}/_{t_{0.5}} = Ae^{-Q/RT} \rightarrow \textbf{[Arrhenius expression]}$$

  where, R= gas constant, A=Arrhenius constant, Q= activation energy, T=temperature (K).
- Rate increases with temperature.
- Rate is often small, so equilibrium is not possible.

Temperature Dependence of Transformation Rate for Copper

Now we are going to discuss about the rate of phase transformations, so transformations follow a characteristics S-shaped or maybe the sigmoidal curve, so modeled by the Avrami equations which is known as the Y = 1 – exponential (-kt to the power n), where K and N are time independent constants. Rate of phase transformation is the reciprocal of time for transformation to proceed half way to completions which is R prime = 1/t0.5 = Ae to the power –Q/RT that is known as the Arrhenius expressions, where R is the gas constant, A is the Arrhenius constant, Q is the activation energy, and the T is the absolute temperature that is in kelvin. Rate increase with temperature, rate is often small, so equilibrium is not possible, so in this particular case you can see that with the temperature that how the percent recrystallizations is taking place, temperature dependence of transformation rate for copper, so this is the example.



Supercooling and Superheating:

- Crossing a phase boundary on composition-temperature phase diagram, phase transformation towards equilibrium state is induced.
- But transition to equilibrium structure takes time and transformation is delayed.
- During cooling, transformation occur at temperatures less than predicted by phase diagram: **supercooling.**
- During heating, transformation occur at temperatures greater than predicted by phase diagram: **superheating.**
- Degree of supercooling/superheating increases with rate of cooling/heating.
- Driving force to nucleate increase as ΔT increases.

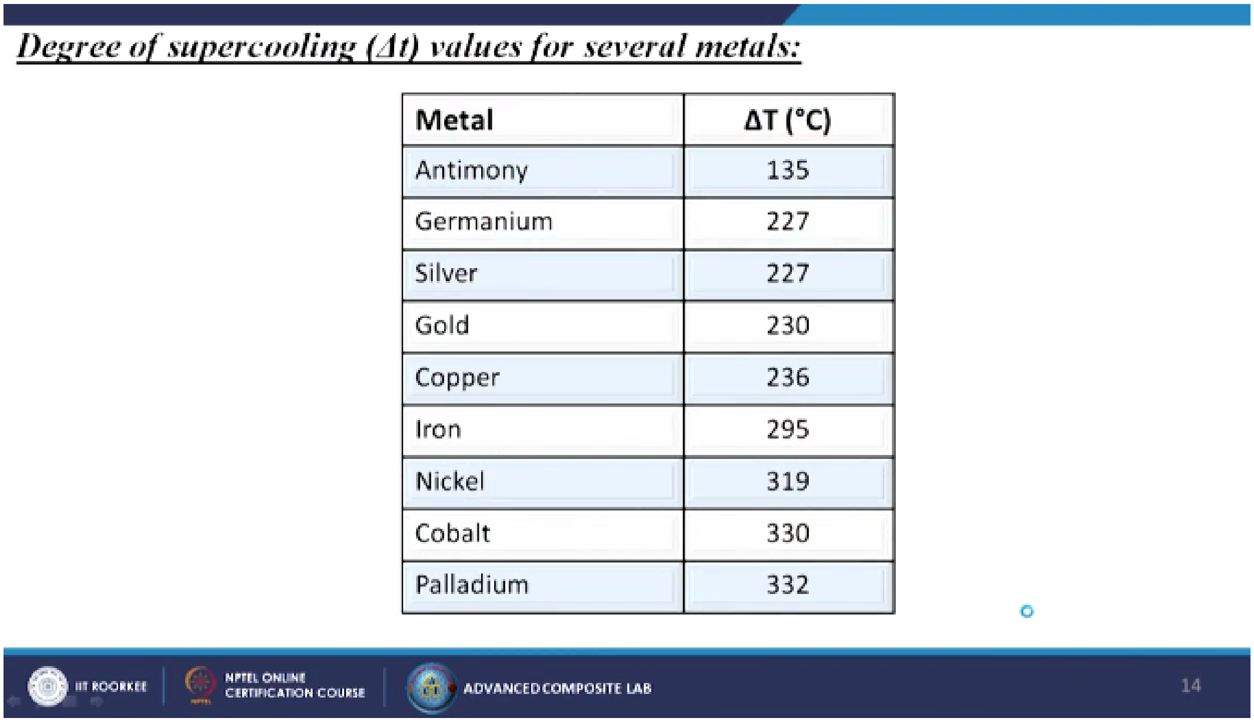
Small supercooling → *Small nucleation rate* → *Few nuclei* → *Large crystals*

Large supercooling → *Rapid nucleation rate* → *Many nuclei* → *Small crystals*

- ✓ Metastable states can be formed as result of fast temperature change.
- ✓ Microstructure is strongly affected by cooling rate.
- ✓ Effect of time on phase transformation is explained using **Iron-carbon alloy**.

Now we are going to discuss about the super cooling and the super heating because super cooling and super heating is having a very high impact on this nucleations or maybe the grain growth, so crossing a phase boundary on composition temperature phase diagram, phase transformations towards equilibrium state is induced, but transitions to equilibrium structure takes time and transformations is delayed. During cooling transformation occur at temperature less than the predicted by the phase diagram that is known as the super cooling. And super heating during heating transformations occurs at temperature greater than the predicted by the phase diagram that is known as the super heating. Degree of super cooling and super heating increase with rate of cooling and heating. Driving force to nucleate increase as del T increases, so small super cooling is the small nucleation rate is few nuclei and large crystals, large super cooling is the rapid nucleation rate, many nuclei and small crystals.

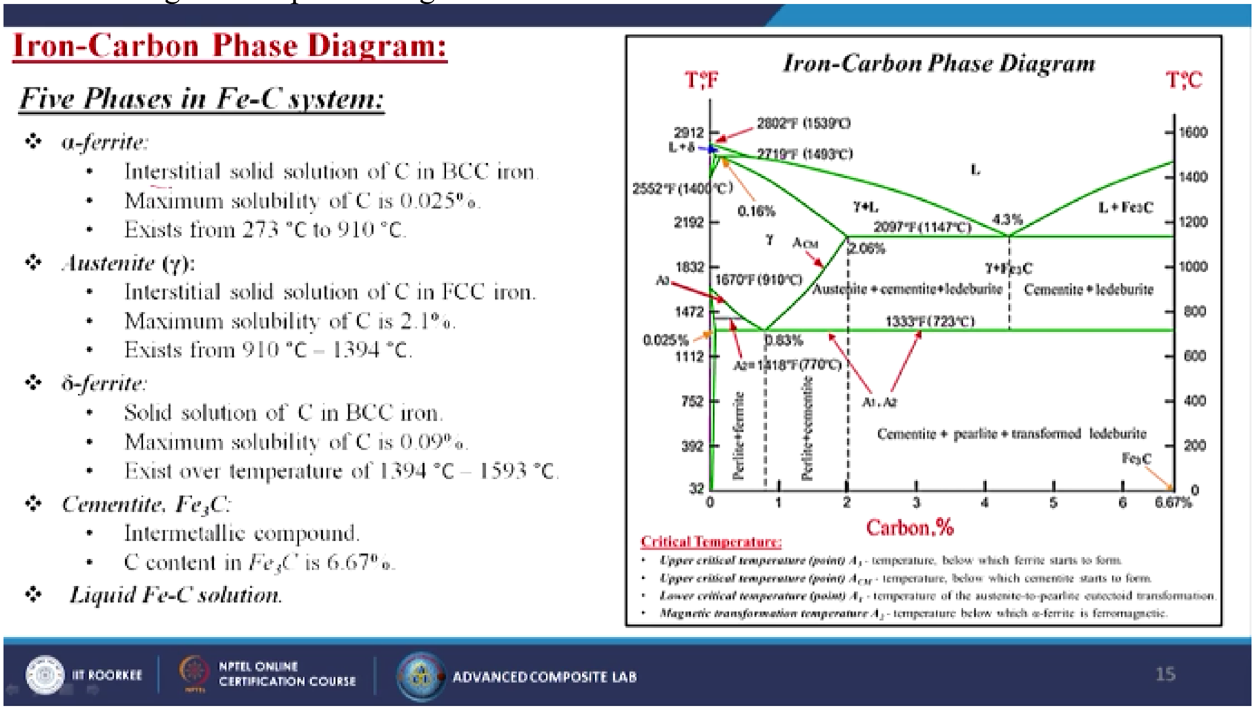
So metastable states can be formed as result of fast temperature change, microstructure is strongly affected by the cooling rate, effect of time on phase transformations is explained during the iron, carbon alloy.



Degree of supercooling (Δt) values for several metals:

Metal	ΔT (°C)
Antimony	135
Germanium	227
Silver	227
Gold	230
Copper	236
Iron	295
Nickel	319
Cobalt	330
Palladium	332

So now degree of super cooling del T values for the several methods, say suppose we take the antimony it is 135 degree centigrade, generally copper is required for us because we are widely using the copper that is 236 degree centigrade, iron is 295 degree centigrade, nickel is 319 degree centigrade, then cobalt is 330 degree centigrade or maybe the gold is 230 degree centigrade so this is the degree of super cooling for various metals.



