LECTURE NOTES ON

PHASE TRANSFORMATIONS & HEAT TREATMENT

6th Semester, MME

For Batches 2013-17, 2014-18 and 2015-19

PHASE TRANSFORMATIONS & HEAT TREATMENT

Course Coordinator

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PHASE TRANSFORMATIONS & HEAT TREATMENT

Course Objective

The aim of this course is to gain an understanding of the role of phase transformations w.r.t. heat treatment on the development of microstructure and properties of metallic materials. The course will highlight a number of commercially-significant applications where phase transformations due to heat treatment are important.

Course Overview

Thermodynamics of phase transformations; solidification of pure metals and alloys; thermal supercooling; constitutional supercooling; interface stability; solute redistribution; Solid state transformations : nucleation and growth of phases; diffusion mechanisms; transformation kinetics; transformation diagrams. Diffusional and Diffusionless transformations: decomposition of solid solutions; ordering reactions, spinodal decomposition; eutectoid, bainitic, martensitic transformations Heat treatment processes, concept of Hardenability and Cast Irons.

Learning Outcomes

Enhanced critical thinking, analytical and problem solving skills in materials science and engineering. An understanding of the principles underlying liquid-to solid and solid-state phase transformations in a range of materials. An understanding of the importance of phase transformations w.r.t. heat treatment for controlling microstructure and properties in engineering alloys.

REFERENCES

☐ Phase Transformations in Metals and Alloys (*This is the major reference for this course*)

D.A.Porter, K.E. Easterling, and M.Y. Sharif

CRC Press , Taylor & Francis Group

☐ Diffusion in solids

Prof. Alok Paul , IISC Banglore

NPTEL Web course

☐ Phase Transformations

Prof. Anandh Subramaniam IIT Kanpur

☐ Steel heat treatment : Metallurgy and Technologies

Geroge E. Totten

CRC Press , Taylor & Francis Group

☐ Heat Treatment : Principles and Techniques

T.V.Rajan, C.P.Sharma and Ashok Sharma

PHI Learning Private Limited

☐ Heat Treatment of Materials

Vijendra Singh

Standard Publishers Distributors, Delhi

☐ Phase Transformations & Heat Treatment
Prof. M.P.Gururajan
NPTEL web course

PHASE TRANSFORMATIONS & HEAT TREATMENT

CONTENTS

Introduction

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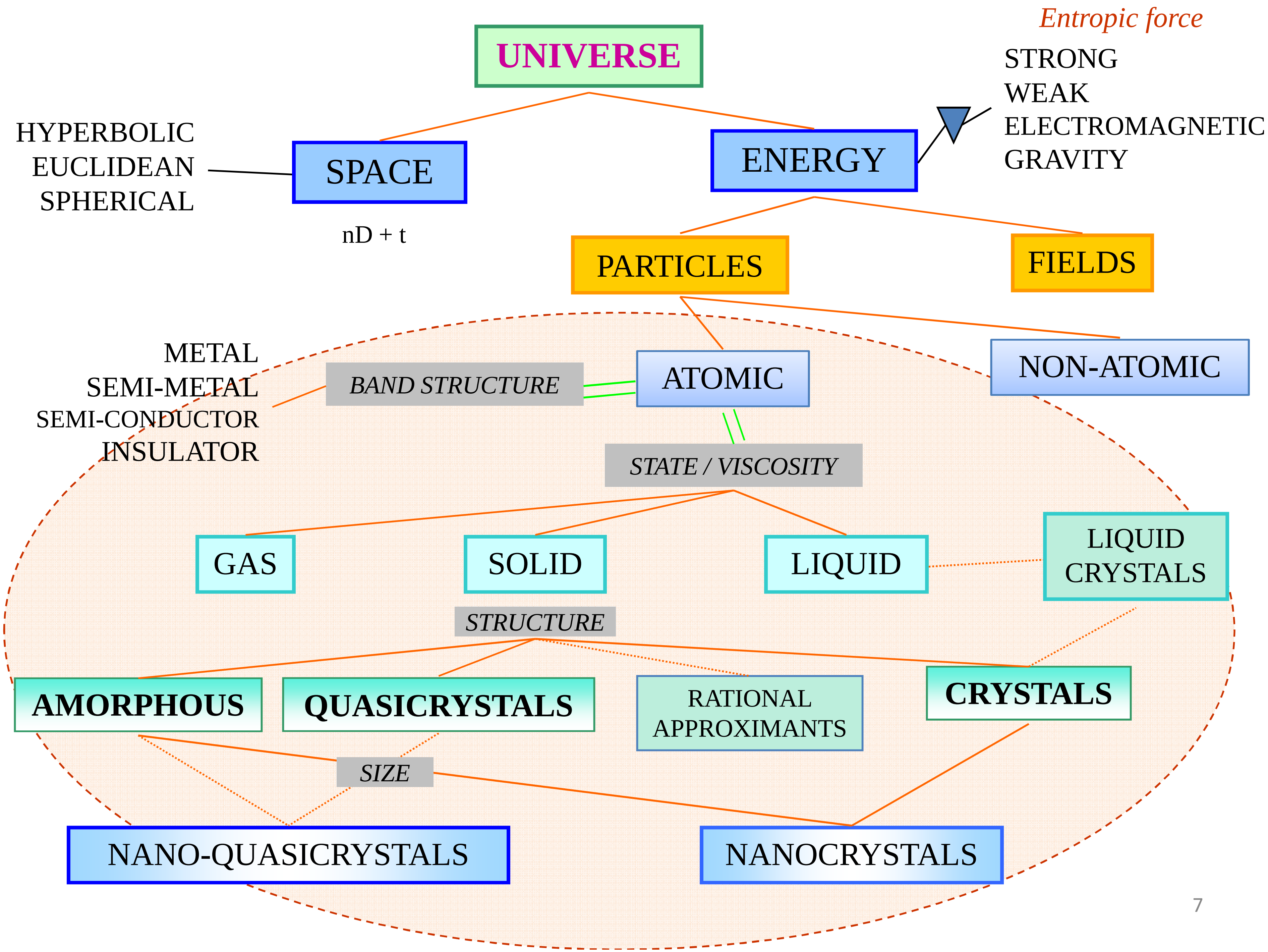


UNIVERSE

SPACE

HYPERBOLIC
EUCLIDEAN
SPHERICAL

nD + t

ENERGY

Entropic force
STRONG
WEAK
ELECTROMAGNETIC
GRAVITY

PARTICLES

FIELDS

ATOMIC

NON-ATOMIC

BAND STRUCTURE

METAL
SEMI-METAL
SEMI-CONDUCTOR
INSULATOR

STATE / VISCOSITY

GAS

SOLID

LIQUID

LIQUID CRYSTALS

STRUCTURE

AMORPHOUS

QUASICRYSTALS

RATIONAL APPROXIMANTS

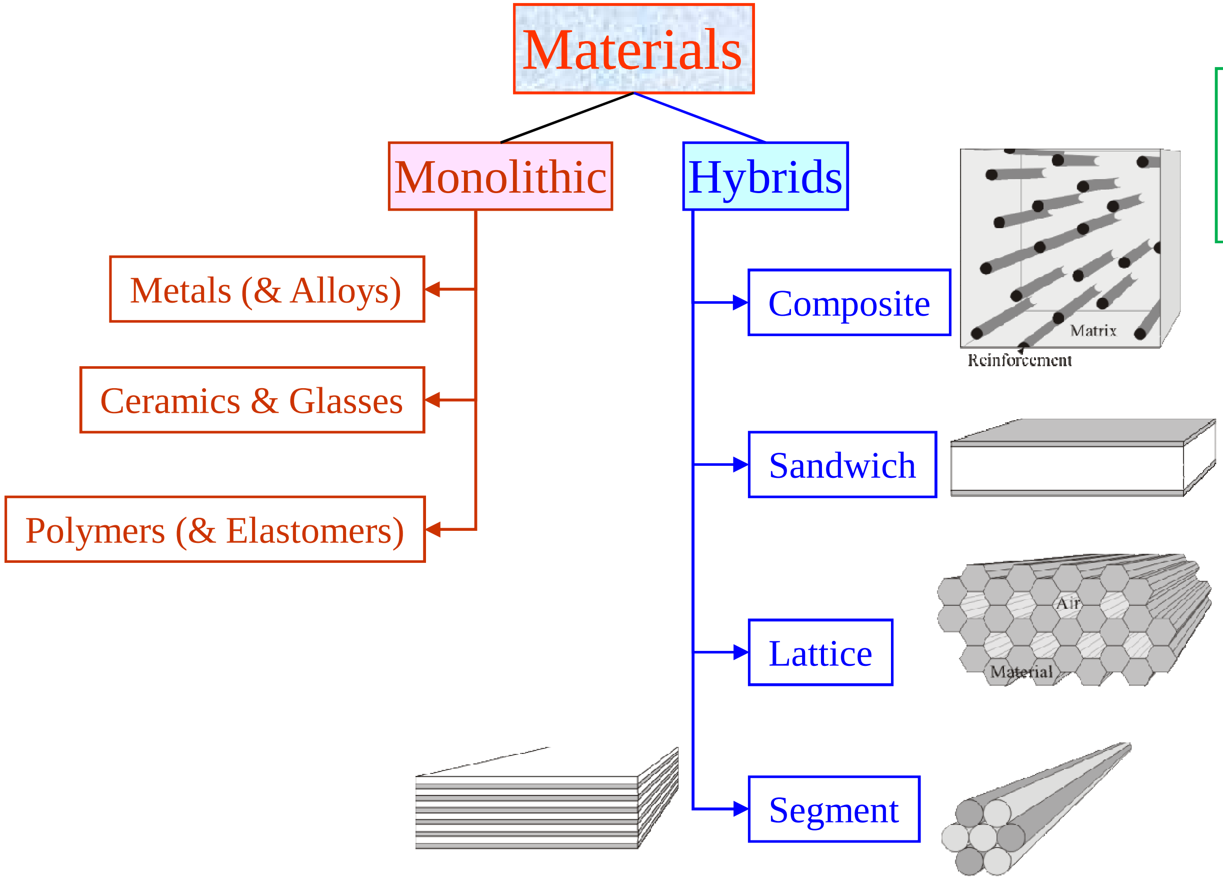
CRYSTALS

SIZE

NANO-QUASICRYSTALS

NANOCRYSTALS

Classification of materials



Materials

- Monolithic
  - Metals (& Alloys)
  - Ceramics & Glasses
  - Polymers (& Elastomers)
- Hybrids
  - Composite
  - Sandwich
  - Lattice
  - Segment

Composites: have two (or more) solid components; usually one is a matrix and other is a reinforcement

Sandwich structures: have a material on the surface (one or more sides) of a core material

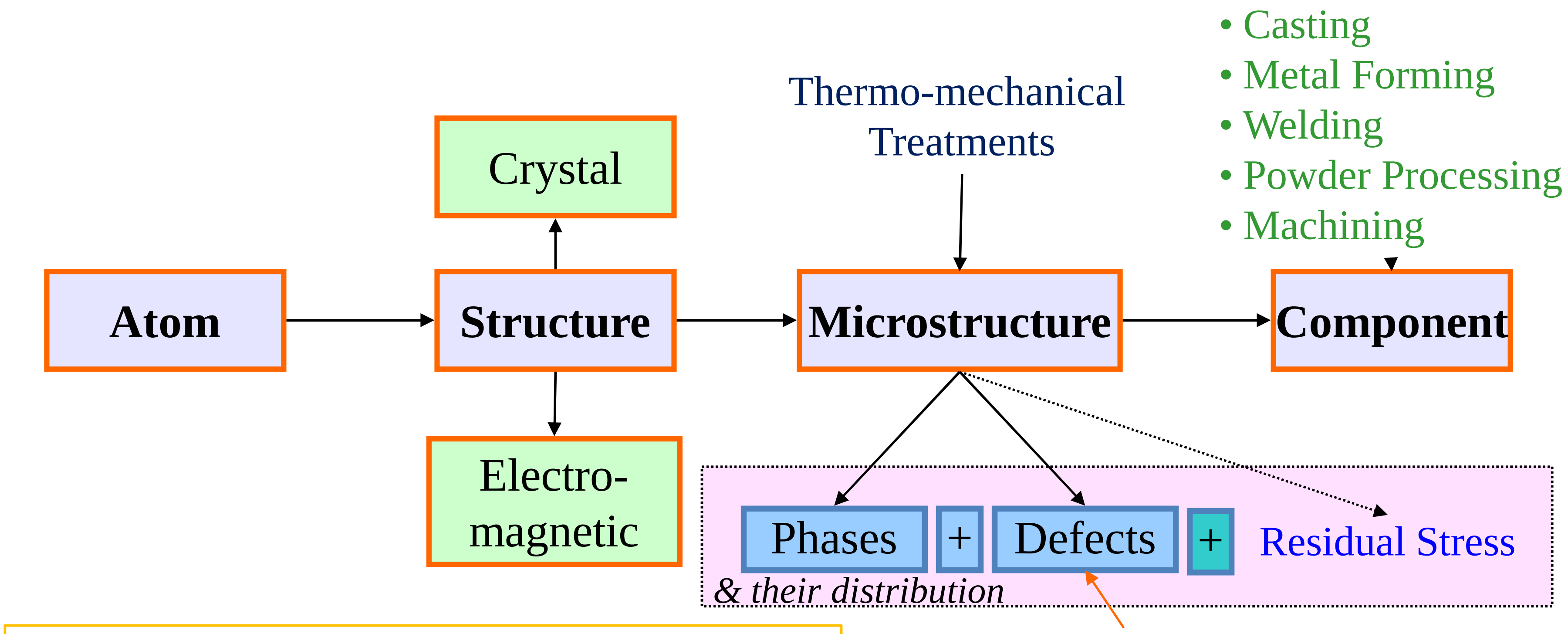
Lattice* Structures: typically a combination of material and space (e.g. metallic or ceramic forms, aerogels etc.).

Segmented Structures: are divided in 1D, 2D or 3D (may consist of one or more materials).

Hybrids are designed to improve certain properties of monolithic materials

*Note: this use of the word 'lattice' should not be confused with the use of the word in connection with crystallography.

Length scales in metallurgy



- Casting
- Metal Forming
- Welding
- Powder Processing
- Machining

Thermo-mechanical Treatments

Atom → **Structure** → **Microstructure** → **Component**

Crystal

Electro-magnetic

Phases + Defects + Residual Stress

& their distribution

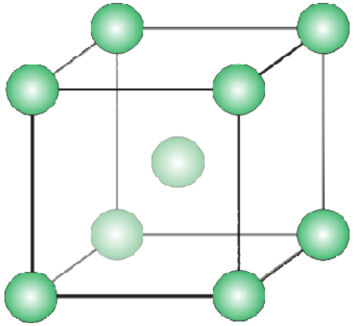
- Vacancies
- Dislocations
- Twins
- Stacking Faults
- Grain Boundaries
- Voids
- Cracks

- ❑ Structure could imply two types of structure:
  - ➢ Crystal structure
  - ➢ Electromagnetic structure
  - ▪ *Fundamentally these aspects are two sides of the same coin*
- ❑ Microstructure can be defined as: (Phases + Defect Structure + Residual Stress) *and their distributions*
- ❑ Microstructure can be 'tailored' by thermo-mechanical treatments

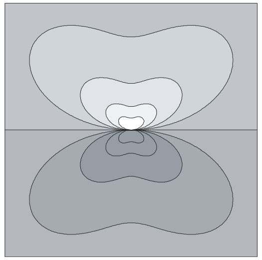
Processing determines shape and microstructure of a component

Length scales in metallurgy

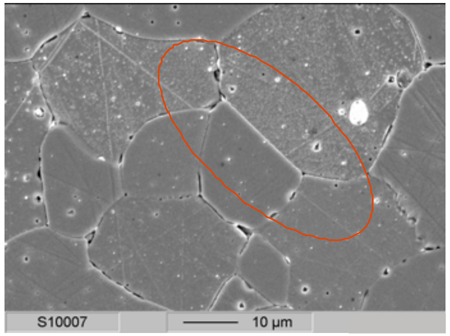
Let us start with a cursory look at the length scales involved in Materials Science



Angstroms

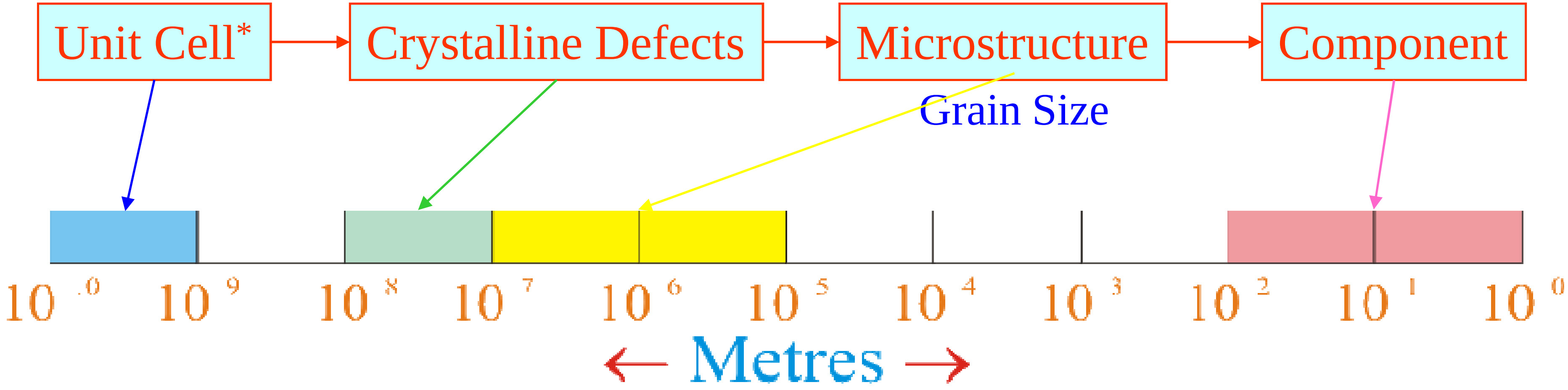


Dislocation Stress fields
→ Nanometers



Microns

Centimeters



Unit Cell* → Crystalline Defects → Microstructure → Component

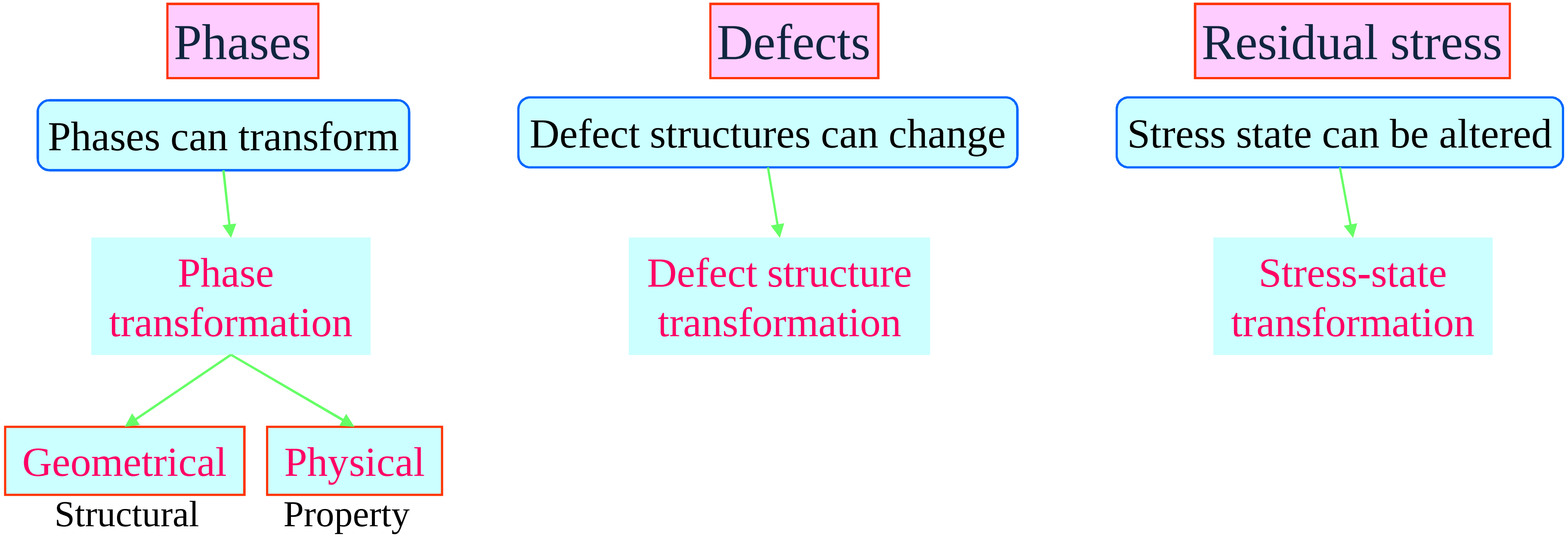
Grain Size

10^{-10} 10^{9} 10^{8} 10^{7} 10^{6} 10^{5} 10^{4} 10^{3} 10^{2} 10^{1} 10^{0}

← Metres →

**Simple Unit Cells*

Transformations in Materials



Phases

Phases can transform

Phase transformation

Geometrical

Structural

Physical

Property

Defects

Defect structures can change

Defect structure transformation

Residual stress

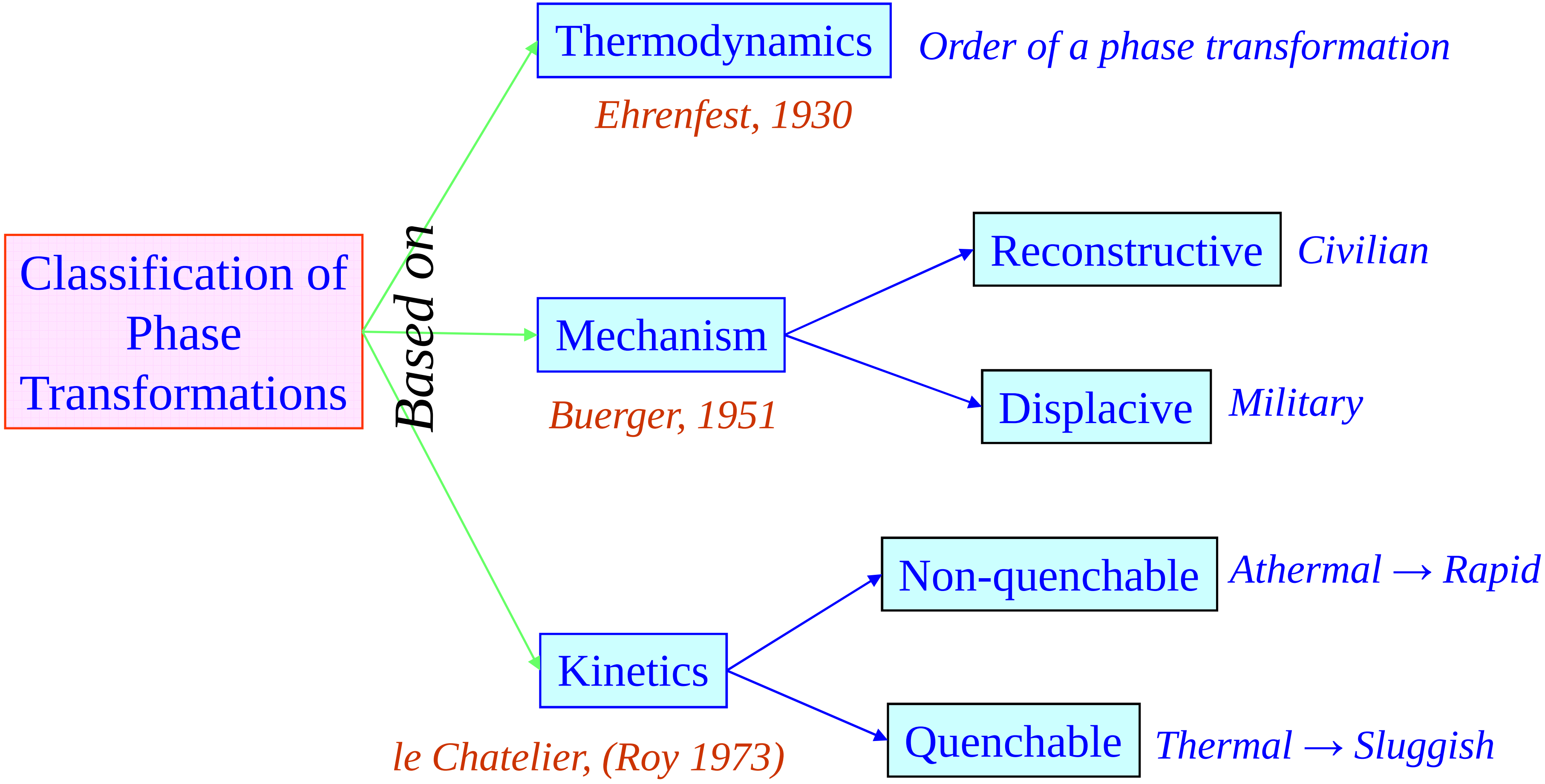
Stress state can be altered

Stress-state transformation

Phases → Microstructure

Phases Transformations → Microstructural Transformations

Classification of Transformations



Classification of Phase Transformations

Based on

Thermodynamics

Order of a phase transformation

Ehrenfest, 1930

Mechanism

Buerger, 1951

- Reconstructive — *Civilian*
- Displacive — *Military*

Kinetics

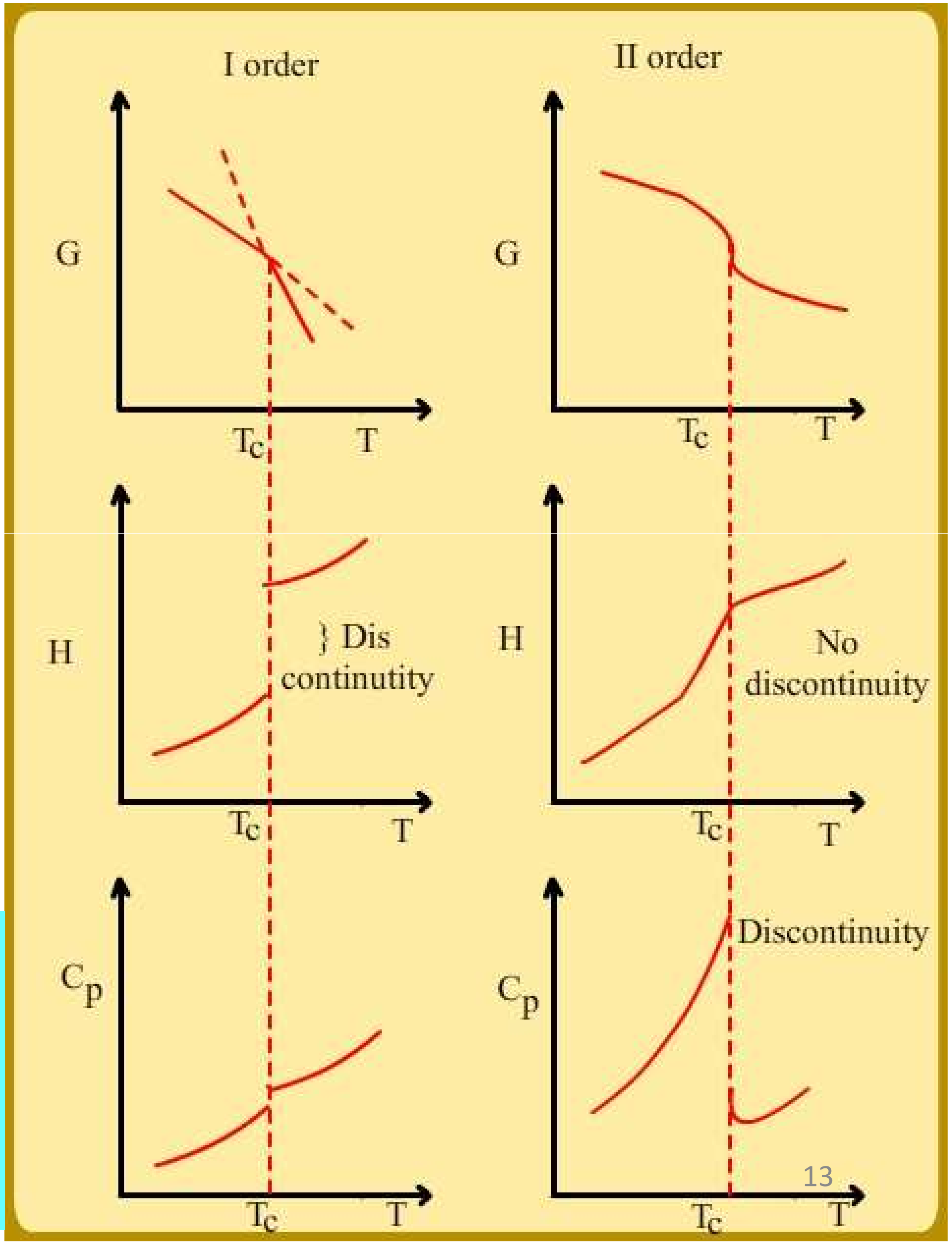
le Chatelier, (Roy 1973)

- Non-quenchable — *Athermal → Rapid*
- Quenchable — *Thermal → Sluggish*

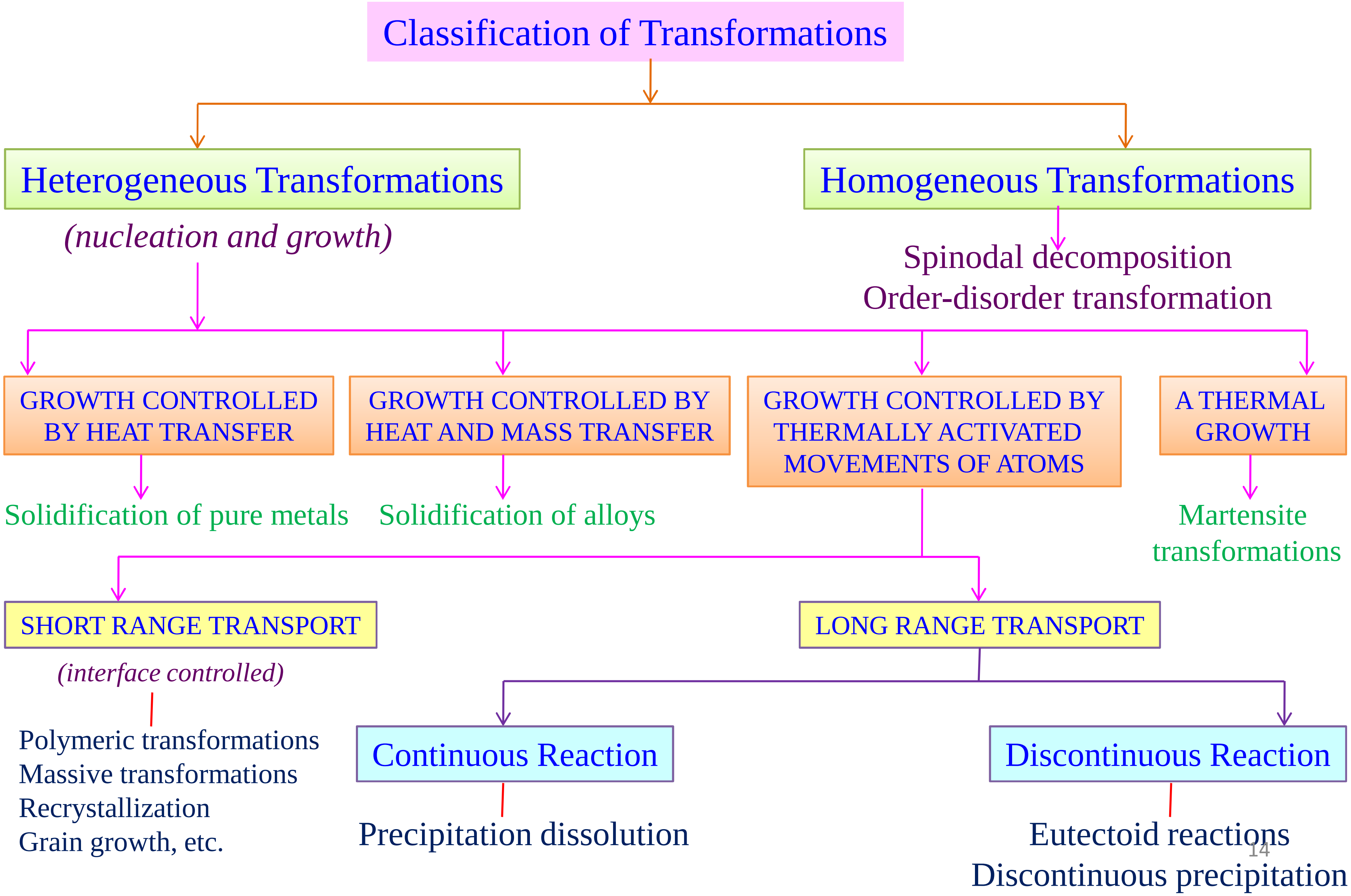
Classification of Transformations

- The thermodynamic characteristics associated with the phase transformations can be used to classify transformations; in this classification methodology, if the nth derivative of free energy (G) with respect to temperature (T) and pressure (P) is discontinuous, it is defined as the nth order transformation.
- As shown in Fig., in transformations such as melting, the first derivative has the discontinuity; hence, melting is a first order transformation; on the other hand, in some of the order/disorder transformations, it is the second derivative which is discontinuous, making it the second order transformation.

Figure: The thermodynamic classification of transformations: the first derivative of the free energy ‘G’ with respect to temperature ‘T’ , that is the enthalpy ‘H’ is discontinuous at the transformation temperature T_c as shown in the first column; the second derivative of the free energy with respective to temperature C_p is discontinuous while ‘H’ is not in the second column, making the order of transformation second.



Classification of Transformations



Classification of Transformations

Heterogeneous Transformations

(nucleation and growth)

Homogeneous Transformations

Spinodal decomposition
Order-disorder transformation

GROWTH CONTROLLED BY HEAT TRANSFER

Solidification of pure metals

GROWTH CONTROLLED BY HEAT AND MASS TRANSFER

Solidification of alloys

GROWTH CONTROLLED BY THERMALLY ACTIVATED MOVEMENTS OF ATOMS

A THERMAL GROWTH

Martensite transformations

SHORT RANGE TRANSPORT

(interface controlled)

Polymeric transformations
Massive transformations
Recrystallization
Grain growth, etc.

LONG RANGE TRANSPORT

Continuous Reaction

Precipitation dissolution

Discontinuous Reaction

Eutectoid reactions
Discontinuous precipitation

Classification of Transformations

- Phase transformations can be classified as homogeneous (transformations which take place through spinodal mechanism in which transformation takes place throughout the material) and heterogeneous (transformations which take place through nucleation and growth mechanism in which transformation takes place heterogeneously at a few places in the material at the start of the transformation).
- Transformations can also be classified as diffusional (or, so called, `civilian') and diffusionless (or, so called `military') depending on the mechanism. In civilian transformations, the nucleation and growth take place via diffusion assisted atomic motion. On the other hand, in the military transformation, the nucleation and growth is by shear and shuffle of atoms by less than one atomic displacement and the movement of all the participating atoms is coordinated.
- There are transformations which are thermally activated (which typically are based on diffusion) while there are others which are athermal.
- The transformations can also be diffusion controlled or interface controlled.
- Transformations can also be differentiated based on whether the interfaces formed are glissile or nonglissile.
- In some transformations there are compositional changes while in some other there are no composition changes.
- Further, transformations which are diffusional can either involve long range diffusion or short range diffusion.

Questions?

1. What is a Phase transformation? How it is depending on Heat treatment?
2. How do the thermodynamic parameters such as G, H, V and C_p vary with temperature for first and second order transformations
3. Explain the classification of phase transformations.
4. What is meant by Glissile transformations?
5. Can a ferromagnetic to paramagnetic change be described as an order-disorder transformation? Explain
6. Give two examples of phase transformations where the proper control of the transformation can result in different combinations of properties.
7. List the possible differences in the nature of short-range diffusion in a polymorphic transformation versus an order-disorder transformation.
8. What types of phase changes require long-range diffusion?
9. In what type of transformation is a composition change not possible?
10. Consider a transformation in which there is a large volume change during transformation. What is the order of such transformation?

Thermodynamics & Kinetics

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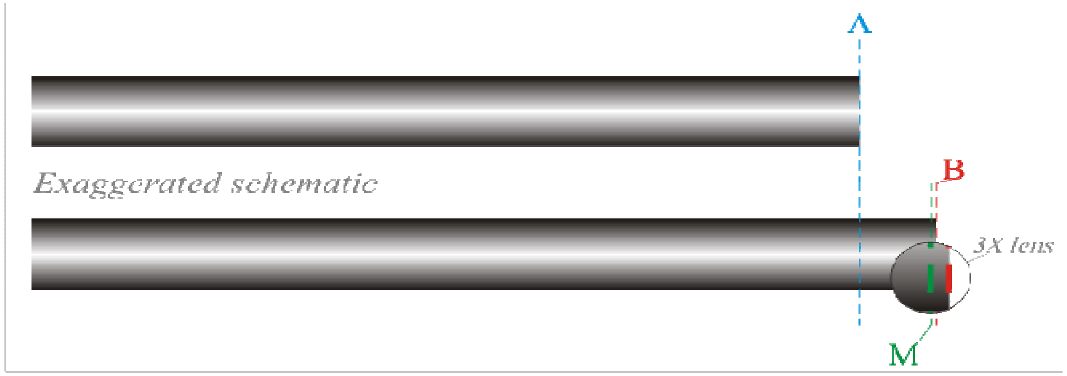
Introduction

- The fields of Thermodynamics and Kinetics are vast oceans and this chapter will introduce the bare essentials required to understand the remaining chapters.
- Let us start by performing the following (thought) experiment:
  Heat a rod of Al from room temperature to 500°C → As expected the rod will expand
  (A → B in figure below).
- The expansion occurs because of two reasons:
  1➢ Vibration of atoms (leading to an increase in average spacing between atoms→ the usual reason) *(A → M in figure below).*
- 2➢ Increase in the concentration of vacancies* (a vacancy is created when a Al atom goes to the surface and for every 4 vacancies created the volume equal to 1 unit cell is added). *(M → B in figure below).* The 2nd reason is a smaller effect in terms of its contribution to the overall increase in length of the specimen



Metal expands on heating due to 2 different physical reasons!

* *It costs energy for the system to put vacancies (broken bonds, distortion to the lattice)*
→ *then why does the system tolerate vacancies?*

Introduction

- Let us next consider the melting of a pure metal at its melting point (MP) (at constant T and P) → by supplying heat to the sample of metal (so that the metal sample is only partly molten). At the MP the liquid metal is in equilibrium with the solid metal.
- The liquid has higher potential energy as well as higher kinetic energy than the solid.
- *Then why does the liquid co-exist with the solid?*
- The answer to this question lies in the fact that internal energy is not the measure of stability of the system *(under the circumstances).*
- We will learn in this chapter that it is the Gibbs Free Energy (G). The molten metal has higher energy (internal energy and enthalpy), but also higher Entropy. So the melting is driven by an increase in Entropy of the system. The molten metal and the crystalline solid metal have the same G → hence they co-exist in equilibrium.

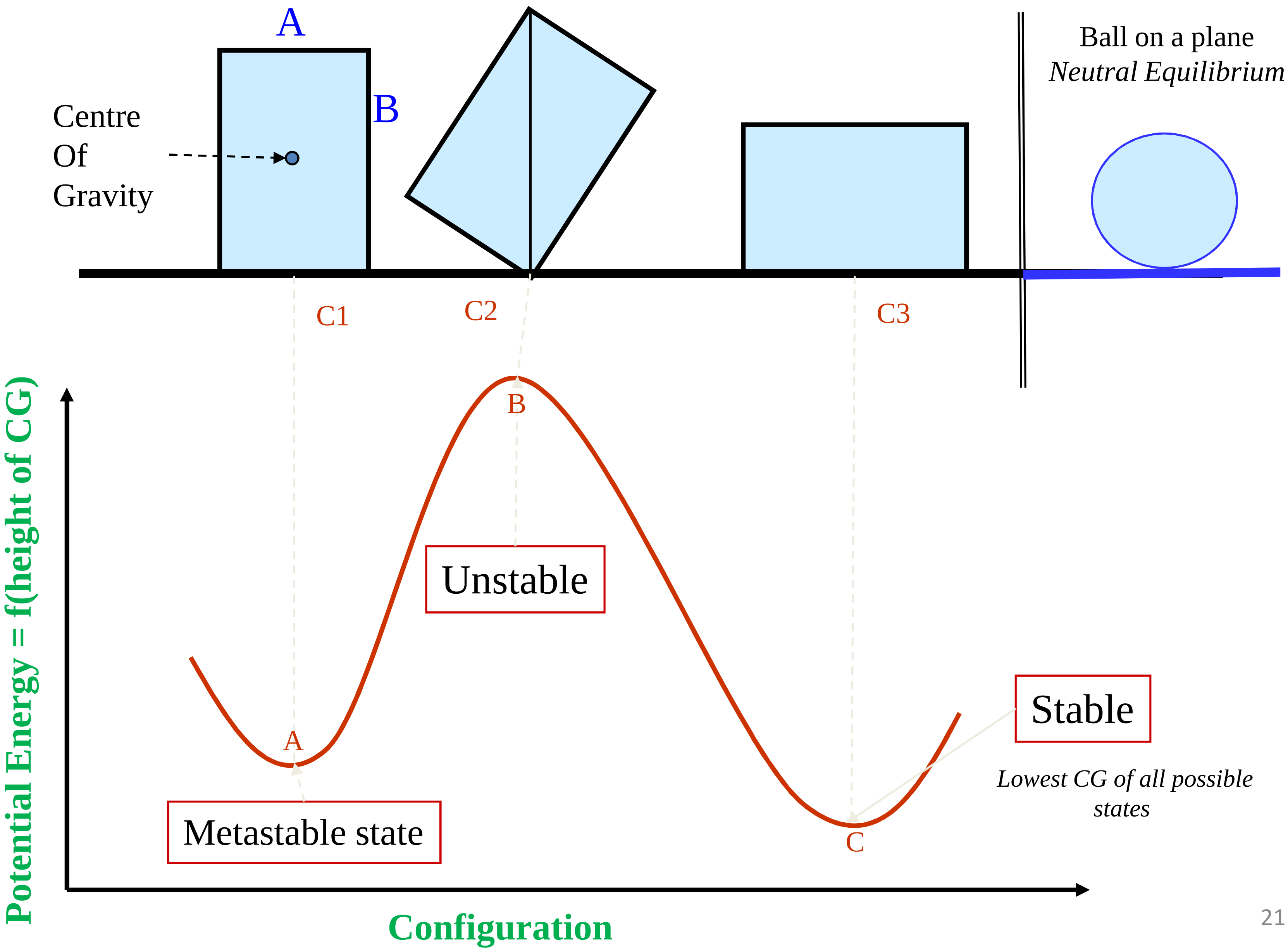
Stability and Equilibrium

- Equilibrium refers to a state → wherein there is a balance of 'forces'* (as we shall see equilibrium points have zero slope in a energy-parameter plot)
- Stability relates to perturbations (usually small perturbations** about an equilibrium state) (as we shall see stable relates to the curvature at the equilibrium points).
- Let us start with a simple mechanical system → a rectangular block *(Figure in next slide)* (under an uniform gravitational potential).
- The potential energy (PE) of the system depends on the height of the centre of gravity (CG).
- The system has higher PE when it rests on face-A, than when it rests on face-B.
- The PE of the system increases when one tilts it from C1 → C2 configuration.
- In configurations such as C1,C2 & C3 the system will be in equilibrium (i.e. will not change its configuration if there are no perturbations).
- In configuration C2 the system has the highest energy (point B) and any small perturbations to the system will take it downhill in energy → Unstable state.
- Configuration C3 has the lowest energy (point C) and the system will return to this state if there are small perturbations → the Stable state.

** Force has been used here in a generalized sense (as an agent which can cause changes)*

** Perturbation is usually a small 'force/displacement' imposed in a short span of time.

Mechanical Equilibrium of a Rectangular Block



Stability and Equilibrium

- Configuration C1 also lies in an 'energy well' (like point C) and small perturbations will tend to bring back the system to state C1. However this state is not the 'global energy minimum and hence is called a Metastable state.
- Additionally, one can visualize a state of neutral equilibrium, like a ball on a plane (wherein the system is in a constant energy state with respect to configurations).
- Points to be noted:
    - A system can exist in many states *(as seen even for a simple mechanical system: block on a plane)*
    - These states could be stable, metastable or unstable
    - Using the relevant (thermodynamic) potential the stability of the system can be characterized (In the case of the block it is the *potential energy*, measured by the height of the CG for the case of the block on the plane)
    - System will 'evolve' towards the stable state provided 'sufficient activation' is provided (in the current example the system will go from C1 to C3 by 'sufficient jolting/shaking' of the plane)

Three kinds of equilibrium (with respect to energy)

- Global minimum → STABLE STATE
- Local minimum → METASTABLE STATE
- Maximum → UNSTABLE STATE

Law’s of Thermodynamics

❑ Zeroth law of Thermodynamics

If two systems are each in thermal equilibrium with a third, then all three are in thermal equilibrium with each other. (Similar to the transitive property of equality in mathematics; i.e. If a = b and b = c, then a = c)

If

&

Then

No heat flows **(A is in equilibrium with B)**

No heat flows **(B is in equilibrium with C)**

No heat flows **(A is in equilibrium with C)**

❑ First law of Thermodynamics

This is a statement of the conservation of energy i.e. When heat (Q) is added to a system, it increases the internal energy (ΔU) of the system and the system does some work (W) on the external world.

$$\Delta U = Q - W$$

For infinitesimal change of the state,

$$dU = \delta Q - \delta W$$

Signs of Q and W	
Q Positive	System gains heat
Q Negative	System loses heat
W Positive	Work done by system
W Negative	Work done on system

Law's of Thermodynamics

❑ Second law of Thermodynamics:

In an isolated system, natural processes are spontaneous when they lead to an increase in disorder, or entropy i.e. The entropy of a system in an adiabatic enclosure always increases for spontaneous/irreversible processes and remains constant during a reversible process but it never decreases.

Entropy S is defined by the equation

$$dS = \frac{\delta Q_{rev}}{T}$$ and is a function of state.

❑ Third law of Thermodynamics:

The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K).

$$\lim_{T \to 0} \Delta S = 0$$

Thermodynamic parameters

- In Materials Science we are mainly interested with condensed matter systems (solids and liquids) (also sometimes with gases)
- The state of such a system is determined by 'Potentials' analogous to the potential energy of the block (which is determined by the centre of gravity (CG) of the block). These potentials are the Thermodynamic Potentials (A thermodynamic potential is a Scalar Potential to represent the thermodynamic state of the system).
- The relevant potential depends on the 'parameters' which are being held constant and the parameters which are allowed to change. More technically these are the State/Thermodynamic Variables (A state variable is a precisely measurable physical property which characterizes the state of the system- It does not matter as to how the system reached that state). Pressure (P), Volume (V), Temperature (T), Entropy (S) are examples of state variables.
- There are 4 important potentials (in some sense of equal stature). These are: Internal Energy, Enthalpy, Gibbs Free Energy, Helmholtz Free Energy.
- Intensive properties are those which are independent of the size of the system
  - P, T
- Extensive Properties are dependent on the quantity of material
  - V, E, H, S, G

Thermodynamic parameters

- **Gibb's free energy**, G can be expressed as G = H-TS
  - H – enthalpy (J/mol) , T – temperature in K, S – entropy (J/mol.K)
- Further H= E+PV
  - E – Internal energy (J/mol), P – Pressure (N/m^2) , V – Volume (m^3/mol)
- In the solid state, the term PV is in general very small (in the temperature and pressure range we consider) and can be neglected.
- On the other hand, internal energy of metals is in the order of kJ/mol. So PV term is less than even 1%.
- **Internal energy** has two components:
  - Potential energy , which depends on atomic bonds and
  - Kinetic energy , which depends on the vibration of atoms at their lattice position
- The relation can be rewritten as H = G + TS
  - H measures the total energy of the body
  - TS measures the useless energy that is the energy which can't be spent for any work or transformation.

Thermodynamic parameters

- So the Gibb’s free energy is defined as the energy that can be “set free” at a particular pressure to do the work or make a particular transformation possible
- Similarly at a particular volume the free energy is called Helmoltz free energy, F, expressed as

  F = E – TS
- We shall consider the Gibb’s free energy since we are going to consider the transformations under constant pressure.
- To determine Gibb’s free energy, we need to determine enthalpy and entropy of the system.

Relation between enthalpy and specific heat

- Let us first consider a **single component system**.
- If we keep the system isolated and do not allow it to interact with the surroundings, the internal energy of the system will not change. This is actually a closed system.
- However, if the system is allowed to interact with the surroundings (that is if it acts as a open system) internal energy might change.
- Suppose the system does work δW in the surroundings and takes heat δQ from the system, then according to the *first law of thermodynamics*, the change in internal energy of the system is

$$\boxed{dE = \delta Q - \delta W}$$

- So after spending some energy for work, rest of the energy is added to the system to increase the internal energy.
- Here exact differential is used for energy because it does not depend on the path and function of the state only. On the other hand heat and work depend on the path.
- If a system changes its volume by dV at a constant pressure P, the work can be expressed as

$$dW = PdV$$

- So, $dE = \delta Q - PdV$, we know $H = E + PV$

$$dH = dE + PdV + VdP$$

$$dH = dQ + VdP$$

Relation between enthalpy and specific heat

- If we divide by *dT* on both sides we get

$$\boxed{\frac{dH}{dT} = \frac{\delta Q}{dT} + V\frac{dP}{dT}}$$

- Specific heat capacity, C_p *at a constant pressure is defined as the heat required* to increase the temperature of the system by one degree. So it can be expressed as

$$\boxed{C_P = \left(\frac{\delta Q}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P}$$

- After integration, we can write

$$\boxed{\int_{H_0}^{H} dH = \int_0^T C_p dT} \qquad \boxed{H_T = H_0 + \int_0^T C_p dT}$$

$$\boxed{H_T = \Delta H_{298} + \int_{298}^T C_p dT}$$

- H_T , H_0 , and ΔH_{298} are the enthalpies at temperature, T, 0, and 298K respectively
- Note that we can not measure absolute thermodynamic values. We rather measure a relative value, H_{298} is considered as reference value.
- For pure metals it considered as zero.

Relation between entropy and specific heat

- As explained before, the knowledge on entropy (which cannot be spent to do a work) is required to determine how much energy is available (free energy) in a system to do useful work from the total heat content or enthalpy.
- Second law of thermodynamics states that the entropy of a system will either remain the same or try to increase.
- When system moves from one equilibrium state 1 to another equilibrium state 2 by changing heat of δQ, the entropy S in a reversible process can be defined as

$$\boxed{S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}}$$

- The value at zero Kelvin is zero and considered as the reference state for entropy, so that the entropy at any temperature T can be expressed as

$$\boxed{S_T = \int_0^T \frac{\delta Q}{T}}$$

- Previously we have seen from the relation $H = E + PV$ and using the first law of thermodynamics

$$\delta Q = dH$$

- We know $dH = C_p\, dT$, So the entropy at T can be expressed as

$$\boxed{S_T = \int_0^T \frac{C_P}{T} dT}$$

Relation between entropy and specific heat

- ❑ Sometimes value of the entropy at the standard state (298 K) is available and can written as

$$\boxed{S_T = \Delta S_{298} + \int_{298}^{T} \frac{C_P}{T} dT}$$

- ❑ So the free energy at temperature, T can be determined

$$G_T = H_T - TS_T$$

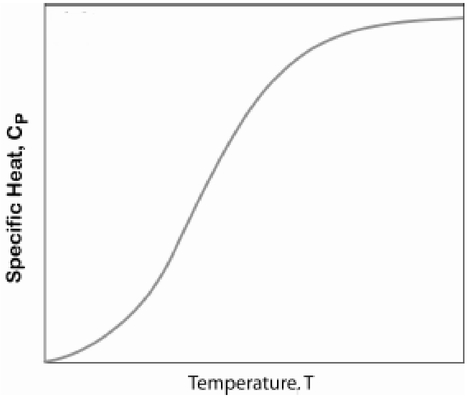
$$G_T = \Delta H_{298} + \int_{298}^{T} C_P dT - T\left(\Delta S_{298} + \int_{298}^{T} \frac{C_P}{T} dT\right)$$

$$G_T = \int_{298}^{T} C_P dT - T\left(\Delta S_{298} + \int_{298}^{T} \frac{C_P}{T} dT\right) \quad \textit{In pure elements}$$

- ❑ Specific heat is expressed as

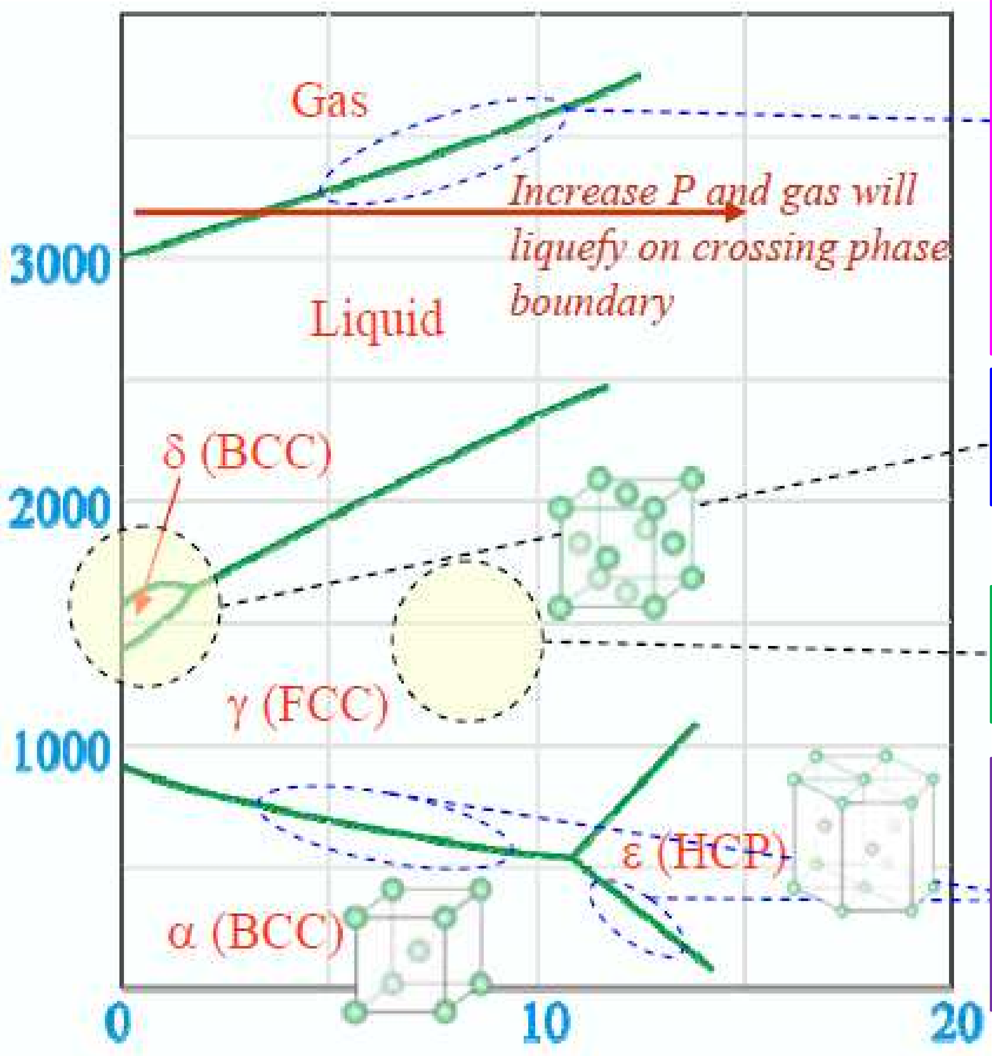
$$C_P = A + BT - \frac{C}{T^2} \qquad \textit{A, B and C are constants.}$$

- ❑ Specific heat is expressed in terms of empirical formula as expressed above.
- ❑ In general the constant values are available in the data book.



Specific heat changes with temperature as shown in the figure

Single component system



This line slopes upward as at constant T if we increase the P the gas will liquefy as liquid has lower volume (similarly the reader should draw horizontal lines to understand the effect of pressure on the stability of various phases- and rationalize the same).

Phase fields of non-close packed structures shrink under higher pressure

Phase fields of close packed structures expand under higher pressure

These lines slope downward as: Under higher pressure the phase with higher packing fraction (lower volume) is preferred

Gibb's free energy change with temperature in a single component system

- An isolated system always tries to maximize the entropy. That means the system is stable when it has maximum possible entropy.
- Instead of considering isolated system, we need to consider the system which interacts with the surroundings because heat transfer is always with respect to the surroundings only.
- Any transformation is possible only when $dS + dS_{Surrou} \geq 0$ where dS is the change in entropy of the system.
- In a reversible process, when system can transform back to its previous state it is equal to zero and in an irreversible process when the system cannot come back to its previous state is greater than zero.
- We need to find the stability with respect to another term, for the sake of convenience, which can be used without referring to the surroundings. We shall show now that free energy is rather a suitable property to define stability of the phases.
- Let us consider that the system absorbs some amount of heat δQ from the system. Since the surrounding is giving away the heat, we can write

$$dS_{surrou} = -\frac{\delta Q}{T}$$

Gibb’s free energy change with temperature in a single component system

- ❑ We have seen before that in an isobaric system $\delta Q = dH$. So we can write

$$dS - \frac{dH}{T} \geq 0$$

$$dH - TdS \leq 0$$

- ❑ We are considering isobaric system. If we consider the transformation at a particular temperature (*T constant, dT = 0)* then

$$dH - TdS - SdT \leq 0$$

$$d(H - TS) \leq 0$$

$$dG \leq 0$$

- ❑ So we have derived a more reasonable relation, which can be used without referring to the surroundings.
- ❑ In an reversible process, such as allotropic transformation or the transformation from solid to liquid or liquid to solid the free energy change is zero. There will be many irreversible transformations (later we shall see these kinds of diffusion controlled transformations), where dG is less than zero.
- ❑ This also indicates that a system will be stable when it has *minimum free energy, so* that it is not possible to get anymore dG less than zero by any further transformation.

Stability of the phases in a single component system

- From previous studies, we understand that system can attain minimum free energy by decreasing enthalpy and/or increasing entropy.

  That means $dH \leq 0$ *and/or* $dS \geq 0$ *since* $dH - TdS \leq 0$
- One component can have different stable phases at different temperature and pressure ranges, for example, solid, liquid and the gas phase.
- One phase is said to be stable, when it has lower free energy compared to other phases in a particular range of temperature and pressure.
- Let us consider constant pressure.
- To compare the stability of different phases in a particular range of temperatures, we need to calculate the free energy of the phases with respect to temperature.
- To determine Gibb's free energy at a particular temperature, we need to determine H and S. Similarly it can be calculated at every temperature to gain knowledge on the change in free energy with temperature.
- As mentioned previously the data on specific heat are available in literature and these parameters can be calculated.

Stability of the phases in a single component system

- From the definition, we know that the slope of the enthalpy at any temperature is equal to the specific heat at that temperature.

$$G = H - TS$$

$$dG = dH - TdS - SdT \qquad (H = E + PV)$$

$$dG = dE + PdV + Vdp - TdS - SdT \qquad (dE = \delta Q - PdV)$$

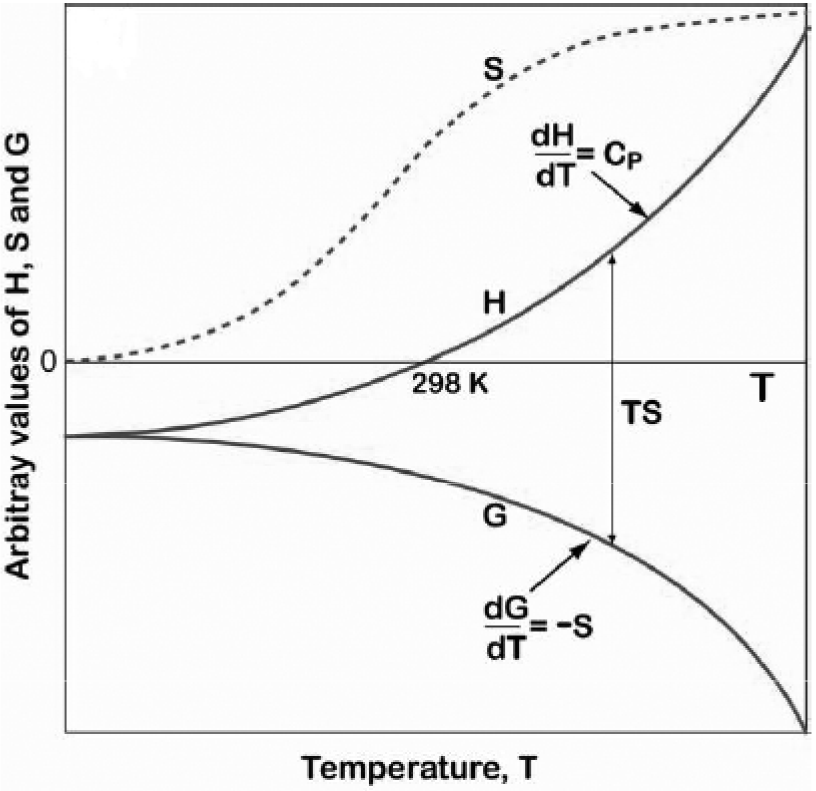
$$dG = \delta Q - PdV + PdV + VdP - TdS - SdT \qquad \frac{\delta Q}{T} = dS$$

$$dG = TdS + VdP - TdS - SdT$$

$$dG = VdP - SdT$$ **(Maxwell's Relation)**

- So at a constant pressure the slope of the free energy curve

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

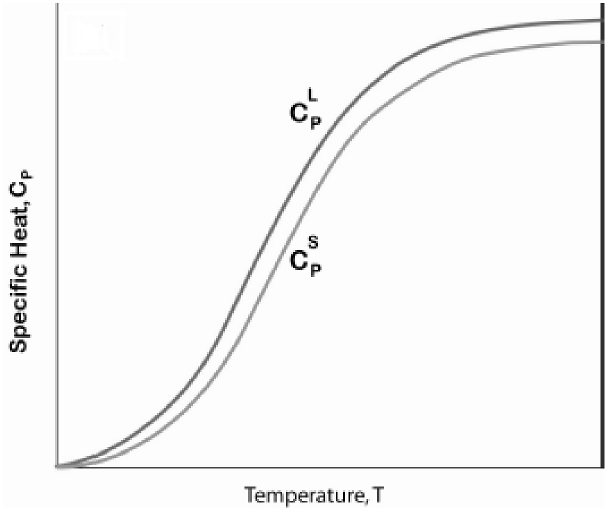


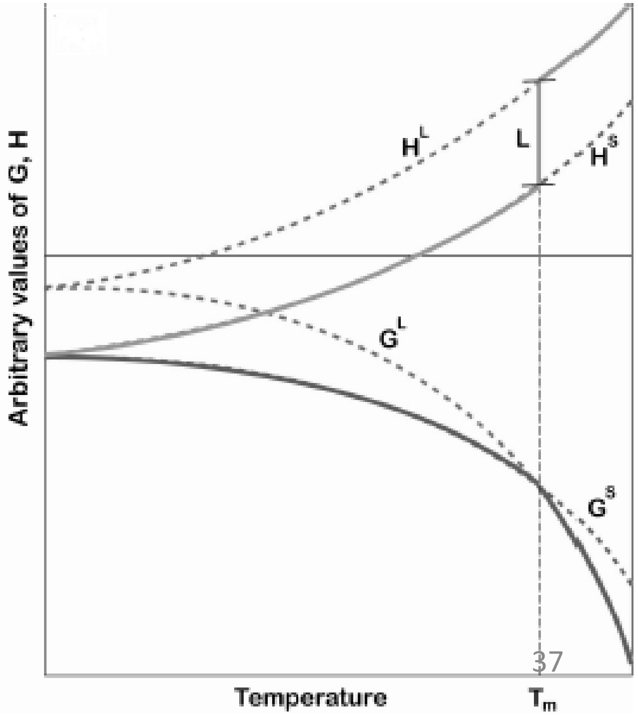
Typical variation of thermodynamic parameters are shown in the figure.

- *If we want to know whether a solid or liquid phase will be stable at a particular temperature or in a temperature range, we need to find free energy for both the phases.*

Stability of the phases in a single component system

- For that we need to know the variation of specific heat with temperature for both the phases as shown in the figure.
- Specific heat for a liquid phase is always higher than the solid phase. That means energy required to increase the temperature by one degree for liquid phase is higher than the solid phase.
- Superscript, S and L denote the solid and liquid phases.
- Free energy for liquid phase changes more drastically compared to the free energy of the liquid phase because entropy of the liquid phase is always higher, which is the slope of the free energy.
- At melting point, free energy for both the phases are the same and the difference between the enthalpy of these two phases is equal to the latent heat of fusion L.

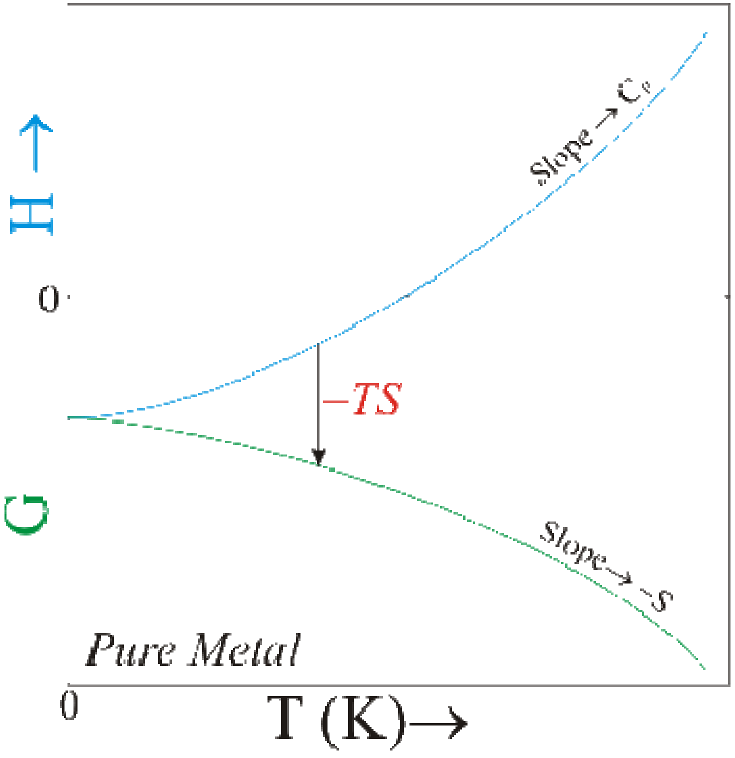


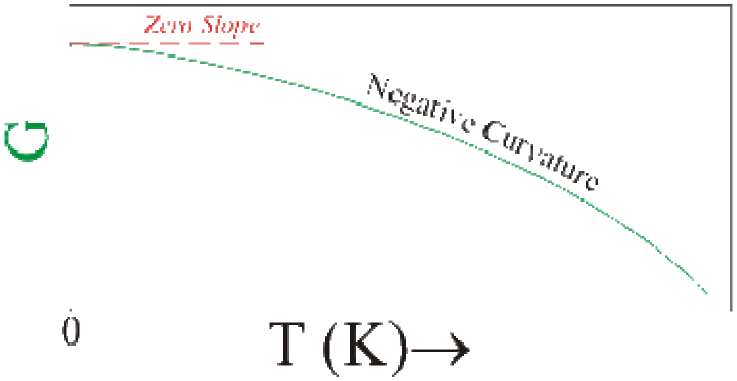


Stability of the phases in a single component system

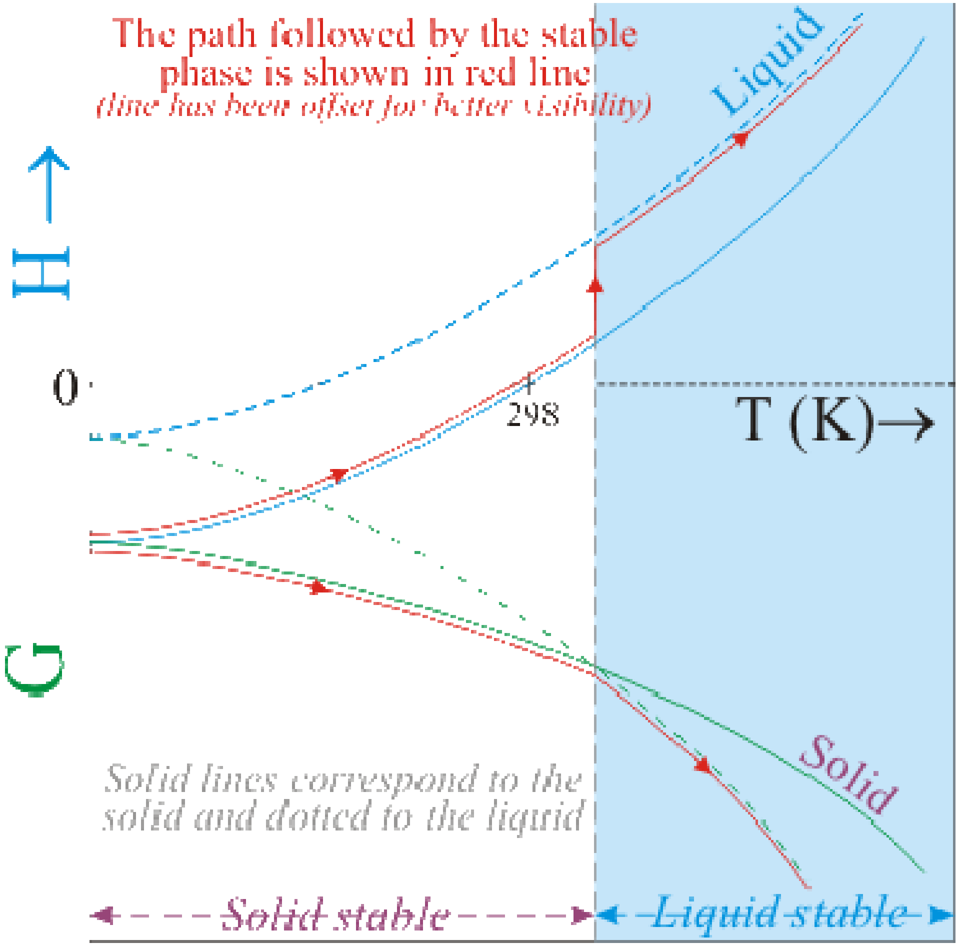
- It must be apparent that one particular phase at certain temperature range will be stable, if the free energy, G is lower of that phase than the other phase.
- At low temperature range, one particular phase will be stable, which has low enthalpy, since "TS" term will not dominate. That is why *solid phase* is stable at *low temperature* range.
- On the other hand, at higher temperature range, phase having higher entropy will be stable since in this range "TS" term will dominate. That is why *liquid phase* is stable at *high temperature* range.
- This is the reason that α-Ti with close packed HCP structure is stable at low temperature range, whereas, at high temperature range β-Ti with relatively more open BCC structure is stable.
- If we fix a temperature, we have seen that one material/element will be stable as one type of phase with a particular state compared to other.
- It can stay in equilibrium if it has minimum free energy and dG=0, it indicates that for small fluctuation it does not move to another state.

Gibbs Free Energy (G) vs T, H, S





Melting transition


The path followed by the stable phase is shown in red line
(line has been offset for better visibility)

Solid lines correspond to the solid and dotted to the liquid

Pressure Effects

From previous studies

$$dG = VdP - SdT$$

$$G^l = G^s \rightarrow \Delta G = 0$$

$$consider : S \rightarrow L$$

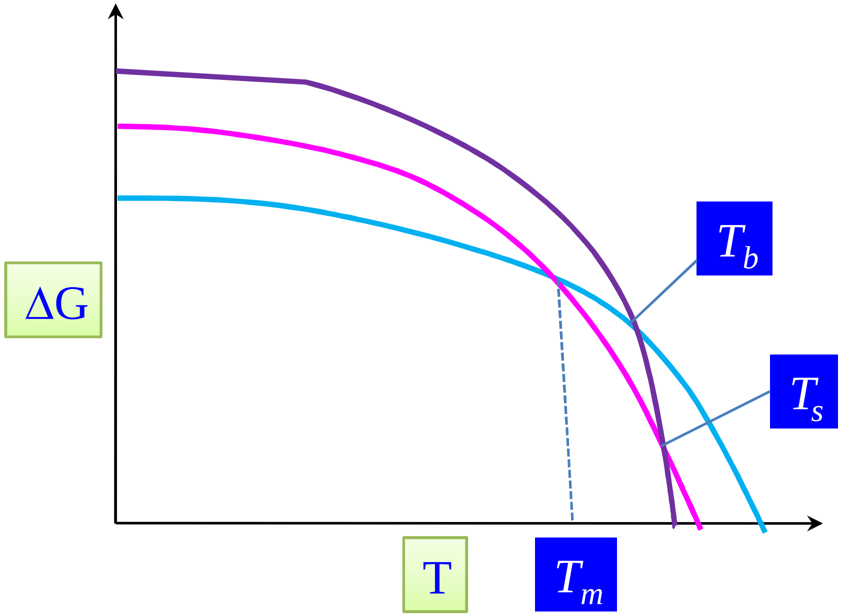
$$dG^S = V^S dT - S^S dT$$

$$dG^L = V^L dT - S^L dT$$

$$(V^S - V^L)dP = (S^S - S^L)dT$$

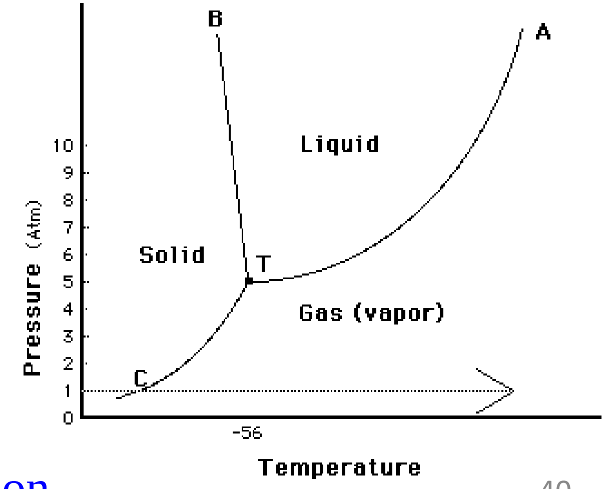
$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S} = \frac{V^S - V^L}{S^S - S^L}$$

$\dfrac{dT}{dP} =$ *The rate of change of transformation temperature as a function of pressure*



$$\boxed{\frac{dT}{dP} = \frac{\Delta V}{\Delta S}}$$

Is known as Clausius-Clapeyron equation



Pressure Effects

- The equation (previous page) can also write
- We know $\Delta G = \Delta H - T\Delta S$
- At equilibrium $\Delta G = 0$ i.e., $\Delta H - T\Delta S = 0$, $\Delta S = \frac{\Delta H}{T}$

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}}$$

Is also known as Clausius-Clapeyron equation

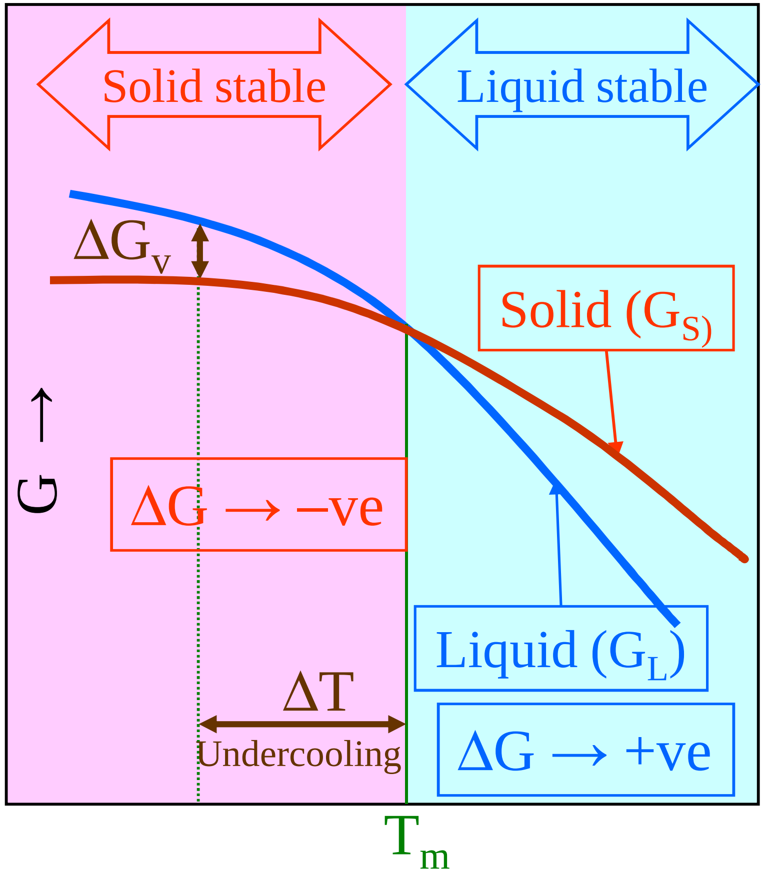
- Example: close packed γ-Fe has a smaller molar volume than α – Fe, $\Delta V = V^{\gamma} - V^{\alpha} < 0$ whereas $\Delta H = H^{\gamma} - H^{\alpha} > 0$ (for the same reason that a liquid has a higher enthalpy than a solid), so that (dP/dT) is negative, i.e., an increase in pressure lowers the equilibrium transition temperature.
- On the other hand the δ/L equilibrium temperature is raised with increasing pressure due to the larger molar volume of the liquid phase. It can be seen that the effect of increasing pressure is to increase the area of the phase diagram over which the phase with the smallest molar volume is stable.

Driving force for solidification

- ❑ In dealing with phase transformations, we are often concerned with the difference in free energy between two phases at temperatures away from the equilibrium temperature.
- ❑ For example if a liquid metal is under cooled by ΔT below T_m before it solidifies, solidification will be accompanied by a decrease in free energy ΔG (J/mol) as shown in figure.
- ❑ This free energy decreases provides the driving force for solidification. The magnitude of this change can be obtained as follows.
- ❑ The free energies of the liquid and solid at a temperature T are given by

$$G^L = H^L - TS^L$$

$$G^S = H^S - TS^S$$



Therefore, at a temperature T $\Delta G = \Delta H - T\Delta S$ →①

Where $\Delta H = H^L - H^S$ *and* $\Delta S = S^L - S^S$

Driving force for solidification

- ❑ At the equilibrium melting temperature T_m the free energies of solid and liquid are equal, i.e., $\Delta G = 0$. Consequently

$$\Delta G = \Delta H - T_m \Delta S = 0$$

- ❑ And therefore at T_m

$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m} \quad \rightarrow ②$$

- ❑ This is known as the entropy of fusion. It is observed experimentally that the entropy of fusion is a constant ≈ R (8.3 J/mol . K) for most metals (Richard's rule).
- ❑ For small undercoolings (ΔT) the difference in the specific heats of the liquid and solid (C_p^L - C_p^S) can be ignored.
- ❑ Combining equations 1 and 2 thus gives

$$\boxed{\Delta G \cong L - T\frac{L}{T_m}}$$

- ❑ i.e., for small ΔT

$$\boxed{\Delta G \cong \frac{L\Delta T}{T_m}}$$

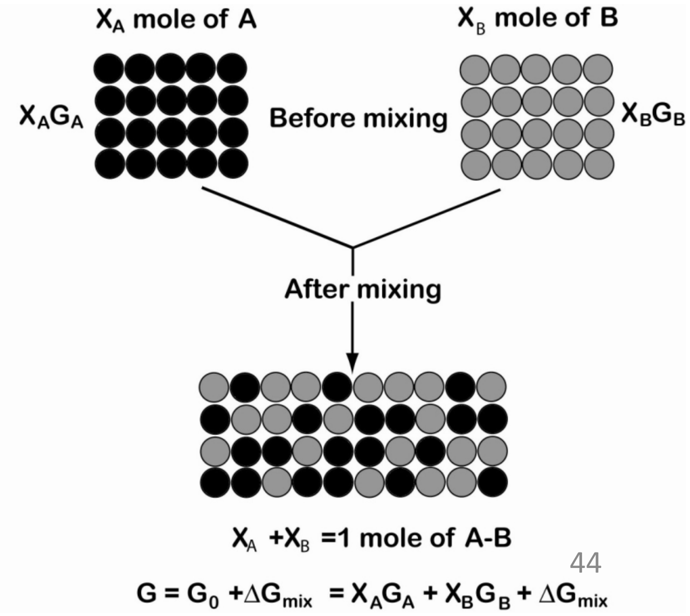
This is called Turnbull's approximation

Thermodynamic parameters in a binary system

- Previously we are considered one element only. Now we consider interaction between two elements. This is not straightforward since elements can interact differently and thermodynamic parameters may change accordingly.
- Let us consider a Binary system with elements A and B. For our analysis, we consider X_A mole of A and X_B mole of B so that $\boldsymbol{X_A + X_B = 1}$
- That means we consider total one mole of the system That further means we consider total number of atoms equal to the Avogadro number, N_0 $(= 6.023 \times 10^{23})$,

$$\text{Where} \quad X_i = \frac{N_i}{N_0} \quad \text{is the number of atoms of element } i.$$

- Unlike single component system, where we determine the change in free energy with temperature, in the binary case we shall find the change in free energy with the change in composition at different constant temperature at a time.
- Let us consider the free energy for one mole of element A is G_A and one mole of B is G_B.



Thermodynamic parameters in a binary system

- So before mixing when kept separately, X_A mole of A and X_B mole of B will have the free energy of $X_A G_A$ *and* $X_B G_B$ respectively

Total free energy before mixing $G_0 = X_A G_A + X_B G_B$

- After mixing there will be change in free energy
- Total free energy after mixing

$$G = G_0 + \Delta G_{mix}$$

- ΔG_{mix} is the free energy change of the alloy because of mixing

$$\Delta G_{mix} = G - G_0 = H - TS - (H_0 - TS_0) = (H - H_0) - T(S - S_0)$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

- So, once we determine the change in free energy because of mixing, we can determine the total free energy after mixing.
- Let us first determine, the enthalpy change because of mixing (ΔH_{mix}) and the change in entropy because of mixing (ΔS_{mix})
- Note that system always tries to decrease enthalpy and increase entropy for stability.

The change in enthalpy because of mixing, ΔH_{mix}

- ☐ We take the following assumptions:
  - ✓ The molar volume does not change because of mixing
  - ✓ Bond energies between the pure elements do not change with the change in composition
  - ✓ We neglect the role of other energies.
- ☐ After mixing, the system can have three different types of bonding, A-A, B-B and A-B
- ☐ Enthalpy of mixing can be expressed as $\Delta H_{mix} = N_0 Z X_A X_B \Delta\varepsilon$

  N_0 - Avogrado number, Z = coordination number

- ☐ The change in internal energy

$$\Delta\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

ε_{AB} is the bond energy between A and B

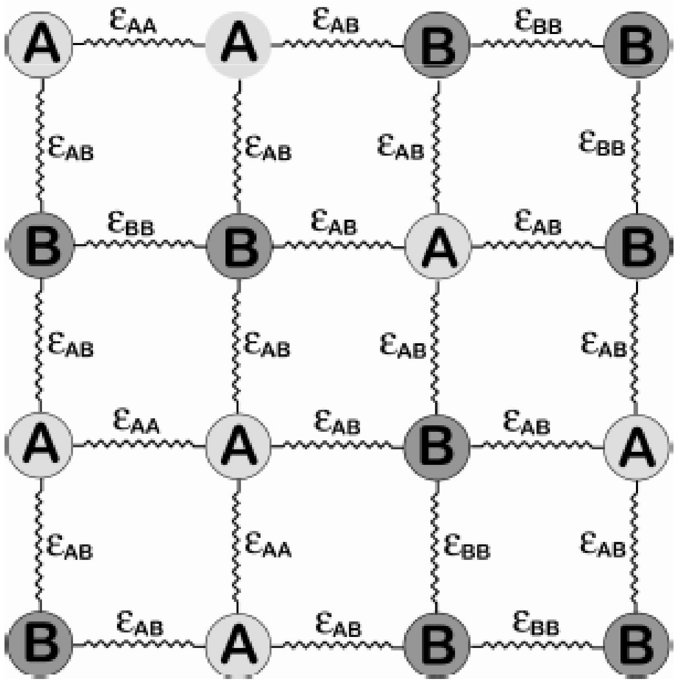
ε_{AA} *is the bond energy between A and A*

ε_{BB} *is the bond energy between B and B*

- ☐ It can be written as

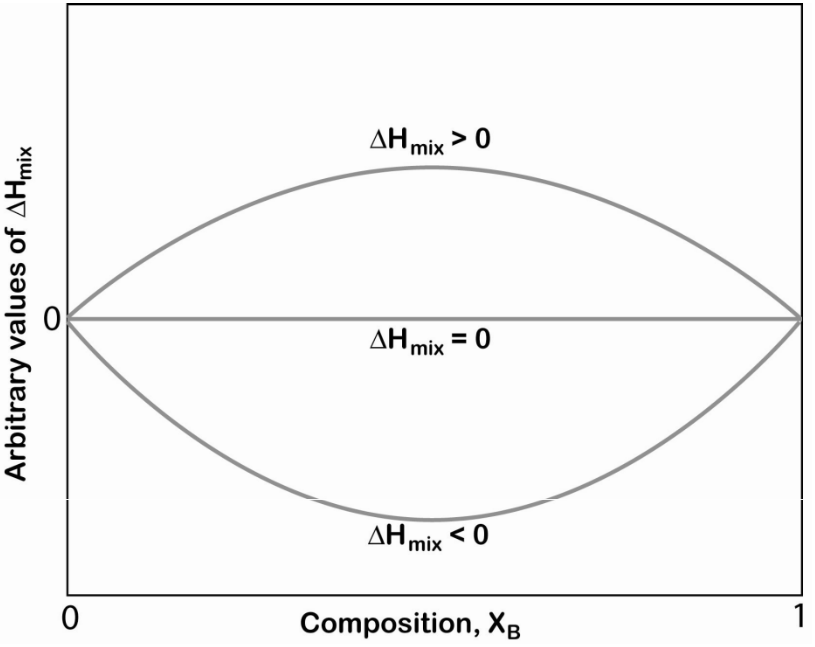
$$\boxed{\Delta H_{mix} = \Omega X_A X_B}$$

Where $\Omega = N_0 Z \Delta\varepsilon$



The change in enthalpy because of mixing, ΔH_{mix}

Situation 1: Enthalpy of mixing is zero



$$\Delta H_{mix} = \Omega X_A X_B = 0$$

That means $\varepsilon_{AB} = \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

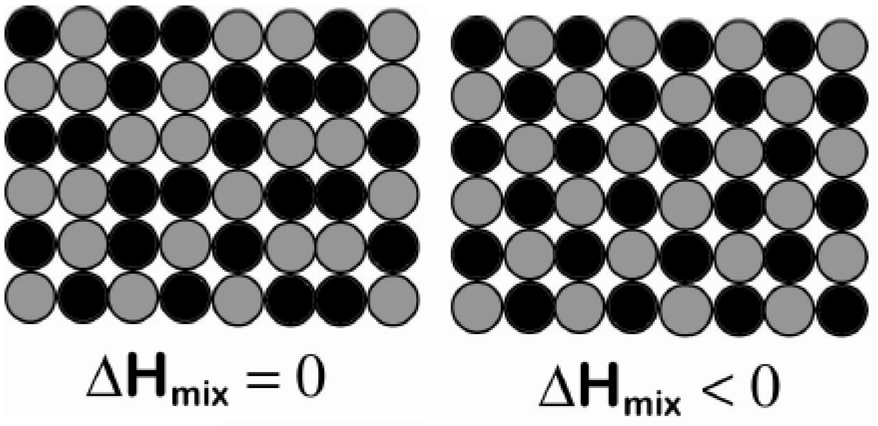
There will be no preference to choose neighboring atoms. Atoms can sit randomly at any lattice points .

Situation 2: Enthalpy of mixing is less than zero

$$\Delta H_{mix} = \Omega X_A X_B < 0$$

That means $\varepsilon_{AB} < \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

Because of transformation internal energy will decrease. That means transformation is exothermic. Atoms will try to maximize A-B bonds.



$\Delta H_{mix} = 0$ $\quad$ $\Delta H_{mix} < 0$

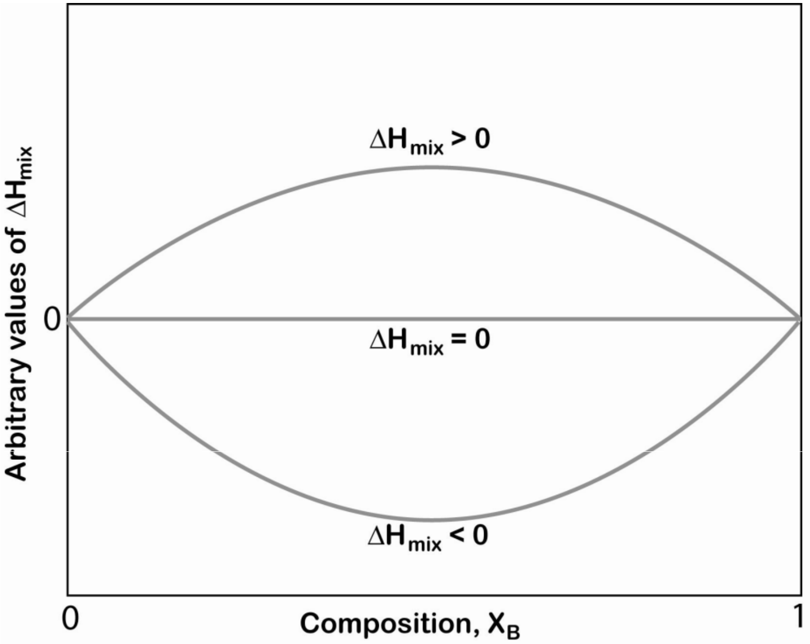
The change in enthalpy because of mixing, ΔH_{mix}

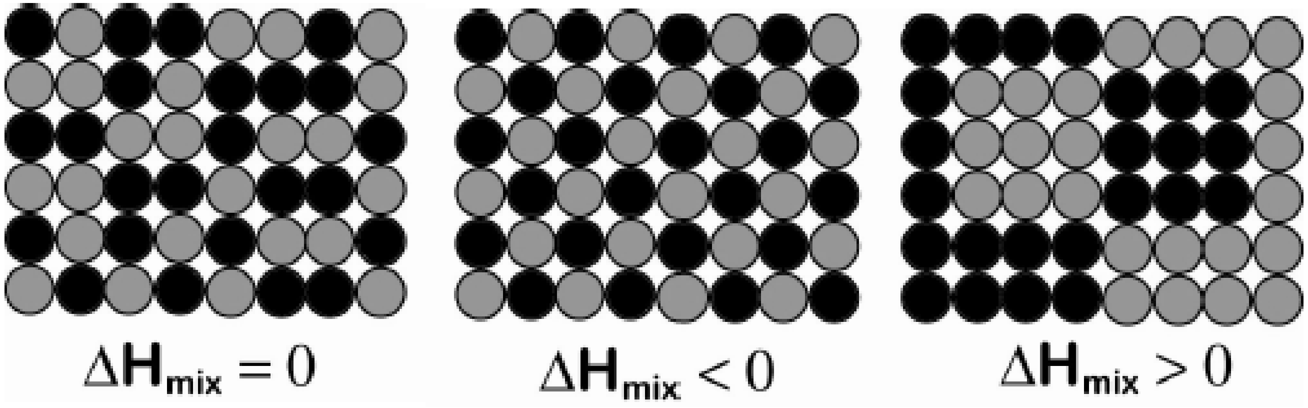
Situation 3: Enthalpy of mixing is greater than zero

$$\Delta H_{mix} = \Omega X_A X_B > 0$$

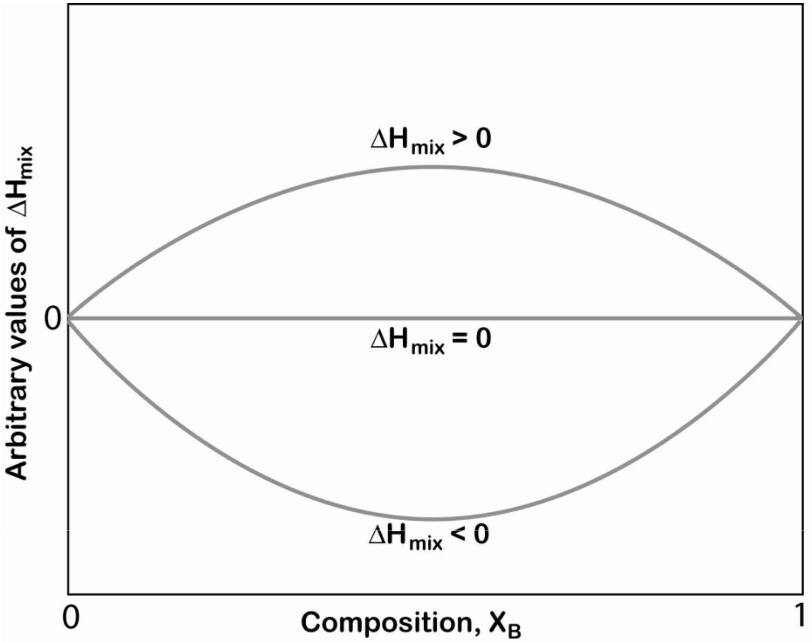
That means $\varepsilon_{AB} > \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

Because of transformation internal energy will increase. That means transformation is to be endothermic. Atoms will try to maximize A-A and B-B bonds.





Slope/maximum/minimum of the enthalpy of mixing curve



$$\Delta H_{mix} = \Omega X_A X_B = \Omega (X_B - X_B^2)$$

$$\frac{d(\Delta H_{mix})}{dX_B} = \Omega(1 - 2X_B)$$

At maximum/minimum $\frac{d(\Delta H_{mix})}{dX_B} = 0$ *This implies X_B = 0.5. That means maximum or minimum will be at X_B =0.5*

Further $\frac{d(\Delta H_{mix})}{dX_B}$ at $X_B \rightarrow 0 = \Omega$ *That means the slope at the beginning has a finite value of x*

The change in entropy because of mixing, ΔS_{mix}

- Since we are considering transformation at a particular temperature, the change in entropy because of the change in temperature can be neglected.
- We need to consider only the configurational entropy change. Configurational entropy change comes from the possibilities of different ways of arrangement of atoms.
- Following statistical thermodynamics the configurational entropy can be expressed as

$$S = l \ln \omega$$

k is the Boltzmann constant
w is the measure of randomness

$$\Delta S_{mix} = S - S_0 = k \ln \omega - k \ln 1 = k \ln \omega$$

since atoms at their pure state before mixing can be arranged in only one way

- If we consider the random solid solution, then

$$\omega = \frac{(n_A + n_B)!}{n_A! n_B!}$$

n_A and n_B are the number of atoms of A and B

- *Following Stirling's approximation* $\ln N! = N \ln N - N$

The change in entropy because of mixing, ΔS_{mix}

❑ ***So, ΔS_{mix} can be written as***

$$\Delta S_{mix} = k \ln \omega = k\{[(n_A + n_B)\ln(n_A + n_B) - (n_A + n_B)] - [n_A \ln n_A - n_A] - [n_B \ln n_B - n_B]\}$$

$$\Delta S_{mix} = -k\left[n_A \ln \frac{n_A}{n_A + n_B} + n_B \ln \frac{n_A}{n_A + n_B} \right]$$

Number of atoms can be related to the mole fraction, X and the Avogadro number N_0 following

$$n_A = X_A N_0 \qquad n_B = X_B N_0$$

$$X_A + X_B = 1 \qquad n_A + n_B = N_0$$

$$\Delta S_{mix} = -kN_0[X_A \ln X_A + X_B \ln X_B]$$

$$= R[X_A \ln X_A + X_B \ln X_B]$$

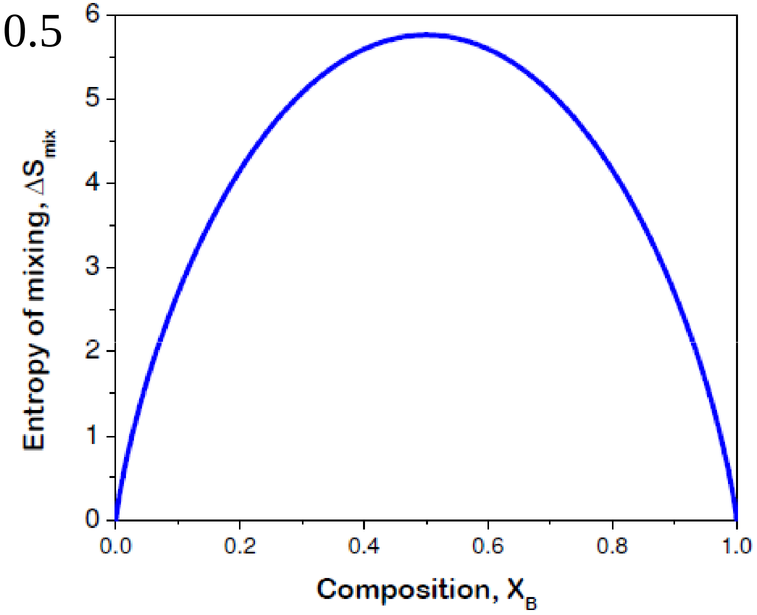
where, R is the gas constant

Slope/maximum of the entropy of mixing curve

$$\frac{d(\Delta S_{mix})}{dX_B} = -R\left[-\ln(1-X_B) - (1-X_B)\frac{1}{(1-X_B)} + \ln X_B + X_B\frac{1}{X_B}\right] = -R\ln\frac{X_B}{1-X_B}$$

$$\frac{d(\Delta S_{mix})}{dX_B} = 0$$ at maximum, this corresponds to $X_B = 0.5$

Further, the slope at $X_B \rightarrow 0$ is infinite. That means the entropy change is very high in a dilute solution



As mentioned earlier the total free energy after mixing can be written as $G = G_0 + \Delta G_{mix}$

where

$$G_0 = X_A G_A + X_B G_B$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta H_{mix} = \Omega X_A X_B$$

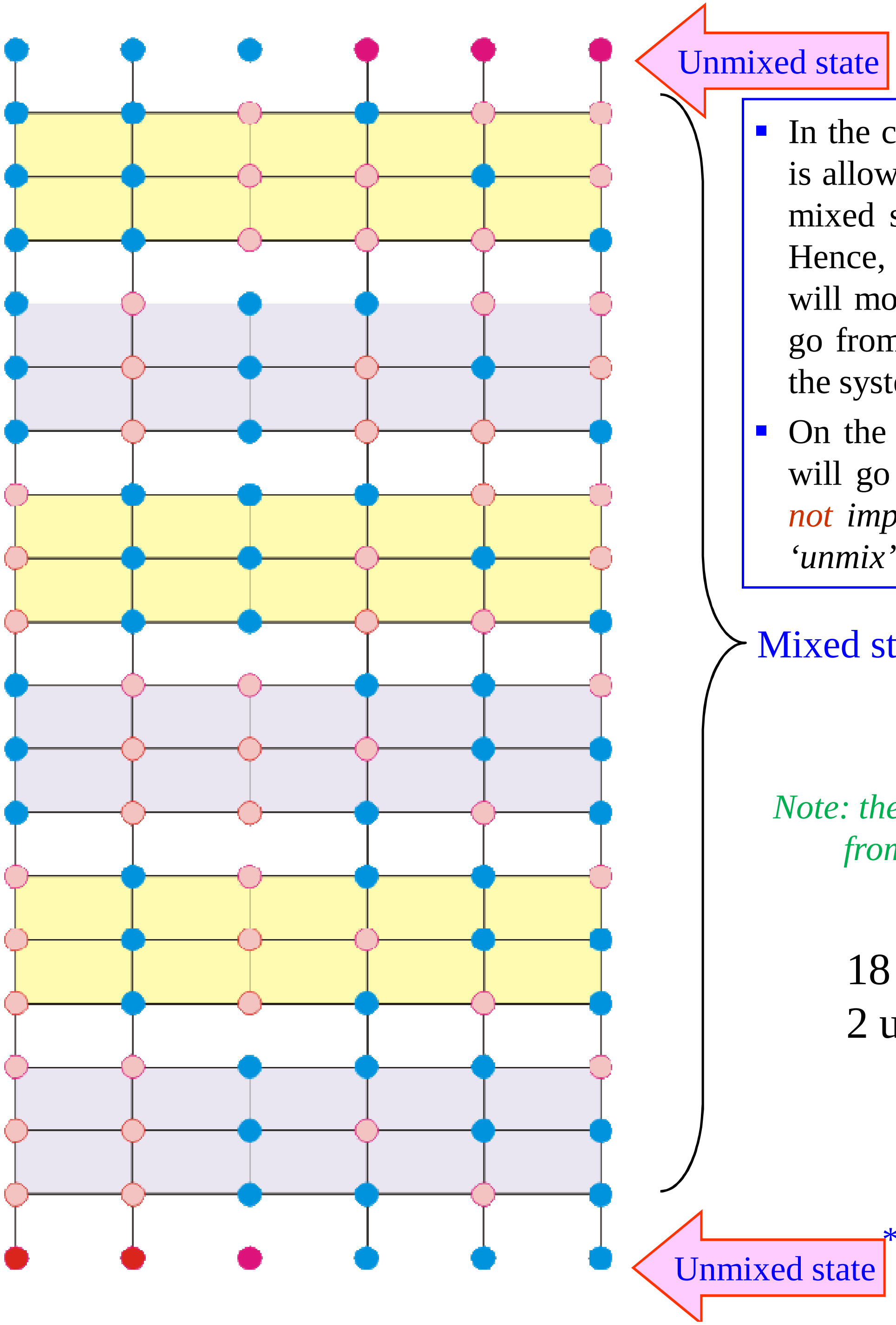
$$\Delta S_{mix} = -R[X_A \ln X_A + X_B \ln X_B]$$

So ΔG_{mix} can be written as $\Delta G_{mix} = \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$

Following, total free energy of the system after mixing can be written as

$$\boxed{G = X_A G_A + X_B G_B + \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]}$$

Entropy of mixing - Schematic



- In the case of two gases initially separated by a barrier, which is allowed to mix on the removal of the barrier: the number of mixed states are very large compared to the unmixed states. Hence, if all configurational states are accessible, the system will more likely found in the mixed state. I.e. the system will go from a unmixed state to a mixed state (worded differently the system will go from 'order' to 'disorder').
- On the other hand it is *unlikely (improbable)* that the system will go from mixed state to a unmixed state. *(Though this is not impossible → i.e. a mixed system can spontaneously get 'unmix' itself!!)*

Mixed states with 'various' degrees of mixing

Note: the profoundness of the concept of entropy comes from its connection to energy (via T)

18 mixed states
2 unmixed states

* *We assume that all states have equal probability of occurring and are all accessible*

Free energy of mixing

We need to consider three situations for different kinds of enthalpy of mixing

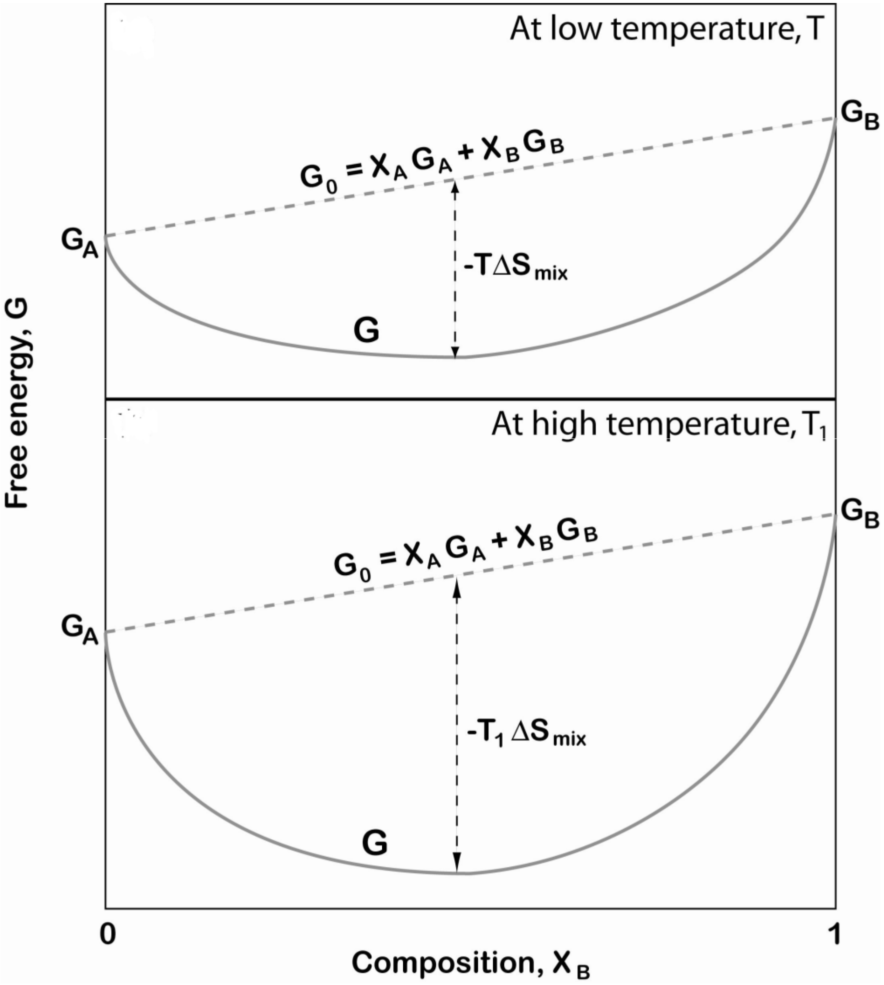
Situation 1: Enthalpy of mixing is zero

$$G = G_0 + \Delta G_{mix}$$

$$= G_0 - T\Delta S_{mix}$$

$$= X_A G_A + X_B G_B + RT[X_A \ln X_A + X_B \ln X_B]$$

- With the increase in temperature, -TΔS_{mix} will become even more negative.
- The values of G_A and G_B also will decrease.
- Following the slope G_o *might change since* G_A *and* G_B will change differently with temperature.



Free energy of mixing

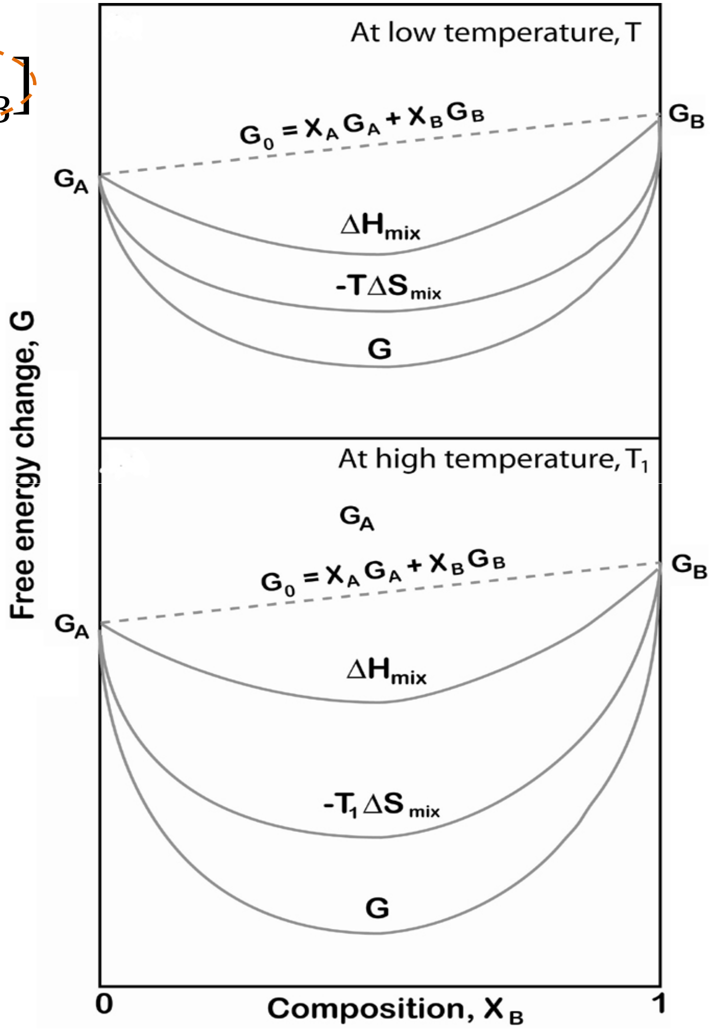
Situation 2: Enthalpy of mixing is negative

$$G=\underbrace{X_AG_A+X_BG_B}_{G_0}+\underbrace{\Omega X_AX_B}_{\text{Negative } \Delta H_{mix}}+\underbrace{RT[X_A\ln X_A+X_B\ln X_B]}_{-T\Delta S_{mix}}$$

- Here both ΔH_{mix} and $-T\Delta S_{mix}$ are negative

- With increasing temperature G will become even more negative.

- Note that here also G_0 may change the slope because of change of G_A and G_B differently with temperature.

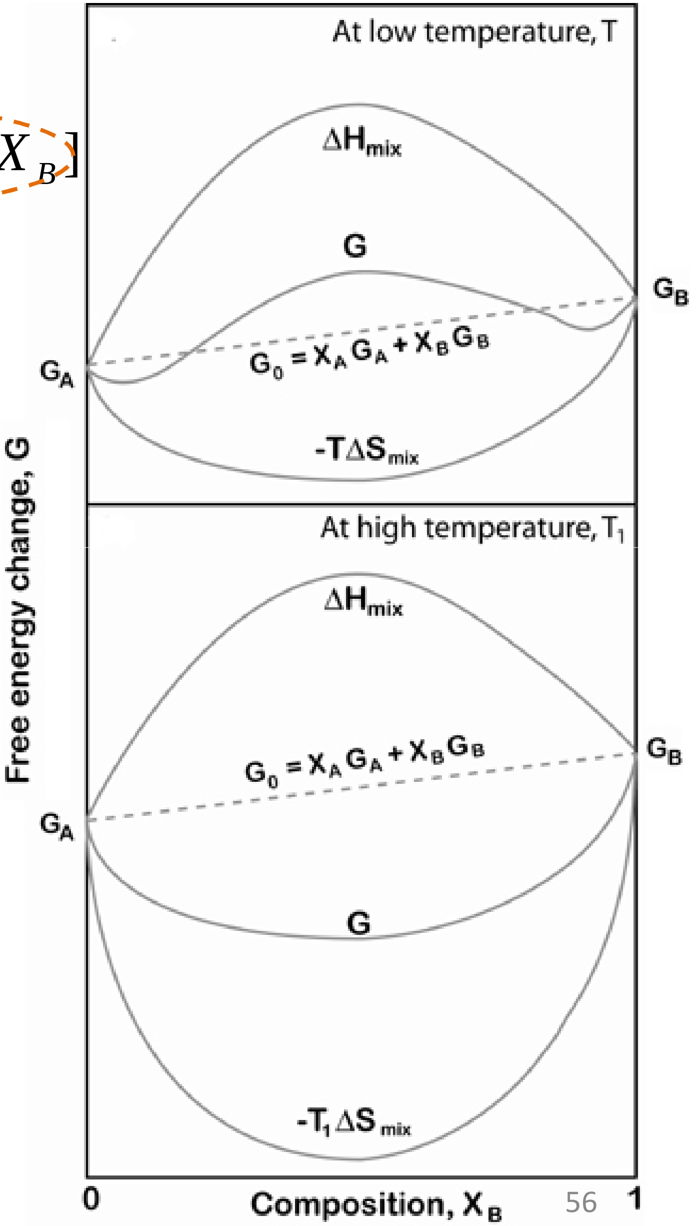


Free energy of mixing

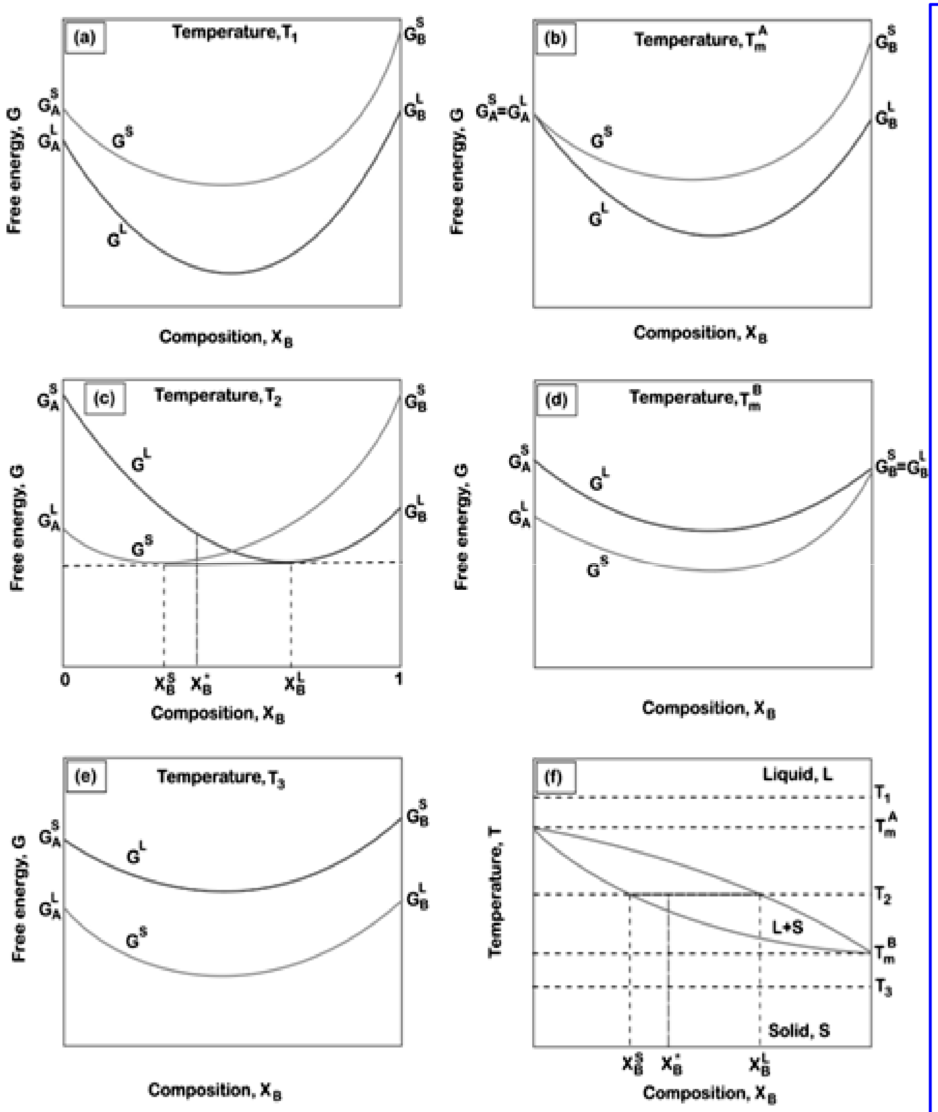
Situation 3: Enthalpy of mixing is positive

$$G = \underbrace{X_A G_A + X_B G_B}_{G_0} + \underbrace{\Omega X_A X_B}_{\text{Positive } \Delta H_{mix}} + \underbrace{RT[X_A \ln X_A + X_B \ln X_B]}_{-T\Delta S_{mix}}$$

- ΔH_{mix} is positive but $-T\Delta S_{mix}$ is negative. At lower temperature, in a certain mole fraction range the absolute value of ΔH_{mix} could be higher than $T\Delta S_{mix}$ so that G goes above the G_0 line.
- However to G_A and G_B, G will always be lower than G_0 , since ΔH_{mix} has a finite slope, where as ΔS_{mix} has infinite slope. The composition range, where G is higher than G_0 will depend on the temperature i.e., $-T\Delta S_{mix}$
- Because of this shape of the G, we see miscibility gap in certain phase diagrams.
- At higher temperature, when the absolute value of $-T\Delta S_{mix}$ will be higher than ΔH_{mix} at all compositions, G will be always lower than G_0



Free energy Vs Composition Phase Diagrams

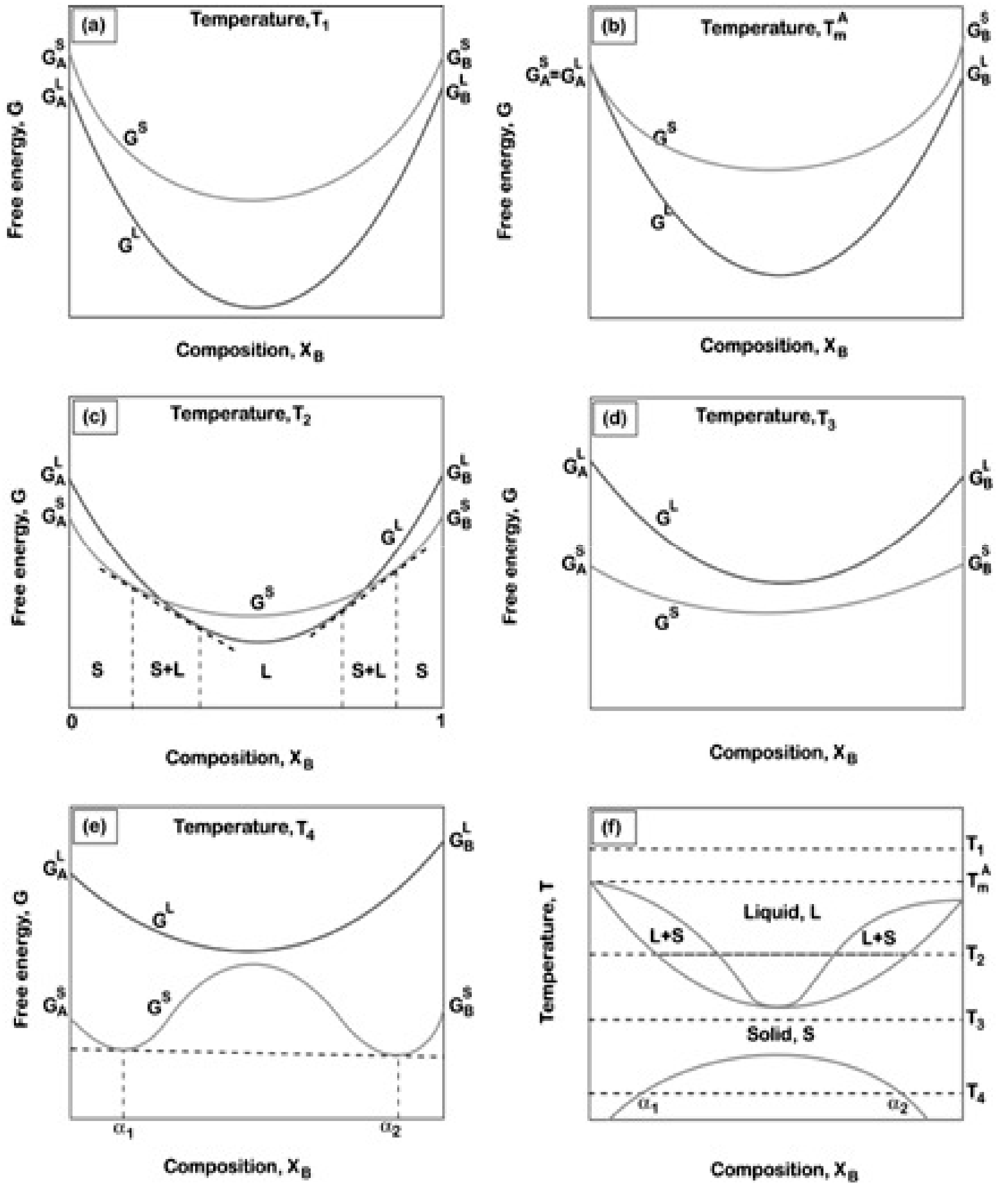


Both the liquid and solid phases can stay together because overall free energy will be less than the free energy when considered separately.

- With decreasing temperature, free energy for the solid, G_S and liquid phase G_L will change differently with different rates of change of G_A and G_B.
- At higher temperature, $G_L < G_S$ (fig a), so that the liquid phase is stable. At lower temperature $G_S < G_L$ (fig e) so that the solid phase is stable.
- In between, G_S and G_L intersects to find the situation as explained in Fig. c.
- Common tangent drawn gives the composition range where both solid and liquid phases can be found together.
- That means, if average composition is X_B* as shown in the phase diagram, it will have the solid phase with composition of X_B^S and the liquid phase with composition of X_B^L

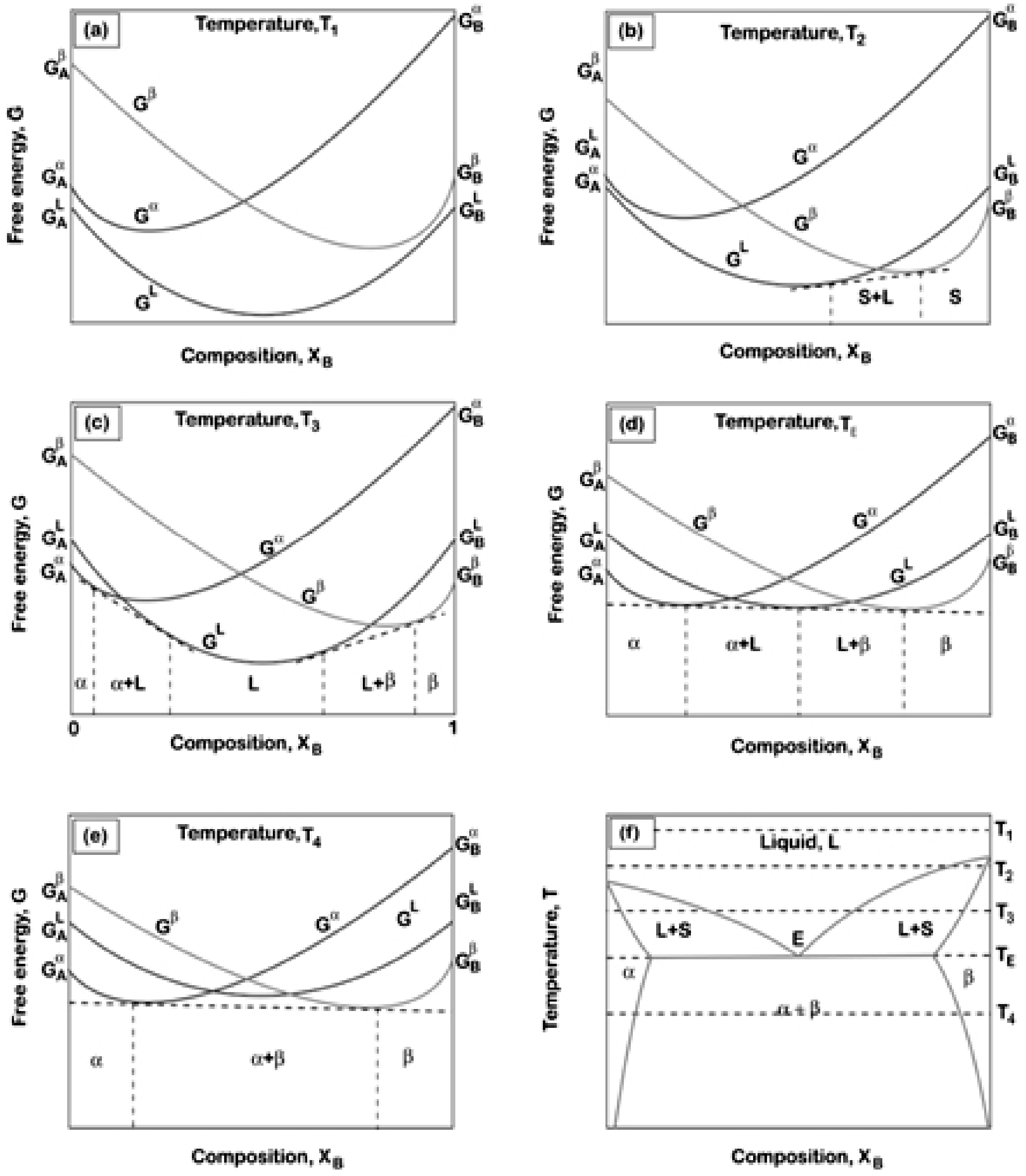
  Phase fractions can be found with the help of lever rule.

Free energy Vs Composition Phase Diagrams



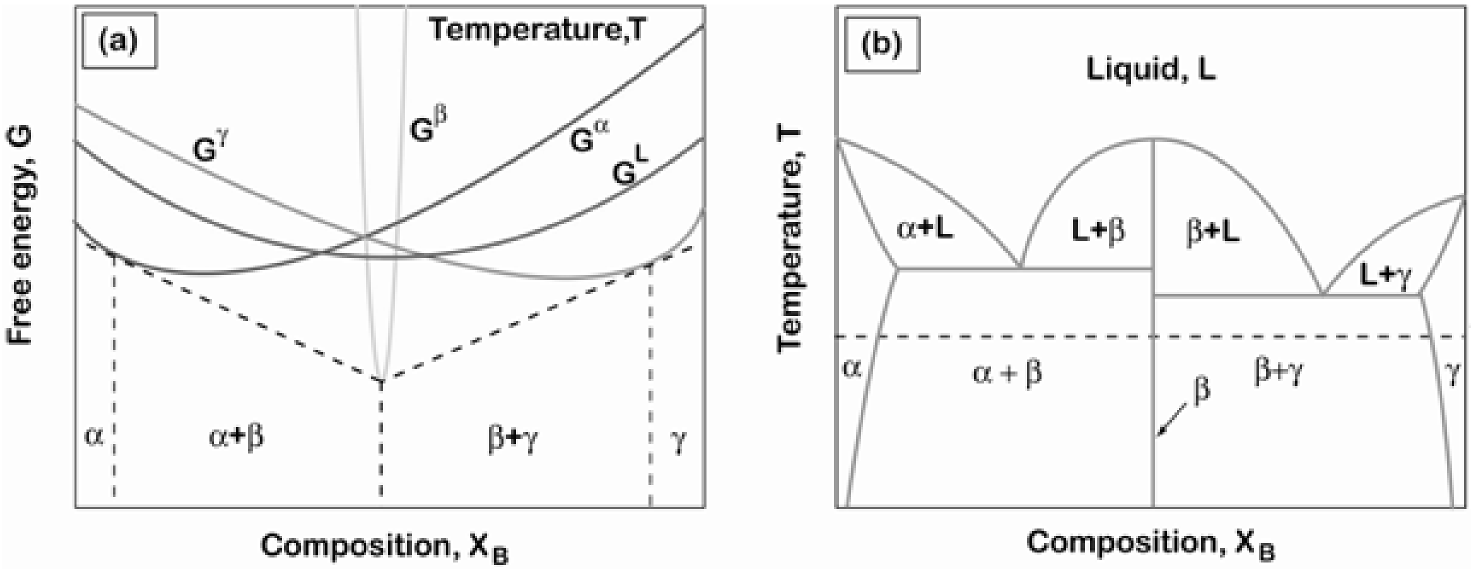
- This kind of phase diagram is found when the system has positive enthalpy of mixing, especially for the solid phase.
- Because of the shape of the G_S at low temperature as as shown in Fig. e, it is possible to draw a common tangent, which indicates that the solid phase with the average composition between α_1 and α_2 will have a phase separation . This corresponds to the miscibility gap in the phase diagram.
- It may also come to the situation, as it is shown in Fig. c, G_L and G_S intersects twice. In that case these will be two separate regions where both the solid and liquid phases coexist.

Free energy Vs Composition Phase Diagrams

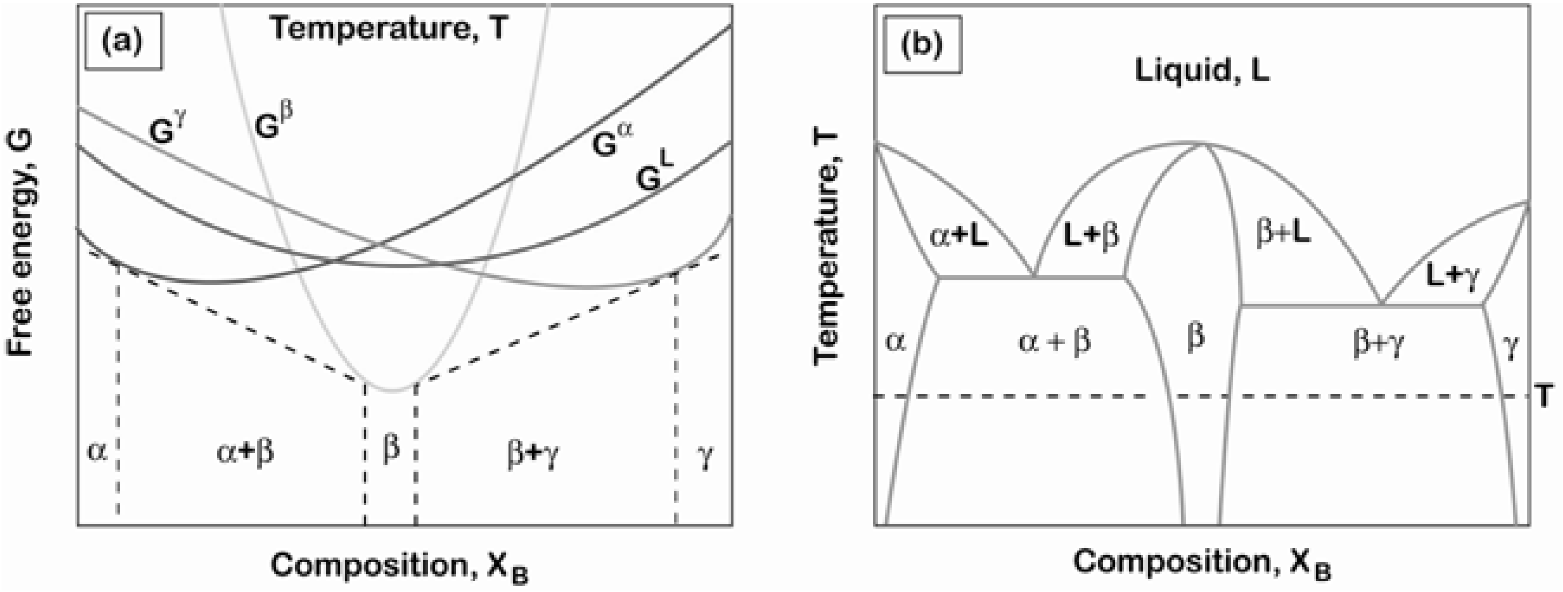


- In this system, there are two solid state phases and one liquid phase. So three free energy curves should be considered.
- At certain temperature, T_E, one common tangent can be drawn, which will touch all the free energy curves.
- This indicates that all the three phases at a particular composition E, as shown in Fig. d and f can coexist. This is called eutectic point.

Free energy Vs Composition Phase Diagrams



β phase is an intermetallic compound that is an ordered phase with very narrow homogeneity range.



Sometimes β phase can be found with wider homogeneity range.

Concept of the chemical potential and the activity of elements

- ☐ Gibb's free energy, G is function of temperature, T, pressure, P and amount of elements, n_A, $n_{B.}$

  $$\boldsymbol{G = G\ (T, P, n_A, n_B \ldots\ldots)}$$

- ☐ At particular temperature and pressure, partial derivative gives

$$dG = \frac{\partial G}{\partial n_A} dn_A + \frac{\partial G}{\partial n_B} dn_B$$

$$= \mu_A dn_A + \mu_B dn_B$$

$\frac{\partial G}{\partial n_A} = \mu_A$ is the chemical potential of element A. It measures the change in free energy because of very minute change of element A.

$\frac{\partial G}{\partial n_B} = \mu_B$ is the chemical potential of element B. It measures the change in free energy because of very minute change of element B.

- ☐ It should be noted here that the change should be so minute that there should not be any change in concentration because the chemical potential is a concentration dependent parameter.

Concept of the chemical potential and the activity of elements

- Let us consider an alloy of total X moles where it has X_A mole of A and X_B mole of B. Note that x is much higher than 1 mole.
- Now suppose we add small amounts of A and B in the system, keeping the ratio of $X_A : X_B$ the same, so that there is no change in overall composition.
- So if we add four atoms of A, then we need to add six atoms of B to keep the overall composition fixed. Following this manner, we can keep on adding A and B and will reach to the situation when X_A mole of A and X_B mole of B are added and total added amount is $X_A + X_B = 1$
- Since previously we have considered that the total free energy of 1 mole of alloy after mixing is G, then we can write

$$G = \mu_A X_A + \mu_A X_B$$

- ***Previously, we derived***

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$$

- ***Further, we can write*** $X_A X_B = X_A^2 X_B + X_A X_B^2$

$$G = X_A (G_A + \Omega X_B^2 + RT \ln X_B) + X_B (G_B + \Omega X_A^2 + RT \ln X_B)$$

Concept of the chemical potential and the activity of elements

Further, comparing the expressions for free energy, we can write

$$\mu_A = G_A + \Omega X_B^2 + RT \ln X_A$$

$$\mu_A = G_A + \Omega(1 - X_A)^2 + RT \ln X_A$$

$$\mu_B = G_B + \Omega(1 - X_B)^2 + RT \ln X_B$$

In terms of activity

$$\mu_A = G_A + RT \ln a_A$$

$$\mu_B = G_B + RT \ln a_B$$

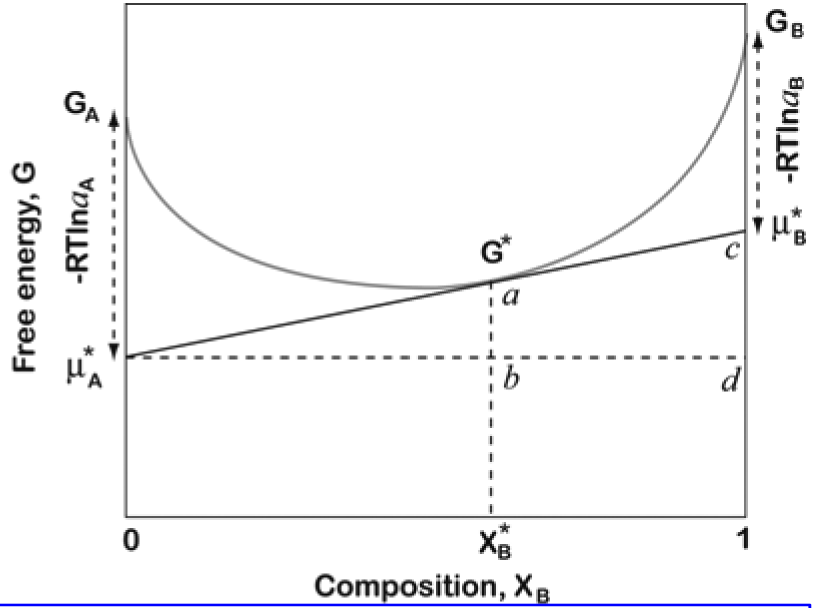
So the relations between the chemical potential and activity are

$$RT \ln a_A = \Omega(1 - X_A)^2 + RT \ln X_A$$

$$RT \ln a_B = \Omega(1 - X_B)^2 + RT \ln X_B$$

Concept of the chemical potential and the activity of elements

- ❑ Activities and chemical potentials are determined from a free energy curve after taking a slope, as explained in the figure.
- ❑ If we are interested to determine the activities or chemical potentials in a binary system A-B, let say at X_B^*, we need to take a slope on the free energy curve at the free energy, G^* and extended it to pure element, A ($X_B = 0$) and pure element B ($X_B = 1$).



- ❑ The point at which it hits $N_B = 0$, the value corresponds to the chemical potential of element A ( ). μ_A^*
- ❑ From previous slide, we can write $-RT\ln a_A = G_A - \mu_A^*$
- ❑ So, once the chemical potential is known, the activity of the element can be calculated using the above equation, as explained in the graph.
- ❑ It can be proved that, by taking slope and then extending to $X_B = 0$ and $X_B = 1$, we can find the chemical potentials. We can write $G^* = \mu_A^* + ab$
- ❑ Further we can write $\dfrac{ab}{X_B^*} = \dfrac{cd}{1}$ $\Rightarrow ab = X_B^* cd = X_B^*(\mu_B^* - \mu_A^*)$ $\boxed{\Rightarrow G^* = \mu_A^* X_A^* + \mu_B^* X_B^*}$

Concept of the chemical potential and the activity of elements

Further, we can write

$$\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1 - X_A)^2$$

$$a_A = X_A \exp\left[\frac{\Omega}{RT}(1 - X_A)^2\right] = \gamma_A X_A$$

$$\gamma_A = \exp\left[\frac{\Omega}{RT}(1 - X_A)^2\right]$$

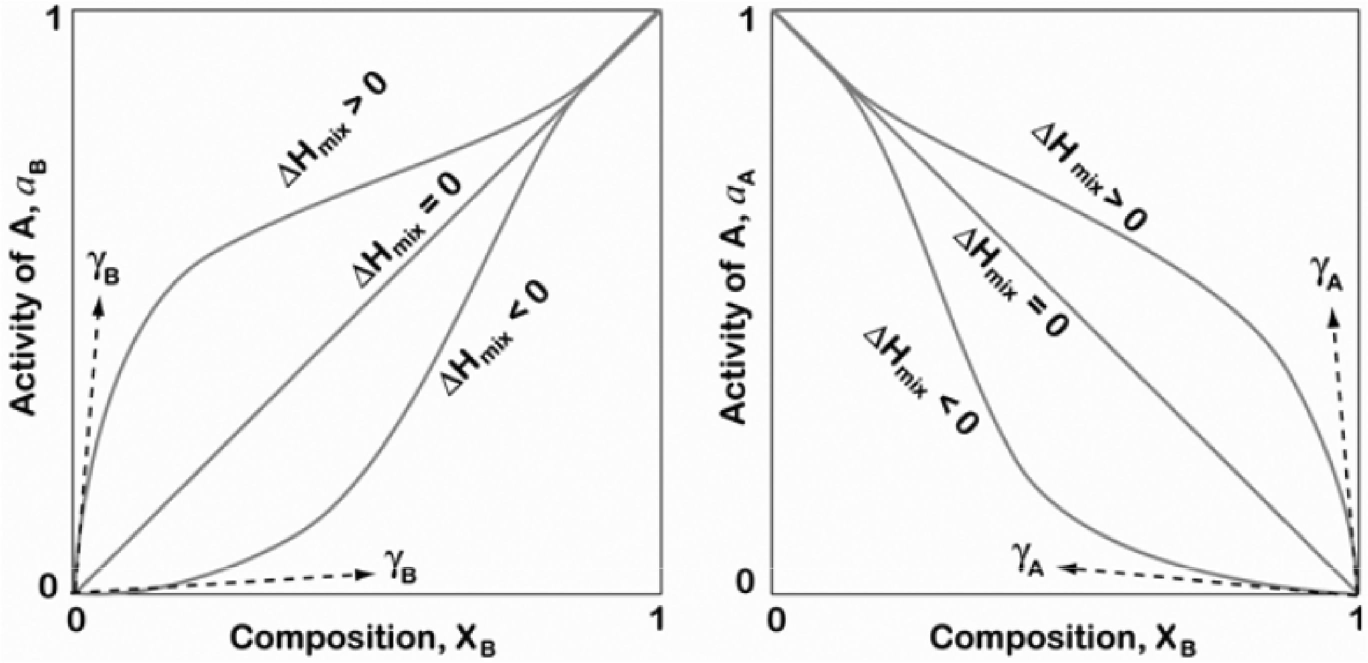
$$\ln\left(\frac{a_B}{X_B}\right) = \frac{\Omega}{RT}(1 - X_B)^2$$

$$a_B = X_B \exp\left[\frac{\Omega}{RT}(1 - X_B)^2\right] = \gamma_B X_B$$

$$\gamma_B = \exp\left[\frac{\Omega}{RT}(1 - X_B)^2\right]$$

- ❑ γ_i are the activity coefficient of element i.
- ❑ In an ideal solution, $\Omega = 0$, and $A_i = X_i$.
- ❑ In a non ideal solution, activity coefficient indicates the deviation from the ideal line.

Concept of the chemical potential and the activity of elements



$$\gamma_A = \exp\left[\frac{\Omega}{RT}(1 - X_A)^2\right]$$

$$\gamma_B = \exp\left[\frac{\Omega}{RT}(1 - X_B)^2\right]$$

In the case of positive enthalpy of mixing, activity deviates positively and in the case of negative enthalpy of mixing activity deviates negatively from the ideal mixing line.

$$X_A \to 0, \gamma_A \to \exp\left(\frac{\Omega}{RT}\right)$$

$$X_B \to 0, \gamma_B \to \exp\left(\frac{\Omega}{RT}\right)$$

$$X_A \to 1, \gamma_A \to 1$$

$$X_B \to 1, \gamma_B \to 1$$

Henry’s law: activity of elements is more or less the constant in a very dilute solution.

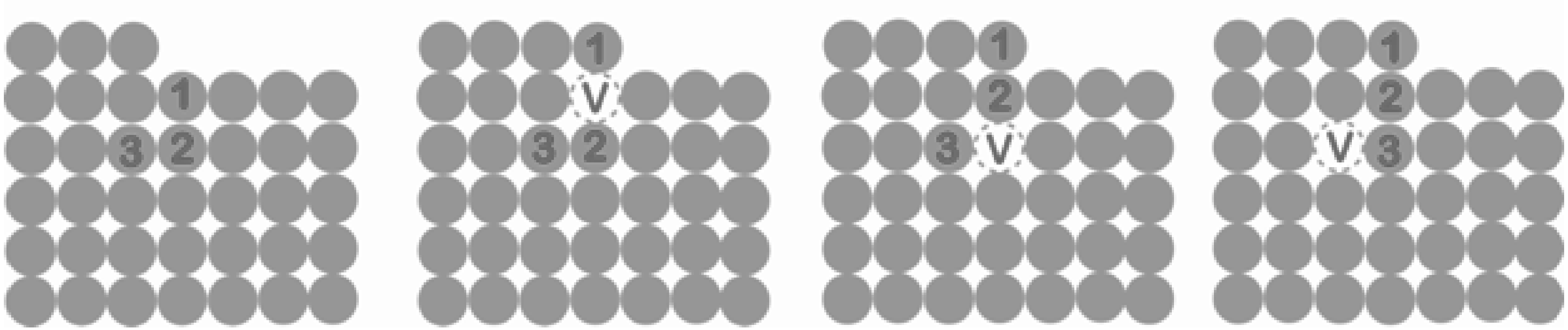
Rault’s law: activity is equal to the mole fraction near the mole fraction of 1.

Equilibrium vacancy concentration

- ☐ Diffusion of elements is possible because of the presence of defects. For example, substitutional diffusion occurs because of exchange of an atom with vacancies. Further, impurities are present at the interstitial positions, which could diffuse to any neighboring vacant interstitial sites. This is called interstitial diffusion.
- ☐ Certain concentration of these impurities are always present in the pure elements in equilibrium condition, which will be discussed here.
- ☐ Further in the intermetallic compounds (ordered phases), antisites defects also could be present along with vacancies. Moreover, different sublattices could have different concentration of defects, which makes the diffusion process complicated.
- ☐ Let us not get confused with the structural defects present in pure elements.
- ☐ To understand simple atomic mechanism of diffusion at this point, we shall calculate the equilibrium concentration of point defects that is the equilibrium concentration of vacancies and interstitial atoms in pure elements
- ☐ Interesting point to be mentioned here that unlike dislocations, grain boundary or interfaces, point defects are equilibrium defects. It means that the system will try to have certain concentration of defects to decrease the free energy.

Let us first calculate the equilibrium concentration of vacancies, because of which lattice substitutional diffusion is possible

Equilibrium vacancy concentration in a pure element



- ❑ Pure elements A and vacancies (V) can be considered as a mixture of two entities and follow the similar treatment as we did to calculate the total free energy after mixing of elements A and B.
- ❑ It can be easily visualized how the movement of atoms can create vacancies in the material in few steps.
- ❑ Equilibrium number of vacancies is so small that we can neglect the interaction between them.
- ❑ This means that we are neglecting V-V interactions. This also means that we are, at this point, neglecting the presence of divacancies, which are actually present in the material.

Equilibrium vacancy concentration in a pure element

- If we consider that the number of vacancies is very small then the increase of enthalpy because of formation of vacancies can be written as

$$\Delta H \approx X_V \Delta H_V$$

ΔX_V ***is the mole fraction of vacancy and***

ΔH_V ***is the increase in enthalpy because of one mole of vacancies***

- There will be the change in the pattern of vibration of atoms next to vacancies because of extra free space. The increase in (thermal) entropy because of the extra freedom of vibration can be written as

$$\Delta S_{thermal} = X_V \Delta S_V$$

ΔS_V ***is the increase in entropy for one mole of vacancies***

- In both the cases, we are actually assuming linear relationship because of very small concentration of vacancies.
- NOTE: In the case of entropy change of A-B mixture, we did not consider the thermal entropy change, since we are considering the change at a particular temperature. However, in this case, although we are considering again at a particular temperature, we still need to consider the contribution because of the change in vibration pattern of atoms next to vacancies.