Iron-Carbon Phase Diagram:

Five Phases in Fe-C system:

- *α-ferrite:*
    - Interstitial solid solution of C in BCC iron.
    - Maximum solubility of C is 0.025%.
    - Exists from 273 °C to 910 °C.
- *Austenite (γ):*
    - Interstitial solid solution of C in FCC iron.
    - Maximum solubility of C is 2.1%.
    - Exists from 910 °C – 1394 °C.
- *δ-ferrite:*
    - Solid solution of C in BCC iron.
    - Maximum solubility of C is 0.09%.
    - Exist over temperature of 1394 °C – 1593 °C.
- *Cementite, Fe_3C:*
    - Intermetallic compound.
    - C content in Fe_3C is 6.67%.
- *Liquid Fe-C solution.*

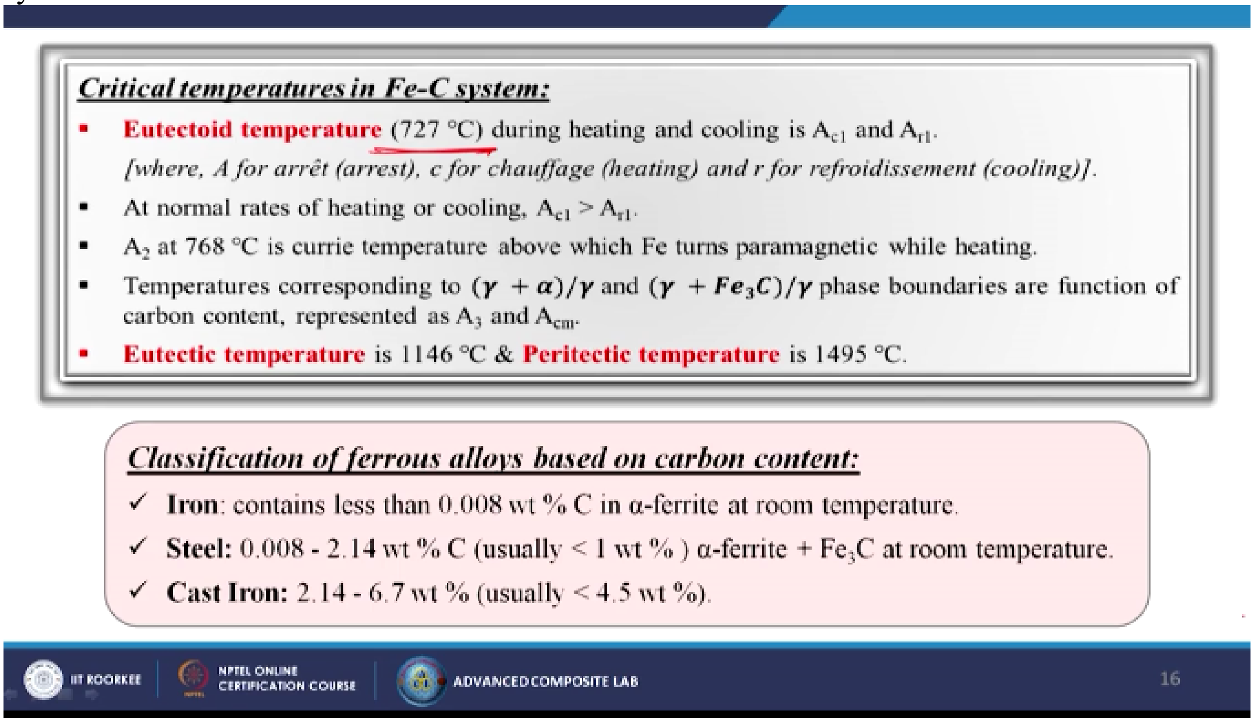
Critical Temperature:

- *Upper critical temperature (point)* A_3 - temperature, below which ferrite starts to form.
- *Upper critical temperature (point)* A_{CM} - temperature, below which cementite starts to form.
- *Lower critical temperature (point)* A_1 - temperature of the austenite-to-pearlite eutectoid transformation.
- *Magnetic transformation temperature* A_2 - temperature below which α-ferrite is ferromagnetic.

Now we are going to discuss about the famous iron-carbon phase diagram, so five phases are present in the iron-carbon systems, so first is called the alpha ferrite, so alpha ferrite it is the interstitial solid solution of carbon in BCC iron, maximum solubility of C is 0.025 after that the

C will not be dissolved into that phase, exists from 273 degree centigrade to 910 degree centigrade, so from this we can get the alpha ferrite and then we are going to austenite that is gamma phase, interstitial solid solution at carbon in FCC iron, maximum solubility of C is 2.1% so solubility of carbon has been enhanced, exists from 910 degree centigrade to 1394 degree centigrade, then we are having the delta ferrite. Solid solution of C in BCC iron C, just we are changing the temperature the solubility of carbon is increasing and also the phase of that material is going to be changed, first it was in C in BCC, then C in FCC and then C in again BCC it is coming, maximum solubility of C is 0.09, it has been reduced.

Exists over temperature of 1394 degree centigrade to 1593 degree centigrade, again we are moving to cementite it is the intermetallic compound, C content in Fe3C is 6.67% and the last one is called the liquid iron carbon solutions, so this is coming in this particular case, so in this particular case you can see there are several things it is the carbon percentage is 0 to 6.67 percentage and temperature is increasing in this directions, so this is into the Fahrenheit and this is into the centigrade scale, so when we are talking about we are getting so many phases cementite + pearlite + transformed ledeburite, in this zone we are getting the pearlite or maybe the cementite when the carbon perishes below 2% and its almost 0.8 to 2%, it is only the pearlite ferrite then we are getting the 910 degree centigrade is up to this case almost, so in this case we can get austenite + cementite + ledeburite or maybe into the higher carbon percentage we are getting the cementite + ledeburite, so this all are the different phase, so based on the carbon compositions and based on the temperature we are getting the different phases of iron-carbon system.



Critical temperatures in Fe-C system:

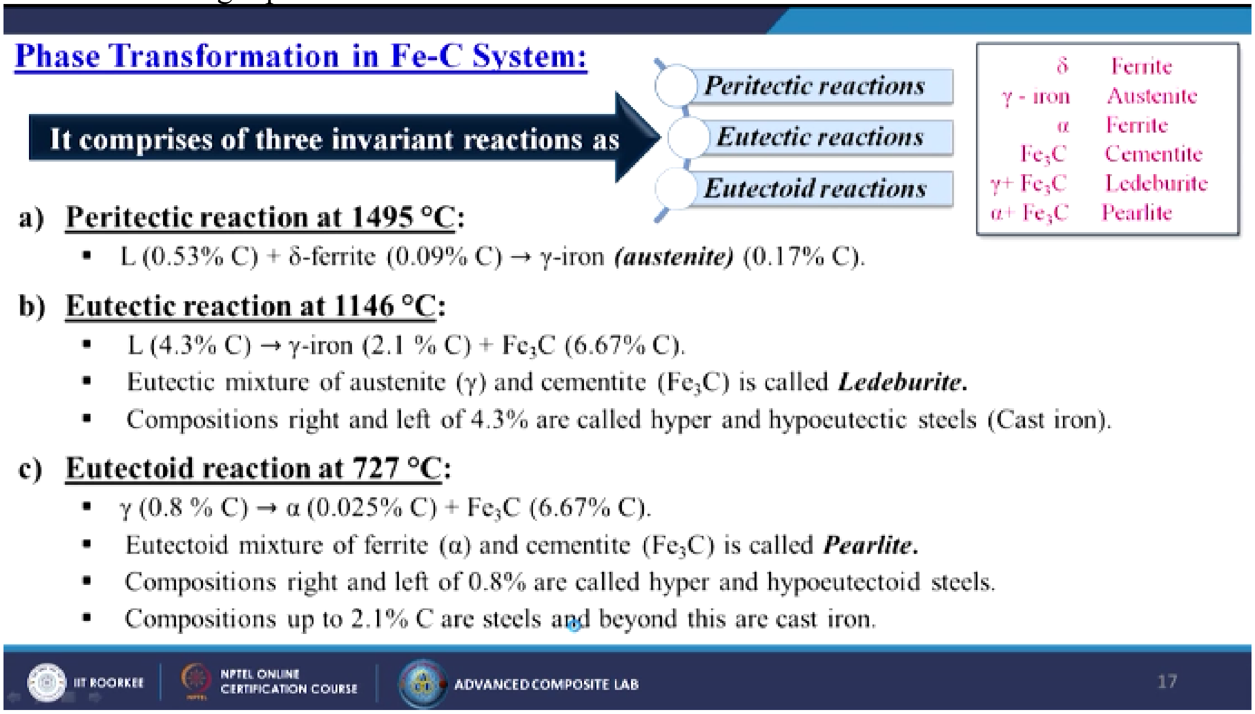
- **Eutectoid temperature** (727 °C) during heating and cooling is A_{c1} and A_{r1}.
  [where, A for arrêt (arrest), c for chauffage (heating) and r for refroidissement (cooling)].
- At normal rates of heating or cooling, $A_{c1} > A_{r1}$.
- A_2 at 768 °C is currie temperature above which Fe turns paramagnetic while heating.
- Temperatures corresponding to $(\gamma + \alpha)/\gamma$ and $(\gamma + Fe_3C)/\gamma$ phase boundaries are function of carbon content, represented as A_3 and A_{cm}.
- **Eutectic temperature** is 1146 °C & **Peritectic temperature** is 1495 °C.

Classification of ferrous alloys based on carbon content:

- ✓ **Iron**: contains less than 0.008 wt % C in α-ferrite at room temperature.
- ✓ **Steel:** 0.008 - 2.14 wt % C (usually < 1 wt %) α-ferrite + Fe_3C at room temperature.
- ✓ **Cast Iron:** 2.14 - 6.7 wt % (usually < 4.5 wt %).

So critical temperatures in the iron carbon systems, eutectoid temperature generally 727 degree centigrade during heating, and cooling is AC1 and AR1, where A for arret that means arrest, C for chauffage that means heating and R for refroidissement that means cooling, at normal rates of heating or cooling AC1 is greater than is equal to AR1, A2 at 768 degree centigrade is currie temperature above which iron turns paramagnetic while heating, temperature corresponding to gamma + alpha/gamma and gamma + Fe3C and gamma phase boundaries are function of carbon content represented as A3 and ACM, eutectic temperature is 1146 degree centigrade and peritectic temperature is 1495 degree centigrade.

Now what is the classifications of ferrous alloys based on carbon content, iron contains less than 0.008 weight percent of carbon in alpha ferrite at room temperature, steel 0.008 that means 2.14 weight percent in carbon usually less than 1 weight percent alpha ferrite + Fe3C at room temperature, cast iron generally carbon percentage varies from 2.14 to 6.7 weight percent usually less than 4.5 weight percent.



Phase Transformation in Fe-C System:

It comprises of three invariant reactions as

- *Peritectic reactions*
- *Eutectic reactions*
- *Eutectoid reactions*

δ	Ferrite
γ - iron	Austenite
α	Ferrite
Fe_3C	Cementite
$\gamma + Fe_3C$	Ledeburite
$\alpha + Fe_3C$	Pearlite

a) Peritectic reaction at 1495 °C:

- L (0.53% C) + δ-ferrite (0.09% C) → γ-iron ***(austenite)*** (0.17% C).

b) Eutectic reaction at 1146 °C:

- L (4.3% C) → γ-iron (2.1 % C) + Fe_3C (6.67% C).
- Eutectic mixture of austenite (γ) and cementite (Fe_3C) is called ***Ledeburite.***
- Compositions right and left of 4.3% are called hyper and hypoeutectic steels (Cast iron).

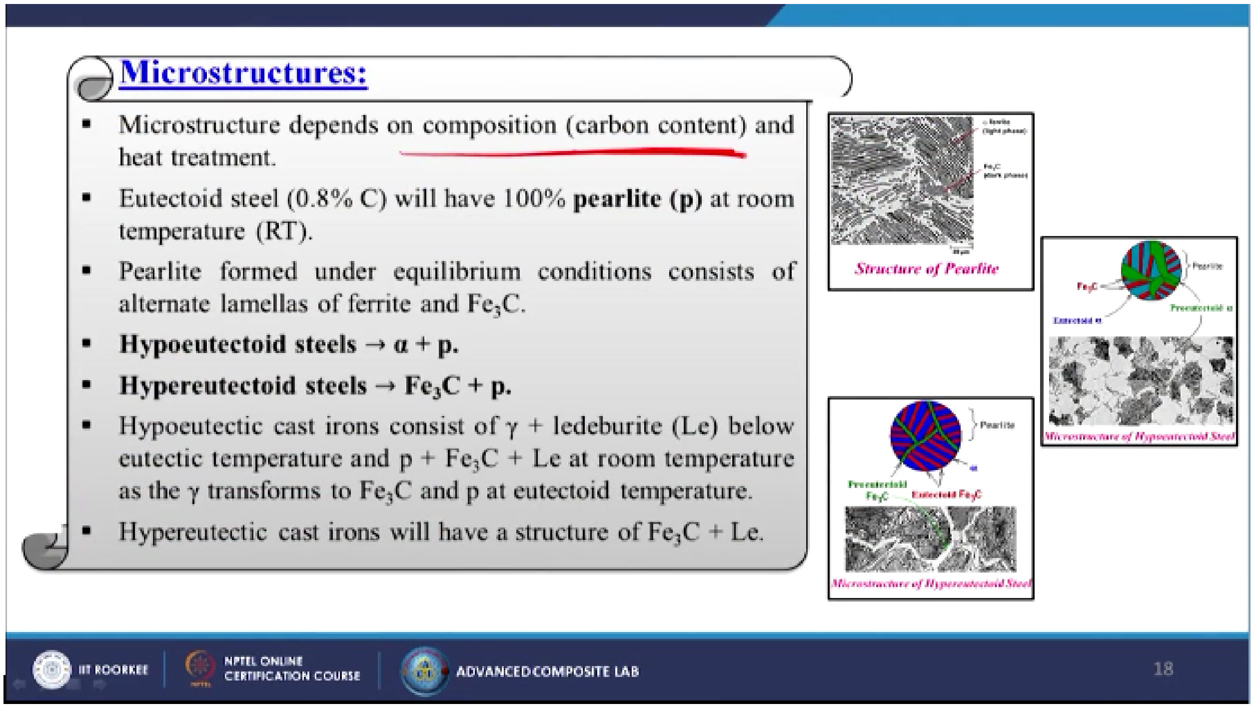
c) Eutectoid reaction at 727 °C:

- γ (0.8 % C) → α (0.025% C) + Fe_3C (6.67% C).
- Eutectoid mixture of ferrite (α) and cementite (Fe_3C) is called ***Pearlite.***
- Compositions right and left of 0.8% are called hyper and hypoeutectoid steels.
- Compositions up to 2.1% C are steels and beyond this are cast iron.

Now phase transformations in iron-carbon systems, so it comprises of three invariant reactions as peritectic reactions, eutectic reactions, and the eutectoid reactions, so in this particular case delta is the ferrite, gamma iron is known as the austenite, alpha is known as the ferrite, Fe3C is known as cementite, gamma + Fe3C is known as ledeburite and alpha + Fe3C is known as pearlite. So what is peritectic reactions at 1495 degree centigrade, so in this particular case the L = 0.53% C + delta ferrite 0.09% of C converts into gamma iron austenite which is having 0.17 percent of C.

What is eutectic reactions at 1146 degree centigrade, L 4.3% of carbon converts into gamma iron that is 2.1% of carbon + Fe3C that is 6.67% carbon. Eutectic mixture of austenite and cementite is called the ledeburite.

Next compositions right and left of 4.3% are called the hyper and hypoeutectic steels or maybe known as the cast iron. Eutectoid reactions at 727 degree centigrade, so gamma 0.8% C converts into alpha 0.025% C + Fe3C 6.67% of C, eutectoid mixture of ferrite and cementite is called the pearlite, compositions right and left of 0.8% are called the hyper and hypoeutectoid steels, compositions up to 2.1% C are steels and beyond this are cast iron, so simple by the presence of carbon with temperature simple we can get that different materials like stainless steel, like cast iron, like mild steel so this can be achievable.



Microstructures:

- Microstructure depends on composition (carbon content) and heat treatment.
- Eutectoid steel (0.8% C) will have 100% **pearlite (p)** at room temperature (RT).
- Pearlite formed under equilibrium conditions consists of alternate lamellas of ferrite and Fe_3C.
- **Hypoeutectoid steels → α + p.**
- **Hypereutectoid steels → Fe_3C + p.**
- Hypoeutectic cast irons consist of γ + ledeburite (Le) below eutectic temperature and p + Fe_3C + Le at room temperature as the γ transforms to Fe_3C and p at eutectoid temperature.
- Hypereutectic cast irons will have a structure of Fe_3C + Le.

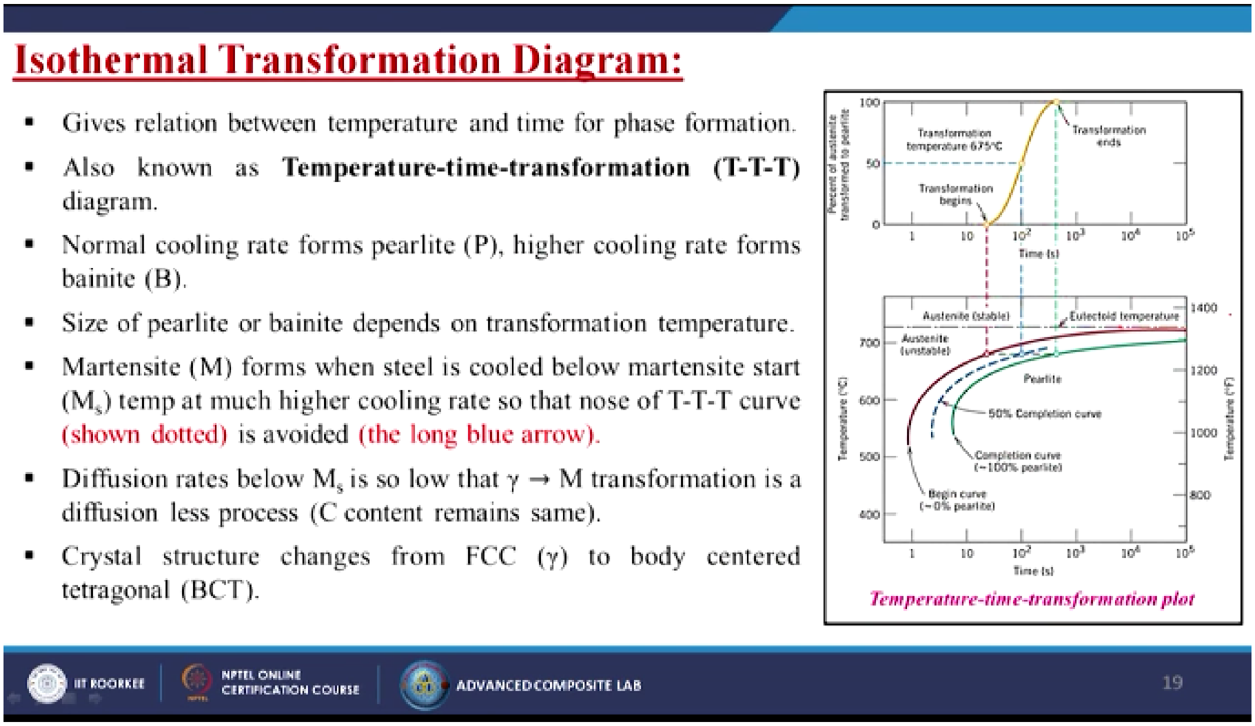
Structure of Pearlite

Microstructure of Hypoeutectoid Steel

Microstructure of Hypereutectoid Steel

Now we are going into the details that about the microstructures, so microstructures depend on compositions that means the carbon content and the heat treatment, eutectoid steel is having 0.8% carbon will have 100% pearlite at room temperature, pearlite formed under equilibrium conditions consist of alternate lamellas of ferrite and Fe3C. Hypoeutectoid steel alpha + pearlite, hypereutectoid steels that is Fe3C + pearlite. Hypoeutectic cast irons consist of gamma + ledeburite below eutectic temperature and pearlite + Fe3C + ledeburite at room temperature as the gamma transforms to Fe3C and pearlite at eutectoid temperature. Hypereutectic cast irons will have a structure of Fe3C + ledeburite, so from this you can understand that structure of the pearlite where we can find the Fe3C into the dark phases and alpha ferrite is into the light phases, so when we are getting the optical microscope image so of the pearlite also, so you can see that this is the hypoeuctectoid Fe3C which is green in colour and the red in colour is that eutectoid Fe3C and alpha phase you are getting into the blue in colour.