Equilibrium vacancy concentration in a pure element

- ☐ Further there will be change in configurational entropy considering the mixing of A and V and can be expressed as (Note that we are considering $X_A + X_V = 1$

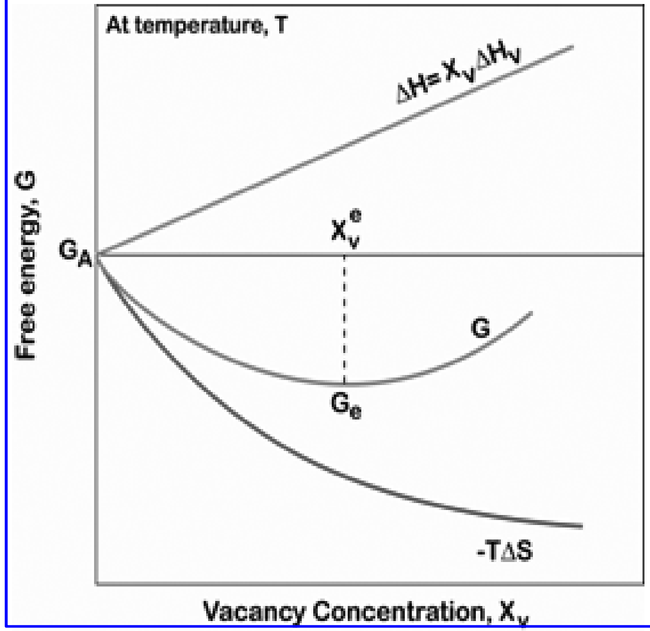
$$\Delta S_{config} = -R[X_V \ln X_V + X_A \ln X_A] = -R[X_V \ln X_V + (1-X_V)\ln(1-X_V)]$$

- ☐ Total entropy of mixing $\Delta S_{mix} = \Delta S_V X_V - R[X_V \ln X_V + (1-X_V)\ln(1-X_V)]$

(Total contribution from thermal and configurational entropy)

- ☐ Total free energy in the presence of vacancies

$$\begin{aligned} G &= G_A + \Delta G \\ &= G_A + \Delta H - T\Delta S \\ &= G_A + X_V \Delta H_V - T\{\Delta S_V - R[X_V \ln X_V + (1-X_V)\ln(1-X_V)]\} \end{aligned}$$



Note here that G of element A when vacancies are present decreases. So always there will be vacancies present in materials. Further G decreases to a minimum value and then increases with the further increase in vacancy concentration. So, in equilibrium condition, certain concentration of vacancies will be present, which corresponds to G_e.

Equilibrium vacancy concentration in a pure element

- ☐ Since the slope is zero at the minima, we can find the equilibrium vacancy concentration from

$$\frac{dG}{dX_V}=0$$

$$\Delta H_V - T\Delta S_V + RT\left[\ln X_V + X_V.\frac{1}{X_V} - \ln(1-X_V) - (1-X).\frac{1}{(1-X_V)}\right]=0$$

- ☐ Since the number of vacancies that can be present in the system is very small

$$1-X_V \approx 1$$

$$\Delta H_V - T\Delta S_V + RT\ln X_V = 0$$

- ☐ The relation for equilibrium concentration of vacancies can be written as

$$X_V^e = X_V = \exp\left(-\frac{\Delta H_V - T\Delta S_V}{RT}\right) = \exp\left(-\frac{\Delta G_V}{RT}\right)$$

- ☐ Although there is increase in configurational entropy because of the presence of vacancies, it is not included in the activation energy barrier, $\Delta G_{V.}$
- ☐ Although there is activation energy barrier present because of formation, vacancies will still be present because of overall decrease in free energy of the materials.

Equilibrium vacancy concentration in a pure element

- From the equation in previous slide, we can also write

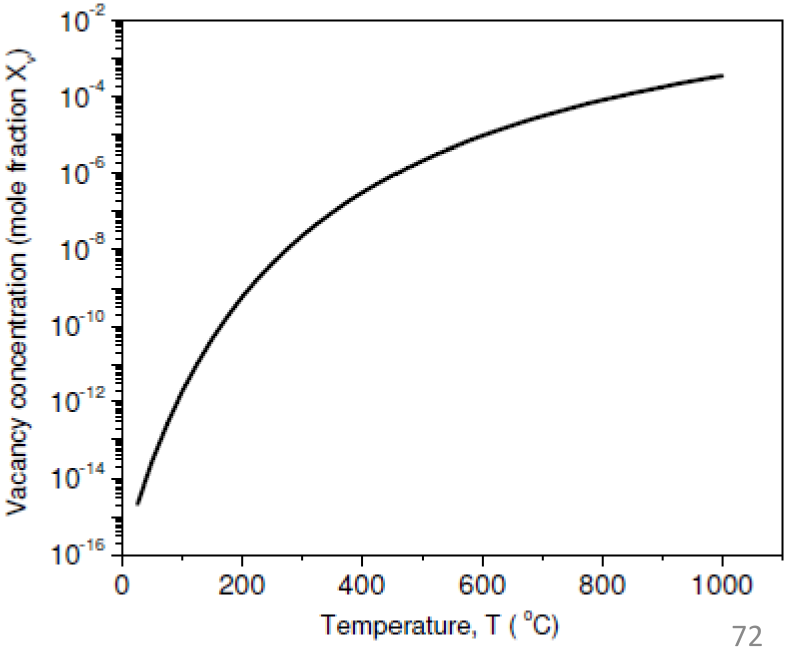
$$X_V^e = X_V^0 \exp\left(-\frac{\Delta H_V}{RT}\right)$$

- ΔH_V is the activation enthalpy for the formation of vacancies and

$$X_V^0 = \exp\left(\frac{\Delta S_V}{R}\right)$$ Is the pre-exponential factor.

- The change in concentration of vacancies in pure Cu is shown in below graph, considering activation energy for vacancy formation to be 83.7 kJ/mole.

The concentration of vacancies in mole fraction at 1000°C is 3.68 × 10^{-4}. *That means in a cube of 14 atoms in each direction, only one vacancy will be present in Cu at this temperature!!!*



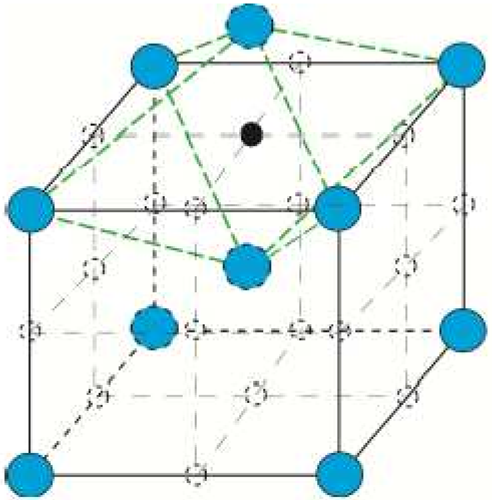
Equilibrium concentration of interstitial atoms

- ❑ In many metals, especially in transition metals, interstitial atoms such as carbon, nitrogen, oxygen, hydrogen can be present up to a certain extent depending on the metal.
- ❑ There are mainly two types of interstitial voids present in the structure, where these atoms can sit: tetrahedral (surrounded by four solvent atoms) and octahedral (surrounded by six solvent atoms).
- ❑ However, since impurities prefer to occupy octahedral interstices, we shall mainly consider this type of voids only.

LET US FIRST CONSIDER A BCC CRYSTAL

- ❑ In general the size of the interstitial atoms is much larger than the interstitial void and lattice surrounding the interstitial will be strained. That means enthalpy of the system will be increased.
- ❑ Consider the increase in enthalpy because of addition of one mole of interstitial atoms is , $\Delta H_{I.}$
- ❑ The enthalpy increment of the system because of addition of X_I is expressed by $\Delta H = X_I \Delta H_I$

$$where X_I = \frac{n_I}{N_o} \quad Number\ of\ interstitial\ atom\ is\ n_I$$



Equilibrium concentration of interstitial atoms

- Further, there will be two different types of contribution on entropy
- Vibration of atoms A, next to interstitial atoms will change from normal mode of vibration and will be more random and irregular because of distortion of the lattice

$$\Delta S_{thermal} = X_I \Delta S_I$$

- ΔS_I is the change of the entropy of one mole of atoms because of change in vibration pattern
- From the crystal structure, we can say that for 2 solvent atoms there are 6 sites for interstitial atoms. So if we consider that there are N_0 numbers of A atoms then there will be $3N_0$ numbers of sites available for interstitial atoms.
- In other sense, we can say that n_I atoms will randomly occupy in $3N_0$ sites available. So the configurational entropy can be written as

$$\Delta S_{config} = k \ln w = k \ln \frac{3N_0!}{n_I!(3N_0 - n_I)} \quad \textit{Following Stirling's approximation} \quad \ln N! = N \ln N - N$$

$$\Delta S_{config} = k[3N_0 \ln 3N_0 - n_I \ln n_I - (3N_0 - n_I)\ln(3N_0 - n_I)]$$

$$\Delta S_{config} = R\left[3\ln 3N_0 - \frac{n_I}{N_0}\ln n_I - \frac{3N_0 - n_I}{N_0}\ln(3N_0 - n_I)\right]$$

Equilibrium concentration of interstitial atoms

$$\Delta S_{config} = R\left[3\ln\frac{3N_0}{3N_0 - n_I} - \frac{n_I}{N_0}\ln\frac{n_I}{3N_0 - n_I}\right]$$

$$\Delta S_{Config} = R\left[3\ln\frac{3}{3 - X_I} - X_I\ln\frac{X_I}{3 - X_I}\right]$$

- ☐ So the total entropy change

$$\Delta S = X_I\Delta S_I + R\left[3\ln\frac{3}{3 - X_I} - X_I\ln\frac{X_I}{3 - X_I}\right]$$

- ☐ Free energy in presence of interstitial impurities

$$G = G_A + \Delta G = G_A + \Delta H - T\Delta S_I$$

$$G = G_A + X_I\Delta H_I - TX_I\Delta S_I - RT\left[3\ln\frac{3}{3 - X_I} - X_I\ln\frac{X_I}{3 - X_I}\right]$$

Equilibrium concentration of interstitial atoms

- To find the equilibrium concentration, we need to take

$$\frac{dG}{dX_I} = 0$$

$$\Delta H_I - T\Delta S_I - RT\left[-\frac{3}{3-X_I} - \frac{X_I}{X_I} - \ln X_I + \ln(3-X_I) - \frac{X_I}{3-X_I} \right] = 0$$

$$\Delta H_I - T\Delta S_I + RT\ln\frac{X_I}{3-X_I} = 0 \qquad \textbf{since} \quad X_I \approx 0$$

$$X_I = 3\exp\left(-\frac{\Delta H_I - T\Delta S_I}{RT} \right) = 3\exp\left(-\frac{\Delta G_I}{RT} \right)$$

- G_I is the activation barrier.

Equilibrium concentration of interstitial atoms

LET US NOW CONSIDER A FCC CRYSTAL

- If we consider FCC crystal, then the number of sites available for interstitial atoms are 4. Further in a FCC unit cell, total 4 solvent atoms are accommodated. So we can say that for N_0 solvent atoms there will be N_0 sites available for interstitial atoms. Like previous example, we consider n_I interstitial atoms which will occupy randomly.
- Then following similar procedure, we can show the equilibrium concentration of interstitial atoms present in a metal with FCC crystal as

$$X_I = \exp\left(-\frac{\Delta G_V}{RT}\right)$$

- So in general, we can write that the equilibrium concentration of interstitial impurities present is

$$X_I = B\exp\left(-\frac{\Delta G_I}{RT}\right) \quad \textit{B depends on the crystal structure}$$

$$X_I = X_I^0 \exp\left(-\frac{\Delta H_I}{RT}\right)$$

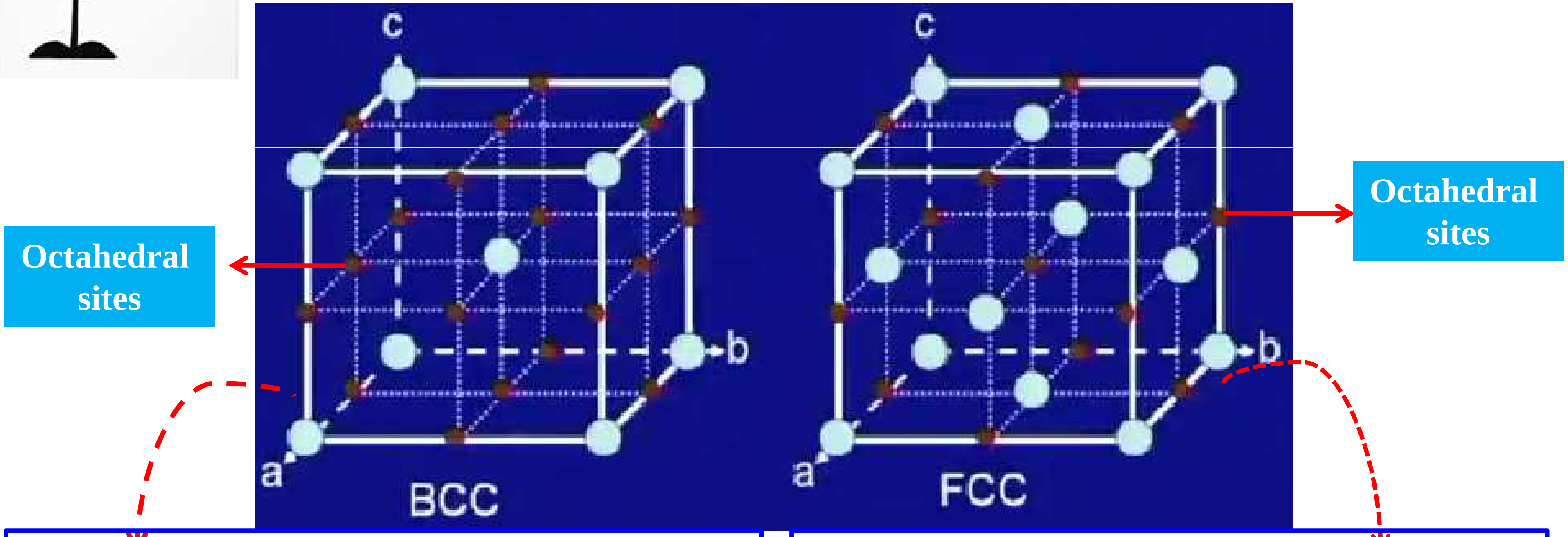
ΔH_I *is the activation enthalpy for interstitial impurities*

$X_I^0 = B\exp\left(\frac{\Delta S}{R}\right)$ *is the pre-exponential factor*

Carbon Solubility in Iron

Solubility of carbon in Fe = f (structure, temperature)

Where is carbon located in iron lattice ?



6 faces sharing with two sides (6/2)=3
12 edges sharing with four sides (12/4)=3
Total sites is (3+3), 6 per unit cell
Every one Fe atom we have 3 interstitial sites

One interstitial site in center plus
12 edges sharing with four sides (12/4)=3
Total sites is (1+3), 4 per unit cell
Every one Fe atom we have 1 interstitial site

Why concentration of carbon in α-Fe with BCC structure is less than γ-Fe with FCC structure?

- FIRST LET US CONSIDER FCC STRUCTURE (γ-Fe)
- Packing factor of FCC lattice 0.74
- This indicates the presence of voids. Let us discuss it more elaborately.
- In a FCC crystal there are mainly two types of voids:
- Tetrahedral: coordination number (CN) is 4. That means the void is surrounded by 4 atoms.
- Octahedral: CN is 6. That means the void is surrounded by 6 atoms.
- There are 8 tetrahedral voids in a unit cell. That means 2 voids per atom.
- There are 4 octahedral voids in a unit cell. That means 1 void per atom.
- However, impurities prefer to occupy octahedral voids.
- Because the ratio of the radius of the tetrahedral void to atom is 0.225 and the same for the octahedral void is 0.414.
- The ratio of the radius of the carbon atom (size is 77 pm) to Fe (when it has FCC crystal) is 0.596.
- So when a carbon atom occupies any void, lattice will be distorted to increase the enthalpy.
- Distortion will be less if it occupies the octahedral voids.
- Although it increases the enthalpy, carbon atoms will be present up to a certain extent because of the gain in entropy, as explained previously, which decreases the free energy.

Carbon Solubility in Iron

FCC

Size of Fe atom
CCP crystal

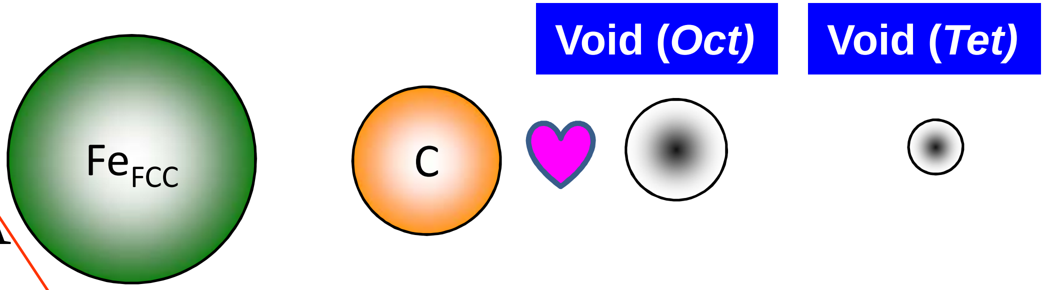
$$r_{FCC}^{Fe} = 1.292\ \mathring{A}$$

Size of the OV

$$x_{FCC}^{Fe}(oct) = 0.534\ \mathring{A}$$

Size of Carbon atom

$$r^{C} = 0.77\ \mathring{A}$$



Relative sizes of voids w.r.t atoms

Note the difference in size of the atoms

BCC

Size of Fe atom
BCC crystal

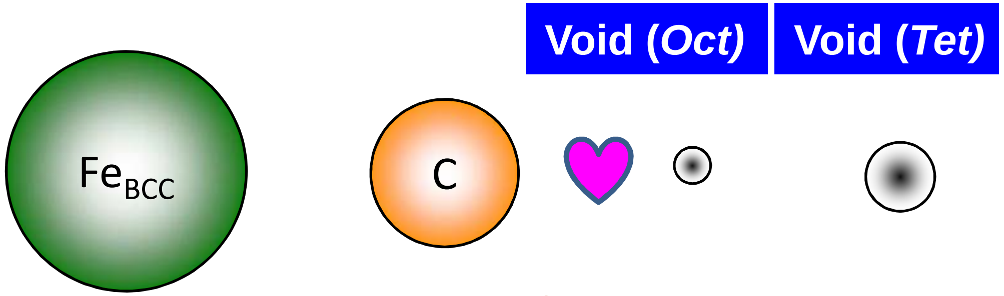
$$r_{BCC}^{Fe} = 1.258\ \mathring{A}$$

Size of the TV

$$x_{BCC}^{Fe}(d.tet) = 0.364\ \mathring{A}$$

Size of the OV

$$x_{BCC}^{Fe}(d.oct) = 0.195\ \mathring{A}$$



Relative sizes of voids w.r.t atoms

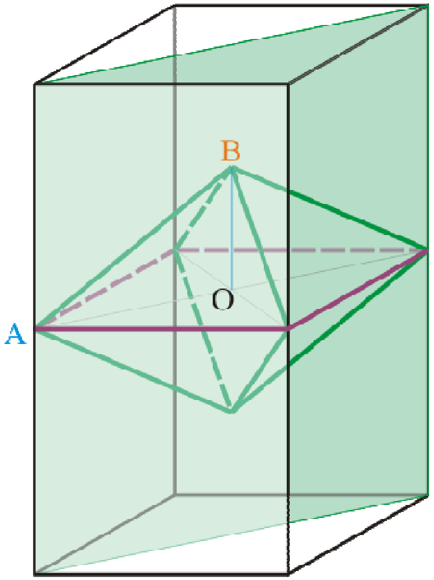
Remember

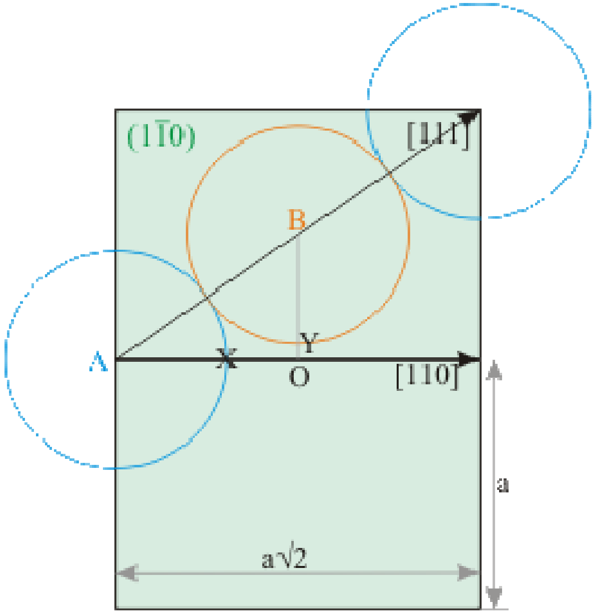
- ❑ **FCC** Size of the largest atom which can fit into the tetrahedral is 0.225 and octahedral void is 0.414
- ❑ **BCC** Size of the largest atom which can fit into the *d.tetrahedral* is 0.29 and *d.octahedral* void is 0.154

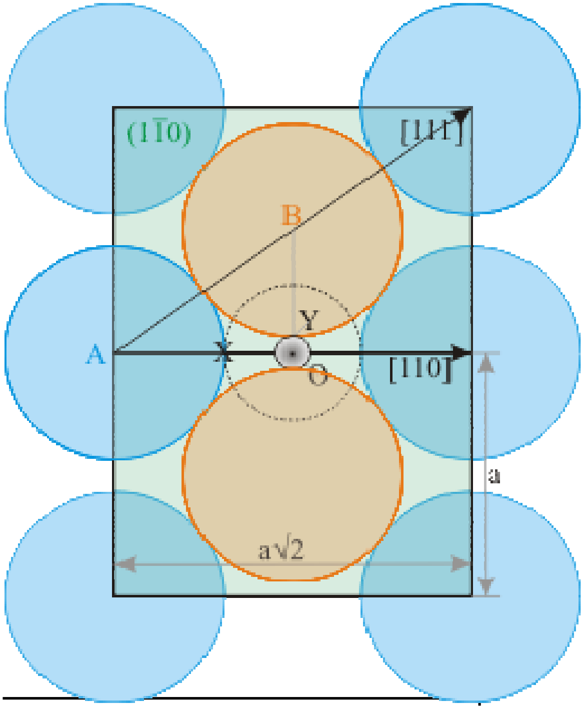
Why concentration of carbon in α-Fe with BCC structure is less than γ-Fe with FCC structure?

- ❑ NOW LET US CONSIDER THE BCC UNIT CELL (α - Fe)
- ❑ Packing factor of BCC lattice 0.68. So total void in a BCC unit cell is higher than FCC cell.
- ❑ However, there are 12 (6 per atom) tetrahedral and 6 (3 per atom) octahedral voids present. This number is higher than the number of voids present in a FCC unit cell.
- ❑ Unlike voids in FCC lattice, in a BCC lattice the voids are distorted. That means if an atom sits in a void, it will not touch all the host atoms.
- ❑ The ratio of the radius of tetrahedral void to atom is 0.29 and the radius of octahedral void to atom is 0.155.
- ❑ The ratio of the radius of the C atom (size is 77 pm) to Fe (when it has BCC crystal) is 0.612. So it is expected that in a BCC unit cell, impurities should prefer tetrahedral voids.
- ❑ However, although the octahedral void size is small, planar radius which has 4 atoms on the same plane is 79.6 pm, which is larger that the C atom size. That means it needs to distort only other two atoms.
- ❑ On the other hand if C sits in the tetrahedral void it has to distort all four atoms. So in α – Fe with BCC unit cell C occupies the octahedral voids
- ❑ Now the octahedral void size in g-Fe (FCC) is higher than a-Fe (BCC). So naturally the distortion in a BCC cell will be higher and the activation energy for impurities to occupy a void in a BCC cell also will be higher.
- ❑ This is the reason that we find much lower solubility limit of C in a-Fe.

Why carbon preferentially sits in the apparently smaller octahedral void in BCC ?







Ignoring the atom sitting at B and assuming the interstitial atom touches the atom at A

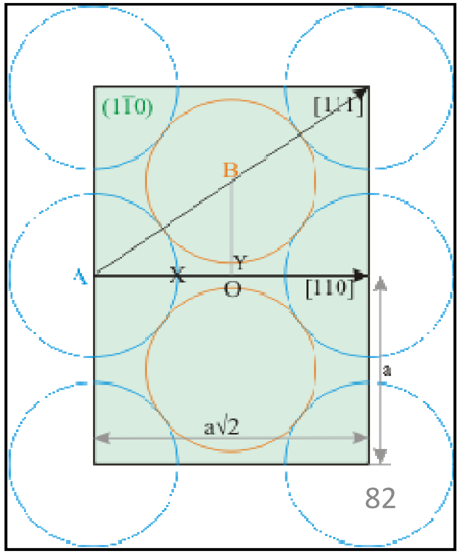
$$OA = r + x_A = \frac{\sqrt{2}a}{2}$$

$$r_{BCC}^{Fe} = 1.258\ \mathring{A}$$

$$BCC : \sqrt{3}a = 4r$$

$$r + x_A = \frac{2\sqrt{6}\,r}{3}$$

$$\frac{x_A}{r} = \left(\frac{2\sqrt{6}}{3} - 1\right) = 0.6329$$

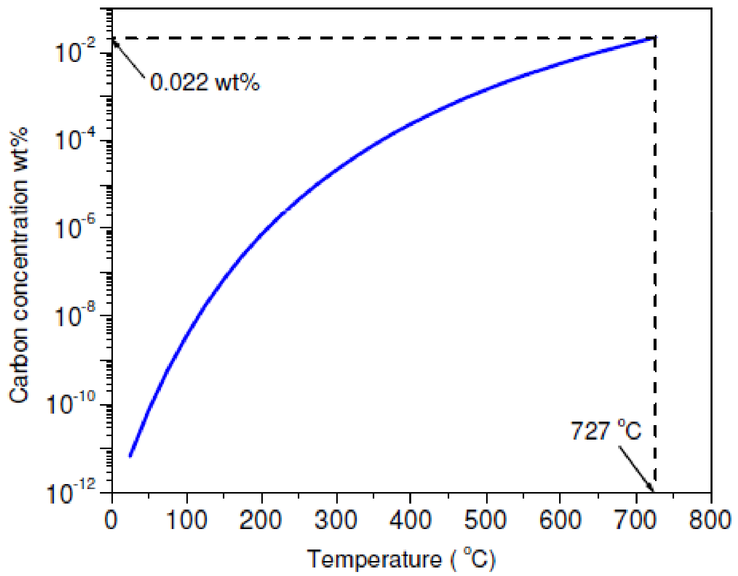


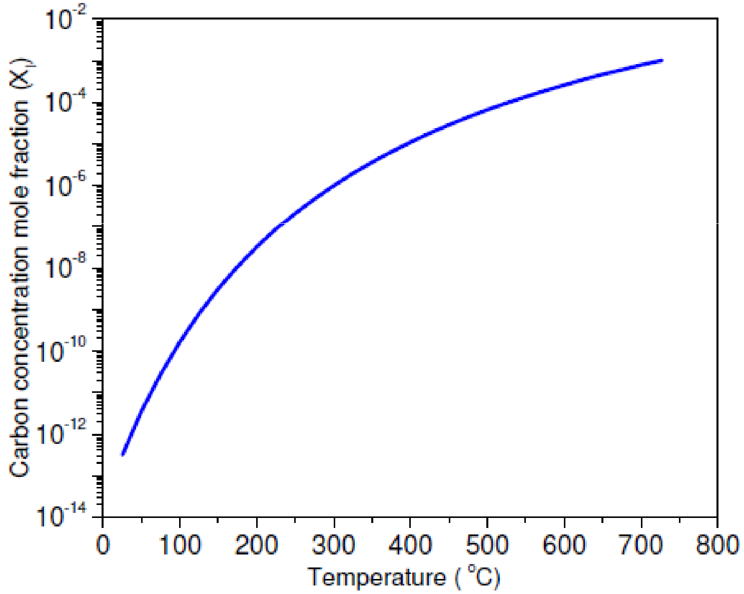
$$OX = x_A = 0.796\ \mathring{A} \qquad OY = x_B = 0.195\ \mathring{A} \qquad x_{BCC}^{Fe}(d.tet) = 0.364\ \mathring{A}$$

Why concentration of carbon in α-Fe with BCC structure is less than γ-Fe with FCC structure?

- ❑ Let us consider the C concentration in α-Fe (BCC)

$$Wt\% = 240\exp\left(-\frac{77300\ {}^{J}\!/\!{}_{mol}}{RT}\right) \quad \textit{In terms of mole fraction} \quad X_1 = 11.2\exp\left(-\frac{77300\ {}^{J}\!/\!{}_{mol}}{RT}\right)$$





- ❑ At 727°C, carbon concentration in α-Fe is maximum (0.022 wt%), which is equivalent to mole fraction of ~10^{-3}. That means there is one C atom present in a cube of 10 atoms in each direction. That further means that only one carbon atom is present in 3000 octahedral voids

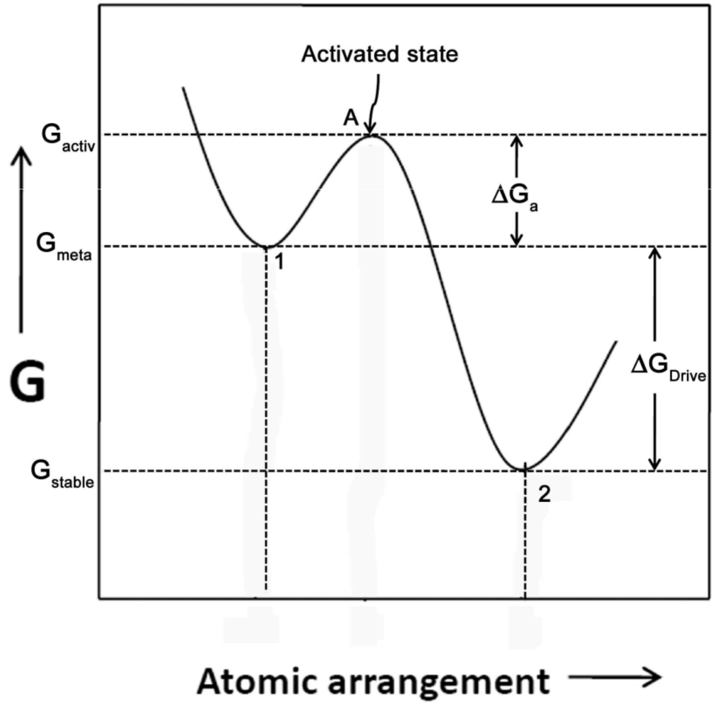
KINETICS

- In earlier we are learned about Equilibrium we had seen that the thermodynamic feasibility of processes is dictated by 'Thermodynamic Potentials' (e.g. Gibbs Free Energy, at constant T, P, N_i).
- If (say) the Gibbs Free Energy for a process is negative then the process CAN take place spontaneously.
- However, IF the process WILL actually take place (and if it will take place- how long will it take to occur?) → will be determined by the 'Kinetics of the process'.
- Deeper the 'metastable energy well', higher will be activation energy required to pull the system out of the 'well' and take it to the equilibrium state (or some other metastable state).
- To give an example: Fe_3C is a metastable phase. it can decompose 3Fe + C after hundreds of years. *'Thermodynamics warrants, Kinetics delays'*
- For a given process to occur heat and mass transfer may have to take place and this would take time → hence in 'kinetics' we deal with time and rates (1/t) .
- Thermodynamics dictates that the state should transform to the stable state. However, how fast this transformation can occur cannot be answered by thermodynamics alone. Determining the rate of such transformation comes under the realm of kinetics.

KINETICS

- For example, consider Figure 1, which shows variation of Gibbs free energy of a system versus an arbitrary unit (say atomic arrangement).
- Thermodynamics tells us that if the system is at some meta-stable state-1, it has to transform to the stable state-2. The difference of Gibbs energy (G_2 - G_1 = ΔG_{Drive}) is the driving force for transformation.

- However, it should be noted that while moving from state-1 to state -2, the system has to actually cross the hump i.e., it has to go through a higher energy state-A. This state-A is called as activated state and the difference in Gibbs energy ($G_A - G_{meta}$) is called as energy barrier since it actually resists the system from transforming from metastable state-1 to stable state-2.
- The energy ΔG_a is also called as Gibbs free energy for activation of the process.



- The energy required to overcome the barrier is usually provided by thermal vibrations of the atoms and hence these processes are called as “thermally activated processes”.

KINETICS

- The kinetics tells us that the rate of the process should be proportional to:

$$Rate \propto \exp\left(\frac{-\Delta G_a}{RT}\right)$$

$$(or)$$

$$Rate = K_o \exp\left(\frac{-\Delta E_a}{RT}\right)$$

K_o is a constant and E_a is the energy (or enthalpy) of activation.

- Most of the transformations are brought about by diffusion mechanisms. The diffusion itself is a thermally activated process. Thus, diffusion coefficient can be expressed as:

$$D = D_o \exp\left(\frac{-Q_D}{RT}\right)$$

D_o is a constant and Q_d is the activation energy of diffusion

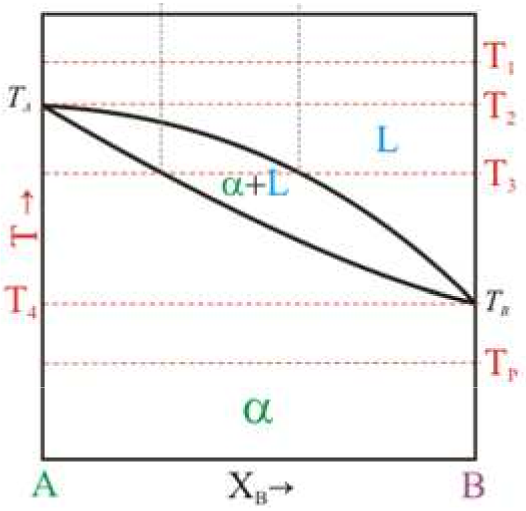
Questions?

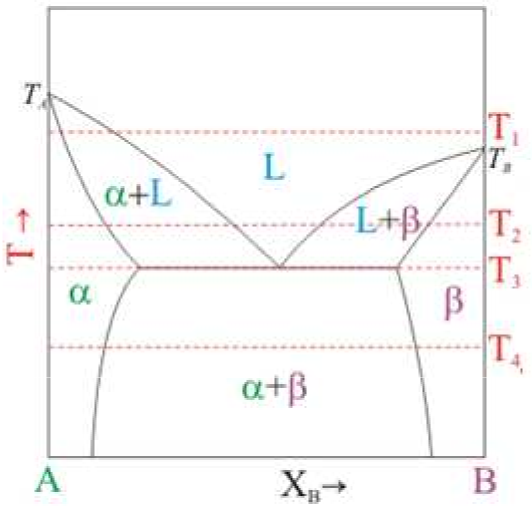
1. The specific heat of solid copper above 300 K is given by $C_P = 22.64 + 6.28\times10^{-3}T\ J\ \text{mole}^{-1}\ \text{K}^{-1}$. By how much does the entropy of copper increase on heating from 300 to 1358 K?
2. Draw the free energy temperature diagram for Fe up to 1600^{o}C showing all the allotropic forms.
3. From the thermodynamic principles show that the melting point of a nanocrystalline metal would be different from that of bulk metal. Will the melting point be different if the nanoparticle is embedded in another metal?
4. What is Clausius-Clapeyron equation? Apply it for the solidification of steels and gray cast iron.
5. If the equilibrium concentration of vacancies in terms of mol fraction at 600 °C is 3x10^{-6} calculate the vacancy concentration at 800 °C. R = 8.314 J/mol.K

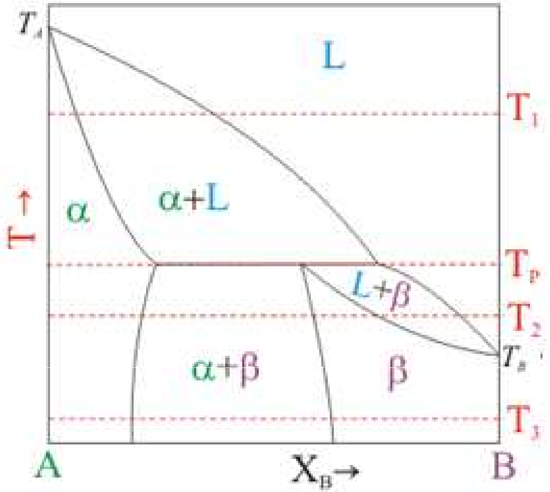
   For aluminium ΔH_V = 0.8 eV atom^{-1} and $\Delta S_V/R$ = 2. Calculate the equilibrium vacancy concentration at 660^{o}C (T_m) at 25^{o}C
6. Derive $\Delta S^{mix}_{Conf} = -R[X_A \ln X_A + X_B \ln X_B]$
7. Show that the free energy of a mixture of two phases in equilibrium in a binary system is given by the point on the common tangent line that corresponds to that overall composition. Show that the free energy of a mixture of phases of any other composition or a single phase is higher.

Questions?

8. Draw the G-X diagrams at the temperatures shown in Fig's. Please note that the crystal structure of both the pure metals in the phase diagram is the same.







9. For a single-component system, why do the allotropes stable at high temperatures have higher enthalpies than allotropes stable at low temperatures.

10. Derive following equations

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

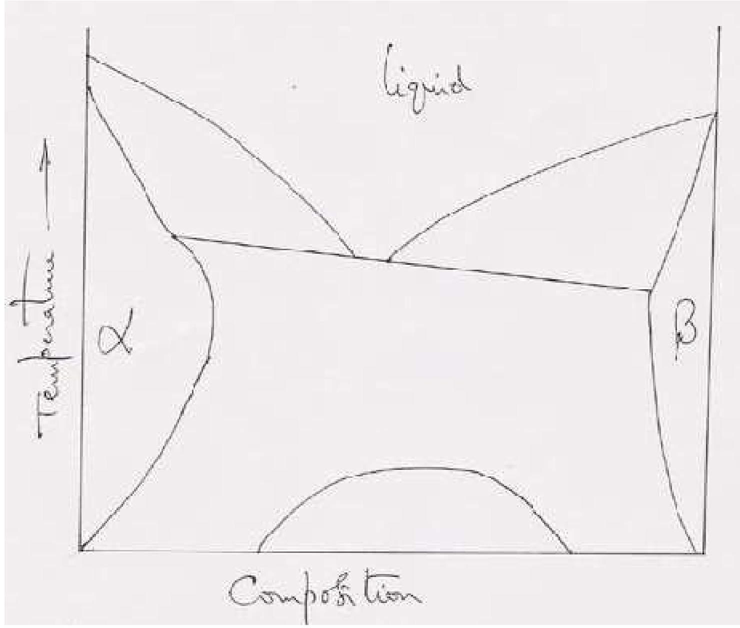
$$\mu_A = G_A + \Omega(1 - X_A)^2 + RT \ln X_A$$

11. Calculate the free energy of Si at 1186 °C from the known values, as given below:

$$A = 23.698, B = 3.305\times10^{-3}, C = 4.35\times10^{5} \; and \; \Delta S_{298}^{\theta} = 18.81 J/mol.k$$

Questions?

12. Identify the errors in the binary phase diagram given in Fig., give the reasons and draw the corrected phase diagram.



13. Consider an alloy of elements A and B, with the composition of X_A=0.25 andX_B=0.75. If the free energy of the pure elements, A (G_A) and B (G_B) are -45.1 kJ and -48.3 kJ/mole at 950°C, then (a) Calculate the free energy after mixing at this temperature for two cases, whenenthalpy of mixing ΔH_{mix}= -3.1 kJ/mole and +2.7 kJ/mole.(b) Further, calculate the activity and chemical potential of element A at thattemperature forΔH_{mix}= -3.1 kJ/mole.
14. Derive the Gibb's phase rule.

Questions?

15. 15 g gold and 25 g of silver are mixed to form a single-phase ideal solid solution

a) How many moles of solution are there?
b) What are the mole fractions of gold and silver?
c) What is the molar entropy of mixing?
d) What is the total entropy of mixing?
e) What is the molar free energy change at 500^{o}C?
f) What are the chemical potentials of Au and Ag at 500^{o}C taking the free Au atom is added? Express your answer in eV atom^{-1}.
g) By how much will the free energy of the solution change at 500^{o}C if one Au atom is added? Express your answer in eV atom^{-1}

DIFFUSION

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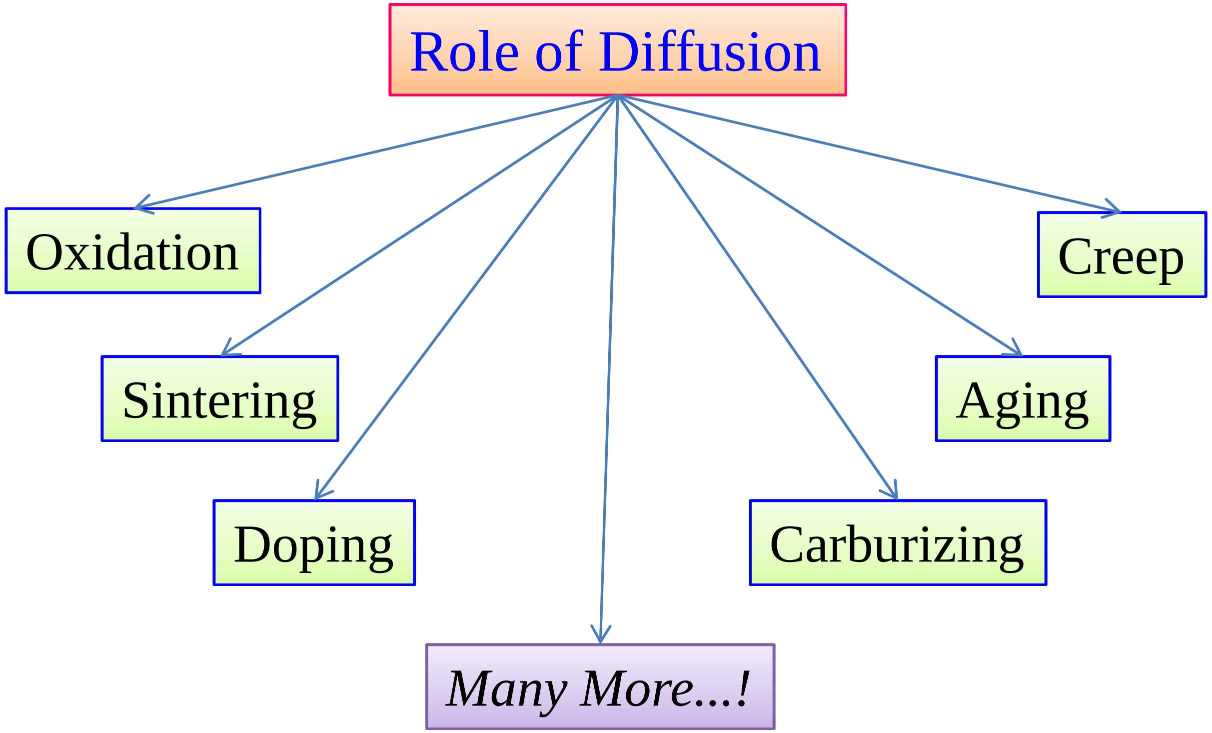
Introduction

- Diffusion is defined as, random movement of atoms/ molecules in solid, liquid and gas. For example dissolution of ink in water and smoke in air
- It can also defined as, Diffusion is a process of mass transport by atomic movement under the influence of thermal energy and a concentration gradient.
- To comprehend many materials related phenomenon one must understand diffusion.



Role of Diffusion

Oxidation

Sintering

Doping

Many More...!

Carburizing

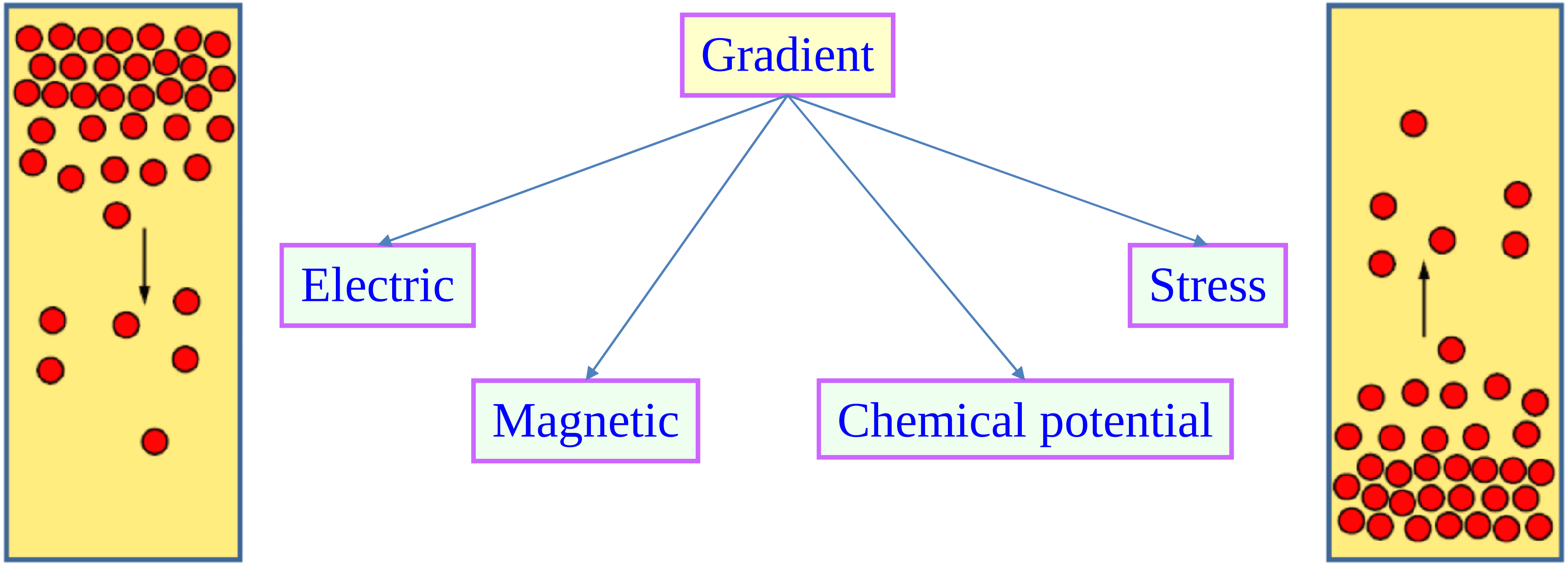
Aging

Creep

Materials Joining : Diffusion Bonding

Diffusion Phenomena

- Mass flow process by which species change their position relative to their neighbors.
- Driven by *thermal energy* and a *gradient*
- Thermal energy → thermal vibrations → Atomic jumps
- Atoms move from higher to lower concentration region. If this movement is from one element to another e.g. Cu to Ni, then it is termed as *Inter-diffusion.* If the movement is within similar atoms as in pure metals, it is termed *self-diffusion.*


Gradient

Electric

Magnetic

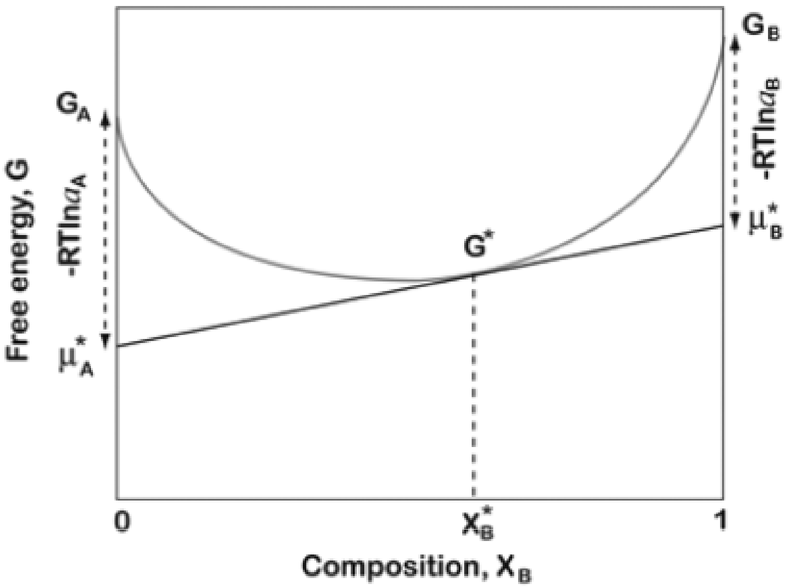
Chemical potential

Stress

Diffusion under thermodynamic driving force

- As explained before and in the figure, the chemical potential of elements at any composition can be determined by taking a slope on the Gibb's free energy curve and then by extending it to X_B = 0 (chemical potential of element A, μ_A) and X_B = 1 (chemical potential of element B, μ_B)
- From the chemical potentials, we can determine the activities, a_A and a_B from the knowledge of free energies of pure elements.

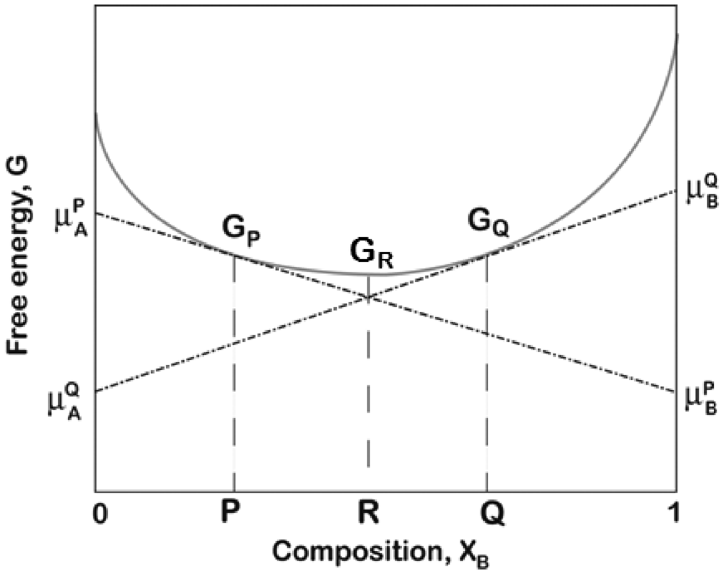
$$-RT\ln a_A = G_A - \mu_A \qquad -RT\ln a_B = G_B - \mu_B$$

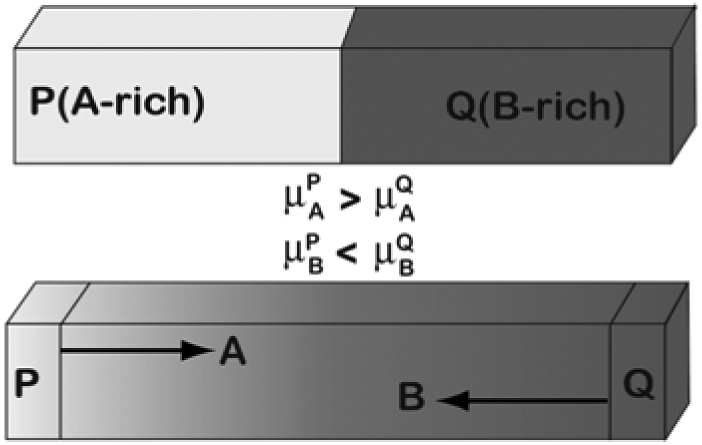


- So it must be clear that μ_B decreases from G_B at X_B = 1 to a infinitely small value close to X_B = 0.
- Following, a_B decreases from 1 at X_B = 1 to 0 at X_B = 0. It may vary ideally, that is $a_B = X_B$ or deviate positively/negatively, as explained previously.
- Similarly, μ_A decreases from G_A at X_B = 0 to a infinitely small value close to X_B = 1. a_B decreases from 1 at X_B = 0 to 0 at X_B = 1
- So, μ_A and a_A, and μ_B and a_B follow the same trend of increasing or decreasing with X_B.

Diffusion under thermodynamic driving force

- ❑ Now let us consider, two different AB alloys P (A rich) and Q (B rich).
- ❑ If these alloys are kept separately, these alloys will have free energy of G_P and G_Q, respectively.
- ❑ However, if we bond these two blocks, they will not be anymore in equilibrium condition.
- ❑ If the amount of material P and Q are taken such that overall mole fraction is R, then the equilibrium free energy will be G_R.
- ❑ So the system will try to move to its new equilibrium free energy.
- ❑ Now if we don't melt the alloy, it can only move to the equilibrium composition by solid state diffusion.

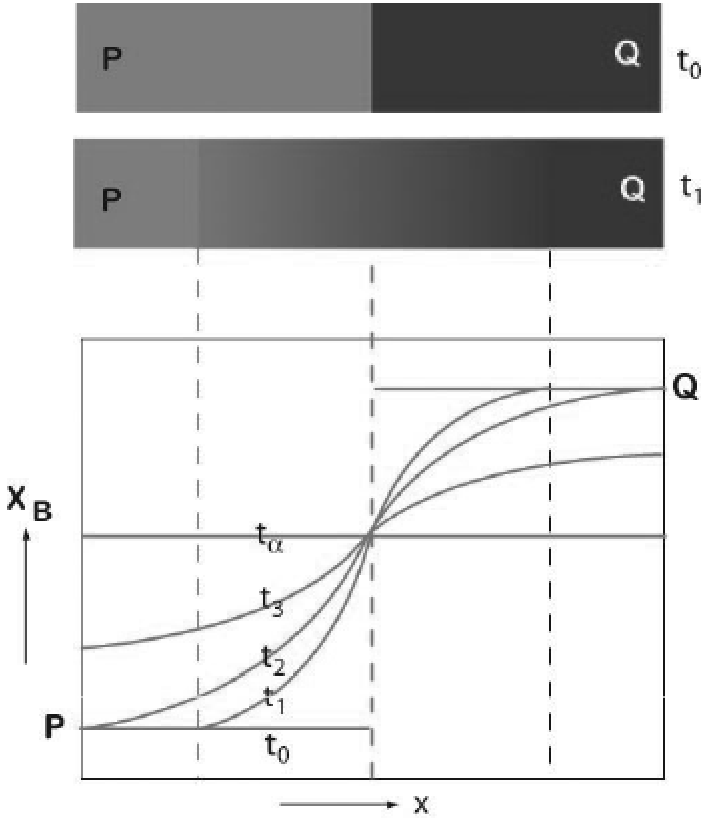




Diffusion under thermodynamic driving force

- If it is held at elevated temperature at which diffusion rate is reasonable, the system will reach to the equilibrium after certain time depending on the diffusion rate.
- It can be seen that at equilibrium alloy R, the chemical potential of A is μ_A^R , which is lower than the chemical potential of the same element, μ_A^P , in alloy P but higher than in alloy Q, that is μ_A^Q .
- On the other hand, μ_B^R is less than μ_B^Q but higher than μ_B^P .
- So to reach the equilibrium, the alloy P should decrease the chemical potential of A and increase the chemical potential of B. On the other hand, the alloy Q should increase the chemical potential of A and decrease the chemical potential of B.
- Since the chemical potential of A decreases from the A rich to the B rich alloy and the chemical potential of B decreases from B rich to A rich alloy, P should decrease the content of A and Q should decrease the content of B.
- In this condition it is possible only by the diffusion of element A out of P and diffusion of element B out of alloy Q, as shown in the figure in the previous slide.
- If we allow the system to go to equilibrium at temperature T, there will be no composition in the blocks P and Q at time zero that is t_0. Then with the increase in time in the order of $t_3 > t_2 > t_1 > t_0$, as shown in the figure (next slide), interaction zone increases. Following, after infinite time of annealing, t_α it will reach to equilibrium composition.

Diffusion under thermodynamic driving force



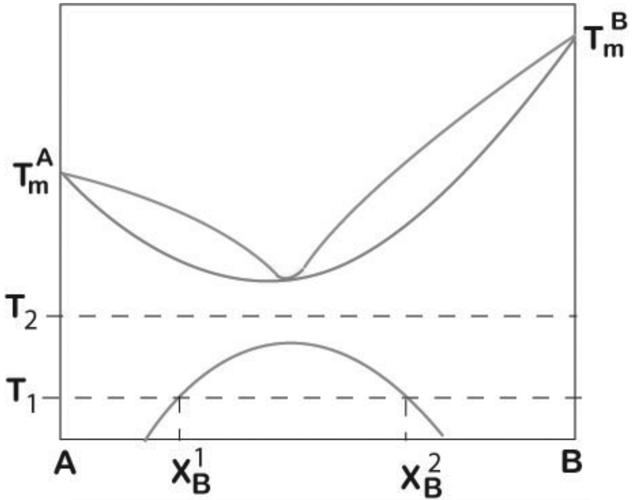
Note here that infinite time is rather notional. It means that long time enough to reach it to equilibrium. So this time will depend on the thickness of the blocks and the diffusion rate at the temperature of annealing.

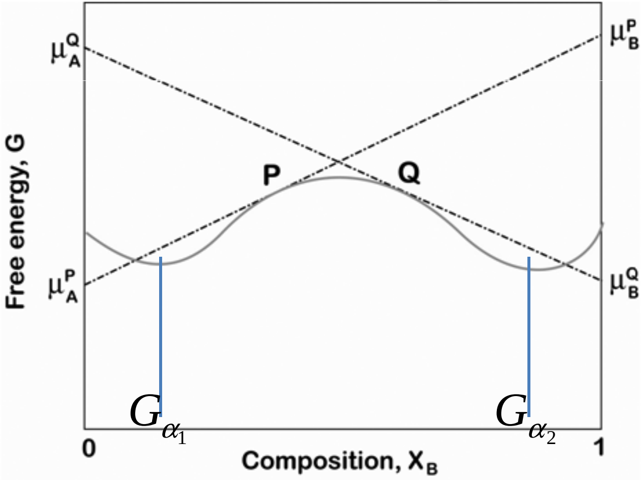
Diffusion under thermodynamic driving force

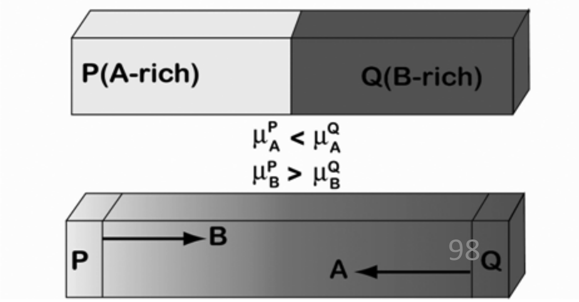
- ☐ Now let us consider a system with miscibility gap.
- ☐ If we anneal two block with any compositions at temperature, T_2, the explanation of the diffusion process will be similar as explained before.
- ☐ However, if we couple two blocks with the composition of P and Q, which are inside the miscibility gap, different situation will happen.
- ☐ From the slopes taken at P and Q, we find

$$\mu_A^P < \mu_A^Q \qquad and \qquad \mu_B^P < \mu_B^Q$$

- ☐ That means, the chemical potential of A is less in A rich alloy, P compared to the A lean alloy, Q.
- ☐ Similarly, the chemical potential of B is higher in B lean alloy, P compared to the B rich alloy, Q.
- ☐ If we couple blocks of P and Q then the average free energy of the systems, let say, R depending on the relative amounts of P and Q.
- ☐ However, since the system always tries to decrease free energy, it will try to reach to the lowest free energy G_{α_1} and G_{α_2}







Diffusion under thermodynamic driving force

- ❑ That means A rich alloy P should increase the content of A and the B rich alloy Q should increase the content of B.
- ❑ From the chemical potential point of view also it must be clear that B will diffuse out of the B lean alloy P towards Q and A will diffuse out of the B lean alloy Q towards P.
- ❑ The direction of elements is just opposite compared to the previous example explained.
- ❑ Since elements diffuse up the concentration gradient instead of down the concentration gradient, it is called uphill diffusion.
- ❑ In terms of chemical potential gradient

$$J_A \alpha \frac{\mu_A^P - \mu_A^Q}{\Delta x} \Rightarrow J_A \alpha \frac{\mu_A^P - \mu_A^Q}{\Delta x} \Rightarrow J_A = -D_A \frac{d\mu_A}{dx}$$

Since A diffuse from Q to P and and B diffuse from P to Q

$$J_B \alpha \frac{\mu_B^Q - \mu_B^P}{\Delta x} \Rightarrow J_A \alpha \frac{\mu_B^Q - \mu_B^P}{\Delta x} \Rightarrow J_B = -D_B \frac{d\mu_B}{dx}$$

- ❑ In terms of concentration gradient

$$J_A = D_A \frac{C_A^P - C_A^Q}{dx} \Rightarrow J_A = D_A \frac{dC_A}{dx}$$

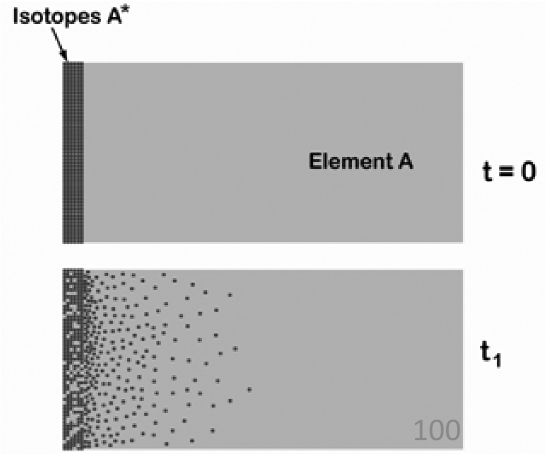
$$J_B = D_B \frac{C_B^Q - C_B^P}{dx} \Rightarrow J_B = D_B \frac{dC_B}{dx}$$

- ❑ It can be seen that negative sign is not present in the Fick’s first law for this case.

Diffusion under thermodynamic driving force

- In previous slides we have shown diffusion of elements because of chemical potential driving forces. However, diffusion occurs even without the presence of thermo dynamical driving force or any other driving forces.
- For example, in pure material, where there are no forces present but atoms still to jump to another position.
- In a low melting point material, like in Sn or Pb, jump of atoms possible even at room temperature. However, jump of atoms in this case is completely random. Presence of driving forces rather make net flux of atoms to a particular direction.
- To test the possibility of diffusion without any driving forces tracer diffusion experiments are conducted. Radiotracer elements which has one or two neutron mass difference are deposited on a material of the same element and then annealed at elevated temperature.
- Concentration of these tracer elements can be measured at different depths even in low concentration because of radiation of different rays

- .As shown in a schematic figure, these tracer elements diffuse inside the material. Since both are pure elements there is no chemical potential difference.
- These tracer elements are used to trace the diffusion of elements.
- There will be very small gain (increase in entropy) because of spreading of these tracer elements.
- If we do not use the tracer elements we will not be able to detect the jump of atoms.

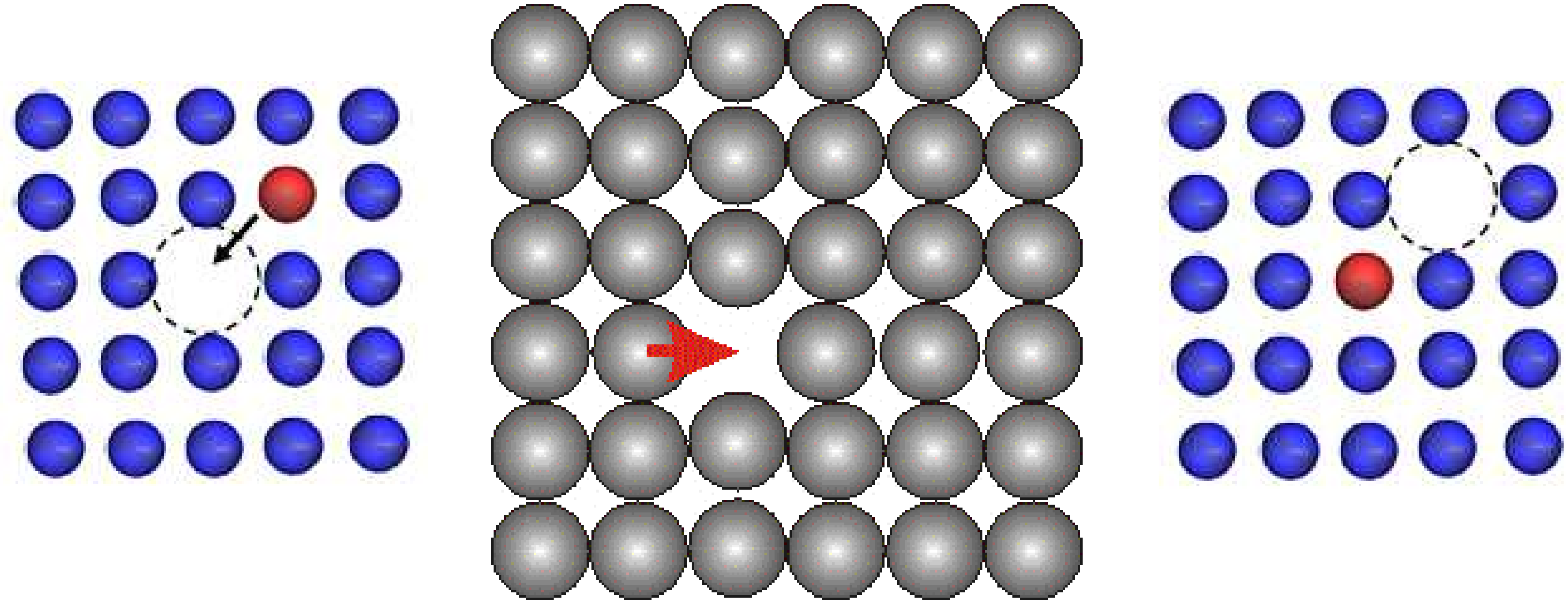


Diffusion Mechanism

- ❑ Diffusion of atoms involves movement in steps from one lattice site to the another. An empty adjacent site and breaking of bonds with the neighbor atoms are the two necessary conditions for this.

Vacancy Mechanism

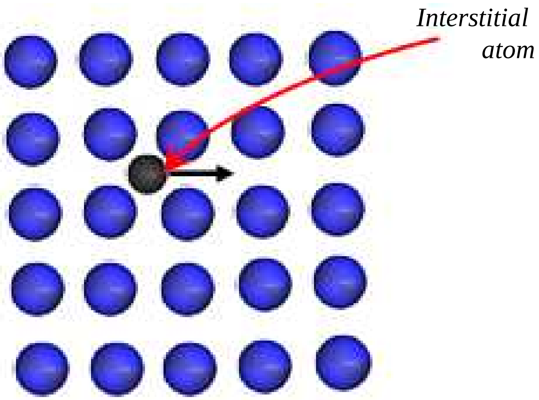
- ❑ This mechanism involves movement of atoms (we are interested in substitutional atoms) from a regular lattice site to an adjacent vacancy. Since vacancy and atoms exchange position, the vacancy flux is in the opposite direction.

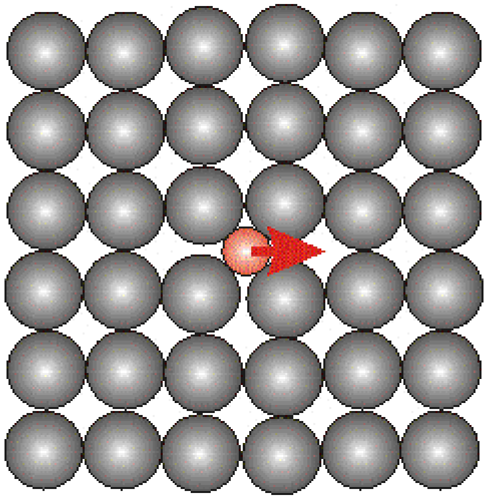


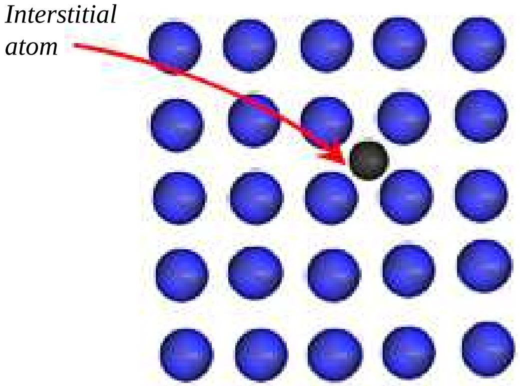
Diffusion Mechanism

Interstitial Mechanism

- This mechanism Involves migration of atoms from one interstitial site to a neighboring empty interstitial site.
- Usually the solubility of interstitial atoms (e.g. carbon in steel) is small. This implies that most of the interstitial sites are vacant. Hence, if an interstitial species wants to jump, ‘most likely’ the neighboring site will be vacant and jump of the atomic species can take place.
- This mechanism is more prevalent for impurity such a hydrogen, carbon, nitrogen, oxygen which are small enough to fit into an interstitial position.



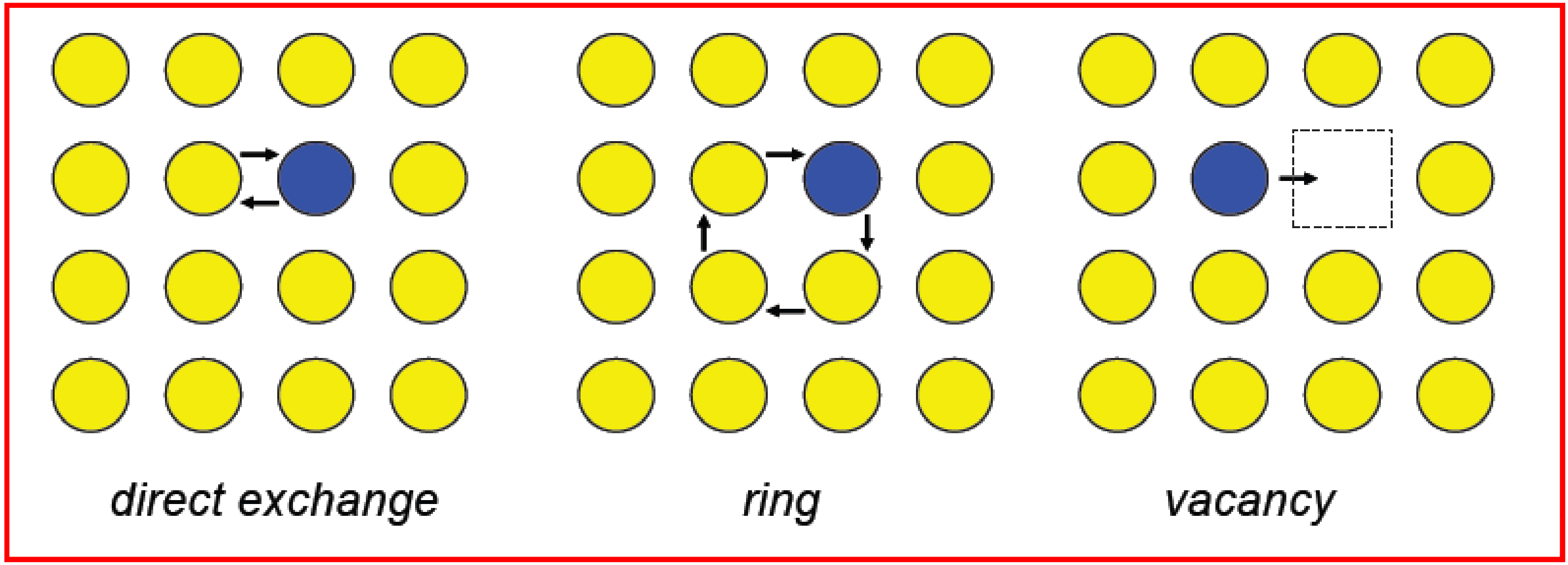




Diffusion Mechanism

Atom Interchange Mechanism

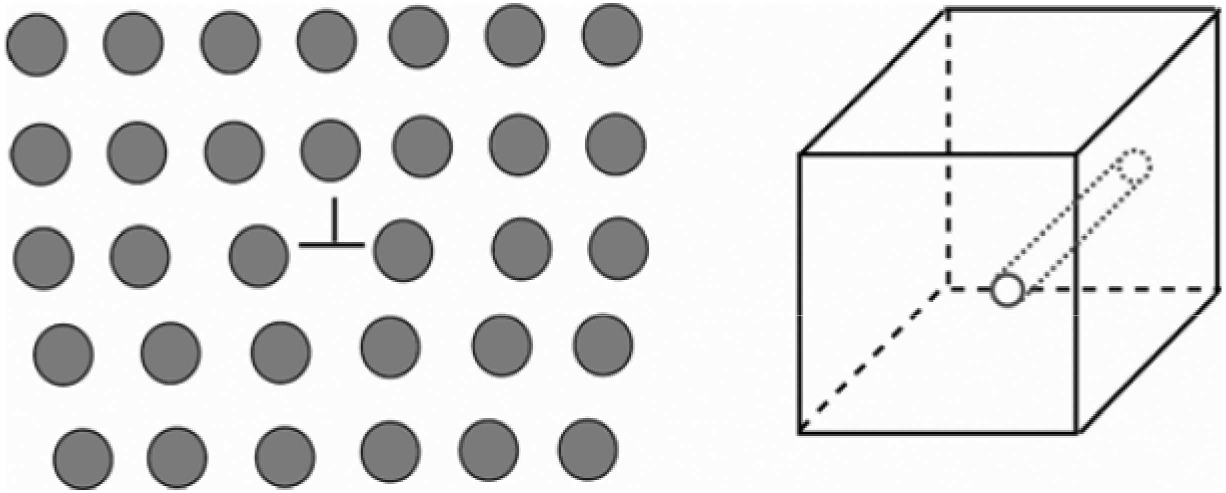
- It is possible for movement to take place by a direct interchange between two adjacent atoms or by a four –atom ring interchange.
- However, these would probably occur only under special conditions, since the physical problem of squeezing between closely packed neighboring atoms would increase the barrier for diffusion.
- Note: The rate of diffusion is much greater in a rapidly cooled alloy than in the same alloy slow cooled. The difference is due to the larger number of vacancies retained in the alloy by fast cooling.



Diffusion Mechanism

Pipe Diffusion

- When diffusion occurs via edge dislocation, it is called pipe diffusion.

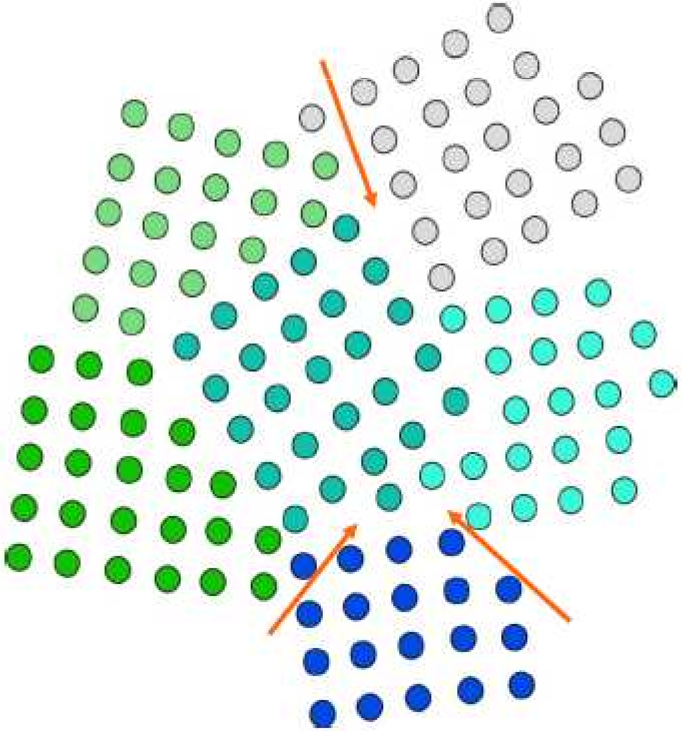


- Since it feels like movement of atoms through a pipe.
- Note that both interstitial and substitutional diffusion can occur via dislocations.
- Even impurities are attracted by the dislocations because of availability of more space and chance to release stress.
- This is also the reason (more open space) that it has lower activation barrier and diffusion rate through dislocation is higher than the diffusion through lattice.

Diffusion Mechanism

Grain boundary diffusion

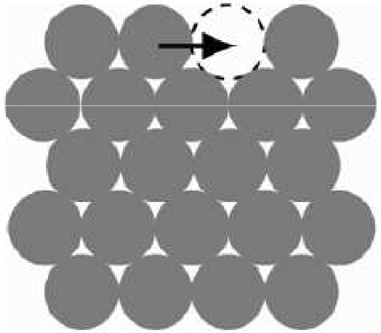
- ❑ Diffusion occurs via grain boundaries even easily and it is called grain boundary diffusion.
- ❑ Since grain boundaries are relatively more open structure compared to atomic structure inside the grains, the barrier for diffusion through grain boundary is much less and the diffusion rate is higher.
- ❑ Rate of diffusion increases with the increase in misorientations.



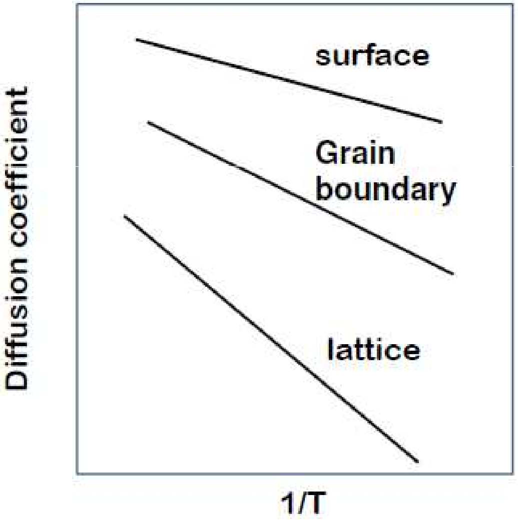
Diffusion Mechanism

Surface diffusion

- When diffusion occurs over a surface, it is called surface diffusion.
- Here activation energy for diffusion is the lowest since there are no atoms above the atom of interest, which exchanges position with the vacancy. So diffusion rate is the highest compared to other diffusion mechanisms.



Surface diffusion

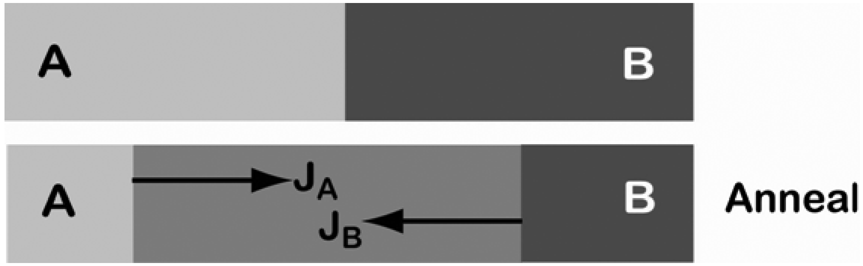


- Note that both interstitial and substitutional diffusion can happen through, lattice, dislocations, grain boundaries and surface.
- Slope of the diffusion coefficient vs. 1/T gives the activation barrier for diffusion. Activation barrier is the lowest and diffusion rate is the highest for the surface diffusion. Activation barrier is the highest and diffusion rate is the lowest for lattice diffusion.

Diffusion Mechanism

Diffusion Couple

- When two blocks with different compositions are joined (coupled) together and annealed to allow diffusion between them, it is called diffusion couple.



Interdiffusion (chemical diffusion)

- Since elements in the diffusion couple interdiffuse to each other, it is called interdiffusion.
- The diffusion coefficient is in general called as interdiffusion coefficient and if sometimes any new compound forms during the diffusion at the interface, occasionally, it is called chemical diffusion coefficient.
- Note that actually elements A and B diffuse. Diffusion of these elements are called intrinsic diffusion of elements.

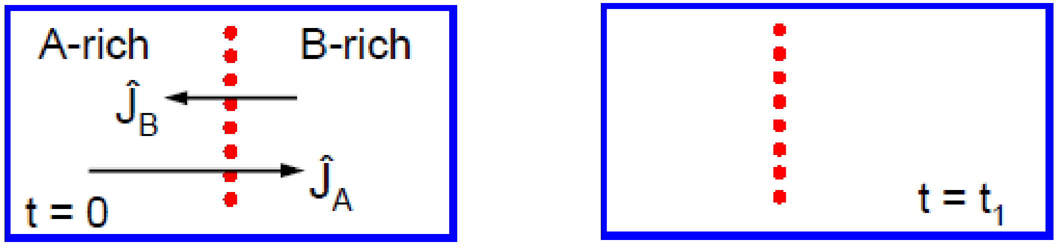
Diffusion Mechanism

Self diffusion

- When diffusion occurs without any presence of driving force, it is called self diffusion.
- Atoms vibrate at their positions and because of some violent jumps, it can cross the activation barrier to make the jump successful.
- Since there is no driving force to direct the jump of atoms to a particular direction, self diffusion is truly random in nature.
- This indicates that when a pure metal is kept at elevated temperature jump of atoms is always happening.
- In low melting point metals, like In or Sn, even at room temperature, atoms exchange their position.
- However, since these are very small in size, we cannot follow a particular atom jump.
- We shall see that the jump can be many orders of magnitude in one second. This makes it even difficult to follow the jump of atoms.
- To obviate this problem, concept of tracer diffusion is introduced.

Kirkendall Effect

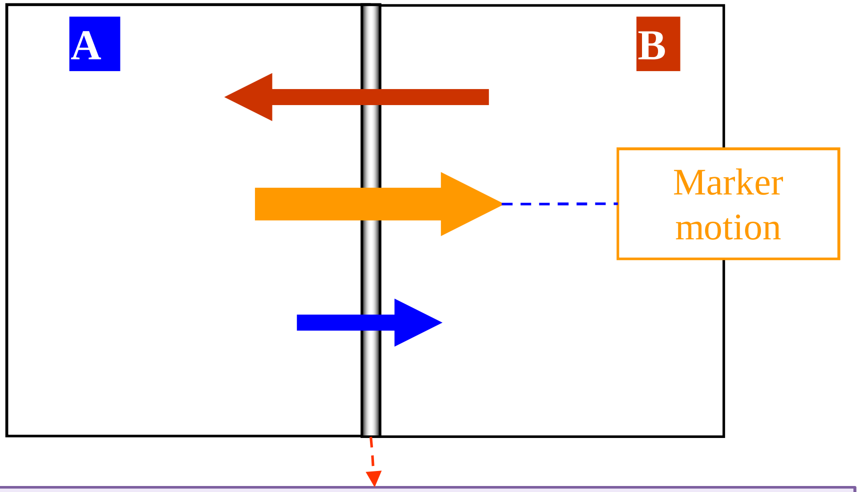
- If the diffusion rates of two metals A and B into each other are different, the boundary between them shifts and moves towards the faster diffusing metal.



Diffusion rate
$\hat{J}_A > \hat{J}_B$
t = time

- This is known as kirkendall effect. Named after the inventor Ernest Kirkendall (1914-2005). It can be demonstrated experimentally by placing an inert marker at the interface

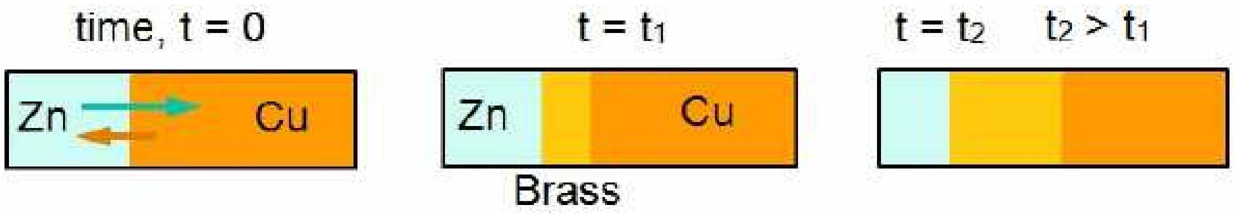
✓ Materials A and B welded together with inert marker and given a diffusion anneal
✓ Usually the lower melting component diffuses faster (say B)



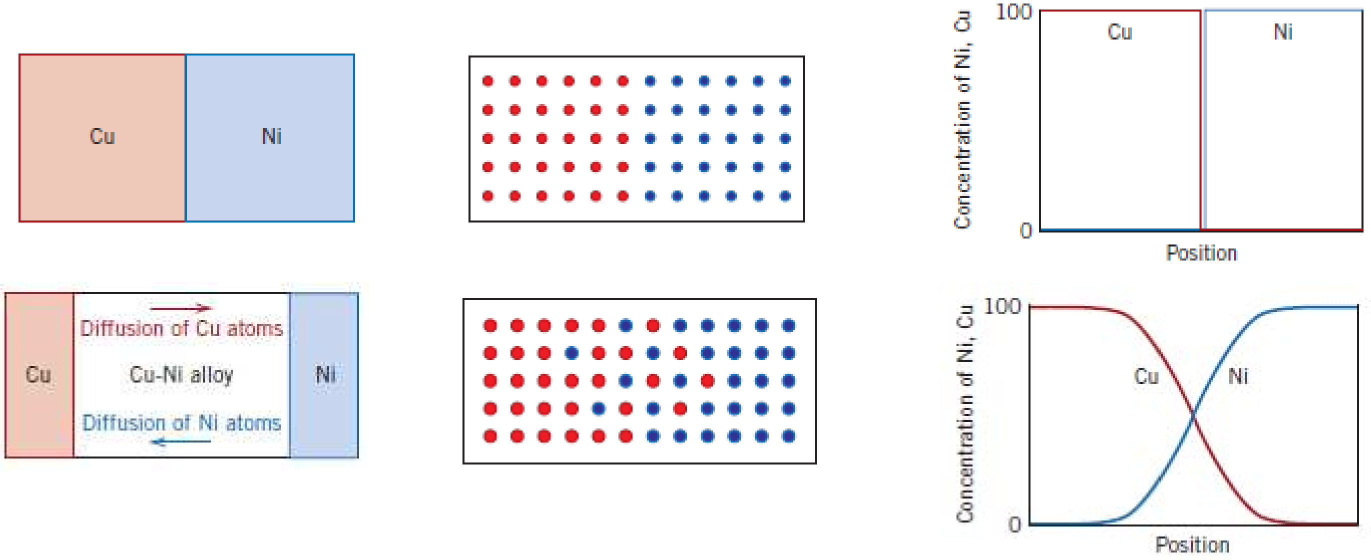
***Inert Marker** – thin rod of a high melting material which is basically insoluble in A & B*

Kirkendall Effect

- Zn diffuses faster into Cu than Cu in Zn. A diffusion couple of Cu and Zn will lead to formation of a growing layer of Cu-Zn alloy (*Brass*).



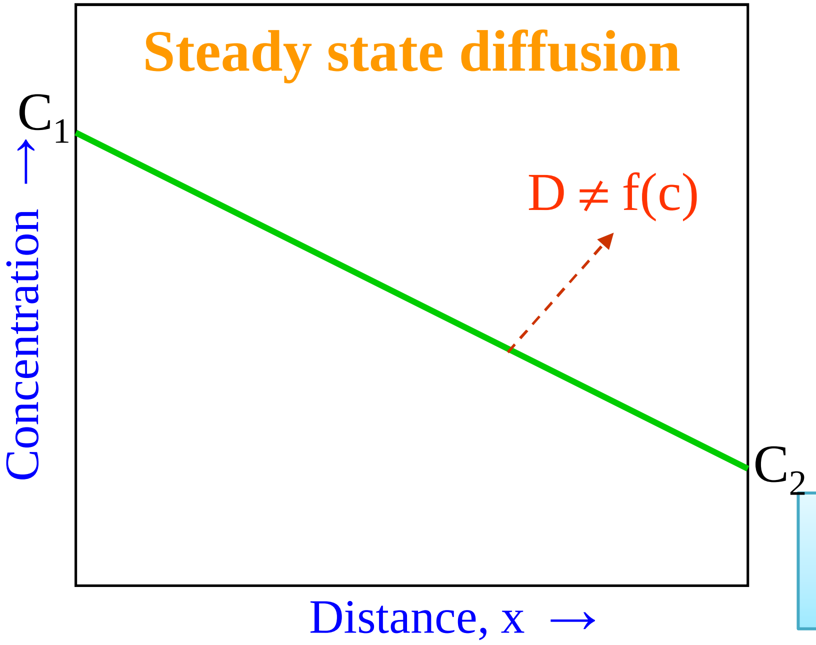
- Same will happen in a Cu-Ni couple as copper diffuses faster in nickel than nickel in copper.
- Since this takes place by vacancy mechanism, pores will form in cu (of the Cu-Ni couple as the vacancy flux in the opposite direction (towards Cu) will condense to form pores.



steady and non-steady state diffusion

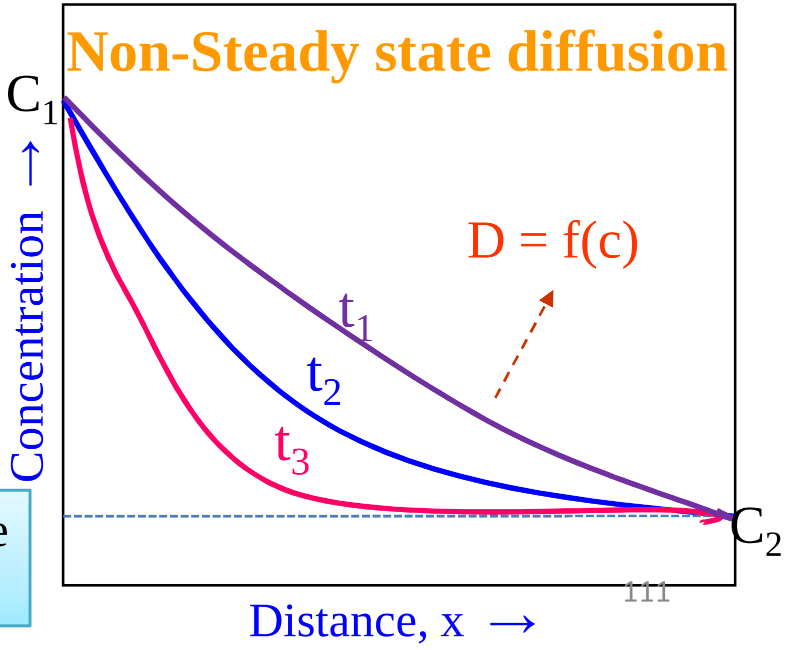
- ❑ Diffusional processes can be either steady-state or non-steady-state. These two types of diffusion processes are distinguished by use of a parameter called flux.
- ❑ It is defined as net number of atoms crossing a unit area perpendicular to a given direction per unit time. **For steady-state diffusion, flux is constant with time, whereas for non-steady-state diffusion, flux varies with time.**
- ❑ A schematic view of concentration gradient with distance for both steady-state and non-steady-state diffusion processes are shown below.

❑ Flux (J) *(restricted definition)* → Flow / area / time [Atoms / m^2 / s]



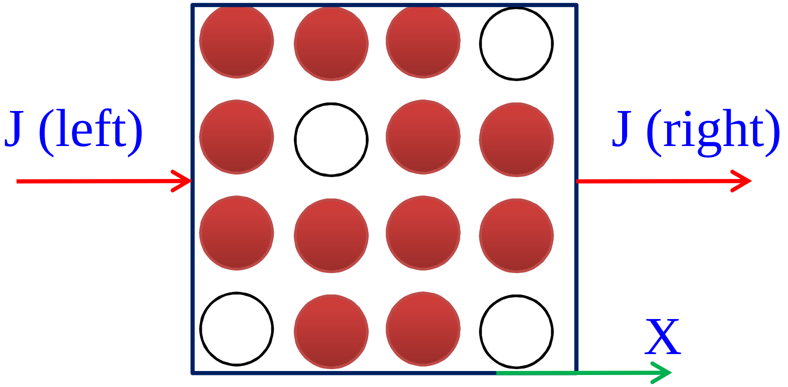
Steady state
$J \neq f(x,t)$

Non-steady state
$J = f(x,t)$



steady and non-steady state diffusion

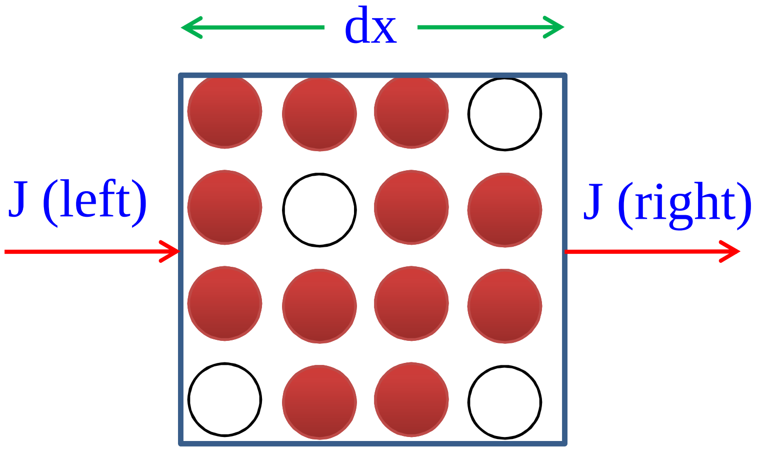
Steady State : Concentration profile not changing with time.



Concentration 'C' in the box doesn't change with time

Steady State
J(x) Left = J(x) Right

Non-Steady State : Concentration profile changes with time.



Concentration accumulating in the box

Non-Steady State
J(x) Left ≠J(x) Right

Fick's I Law

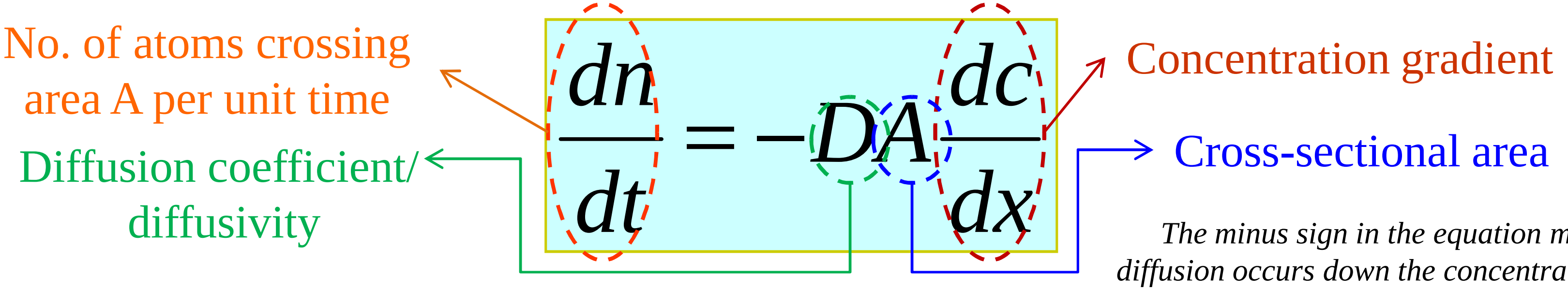
- ❑ Steady-state diffusion is described by Fick's first law which states that flux, J, is proportional to the concentration gradient.
- ❑ The constant of proportionality is called diffusion coefficient (diffusivity), D (cm^2/sec). diffusivity is characteristic of the system and depends on the nature of the diffusing species, the matrix in which it is diffusing, and the temperature at which diffusion occurs.
- ❑ Thus under steady-state flow, the flux is independent of time and remains the same at any cross-sectional plane along the diffusion direction. for the one-dimensional case, Fick's first law is given by

$$J \equiv atoms\,/\,area\,/\,time \propto concentration\ gradient$$

$$J \propto \frac{dc}{dx} \longrightarrow J = -D\frac{dc}{dx} \longrightarrow J = \frac{1}{A}\frac{dn}{dt} = -D\frac{dc}{dx}$$

Steady state

$J \neq f(x,t)$



$$\frac{dn}{dt} = -DA\frac{dc}{dx}$$

No. of atoms crossing area A per unit time

Diffusion coefficient/ diffusivity

Concentration gradient

Cross-sectional area

The minus sign in the equation means that diffusion occurs down the concentration gradient

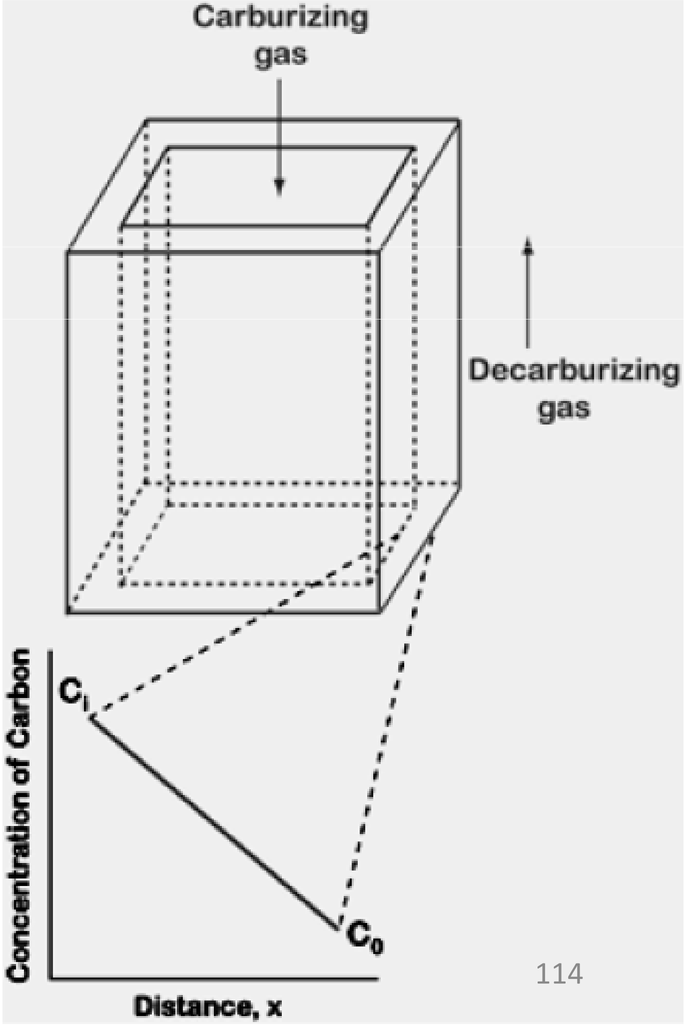
Fick’s I Law

- ❑ In Ficks I law, minus sign comes from the fact that matter flows down the concentration gradient. It is not necessarily true in all the cases.
- ❑ Matter may also diffuse up the concentration gradient, which is called uphill diffusion.

- ❑ Fick’s first law can directly be applied in the case of steady state, as shown in the example below.
- ❑ Steady state means that there will not be any change in the composition profile with time.
- ❑ If we pass carburizing gas through the pipe as shown in the figure and decarburizing gas outside the pipe, a steady composition profile may develop.
- ❑ Concentration gradient can be calculated following:

$$\frac{dc}{dx} = -\frac{C_i - C_0}{d} = -\frac{C_0 - C_i}{d}$$

- ❑ From this, one can calculate the flux from the known diffusion coefficients of carbon or the diffusion coefficient from the flux determined.



Solved Example -1

The steady-state diffusion is found in the purification of hydrogen gas. Compute the number of kilograms of hydrogen that pass per hour through a 6-mm-thick sheet of palladium having an area of 0.25 m^2 at 600°C. Assume a diffusion coefficient of 1.7×10^{-8} m^2 / s, that the concentrations at the high- and low-pressure sides of the plate are 2.0 and 0.4 kg of hydrogen per cubic meter of palladium, and that steady-state conditions have been attained.

This Problem calls for the mass of hydrogen, per hour, that diffuses through a pd sheet.

From the Fick's I law:

$$\boxed{M = JAt = -DAt\frac{\Delta c}{\Delta x}}$$

$$\boxed{= -(1.7\times10^{-8} m^2/s)(0.25m^2)(3600s/h)\left[\frac{0.4-2.0kg/m^3}{6\times10^{-3}s}\right]}$$

$$\boxed{= 4.1\times10^{-3} kg/h}$$

Solved Example -2

A sheet of BCC iron 2 mm thick was exposed to a carburizing gas atmosphere on one side and a decarburizing atmosphere on the other side at *675ºC*. After having reached steady state, the iron was quickly cooled to room temperature. The carbon concentrations at the two surfaces of the sheet were determined to be 0.015 and 0.0068 wt%. Compute the diffusion coefficient if the diffusion flux is 7.36×10^{-9} kg/m^2-s *(Hint : convert the concentrations from weight percent to kilograms of carbon per cubic meter of iron.*

This problem calls for computation of the diffusion coefficient for a steady-state diffusion situation. Let us first convert the carbon concentrations from weight percent to kilograms carbon per meter cubed using below equation.

For 0.015 wt% C

$$C'_C = \left[\frac{C_C}{\frac{C_C}{\rho_C} + \frac{C_C}{\rho_{Fe}}} \times 10^3 \right]$$

$$C'_C = \left[\frac{0.015}{\frac{0.015}{2.25} + \frac{99.985}{7.87}} \times 10^3 \right]$$

$$= 1.18 kgC / m^3$$

Similarly, for 0.0068 wt% C

$$C''_C = \left[\frac{0.0068}{\frac{0.0068}{2.25} + \frac{99.9932}{7.87}} \times 10^3 \right]$$

$$= 0.535 kgC / m^3$$

$$D = -J \frac{X_A - X_B}{C_A - C_B}$$

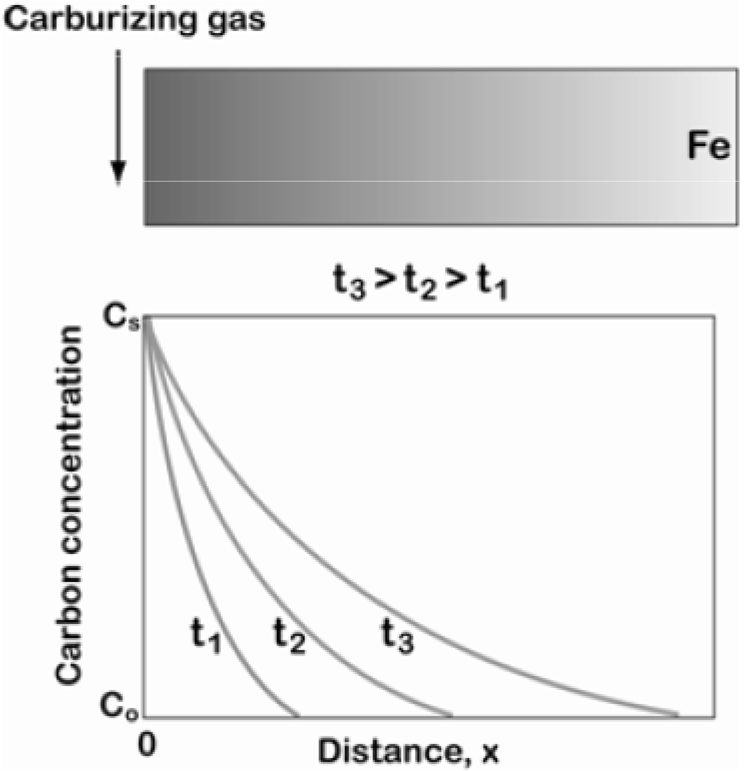
$$= -(7.36 \times 10^{-9} Kg / m^2 - s) \left[\frac{-2 \times 10^{-3} m}{1.18 Kg / m^3 - 0.535 Kg / m^3} \right]$$

$$= 2.3 \times 10^{-11} m^2 / s$$

Fick’s II Law

- However, just the Fick’s first law may not be useful to relate the flux and the concentration profile, since, in most of the cases, systems develop non steady state concentration profile.
- It means that concentration at a particular position changes with time.
- For example, if we keep concentration of carbon on one of the Fe surfaces anneal, composition profile will change with time , as shown in the figure.

- We can’t apply Fick’s first law directly to evaluate the concentration profile that develops during diffusion in this case, since, as shown in the figure, composition changes with annealing time at a particular position.
- So we need to have a relation, which can relate time along with the concentration and the position.
- For that Fick’s second law is derived. It is derived using conservation of mass and Fick’s first law.



Fick’s II Law

- ❑ Let us consider a very thin slab in the material.
- ❑ J_1 is the incoming flux, J_2 is the outgoing flux
- ❑ So the amount of carbon coming in short time δt is $J_1\ \delta t$ (mole/m^2) and going out is $J_2 \delta t$ (here $J_1 > J_2$)
- ❑ If the slab thickness is Δx, then

$$\delta C = \frac{(J_1 - J_2)\delta t}{\Delta x} \quad \text{Equation 1}$$

- ❑ Further, flux change in the thin slab can be considered, linear and we can write

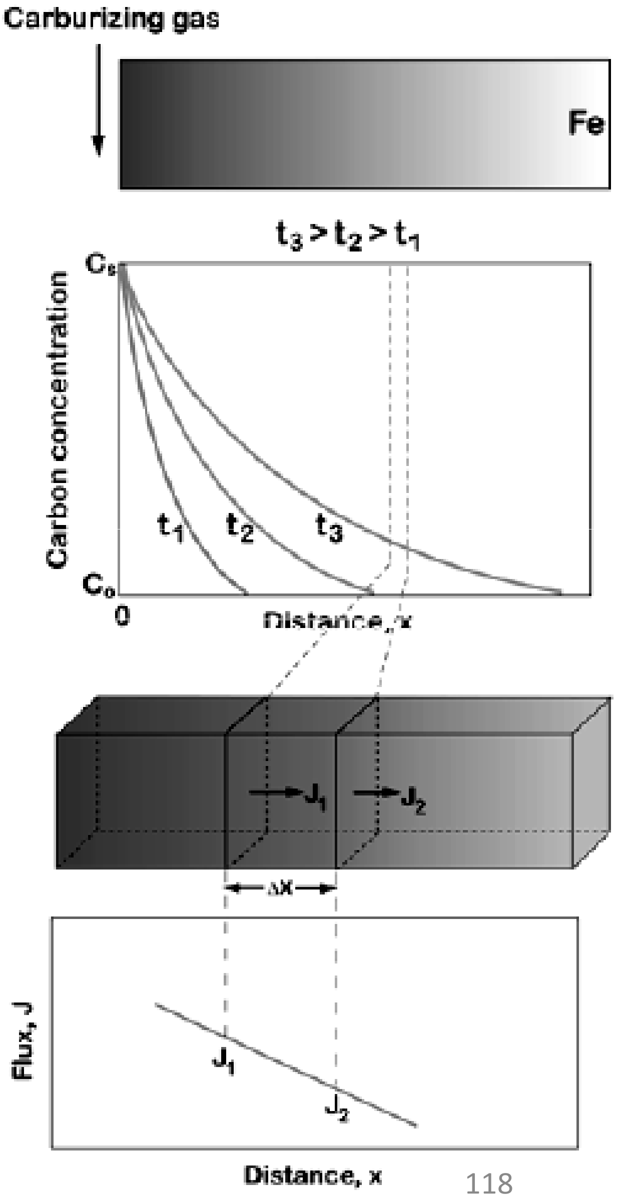
$$\frac{\partial J}{\partial x} = \frac{J_2 - J_1}{\Delta x} = -\frac{J_1 - J_2}{\Delta x} \quad \text{Equation 2}$$

- ❑ **From Eq. 1 and Eq. 2**

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}$$

- ❑ Using Fick’s first law

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial J}{\partial x}\right) \quad \textbf{\textit{If D is Constant}} \rightarrow \quad \frac{\partial C}{\partial t} = D\frac{\partial^2 J}{\partial x^2}$$



Solutions to Fick’s second Law

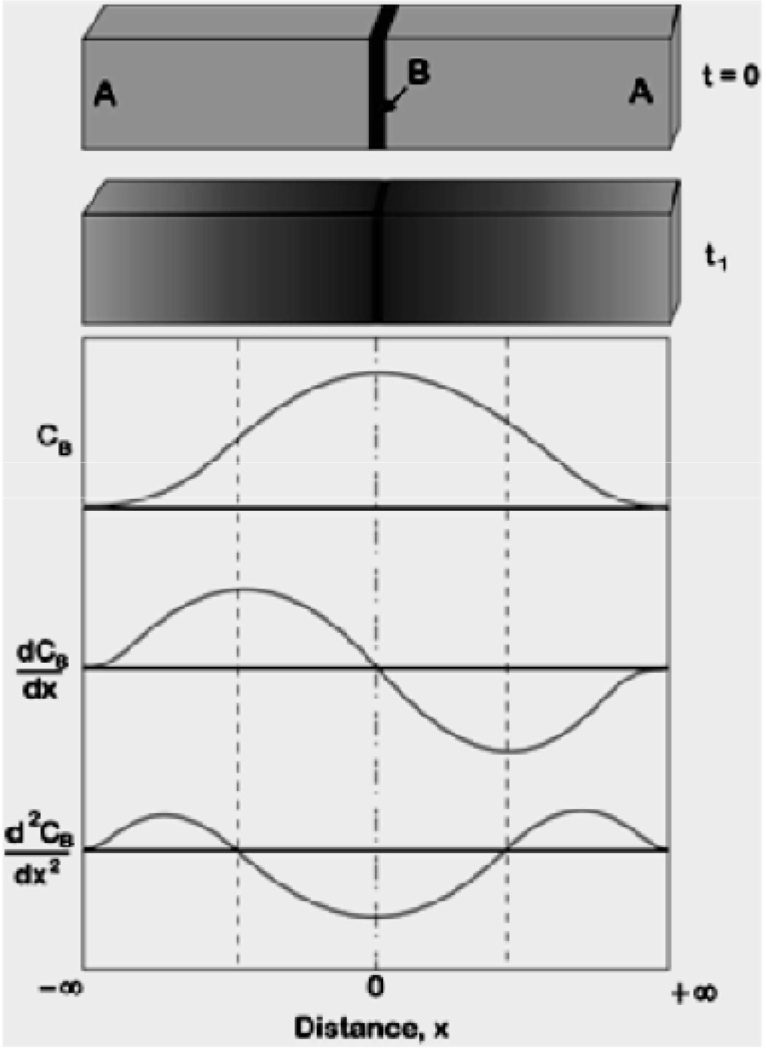
- Solution of the Fick’s second law depends on initial and boundary conditions.
- Further, D, in some cases, may be considered constant. That means D does not change with concentration or position.
- However, this condition meets only in very limited cases.
- In most of the practical examples, D is a function of concentration. In this case, solution to the Fick’s second law is complicated.
- So in the beginning, we shall solve the Fick’s second law for constant D.
- Solutions are mainly for two different types of conditions, small and large time values.
- When diffusion annealing time is small, solution is expressed with integrals or error functions. For long annealing time, it is expressed in terms of trigonometrical series.
- Note that the long or short annealing time is rather relative. By saying long annealing time, we mean that the complete sample is affected by the diffusion process and may lead to homogenization.
- By saying short annealing time, we mean that experiments are conducted such that whole material is not affected by the diffusion process.

Solution for a thin film source

- ❑ Let us consider that D is constant. That means D does not change with the composition. Since at a particular location C changes continuously with annealing time, t or a particular C changes its location continuously. From the assumption, we can state that D is the same at any location.
- ❑ The meaning of the above statement will be more clear, when we shall consider the change of D with the change in C concentration.
- ❑ Let us consider the situation, when a very thin film of element B is sandwiched between material A and then annealed at elevated temperature.

Note: One might ask, how thin it is?

- ❑ By saying "thin" we mean that the amount of material B is very low and even after total mixing (full homogenization) element B can be considered as impurities in the material A.
- ❑ That means, after deposition of B on A, the chemical potential gradient is negligible.



Solution for a thin film source

- ❑ In other sense, we can consider this as an example of diffusion in the absence of any driving force (although small driving force will be there from entropy of mixing)
- ❑ Actual meaning will be clear, when we discuss about the atomic mechanism of diffusion!
- ❑ We can consider that D is constant, since the material in which it diffuses has fixed composition.
- ❑ For constant D, the Fick's II law can be written as $\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x} \right) = D\frac{\partial^2 C}{\partial x^2}$
- ❑ As shown in the previous slide, it is seen that the element distribution after the diffusion can be expressed by exponential relation.
- ❑ Following the Fick's second law the distribution of element B in A can be expressed as

$$C_B(x) = \frac{C_0}{t^{1/2}} \exp\left(-\frac{x^2}{4D_B t} \right) \quad \text{where } C_o \text{ is a constant}$$

- ❑ This relation is developed based on the fact that composition profile shows exponential decay from thin film source.
- ❑ The correctness of the solution can be checked by differentiation of the equation with respect to t and x and then using them in the Fick's second law to find the equal values on both the sides.

Solution for a thin film source

- Further, the boundary condition that $C_B = 0$, at $x = \infty$ at t = 0 and $C_B = \infty, at$ x = 0 at t = 0 also meet.
- Now one might get confused, when we say $C_B = \infty$, since concentration of element B (= X_B / V_m = 1/ V_m) can't be infinite any time and will have some definite value even at completely pure state.
- Here $C_B = \infty$ is notional and means that the element B is not diluted by any other element, which further means that it is in pure state and for system it means that it has infinite source of element B before starting the experiment.
- We shall show that the absolute values of C_B (x) or C_0 are not important but the ratio $C_B(x)/C_0$ is important, where this solution is actually used to calculate the tracer or impurity diffusion coefficient of the species.
- Total material B (mole/m^2) that was sandwiched before annealing can be found following.

$$M_B = \int_{-\infty}^{+\infty} C_B$$

- So we can write $$M_B = \int_{-\infty}^{+\infty} \frac{C_B}{t^{1/2}} \exp\left(-\frac{x^2}{4D_Bt}\right) dx$$
- Further, we consider $\lambda = \dfrac{x}{2\sqrt{D_Bt}}$ means $dx = (2\sqrt{D_Bt})d\lambda$

Solution for a thin film source

- Since integration gives √Π, we get

$$M_B = 2C_0\sqrt{D_B}\int_{-\infty}^{+\infty}\exp(-\lambda^2)\,d\lambda = 2C_0\sqrt{\pi D_B}$$

- Replacing this for M_B we find

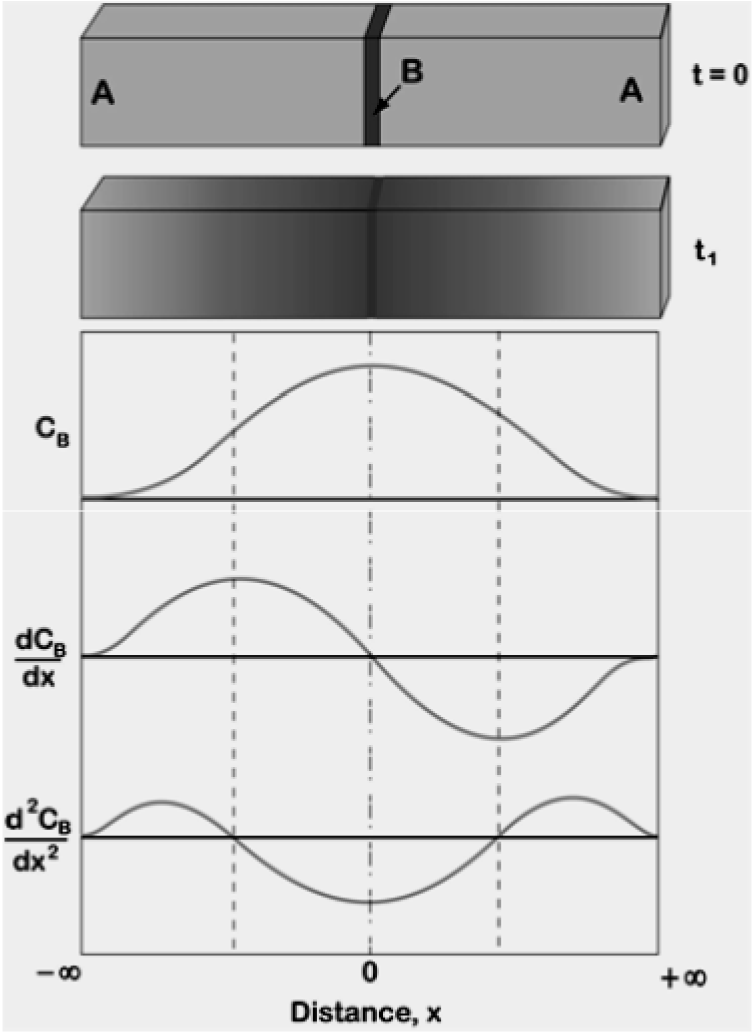
$$C_B(x) = \frac{M_B}{2\sqrt{\pi D_B t}}\exp\left(-\frac{x^2}{4D_B t}\right)$$

- C_B vs. x describes the distribution of elements B.
- dC_B/dx describes (following the Fick's law) the change in flux with respect to distance at a particular annealing time.

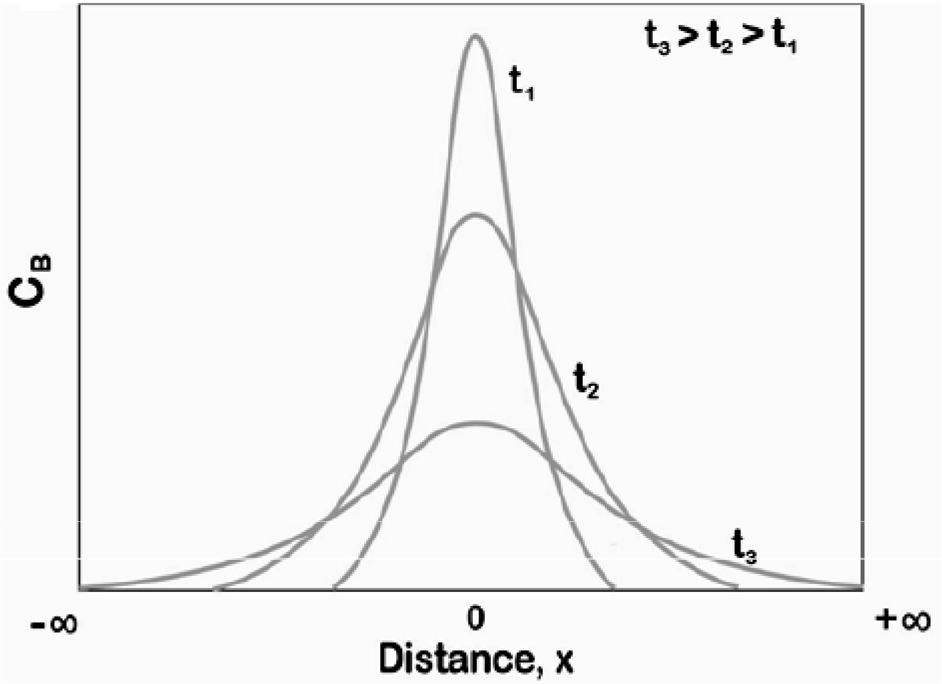
$$\frac{d^2C_B}{dx^2} = \frac{dC_B}{dt}\,vs.x$$

It explains the rate of change of element B

- The negative values indicate the region, where it loses the element B and positive value indicates that the region where it gains the element B. Note that the region where it is losing or gaining the element B depends on the time of annealing.



Solution for a thin film source



- ☐ The change in distribution of elements B with the increase in time is shown in the figure.

$$C_B(x) = \frac{M_B}{\boxed{2}\sqrt{\pi D_B t}} \exp\left(-\frac{x^2}{4D_B t}\right)$$

- ☐ Factor 2 comes from the fact that elements diffuse both the sides from the source

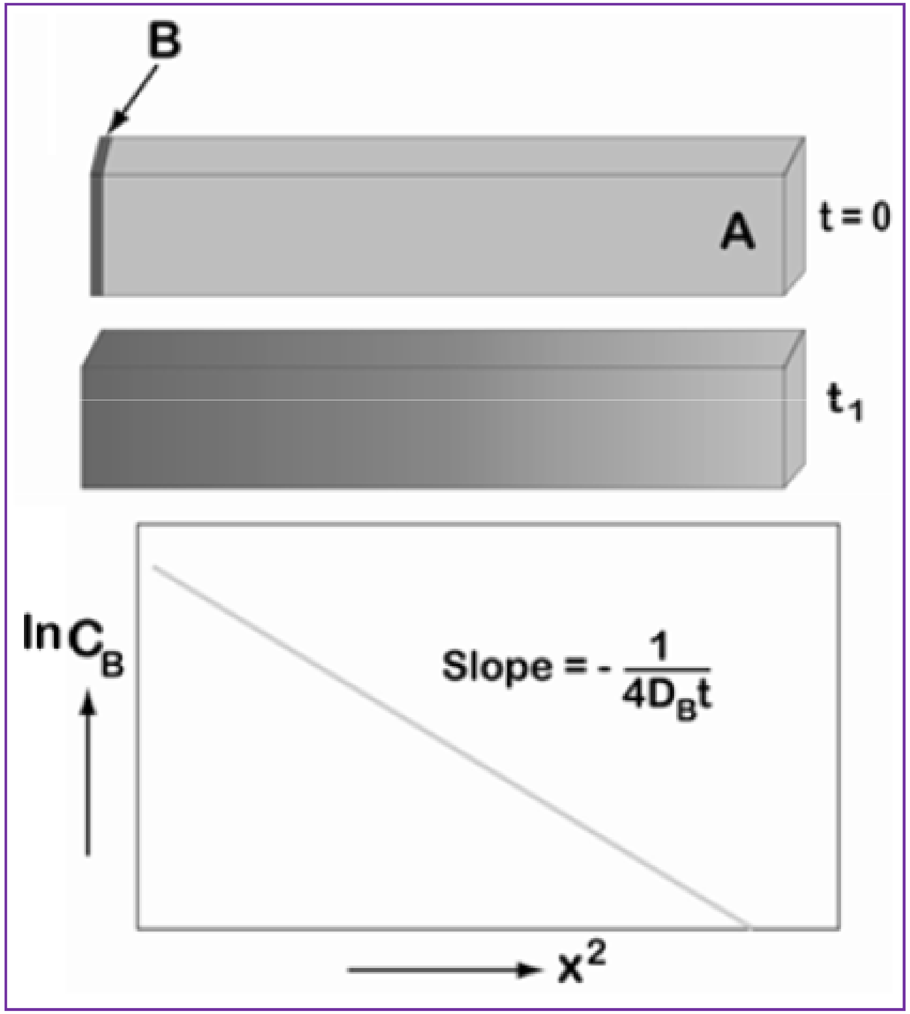
Solution for a thin film source

- ❑ If the element B diffuses to one direction then the factor 2 should not be considered.

$$C_B(x) = \frac{M_B}{\sqrt{\pi D_B t}} \exp\left(-\frac{x^2}{4D_B t} \right)$$

$$\ln C_B(x) = \ln \frac{M_B}{\sqrt{\pi D_B t}} - \frac{x^2}{4D_B t}$$

- ❑ From the calculated slope, one can determine the diffusion coefficient from the known annealing time.

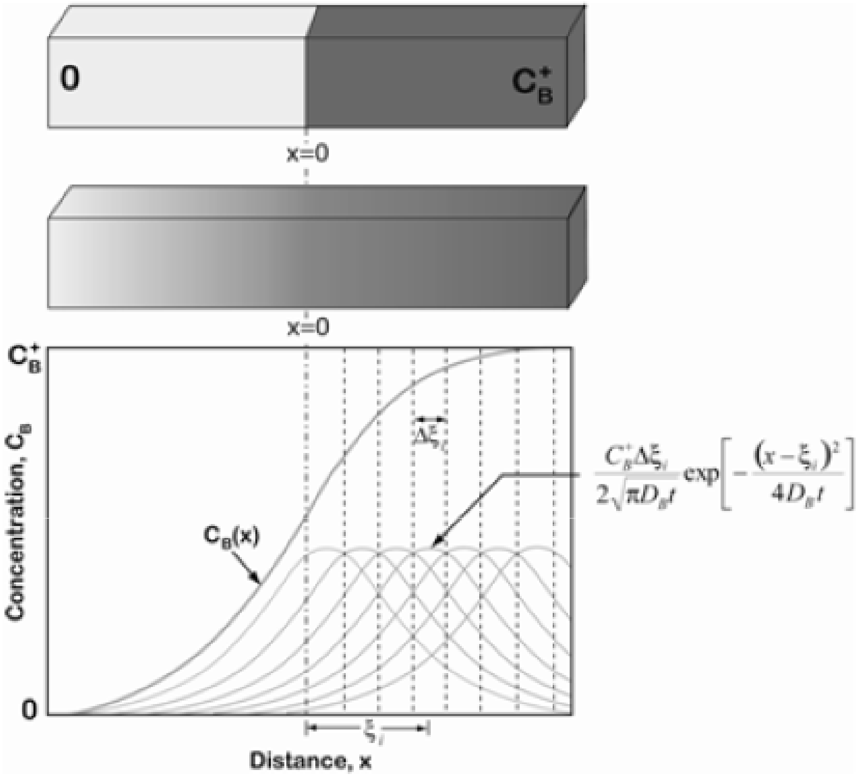


Solution in semi infinite diffusion couples (error function analysis)

- ❑ Let us consider now the semi infinite diffusion couple of two blocks with concentration of

$$C_B = 0 \quad and \quad C_B = C_B^+$$

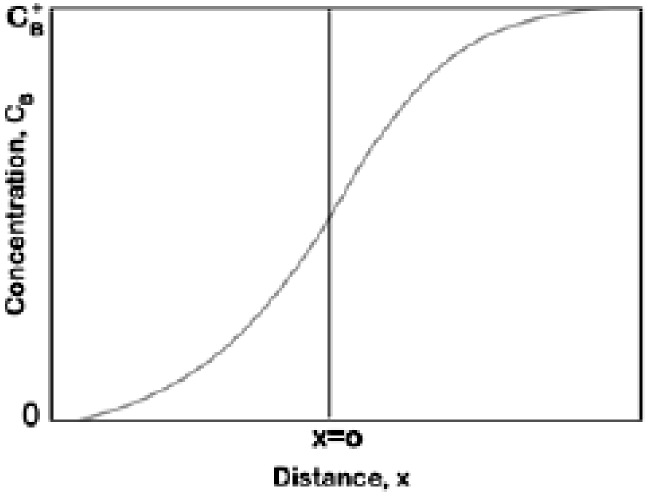
- ❑ It means that, in a A-B binary system, it is bonding between two blocks made of pure A and an alloy of AB.
- ❑ Unlike the previous case, here, because of the difference in the composition, diffusion will be driven by the chemical potential gradient.



- ❑ However, we shall show later that the solution we are going to derive, can be used only in the case where the concentration and the chemical potential difference of the end members is not much. That means diffusion coefficients do not vary significantly with the composition.
- ❑ Semi infinite means that, we anneal for a certain annealing time such that the end of the initial materials are not affected by the diffusion of elements.

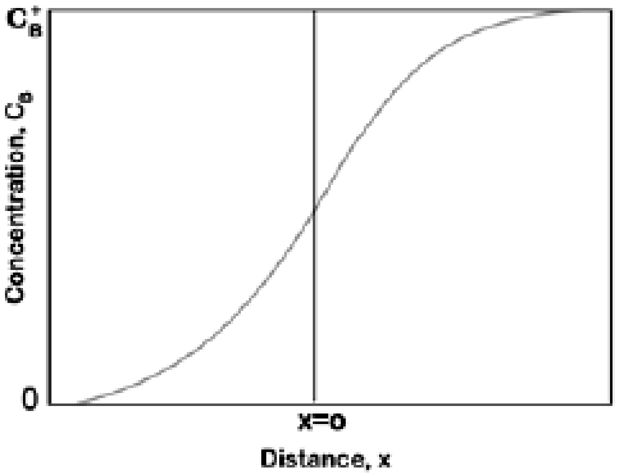
Solution in semi infinite diffusion couples (error function analysis)

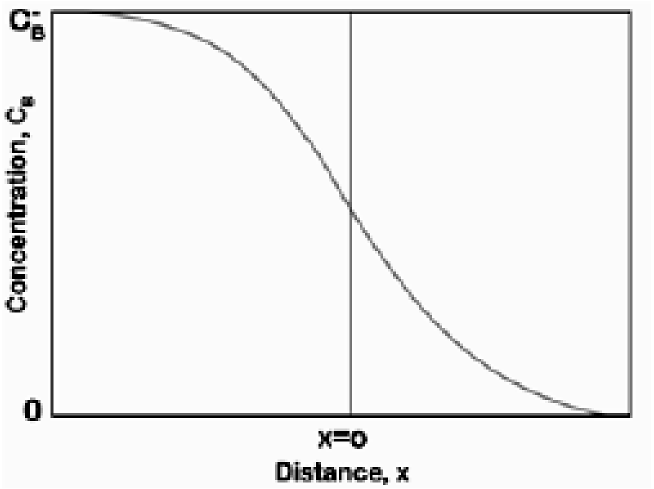
- ☐ Although the meaning of the semi infinite indicates that a good part of the end of the diffusion couple should not be affected but actually even with one unaffected atomic layer in the end is sufficient to consider the system as semi infinite diffusion couple!
- ☐ This is important since otherwise we can’t apply the relation derived here to determine the diffusion parameter or to calculate the concentration profile from the known diffusion parameter.
- ☐ If this kind of situation shown below, one can calculate no. of B atoms are diffusing in a metal is following way



$$\frac{C_B(x)}{C_B^+} = \frac{1}{2}\left[1 + erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right]$$

Solution in semi infinite diffusion couples (error function analysis)





$$\frac{C_B(x)}{C_B^+} = \frac{1}{2}\left[1 + erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right]$$

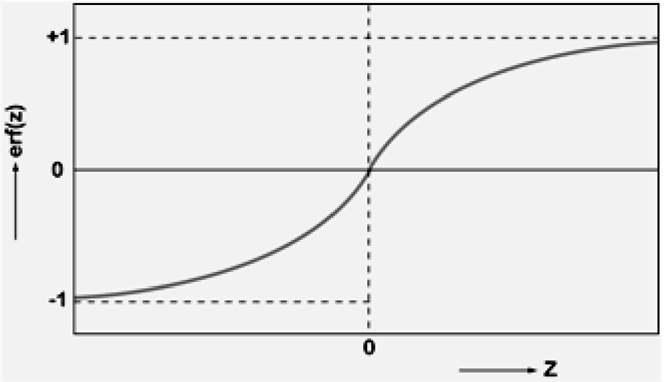
$$\frac{C_B(x)}{C_B^-} = \frac{1}{2}\left[1 - erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right]$$

- It is apparent that the sign of x will depend on which side of the x = 0, we are interested to calculate.
- Further, if the composition profile is just the opposite compared to the first example, it can be shown that the relation becomes $$\frac{C_B(x)}{C_B^-} = \frac{1}{2}\left[1 - erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right]$$

Note: We always use "+" at superscript for the concentration to denote right hand side of the couple and "-" for the left hand side of the couple.

Tabulated error function values

z	erf(z)	z	erf(z)	z	erf(z)	z	erf(z)	z	erf(z)
0	0	0.5	0.5204999	1	0.8427007	1.5	0.9661051	2	0.9953223
0.01	0.0112834	0.51	0.5292436	1.01	0.8468104	1.51	0.9672767	2.01	0.9955248
0.02	0.0225646	0.52	0.5378986	1.02	0.850838	1.52	0.9684135	2.02	0.9957195
0.03	0.0338412	0.53	0.5464641	1.03	0.8547842	1.53	0.9695162	2.03	0.9959063
0.04	0.0451111	0.54	0.5549392	1.04	0.8586499	1.54	0.9705857	2.04	0.9960858
0.05	0.056372	0.55	0.5633234	1.05	0.8624361	1.55	0.9716227	2.05	0.9962581
0.06	0.0676216	0.56	0.5716158	1.06	0.8661435	1.56	0.9726281	2.06	0.9964235
0.07	0.0788577	0.57	0.5798158	1.07	0.8697733	1.57	0.9736026	2.07	0.9965822
0.08	0.0900781	0.58	0.5879229	1.08	0.8733261	1.58	0.974547	2.08	0.9967344
0.09	0.1012806	0.59	0.5959365	1.09	0.8768031	1.59	0.975462	2.09	0.9968805
0.1	0.1124629	0.6	0.6038561	1.1	0.880205	1.6	0.9763484	2.1	0.9970205
0.11	0.1236229	0.61	0.6116812	1.11	0.883533	1.61	0.9772068	2.11	0.9971548
0.12	0.1347584	0.62	0.6194115	1.12	0.8867879	1.62	0.9780381	2.12	0.9972836
0.13	0.1458671	0.63	0.6270464	1.13	0.8899706	1.63	0.9788428	2.13	0.997407
0.14	0.156947	0.64	0.6345858	1.14	0.8930823	1.64	0.9796218	2.14	0.9975253
0.15	0.167996	0.65	0.6420293	1.15	0.8961238	1.65	0.9803756	2.15	0.9976386
0.16	0.1790118	0.66	0.6493767	1.16	0.8990962	1.66	0.9811049	2.16	0.9977472
0.17	0.1899925	0.67	0.6566277	1.17	0.9020004	1.67	0.9818104	2.17	0.9978511
0.18	0.2009358	0.68	0.6637822	1.18	0.9048374	1.68	0.9824928	2.18	0.9979506
0.19	0.2118399	0.69	0.6708401	1.19	0.9076083	1.69	0.9831526	2.19	0.9980459
0.2	0.2227026	0.7	0.6778012	1.2	0.910314	1.7	0.9837905	2.2	0.9981372
0.21	0.2335219	0.71	0.6846653	1.21	0.9129555	1.71	0.984407	2.21	0.9982244
0.22	0.2442959	0.72	0.6914328	1.22	0.9155339	1.72	0.9850028	2.22	0.9983079
0.23	0.2550226	0.73	0.6981037	1.23	0.9180501	1.73	0.9855785	2.23	0.9983878
0.24	0.2657001	0.74	0.7046778	1.24	0.9205052	1.74	0.9861346	2.24	0.9984642
0.25	0.2763264	0.75	0.7111554	1.25	0.9229001	1.75	0.9866717	2.25	0.9985373
0.26	0.2868997	0.76	0.7175365	1.26	0.9252359	1.76	0.9871903	2.26	0.9986071
0.27	0.2974182	0.77	0.7238214	1.27	0.9275136	1.77	0.9876909	2.27	0.9986739
0.28	0.3078801	0.78	0.7300102	1.28	0.9297342	1.78	0.9881742	2.28	0.9987377
0.29	0.3182835	0.79	0.7361032	1.29	0.9318986	1.79	0.9886405	2.29	0.9987986
0.3	0.3286268	0.8	0.7421008	1.3	0.9340079	1.8	0.9890905	2.3	0.9988568
0.31	0.3389082	0.81	0.7480031	1.31	0.9360631	1.81	0.9895245	2.31	0.9989124
0.32	0.349126	0.82	0.7538106	1.32	0.9380651	1.82	0.9899432	2.32	0.9989655
0.33	0.3592787	0.83	0.7595236	1.33	0.940015	1.83	0.9903468	2.33	0.9990162
0.34	0.3693645	0.84	0.7651426	1.34	0.9419137	1.84	0.9907359	2.34	0.9990646
0.35	0.3793821	0.85	0.7706679	1.35	0.9437622	1.85	0.991111	2.35	0.9991107
0.36	0.3893297	0.86	0.7761001	1.36	0.9455614	1.86	0.9914725	2.36	0.9991548
0.37	0.399206	0.87	0.7814397	1.37	0.9473124	1.87	0.9918207	2.37	0.9991968
0.38	0.4090095	0.88	0.7866872	1.38	0.949016	1.88	0.9921562	2.38	0.9992369
0.39	0.4187387	0.89	0.7918431	1.39	0.9506733	1.89	0.9924793	2.39	0.9992751
0.4	0.4283924	0.9	0.7969081	1.4	0.9522851	1.9	0.9927904	2.4	0.9993115
0.41	0.4379691	0.91	0.8018827	1.41	0.9538524	1.91	0.9930899	2.41	0.9993462
0.42	0.4474676	0.92	0.8067676	1.42	0.9553762	1.92	0.9933782	2.42	0.9993793
0.43	0.4568867	0.93	0.8115635	1.43	0.9568572	1.93	0.9936556	2.43	0.9994108
0.44	0.4662251	0.94	0.8162709	1.44	0.9582966	1.94	0.9939226	2.44	0.9994408
0.45	0.4754817	0.95	0.8208907	1.45	0.959695	1.95	0.9941793	2.45	0.9994694
0.46	0.4846554	0.96	0.8254236	1.46	0.9610535	1.96	0.9944263	2.46	0.9994966
0.47	0.4937451	0.97	0.8298702	1.47	0.9623729	1.97	0.9946637	2.47	0.9995226
0.48	0.5027497	0.98	0.8342314	1.48	0.9636541	1.98	0.994892	2.48	0.9995472
0.49	0.5116683	0.99	0.838508	1.49	0.9648979	1.99	0.9951114	2.49	0.9995707



$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\eta^2) d\eta$$

$$= \frac{2}{\sqrt{\pi}} \left[z - \frac{z^3}{3\times 1!} + \frac{z^5}{5\times 2!} - \frac{z^7}{7\times 3!} ..... \right]$$

$$erf(-z) = -erf(z)$$

- *Advantage of using this error function is that one can determine the values from a table.*

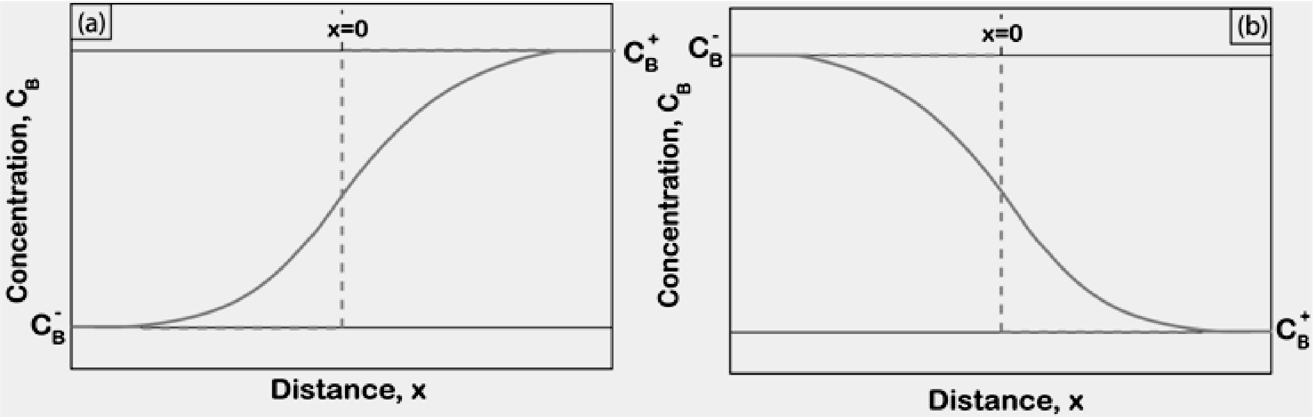
Solution in semi infinite diffusion couples (error function analysis)

- ☐ In the previous case, we considered the diffusion between the diffusion couple of two different blocks with composition $C_B = 0$, and C_B^+ or otherwise $C_B = C_B^-$ and 0.
- ☐ That means in both the cases, it was a couple between one pure element and an alloy of AB.
- ☐ Error function solutions given previously can be rewritten interms of normalized concentration profiles as

$$\frac{C_B(x)-0}{C_B^- -0}=\frac{1}{2}\left[1+erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right] \qquad \frac{C_B(x)-0}{C_B^- -0}=\frac{1}{2}\left[1-erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right]$$

- ☐ In some cases, it is possible that two alloys of AB are couples.
- ☐ Now if we consider the diffusion couple between C_B^- and C_B^+, where $C_B^+ > C_B^-$ the relation can be written as shown in Fig a.

$$\frac{C_B(x)-C_B^-}{C_B^+ -C_B^-}=\frac{1}{2}\left[1+erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right] \quad or \quad C_B(x)=\frac{C_B^+ + C_B^-}{2}+\frac{C_B^+ - C_B^-}{2}erf\left(\frac{x}{2\sqrt{D_B t}}\right)$$

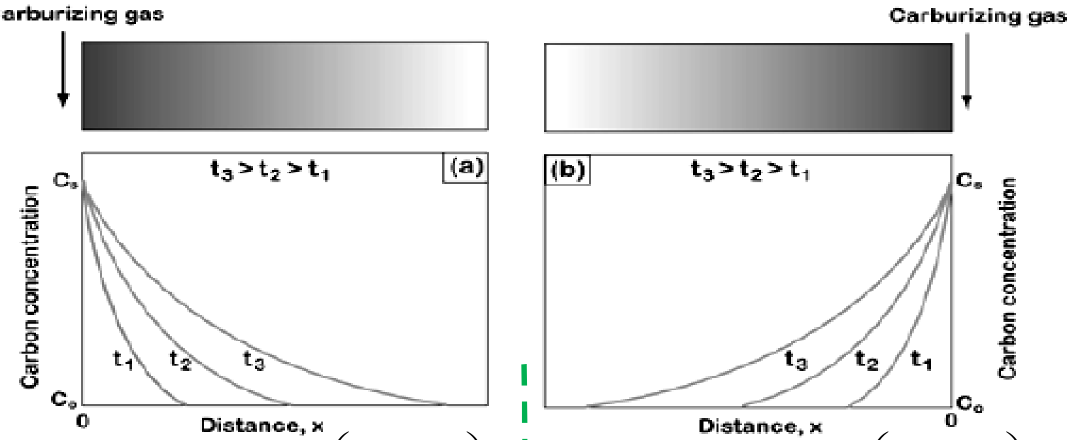


Solution in semi infinite diffusion couples (error function analysis)

- ❑ Further, the relation in the case of diffusion couple, where C_B^- and C_B^+ and $C_B^- > C_B^+$ as shown in figure b. (in the previous slide), it can be expressed as

$$\frac{C_B(x)-C_B^+}{C_B^- - C_B^+} = \frac{1}{2}\left[1-erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right] \quad Or \quad C_B(x) = \frac{C_B^- + C_B^+}{2} - \frac{C_B^- - C_B^+}{2} erf\left(\frac{x}{2\sqrt{D_B t}}\right)$$

- ❑ In the case of carburizing, we can see that the relation will be the same, irrespective of the side on which carburizing is done, since in the case of Fig. a, x is positive but in Fig. b, x is negative



$$\frac{C(x)-C_0}{C_S - C_0} = 1-erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{C(x)-C_0}{C_S - C_0} = 1+erf\left(\frac{-x}{2\sqrt{Dt}}\right) = 1-erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$C(x) = C_S - (C_S - C_0)erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$C(x) = C_S\left[1-erf\left(\frac{x}{2\sqrt{Dt}}\right)\right] \qquad for \quad C_0 = 0$$

Few important notes

- So from the previous relations, it is apparent that the sign of x (whether positive or negative) will depend on in which side of the x = 0, we are interested to calculate.
- Note again that D will be more or less the constant at any position it is calculated. It was also one of the assumptions for this derivation.
- From the error function analysis above, we can see that, at x =0

from the relation $\frac{C_B(x)-C_B^-}{C_B^+-C_B^-}=\frac{1}{2}\left[1+erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right]$ ***it comes*** $\frac{C_B(x=0)-C_B^-}{C_B^+-C_B^-}=\frac{1}{2}\Rightarrow C_B(x=0)=\frac{1}{2}(C_B^+ + C_B^-)$

from the relation $C(x)=C_S-(C_S-C_0)erf\left(\frac{x}{2\sqrt{Dt}}\right)$ ***it comes*** $C(x=0)=C_S$

- It indicates that in a system, where two blocks with different concentrations are coupled, at x =0, which is basically the initial contact plane, the concentration will be always average of the concentration of the initial materials.
- Note that we need to locate anyway the initial contact plane after the diffusion process, since x in the equation is actually measured from the location of the initial contact plane.
- This also indicates that this equation can only be used when end parts of the couple is not affected by the diffusion process, since otherwise at x =0, it will have another average value depending on how much of the end members are affected.

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$$\textit{from the relation}\quad \frac{C_B(x)-C_B^-}{C_B^+-C_B^-}=\frac{1}{2}\left[1+erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right]\quad \textbf{\textit{it comes}}\ \frac{C_B(x=0)-C_B^-}{C_B^+-C_B^-}=\frac{1}{2}\Rightarrow C_B(x=0)=\frac{1}{2}(C_B^+ + C_B^-)$$

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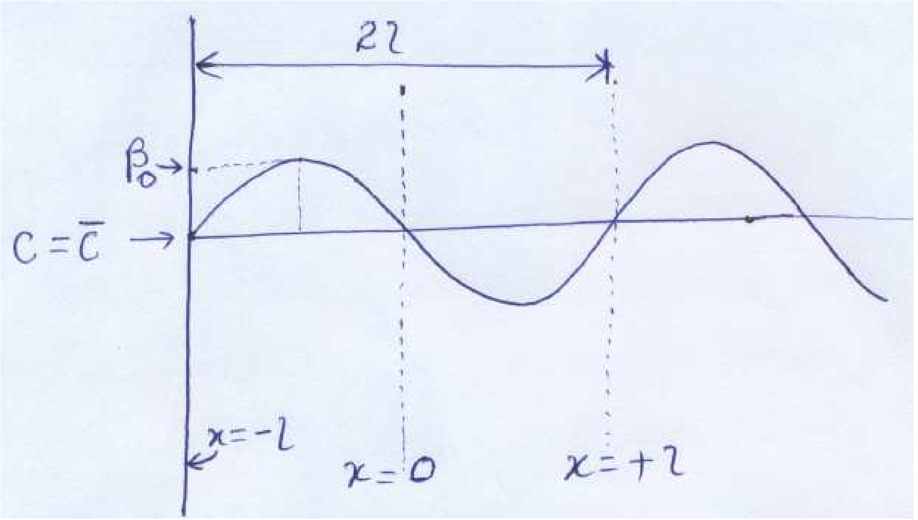
Solution for homogenization

- Let us consider a system with a relatively long time of annealing such that system may reach to homogenization.
- Time is rather relative. In a small system, relatively small time can be considered as long time because it will not take much time to homogenize. On the other hand in a large system, even longer time also may not be sufficient.
- The coring effect generally seen as cast alloys during solidification, the first solid that forms is poor in solute. As the solidification progress, the new solid formed becomes richer & richer in solute.
- This give rise to coring i.e., continuous change of solute concentration from center of a dendrite towards its surface. Thus, the concentration profile in a cored dendritic structure can be approximated to a sinusoidal wave form as shown in figure.