Same thing the microstructure of the hypoeutectoid steel, so you can get the Fe3C, you can get the pearlite, you can get the proeutectoid alpha, but in this particular case, but in this particular case what happen, you can see the grain structure is totally different than this one, when we are talking about the microstructure of the hypereutectoid steel, so you are getting the proeutectoid Fe3C, eutectoid Fe3C alpha and the pearlite, so total the microstructure is changing.



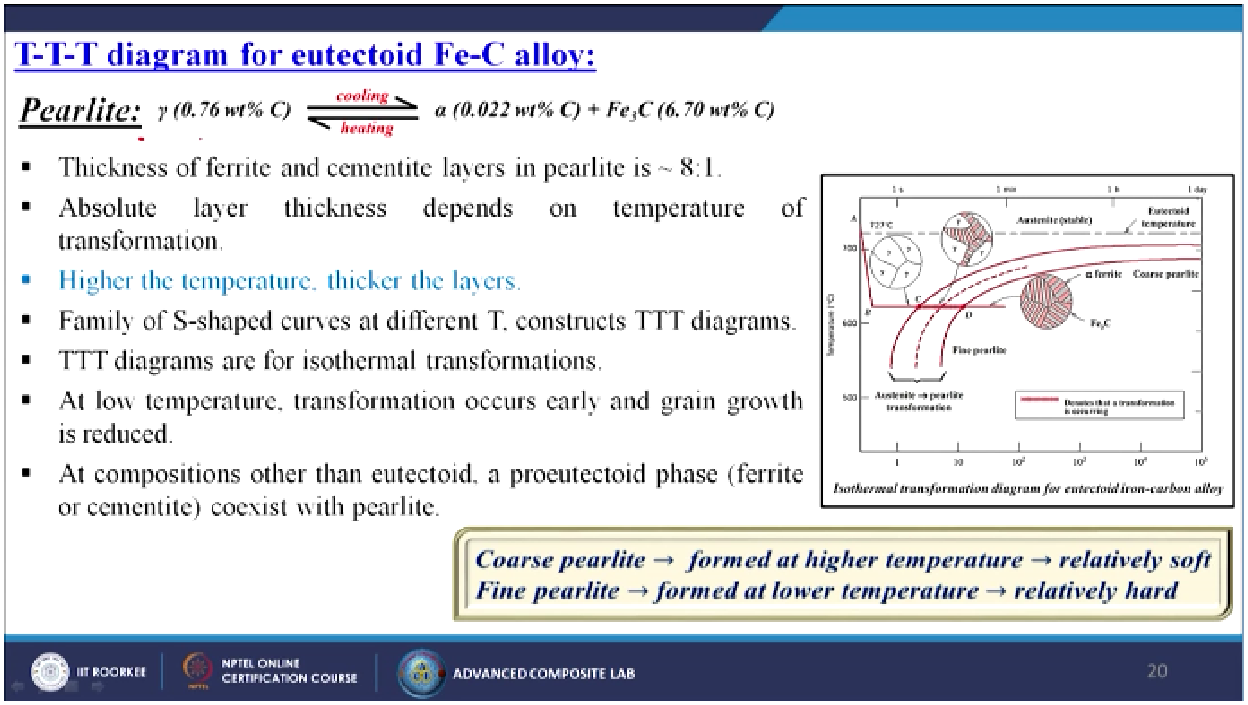
Isothermal Transformation Diagram:

- Gives relation between temperature and time for phase formation.
- Also known as **Temperature-time-transformation (T-T-T)** diagram.
- Normal cooling rate forms pearlite (P), higher cooling rate forms bainite (B).
- Size of pearlite or bainite depends on transformation temperature.
- Martensite (M) forms when steel is cooled below martensite start (M_s) temp at much higher cooling rate so that nose of T-T-T curve (shown dotted) is avoided (the long blue arrow).
- Diffusion rates below M_s is so low that $\gamma \rightarrow M$ transformation is a diffusion less process (C content remains same).
- Crystal structure changes from FCC (γ) to body centered tetragonal (BCT).

Temperature-time-transformation plot

Now we are going to discuss about the isothermal transformation diagram, so it gives the relation between temperature and the time of phase formations, so this is the time versus the temperature, so how the temperature or maybe the transformation is taking place, so through this graph you can get the time and transformation begins in this particular point then transformation is taking places and the transformation ends in this particular point which is nothing but the percent of austenite transform to the pearlite, so it is also known as temperature time transformations or maybe that T-T-T diagram, normal cooling rate forms the pearlite, higher cooling rate forms the bainite. Size of pearlite or bainite depends on transformation temperature, martensite forms when steel is cooled below martensite start temperature at much higher cooling rate so that nose of T-T-T curve shown in that dotted, so this dotted line, this dotted line is avoided, the long blue arrow over there.

Diffusion rate below Ms is so low that gamma tends to M transformations is a diffusion less process C content remains the same, means carbon content is not going to be changed. Crystal structure changes from FCC gamma to body centered tetragonal or maybe the BCT in structure.



T-T-T diagram for eutectoid Fe-C alloy:

Pearlite: $\gamma\ (0.76\ wt\%\ C) \underset{heating}{\overset{cooling}{\rightleftharpoons}} \alpha\ (0.022\ wt\%\ C) + Fe_3C\ (6.70\ wt\%\ C)$

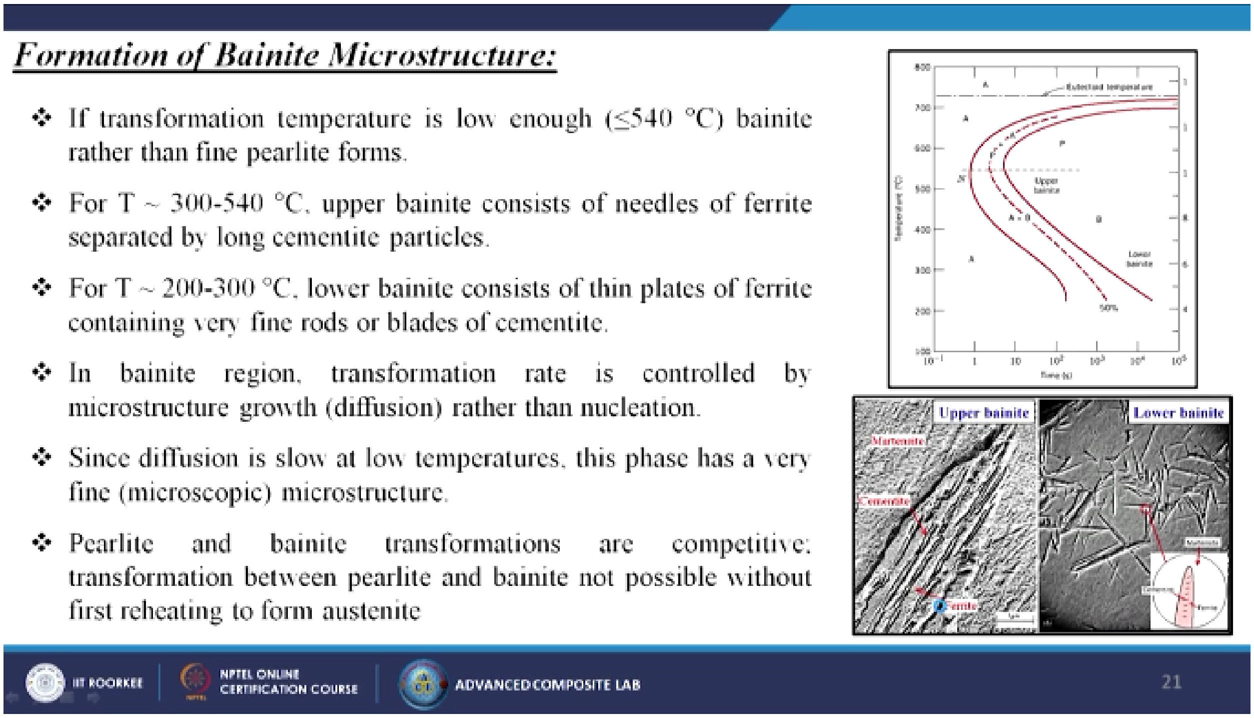
- Thickness of ferrite and cementite layers in pearlite is ~ 8:1.
- Absolute layer thickness depends on temperature of transformation.
- Higher the temperature, thicker the layers.
- Family of S-shaped curves at different T, constructs TTT diagrams.
- TTT diagrams are for isothermal transformations.
- At low temperature, transformation occurs early and grain growth is reduced.
- At compositions other than eutectoid, a proeutectoid phase (ferrite or cementite) coexist with pearlite.

Isothermal transformation diagram for eutectoid iron-carbon alloy

Coarse pearlite → formed at higher temperature → relatively soft
Fine pearlite → formed at lower temperature → relatively hard

Now again we are going to discuss about the T-T-T diagram for the eutectoid iron-carbon alloy, so pearlite which is gamma having 0.76 weight percent of C either we can heating or cooling both at certain conditions, alpha is 0.022 weight percent carbon + Fe3C 6.70 weight percent C, so thickness of ferrite and cementite layers in pearlite is 8:1, absolute layer thickness depends on temperature of the transformation, so you can see in all this cases the temperature is the vital factor over there, higher the temperature thicker the layers, family of S shaped curves at different T constructs TTT diagrams, TTT diagrams are for isothermal transformations, at low temperature transformation occurs early and grain growth is reduced, at compositions other than eutectoid a proeutectoid phase ferrite or cementite coexist with pearlite.

So in this particular case, in this regions you can see that there are several structures are present over there when the austenite to pearlite transformation is taking place, so this is the temperature versus the time diagram over there so with temperature and with time how the material is changing. So course pearlite tends to formed at higher temperature that is relatively soft, fine pearlite which is forming at lower temperature which is relatively hard in nature.

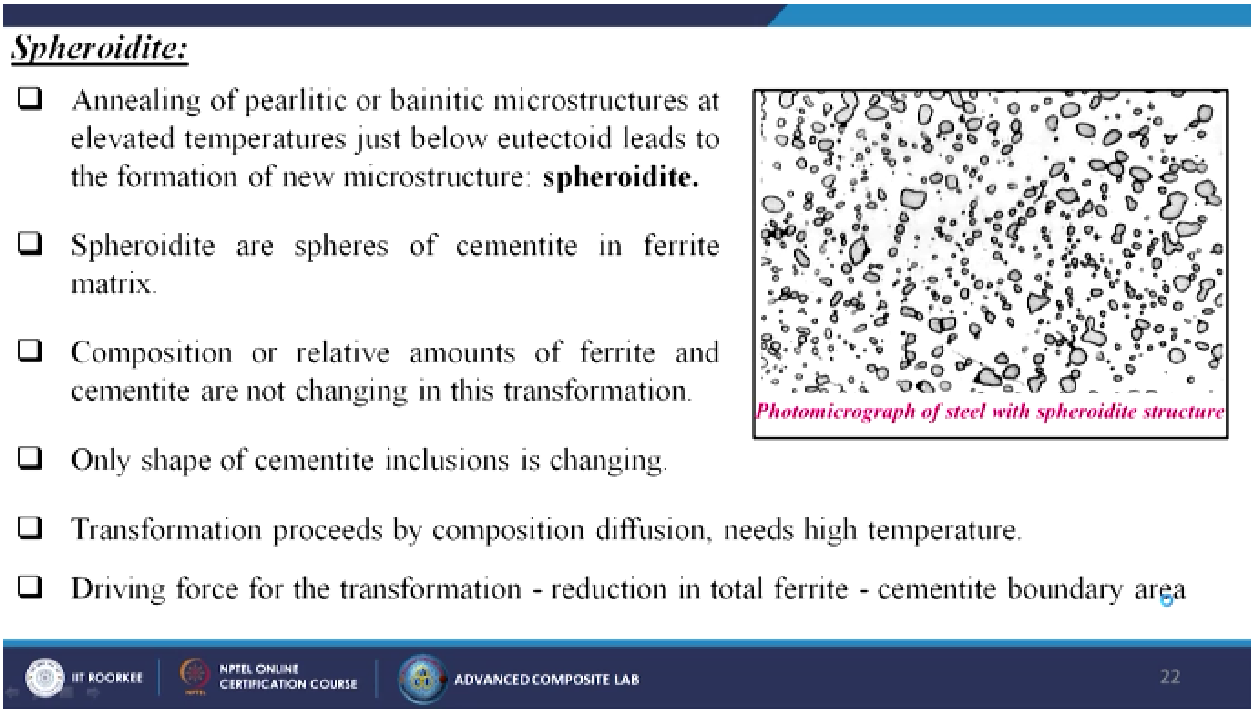


Formation of Bainite Microstructure:

- If transformation temperature is low enough (≤540 °C) bainite rather than fine pearlite forms.
- For T ~ 300-540 °C, upper bainite consists of needles of ferrite separated by long cementite particles.
- For T ~ 200-300 °C, lower bainite consists of thin plates of ferrite containing very fine rods or blades of cementite.
- In bainite region, transformation rate is controlled by microstructure growth (diffusion) rather than nucleation.
- Since diffusion is slow at low temperatures, this phase has a very fine (microscopic) microstructure.
- Pearlite and bainite transformations are competitive; transformation between pearlite and bainite not possible without first reheating to form austenite

Now formation of the bainite microstructure, if transformation temperature is low enough that is less than 540 degree centigrade, bainite rather than fine pearlite forms, for temperature 300 - 540 degree centigrade upper bainite consists of needless of ferrite separated by long cementite particles, for T more than equal to 200 to 300 degree centigrade, lower bainite consists of thin plate of ferrite containing very fine rods or blades of cementite. In bainite region transformation rate is controlled by microstructure growth that means diffusion rather than the nucleation.

Since diffusion is slow at low temperature this phase has a very fine microscopic microstructure. Pearlite and bainite transformations are competitive, transformation between pearlite and bainite not possible without first reheating to form the austenite, so this is known as the upper bainite structure where we can see the martensite, cementite and the ferrite and this is the lower bainite where we can see the martensite is looks like this, cementite is in to the, in this shapes and ferrite is into this confinement.

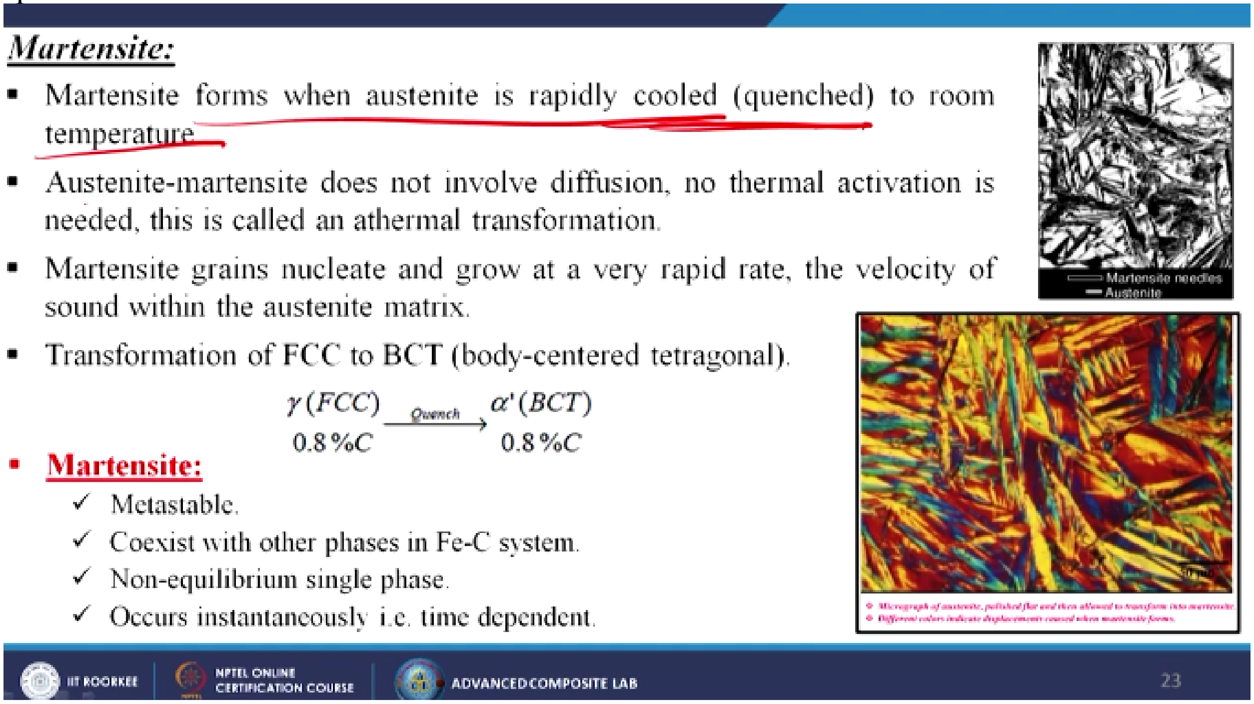


Spheroidite:

- ☐ Annealing of pearlitic or bainitic microstructures at elevated temperatures just below eutectoid leads to the formation of new microstructure: **spheroidite.**
- ☐ Spheroidite are spheres of cementite in ferrite matrix.
- ☐ Composition or relative amounts of ferrite and cementite are not changing in this transformation.
- ☐ Only shape of cementite inclusions is changing.
- ☐ Transformation proceeds by composition diffusion, needs high temperature.
- ☐ Driving force for the transformation - reduction in total ferrite - cementite boundary area

Photomicrograph of steel with spheroidite structure

Now we are going to discuss about the spheroidite, so annealing of pearlite or bainite microstructures at elevated temperature just below the eutectoid leads to the formation of new microstructure which is known as the spheroidite. Spheroidite are spheres of cementite in ferrite matrix, composition or relative amounts of ferrite and cementite are not changing in this transformations, only shape of cementite inclusions is changing, transformation proceeds by composition, diffusion, needs high temperature, driving force for the transformation, reduction in total ferrite that means cementite boundary area, so this is the photomicrograph of steel with spheroidite structure.