Solution for homogenization

- Now if the temperature of a two phase alloy is raised, it may form a single phase alloy by dissolution of second phase i.e., the solute will diffuse from precipitate into the matrix & the concentration of matrix will keep increasing.
- The diffusion process will continue until the whole matrix achieves a uniform composition. Similarly in a heterogeneous alloy with large micro-segregation (as in a cored structure), we often need to apply homogenization treatment, during which the solute diffuses into matrix & until the whole alloy achieves a uniform composition.
- We are interested in finding out the concentration profile changes with time during homogenization, which in turn is used to decide the optimum homogenization time. Although diffusion in three dimension does occur during homogenization, we assume that the length dimension is much larger compared to the width of a layer.
- The diffusion along width is more crucial for homogenization & we can approximate our problem to unidirectional diffusion.
- Let's assume that the initial segregation pattern is defined by a sinusoidal function as shown in figure (before page).
- We can apply Fick's II law for constant diffusion coefficient : $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$
- Initial condition is given as : **at t = 0** , $C_{(x,0)} = \bar{C} + \beta_0 \sin\left(\frac{\Pi x}{l}\right)$

  $\bar{C}$ *is the mean concentration &* β_0 *is the amplitude of the segregation pattern*

Solution for homogenization

- It is clear that the curvature of the profile between x = -l to x = 0 is negative & hence, the concentration will decrease in this region. Between x = 0 & x = +l , the curvature is positive & hence the concentration in this region will increase.
- At x = -l, x = 0 & x = 1, the curvature being zero, no change in concentration will occur i.e.,

$$C_{(-l,t)} = \bar{C}, \qquad C_{(0,t)} = \bar{C} \qquad C_{(l,t)} = \bar{C}$$

- One can write solution for C (x,t) using fick's II law is

$$C_{(x,t)} = \overline{C} + \beta_0 \sin\left(\frac{n\Pi x}{l}\right).\exp\left(\frac{-n^2\Pi^2}{l^2}Dt\right) \quad \text{or}$$

$$C_{(x,t)} = \overline{C} + \beta_0 \sin\left(\frac{\Pi x}{l}\right).\exp\left(\frac{-t}{\tau}\right) \text{ where } \tau = \frac{l^2}{n^2 D}$$

- τ is called relaxation time. Thus (l/τ) gives the rate of homogenization. It can be seen that the rate of homogenization increases if diffusion coefficient increases. Similarly, rate of homogenization is lower for larger values of period (2l).
- The amplitude β(t) of the concentration profile at any time (t) is given by

$$\beta_{(t)} = \beta_0 \exp\left(\frac{-t}{\tau}\right)$$

$$at\ \mathrm{t} = \tau,\ \beta_{(\tau)} = \frac{1}{e} \times \beta_0$$

Thus, relaxation time is the time at which the amplitude of the profile drops to (1/e) times of it's original amplitude.

Similarly, at t = 2τ, the amplitude drops to $(\frac{\beta_0}{e^2})$ *& so on.*

Summary on Fick’s II Law

Process	Solution	
Carburisation	$C = C_S - (C_S - C_0)\,erf\left(\frac{x}{2\sqrt{Dt}}\right)$	Cs = Surface concentration C0 = Bulk concentration
Decarburisation	$C = C_0\,erf\left(\frac{x}{2\sqrt{Dt}}\right)$	C0 =Initial Bulk concentration
Diffusion couple	$C = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right) erf\left(\frac{x}{2\sqrt{Dt}}\right)$	C1 = Concentration of steel 1 C2 = Concentration of steel 2
Homogenisation	$C = C_{mean} + \beta_0 \sin\left(\frac{\pi x}{\lambda}\right) \exp\left(-\frac{t}{\tau}\right)$	Cmean = Mean concentration β0 = Initial concentration amplitude λ = half wavelength t = relaxation time

Solved Example - 3

An FCC iron–carbon alloy initially containing 0.55 wt% C is exposed to an oxygen-rich and virtually carbon-free atmosphere at 1325 K (1052ºC). Under these circumstances the carbon diffuses from the alloy and reacts at the surface with the oxygen in the atmosphere; that is, the carbon concentration at the surface position is maintained essentially at 0 wt% C. (This process of carbon depletion is termed *decarburization.) At what position will the* carbon concentration be 0.25 wt% after a 10-h treatment? The value of *D at 1325 K is* 4.3×10^{-11} m²/s.

This problem asks that we determine the position at which the carbon concentration is 0.25 wt% after a 10-h heat treatment at 1325 K when C_o = 0.55 wt% C.

$$\frac{C_x - C_o}{C_s - C_o} = \frac{0.25 - 0.55}{0 - 0.55} = 0.5455 = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4545$$

Z	Erf (Z)
0.40	0.4284
Z	0.4545
0.45	0.4755

Using tabulation of error function values and linear interpretation

$$\frac{Z - 0.40}{0.45 - 0.40} = \frac{0.4545 - 0.4284}{0.4755 - 0.4284}$$

$$Z = 0.4277$$

$$\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4277$$

$$x = 2(0.4277)\sqrt{Dt} = (0.8554)\sqrt{(3.6\times10^{4}\,s)(4.3\times10^{-11}\,m^{2}/s)}$$

$$= 1.06\times10^{-3}\,m = 1.06mm$$

Solved Example - 4

Nitrogen from a gaseous phase is to be diffused into pure iron at 675ºC. If the surface concentration is maintained at 0.2 wt% N, what will be the concentration 2 mm from the surface after 25 h? The diffusion coefficient for nitrogen in iron at 675ºC is 1.9×10^{-11} m^2/s .

This problem asks us to compute the nitrogen concentration C_x at the 2 mm position after a 25 h diffusion time, when diffusion is non steady-state.

$$\frac{C_x - C_o}{C_s - C_o} = \frac{C_x - 0}{0.2 - 0} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$= 1 - \mathrm{erf}\left(\frac{2\times10^{-3}\,m}{2\sqrt{(1.9\times10^{-11}\,m^2/s)(25h)(3600s/h)}}\right)$$

$$= 1 - erf(0.765)$$

Using tabulation of error function values and linear interpretation

Z	Erf (Z)
0.750	0.7112
0.765	y
0.800	0.7421

$$\frac{0.765 - 0.750}{0.800 - 0.750} = \frac{y - 0.7112}{0.7421 - 0.7112}$$

$$y = erf(0.765) = 0.7205$$

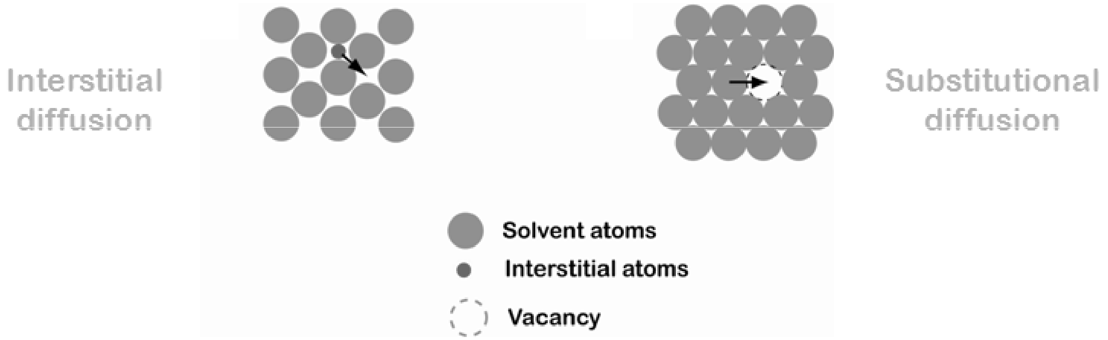
$$\frac{C_x - 0}{0.2 - 0} = 1.0 - 0.7205$$

$$C_x = 0.056 wt\% N$$

Atomic mechanism of diffusion

- Till now, we discussed the diffusion process without going to the atomic level. By measuring concentration profile, one can measure the diffusion coefficients.
- However, to get further insights on the diffusion process, we need to understand the atomic mechanism.
- It is almost impossible to track the jump of any particular atom. However, based on the experimental results, we can use logical arguments to explain the process in the atomic level.

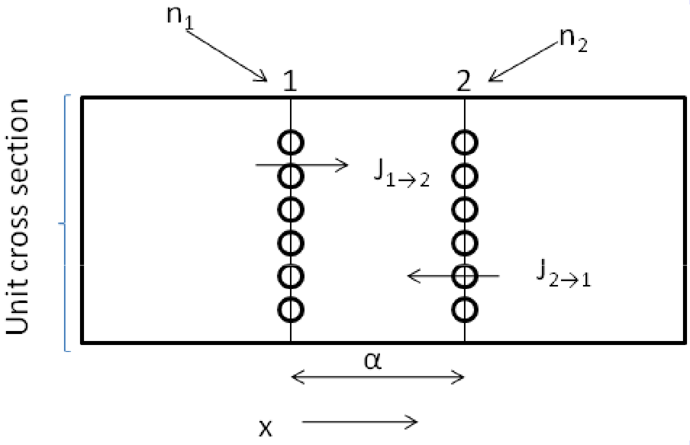
Mainly there can be two types of diffusion:



- As we have seen before that all elements will have some impurities. C, O, H etc. are present in most of the metals in interstitial voids. So, here diffusion occurs by interstitial diffusion mechanism.
- Similarly vacancies are also always present. So substitutional diffusion is possible because of presence of vacancies.
- *Let us first consider random jump of atoms that is diffusion without the presence of any driving force.*

Activation energy for diffusion

- In a crystal, consider two adjacent interatomic planes separated by a distance α and perpendicular to the diffusion direction x. Let there be n_1 moles of the diffusing specie per unit area in plane 1 and n_2 in plane 2, with $n_1 > n_2$.
- If ν' is the frequency with which atoms jump from one plane to a neighboring plane (the jump may be in either the forward direction or the backward direction)



$$J_{1\to 2} = \frac{1}{2} n_1 \nu'$$

$$J_{2\to 1} = \frac{1}{2} n_2 \nu'$$

$$J_{1\to 2(net)} = \frac{1}{2} \nu' (n_1 - n_2) \text{ Equation} \to 1$$

$$C_1 = \frac{n_1}{\alpha}, \mathrm{n}_1 = \mathrm{C}_1\alpha \text{ and } C_2 = \frac{n_2}{\alpha}, n_2 = C_2\alpha \quad \text{(put in Eq.1)}$$

$$J_{net} = \frac{1}{2} \nu' (C_1 - C_2)\alpha \text{ Equation} \to 2$$

$$\frac{dc}{dx} = \frac{C_2 - C_1}{\alpha} \Rightarrow C_2 - C_1 = \alpha \frac{dc}{dx} \text{ (or) } \mathrm{C}_1 - C_2 = -\alpha \frac{dc}{dx} \quad \text{(put in Eq. 2)}$$

$$\mathrm{J}_{\mathrm{net}} = -\frac{1}{2} \nu' \alpha^2 \frac{dc}{dx} \quad \Rightarrow \mathrm{J}_{\mathrm{net}} = \frac{1}{2} \nu' \alpha^2 \left(-\frac{dc}{dx} \right) \to \text{Equation 3}$$

Activation energy for diffusion

- Comparing Equation →3, with Fick's first law, we see that $D = \frac{1}{2}\alpha^2\vartheta'$
- If we take into account the probability of jumps in three mutually peripendicular directions, we can rewrite $D = \frac{1}{6}\alpha^2\vartheta'\ \ Equation \rightarrow 4$
- For a substitutional atom diffusing via the vacancy mechanism, we have to consider the availability of a neighboring vacant site for the atom to jump into.
- The probability that the diffusing atom will find a particular neighboring site to be vacant is equal to $\exp\left(-\frac{\Delta G_f}{RT}\right), where\ \Delta G_f is\ the\ free\ energy\ of\ formation\ of\ a.$ mole of vacancies.
- The number of successful jump attempts by an atom is given by $\vartheta\exp\left(\frac{-\Delta G_m}{RT}\right)$, where ν is the lattice vibration frequency and ΔG_m is the free energy maximum (per mole) along the path to the vacant site.
- ΔG_m is called the free energy of motion of a vacancy. The frequency ν' with which an atom exchanges position with any of the neighboring sites is then given by

$$\nu' = Z\nu\exp\left(-\frac{\Delta G_m}{RT}\right)\exp\left(-\frac{\Delta G_f}{RT}\right) \rightarrow Equation\, 5$$

- Where Z is the coordination number. Substituting Eq.5 in Eq. 4, we obtain

$$D = \frac{1}{6}\alpha^2 Z\nu\exp\left[-\left(\frac{\Delta G_m + \Delta G_f}{RT}\right)\right]$$

Activation energy for diffusion

- In simple cubic, FCC and BCC crystals, it turns out that $\frac{1}{6}\alpha^2 Z = a_0^2$
- Where a_0 is the lattice parameter of the cubic crystals. In such cases, therefore,

$$D = a_0^2 \nu \exp\left[-\left(\frac{\Delta G_m + \Delta G_f}{RT}\right)\right] \rightarrow \text{Equation 6}$$

- Using ΔG = ΔH - TΔS, we can write Equation 6 is

$$D = a_0^2 \nu \exp\left(\frac{\Delta S_m + \Delta S_f}{R}\right) \exp\left[-\left(\frac{\Delta H_m + \Delta H_f}{RT}\right)\right] \rightarrow \text{Equation 7}$$

- Experimental data show that $D = D_0 \exp\left(-\frac{Q}{RT}\right) \rightarrow Equation\,8$
- Values of D_0 (called the frequency factor) and Q (called the activation energy for diffusion) are obtained from measurements of D at different temperatures.
- Comparing Equation 7 & 8, it is seen that $Q = \Delta H_m + \Delta H_f$ and $D_0 = a_0^2 \nu \exp\left(\frac{\Delta S_m + \Delta S_f}{R}\right)$
- For interstitial diffusion in a dilute interstitial solution, the jump frequency into a given neighboring interstitial site is $\vartheta \exp\left(-\frac{\Delta G_m}{RT}\right)$. Here, ΔG_m represents the free energy increase, as the diffusing atom moves from one interstitial site to the next. It is called the free energy of motion of an interstitial.

Activation energy for diffusion

- The probability that the adjacent site will be vacant is almost unity. Then the following expression for D as a function of temperature results:

$$D = a_0^2 \nu \exp\left(\frac{-\Delta G_m}{RT}\right)$$

$$D = \nu a_0^2 \exp\left(\frac{-\Delta G_m}{RT}\right) = \nu a_0^2 \exp\left(\frac{-Q}{RT}\right) = D_0 \exp\left(-\frac{Q}{RT}\right)$$

- Now $Q = \Delta G_m = \Delta H_m - T\Delta S_m$ activation energy for migration

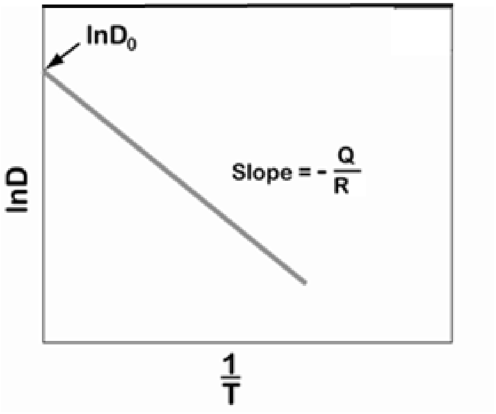
$$D = D_0 \exp\left(-\frac{\Delta H_m}{RT}\right) \quad \textit{where} \quad D_0 = \nu a_0^2 \exp\left(-\frac{\Delta S_m}{R}\right) \quad \textit{pre exponential factor}$$

ΔH_m *activation enthalpy for migration*

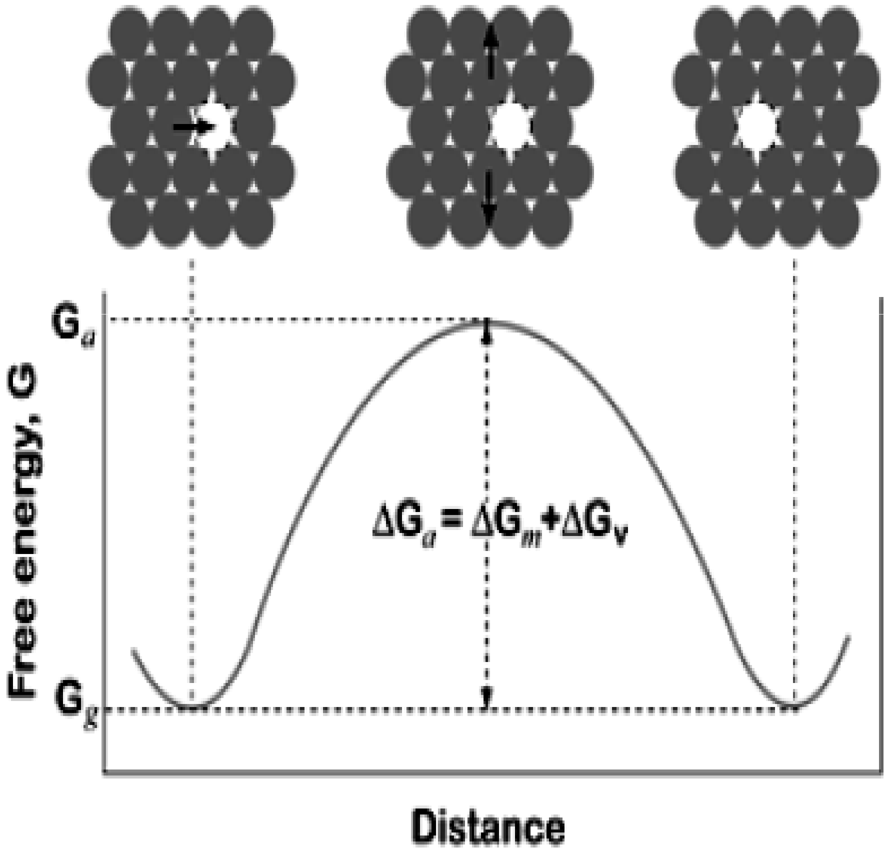
- Activation energy can be determined from the diffusion coefficients calculated at different temperatures.

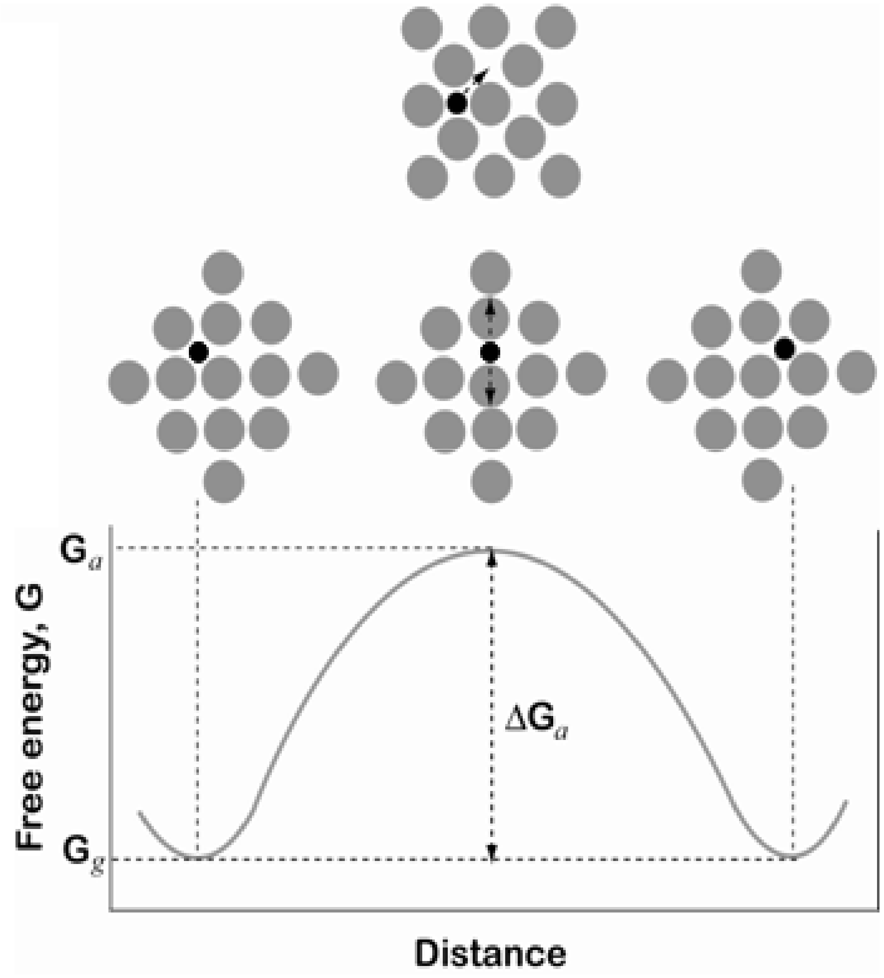
$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \Rightarrow \ln D = \ln D_0 - \frac{Q}{RT}$$

- So if we plot lnD vs. 1/T, we can determine the activation energy for diffusion, Q.



Activation energy for diffusion





Factors affecting Diffusion

Ease of a diffusion process is characterized by the parameter *D*, *diffusivity*. The value of diffusivity for a particular system depends on many factors as many mechanisms could be operative.

Diffusing species

If the diffusing species is able to occupy interstitial sites, then it can easily diffuse through the parent matrix. On the other hand if the size of substitutional species is almost equal to that of parent atomic size, substitutional diffusion would be easier. Thus size of diffusing species will have great influence on diffusivity of the system.

Lattice structure

Diffusion is faster in open lattices or in open directions than in closed directions.

Presence of defects

As mentioned in earlier section, defects like dislocations, grain boundaries act as short-circuit paths for diffusing species, where the activation energy is diffusion is less. Thus the presence of defects enhances the diffusivity of diffusing species.

Factors affecting Diffusion

Temperature

- ❑ Temperature has a most profound influence on the diffusivity and diffusion rates. It is known that there is a barrier to diffusion created by neighboring atoms those need to move to let the diffusing atom pass. Thus, atomic vibrations created by temperature assist diffusion.
- ❑ Empirical analysis of the system resulted in an Arrhenius type of relationship between diffusivity and temperature.

$$D = D_0 \, e^{\left(-\frac{Q}{kT}\right)}$$

- ❑ Where D_0 is a pre-exponential constant, Q is the activation energy for diffusion, R is gas constant (Boltzmann's constant) and T is absolute temperature.
- ❑ From the above equation it can be inferred that large activation energy means relatively small diffusion coefficient. It can also be observed that there exists a linear proportional relation between (lnD) and (1/T). Thus by plotting and considering the intercepts, values of Q and D_0 can be found experimentally (*see in next slide for clear understanding*).

Diffusion paths with lesser resistance

Experimentally determined activation energies for diffusion…!

$$Q_{surface} < Q_{grain\ boundary} < Q_{pipe} < Q_{lattice}$$

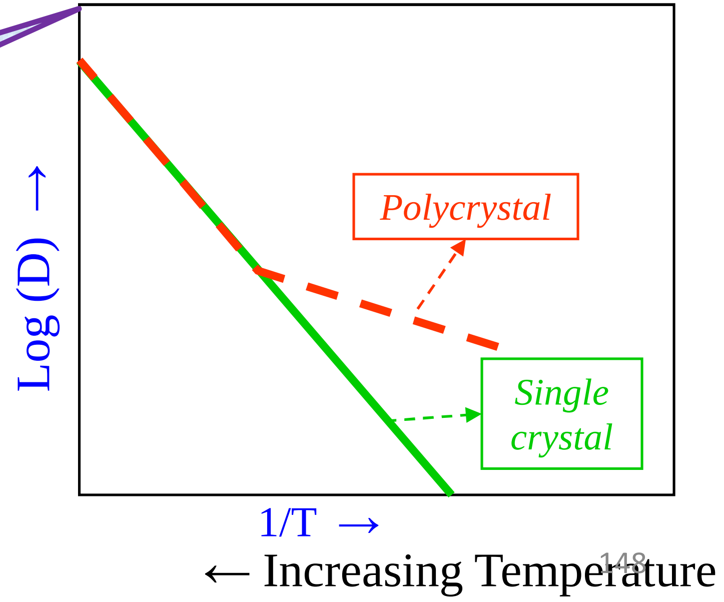
Lower activation energy automatically implies higher diffusivity

Core of dislocation lines offer paths of lower resistance PIPE DIFFUSION

Diffusivity for a given path along with the available cross-section for the path will determine the diffusion rate for that path

Comparison of Diffusivity for self-diffusion of Ag → Single crystal vs. polycrystal

- $Q_{grain\ boundary} = 110\ kJ\ /mole$
- $Q_{Lattice} = 192\ kJ\ /mole$



Solved Example - 5

Using the following diffusion data, compute the value of D for the diffusion of magnesium in aluminum at 400ºC.

$D_{o(\text{Mg in Al})} = 1.2 \times 10^{-4}\ m^2/s$ $Q_d = 131$ KJ/mol

This problem asks us to compute the magnitude of D for the diffusion of Mg in Al at 400ºC (673K).

$$D = (1.2\times10^{-4}\, m^2/s)\exp\left[-\frac{131{,}000\, J/mol}{(8.31 J/mol-k)(673k)}\right]$$

$$= 8.1\times10^{-15}\, m^2/s$$

Solved Example - 6

At what temperature will the difusion coefficient for the diffusion of zinc in copper have a value of 2.6×10^{-16} m²/s
$D_o = 2.4 \times 10^{-5}$ m²/s Q_d=189 KJ/mol

We are asked to calculate the temperature at which the diffusion coefficient for the diffusion of Zn in Cu has a value of 2.6×10^{-16} m²/s. Solving for T from below equation

$$\boxed{T = -\frac{Q_d}{R(\ln D_o - \ln D)}}$$

By using the given data we can get

$$\boxed{T = \left[-\frac{189{,}000 J/mol}{(8.31 J/mol-k)[\ln(2.6\times10^{-16} m^2/s) - \ln(2.4\times10^{-5} m^2/s)} \right]}$$

$$\boxed{= 901K = 628^0 C}$$

Solved Example - 7

The diffusion coefficients for nickel in iron are given at two temperatures:

At 1473K 2.2×10^{-15} m²/s

At 1673K 4.8×10^{-14} m²/s

a) Determine the values of D_o and the activation energy $Q_{d.}$

b) What is the magnitude of D at 1300°C (1573K)

$$T = -\frac{Q_d}{R(\ln D_o - \ln D\ )}$$

From this equation we can compute two simultaneous equations they are

$$\ln D_1 = \ln D_0 - \frac{Q_d}{R}\{\frac{1}{T_1}\}$$

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\{\frac{1}{T_2}\}$$

⇨

$$Q_d = -R\frac{\ln D_1 - \ln D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$Q_d = -(8.314 J/mol - K)\frac{[\ln(2.2\times10^{-15}) - \ln(4.8\times10^{-14})}{\frac{1}{1473K} - \frac{1}{1673K}}$$

$$\boxed{= 315{,}700 J/mol}$$

Now we can solve D_o from this equation

$$D_0 = D_1\, e^{\left(-\frac{Q_d}{RT_1}\right)}$$

$$= (2.2\times10^{-15} m^2/s)\exp\left[\frac{315{,}700 J/mol}{(8.31 J/mol-k)(1473k)}\right]$$

$$= 3.5\times10^{-4} m^2/s$$

(b) Using these values of D_o and $Q_{d,}$ D $_{at}$ 1573K is just

$$D = (3.5\times10^{-4} m^2/s)\exp\left[-\frac{315{,}700 J/mol}{(8.31 J/mol-k)(1573k)}\right]$$

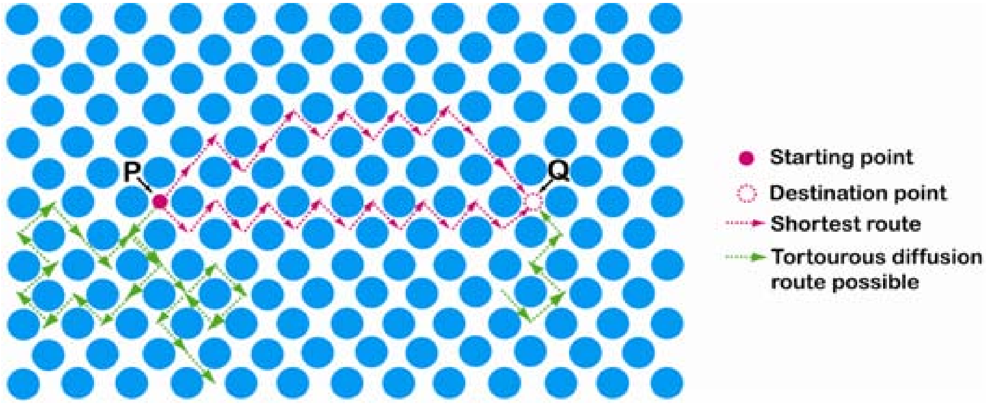
$$= 1.1\times10^{-14} m^2/s$$

Concept of random walk

- ☐ We related the jump frequency without going into details of the possibility of next jump after making a successful jump.
- ☐ However, we find a very strange fact when we try to relate diffusion coefficient with the jump distance.
- ☐ The diffusion coefficient of carbon in γ- iron with FCC structure at 1100°C is in the order of 10^{-10} m^2/s.
- ☐ The jump distance can approximately be considered as $\Delta x \approx 10^{-10}$ m
- ☐ From the relation derived between diffusion coefficient and the jump frequency, we can write $\Gamma \approx 10^{10}$ /s
- ☐ This means, atoms change their position in the order of 10^{10} times per second!
- ☐ This number sounds very high, however, if we consider Debye frequency, it sounds reasonable.
- ☐ That means atoms make successful jump one out of 10^3 attempts only, since vibration frequency or Debye frequency is roughly in the order of 10^{13}/s.
- ☐ Now suppose for the sake of explanation, we consider that atom can jump on a straight line and always goes forward.
- ☐ Then after 1 hour, jump distance will be 10^{-10} x10^{10}x 60x60 = 3.6 kms! The same after 10 hrs will be 36 kms!

Concept of random walk

- However, previously we have seen that the typical diffusion length is in micron.
- This indicates that jump of atom is not linear and possibly many times jumps back to previous position to have resultant jump distance zero.
- Jump is random, as we are considering the jump of atom without any driving force, the jump of atoms will be random.
- This must be the reason to find much smaller diffusion length in practice.
- This is the reason to say that when there is no driving force atoms go through a random walk.
- So we need to relate this random walk with the actual jump distance and the diffusion coefficient of atoms.
- This sounds very difficult, but can be done following simple approach, without making too many assumptions.



Concept of random walk

- ❑ For the sake of explanation, let us consider first atomic arrangement in two dimension.
- ❑ Host atoms are shown as blue balls and the interstitial atom as small red ball.
- ❑ As mentioned previously, we are considering very small concentration of interstitial atoms (one in few thousands voids) and we may assume that no other interstitial atom is present in the close vicinity.
- ❑ Let us consider that the interstitial atom reaches to the point Q from P after certain number of jumps.
- ❑ Now question is after how many jumps one atom will reach to that point.
- ❑ One can easily count that there are few paths (shown by red arrows) through which it can reach to Q after 14 jumps.
- ❑ However, actually, chance is very less that atoms will follow this route.
- ❑ It can follow a very torturous long route, as shown by green arrows, to arrive at Q.
- ❑ For a number of random jumps, n, the mean distance x, after time 't' is given by

$$x = \lambda\sqrt{n} \Rightarrow \lambda\sqrt{\nu t}$$

- ❑ Hence the diffusion distance is proportional to √t
- ❑ Since the jump of atoms is random in nature, there can be huge difference in the number of jumps that different atoms will make to reach to a particular distance.

Concept of random walk

- Now let us go back to our discussion on diffusion of carbon in iron.
- We have calculated that the average jump of carbon atoms in g-iron at 1100°C is 10^{10} /s.
- If we consider that each jump distance is about 10^{-10} m, then each carbon atom travels total distance of 3.6 kilometers in 1 hr .
- However, because of random nature of jump, on average, atoms will travel the effective distance of

$$x = \sqrt{10^{10} \times 3600} \times 10^{-10} m = 6 \times 10^{6} \times 10^{-10} m = 0.6mm = 600 \mu m$$

- Note that this is the order of diffusion length we actually see in carburized steel.

Summary

Diffusion Faster for	Diffusion Slower for
Open crystal structures	Close packed structures
Lower melting temperature materials.	Higher melting temperature materials
Smaller diffusing atoms	Larger diffusing atoms
Cations	Anions
Materials with secondary bonding	Materials with covalent bonding
Lower density materials	Higher density materials

Questions?

1. What is the number of atoms in a cubic meter of copper? The gram-atomic weight of copper is 63.54 gm/mole and the atomic volume of copper is 7.09 cm^3 per gram-atom. Next, compute the number of copper atoms per m^3 given that the lattice constant, a, of copper is 0.36153 nm and that there are 4 atoms per unit cell in a face-centered cubic crystal.
2. A diffusion couple, made by welding a thin one centimeter square slab of pure metal A to similar slab of pure metal B, was given a diffusion anneal at an elevated temperature and then cooled to room temperature. On chemically analyzing successive layers of the specimen, cut parallel to the weld interface, it was observed that, at one position, over a distance of 5000 nm, the atom fraction of metal A, N_A, changed from 0.30 to 0.35. Assume that the number of atoms per m^3 of bothe pure metals is 9×10^{28}. First determine the concentration gradient dn_a/dx. Then if the diffusion coefficient, at the point in question and annealing temperature, was 2×10^{-14} m^2/s, determine the number of A atoms per second that would pass through this cross-section at the annealing temperature.
3. On the assumption that the self-diffusion coefficient of a simple cubic metal whose lattice constant , a, equals 0.300 nm is given by the equation

$$D = 10^{-4} e^{-200,000/RT}, m^2/s$$

   Determine the value of the diffusion coefficient at 1200 K and use this to determine the mean time of stay, τ, of an atom at a lattice site.

Questions?

4. Do you expect any difference in room temperature self diffusion coefficients of Al just quenched from 600^0C to room temperature and the one slowly cooled to room temperature? Explain.
5. The diffusivity of gallium in silicon is 8×10^{-17} m^2/s at 1100^0C and 1×10^{-14} m^2/s at 1300^0C. Determine D_0 and Q_d for diffusion of gallium in silicon and calculate diffusivity at 1200^0C.
6. Using the data given below, make a plot of log D versus 1/T, and estimate, by eye, the best straight line through the points.

   Calculate ΔH and D_0 for this line.

   Calculate ΔH and D_0 using a least squares procedure and assuming all error to be in the values of D. Plot least squares line on the graph.

D (m^2/s)	10^{-12}	10^{-13}	10^{-14}	10^{-15}
T(K)	1350	1100	950	800

7. Concentration of copper in an aluminium slab decreases linearly from 0.4 at % Cu at the surface to 0.2 at% Cu at 1 mm below the surface. Calculate the flux of copper atoms across a plane 0.5 mm below the surface at 500^0C. Lattice parameter of Al is 0.405 nm.
8. Explain why activation energy for the grain boundary diffusion is lower than the activation energy for the lattice diffusion.

Questions?

9. Derive Fick’s second law from the mass conservation with the help of Fick’s first law.
10. Take derivative of the thin film solution and replace in the Fick’s second law to show the correctness of the relation.
11. A small amount (*M*) of component *i* was deposited in the form of an infinitesimally thin layer onto another element *j*. The assembly was then annealed at a constant temperature (*T*) in vacuum so that *i* diffused into *j*. We need to predict the concentration (C_i) as a function of depth (*x*) into the material and time (*t*). Answer the following question for this diffusion problem.
    a) Write the diffusion equation for C_i
    b) Describe the initial condition
    c) Describe the boundary condition
    d) Describe the constraint on the total mass (M) of the component i.
    e) Verify that each of the conditions in (a), (b), (c) and (d) satisfy the following equation for C_i. (D is the constant diffusion coefficient at T).

$$C_i(x,t) = \frac{M}{\sqrt{\sqrt{\Pi} dt}} \exp\left(\frac{-x^2}{4Dt}\right)$$

For answering part(e), you can use the following information

$$\frac{2}{\sqrt{\Pi}} \int_0^Z \exp(-\eta^2) d\eta = erf(z), \text{ where erf } (z) \text{ is ca;;ed error function z}$$

$$\text{erf}(0) = 0, \text{erf}(\infty) = 1$$

Questions?

12. A binary solid-solid diffusion couple is assembled with two alloys having initial concentrations of 80 atom% and 20 atom% for component *i* and annealed at a temperature T for 1 day. Assuming a constant binary interdiffusion coefficient . of 10^{-8} cm^2/s and constant molar volume of 8 cm^3/mole, calculate the position of the plane having concentration of *i* to be 4.8 cm^3/mole.

13. A thick steel part with initial carbon content of 0.18 wt% was exposed to a carburizing atmosphere at 820°C with constant surface concentration of carbon at 0.8 wt%. **a)** If the case depth of the carburized steel is taken as the depth at which carbon concentration drops to 0.4 wt%, determine the time required for achieving a case depth of 0.8mm. Use the following data for diffusion of carbon in austenite. What will be the case depth if carburizing time is doubled?

Activation Energy (Q) (KJ/mol)	Frequency Factor (D_0) m^2/s
136	1×10^{-5}

14. Pure aluminium was quenched from 500^0C to 25^0C to retain all the vacancy concentration. What should be the self diffusion coefficient for Al at 25^0C immediately after this quenching? The enthalpy of migration and vacancy formation for Al are respectively 0.68 eV and 0.72eV. Frequency factor for Al self diffusion is 0.047 cm^2/s. Assume no divacancy concentration.

15. Briefly explain the concept of a driving force. And what is the driving force for steady-state diffusion?

Questions?

16. A steel of eutectoid composition was found to have the lamellar spacing of pearlite to be 2*l*. The average thickness of each cementite layer is 2*h*. This steel was heated to 850°C for austenitization, which proceeds by diffusion of carbon atoms from cementite into austenite. Assuming that the transformation of ferrite to austenite does not take much time, derive the equation for concentration profile of carbon developed in a pearlite colony during the austenitization. You can assume square wave type initial profile in pearlite with zero% carbon in ferrite before the dissolution starts. Assume no discontinuity of concentration at the interface.

Hint i) No flow conditions exists i.e. the concentration gradients are zero at the boundaries and at the middle of the profile i.e. at x = 0, x = l, and x = -l.

Hint ii) If a periodic function f(x) is defined between –l and +l, it can be expresses as a fourier series as follows:

$$f(x) = A_0 + \sum_{n=1}^{\infty}\left(A_n \cos\frac{n\pi x}{l} + B_n \sin\frac{n\pi x}{l}\right)$$

where,

$$A_0 = \frac{1}{2l}\int_{-l}^{+l} f(x)\,dx$$

$$A_n = \frac{1}{l}\int_{-l}^{+l} f(x)\cos\frac{n\pi x}{l}\,dx$$

$$B_n = \frac{1}{l}\int_{-l}^{+l} f(x)\sin\frac{n\pi x}{l}\,dx$$

Questions?

17. A thick steel slab with 0.2 wt% carbon concentration is exposed to a carburizing atmosphere at 900°C. Carbon concentration at the surface of the slab is kept constant at 1.3 wt%. Case depth is considered as the depth from the surface at which carbon concentration drops to 0.6 wt%. (See the error function tables and the interdiffusion data for C in steel given at the end).
    a) Calculate the time required for achieving a case depth of 0.5mm
    b) What should be the temperature of carburizing if the same case depth is required to be achieved in exactly half the time
    c) At 900°C, a particular plane of composition C’ was observed to be at a depth of 0.7mm at the end of carburizing cycle. What should be the position of the plane C’ after double the carburizing time at 900°C?
18. A sheet of steel 2.5 mm thick has nitrogen atmospheres on both sides at 900^0C and is permitted to achieve a steady-state diffusion condition. The diffusion coefficient for nitrogen in steel at this temperature is $1.2 \times 10^{-10} m^2/s$, and the diffusion flux is found to be $1.0 \times 10^{-7} kg/m^2$-s. Also, it is known that the concentration of nitrogen in the steel at the high-pressure surface is 2 kg/m^3. How far into the sheet from this highpressure side will the concentration be 0.5 kg/m^3? Assume a linear concentration profile.
19. If iron is kept at 1200˚K in a carburizing atmosphere for 8hrs to obtain a carbon concentration of 0.75 at a depth of 0.5mm. Find the time it would take to reach same carbon concentration at depth of 7.5mm at 1250˚K. (Given D_0 = 0.2x10-4 m2/s & Q = 143kJ/mole/˚K)

Questions?

20. The concentration of carbon on the surface of iron is maintained at 1.00% at 1175˚K for 2hours. Estimate the depth at which % C would be 0.5%. Use the diffusivity values given D_0 = 0.2x10-4 m2/s & Q = 143kJ/mole/˚K. Assume initial carbon content of iron to be negligible.

SOLIDIFICATION

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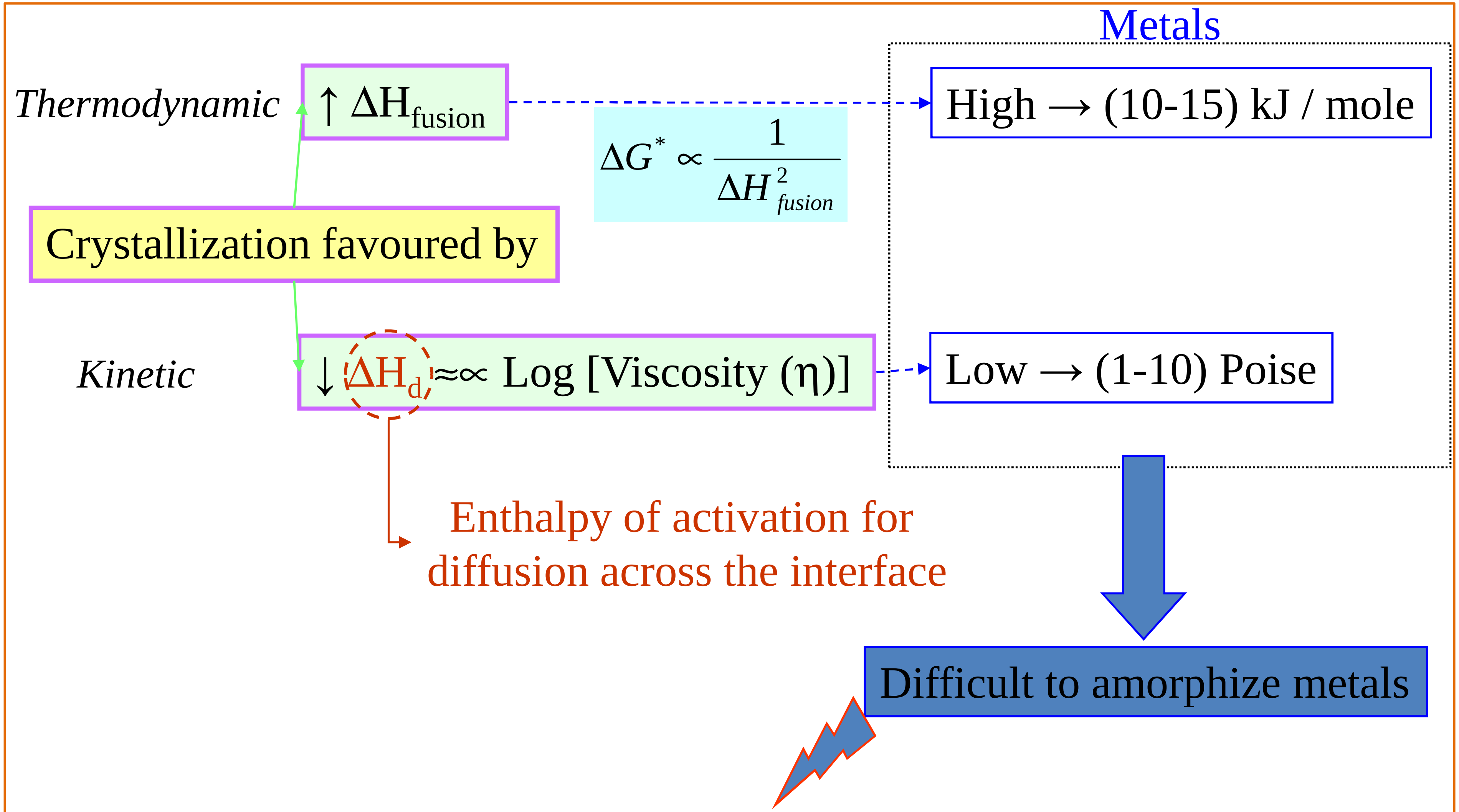
Introduction

- Let us start understanding phase transformations using the example of the solidification of a pure metal.
- Three states of matter are distinguishable: gas, liquid, and solid
- In the gaseous state the metal atoms occupy a great deal of space because of their rapid motion. The atoms move independently and are usually widely separated so that the attractive forces between atoms are negligible. The arrangement of atoms in a gas is one of complete disorder.
- At some lower temperature, the kinetic energy of the atoms has decreased so that the attractive forces become large enough to bring most of the atoms together in a liquid. And there is a continual interchange of atoms between the vapor and liquid across the liquid surface.
- The attractive forces between atoms in a liquid may be demonstrated by the application of pressure. A gas may be easily compressed into a smaller volume, but it takes a high pressure to compress a liquid. There is, however, still enough free space in the liquid to allow the atoms to move about irregularly.
- As the temperature is decreased, the motions are less vigorous and the attractive forces pull the atoms closer together until the liquid solidifies. Most materials contract upon solidification, indicating a closer packing of atoms in the solid state.
- The atoms in the solid are not stationary but are vibrating around fixed points, giving rise to the orderly arrangement of crystal structures.

Mechanism of Crystallization

- Crystallization is the transition from the liquid to the solid state and occurs in two stages:
  - Nuclei formation
  - Crystal Growth
- Although the atoms in the liquid state do not have any definite arrangement, it is possible that some atoms at any given instant are in positions exactly corresponding to the space lattice they assume when solidified.
- These chance aggregates or groups are not permanent but continually break up and reform at other points.
- The higher the temperature, the greater the kinetic energy of the atoms and the shorter the life of the group. When the temperature, of the liquid is decreased, the atom movement decreases, lengthening the life of the group, and more groups will be present at the same time.
- *Atoms in a material have both kinetic and potential energy. Kinetic energy is related to the speed at which the atoms move and is strictly a function of temperature. The higher the temperature, the more active are the atoms and the greater is their kinetic energy. Potential energy, on the other hand, is related to the distance between atoms. The greater the average distance between atoms, the greater is their potential energy.*

Mechanism of Crystallization



Metals

Thermodynamic ↑ ΔH_{fusion}

High → (10-15) kJ / mole

$$\Delta G^{*} \propto \frac{1}{\Delta H^{2}_{fusion}}$$

Crystallization favoured by

Kinetic ↓ $\Delta H_d \approx\propto$ Log [Viscosity (η)]

Low → (1-10) Poise

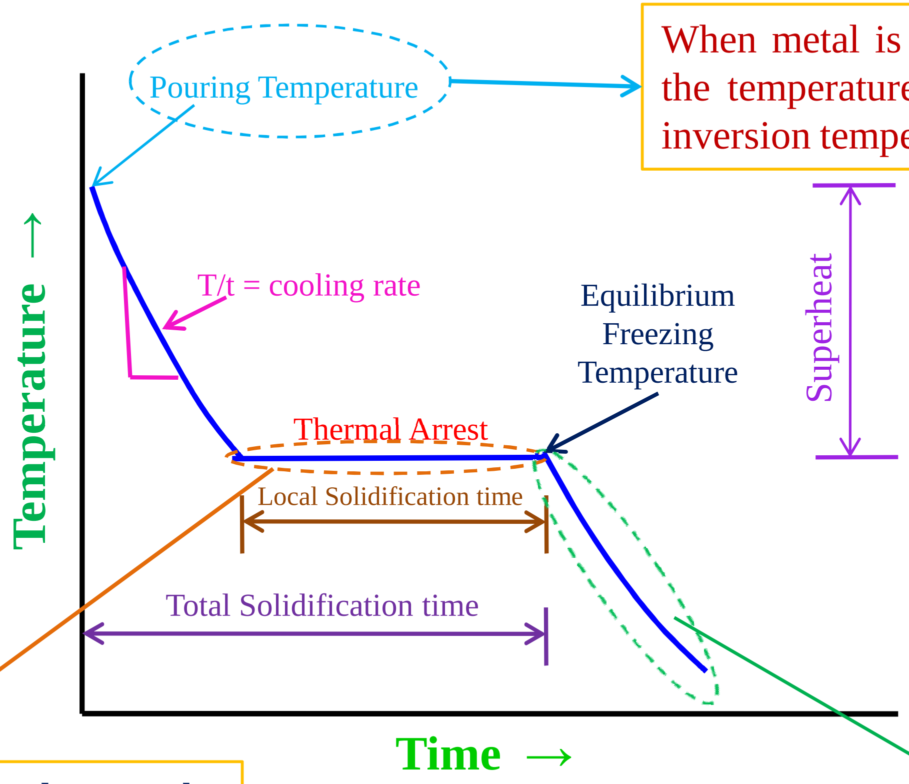
Enthalpy of activation for diffusion across the interface

Difficult to amorphize metals

Very fast cooling rates ~10^6 K/s are used for the amorphization of alloys

→ *splat cooling*, *melt-spinning.*

Solidification (or) Freezing



When metal is poured into the mould, the temperature will be as high as its inversion temperature.

It gets cooled when poured into the mould and molten metal in the liquid form will solidify. This time is called local solidification time

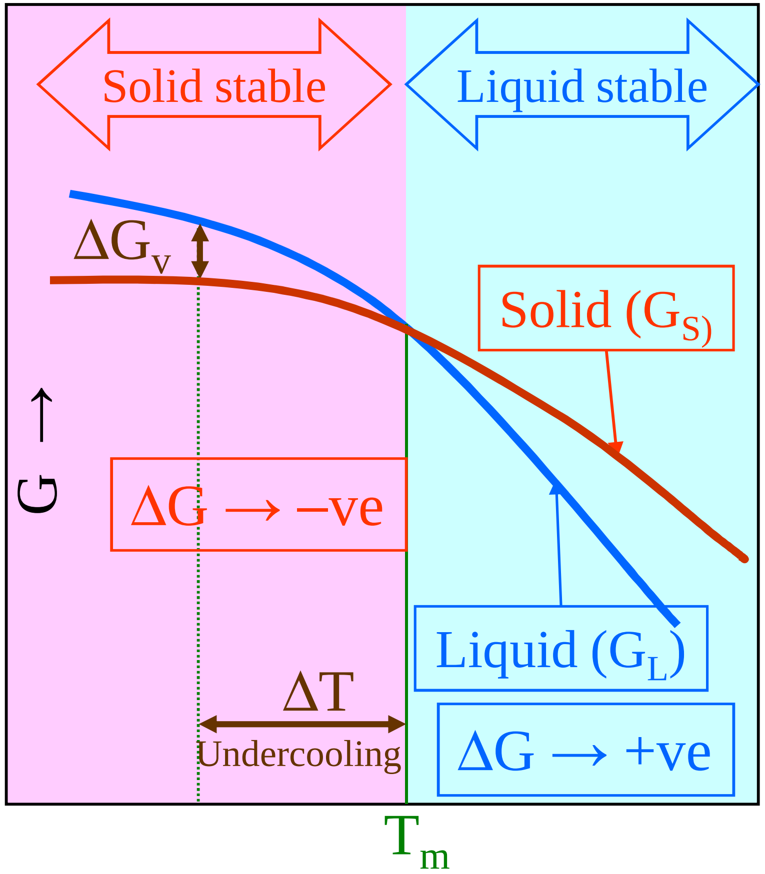
The solidified metal in the mould (called casting) gets cooled in the mould to the temperature of the surroundings

Driving force for solidification

- In dealing with phase transformations, we are often concerned with the difference in free energy between two phases at temperatures away from the equilibrium temperature.
- For example if a liquid metal is under cooled by ΔT below T_m before it solidifies, solidification will be accompanied by a decrease in free energy ΔG (J/mol) as shown in figure.
- This free energy decreases provides the driving force for solidification. The magnitude of this change can be obtained as follows.
- The free energies of the liquid and solid at a temperature T are given by

$$G^L = H^L - TS^L$$

$$G^S = H^S - TS^S$$



Therefore, at a temperature T $\Delta G = \Delta H - T\Delta S$ →①

Where $\Delta H = H^L - H^S$ *and* $\Delta S = S^L - S^S$

Driving force for solidification

- ❑ At the equilibrium melting temperature T_m the free energies of solid and liquid are equal, i.e., $\Delta G = 0$. Consequently

$$\Delta G = \Delta H - T_m \Delta S = 0$$

- ❑ And therefore at T_m

$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m} \rightarrow ②$$

- ❑ This is known as the entropy of fusion. It is observed experimentally that the entropy of fusion is a constant ≈ R (8.3 J/mol . K) for most metals (Richard's rule).
- ❑ For small undercoolings (ΔT) the difference in the specific heats of the liquid and solid (C_p^L - C_p^S) can be ignored.
- ❑ Combining equations 1 and 2 thus gives

$$\Delta G \cong L - T\frac{L}{T_m}$$

- ❑ i.e., for small ΔT

$$\boxed{\Delta G \cong \frac{L\Delta T}{T_m}}$$

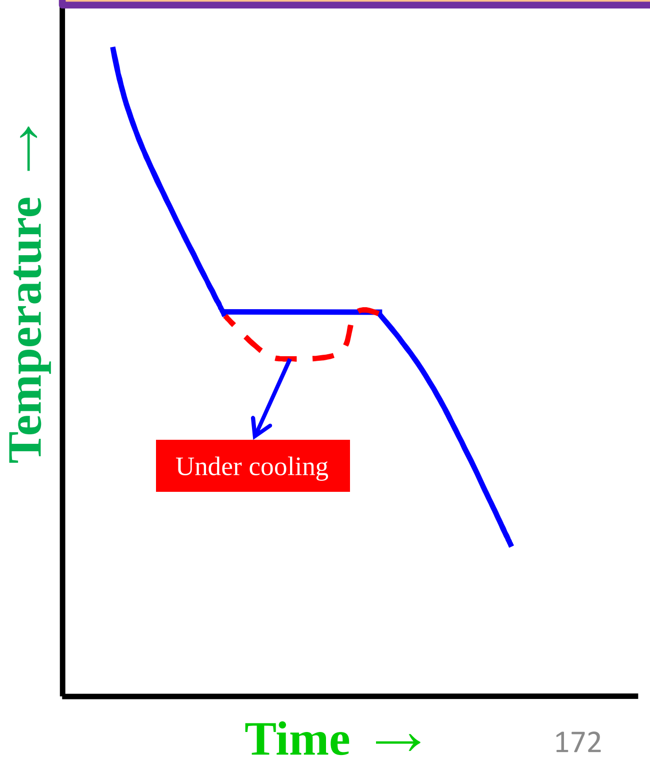
This is called Turnbull's approximation

Solidification of pure metal : Supercooling

- In a pure metal at its freezing point where both the liquid and solid states are at the same temperature. The kinetic energy of the atoms in the liquid and the solid must be the same, but there is a significant difference in potential energy.
- The atoms in the solid are much closer together, so that solidification occurs with a release of energy. This difference in potential energy between the liquid and solid states is known as the *latent heat of fusion.*

- However, energy is required to establish a surface between the liquid and solid. In pure materials at the freezing point insufficient energy is released by the heat of fusion to create a stable boundary, and some under cooling is always necessary to form stable nuclei.
- Subsequent release of the heat of fusion will raise the temperature to the freezing point. The amount of undercooling required may be reduced by the presence of solid impurities which reduce the amount of surface energy required.

Cooling Curve for a pure metal



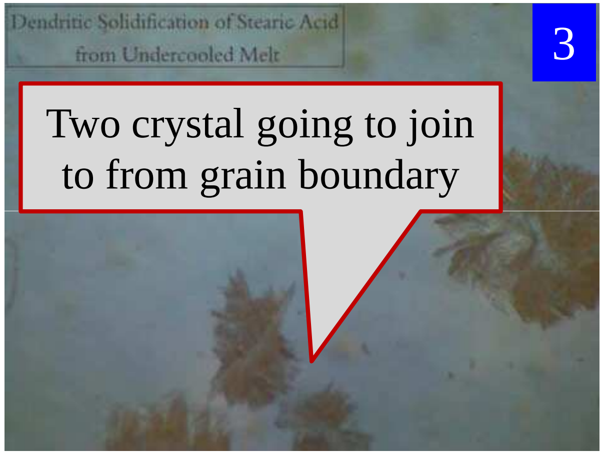
Solidification of pure metal

- When the temperature of the liquid metal has dropped sufficiently below its freezing point, stable aggregates or nuclei appear spontaneously at various points in the liquid. These nuclei, which have now solidified, act as centers for further crystallization.
- As cooling continues, more atoms tend to freeze, and they may attach themselves to already existing nuclei or form new nuclei of their own. Each nucleus grows by the attraction of atoms from the liquid into its space lattice.
- Crystal growth continues in three dimensions, the atoms attaching themselves in certain preferred directions, usually along the axes of the crystal this gives rise to a characteristic treelike structure which is called a dendrite.
- Since each nucleus is formed by chance, the crystal axes are pointed at random and the dendrites growing from them will grow in different directions in each crystal. Finally, as the amount of liquid decreases, the gaps between the arms of the dendrite will be filled and the growth of the dendrite will be mutually obstructed by that of its neighbors. This leads to a very irregular external shape.
- The crystals found in all commercial metals are commonly called grains because of this variation in external shape. The area along which crystals meet, known as the grain boundary, is a region of mismatch.

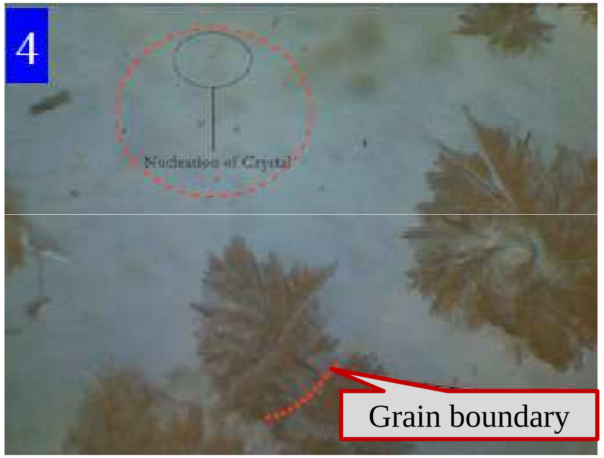
Liquid to Solid Phase Transformation : Solidification

Solid

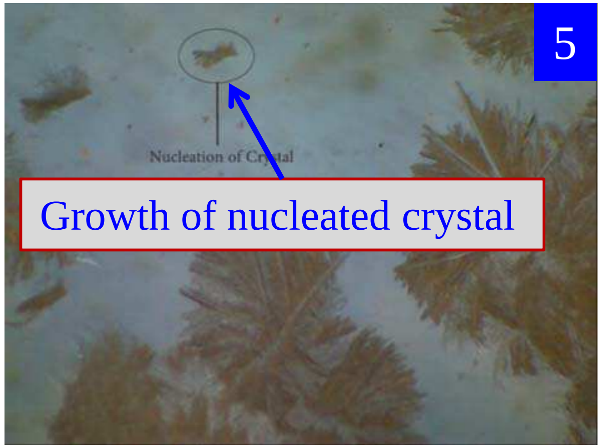
Growth of crystal



Two crystal going to join to from grain boundary

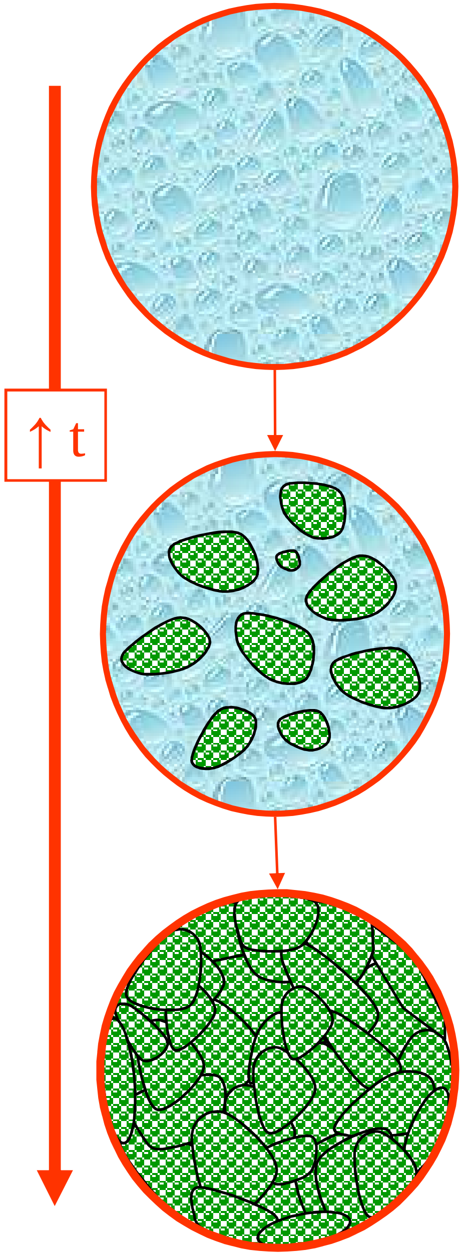


Grain boundary



Growth of nucleated crystal

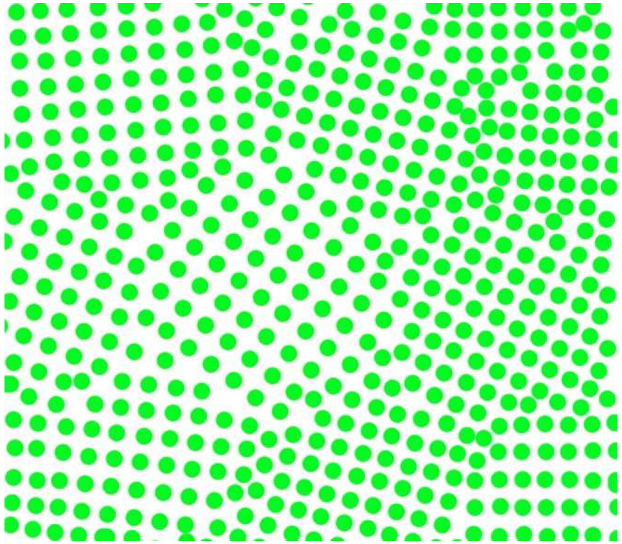
Solidification Complete

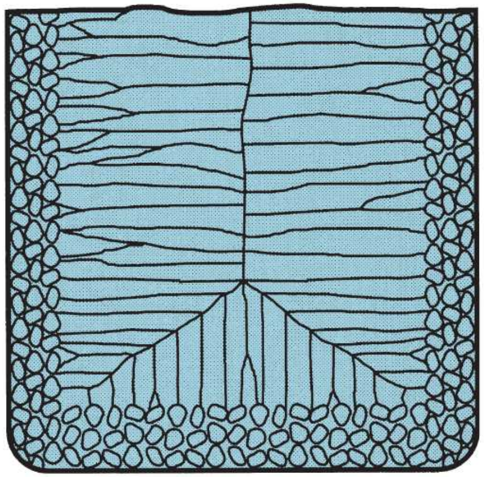


"For sufficient Undercooling"

Solidification of pure metal

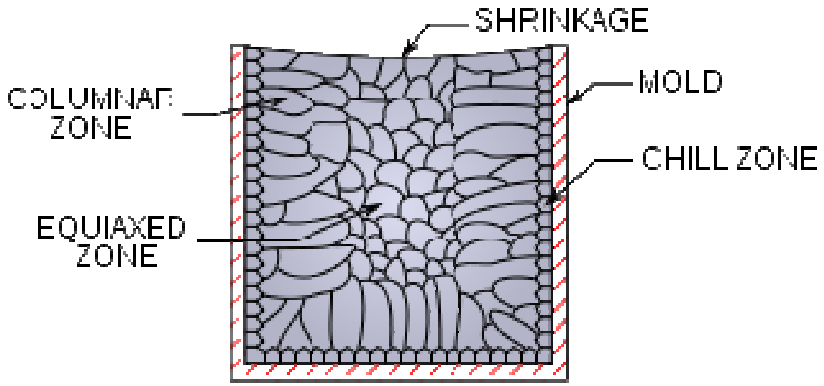
- This mismatch leads to a noncrystalline (amorphous) structure at the grain boundary with the atoms irregularly spaced.
- Since the last liquid to solidify is generally along the grain boundaries, there tends to be higher concentration of impurity atoms in that area. Figure (previous page) shows schematically the process of crystallization from nuclei to the final grains.
- Due to chilling action of mold wall, a thin skin of solid metal is formed at the wall surface immediately after pouring.
- Grain structure in a casting of a pure metal, showing randomly oriented grains of small size near the mold wall, and large columnar grains oriented toward the center of the casting.

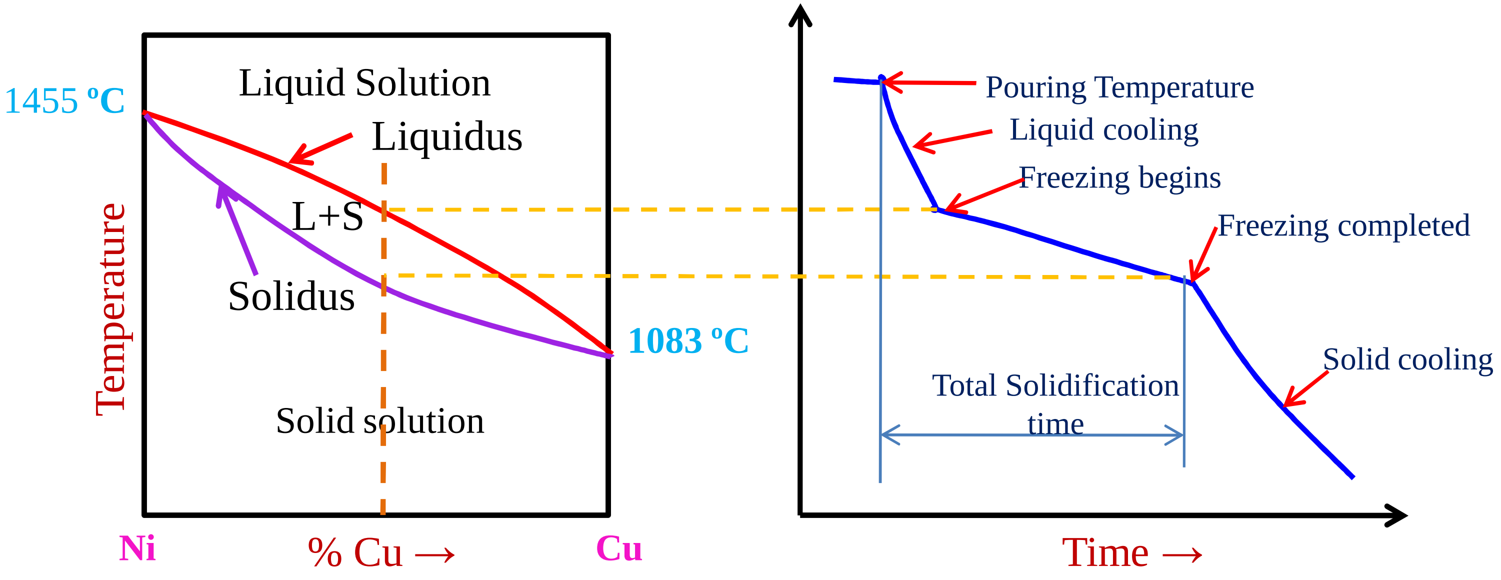




Solidification of Alloys

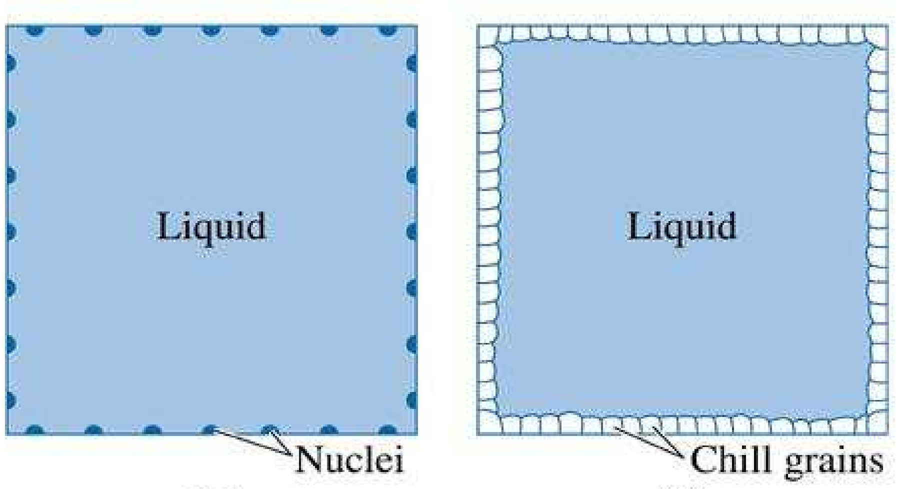
- ❑ Most alloys freeze over a temperature range
- ❑ Phase diagram for a Cu-Ni alloy system and cooling curve for different alloy systems.
- ❑ Characteristic grain structure in an alloy casting, showing segregation of alloying components in center of casting.





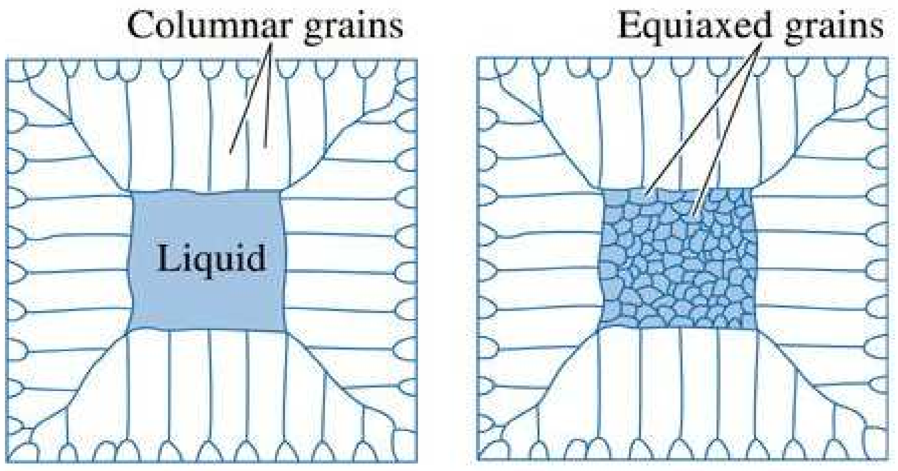
Cast Structure

- Chill Zone: A region of small, randomly oriented grains that forms at the surface of a casting as a result of heterogeneous nucleation.
- Columnar Zone: A region of elongated grains having a preferred orientation that forms as a result of competitive growth during the solidification of a casting.
- Equiaxed Zone: A region of randomly oriented grains in the center of a casting produced as a result of widespread nucleation.



Nucleation begins

Chill zone forms



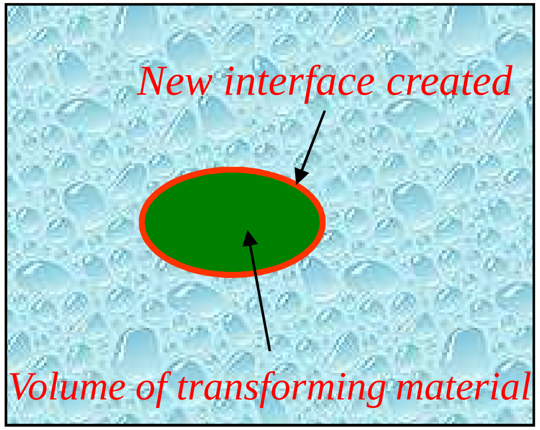
preferred growth produces the columnar zone

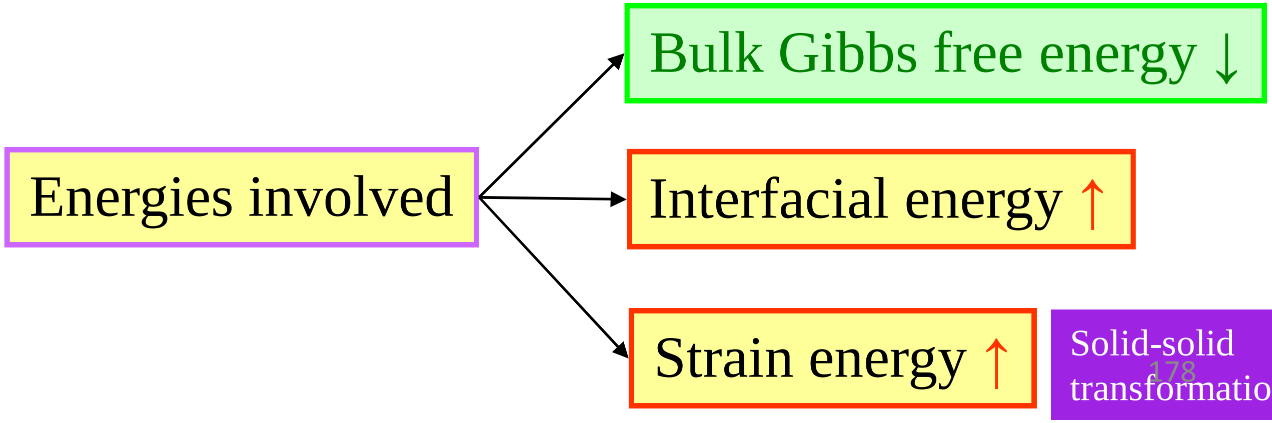
additional nucleation creates the equiaxed zone

Figure: Development of the ingot structure of a casting during solidification:

Remember….!

- We have seen phase transformations using the example of the solidification of a pure metal.
- There is no change in composition involved as we are considering a pure metal. If we solidify an alloy this will involve long range diffusion.
- When a volume of material (V) transforms three energies have to be considered :
  - reduction in G (assume we are working at constant T & P),
  - increase in γ (interface free-energy),
  - increase in strain energy.
- In a liquid to solid phase transformation the strain energy term can be neglected as the liquid melt can flow to accommodate the volume change (assume we are working at constant T & P).
- The process can start only below the melting point of the liquid (as only below the melting point the $G_{Liquid} < G_{Solid}$). I.e. we need to Undercool the system. As we shall note, under suitable conditions (e.g. container-less solidification in zero gravity conditions), melts can be undercooled to a large extent without solidification taking place.





Energies involved

Bulk Gibbs free energy ↓

Interfacial energy ↑

Strain energy ↑

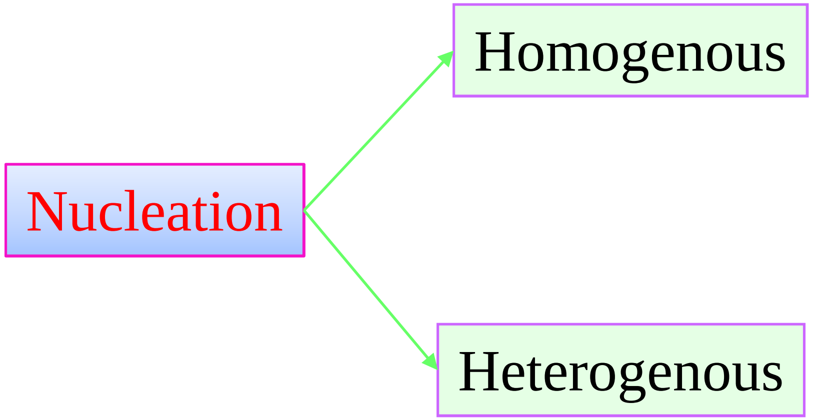
Solid-solid transformation

Nucleation

Solidification = Nucleation + Growth

- Nucleation: localized formation of a distinct thermodynamic phase.
- Nucleation an occur in a gas, liquid or solid phase. Some examples of phases that may form via nucleation include:
  - In gas-creation of liquid droplets in saturated vapor
  - In liquid-formation of gaseous bubbles crystals (e.g., ice formation from water) or glassy regions.
  - In solid-Nucleation of crystalline, amorphous and even vacancy clusters in solid materials. Such solid state nucleation is important, for example, to the semi conductor industry.
- Most nucleation processes are physical, rather than chemical.
- There are two types of nucleation : homogeneous and heterogeneous. This distinction between them made according to the site at which nucleating events occur. For the homogeneous type, nuclei of the new phase form uniformly throughout the parent phase, where as for the heterogeneous type, nuclei form preferentially at structural inhomogeneities such as container surfaces insoluble impurities grain boundaries, dislocations and so on

Nucleation



Nucleation

Homogenous

Heterogenous

- *It occurs spontaneously and randomly, but it requires superheating or supercooling of the medium.*

- Liquid → solid

  walls of container, inclusions

- Solid → solid

  inclusions, grain boundaries, dislocations, stacking faults

- ☐ The probability of nucleation occurring at point in the parent phase is same throughout the parent phase
- ☐ In heterogeneous nucleation there are some preferred sites in the parent phase where nucleation can occur

Homogeneous Nucleation

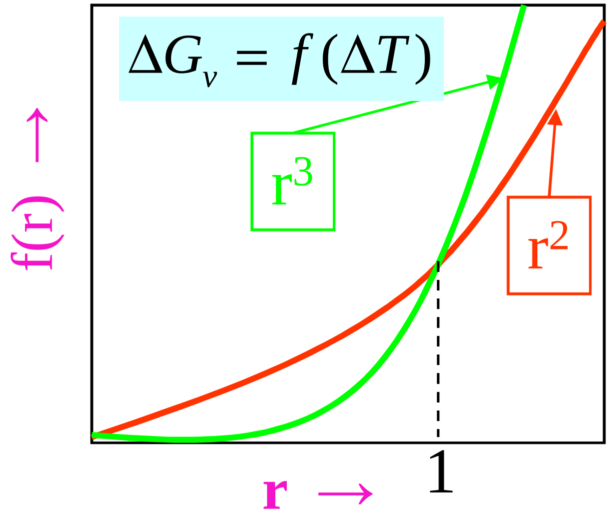
- ❑ Let us consider L→S transformation taking place by homogenous nucleation. Let the system be undercooled to a fixed temperature ΔT. Let us consider the formation of a spherical crystal of radius ‘r’ from the melt. We can neglect the strain energy contribution.
- ❑ Let the change in ‘G’ during the process be ΔG. This is equal to the decrease in bulk free energy + the increase in surface free energy. This can be computed for a spherical nucleus as below.

Free energy change on nucleation =

Reduction in bulk free energy + increase in surface energy + increase in strain energy

Neglected in L → S transformations

$$\Delta G = (\text{Volume}).(\Delta G) + (\text{Surface}).(\gamma)$$



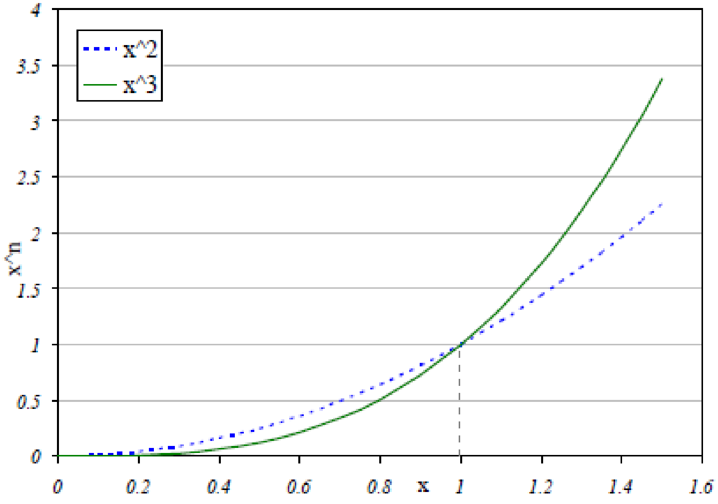
$$\Delta G = \left(\frac{4}{3}\pi r^3\right).(\Delta G_v) + \left(4\pi r^2\right).(\gamma)$$

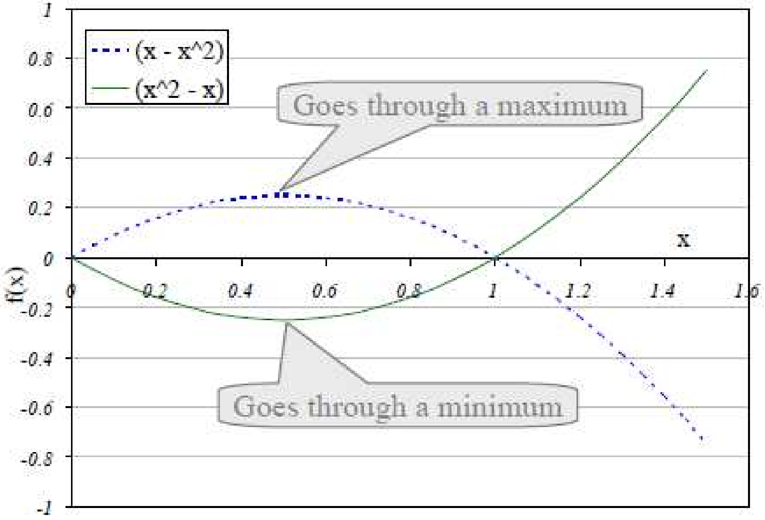
✓Note that below a value of ‘1’ the lower power of ‘r’ dominates; while above ‘1’ the higher power of ‘r’ dominates.
✓In the above equation these powers are weighed with other ‘factors/parameters’, but the essential logic remains.

Homogeneous Nucleation

$$\Delta G = \left(\frac{4}{3}\pi r^{3}\right).(\Delta G_{v}) + \left(4\pi r^{2}\right).(\gamma)$$

- ❑ In the above equation, the r^3 term is +ve and the r^2 term is -ve. Such kinds of equations are often encountered in materials science, where one term is opposing the process and the other is supporting it. Example of such processes are crack growth (where surface energy opposes the process and the strain energy stored in the material supports crack growth).
- ❑ In the current case it is the higher power is supporting the phase transformation. Since the higher power dominates above '1', the function will go through a maximum as in fig. below. This implies the ΔG function will go through a maximum. I.e. if the process just even starts it will lead to an increase in ΔG!
- ❑ On the other hand the function with -ve contribution from the lower power (to ΔG) will go through a minimum (fig. below) and such a process will take place down-hill in G and stop.





Homogeneous Nucleation

- As we have noted previously ΔG vs r plot will go through a maximum (implying that as a small crystal forms 'G' will increase and hence it will tend to dissolve). The maximum of ΔG vs r plot is obtained by, by setting dΔG/dr = 0. The maximum value of ΔG corresponds to a value of 'r' called the critical radius (denoted by superscript *).
- If by some 'accident' (technically a 'statistical random fluctuation') a crystal (of 'preferred' crystal structure) size > r* (called supercritical nuclei) forms then it can grow down-hill in 'G'. Crystals smaller than r* (called embryos) will tend to shrink to reduce 'G'. The critical value of ΔG at r* is called ΔG*. Reduction in G (below the liquid state) is obtained only after r_0 is obtained (which can be obtained by setting ΔG = 0).

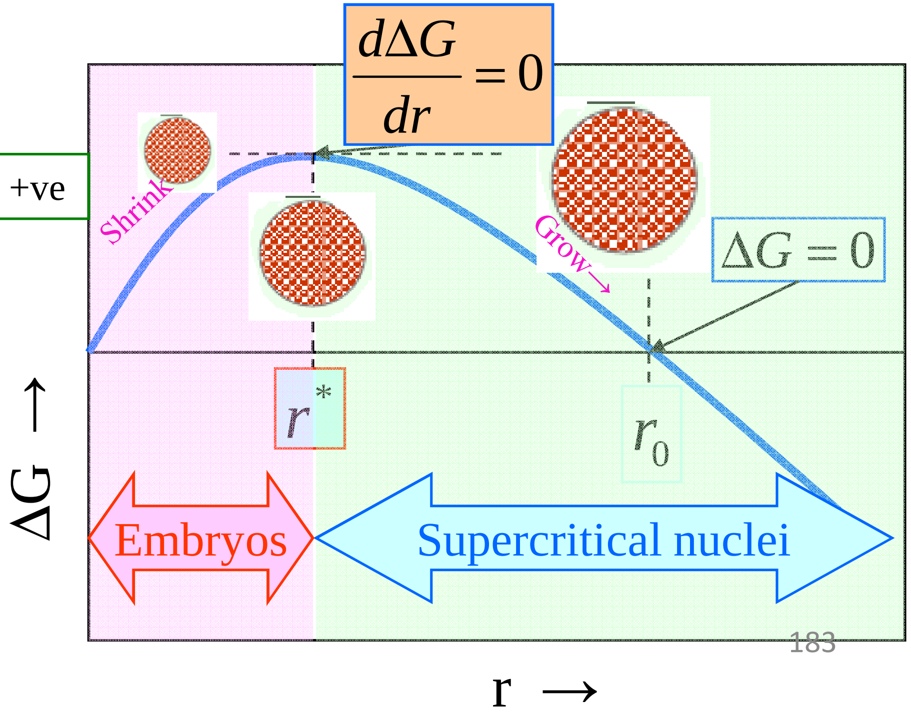
$$\frac{d\Delta G}{dr} = 0 \Rightarrow \begin{cases} r_1^* = 0 & \text{Trivial} \\ r_2^* = -\dfrac{2\gamma}{\Delta G_v} \end{cases}$$

As ΔG_v is –ve, r^* is +ve

$$\boxed{r^* = -\frac{2\gamma}{\Delta G_v}}$$

$$\boxed{\Delta G^* = \frac{16}{3}\pi\frac{\gamma^3}{\Delta G_v^2}}$$

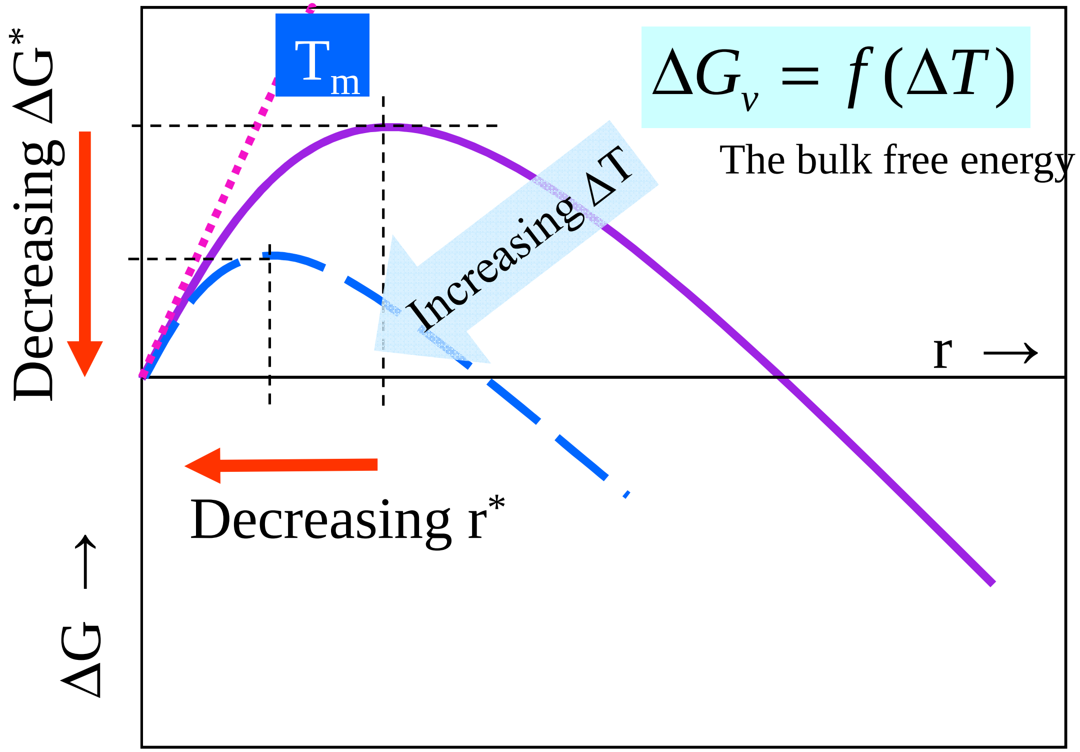
$$\Delta G = 0 \Rightarrow r_0 = -\frac{3\gamma}{\Delta G_v}$$



Homogeneous Nucleation

What is the effect of undercooling (ΔT) on r* and ΔG*?

- ☐ We have noted that ΔG_V is a function of undercooling (ΔT). At larger undercooling ΔG_V increases and hence r* and ΔG* decrease. This is evident from the equations for r* and ΔG* as below
- ☐ At T_m , ΔG_V is zero and r* is infinity! → That the melting point is not the same as the freezing point!! This energy (G) barrier to nucleation is called the *'nucleation barrier'*.



$$\Delta G_v = f(\Delta T)$$

The bulk free energy reduction is a function of undercooling

$$r^* = -\frac{2\gamma}{\Delta G_v}$$

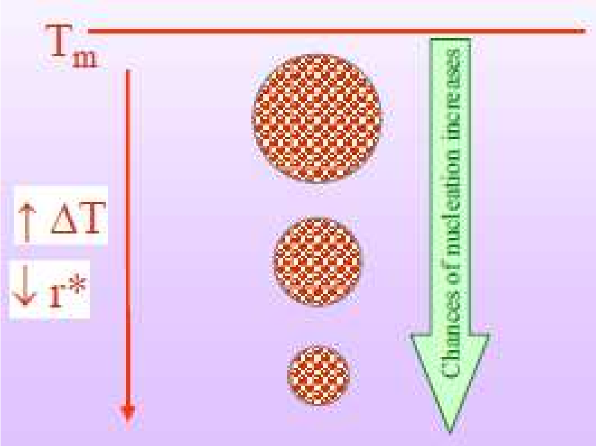
$$\Delta G^* = \frac{16}{3}\pi\frac{\gamma^3}{\Delta G_v^2}$$

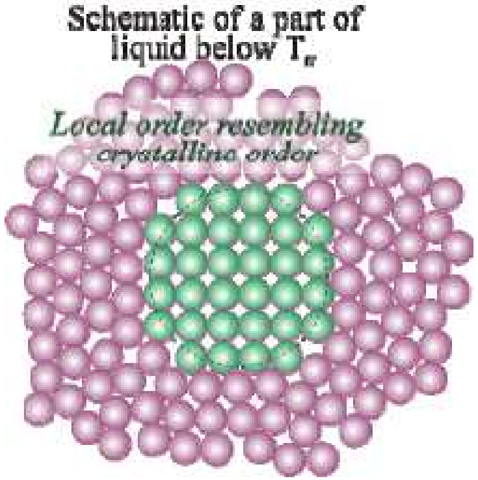
Using the Turnbull approximation (linearizing the G-T curve close to T_m), we can get the value of ΔG interms of the enthalpy of solidification.

$$\Delta G^* = \frac{16}{3}\pi\gamma^3\frac{T_m^2}{\Delta T^2\ \Delta H^2}$$

How are atoms assembled to form a nucleus of r* →“Statistical Random Fluctuation”

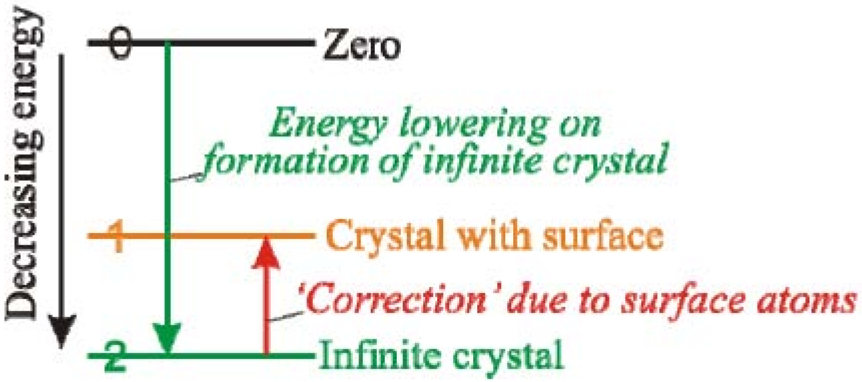
- To cause nucleation (or even to form an embryo) atoms of the liquid (which are randomly moving about) have to come together in a order, which resembles the crystalline order, at a given instant of time. Typically, this crystalline order is very different from the order (local order), which exists in the liquid.
- This ‘coming together’ is a random process, which is statistical in nature →i.e. the liquid is exploring ‘locally’ many different possible configurations and randomly (by chance), in some location in the liquid, this order may resemble the preferred crystalline order.
- Since this process is random (& statistical) in nature, the probability that a larger sized crystalline order is assembled is lower than that to assemble a smaller sized ‘crystal’.
- Hence, at smaller undercoolings (where the value of r* is large) the chance of the formation of a supercritical nucleus is smaller and so is the probability of solidification (as at least one nucleus is needed → which can grow to cause solidification). At larger undercoolings, where r* value is relatively smaller, the chance of solidification is higher.

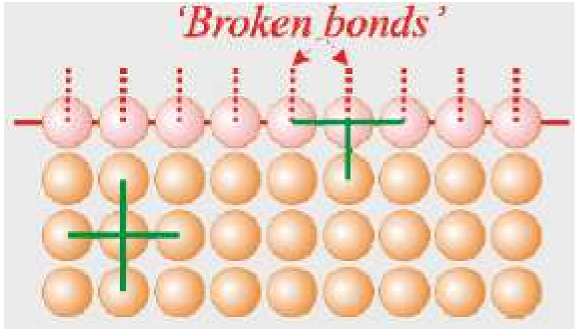




What is meant by the 'Nucleation Barrier' →an alternate perspective

- Here we try to understand: "What exactly is meant by the nucleation barrier?".
- It is sometime difficult to fathom out as to the surface energy can make freezing of a small 'embryo' energetically 'infeasible' *(as we have already noted that unless the crystallite size is* $> r_0$ *the energy of the system is higher)*. Agreed that for the surface the energy lowering is not as much as that for the bulk*, but even the surface (with some 'unsaturated bonds') is expected to have a lower energy than the liquid state (where the crystal is energetically favored). I.e. the specific concern being: "can state-1 in figure below be above the zero level (now considered for the liquid state)?" →"Is the surface so bad that it even negates the effect of the bulk lowering?"
- We will approach this mystery from a different angle - by first asking the question: "what is meant by melting point?" & "what is meant by undercooling?".

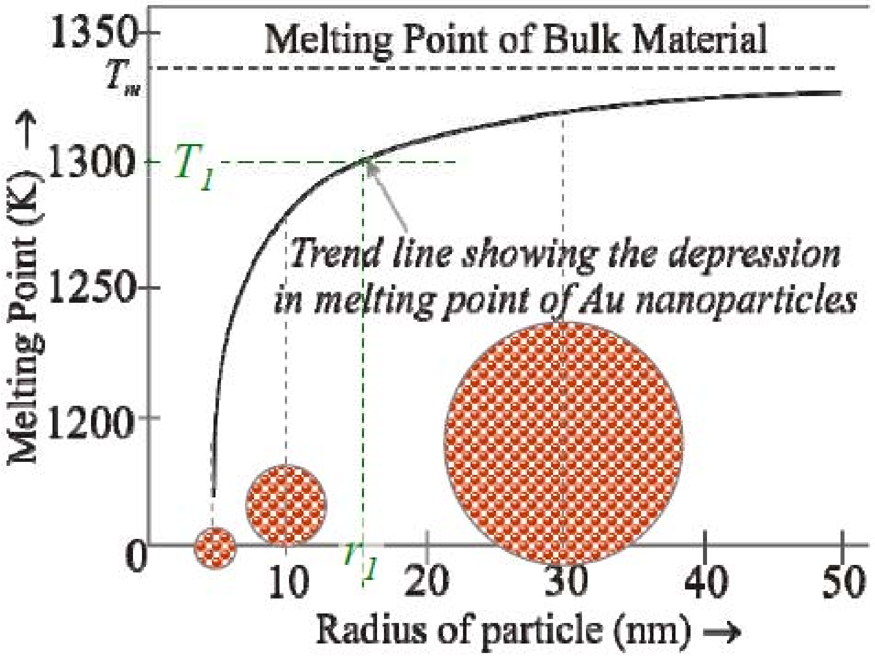




Melting point, undercooling, freezing point

- ❑ The plot below shows melting point of Au nanoparticles, plotted as a function of the particle radius. It is to be noted that the melting point of nanoparticles decreases below the 'bulk melting point' (a 5nm particle melts more than 100 ^{0}C below T_m^{Bulk}). This is due to surface effects (surface is expected to have a lower melting point than bulk!?*) →actually, the current understanding is that the whole nanoparticle melts simultaneously (not surface layer by layer).

- ❑ Let us continue to use the example of Au. Suppose we are below T_m^{Bulk} (1337K=1064 ^{0}C, i.e. system is undercooled w.r.t the bulk melting point) at T_1 (=1300K →ΔT = 37K) and suppose a small crystal of r_2 = 5nm forms in the liquid. Now the melting point of this crystal is ~1200K →this crystal will 'melt-away'. Now we have to assemble a crystal of size of about 15nm (= r_1) for it 'not to melt'. This needless to say is much less probable (and it is better to undercool even further so that the value of r* decreases). Thus the mystery of 'nucleation barrier' vanishes and we can 'think of' melting point ≡ freezing point (for a given size of particle)!



Other materials like Pb, Cu, Bi, Si show similar trend lines

- ❑ T_m is in heating for the bulk material and in cooling if we take into account the size dependence of melting point everything 'sort-of' falls into place .

Homogenous Nucleation Rate

- ❑ The process of nucleation (of a crystal from a liquid melt, below T_m^{Bulk}) we have described so far is a dynamic one. Various atomic configurations are being explored in the liquid state - some of which resemble the stable crystalline order. Some of these 'crystallites' are of a critical size $r^*_{\Delta T}$ for a given undercooling (ΔT). These crystallites can grow to transform the melt to a solid→by becoming supercritical. Crystallites smaller than r* (embryos) tend to 'dissolve'.
- ❑ As the whole process is dynamic, we need to describe the process in terms of 'rate' →the nucleation rate [dN/dt ≡ number of nucleation events/time].
- ❑ Also, true nucleation is the rate at which crystallites become supercritical. To find the nucleation rate we have to find the number of critical sized crystallites (N*) and multiply it by the frequency/rate at which they become supercritical.
- ❑ If the total number of particles (which can act like potential nucleation sites - in homogenous nucleation for now) is N_t , then the number of critical sized particles given by an Arrhenius type function with a activation barrier of ΔG^*.

$$N^* = N_t\, e^{\left(-\frac{\Delta G^*}{kT}\right)}$$

- ❑ The number of potential atoms, which can jump to make the critical nucleus supercritical are the atoms which are ‘adjacent’ to the liquid→let this number be s*.
- ❑ If the lattice vibration frequency is ν and the activation barrier for an atom facing the nucleus (i.e. atom belonging to s*) to jump into the nucleus (to make in supercritical) is ΔH_d, the frequency with which nuclei become supercritical due atomic jumps into the nucleus is given by: $\nu' = S^* \nu e^{\left(-\frac{\Delta H_d}{kT}\right)}$

Rate of nucleation = No. of critical sized particles x Frequency with which they become supercritical

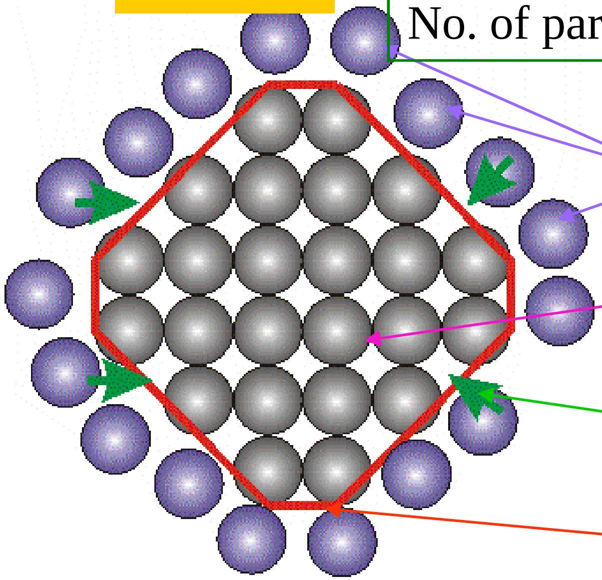
$$I = \frac{dN}{dt}$$

$$N^* = N_t e^{\left(-\frac{\Delta G^*}{kT}\right)}$$

No. of particles/volume in L

$$\nu' = s^* \nu e^{\left(-\frac{\Delta H_d}{kT}\right)}$$

ν → lattice vibration frequency (~10^{13} /s)



s^* atoms of the liquid facing the nucleus

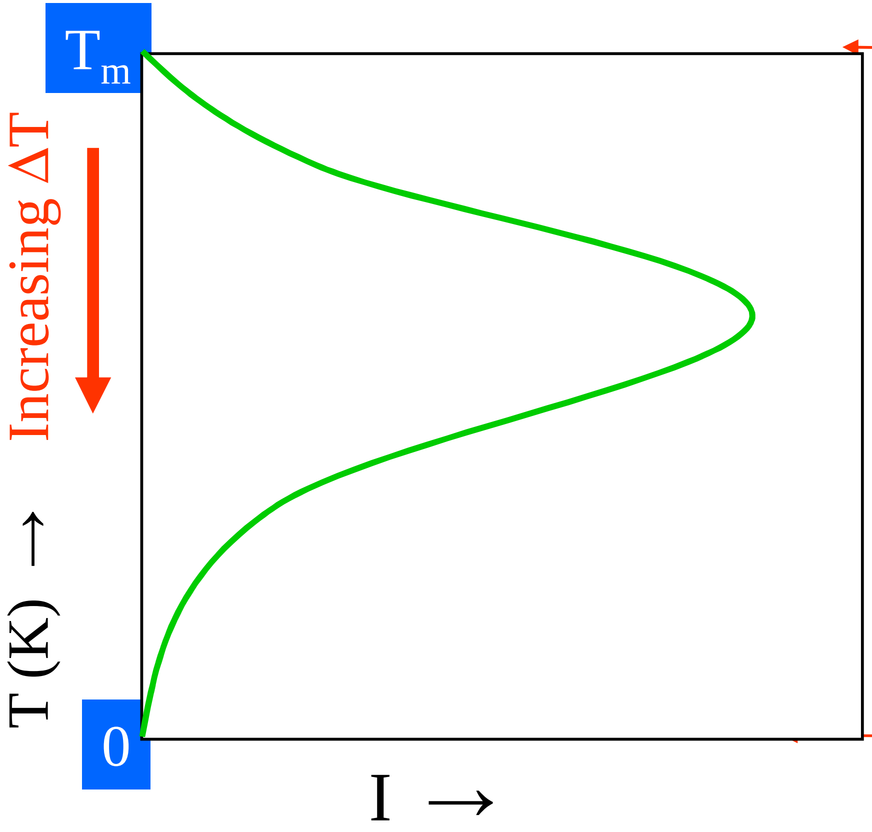
Critical sized nucleus

Jump taking particle to supercriticality → nucleated *(enthalpy of activation = ΔH_d)*

Critical sized nucleus

Homogenous Nucleation Rate

- The nucleation rate (I = dN/dt) can be written as a product of the two terms as in the equation below.
- How does the plot of this function look with temperature?
- At T_m , ΔG^* is ∞→I = 0 (as expected if there is no undercooling there is no nucleation).
- At T = 0K again I = 0
- This implies that the function should reach a maximum between $T = T_m$ and T = 0.
- A schematic plot of I(T) (or I(ΔT)) is given in the figure below. An important point to note is that the nucleation rate is not a monotonic function of undercooling.



$T = T_m \rightarrow \Delta G^* = \infty \rightarrow I = 0$

$$I = N_t\, s^*\, \nu\, e^{-\left(\frac{\Delta G^* + \Delta H_d}{kT}\right)}$$

Note: ΔG^* is a function of T

- $\Delta G^* \uparrow \;\Rightarrow I \downarrow$
- $T \uparrow \;\Rightarrow I \uparrow$

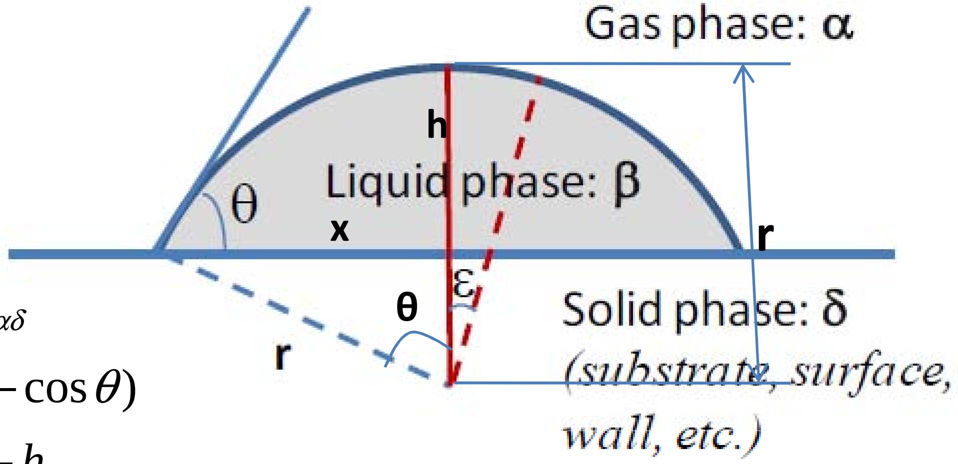
$T = 0 \rightarrow I = 0$

Heterogenous Nucleation

- Heterogeneous nucleation can be considered as a surface catalyzed or assisted nucleation process. The extent of how a surface can catalyze or facilitate the nucleation depends on the contact angle of the nucleus with respect to the substrate. The smaller the angle (or the stronger the wetting of the surface), the lower the free energy change, and the lower the nucleation barrier will be.
- Critical radius of the nucleus (r*) for a heterogeneous nucleation is the same as that for a homogeneous nucleation, whereas the critical volume of the nucleus (like the droplet for liquid nucleated from gas/vapor phase) is usually smaller for heterogeneous nucleation than for homogeneous nucleation, due to the surface wetting (spreading).
- Heterogeneous nucleation occurs much more often than homogeneous nucleation. Heterogeneous nucleation applies to the phase transformation between any two phases of gas, liquid, or solid, typically for example, condensation of gas/vapor, solidification from liquid, bubble formation from liquid, etc.
- In the solidification of a liquid this could be the mold walls. For solid state transformation suitable nucleation sites are: non-equilibrium defects such as excess vacancies, dislocations, grain boundaries, stacking faults, inclusions and surfaces.
- One way to visualize the ease of heterogeneous nucleation → heterogeneous nucleation at a defect will lead to destruction/modification of the defect (make it less “‘defective’”). This will lead to some free energy ΔG_d being released →thus reducing the activation barrier.

Heterogenous Nucleation : Derivation

- There are three different surface energies of interest:



$$\gamma_{\alpha\beta} = \mathit{Surface}\ \text{of gas/liquid}$$

$$\gamma_{\beta\delta} = \mathit{Surface}\ \text{of liquid/solid}$$

$$\gamma_{\alpha\delta} = \text{Surface of gas/solid}$$

$$\Delta \text{G} = \text{V}.\Delta \text{G}_\text{V} + A.\gamma$$

$$\text{Surface energy} = A_{\alpha\beta}\gamma_{\alpha\beta} + A_{\beta\delta}\gamma_{\beta\delta} + A_{\alpha\delta}\gamma_{\alpha\delta}$$

$$A_{\alpha\beta} = 2\pi rh \Rightarrow 2\pi r(r - r\cos\theta) \Rightarrow 2\pi r^2(1-\cos\theta)$$

$$Cos\,\theta = \frac{r-h}{r}$$

$$h = r - r\cos\theta$$

$$A_{\beta\alpha} = \pi r^2 \Rightarrow \pi\left(r\sin\theta\right)^2 \Rightarrow \pi r^2 \sin^2\theta$$

$$A_{\alpha\delta} = \text{Total area - A}_{\beta\alpha} \Rightarrow A_o - \pi r^2 \sin^2\theta (\therefore A_o = \mathit{Total\ area})$$

$$\text{Surface energy} = \gamma_{\alpha\beta} 2\pi r^2(1-\cos\theta) + \gamma_{\beta\delta}\pi r^2 \sin^2\theta + \gamma_{\alpha\delta}A_o - \pi r^2 \sin^2\theta$$

Neglect the $\gamma_{\alpha\delta}A_o$ term, then above equation becomes

$$\text{Surface energy} = \gamma_{\alpha\beta} 2\pi r^2(1-\cos\theta) + \gamma_{\beta\delta}\pi r^2 \sin^2\theta - \pi r^2 \sin^2\theta \Rightarrow Eq.1$$

Heterogenous Nucleation : Derivation

$$\text{Volume of spherical cap} = \text{Area} \times \text{Height}$$

$$\text{Volume} = \int_0^\theta \pi(\text{r}\sin\varepsilon)^2 \times dH$$

$$\text{we know } H = r - r\cos\varepsilon \Rightarrow dH = r\sin\varepsilon\, d\varepsilon$$

$$= \int_0^\theta \pi \text{r}^2 \sin^2\varepsilon \times r\sin\varepsilon\, d\varepsilon$$

$$= \int_0^\theta \pi \text{r}^3 \sin^2\varepsilon \times \sin\varepsilon\, d\varepsilon$$

$$= \pi \text{r}^3 \int_0^\theta (1 - \cos^2\varepsilon)\sin\varepsilon\, d\varepsilon$$

$$= \pi \text{r}^3 \int_0^\theta (\sin\varepsilon - \sin\varepsilon\cos^2\varepsilon) d\varepsilon$$

$$= \pi \text{r}^3 \int_0^\theta \sin\varepsilon - \pi \text{r}^3 \int_0^\theta \sin\varepsilon\cos^2\varepsilon\, d\varepsilon$$

$$let \text{ us take t} = \cos\varepsilon \Rightarrow \frac{\text{dt}}{\text{d}\varepsilon} = -\sin\varepsilon \Rightarrow d\varepsilon = \frac{-dt}{\sin\varepsilon}$$

$$= \pi \text{r}^3 (-\cos\varepsilon)_0^\theta - \pi \text{r}^3 \int_0^\theta \sin\varepsilon . t^2 . -\frac{dt}{\sin\varepsilon}$$

$$= \pi \text{r}^3 (-\cos\varepsilon)_0^\theta + \pi \text{r}^3 \int_0^\theta t^2 dt$$

$$= \pi \text{r}^3 (-\cos\theta + 1) + \pi \text{r}^3 \left(\frac{t^3}{3}\right)_0^\theta$$

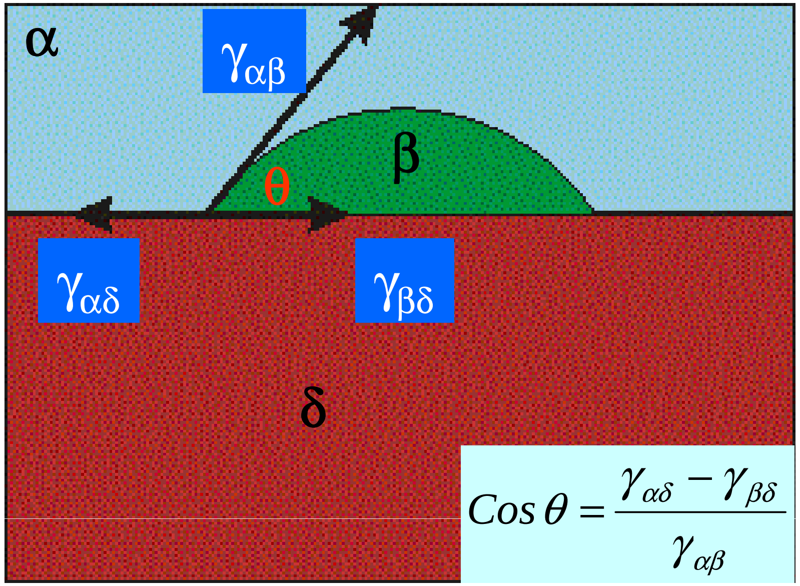
Heterogenous Nucleation : Derivation

$$= \pi r^3(1-\cos\theta) + \frac{\pi r^3}{3}(\cos^3\theta - \cos^3 0)$$

$$= \pi r^3(1-\cos\theta) + \frac{\pi r^3}{3}(\cos^3\theta - 1)$$

$$= \pi r^3\left[\frac{3-3\cos\theta+\cos^3\theta-1}{3}\right]$$

$$= \frac{\pi r^3}{3}[2-3\cos\theta+\cos^3\theta]$$



Surface tension force balance

$$Cos\theta\gamma_{\alpha\beta} = \gamma_{\alpha\delta} - \gamma_{\beta\delta}$$

$$Cos\theta = \frac{\gamma_{\alpha\delta}-\gamma_{\beta\delta}}{\gamma_{\alpha\beta}} \Rightarrow Eq.2$$

$$\Delta G = \frac{\pi r^3}{3}[2-3\cos\theta+\cos^3\theta]\Delta G_V + \gamma_{\alpha\beta}2\pi r^2(1-\cos\theta) + \pi r^2\sin^2\theta(\gamma_{\beta\delta}-\gamma_{\alpha\delta})$$

$$put\ \gamma_{\beta\delta}-\gamma_{\alpha\delta} = -\gamma_{\alpha\beta}\cos\theta$$

Heterogenous Nucleation : Derivation

$$= \frac{\pi r^3}{3}[2-3\cos\theta+\cos^3\theta]\Delta G_V + \gamma_{\alpha\beta}2\pi r^2(1-\cos\theta)-\gamma_{\alpha\beta}\pi r^2\sin^2\theta\cos\theta$$

$$= \frac{4\pi r^3}{3}\frac{[2-3\cos\theta+\cos^3\theta]}{4}\Delta G_V + \pi r^2\gamma_{\alpha\beta}(2-2\cos\theta-\sin^2\cos\theta)$$

$$= \frac{4\pi r^3}{3}\frac{[2-3\cos\theta+\cos^3\theta]}{4}\Delta G_V + \pi r^2\gamma_{\alpha\beta}(2-2\cos\theta-(1-\cos^2\theta)\cos\theta)$$

$$= \frac{4\pi r^3}{3}\frac{[2-3\cos\theta+\cos^3\theta]}{4}\Delta G_V + 4\pi r^2\gamma_{\alpha\beta}\frac{[2-3\cos\theta+\cos^3\theta]}{4}$$

$$= \frac{[2-3\cos\theta+\cos^3\theta]}{4}[\frac{4\pi r^3}{3}\Delta G_V + 4\pi r^2\gamma_{\alpha\beta}]$$

$$= [\frac{4\pi r^3}{3}\Delta G_V + 4\pi r^2\gamma_{\alpha\beta}]f(\theta) \rightarrow where\ \ f(\theta) = \frac{[2-3\cos\theta+\cos^3\theta]}{4}$$

$$\Delta G_{Hetero} = \Delta G_{Homo}.f(\theta)$$

$$\Delta G^*_{Hetero} = \Delta G_{Hetero}(r*) = \Delta G_{Homo}(r*).f(\theta) = \Delta G^*_{Homo}\ f(\theta)$$

Nucleation barrier can be significantly lower for heterogeneous nucleation due to wetting angle affecting the shape of the nucles

Heterogenous Nucleation

- ☐ Using the procedure as before (for the case of the homogenous nucleation) we can find r* for heterogeneous nucleation. Using the surface tension balance equation we can write the formulae for r*and ΔG* using a single interfacial energy $\gamma_{\alpha\beta}$ (and contact angle θ).
- ☐ Further we can write down $\Delta G^*_{\text{hetero}}$ in terms of ΔG^*_{homo} and contact angle θ.

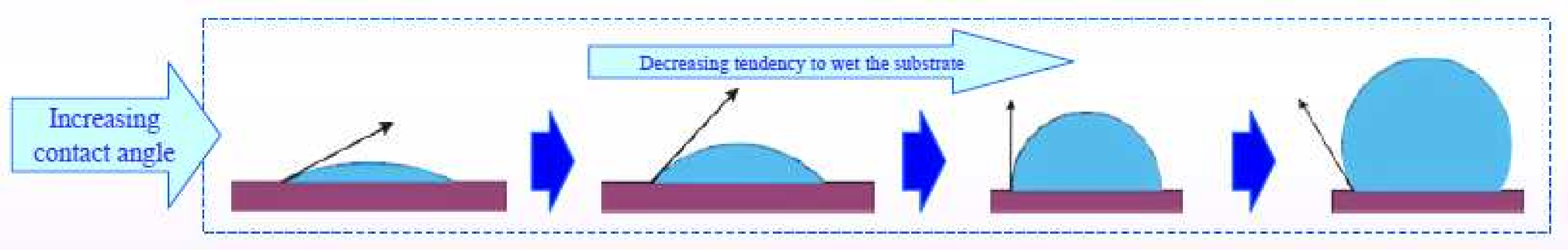
$$\frac{d\Delta G}{dr} = 0 \quad \Rightarrow \quad r^*_{hetero} = -\frac{2\gamma_{\alpha\beta}}{\Delta G_V}$$

$$\Delta G^*_{hetero} = \frac{4}{3}\pi \frac{\gamma^3_{\alpha\beta}}{\Delta G_V^2}\left(2 - 3Cos\theta + Cos^3\theta\right)$$

$$\Delta G^*_{hetero} = \frac{1}{4} G^*_{\text{homo}}\left(2 - 3Cos\theta + Cos^3\theta\right)$$

$$\frac{\Delta G^*_{hetero}}{G^*_{\text{homo}}} = \frac{1}{4}\left(2 - 3Cos\theta + Cos^3\theta\right)$$

Just a function of θ →
The contact angle

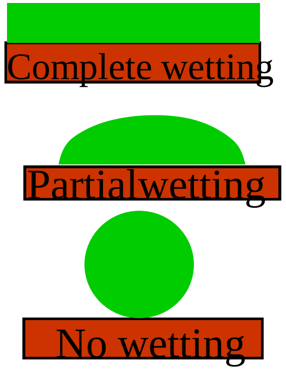


$$\frac{\Delta G^*_{hetero}}{G^*_{\text{homo}}} = \frac{1}{4}\left(2 - 3Cos\theta + Cos^3\theta\right) = f(\theta)$$

$\theta = 0^0 \rightarrow f(\theta) = 0$

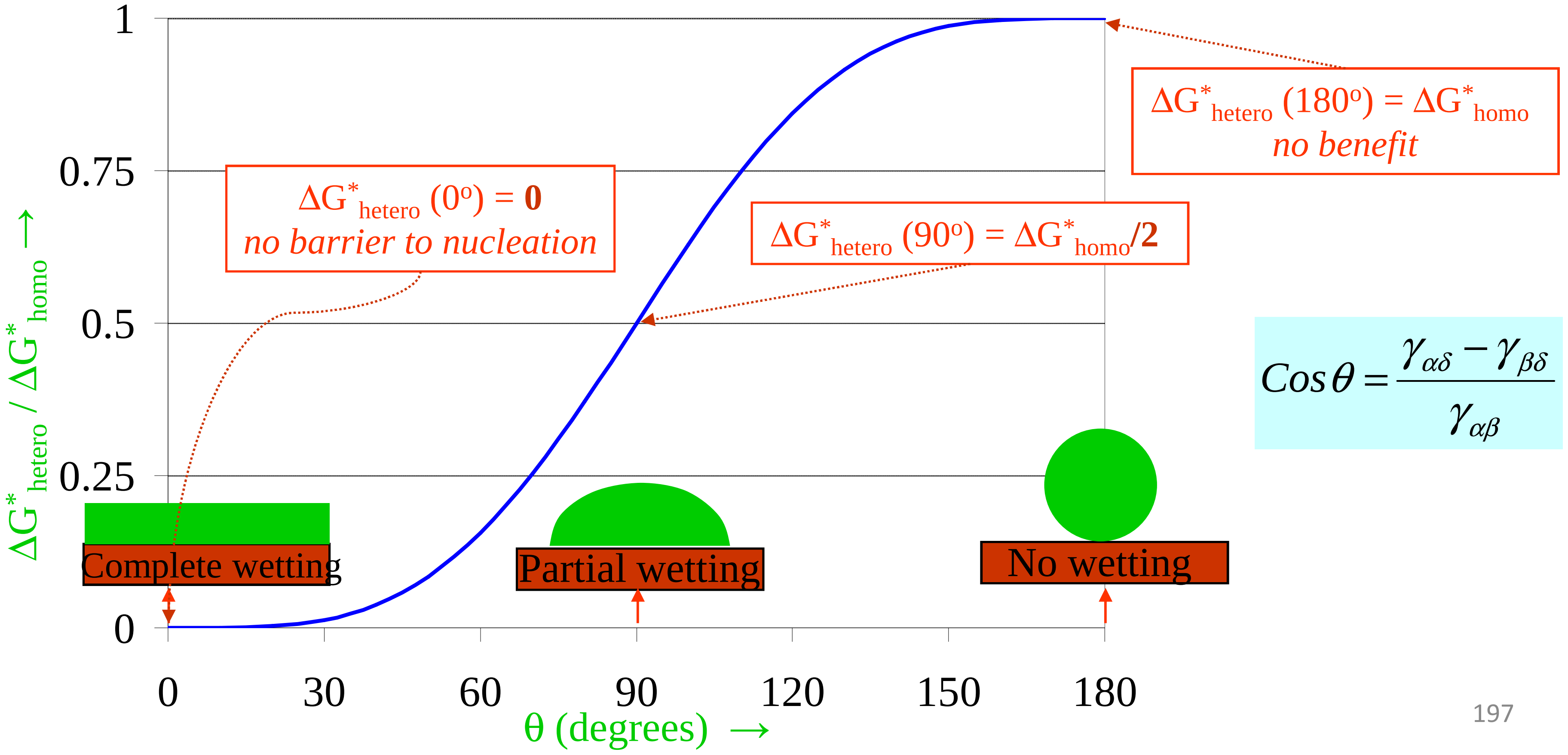
$\theta = 90^0 \rightarrow f(\theta) = 1/2$

$\theta = 180^0 \rightarrow f(\theta) = 1$



The plot of $\Delta G^*_{hetero} / \Delta G^*_{homo}$ is shown in the next page

- Plot of $\Delta G^*_{hetero} / \Delta G^*_{homo}$ is shown below. This brings out the benefit of heterogeneous nucleation vs homogenous nucleation
- If the β phase nucleus (lens shaped) completely wets the substrate/inclusion (δ-phase) (i.e. $\theta = 0^o$) →then $\Delta G^*_{hetero} = 0$ →there is no barrier to nucleation.
- On the other extreme if β-phase does not we the substrate (i.e. $\theta = 180^o$) → $\Delta G^*_{hetero} = \Delta G^*_{homo}$ → there is no benefit of the substrate. In reality the wetting angle θ is somewhere between 0°-180°.
- Hence, we have to chose a heterogeneous nucleating agent with a minimum 'θ' value



ΔG^*_{hetero} (0°) = **0**
no barrier to nucleation

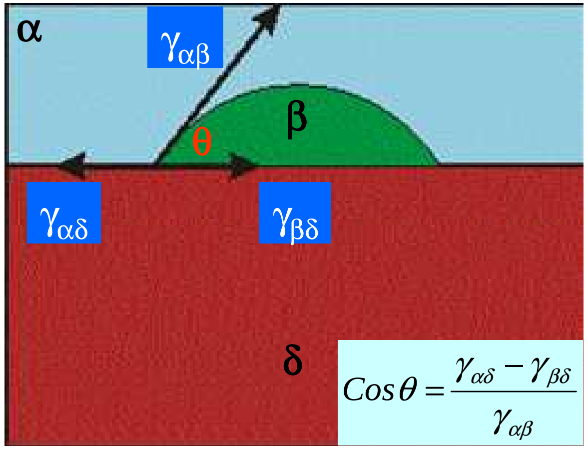
ΔG^*_{hetero} (90°) = ΔG^*_{homo}**/2**

ΔG^*_{hetero} (180°) = ΔG^*_{homo}
no benefit

$$Cos\,\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}}$$

Choice of heterogeneous nucleating agent

- Heterogeneous nucleation has many practical applications.
- During the solidification of a melt if only a few nuclei form and these nuclei grow, we will have a coarse grained material *(which will have a lower strength as compared to a fine grained material- due to Hall-Petch effect).*
- Hence, nucleating agents are added to the melt (e.g. Ti for Al alloys, Zr for Mg alloys) for grain refinement.



$$Cos\,\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}}$$

How to get a small value of θ? (so that 'easy' heterogeneous nucleation).

- Choosing a nucleating agent with a low value of $\gamma_{\beta\delta}$ (low energy βδ interface)
- (Actually the value of $(\gamma_{\alpha\delta} - \gamma_{\beta\delta})$ will determine the effectiveness of the heterogeneous nucleating agent → high $\gamma_{\alpha\delta}$ or low $\gamma_{\beta\delta}$)

How to get a low value of $\gamma_{\beta\delta}$

- We can get a low value of $\gamma_{\beta\delta}$
  - Crystal structure of β and δ are similar
  - lattice parameters are as close as possible
- Examples of such choices are
  - ✓ Seeding rain-bearing clouds → AgI or NaCl → nucleation of ice crystals
  - ✓ Ni (FCC, a = 3.52 Å) is used a heterogeneous nucleating agent in the production of artificial diamonds (FCC, a = 3.57 Å) from graphite

Heterogeneous nucleation rate

- The rate of heterogeneous nucleation can be expressed in a form similar to that of Homogeneous nucleation rate. In addition to the difference in the ΔG* term and the pre-exponential term will include only the number of preferred nucleation sites, which is many orders of magnitude smaller than the number of atoms per unit voulme used in the homogeneous case
- In order of magnitude , the number of nucleation sites for various situations is typically as folllows:
- If N_i is the number of sites per unit volume having a nucleation barrier ΔG_i *, then we can write expression for heterogeneous nucleation rate will be

$$I_{het} = N_i \, s_i^* \, \nu \, e^{-\left(\frac{\Delta G^* + \Delta G_d}{RT}\right)}$$

$N_{homogeneous}$	$\sim 10^{29}\ m^{-3}$
$N_{grain\ boundary}$	$\sim 10^{23}\ m^{-3}$
$N_{grain\ edge}$	$\sim 10^{17}\ m^{-3}$
$N_{grain\ corner}$	$\sim 10^{11}\ m^{-3}$
$N_{dislocation}$	$\sim 10^{13}\ m^{-3}$

- Usually, $I_{het} > I_{homo}$, because $\Delta G^*_{het} < \Delta G^*_{homo}$ dominates

  the result through the pre-exponential factor may be much smaller for heterogeneous nucleation as compared to the homogeneous case.

Why does heterogeneous nucleation rate dominate?

- ❑ To understand the above questions, let us write the nucleation rate for both cases as a pre-exponential term and an exponential term. The pre-exponential term is a function of the number of nucleation sites.
- ❑ However, the term that dominates is the exponential term and due to a lower ΔG* the heterogeneous nucleation rate is typically higher.

$$I_{\text{homo}} \propto I^{0}_{\text{homo}} \, e^{-\left(\frac{\Delta G^{*}_{\text{homo}}}{kT}\right)}$$

= f(number of nucleation sites)

$\sim 10^{42}$

$$I_{\text{hetero}} \propto I^{0}_{\text{hetero}} \, e^{-\left(\frac{\Delta G^{*}_{\text{hetero}}}{kT}\right)}$$

= f(number of nucleation sites)

$\sim 10^{26}$

BUT

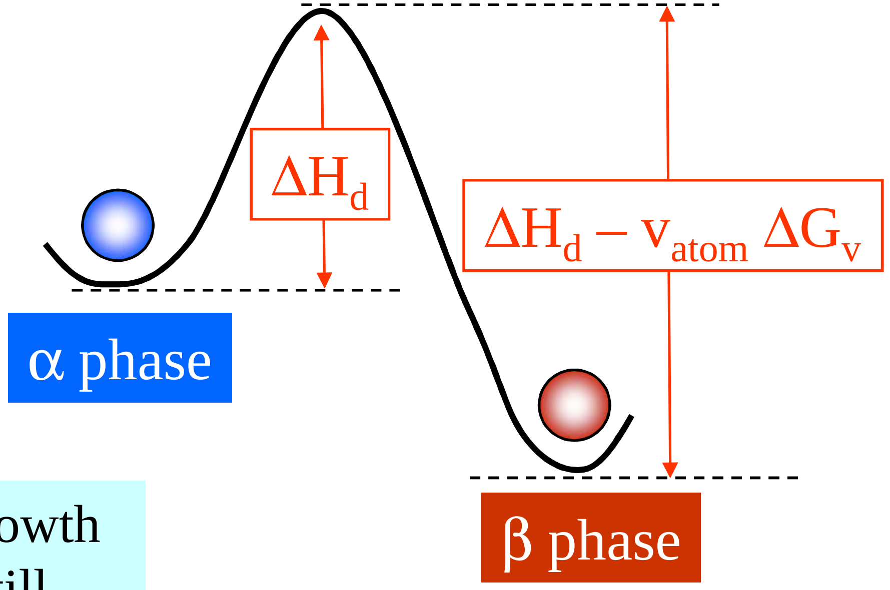
the exponential term dominates

$$I_{\text{hetero}} > I_{\text{homo}}$$

Growth of a Pure solid

- At transformation temperature the probability of jump of atom from α → β (across the interface) is same as the reverse jump
- Growth proceeds below the transformation temperature, wherein the activation barrier for the reverse jump is higher.
- There are basically two different types of solid/liquid interface: an atomically rough or diffuse interface associated with metallic systems, and an atomically flat or sharply defined interface often associated with nonmetals.

- Because of the differences in atomic structure these two types of interface migrate in quite different ways . Rough interface migrate by a **continuous growth** processes while flat interface migrate by **lateral growth (Spiral growth and surface nucleation)** process involving ledges.



Trasformation $\alpha \rightarrow \beta$ = Nucleation of β phase + Growth till α is exhausted

Summary

- Compared to the heterogeneous nucleation (which starts at nucleation sites on surfaces) homogeneous nucleation occurs with much more difficulty in the interior of a uniform substance. The creation of a nucleus implies the formation of an interface at the boundaries of a new phase.
- Liquids cooled below the maximum heterogeneous nucleation temperature (melting temperature) but which are above the homogeneous nucleation temperature. (pure substance freezing temperature) are cooled super cooled.
- An example of supercooling: pure water freezes at -42ºC rather than at its freezing temperature 0ºC.

Nucleation - The physical process by which a new phase is produced in a material.

Critical radius (r^*) - The minimum size that must be formed by atoms clustering together in the liquid before the solid particle is stable and begins to grow.

Undercooling - The temperature to which the liquid metal must cool below the equilibrium freezing temperature before nucleation occurs.

Homogeneous nucleation - Formation of a critically sized solid from the liquid by the clustering together of a large number of atoms at a high undercooling (without an external interface).

Heterogeneous nucleation - Formation of a critically sized solid from the liquid on an impurity surface.

Questions?

1. (a). Suppose that 0.100 kg of liquid copper is supercooled 250 K, where it is allowed to nucleate and solidify adiabaticall (no heat is lost to the surroundings). Calculate how much copper will solidify until the temperature recalesces to its melting point of 1356 K. The specific heats of solid and liquid copper in the temperature range of interest are, respectively:

   $$C_{P(s)} = 22.64 + 5.86\times10^{-3}T, J/mol.K$$

   $$C_{P(l)} = 31.4 J/mol.K$$

   Where T is the temperature in degrees Kelvin. The heat of fusion of copper is 13.20 kJ/mol and its molar weight is 0.0635 kg/mol.

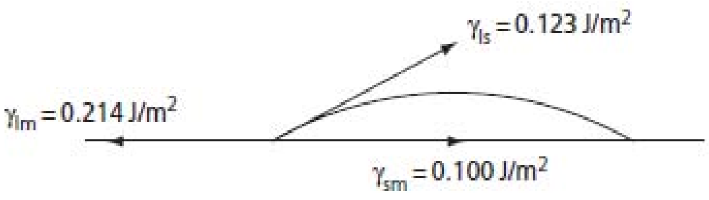
   (b). How much supercooling would be necessary in order to solidify the entire sample adiabatically?
2. Derive the expression for Homogeneous nucleation (ΔG* and r*) and it's rate, and heterogeneous nucleation (ΔG* and r*) and its rate (neglect the strain energy).
3. Briefly explain Heterogeneous nucleation on grain boundaries, Grain edges grain corners, inclusions and dislocations.
4. Derive the expressions for Homogeneous and heterogenerous nucleation by considering the strain energy term.
5. Derive an expression for the critical size and activation energy for a cubic nucleus. Under what conditions is such a nucleus most likely to occur?

Questions?

6. Assume for the solidification of nickel that nucleation is homogeneous, and the number of stable nuclei is 10^6 nuclei per cubic meter. Calculate the critical radius and the number of stable nuclei that exist at the following degrees of supercooling: 200 K and 300 K. and What is significant about the magnitudes of these critical radii and the numbers of stable nuclei? [r_{Ni} – 0.255 J/m^2, ΔH_f = -2.53×10^9 J/m^3, Super cooling value for Ni = 319^{o}C]
7. Calculate the homogeneous nucleation rate in liquid copper at under coolings of 180, 200, and 220K, using the given data: L =1.88×10^9 J m^{-3}, T_m = 1356K, γ_{sL} = 0.177 J m^{-2}, f_0 = 10^{11} s^{-1}, C_0 = 6×10^{28} atoms m^{-3}, k = 1.38×1
8. Explain the concept constitutional Supercooling. When does this take place? And explain dendritic formation
9. The surface energy of pure metal liquid , γ, is 600 dynes/ cm; The volume of an atom of this metal in the liquid is 2.7×10^{-25}cm^3; and the free-energy difference between an atom in the vapor and liquid , ΔG^{vl}, is -2.37J. Under these conditions, what would be the critical radius of a droplet, r_0 in nm and the free energy of the droplet, $\Delta G_{r0,}$ in J?
10. Write a short note on ‘Grwoth of a pure solid’ ?
11. Differentiate between Homogeneous and Heterogeneous nucleation? In which case nucleation rate will be high? Why.
12. Explain the effect of undercooling on Nucleation rate, growth rate, r* and G*? And what is the glass transition temperature. And how it is related to undercooling.

Questions?

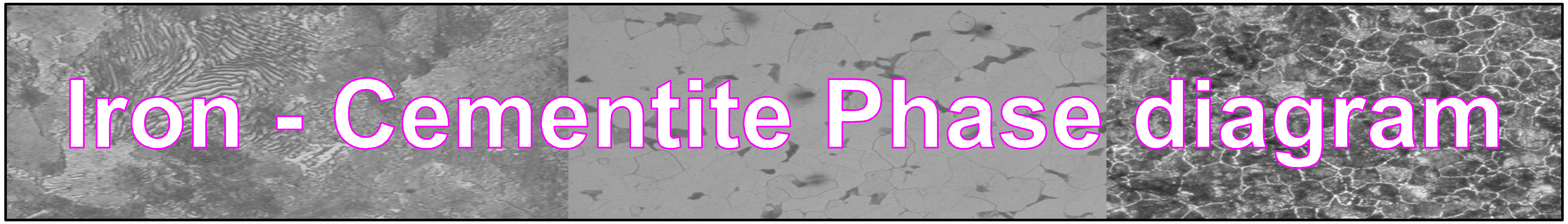
13. The following data concern liquid magnesium at a temperature close to its boiling point of 1380 K: the surface energy of the liquid-vapor interface is 0.440 J/m^2; the density of the liquid phase is 1.50 ×10^3 kg/m^3; and the atomic weight is 0.02432 kg/mol.
    a) First determine v_l, the volume of the liquid per atom. To do this, use the density and the atomic weight.
    b) Now compute the number of embryos in the vapor at a temperature just above the boiling point, that contain 10 magnesium atoms.
14. The accompanying diagram is for a hypothetical embryo of silver growing against an arbitrary mold wall. With the aid of this diagram,
    a) Compute the angle of contact,θ of the embryo with the mold wall.



    b) Determine the magnitude of the factor that may be used to convert the homogeneous free energy needed to obtain a nucleus into that of the corresponding heterogeneous free energy.
15. An alloy having solute concentration C is held at a temperature T within solid – liquid range and the liquid is filtered out. If this process is repeated by heating & filtering out the liquid will it ultimately give pure A? Is this a practical method of purification?

Questions?

16. Estimate entropy change during solidification of the following elements and comment on the nature of the interface between solidifying crystal and liquid. The latent heat and melting point are given with brackets. (a) Al [10.67kJ/mole, 660C] (b) Si [46.44kJ/mole, 1414^{0}C]
17. What is partition coefficient? Derive Scheil equation for solidification of binary alloys. State the assumptions made during its derivation. What is the composition of the last solid that forms during solidification of a terminal solid solution of a binary eutectic system?
18. Estimate the temperature gradient that is to be maintained within solid aluminum so that the planar solidification front moves into liquid aluminum maintained at its melting point at a velocity of 0.001m/s. Given thermal conductivity of aluminum = 225 W/mK, latent heat of fusion = 398 KJ/kg and density = 2700kg/m^3 .
19. In cobalt, a coherent interface forms during HCP to FCC transformation. The lattice parameter of the FCC phase is 3.56 A^{o}. The distance between nearest neighbours along a close packed direction in the basal plane of the HCP phase is 2.507A^{o}. show that the misfit to be accommodated by coherency strains is small.
20. Suppose that an iron specimen containing 0.09 atomic percent carbon is equilibriated at 720°C (993 K) and then rapidly quenched to 300°C (573 K). Determine the length of the time needed for one side of a plate shaped carbide precipitate to grow out by 10^3 nm.
    - p) How wide a layer of the matrix next to a plate would have its carbon concentration lowered from 0.09 percent carbon to that corresponding to n_{α}^{e} *to* form a layer of cementite 10^3 nm thick?
    - q) How long would it take to increase one side of the plate by 10 nm?



Iron - Cementite Phase diagram

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History

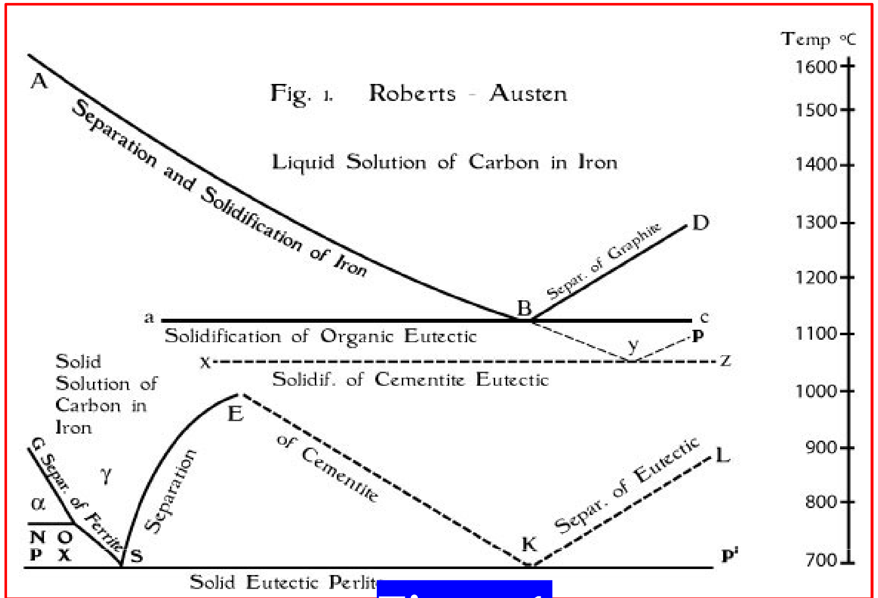


Figure 1

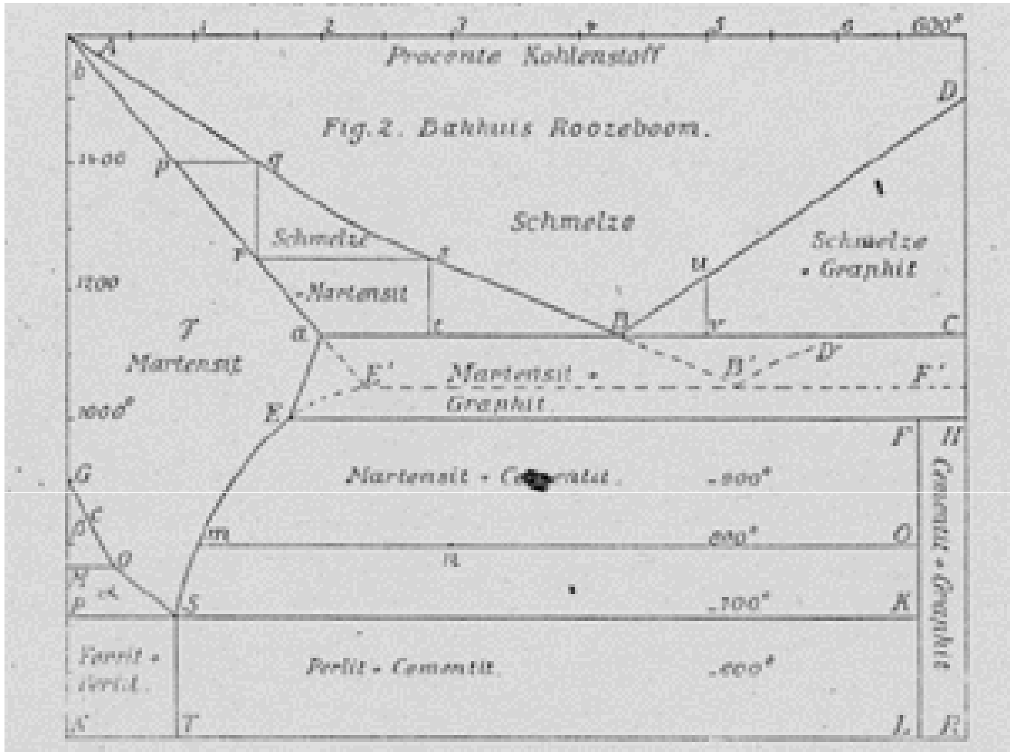


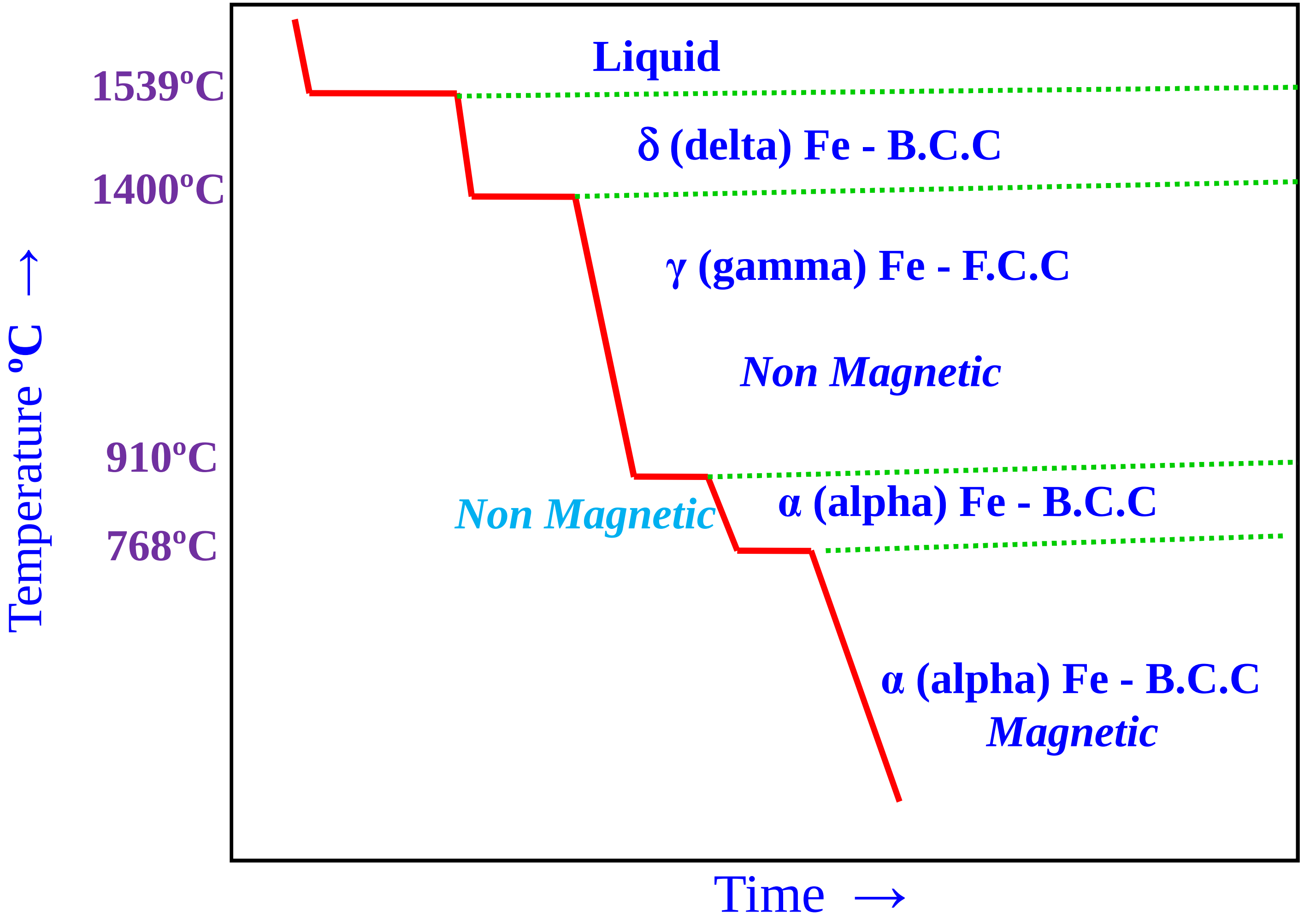
Figure 2

- Iron – carbon (Fe-C) diagram and first phase diagram of any alloy to be established, done by Roberts –Austen in 1898 after whom austenite came to be named. (Figure 1)

- The Iron Carbon diagram, adjusted by Bakhuis-Roozeboom in 1900. Notice line A-a and the temperature range between 1000 and 1100°C, where carbide formation was suppose to take place as the result of a chemical reaction between graphite and austenite (at that time called martensite! (Figure 2)

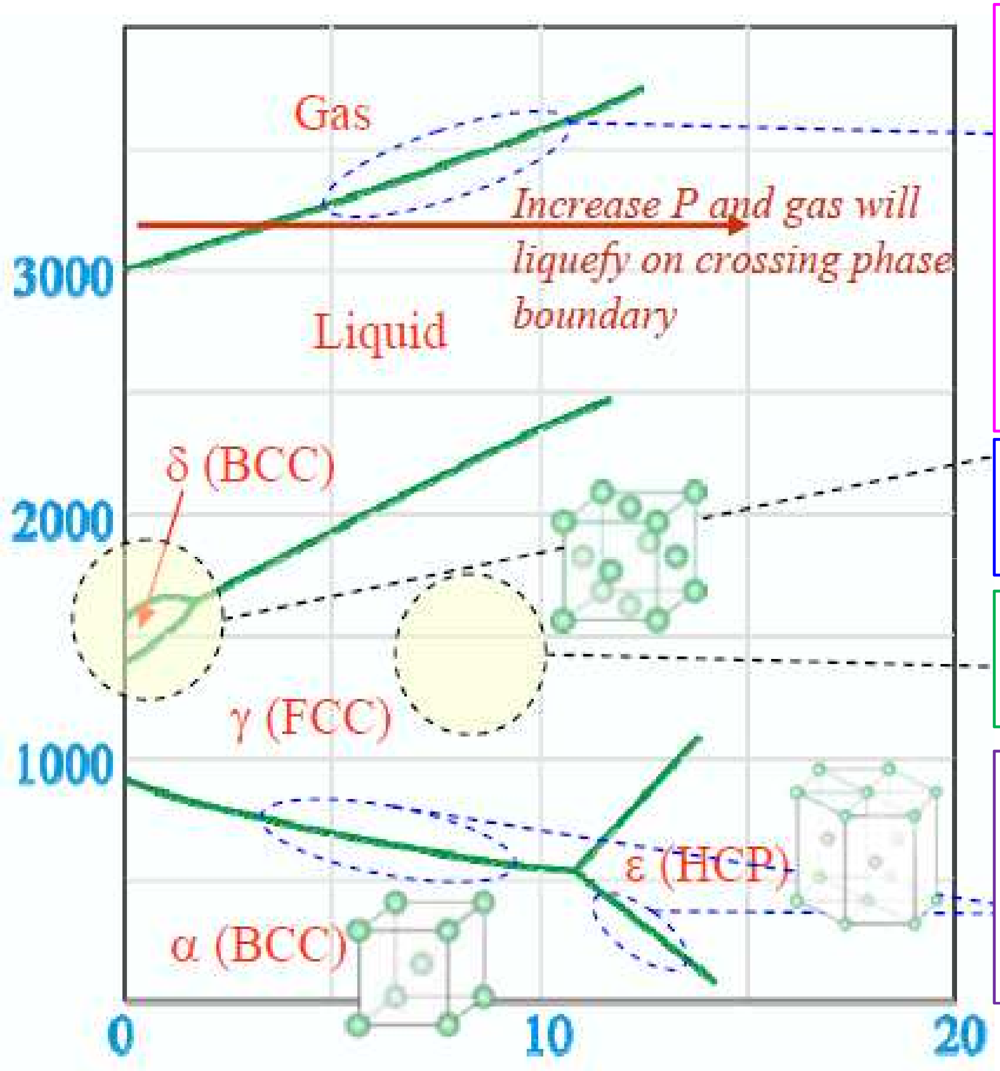
Allotropic Transformation in Iron

- Iron is an allotropic metal, which means that it can exist in more than one type of lattice structure depending upon temperature. A cooling curve for pure iron is shown below:



Can be other allotropic structures are possible….?

Effect of pressure on allotropy of Iron



This line slopes upward as at constant T if we increase the P the gas will liquefy as liquid has lower volume (similarly the reader should draw horizontal lines to understand the effect of pressure on the stability of various phases- and rationalize the same).

Phase fields of non-close packed structures shrink under higher pressure

Phase fields of close packed structures expand under higher pressure

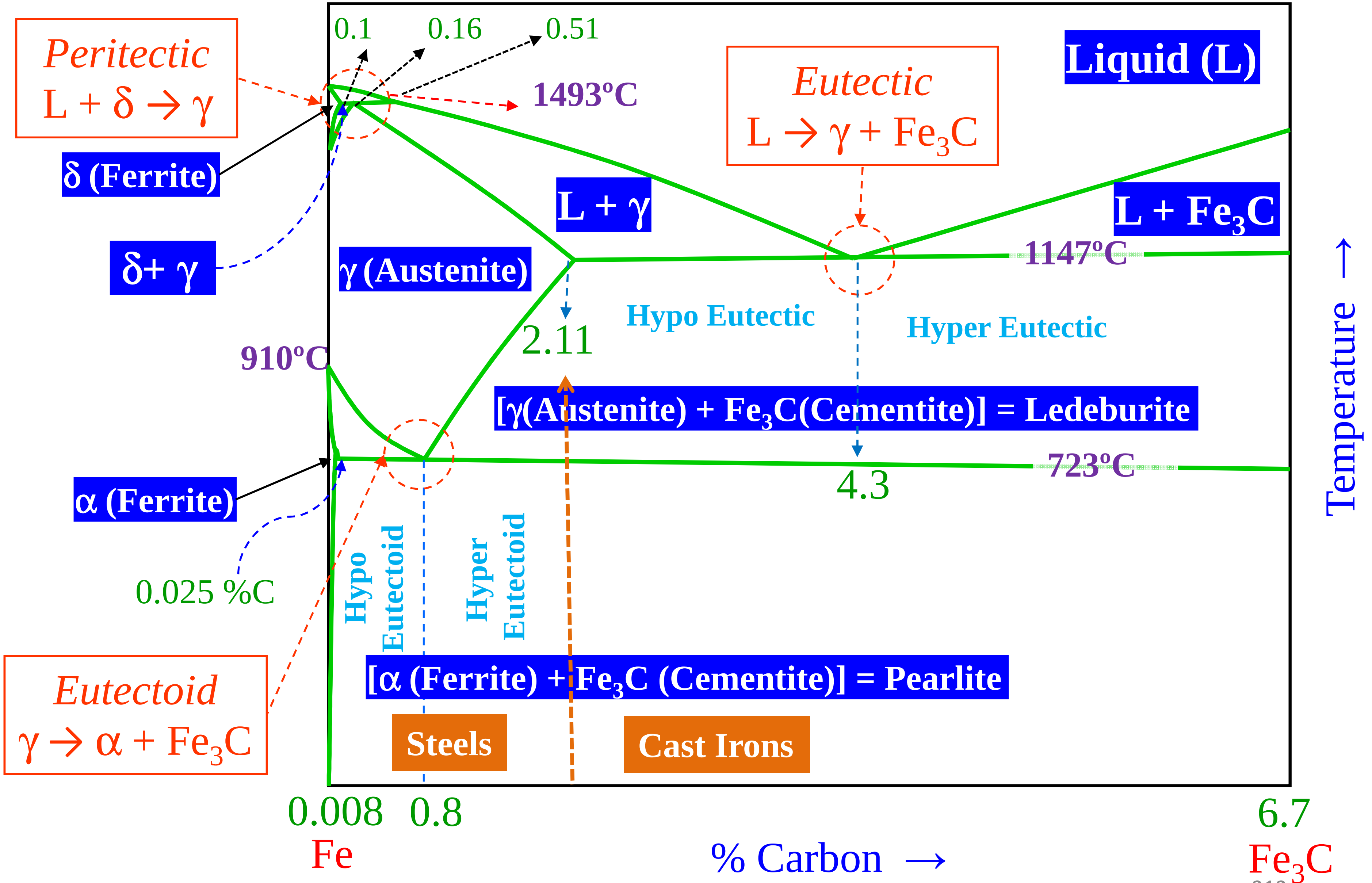
These lines slope downward as: Under higher pressure the phase with higher packing fraction (lower volume) is preferred

The face centered tetragonal (FCT) iron is coherently deposited iron grown as thin film on a {100} plane of copper substrate. Growing Trigonal iron on mis-fiting {111} surface of a face centered cubic copper substrate.

Iron - Cementite phase diagram

- The Fe-C (or more precisely the Fe-Fe_3C) diagram is an important one. Cementite is a metastable phase and ‘strictly speaking’ should not be included in a phase diagram. But the decomposition rate of cementite is small and hence can be thought of as ‘stable enough’ to be included in a phase diagram. Hence, we typically consider the Fe-Fe_3C part of the Fe-C phase diagram.
- In the phase diagram, temperature is plotted against composition. Any point on the diagram therefore represents a definite composition and temperature. The phase diagram indicates the phases present and the phase changes that occur during heating and cooling. The relative amounts of the phases that exist at any temperature can also be estimated with the help of lever rule.
- A portion of the Fe-C diagram – the part from pure Fe to 6.67 wt.% carbon (*corresponding to cementite, Fe_3C) – is technologically very relevant.*
- Cementite is not a equilibrium phase and would tend to decompose into Fe and graphite. This reaction is sluggish and for practical purpose (at the microstructural level) cementite can be considered to be part of the phase diagram. Cementite forms as it nucleates readily as compared to graphite.
- Compositions upto 2.1%C are called steels and beyond 2.1% are called cast irons. *In reality the calssification should be based on ‘castability’ and not just on carbon content.*
- Heat treatments can be done to alter the properties of the steel by modifying the microstructure → we will learn about this in coming chapters.

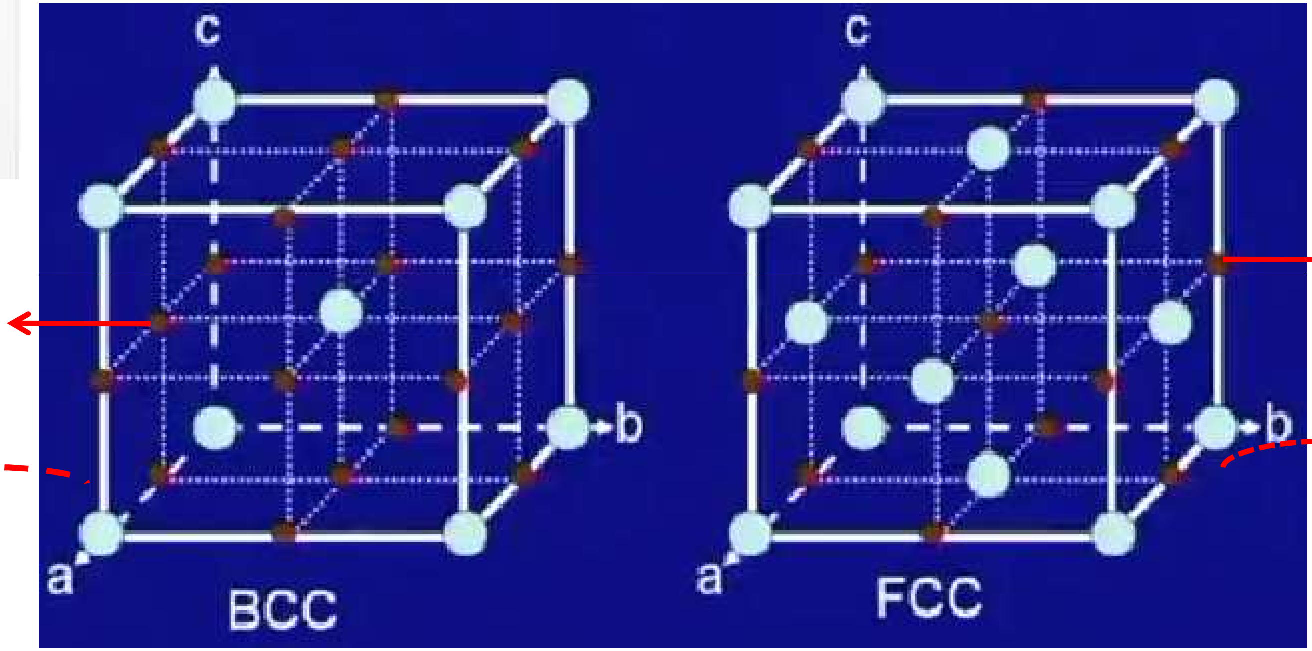
Fe-Fe_3C metastable phase diagram



Carbon Solubility in Iron

Solubility of carbon in Fe = f (structure, temperature)

Where is carbon located in iron lattice ?



Octahedral sites

Octahedral sites

6 faces sharing with two sides (6/2)=3
12 edges sharing with four sides (12/4)=3
Total sites is (3+3), 6 per unit cell
Every one Fe atom we have 3 interstitial sites

One interstitial site in center plus
12 edges sharing with four sides (12/4)=3
Total sites is (1+3), 4 per unit cell
Every one Fe atom we have 1 interstitial site

Why concentration of carbon in α-Fe with BCC structure is less than γ-Fe with FCC structure?

- ❑ FIRST LET US CONSIDER FCC STRUCTURE (γ-Fe)
- ❑ Packing factor of FCC lattice 0.74
- ❑ This indicates the presence of voids. Let us discuss it more elaborately.
- ❑ In a FCC crystal there are mainly two types of voids:
- ❑ Tetrahedral: coordination number (CN) is 4. That means the void is surrounded by 4 atoms.
- ❑ Octahedral: CN is 6. That means the void is surrounded by 6 atoms.
- ❑ There are 8 tetrahedral voids in a unit cell. That means 2 voids per atom.
- ❑ There are 4 octahedral voids in a unit cell. That means 1 void per atom.
- ❑ However, impurities prefer to occupy octahedral voids.
- ❑ Because the ratio of the radius of the tetrahedral void to atom is 0.225 and the same for the octahedral void is 0.414.
- ❑ The ratio of the radius of the carbon atom (size is 77 pm) to Fe (when it has FCC crystal) is 0.596.
- ❑ So when a carbon atom occupies any void, lattice will be distorted to increase the enthalpy.
- ❑ Distortion will be less if it occupies the octahedral voids.
- ❑ Although it increases the enthalpy, carbon atoms will be present up to a certain extent because of the gain in entropy, as explained previously, which decreases the free energy.

Carbon Solubility in Iron

FCC

Size of Fe atom
CCP crystal

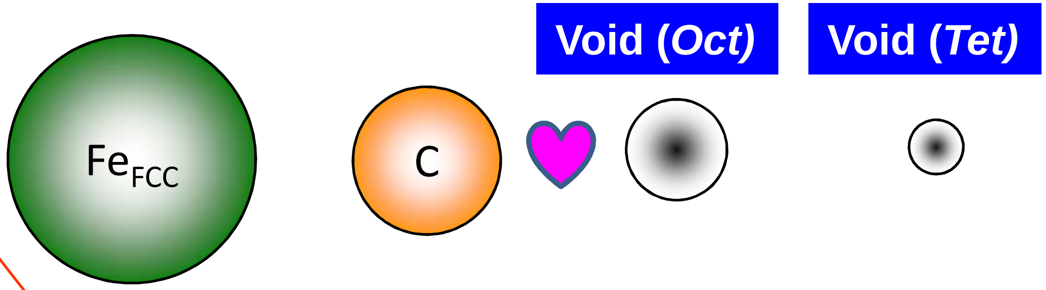
$$r^{Fe}_{FCC} = 1.292\,\mathring{A}$$

Size of the OV

$$x^{Fe}_{FCC}(oct) = 0.534\,\mathring{A}$$

Size of Carbon atom

$$r^{C} = 0.77\,\mathring{A}$$



Relative sizes of voids w.r.t atoms

Note the difference in size of the atoms

BCC

Size of Fe atom
BCC crystal

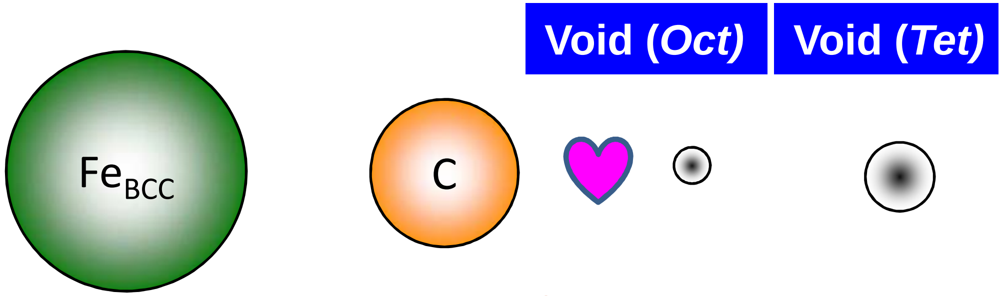
$$r^{Fe}_{BCC} = 1.258\,\mathring{A}$$

Size of the TV

$$x^{Fe}_{BCC}(d.tet) = 0.364\,\mathring{A}$$

Size of the OV

$$x^{Fe}_{BCC}(d.oct) = 0.195\,\mathring{A}$$



Relative sizes of voids w.r.t atoms

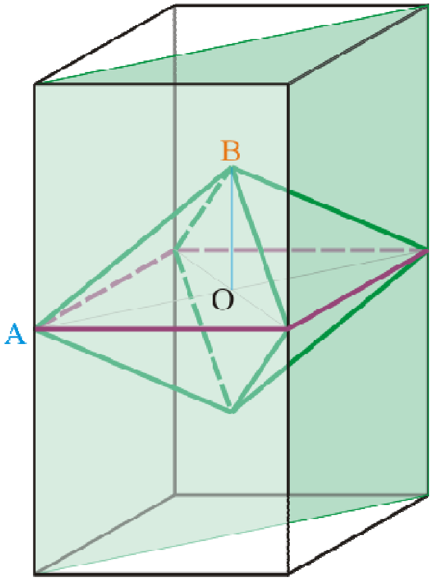
Remember

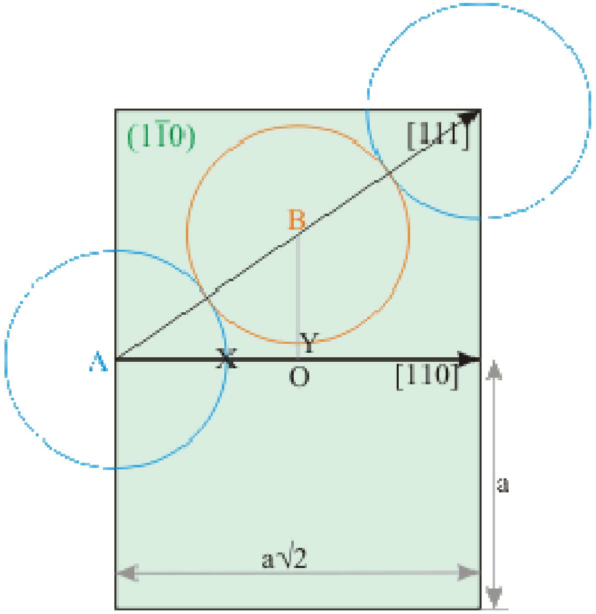
- ❑ **FCC** Size of the largest atom which can fit into the tetrahedral is 0.225 and octahedral void is 0.414
- ❑ **BCC** Size of the largest atom which can fit into the *d.tetrahedral* is 0.29 and *d.octahedral* void is 0.154

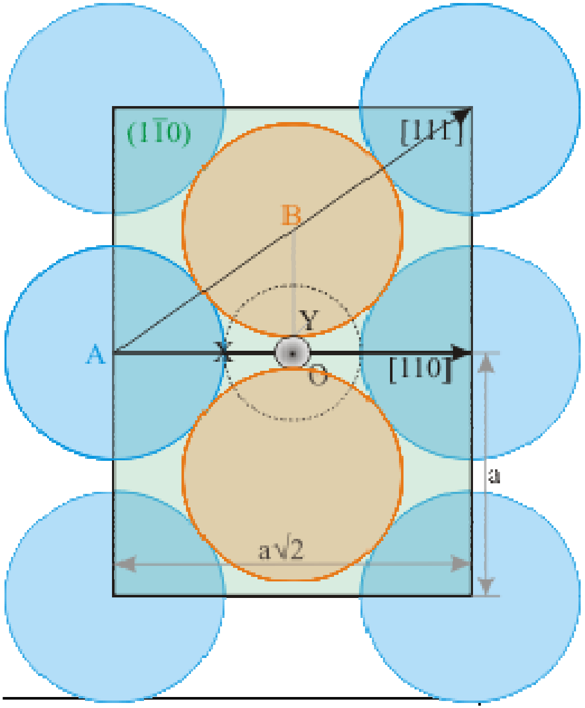
Why concentration of carbon in α-Fe with BCC structure is less than γ-Fe with FCC structure?

- NOW LET US CONSIDER THE BCC UNIT CELL (α - Fe)
- Packing factor of BCC lattice 0.68. So total void in a BCC unit cell is higher than FCC cell.
- However, there are 12 (6 per atom) tetrahedral and 6 (3 per atom) octahedral voids present. This number is higher than the number of voids present in a FCC unit cell.
- Unlike voids in FCC lattice, in a BCC lattice the voids are distorted. That means if an atom sits in a void, it will not touch all the host atoms.
- The ratio of the radius of tetrahedral void to atom is 0.29 and the radius of octahedral void to atom is 0.155.
- The ratio of the radius of the C atom (size is 77 pm) to Fe (when it has BCC crystal) is 0.612. So it is expected that in a BCC unit cell, impurities should prefer tetrahedral voids.
- However, although the octahedral void size is small, planar radius which has 4 atoms on the same plane is 79.6 pm, which is larger that the C atom size. That means it needs to distort only other two atoms.
- On the other hand if C sits in the tetrahedral void it has to distort all four atoms. So in α – Fe with BCC unit cell C occupies the octahedral voids
- Now the octahedral void size in g-Fe (FCC) is higher than a-Fe (BCC). So naturally the distortion in a BCC cell will be higher and the activation energy for impurities to occupy a void in a BCC cell also will be higher.
- This is the reason that we find much lower solubility limit of C in a-Fe.

Why carbon preferentially sits in the apparently smaller octahedral void in BCC ?







Ignoring the atom sitting at B and assuming the interstitial atom touches the atom at A

$$OA = r + x_A = \frac{\sqrt{2}a}{2}$$

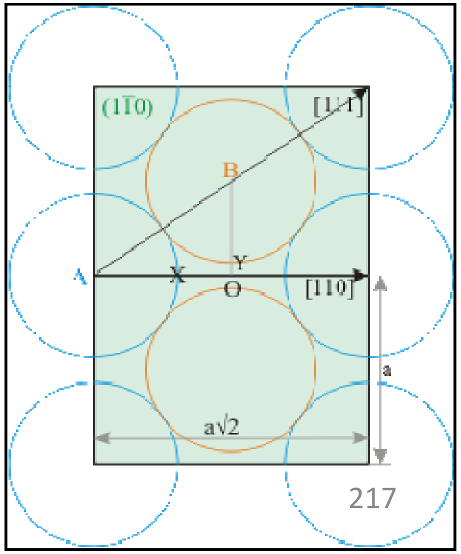
$$r_{BCC}^{Fe} = 1.258\ \mathring{A}$$

$$r + x_A = \frac{2\sqrt{6}\,r}{3}$$

$$BCC : \sqrt{3}a = 4r$$

$$\frac{x_A}{r} = \left(\frac{2\sqrt{6}}{3} - 1\right) = 0.6329$$

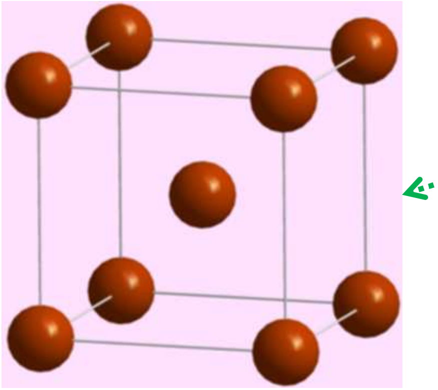
$$OX = x_A = 0.796\ \mathring{A} \qquad OY = x_B = 0.195\ \mathring{A} \qquad x_{BCC}^{Fe}(d.tet) = 0.364\ \mathring{A}$$



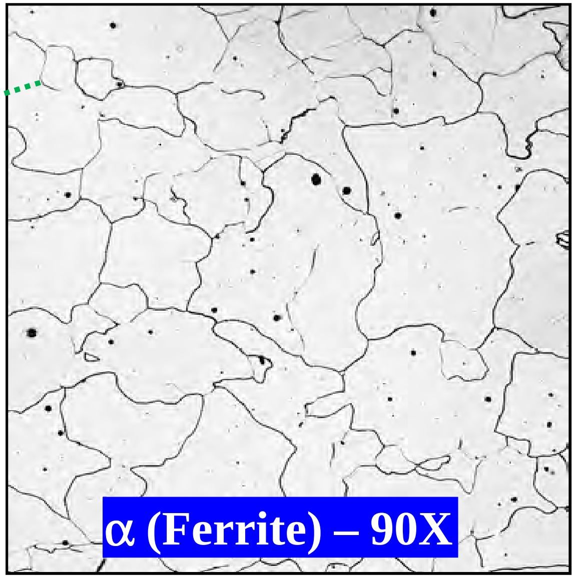
Characteristics of phases appeared in Fe-Fe_3C phase diagram

Ferrite (α)

- It is an interstitial solid solution of a small amount of carbon dissolved in α iron. The maximum solubility is 0.025%C at 723°C and it dissolves only 0.008%C at room temperature. *It is the softest structure that appears on the diagram.*
- *Ferrite is ferromagnetic at low temperatures but loses its magnetic properties with the rise of temperatures with major loss at curies temperatures, 768*°C and above this temperature, it becomes non magnetic (paramagnetic).
- The crystal structure of ferrite (α) is B.C.C
- Tensile strength – 245 Mpa, Yield strength 118 Mpa
- Elongation – 40-50% in 2 in.
- Hardness - 95 VPN



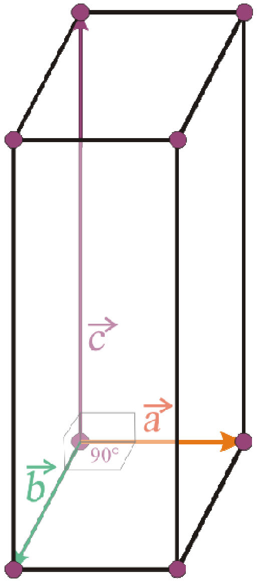
α(Ferrite) contains B.C.C structure



α (Ferrite) – 90X

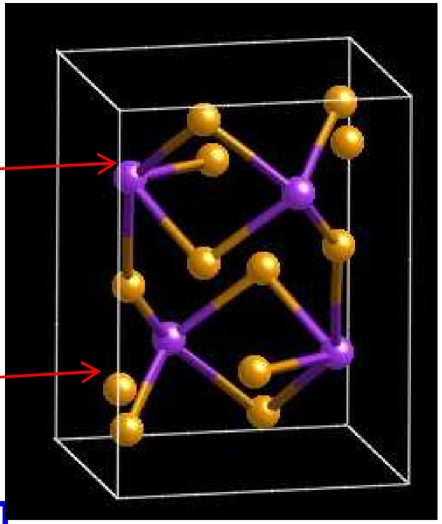
Cementite (Fe_3C)

- Cementite or iron carbide, chemical formula Fe_3C, contains 6.67%C by weight and it is a metastable phase.
- It is typically hard and brittle interstitial compound of low tensile strength (35 Mpa) but high compressive strength and high hardness ~800VPN.
- It is the hardest structure that appears on the diagram.
- It has a complex orthorhombic crystal structure with 12 iron atoms and 4 carbon atoms per unitcell.
- It is slightly ferromagnetic up to 210ºC and paramagnetic above it. Melting point around 1227ºC.



Orthorhombic

$a \neq b \neq c$
$\alpha = \beta = \gamma = 90^\circ$



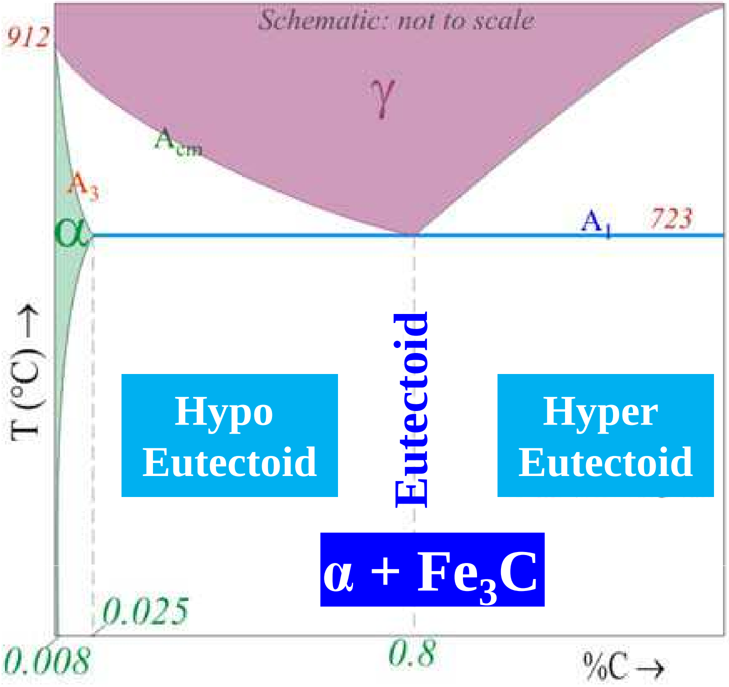
Carbon (4 atoms)

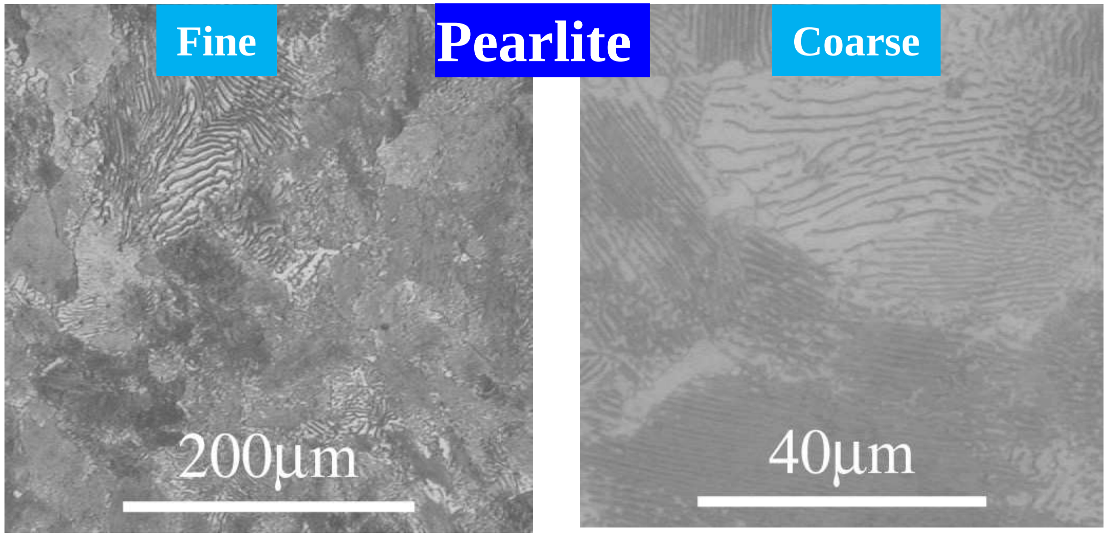
Iron (12 atoms)

Cementite network

Pearlite ($\alpha+Fe_3C$)

- ❑ Pearlite is the eutectoid mixture containing 0.80 %C and is formed at 723ºC on very slow cooling.
- ❑ It is very fine platelike or lamellar mixture of ferrite and cementite. The fine fingerprint mixture called pearlite is shown in below figure.
- ❑ The weight % of these two phases are thus in ratio 8:1
- ❑ Tensile strength – 120,000 psi or 825 Mpa
- ❑ Elongation – 20 percent in 2 in.
- ❑ Hardness – HRC 20, HRB 95-100, or BHN 250-300



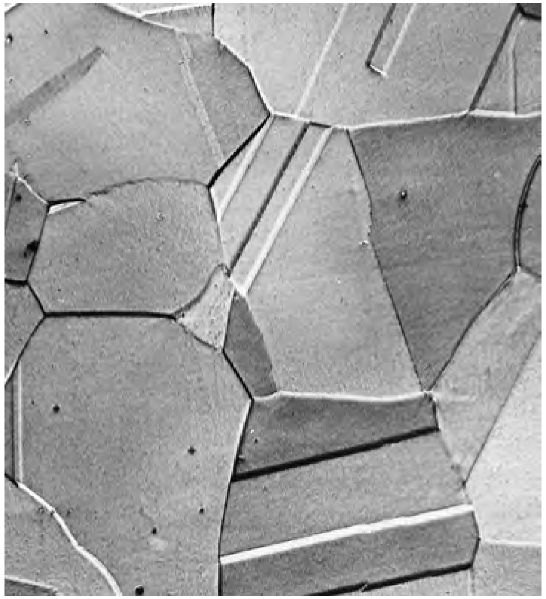


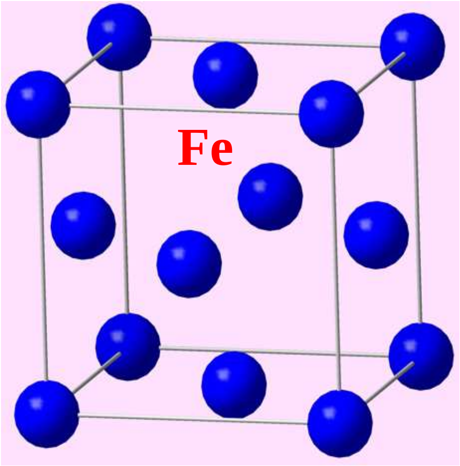
Remember…!

Pearlite is a not a phase but combination of two phases (ferrite + cementite)

Austenite (γ)

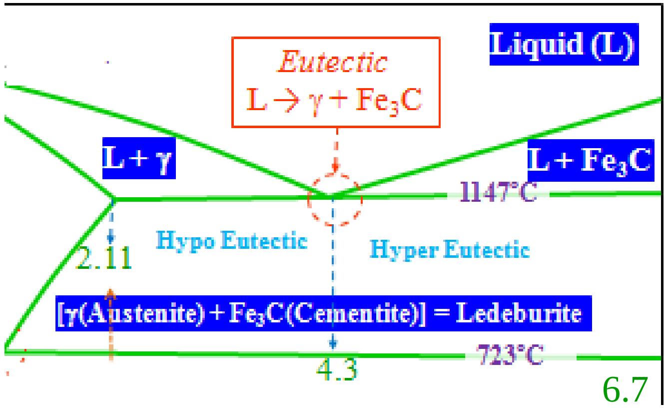
- ☐ It is an interstitial solid solution of a small amount of carbon dissolved in γ iron and has FCC crystal structure. The maximum solubility is 2.1%C at 1147ºC.
- ☐ Austenite is soft, ductile tough and malleable (FCC structure) and non magnetic (paramagnetic).
- ☐ Steels are commonly rolled and forged above about 1100ºC when they are in austenite state due to its high ductility and malleability, which is also due to its FCC structure.
- ☐ Tensile strength – 150,000 psi or 1035 Mpa
- ☐ Elongation – 10% in 2 in.
- ☐ Hardness - 395 VPN and Toughness is high.



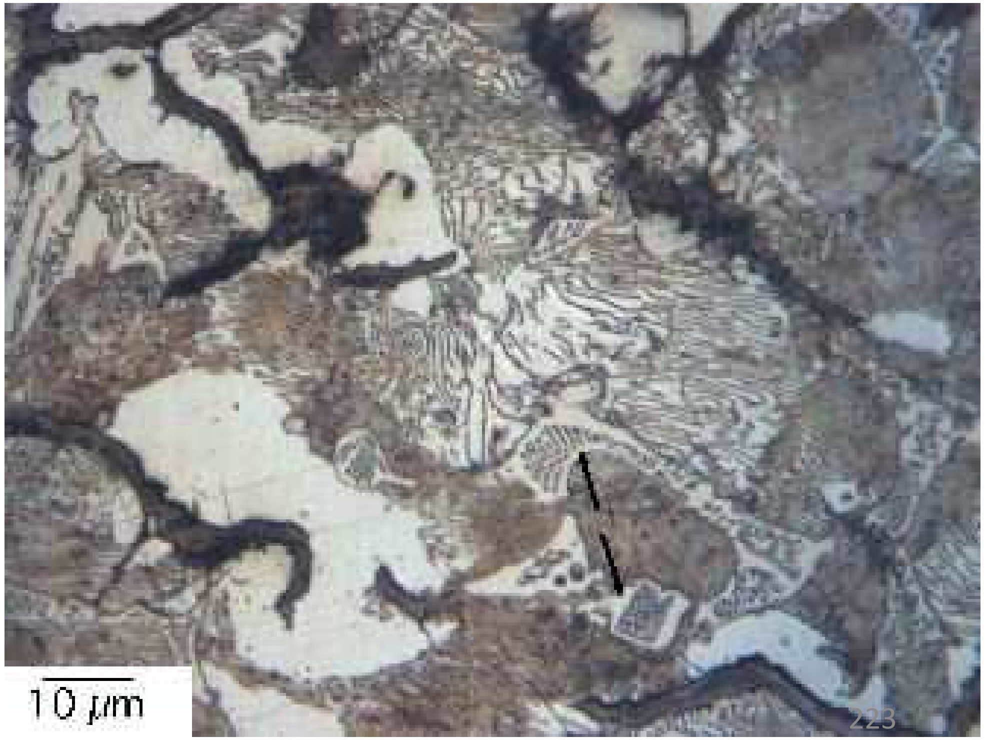


Ledeburite (γ+Fe_3C)

- Ledeburite is the eutectic mixture of austenite and cementite. It contains 4.3%C and is formed at 1147ºC
- Structure of ledeburite contains small islands of austenite are dispersed in the carbide phase.
- Not stable at room temperature

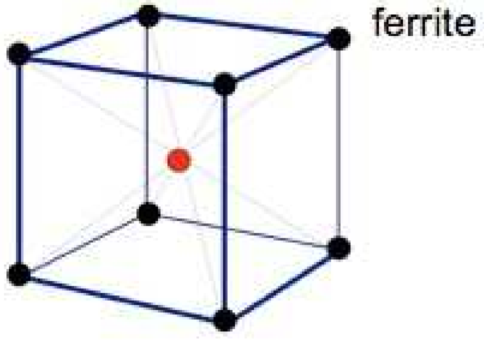


The pearlite is resolved in some regions where the sectioning plane makes a glancing angle to the lamellae. The ledeburite eutectic is highlighted by the arrows. At high temperatures this is a mixture of austenite and cementite formed from liquid. The austenite subsequently decomposes to pearlite.

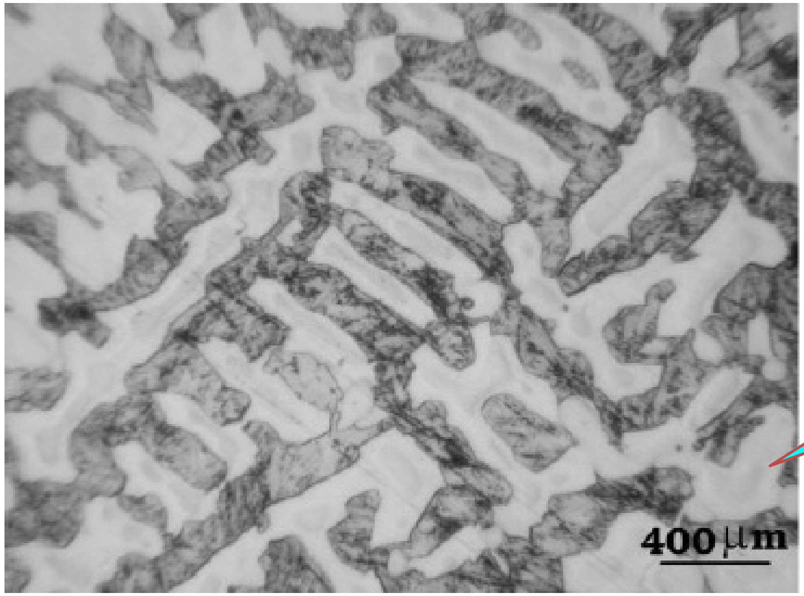


Ferrite (δ)

- ❑ Interstitial solid solution of carbon in iron of body centered cubic crystal structure. (δ iron) of higher lattice parameter (2.89Å) having solubility limit of 0.09 wt% at 1495°C with respect to austenite. The stability of the phase ranges between 1394-1539°C.
- ❑ It is a high temperature phase and is a high temperature manifestation of α ferrite.



- ❑ This is not stable at room temperature in plain carbon steel. However it can be present at room temperature in alloy steel specially duplex stainless steel.



δ-ferrite in dendrite form in as-cast Fe-0.4C-2Mn-0.5Si-2 Al0.5Cu

Invariant Reactions in Fe-Fe_3C Phase Diagram

Peritectic Reaction

- The invariant peritectic reaction in Fe-Fe_3C diagram is given by

$$\underset{0.51\%C}{L} + \underset{0.1\ \%C}{\delta\text{-ferrite}} \underset{1495^{o}C}{\overset{\text{Cool}}{\rightleftharpoons}} \underset{0.17\%C}{\text{Austenite }(\gamma)}$$

- Thus Liquid, wt% is $$L = \frac{0.16-0.1}{0.51-0.1}\times 100 = 14.63\%$$

- Thus δ ferrite, wt % is $$\delta(ferrite) = \frac{0.51-0.16}{0.51-0.1}\times 100 = 85.37\%$$

- Fe-0.16%C steel is a peritectic steel because only this steel undergoes above reaction completely.
- Peritectic reaction is of some importance during freezing of steels (carbon from 0.1 to 0.51% particularly under fast cooling conditions, when micro segregation may result, otherwise no commercial heat treatment is done in this region.
- Unfortunately these temperatures are attained during heating of steels for forging or rolling etc., then severe overheating and burning results in steels turning them to scrap form.

Eutectic Reaction

- The invariant Eutectic reaction in Fe-Fe_3C diagram is given by

$$\begin{array}{ccccc} \textbf{Liquid (L)} & \underset{\textbf{1147}^{o}\textbf{C}}{\overset{\text{Cool}}{\rightleftharpoons}} & \textbf{Austenite }(\gamma) & + & \textbf{Cementite} \\ \textbf{0.17\%C} & & \textbf{2.11\%C} & & \textbf{6.67 \%C} \end{array}$$

- Thus Austenite, wt% is $\gamma = \dfrac{6.67-4.3}{6.67-2.11} \times 100 = 51.97\%$

- Thus cementite, wt % is $Fe_3C = \dfrac{4.3-2.11}{6.67-2.11} \times 100 = 48.03\%$

- Fe-4.3%C alloy is called eutectic cast iron as it is the lowest melting point alloy, which is single phase liquid (100%) of 4.3% carbon at the eutectic temperature, 1147°C just attained and undergoes eutectic reaction completely at this constant eutectic temperature to give a mixture of two different solids, namely austenite and cementite, solidifying simultaneously. The eutectic mixture called *Ledeburite*.

- As Fe-C alloys having more than 2.11% carbon are classed as cast irons, the Fe-C alloys having carbon between 2.11 and 4.3% are called *hypo eutectic cast irons*, where as those having carbon between 4.3% and 6.67% are called *hypereutectic cast irons*. Alloys of Fe with 4.3% carbon is called *eutectic cast iron*.

Eutectoid Reaction

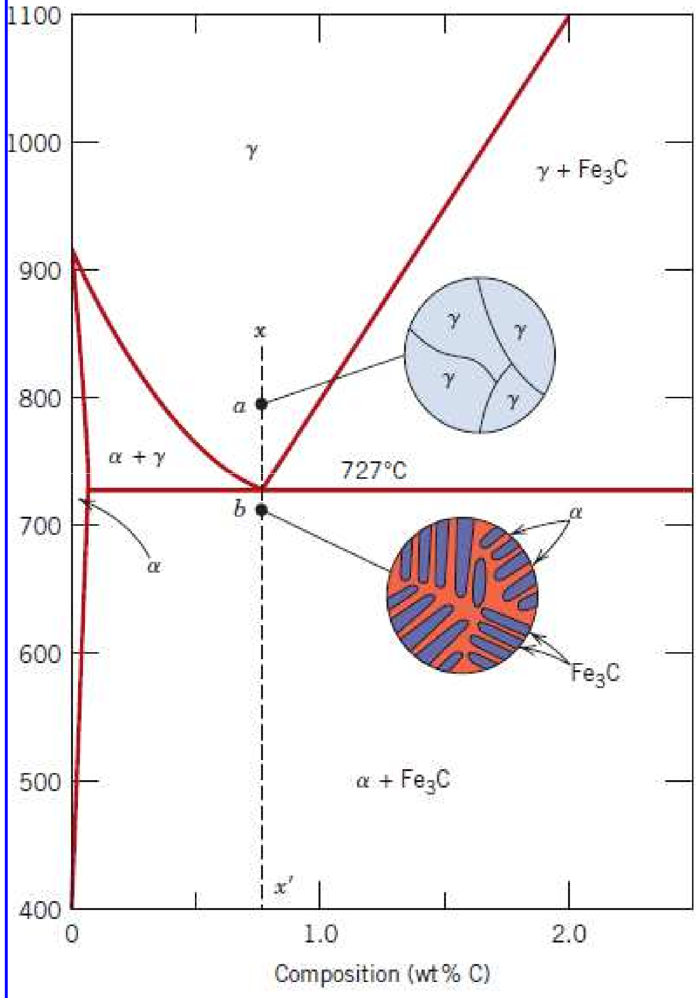
- ☐ The invariant Eutectoid reaction in Fe-Fe_3C diagram is given by

$$\underset{0.8\%C}{\textbf{Austenite }(\gamma)} \xrightleftharpoons[727^{\circ}C]{\text{Cool}} \underset{0.02\%C}{\textbf{Ferrite }(\alpha)} + \underset{6.67\ \%C}{\textbf{Cementite}}$$

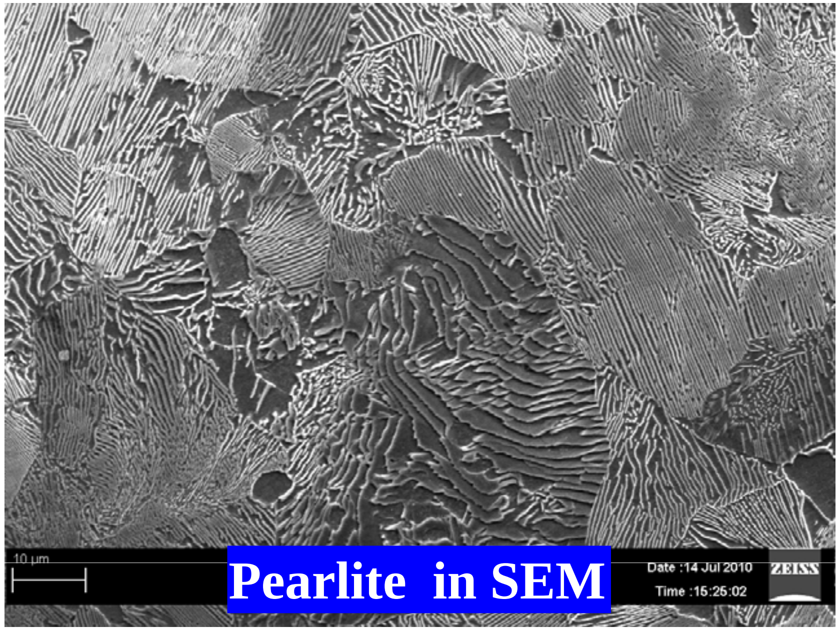
- ☐ Thus Ferrite, wt% is $$\alpha = \frac{6.67-0.8}{6.67-0.02} \times 100 = 88\%$$
- ☐ Thus cementite, wt % is $$Fe_3C = \frac{0.8-0.02}{6.67-0.02} \times 100 = 12\%$$
- ☐ During cooling austenite of 0.8% at constant eutectoid temperature, 727°C undergoes eutectoid transformation to form a mixture of ferrite (C%=0.02%) and cementite i.e., there are alternate lamellae of ferrite and cementite .
- ☐ This eutectoid mixture of ferrite and cementite is called PEARLITE, because of its pearly appearance under optical microscope.
- ☐ The weight % of these phases are thus 8:1. The densities are (α-7.87 gm/cm^3) and (Fe_3C- -7.70 gm/cm^3) are quite comparable. Thus the Volume % also approx 8:1. Thus ferrite lamilla is 8 times thicker than cementite lamilla. as the two boundaries of cementite plate are close together, they may not resolved separately under the microscope, instead of two lines, it appears a single dark line.

Eutectoid Reaction

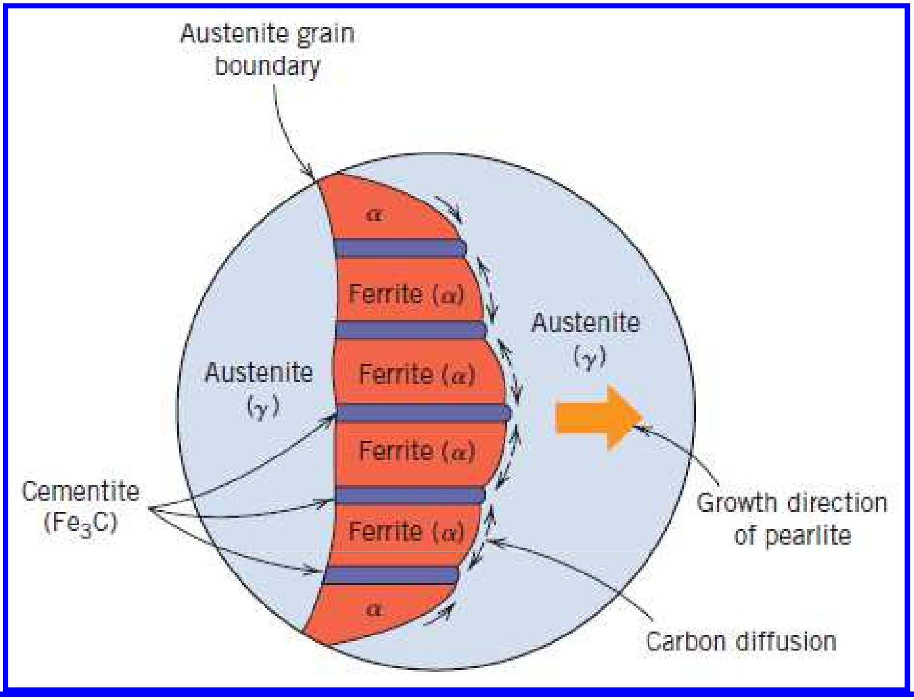
- Phase changes that occur upon passing from the γ region into the α+ Fe_3C phase field.
- Consider, for example, an alloy of eutectoid composition (0.8%C) as it is cooled from a temperature within the γ phase region, say 800ºC – that is, beginning at point ‘a’ in figure and moving down vertical xx’. Initially the alloy is composed entirely of the austenite phase having composition 0.8 wt.% C and then transformed to α+ Fe_3C [pearlite]
- The microstructure for this eutectoid steel that is slowly cooled through eutectoid temperature consists of alternating layers or lamellae of the two phases α and Fe_3C
- The pearlite exists as grains, often termed “colonies”; within each colony the layers are oriented in essentially the same direction, which varies from one colony to other.
- The thick light layers are the ferrite phase, and the cementite phase appears as thin lamellae most of which appear dark.



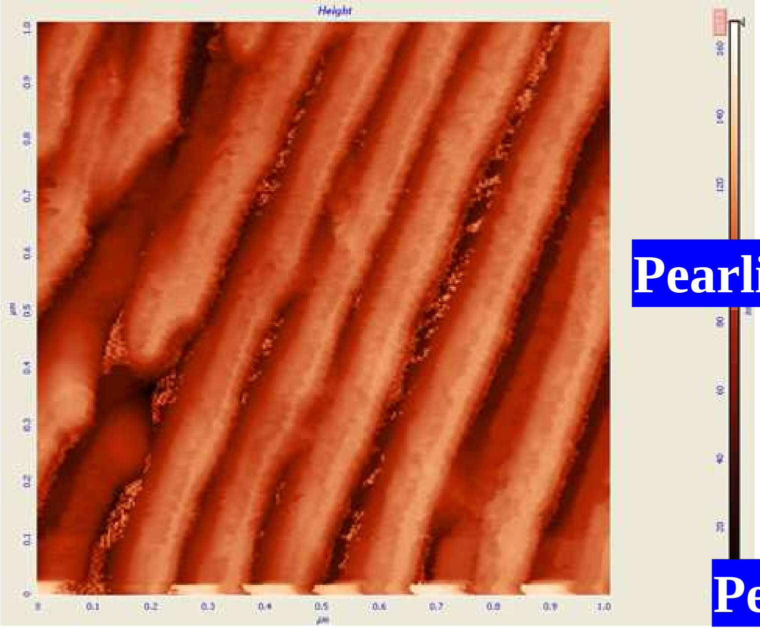
Eutectoid Structure



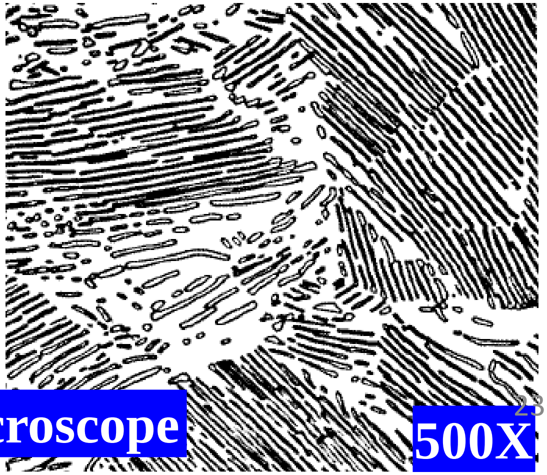
Pearlite in SEM



Schematic representation of the formation of pearlite from austenite; direction of carbon diffusion indicated by arrows



Pearlite in AFM

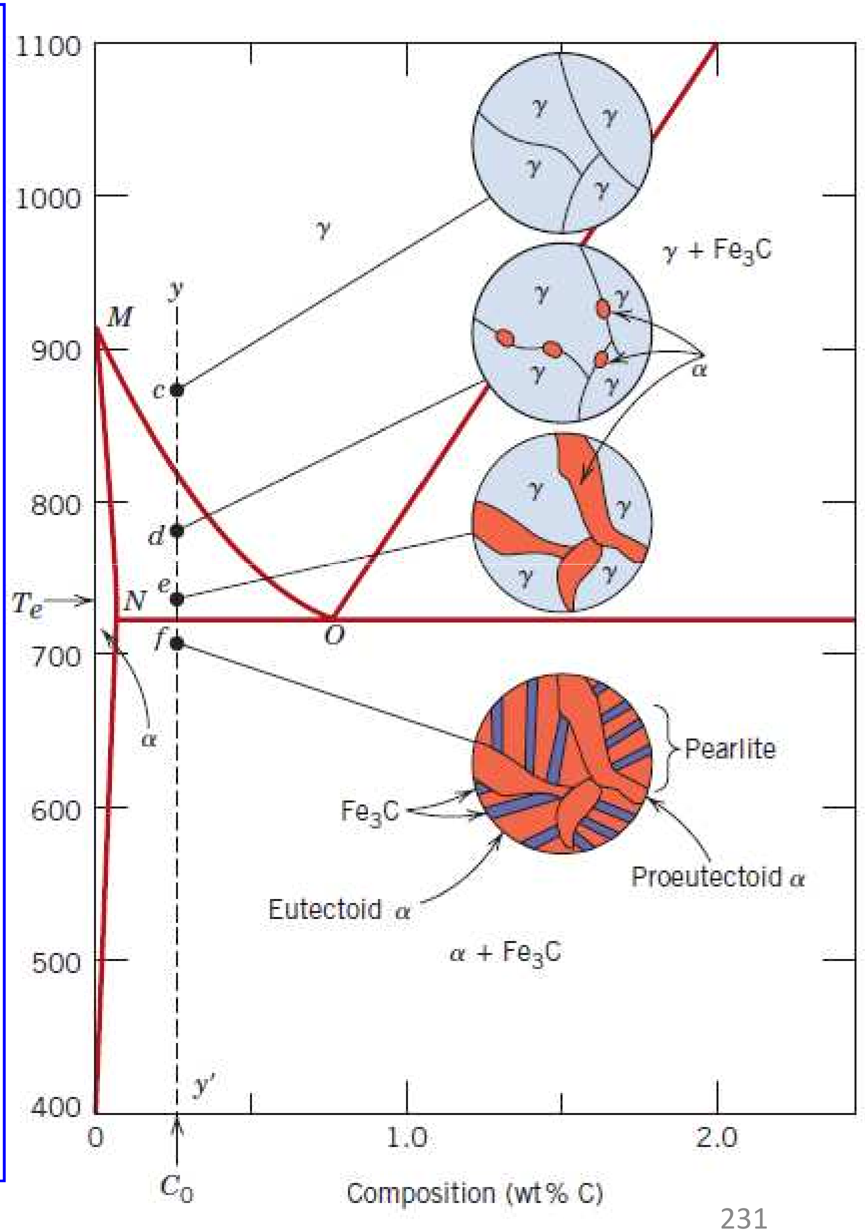


Pearlite in optical microscope

500X

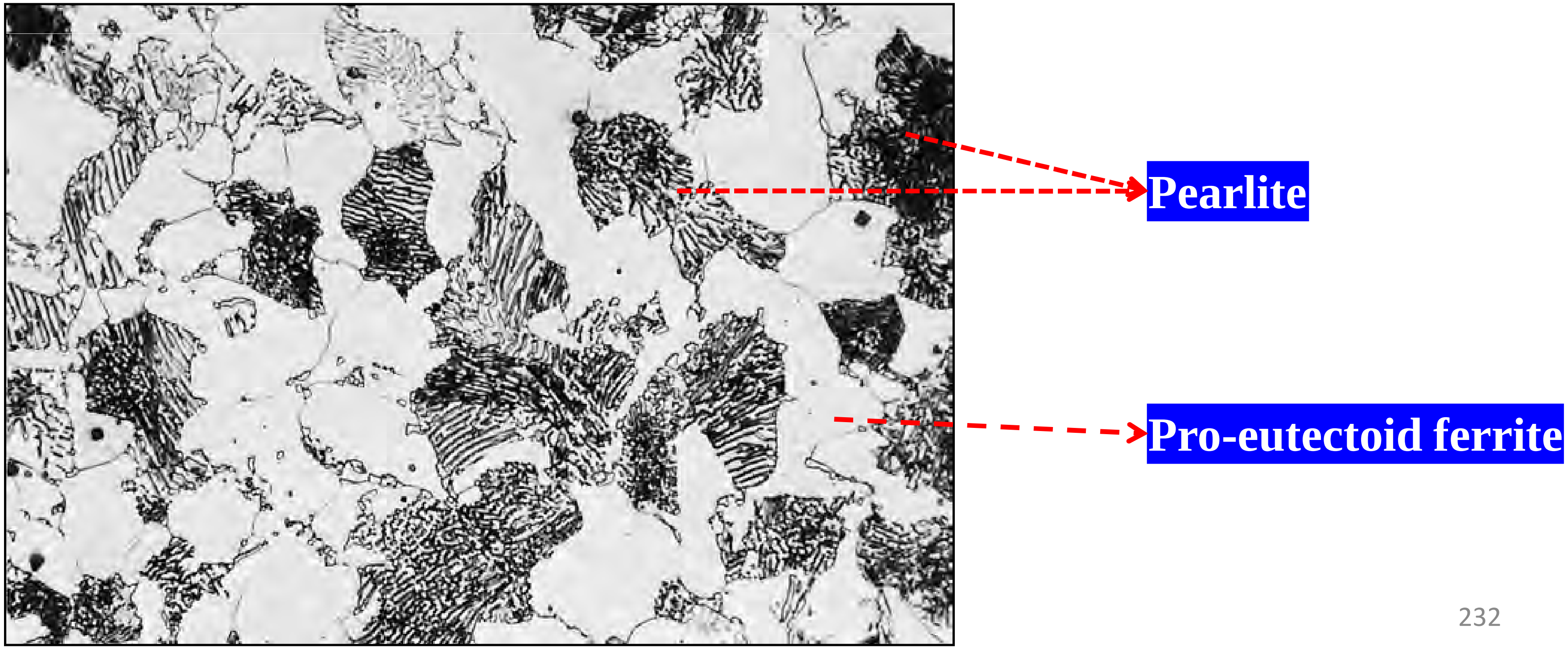
Hypo Eutectoid Region

- ❑ Hypo eutectoid region – 0.008 to 0.8 %C
- ❑ Consider vertical line yy’ in figure, at about 875ºC, point c, the microstructure will consist entirely of grains of the γ phase.
- ❑ In cooling to point d, about 775ºC, which is within the α+γ phase region, both these phases will coexist as in the schematic microstructure Most of the small α particles will form along the original γ grain boundaries.
- ❑ Cooling from point d to e, just above the eutectoid but still in the α+γ region, will produce an increased fraction of the α phase and a microstructure similar to that also shown: the α particles will have grown larger.



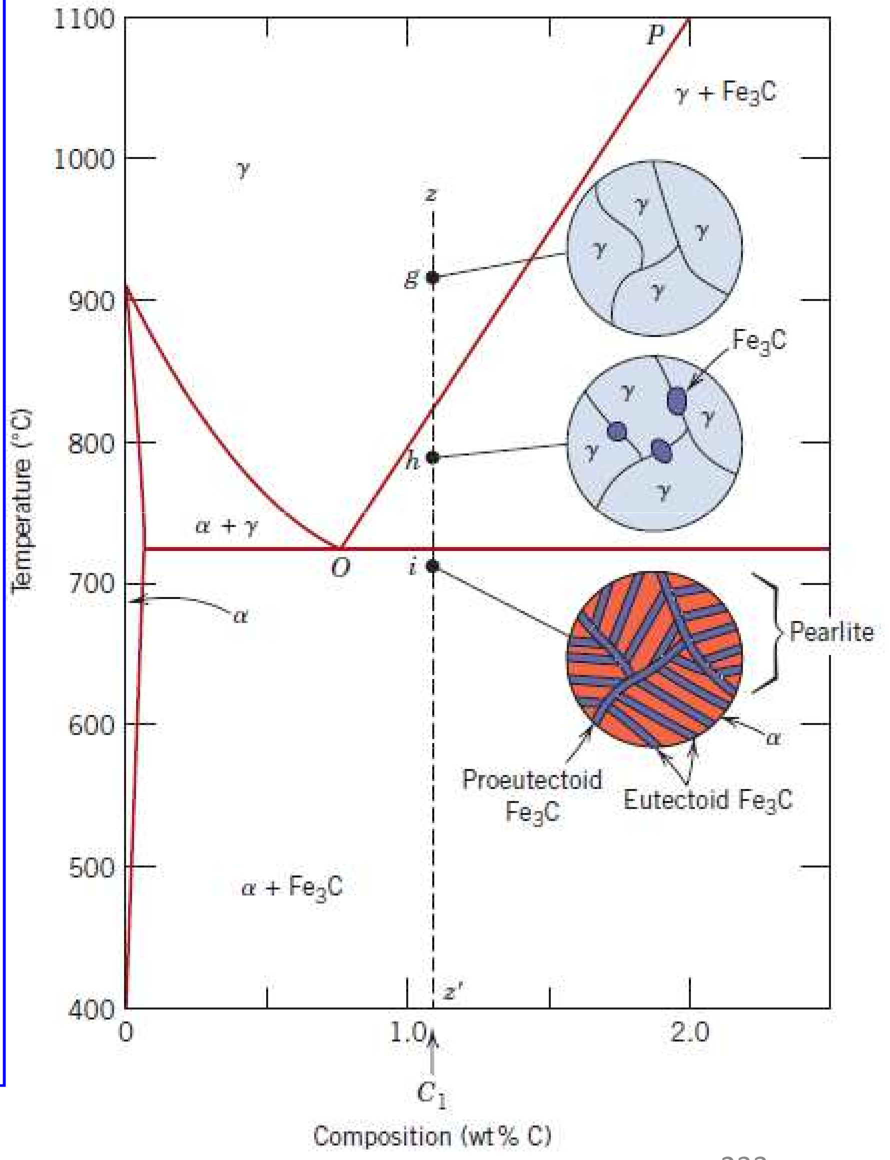
Hypo Eutectoid Region

- ❑ Just below the eutectoid temperature, at point f, all the γ phase that was present at temperature e will transform pearlite. Virtually there is no change in α phase that existed at point e in crossing the eutectoid temperature – it will normally be present as a continuous matrix phase surrounding the isolated pearlite colonies.
- ❑ Thus the ferrite phase will be present both in the pearlite and also as the phase that formed while cooling through the α+γ phase region. The ferrite that is present in the pearlite is called eutectoid ferrite, whereas the other, is termed proeutectoid (meaning pre- or before eutectoid) ferrite.



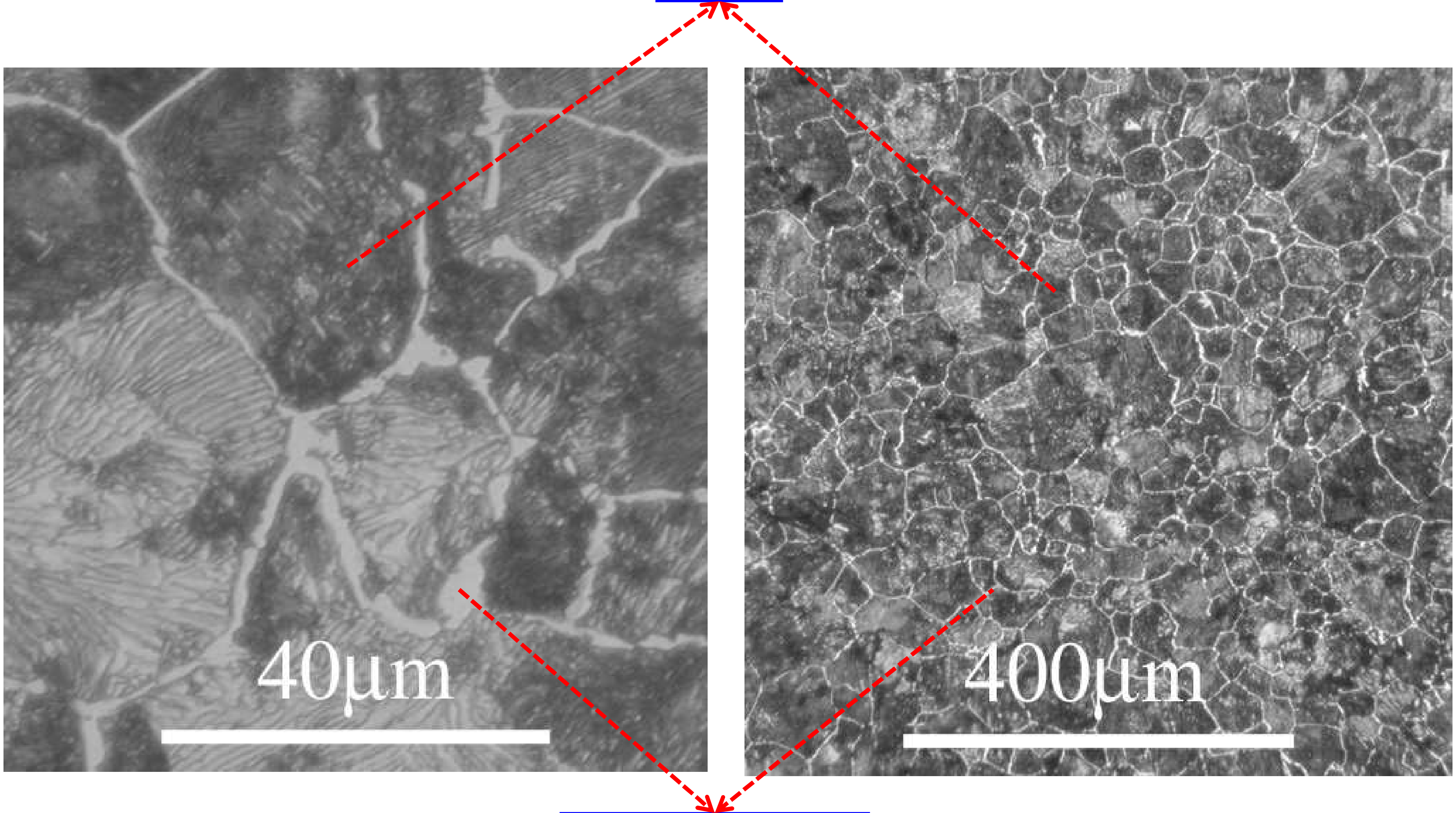
Hyper Eutectoid Region

- Hyper eutectoid region – 0.8 to 2.1 %C
- Consider an alloy of composition C_1 in figure that, upon cooling, moves down the line zz'. At point g only the γ phase will be present and the microstructure having only gamma grains.
- Upon cooling into the γ+ Fe_3C phase field – say to point h – the cementite phase will began to form along the initial γ grain boundaries, similar to the α phase in point d. this cementite is called *proeutectoid cementite* that which forms before the eutectoid reaction.
- As the temperature is lowered through the eutectoid to point I, all remaining austenite of eutectoid composition is converted into pearlite; thus the resulting microstructure consists of pearlite and proeutectoid cementite as microconstituents.



Hypo Eutectoid Region

Pearlite



Cementite network

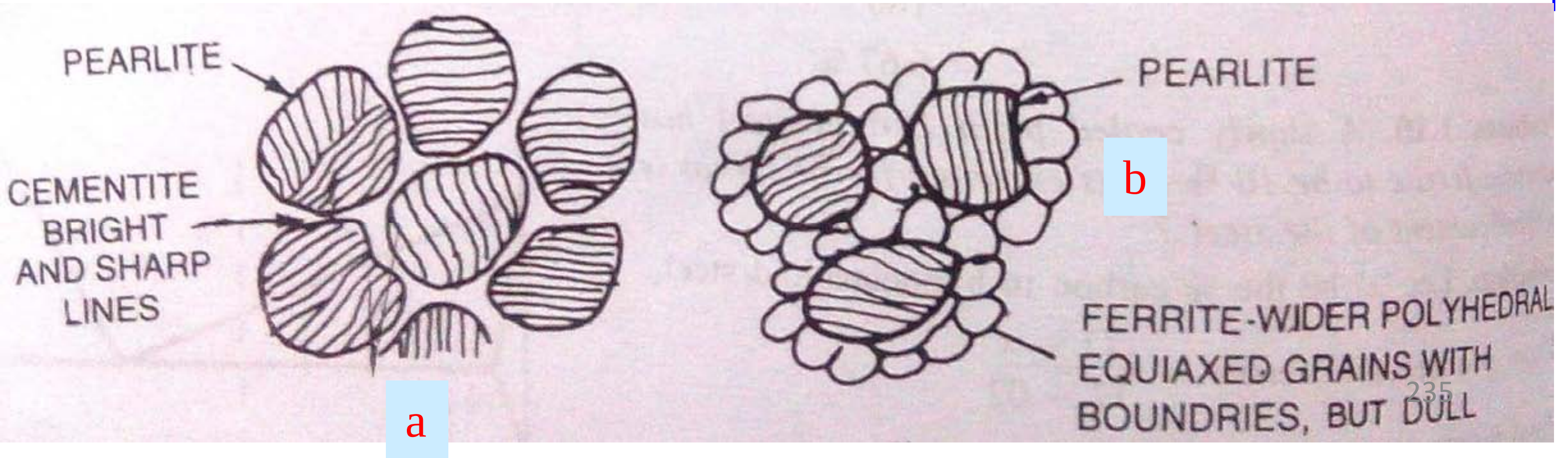
Concept of Primary Ferrite & Primary Cementite

- When the carbon content of steels is much away from the eutectoid carbon, then distinction can easily be made between hypoeutectoid steels and the hypereutectoid steel. Nital is the common etching agent.

Shape of the phases

- Proeutectoid ferrite appears as grains which are quite wide, polyhedral and the grain boundaries in between neighboring ferrite grains can be seen.
- The films of pro eutectoid cementite generally are much thinner, have irregular outlines and bounded by sharp lines. These are present as network of needles or platelets. Cementite looks much brighter and sharp because of its hardness and etching characteristics.
- Major difference is cementite is present as network at the grain boundaries of pearlite (at RT), whereas ferrite is present as grains (equiaxed polyhedral grains) with grain boundaries in between ferrite grains (if etched properly).

Microstructures of (a) Hypereutectoid steel (b) Hypoeutectoid steel

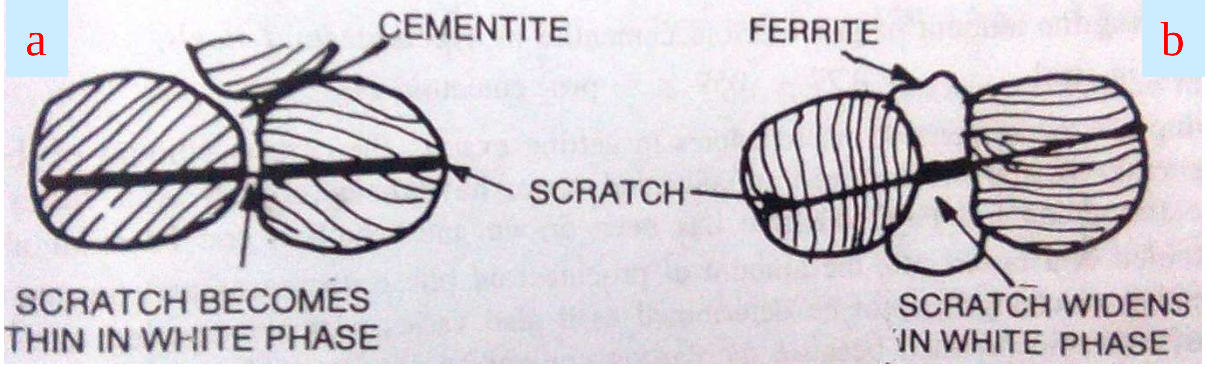


Concept of Primary Ferrite & Primary Cementite

Relative Hardness

- Cementite is very hard (~800 VPN) and ferrite is (~95 VPN). Micro hardness testing can be done to distinguish between ferrite and cementite.
- A simple scratch test can be done. Make a scratch on the polished and etched surface of the steel and then, examine the point of the scratch where it enters the white proeutectoid phase from the pearlite.
- If the scratch widens on entering, it is the soft phase ferrite, and if it thins in white phase, then the white phase is much harder than pearlite, i.e, it is cementite.

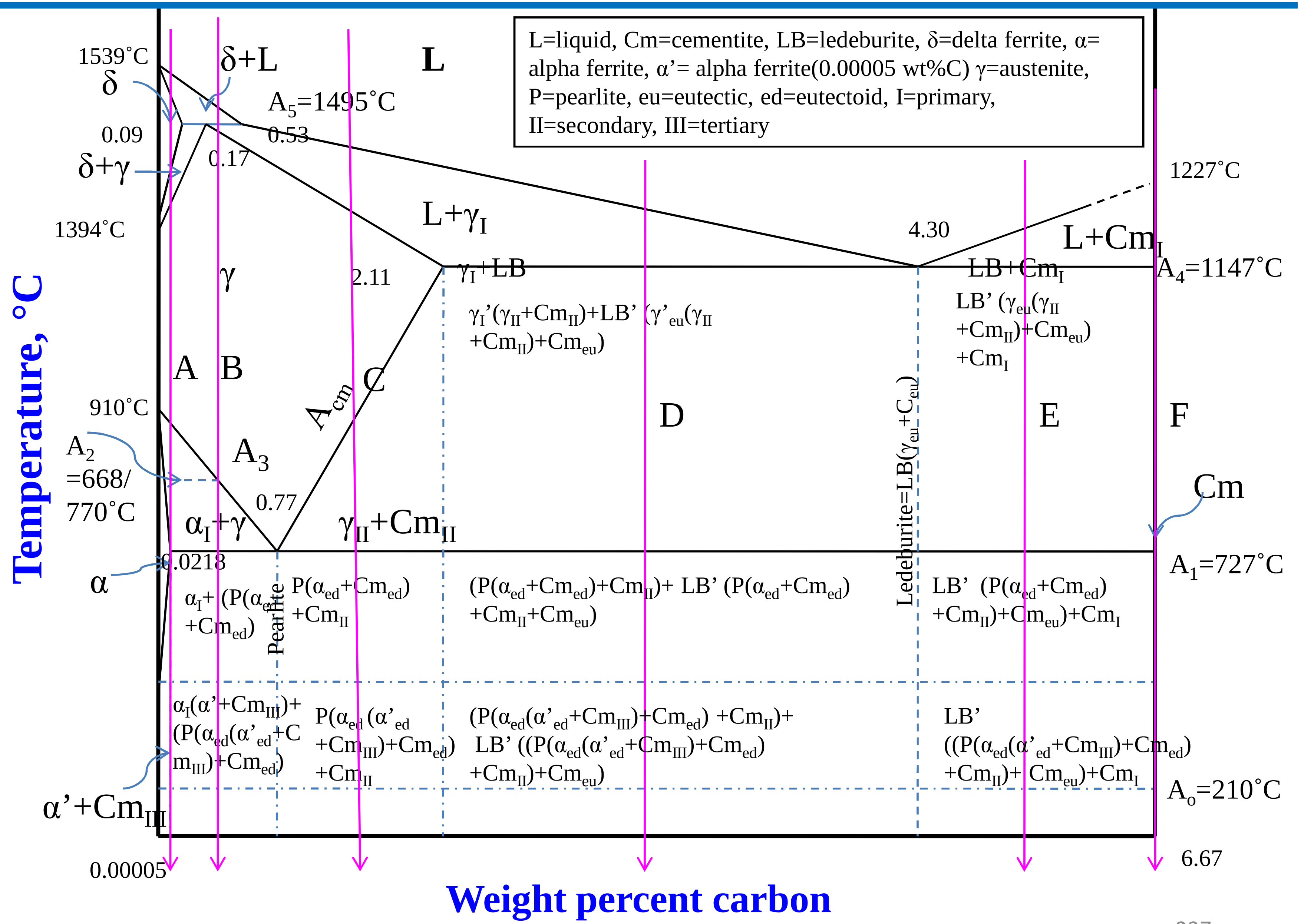
Relative hardness of ferrite and cementite distinguishes them (a) Hypereutectoid steel (b) Hypoeutectoid steel



Special Etchants

- Nital etching causes cementite as well as ferrite to look white under microscope
- A sodium picrate solution used either boiling or electrolytically, darkens Fe_3C but not ‘α’
- Another etchant based on sodium thiosulphate and ammonium nitrate gives colors ferrite but not cementite.

Fe-Fe$_3$C phase diagram (microstructural aspects)



L=liquid, Cm=cementite, LB=ledeburite, δ=delta ferrite, α= alpha ferrite, α'= alpha ferrite(0.00005 wt%C) γ=austenite, P=pearlite, eu=eutectic, ed=eutectoid, I=primary, II=secondary, III=tertiary

Evolution of Microstructures on equilibrium cooling

- Sequence of evolution of microstructure can be described by the projected cooling on compositions A, B, C, D, E, F.
- At composition A

$$L \rightarrow \delta + L \rightarrow \delta \rightarrow \delta + \gamma \rightarrow \gamma \rightarrow \gamma + \alpha_I \rightarrow \alpha \rightarrow \alpha^{'} + Cm_{III}$$

- At composition B

$$L \rightarrow \delta + L \rightarrow L + \gamma_I \rightarrow \gamma \rightarrow \alpha_I + \gamma \rightarrow \alpha_I + (P(\alpha_{ed} + Cm_{ed}) \rightarrow \alpha_I(\alpha^{'} + Cm_{III}) + P(\alpha_{ed}(\alpha_{ed}^{'} + Cm_{III}) + Cm_{ed})$$

- At composition C

$$L \rightarrow L + \gamma_I \rightarrow \gamma \rightarrow \gamma_{II} + Cm_{II} \rightarrow P(\alpha_{ed} + Cm_{ed}) + Cm_{II} \rightarrow P(\alpha_{ed}(\alpha_{ed}^{'} + Cm_{III}) + Cm_{ed}) + Cm_{II}$$

- At composition D

$$L \rightarrow L + \gamma_I \rightarrow \gamma_I + LB \rightarrow \gamma_I^{'}(\gamma_{II} + Cm_{II}) + LB^{'}(\gamma_{eu}^{'}(\gamma_{II} + Cm_{II}) + Cm_{eu})$$

$$\rightarrow (P(\alpha_{ed} + Cm_{ed}) + Cm_{II}) + LB^{'}(P(\alpha_{ed} + Cm_{ed}) + Cm_{II} + Cm_{eu}$$

$$\rightarrow (P(\alpha_{ed}(\alpha_{ed}^{'} + Cm_{III}) + Cm_{ed}) + Cm_{II}) + LB^{'}((P(\alpha_{ed}(\alpha_{ed}^{'} + Cm_{III}) + Cm_{ed}) + Cm_{II}) + Cm_{eu})$$

Evolution of Microstructures on equilibrium cooling

- Sequence of evolution of microstructure can be described by the projected cooling on compositions A, B, C, D, E, F.
- At composition E

$$L \rightarrow L + Cm_I \rightarrow LB(\gamma_{eu} + Cm_{eu} + Cm_I) \rightarrow LB^{'}(\gamma_{eu}(\gamma_{II} + Cm_{II}) + Cm_{eu}) + Cm_I$$

$$\rightarrow LB^{'}(P(\alpha_{ed} + Cm_{ed}) + Cm_{II}) + Cm_{eu}) + Cm_I$$

$$\rightarrow LB^{'}((P(\alpha_{ed}(\alpha^{'}_{ed} + Cm_{III}) + Cm_{ed}) + Cm_{II}) + Cm_{eu}) + Cm_I$$

- At composition F

$$L \rightarrow Fe_3C$$

Application of Lever rule in Fe-Fe_3C phase diagram

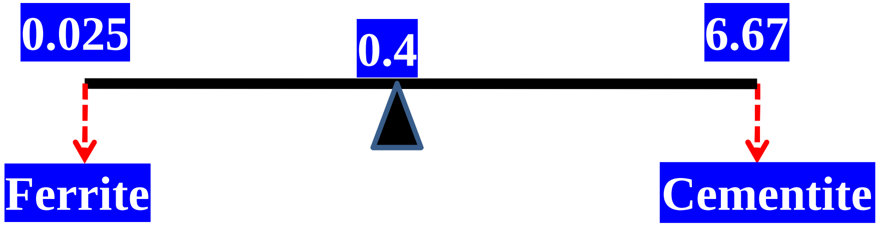
Solved Example

For a 99.6 wt% Fe-0.40 wt% C at a temperature just below the eutectoid, determine the following:

a) The amount of Fe_3C, ferrite (α) and pearlite

b) The amount of pearlite and proeutectoid ferrite (α)

a) The amount of Fe_3C and ferrite (α)



0.025

0.4

6.67

Ferrite

Cementite

Percentage of $\mathbf{Fe_3C}$ = $\dfrac{0.4-0.025}{6.67-0.025} * 100$

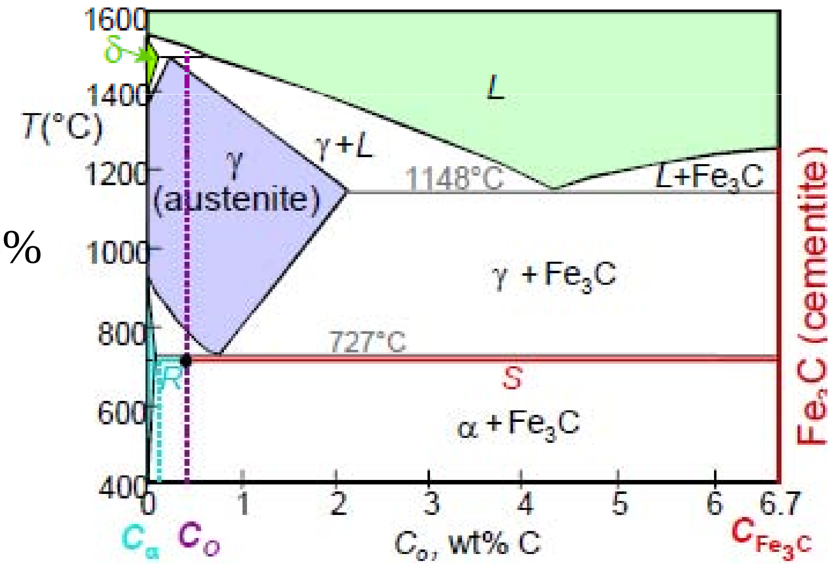
Percentage of Fe_3C in 0.4 %C steel is 5.64 %

Percentage of Ferrite (α) in 0.4 %C steel = (100- 5.64)%

Percentage of ferrite in 0.4 %C steel = 94.36%

or

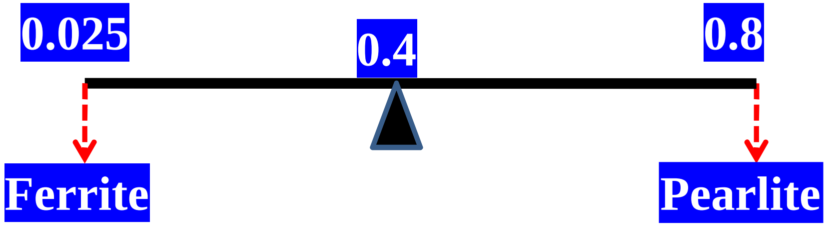
Percentage of ferrite$=\dfrac{6.67-0.4}{6.67-0.025} * 100$ **= 94.36%**



b) Phase fraction of pearlite and proeutectoid ferrite (α)

$$Percentage\ of\ pearlite = \frac{0.4 - 0.025}{0.8 - 0.025} * 100$$

Percentage of pearlite = 48 %


0.025

0.4

0.8

Ferrite

Pearlite

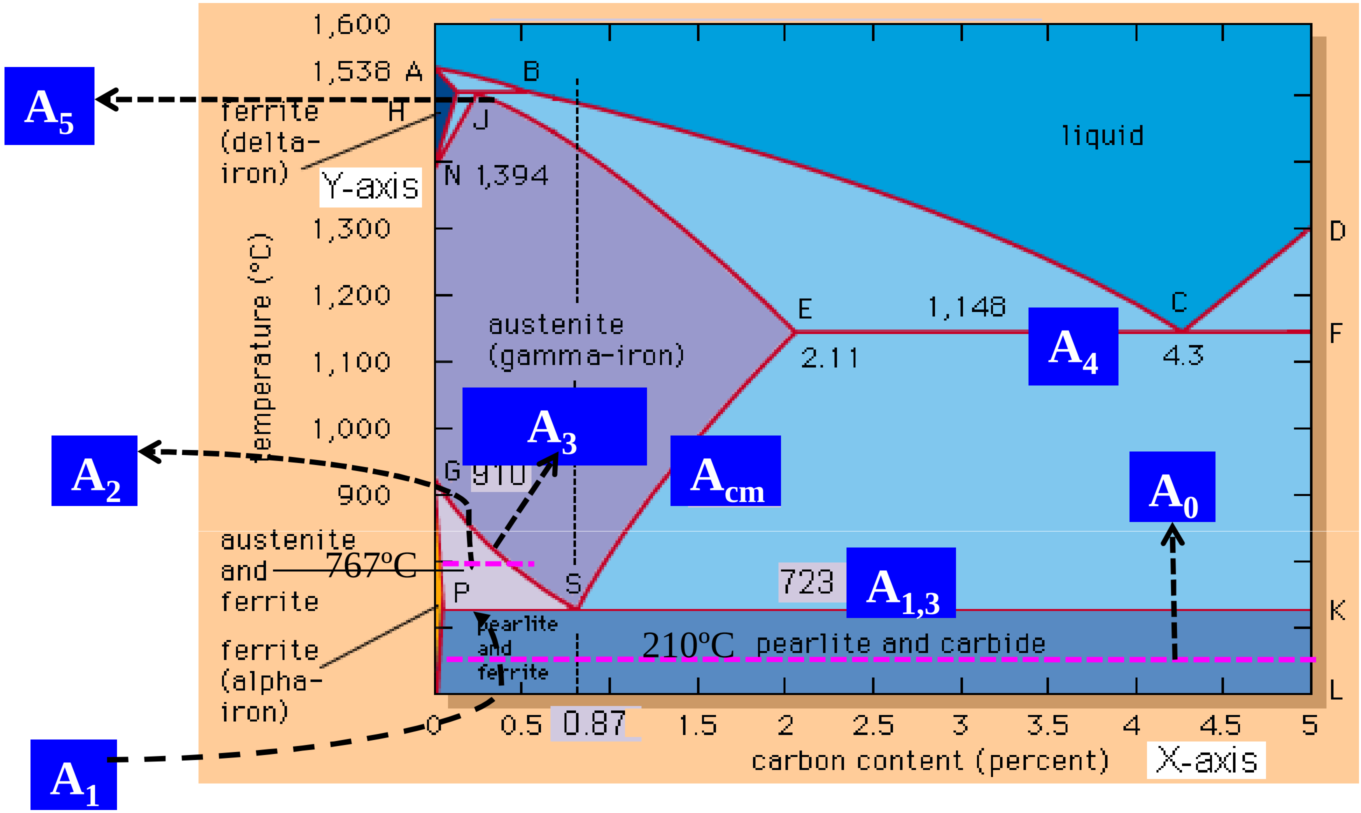
Percentage of proeutectoid ferrite (α) in 0.4 %C steel = (100- 48)%

Percentage of proeutectoid ferrite (α) = 52 %

or

$$Percentage\ of\ proeutectoid\ ferrite = \frac{0.8 - 0.4}{0.8 - 0.025} * 100 = 52\%$$

Critical Temperature lines



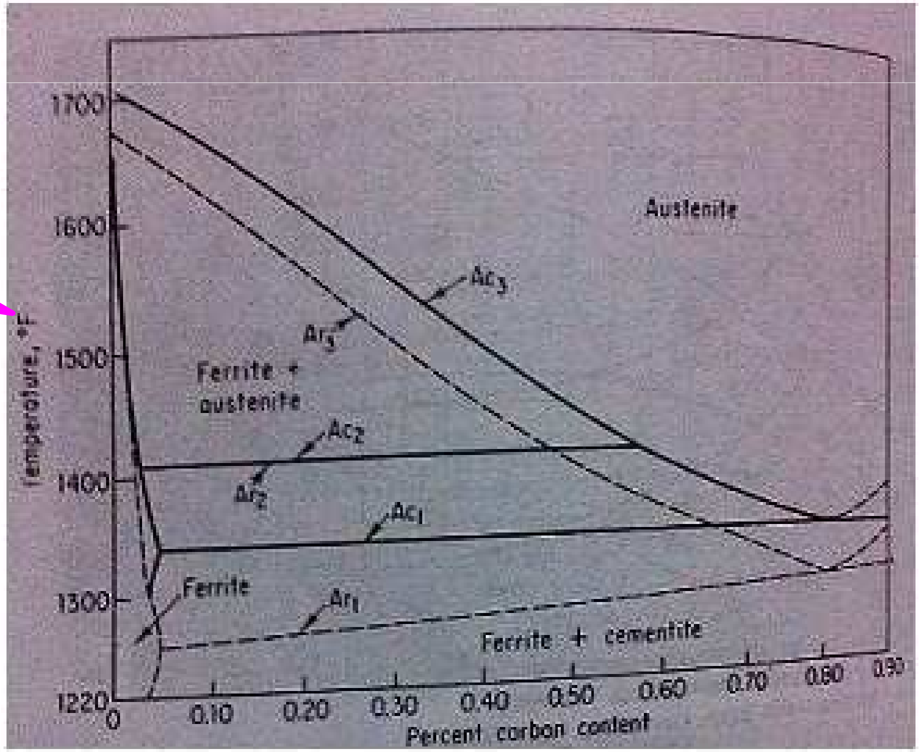
- ❑ In general, A_0 – Subcritical temperature, A_1 - lower critical temperature, A_3 - upper critical temperature, A_4 – Eutectic temperature, A_5 – Peritectic temperature and A_{cm} - γ/γ+cementite phase field boundary.
- ❑ While heating we denoted as $Ac_{1,}$ $Ac_{2,}$ Ac_3 etc., *'c' stands for chauffage (French word), which means heating* and while cooling we denoted as $Ar_{1,}$ $Ar_{2,}$ Ar_3 etc., *'r' stands for refroidissement, (French word) which means cooling.*

Critical Temperature lines

- The upper – and lower critical temperature lines are shown as single lines under equilibrium conditions and are sometimes indicated as **A_{e3}, A_{e1}** etc. When the critical lines are actually determined, it is found that they do not occur at the same temperature.
- The critical line on heating is always higher than the critical line on cooling. Therefore, the upper critical line of a hypo eutectoid steel on heating would be labeled **A_{C3}** and the same line on cooling **A_{r3}**. The rate of heating and cooling has a definite effect on the temperature gap between these lines.

The results of thermal analysis of a series of carbon steels with an average heating and cooling rate of 11°F/min are shown in figure.

Final word…! with infinitely slow heating and cooling they would probably occur at exactly the same temperature.



Effect of alloying elements on Fe-Fe_3C phase diagram

Based on stabilizing Austenite

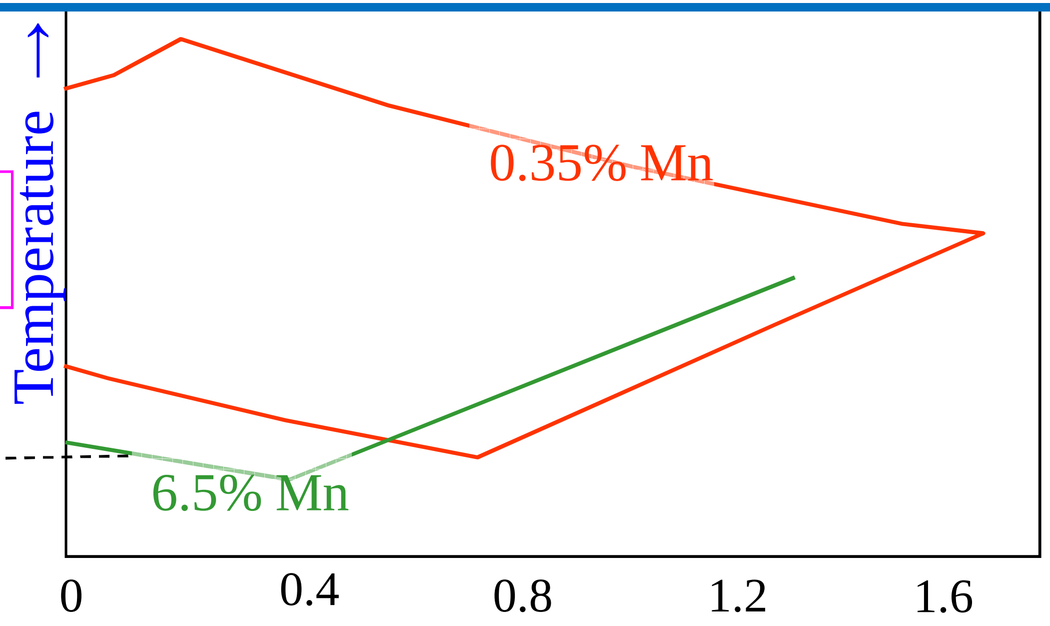
- ❑ Mn, Ni, Co, Cu, Zn increase the range in which γ-phase, or austenite is stable [by raising A_4 and lowering A_3 temperature and also tend to retard the separation of carbides.
- ❑ These elements have γ-phase FCC crystal structure (or similar structure) in which these elements are more soluble than ferrite, and that is why, in the (α+γ) two phase equilibrium, these segregate in austenite in preference to ferrite.
- ❑ Elements like carbon and nitrogen (interstitial solid solution forming elements) are also austenite stabilizers.

Based on stabilizing Ferrite

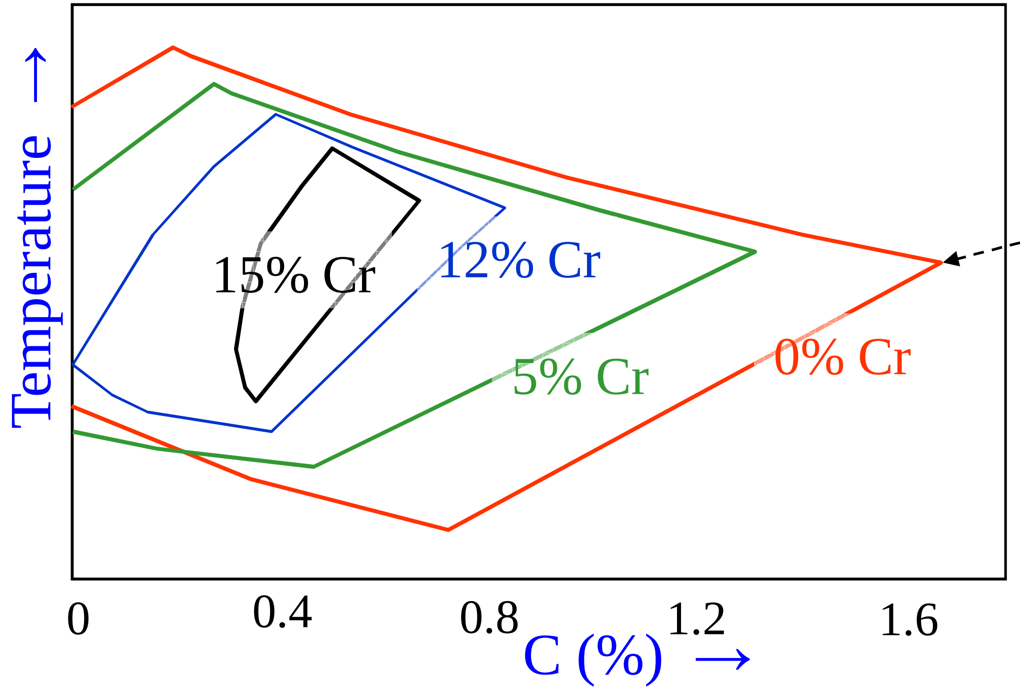
- ❑ Cr, W, Mo, V, Si, Al, Be, Nb, P, Sn, Ti, Zr increase the range of α-phase (by lowering A_4 and raising A_3 temperatures).
- ❑ These elements have α phase BCC crystal structure (or similar structure) and thus in (α+γ) two phase equilibrium , these elements segregate in ferrite in preference to austenite. These elements decrease the amount of carbon soluble in austenite, and thus tend to increase the volume of the free carbide in the steel for a given carbide content.
- ❑ Chromium is a special case of these elements as at low concentrations , chromium lowers A_3 temperature and raises A_4 , but at high concentrations raises A_3 temperature. Overall, the stability of austenite is continuously decreased.

Effect of alloying elements on Austenite phase region Mn, Cr

- Mn is Austenite stabilizer
- Expansion of γ phase field with ↑ Mn



Outline of the γ phase field



Outline of the γ phase field

- Cr is Ferrite stabilizer
- Shrinking γ phase field with ↑ Cr

Effect of alloying elements on Fe-Fe_3C phase diagram

Carbide forming elements

- Important elements, in this class, are arranged in order of increasing affinity for carbon, and thus the carbide forming potential of the element :

$$Fe \rightarrow Mn \rightarrow Cr \rightarrow W \rightarrow Mo \rightarrow V \rightarrow Ti \rightarrow Nb \rightarrow Ta \rightarrow Zr$$

- For example, vanadium is added in steel having chromium and molybdenum with insufficient carbon, then vanadium first removes carbon from chromium carbide, the remaining vanadium then removes carbon from molybdenum carbide and forms its own carbide. The released Cr and Mo dissolve to form solid solution in austenite.

Graphitising elements

- Si, Ni, Cu, Al are common graphitizes. Small amount of these elements in steel can graphitise it and thus, impair the properties of steel unless elements of austenite stabilizers are present to counteract the effect.

Neutral element

- Co is the only element which neither forms carbide, nor causes graphitisation.

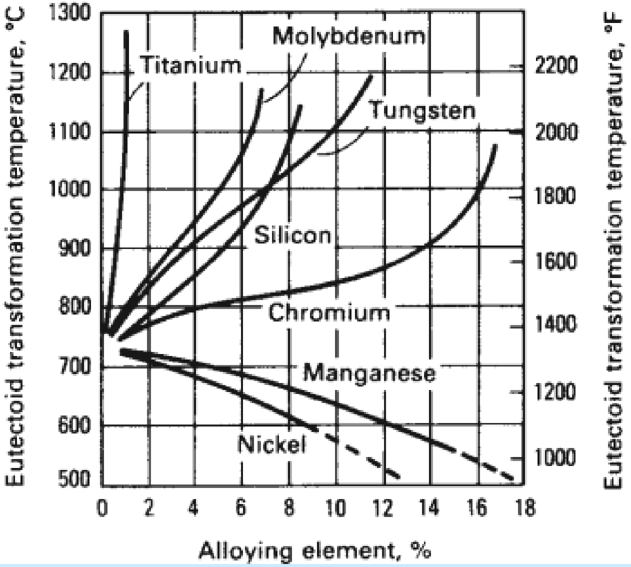
Effect of alloying elements on Fe-Fe_3C phase diagram

Effect on Eutectoid composition

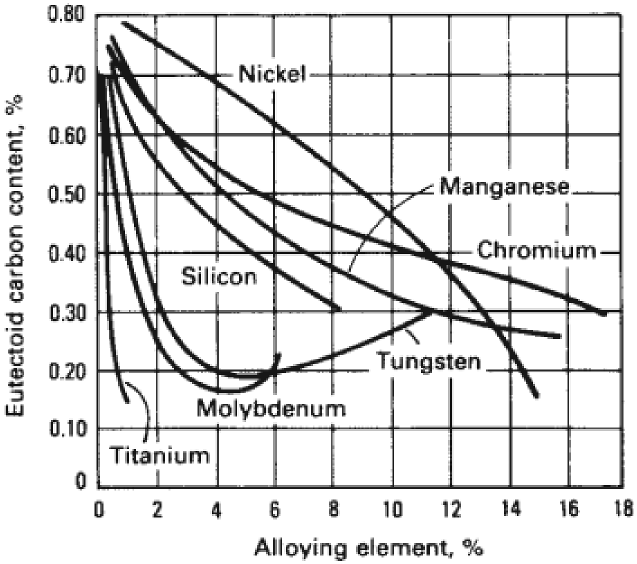
- ❑ All the elements lower the eutectoid carbon content. Titanium and molybdenum are the most effective in lowering it.
- ❑ For example, a steel with 5% Cr has its eutectoid point at 0.5%C as compared to 0.8% in carbon steels. High speed steel has eutectoid point at 0.25% carbon.

Effect on Eutectoid temperature

- ❑ Elements like Ni, Mn i.e., the austenite stabilizers lower the eutectoid temperature (727°C). Ferrite stabilizers like Cr, V, W etc. raise the eutectoid temperature.



Effect of alloying element on eutectoid temperature



Effect of alloying element on effective carbon content

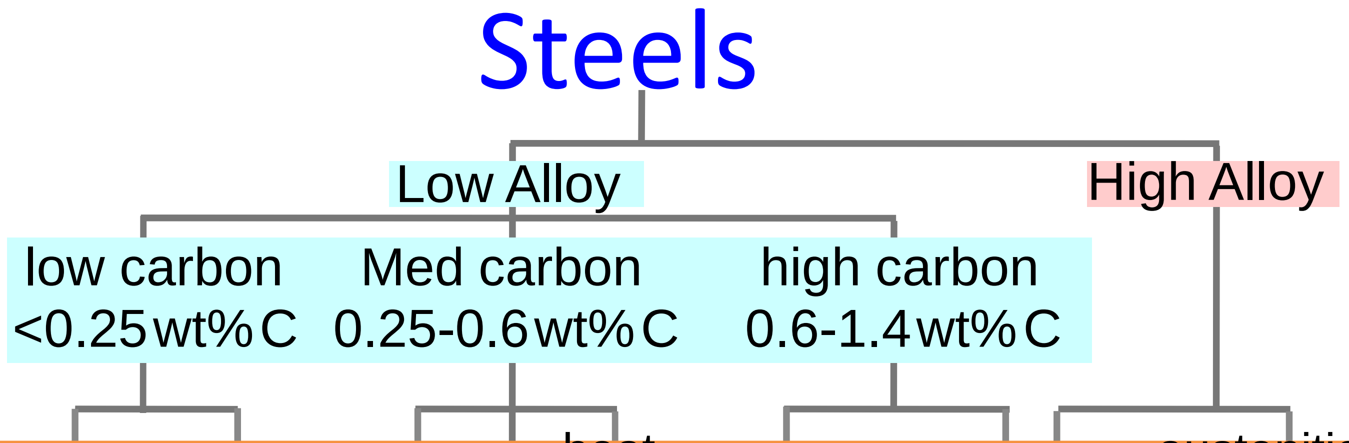
Limitations on Fe-Fe_3C phase diagram

- Fe-Fe_3C diagram represents behavior of steels under equilibrium conditions, whereas the actual heat treatments of steels are normally under non-equilibrium conditions.
- The diagram does not indicate the character of transformation of austenite such as to bainite, or martensite.
- The diagram does not indicate the presence of metastable phases like martensite, or bainite.
- It does not indicate the temperature of start of martensite M_s or bainite B_s .
- It does not indicate the kinetics of the transformation of austenite to martensite, bainite or even pearlite.
- It does not indicate the possibilities of suppressing the pearlitic or bainitic transformations.

Classification of steels

- Compositions, such as carbon (or non alloy), low -alloy, and alloy steels
- Manufacturing methods , such as converter, electric furnace, or electroslag remelting methods
- Application or main characteristic, such as structural , tool, stainless steel, or heatresistant steels.
- Finishing methods, such as hot rolling, cold rolling, casting, or controlled rolling and controlled cooling.
- Product shape, such as bar, plate, strip, tubing, or structural shape
- Oxidation practice employed, such as rimmed, killed, semikilled, and capped steels.
- Microstructure, such as ferritic, pearlitic, martensitic, and austenitic
- Required strength level, as specified in the American Society for Testing and Materials (ASTM) standards.
- Heat treatment, such as annealing, quenching and tempering, air cooling (normalization), and thermo-mechanical processing.
- Quality descriptors and classifications, such as forging quality and commercial quality.

Classification of steels



Steels

Low Alloy

High Alloy

low carbon <0.25 wt% C

Med carbon 0.25-0.6 wt% C

high carbon 0.6-1.4 wt% C

Name	plain	HSLA	plain	heat treatable	plain	tool	austenitic stainless
Additions	none	Cr,V Ni, Mo	none	Cr, Ni Mo	none	Cr, V, Mo, W	Cr, Ni, Mo
Example	1010	4310	1040	4340	1095	4190	304
Hardenability	0	+	+	++	++	+++	0
TS	-	0	+	++	+	++	0
EL	+	+	0	-	-	--	++
Uses	auto struc. sheet	bridges towers press. vessels	crank shafts bolts hammers blades	pistons gears wear applic.	wear applic.	drills saws dies	high T applic. turbines furnaces V. corros. resistant

increasing strength, cost, decreasing ductility →

TTT & CCT Diagrams

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Time-Temperature-Transformation (TTT) Diagrams

- ❑ The temperature of transformation controls the nature of decomposed product (of austenite) which in turn decides the resultant properties of steel.
- ❑ The kinetics of austenitic transformation can be studied best at a constant temperature rather than by continuous cooling.
- ❑ The constant temperature transformation is also referred to as isothermal transformation which is studied by the following experiment.
- ❑ Davenport and Bain were the first to develop the TTT diagram of eutectoid steel. They determined pearlite and bainite portions whereas Cohen later modified and included M_S and M_F temperatures for martensite.
- ❑ There are number of methods used to determine TTT diagrams. The most popular method is salt bath techniques combined with metallography and hardness measurement with addition of this we have other techniques like dilatometry, electrical resistivity method, magnetic permeability, i*n situ* diffraction techniques (X-ray, neutron), acoustic emission, thermal measurement techniques, density measurement techniques and thermodynamic predictions.
- ❑ TTT diagrams, also called as Isothermal (*temperature constant)* Transformation diagrams.
- ❑ For every composition of steel we should draw a different TTT diagram.

Determination of TTT diagram for eutectoid steel

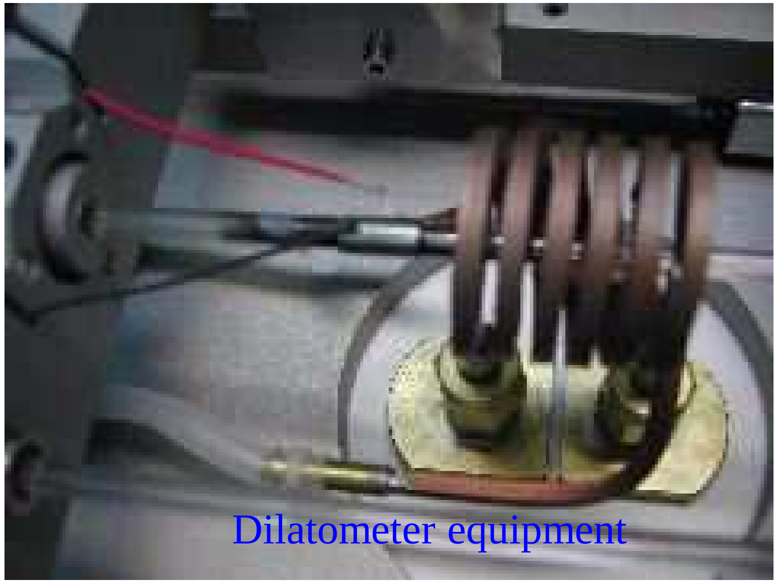
- ☐ For the determination of isothermal transformation (or) TTT diagrams, we consider *molten salt bath technique* combined with metallography and hardness measurements.
- ☐ In *molten salt bath technique* two salt baths and one water bath are used.
- ☐ Salt bath I is maintained at austenising temperature (780˚C for eutectoid steel).
- ☐ Salt bath II is maintained at specified temperature at which transformation is to be determined (below A_{e1}), typically 700-250°C for eutectoid steel.
- ☐ Bath III which is a cold water bath is maintained at room temperature.
- ☐ In bath I number of samples are austenite at A_1+20-40°C for eutectoid, A_3+20-40°C for hypo-eutectoid steel and A_{Cm}+20-40°C for hyper-eutectoid steels for about an hour.
- ☐ Then samples are removed from bath I and put in bath II and each one is kept for different specified period of time say t_1, t_2, t_3, t_4,…..........,t_n etc.
- ☐ After specified times, the samples are removed and quenched in cold water.
- ☐ The microstructure of each sample is studied using metallographic techniques. The type, as well as quantity of phases, is determined on each sample.
- ☐ Transformation of austenite to ferrite-cementite mixtures occurs after a definite time (say t_1) This time during which transformation does not proceed is known as incubation period.
- ☐ The magnitude of incubation period provides a qualitative idea about the relative stability of supercooled austenite. Smaller incubation period corresponds to lesser stability of austenite.

Equipments for determination of TTT Diagrams

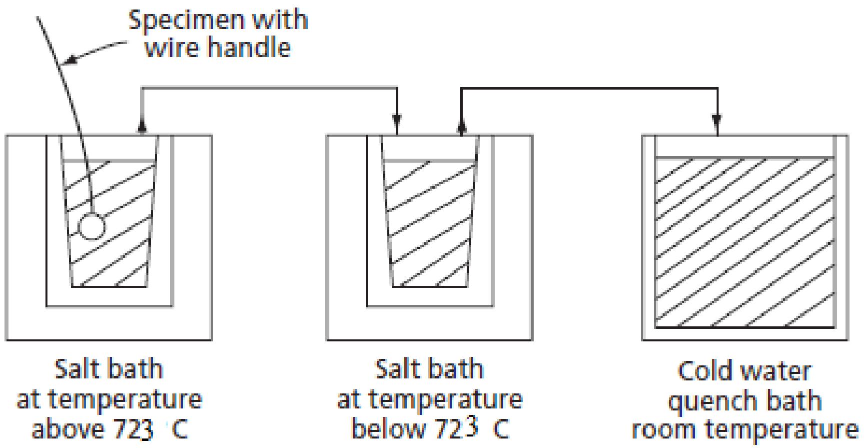

Salt bath I
Austenitisation heat treatment


Salt bath II
Low-temperature for isothermal treatment

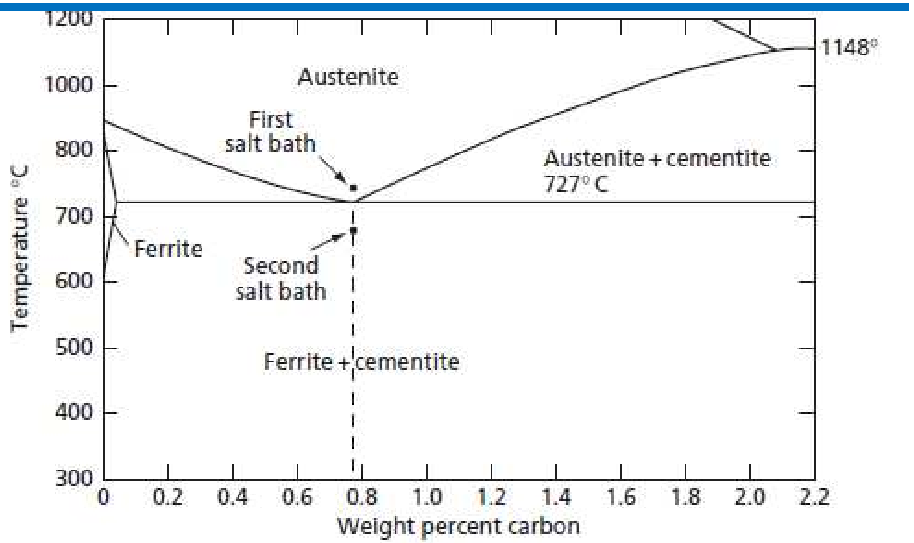

Sample and fixtures
for dilatometric measurements


Dilatometer equipment

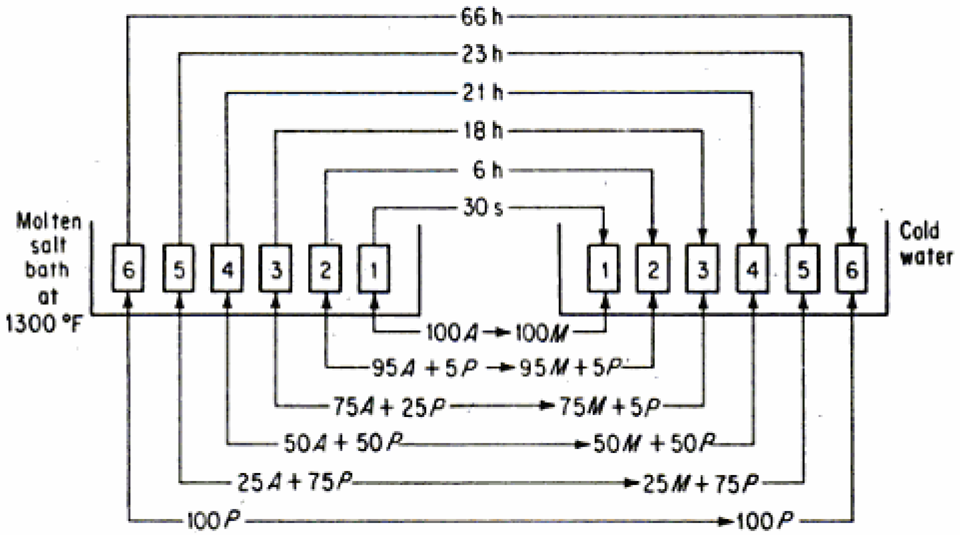
Determination of TTT diagram for eutectoid steel



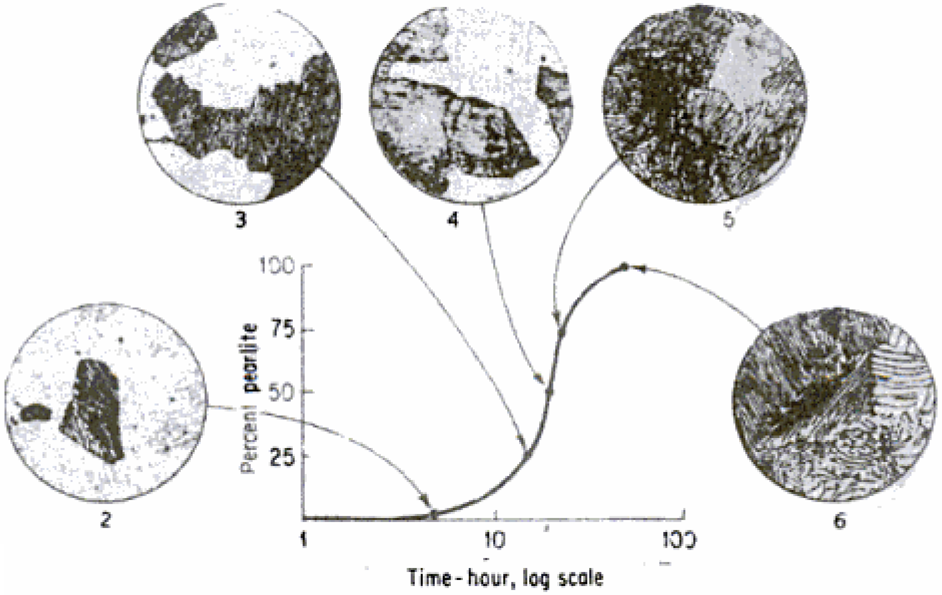
Simple experimental arrangement for determining
The kinetics of isothermal austenitic transformation



Eutectoid section of the iron - carbon diagram

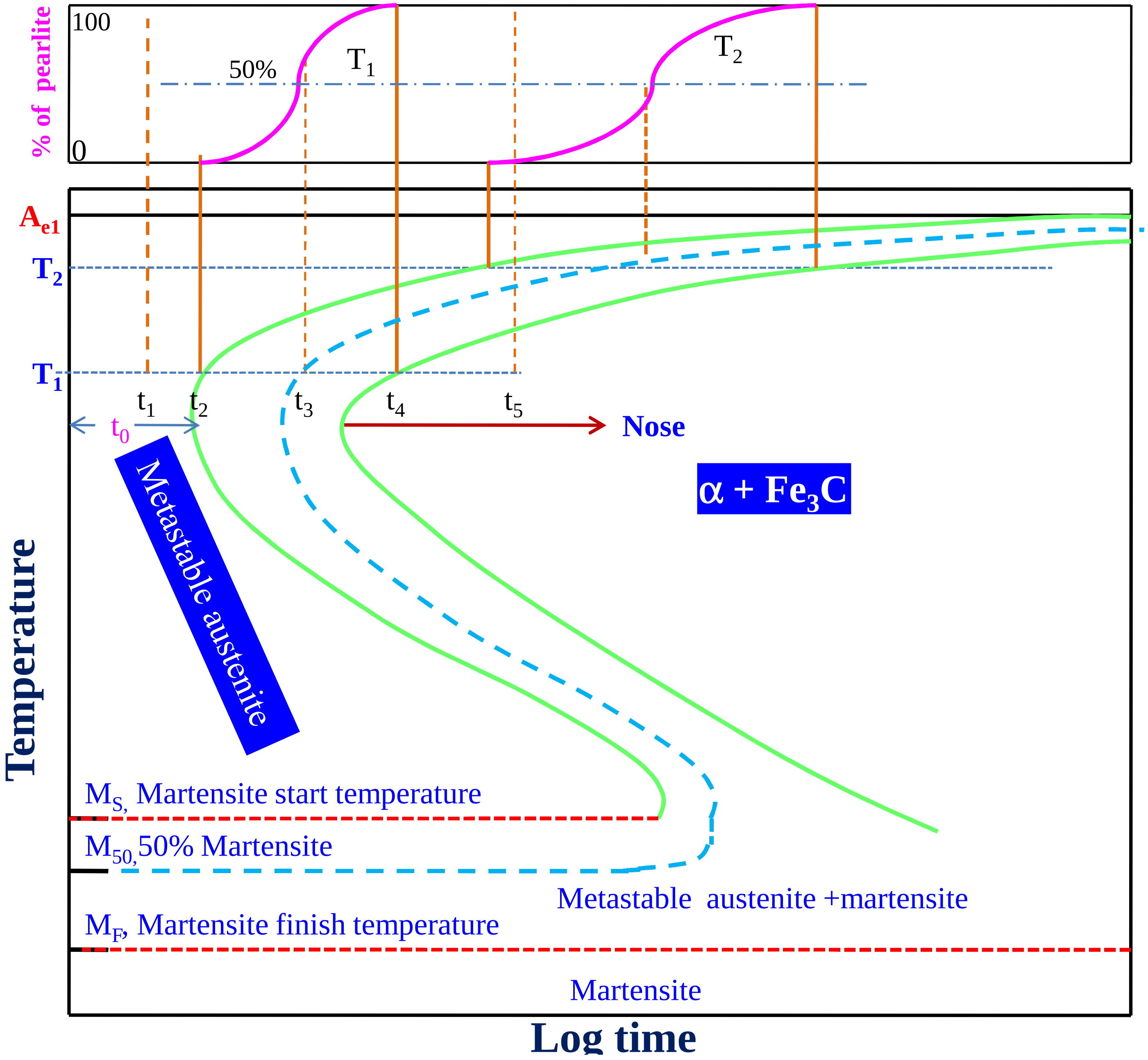


The progress of austenite transformation
A-austenite, P-pearlite, M-martensite



TTT curve of austenite to pearlite for 1080 steel

Determination of TTT diagram for eutectoid steel



✓At T_1, incubation period for pearlite=t_2, Pearlite finish time =t_4

✓Minimum incubation period t_0 at the nose of the TTT diagram,

Important points to be noted:

✓ The x-axis is log scale. ‘Nose’ of the ‘C’ curve is in ~sec and just below **T_E** transformation times may be ~day.

✓ The starting phase (left of the C curve) has to γ.

✓ To the right of finish C curve is (γ+ Fe_3C) phase field. This phase field has more labels included.

Determination of TTT diagram for eutectoid steel

Important points to be noted:

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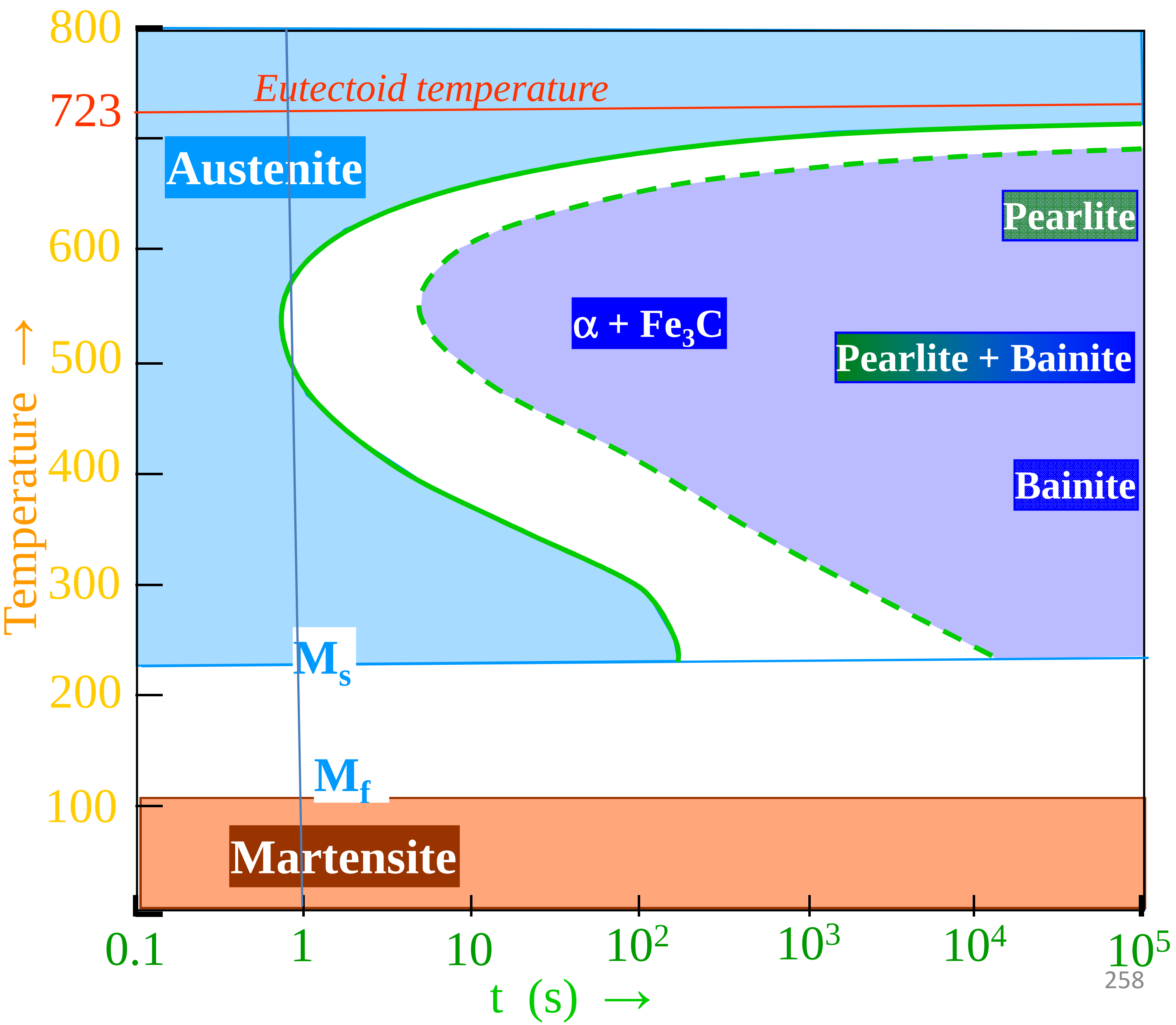
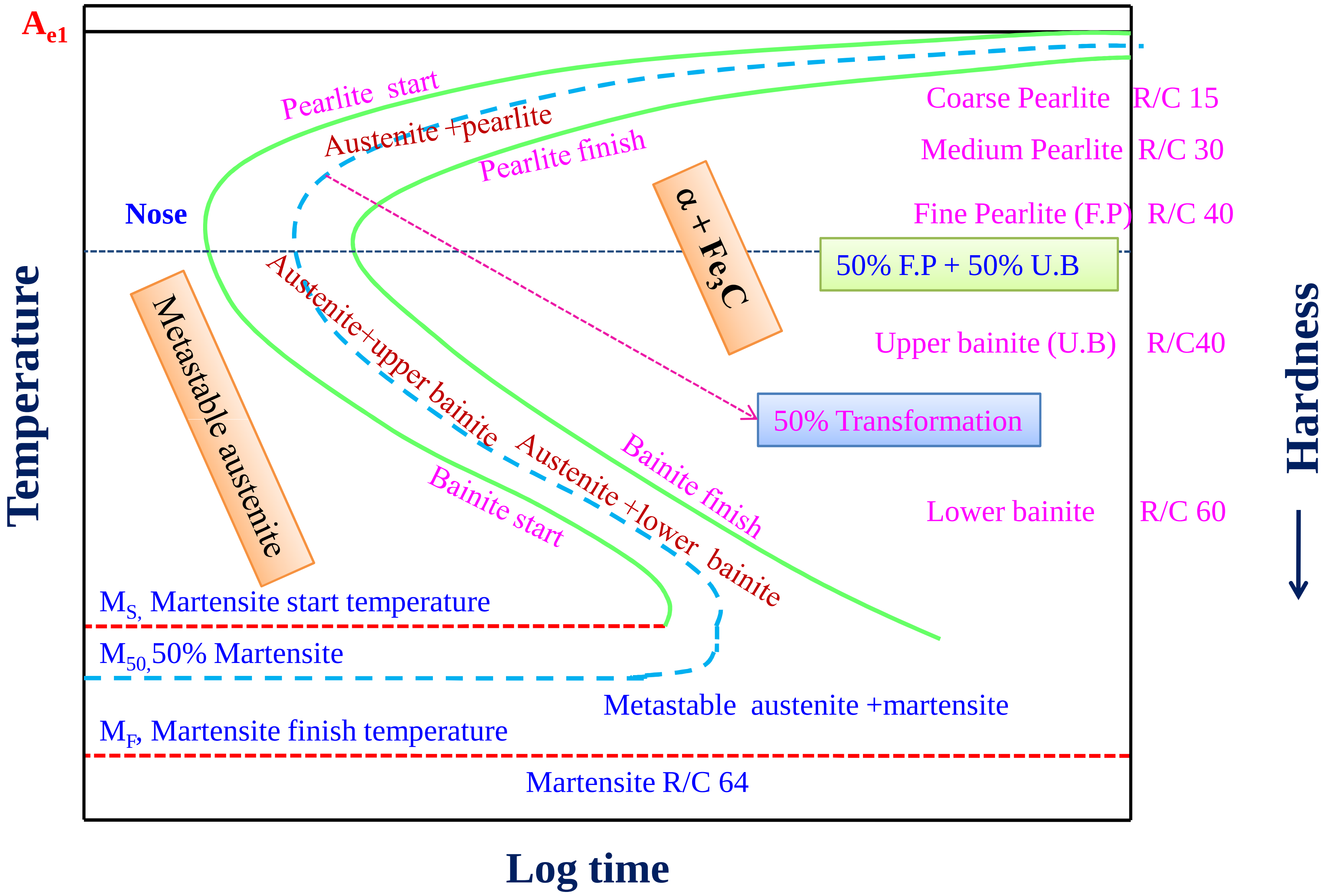


Possible phases in TTT diagram for eutectoid steel



Isothermal Transformation diagram for eutectoid steel

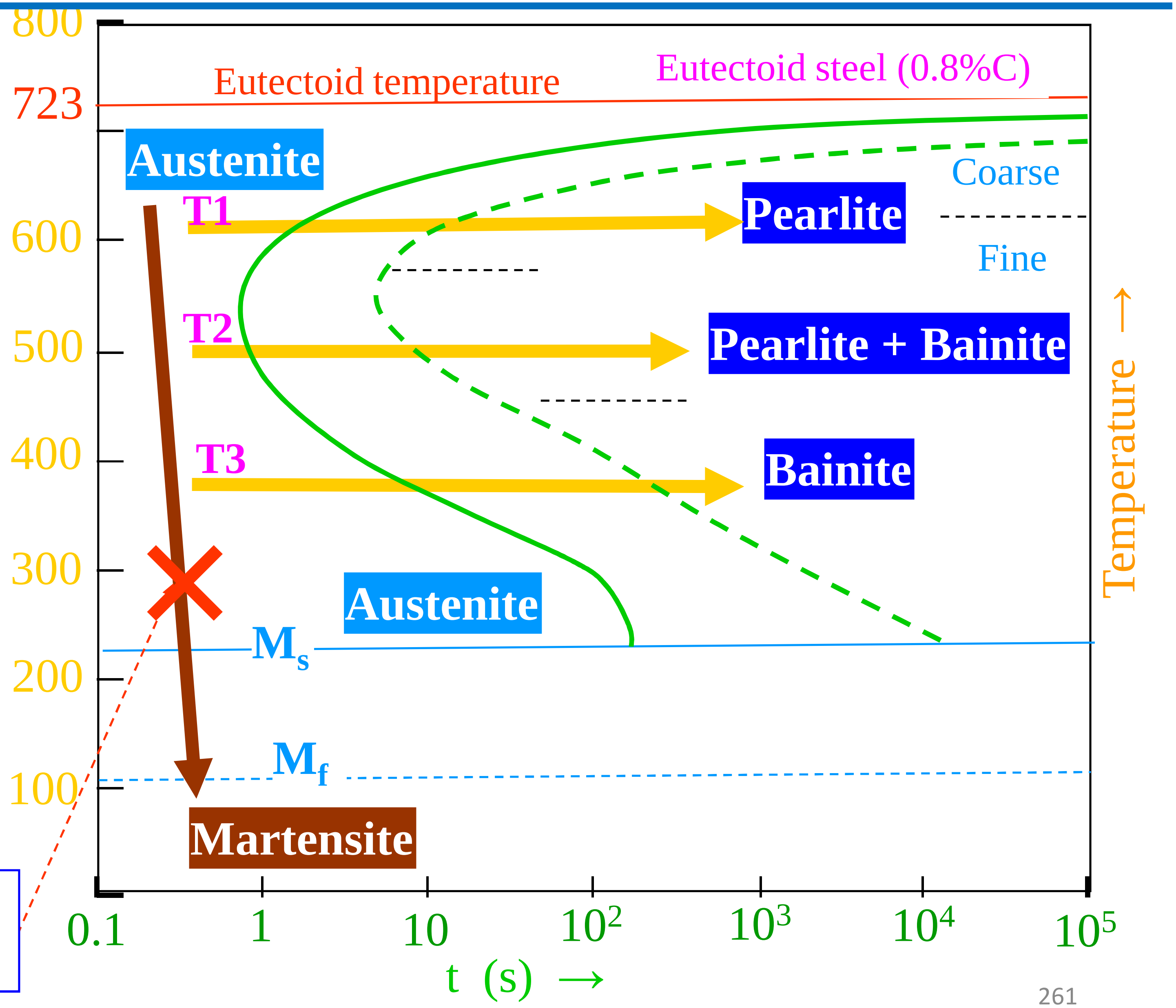
- ❑ As pointed out before one of the important utilities of the TTT diagrams comes from the overlay of micro-constituents (microstructures) on the diagram.
- ❑ Depending on the T, the (γ+ Fe_3C) phase field is labeled with micro-constituents like Pearlite, Bainite.
- ❑ The time taken to 1% transformation to, say pearlite or bainite is considered as transformation start time and for 99% transformation represents transformation finish.
- ❑ We had seen that TTT diagrams are drawn by instantaneous quench to a temperature followed by isothermal hold.
- ❑ Suppose we quench below (~225°C, below the temperature marked M_s), then Austenite transforms via a diffusionless transformation *(involving shear) to a (hard)* phase known as Martensite. Below a temperature marked M_f this transformation to Martensite is complete. Once γ is exhausted it cannot transform to (γ + Fe_3C).
- ❑ Hence, we have a new phase field for Martensite. The fraction of Martensite formed is not a function of the time of hold, but the temperature to which we quench (between M_s and M_f).
- ❑ Strictly speaking cooling curves (including finite quenching rates) should not be overlaid on TTT diagrams *(remember that TTT diagrams are drawn for isothermal holds!).*

Isothermal Transformation diagram for eutectoid steel

✓ Isothermal hold at: (i) T1 gives us Pearlite, (ii) T2 gives Pearlite+Bainite, (iii) T3 gives Bainite. *Note that Pearlite and Bainite are both* α*+*Fe_3C *(but their morphologies are different).*

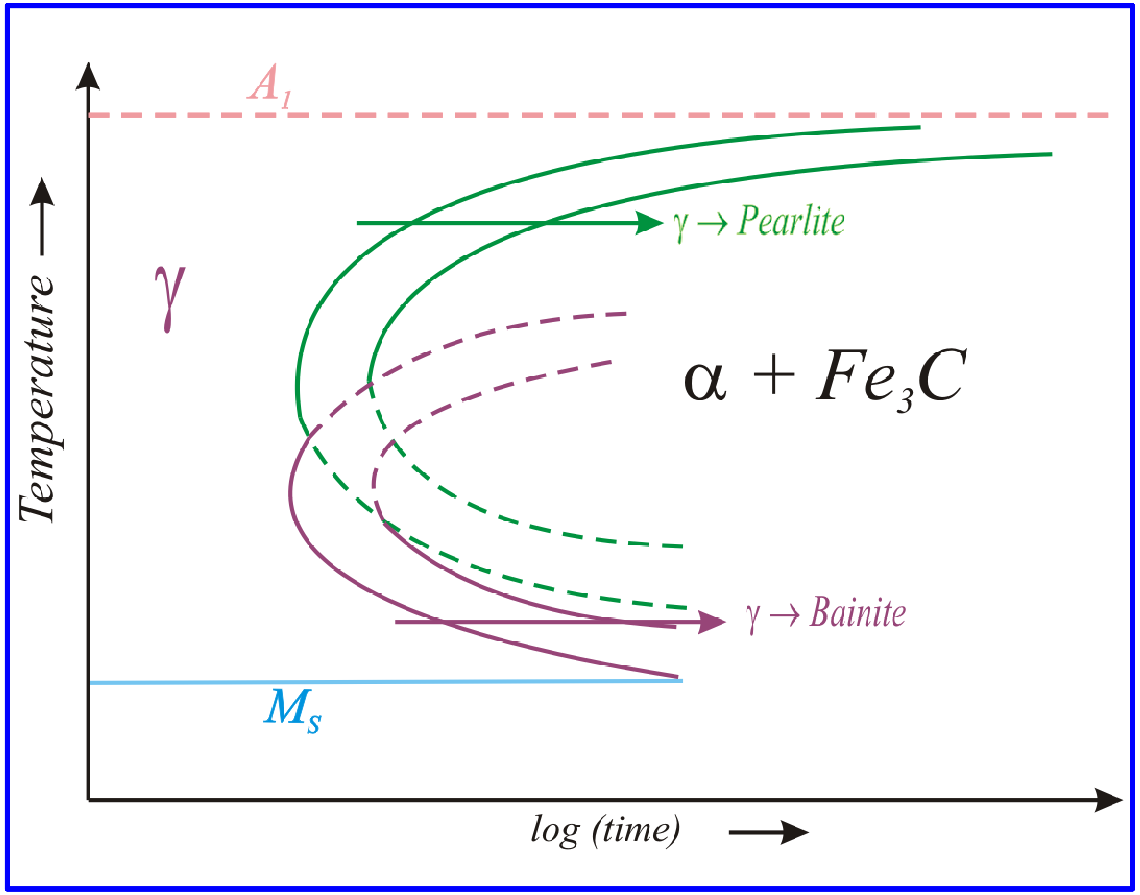
✓ To produce Martensite we should quench at a rate such as to avoid the nose of the start 'C' curve. Called the critical cooling rate.