Martensite:

- Martensite forms when austenite is rapidly cooled (quenched) to room temperature
- Austenite-martensite does not involve diffusion, no thermal activation is needed, this is called an athermal transformation.
- Martensite grains nucleate and grow at a very rapid rate, the velocity of sound within the austenite matrix.
- Transformation of FCC to BCT (body-centered tetragonal).

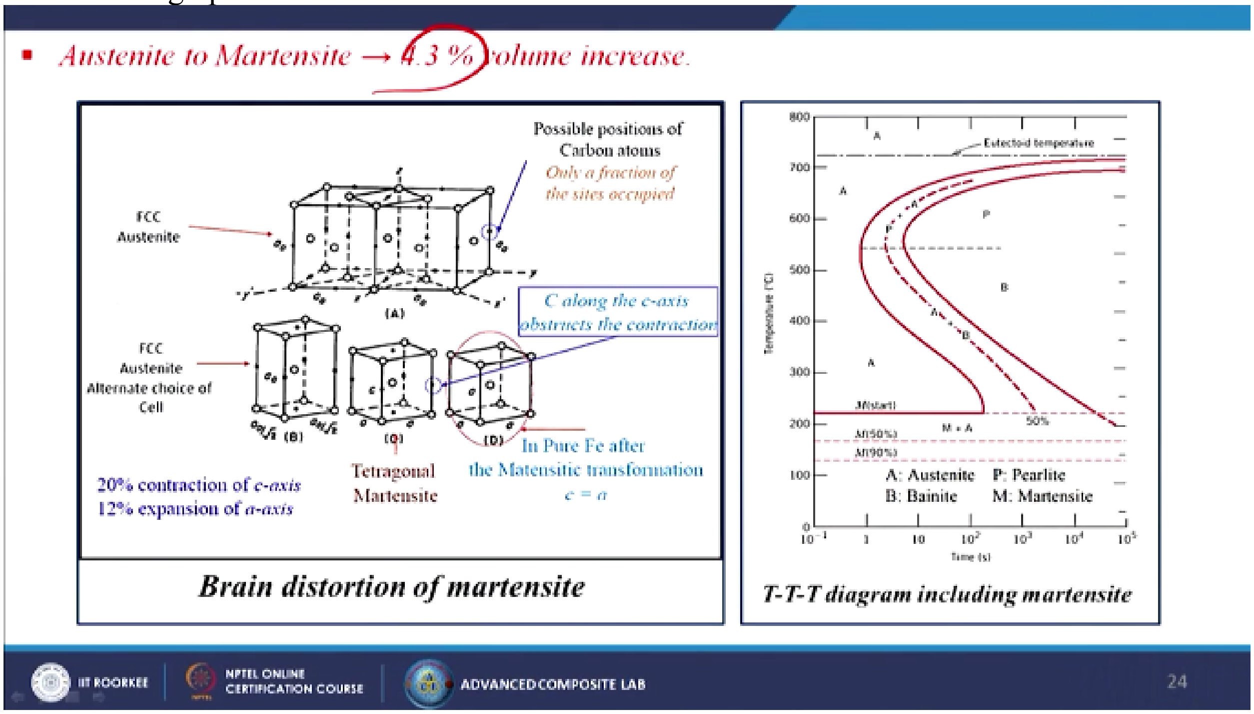
$$\underset{0.8\%C}{\gamma(FCC)} \xrightarrow{Quench} \underset{0.8\%C}{\alpha'(BCT)}$$

- **Martensite:**
  - ✓ Metastable.
  - ✓ Coexist with other phases in Fe-C system.
  - ✓ Non-equilibrium single phase.
  - ✓ Occurs instantaneously i.e. time dependent.

- Micrograph of austenite, polished flat and then allowed to transform into martensite.
- Different colors indicate displacements caused when martensite forms.

Now we are going to discuss about the martensite, so martensite forms when the austenite is rapidly cooled or maybe the quenched that means we are rising the material up to high temperature and then suddenly we are dipping that materials into some water or maybe some oil to do the quenching to room temperature, so suddenly from high temperature the material is coming to the low temperature or maybe the room temperature, austenite martensite does not involve diffusion, no thermal activation is needed this is called an athermal transformations.

Martensite grains nucleate and grow at a very rapid rate, the velocity of sound within the austenite matrix, transformation of FCC to BCT, body centered tetragonal, how it is taking place? That gamma FCC 0.8% of carbon just we are doing the quench, we are getting the alpha prime BCT so the carbon percentage is not going to be changed, so martensite, the properties are metastable in nature coexist with other phases in iron carbon systems, non-equilibrium single phase occurs instantaneously that is time dependent, so this is the micrograph or maybe the colour micrograph of the martensite structure.



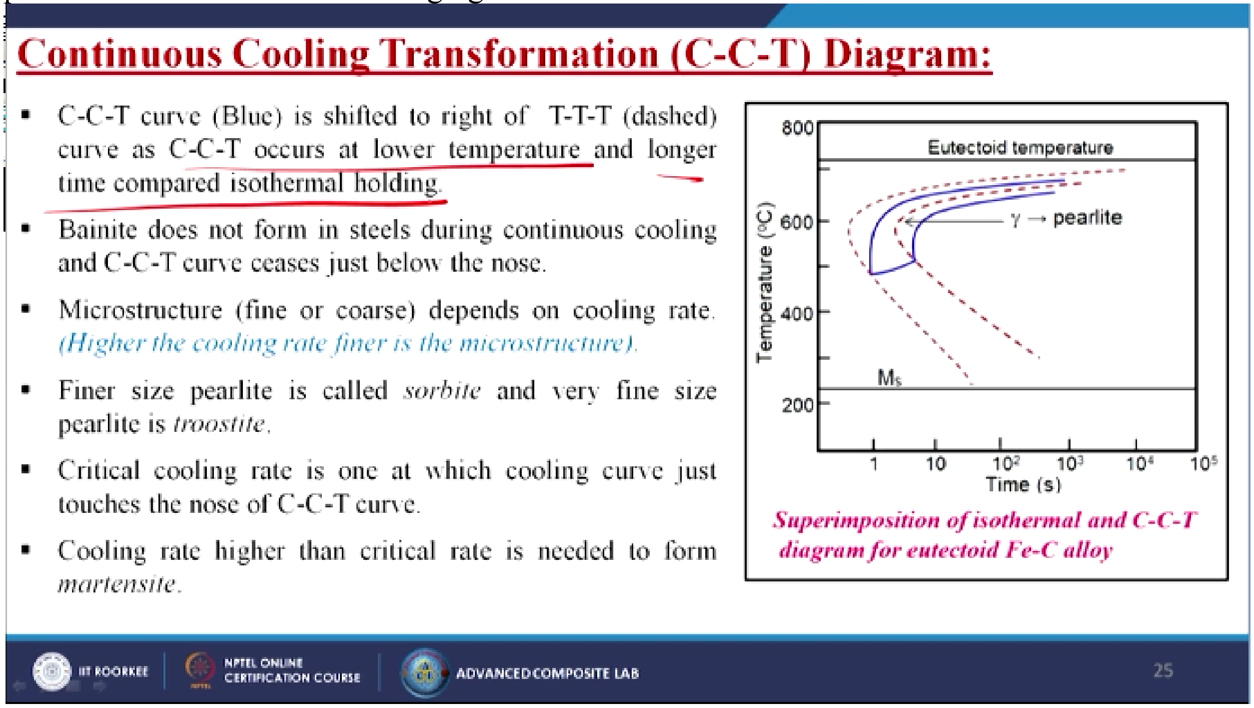
- *Austenite to Martensite → 4.3 % volume increase.*

Brain distortion of martensite

T-T-T diagram including martensite

Now how it is changing from austenite to martensite, that means nothing only the volume is going to be increased, because we are heating that materials and suddenly we are cooling down the materials, so generally 4.3% of volume is increasing at that particular conditions, so in this case you can see the martensite region is this zone, and then after that we are having the bentonite, then austenite, then pearlite, then again austenite and this is the eutectoid temperature of that particular materials that is nothing but the 727 degree centigrade, so in this particular case you can see that at lower temperature because I told that from higher temperature to lower temperature the martensite formation will be taking place, so at lower temperature we are getting, so at more than 200 degree centigrade the martensite start, below that the martensite is 50% and it is just above the 100 degree or maybe 120 degree then martensite is 90% are present over there, and this zone is martensite + austenite so this is totally time dependent and the temperature dependent over there, in this particular case you can understand that only the changing, only the changing because some atoms over here that is C along that, carbon along the

C axis obstructs the contractions, so just only the volume expansion is taking place in this particular case when we are changing it from the austenite to martensite.

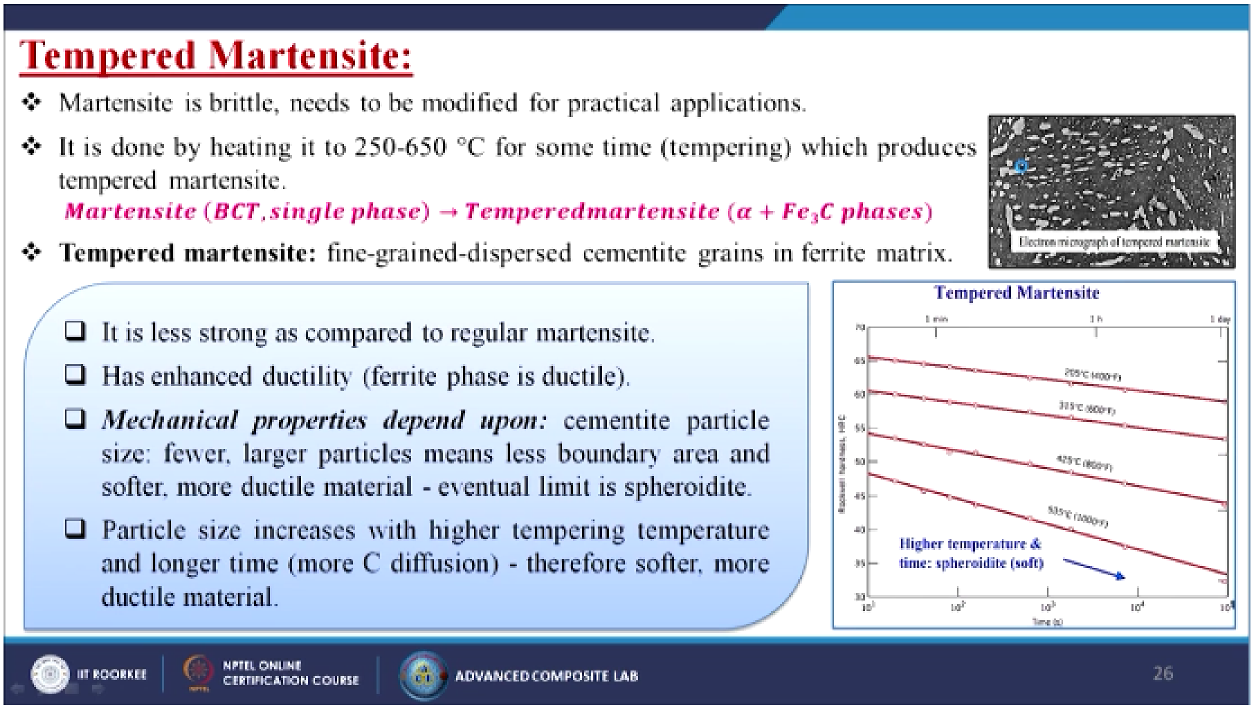


Continuous Cooling Transformation (C-C-T) Diagram:

- C-C-T curve (Blue) is shifted to right of T-T-T (dashed) curve as C-C-T occurs at lower temperature and longer time compared isothermal holding.
- Bainite does not form in steels during continuous cooling and C-C-T curve ceases just below the nose.
- Microstructure (fine or coarse) depends on cooling rate. *(Higher the cooling rate finer is the microstructure).*
- Finer size pearlite is called *sorbite* and very fine size pearlite is *troostite*.
- Critical cooling rate is one at which cooling curve just touches the nose of C-C-T curve.
- Cooling rate higher than critical rate is needed to form *martensite*.

Superimposition of isothermal and C-C-T diagram for eutectoid Fe-C alloy

Now there is another famous graph which is known as the continuous cooling transformations or maybe the C-C-T diagram, so generally the C-C-T curve which is in blue in nature and your dotted is the, or maybe the dashed curve is the T-T-T curve. As C-C-T occurs at lower temperature and longer time compared isothermal holding, bainite does not form in steels during continuous cooling and C-C-T curve ceases just below the nose. Microstructure fine or coarse depends on cooling rate, higher the cooling rate finer is the microstructure, so finer size pearlite is called sorbite, and very fine size pearlite is called the troostite. Critical cooling rate is one at which cooling curve just touches the nose of C-C-T curve, cooling rate higher than critical rate is needed to form the martensite, so it is the super impositions of the isothermal and C-C-T diagram for the eutectoid iron-carbon alloy, so sometimes some cases like critical cooling rate is one at which the cooling curve just touches the nose of C-C-T curve, so in this particular case it is going to touch.



Tempered Martensite:

- ❖ Martensite is brittle, needs to be modified for practical applications.
- ❖ It is done by heating it to 250-650 °C for some time (tempering) which produces tempered martensite.
  $Martensite\ (BCT, single\ phase) \rightarrow Temperedmartensite\ (\alpha + Fe_3C\ phases)$
- ❖ **Tempered martensite:** fine-grained-dispersed cementite grains in ferrite matrix.

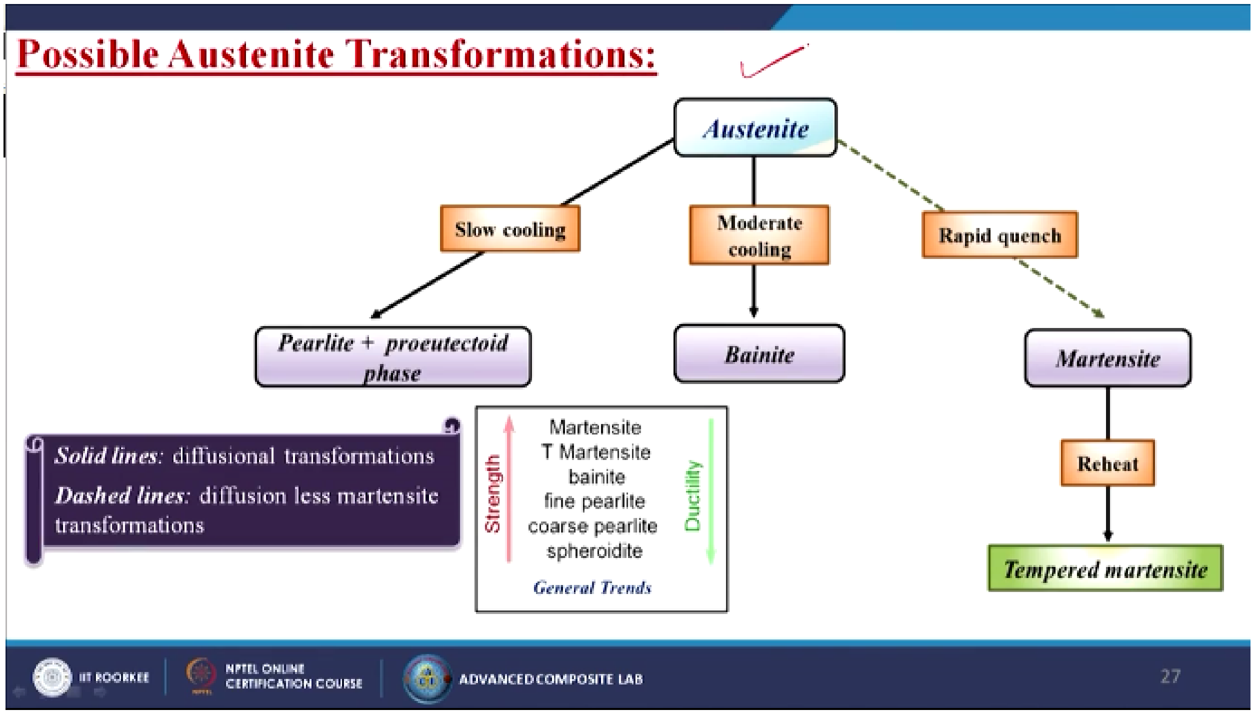
Electron micrograph of tempered martensite

- ☐ It is less strong as compared to regular martensite.
- ☐ Has enhanced ductility (ferrite phase is ductile).
- ☐ ***Mechanical properties depend upon:*** cementite particle size: fewer, larger particles means less boundary area and softer, more ductile material - eventual limit is spheroidite.
- ☐ Particle size increases with higher tempering temperature and longer time (more C diffusion) - therefore softer, more ductile material.

Tempered Martensite

Now next one is called the tempered martensite, so martensite is brittle needs to be modified for practical applications, it is done by heating that is 250 to 650 degree centigrade, for some time tempering which produces the tempered martensite, martensite which is BCT and single phase converts into the tempered martensite that is alpha + Fe3C phases, Fe3C is nothing but the cementite, tempered martensite fine-grained dispersed cementite grains in ferrite matrix, so this is the electron micrograph of the tempered martensite where you can find the fine grain, the small, small grain of the cementite at present inside the matrix, it is less strong as compared to regular martensite has enhanced the ductility, ferrite phase is ductile over here, so elasticity kind of things we can get it for over, from here, it is not brittle in nature.

Mechanical properties depend upon cementite particles size fewer, larger particles means less boundary area and softer more ductile material eventual limit is spheroidite. Particle size increases with higher tempering temperature and longer time that means more carbon diffusion is taking place therefore softer and more ductile in nature, so when we are talking about the hardness so this is the time, so when we are talking about the higher temperature and time spheroidite is becoming softer, because it's hardness is going down, and this is the tempered martensite, that means at higher temperature it is becoming softer.