✓ If we quench between M_s and M_f we will get a mixture of Martensite and γ *(called retained Austenite).*



Not an isothermal transformation

Isothermal Transformation diagram for eutectoid steel



In principle two curves exist for Pearlitic and Bainitic transformations

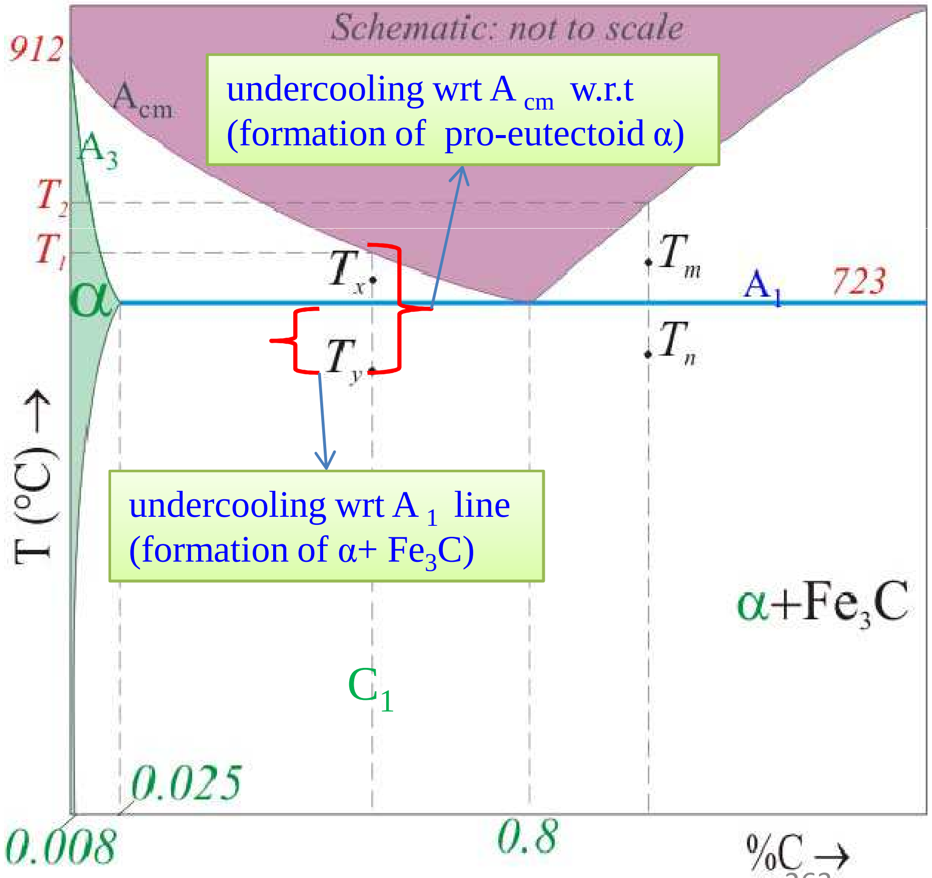
→ they are usually not resolved in plain C steel

(In alloy steels they can be distinct)

TTT diagram for Hypo-eutectoid steel

- In hypo- (and hyper-) eutectoid steels (say composition C_1) there is one more branch to the 'C' curve-NP *(next slide: marked in red).*
- The part of the curve lying between T_1 and T_E (marked in fig : n*ext slide*) is clear, because in this range of temperatures we expect only pro-eutectoid α to form and the final microstructure will consist of α and γ. *(E.g. if we cool to T_x and hold).*

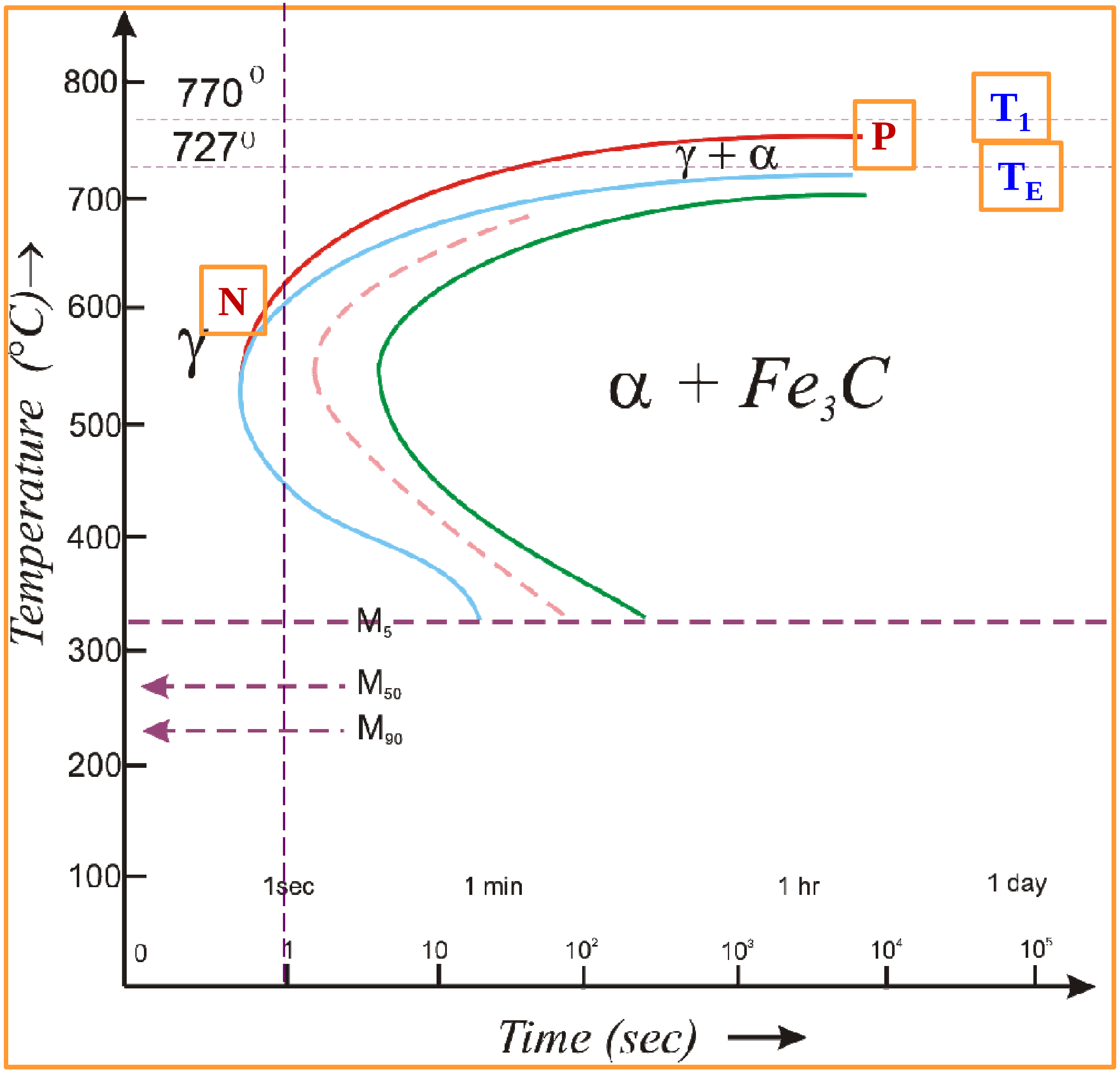
- The part of the curve below T_E is a bit of a 'mystery' *(since we are instantaneously cooling to below T_E, we should get a mix of $\alpha + Fe_3C \Rightarrow$ what is the meaning of a 'pro'-eutectoid phase in a TTT diagram? (remember 'pro-' implies 'pre-')*
- Suppose we quench instantaneously an hypo-eutectoid composition C_1 to T_x we should expect the formation of $\alpha + Fe_3C$ (and not pro-eutectoid α first).
- The reason we see the formation of pro-eutectoid α first is that the undercooling w.r.t to A_{cm} is more than the undercooling w.r.t to A_1. Hence, there is a higher propensity for the formation of pro-eutectoid α.



undercooling wrt A_{cm} w.r.t (formation of pro-eutectoid α)

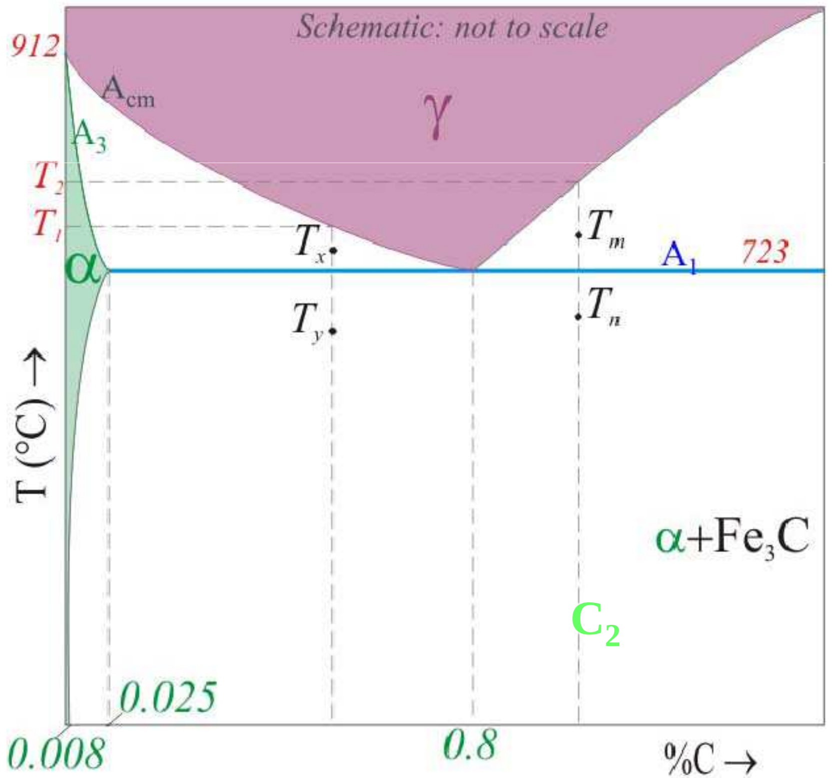
undercooling wrt A_1 line (formation of $\alpha + Fe_3C$)

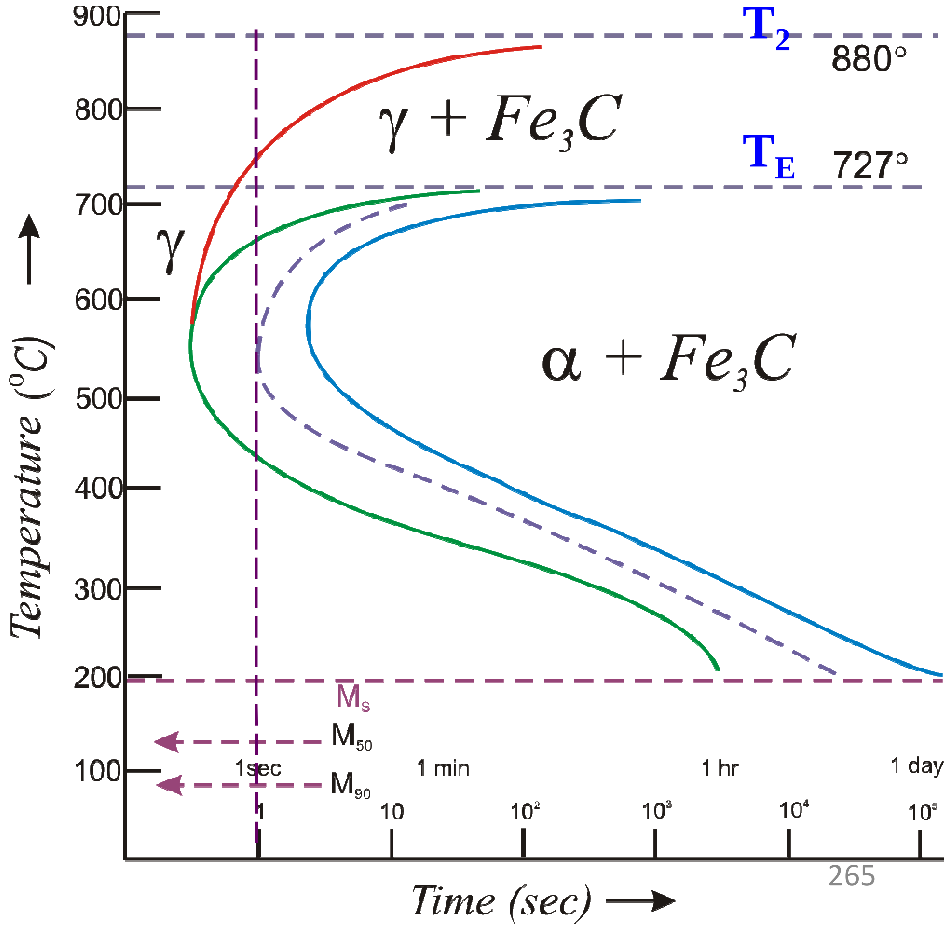
TTT diagram for Hypo-eutectoid steel



TTT diagram for Hyper-eutectoid steel

- Similar to the hypo-eutectoid case, hyper-eutectoid compositions C_2 have a γ+Fe_3C branch.
- For a temperature between T_2 and T_E (say T_m (not melting point- just a label)) we land up with γ+Fe_3C.
- For a temperature below T_E (but above the nose of the 'C' curve) (say T_n), first we have the formation of pro-eutectoid Fe_3C followed by the formation of eutectoid γ+Fe_3C.





Transformation Mechanism

- ❑ TTT diagrams involve nucleation and growth. Nucleation involves the formation of a different phase from a parent phase (e.g. crystal from melt). Growth involves attachment of atoms belonging to the matrix to the new phase (e.g. atoms ‘belonging’ to the liquid phase attach to the crystal phase).
- ❑ Nucleation we have noted is ‘uphill’ in ‘G’ process, while growth is ‘downhill’ in G.
- ❑ Growth can proceed till all the ‘prescribed’ product phase forms (by consuming the parent phase).

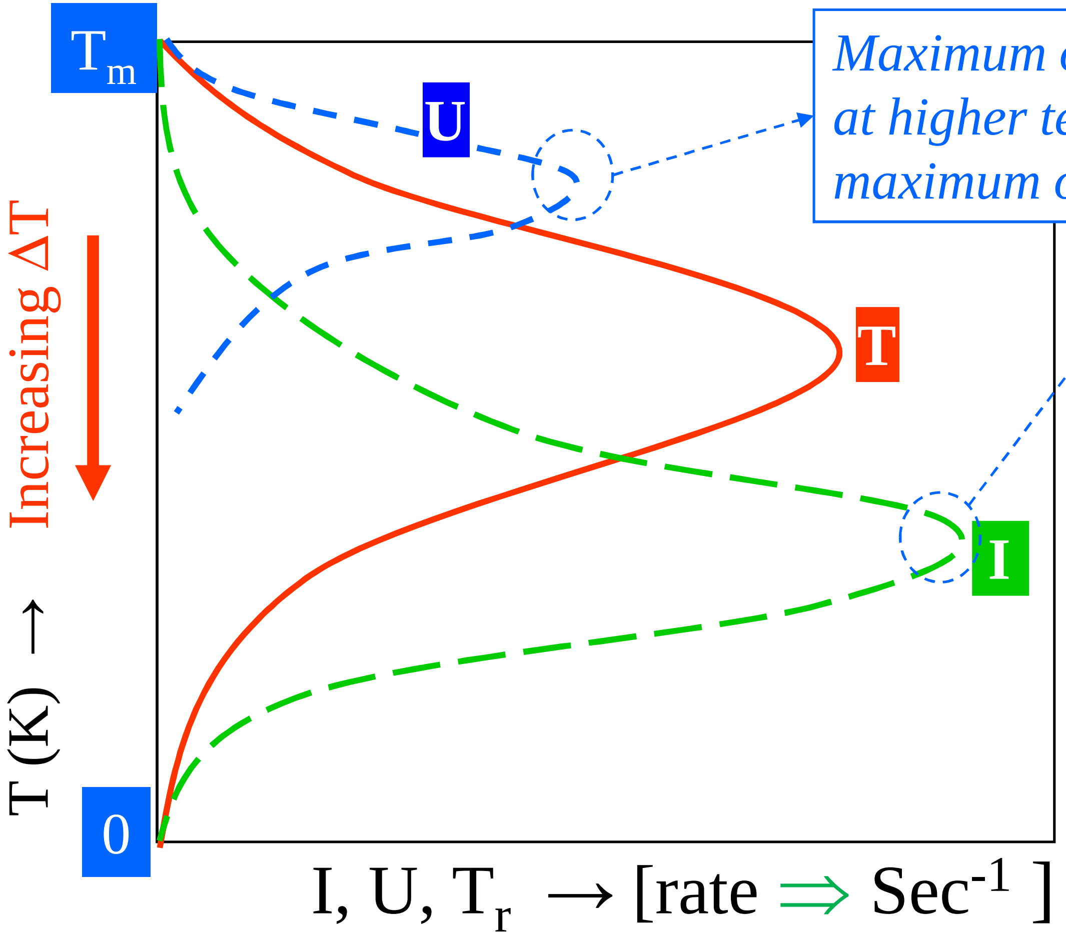
Transformation rate

- ❑ As expected transformation rate (T_r) is a function of nucleation rate (I) and growth rate (U).
- ❑ In a $\alpha \rightarrow \beta$ transformation, if X_β is the fraction of β-phase formed, then dX_β/dt is the transformation rate.
- ❑ The derivation of T_r as a function of I & U is carried using some assumptions (e.g. *Johnson-Mehl and Avarami models*).
- ❑ We have already seen the curve for the nucleation rate (I) as a function of the undercooling.
- ❑ The growth rate (U) curve as a function of undercooling looks similar. The key difference being that the maximum of U-ΔT curve is typically above the I-ΔT curve.
- ❑ This fact that $T(U_{max}) > T(I_{max})$ give us an important ‘handle’ on the scale of the transformed phases forming.

Transformation Rate

Transformation rate = f(Nucleation rate, Growth rate)

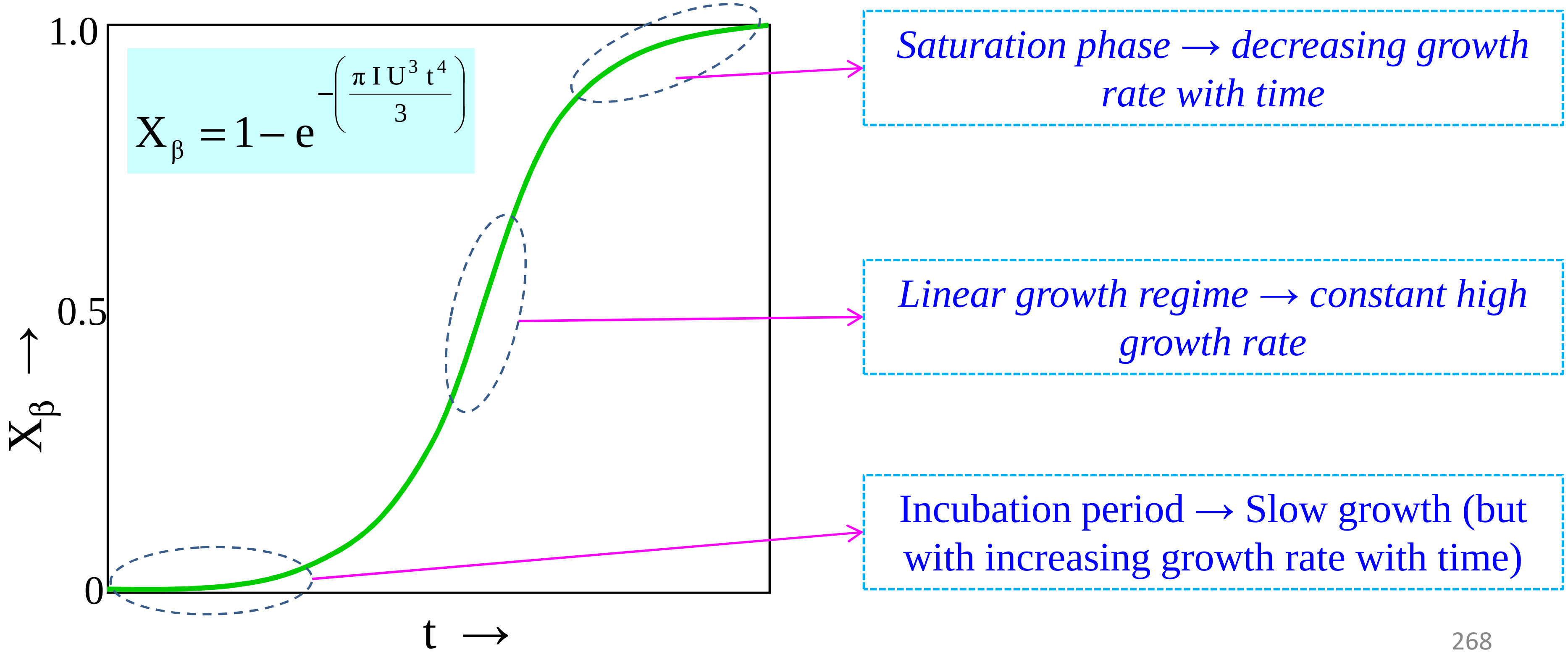
$$\boxed{T} = \frac{dX_\beta}{dt} = f\left(\boxed{I}, \boxed{U}\right)$$



Maximum of growth rate usually at higher temperature than maximum of nucleation rate

Transformation Rate

- ❑ Fraction of the product (β) phase forming with time →the sigmoidal growth curve
- ❑ Many processes in nature (etc.), e.g. growth of bacteria in a culture (number of bacteria with time), marks obtained versus study time(!), etc. tend to follow a universal curve the sigmoidal growth curve.
- ❑ In the context of phase transformation, the fraction of the product phase (X_β) forming with time follows a sigmoidal curve (function and curve as below).



$$X_\beta = 1 - e^{-\left(\frac{\pi I U^3 t^4}{3}\right)}$$

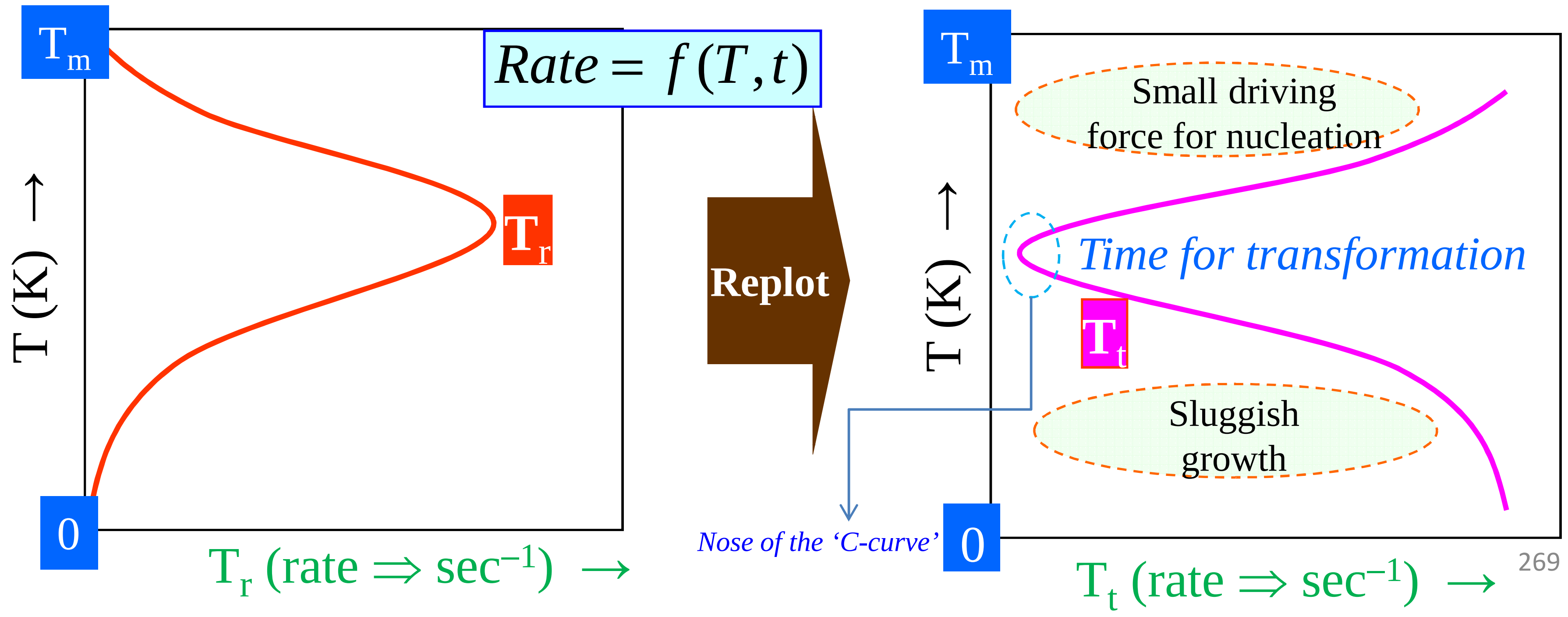
Saturation phase → decreasing growth rate with time

Linear growth regime → constant high growth rate

Incubation period → Slow growth (but with increasing growth rate with time)

From ‘Rate’ to ‘time’ : The Origin of TTT diagrams

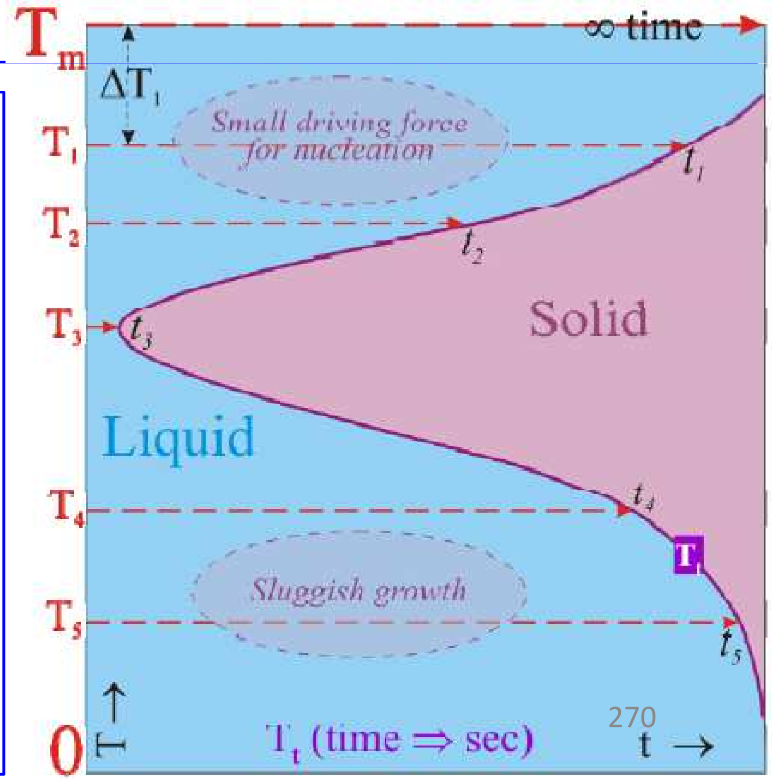
- The transformation rate curve (T_r -T plot) has hidden in it the I-T and U-T curves.
- An alternate way of plotting the Transformation rate (T_r) curve is to plot Transformation time (T_t) [i.e. go from frequency domain to time domain]. Such a plot is called the Time-Temperature-Transformation diagram (TTT diagram).
- High rates correspond to short times and vice-versa. *Zero rate implies ∞ time (no transformation).*
- This T_t -T plot looks like the ‘C’ alphabet and is often called the ‘C-curve. The minimum time part is called the nose of the curve.



Understanding the TTT diagram

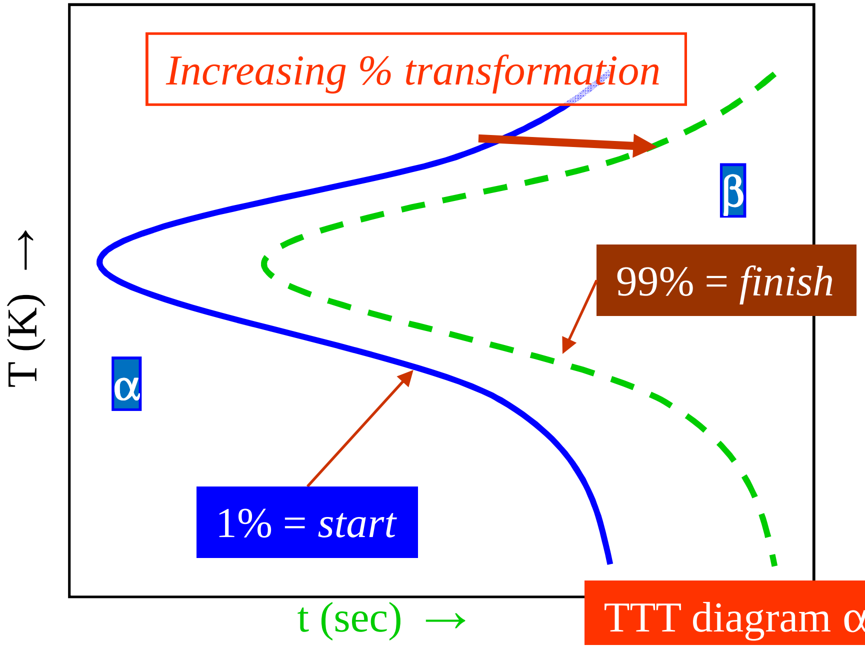
- Though we are labeling the transformation temperature T_m , it represents other transformations, in addition to melting.
- Clearly the T_t function is not monotonic in undercooling. At T_m it takes infinite time for transformation.
  - ✓ Till T_3 the time for transformation decreases (with undercooling) [i.e. $T_3 < T_2 < T_1$] →due to small driving force for nucleation.
  - ✓ After T_3 (the minimum) the time for transformation increases [i.e. $T_3 < T_4 < T_5$]→due to sluggish growth.

- The diagram is called the TTT diagram because it plots the time required for transformation if we hold the sample at fixed temperature (say T_1) or fixed undercooling (ΔT_1). The time taken at T_1 is t_1.
- To plot these diagrams we have to isothermally hold at various undercoolings and note the transformation time. I.e. instantaneous quench followed by isothermal hold.
- Hence, these diagrams are also called Isothermal Transformation Diagrams. Similar curves can be drawn for α→β *(solid state) transformation.*



Transformation Rate

- ❑ This is a phase diagram where the blue region is the Liquid (parent) phase field and purplish region is the transformed product (crystalline solid).
- ❑ Clearly the picture of TTT diagram presented before is incomplete → transformations may start at a particular time, but will take time to be completed *(i.e. between the Liquid phase field and solid phase field there must be a two phase region L+S).*
- ❑ This implies that we need two 'C' curves → one for start of transformation and one for completion. A practical problem in this regard is related to the issue of how to define start and finish *(is start the first nucleus which forms? Does finish correspond to 100%?)* . Since practically it is difficult to find 'β%' and '100%', we use practical measures of start and finish, which can be measured experimentally. Typically this is done using optical metallography and a reliable 'resolution of the technique is about 1% for start and 99% for finish.



TTT diagram α → β phase transformation

- ❑ Another obvious point: as x-axis is time any 'transformation paths' have to be drawn such that it is from left to right (i.e. in increasing time).

How do we define the fractions transformed?

Fraction transformed

$$\alpha' \rightarrow \alpha + \beta$$

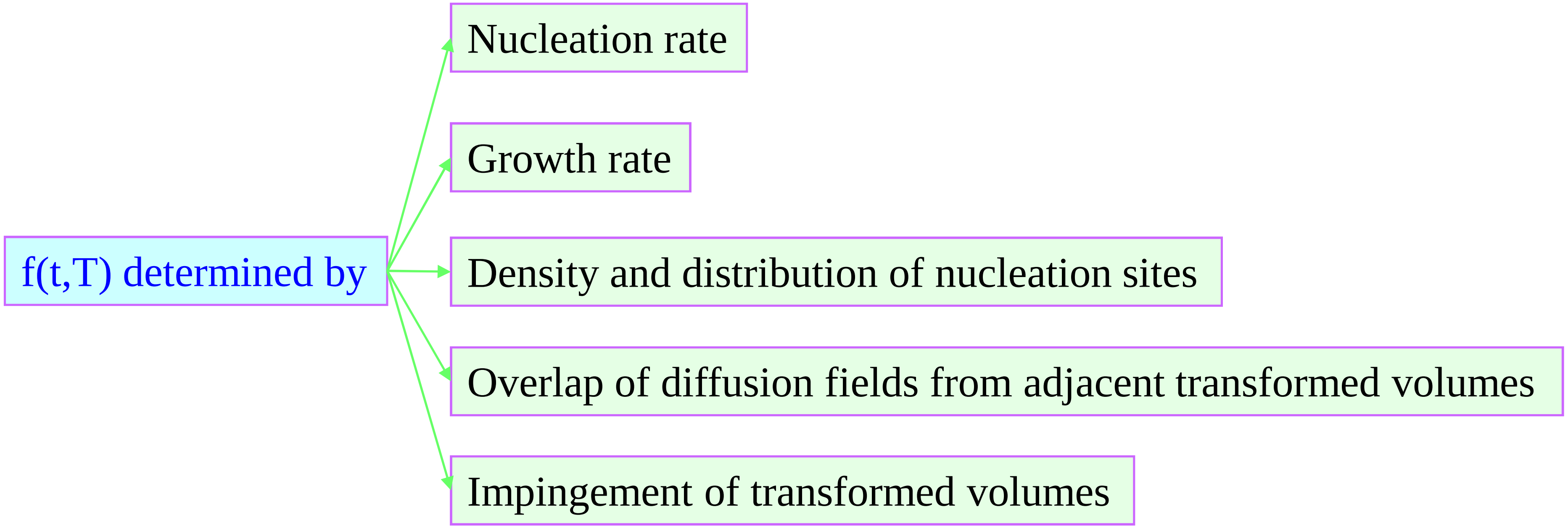
$$f \rightarrow \frac{volume\ fraction\, of\ \beta\ at\ t}{final\ volume\, of\ \beta}$$

$$\alpha \rightarrow \beta$$

$$f \rightarrow volume\ fraction\, of\ \beta$$

Overall Transformation Kinetics

- ❑ The ‘C’ curve depends on various factors as listed in diagram below.



f(t,T) determined by

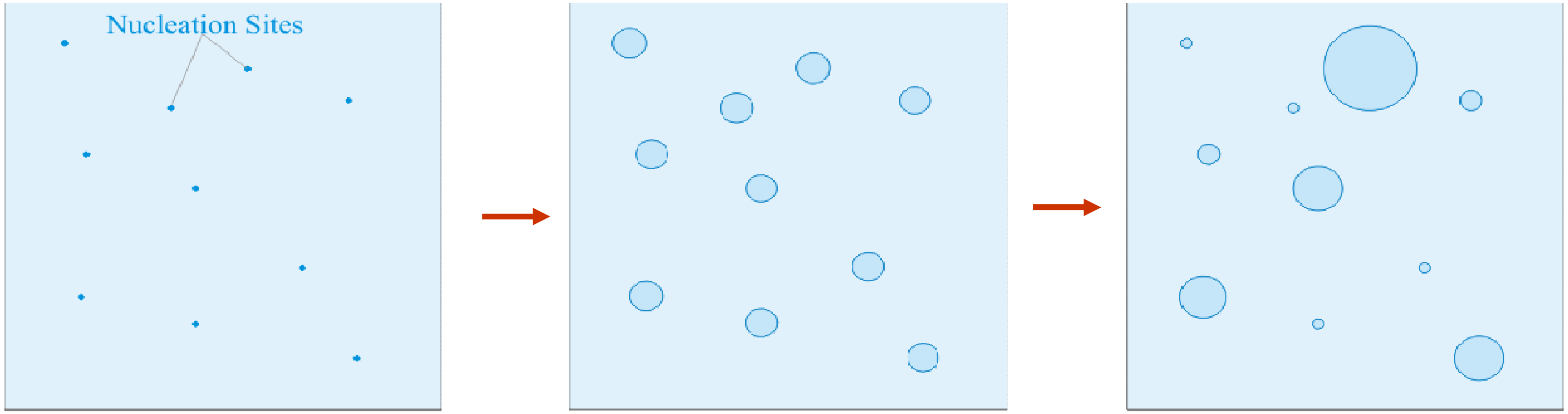
- Nucleation rate
- Growth rate
- Density and distribution of nucleation sites
- Overlap of diffusion fields from adjacent transformed volumes
- Impingement of transformed volumes

- ❑ Some common assumptions used in the derivation are
  - ➢ constant number of nuclei
  - ➢ constant nucleation rate
  - ➢ constant growth rate.

Overall Transformation Kinetics

Constant number of nuclei

- ☐ Generally constant number of nuclei will form at the beginning of the transformation.
- ☐ One assumption to simplify the derivation is to assume that the number of nucleation sites remain constant and these form at the beginning of the transformation.
- ☐ This situation may be approximately valid for example if a nucleating agent (inoculant) is added to a melt (the number of inoculant particles remain constant).
- ☐ In this case the transformation rate is a function of the number of nucleation sites (fixed) and the growth rate (U). Growth rate is expected to decrease with time.
- ☐ In Avrami model the growth rate is assumed to be constant (till impingement).



$$f = F(\mathit{number\ of\ nucleation\ sites, growth\ rate})$$

$\mathit{growth\ rate} \downarrow \mathit{with\ time}$

Overall Transformation Kinetics

Constant growth rate

- ❑ Generally in cellular transformations constant growth rate is observed.

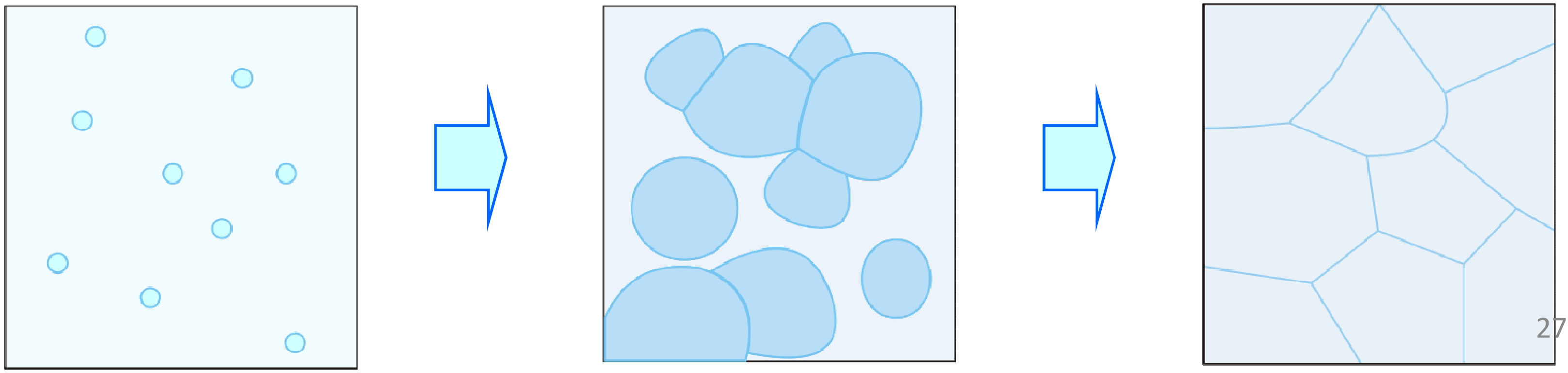
Cellular Transformations → Constant growth rate

- Pearlitic transformation
- Cellular Precipitation
- Massive Transformation
- Recrystallization

All of the parent phase is consumed by the product phase

$\boxed{\alpha \rightarrow \beta + \gamma}$ $\boxed{\alpha \rightarrow \beta}$

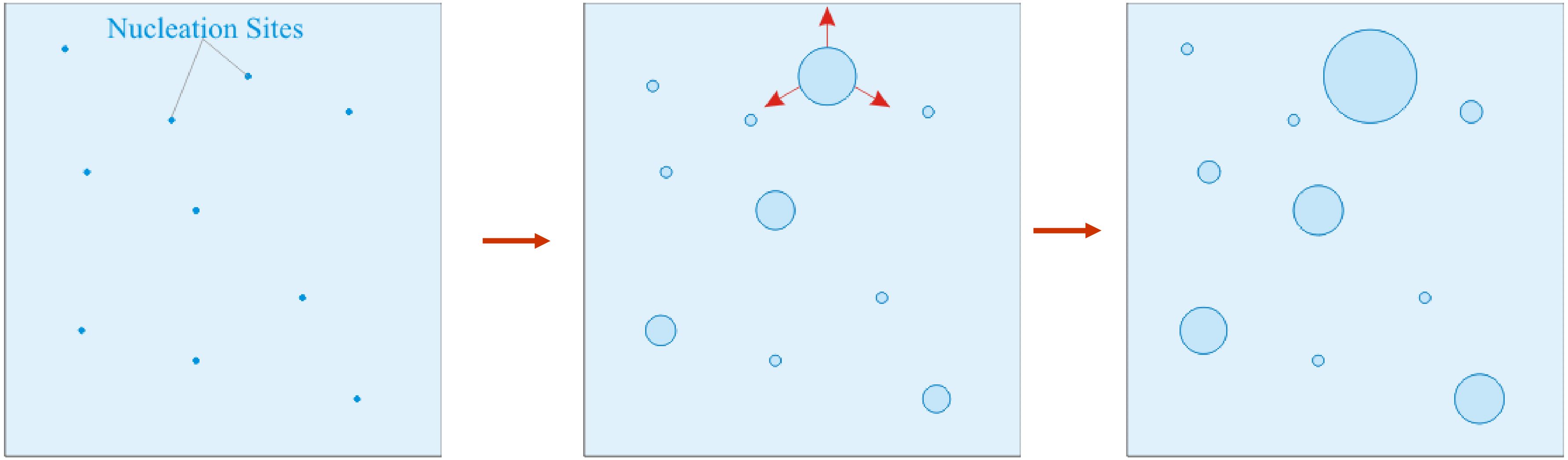
- ❑ Termination of transformation does not occur by a gradual reduction in the growth rate but by the impingement of the adjacent cells growing with a constant velocity.



Overall Transformation Kinetics

Constant nucleation rate

- ❑ Another common assumption is that the nucleation rate (I) is constant.
- ❑ In this case the transformation rate is a function of both the nucleation rate (fixed) and the growth rate (U).
- ❑ Growth rate decreases with time.
- ❑ If we further assume that the growth rate is constant (till impingement), then we get the Johnson-Mehl model.



$$f = F(number\ of\ nucleation\ sites, growth\ rate)$$

$growth\ rate \downarrow with\ time$

Derivation of f(T,t) : Avrami Model

- Parent phase has a fixed number of nucleation sites N_n per unit volume (and these sites are exhausted in a very short period of time
- Growth rate ($U = dr/dt$) constant and isotropic (as spherical particles) till particles impinge on one another.
- At time t the particle that nucleated at $t = 0$ will have a radius $r = Ut$
- Between time $t = t$ and $t = t + dt$ the radius increases by $dr = Udt$
- The corresponding volume increase $dV = 4\pi r^2\,dr$
- Without impingement, the transformed volume fraction (f) *(the extended transformed volume fraction)* of particles that nucleated between $t = t$ and $t = t + dt$ is:

$$\boxed{f = N_n\,4\pi r^2\left(dr\right) = N_n\,4\pi\left[Ut\right]^2\left(Udt\right) = N_n\,4\pi U^3 t^2 dt}$$

- This fraction (f) has to be corrected for impingement. The corrected transformed volume fraction (X) is lower than f by a factor (1–X) as contribution to transformed volume fraction comes from untransformed regions only:

$$\boxed{f = \frac{dX}{1-X}} \Rightarrow \boxed{\frac{dX}{1-X} = N_n\,4\pi U^3 t^2 dt} \Rightarrow \boxed{\int_0^X \frac{dX}{1-X} = \int_{t=0}^{t=t} N_n\,4\pi U^3 t^2 dt}$$

$$X_\beta = 1 - e^{-\left(\frac{4\pi\,N_n U^3\,t^3}{3}\right)}$$

- *Based on the assumptions note that the growth rate is not part of the equation →it is only the number of nuclei.*

Derivation of f(T,t): Johnson-Mehl Model

- Parent phase completely transforms to product phase (α → β)
- Homogenous Nucleation rate of β in untransformed volume is constant (I)
- Growth rate (U = dr/dt) constant and isotropic (as spherical particles) till particles impinge on one another

- At time t the particle that nucleated at t = 0 will have a radius $r = Ut$
- The particle which nucleated at t = τ will have a radius $r = U(t-\tau)$
- Number of nuclei formed between time t = τ and t = τ + dτ → $Id\tau$
- Without impingement, the transformed volume fraction (f) *(called the extended transformed volume fraction)* of particles that nucleated between t = τ and t = τ + dτ is:

$$\boxed{f = \frac{4}{3}\pi r^3 \left(Id\tau\right) = \frac{4}{3}\pi\left[U(t-\tau)\right]^3 \left(Id\tau\right)}$$

- This fraction (f) has to be corrected for impingement. The corrected transformed volume fraction (X) is lower than f by a factor (1–X) as contribution to transformed volume fraction comes from untransformed regions only:

$$\boxed{f = \frac{dX}{1-X}} \Rightarrow \boxed{\frac{dX}{1-X} = \frac{4}{3}\pi r^3 \left(Id\tau\right) = \frac{4}{3}\pi\left[U(t-\tau)\right]^3 \left(Id\tau\right)}$$

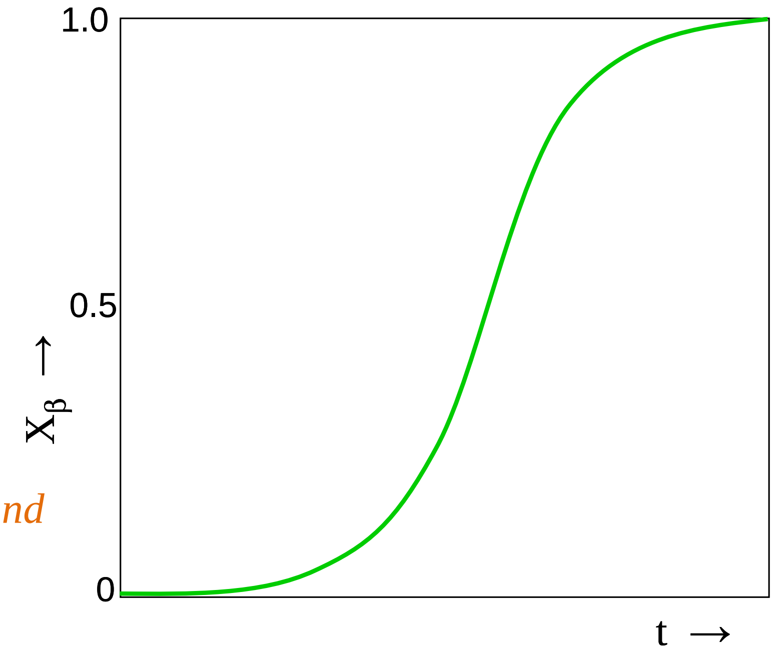
Derivation of f(T,t): Johnson-Mehl Model

$$\int_0^X \frac{dX}{1-X} = \int_{\tau=0}^{\tau=t} \frac{4}{3}\pi\left[U(t-\tau)\right]^3 (I d\tau)$$

$$X_\beta = 1 - e^{-\left(\frac{\pi I U^3 t^4}{3}\right)}$$

Note that X_β is both a function of I and U. I & U are assumed constant

For a isothermal transformation



$\left(\frac{\pi I U^3}{3}\right)$ → is a constant during isothermal transformation

Effect of alloying elements on TTT diagram

- ☐ Almost all alloying elements (except, Al, Co, Si) increases the stability of supercooled austenite and retard both proeutectoid and the pearlitic reaction and then shift TTT curves of start to finish to right or higher timing. This is due to
  - ✓ low rate of diffusion of alloying elements in austenite as they are substitutional elements,
  - ✓ reduced rate of diffusion of carbon as carbide forming elements strongly hold them.
  - ✓ Alloyed solute reduce the rate of allotropic change, i.e. γ→α, by solute drag effect on γ→α interface boundary.
- ☐ Additionally those elements (Ni, Mn, Ru, Rh, Pd, Os, Ir, Pt, Cu, Zn, Au) that expand or stabilise austenite, depress the position of TTT curves to lower temperature. In contrast elements (Be, P, Ti, V, Mo, Cr, B, Ta, Nb, Zr) that favour the ferrite phase can raise the eutectoid temperature and TTT curves move upward to higher temperature.
- ☐ However Al, Co, and Si increase rate of nucleation and growth of both ferrite or pearlite and therefore shift TTT diagram to left. In addition under the complex diffusional effect of various alloying element the simple C shape behaviour of TTT diagram get modified and various regions of transformation get clearly separated. There are separate pearlitic C curves, ferritic and bainitic C curves and shape of each of them are distinct and different.

Effect of alloying elements on TTT diagram

- ❑ The effect of alloying elements is less pronounced in bainitic region as the diffusion of only carbon takes place (either to neighboring austenite or within ferrite) in a very short time (within a few second) after supersaturated ferrite formation by shear during bainitic transformation and there is no need for redistribution of mostly substitutional alloying elements.
- ❑ Therefore bainitic region moves less to higher timing in comparison to proeutectoid/pearlitic region. Addition of alloying elements lead to a greater separation of the reactions and result separate C-curves for pearlitic and bainitic region. Mo encourage bainitic reaction but addition of boron retard the ferrite reaction. By addition of B in low carbon Mo steel the bainitic region (almost unaffected by addition of B) can be separated from the ferritic region.
- ❑ However bainitic reaction is suppressed by the addition of some alloying elements. B_S temperature (empirical) has been given by Steven & Haynes

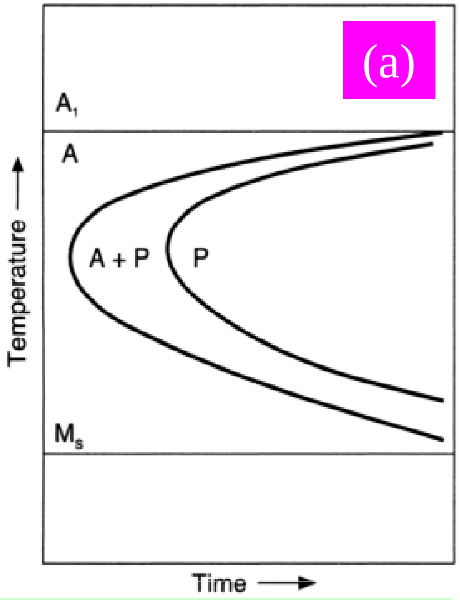
$$B_s(^0C) = 830 - 270(\%C) - 90(\%Mn) - 37(\%Ni) - 70(\%Cr) - 83(\%Mo)$$

- ❑ Most alloying elements which are soluble in austenite lower M_S, M_F temperature except Al, Co. Andrews gave best fit equation for M_S:

$$M_s(^0C) = 539 - 423(\%C) - 30.4Mn - 17.7Ni - 12.1Cr - 7.5Mo + 10Co - 7.5Si$$

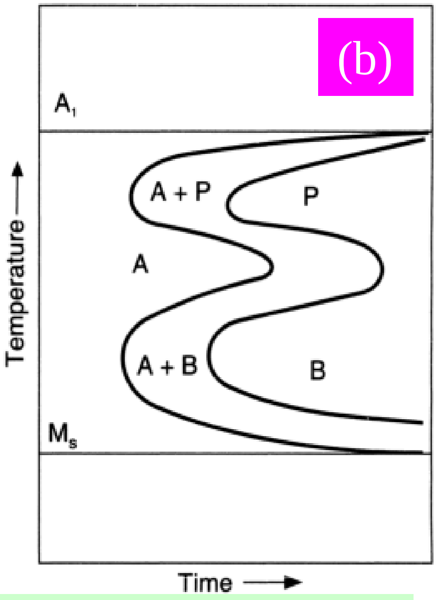
- ❑ Effect of alloying elements on M_F is similar to that of M_S. Therefore, subzero treatment is must for highly alloyed steels to transform retained austenite to martensite.

Various types of TTT diagrams for alloy steels



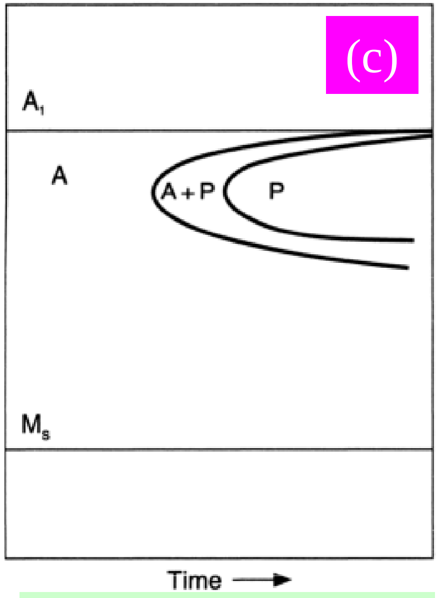
With resembalance of plain carbon steel

The (a) type of TTT diagram is similar to that of carbon steel. In the presence of carbide forming elements super cooled austenite decomposes to a mixture of ferrite and carbides rather than to aggregate of ferrite and cementite.



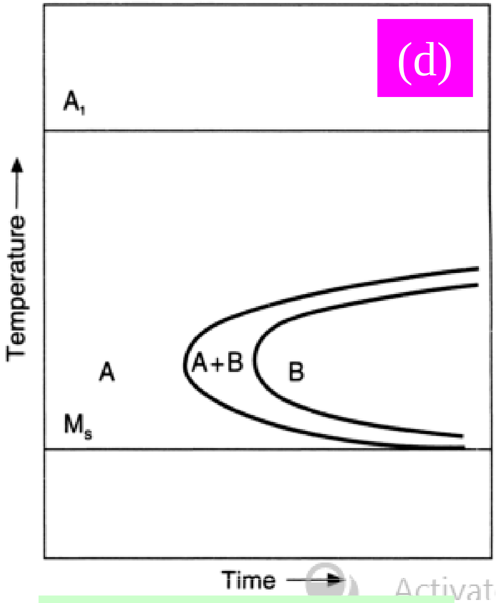
With both pearlitic and bainitic bays

The (b) type of TTT diagram consists of two minima with respect to the stability of austenite. The upper bay (γ → pearlite), lower bay (γ→ bainite). Very few steels exhibit such a TTT diagram.



With out bainitic bay

The (c) type of TTT diagram is peculiar in the sense that bainitic region is not present. Such a TTT diagram is obtained , in general, for high alloy steels and Ms region shifted to sub zero region



With out pearlitic bay

The (d) type of TTT diagram does not exhibit pearlitic bay. Under normal conditions either bainite or martensite can be formed.

Factors affecting on TTT diagram

Composition of steel

- Carbon and alloying elements affect the transformation of austenite in many ways. As the amount of carbon and most alloying elements increase in steel, the lower part of the curves is progressively lowered because except for aluminium, all the elements lower the M_s temperature.
- The austenite stabilizers lower the Ac_3 as well as Ac_1 temperatures, i.e., these elements (Ni, Mn, C etc) lower the upper part of the TTT curve. This probably is the reason of having overlapping 'C' curves for pearlitic and bainitic transformations in plain carbon steel as well as in steels having Ni, etc.
- Ferrite stabilizers raise Ac_3 as well as Ac_1 temperatures. As the TTT curve for such steels get raised upward as well as gets lowered down ward, there are invariably two 'C' curves- one for pearlitic and the other for bainitic transformations. For example, presence of 0.8% Cr and 0.33% Mo in steel yield two 'C' curves.
- Andrew suggests the effect of the elements on Ac_3 and Ac_1 by equations :

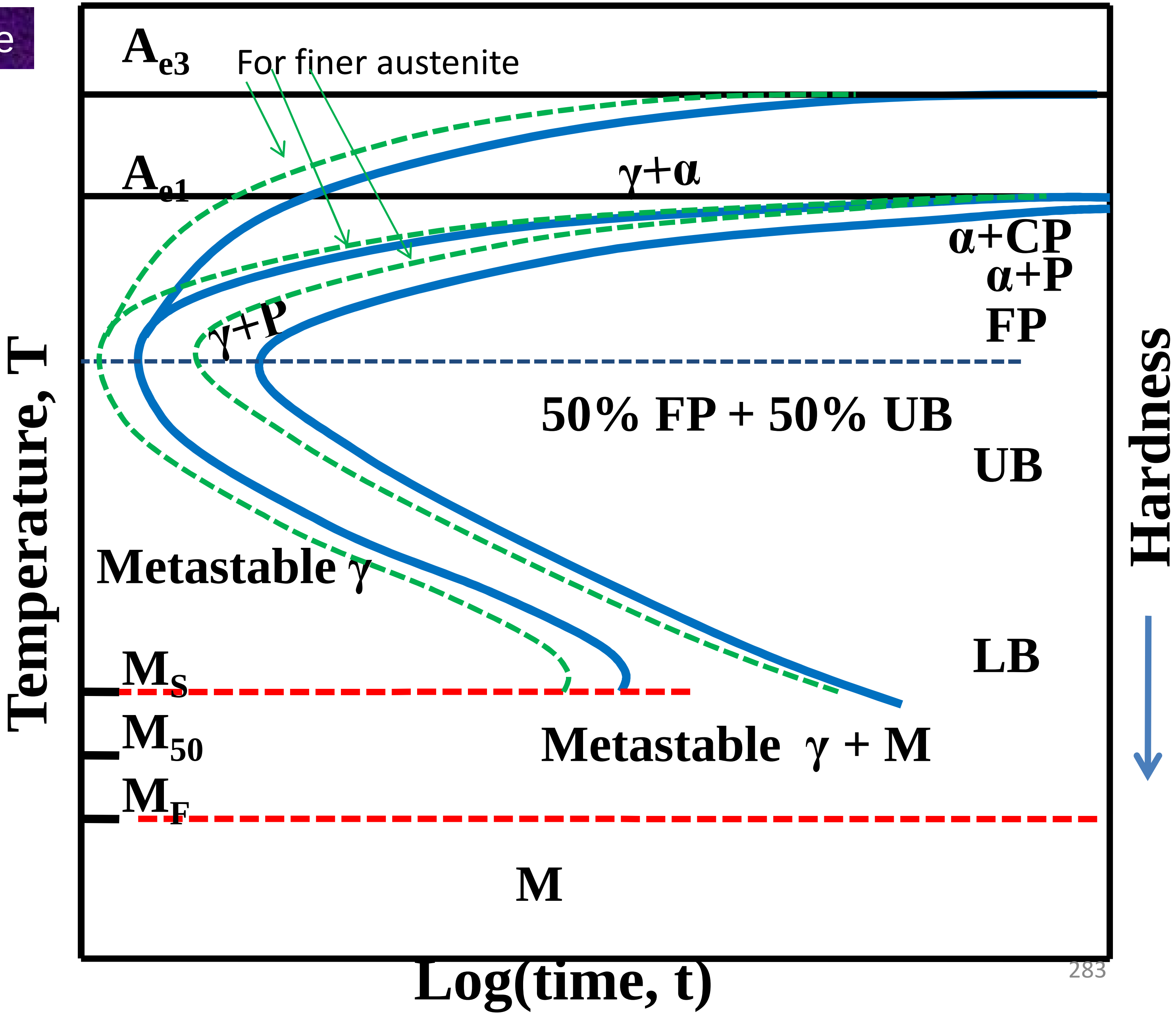
$$\boxed{Ac_3 = 910 - 203\sqrt{\%C} - 15.2(\%Ni) + 44.7(\%Si) + 104(\%V) + 31.5(\%Mo) + 13.1(\%W)}$$

$$\boxed{Ac_1 = 727 - 10.7(\%Mn) - 16.9(\%Ni) + 29.1(\%Si) + 290(\%As) + 16.9(\%Cr) + 6.38(\%W)}$$

Factors affecting on TTT diagram

Effect of grain size

γ=austenite
α=ferrite
CP=coarse pearlite
P=pearlite
FP=fine pearlite
UB=upper Bainite
LB=lower Bainite
M=martensite
M_S=Martensite start temperature
M_{50}=temperature at which 50% martensite is obtained
M_F= martensite finish temperature



Factors affecting on TTT diagram

Effect of grain size

- All the composition products of austenite nucleate heterogeneously preferentially at the grain boundaries.
- A fine grained steel has larger grain boundary area than a coarse grained steel, and consequently favors nucleation of pearlite, bainite, ferrite, cementite and thus, reduces the incubation period, that means the TTT curve of the fine grained steel is more towards left, significantly in the pearlitic range, than a coarse grained steel of same composition.

Effect of Heterogeneity of Austenite

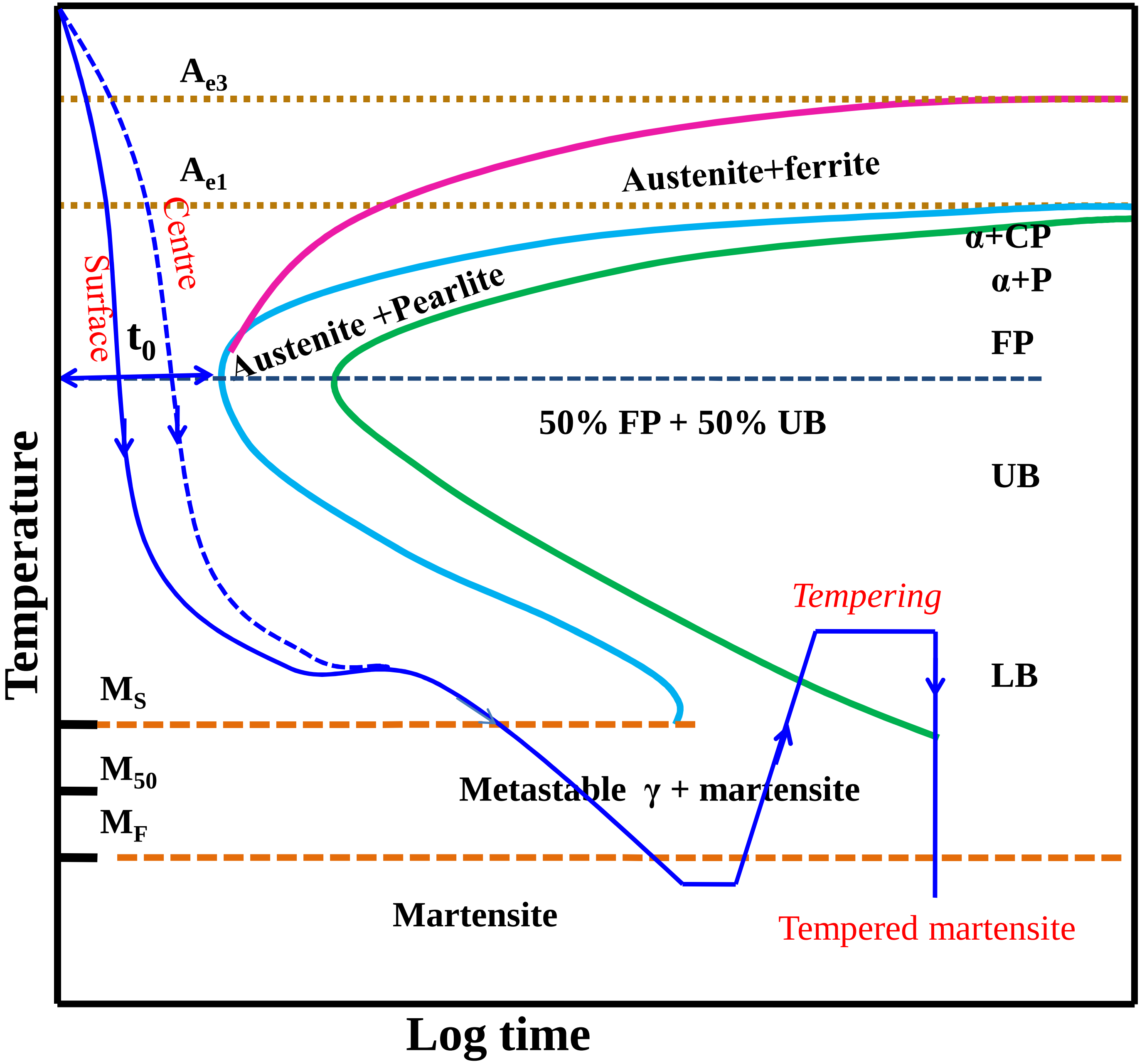
- Heterogeneous austenite increases transformation time range, start to finish of ferritic, pearlitic and bainitic range as well as increases the transformation temperature range in case of Martensitic transformation and bainitic transformation. Undissolved cementite, carbides act as powerful inoculants for pearlite transformation. Therefore heterogeneity in austenite increases the transformation time range in Diffusional transformation and temperature range of shear transformation products in TTT diagram.
- This heterogeneity of austenite, when the steel is heated to temperatures not higher than 50°C above A_1 is put to advantage to obtain spheroidized pearlite by letting it decompose within 50°C below A_1 to improve the ductility and the machinability (high carbon steels).

Applications of TTT diagrams

MARTEMPERING

- This heat treatment is given to oil hardenable and air hardenable steels and thin section of water hardenable steel sample to produce martensite with minimal differential thermal and transformation stress to avoid distortion and cracking.
- The steel should have reasonable incubation period at the nose of its TTT diagram and long bainitic bay.
- The sample is quenched above M_S temperature in a salt bath to reduce thermal stress (instead of cooling below M_F directly) Surface cooling rate is greater than at the centre.
- The cooling schedule is such that the cooling curves pass behind without touching the nose of the TTT diagram. The sample is isothermally hold at bainitic bay such that differential cooling rate at centre and surface become equalize after some time.
- The sample is allowed to cool by air through M_S-M_F such that martensite forms both at the surface and centre at the same time due to not much temperature difference and thereby avoid transformation stress because of volume expansion. The sample is given tempering treatment at suitable temperature.
- The rate of cooling from austenising temperature should avoid formation of pearlitic and bainite. Thus the success of Martempering depends on the incubation period at the pearlitic nose, and also at the bainitic bay, and thus the steel suitable for Martempering should have sufficient hardenability. *Plain carbon steels with dia. > 10mm are difficult to mar-temper and thus, this process is restricted to alloy steels.*

Martempering



γ=austenite
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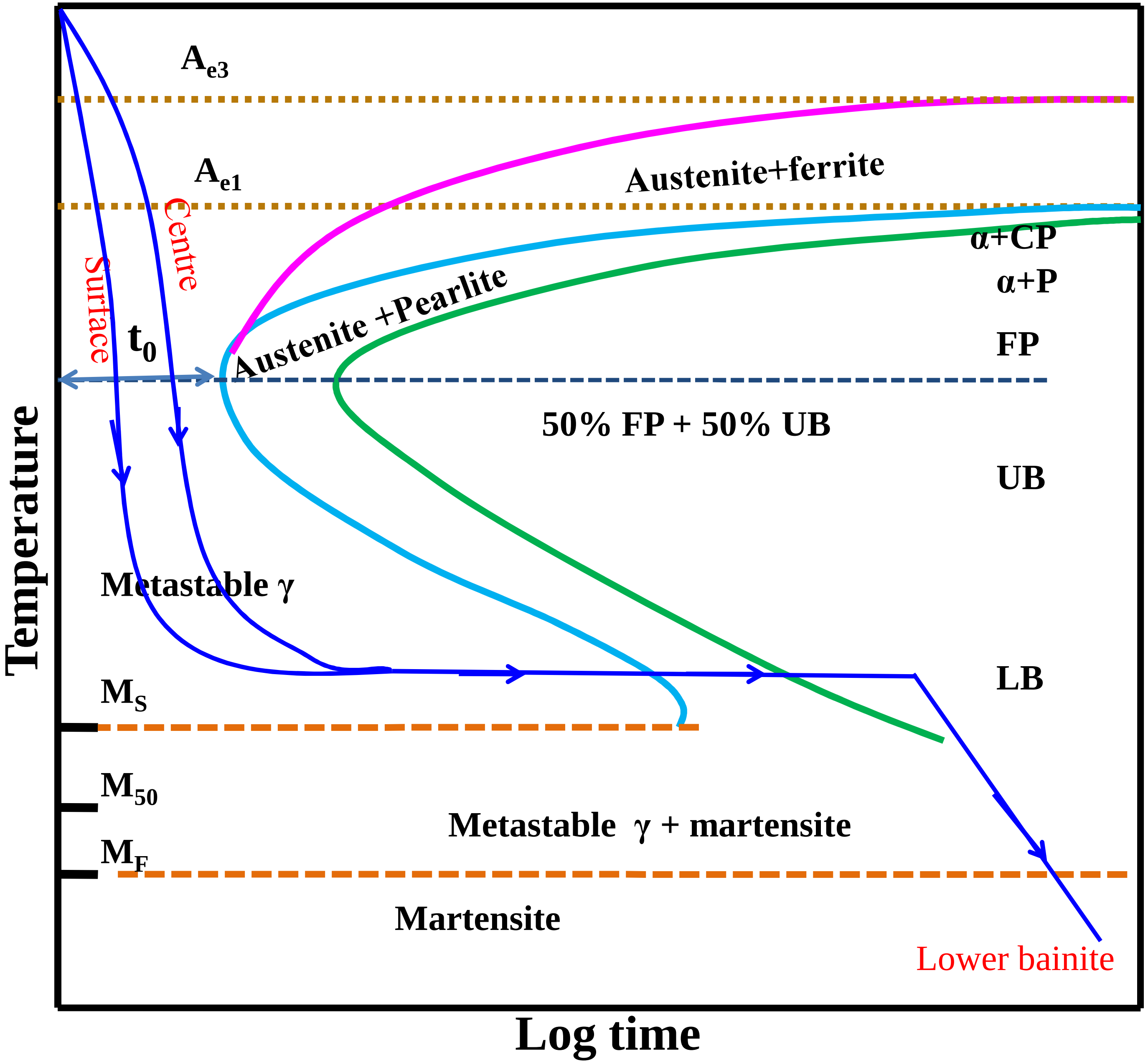
CP=coarse pearlite
P=pearlite
FP=fine pearlite
t_0=minimum incubation period
UB=upper bainite
LB=lower bainite
M=martensite
M_S=Martensite start temperature
M_{50}=temperature at which 50% martensite is obtained
M_F= martensite finish temperature

Applications of TTT diagrams

AUSTEMPERING

- ☐ Austempering heat treatment is given to steel to produce lower bainite in high carbon steel without any distortion or cracking to the sample.
- ☐ The heat treatment is cooling of austenite rapidly in a bath maintained at lower bainitic temperature (above M_s) temperature (avoiding the nose of the TTT diagram) and holding it here to equalize surface and centre temperature and till bainitic finish time.
- ☐ At the end of bainitic reaction sample is air cooled. The microstructure contains fully lower bainite. This heat treatment is given to 0.5-1.2 wt%C steel and low alloy steel.
- ☐ The product hardness and strength are comparable to hardened and tempered martensite with improved ductility and toughness and uniform mechanical properties. Products do not required to be tempered.
- ☐ TTT diagram is great help in scheduling Austempering as it fixes
  - ✓ Temperature of holding of the bath
  - ✓ Duration of holding time
  - ✓ Section which can be quenched to avoid pearlite formation
  - ✓ Whether Austempering is worth while , or not, as the time at the bay may be too long.

Austempering



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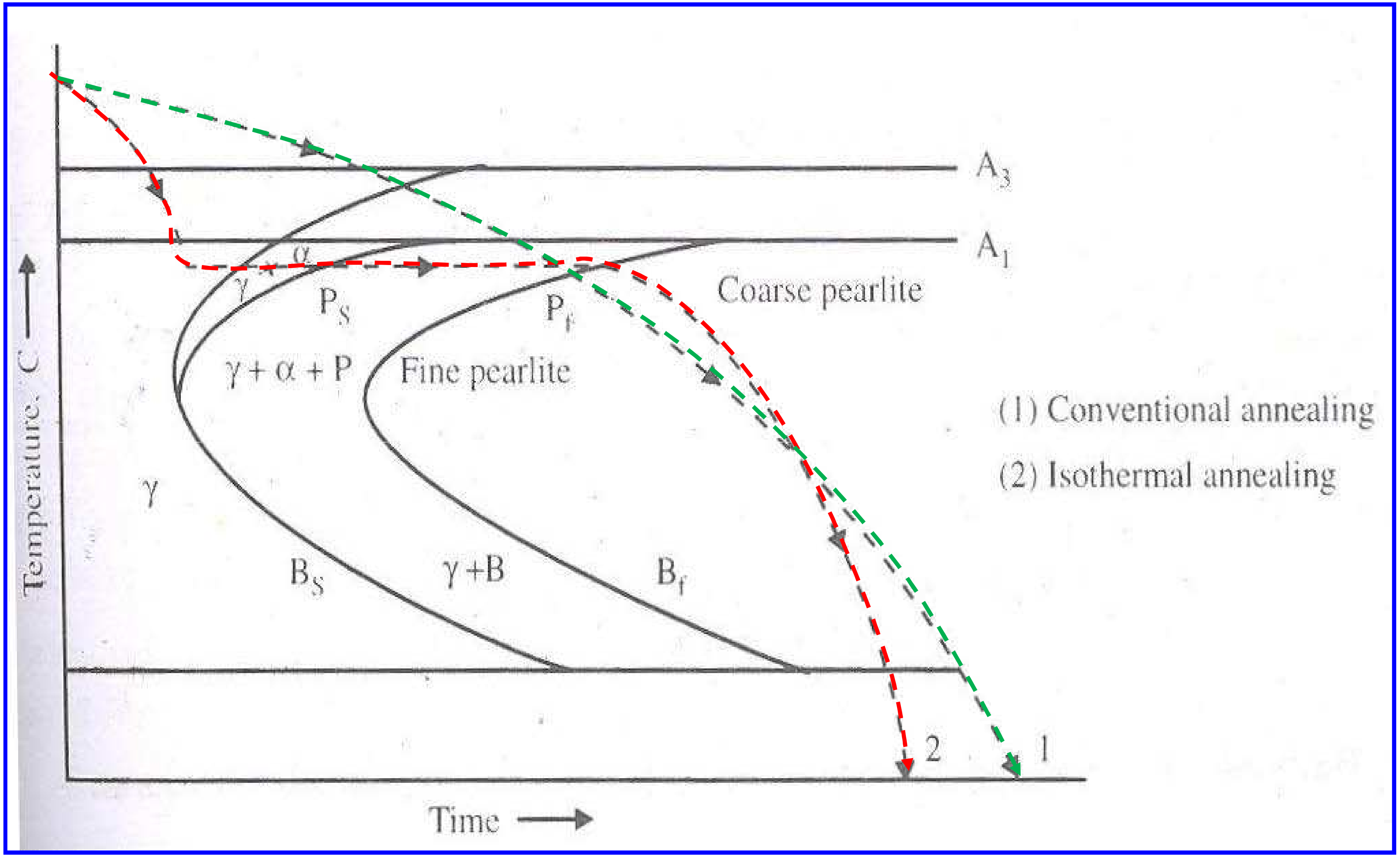
M_S=Martensite start temperature
M_{50}=temperature at which 50% martensite is obtained
M_F= martensite finish temperature

Applications of TTT diagrams

ISOTHERMAL ANNEALING

- Isothermal annealing consists of four steps.
    - The first step is heating the steel components similar as in the case of full annealing.
    - The second step is slightly fast cooling from the usual austenitizing temperature to a constant temperature just below A_1.
    - The third step is to hold at this reduced temperature for sufficient soaking period for the completion of transformation and the final step involves cooling the steel component to room temperature in air.
- Figure (nextslide) depicts the heat treatment cycles of full annealing and isothermal annealing. The terms α, γ, P, P_s and P_F refer to ferrite, austenite, pearlite, pearlite starting and pearlite finish, respectively.
- Isothermal annealing has distinct advantages over full annealing which are given below.
    - ✓ Reduced annealing time, especially for alloy steels which need very slow cooling to obtain the required reduction in hardness by the full annealing.
    - ✓ More homogeneity in structure is obtained as the transformation occurs at the same time throughout the cross section.
    - ✓ Improved machinability and surface finish is obtained after machining as compared to that of the full annealed components.

Isothermal Annealing



Isothermal annealing is primarily used for medium carbon, high carbon and some of the alloy steels to improve their machinability.

Applications of TTT diagrams

PATENTING

- ☐ Patenting is an isothermal heat treatment processes used for producing high strength ropes, springs, and piano wires of normally 0.45% to 1.0% carbon steel. In fact, the strongest material in commercial quantities is the patented and cold drawn wire made from 0.80% to 1.0% carbon steel, containing no martensite. Wires having high ultimate tensile strength of 4830MN/m^2 with 20% elongation have been reported.
- ☐ Patenting consists of austenitising steel in continuous furnace to temperature 150-200°C above Ac_3 , then cooling rapidly in and holding in a lead, or salt bath maintained at a temperature of 450-550°C (near the pearlitic nose of its TTT curve, i.e., in the lower temperature limit of pearlitic transformation) for sufficient time for austenite to completely transform to finest pearlite (some upper bainite may also form), and then wound on to driven drum
- ☐ The eutectoid steel after patenting may have interlamellar spacing as small as 40nm with strength as 1240-1450 Mpa. The process of patenting helps in two ways to obtain high strengths. Patented wires can be cold drawn by large extent (80-90%) without fracture as the soft , weak primary ferrite or brittle cementite is absent and the interlamellar spacing is same every where.
- ☐ TTT diagram help to fix the time and temperature of holding. The speed of motion of the wire through the bath should be such that it remains in bath for a time slightly greater than the time of completion of pearlitic transformation to avoid any chance of untransformed austenite to bainite or martensite later.

Patenting

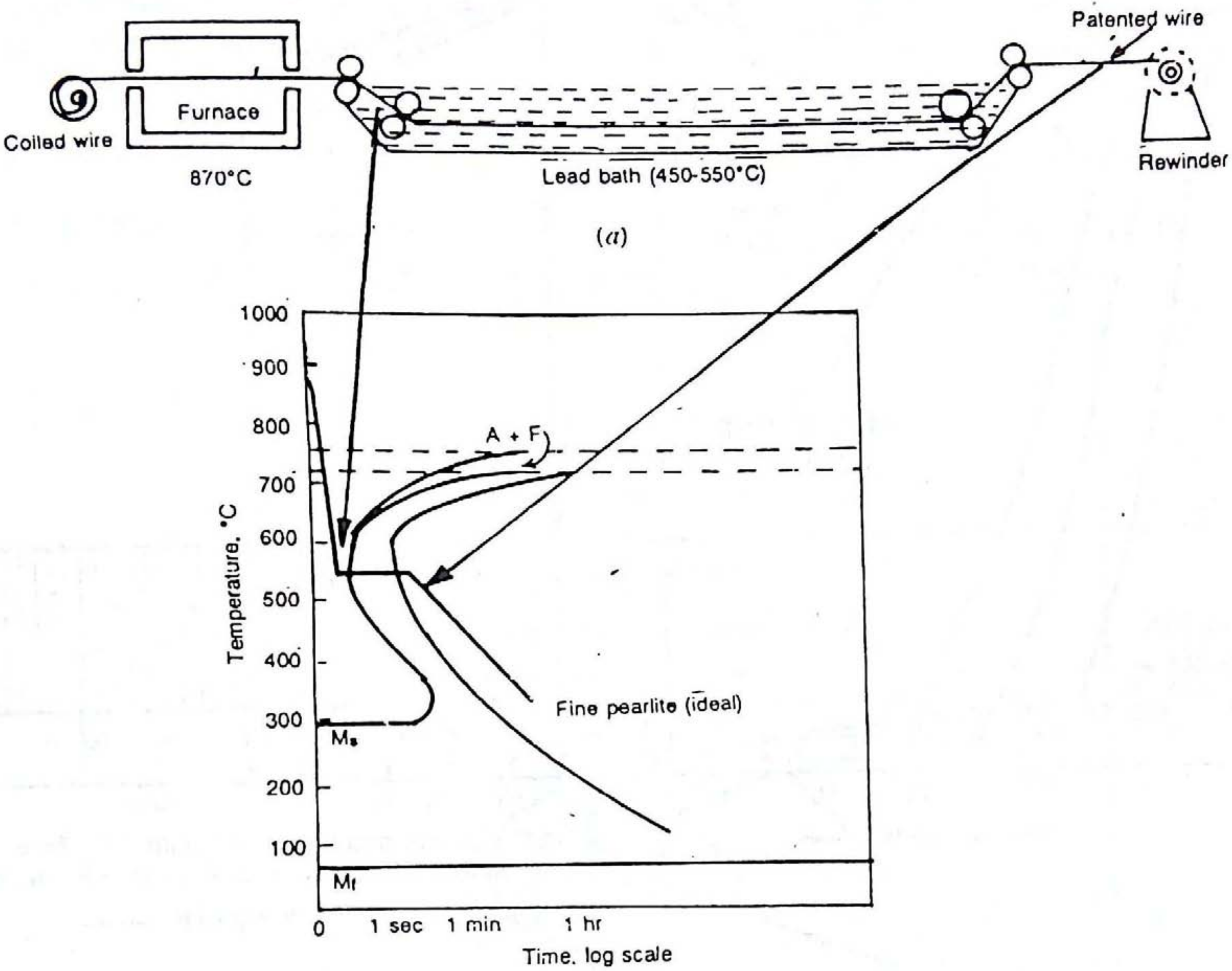


Figure : Patenting (a) Schematic process of patenting, (b) TTT diagram of 0.6% carbon steel

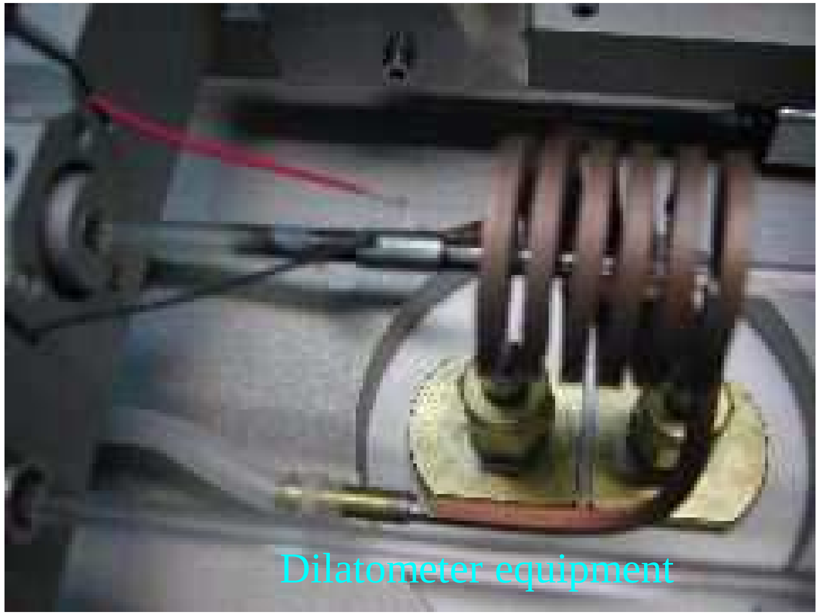
Continuous Cooling Transformation (CCT) diagrams

- ❑ The TTT diagrams are also called Isothermal Transformation Diagrams, because the transformation times are representative of isothermal hold treatment (following a instantaneous quench).
- ❑ In practical situations we follow heat treatments (T-t procedures/cycles) in which (typically) there are steps involving cooling of the sample. The cooling rate may or may not be constant. The rate of cooling may be slow (as in a furnace which has been switch off) or rapid (like quenching in water).
- ❑ Hence, in terms of practical utility TTT curves have a limitation and we need to draw separate diagrams called Continuous Cooling Transformation diagrams (CCT), wherein transformation times (also: products & microstructure) are noted using constant rate cooling treatments.
- ❑ A diagram drawn for a given cooling rate (dT/dt) is typically used for a range of cooling rates (thus avoiding the need for a separate diagram for every cooling rate).
- ❑ However, often TTT diagrams are also used for constant cooling rate experiments- keeping in view the assumptions & approximations involved.
- ❑ *Important difference between the CCT & TTT transformations is that in the CCT case Bainite cannot form.*
- ❑ The CCT diagram for eutectoid steel is considered next.

Determination of CCT diagram for eutectoid steel

- ❑ CCT diagrams are determined by measuring some physical properties during continuous cooling. Normally these are specific volume and magnetic permeability. However, the majority of the work has been done through specific volume change by dilatometric method. This method is supplemented by metallography and hardness measurement.
- ❑ In dilatometry the test sample is austenitised in a specially designed furnace and then controlled cooled. Sample dilation is measured by dial gauge/sensor. Slowest cooling is controlled by furnace cooling but higher cooling rate can be controlled by gas quenching

Sample and fixtures
for dilatometric measurements



Dilatometer equipment

Determination of CCT diagram for eutectoid steel

- ❑ Cooling data are plotted as temperature versus time (Fig. a). Dilation is recorded against temperature (Fig. b). Any slope change indicates phase transformation. Fraction of transformation roughly can be calculated based on the dilation data as explained below.

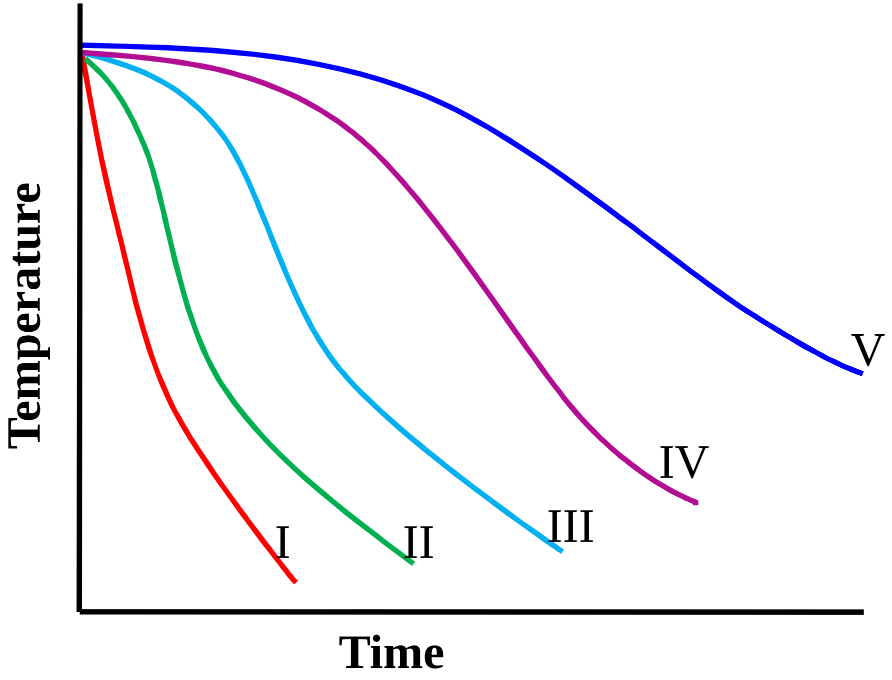


Fig. a : Schematic cooling curves

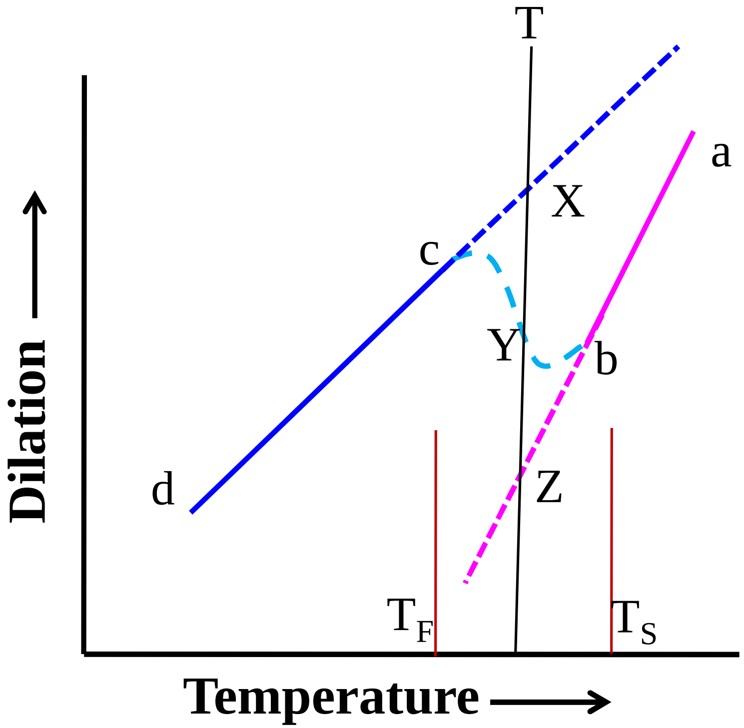


Fig. b : Dilation-temperature plot for a cooling curve

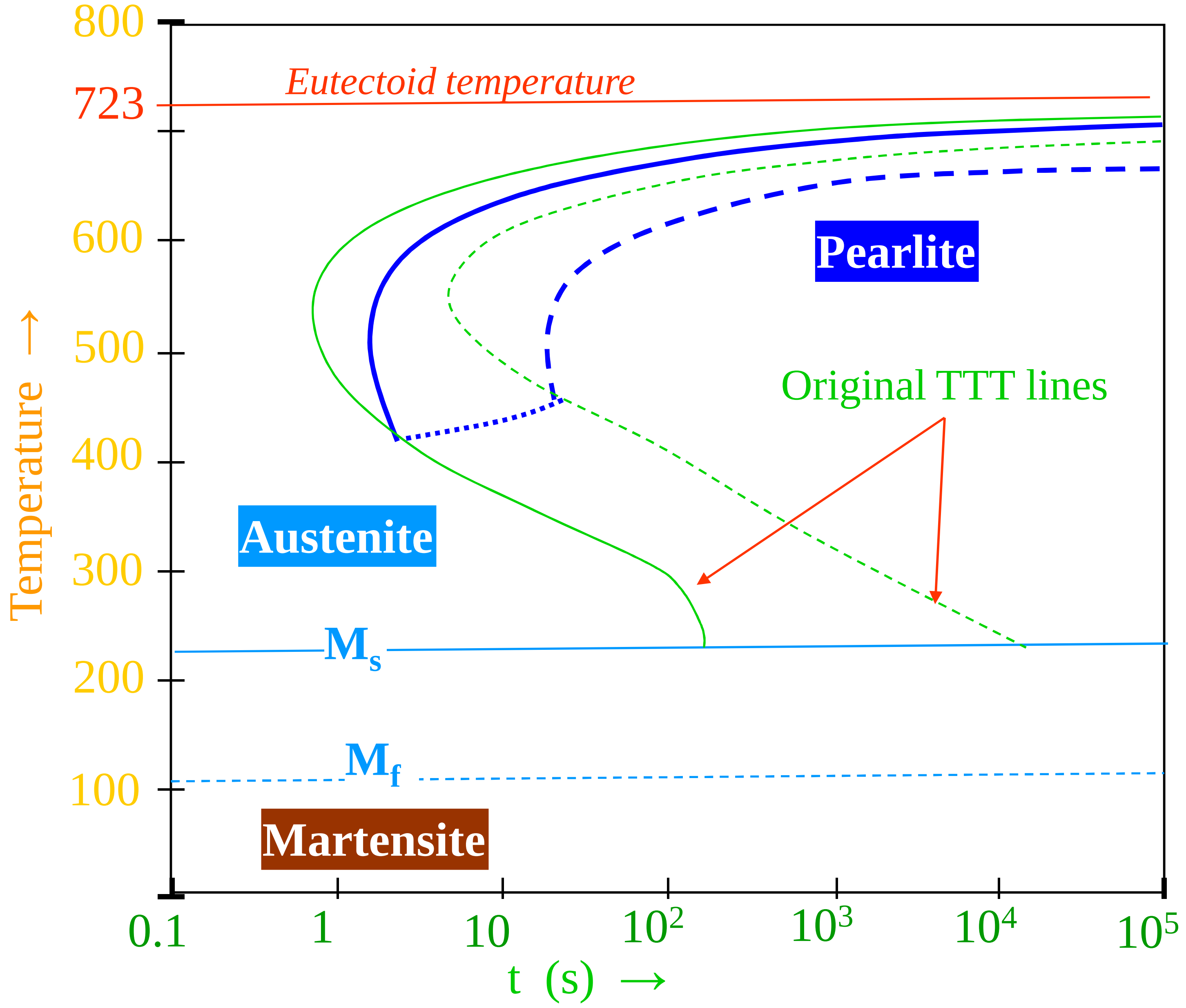
Determination of CCT diagram for eutectoid steel

- ☐ In **Fig. a** curves I to V indicate cooling curves at higher cooling rate to lower cooling rate respectively.
- ☐ **Fig. b** gives the dilation at different temperatures for a given cooling rate/schedule.
- ☐ In general slope of dilation curve remains unchanged while amount of phase or the relative amount of phases in a phase mixture does not change during cooling (or heating) however sample shrink or expand i.e. dilation takes place purely due to thermal specific volume change because of change in temperature.
- ☐ Therefore in **Fig. b** dilation from a to b is due to specific volume change of high temperature phase austenite. But at T_S slope of the curve changes.
- ☐ Therefore transformation starts at T_S. Again slope of the curve from c to d is constant but is different from the slope of the curve from a to b.
- ☐ This indicates there is no phase transformation between the temperature from c to d but the phase/phase mixture is different from the phase at a to b.
- ☐ Slope of the dilation curve from b to c is variable with temperature. This indicates the change in relative amount of phase due to cooling.
- ☐ The expansion is due to the formation of low density phase(s). Some part of dilation is compensated by purely thermal change due to cooling.
- ☐ Therefore dilation curve takes complex shape. i.e first slope reduces and reaches to a minimum value and then increases to the characteristic value of the phase mixture at c.

Determination of CCT diagram for eutectoid steel

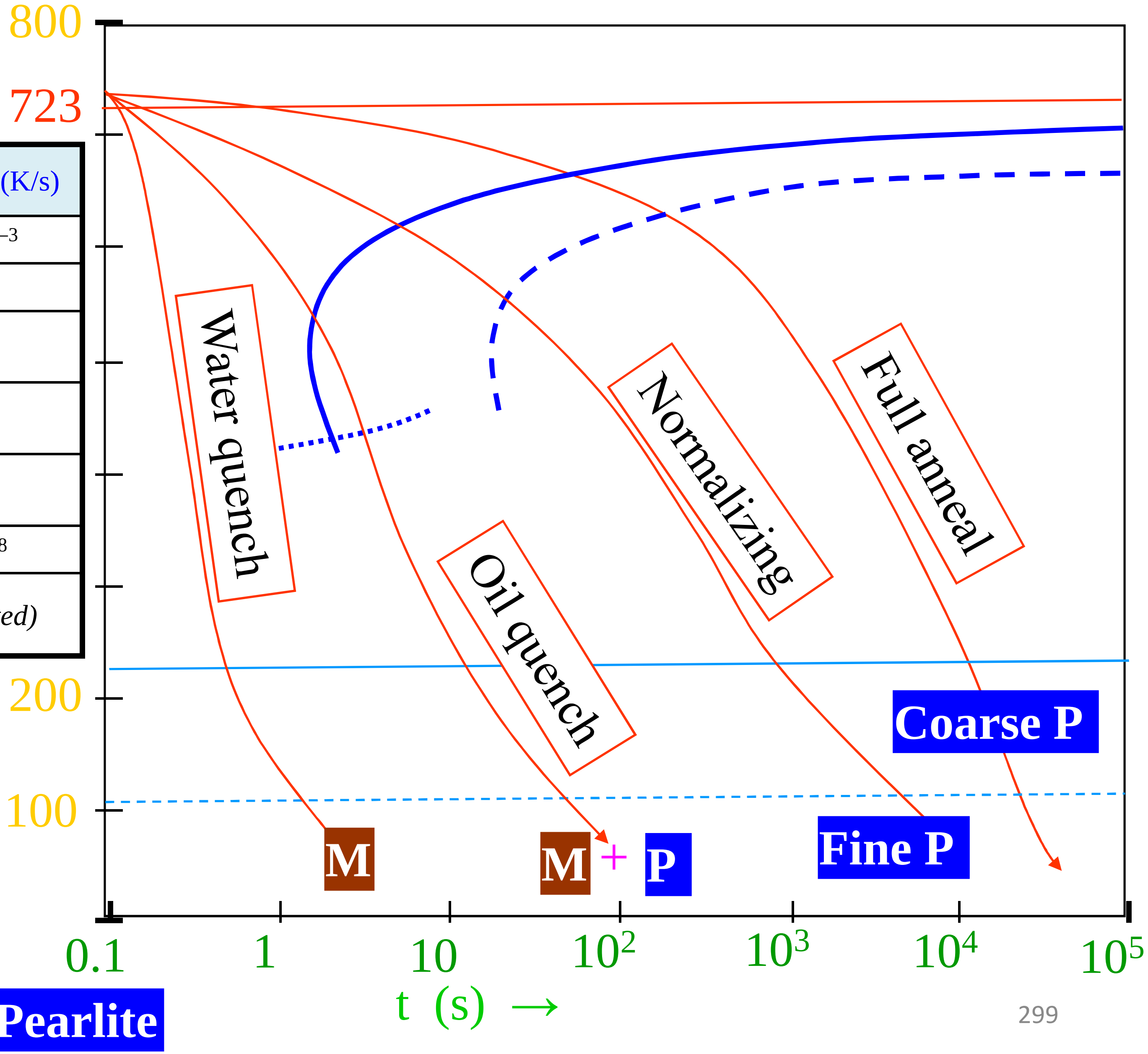
- Therefore phase transformation start at b i.e. at temperature T_S and transformation ends or finishes at c or temperature T_F. The nature of transformation has to be determined by metallography.
- When austenite fully transforms to a single product then amount of transformation is directly proportional to the relative change in length. For a mixture of products the percentage of austenite transformed may not be strictly proportional to change in length, however, it is reasonable and generally is being used.
- Cumulative percentage of transformation at in between temperature T is equal to YZ/XZ*100 where X, Y and Z are intersection point of temperature T line to extended constant slope curve of austenite (ba), transformation curve (bc) and extended constant slope curve of low temperature phase (cd) respectively.
- So at each cooling rate transformation start and finish temperature and transformation temperature for specific amount (10 %, 20%, 30% etc.) can also be determined.
- For every type of transformation, locus of start points, is percentage points and finish points give the transformation start line, is percentage lines and finish line respectively and that result CCT diagram.
- Normally at the end of each cooling curve hardness value of resultant product at room temperature and type of phases obtained are shown.

CCT diagram for eutectoid steel



Different cooling rates for eutectoid steel

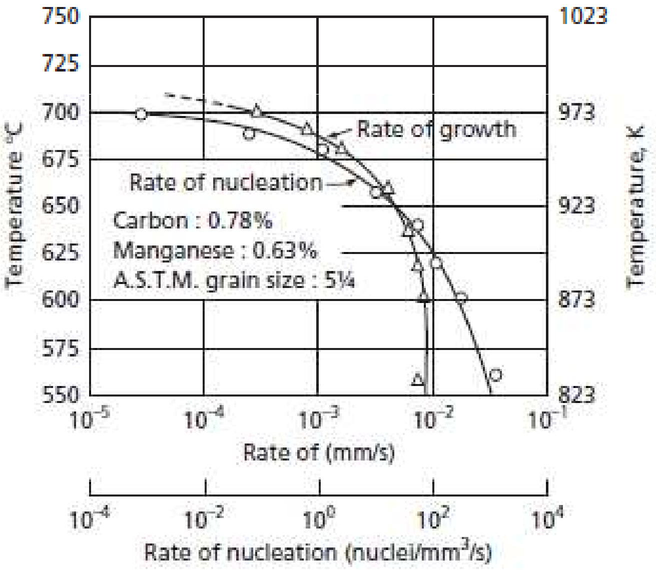
Process	Cooling rate (K/s)
Annealing	10^{-5} – 10^{-3}
Air Cooling	1 – 10
Oil Quenching	~100
Water Quenching	~500
Splat Quenching	10^5
Melt-Spinning	10^6 – 10^8
Evaporation, sputtering	10^9 *(expected)*



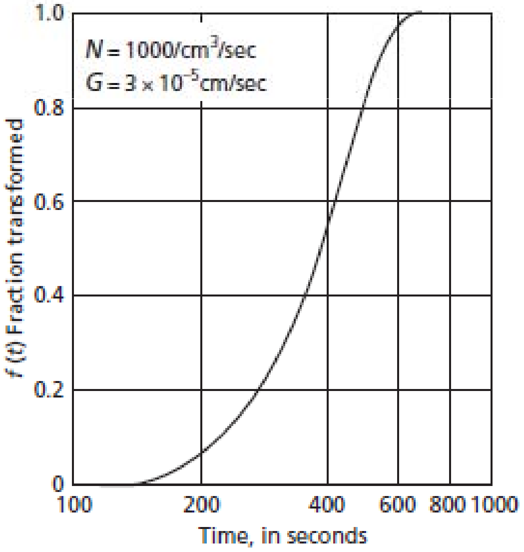
M = Martensite **P = Pearlite**

Questions?

1. The Johnson-Mehl equation, in most cases adequately describes the kinetics of the austenite to pearlite transformations. This can be demonstrated by taking several sets of N and G values, which contains data from a 0.8% C plain carbon steel. This figure indicates that at 700^0C, N = 6.31×10^{-4} nuclei per mm^3 per sec and G = 3.16×10^{-4} mm per sec. Substitute these values of N and G into J-M equation, and obtain the pearlite reaction curves for this steel at 700 and 500^0C. Plot the fraction transformed , f(t), versus log(t) as in fig b.



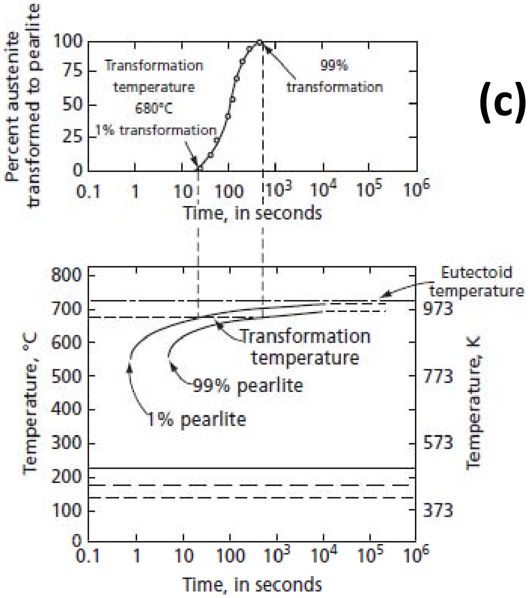
(a)



(b)

Questions?

2. Determine, using the curves obtained in problem 1, the times required to obtain 1% and 99% pearlite at 700 and 550^{o}C. Compare these times with the experimental data for an eutectoid plain carbon steel shown in the T-T-T in fig c. is the agreement reasonable?
3. In a slowly cooled hypereutectoid iron-carbon steel, the pearlite colonies are normally separated from each other by a more or less continuous boundary layer of cementite. Explain how this microstructure develops. Use simple sketches to illustrate your answer.



(c)

4. In slowly cooled hypoeutectoid steels one normally finds a microstructure in which the pearlite colonies are surrounded by ferrite grains. Explain.
5. After being slowly cooled from the austenite region, a simple iron-carbon steel exhibits a microstructure consisting of 40 percent pearlite and 60 percent ferrite.
   a) Estimate the carbon concentration of the steel.
   b) Describe the equilibrium microstructure that would be obtained if the steel were heated to 730°C and held there for a long period of time.
   c) What would be the equilibrium structure of this steel if it were heated to 850°C?
   d) Make sketches of all of these microstructures.

Questions?

6. Consider an iron-carbon alloy containing 1.0 percent carbon.
   a) If this composition is slowly cooled from the austenite region, what would be the respective percentages of the constituents and the phases in its microstructure?
   b) Now assume that it has been cooled at a rate rapid enough to yield a proeutectoid constituent of only 1.2 percent. What would be the percentages of the constituents and the phases in this case?
7. Explain in detail how bainite differs from martensite and from pearlite. How do upper and lower bainite differ?
8. Describe the meaning of the term partitioning coefficient.
9. Explain why C occupies an octahedral void not the tetrahedral void in $\alpha-$Fe.
10. In the Fe-C system Fe_3C is only a metastable phase, while graphite is the most stable carbon rich phase. By drawing schematic free energy-composition diagrams show how the Fe-graphite phase diagram compares to the Fe-Fe_3C phase diagram from 0 to 2 wt% Fe.
11. An iron-carbon steel containing 0.5 percent of carbon has a microstructure consisting of 85 percent pearlite and 15 percent ferrite.
    a) Are these the amounts of these constituents that one would expect to find in the steel if it had been slowly cooled from the austenite region?
    b) In a slowly cooled microstructure, pearlite normally has a 7 to 1 ratio of the widths of the ferrite and cementite lamellae. What would this ratio be in the present case?

Questions?

12. Answer the following with regard to the *T-T-T* diagram of a steel of eutectoid composition, and assume that the specimens involved in the various cooling paths were cut from a thin sheet and austenitized at 750°C before cooling. Describe the microstructure resulting from being:
    a) Cooled to room temperature in less that 1 s.
    b) Cooled to 160°C in less than 1 s and then maintained at this temperature for several years.
    c) Quenched to 650°C and held at this temperature for 1 day, then quenched to room temperature.
    d) Quenched to 550°C and held at this temperature for 1 day, then quenched to room temperature.

13. A high-carbon steel containing 1.13 percent carbon, with a microstructure similar to that in Fig. d, is heated to 730°C and allowed to come to equilibrium. It is then quenched to room temperature. Make a sketch of the resulting microstructure, identifying the constituents.

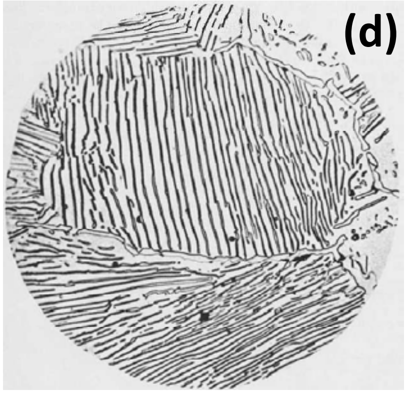
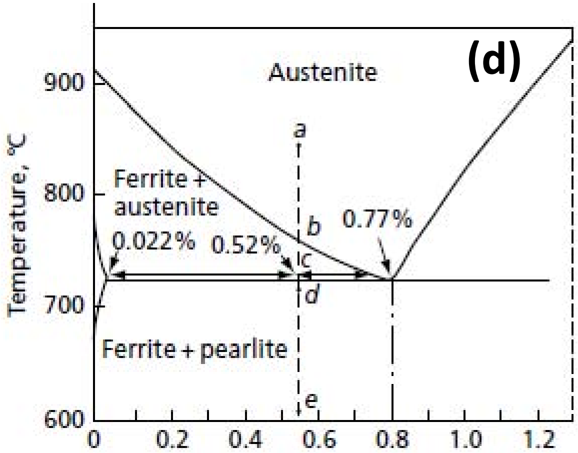


Fig. d: Hypereutectoid-steel microstructure. Notice the band of cementite plates outlining the pearlite colony in the center of the photograph. 1000X

Questions?

14. Assume that the 0.52 percent carbon steel of Fig. (e) is slowly cooled to the temperature of point *c* and then quenched to 450°C and held at this latter temperature for a period of a day. Describe the microstructure that one might find. Determine the percentages of the constituents.
15. Transpose paths 1, 2, and 3 of Fig. **g** to Fig. **f** and determine the microstructures corresponding to these paths in the hypereutectoid steel.



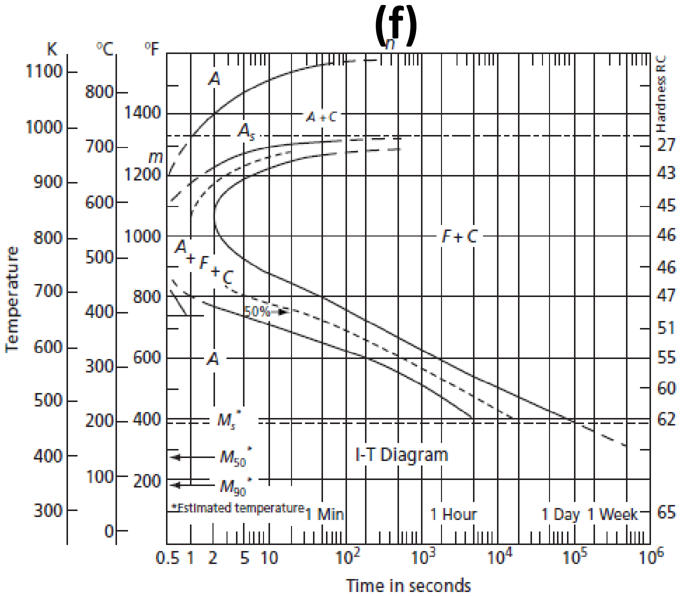


Fig. f: Isothermal transformation diagram for a hypereutectoid steel: 1.13 percent carbon, 0.30 percent manganese.

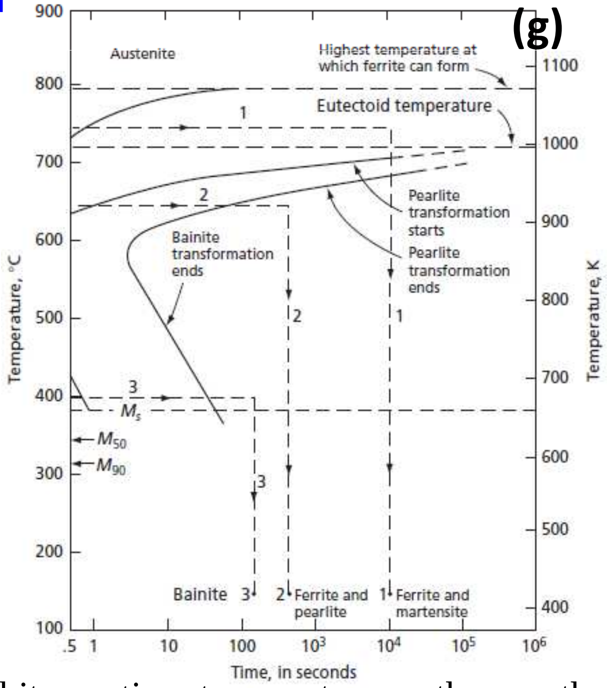


Fig. g: Arbitrary time-temperature paths on the isothermal diagram of a hypoeutectoid steel

Questions?

16. With regard to the data for eutectoid steels in Figure h.
    a) What is the interlamellar spacing in the pure Fe-C alloy at 660°C?
    b) How much smaller is it at this temperature when the steel contains 1.8 percent chromium?
    c) How much larger is it in the steel with 1.8 % manganese?

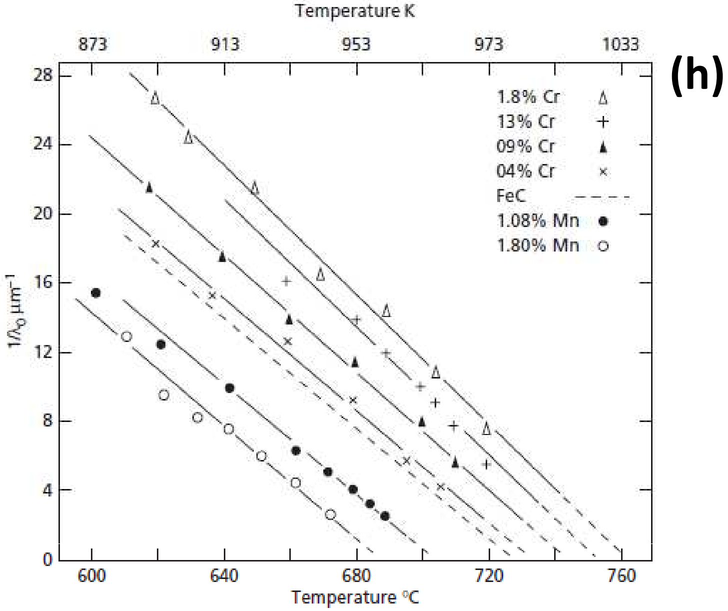


Fig. h: Minimum interlamellar spacing data for eutectoid steel containing additions of manganese and chromium

17. Estimate %Cm in Ledeburite just below eutectic and just above eutectoid temeratures. What is its structure at room temperature?
18. Use the concept of Bain distortion to estimate maximum displacement experienced by iron atom during martensitic transformation. Lattice parameters of austenite and ferrite are 0.356nm & 0.286 respectively. Assume c/a ratio of martensite to be 1.15.
19. Carbon atoms occupy octahedral interstitial sites in austenite and ferrite. Estimate fraction of these sites that are occupied in these if carbon contents are 0.1 and 0.01wt% respectively.

Questions?

20. Show that the inter-lamellar spacing of pearlite is inversely proportional to the degree of under cooling.
21. Which is the more stable, the pearlitic or the spheroiditic microstructure? Why?
22. How are the critical temperatures in steel designated? What is the critical range?
23. Draw the Fe-Fe_3C phase diagram and label the phase fields. Discuss in brief the different reactions that takes place in this system.
24. Compute the following
    a) % pearlite and cementite in asteel containing 1.2% C.
    b) % austenite and ledeburite in cast iron containing 3.5% C.
    c) % ferrite and cementite in a steel containing 0.8% carbon.
25. Discuss in brief the effect of alloying elements in Fe-Fe_3C phase diagram.
26. Discuss in brief the effect of along elements in TTT & CCT diagrams
27. Draw the TTT diagram for Hypo eutectoid, Eutectiod and Hyper eutectoid steels.
28. Draw the CCT diagram for Hypo eutectoid, Eutectiod and Hyper eutectoid steels.
29. CCT curve of eutectoid steel is displaced towards right and lowered as compared to its TTT curve. Why?
30. What are the limitations of Fe-Fe_3C diagram, TTT diagram and CCT diagram?

Diffusional Transformations

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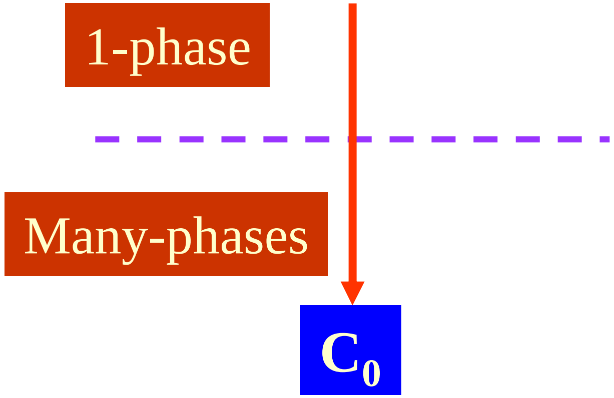
Introduction

- The majority of phase transformations that occur in the solid state takes place by thermally activated atomic movements.
- The transformations that will be dealt with in this chapter are those that are induced by a change of temperature of an alloy that has a fixed composition.



- Usually we will be concerned with the transformations caused by a temperature change from a single phase region of a (binary) phase diagram to a region where one or moreother phases are stable.
- The different types of phase transformations that are possible can be roughly divided in to several groups (*see in next slide).*

Classification of Diffusional transformations

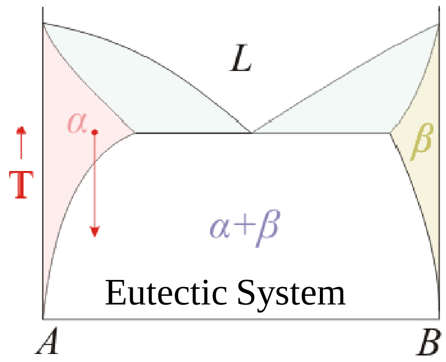
Diffusional Transformations

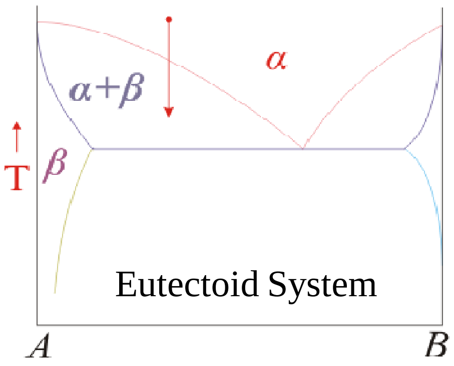
- Precipitation $\alpha' \rightarrow \alpha + \beta$
  - $\alpha' \rightarrow$ metastable supersaturated solid solution
- Eutectoid $\gamma \rightarrow \alpha + \beta$
- Polymorphic $\beta_{crystal-1} \rightarrow \alpha_{crystal-2}$
- Ordering $\alpha(disordered) \rightarrow \alpha'(ordered)$
- Massive $\beta \rightarrow \alpha$

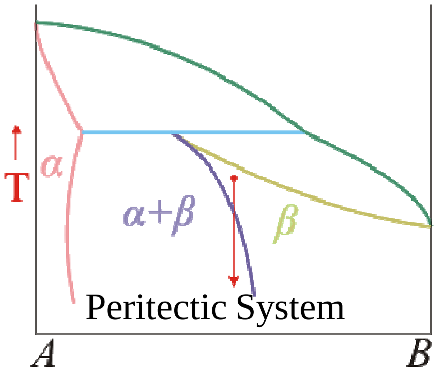
Original phase decomposes to one or more new phases which have the same composition as the parent phase but different crystal structures

Classification of Diffusional transformations

Precipitation

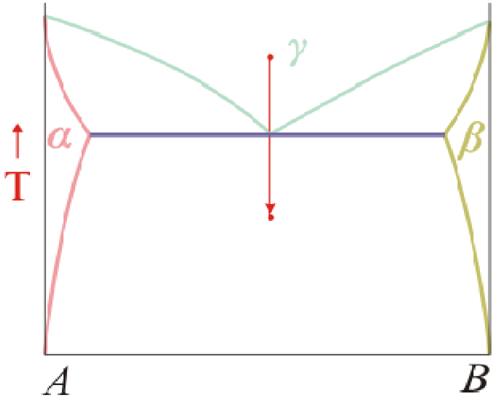






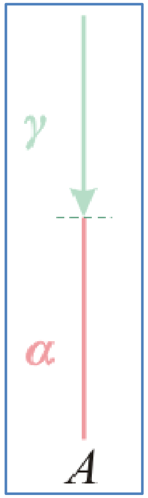
$$\alpha' \rightarrow \alpha + \beta$$

Eutectoid



$$\gamma \rightarrow \alpha + \beta$$

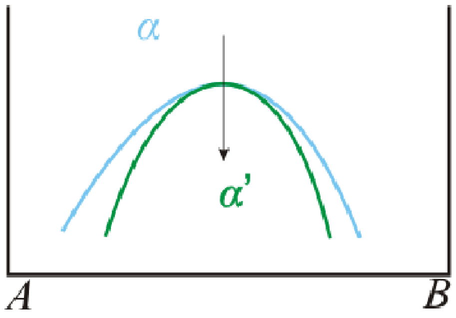
Polymorphic

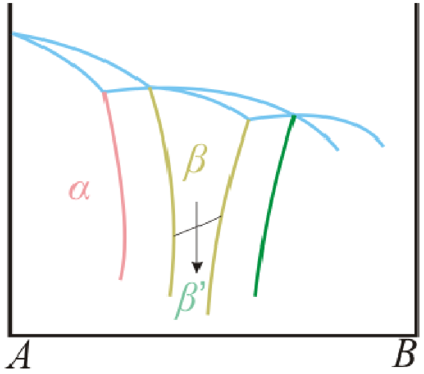


$$\beta_{crystal-1} \rightarrow \alpha_{crystal-2}$$

Classification of Diffusional transformations

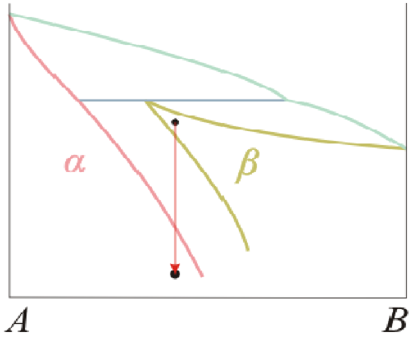
Ordering

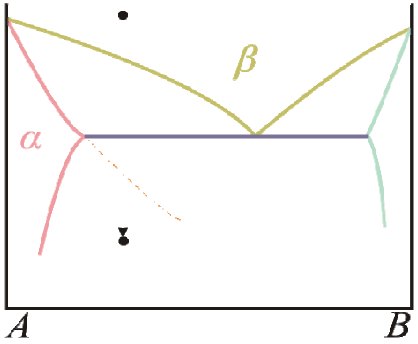




$$\boxed{\alpha(disordered) \rightarrow \alpha'(ordered)}$$

Massive



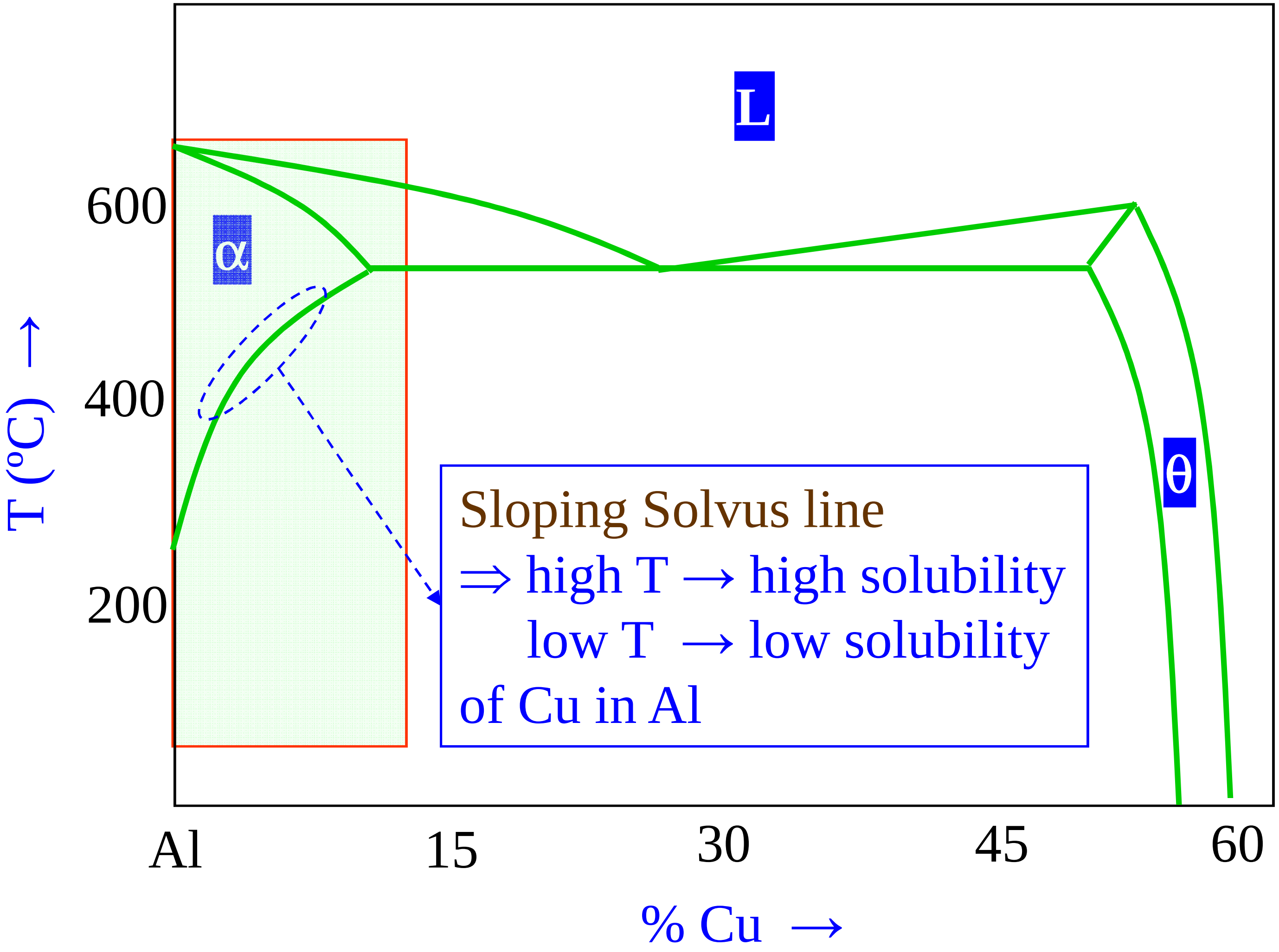


$$\boxed{\beta \rightarrow \alpha}$$

Precipitation Hardening

- The most important heat treating process for non ferrous alloys is *age hardening*, or *precipitation hardening*.
- In order to apply this heat treatment, the equilibrium diagram must show partial solid solubility, and the slope of the solvus line must be such that there is greater solubility at a higher temperature than at a lower temperature.
- The purpose of precipitation hardening treatment is to improve strength of the materials. It can explained by with respect to dislocations.
- The presence of dislocation weakens the crystal → easy plastic deformation
- Putting hindrance to dislocation motion increases the strength of the crystal
- Fine precipitates dispersed in the matrix provide such an impediment.
- For example: Strength of Al → 100 MPa
  Strength of Duralumin (Al + 4% Cu + other alloying elements) → 500 Mpa
- Two stages are generally required in heat treatment to produce age hardening:
  - ✓ Solution treatment
  - ✓ Aging

Precipitation Hardening

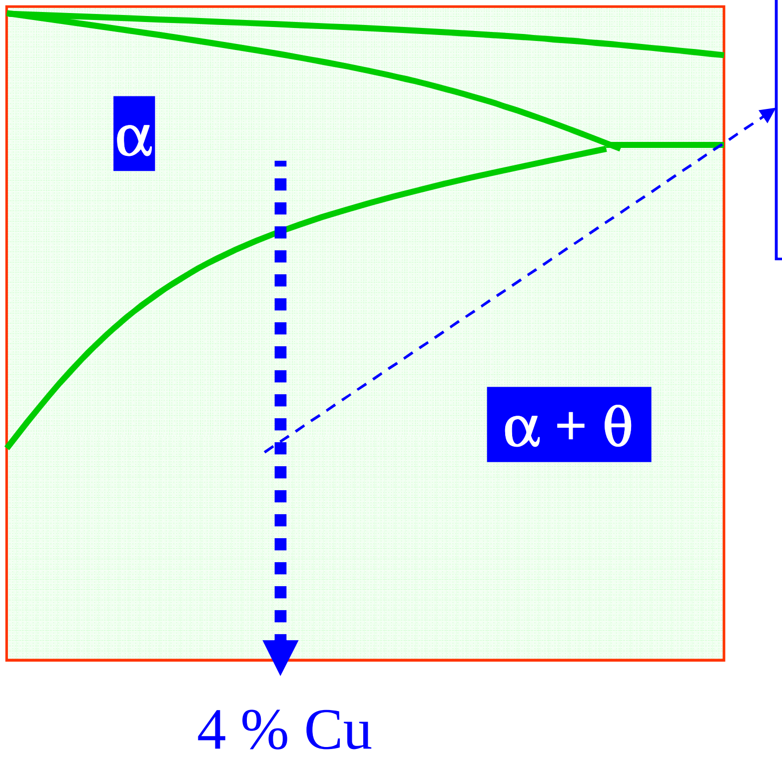


Sloping Solvus line
⇒ high T → high solubility
low T → low solubility
of Cu in Al

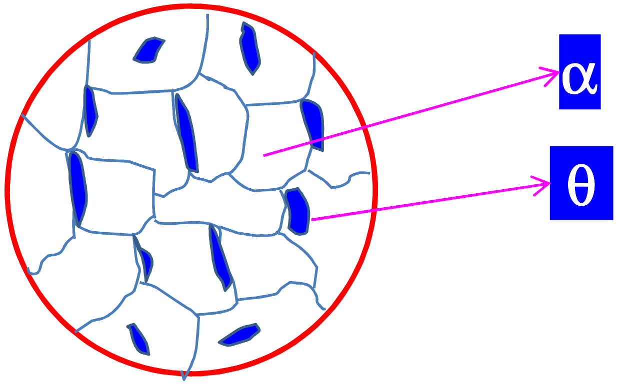
Al rich end of the Al-Cu phase diagram

Precipitation Hardening

On Equilibrium cooling



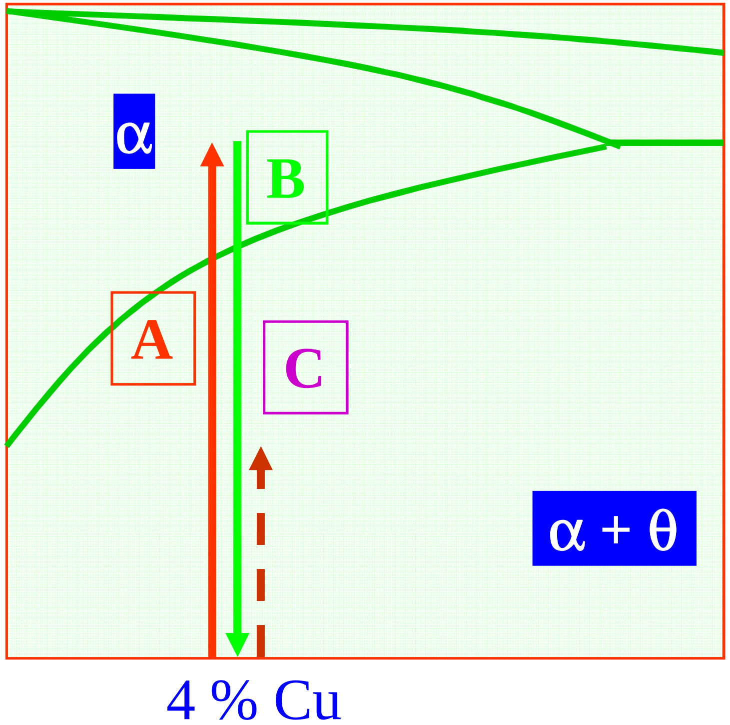
- α → α + θ
- Slow equilibrium cooling gives rise to coarse θ precipitates which is not good in impeding dislocation motion.*



$$\begin{pmatrix} \alpha\,(FCC) \\ 4\,\%\,Cu \\ 550^{o}\,C \end{pmatrix} \xrightarrow{slow\ cool} \begin{pmatrix} \alpha\,(FCC) \\ 0.5\,\%\,Cu \\ RT \end{pmatrix} + \begin{pmatrix} \theta\ CuAl_2\,(Tetragonal) \\ 52\,\%\,Cu \\ RT \end{pmatrix}$$

Precipitation Hardening

To obtain a fine distribution of precipitates the cycle A → B → C is used



Solution treating at high temperature, then quenching (second phase is in solid solution)
→Cycle A and B

A Heat (to 550^{o}C) → solid solution α

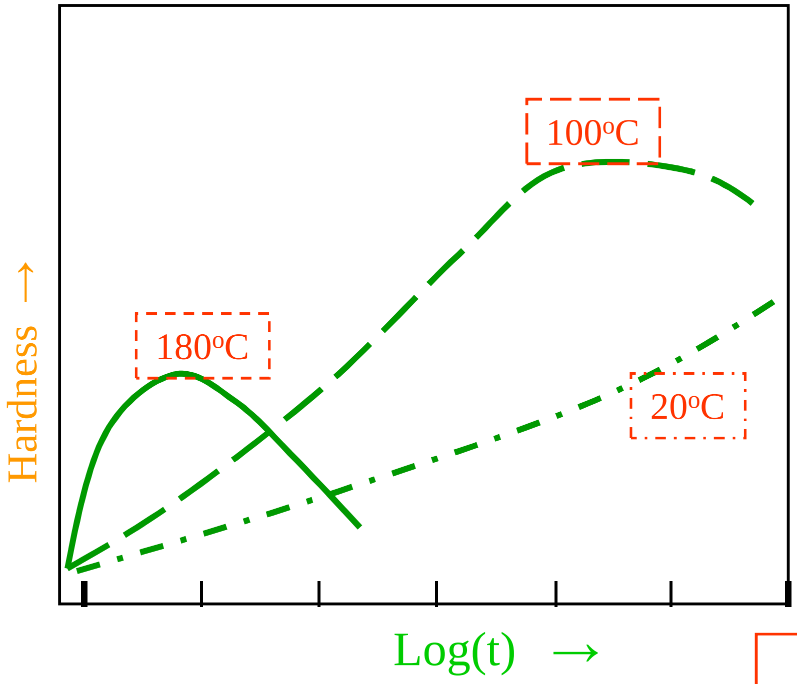
B Quench (to RT) →
- supersaturated solution
- Increased vacancy concentration

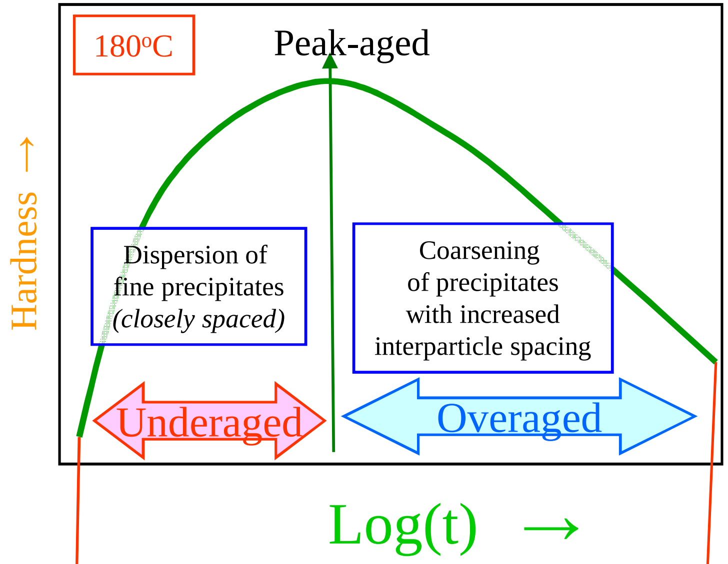
Ageing at room temperature or slightly higher temperature (Precipitation of second phase, giving strengthening effect) →Cycle C

C Age (*reheat* to 200^{o}C) → fine precipitates

Note: Treatments A, B, C are for the same composition

Precipitation Hardening





Dispersion of fine precipitates *(closely spaced)*

Coarsening of precipitates with increased interparticle spacing

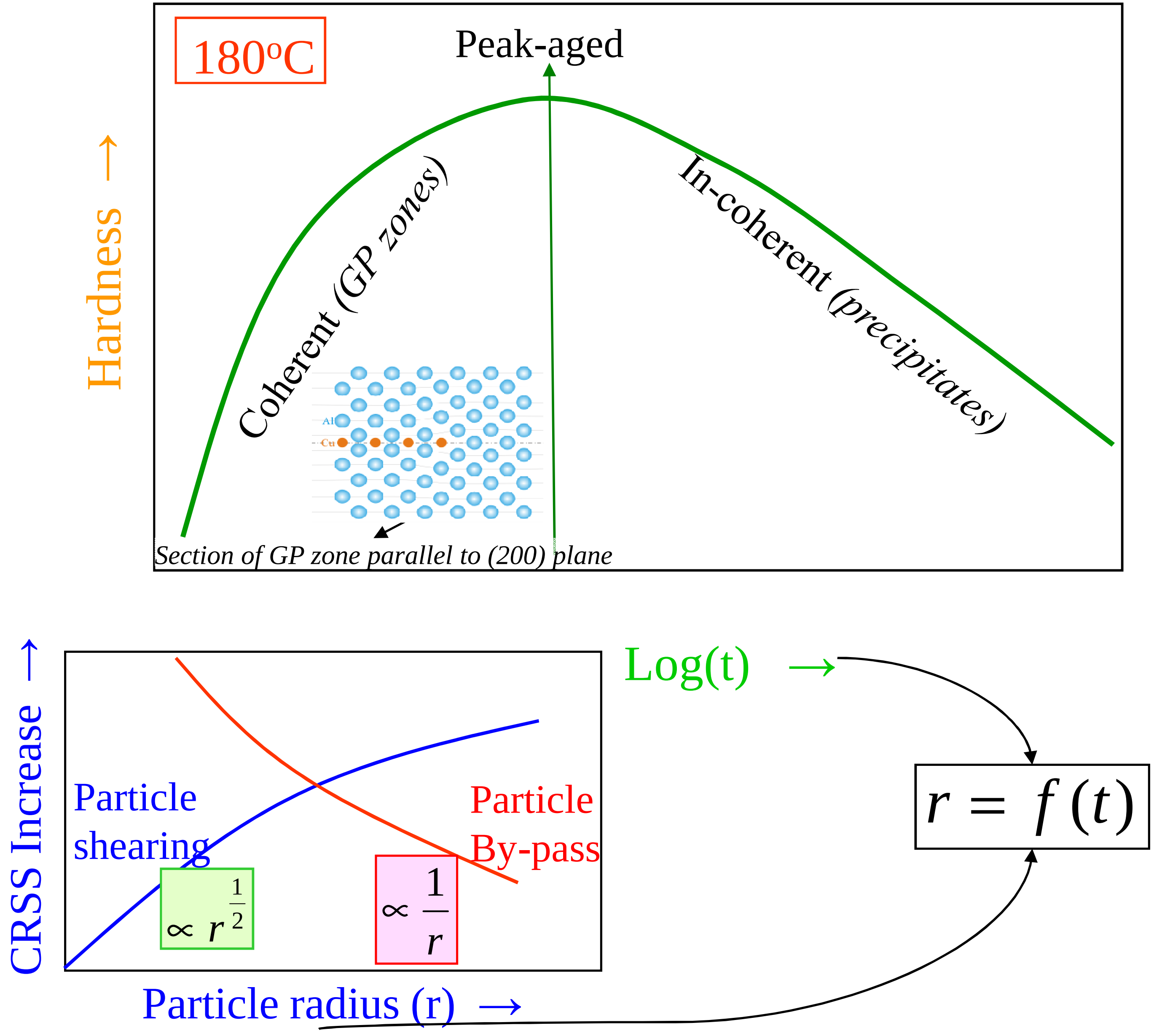
Region of solid solution strengthening *(no precipitation hardening)*

Region of precipitation hardening *(but little/some solid solution strengthening)*

- ❑ Higher temperature ⇒ less time of aging to obtain peak hardness
- ❑ Lower temperature ⇒ increased peak hardness

⇒ optimization between time and hardness required

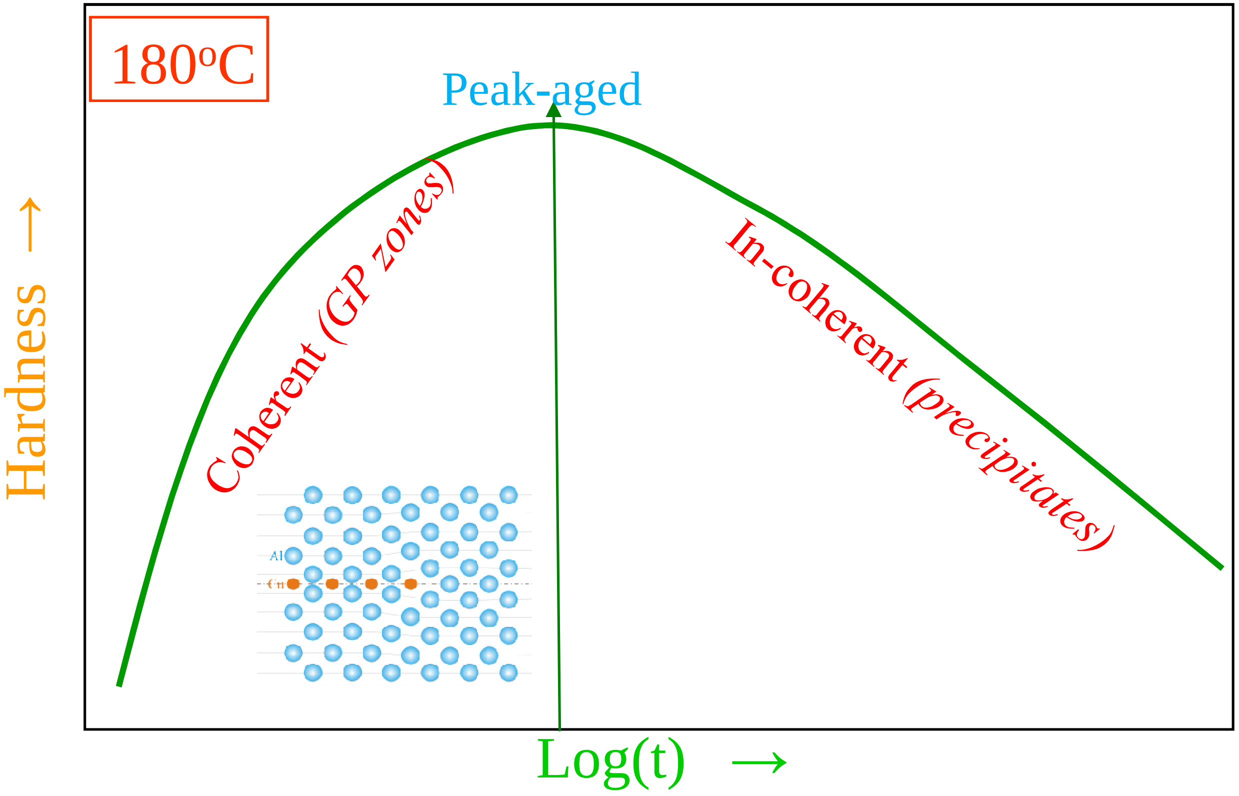
Precipitation Hardening



$$r = f(t)$$

Precipitation Hardening

A complex set of events are happening parallely/sequentially during the aging process → These are shown schematically in the figure ⇒



Increasing size of precipitates with increasing interparticle (inter-precipitate) spacing

Interface goes from coherent to semi-coherent to incoherent

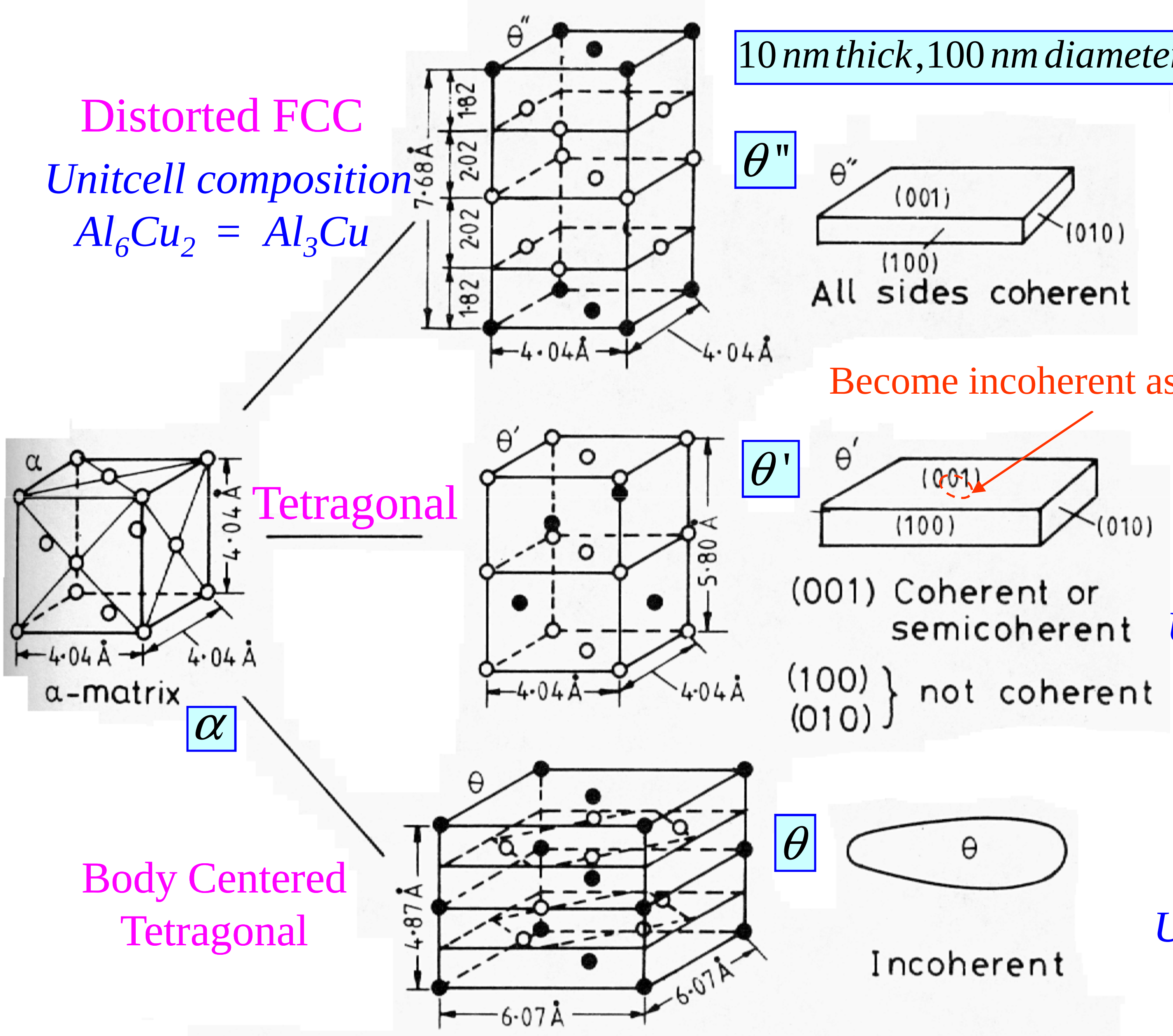
Precipitate goes from GP zone → θ'' → θ' → θ

Precipitation Hardening

GP Zones

- ☐ Cu rich zones fully coherent with the matrix → low interfacial energy
- ☐ (Equilibrium θ phase has a complex tetragonal crystal structure which has incoherent interfaces)
- ☐ Zones minimize their strain energy by choosing disc-shape ⊥ to the elastically soft <100> directions in the FCC matrix
- ☐ The driving force ($\Delta G_v - \Delta G_s$) is less but the barrier to nucleation is much less (ΔG^*)
- ☐ 2 atomic layers thick, 10nm in diameter with a spacing of ~10nm
- ☐ The zones seem to be homogenously nucleated (excess vacancies seem to play an important role in their nucleation)
- ☐ Due to large surface to volume ratio the fine precipitates have a tendency to coarsen → small precipitates dissolve and large precipitates grow
- ☐ Coarsening
  - ⇒ ↓ in number of precipitate
  - ⇒ ↑ in interparticle (inter-precipitate) spacing
    - ⇒ reduced hindrance to dislocation motion ($\tau_{max} = Gb/L$)

Precipitation Hardening



Structure and morphology of θ″, θ′ and θ in Al–Cu (○ Al, ● Cu).

Distorted FCC

Unitcell composition

$Al_6Cu_2 = Al_3Cu$

$10\,nm\,thick, 100\,nm\,diameter$

θ''

$(001)_{\theta''} \| (001)_{\alpha}$

$[100]_{\theta''} \| [100]_{\alpha}$

Become incoherent as ppt. grows

Tetragonal

θ'

$(001)_{\theta'} \| (001)_{\alpha}$

$[100]_{\theta'} \| [100]_{\alpha}$

Unitcell composition

$Al_4Cu_2 = Al_2Cu$

α

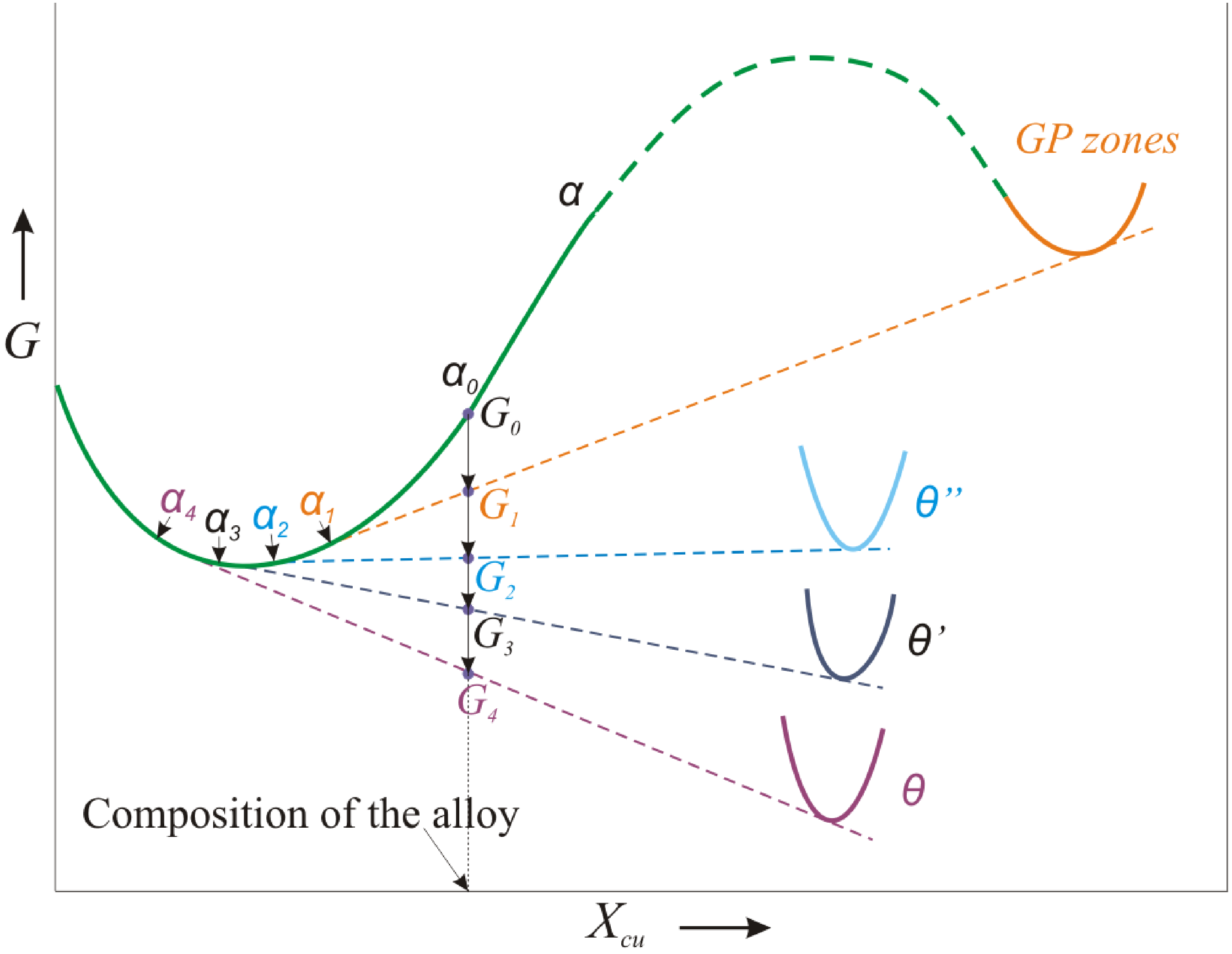
Body Centered Tetragonal

θ

Unitcell composition

$Al_8Cu_4 = Al_2Cu$

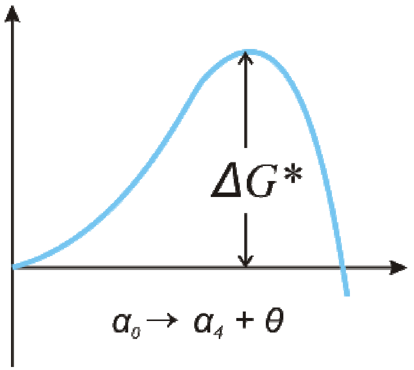
Precipitation Hardening



Schematic diagram showing the lowering of the Gibbs free energy of the system on sequential transformation:

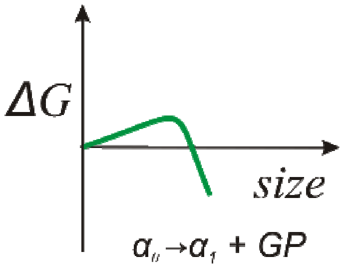
GP zones → θ'' → θ' → θ

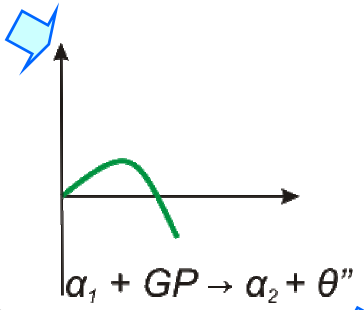
Precipitation Hardening

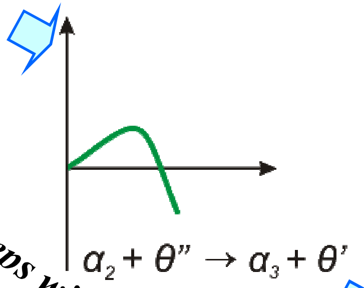


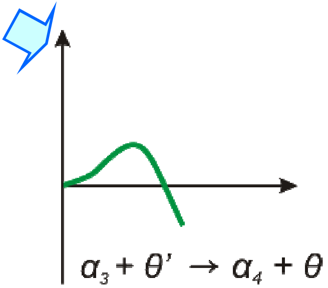
The activation barrier for precipitation of equilibrium (θ) phase is large

If the transformation is broken down into a series of steps with smaller activation barrier the processes can take place even with low thermal activation

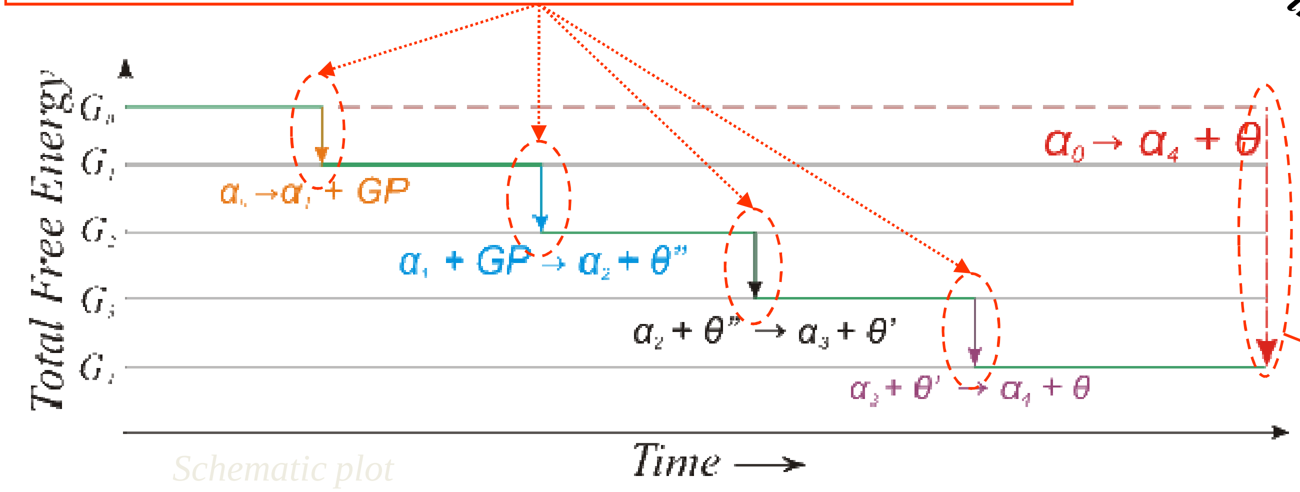






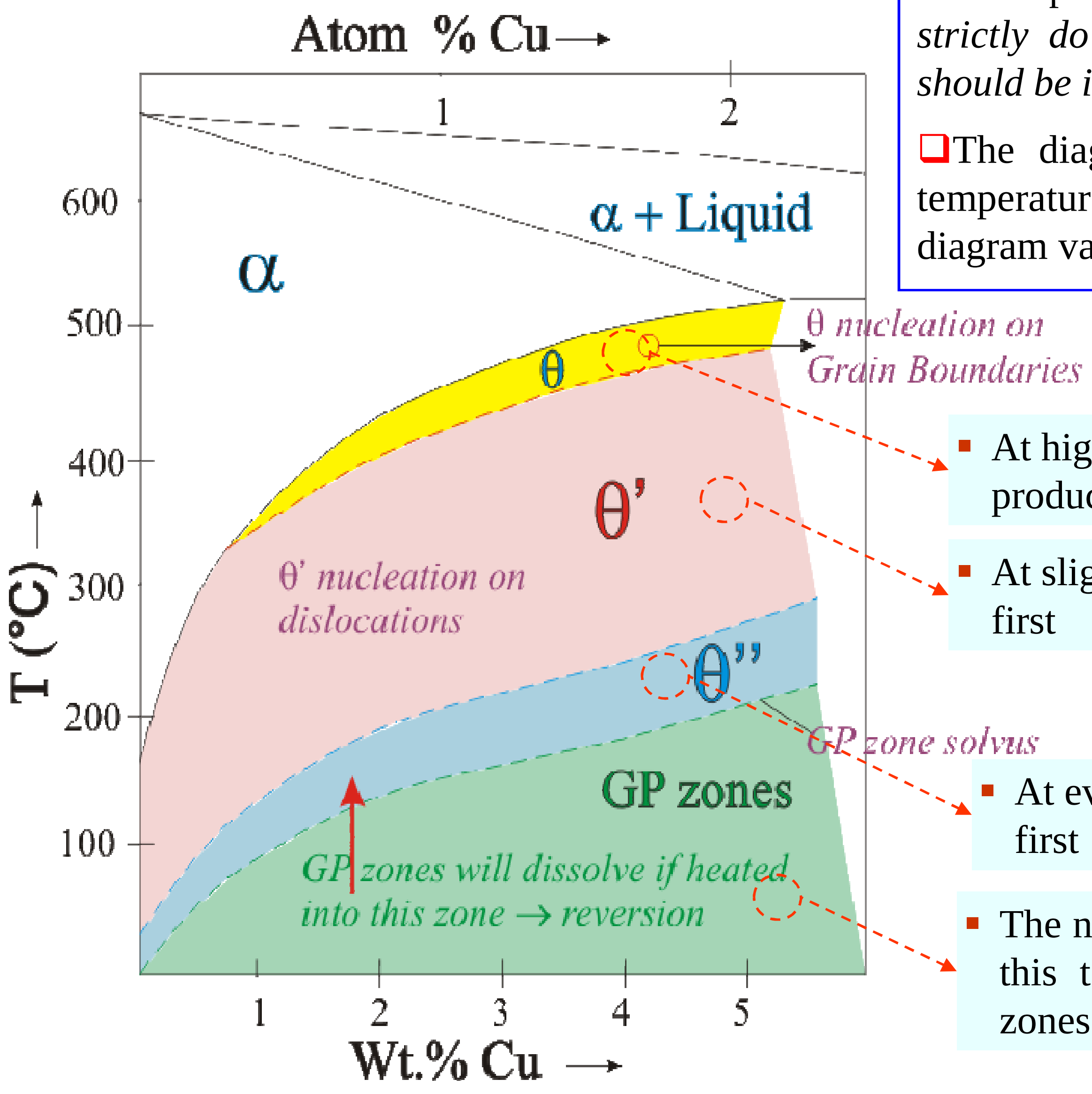


But, the free energy benefit in each step is small compared to the overall single step process



Single step ('equilibrium') process

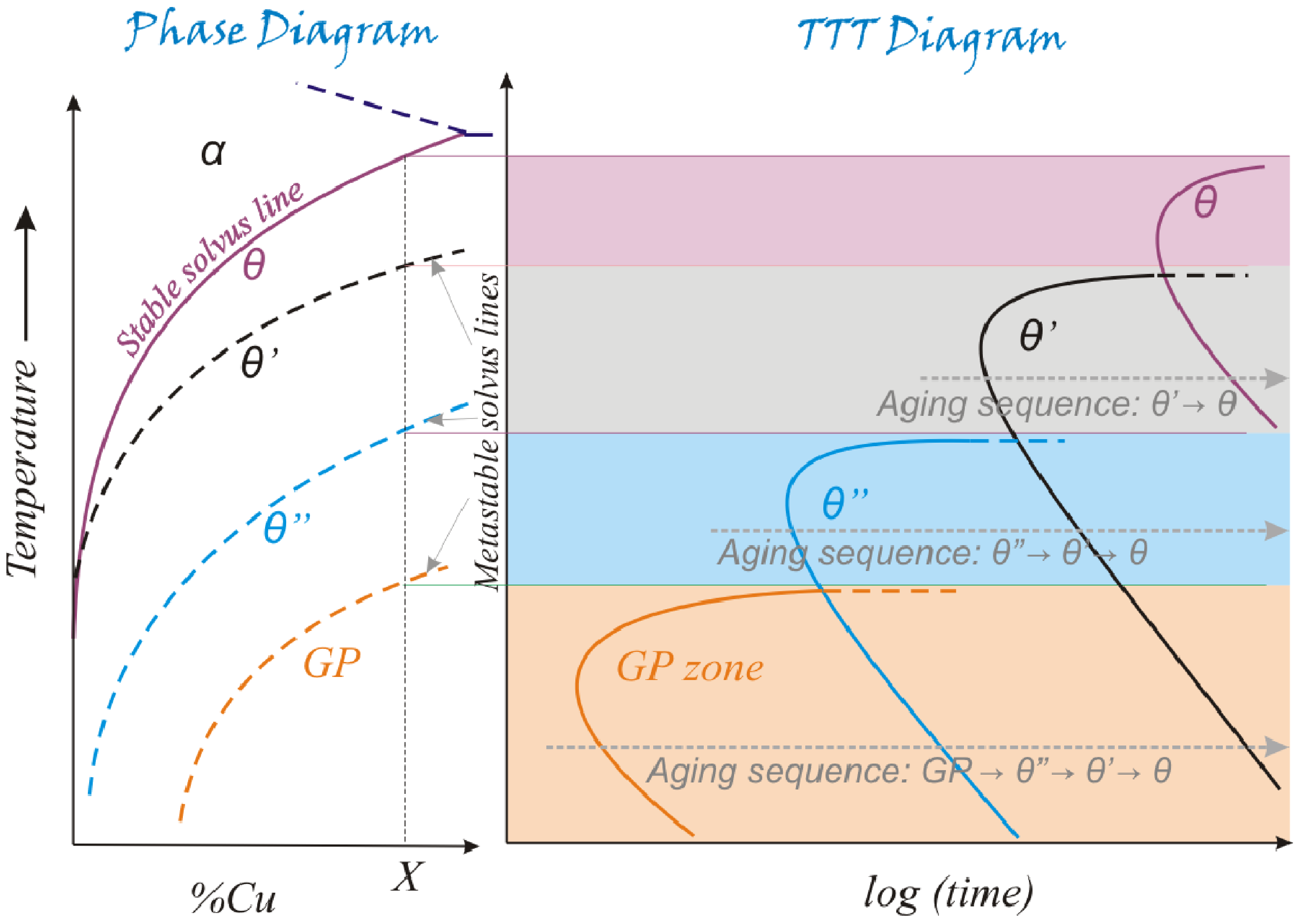
Precipitation Hardening



- In this diagram additionally information has been superposed onto the phase diagram *(which strictly do not belong there- hence this diagram should be interpreted with care)*
- The diagram shows that on aging at various temperatures in the α + θ region of the phase diagram various precipitates are obtained first

- At higher temperatures the stable θ phase is produced directly
- At slightly lower temperatures θ' is produced first
- At even lower temperatures θ'' is produced first
- The normal artificial aging is usually done in this temperature range to give rise to GP zones first

Phase and TTT diagrams



Phase and TTT diagrams

- In previous slide, we show the Al-rich portion of the Al-Cu phase diagram (schematically). From the phase diagram, it is clear that the Al with a few percent copper is cooled from high temperature leads to the formation of a microstructure in which the θ phase precipitates out of the supersaturated α matrix.
- However, if an alloy of composition Al - 4 wt. %Cu is solutionised at say, 540°C, and the resultant phase is rapidly quenched to room temperature, the solid solution is largely retained; if this alloy is kept at room temperature (or at any temperature below 180°C), a metastable phase known as Guinier-Preston zones (GP zones) is formed.
- Similarly, the aging treatment at other temperatures can produce other precipitates such as θ’’ and θ’.
- The solvus for these metastable phases in shown in Fig. Further, we also show the corresponding time-temperature-transformation curves for these metastable phase as well as the stable phase.
- we already discussed the crystallography and interface structure of all these phases as well as the reasons for their formation.

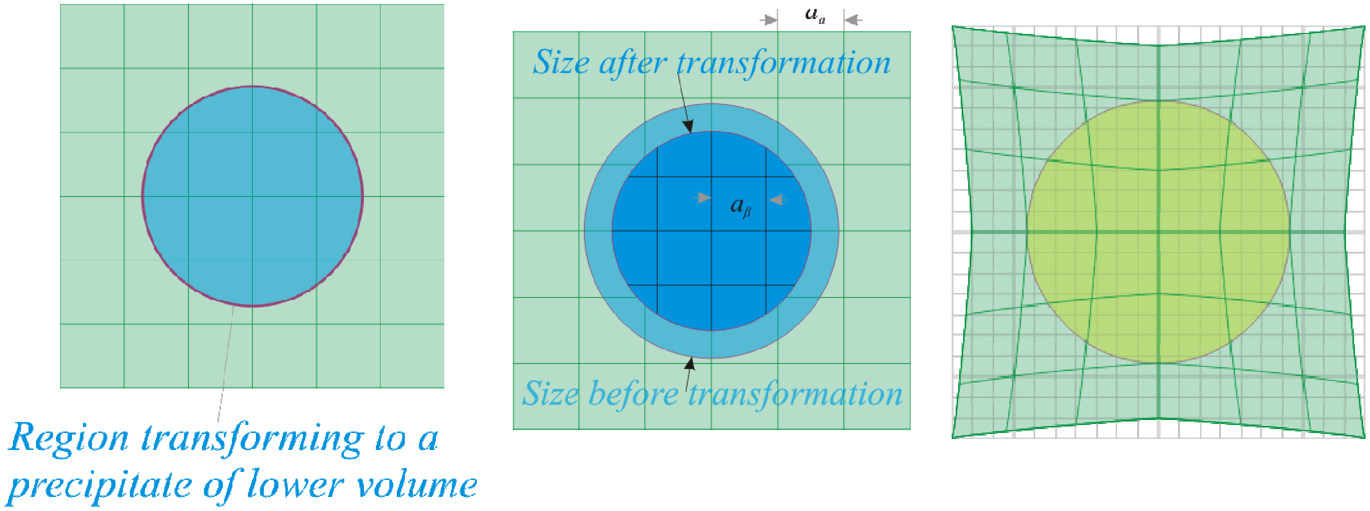
Misfit strain effects : Coherent precipitate

- The equilibrium shape of a coherent precipitate or zone is, when the misfit between the precipitate and matrix is small.
- When misfit is present is present the formation of coherent interfaces raises the free energy of the system on accounted of the elastic strain fields that arise.
- If the elastic strain energy is denoted by ΔG_s the condition for equilibrium becomes

$$\boxed{\sum A_i \gamma_i + \Delta G_s = \min imum}$$

- If the lattice parameters of the unstrained precipitate and matrix are a_p and a_m , respectively, the unconstrained misfit (δ) is defined by

$$\boxed{\delta = \frac{a_p - a_m}{a_m}}$$

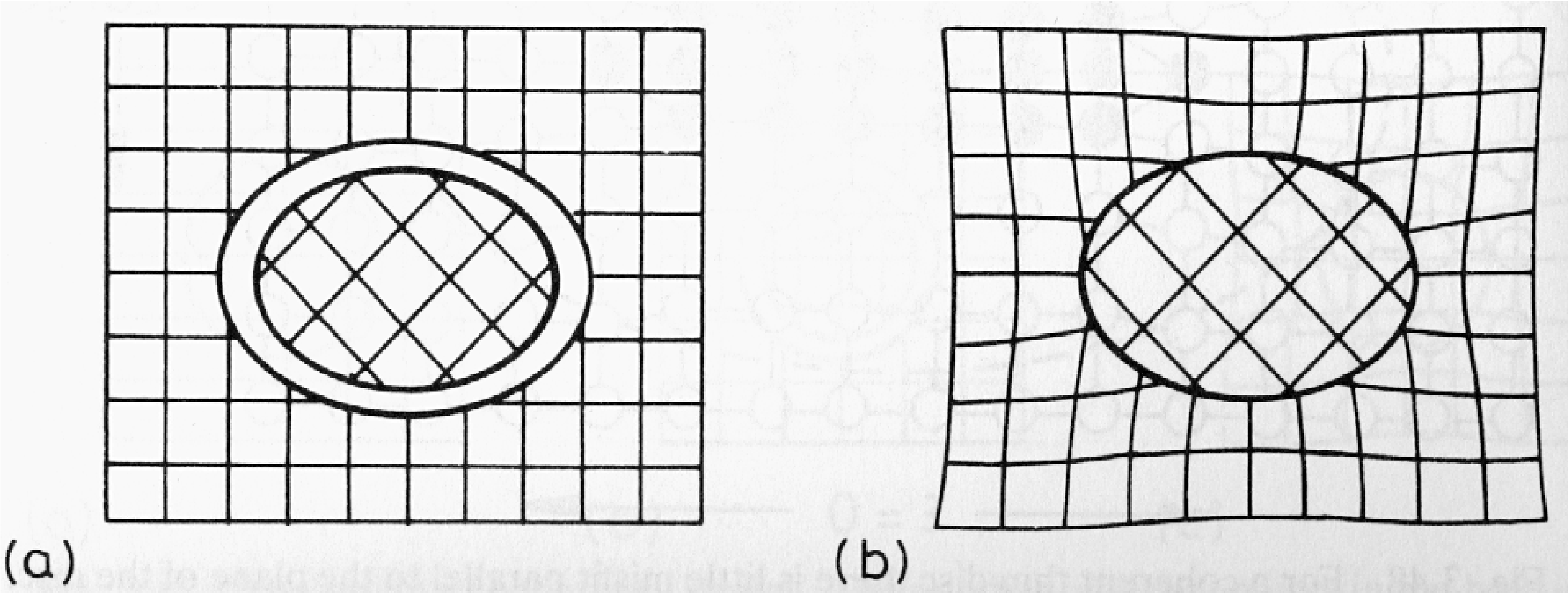


Schematic showing a coherent precipitate and the origin of coherency strains

Misfit strain effects : Coherent precipitate

- When the precipitate is incoherent with the matrix, there is an attempt at matching the two lattices and lattice sites are not conserved across the interface.
- Under these circumstances there are no coherency strains. Misfit strains can, however, still arise if the precipitate is the wrong size for the hole it is located.
- In this case the lattice misfit δ has no significance and it is better to consider the volume misfit Δ as defined by

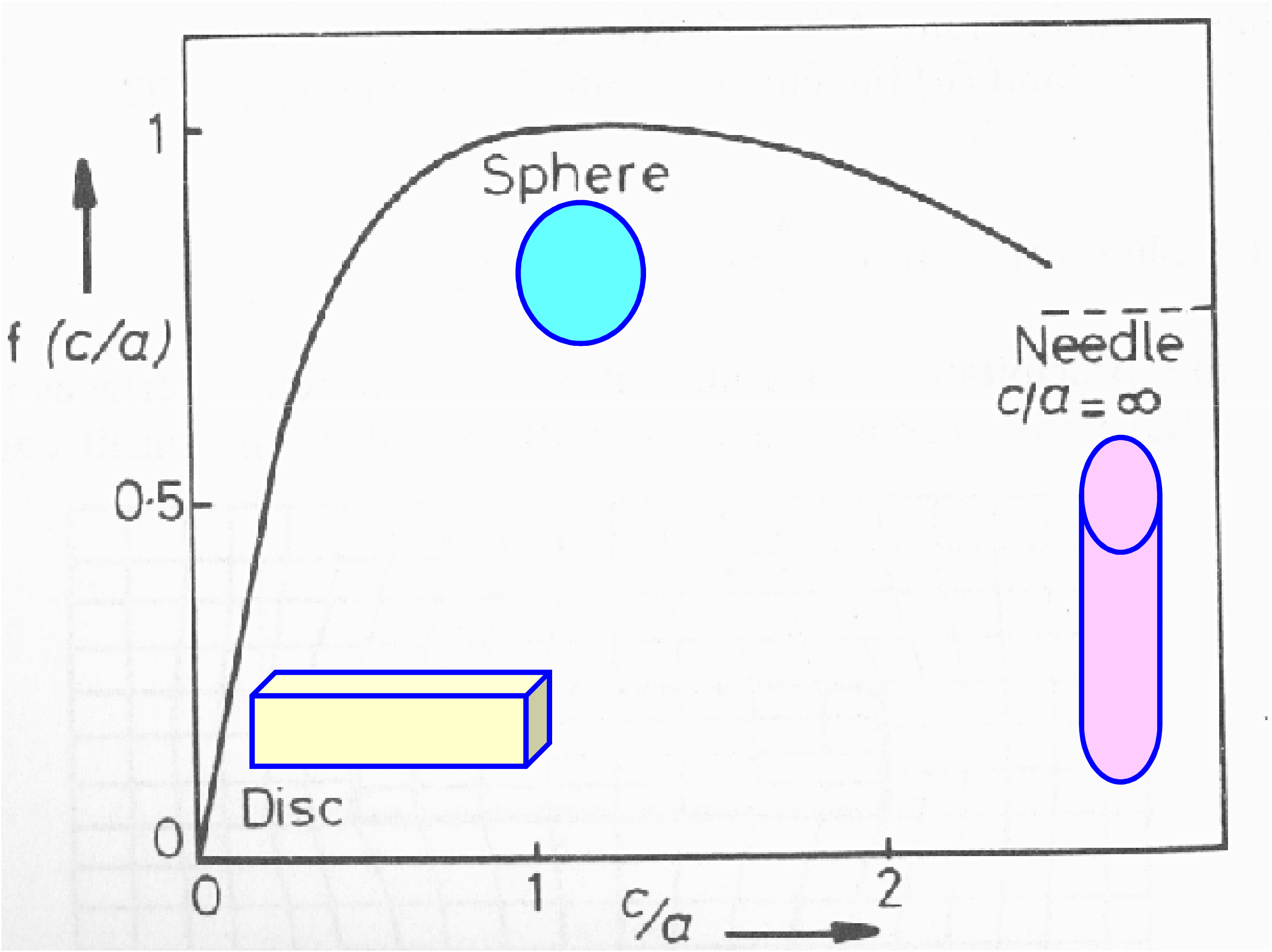
$$\Delta = \frac{V_p - V_m}{V_m}$$



The origin of misfit strain for an incoherent precipitate (no lattice matching

Misfit strain effects : Coherent precipitate

- ☐ Choose particle shape → minimize the free energy of system



The variation of misfit strain energy with aspect ratio of ellipsoid shape

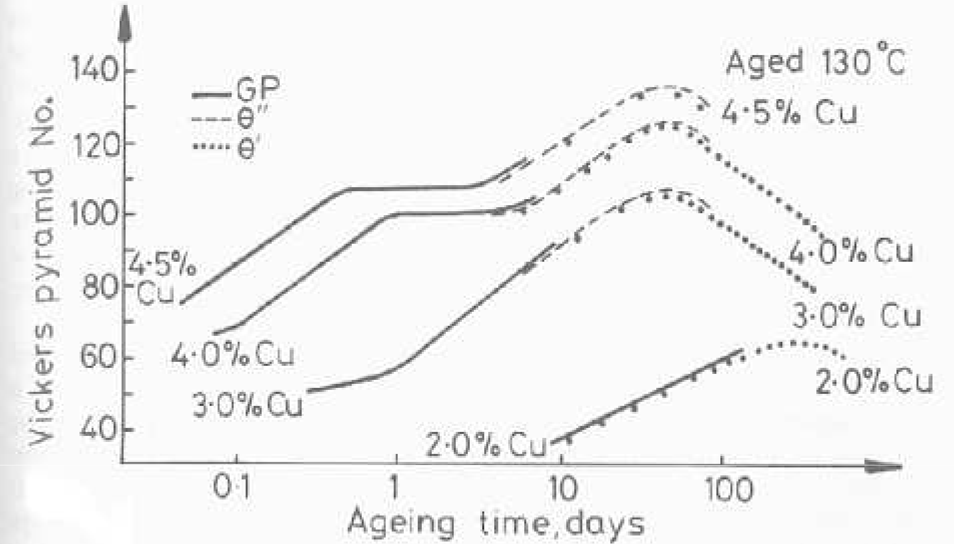
Precipitation Hardening

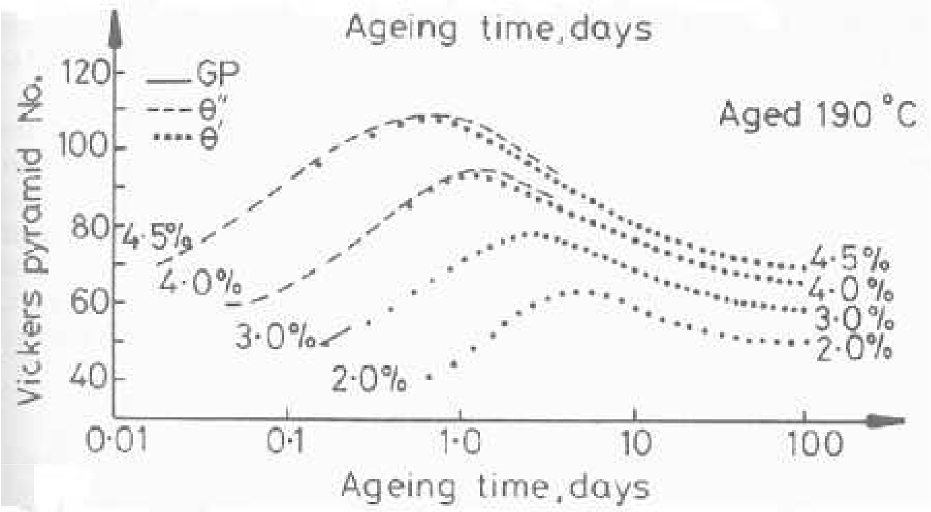
Precipitation Sequence in some precipitation hardening systems

Base Metal	Alloy	Precipitation Sequence
Aluminium	Al-Ag	GPZ (spheres) → γ' (plates) → γ (Ag_2Al)
	Al-Cu	GPZ (discs) → θ'' (discs) → θ' (plates) → θ ($CuAl_2$)
	Al-Cu-Mg	GPZ (rods) → S' (laths) → S ($CuMgAl_2$) (laths)
	Al-Zn-Mg	GPZ (spheres) → η' (plates) → η ($MgZn_2$) (plates or rods)
	Al-Mg-Si	GPZ (rods) → β' (rods) → β (Mg_2Si) (plates)
Copper	Cu-Be	GPZ (discs) → γ' → γ (CuBe)
	Cu-Co	GPZ (spheres) → β (Co) (plates)
Iron	Fe-C	ε-carbide (discs) → Fe_3C
	Fe-N	α'' (discs) → Fe_4N
Nickel	Ni-Cr-Ti-Al	γ' (cubes or spheres)

Precipitation Hardening

Details in ‘practical’ aging curves

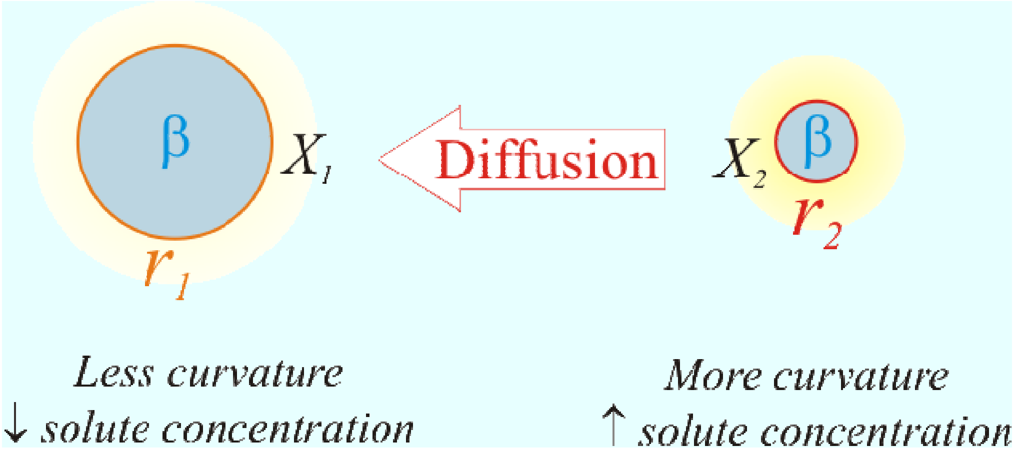




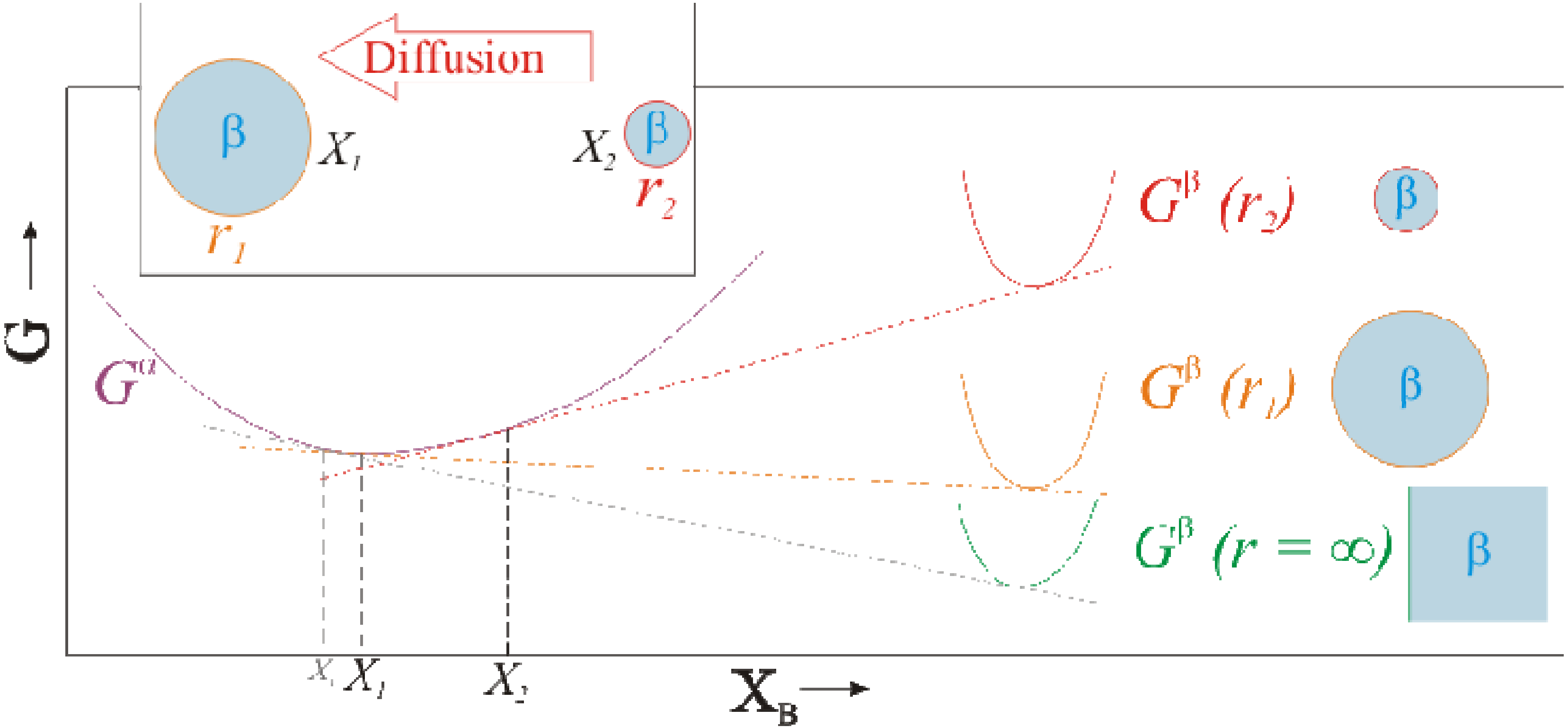
- In low T aging (130ºC)→The aging curves have more detail than the single peak as discussed schematically before.
- In low T aging (130ºC)→ the full sequence of precipitation is observed (GPZ →θ''→ θ').
- At high T aging (190ºC)→ θ'' directly forms (i.e. the full precipitation sequence is not observed).
- Peak hardness increases with increasing Cu%.
- For the same Cu%, the peak hardness is lower for the 190ºC aging treatment as compared to the 130ºC aging treatment.
- Peak hardness is achieved when the microstructure consists of a θ' or combination of (θ' + θ'').

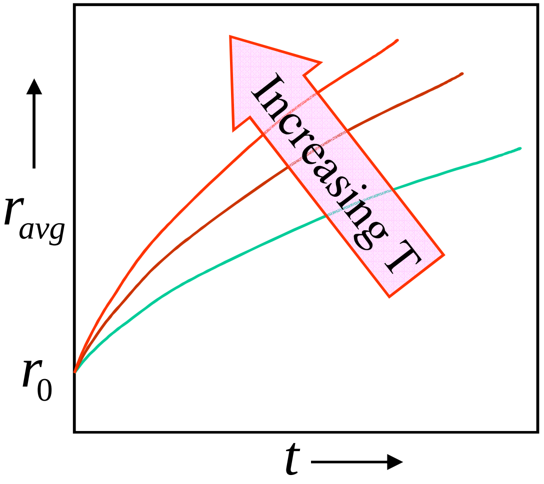
Particle/precipitate Coarsening

- ☐ There will be a range of particle sizes due to time of nucleation and rate of growth
- ☐ As the curvature increases the solute concentration (X_B) in the matrix adjacent to the particle increases
- ☐ Concentration gradients are setup in the matrix → solute diffuses from near the small particles towards the large particles
  ⇒ small particles shrink and large particles grow
- ☐ ⇒ with increasing time * Total number of particles decrease
  * Mean radius (r_{avg}) increases with time



Particle/precipitate Coarsening





$$\boxed{r_{avg}^3 - r_0^3 = kt}$$

$$\boxed{k \propto D\,\gamma\,X_e}$$

- $r_0 \rightarrow r_{avg}$ at $t = 0$
- D → Diffusivity
- $X_e \rightarrow X_B\ (r = \infty)$

D is a exponential function of temperature
⇒ coarsening increases rapidly with T

Particle/precipitate Coarsening

Rate controlling factor

- Volume diffusion rate

$$\frac{dr_{avg}}{dt} \propto \frac{k}{r_{avg}^2}$$

$\Rightarrow$ *small ppts coarsen more rapidly*

Linear r_{avg}^3 versus t relation may break down due to diffusion short-circuits or if the process is interface controlled

- Interface diffusion rate

Rate of coarsening

- Diffusion coefficient (D)
- Interfacial energy
- Equilibrium solubility of very large particles (X_e)

- Precipitation hardening systems employed for high-temperature applications must avoid coarsening by having low: γ, X_e or D

Rate of coarsening

Low γ

- In superalloys, Strength obtained by fine dispersion of γ' [ordered FCC $Ni_3(TiAl)$] precipitate in FCC Ni rich matrix
- Matrix (Ni SS)/ γ' matrix is fully coherent [low interfacial energy $\gamma = 30$ mJ/m^2]
- Misfit = f(composition) → varies between 0% and 0.2%
- Creep rupture life increases when the misfit is 0% rather than 0.2%

Low X_e

ThO_2 dispersion in W (or Ni) *(Fine oxide dispersion in a metal matrix)*

- Oxides are insoluble in metals
- Stability of these microstructures at high temperatures due to low value of X_e
- The term $D\gamma X_e$ has a low value

Low D

ThO_2 dispersion in W (or Ni) *(Fine oxide dispersion in a metal matrix)*

- Cementite dispersions in tempered steel coarsen due to high D of interstitial C
- If a substitutional alloying element is added which segregates to the carbide → rate of coarsening ↓ due to low D for the substitutional element

Spinodal decomposition/Spinodal clustering

- Phase diagrams showing miscibility gap correspond to solid solutions which exhibit clustering tendency.
- Within the miscibility gap the decomposition can take place by either
  - *Nucleation and Growth* or by
  - *Spinodal Mechanism*
- If the second phase is not coherent with the parent then the region of the spinodal is called the chemical spinodal
- If the second phase is coherent with the parent phase then the spinodal mechanism is operative only inside the coherent spinodal domain
- As coherent second phases cost additional strain energy to produce (as compared to a incoherent second phase – only interfacial energy involved) → this requires additional undercooling for it to occur
- Spinodal decomposition is not limited to systems containing a miscibility gap
- Other examples are in binary solid solutions and glasses
- All systems in which GP zones form (e.g.) contain a metastable coherent miscibility gap → THE GP ZONE SOLVUS
- Thus at high supersaturations it is GP zones can form by spinodal mechanism.

Spinodal mechanism

- In phase separating systems, at low temperatures, the Gibbs free energy consists of regions of concave curvature (as shown Fig. 1) and in such regions the binary alloy separated into a mechanical mixture of A and B-rich regions instead of remaining a solid solution. This is because such a phase separation into mechanical mixture reduces the free energy of the system.
- Further, in such systems with concavity of free energy, for certain compositions, the mechanism of phase separation changes from the classical nucleation and growth to spinodal decomposition. The change over in the mechanism is related to the curvature of the free energy curve as shown in Fig. 2.

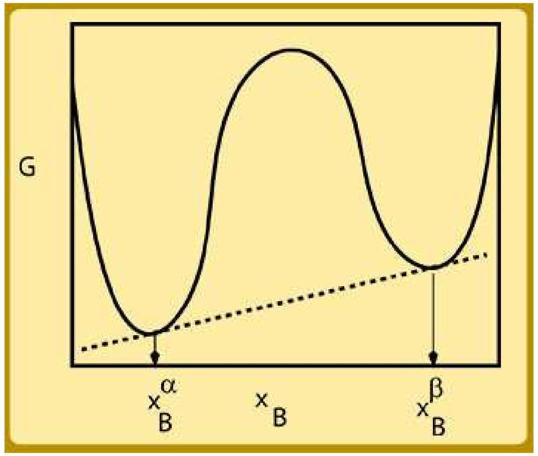


Fig. 1

The free energy of a system with concave curvature. In the concave curvature region, the system becomes a mechanical mixture of A rich and B rich phases with the given compositions marked in this figure.

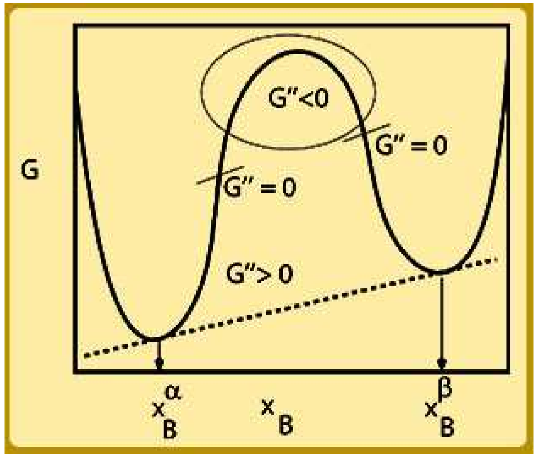


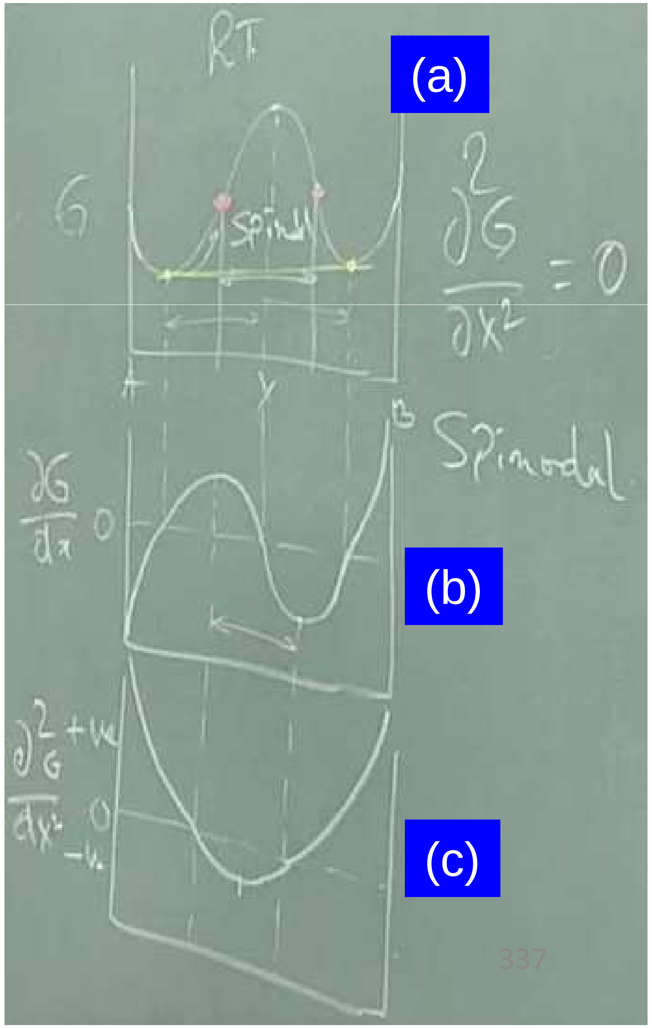
Fig. 2

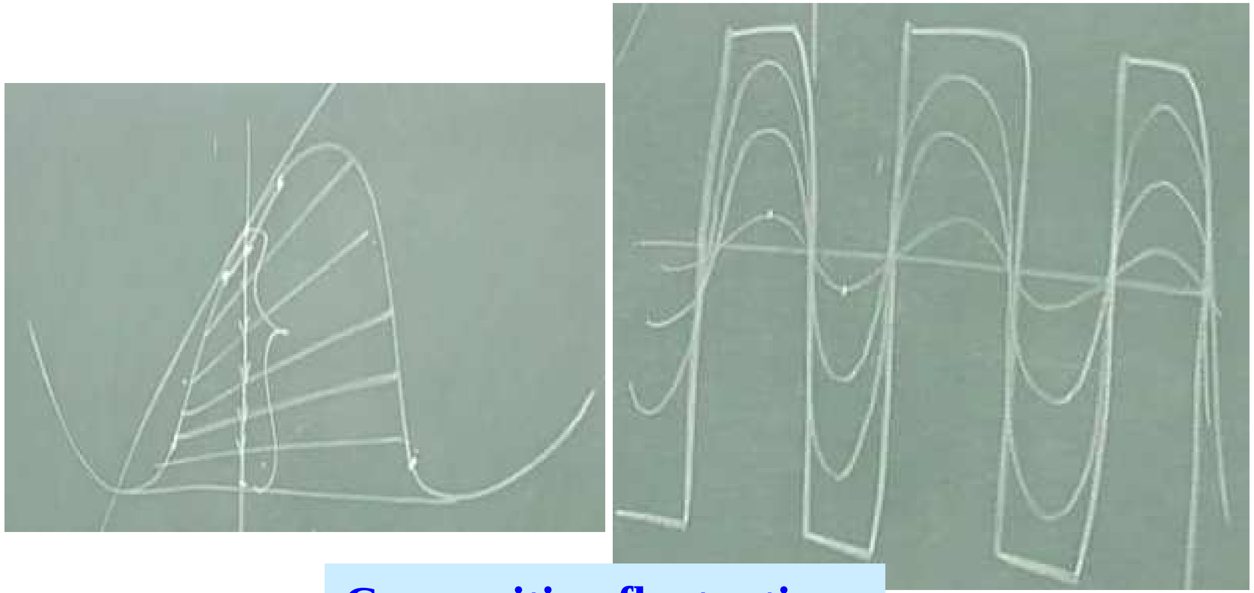
Positive curvature (nucleation) and negative curvature (spinodal) regions of the free energy versus composition diagram; phase separation mechanism changes from nucleation to spinodal at the point of zero curvature.

Spinodal mechanism $\Rightarrow \frac{d^2G}{dx^2} < 0$

- ❑ When/How it is possible?
- ❑ We always know that, towards the two pure metal ends, the slope of free energy verses composition is minus infinity.

- ❑ We will understand the Spinodal decomposition better, if we try to see, what is the first and second derivatives of this free energy.
- ❑ $\partial G / \partial x$ is nothing but slope of the curve (a) and it will be given in Fig. (b).
- ❑ $\partial G^2 / \partial x^2$ is slope of the curve (b) and it will be given in Fig. (c).





Composition fluctuations

Spinodal mechanism

- Consider a system with an interdiffusion coefficient D and undergoing spinodal decomposition. Within the spinodal region, the composition fluctuations grow as shown in Fig. (previous slide); the fluctuations grow with a characteristic time constant

$$\boxed{\tau = -\lambda^2 / 4\pi^2 D}$$

where λ is the wavelength of the composition modulation (assuming one-dimensional modulations).

- Thus, for smaller λ, the rate of transformation becomes high; however, there is a minimum λ below which spinodal decomposition cannot occur; this is because, during spinodal decomposition, as A- and B-rich regions are forming, there are also interfaces between these regions where AB bonds are formed which are energetically costlier; these regions give rise to an increase in free energy; the `incipient' interfacial energy associated with the formation of these regions with large AB bonds are the ones which set the lower wavelength limit. The lower limit on the wavelength λ can be obtained using the following argument.
- Consider a homogeneous alloy of composition x_B^0 decomposing into two parts: one with composition $x_B^0 + \Delta x$ and another with composition . It can be shown that the total free energy change associated with this decomposition is

$$\boxed{\Delta G_{chem} = \frac{1}{2}\frac{d^2G}{dx_B^2}(\Delta x)^2}$$

Spinodal mechanism

- As noted earlier, the AB bonds in the incipient interface regions also contribute to the free energy; this free energy contribution, thus, is associated with the gradients in composition. Consider a sinusoidal composition modulation of wavelength λ and amplitude Δx ; the maximum composition gradient is thus Δx/λ and the gradient energy contribution is

$$\Delta G_{grad} = \kappa\left(\frac{\Delta x}{\lambda}\right)^2$$

where ΔG_{grad} *is a proportionality constant which is dependent on the difference between AB and AA and BB bond energies.*

- The total change in free energy associated with a composition fluctuation of wavelength λ is thus given by the addition of the chemical and gradient terms

$$\Delta G = \Delta G_{chem} + \Delta G_{grad} = \left(\frac{d^2G}{dx_B^2} + \frac{2\kappa}{\lambda^2}\right)\frac{(\Delta x)^2}{2}$$

- From the above expression, it is clear that for spinodal decomposition

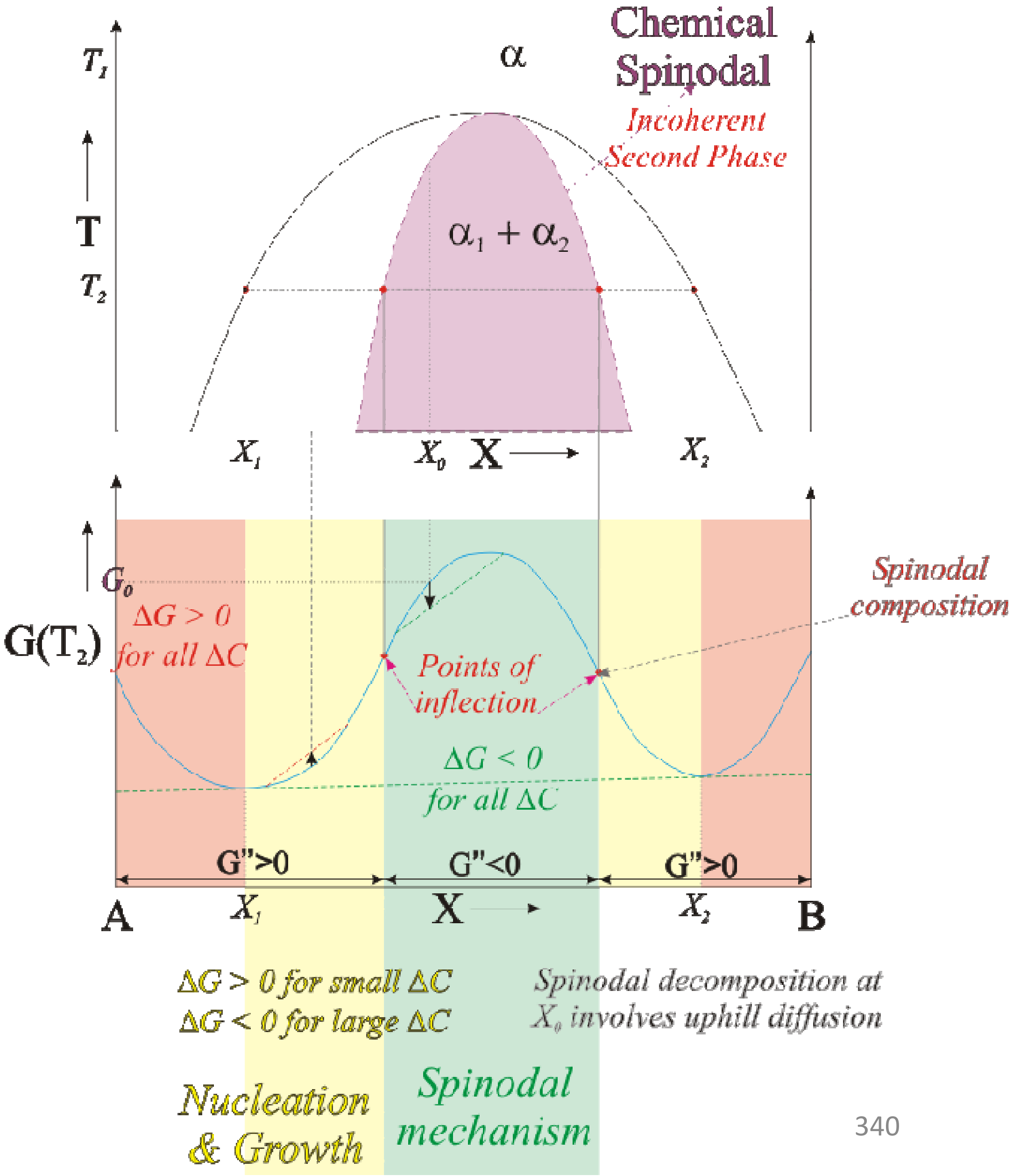
$$-\frac{d^2G}{dx_B^2} > \frac{2\kappa}{\lambda^2}$$

- Or

$$\lambda^2 > -\frac{2\kappa}{\frac{d^2G}{dx_B^2}}$$

Spinodal mechanism

- ❑ In this figure we show the phase separation region along with the points at every temperature at which the curvature of the free energy versus composition plot changes its sign; the locus of these points is as shown and is known as chemical spinodal.
- ❑ In the case of spinodal phase separation, any small composition fluctuation grows leading to A-rich regions becoming richer in A and B-rich regions becoming richer in B. This is because such a process leads to a decrease in free energy.
- ❑ Thus, the process of spinodal decomposition is in contrast to the classical diffusion equation scenario which predicts that regions with positive curvature for composition profile grow in time while those with negative curvature decay leading to homogenisation.



Spinodal Ordering

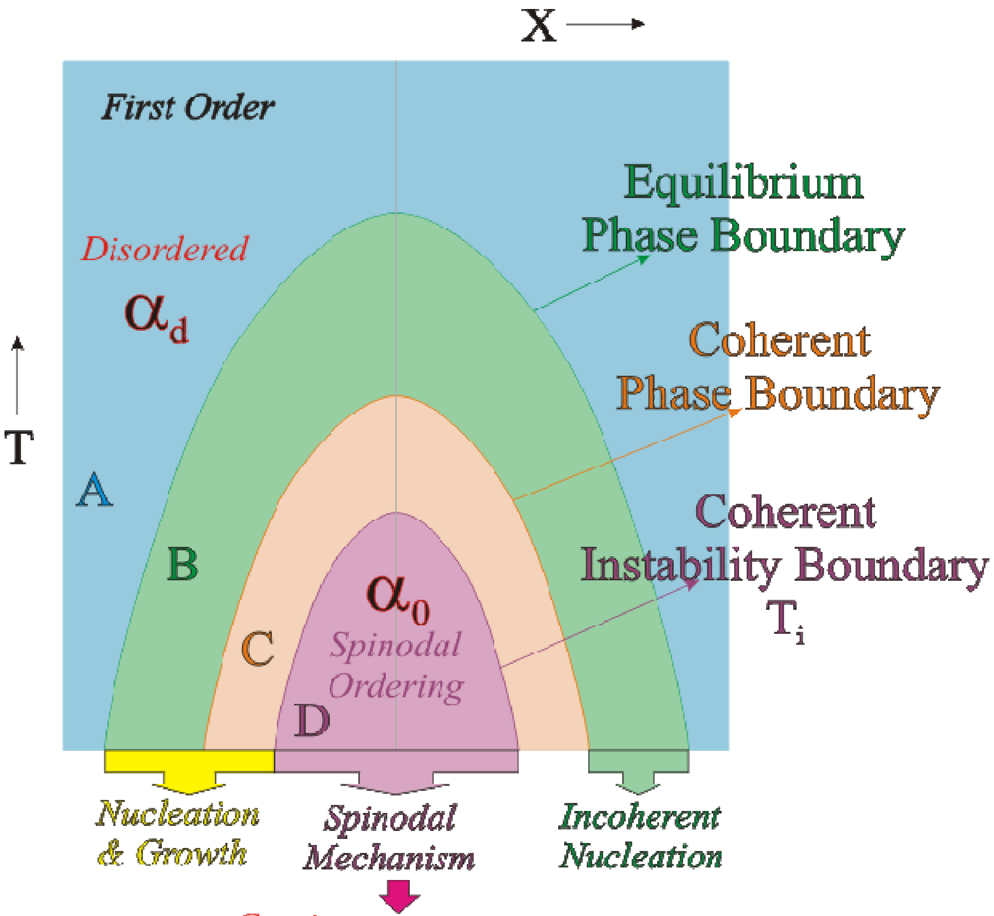
- Ordering leads to the formation of a superlattice
- Ordering can take place in *Second Order or First Order (in continuous mode below T_i)* modes
- Any change in the lattice dimensions due to ordering introduces a third order term in the Landau equation

$$\Delta G = A\eta^2 + \boxed{B}\eta^3 + C\eta^4 \ldots$$

Not zero

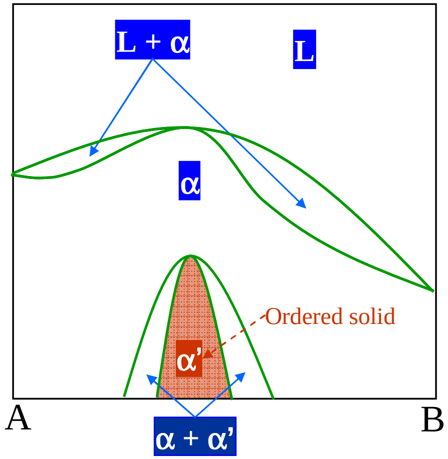
- Continuous ordering as a first order transformation requires a finite supercooling below the Coherent Phase Boundary to the Coherent Instability (T_i) boundary
- These (continuous ordering) 1st order transitions are possible in cases where the symmetry elements of the ordered structure form a subset of the parent disordered structure

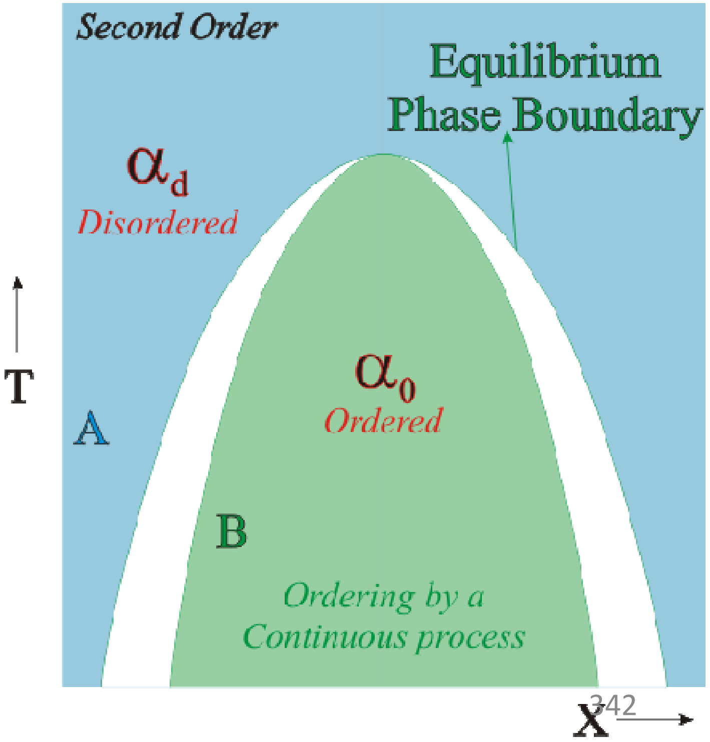
Spinodal Ordering



Continuous process but FIRST ORDER

- A→Disordered solid solution
- B→Nucleation of incoherent ordered phase
- C→Nucleation of coherent ordered phase
- D→Ordered phase by Spinodal mechanism

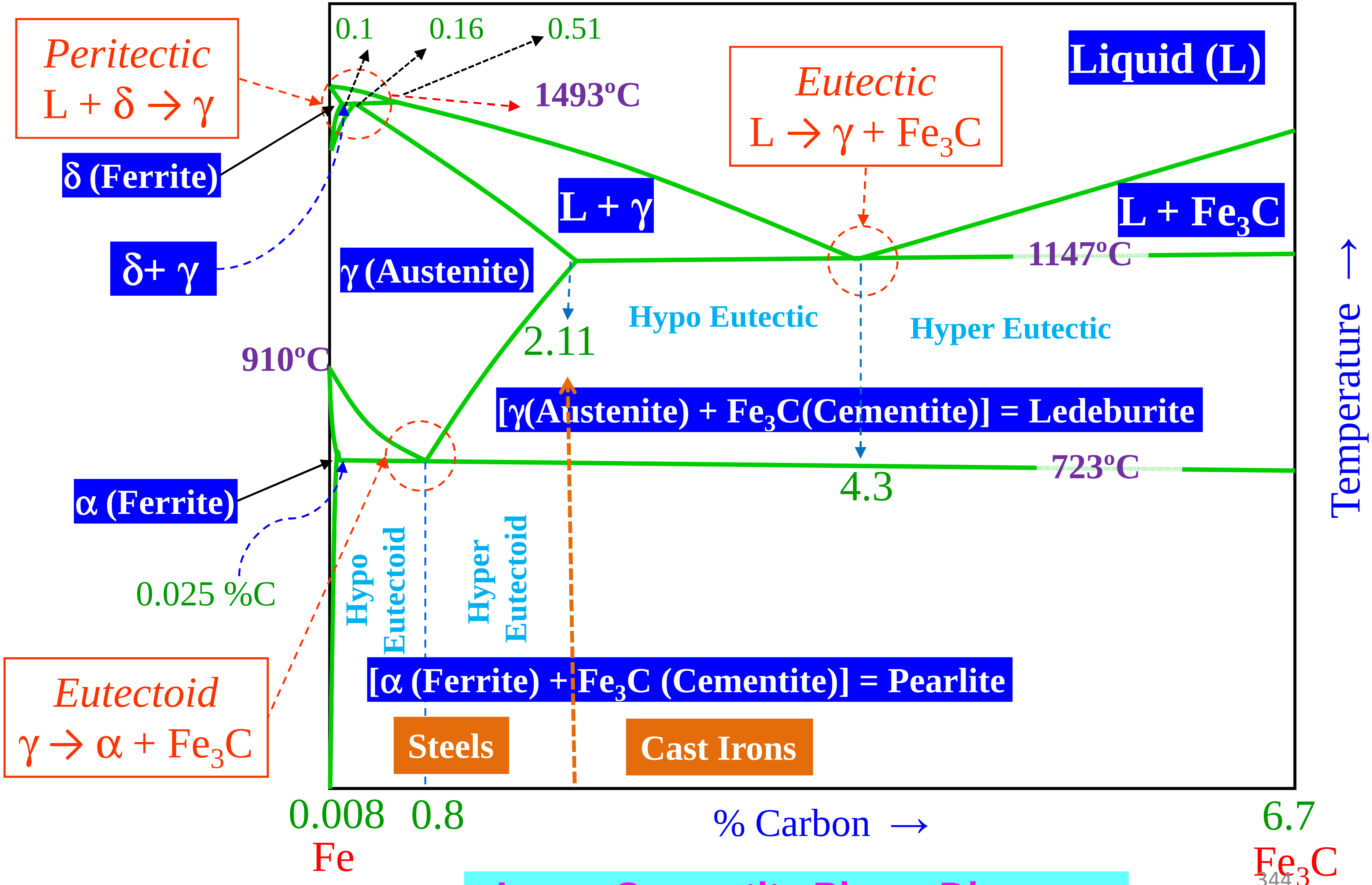




Summary

Nucleation & Growth	Spinodal
The composition of the second phase remains unaltered with time	A continuous change of composition occurs until the equilibrium values are attained
The interfaces between the nucleating phase and the matrix is sharp	The interface is initially very diffuse but eventually sharpens
There is a marked tendency for random distribution of both sizes and positions of the equilibrium phases	A regularity- though not simple- exists both in sizes and distribution of phases
Particles of separated phases tend to be spherical with low connectivity	The separated phases are generally non-spherical and posses a high degree of connectivity

Eutectoid Transformation in Fe-Fe_3C phase diagram



Peritectic

$L + \delta \rightarrow \gamma$

Eutectic

$L \rightarrow \gamma + Fe_3C$

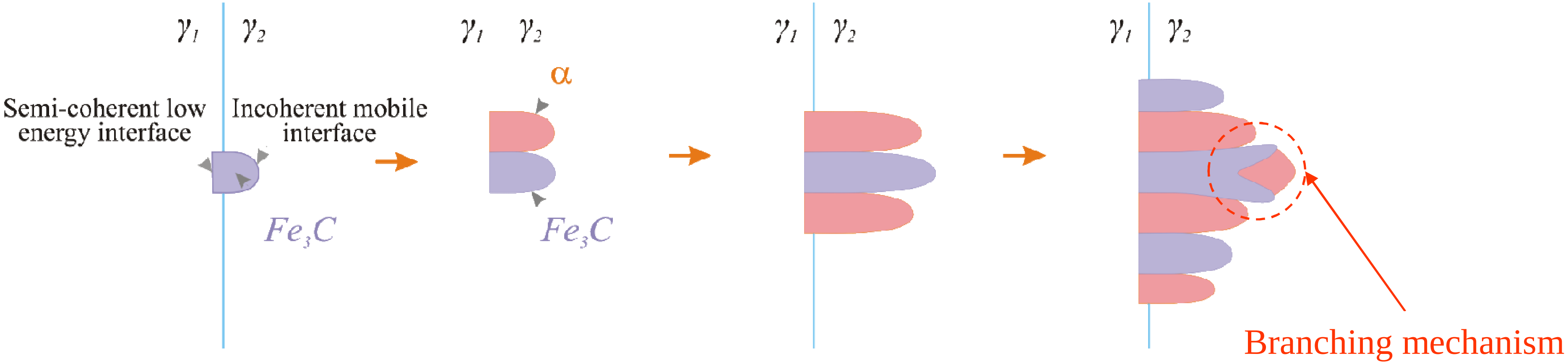
Eutectoid

$\gamma \rightarrow \alpha + Fe_3C$

Iron – Cementite Phase Diagram

Eutectoid Transformation : Nucleation of Pearlite

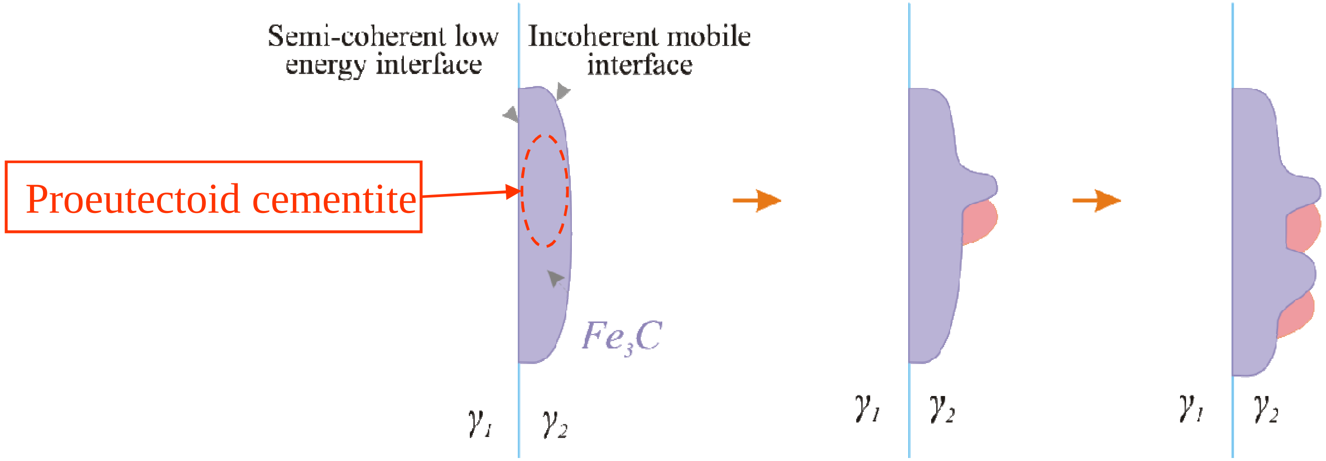
- ❑ Pearlite typically forms on the grain boundaries of the austenite phase by the nucleation of either the ferrite or cementite; the exact phase that nucleates is decided both by the composition and the structure of the grain boundary.
- ❑ The nucleation is such that the barrier for nucleation is the lowest; in other words, the nuclei has a orientation relationship with one of the grains such that the interfacial free energy is minimized.
- ❑ Suppose the first phase to nucleate is cementite; this leads to a depletion of the carbon surrounding this region leading to ferrite nucleation. Ferrite nucleation is also such that the interfacial free energy is minimized; thus, it also has an orientation relationship with the cementite. This process is repeated with the entire grain boundary coated with alternating cementite and ferrite nuclei.



Nucleation of the eutectoid phases in a system with eutectoid composition

Eutectoid Transformation : Nucleation of Pearlite

- ❑ If the composition of the steel is not the eutectoid composition, then, it is possible that proeutectoid ferrite or cementite is nucleated at the grain boundary. The other phase, be it cementite or ferrite, then forms on the incoherent boundary of this proeutectoid phase. This process is shown schematically in Fig.



Orientation Relation:
Kurdyumov-Sachs

$$(100)_c \parallel (1\bar{1}1)_\gamma$$

$$(010)_c \parallel (110)_\gamma$$

$$(001)_c \parallel (\bar{1}12)_\gamma$$

Nucleation of the eutectoid phases in a system with pro-eutectoid composition

- ❑ The development of Pearlitic microstructure requires cooperative growth of Ferrite and Cementite
- ❑ If this cooperation is not established then the resulting microstructure is non-lamellar → *Degenerate Pearlite*

Eutectoid Transformation : Nucleation of Pearlite

Eutectoid Transformations

Nucleation at GB

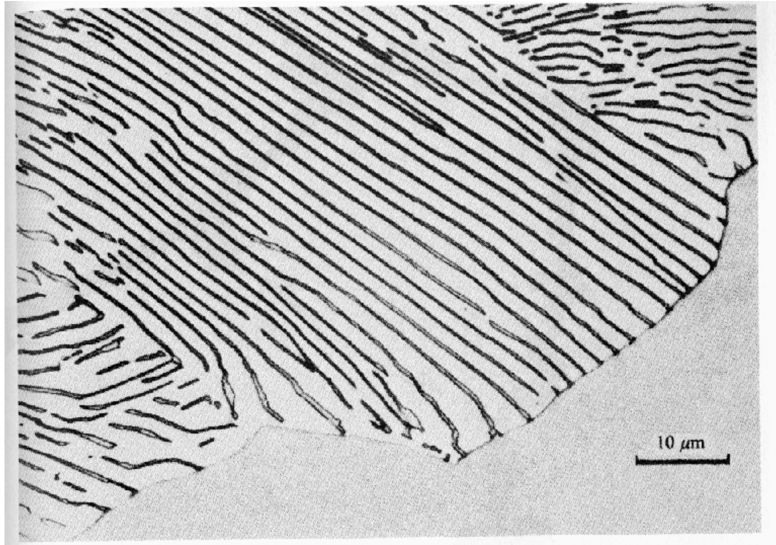
Pearlite in Fe-C alloys $\boxed{\gamma \rightarrow \alpha + Fe_3C}$

Low undercooling (below A_1)

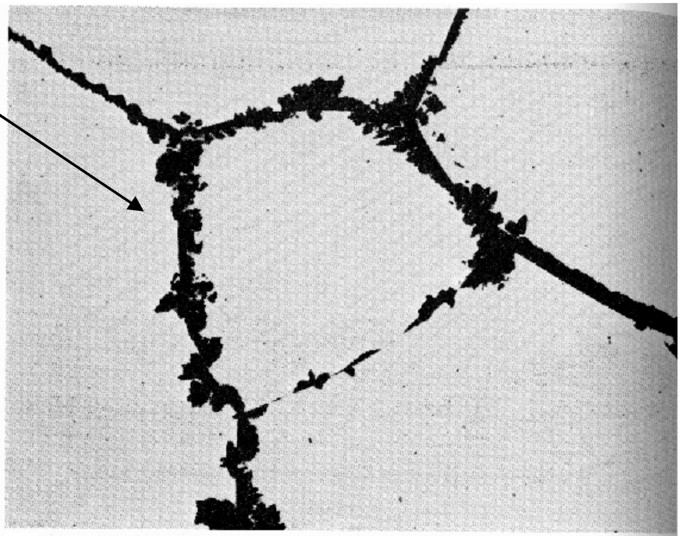
Small number of nuclei form which grow without interference

Large undercooling (below A_1)

High nucleation rate → Site saturation along GB



A pearlite colony advancing into an austenite grain. (After L.S. Darken and R.M. Fisher in *Decomposition of Austenite by Diffusional Processes*, V.F. Zackay and H.I. Aaronson (Eds.), by permission of The Metallurgical Society of AIME.



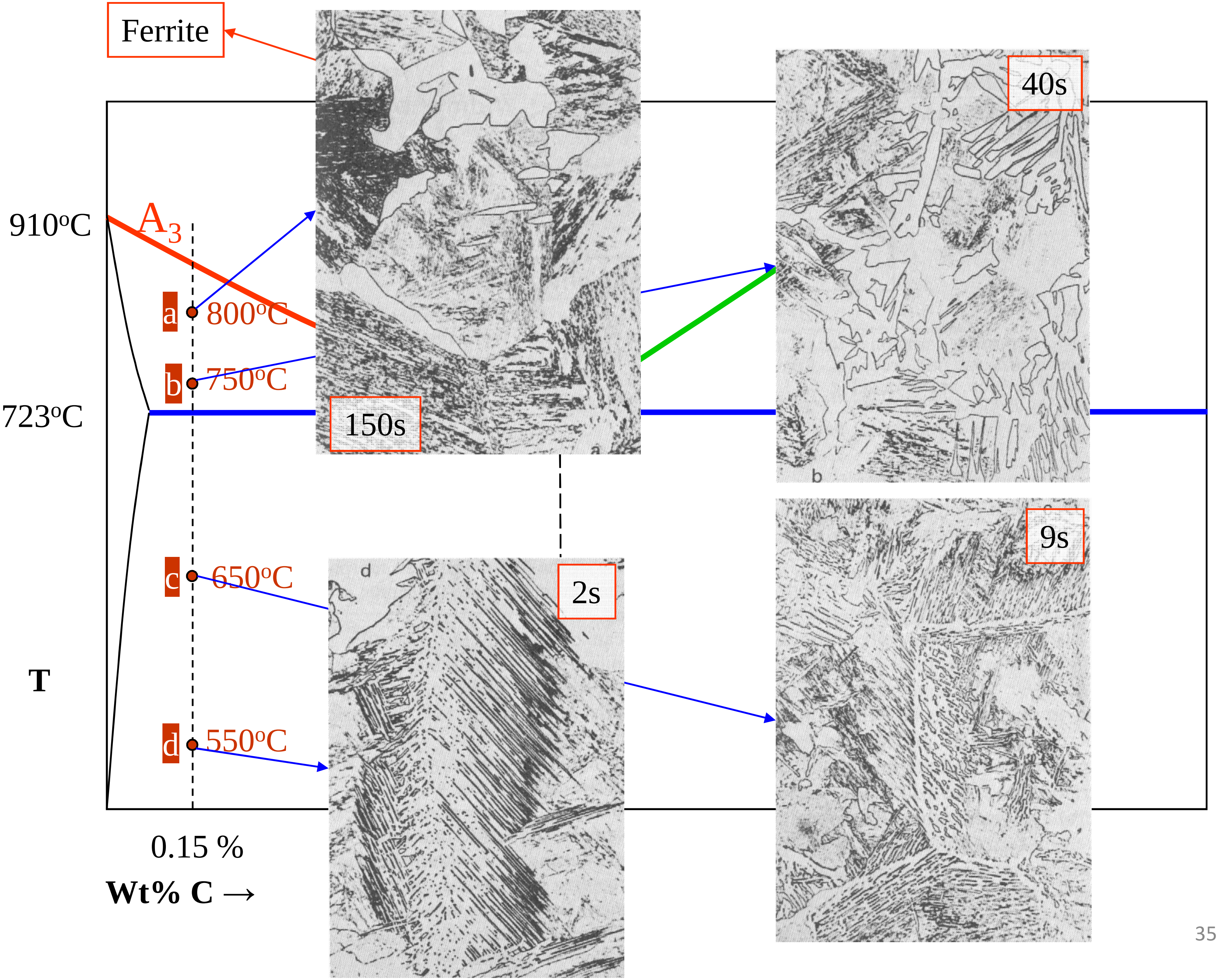
A partially transformed eutectoid steel. Pearlite has nucleated on grain boundaries and inclusions (× 100). (After J.W. Cahn and W.C. Hagel in *Decomposition of Austenite by Diffusional Processes*, V.F. Zackay and H.I. Aaronson (Eds.), 1962, by permission of The Metallurgical Society of AIME.)

Decomposition of Austenite

- The transformation of austenite on cooling is a complex processes in the sense that compositional as well as configurational changes are involved. Carbon present in the austenite adjusts itself in such a way that at one end it leaves behind an almost carbon free phase (ferrite) and on the other it combines with iron to form cementite.
- Similarly large scale redistribution of alloying elements takes place when the solubility of the element is restricted in alpha iron, and/or there is a strong tendency for the element to form carbides. Also, the crystal structure changes from γ-iron to α-iron.
- The process of decomposition of austenite to ferrite-cementite aggregate is essentially a diffusion controlled processes and proceeds by nucleation and growth mechanism. Therefore, any factor, which is able to vary either the rate of nucleation/ the rate of growth or both is also able to change the nature of ferrite cementite mixture.
- Some of These factors are: *nature of austenite under consideration, the temperature of transformation and the presence of alloying elements.*
- The more the homogeneity of austenite, the better is the probability of getting a lamellar structure. A heterogeneous austenite may result in the transformation of austenite to spheroidized structure. With lowering of the transformation temperature, a harder and finer aggregate of ferrite and cementite results.
- The microstructures evolving during austenite decomposition are Ferrite with different morphologies (grain boundary allotriomorphic ferrite, idiomorphic ferrite, Widmanstatten ferrite, and intragranular ferrite) , cementite, Pearlite, Bainite and Martensite.

Precipitation of Ferrite from Austenite

- ☐ In this topic we will be concerned with phase transformations in which the first phase to appear is that given by the equilibrium phase diagram.
- ☐ Here we will consider to the diffusional transformation of Fe-C austenite into ferrite.
- ☐ However, many of the principles are quite general and have analogues in other systems where the equilibrium phases are not preceded by the precipitation of transition phases.
- ☐ Under these conditions the most important nucleation sites are grain boundaries and the surface of inclusions.
- ☐ It can be seen in figure (next slide) that ferrite can also precipitate within the austenite grains (intragranular ferrite). Suitable heterogeneous nucleation sites are thought to be inclusions and dislocations. These precipitates are generally equiaxed at low undercoolings and more platelike at higher undercoolings.
- ☐ In general the nucleation rate within grains will be less than on grain boundaries. Therefore, whether or not intergranular precipitates are observed depends on the grain size of the specimen.
- ☐ In fine grained austenite for example, the ferrite that forms on grain boundaries will rapidly raise the carbon concentration with in the middle of the grains, thereby reducing the undercooling and making nucleation even more difficult.
- ☐ In a large grained specimen, however, it takes a longer time for the carbon rejected from the ferrite to reach the centers of the grains and meanwhile there will be time for nucleation to occur on the less favorable intragranular sites.


Ferrite
910°C
A3
a 800°C
b 750°C
723°C
c 650°C
d 550°C
T
0.15 %
Wt% C →
150s
40s
9s
2s

Ferrite nucleates on Austenite grain boundaries and grows with a blocky appearance
→ *Grain Boundary Allotriomorphs*

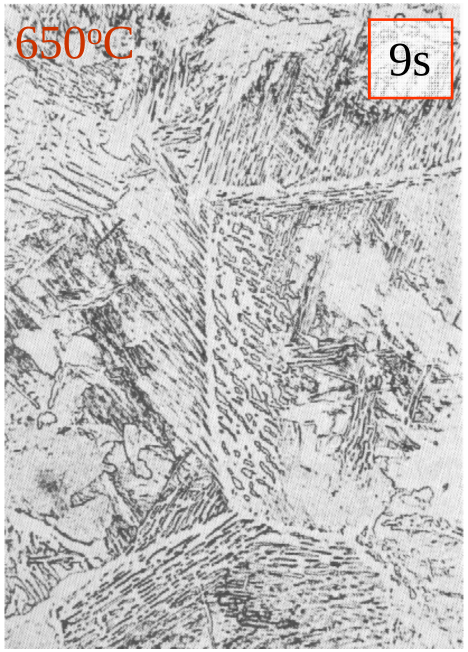
Small ΔT

Curved interfaces → incoherent
Faceted interfaces → semicoherent

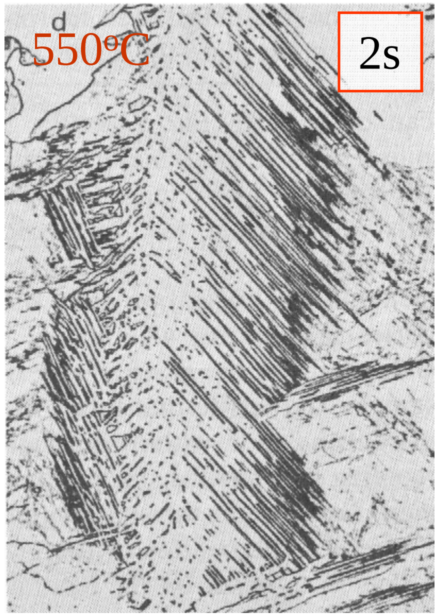
Larger undercooling – Ferrite grows as plates from GB
→ *Widmannstätten side-plates*

Large ΔT

Ferrite can also nucleate within the γ grains heterogeneously at inclusions and dislocations → equiaxed at low undercoolings and plate-like at higher undercoolings.



Widmannstätten side-plates → become finer with larger undercooling



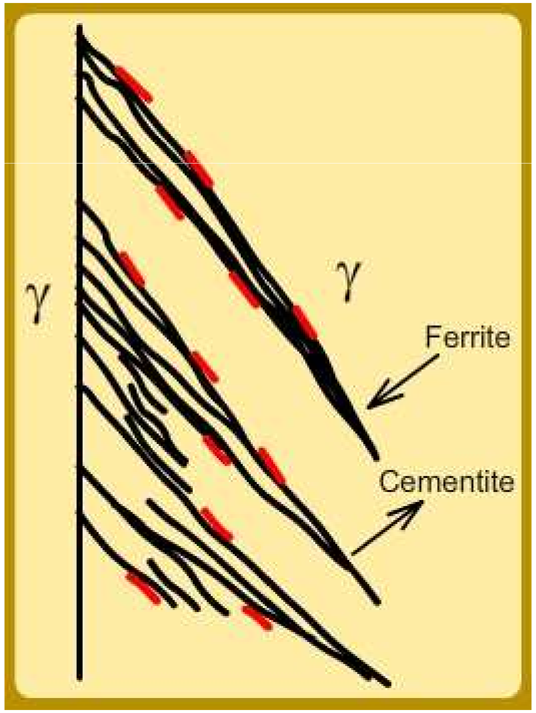
Very Large undercooling – Ferrite grows as needles GB → Widmannstätten needles

Eutectoid Transformation : Bainite transformation

- ☐ At relatively larger supersaturations (austenite cooled below the nose of the pearlite transformaton), there is another eutectoid product that develops known as bainite; bainite is also a mixture of ferrite and cementite; however, it is microstructurally quite distinct. In the next two subsections, we discuss these microstructural features.

Upper bainite

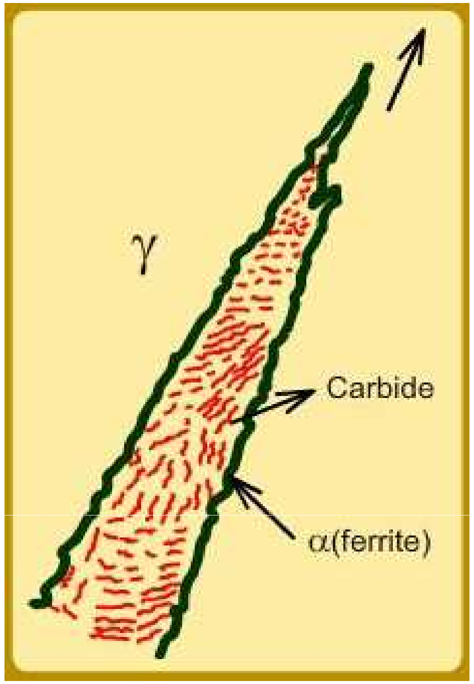
- ☐ At the higher end of the temperatures (350-550˚C), the microstructure consists of needles of laths of ferrite nucleated at the grain boundary and grown into one of the grains with cementite precipitates between the ferrites; see in Fig.
- ☐ The ferrite formed is Widmanstatten; it has a Kurdjumov-Sachs orientation relationship with the austenite grain into which it is growing; it is in this respect, namely the orientation relationship between the ferrite/cementite and the austenite grain in which they grow, that the bainite differs from pearlite.



Eutectoid Transformation : Bainite transformation

Lower bainite

- ❑ At low enough temperatures, the bainitic microstructure changes to that of plates of ferrite and very finely dispersed carbides; since the diffusion of carbon is very low at these temperatures (especially in the austenite phase as compared to ferrite), the carbides precipitate in ferrite (and, with an orientation relationship). These carbides that precipitate could be the equilibrium cementite or metastable carbides (such as ε carbide for example). A schematic of lower bainite plate that is formed is shown in Fig.

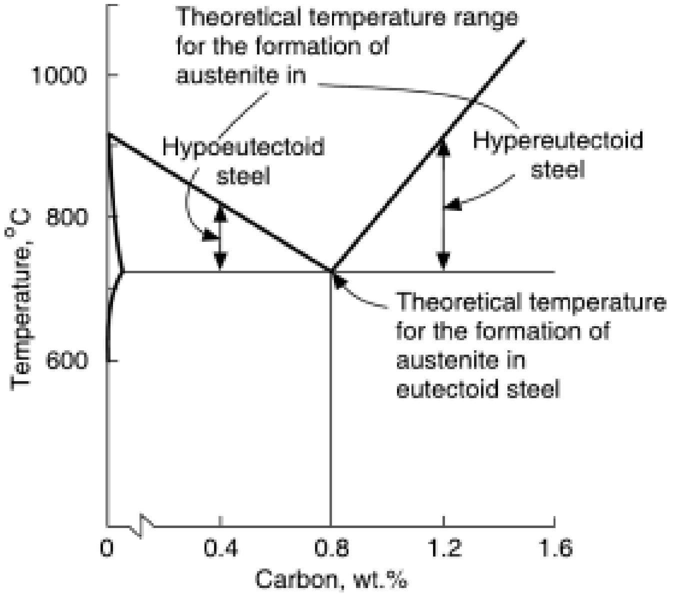


$$\gamma \rightarrow \alpha + Fe_3C^{**}$$

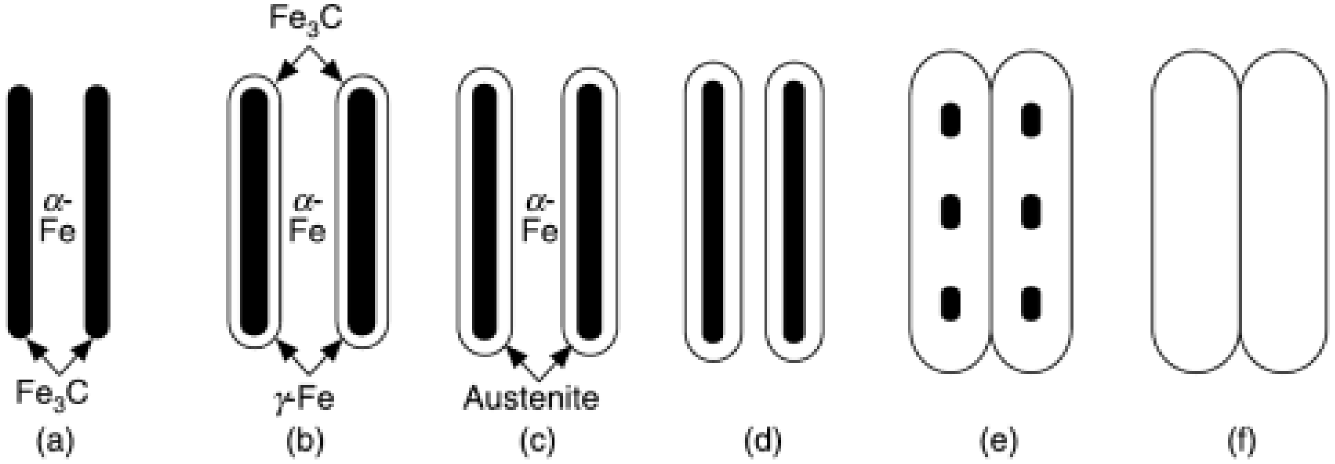
- ❑ Pearlite is nucleated by a carbide crystal, bainite is nucleated by a ferrite crystal, and this results in a different growth pattern.
- ❑ Acicular, accompanied by surface distortions
- ❑ ** Lower temperature → carbide could be ε carbide (hexagonal structure, 8.4% C)
- ❑ Bainite plates have irrational habit planes
- ❑ Ferrite in Bainite plates possess different orientation relationship relative to the parent Austenite than does the Ferrite in Pearlite

Formation of Austenite

- Formation of austenite is a preliminary step for any heat treatment process.
- Formation of austenite in eutectoid steel differs from that of hypoeutectoid and hypereutectoid steels in the sense that in the former case it occurs at a particular temperature (A_{C1}) where as for the latter it takes place a over range of temperature.
- At 1147°C, the maximum solubility of carbon in FCC iron is about 2 percent. Therefore, at this temperature, regions around the cementite layer will be enriched with carbon because of diffusion.



Temperature ranges for the formation of austenite on heating for steels.

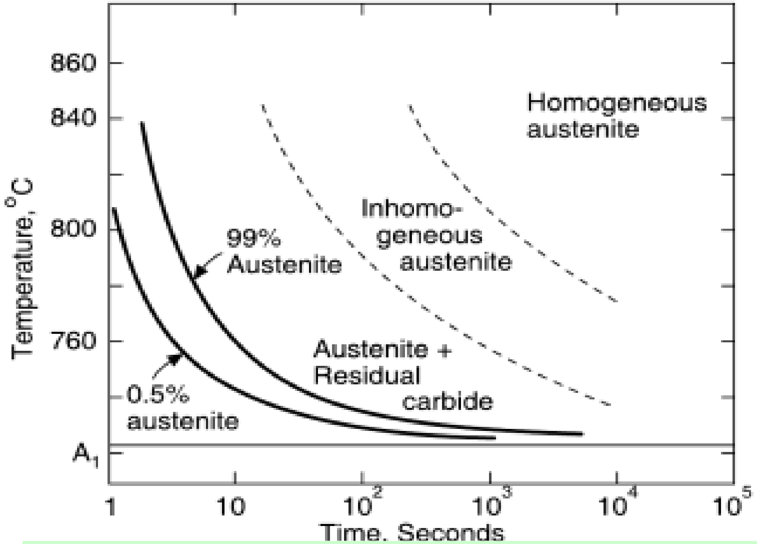


Steps associated with transformation of pearlite to austenite

Formation of Austenite

- The maximum diffusion of carbon atoms will take place from the cementite at the ferrite-cementite interface. As sufficient number of interfaces are available, austenite nuclei will be formed at the interface.
- By gradual dissolution of carbon of cementite into gamma iron, primary austenite/grains are formed. These primary austenitic grains dissolve the surrounding ferrite and austenitic grains grow at the expense of ferrite.
- The growth rate of austenite is higher than the rate of dissolution of the cementite into austenite because austenitic grain growth takes place because of the transformation of alpha iron to gamma iron and diffusion of carbon atoms from austenite to ferrite. This explains the experimentally observed fact that dissolving of ferrite is completed before that of cementite.

- The austenite thus formed at eutectoid temperature is not homogeneous. The carbon concentration is higher in these regions which are adjacent to the original cementite lamellae than those which are adjacent to the ferrite mass.
- Chemically homogeneous austenitic grains are obtained by holding (holding time should be sufficient to diffuse properly) steel above the eutectoid temperature

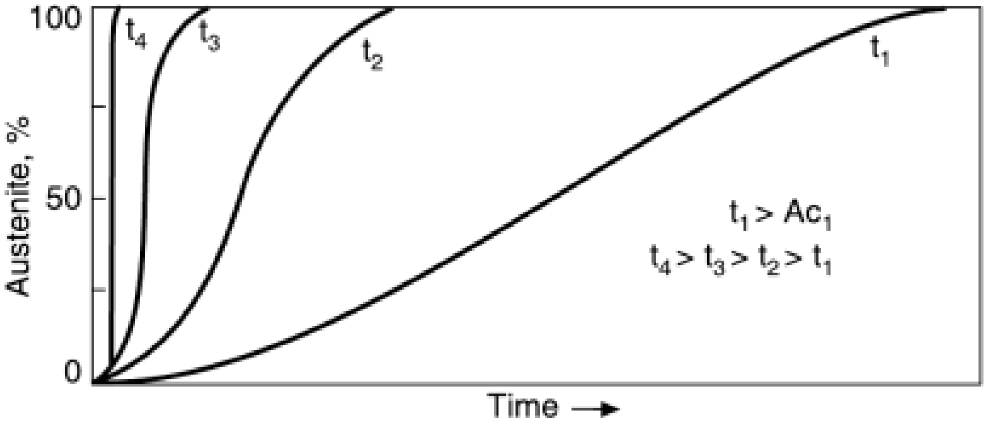


Effect of temperature and time on the austenite formed from pearlite in 0.3% carbon steel

Kinetics formation of Austenite

- The formation of austenite on heating always occurs at a temperature higher than that predicted by the Fe-Cementite phase diagram.
- To study the kinetics of austenite formation is to heat a number of steel samples to different temperatures above the eutectoid temperature.
- Heating is done by immersing samples in constant temperature baths. A number of samples are immersed in a constant temperature bath and are taken out one by one after a definite interval of time followed by immediate quenching which will result in the formation of austenite from transformed austenite.
- The amount of martensite formed will depend on the amount of transformed austenite which in turn will depend on the temperature at which the steel sample has been heated and the holding time at that temperature.

- From the figure, we can concluded that the lower transformation temperature, the more is the time required to complete the transformation
- Any property which changes with the formation of austenite, and/or with martensite formed by quenching of transformed austenite, can be utilized this purpose

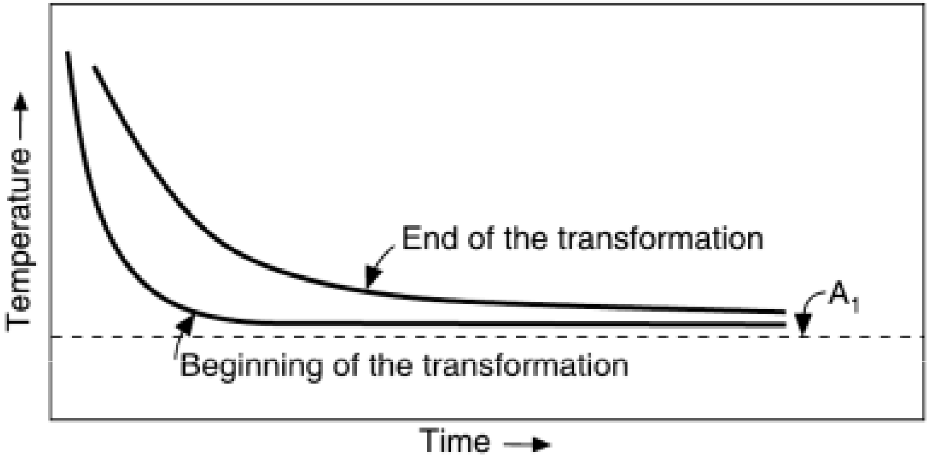


Transformation of pearlite to austenite as a function of time

Kinetics formation of Austenite

- ❑ The relationship between transformation temperature and transformation time has been derived by taking into consideration the effect of superheating. An analysis of figure leads to the following conclusions:

- ❑ Transformation is completed in a short period at high transformation temperature.
- ❑ For Higher heating rates, transformation will start at higher temperature, whereas for slower heating rate, transformation will start at lower temperature.
- ❑ For any given practical rate of heating , the formation of austenite will occur over a range of temperature, and not at constant temperature.



Effect of temperature on the time required for start and completion of transformation of pearlite to austenite

- ❑ For the formation of austenite at a constant temperature, the heating rate should be extremely slow, and the two curved lines will converge to a single point located at eutectoid temperature line.
- ❑ The end of transformation curve does not reveal any information about the nature (homogeneity) of austenite. The curved line ensures that all the pearlite has been transformed into austenite. In order to attain homogeneous austenite, the steel has to be heated to still higher temperatures.

Kinetics formation of Austenite

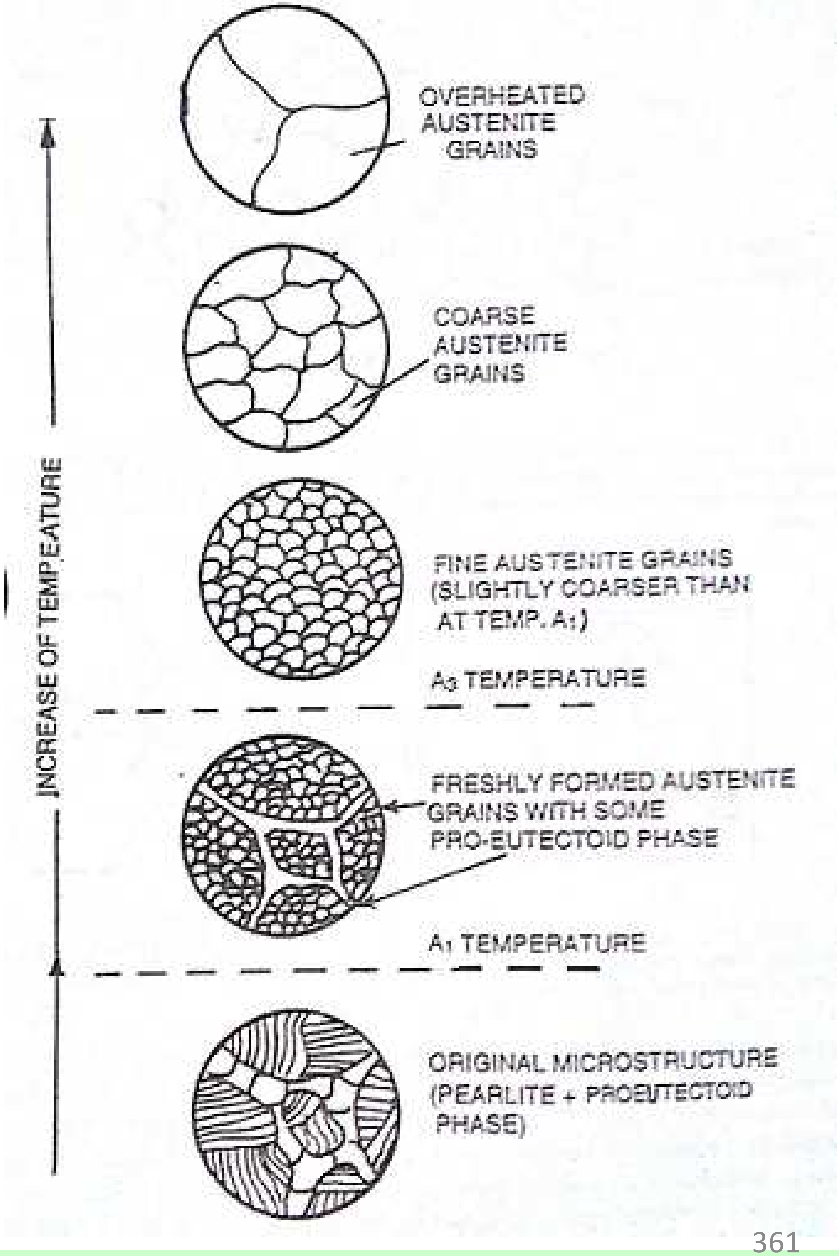
- The processes of austenite formation on heating proceeds by nucleation and growth reaction. Therefore, the factors which can vary either the rate of nucleation or the rate of growth or both will change the kinetics of austenite formation. Two such parameters are transformation temperature and holding time at transformation temperature.
- The kinetics of austenite transformation is governed to great extent, by the nature of pearlite. The number of possible austenite nuclei will increase with the increase in interfacial area. The interfacial area can be increased in two ways: by increasing the cementite contents, and by decreasing the interlamellar spacing. This is the reason why high carbon steels austenitize more rapidly than low carbon steels.
- The closer the ferrite-cementite lamellae, the higher will be the rate of nucleation. Also, the carbon atoms have to diffuse for smaller distances in order to enrich low carbon regions.
- Therefore, the rate of growth of primary austenitic grains will also be higher in this case . This explains why pearlitic structure with less interlamellar spacing is transformed faster to austenite.
- The kinetics of austenite transformation for coarse pearlitic structure is slow for the reason given above. The kinetics of austenitic transformation from granular pearlite is slower than that of lamellar pearlite for same reasons.
- The kinetics of transformation will further decrease with increase in the size of globular cementite particles. Quenched structure will also transform to austenite more rapidly than the granular pearlitic structure.

Austenitic Grain Size

- ☐ The size of austenitic grains is the most important structural characteristic of heated steel. The austenitic grain size strongly effects its own transformation behavior and the mechanical properties of the microstructures formed from austenite.
- ☐ Austenitic grain boundaries are preferred sites for the nucleation of pro-eutectoid phases and pearlite, which are diffusion controlled transformation products.
- ☐ Coarse austenitic grains having less grain boundary area, have fewer nucleating sites, thus diffusion-controlled transformation of austenite is retarded paving way for easy transformation to martensite (Diffusionless transformation product).
- ☐ The impact toughness of steel is most sensitive to the size of the austenite grains in the hardened and tempered state. The charpy impact value improves with decreasing austenitic grain size to the extent that its value for a fine-grained steel can exceed several times that of a coarse grained steel of the same grade.
- ☐ The reason, partly is due to segregation of impurity atoms to the austenitic grain boundaries during Austenitisation (more segregation takes place if grain boundary area is less as is the case in coarse grained steels), and thus the fracture frequently takes place along prior austenitic grain boundaries.
- ☐ The co-segregation of impurities like Sb, P, Sn, As along the large angle grain boundaries of austenitic grains weakens the adhesion at these boundaries to cause fracture along them. Such intergranular fracture is quite brittle.
- ☐ In alloys of Fe-Ni, and Fe-Ni-C, the M_s temperature is lowered significantly by decreasing the austenitic grain size, probably due to higher strength of fine grained austenite , which in turn increases the shear resistance of austenite to transform martensite.

Austenitic Grain Size

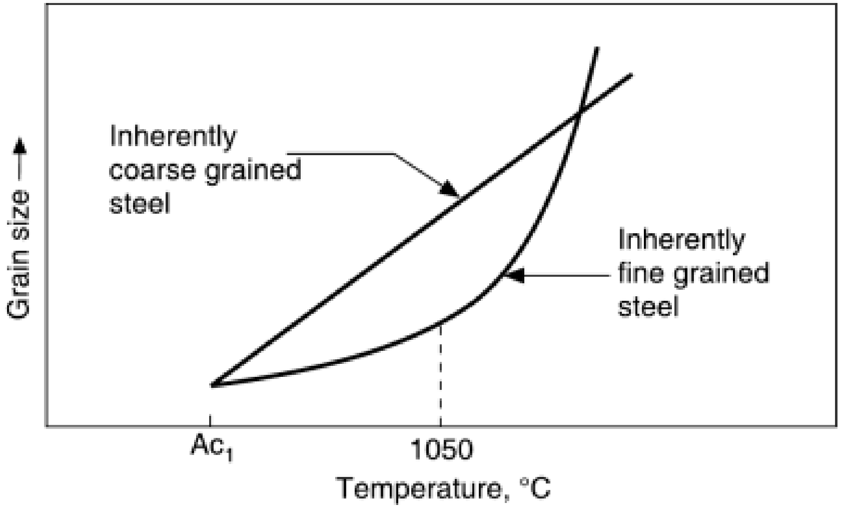
- At temperatures just above the upper critical temperature, when the structure is fully austenitic, that is just after the transformation is complete, the initial grain size of austenite is fine (though more disperse is the initial structure, the finer is the austenite grain formed).
- As the temperature is raised further, or holding time at a given temperature is increased, then grain coarsening occurs. This behavior is schematically illustrated.
- Austenitic grain growth is a natural spontaneous process and is caused by the tendency to reduce the surface energy by reducing the total surface area of the grain boundaries. A high temperature accelerates the rate of this processes.
- Driving force is the surface energy stored as grain boundary energy. Certain grains grow at the expense of smaller grains, which due to their less stable.



Schematic illustration of changes in microstructure of steel on heating

Austenitic Grain Size

- ❑ Depending on the tendency of steel to grain growth, steels can be classified into two broad groups:
  - ✓ Inherently fine grained steels
  - ✓ Inherently coarse grained steels
- ❑ Inherently fine grained steel resists the growth of austenitic grains with increasing temperature. The kinetics of austenite grain growth is very slow and the steel remains fine grained even at temperatures as high as 1000°C or 1050°C.



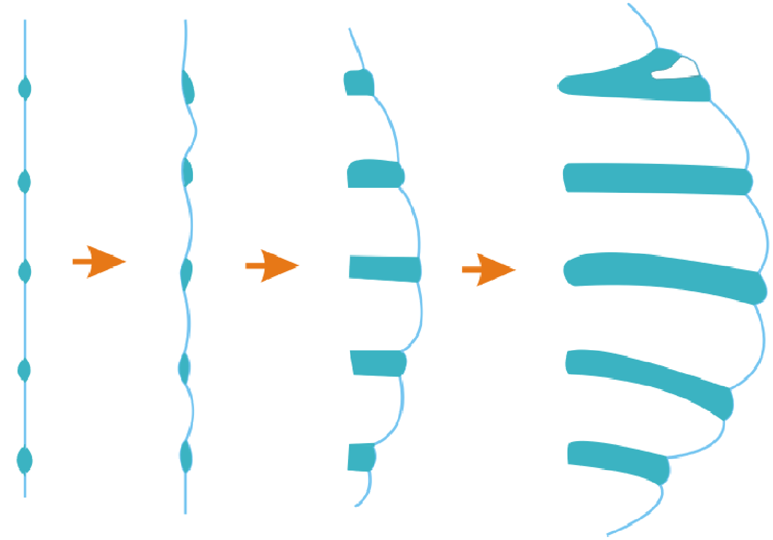
Comparison of austenitic grain growth characteristics of inherently fine grained and course grained eutectoid steel

- ❑ On the other hand, grains of inherently coarse grained steel grow abruptly with increasing temperature, and so a steel with coarse grains is obtained.
- ❑ In the presence of ultramicroscopic particles of oxides, carbides and nitrides which prevent grain growth. These particles are refractory in nature, i.e., they can withstand high temperatures and are generally present at grain boundaries of austenite. Therefore, they act as barriers to the growth of austenitic grains.
- ❑ Intensive grain coarsening of inherently fine grained steels above a particular temperature is due to the dissolution of ultrafine particles of carbides, oxides and nitrides in the matrix (austenite). After dissolution, no particles are left to offer resistance to grain growth.

Cellular Precipitation (Discontinuous Precipitation)

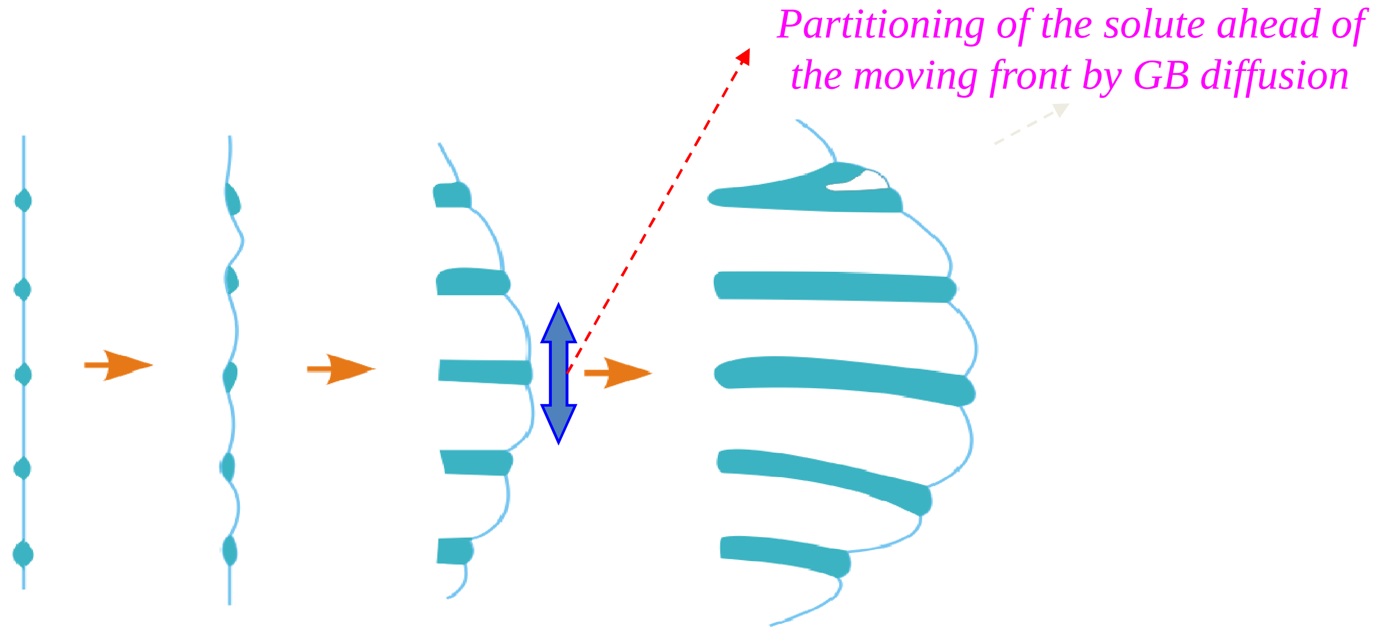
- Grain boundary precipitation may also occur by cellular precipitation *(apart from Allotriomorphs, Widmannstätten side plates & needles)*
- Main Feature → boundary moves with the tip of the precipitates
- The mechanism by which GB ppt. develops into cellular precipitation is system specific called *discontinuous precipitation* as the composition of the matrix changes discontinuously as the cell front passes
- (Continuous precipitation- *not* cellular- occurs throughout the matrix and the matrix composition changes continuously with time

$$\alpha'(\text{higher solute concentration}) \rightarrow \alpha(\text{lower solute concentration}) + \beta$$



Cellular Precipitation (Discontinuous Precipitation)

- ☐ In the previous section, we discussed the effect of grain boundaries on the nucleation of precipitates with specific reference to ferrite (α) on austenite (γ). We saw that there exist two morphologies, namely, grain boundary allotriomorphs and Widmanstatten side plates.
- ☐ In some cases, the precipitates that are nucleated at the grain boundary, when they grow, also carry the grain boundary along with them. This process is shown schematically in Fig. Such a process leads to a cellular microstructure as shown. This kind of process is known as cellular precipitation.


Partitioning of the solute ahead of the moving front by GB diffusion

$$\boxed{\alpha'(\text{higher solute concentration}) \rightarrow \alpha(\text{lower solute concentration}) + \beta}$$

Cellular Precipitation (Discontinuous Precipitation)

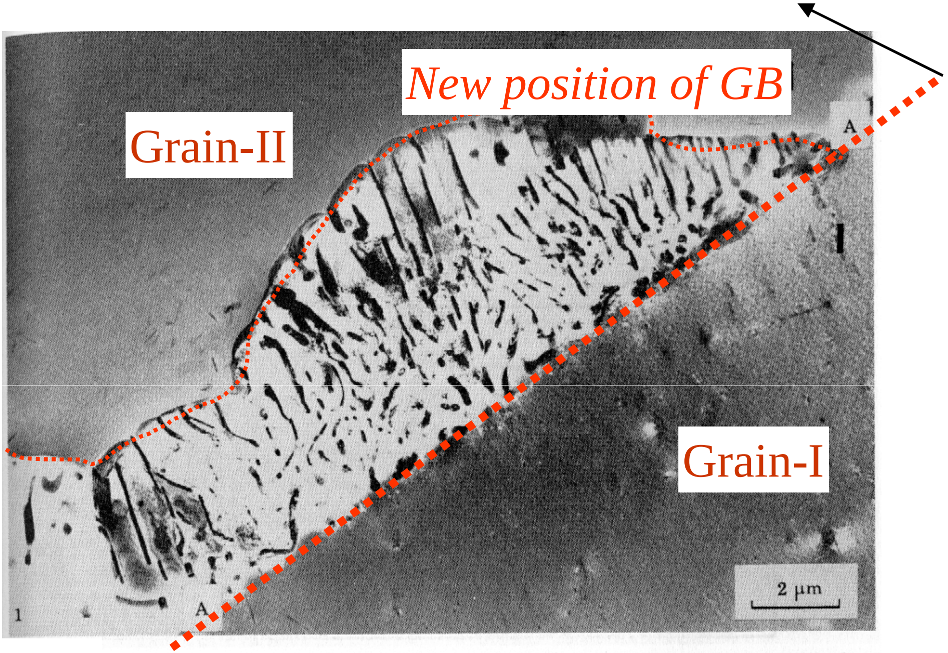
- Cellular precipitation is also known discontinuous precipitation because of the sudden change in composition of matrix across the moving grain boundary as shown below; on the other hand, noncellular precipitation is known as continuous because the composition of the matrix phase decreases continuously at any point. In general, continuous precipitation leads to much better mechanical properties (due to the more uniform distribution of precipitates, which nucleate throughout the matrix (on dislocations for example) and hence, much smaller size distribution) as opposed to discontinuous precipitation.
- Cellular precipitation leads to microstructures that are very similar to eutectoid transformations. In fact, the only difference between cellular precipitation and eutectoid transformation is that while in eutectoid transformation both the phases that form are different from the original phase, in cellular precipitation one of the phases remains the same as the original phase (albeit with a different composition):

$$\boxed{\alpha' \rightarrow \alpha + \beta}$$

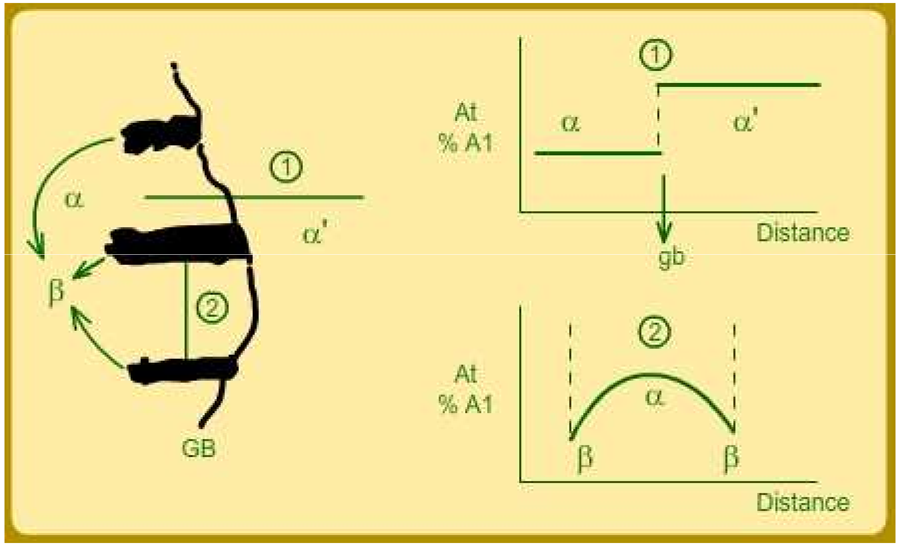
- α' is the supersaturated matrix, and is the matrix phase with a composition closer to equilibrium as compared to α ' and β is the precipitate phase.

Cellular Precipitation (Discontinuous Precipitation)

Original position of GB



Cellular precipitation of $Mg_{17}Al_{12}$ in an Mg–9 at% Al alloy solution treated and aged 1 h at 220 °C followed by 2 min at 310 °C. Some general $Mg_{17}Al_{12}$ precipitation has also occurred on dislocations within the grains.



The cellular precipitation that takes place during the aging treatment leads to microstructures

The composition profiles across the boundary as well as parallel to the boundary

Cellular Precipitation (Discontinuous Precipitation)

- Consider the phase diagram of the Al-Mg system, The β phase is the $Mg_{17}Al_{12}$ phase and the phase is the solid solution of Mg and Al. Consider an alloy of 9 at % Al, which is solution treated (at, say 410^{o}C) and aged for an hour at 220^{o}C.
- The cellular precipitation that takes place during the aging treatment leads to microstructures as shown schematically in Fig. (next slide).
- The composition profiles across the boundary as well as parallel to the boundary are as shown in Fig. (next slide).
- The discontinuous nature of the composition in the phase across the moving boundary indicates that the mechanism of diffusion which leads to the formation of cellular structures is the diffusion of solutes through the moving grain boundary (since, if the diffusion took place through the matrix on either side of the boundary, it would have led to composition gradients).
- The composition of the α in the profile parallel to the moving boundary indicates that composition is still not equilibrated after the precipitation of β.
- When the mechanism of phase transformation changes from nucleation and growth to spinodal decomposition, it is possible for discontinuous spinodal to take place; in such cases, phase separation starts near the grain boundary and the boundary moves with the phase separation (reaction) front.

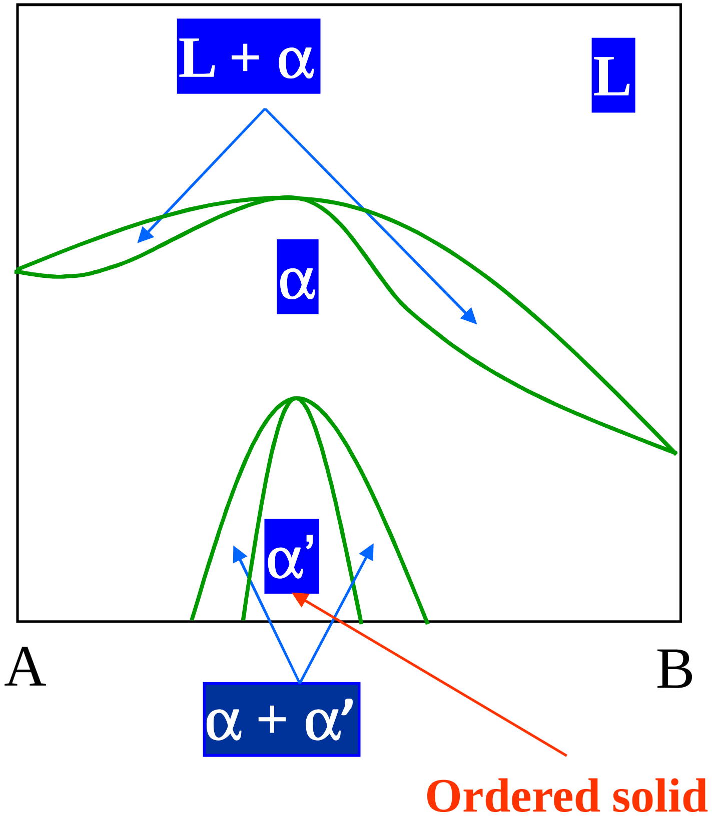
Ordering Transformations

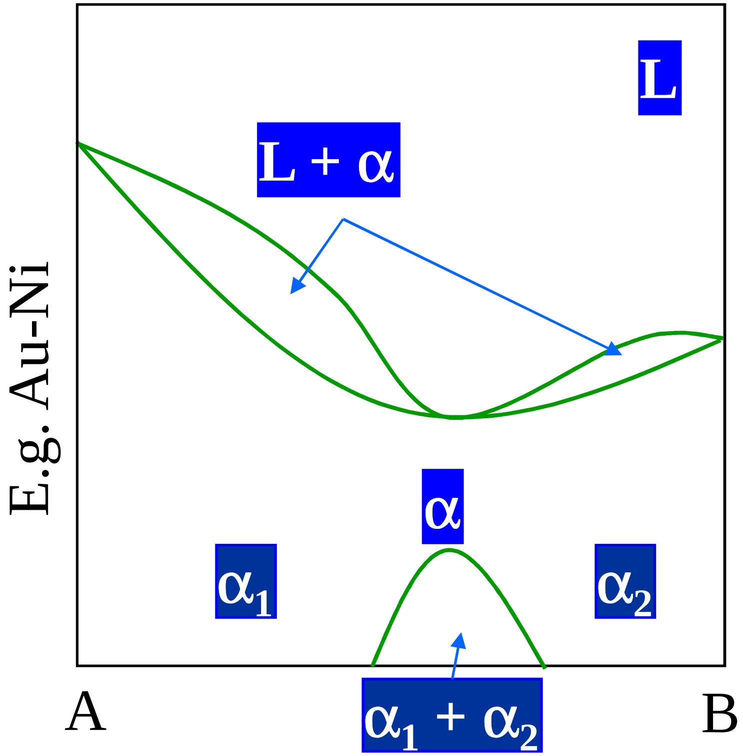
- In the thermodynamics & kinetics topic, we considered a system with $\Omega > 0$. In such systems, at lower temperatures, the free energy develops a concave curvature leading to a phase separation into mechanical mixture.
- Now, consider a system with , that is, the AB bonds are preferred over AA/BB bonds. What happens to such systems at low temperatures?
- In systems with $\Omega < 0$, that is, systems in which AB bonds are preferred over AA/BB bonds are preferred, at lower temperatures, the system becomes ordered. This ordering is over and above the crystallographic ordering. In the crystalline lattice, specific lattice positions are occupied by specific atoms, thus leading to more of the preferred unlike bonds.
- Consider for example a bcc lattice occupied by A and B atoms. If it is disordered, then, the probability of the cube corners and cube centers are occupied by the A or B atoms is 50% (that is, the same as the alloy composition in at%). However, when this system orders, the cube corners preferentially occupy one of the positions, say, cube corners while the other preferentially occupies the cube centers.
- That is, the bcc lattice now can be considered to be consisting of two interpenetrating cubic lattices. Such a structure is known as B_2. Notice that in the (ideal) B_2 structure, there are only AB bonds and no AA/BB bonds. NiAl is a system in which, for example, such B_2 ordered structure is known. There are also fcc based ordered structures such as $L1_2$ (example: Ni_3Al) and $L1_0$ (example: CuAu).

Ordering Transformations

- A–B bonds stronger than A–A and B–B bonds
- Solid stabilized → Ordered solid formation

- A–A and B–B bonds stronger than A–B bonds
- Liquid stabilized → Phase separation in the solid state

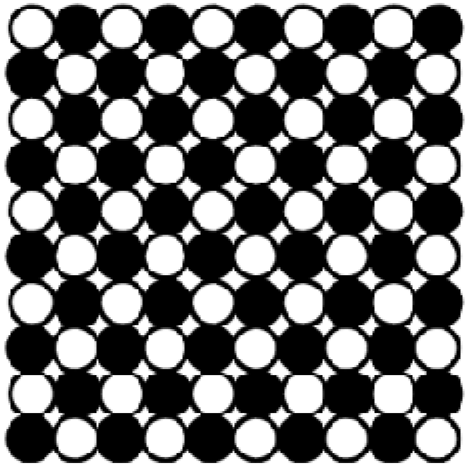




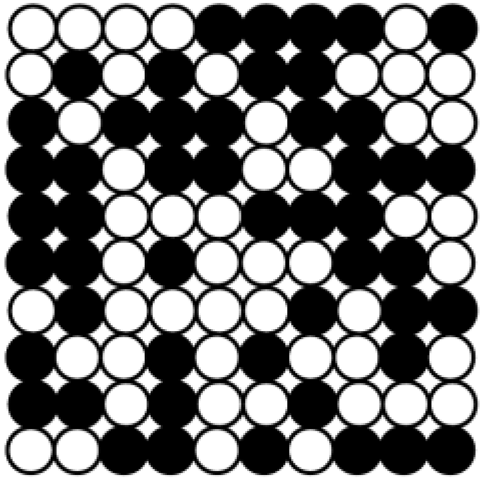
α_1 & α_2 are different only in lattice parameter

Variations to the isomorphous phase diagram

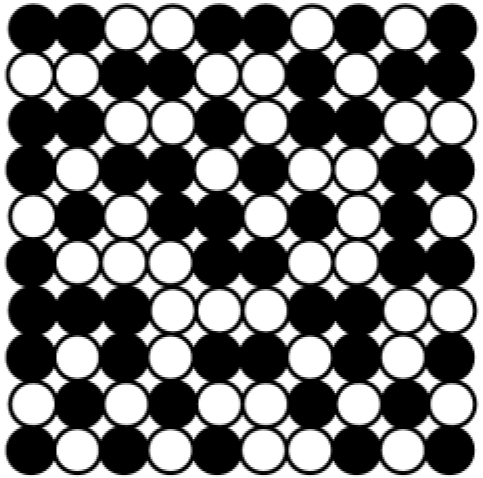
Ordered Phases



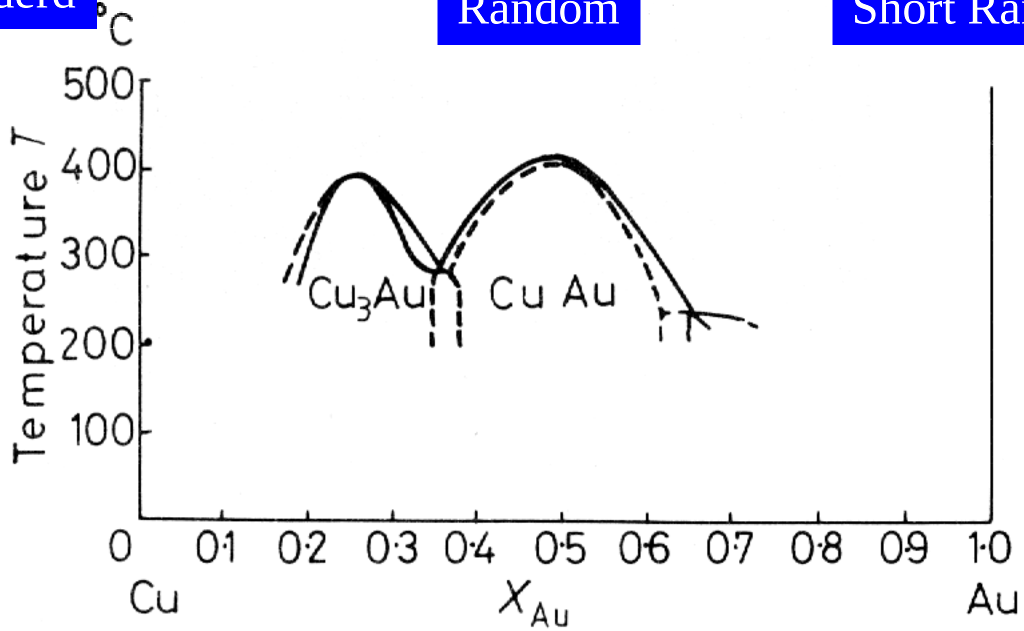
Orderd



Random

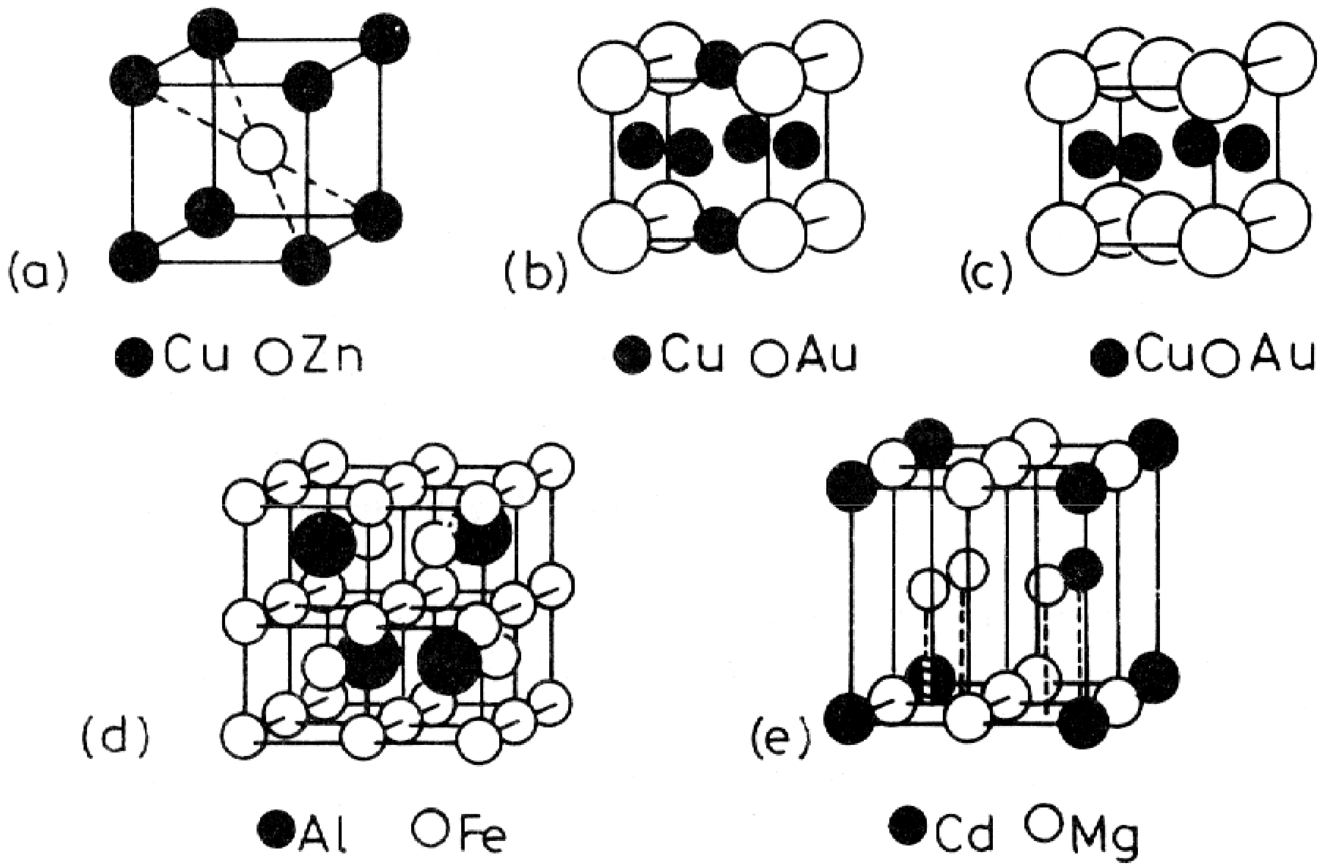


Short Range Orderd



Part of the Cu-Au phase diagram showing the regions where the Cu_3Au and CuAu superlatices are stable.

Ordered Phases



The five common ordered lattices, examples of which are: (a) $L2_0$: CuZn, FeCo, NiAl, FeAl, AgMg; (b) $L1_2$: Cu_3Au, Au_3Cu, Ni_3Mn, Ni_3Fe, Ni_3Al, Pt_3Fe; (c) $L1_0$: CuAu, CoPt, FePt; (d) $D0_3$: Fe_3Al, Fe_3Si, Fe_3Be, Cu_3Al; (e) $D0_{19}$: Mg_3Cd, Cd_3Mg, Ti_3Al, Ni_3Sn. (After R.E. Smallman, *Modern Physical Metallurgy, 3rd edition*, Butterworths, London, 1970.)

Long range and short range order parameters

- There are two different order parameters that one can define. The first is the short range order parameter (S) defined as :

$$S = \frac{P_{AB} - P_{AB}(random)}{P_{AB}(\max) - P_{AB}(random)}$$

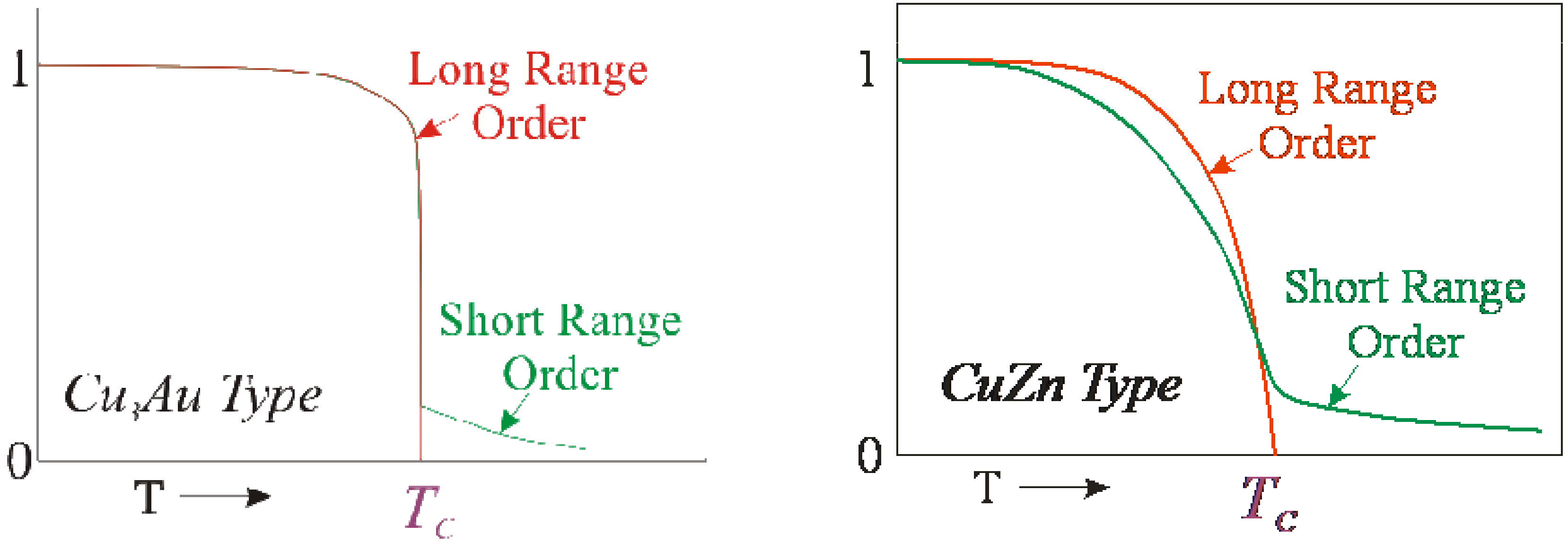
- Here, P_{AB}(max)and P_{AB}(random) refer to the maximum number of bonds that can exist and the number of bonds in a random solution. As one can see, the short range order parameter is closely related to the, regular solution parameter; this type of ordering is possible in alloys of all compositions.
- In case the alloy composition is in simple ratios of the constituent atoms, then, one can define the so called long range order parameter L in terms of the alloy composition as x given as:

$$L = \frac{p - x}{1 - x}$$

- Where p is the probability of occupancy of the given site by the right kind of atom.
- At absolute zero, the system will choose a state with L = 1; however, as temperature increases, the effects of configurational entropy come into play; so the value of L decreases from unity and eventually reaches zero. The temperature at which this change of Long Range Order (LRO) from unity to zero takes place is known as the critical temperature (T_c) for the order-disorder transformation.

Long range and short range order parameters

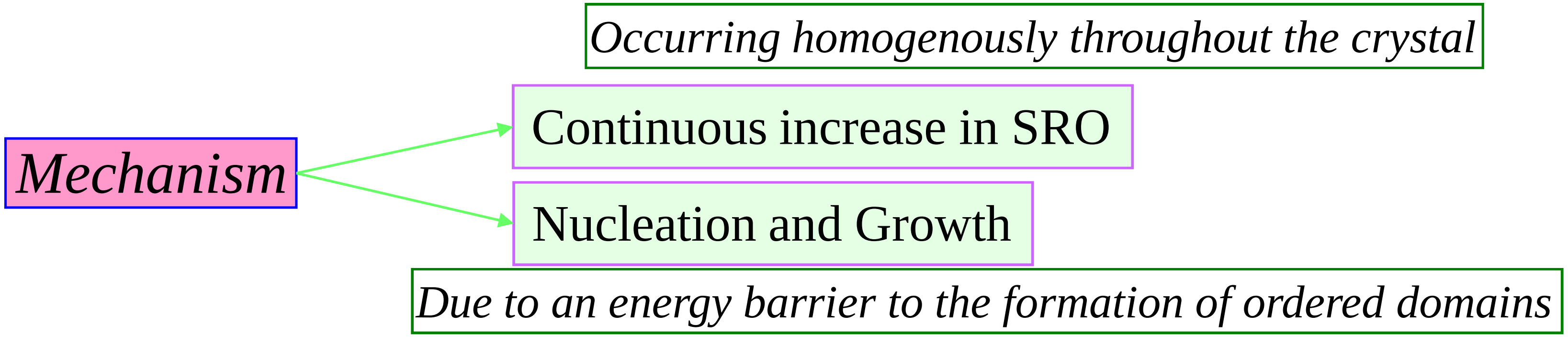
- In Fig. we show the variation of *L* and *S* with temperature in two systems, namely, one that undergoes an order-disorder transformation from B_2 to disordered bcc and another that undergoes an order-disorder transformation from $L1_2$ to disordered fcc.
- It is clear from the figures, the changes are of two different types; in the equiatomic case of B_2 to bcc (CuZn type), the variation is continuous; however, in the case of $L1_2$ to fcc (Cu_3Au type), the variation is abrupt. These differences in the behavior is a consequence of the differences in atomic configurations in the two ordered lattices.



Order parameter variation with temperature: continuous (B_2 type) and abrupt ($L1_2$).

Ordering Transformations : Microstructural features

- ❑ The order-disorder transformation can take place both through the nucleation and growth mechanism and spinodal mechanisms. In spinodal mechanism there is continuous increase in, homogeneously all through the crystal leading to the transformation. In the nucleation and growth mechanism, small regions form overcoming an energy barrier and these regions grow.
- ❑ In ordered alloys, the two phases have near-identical lattice parameters and the interfacial energies between the ordered and disordered phases is very low. Hence, the barrier for nucleation is very small. Hence, order-disorder transformation, when takes place through the nucleation and growth mechanism, takes place through homogeneous nucleation.



Occurring homogenously throughout the crystal

Mechanism

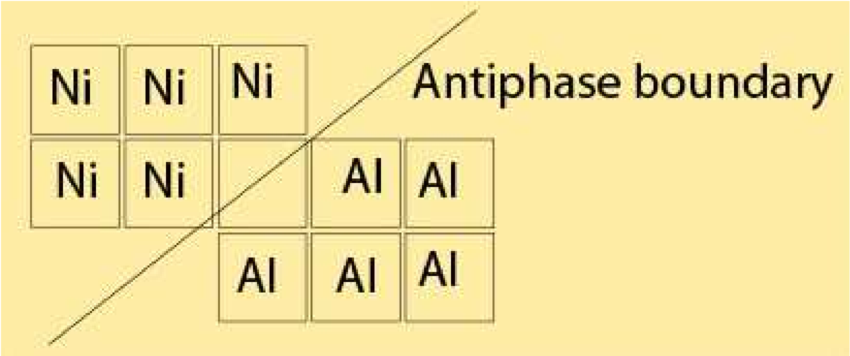
Continuous increase in SRO

Nucleation and Growth

Due to an energy barrier to the formation of ordered domains

Antiphase boundary

- In ordered alloys, there exist surface defects which are known as antiphase boundaries. This is because the two different ordered domains formed at different regions, when impinge, it can so happen that there is no matching across the interface; see the schematic in Figure.
- The different ordered domains are possible because in B2 for example, the two sites are equivalent and hence what is cube center in one domain could be the cube corner in another.
- In the schematic shown in the Fig., for example, in the left upper portion, the cube centers are occupied by Ni while in the lower right portion cube centers are occupied by Al. So, when these two domains meet an antiphase boundary is formed. Since the antiphase boundary consists of NiNi and AlAl bonds, they increase the energy of the system. Hence, given a chance the system would like to get rid of them.



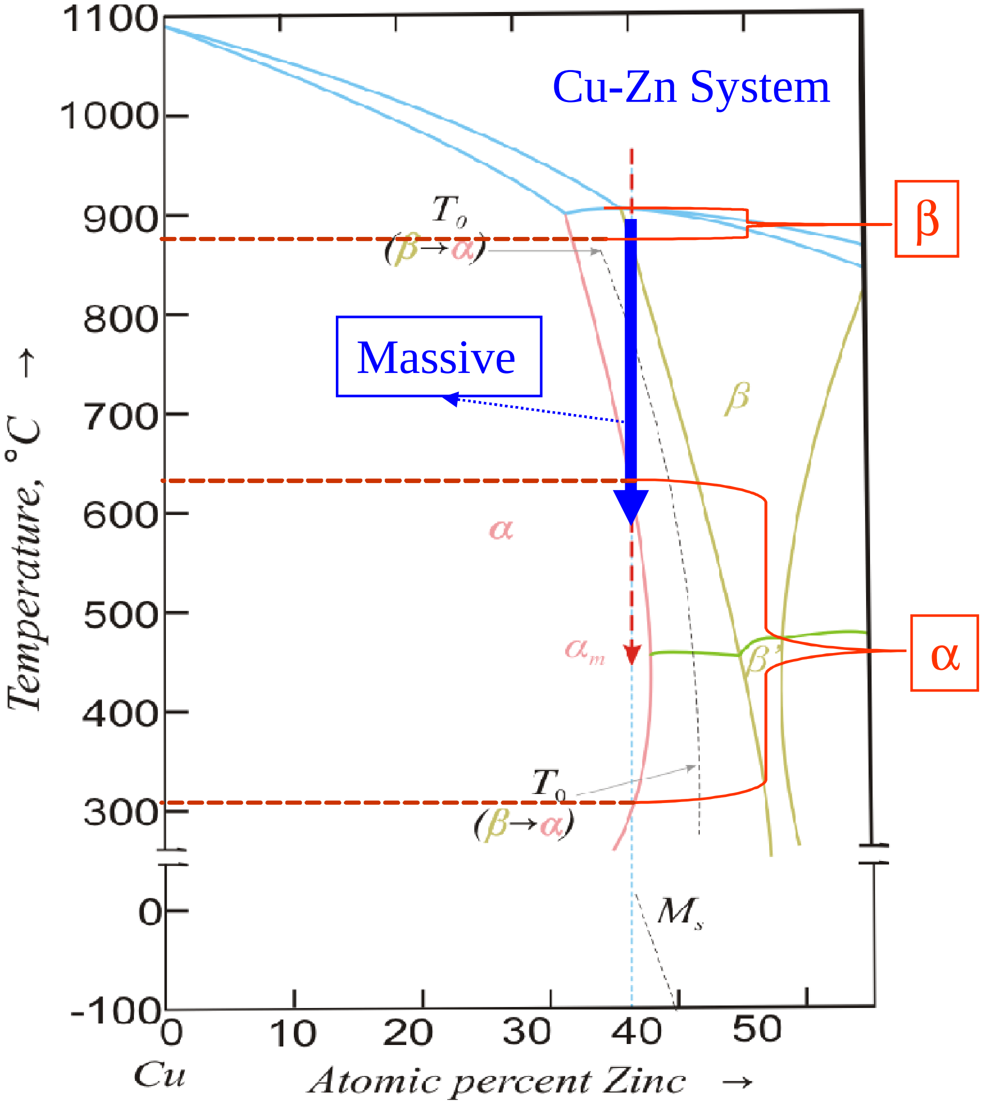
The schematic of the formation of antiphase boundaries in an ordered alloy due to the accidents of growth.