Possible Austenite Transformations:

Austenite

Slow cooling

Moderate cooling

Rapid quench

Pearlite + proeutectoid phase

Bainite

Martensite

Reheat

Tempered martensite

Solid lines: diffusional transformations

Dashed lines: diffusion less martensite transformations

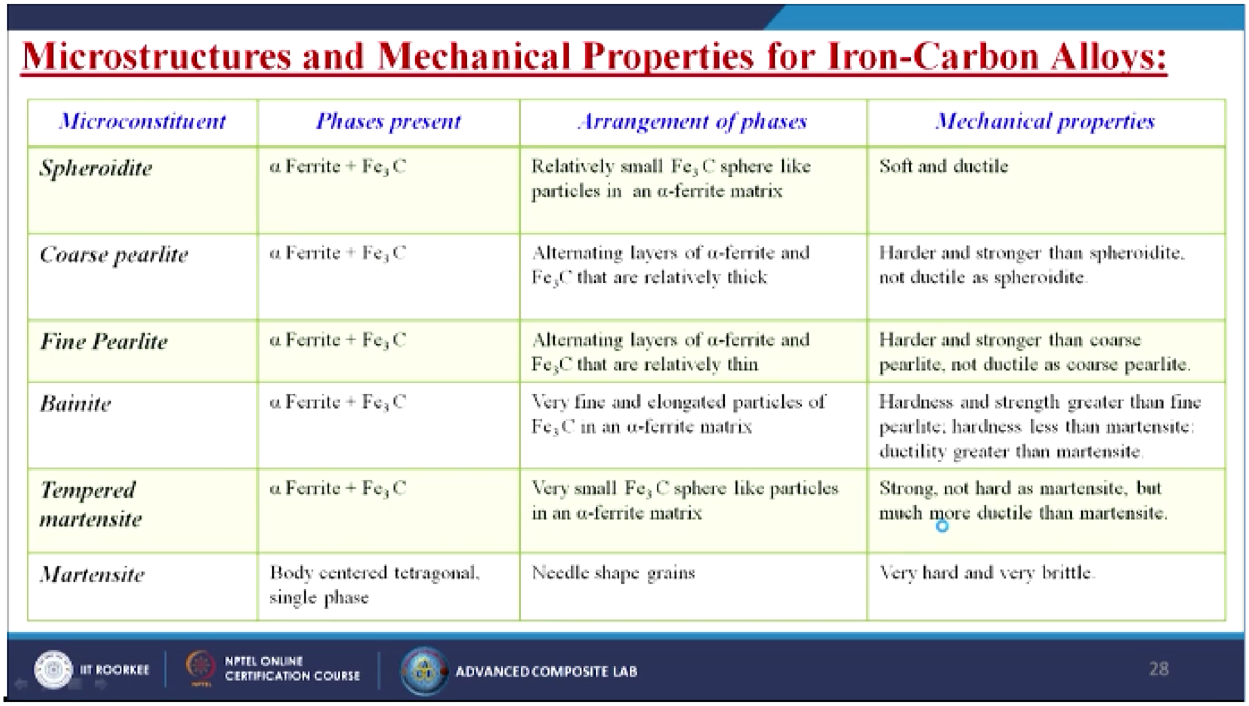
Strength

Martensite
T Martensite
bainite
fine pearlite
coarse pearlite
spheroidite

Ductility

General Trends

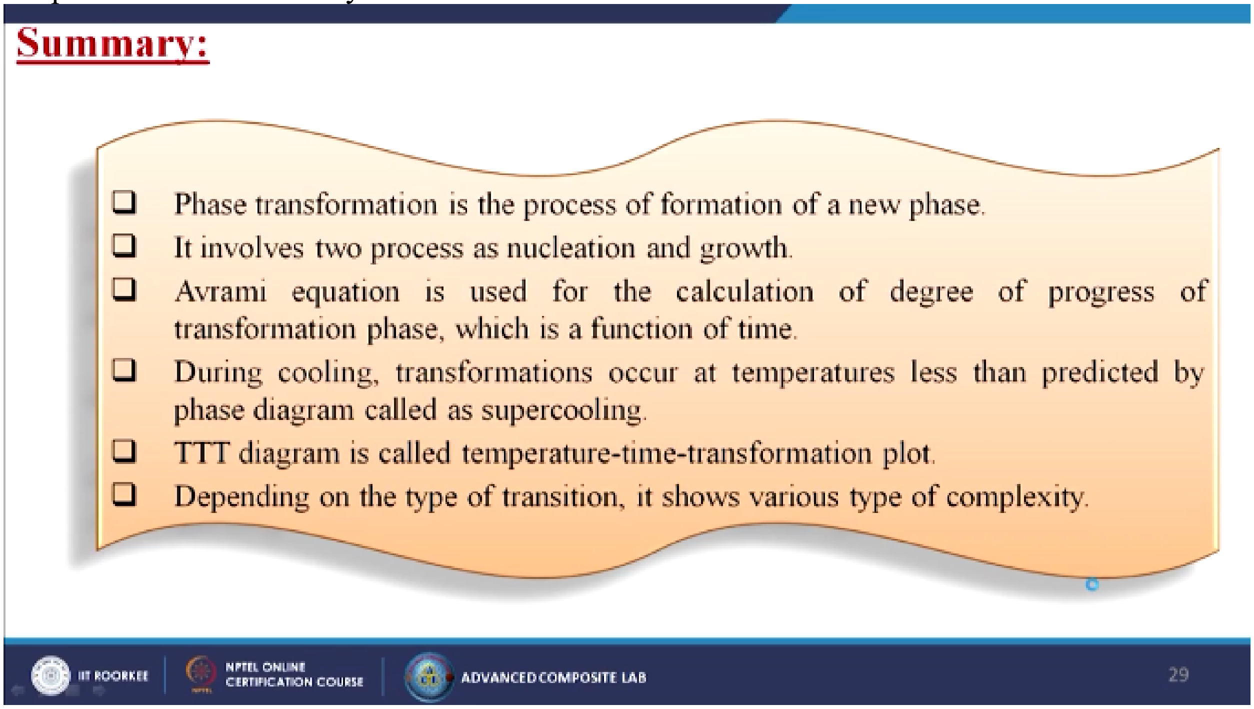
Now possible austenite transformations, there are so many possible ways for the austenite transformations, so first is that austenite then if you do the slow cooling over there it will become pearlite and the proeutectoid phase, if you do the moderate cooling then you will find the bainite in structure, if you do the rapid quench as I told already you are getting the martensite and then if you reheat the martensite you can get the tempered martensite over there, so solid lines this solid lines which is known as the diffusional transformations and this dashed lines is known as the diffusion less martensite transformations. So if we talk about the strength, so strength is maximum for the martensite and very less for the spheroidite, and of course it is the vise-versa or maybe the opposite for the ductility one, so for martensite that ductility is very, very less and for spheroidite the ductility is maximum.



Microstructures and Mechanical Properties for Iron-Carbon Alloys:

Microconstituent	*Phases present*	*Arrangement of phases*	*Mechanical properties*
Spheroidite	α Ferrite + Fe_3C	Relatively small Fe_3C sphere like particles in an α-ferrite matrix	Soft and ductile
Coarse pearlite	α Ferrite + Fe_3C	Alternating layers of α-ferrite and Fe_3C that are relatively thick	Harder and stronger than spheroidite, not ductile as spheroidite.
Fine Pearlite	α Ferrite + Fe_3C	Alternating layers of α-ferrite and Fe_3C that are relatively thin	Harder and stronger than coarse pearlite, not ductile as coarse pearlite.
Bainite	α Ferrite + Fe_3C	Very fine and elongated particles of Fe_3C in an α-ferrite matrix	Hardness and strength greater than fine pearlite; hardness less than martensite; ductility greater than martensite.
Tempered martensite	α Ferrite + Fe_3C	Very small Fe_3C sphere like particles in an α-ferrite matrix	Strong, not hard as martensite, but much more ductile than martensite.
Martensite	Body centered tetragonal, single phase	Needle shape grains	Very hard and very brittle.

So now microstructure and mechanical properties for iron-carbon alloys, so this is a overall comparison table, so micro constituents like spheroidite, phases present is alpha ferrite + Fe3C, arrangement of phases relatively small Fe3C sphere like particles in an alpha ferrite matrix, mechanical properties it is soft and ductile, so like this way just we have summarized all this for the spheroidite, course pearlite, fine pearlite, bainite, tempered martensite and the martensite. So for martensite it is having the body centered tetragonal BCT, it is single phase, needle shape grains generally it is showing, it is very hard and very brittle because sometimes it is having that tempered martensite or maybe the normal martensite.



Summary:

- ☐ Phase transformation is the process of formation of a new phase.
- ☐ It involves two process as nucleation and growth.
- ☐ Avrami equation is used for the calculation of degree of progress of transformation phase, which is a function of time.
- ☐ During cooling, transformations occur at temperatures less than predicted by phase diagram called as supercooling.
- ☐ TTT diagram is called temperature-time-transformation plot.
- ☐ Depending on the type of transition, it shows various type of complexity.

So now we have reached to the last slide of this particular lecture, so we have to summarize the whole lecture, so in this particular lecture we have discussed about the phase transformations which is the process of formations of the new phases, which involves the two process generally one is the nucleations another one is the growth, Avrami equations is used here for the calculation of degree of progress of transformation phases, which is a function of time. During cooling transformation occurs at temperature less than predicted by phase diagram called as super cooling, TTT diagram is called the temperature time transformation plot, depending on the type of transition it shows various types of complexity, so simple in this lecture we have seen that changing the temperature, changing the time how the material, same composition is behaving or maybe the showing the difference phases and the different physical properties. Thank you.

For Further Details **Contact**

Coordinator, Educational Technology Cell
Indian Institute of Technology Roorkee
Roorkee- 247 667
E Mail: etcell@iitr.ernet.in, etcell.iitrke@gmail.com
Website: www.nptel.iitm.ac.in

For Further Details Contact
Coordinator Educational Technology Cell
Indian Institute of Technology Roorkee
Roorkee-247 667
E Mail:- etcell@iitr.ernet.in, etcell@iitrke@gmail.com
Website:- www.nptel.iitm.ac.in
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Prof. Ajit Kumar Chaturvedi
Director, IIT Roorkee
NPTEL Coordinator
Prof. B.K Gandhi
Subject Expert
Dr. Kaushik Pal
Department of Mechanical and Industrial
Engineering
IIT Roorkee
Produced By

Mohan Raj. S
Graphics
Binoy. V.P
Web Team
Dr. Nibedita Bisoyi
Neetesh Kumar
Jitender Kumar
Vivek Kumar
Dharamveer Singh
Gaurav Kumar
An Educational Technology Cell
IIT Roorkee Production