Massive Transformation

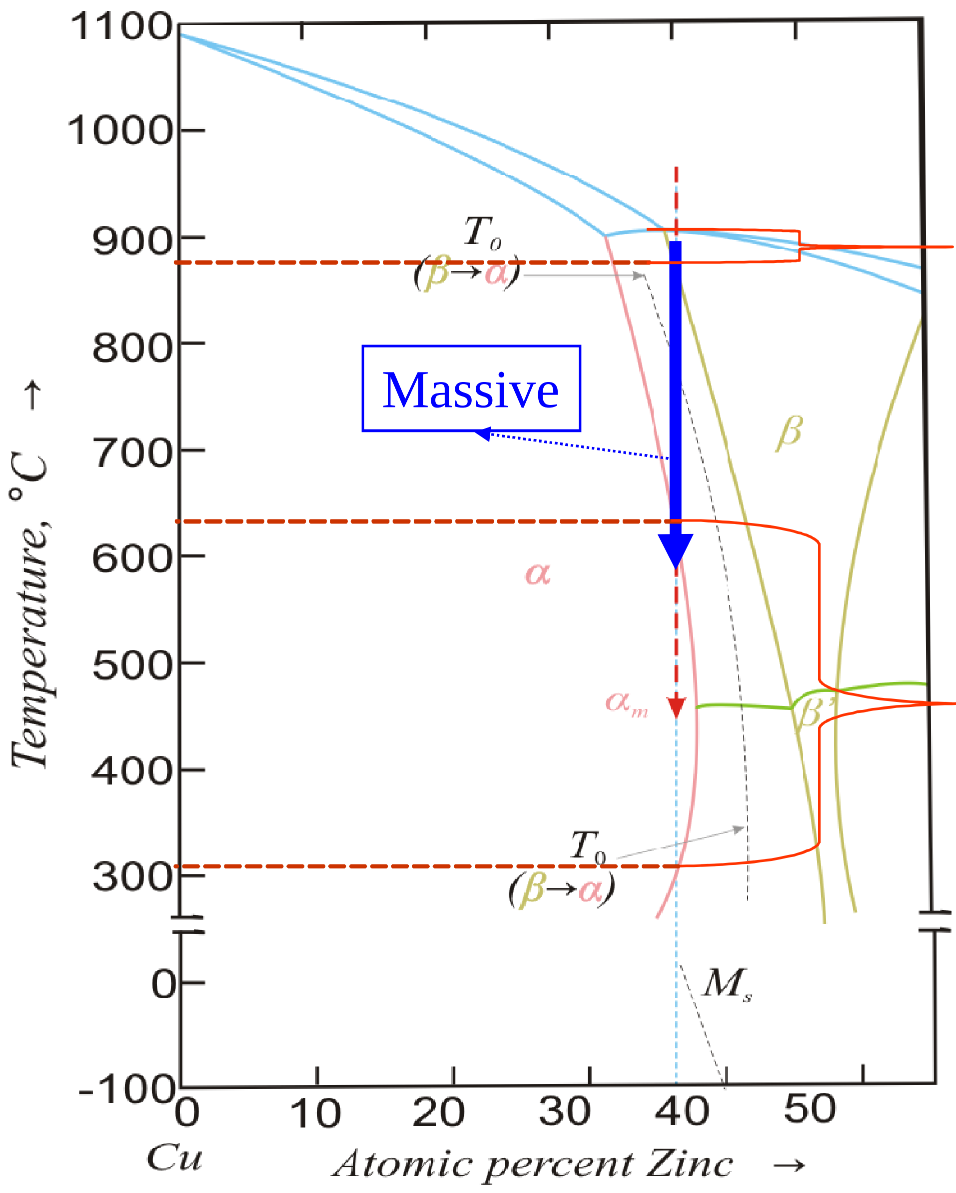
- ❑ The type of transformation that occurs in cooling (e.g. Cu-38 at% Zn alloy) depends on the cooling rate
  - Slow cooling → transformation at small undercoolings ⇒ equiaxed α
  - Faster cooling → transformation at lower T ⇒ *Widmannstätten α needles*
  - Even faster cooling (brine quench) → no time for diffusion ⇒ *Transformation of β →α without change in composition* (MASSIVE TRANSFORMATION)
- ❑ α richer in Cu ⇒ growth of α requires long-range diffusion of Zn away from advancing α/β interface
- ❑ MASSIVE Tr.
  - Nucleation at GB and rapid growth into β
  - Irregular appearance
  - No change in composition ⇒ Only short range jumps (thermally activated) across the interface (α/β) *(no long range diffusion required)→ fast growth rate*
    (thermally activated migration of incoherent interfaces → diffusionless civilian)
- ❑ Separate transformation curve (in TTT & CCT diagrams)
- ❑ ~ to GB migration during recrystallization → *but driving force v.high*

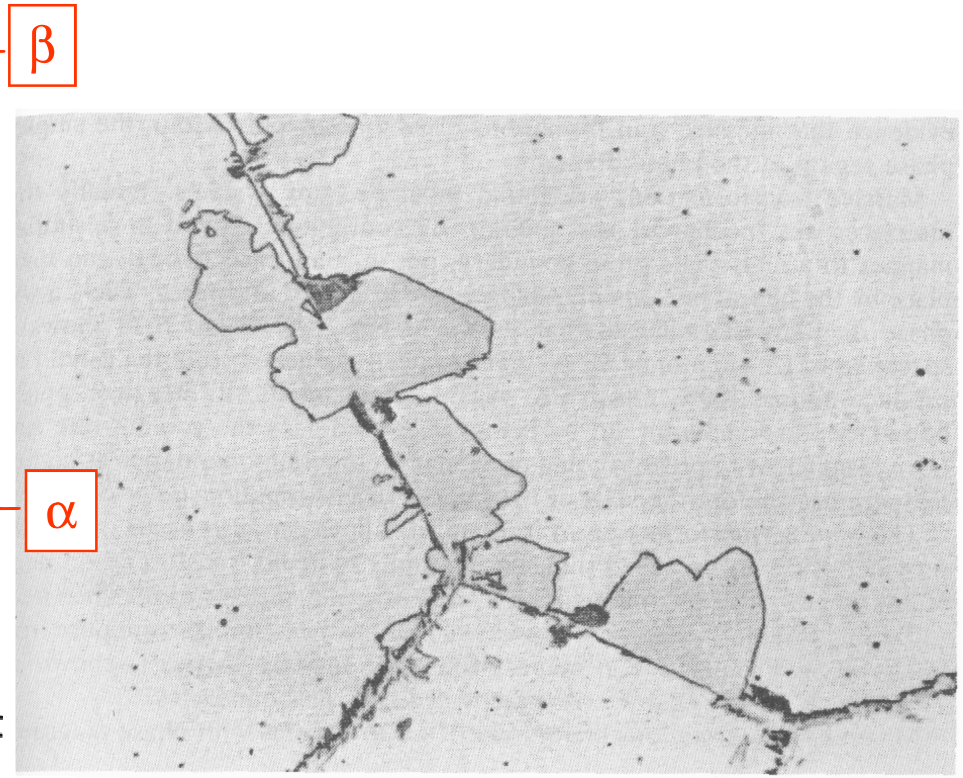
Massive Transformation

- An example of massive transformation is shown in Fig.: in Cu-Zn system, when an alloy of 38 at.% Zn is cooled from 850°C to say 400°C at fast enough cooling rates, the structure changes from that of β to α albeit with the same composition.
- Since the composition is the same, there is no need for long range diffusion and hence the transformation is very fast.
- Such changes in structure without changes in composition can be achieved in two ways: massive which is through thermally activated jumps of atoms from regions of one phase to another and martensitic which is through diffusionless (military)



Massive Transformation

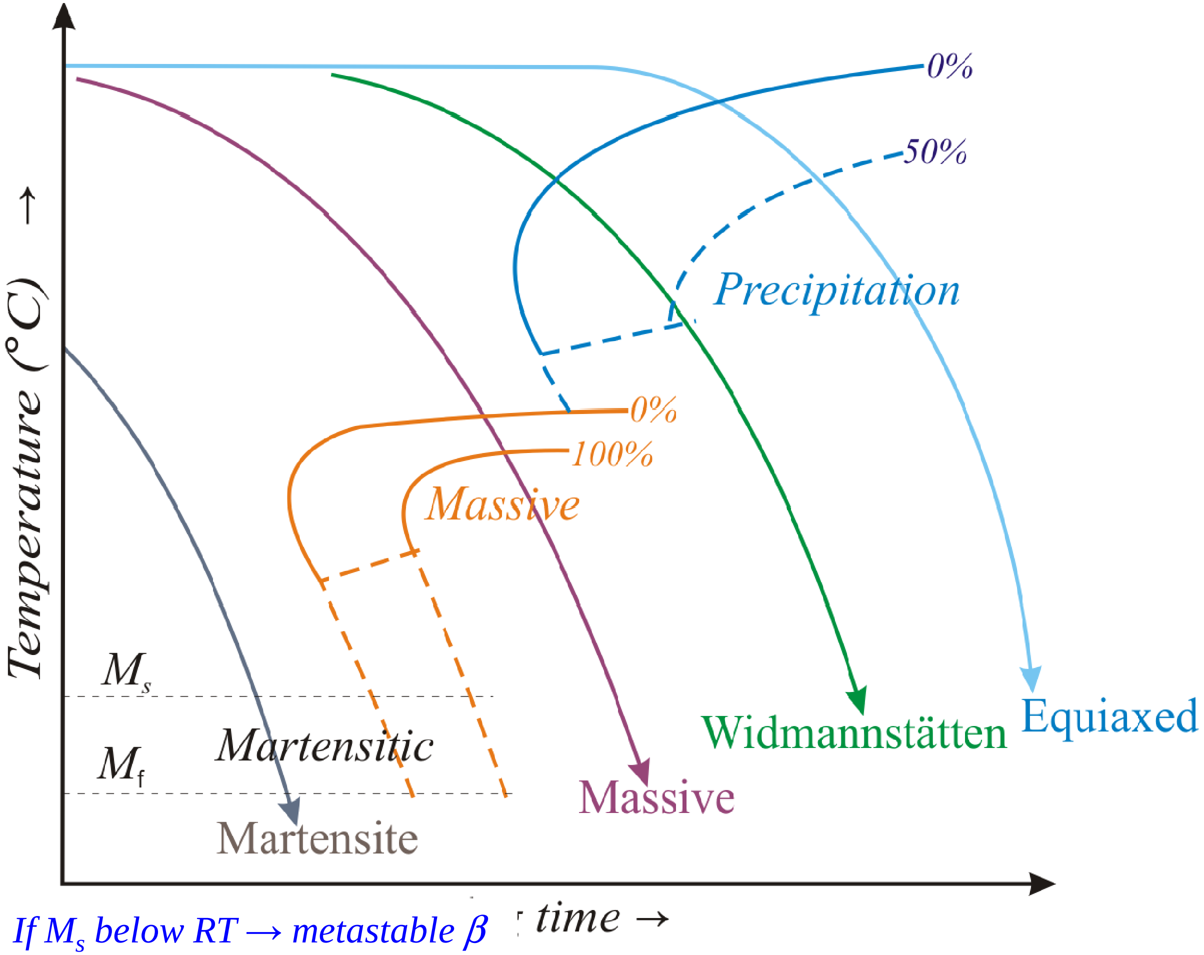




Massive α formed at the grain boundaries of β in Cu–38.7 wt% Zn quenched from 850 °C in brine at 0 °C. Some high temperature precipitation has also occurred on the boundaries. (From D. Hull and K. Garwood, *The Mechanism of Phase Transformations in Metals*, Institute of Metals, London, 1956.)

Massive Transformation

- ❑ Typically, systems which undergo massive transformation also undergo martensitic transformation at higher cooling rates; this is indicated in the schematic CCT diagram in Fig. The mechanism of formation of massive transformation can be understood with reference to this CCT diagram.

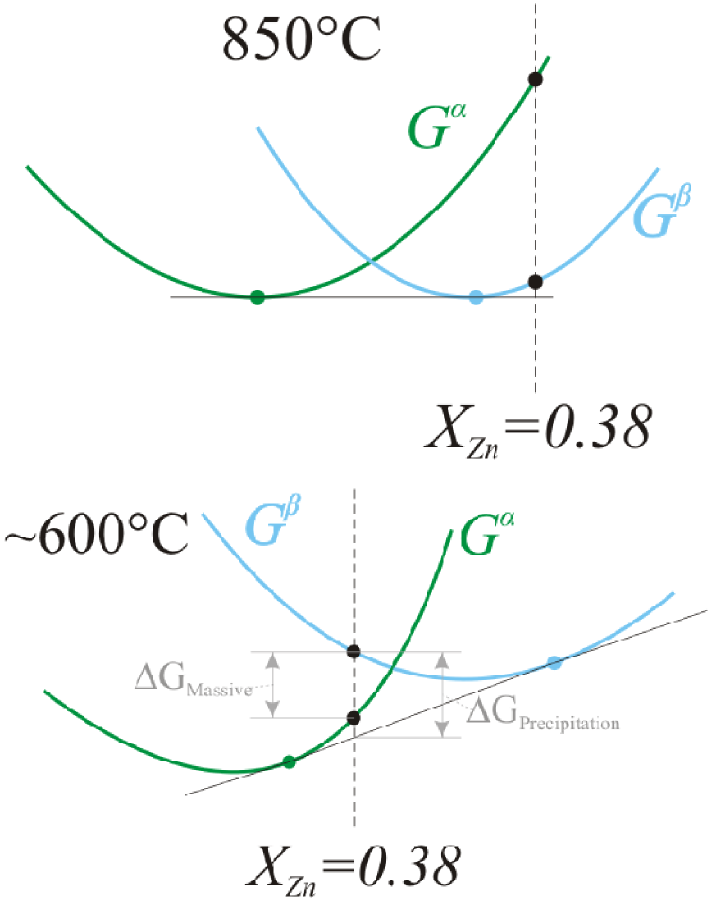


If M_s below RT → metastable β

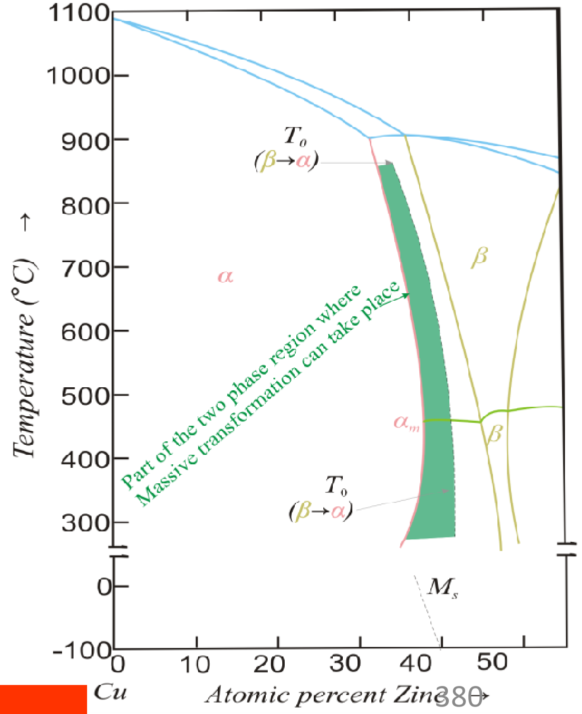
- ❑ At slow cooling rates and at smaller undercoolings, precipitation and growth of α leads to equiaxed α. At higher cooling rates and larger undercoolings Widmanstatten α formation takes place.
- ❑ In both these cases, since the growth of α requires long range diffusion (see Cu-Zn phase diagram for example, where it is the long range diffusion of Zn that is needed), it requires long time to form.

Massive Transformation

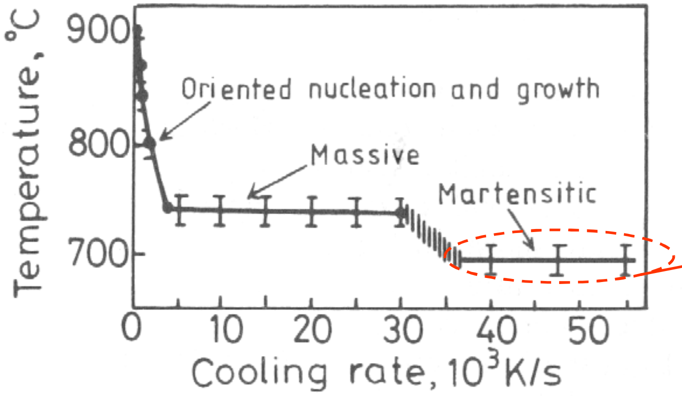
- However, relatively faster cooling rates would nucleate the α phase at the grain boundaries; since the growth of this α only requires that atoms jump across the α -β interface, and since the driving forces for the formation of α are very large (see in Fig.)



Free energy composition curves (schematic) for α and β in the Cu-Zn system



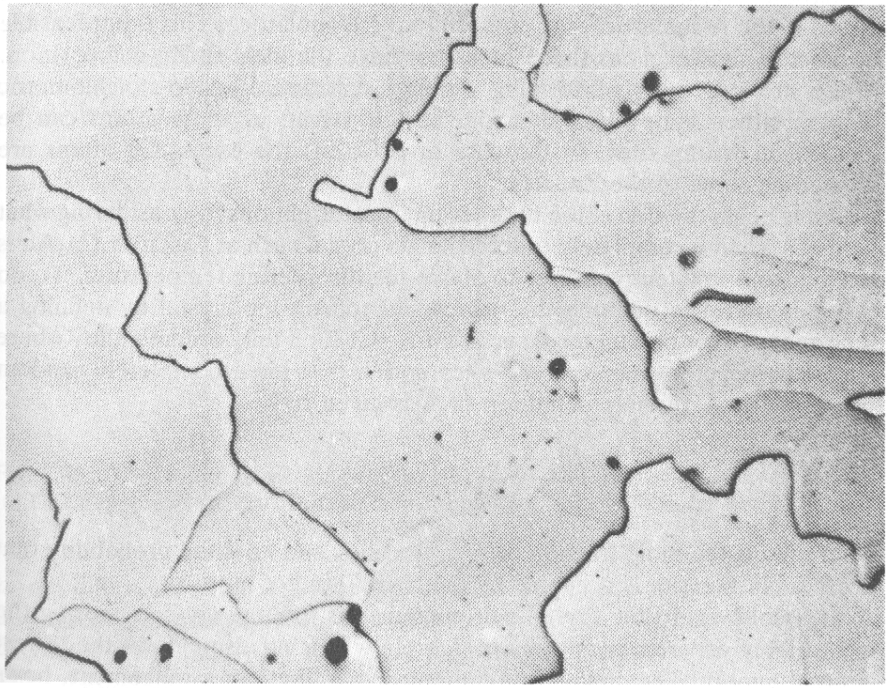
Massive Transformation



The effect of cooling rate on the transformation temperature of pure iron. (After M.J. Bibby and J.G. Parr, *Journal of the Iron and Steel Instit*
100.)

V.High cooling rate will produce Martensite

Massive Tr. can also occur in Fe-C system



Massive α in an Fe–0.002 wt% C quenched into iced brine from 1000 °C. Note the irregular α/α boundaries. (After T.B. Massalski in *Metals Handbook*, 8th edn., Vol. 8, American Society for Metals, 1973, p. 186.)

Questions?

1. What is the condition for the development of a miscibility gap in an isomorphous phase diagram?
2. Where do the eutectic and peritectic reactions get the driving force for the progress of the reaction?
3. Show that coupled growth (growth of α and β together as is observed in case of eutectic solidification) is not possible in peritectic solidification.
4. What is the need for the formation of coherent precipitates at high undercooling?
5. What would be the positions of the GP zones, θ”, θ’ solvus lines in relation to that of θ in Al-Cu phase diagram? Explain based on thermodynamic principles.
6. How do you know the driving force for the nucleation during precipitation of a second phase from a supersaturated solid solution using the G-X diagram?
7. Identify the differences between the composition outside and inside the spinodal in terms of (a) driving force for the transformation and (b) the progress of transformation.
8. Usually massive transformations are observed in single phase field instead of a two phase field. Why?
9. Why do massive transformations generally occur at lower temperatures but higher rates than precipitation transformations.
10. How does pressure influence the austenite-martensite transformation in steels?

Questions?

11. Define interlamellar spacing. Is it characteristic of a temperature of transformation? How is it that it appears different in different colonies in a microstructure?
    a) Derive an expression to prove that growth rate of pearlite is proportional to square of the amount of under cooling. Why does the growth rate decrease after becoming a maximum with the fall of temperature
    b) What is the kinetics of pearlitic transformation? How is the volume rate of pearlite formation related to growth rate and grain size of austenite?
12. Why does the flow stress increase as the carbon content of annealed steels increases?
13. Distinguish between two types of bainites.
    a) Discuss at least four characteristics of bainitic transformation
    b) Compare the characteristics of bainitic transformation with pearlitic and with martensitic reaction
    c) Discuss the mechanism of formation of bainites.
    d) What makes lower bainite to have more applications than upper bainite?
14. Explain the term active nucleus. Name the active nucleus for (i) Pearlitic transformation and (ii) bainitic transformation. Give reasons in support of your answer.
15. What is cellular precipitation? What is the mechanism involved in it. How it is different from Precipitation hardening.
16. What is meant by ordering parameter? How it influences the material property? Define SRO and LRO.

Questions?

17. What is super lattice? Give some of examples. And what are the criteria to form a super lattice. What are the techniques available to find out a super lattice?
18. Write short note on Spinodal decomposition. Compare with Nucleation and Growth.
19. Explain the thermodynamics and kinetics of solid state phase transformation with reference to the following factors;

    Volume free energy, surface energy and strain energy components.

    Why does solid state phase transformation generally require under cooling to start nucleation?
20. Explain the Hull-Mehl mechanism of pearlitic transformation by citing Hultgren's extrapolation technique.

    What is Johnson-Mehl equation of kinetics of pearlitic transformation

    Explain the parameters affecting inter-lamellar spacing of pearlitic structure and also states its roles on mechanical properties.

Diffusionless Transformations

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Martensitic transformations - Introduction

- ☐ The name martensite is after the German scientist Martens. It was used originally to describe the hard microconstituent found in quenched steels. Martensite remains of the greatest technological importance in steels where it can confer an outstanding combination of strength (> 3500 MPa) and toughness (> 200 Mpa/m^2).
- ☐ Martensitic transformation is the name for any transformation that takes place in a diffusionless and military manner - that is, these transformations take place through atomic movements which are less than one atomic spacing; and in these transformations atoms change their positions in a coordinated manner (unlike thermally activated diffusional, or, so-called, civilian processes).
- ☐ In shape memory alloys such as Ni-Ti (nitinol), it is the martensitic transformation that is responsible for the shape memory effect.
- ☐ In this topic, we describe some characteristic features of the martensitic transformations (with specific reference to steels in which, this transformation is repsonsible for hardening by quenching).
- ☐ Since martensitic transformations are diffusionless, necessarily, the composition does not change during the transformation. It is only the crystal structure that changes. For example, in Fe-C alloys, the austenite (fcc) transforms into martensite (bct);
- ☐ in Ni-Ti, an ordered bcc (called austenite) transforms to another ordered CsCl type structure (called martensite). Note that since martensitic transformation is diffusionless, if the austenitic phase is ordered, the martensitic phase is also ordered.

Characteristics of martensitic transformation

- Occur at high super saturations, without change in composition
- No long range diffusion → Movement of atoms a fraction of the inter-atomic distance
- Nearest neighbour configuration remains unchanged
- Cooperative movement of a large group of atoms → transformation proceeds at the speed of sound in the material
- Thermal activation does not play a role in the growth of the martensitic phase Thermal activation may play a role in the nucleation of martensite
- Usually martensite crystals nucleate and grow across the whole grain (in some cases this growth is a function of temperature)
- In some cases the transformation occurs over a period of some time (due to thermally assisted nucleation)
- Martensitic crystals have a specific orientation relationship (OR) with the parent phase
- Planes of the parent lattice on which Martensitic crystals from → Habit planes *(irrational Indices)*
- Interface between Martensite and parent phase → Coherent or Semi-coherent
- At a given temperature (between M_s and M_f) the fraction transformed ↑ with plastic deformation (in some cases elastic stress also has a similar effect)
- With prior plastic deformation the transformation temperature can be increased to M_d

Characteristics of martensitic transformation

- ❑ Shape of the Martensite formed → Lathe and Plate morphologies
- ❑ Associated with shape change (shear)
- ❑ But: Invariant plane strain *(observed experimentally)* → Interface plane between Martensite and Parent remains undistorted and unrotated
- ❑ This condition requires
  1) Bain distortion → Expansion or contraction of the lattice along certain crystallographic directions leading to homogenous pure dilation
  2) Secondary Shear Distortion → Slip or twinning
  3) Rigid Body rotation

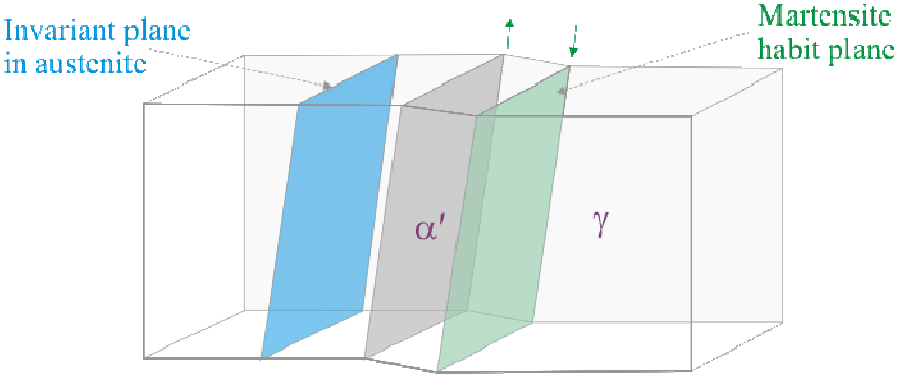
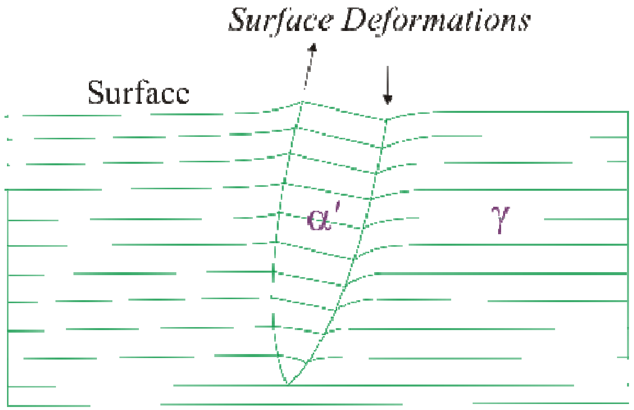


Illustration of the coherence of the martensitic plate with the surrounding austenite

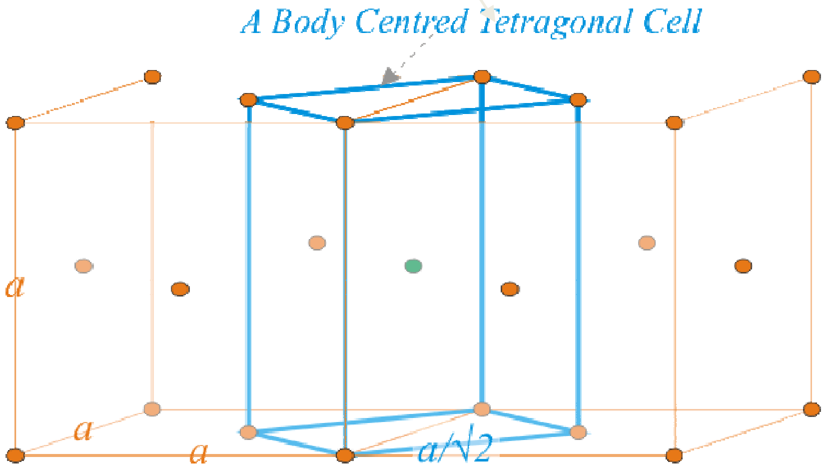


Characteristics of martensitic transformation

- Martensitic transformation can be understood by first considering an alternate unit cell for the Austenite phase as shown in the figure below.
- If there is no carbon in the Austenite (as in the schematic below), then the Martensitic transformation can be understood as a ~20% contraction along the c-axis and a ~12% expansion of the a-axis → accompanied by no volume change and the resultant structure has a BCC lattice (the usual BCC-Fe) → c/a ratio of 1.0.

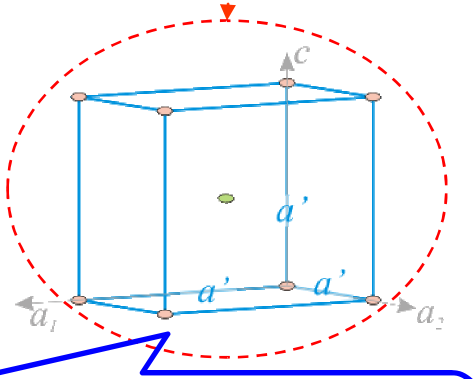
$$\underset{0.8\%C}{\gamma\,(FCC)} \xrightarrow{Quench} \underset{0.8\%C}{\alpha'\,(BCT)}$$

FCC Austenite alternate choice of Cell



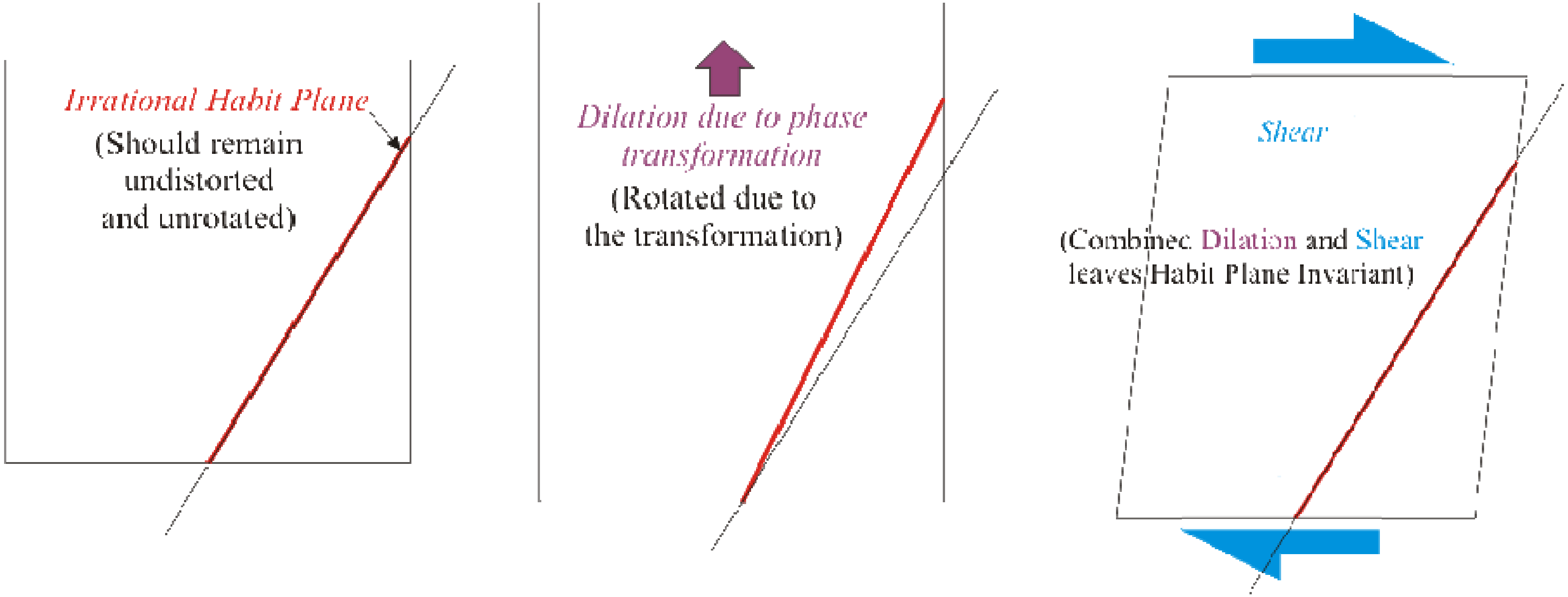
FCC → BCC

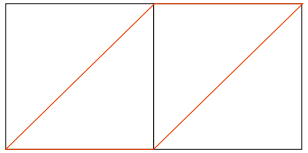
In Pure Fe after
the Martensitic transformation
$c = a$



~20% contraction of *c-axis*
~12% expansion of *a-axis*

Characteristics of martensitic transformation

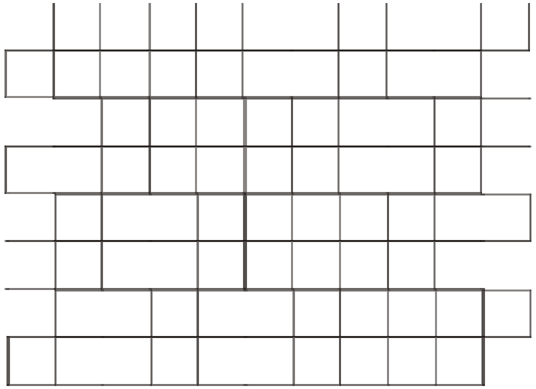




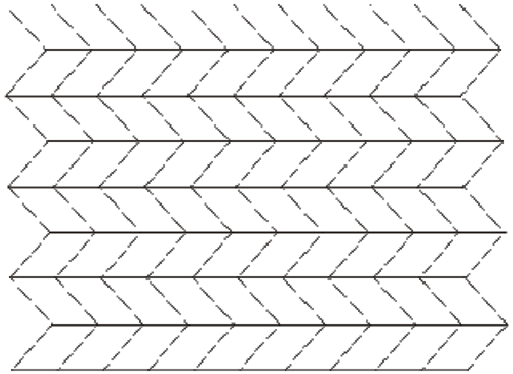
But shear will distort the lattice!

Slip

Twinning



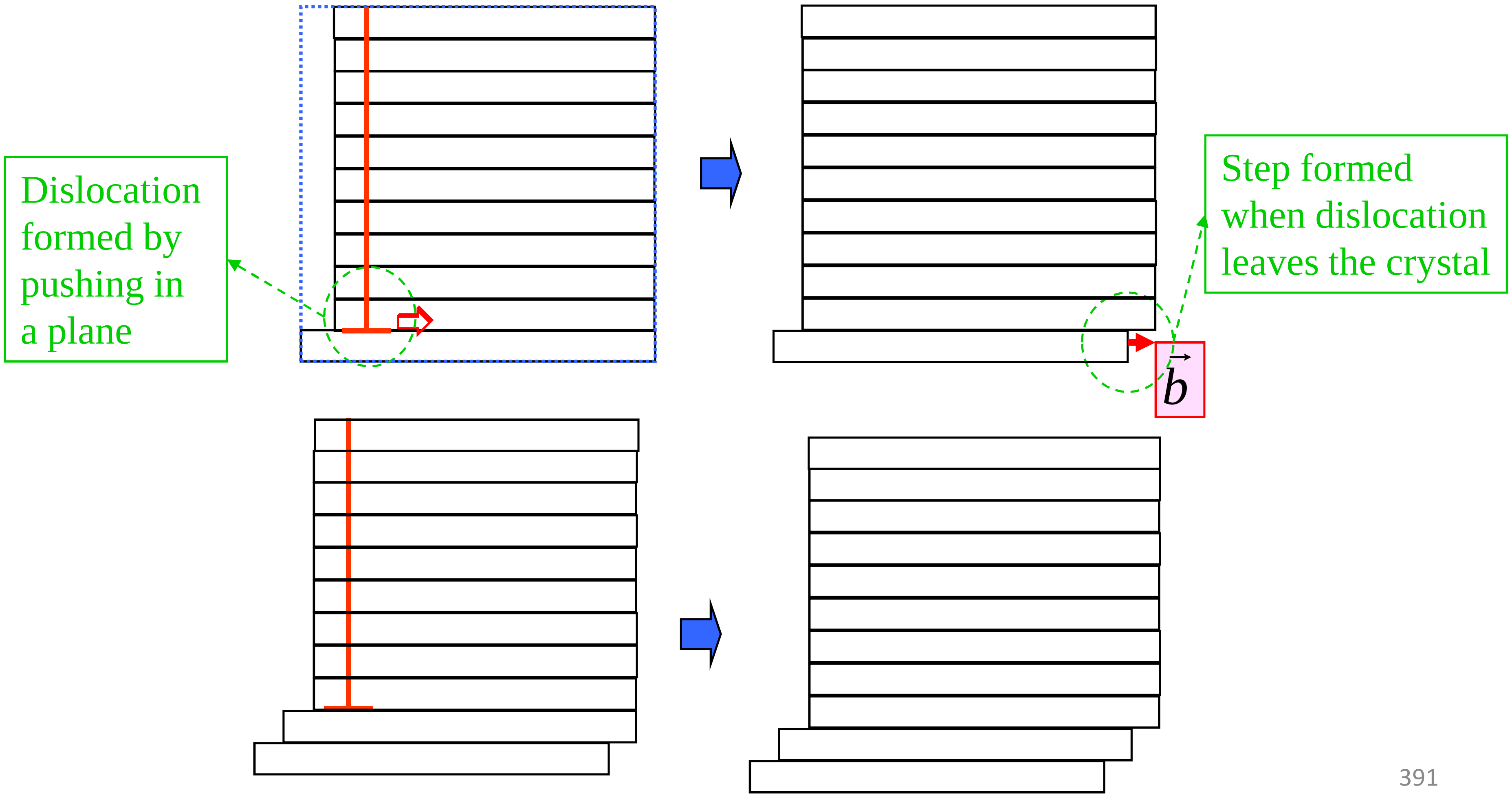
Average shape remains undistorted



Characteristics of martensitic transformation

How does the motion of dislocations lead to a macroscopic shape change?

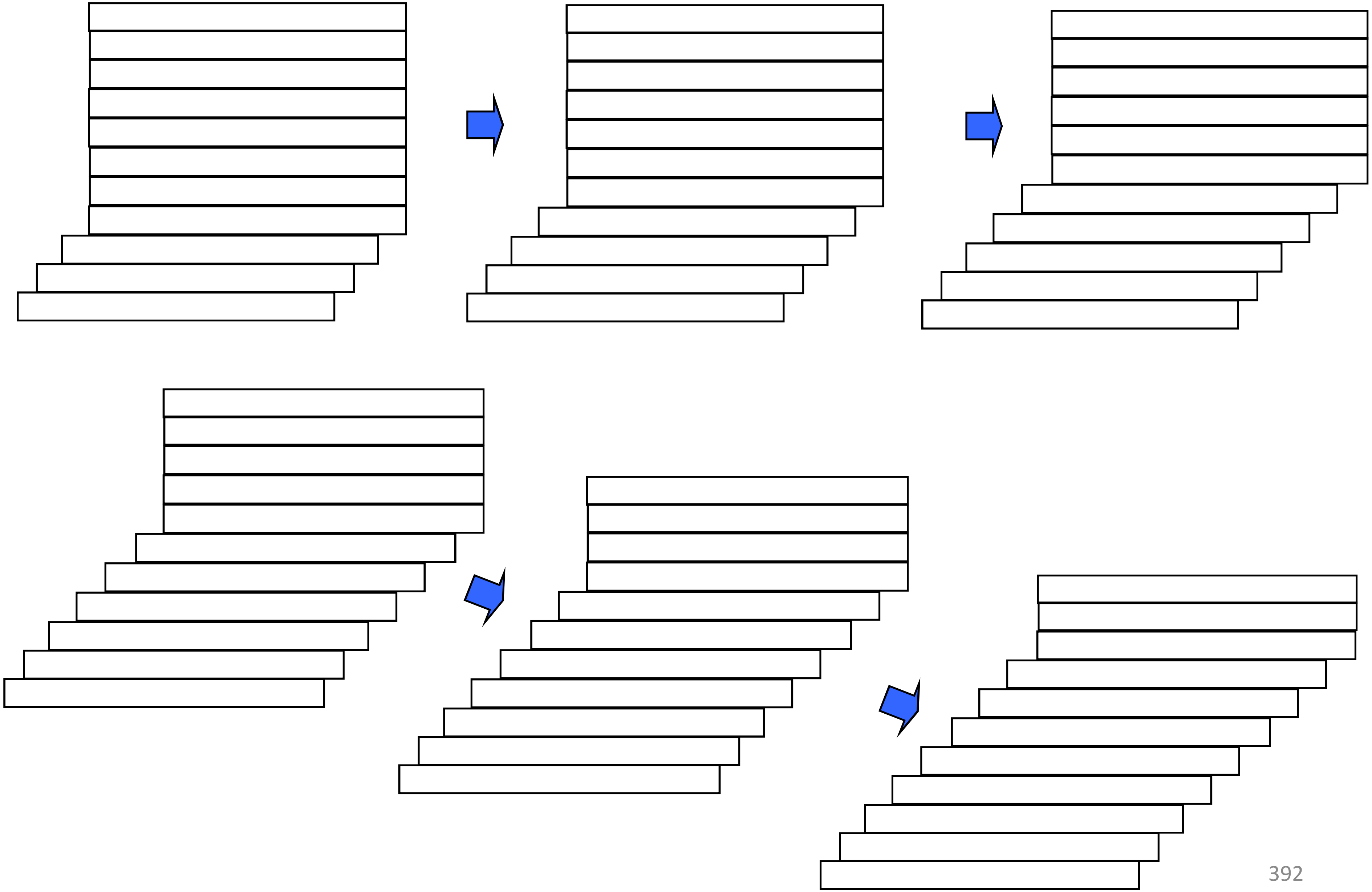
(From microscopic slip to macroscopic deformation ⇨ a first feel!)



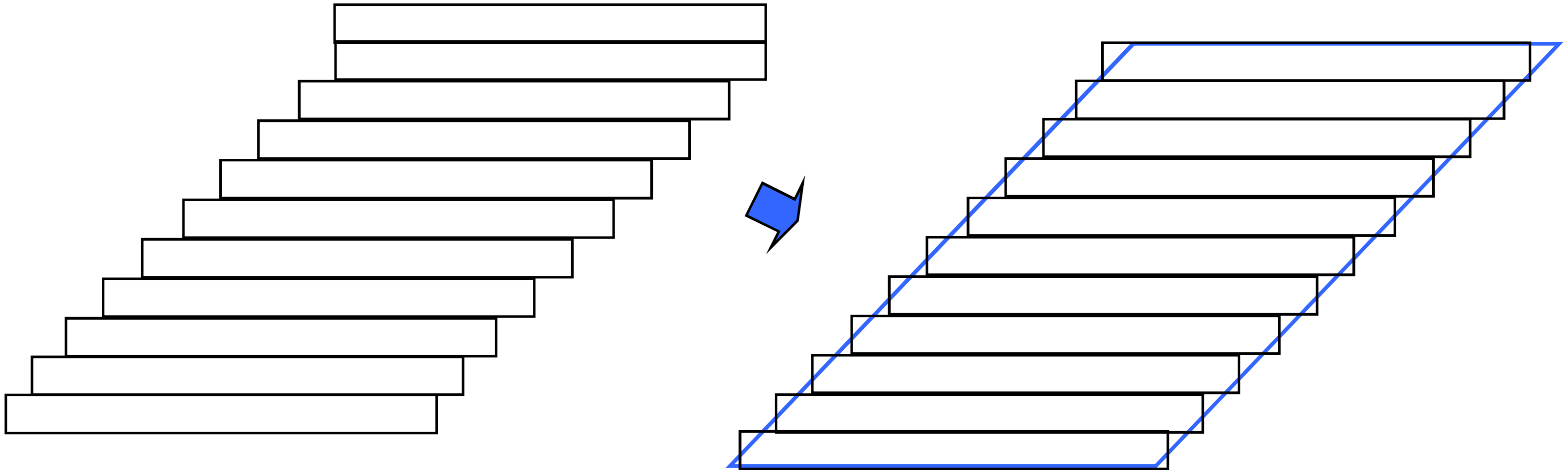
Dislocation formed by pushing in a plane

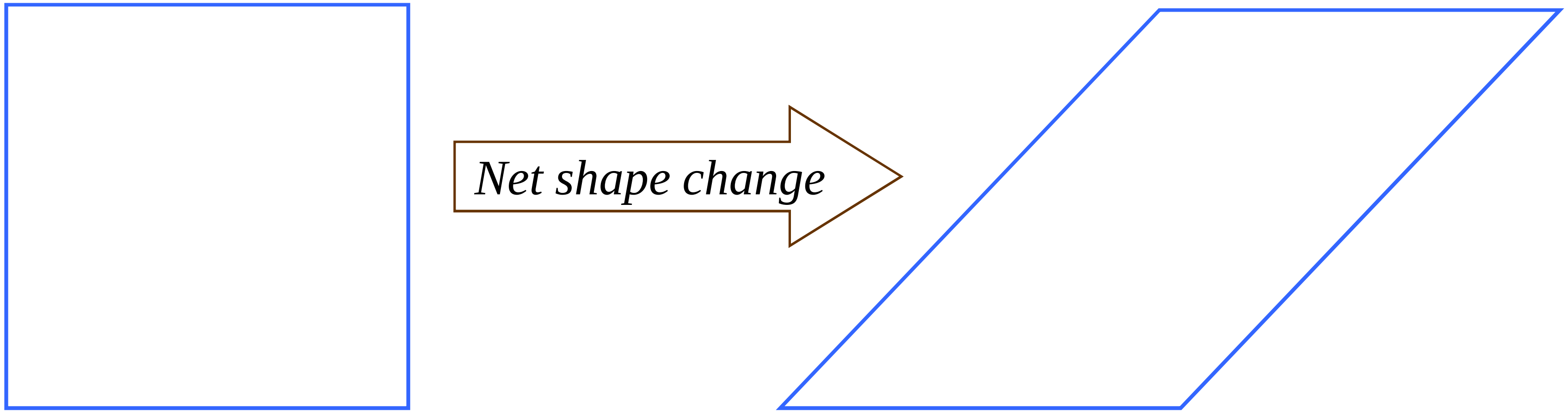
Step formed when dislocation leaves the crystal

Characteristics of martensitic transformation



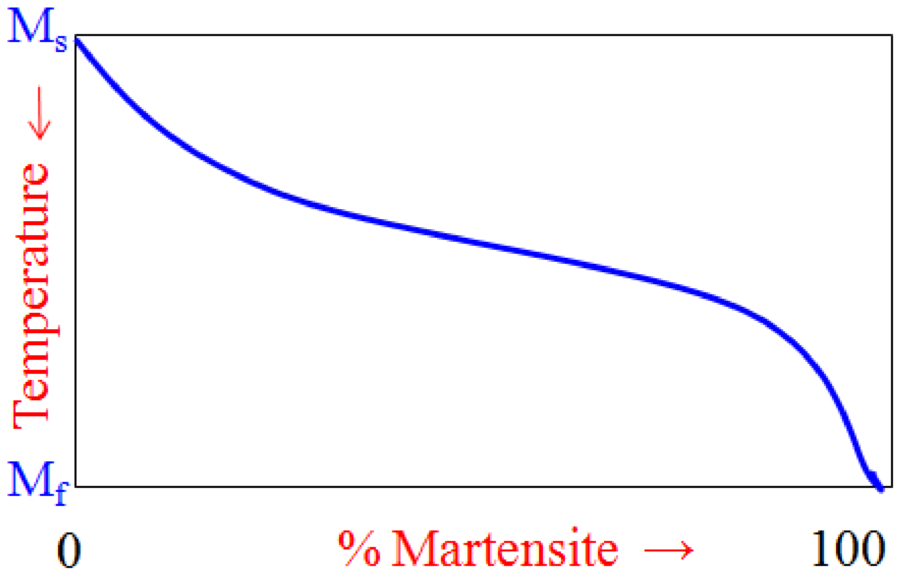
Characteristics of martensitic transformation

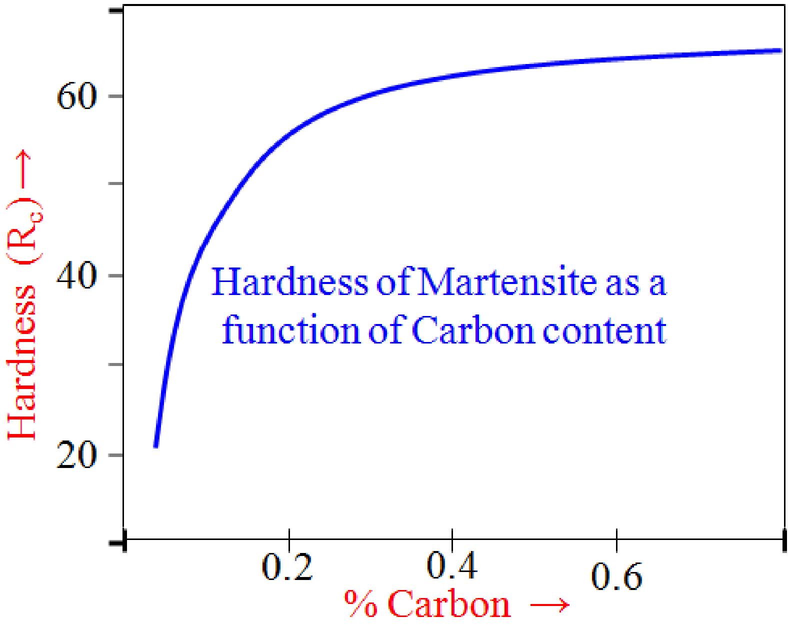




Net shape change

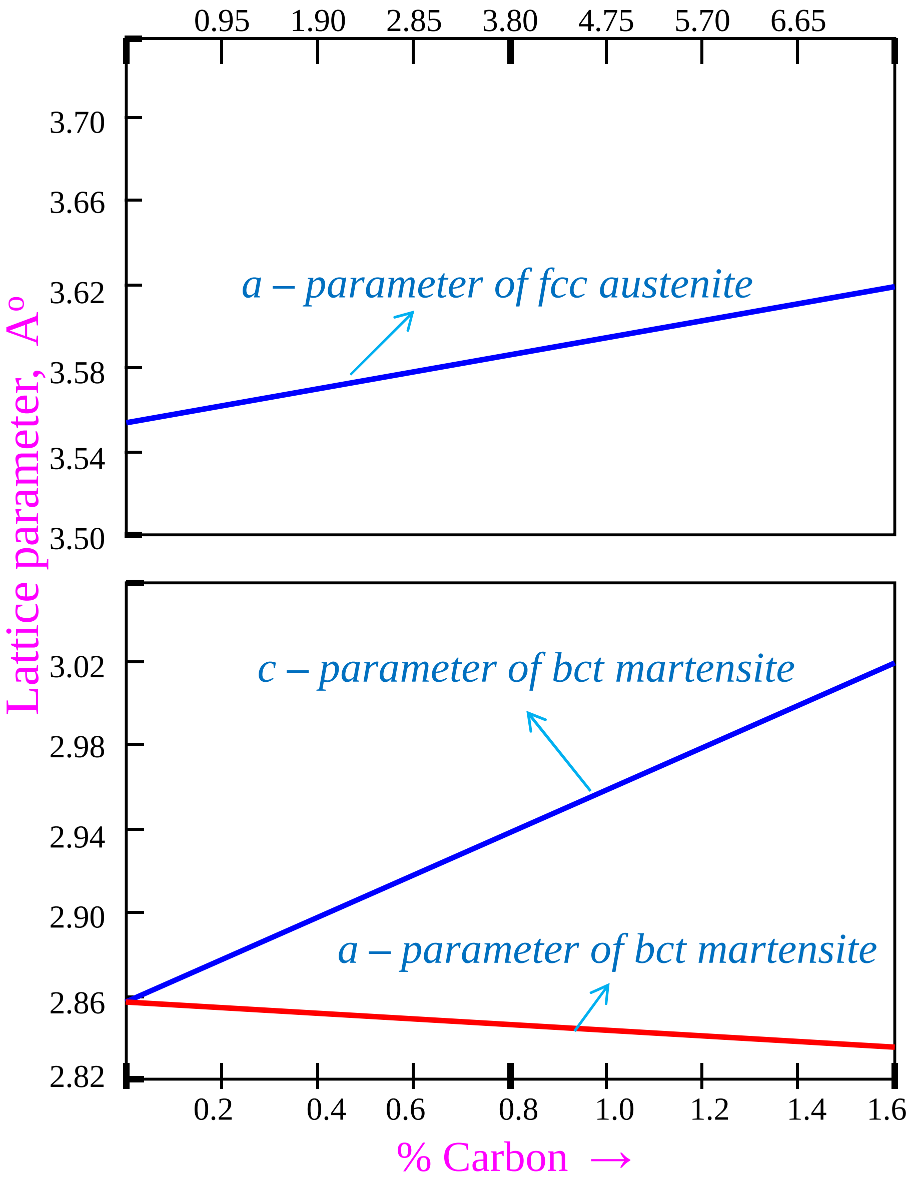
Characteristics of martensitic transformation

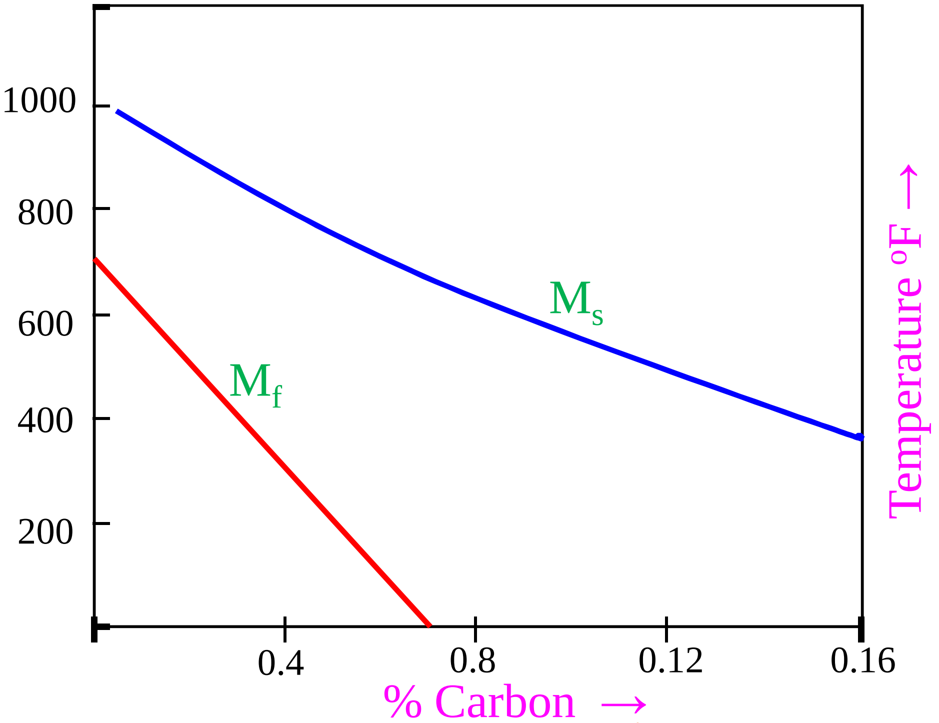




Properties of 0.8% C steel		
Constituent	Hardness (R_c)	Tensile strength (MN / m^2)
Coarse pearlite	16	710
Fine pearlite	30	990
Bainite	45	1470
Martensite	65	-
Martensite tempered at 250 °C	55	1990

Characteristics of martensitic transformation





Influence of carbon on the martensite range

Effect carbon on lattice parameters of austenite and martensite

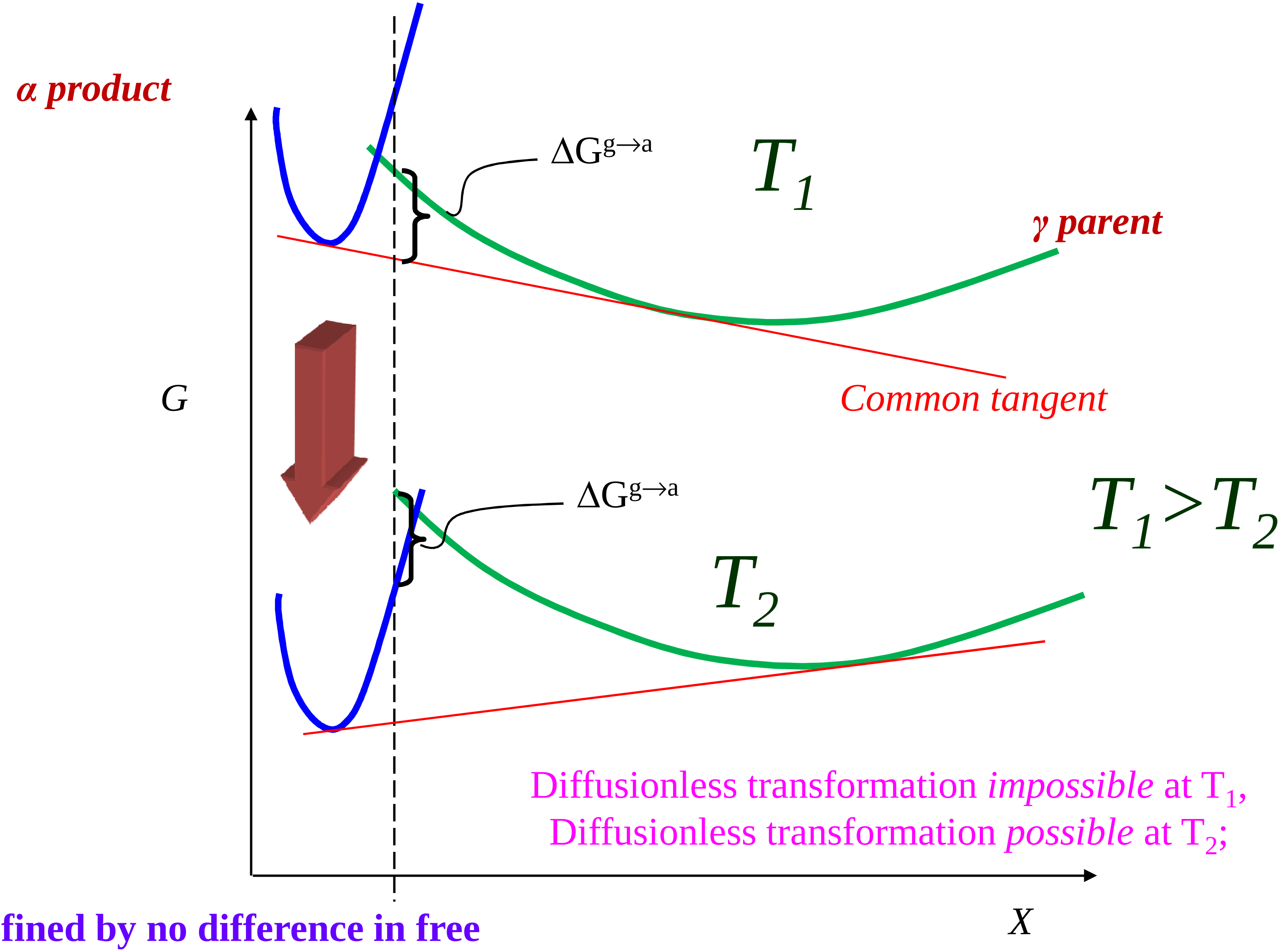
Driving force for martensitic transformation

- Diffusionless transformations require larger driving forces than for diffusional transformations
- Why? In order for a transformation to occur without long range diffusion, it must take place *without a change in composition*
- This leads to the so-called T_0 concept, which is the temperature at which the new phase can appear with a net decrease in free energy *at the same composition as the parent (matrix) phase*.
- As the following diagram demonstrates, the temperature, T_0, at which segregation-less transformation becomes possible (i.e. a decrease in free energy would occur), is always less than the solvus (liquidus) temperature.
- The driving force for a martensitic transformation can be estimated in exactly the same way as for other transformations such as solidification.
- Provided that an enthalpy (latent heat of transformation) is known for the transformation, the driving force can be estimated as proportional to the latent heat and the undercooling below T_0.

$$\Delta G^{\gamma \to \alpha'} = \Delta H^{\gamma \to \alpha'} \frac{T_0 - M_S}{T_0}$$

.

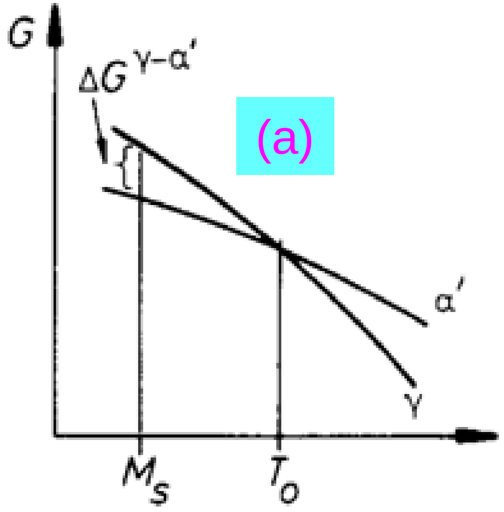
Driving force for martensitic transformation

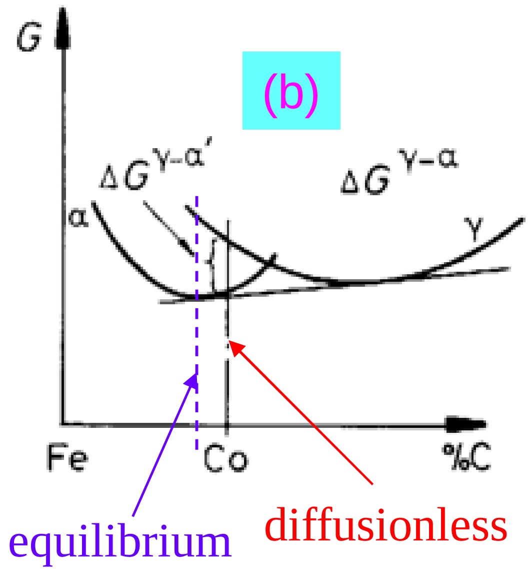


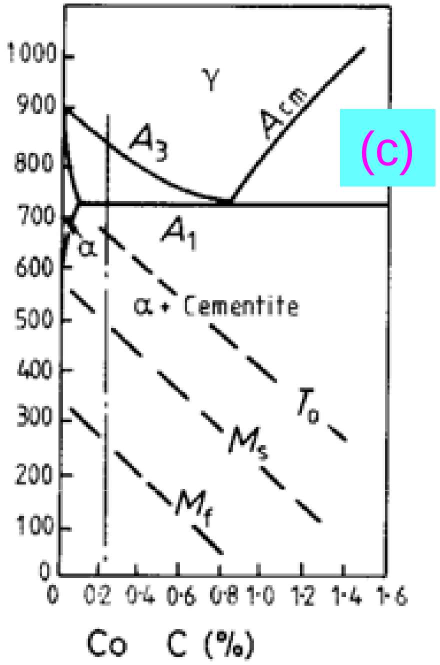
Diffusionless transformation *impossible* at T_1,
Diffusionless transformation *possible* at T_2;

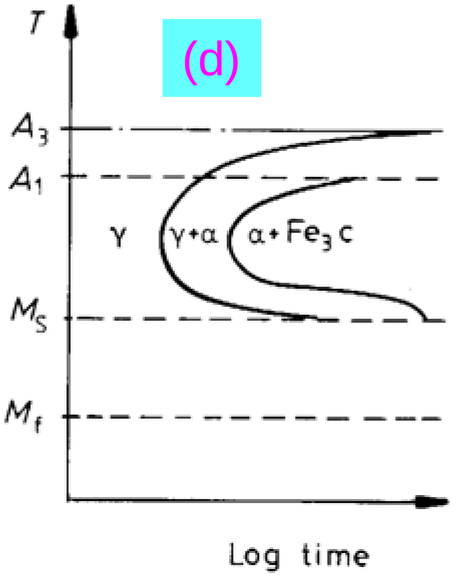
“T_0” is defined by no difference in free energy between the phases, $\Delta G=0$.

Various ways of showing Martensitic Transformations









(a) Free energy – temperature diagram for Austenite and martensite of fixed carbon concentration

(b) Free energy – composition diagram for the austenite and martensite phases at the M_s temperature.

(c) Iron-carbon phase diagram with T_0 as defined in (a), M_s and M_f superimposed.

(d) M_s and M_f in relation to the TTT diagram for alloy C_0 in C

Why tetragonal Fe-C martensite?

- At this point, it is worth stopping to ask why a tetragonal martensite forms in iron. The answer has to do with the preferred site for carbon as an interstitial impurity in bcc Fe.
- Remember: Fe-C martensites are unusual for being so strong (& brittle). Most martensites are not significantly stronger than their parent phases.
- Interstitial sites:
  FCC: octahedral sites radius= 0.052 nm
  tetrahedral sites radius= 0.028 nm
  BCC: octahedral sites radius= 0.019 nm
  tetrahedral sites radius= 0.036 nm

Carbon atom radius = 0.08 nm.

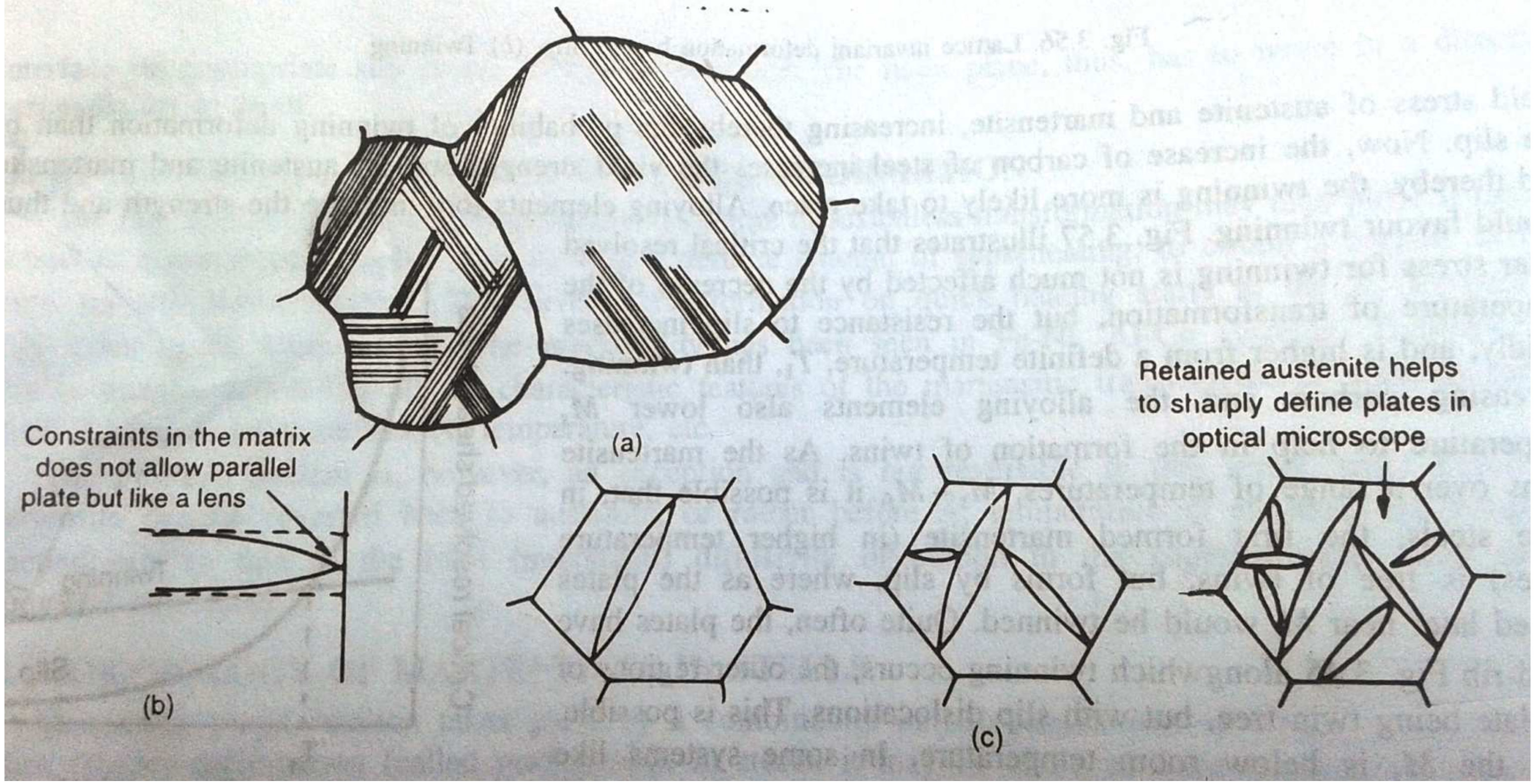
- Surprisingly, it occupies the octahedral site in the bcc Fe structure, despite the smaller size of this site (compared to the tetrahedral sites) presumably because of the low modulus in the <100> directions.
- One consequence of the occupation of the octahedral site in ferrite is that the carbon atom has only two nearest neighbors. Each carbon atom therefore distorts the iron lattice in its vicinity. The distortion is a *tetragonal distortion*.
- If all the carbon atoms occupy the *same type of site* then the entire lattice becomes tetragonal, as in the martensitic structure.
- Switching of the carbon atom between adjacent sites leads to strong internal friction peaks at characteristic temperatures and frequencies.

Massive vs. Martensitic Transformations

- There are two basic types of *diffusionless* transformations.
- One is the *massive transformation*. In this type, a diffusionless transformation takes place without a definite orientation relationship. The interphase boundary (between parent and product phases) migrates so as to allow the new phase to grow. *It is, however, a civilian transformation because the atoms move individually.*
- The other is the *martensitic transformation*. In this type, the change in phase involves a definite orientation relationship because the atoms have to move in a coordinated manner. There is always a change in shape which means that there is a strain associated with the transformation. The strain is a general one, meaning that all six (independent) coefficients can be different.

	CIVILIAN	MILITARY
Diffusion Required	Precipitation, Spinodal Decomposition	-
Diffusionless	Massive Transformations	Martensitic Transformations

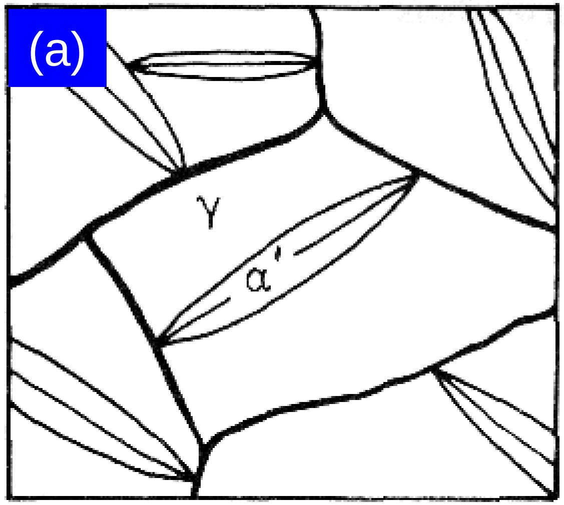
Morphology of Martensite

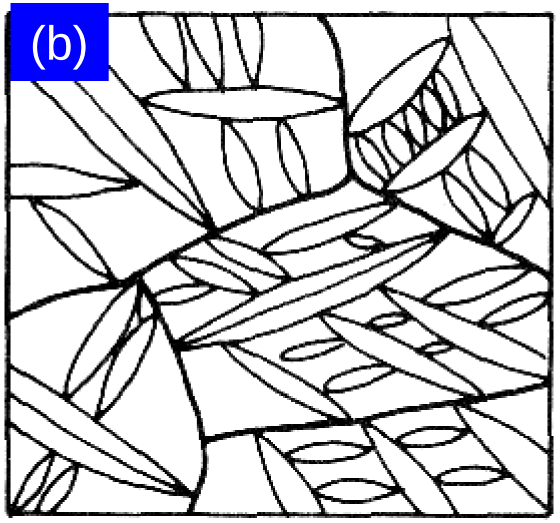


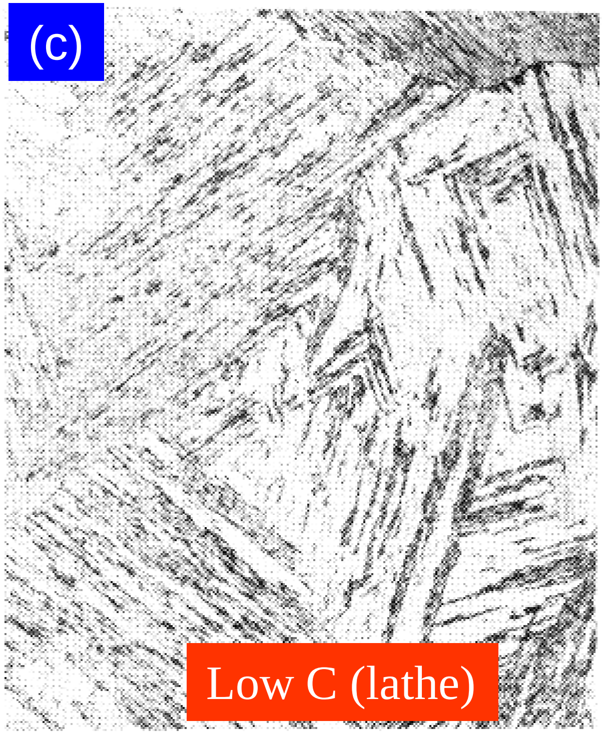
Formation of **(a)** Lath martensite **(b)**, **(c)** plate martensite. (a) Schematic illustration of mode of nucleation and growth of lathe martensite. (b) Lens Shaped martensite (c) Successive partioning of austenite grain with the formation of plates of martensite

- ❑ In steels, two distinct morphologies of martensite are seen **Lathe Martensite** and **Plate (Lenticular) Martensite.**
- ❑ Low carbon martensite – Lathe martensite
- ❑ Medium carbon martensite – Mixed martensite –lathe as well as plate martensite
- ❑ High carbon martensite – Lenticular plates

Morphology of Martensite







Low C (lathe)

Medium C (plate)

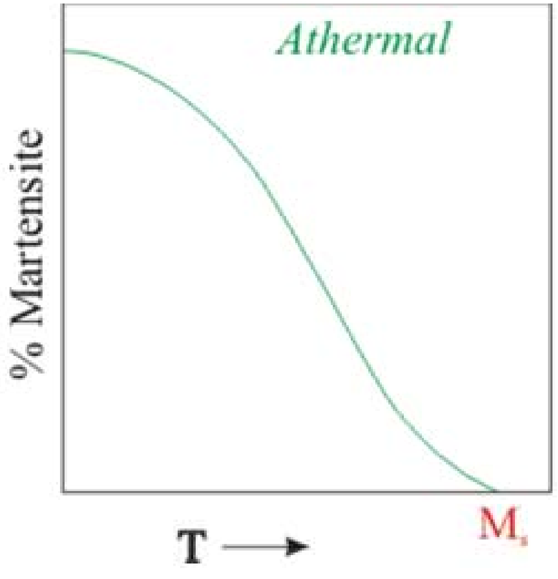
Fe-Ni: Plate

(a, b) Growth of martensite with increasing cooling below M_s
(c-e) Different martensite morphologies in iron alloys

Kinetics of Martensitic transformations

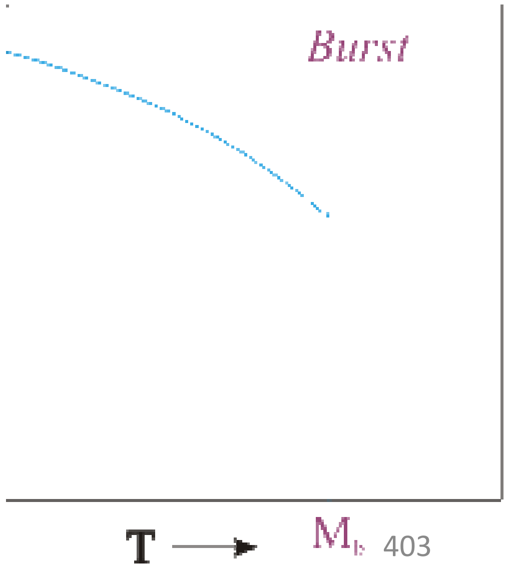
Athermal

- Fraction transformed = f(T) *only (between* M_s *and* M_f*)*
- At a given T a certain number of nuclei form which grow at the speed of sound in the material across the whole grain
- The number of nuclei forming increases with decreasing T ⇒ more transformation
- M_s and M_f temperatures increase with increasing grain size



Burst

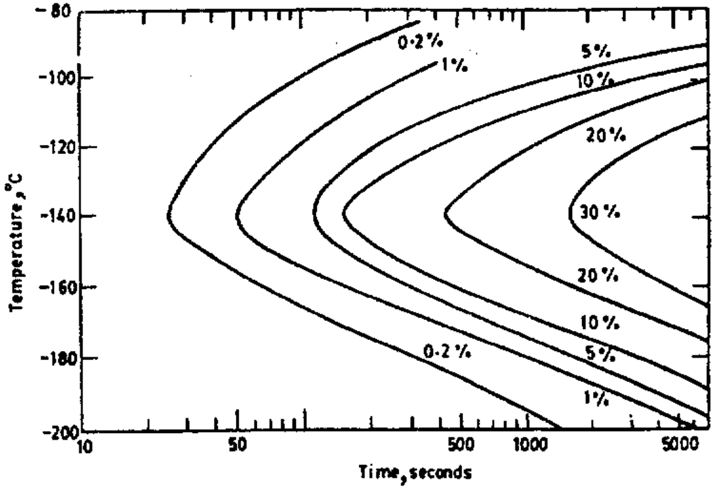
- At some T *(M_b)* → *sudden transformation of a large fraction of parent to Martensite* (often with a acoustic effect-click)
- % transformed during the "burst" → few-over 50%
- The 'burst' can be thought of as an extreme form of autocatalytic effect
- Remaining transformation is completed at → ◆ lower T ◆ longer t



Kinetics of Martensitic transformations

Isothermal

- Fraction transformed at a given T *(between M_s and M_f)* = f(t)
  → *observed in some alloys at subzero T*
- At the low T thermal activation of growth does not occur (as usual fast)
- "t effect" is due to small thermal activation required for nucleation of Martensitic plates and autocatalytic effect
- Rate of transformation at a given T ↑ with ↑ grain size *(fewer nucleation events give more transformed fraction)*



Isothermal Transformation diagram for Martensitic Transformation in Fe-Ni-Mn alloy

Questions?

1. Differentiate between the following transformations

   Pearlite, (b) Bainitic (c) Martensitic, based on Diffusion, Temperature range, Nuclei, Kinetics of reaction, Crystallography, Density of dislocation, Surface relief, and Growth rate.
2. Where the carbon atoms sitting in BCT martensite
   a) Why does martensite has BCT structure?
   b) Why martensitic transformation is not reversible in steels?
   c) Slip in the cause of lattice invariant deformation in low carbon martensite, while twinning is the cause in high carbon martensite. What is the relationship as the temperature of transformation drops
3. Give an exact definition of the habit plane of martensite. Describe how this habit plane might be measured experimentally. Give possible reasons why there is so much scatter of habit plane measurements in given sample.
4. Draw a diagram to illustrate Bain's homogeneous deformation model for the fcc → tbcc diffusionless transformation. Assuming $\alpha_{\gamma} = 3.56\ A^{o}$ and $\alpha_{\alpha} = 2.86\ A^{o}$, and that c/a for martensite is 1.15 calculate the maximum movement experienced by atoms during the transformation. Assume that c/a = 1.1.
5. What is the role of austenitic grain size in martensitic transformations? Is austenitic grain size is important to the strength of martensite? What other factors are important to the strength and toughness in technological hardened steels?

Questions?

6. Calculate the volume change associated with austenite to martensite transformation in 1 % carbon steel
7. Explain why martensite is hard? What is the crystal structure of martensite? Show the positions of carbon atoms in unit cell of martensite.
8. What is the impact of tetragonal expansion (due to carbon) on the locking of dislocations.
9. Explain the role of applied stress on martensitic transformation and also enumerate a thermal and isothermal kinetics of martensite formation.
10. Classify martensite based on the morphology and what is the effect of carbon on it?

Heat Treatment Processes

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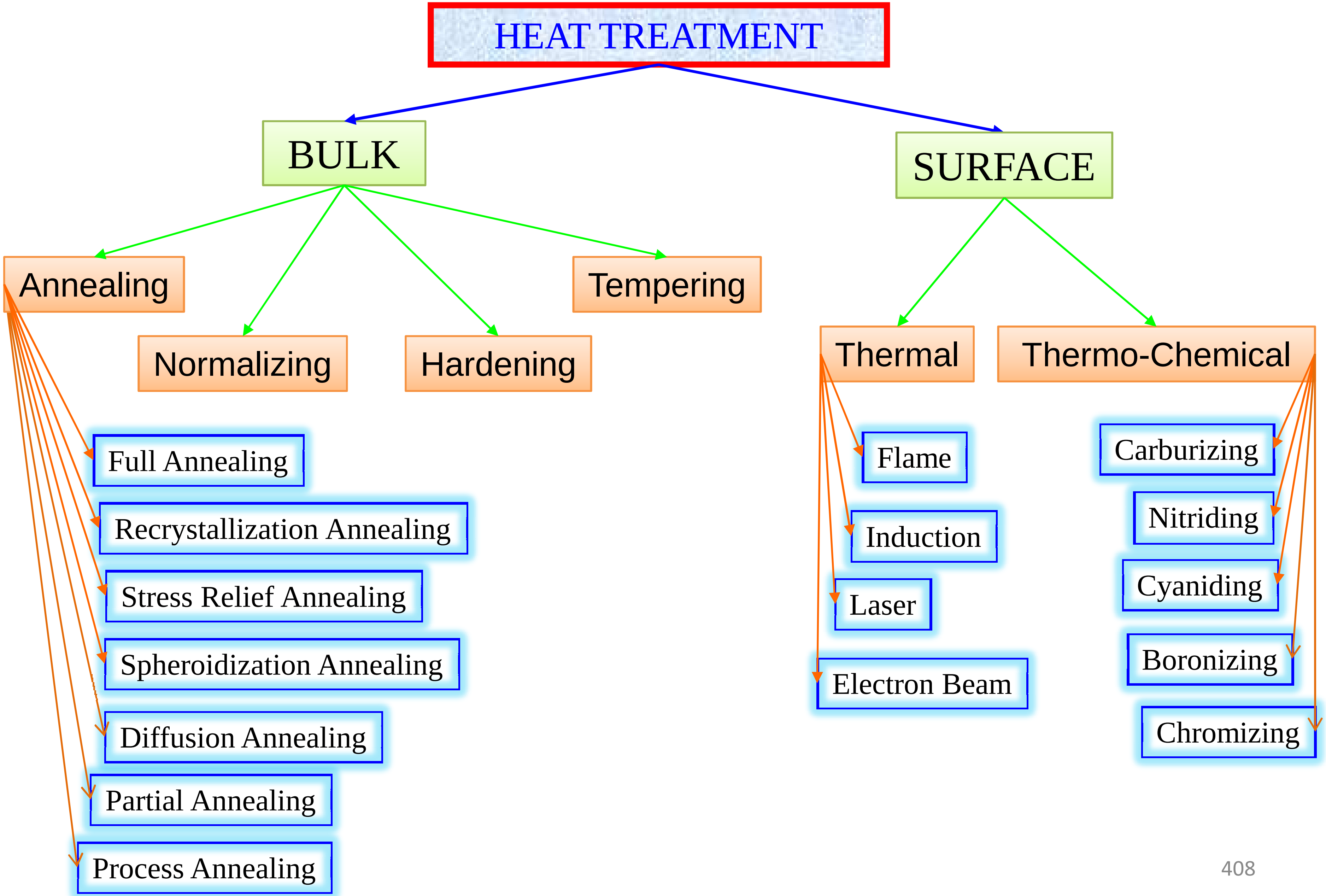
Classification



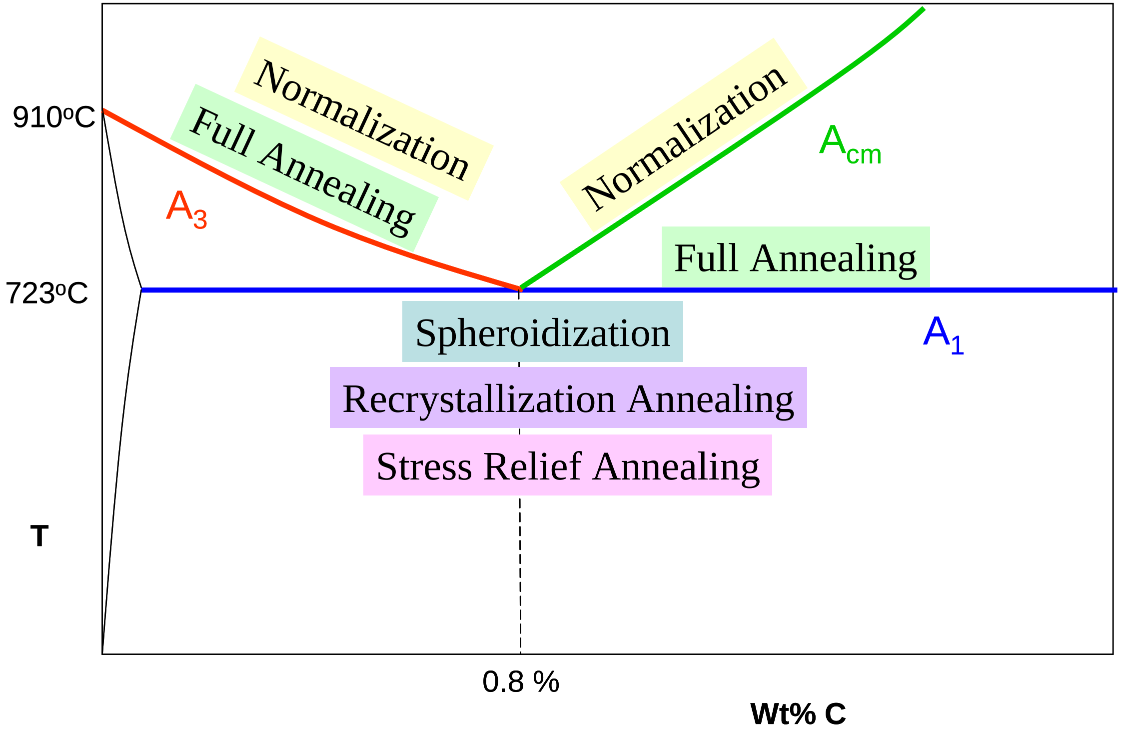
HEAT TREATMENT

- BULK
  - Annealing
    - Full Annealing
    - Recrystallization Annealing
    - Stress Relief Annealing
    - Spheroidization Annealing
    - Diffusion Annealing
    - Partial Annealing
    - Process Annealing
  - Normalizing
  - Hardening
  - Tempering
- SURFACE
  - Thermal
    - Flame
    - Induction
    - Laser
    - Electron Beam
  - Thermo-Chemical
    - Carburizing
    - Nitriding
    - Cyaniding
    - Boronizing
    - Chromizing

Annealing

Full Annealing

- ❑ The steel is heated above A_3 (for hypo-eutectoid steels) | A_1 (for hyper-eutectoid steels) →(hold) →then the steel is furnace cooled to obtain Coarse Pearlite
- ❑ Coarse Pearlite has ↓ Hardness, ↑ Ductility
- ❑ Not above A_{cm} →to avoid a continuous network of proeutectoid cementite along grain boundaries (→path for crack propagation)



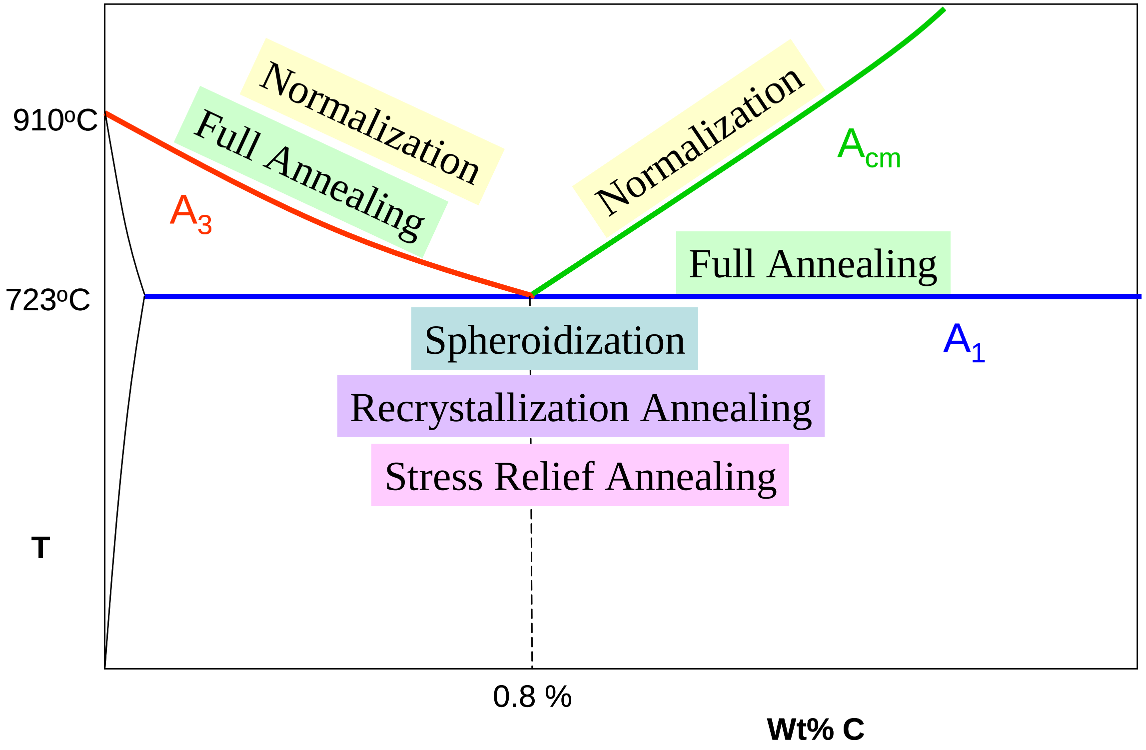
Annealing

Recrystallization Annealing

- ☐ The Heat below A_1 → Sufficient time → Recrystallization

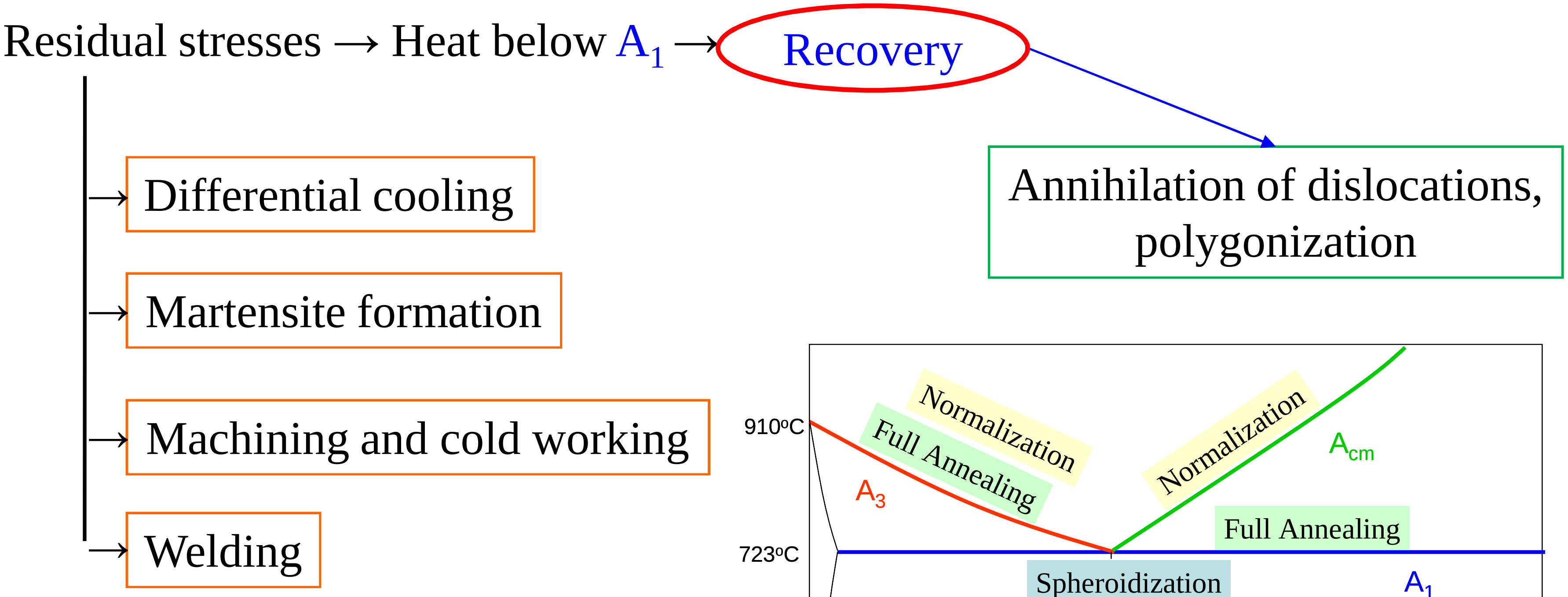
  Cold worked grains → New stress free grains

- ☐ Used in between processing steps (e.g. Sheet Rolling)



Annealing

Stress Relief Annealing



Residual stresses → Heat below A_1 → Recovery

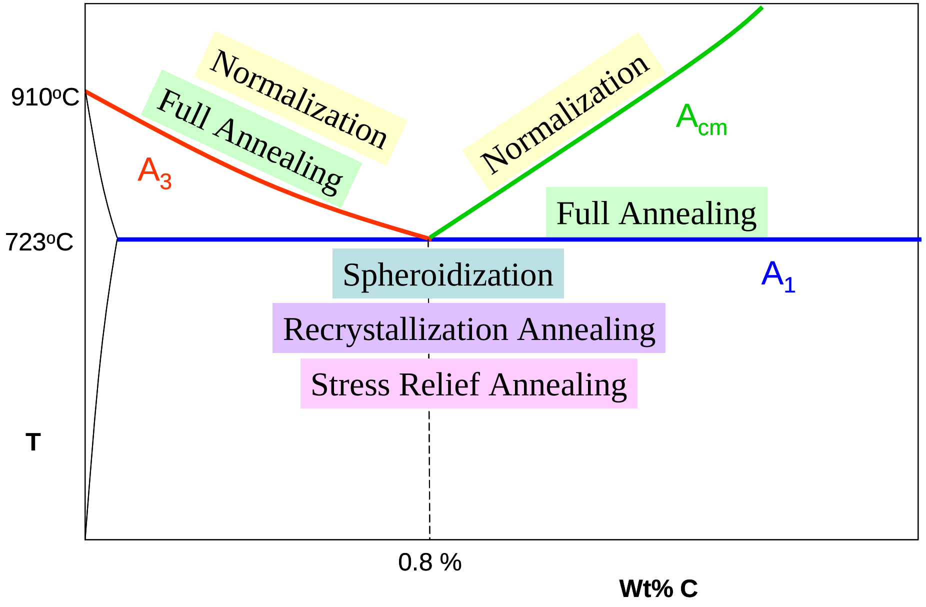
Annihilation of dislocations, polygonization

→ Differential cooling

→ Martensite formation

→ Machining and cold working

→ Welding



Annealing

Spheroidization Annealing

Heat below/above A_1 (Prolonged holding*)
Cementite plates → Cementite spheroids → ↑ Ductility

- ☐ *Used in high carbon steel requiring extensive machining prior to final hardening and tempering*
- ☐ *Driving force is the reduction in interfacial energy*

- ☐ The spheroidized structure is desirable when minimum hardness, maximum ductility, or(in high-carbon steels) maximum machinability is important.
- ☐ Low-carbon steels are seldom spheroidized for machining, because in the spheroidized condition they are excessively soft and "gummy".
- ☐ Medium-carbon steels are sometimes spheroidization annealed to obtain maximum ductility.

**If the steel is kept too long at the spheroidized-annealing temperature, the cementite particles will coalesce and become elongated thus reducing machinability*

Annealing

Diffusion Annealing

- ❑ This process also known as homogenizing annealing, is employed to remove any structural non-uniformity.
- ❑ Dendrites, columnar grains and chemical inhomogeneities are generally observed in the case of ingots, heavy plain carbon steel casting, and high alloy steel castings. These defects promote brittleness and reduce ductility and toughness of steel.
- ❑ In diffusion annealing treatment, steel is heated sufficiently above the upper critical temperature (say, 1000-1200°C), and is held at this temperature for prolonged periods, usually 10-20 hours, followed by slow cooling.
- ❑ Segregated zones are eliminated and a chemically homogeneous coarse grain steel is obtained by this treatment as a result of diffusion.
- ❑ The coarse grained structure can be refined either by plastic working for ingots or by employing a second heat treatment for castings.
- ❑ Hypoeutectoid and eutectoid steel castings are given full annealing treatment, whereas hypereutectoid steel castings are either normalized or partially annealed for this purpose.

Annealing

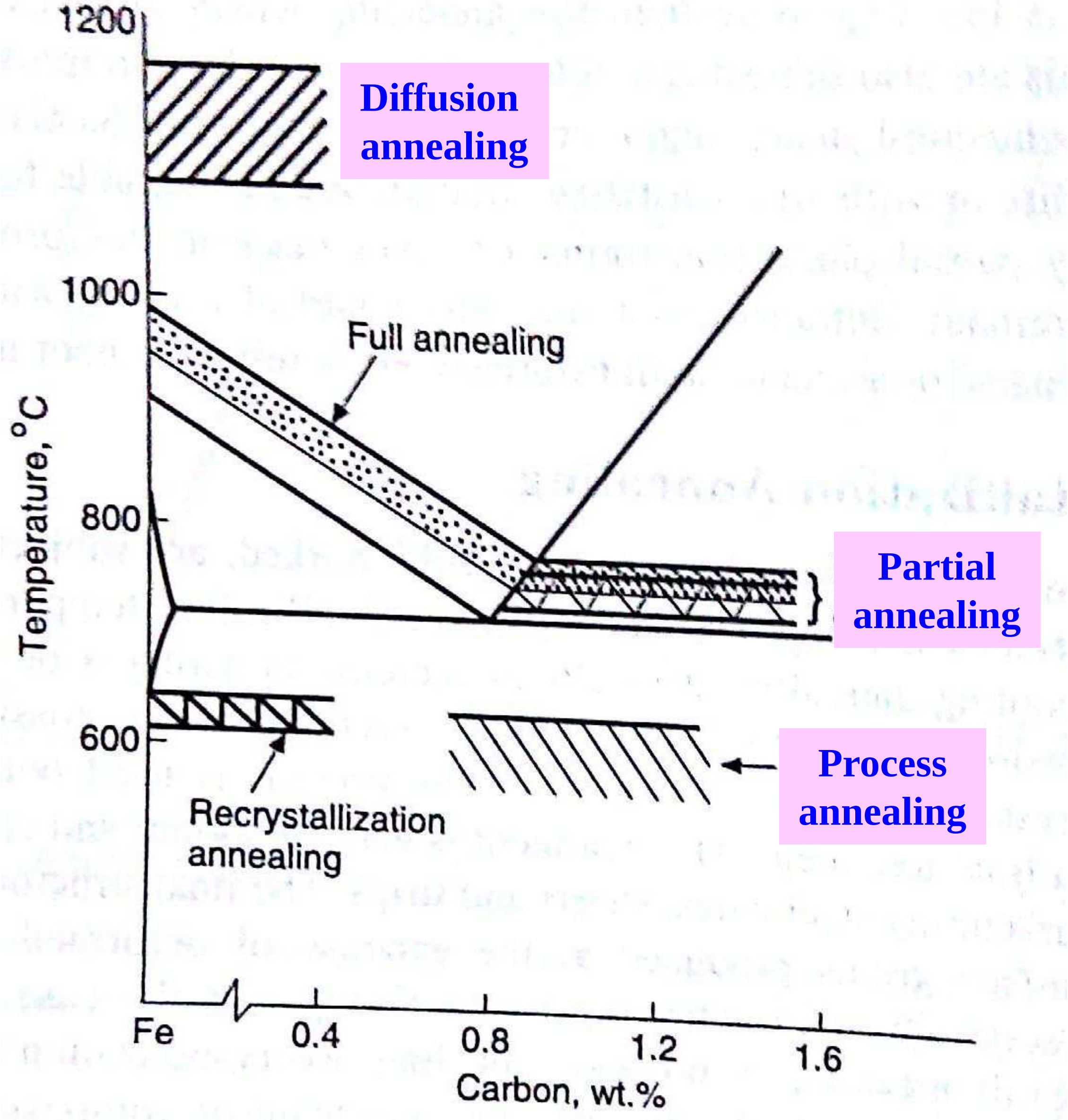
Partial Annealing

- ☐ Partial annealing is also referred to as intercritical annealing or incomplete annealing. In this process, steel is heated between the A_1 and the A_3 or A_{cm}. It is followed by slow cooling.
- ☐ Generally, hypereutectoid steels are subjected to this treatment. Resultant microstructure consists of fine pearlite and cementite. The reason for this is that grain refinement takes place at a temperature of about 10 to 30°C above Ac_1 for hypereutectoid steels.
- ☐ As low temperature are involved in this process, so it is cost effective than full annealing

Process Annealing

- ☐ In this treatment steel is heated to a temperature below the lower critical temperature, and is held at this temperature for sufficient time and then cooled. Since it is a subcritical annealing, cooling rate is of little importance
- ☐ The purpose of this treatment is to reduce hardness and to increase ductility of cold-worked steel so that further working may be carried out easily. It is an Intermediate operation and is sometimes referred to as in process annealing. The process is less expensive than Recrystallization annealing.

Annealing



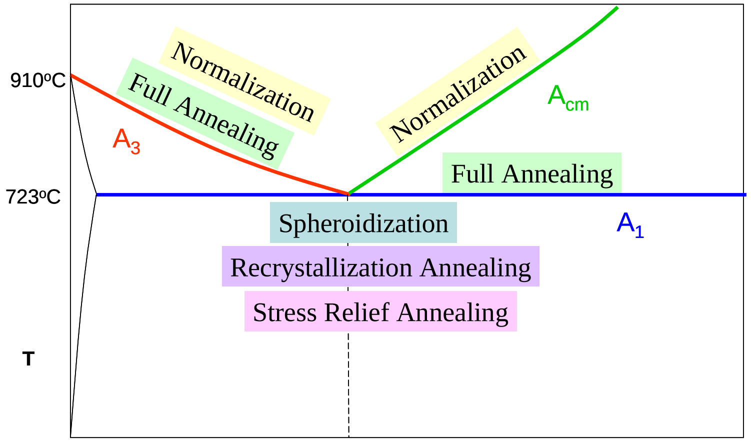
Temperature ranges for various types of annealing processes

Normalizing

Heat above A_3 | A_{cm} → Austenization → Air cooling → Fine Pearlite (Higher hardness)

Purposes

- Refine grain structure prior to hardening
- To harden the steel slightly
- To reduce segregation in casting or forgings



- ❑ In hypo-eutectoid steels normalizing is done 50°C above the annealing temperature
- ❑ In hyper-eutectoid steels normalizing done above A_{cm} → due to faster cooling cementite does not form a continuous film along GB

Annealed Vs Normalized

Annealed	Normalized
Less hardness, tensile strength and toughness	Slightly more hardness, tensile strength and toughness
Pearlite is coarse and usually gets resolved by the optical microscope	Pearlite is fine and usually appears unresolved with optical microscope
Grain size distribution is more uniform	Grain size distribution is slightly less uniform
Internal stresses are least	Internal stresses are slightly more

Hardening

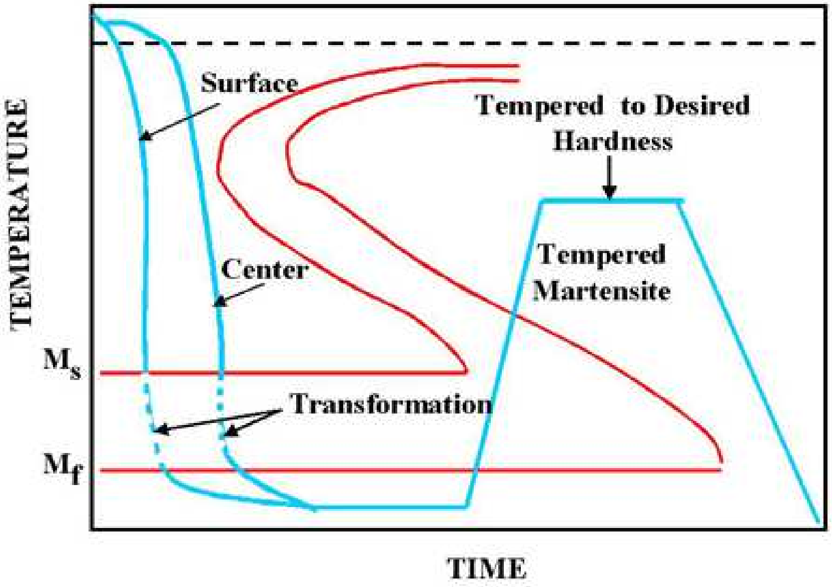
Heat above A_3 | A_{cm} → Austenization → Quench (higher than critical cooling rate)

- ☐ Certain applications demand high tensile strength and hardness values so that the components may be successfully used for heavy duty purposes. High tensile strength and hardness values can be obtained by a processes known as Hardening.
- ☐ hardening process consists of four steps. The first step involves heating the steel to above A_3 temperature for hypoeutectoid steels and above A_1 temperature for hypereutectoid steels by 50^0C.
- ☐ The second step involves holding the steel components for sufficient soaking time for homogeneous austenization.
- ☐ The third step involves cooling of hot steel components at a rate just exceeding the critical cooling rate of the steel to room temperature or below room temperature.
- ☐ The final step involves the tempering of the martensite to achieve the desired hardness. Detailed explanation about tempering is given in the subsequent sections. In this hardening process, the austenite transforms to martensite. This martensite structure improves the hardness.
- ☐ In the hardening process, which involves quenching and tempering. During quenching outer surface is cooled quicker than the center. In other words the transformation of the austenite is proceeding at different rates. Hence there is a limit to the overall size of the part in this hardening process.

Hardening

A few salient features in hardening of steel

- ❑ Proper quenching medium should be used such that the component gets cooled at a rate just exceeding the critical cooling rate of that steel.
- ❑ Alloy steels have less critical cooling rate and hence some of the alloy steels can be hardened by simple air cooling.
- ❑ High carbon steels have slightly more critical cooling rate and has to be hardened by oil quenching.
- ❑ Medium carbon steels have still higher critical cooling rates and hence water or brine quenching is necessary.



Hardening

Factors affecting Hardening Processes

- Chemical composition of steel
- Size and shape of the steel part
- Hardening cycle (heating/cooling rate, temp, soak time
- Homogeneity and grain size of austenite
- Quenching media
- Surface condition of steel part

Hardening Methods

- Conventional or direct quenching
- Quenching in stages in sequence in different media
- Spray Quenching
- Quenching with self tempering
- Austempering or Isothermal Quenching
- Martempering

Retained Austenite

- Austenite that is present in in the ferrous alloys even after the completion of the heat treatment process is referred to as retained austenite. In simple words, retained austenite is the untransformed austenite.
- Austenite transforms to martensite between M_s and M_f temperatures as it is essentially an athermal transformation. However, this transformation never goes to completion, i.e., 100% martensite (M_f temperature line is illustrated as dotted line in TTT diagrams).
- This is because at M_f , a small amount of (~1%) of austenite is present in highly stressed state along with ~99% martensite, and can not transform to martensite because unfavourable stress conditions.
- Both M_s and M_f temperatures decrease with increase in carbon content. Therefore amount of retained austenite in hardened steels increase with increase in carbon content.
- All alloying elements, except Al and Co, lower the M_s temperature and hence enhance the amount of retained austenite. Therefore, both high carbon steels and high alloy steels are more prone to the presence of retained austenite.
- The substructure of retained austenite differs from that of the original austenite as it has as a higher density of imperfections like dislocations, stacking faults, etc. which are created by local plastic deformation of the austenite by martensite crystals.
- Tool steels may have retained- austenite in the range of 5-35%. At the surface of a quenched steel, that restrains are minimum. R.A is less at surface than center of the part.

Retained Austenite

Advantages

- Ductility of austenite can help to relieve some internal stresses developed due to hardening, to reduce danger of distortion and cracks. 10% retained austenite along with martensite is desirable.
- The presence of 30-40% retained austenite makes straightening operation of the components possible after hardening. Straightening increases the hardness slightly.
- Non-distorting steels owe their existence to retained austenite. Here enough austenite is retained to balance the transformational contracting during heating, on the formation of austenite from ferrite carbide aggregate on the one hand, and the expansion corresponding to the formation of martensite during cooling, on the other, Here, the basis of dimensional stability of non-distorting steels is the presence of retained austenite.

disadvantages

- The soft austenite if present, in large amounts, decreases the hardness of hardened steels.
- As retained austenite may transform to lower bainite, or to martensite, there takes place increase in dimensions of the part. Not only it creates problems in precision gauges, or dies, the neighboring parts may be put under stress by it. In the component itself, stresses may be created to cause distortion or cracking.
- Retained austenite decreases the magnetic properties of the steel.

Sub-Zero treatment

- The retained austenite is generally undesirable, sub-zero treatment is one of the method to eliminate retained austenite.
- As the room temperature lies between M_s and M_f temperatures of steel, quenching to room temperature results in retained austenite.
- Subzero treatment consists in cooling the hardened steel to a temperature below 0°C. The temperature of the sub zero treatment depends on the position of M_f temperature of the steel.
- A steel can be cooled much below the M_f temperature, but it, evidently achieves nothing, because it cannot bring about any additional increase of hardness, or any additional increase of martensite, because the Martensitic transformation ends at M_f temperature.
- Sub-zero treatment is more effective, if it is carried out immediately after quenching operation. Any lapse of time between hardening and the cold treatment causes the stabilization of austenite, makes the retained austenite resistant to further transformation.
- Most steels can be cooled by subzero treatment in a low cooling unit with one of the mediums as given in table (next page) .
- The low-cooling unit consists of two vessels, the interior one of copper, where the parts or tools to be deep frozen, are placed and the exterior one of steel provided with a good heat insulation.

Sub-Zero treatment

Table : Subzero Coolants with Temperature of Application

Coolant	Minimum temperature °C
Dry ice (solid Co_2) + Acetone	-78
Ice + Salt (NaCl)	-23
Ice + Salt ($CaCl_2$)	-55
Liquid air	-183
Liquid Nitrogen	-196
Liquid Pentane	-129
Freon	-111

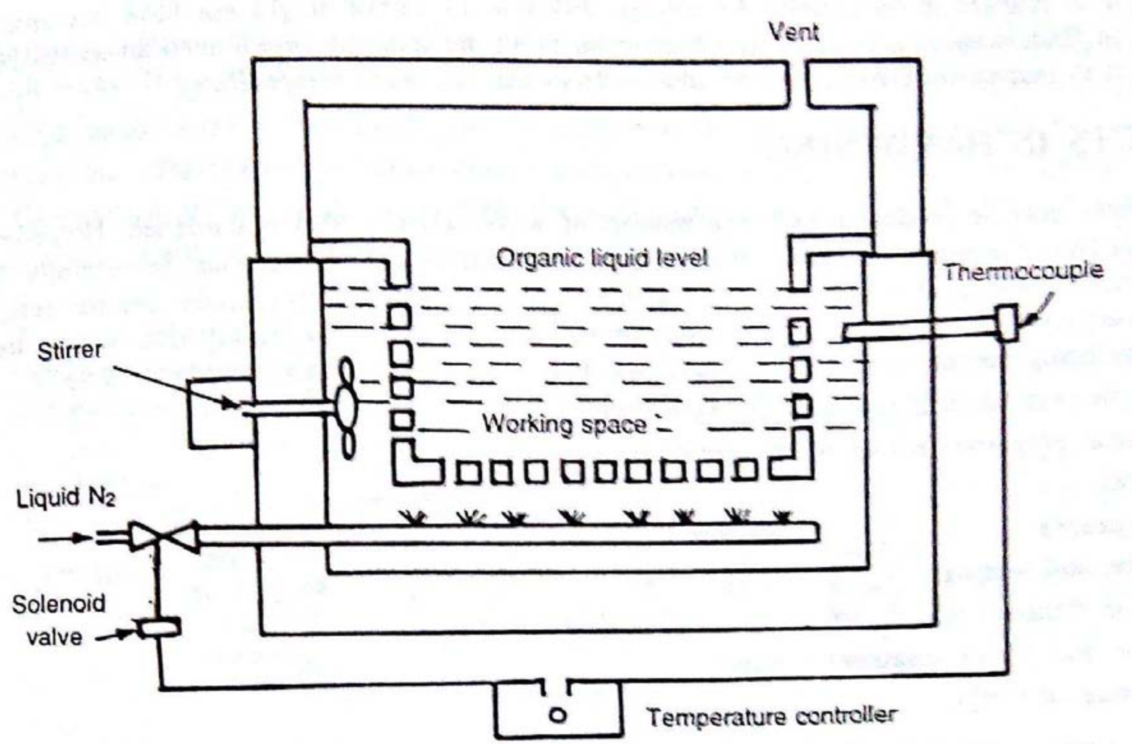


Figure : Liquid cooled (liquid N_2) system. Components are immersed in a bath of alcohol, or trichloro ethylene, which is cooled by a submerged liquid nitrogen spray (-150°C), cooling rates can be controlled.

Sub-Zero treatment

- The space in between the vessels is filled with one of the chosen medium, or a system (figure in previous page) which is inexpensive and can be used.
- Usually the temperature range used is in range of -30°C to -150°C, and total time of cooling and holding at that temperature (M_f) varies from ½ - 1 hour. The hardness increased by 2-4 HRc.
- As the amount of martensite increases by sub-zero treatment, it increases hardness, abrasion resistance, fatigue resistance and eliminates the danger of developing grinding cracks.
- As the newly formed martensite may add further to unfavorable stresses to cause distortion and cracks, the complicated, or intricate shaped components may be first tempered at 150-160°C immediately after first quenching and then given the sub-zero treatment.

Sub-zero treatment has been most extensively used for…!

- Alloyed tool steels – like high speed steel, which now shall need only single stage tempering.
- Tools and components which need exact dimensions – gauges
- Carburized steels, especially alloy steels (having elements like Ni in it) to increase their hardness and wear resistance
- Steels having 0.8 to 1.1%C as hardness increases by 1-3 HRc

Tempering

Objective

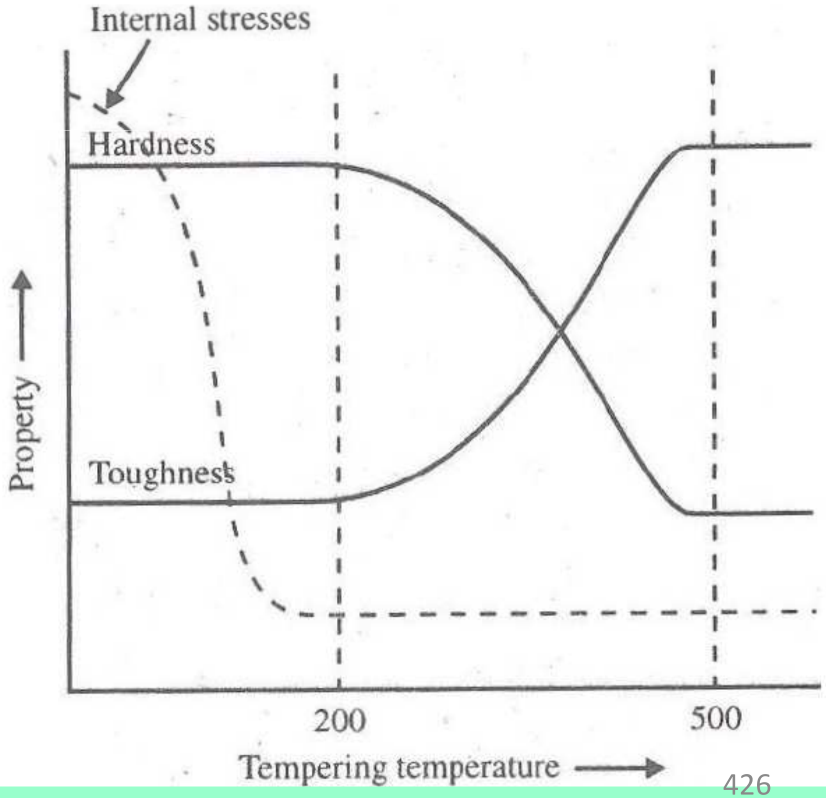
- Relieve Internal stresses
- Restore ductility and toughness
- To improve dimensional stability
- To improve magnetic properties

Structure in as Quenched state

- Highly supersaturated martensite
- Retained austenite
- Undissolved carbides
- Rods, or plates of carbide particles produced during ‘auto-tempering’
- Segregation of carbon

Tempering

- ❑ The hardened steel is not readily suitable for engineering applications. It possesses following three drawbacks.
  - ✓ Martensite obtained after hardening is extremely brittle and will result in failure of engineering components by cracking.
  - ✓ Formation of martensite from austenite by quenching produces high internal stresses in the hardened steel.
  - ✓ Structures obtained after hardening consists of martensite and retained austenite. Both these phases are metastable and will change to stable phases with time which subsequently results in change in dimensions and properties of the steel in service.
- ❑ Tempering helps in reduce these problems. Tempering is the process of heating the hardened steel to a temperature maximum up to lower critical temperature (A_1), soaking at this temperature, and then cooling, normally very slowly.



Variation in properties with tempering temperature

Tempering of plain carbon steels

First stage of Tempering

- First Stage of tempering temperature extends from room temperature to 200°C. The tempering reactions in steels, containing carbon less than 0.2%, differ somewhat from the steels containing more than 0.2% carbon.
- In the former, if carbon atoms have not yet segregated (during quenching) to dislocations, these diffuse and segregate around the dislocations and lath boundaries in the first stage of tempering. No ε-carbide forms as all the carbon gets locked up to the dislocations (defects).
- Martensite in steels with more than 0.2% carbon is highly unstable because of super saturation, and interstitial diffusion of carbon in BCT martensite can occur. Thus in the first stage of tempering, the decomposition of martensite into low-tetragonality martensite (containing ~0.2%C, c/a ~ 1.014) and ε-carbide, $Fe_{2.4}C$ occurs. (*There are reports of precipitation of eta-carbide,* Fe_2C and Haggs carbide, $Fe_{2.2}C$.
- ε-carbide is a separate phase and is not a preliminary step in the formation of cementite, but it nucleates and grows more rapidly than cementite. It has HCP structure with c = 4.33A°, a = 2.73A°, c/a = 1.58A° and forms as small (0.015-0.02 μm) platelets, or needles observed under electron microscope.
- The structure at this stage referred to as tempered martensite, which is double phase mixture of low tetragonal martensite and ε-carbide.
- In this stage volume ↓ because specific volume of martensite ↓ due to rejecting of C atoms.

Tempering of plain carbon steels

Second stage of Tempering

- Second Stage of tempering temperature lies between 200-300°C. The amount of retained austenite in the as-quenched steel depends mainly on the composition of the steel, and the temperature to which steel is quenched.
- In the second stage of tempering retained austenite transforms to lower bainite (the carbide in bainite is ε-carbide). The matrix in lower bainite is cubic ferrite ($c/a = 1$), where as in tempered martensite, the low tetragonal martensite has $c/a \sim 1.014$
- When retained austenite changes to lower bainite, their takes place increase in volume.

Third stage of Tempering

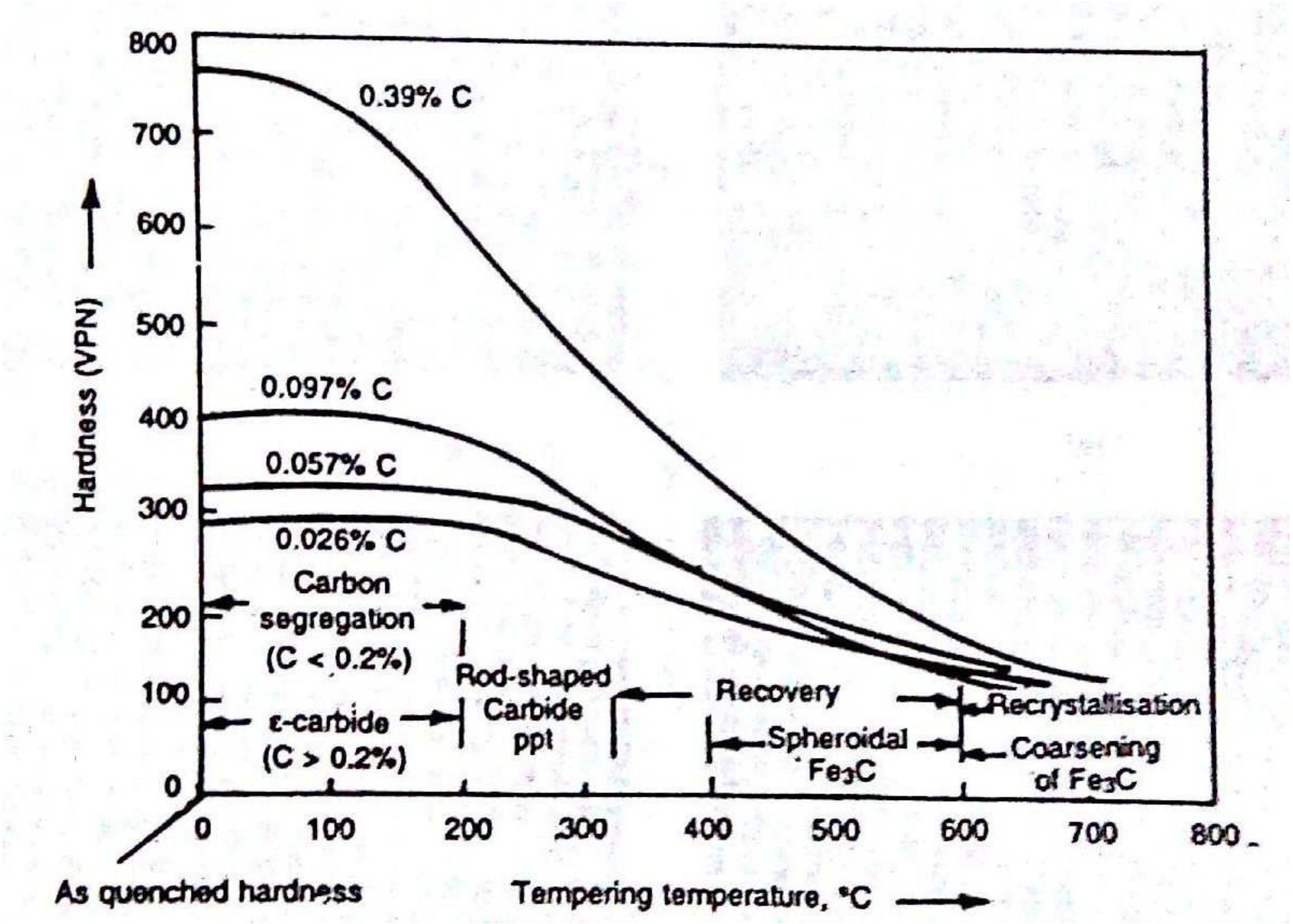
- Third Stage of tempering temperature lies between 200-350°C. In this stage of tempering, ε-carbide dissolves in matrix, and low tetragonal martensite losses its completely its carbon and thus, the tetragonality to become ferrite .
- Cementite forms as rods at interfaces of ε-carbide and matrix, twin boundaries, interlath boundaries, or original austenite grain boundaries.
- During this stage, volume decreases just as in stage one, due to complete loss of tetragonality. In a 1% carbon steel , the total decrease in length in the first and third stages in around 0.25%

Tempering of plain carbon steels

Fourth stage of Tempering

- Fourth Stage of tempering temperature lies between 350-700°C.
- Growth and spheroidisation of cementite, as well as recovery and Recrystallization of ferrite occur. Though the growth of cementite starts above 300°C, its spheroidisation starts above 400°C to 700°C.
- Spheroidisation takes place due to reduction in interfacial energy of ferrite-cementite interfaces. As quenched martensite has high concentration of lattice defects. Though their annealing out starts in the third stage of tempering, but the cementite precipitates retard the recovery processes.
- Substantial recovery processes starts occurring only above 400°C. original lathe boundaries are stable up to 600°C, but above this, these are replaced by equiaxed-ferrite grain boundaries – the process, which is best described as 'Recrystallization'.
- In the end, the optical microstructure consists of equiaxed ferrite grains with coarse Spheroidal particles of cementite, and then the structure is called globular pearlite, or spheroidized cementite.
- The structure perhaps is the most stable of all ferrite- cementite aggregates, and is the softest with highest ductility with best machinability.

Effect of carbon on Tempering



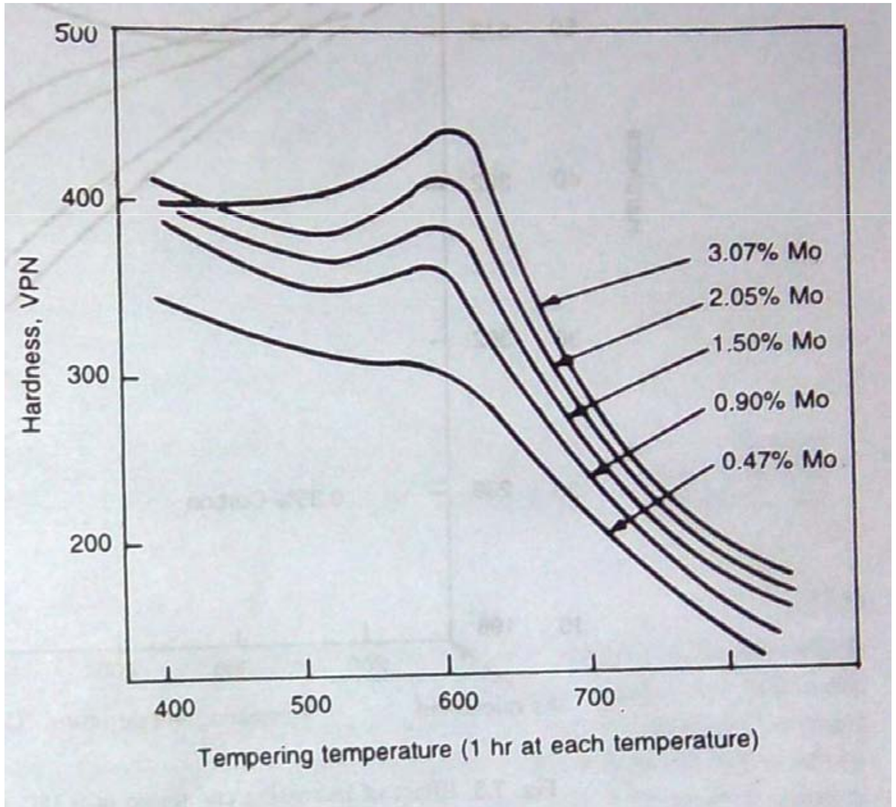
Effect of tempering temperature(1 hour at each temperature) on hardness and reactions

Tempering of alloy steels

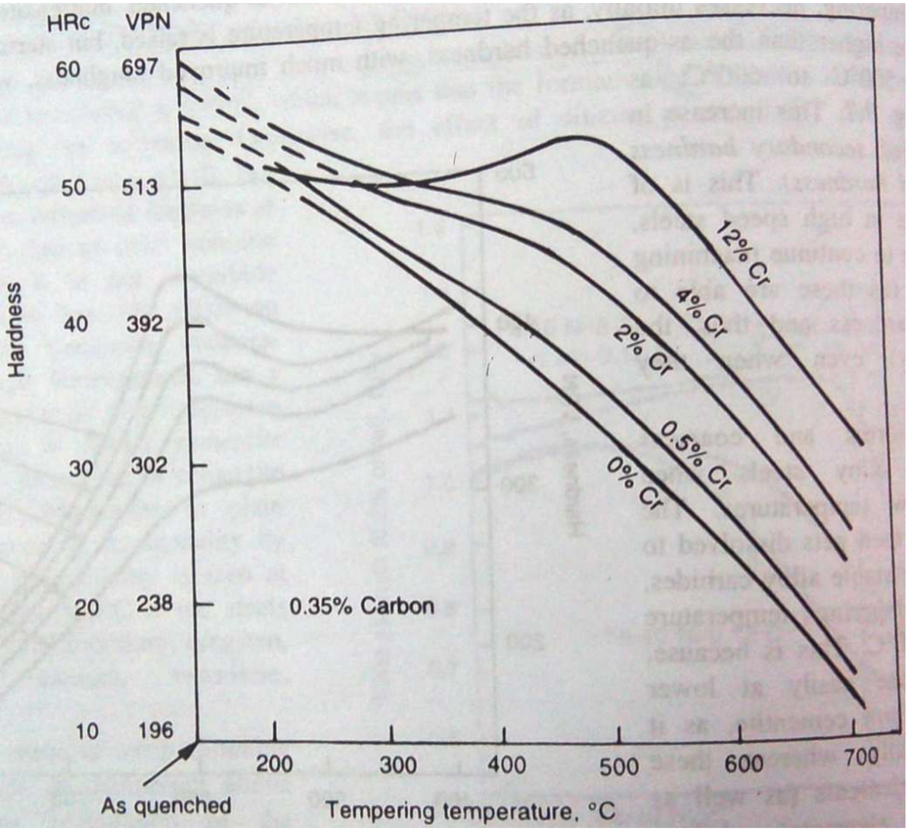
- The presence of alloying elements, steels can change their nature and properties effectively.
- Most common elements (except cobalt) shift the CCT curve to longer times, which essentially result in the increase of hardenability of the steels, so that pearlitic transformation can be avoided easily to obtain Martensitic structure, even at a slower trate of cooling and in thicker parts.
- Alloying elements also lower M_s and M_f temperatures, increasing further the amount of retained austenite. The decomposition of retained austenite on tempering, plays quite a significant role on the properties of tempered steels, specially having high carbon and high alloying elements.
- Some elements, that are not found in carbides, but are present as solid solution in ferrite, are Al, Cu, Si, P, Ni, and Zr. Some elements arranged in order of increasing tendency to form carbides are Mn, Cr, W, Mo, V and Ti. These carbide forming elements retard most effectively the rate of softening during tempering of the steel.
- The first stage of tempering does not appear to be effected by the presence of the alloying elements. However, most of the alloying elements in steels tends to increase the hardness after tempering than a plain carbon steel with the same carbon content.
- At smaller concentration, they merely retard the tempering processes hence the softening, particularly at higher temperature (> 500°C), where these elements have good diffusivity to take part in tempering reactions.

Tempering of alloy steels

- When alloy carbides are formed, the drop in hardness during tempering is not only retarded but is significantly increased. The steel is then said to secondary hardening.
- Thus, 0.5% chromium , or less than 0.5% Mo resists softening but secondary hardening is produced by either 12% chromium, or 2 % Mo.. Stronger the carbide, the more potent is the secondary hardening.



Effect of increasing Mo on tempering of as quenched 0.1%C steel



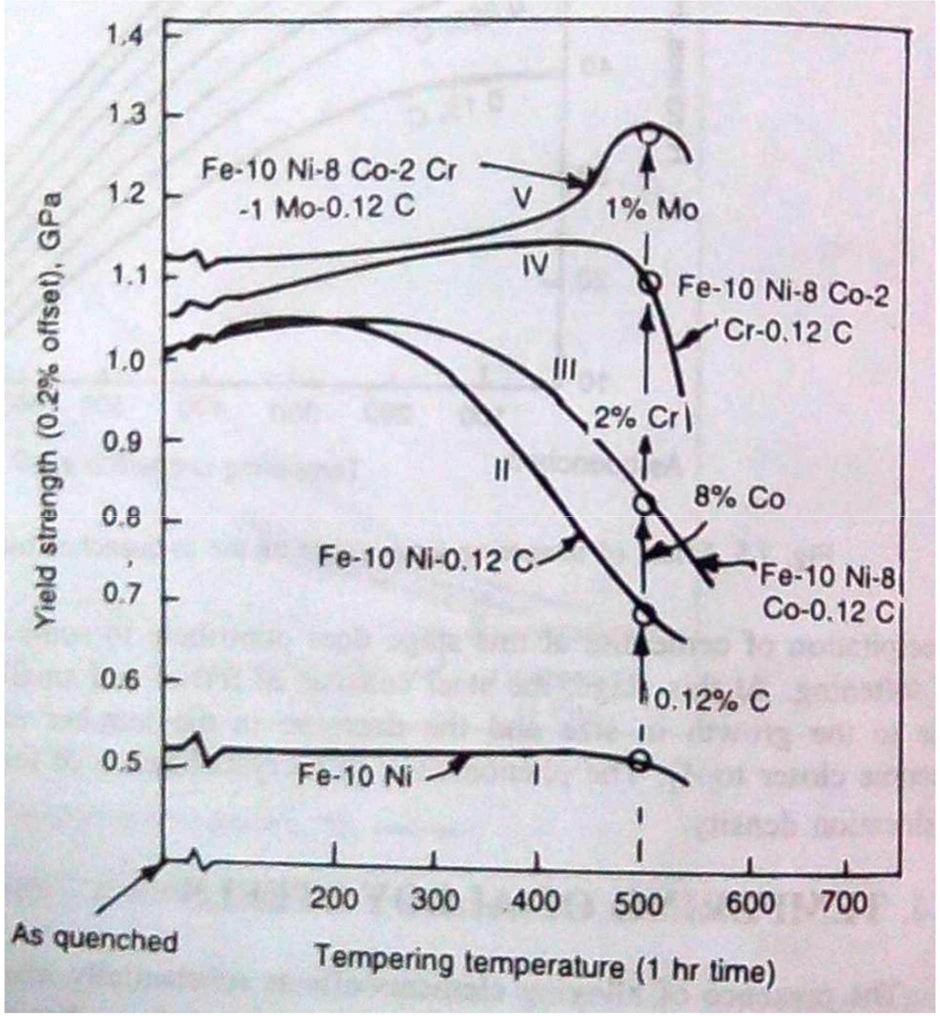
Effect of increasing chromium in 0.35%C steel on tempering

Tempering of alloy steels

- Element, such as, silicon dissolves in ε-carbide to stabilize it. Steels with 1-2% silicon have ε-carbide present even after tempering at 400°C, which means that the formation of cementite is delayed considerably, and thus, resisting the softening. Otherwise, the effect of silicon is essentially due to solid solution strengthening.
- Nickel has a small, but constant effect on tempered hardness at all temperatures due to solid solution strengthening as it is not a carbide former.
- Manganese has little effect on softening at low tempering temperatures, but at high temperatures, has a strong effect on due to its faster diffusion then, and thus, it resists cementite coarsening as it is present in cementite as $(Fe, Mn)_3C$.
- Martensite in plain carbon steels losses its tetragonality by 300°C, but the tetragonality is seen at 450°C, or even at 500°C if the steels have elements like Cr, W, Mo, Ti, V and Si.
- The basic cause of steep softening in carbon steels on tempering above 400°C, is the coagulation of the cementite particles. Alloying elements notably Si, Cr, Mo, V, when present in steels, retard the coalescence and the coarsening of cementite particles., resulting in enhanced hardening over and above the solid solution hardening effect.
- Elements like Cr, Si, Mo, or W delay coarsening to temperature range of 500-550°C. up to tempering temperature 500°C, the carbides formed are of iron with proportional alloying elements in it, but above 500°C, alloying elements can form their own carbides and thus, coarse cementite particles are replaced by fine dispersion of more stable alloy carbides.

Tempering of alloy steels

- An Fe-10 Ni alloy shows constant hardness on tempering up to 450°C and then, there takes place some decrease in strength (curve I).
- Addition of 0.12% carbon increases the as quenched strength to almost double, and slow decrease of hardness occurs on tempering to fall to 0.7 GPa at 500°C.
- A 8% cobalt addition, which doesn't enter the carbide, delays the softening to have strength of 0.8 GPa at 500°C .
- Addition of 2% Cr almost continuously but slowly ↑ hardness to start falling at above ~450°C to become 1.1 GPa at 500°C by fine dispersion of Cr carbide.
- Addition of Mo causes secondary hardening, as it is very strong carbide forming element, to attain a hardness of 1.3 Gpa at 500°C



Effect of C, Co, Cr, and Mo on tempering of Fe-10Ni steels

Tempering of alloy steels : Secondary Hardening

- In alloy steels, having larger amounts of strong carbide forming elements like Mo, Ti, V, Nb, W, Cr etc., and carbon , a peculiar phenomena occurs, the hardness of the as-quenched martensite (called primary hardness) on tempering, decreases initially, as the tempering temperatures is raised, but starts increasing again to often become higher than the as quenched hardness, with much improved toughness, when tempered in the range of 500 to 600°C. This increase in hardness is called secondary hardness (also called red hardness).
- This is great importance in high speed steels, as these are able to continue machining, at high speeds (as these are able to resist fall in hardness and thus, the cutting property) even when they become red hot.
- Secondary hardening is a process, similar to age hardening, in which coarse cementite particles are replace by a new and much finer alloy carbide dispersion of V_4C_3, Mo_2C, W_2C (which normally form on dislocations). As in aging a critical dispersion causes a peak in the hardness and strength of the alloy, and as over aging takes place, i.e., carbide dispersion slowly coarsens, the hardness decreases.
- Secondary hardening is best shown in steels containing Mo, V, W, Ti and also in Cr steels at high chromium concentrations.
- The amount of secondary hardening in an alloy steel is directly proportional to the volume fraction of the alloy carbides, and thus is directly proportional to the concentration of strong carbide forming elements present in steels. The alloy carbides must precipitate as fine dispersion in ferrite matrix rather than massive carbide particles.

Time and Temperature relationship in Tempering

- For a given steel, a heat treater might like to choose some convenient tempering time, say over night, otherwise different than 1 hour, and thus, wants to calculate the exact temperature required to achieve the constant hardness.
- Hollomon and Jaffe's "tempering parameter" may be used for this purpose as it relates the hardness, tempering temperature and tempering time. For a thermally activated process, the usual rate equation is :

$$Rate = \frac{1}{t} = Ae^{-Q/RT}$$

- Where, t is the time of tempering to develop a given hardness, and Q is the 'empirical activation energy' . 'Q' is not constant in the complex tempering processes but varies with hardness. Thus, hardness was assumed to be a function of time and temperature:

$$H = f[te^{-Q/RT}]$$

- Interestingly, $[te^{-Q/RT}]$ is a constant, and let it be $t_{0.}$ Equating activation energies of eq (1) and (2) gives,

$$Q = T[\ln t - \ln t_0] = f(H)$$

- As t_0 constant then

$$H = f[T(C + \ln t)]$$

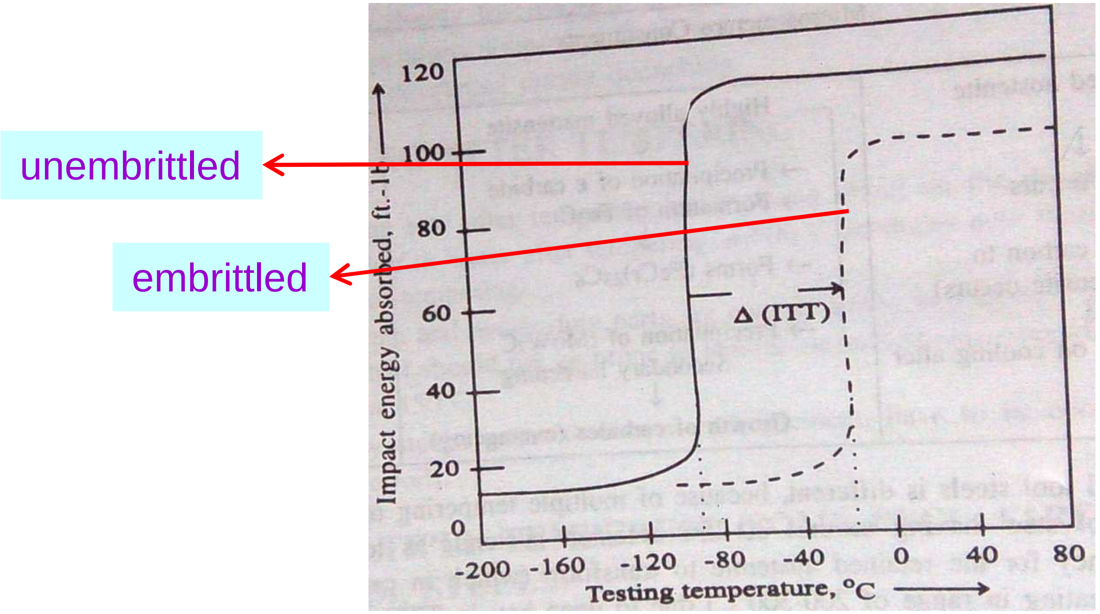
- Where, C is a constant, whose value depends on the composition of austenite. The single parameter which expresses two variables time and the temperature i.e., **T (C + ln t)** is called the Hollomon and Jaffe tempering parameter. (hardness in vickers is preferable)

Temperature and colours for Heating and Tempering of Steel

	Colours of Hot Solid metal	℃	Process of Heat treatment
HEAT COLOURS	White	1500	
	Yellow white	1300	High speed steel hardening (1230-1300°C)
	Yellow	1100	
	Orange Red	1000	Alloy steel hardening (800-1100°C)
	Light-Cherry-Red	900	
	Cherry-red	800	Carbon steel hardening
	Dark-red	700	
	Vary dark-red	500	High speed steel tempering (500-600°C)
	Black red in dull light, or darkness	400	
	Steel gray	300	Carbon steel tempering (150-575°C)
TEMPER COLOURS	Colour of Oxide film	℃	Parts Heat treated
	Steel Gray	327	Cannot be used for cutting tools
	Pale-light blue	310	For springs
	Purple	282	Spring and screw drivers
	Brown	270	Axes, wood cutting tools
	Gold	258	Shear blades, hammer faces, cold chisels
	Dark-straw-light-brown	240	Punches and Dies
	Light-Straw-Yellow	220	Steel cutting tools, files, paper cutters

Embrittlement during Tempering

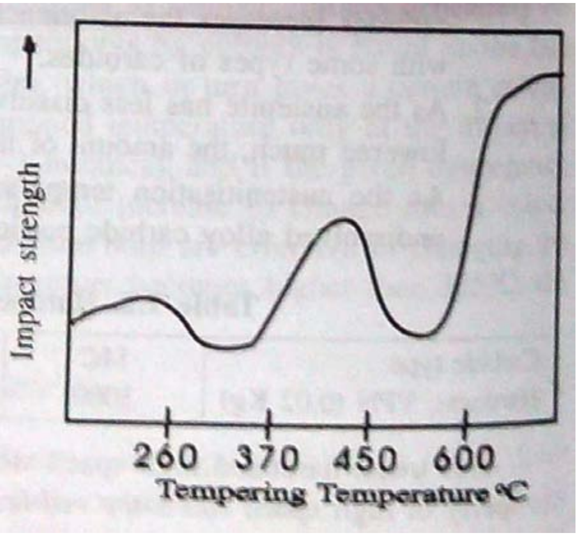
- ❑ Normally, as the tempering progresses, the hardness and the strength decreases, but the ductility and impact strength increase. But in certain steels, there is an unexpected decrease of the impact strength in certain ranges of temperatures. This indicates that there are two main types of embrittlement during tempering.
  - Tempered Martensite Embrittlement (TME)
  - Temper Embrittlement
- ❑ Both these embrittlement raise the impact transition temperature (ITT) to higher temperature. Figure (below) indicates the increase in *impact transition temperature*, Δ(ITT) due to TE in SAE 3140 steel.



Temper-embrittlement in SAE 3140 steel shifts the impact transition temperature to higher temperature . Δ(TTT) indicates the amount of increase.

Embrittlement during Tempering

- ❑ Normally, the degree of both type of embrittlement is expressed in terms of relative displacements of ITT i.e., by Δ (ITT) illustrated in figure (in previous slide).
- ❑ In both the transgranular fracture mode is replaced by an intergranular (IG) mode below the transition temperature, i.e., these show bright inter crystalline fracture along original austenite grain boundaries.
- ❑ Inspite of these similar effects, the two types of embrittlement are two separate phenomena, which occur in two different temperature ranges. Moreover, TME is a much faster process usually occurring in one hour, where as TE takes many hours.
- ❑ Temper embrittlement is of mush greater concern from practical point of view, as the rotors and shafts of power generating equipment even after tempering above 600°C, develop it when thick section cool very slowly through the range (450-600°C)



Schematic illustration of effect of tempering temperature on impact strength in steels prone to embrittlement during tempering.

Tempered Martensite embrittlement

- ❑ As TME develops after tempering in range 260°C to 370°C, it is called as "350°C" embrittlement, or 500°F embrittlement. It is called 'one-step embrittlement' as during heating only in this range, TME develops. It is also called 'irreversible embrittlement because a steel embrittled by tempering in this range , if heated further to above 400°C (above the critical range), becomes tougher, and the tempered martensite embrittlement does not occur again if cooled down to or tempered in the range of 260°C to 370°C again.
- ❑ All steels, including the plain carbon steels are prone to irreversible embrittlement to some extent, and that is why tempering range of 260°C- 370°C is avoided in all steels, though it is a malady of low alloy steels.
- ❑ The embrittlement is associated with the change in the structure of carbide from epsilon (ε) to cementite in the form of a film at the grain boundaries.
- ❑ On tempering at higher temperatures, this film disappears and can not be restored, on repeated heating in 260°C-370°C temperature range.
- ❑ Although, tempered martensite embrittlement is concurrent with the precipitation of cementite, but such precipitation is not in itself the cause of loss of impact toughness, as the embrittlement is does not occur if P, Sb, Sn, As, or N are not present in steel.
- ❑ Addition of sufficient silicon to the steel inhibits the formation of cementite in the critical range, as silicon dissolved in epsilon carbide, increases its stability, and thus embrittlement does not occur

Temper embrittlement

- The sickness of alloy steels occurs when they are tempered in the range 450°C to 600°C. it is also called reversible embrittlement (as well as two step embrittlement), because it occurs, when steels are tempered in this range, but gets removed, when heated to high temperatures, but occurs again on slow continuous cooling through this range from that high temperature (>600°C). The degree of embrittlement depends on the rate of cooling in the range 600-450°C.
- The phenomena of temper embrittlement results in loss of toughness as measured by notched impact test (without affecting very much the hardness, Y.S, UTS, elongation and fatigue properties), and a rise in ductile to brittle transition temperature occurs, with an intergranular (IG) fracture, below the transition temperature along the original austenitic grain boundaries.
- Carbon steels in general, but with less than 0.5% Mn, do not show temper embrittlement. Alloy steels of high purity do not show it. It is caused primarily by Sb and P and secondarily by Sn or As (even in amounts as low as 0.01%) in presence of elements like Ni, Mn, Cr, Si in steels. The highest effect is in Ni-Cr and Mn-Cr steels. Presence of elements like Mo, Ti, Zr delay, or remove embrittlement.
- The characteristic features of temper embrittlement are best explained by the concept of co-segregation. The impurity solutes are the surface active elements in iron, i.e., these reduce the grain boundary energy, and thus reduce the cohesion. Elements like Sb, P, As, Sn, interact with certain elements like Ni and Mn in steels.

Temper embrittlement

- ☐ These interactions leads to co-segregation of alloying elements and the impurity elements such as between Ni-Sb, Ni-P-Ni-Sn and Mn-Sb. The reason of co-segregation is the stronger interaction between them than, between either of these and iron.
- ☐ If the interaction is very strong then, co-segregation does not occur, but a scavenging effect is got, as happens between Mo-P, Ti-P, which is the cause of elimination of embrittlement by 0.5% Mo in such steels. If larger amount of Mo, Ti, Zr are present , then these elements slowly react with carbon to form stable carbides releasing the impurity atoms to segregate to the boundaries.
- ☐ Additional segregation may take place, when two alloying elements are present simultaneously, such as Ni and Cr. At high temperatures (>600°C), thermal vibrations make the equilibrium segregation low enough not to cause embrittlement., and at lower temperature (<450°C), the diffusion of the elements is too low to cause enough co-segregation with in the normal tempering time.
- ☐ The following methods are normally recommended to minimize the effect of Temper embrittlement
    - ✓ Keep the impurities such as Sb, P, Sn, As as low as possible
    - ✓ Alloy the steel with Mo (0.5-0.75%)
    - ✓ Quench from tempering at higher temperatures

Heat Treatment Defects

- Heat treatment of steels or aluminum can lead to several defects. The principal types of defects found in quenching of steels are internal and external cracks in the work, distortion and warping.
- CRACK : When the internal tensile stresses exceed the resistance of the steel to separation the crack occurs. The insertion of the tools in the furnace without preheating for tempering is one of the main causes of crack propagation. The crack formation is reduced by preheating the tool between 200^0Cto 300^0C.
- DISTORTION : Distortion occurs due to uneven heating, too fast cooling, part incorrectly supported in furnace, incorrect dipping in quenching and stresses present before preheating. Distortion can be prevented by preheating the tool or check furnace capacity, reduce the hardening temperature, and by reviewing the method of dipping.
- WARPING : Asymmetrical distortion of the work is often called warping in heat-treating practice. Warping is usually observed upon non-uniform heating or over heating for hardening. It also occurs when the work is quenched in the wrong position and when the cooling rate is too high in the temperature range of the martensite transformation. An elimination of these causes should subsequently reduce warping.
- The properties required in the heat treated part are obtained without the parts being distorted beyond the acceptable limits.
- The ideal design for a heat treatable part is the shape that when heated (or cooled) would have the same temperature at every point with in the part.

Recovery Recrystallization & Grain Growth

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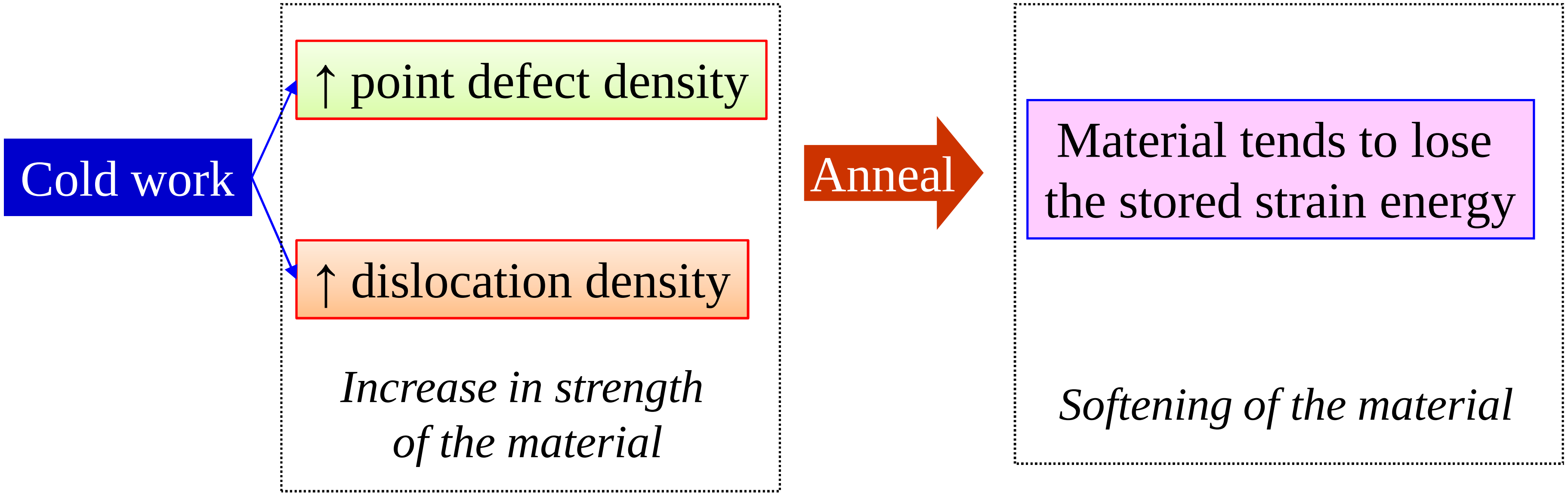
Introduction

Plastic deformation in the temperature range (0.3 – 0.5) T_m → COLD WORK

- Point defects and dislocations have strain energy associated with them
- (1 -10) % of the energy expended in plastic deformation is stored in the form of strain energy (in these defects) → *The material becomes battery of energy..!*
- The cold worked material is in a micro structurally metastable state.
- Depending on the severity of the cold work the dislocation density can increase 4-6 orders of magnitude more. The material becomes stronger, but less ductile.
- The cold worked material is stronger (harder), but is brittle.
- Heating the material (typically below $0.5T_m$) is and holding for sufficient time is a heat treatment process called annealing.
- Depending on the temperature of annealing processes like Recovery at lower temperatures) or Recrystallization (at higher temperatures) may take place. During these processes the material tends to go from a micro structurally metastable state to a lower energy state (towards a stable state).
- Further 'annealing' of the recrystallized material can lead to grain growth.

$$\begin{array}{ccc} \textit{Annealed material} & \xrightarrow{\textit{Cold work}} & \textit{Stronger material} \\ \rho_{\text{dislocation}} \sim (10^{6} - 10^{9}) & & \rho_{\text{dislocation}} \sim (10^{12} - 10^{14}) \end{array}$$

Introduction



Cold work

↑ point defect density

↑ dislocation density

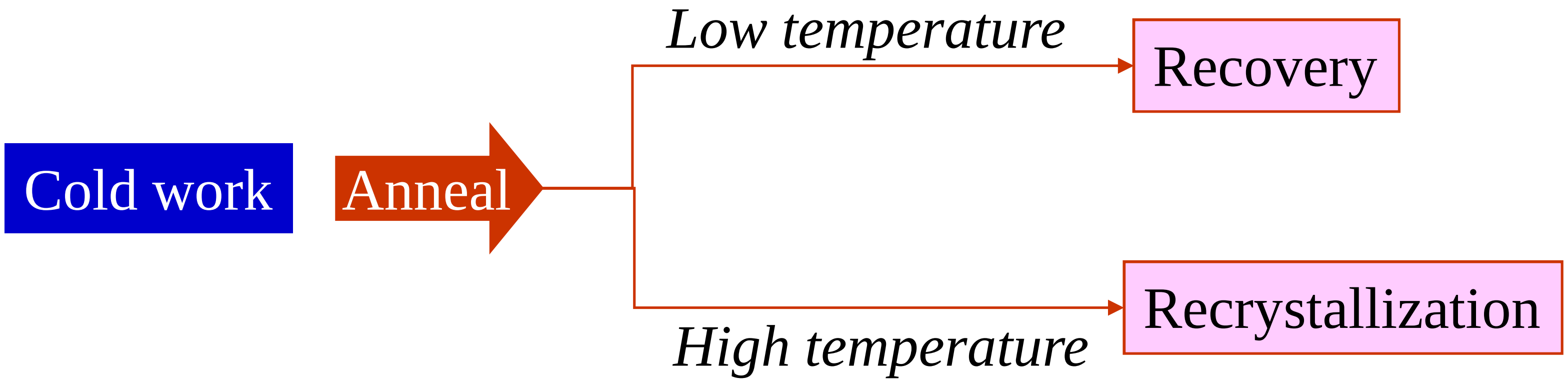
Increase in strength of the material

Anneal

Material tends to lose the stored strain energy

Softening of the material

- ❑ During cold work the point defect density (vacancies, self interstitials…) and dislocation density increase. Typical cold working techniques are rolling, forging, extrusion etc.
- ❑ Cold working is typically done on ductile metals (e.g. Al, Cu, Ni)



Cold work

Anneal

Low temperature

Recovery

High temperature

Recrystallization

Overview of processes taking place during annealing

Cold work

Anneal

Recovery

Driving force is free energy stored in point defects and dislocations

Recrystallization

Driving force is free energy stored in dislocations

Grain growth

Driving force is free energy stored in grain boundaries

Cold work

↑ Strength

↑ Hardness

↑ Electrical resistance

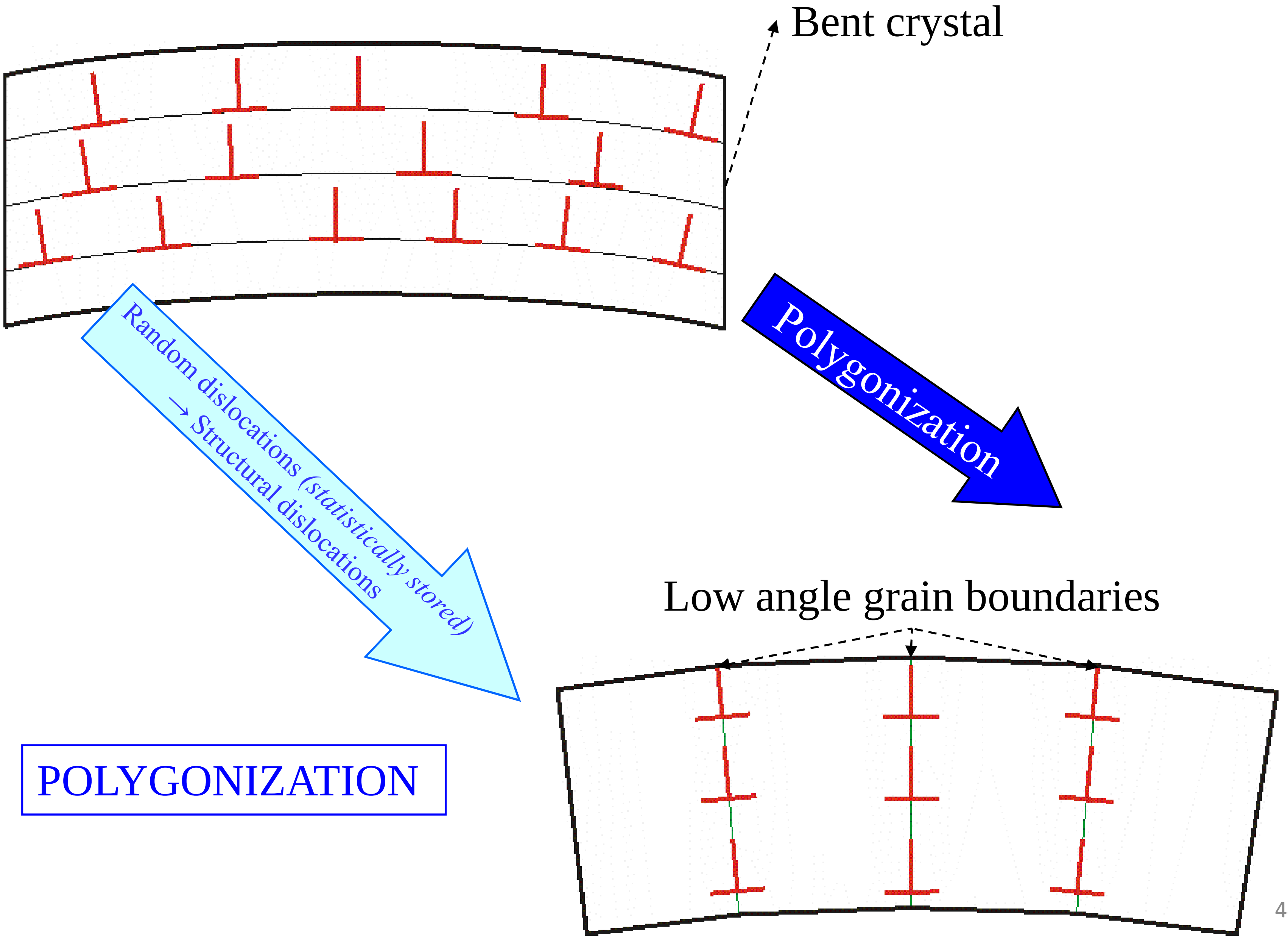
↓ Ductility

Changes occur to almost all physical and mechanical properties

Recovery

- ❑ Recovery takes place at low temperatures of annealing
- ❑ "Apparently no change in microstructure"
- ❑ Excess point defects created during Cold work are absorbed:
  - ▶ at surface or grain boundaries
  - ▶ by dislocation climb
- ❑ Random dislocations of opposite sign come together and annihilate each other
- ❑ Dislocations of same sign arrange into low energy configurations:
  - ▶ Edge → Tilt boundaries
  - ▶ Screw → Twist boundaries
    - ➔ POLYGONIZATION
- ❑ Overall reduction in dislocation density is small
- ❑ At the early stage of annealing of cold formed metals, external thermal energy permits the dislocations to move and form the boundaries of a polygonized subgrain structure while the dislocation density stays almost unchanged. This process also removes the residual stresses formed due to cold working significant. The recovering of physical and mechanical properties varies with the temperature and time.

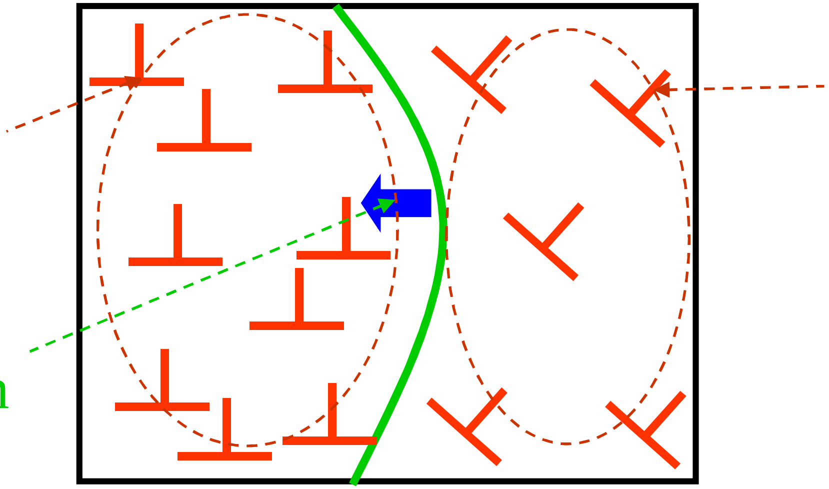
POLYGONIZATION



POLYGONIZATION

Recrystallization

- $T_{recrystallization} \in (0.3 - 0.5)\, T_m$
- “Nucleation” and growth of new, strain free crystals
- Nucleation of new grains in the usual sense may not be present and grain boundary migrates into a region of higher dislocation density
- $\Delta G\ (\text{recrystallization}) = G\ (\text{deformed material}) - G\ (\text{undeformed material})$
- $T_{Recrystallization}$ is the temperature at which 50 % of the material recrystallizes in 1 hour



Region of higher dislocation density

Direction of grain boundary migration

Region of lower dislocation density

Recrystallization

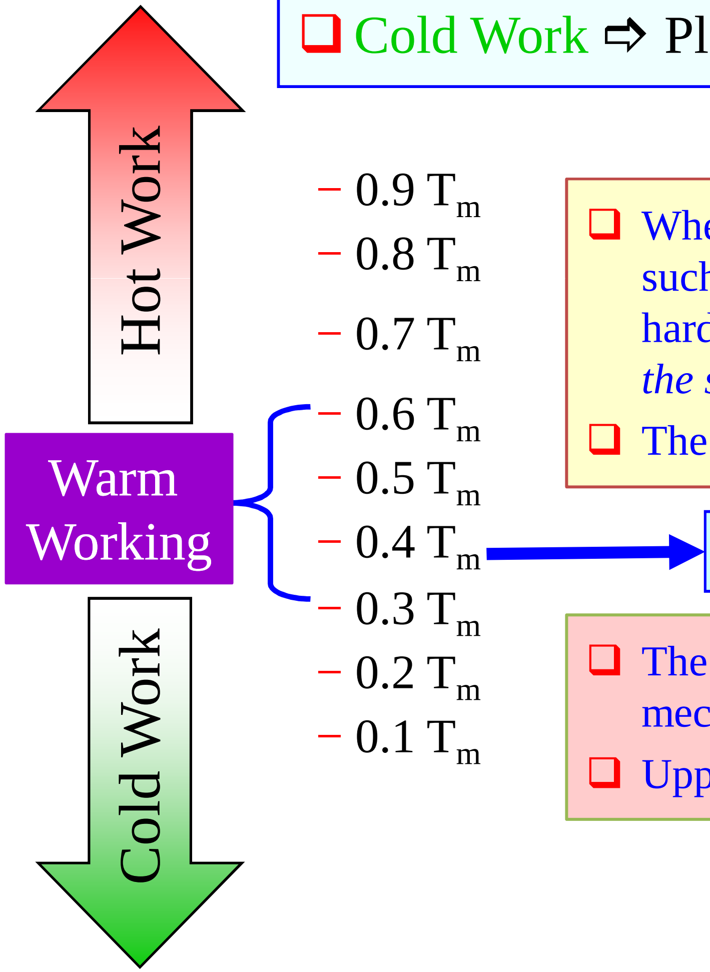
- Deformation ↑ ⇒ recrystallization temperature ($T_{recrystallization}$) ↓
- Initial grain size ↓ ⇒ recrystallization temperature ↓
- High cold work + low initial grain size ⇒ finer recrystallized grains
- ↑ cold work temperature ⇒ lower strain energy stored
  ⇒ ↑ recrystallization temperature
- Rate of recrystallization = exponential function of temperature
- $T_{recrystallization}$ = strong function of the purity of the material
  $T_{recrystallization}$ (very pure materials) ~ 0.3 T_m
  $T_{recrystallization}$ (impure) ~ (0.5 – 0.6) T_m

  ► $T_{recrystallization}$ (99.999% pure Al) ~ 75°C
  $T_{recrystallization}$ (commercial purity) ~ 275°C
- The impurity atoms segregate to the grain boundary and retard their motion → *Solute drag* (can be used to retain strength of materials at high temperatures)
- Second phase particles also pin down the grain boundary during its migration

Hot Work and Cold Work

Often the range is further subdivided into Hot, Cold and Warm working as in the figure

- Hot Work ⇨ Plastic deformation above $T_{\text{Recrystallization}}$
- Cold Work ⇨ Plastic deformation below $T_{\text{Recrystallization}}$



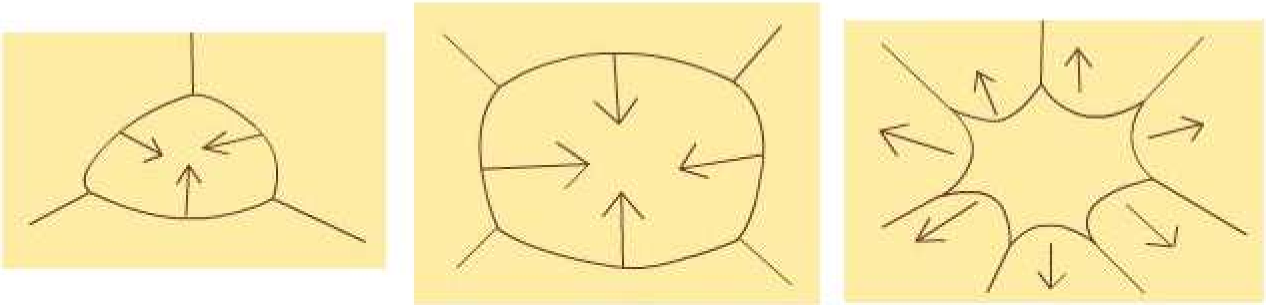
- When a metal is hot worked. The conditions of deformation are such that the sample is soft and ductile. The effects of strain hardening are negated by dynamic and static processes (*which keep the sample ductile)*
- The lower limit of temperature for hot working is taken as $0.6\ T_m$

Recrystallization temperature (~ $0.4\ T_m$)

- The effects of strain hardening is not negated. Recovery mechanisms involve mainly motion of point defects.
- Upper limit ►$0.3\ T_m$

Grain growth

- The interfaces in a material cost the system energy: the excess free energy associated with the interfaces is the interfacial free energy.
- Grain boundaries are the interfaces between two crystallites which are differently oriented in space; the excess free energy associated with the grain boundary is the grain boundary energy.
- The grain boundary energy acts as the driving force for the movement of grain boundaries. Hence, if a recrystallised material is further annealed, then grains growth takes place; bigger grains grow at the cost of smaller ones. This process is known as grain growth.
- Since the driving force for grain growth is the interfacial energy, and since the excess energy associated with a system due to interfaces is related to the curvature of the interface, the grain growth is curvature driven. In Figure we shown the direction of movement of grain boundaries and their relationship to curvature (in 2D systems).



Curvature driven growth of grains (in 2D)

Grain growth

- ❑ It is the velocity of the interface, then $v \propto \kappa$ where κ is the curvature $\left(\frac{1}{r}\right)$. More specifically

$$v = M\frac{2\gamma}{r}$$

- ❑ where M is the mobility, and ϒ is the grain boundary energy. In terms of the diameter (D) of the grains,

$$\frac{dD}{dt} = \frac{4M\gamma}{D}$$

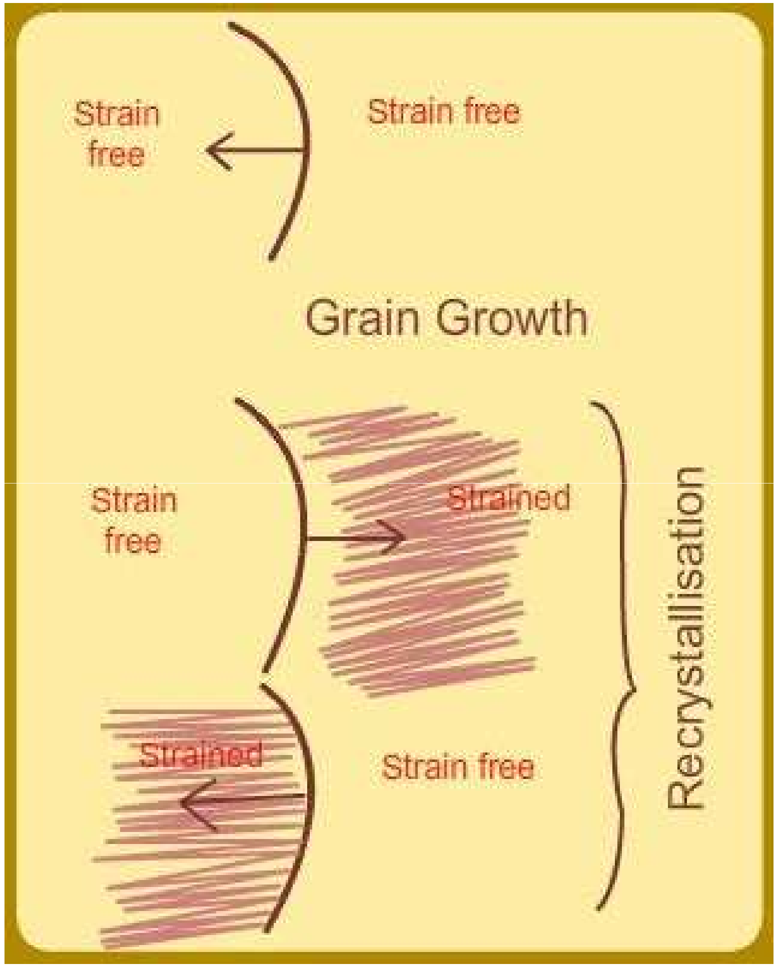
- ❑ The solution to this equation is given by

$$D^2 = D_0^2 + 4M\gamma t$$

- ❑ where D_0 is the mean size of the grain at time t = 0 and D is the mean diameter of the grains in the system.
- ❑ Experimentally, it is found that the grain size as a function of time does follow an expression of the type $D = Kt^n$,where K is a temperature dependent proportionality constant and *n is a number* much less than 0.5. The deviation of the exponent from 0.5 is not yet clearly understood.

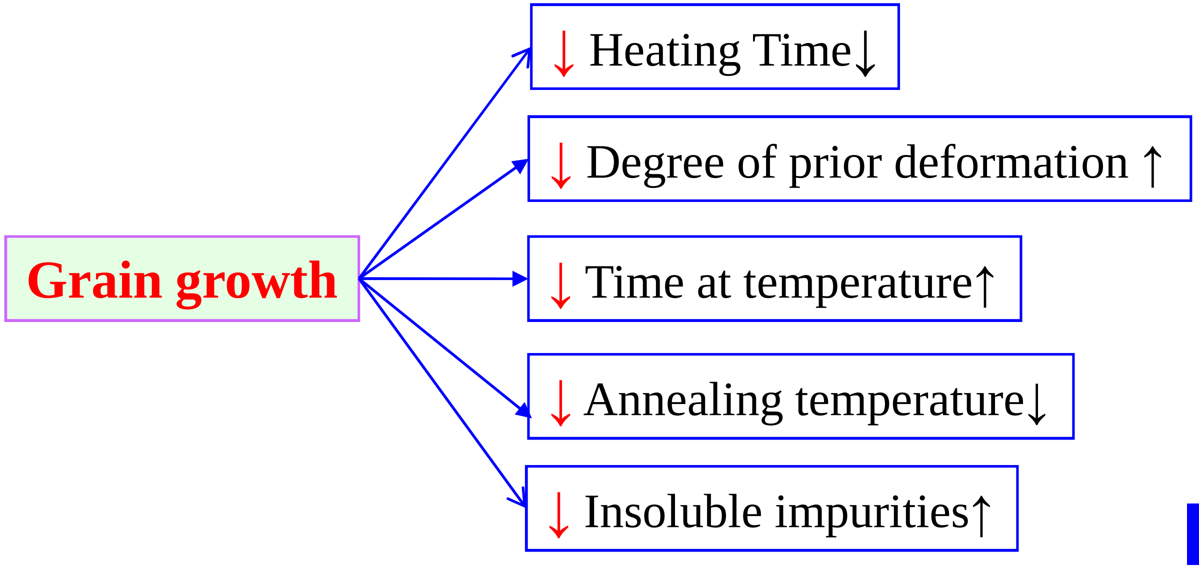
Grain growth

- ☐ Due to the differences in the driving forces for recrystallisation and grain growth, as shown in Figure the movement of the interface in these two cases are different in character; recrystallisation, as long as the growing grain is free of strain and eats into the strained grain, will proceed irrespective of the curvature of the grain; however, during grain growth, the movement of the interface is dependent on the curvature of the grain.
- ☐ During grain growth, the direction of movement of the grain boundary is completely decided by curvature. On the other hand, during recrystallisation it is decided by the strains in the grains; the strained one is eaten up by the strain free crystal; hence, the growth can sometimes be such that the boundary moves away from its centre of curvature.



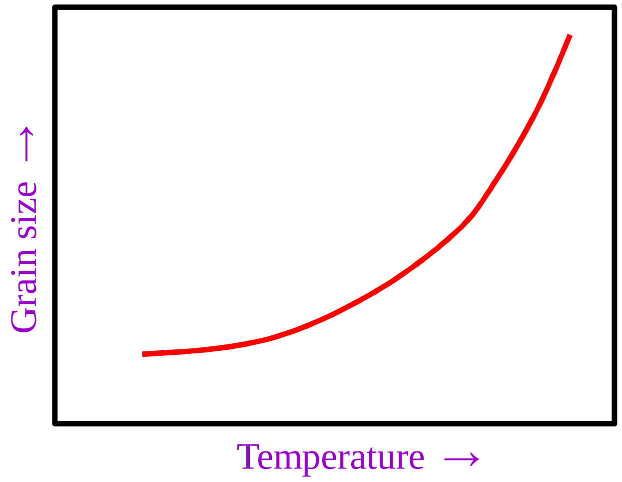
Grain growth

- ❑ Large grains have lower free energy than small grains. This is associated with the reduction of the amount of grain boundary.
- ❑ Therefore, under ideal conditions, the lower energy state for a metal would be as a single crystal. This is driving force for grain growth.
- ❑ Opposing this force is the rigidity of the lattice. As the temperature increases, the rigidity of the lattice decreases and the rate of grain growth is more rapid.
- ❑ At any given temperature there is a maximum grain size at which these two effects are in equilibrium



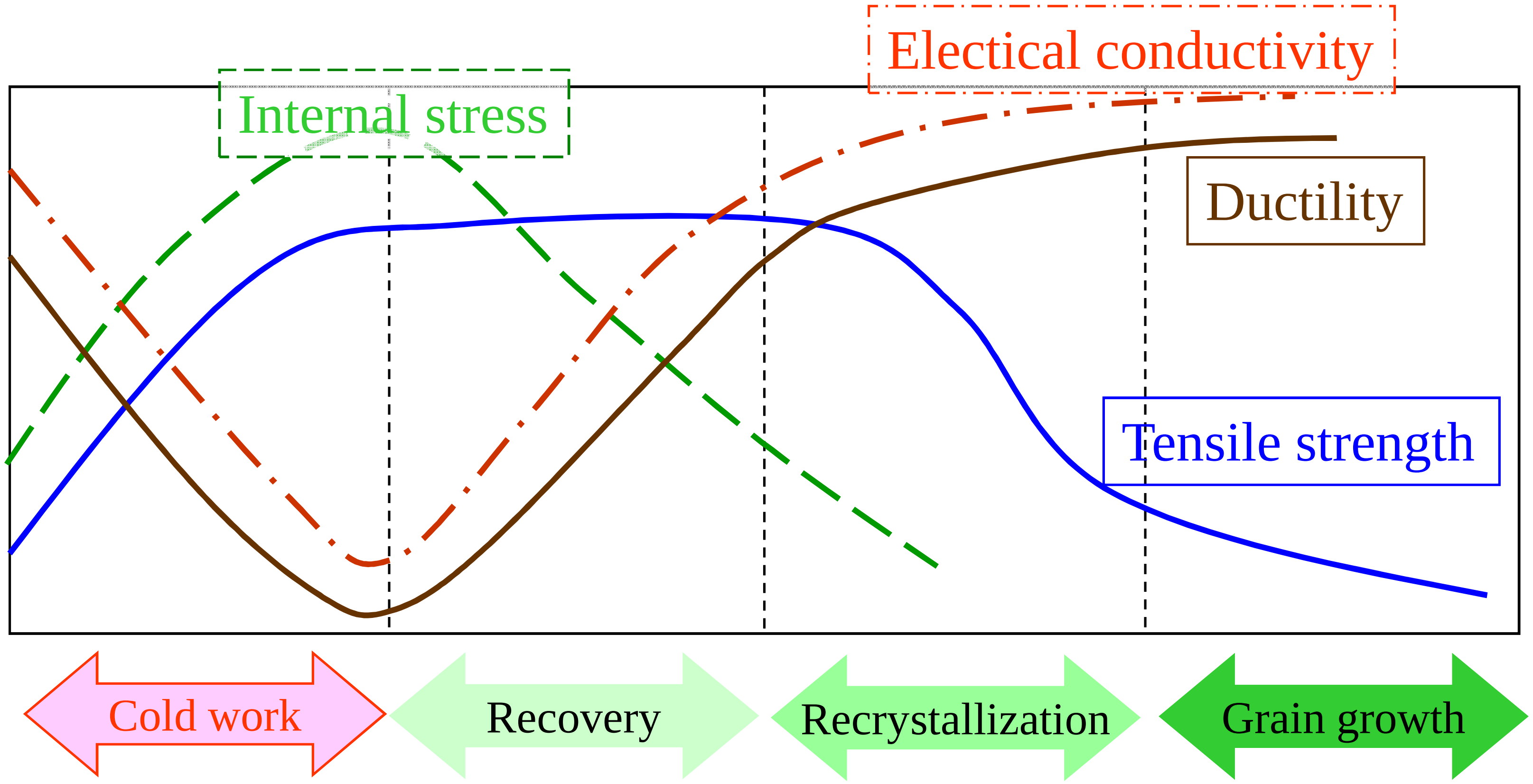
Grain growth

- ↓ Heating Time↓
- ↓ Degree of prior deformation ↑
- ↓ Time at temperature↑
- ↓ Annealing temperature↓
- ↓ Insoluble impurities↑



Effect of temperature on recrystallized grain size

Recovery Recrystallization Graingrowth



Change of properties with increased annealing temperature of a cold worked sample. Note that there are changes in properties beyond recrystallisation temperatures too due to grain growth.

Questions?

1. What is annealing? What are its aims? Discuss the different types of annealing processes giving the temperature ranges and the aims of each type.
2. Differentiate between:
   a) Process annealing and recrystallization annealing
   b) Diffusion annealing and spheroidising
   c) Normalising and annealing
   d) Stress-relieving and tempering
3. With the help of a suitable diagram, show normalizing and hardening temperature ranges for plain carbon hypereutectoid steels. What is the criteria for the selection of these temperature ranges?
4. Discuss the merits and demerits of the following hardening processes:
   a) Direct quenching
   b) Auto-tempering
   c) Interrupted quenching
5. Explain why hardening by quenching is followed by tempering treatment? How do mechanical properties vary with tempering temperature?

Questions?

6. Describe the structural changes that take place during tempering. Is there any fourth stage of tempering? Which type of steels exhibit hardening and why?
7. What is the meant by temper brittleness? Why does it occur? Are there any remedies for it? Discuss.
8. With the help of suitable diagram, explain the process of martempering. How does it differ from austempering? What do the microstructures of martempered and austempered steels consists of? What are limitations.
9. Distinguish between tempered martensite embrittlement (TME) and temper embrittlement (TE) based on (i) rate of embrittlement (ii) reversibility (iii) no. of steps (iv) types of steels (v) mechanism (vi) range of temperature.
10. Consider cold worked aluminium in which the dislocation density is increased from 10^{10} to 10^{14} per m^2. Calcualte the driving force for recrystallisation
11. Most of the materials that we encounter in our daily lives are polycrystalline. If the grain boundary energy does increase the free energy of the system, why do they not disappear leaving behind a single crystal?
12. Describe the following processes
    a) Sub zero treatment
    b) Patenting

Questions?

13. What is the role of cold working in the recovery and recrystallization processes? Is it important in the grain growth process?
14. What is the role of diffusion in the heat treatments applied to the alloy studied in this experiment?
15. Why do grains grow? What is the upper limit for grain size? Lower limit?

Hardenability

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Introduction

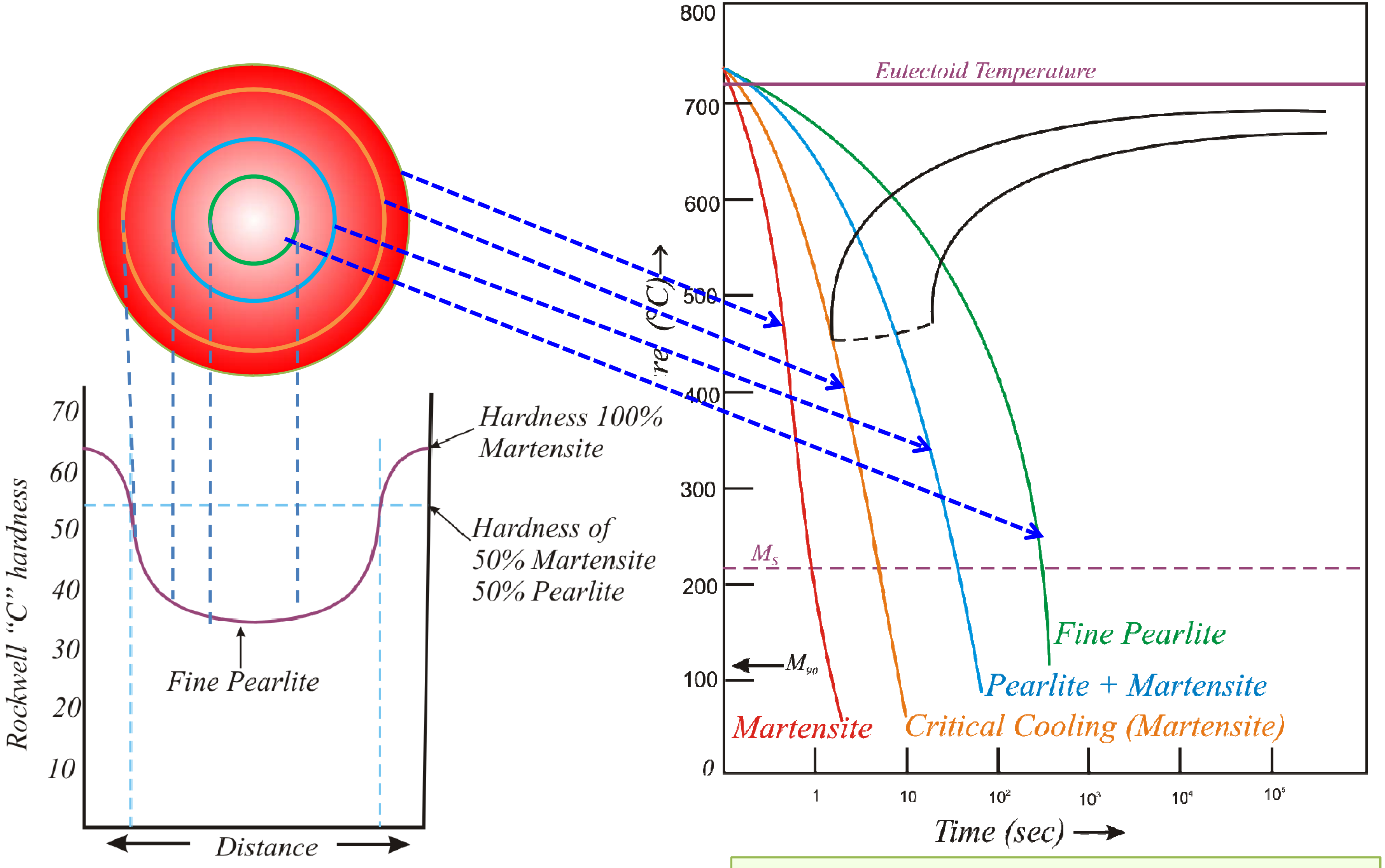
- Hardenability is one of the most important properties of a steel because it describes the ease with which a given steel can be quenched to form martensite or the depth to which martensite is formed on a given quench.
- It is an important property for welding, since it is inversely proportional to weldability, that is, the ease of welding a material.
- The ability of steel to form martensite on quenching is referred to as the hardenability.
- **Hardenability** is a measure of the capacity of a steel to be hardened in depth when quenched from its austenitizing temperature.
- **Steels with high hardenability form martensite even on slow cooling.**
- High hardenability in a steel means that the steel forms martensite not only at surface but to a large degree throughout the interior.
- For the optimum development of strength, steel must be fully converted to martensite.
- To achieve this, the steel must be quenched at a rate sufficiently rapid to avoid the decomposition of austenite during cooling to such products as ferrite, pearlite and bainite.
- Hardenability of a steel should not be confused with the hardness of a steel.

Hardness ≠ Hardenability

The Hardness of a steel is a measure of a sample's resistance to indentation or scratching,

Hardenability refers to its ability to be hardened to a particular depth under a particular set of conditions.

Hardness profile in a cylinder from case to core

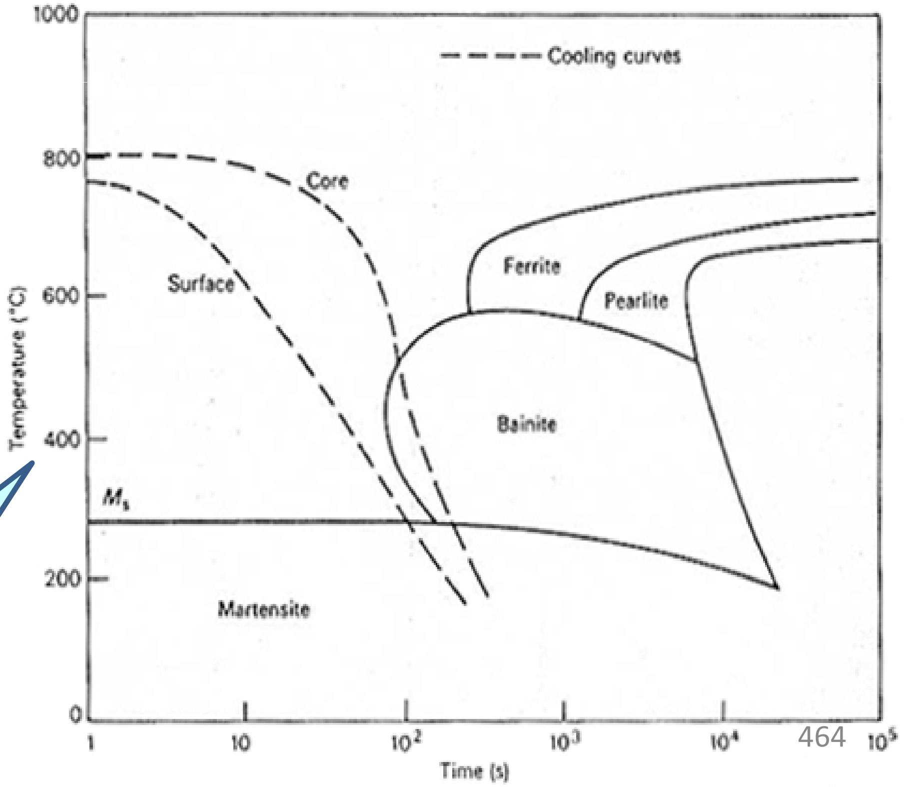


Typical hardness test survey made along a diameter of a quenched cylinder

Schematic showing variation in cooling rate from surface to interior leading to different microstructures

Hardenability

- **It is a qualitative measure of the rate at which hardness drops off with distance into the interior of a specimen as a result of diminished martensite content.**
- Hardenability is more related to depth of hardening of a steel upon heat treat.
- The depth of hardening in a plain carbon steel may be 2-3 mm Vs 50 mm in an alloy steel.
- A large diameter rod quenched in a particular medium will obviously cool more slowly than a small diameter rod given a similar treatment. Therefore, the small rod is more likely to become fully martensitic.
- The hardenability of a steel is the maximum diameter of the rod which will have 50% martensite even in the core when quenched in an ideal quenchants. This diameter is known as D_i or ideal diameter.



Relation between cooling curves for the surface and core of an oil-quenched 95 mm diameter bar

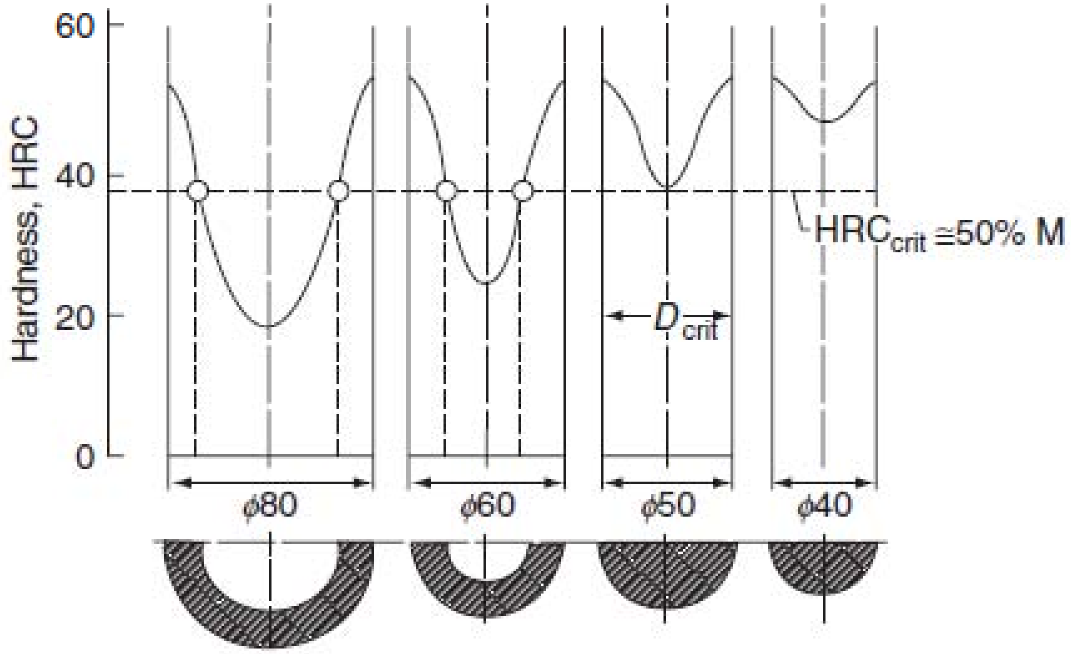
Determination of Hardenability

❑ **Hardenability of steel is determined by the following methods**

- ✓ Grossman’s critical diameter method
- ✓ Jominy end quench test
- ✓ Estimation of hardenability from chemical composition
- ✓ Fracture test

Grossman’s critical diameter method

- In Grossman’s method, we use round bars of different diameters.
- These bars are quenched in a suitable quenchants.
- Further, we determine the critical diameter (D_c) which is the maximum diameter of the rod which produced 50% martensite on quenching.
- The ideal diameter (D_i) is then determined from the curve.
- This type of experiment requires multiple Austenitisation and quenching treatments on specimens of varying diameter just to quantify the hardenability of a single material.



Determination of the critical diameter D_{crit} according to Grossmann

Severity of Quenching media

Process	Variable	H Value
Air	No agitation	0.02
Oil quench	No agitation	0.2
"	Slight agitation	0.35
"	Good agitation	0.5
"	Vigorous agitation	0.7
Water quench	No agitation	1.0
"	Vigorous agitation	1.5
Brine quench (saturated Salt water)	No agitation	2.0
"	Vigorous agitation	5.0
Ideal quench		∞

If the increase in rate of heat conduction is greater than the decrease due to persistence of the vapor film, the net result will be an increase in the actual cooling rate. However if the reverse is true, then the result will be decrease in cooling rate.

Severity of Quench as indicated by the heat transfer equivalent H

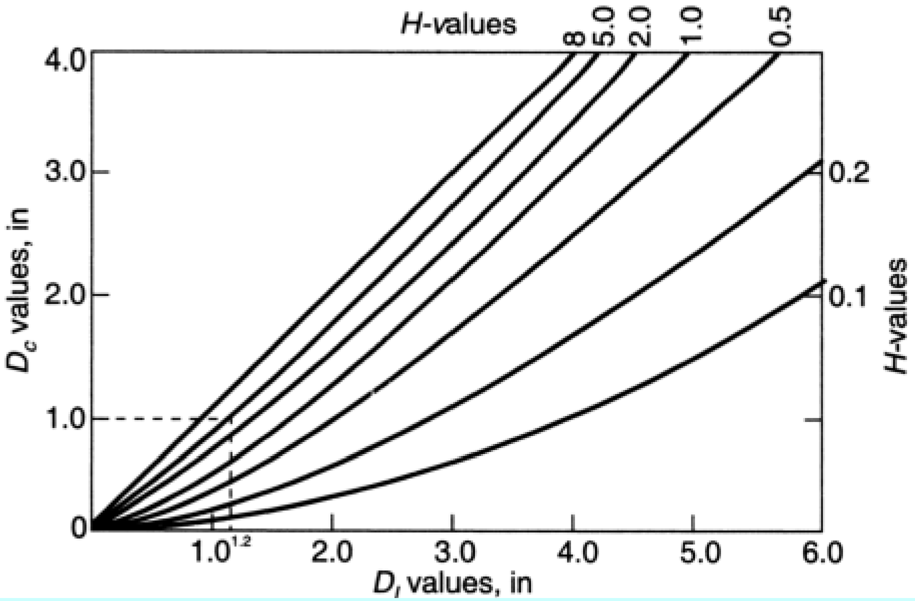
$$H = \frac{f}{K} \qquad [m^{-1}]$$

f → heat transfer factor
K → Thermal conductivity

Note that apart from the nature of the quenching medium, the vigorousness of the shake determines the severity of the quench. When a hot solid is put into a liquid medium, gas bubbles form on the surface of the solid (interface with medium). As gas has a poor conductivity the quenching rate is reduced. Providing agitation (shaking the solid in the liquid) helps in bringing the liquid medium in direct contact with the solid; thus improving the heat transfer (and the cooling rate). The H value/index compares the relative ability of various media (gases and liquids) to cool a hot solid. Ideal quench is a conceptual idea with a heat transfer factor of ∞ ($\Rightarrow$ H = ∞)

Grossman’s critical diameter method

- The relation between ideal critical diameter D_I and critical diameter D_C and severity of quench (H) can be determined from thermodynamic considerations.
- These relations are shown in Grossman’s master graph. In this figure the D_I is plotted as the abscissa, and the D_C is plotted as ordinate.
- A number curves are plotted in this graph and each belongs to different rates of cooling. In every case, the rate of cooling is measured by the H-value or the severity of quench.
- From this graph, by knowing the value of D_C, the corresponding value for D_I can be found out. For example, assuming D_C = 1inch and H = 5 (for agitated brine quench), the critical diameter or hardenability works out to 1.2inch with help of figure.



From figure it can be observed that

$D_I = D_C$ for $H = \infty$

$D_I > D_C$ for $H < \infty$

The relation between ideal critical diameter D_I and critical diameter D_C that can be fully hardened by using a quenching medium with a given cooling power H.

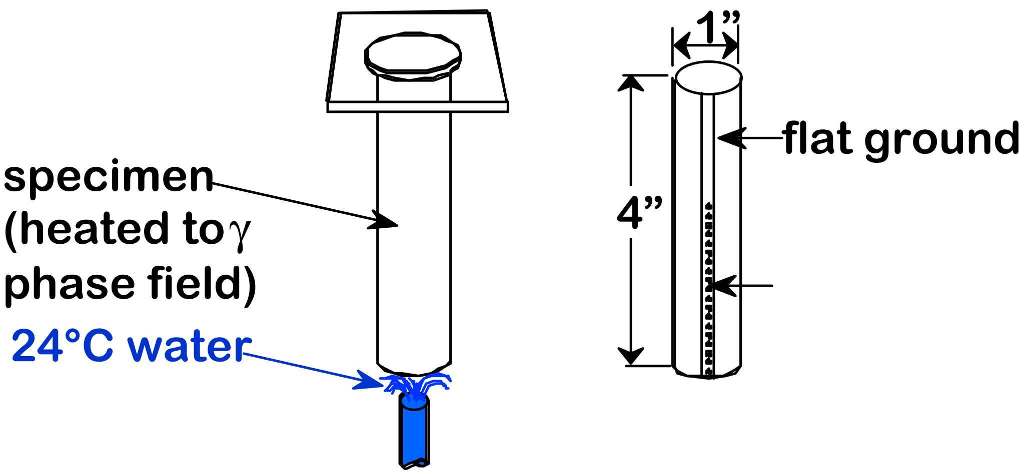
Jominy End Quench method

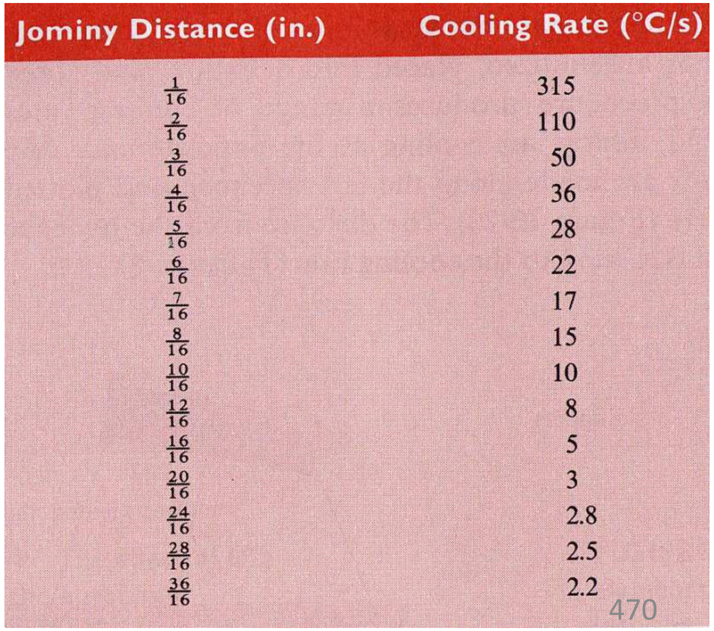
- The most commonly used method for determining hardenability is the end quench test developed by Jominy and Boegehold
- Grossmans method requires multiple Austenitisation and quenching treatments on specimens of varying diameter just to quantify the hardenability of a single material.
- An alternative approach is to develop a more convenient standard test method that can be used for relative comparison of hardenability. The Jominy end-quench test is one such approach.
- The Jominy end-quench test is specified in ASTM standard A255 and is a widely used method for quantifying hardenability. Its wide use adds to its value, since the utility of empirical relations and data comparison becomes more reliable as more data are accumulated.
- Moreover, Jominy data have been collected on a large enough scale to offer a high degree of statistical certainty for many steels.
- These data have been correlated with measurements and/or calculations of D_C.
- By using these correlations, a single Jominy test can be used to estimate D_C and D_I for a given steel (and austenite grain size).
- Information gained from this test is necessary in selecting the proper combination of alloy steel and heat treatment to minimize thermal stresses and distortion when manufacturing components of various sizes.

Jominy End Quench method - Principle

- The hardenability of a steel is measured by a Jominy test with following procedure.
- In conducting this test, a 1 inch round specimen 4 inch long is heated uniformly to the proper austenising temperature. It is then removed from the furnace and placed on a fixture where a jet of water impinges on the bottom face of the sample.
- After 10 min. on the fixture, the specimen is removed, and to cut along the longitudinal direction.
- And then Rockwell C scale hardness readings are taken at 1/16 inch, intervals from the quenched end. The results are expressed as a curve of hardness values Vs. distance from the quenched end. A typical hardenability curve shown below for eutectoid steel.

Jominy Sample

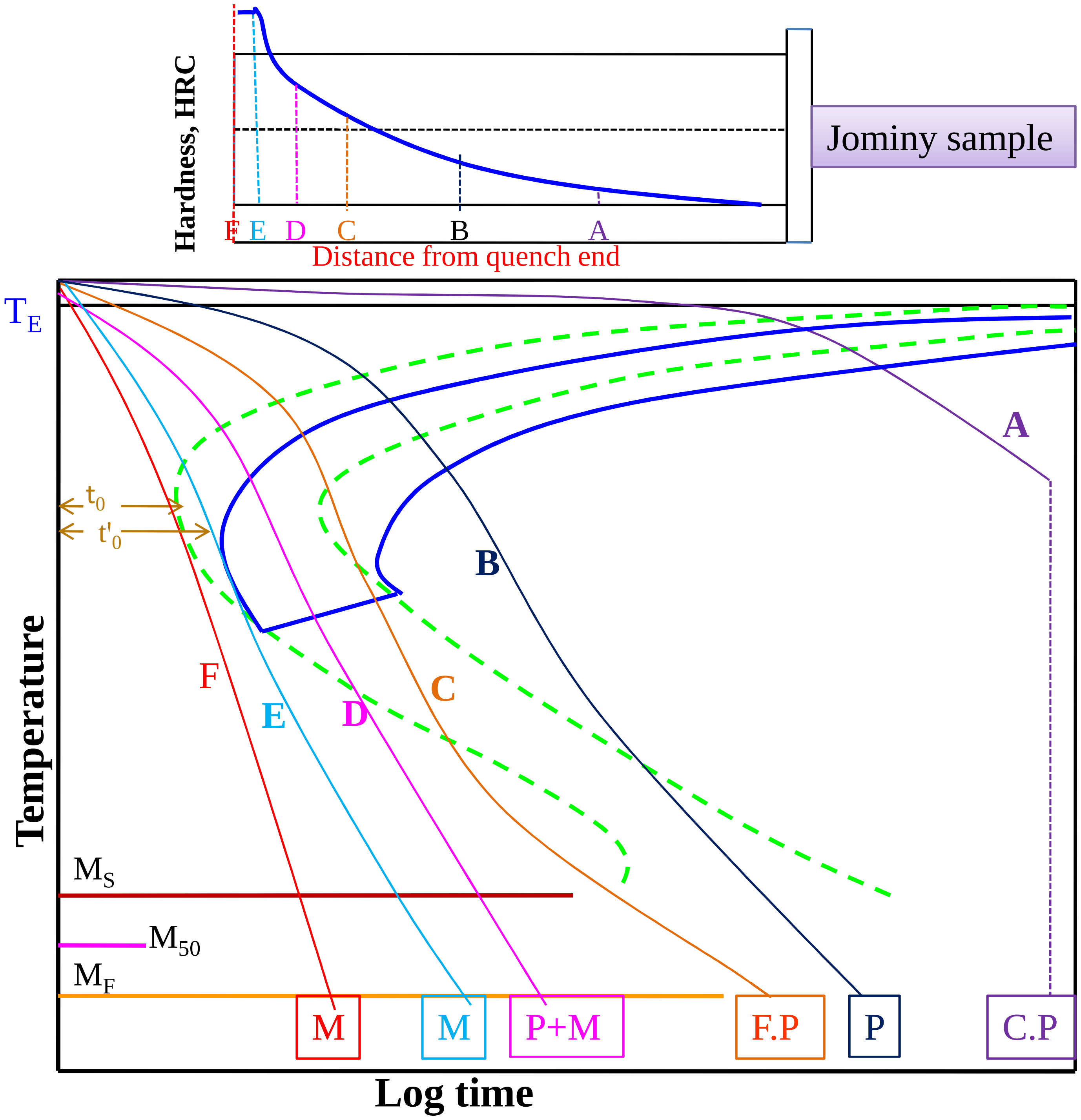




Jominy Distance (in.)	Cooling Rate (°C/s)
$\frac{1}{16}$	315
$\frac{2}{16}$	110
$\frac{3}{16}$	50
$\frac{4}{16}$	36
$\frac{5}{16}$	28
$\frac{6}{16}$	22
$\frac{7}{16}$	17
$\frac{8}{16}$	15
$\frac{10}{16}$	10
$\frac{12}{16}$	8
$\frac{16}{16}$	5
$\frac{20}{16}$	3
$\frac{24}{16}$	2.8
$\frac{28}{16}$	2.5
$\frac{36}{16}$	2.2

Jominy End Quench method - Principle

- A number of Jominy end quench samples are first end- quenched for a series of different times and then each of them (whole sample) is quenched by complete immersion in water to freeze the already transformed structures.
- Cooling curves are generated putting thermocouple at different locations and recording temperature against cooling time during end quenching.
- Microstructures at the point where cooling curves are known, are subsequently examined and measured by quantitative metallography. Hardness measurement is done at each investigated point.
- Based on metallographic information on investigated point the transformation start and finish temperature and time are determined. The transformation temperature and time are also determined for specific amount of transformation.
- These are located on cooling curves plotted in a temperature versus time diagram. The locus of transformation start, finish or specific percentage of transformation generate CCT diagram (*see next slide*).
- A, B, C, D, E, F are six different locations on the Jominy sample shown in *Figure (before slide)* that gives six different cooling rates. The cooling rates A, B, C, D, E, F are in increasing order.
- The corresponding cooling curves are shown on the temperature log time plot. At the end of the cooling curve phases are shown at room temperature. Variation in hardness with distance from Jominy end is also shown in the diagram.

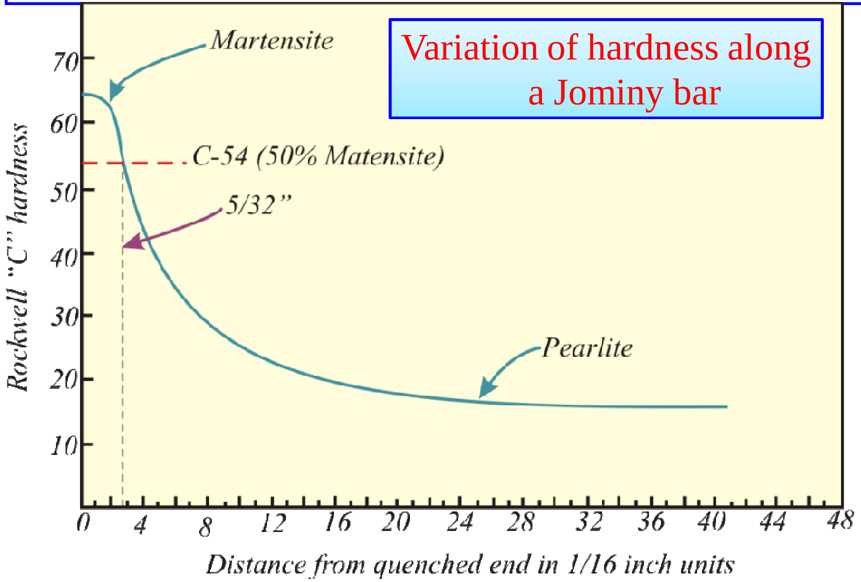


t_o=Minimum incubation period at the nose of the TTT diagram,
t'_o=minimum incubation period at the nose of the CCT diagram

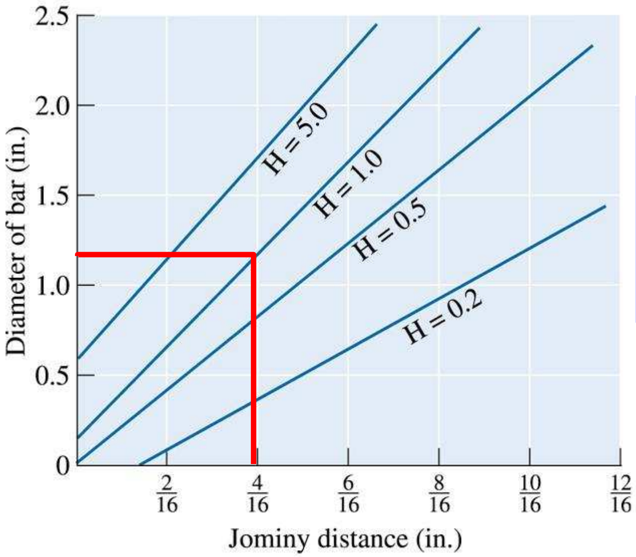
M – Martensite
P – Pearlite
F.P – Fine pearlite
C.P – Coarse pearlite
M_S – Martensite start
M_F – Martensite finish
T_E – Eutectoid temp.

Determination of Hardenability from Jominy curve

- After plotting the Jominy distance Vs Hardness curve, the Jominy distance having hardness equal to 50 % martensite is determined.
- Then the diameter of a rod having cooling rate similar to the cooling rate at the Jominy distance having 50 % martensite is determined from the graph correlating the Jominy distance with the diameter of the rod having similar cooling rate for water quenching.
- This diameter gives the hardenability of the steel in water quenching (having H value equal to 1).
- Hardenability in any other quenchants can be determined from the same graph.
- D_I (hardenability in ideal quenching medium) can also be determined in a similar manner.
- We can determine hardenability for any other amount of martensite in the core in any quenchants in a similar way.



Variation of hardness along a Jominy bar

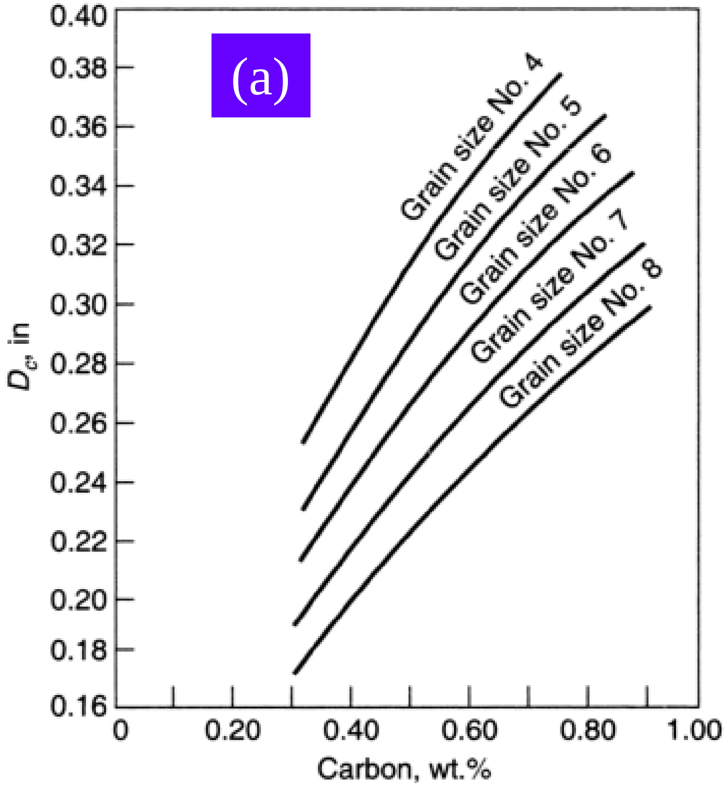


Grossman chart used to determine the hardenability of a steel bar

Estimation of Hardenability from chemical composition

- Although the ideal critical diameter is generally determined experimentally, it is also possible to estimate it from chemical composition and the grain size of steel
- This method is based on the fact that the hardening of steel is controlled basically by the carbon content.
- Every steel has a base hardenability which depends only on carbon content and grain size. Alloying additions change the rate of reaction.

- Furthermore, the effect of each alloying element is independent of other alloying elements. The effect is also independent of carbon content and grain size.
- Figure gives base hardenability in terms of ideal critical diameter. It is clear from the figure that, as the carbon content and grain size decreases, the base diameter value also declines.
- The effect of alloying elements in the hardenability is shown in Figure (b) (next page).
- Mo, Mn and Cr are seen to very effective. The base diameter obtained from Figure (a) is multiplied by the multiplying factors F for each of the alloying elements given in figure (b)

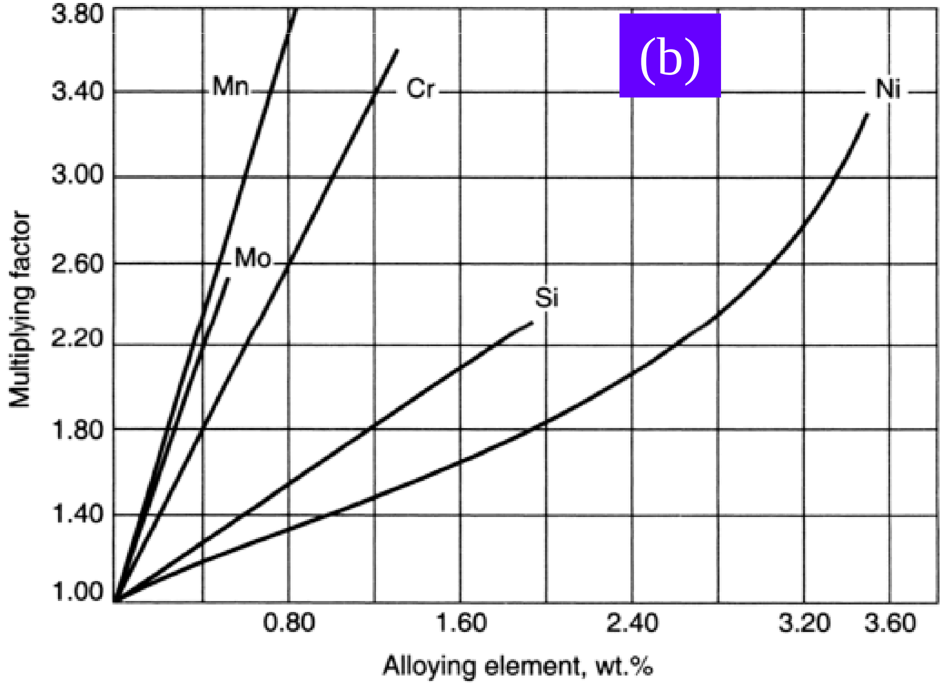


Base diameter as function of carbon content and grain size

Estimation of Hardenability from chemical composition

$$D_I = D_C(basediameter) \times F_{Mn} \times F_{Cr} \times F_{Ni}$$

- For example, for a steel of grain size ASTM 8, with 0.5% carbon, 0.6% Mn, 1% Cr and 2%Ni, D_I = 0.22 (From figure a) × 3.00 (Mn factor from figure b) × 3.17 (Cr factor from figure b) × 1.77 (Ni factor from figure b) = 3.70 inches
- Sulphur and phosphorous are present in low concentrations in steel as impurity. Their combined effect can be ignored in most of the cases. Multiplying factors for sulphur and phosphorus are unity



Multiplying factor F as a function of weight % for a set of alloying elements

Significance of Hardenability Multiplying factor

- The Hardenability Multiplying Factor shows the rate at which the hardening depth is increased with the percentage of the alloying element
- The ideal diameter (D_I) is calculated from: $D_I = D_{Critical} \times F_{Mn} \times F_{Cr} \times F_{Ni} \times F_{Si} \times F_{Mo}$
- Where D_{IC} is the basic D_I factor for carbon and fx is the multiplying factor for the alloying element x.

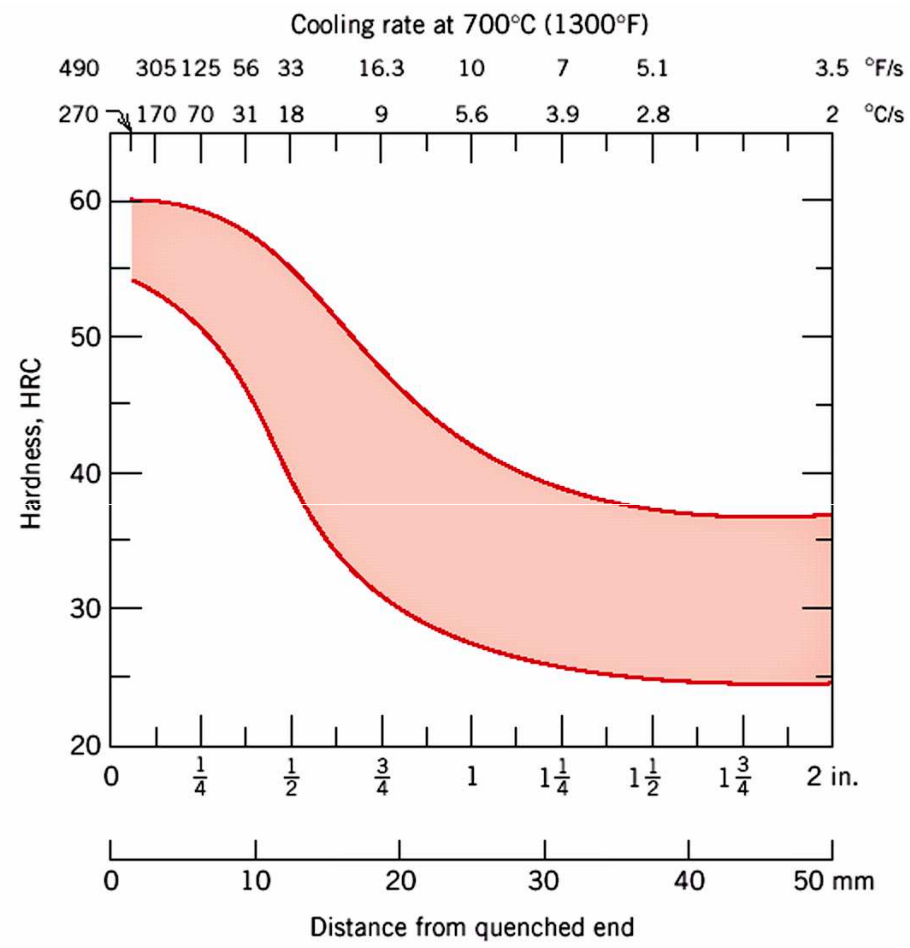
Carbon	grain size			Alloying factor, *fX*				
%	No. 6	No. 7	No.8	Mn	Si	Ni	Cr	Mo
0.05	0.0814	0.0750	0.0697	1.167	1.035	1.018	1.1080	1.15
0.10	0.1153	0.1065	0.0995	1.333	1.070	1.036	1.2160	1.30
0.15	0.1413	0.1315	0.1212	1.500	1.105	1.055	1.3240	1.45
0.20	0.1623	0.1509	0.1400	1.667	1.140	1.073	1.4320	1.60
0.25	0.1820	0.1678	0.1560	1.833	1.175	1.091	1.5400	1.75
0.30	0.1991	0.1849	0.1700	2.000	1.210	1.109	1.6480	1.90
0.35	0.2154	0.2000	0.1842	2.167	1.245	1.128	1.7560	2.05
0.40	0.2300	0.2130	0.1976	2.333	1.280	1.246	1.8640	2.20
0.45	0.2440	0.2259	0.2090	2.500	1.315	1.164	1.9720	2.35
0.50	0.2580	0.2380	0.2200	2.667	1.350	1.182	2.0800	2.50
0.55	0.2730	0.2510	0.2310	2.833	1.385	1.201	2.1880	2.65
0.60	0.284	0.262	0.2410	3.000	1.420	1.219	2.2960	2.80
0.65	0.295	0.273	0.2551	3.167	1.455	1.237	2.4040	2.95
0.70	0.306	0.283	0.260	3.333	1.490	1.255	2.5120	3.10
0.75	0.316	0.293	0.270	3.500	1.525	1.273	2.6200	3.25
0.80	0.326	0.303	0.278	3.667	1.560	1.291	2.7280	3.40
0.85	0.336	0.312	0.287	3.833	1.595	1.309	2.8360	3.55
0.90	0.346	0.321	0.296	4.000	1.630	1.321	2.9440	3.70
0.95	-	-	-	4.167	1.665	1.345	3.0520	-
1.00	-	-	-	4.333	1.700	1.364	3.1600	-

Fracture Test

- There is a contrast in the nature of fracture undergone by martensitic and pearlitic regions.
- Whereas martensite formed on the case exhibits brittle fracture, the pearlite formed in the core undergoes ductile fracture.
- Where there is changeover from martensitic to pearlitic structure, there is corresponding sharp change from brittle to ductile fracture.
- It is similar to a sudden change in hardness or microstructure as one passes from martensitic to pearlite region.
- This region of sudden change is the one that contains 50% pearlite and 50% martensite.
- The method based on the nature of fractured surface is successful when the transformation processes is quick and a sharp boundary is formed.
- When the transformation is sluggish, the method cannot be applied since the gradient in hardness is gradual, and it is not possible to get a clear demarcating boundary.

Hardenability Band

- The industrial products of steels may change composition and average grain size from batch to batch, therefore, the measured hardenability of a given type of steel should be presented as a band rather than a single line, as demonstrated by the Figure at right
- Hardenability data now exists for a wide range of steels in the form of maximum and minimum end-quench hardenability curves, usually referred to as hardenability bands.
- This data is, available for very many of the steels listed in specifications such as those of the American Society of Automotive Engineers (SAE), the American Iron and Steel Institute (AISI) and the British Standards.



Factors effecting Hardenability

- **Slowing the phase transformation of austenite to ferrite and pearlite** increases the hardenability of steels.
- The most important variables which influence hardenability are
  - Quenching conditions
  - Austenitic grain size
  - Carbon content
  - Alloying elements

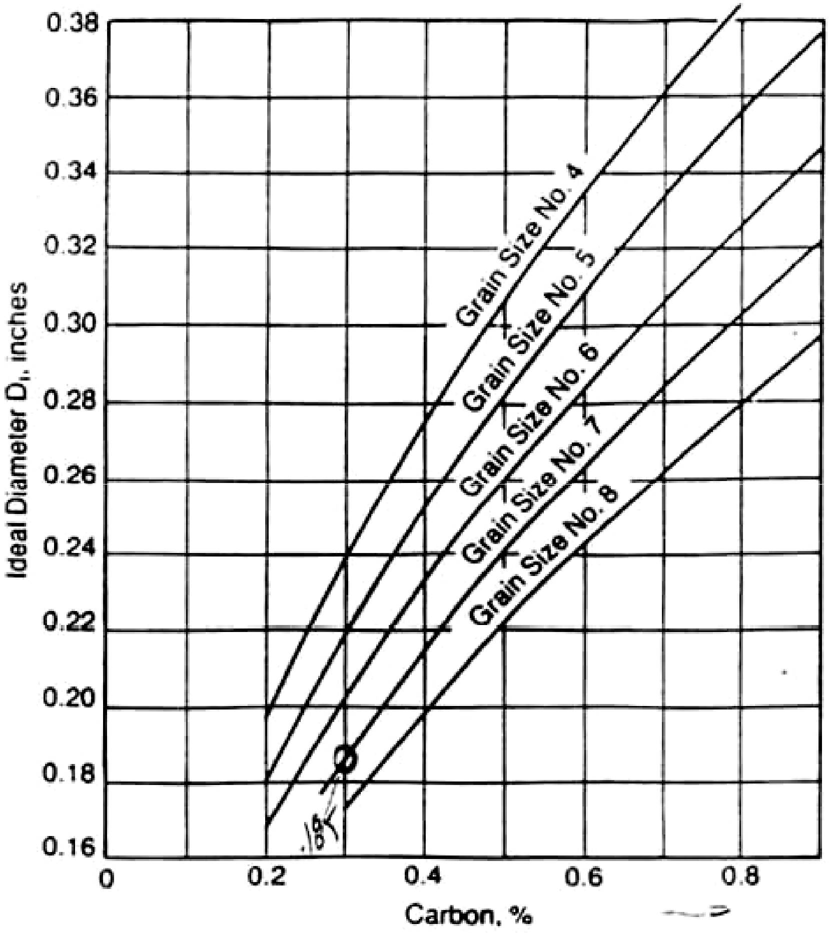
Quenching Conditions

- The fluid used for quenching the heated alloy effects the hardenability.
- Each fluid has its own thermal properties like..
  - ✓ Thermal conductivity
  - ✓ Specific heat
  - ✓ Heat of vaporization
- These cause rate of cooling differences
- Ideal quenchant : It is one which brings down the surface temperature to room temperature instantaneously and keeps it at that temperature thereafter.

Factors effecting Hardenability

Austenitic grain size

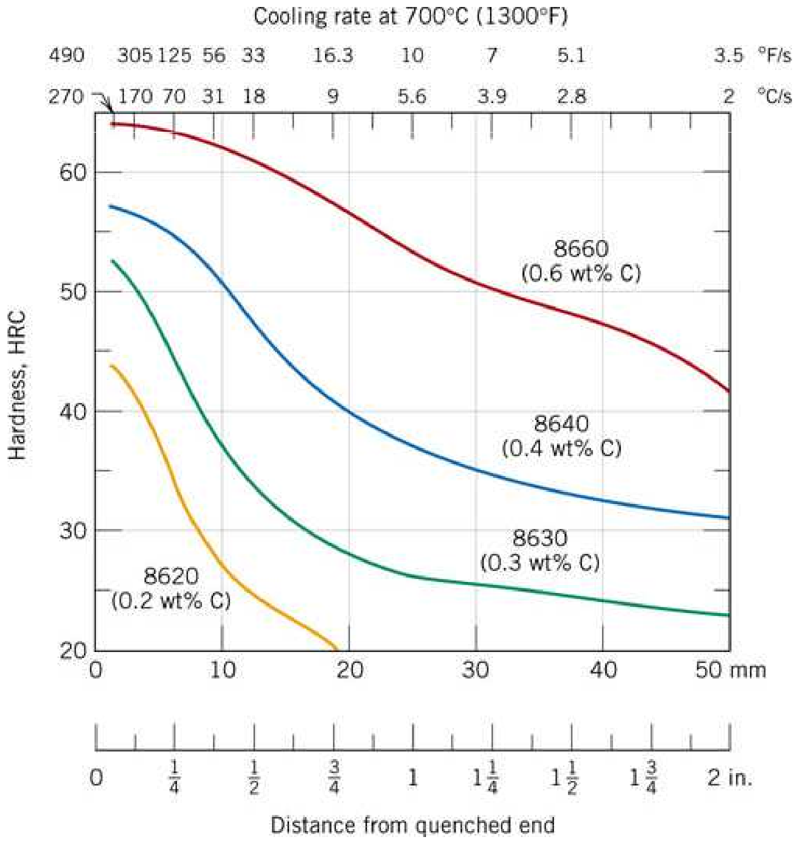
- The hardenability increases with increasing austenite grain size, because the grain boundary area which act as nucleating site is decreasing.
- This means that the sites for the nucleation of ferrite and pearlite are being reduced in number, with the result that these transformations are slowed down, and the hardenability is therefore increased.
- The more γ-grain boundary surface the easier it is for pearlite to form rather than martensite
- Smaller γ-grain size → lower hardenability
- Larger γ-grain size → higher hardenability



Factors effecting Hardenability

Percentage of carbon

- ❑ Carbon is primarily a hardening agent in steel.
- ❑ It also increases hardenability by slowing the formation of pearlite and ferrite.
- ❑ But its use at higher levels is limited, because of the lack of toughness which results in greater difficulties in fabrication and, most important, increased probability of distortion and cracking during heat treatment and welding.

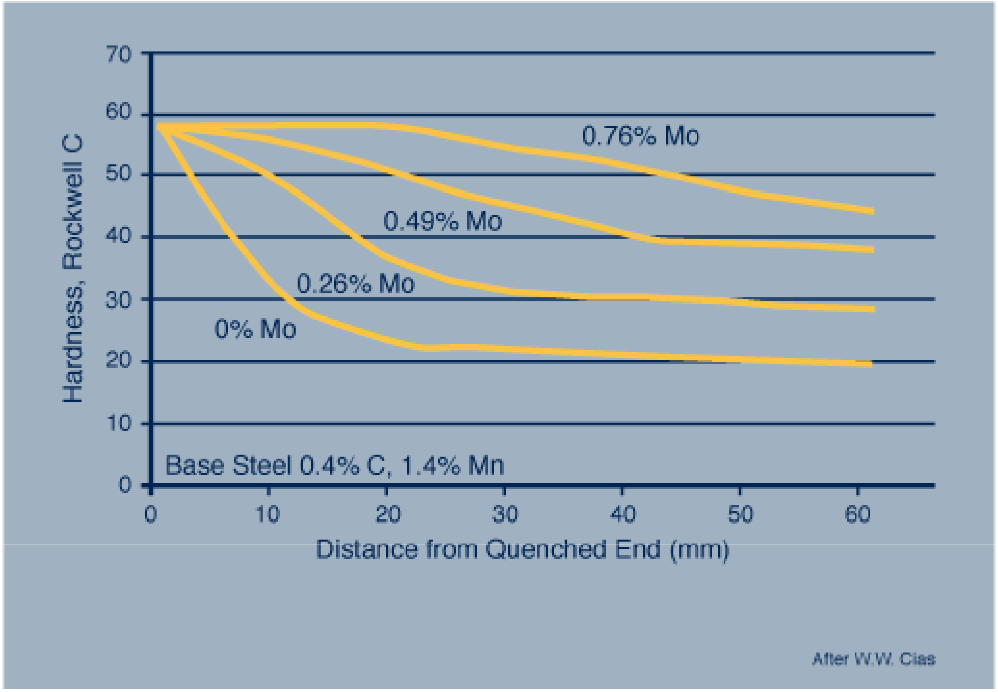


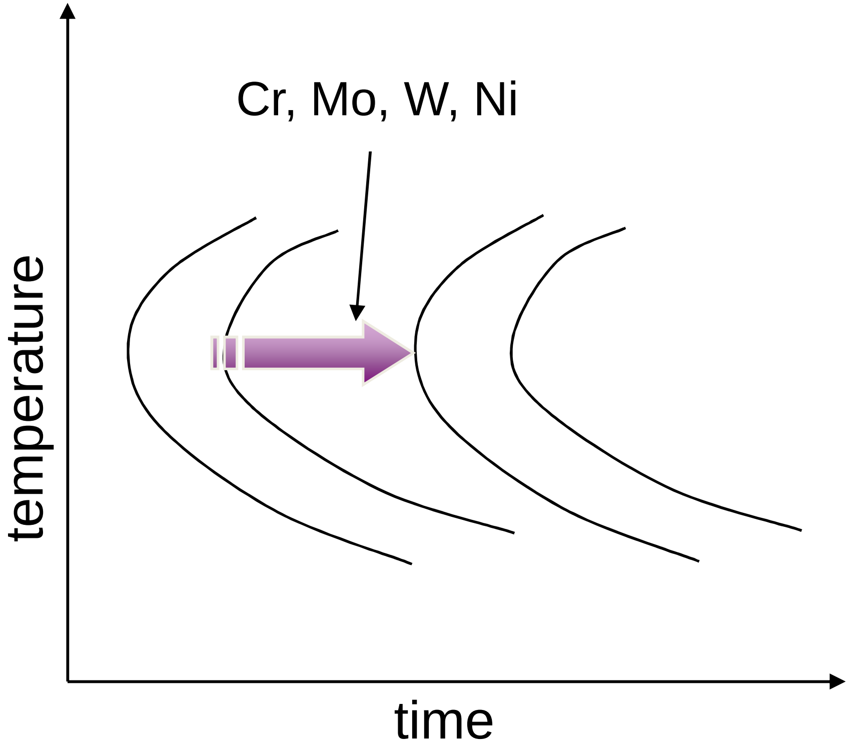
Factors effecting Hardenability

Effect of alloying elements

- Most metallic alloying elements slow down the ferrite and pearlite reactions, and so also increase hardenability. However, quantitative assessment of these effects is needed.
- Chromium, Molybdenum, Manganese, Silicon, Nickel and Vanadium all effect the hardenability of steels in this manner. Chromium, Molybdenum and Manganese being used most often.
- Boron can be an effective alloy for improving hardenability at levels as low as .0005%.
- Boron has a particularly large effect when it's added to fully deoxidized low carbon steel, even in concentrations of the order of 0.001%, and would be more widely used if its distribution in steel could be more easily controlled.
- The most economical way of increasing the hardenability of plain carbon steel is to increase the manganese content, from 0.60 wt% to 1.40 wt%, giving a substantial improvement in hardenability.
- Chromium and molybdenum are also very effective, and amongst the cheaper alloying additions per unit of increased hardenability.
- Hardenability of a steel increases with addition of alloying elements such as Cr, V, Mo, Ni, W $\rightarrow$ TTT diagram moves to the right.

Factors effecting Hardenability

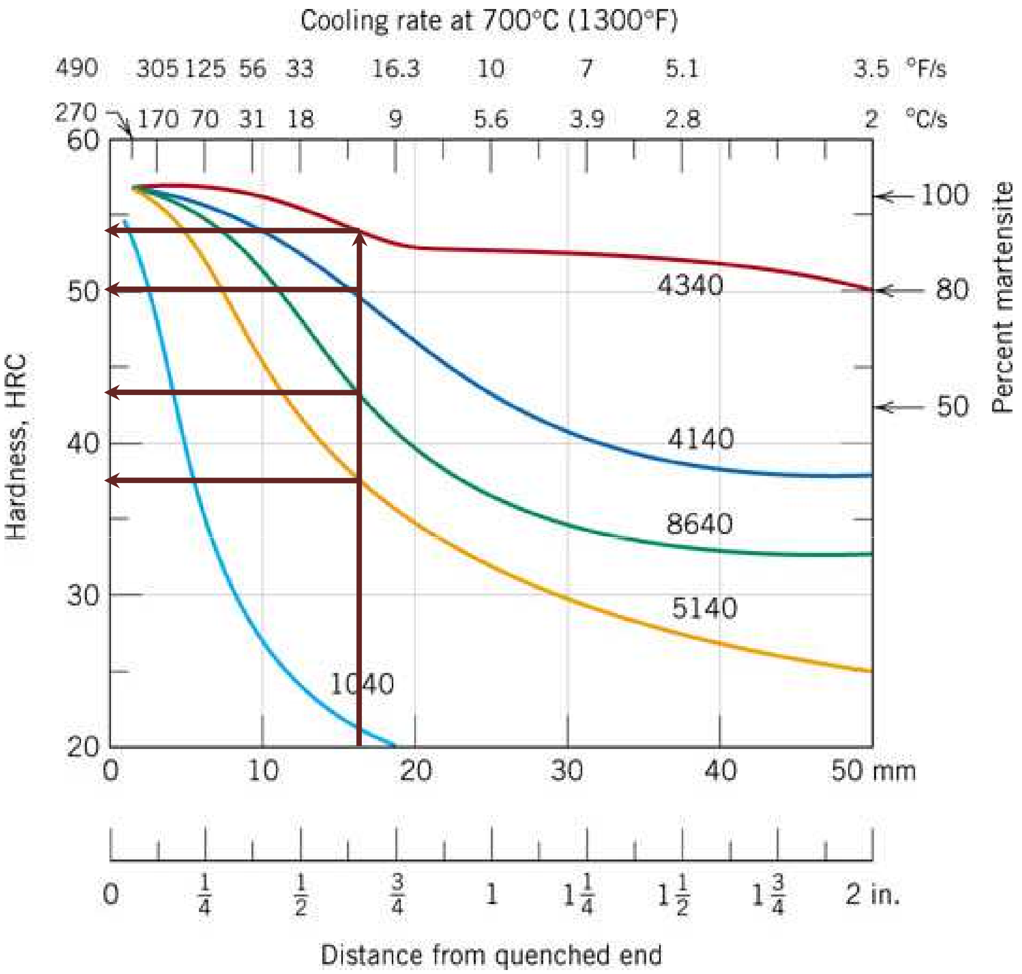




Exceptions

- ❑ S - reduces hardenability because of formation of MnSand takes Mn out of solution as MnS
- ❑ Ti - reduces hardenability because it reacts with C to form TiC and takes C out of solution; TiC is very stable and does not easily dissolve
- ❑ Co - reduces hardenability because it increases the rate of nucleation and growth of pearlite

Factors effecting Hardenability



Hardness at center of a 3 inch bar is different for different steels indicating different amounts of martensite at the center

- ❑ All steels have 0.4wt% C, but with different alloying elements. (in the figure shown)
- ❑ At the quenched end all alloys have the same hardness, which is a function of carbon content only.
- ❑ The hardenability of the 1040 is low because the hardness of the alloy drops rapidly with Jominy distance. The drop of hardness with Jominy distance for the other alloys is more gradual.
- ❑ The alloying elements delay the austenite-pearlite and/or bainite reactions, which permits more martensite to form for a particular cooling rate, yielding a greater hardness.

Effect of boron on Hardenability

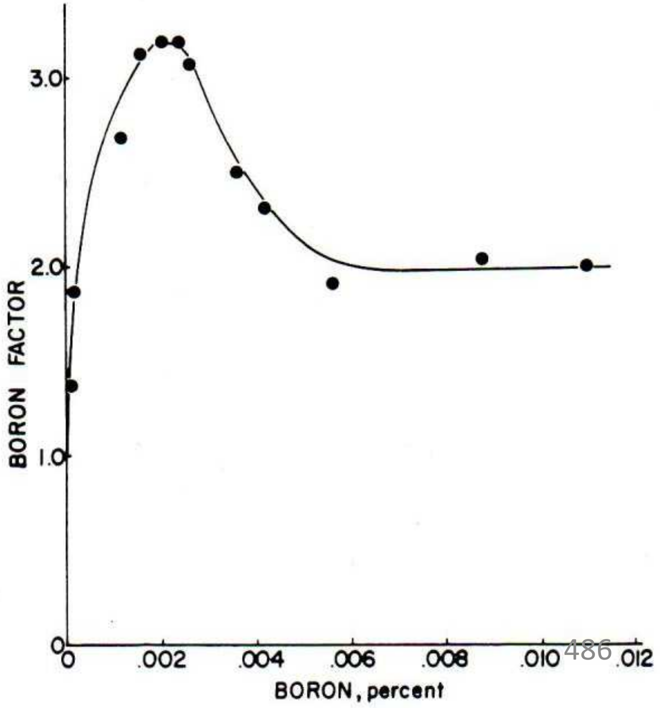
- Boron is added to steel for only one reason-to increase hardenability. Boron-treated steels have certain peculiar characteristics
- Boron increases hardenability in hypoeutectoid steel, has no effect on eutectoid steel, and decreases hardenability in hypereutectoid stee.
- As the austenite grain site becomes finer, the hardenability effect of B increases.
- Austenitizing at high temperature reduces the hardneability effect of B.
- For the maximum B effect, the concentration should be in the range 0.0005 to 0.003 wt%.
- Increasing hardenability by adding B does not decrease the M_s temperature.
- These arise because of the manner in which B produces its effect and the interactions of B with other elements in steel.
- To be effective, B must be in solid solution in austenite. The solubility of B in austenite is very low, for example, the solubility at 912°C is about 0.001 wt% , increasing with temperature to a maximum value of about 0.005 wt% at the eutectic.
- In α-iron, the solubility is essentially zero, but is influenced by the impurities present. Because of its low solubility in austenite, B can be highly concentrated in grain boundaries.
- When a boron steel is cooled from the hardening temperature the solubility of boron is reduced, which results in a still greater concentration of B at the grain boundaries.
- Minute grains of boron carbide $Fe_{23}(BC)_6$ are formed there and to some extent they assume an orientation coherent with one of the two austenite grains between them which separate out.

Effect of boron on Hardenability

- Atomic contact is thereby established between $Fe_{23}(BC)_6$ and austenite, resulting in a reduction in the surface tension and grain-boundary energy.
- The presence of boron in solid solution and coherent boron carbide in the grain boundaries delays the formation of ferrite and pearlite and also to some extent, bainite; hence increasing the hardenability of the steel
- The effect of B may be expressed quantitatively as the boron factor, which is the ratio of the ideal diameters, D_i, (according to Grossmann) for the steel with and without boron

$$B_F = \frac{D_i with' B'}{D_i without' B'}$$

- D_i (with boron) is derived from the Jominy end-quench hardenability curve; D_i (without boron) is calculated from the chemical composition of the steel.
- The optimum B content, near 0.002 wt%, for increasing hardenability in 0.2% C, 0.65% Mn, 0.55% Mo (wt%) steel is shown in Fig. 15. Boron contents above about 0.003 wt% lead to a loss in hardenability, and B in excess of about 0.004 wt% causes a loss in toughness through precipitation of Fe_2B in austenite grain boundaries.



Questions?

1. Define hardenability? What is the common criterion of hardenability of steels, and why? Enumerate five factors effecting the hardenability of the steel.
2. What is the effect of the presence of a carbide forming elements (on the hardenability of steel) that is not dissolved in austenite prior to hardening processes? And how do the nonmetallic inclusions effects the hardenability of steel?
3. Calculate the hardenability (D_I) of steel composition:

   C = 0.4%, Mn = 0.7, P = 0.04, S = 0.04, Si = 0.3, Ni = 1.8, Cr = 0.8, Mo = 0.25, and ASTM grain size = 8, what could be critical diameter (D_C) in water and oil. What severity of quench would be required to fully harden the bar of 3” in diameter?
4. Differentiate between hardness and hardenability
5. Define and explain the term severity of quench. Explain the its impact on hardenability
6. Discuss how hardenability is affected by: (i) austenitic grain size (ii) carbon content (iii) presence of alloying elements
7. Distinguish between
   a) Pearlitic hardenability and bainitic hardenability
   b) Core and case hardenability
   c) Shallow hardening and deep hadening steels

Questions?

8. Discuss the effect of boron on hardenability
    a) "Boron is added in steels to increase the hardenability" comment
    b) What is the effect austenitising temperature, increased carbon, on boron hardenability.
9. Which elements are commonly used to increase hardenability of the steels? And what are the disadvantages of steels of high hardenability?
10. What are the various methods of determining hardenability?

Iron - Graphite Phase diagram

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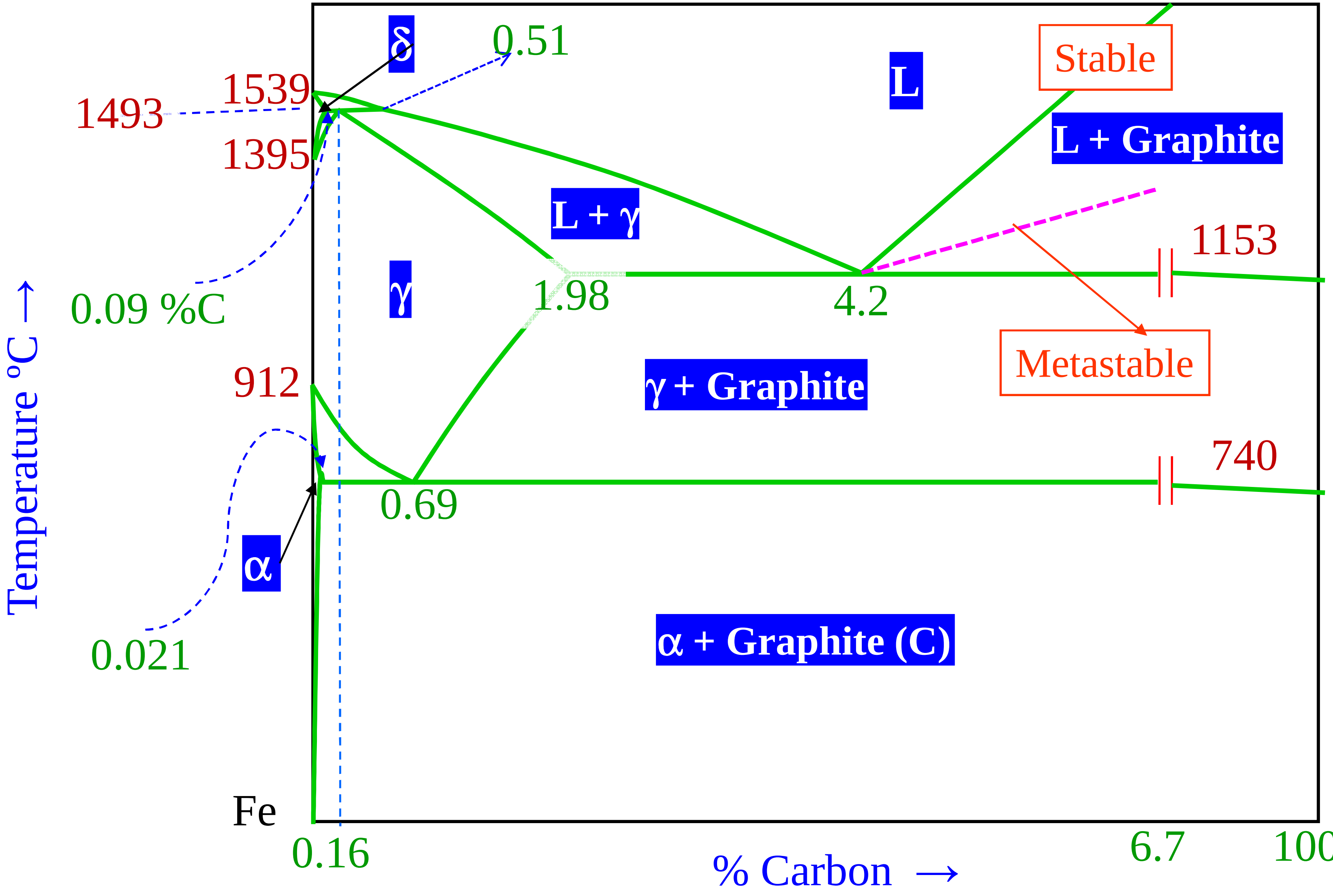
Iron – Graphite Phase Diagram

- ❑ The true equilibrium diagram for iron and carbon is generally considered as iron-graphite phase diagram *(next slide)*.
- ❑ Earlier we learn about iron-iron carbide phase diagram and it is not a true equilibrium diagram, generally it is called metastable iron - iron carbide phase diagram.
- ❑ Cementite (Fe_3C) is a metastable compound, and under some circumstances it can be made to dissociate or decompose to form ferrite and graphite, according to the reaction

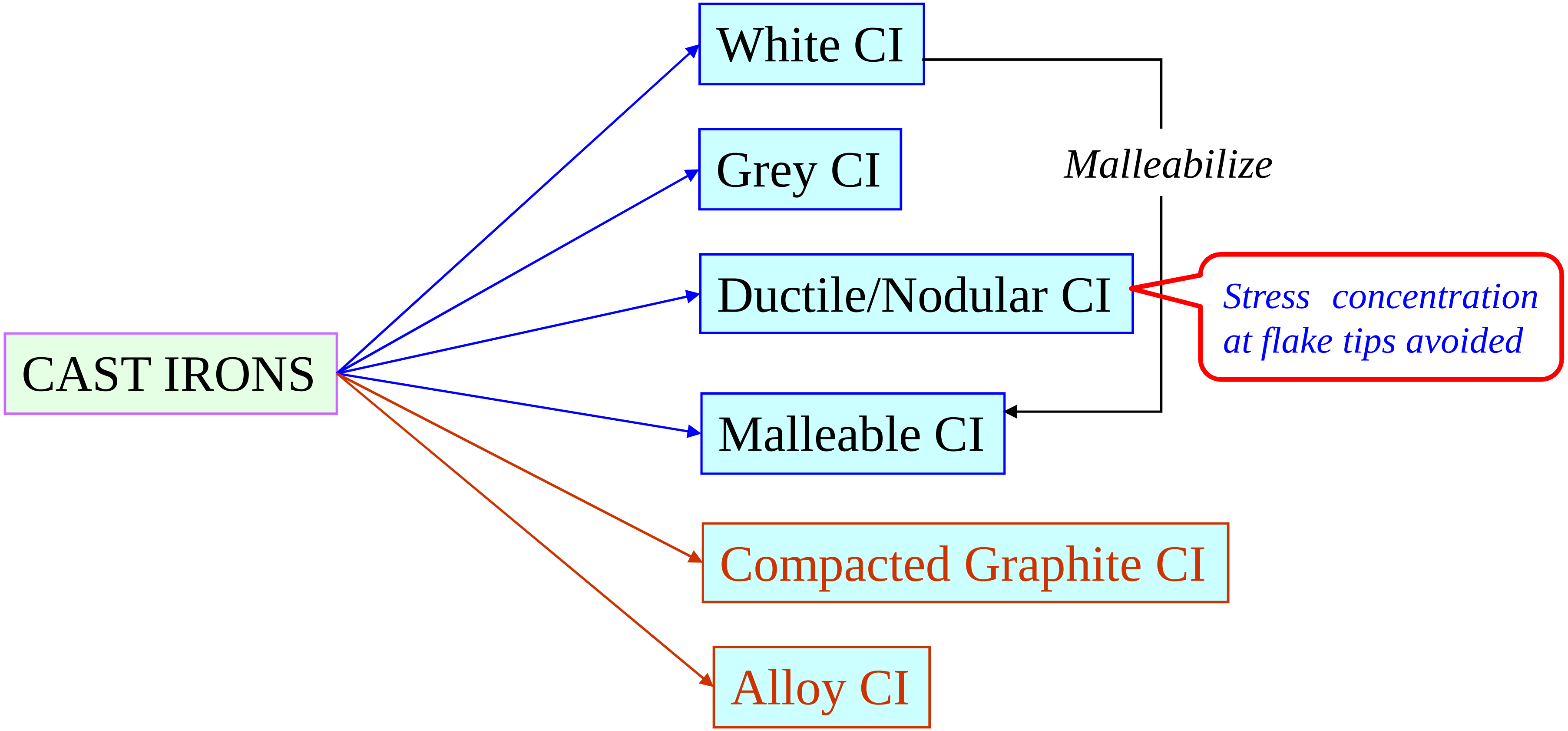
$$\boxed{Fe_3C \rightarrow 3Fe + C}$$

- ❑ For explain of cast irons we will refers to both Iron-Iron carbide phase diagram and Iron-Graphite phase diagram.
- ❑ Earlier we are studied steel microstructures from Iron-Cementite phase diagram. Same as earlier now we will learn the characteristic features of CAST IRONS with the help of Iron-Graphite phase diagram.
- ❑ Cast irons are a class of ferrous alloys with carbon contents above 2.14 wt%; in practice, however, most cast irons contain between 3.0 and 4.5 wt% C and, in addition, other alloying elements .
- ❑ The ductility of cast iron is very low and brittle, it cannot be rolled, drawn, or worked at room temperature. However they melt readily and can be cast into complicated shapes which are usually machined to final dimensions. Since casting is the only suitable process applied to these alloys, they are known as cast irons.

Iron – Graphite Phase Diagram



Classification of cast irons



CAST IRONS

White CI

Grey CI

Ductile/Nodular CI

Malleable CI

Compacted Graphite CI

Alloy CI

Malleabilize

Stress concentration at flake tips avoided

Good castability ⇒ C > 2.4%

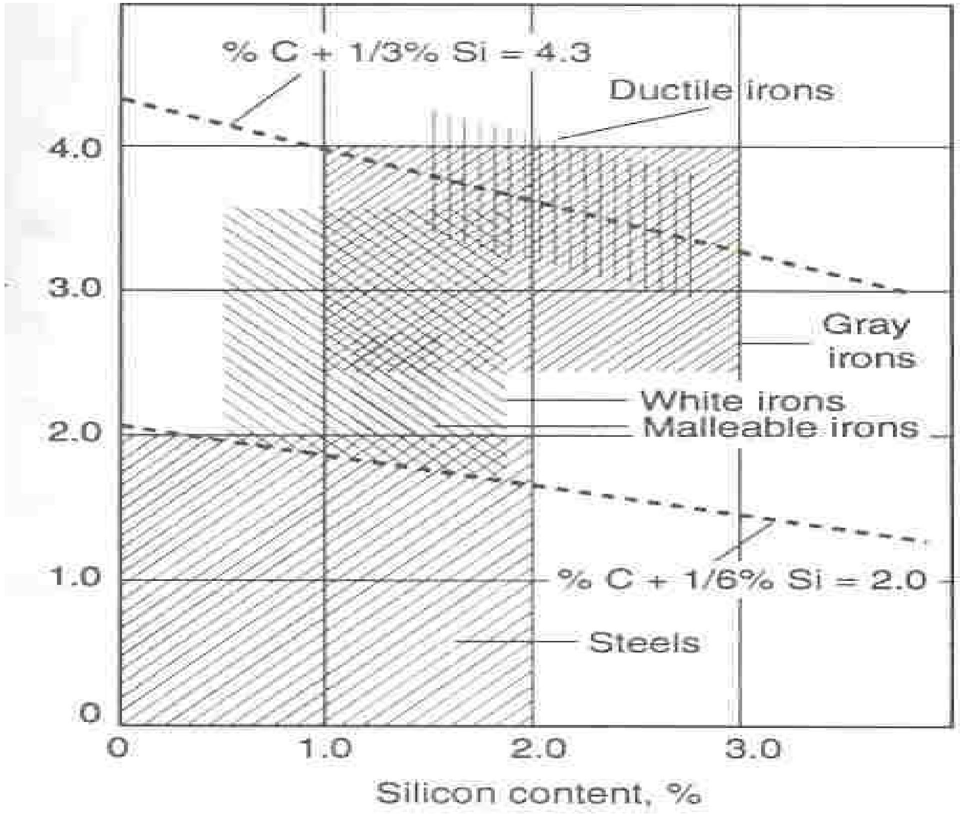
Cast Irons Alloying System

- Most common alloying element of Cast Irons is Silicon for various reasons, which include the manipulation of temperatures required to achieve desired microstructures.
- For example Increases the stability of solidification of Graphite phases. Decreases the stability of the solidification of Fe_3C. Eutectic and eutectoid temperatures change from single values to temperature ranges. Eutectic and eutectoid compositions are affected.

- Carbon Equivalent (CE): a measure of the equivalency of Carbon coupled with other alloying elements to that of just Carbon.   An easier basis for classifying the properties of a multi alloy material.

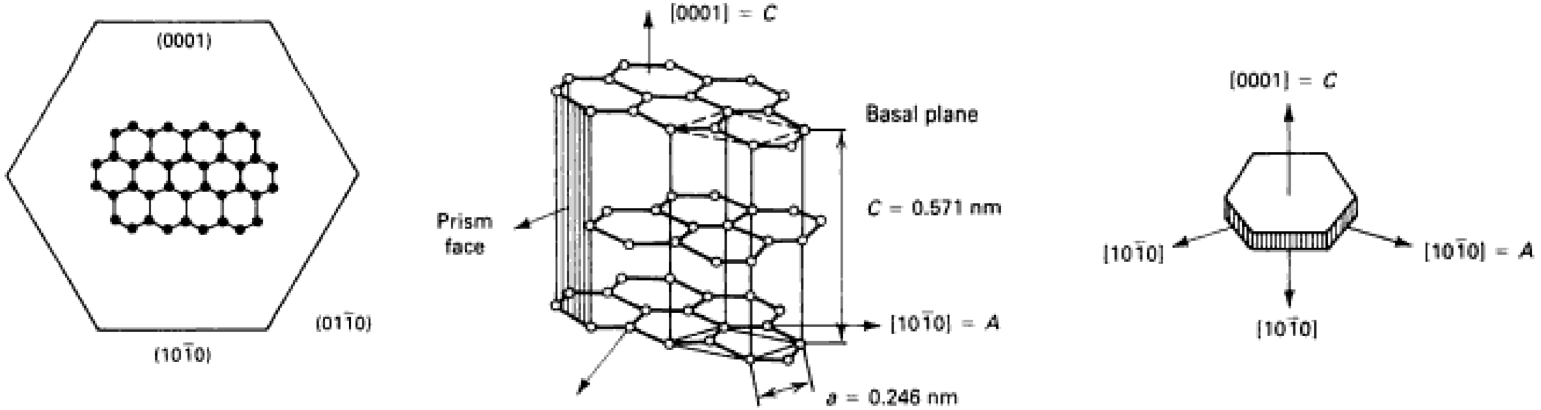
  CE = %C + 1/3%Si = 4.3

- (hypoeutectic) < CE = 4.3 < (hypereutectic), with the addition phosphorus CE = %C + 1/3(%P + %Si)



Solidification of phases in cast irons

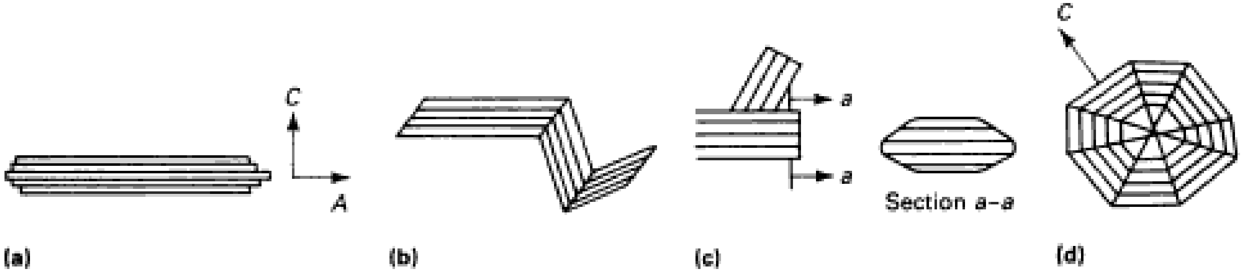
- Graphite structure is a factored crystal bounded by low index planes.
- Growth occurs along $\left(10\bar{1}0\right)$ & (0001) planes (direction A & C). Unstable growth occurs along direction A, giving the Graphite microstructure rough, poorly defined, edges in certain areas.
- When grown from the solidification of liquid Iron Carbon alloys, Graphite takes on a layer structure. Among each layer covalent chemical bonds with strengths between (4.19×10^5 to 5×10^5 J/mol.) exist. Between layers weaker bonds exist on the order of ($4.19 \times 10^3 – 8.37 \times 10^3$)J/mol.
- The structure of the Graphite depends on the chemical composition, the ratio of temperature gradient to growth rate, and the cooling rate. Such structures are:



Crystalline structure of graphite, A and C possible growth directions

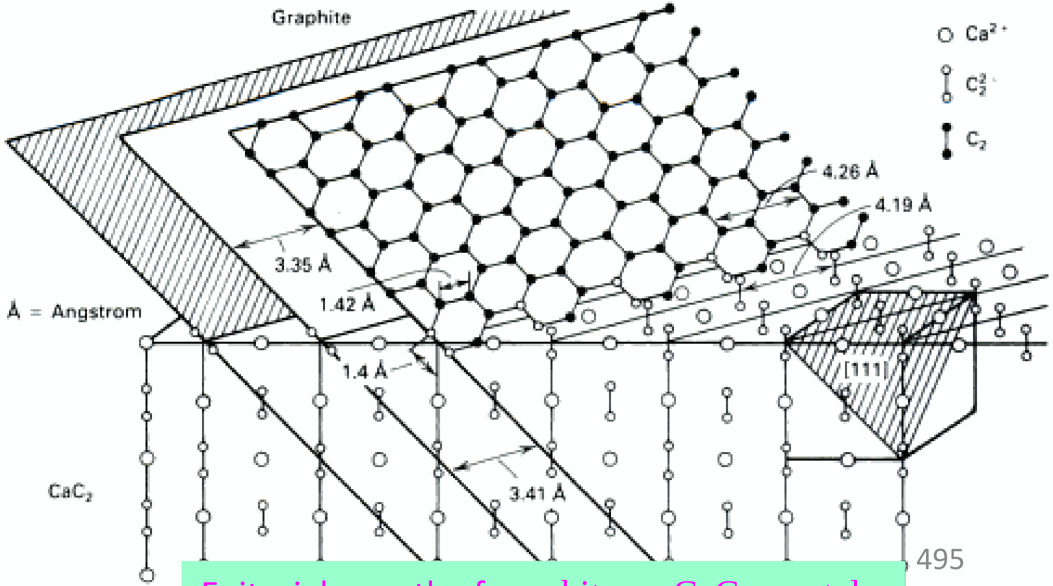
Nucleation of Flake and Spheroidal Graphite

- Such structures are (a) Flake or Plate Graphite, (b) Compacted vermicular graphite, (c) Coral Graphite, (d) Spheroidal Graphite.



- A wide variety of compounds and certain metals have been claimed to serve as either inoculants or nuclei for Flake Graphite growth. (Silicon dioxide, silicates, sulfides, boron nitride, carbides, sodium, potassium, calcium, etc..!)

- Two methods of growth is possible. The nucleation of Flake Graphite Iron occurs mainly on silicon dioxide particles. Another one, Salt like carbides containing the ion Carbon are used as inoculants. Such carbides include $NaHC_2$ & KHC_2 from Group I, CaC_2, SrC_2, BaC_2 from group II, and YC_2 & LaC_2 from group III.



Epitaxial growth of graphite on CaC_2 crystal

Cooling Curve Analysis

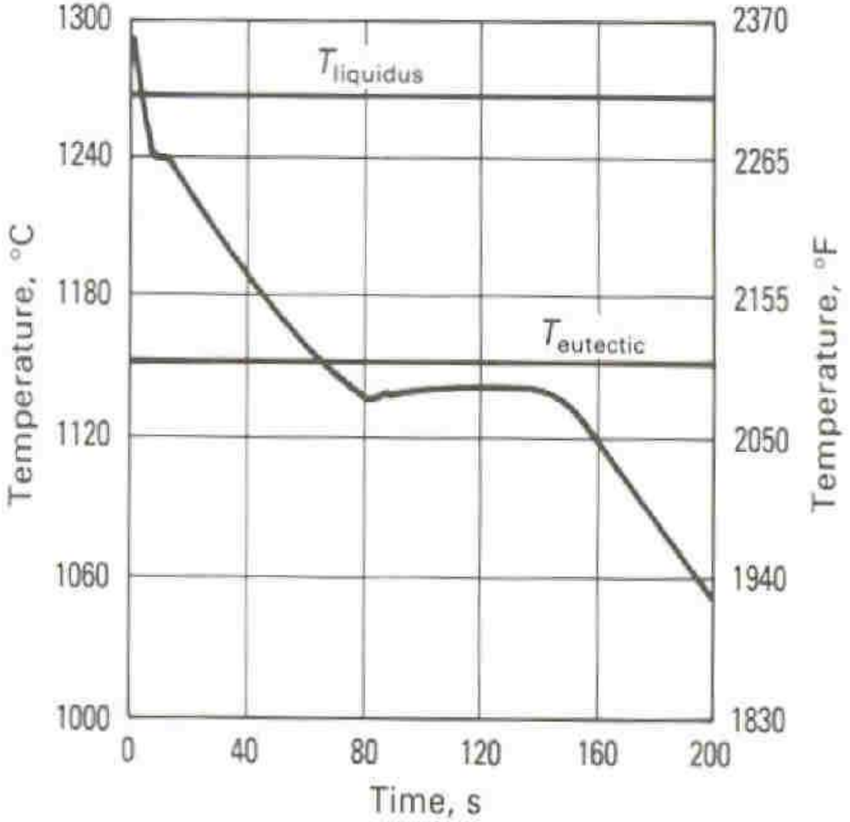
- The solidification of a sample is represented mathematically by the relationship

$$\frac{dQ}{dT} = V\rho C_P \, dT/dt$$

- Where V is the volume of the sample, ρ is the density, C_P is the heat capacity, and dT/dt is the cooling rate of the liquid. dT/dt is the slope of the cooling curve before solidification begins.
- When the liquid cools below the liquidus temperature, crystals nucleate and begin to grow. The rate is thus re-expressed as

$$\frac{dQ}{dT} = (V\rho C_P + \rho \Delta H \, df/dt) dT/dt$$

- Where ΔH is the heat of solidification and df/dt is the volume fraction of solid formed at a changing temperature



Cooling curve for an Iron-carbon alloy with 3.2%C. The solidification starts with a primary precipitation of austenite, followed by a eutectic temperature

White Cast Iron

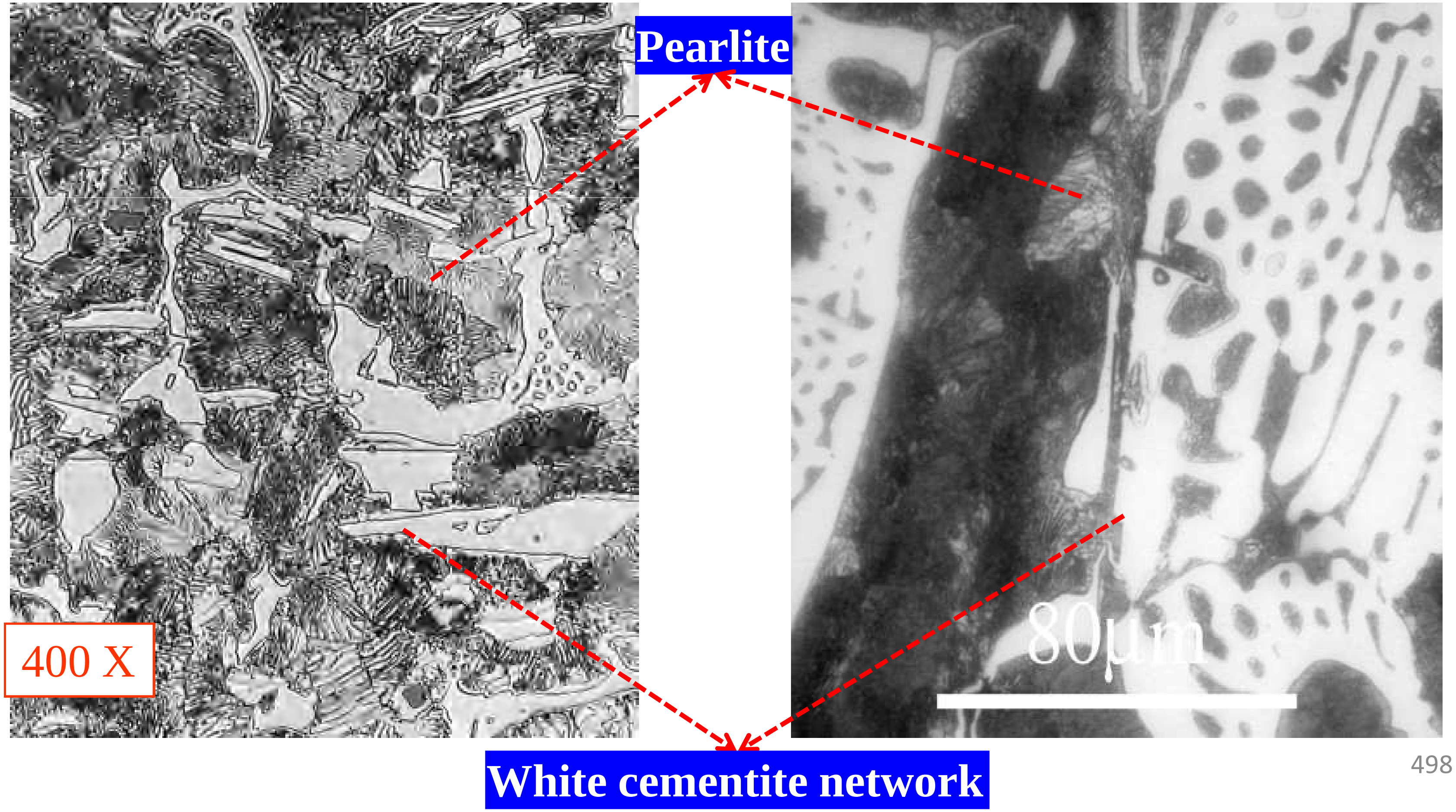
- In which all the C is in the combined form as Fe_3C (Cementite)
- The typical microstructure of white cast iron *(see next slide)*, consisting of dendrites of transformed austenite (pearlite) in a white interdendritic network of cementite.

Microstructure → Pearlite + Ledeburite + Cementite

- White cast iron contains a relatively large amount of cementite as a continuous interdendritic network, it makes the cast iron hard and wear-resistant but extremely brittle and difficult to machine.
- 'completely white' cast irons are limited in engineering applications because of this brittleness and lack of machinability. mainly used in liners for cement mixers, ball mills and extrusion nozzles.
- A large tonnage of white cast iron is used as a starting material for the manufacturer of malleable cast iron.
- Hardness : 375 to 600 BHN, Tensile strength : 135-480 Mpa, Compressive strength: 1380 - 1725 Mpa
- White cast irons fall into three major groups: **Nickel Chromium White Irons**: containing 3-5%Ni, 1-4%Cr. Identified by the name Ni-Hard iron. The **chromium-molybdenum irons** (high chromium irons): 11-23%Cr, 3%Mo, and sometimes additionally alloyed with Ni or Cu. **25-28%Cr White Irons**: contain other alloying additions of Molybdenum and/or Nickel up to 1.5%

White Cast Iron

- ❑ Typical white cast iron contains 2.5-3.5% C, 0.4-1.5% Si, 0.4-0.6% Mn, 0.1-0.4% P, 0.15% S, and balance Fe.
- ❑ During solidification, high internal stresses may be developed due to varying cooling rates across the cross section . These stresses can be relieved by heating white cast iron to about 500-550°C

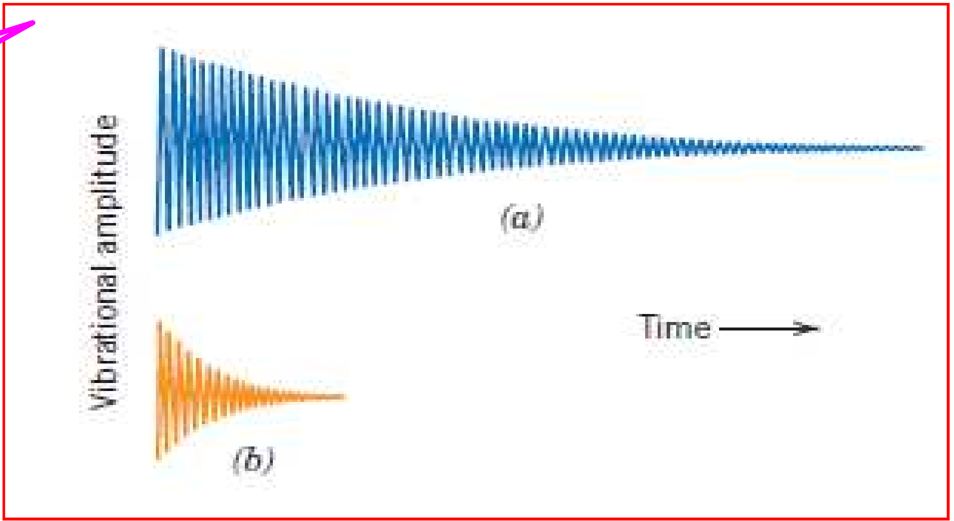


Grey Cast Iron

- ❑ Gray cast iron is obtained by cooling the molten metal slowly during solidification. A typical gray cast iron contains 2.5-3.5% C, 1.4-2.8% Si, 0.5-0.8% Mn, 0.1-0.9% P, and 0.06-0.12% S.
- ❑ Fractured surface of gray cast iron appears grey because of the presence of graphite. Hence the alloy is termed gray cast iron.
- ❑ In the manufacture of gray cast iron the tendency of cementite to separate into graphite and austenite or ferrite is favored by controlling alloy additions and cooling rates.
- ❑ These alloys solidify by first forming primary austenite. The initial appearance of combined carbon is in the cementite resulting from the eutectic reaction. With proper control of carbon content, temperature and the proper amount of graphitizing elements notably silicon, magnesium cerium and, alloy will follow the stable iron – graphite equilibrium diagram.
- ❑ For most of these cast irons, the graphite exists in the form of flakes (similar to corn flakes), which are normally surrounded by an α-ferrite or pearlite matrix.
- ❑ Mechanically, gray iron is comparatively weak and brittle in tension as a consequence of its microstructure; the tips of graphite flakes are sharp and pointed, and may serve as points of stress concentration when an external tensile stress is applied. Strength and ductility are much higher under compressive loads.
- ❑ Gray irons are very effective in damping vibrational energy. Base structures for machines and heavy equipment that are exposed to vibrations are frequently constructed of this material. In addition, gray irons exhibit a high resistance to wear.

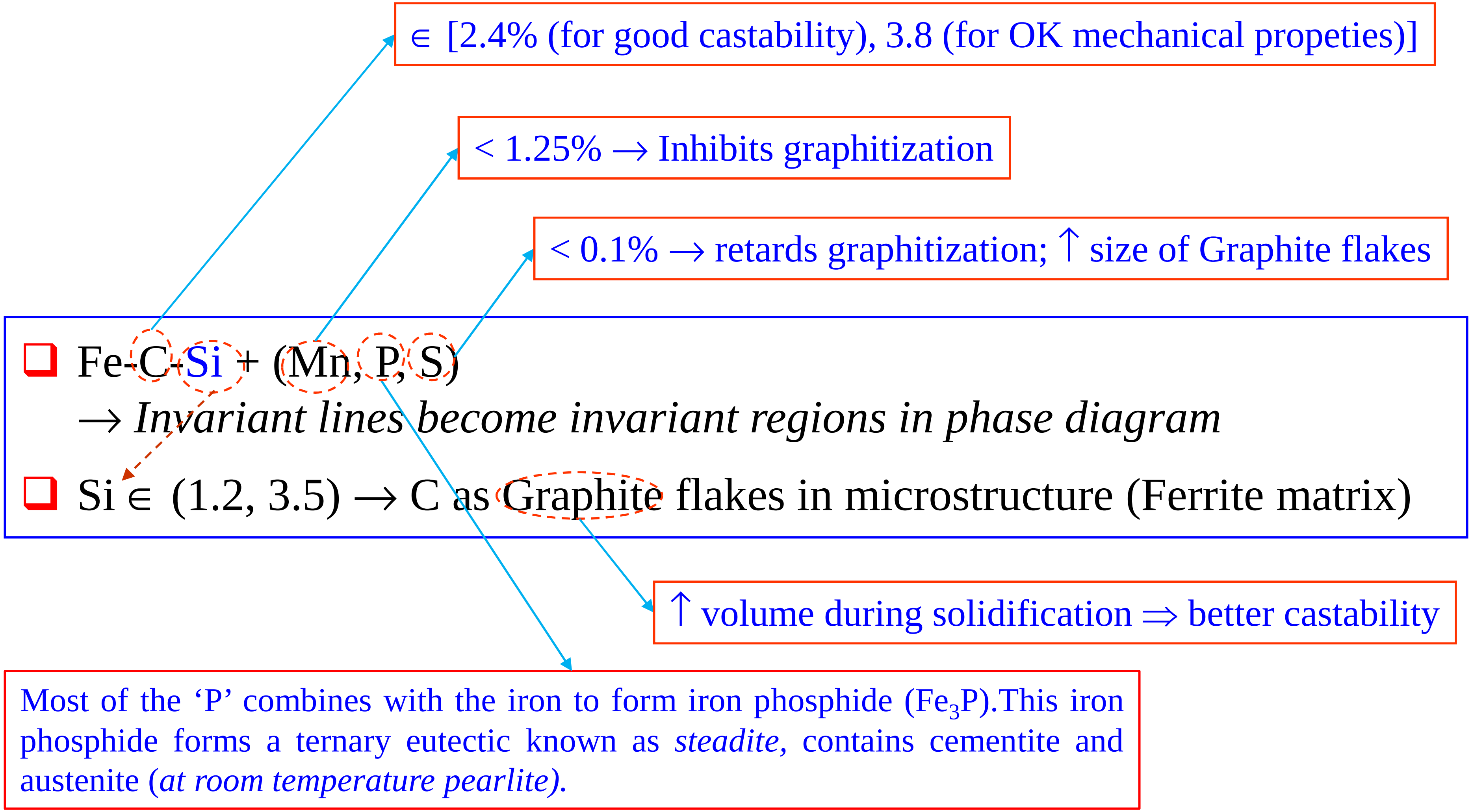
Grey Cast Iron

- Furthermore, in the molten state they have a high fluidity at casting temperature, which permits casting pieces having intricate shapes; also, casting shrinkage is low.
- Finally, and perhaps most important, gray cast irons are among the least expensive of all metallic materials.
- Gray irons having different type of microstructures, it may be generated by adjustment of composition and/or by using an appropriate heat treatment.
- For example, lowering the silicon content or increasing the cooling rate may prevent the complete dissociation of cementite to form graphite. Under these circumstances the microstructure consists of graphite flakes embedded in a pearlite matrix.
- Tensile strength of gray cast iron varies from 100 Mpa to 340 Mpa



Comparison of the relative vibrational damping capacities of *(a) steel and (b) gray cast iron*

Grey Cast Iron



$\in$ [2.4% (for good castability), 3.8 (for OK mechanical propeties)]

< 1.25% → Inhibits graphitization

< 0.1% → retards graphitization; ↑ size of Graphite flakes

- ❑ Fe-C-Si + (Mn, P, S)
  → *Invariant lines become invariant regions in phase diagram*
- ❑ Si $\in$ (1.2, 3.5) → C as Graphite flakes in microstructure (Ferrite matrix)

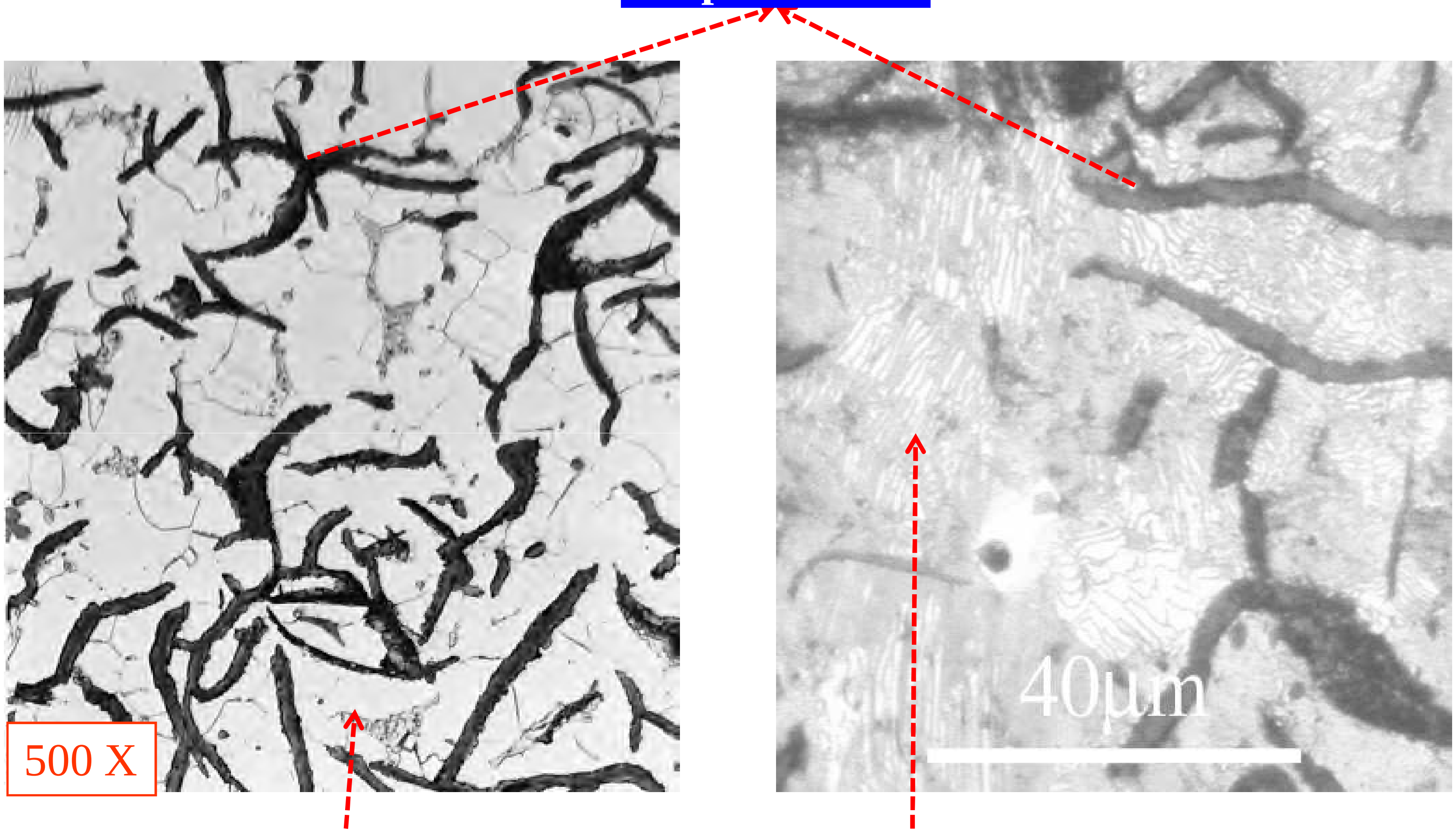
↑ volume during solidification ⇒ better castability

Most of the ‘P’ combines with the iron to form iron phosphide (Fe_3P).This iron phosphide forms a ternary eutectic known as *steadite*, contains cementite and austenite (*at room temperature pearlite).*

$$\mathrm{L} \rightarrow \underbrace{\gamma + (Fe_3C)}_{Ledeburite} \rightarrow \underbrace{\alpha + Fe_3C}_{Pearlite} + (Fe_3C)$$

$$\mathrm{Si}\uparrow \Rightarrow \overleftarrow{C}_{eutectoid}$$

Grey Cast Iron



Graphite flakes

Ferrite matrix

Pearlite matrix

Grey Cast Iron : Heat treatment

The heat treatment given to grey cast iron may be classified is

- ☐ Stress relieving
- ☐ Annealing
  - ✓ Ferritizing annealing
  - ✓ Full annealing
  - ✓ Graphitizing annealing
- ☐ Normalizing
- ☐ Hardening and Tempering

Stress Relieving

- ☐ The purpose of stress relieving in grey cast iron is to relieve residual stresses introduced during solidification, due to different cooling rates prevalent at various section of castings.
- ☐ Residual stresses adversely affect strength and cause distrotion and may even result in cracking in some cases.
- ☐ The temperature of stress relieving is kept much below Ac_1 temperature. For maximum stress relief without changing the microstructure, a temperature range 538-565°C is recommended.
- ☐ In this temperature range, about 80% of the residual stresses are removed with holding time of about one hour. When held at 590°C, more than 85% of the stresses can be removed

Grey Cast Iron : Heat treatment

Annealing

- The purpose of annealing is to soften the grey cast iron and to improve its machinability by minimizing or eliminating massive eutectic carbides.
- Three types of annealing treatment are given to grey cast iron : ferritizing annealing, full annealing, and graphitizing annealing.
- FERRITIZING ANNEALING : To improve machinability in unalloyed or low alloy grey cast iron of normal composition, ferritizing annealing treatment is carried out.
- In this treatment, pearlitic carbide transforms to ferritic matrix and graphite. Ferritic matrix is soft. Above 590°C, the rate of decomposition of iron carbide to ferrite and graphite increases significantly, and at 760°C the rate of decomposition is maximum.
- Therefore for most gray cast irons, the ferritizing annealing temperature is kept between 700°C and 760°C, and the recommended holding time is 1 hour per 25 mm of section.
- Normally, After ferritizing annealing, the annealed specimens are cooled at a rate varying from 100°C/hour to 300°C/hour.
- FULL ANNEALING : If alloy content is high in grey cast iron, then it is difficult to decompose iron carbide into ferrite and graphite at 760°C.
- Therefore, under such conditions, full annealing treatment is adopted. For this treatment, casting is heated to a suitable temperature between 790°C and 900°C and held about 1 hour. Then it is cooled slowly between 790°C and 680°C.

Grey Cast Iron : Heat treatment

Annealing

- GRAPHITIZING ANNEALING : The purpose of graphitizing annealing is to convert massive iron carbide into pearlite and graphite. The treatment is carried out at 900-955°C.
- At this temperature, massive carbide dissolves in austenite which later decomposes to pearlite and graphite on cooling.
- Above 925°C, Fe_3P may also melt. Holding time varies from 15 minutes to several hours.

Normalizing

- The purpose of normalizing treatment for grey cast is to improve mechanical properties such as hardness and tensile strength.
- This treatment also helps restore as cast properties which have been modified by other heating processes such as graphitizing or pre-heat and post-heat treatment of welded joints.
- Normalizing temperature is kept above transformation range, i.e., 885-925°C. Holding time recommended for gray cast iron at normalizing temperature is about 1 hour per 25 mm of maximum thickness.
- Heating temperature significantly affects the mechanical properties, e.g., hardness and tensile strength as also the microstructure.
- Alloying elements such as Cr, Mo, and Ni enhance the strengthening due to normalizing.

Grey Cast Iron : Heat treatment

Hardening and Tempering

- ❑ The purpose of hardening and tempering in grey iron is to improve its strength and wear resistance. After this treatment, the wear resistance of pearlitic grey cast iron increases four to five times.
- ❑ Ordinarily, grey iron is furnace or salt bath hardened from a temperature of about 860-870°C. The transformation range can extend by more than 55°C above the Ac_1 temperature. Approximately Ac_1 temperature of unalloyed grey iron is related to silicon and Manganese content by the relation

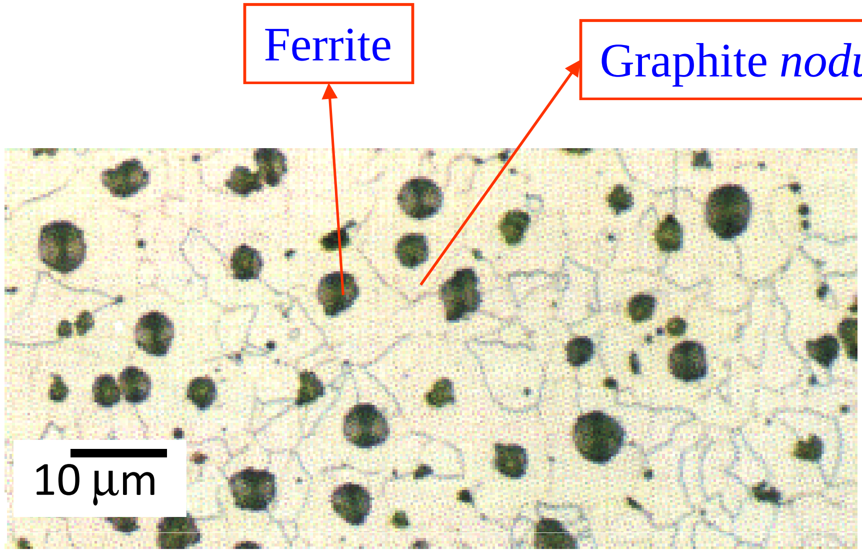
$$Ac_1\ (^\circ C) = 730 + 28.0\ (\%Si) - 25.0\ (\%Mn)$$

- ❑ Tempering treatment increases the toughness and relieves internal stresses which may be developed during quenching. Due to tempering hardness decreases.
- ❑ To achieve maximum toughness in grey iron, tempering temperature of about 370°C is recommended. After tempering at this temperature, the matrix retains a hardness level of 472 BHN.
- ❑ Increase in wear resistance in grey cast iron is achieved by producing a structure consisting of graphite embedded in a martensitic matrix through heat treatment.
- ❑ Flame or induction hardening of grey iron is not so common as furnace hardening because, for adopting the first two methods, a relatively large content of combined carbon is required since very little time is available for carbon to dissolve in austenite. Water is often used as a quenchant with flame or induction hardening where only the outer case is hardened.

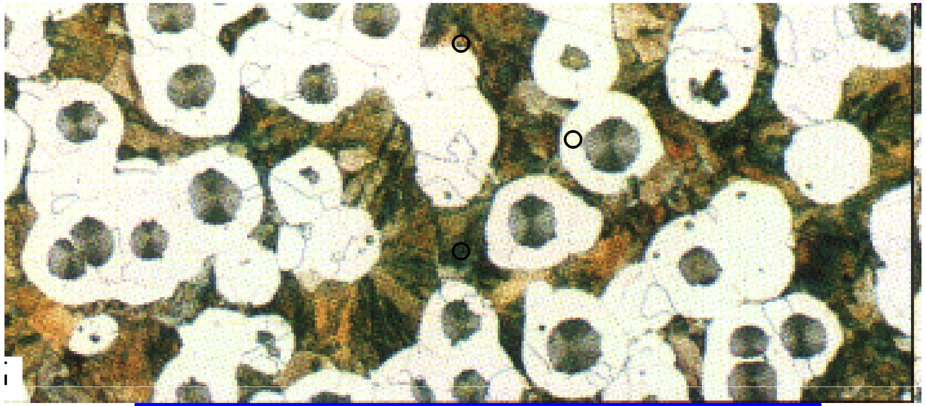
Ductile Cast Iron : Spheroidal Graphite (SG) iron

- Ductile cast iron also called as Nodular cast iron, and Spherulitic cast iron.
- Graphite nodules instead of flakes *(in 2D section)*
- Mg (0.03-0.06)%, Ce, Ca (or other spheroidizing) elements are added
- The elements added to promote spheroidization react with the solute in the liquid to form heterogeneous nucleation sites
- The alloying elements are injected into mould before pouring
- It is thought that by the modification of the interfacial energy the ‘c’ and ‘a’ growth direction are made comparable leading to spheroidal graphite morphology
- The graphite phase usually nucleates in the liquid pocket created by the pro-eutectic γ
- As compared to flaky graphite in grey cast iron, spheroidal graphite does not weaken the matrix considerably. For this reason the mechanical properties of SG iron are superior to gray iron.
- SG iron has tensile strength of 400-700 Mpa, Yield strength 270-390 Mpa, and percentage of elongation 10-20.
- Approx. chemical composition of SG iron is 3.0-3.6%C, 2.0-2.5%Si, 0.6%Mn, 0.04 max P, 0.04 max S, and balance Fe.

Ductile Cast Iron : Spheroidal Graphite (SG) iron



With Ferritic Matrix



With (Ferrite + Pearlite) Matrix

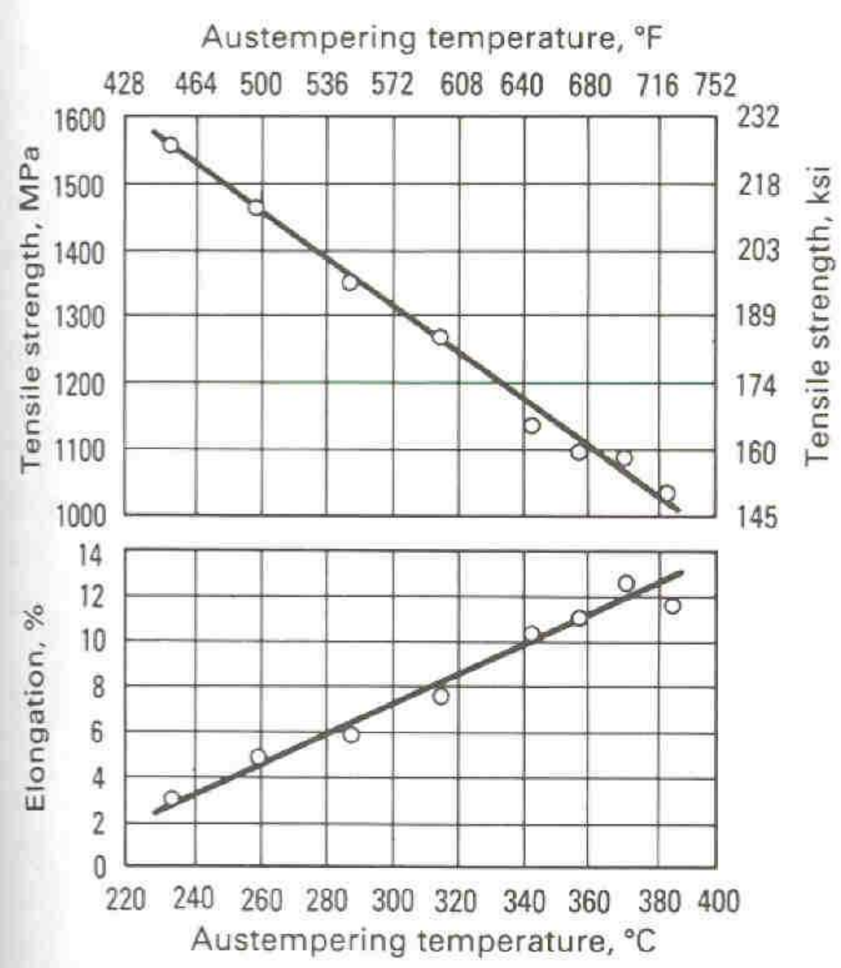
With Pearlitic matrix

Spheroidal Graphite (SG) iron : Heat treatment

- The normalizing, hardening, and austempering heat treatment, which involve Austenitisation, followed by controlled cooling or isothermal reaction, or a combination of the two, can produce a variety of microstructures and greatly extend the limits on the mechanical properties of ductile cast iron.
- These microstructures can be separated into two broad classes
  - Those in which the major iron-bearing matrix phase is the thermodynamically stable body-centered cubic (ferrite) structure.
  - Those with a matrix phase that is a meta-stable face-centered cubic (austenite) structure. The former are usually generated by the annealing, normalizing, normalizing and tempering, or quenching and tempering processes.
- The latter are generated by austempering, an isothermal reaction process resulting in a product called austempered ductile iron (ADI).
- Other heat treatments in common industrial use include stress-relief annealing and selective surface heat treatment. Stress-relief annealing does not involve major micro-structural transformations, whereas selective surface treatment (such as flame and induction surface hardening) does involve microstructural transformations, but only in selectively controlled parts of the casting

Spheroidal Graphite (SG) iron : Heat treatment

- ❑ Stress Relieving: 540 - 595˚C reduces warping and distortion during subsequent machining.
- ❑ Annealing: Full feritizing Annealing used to remove carbides and stabilized Pearlite, heat to 900˚C, holding long enough to dissolve carbides, then cooling at a rate of 85˚C/h to 705˚C, and still air cooling to room temperature. Also improves low temperature fracture resistance but reduces fatigue strength.
- ❑ Normalizing, Quenching, And Tempering: heated to 900˚C, held for 3 hours (allowing 1h/25mm or 1h/in of cross section to reach that temperature). The air blasted or oil quenched. Followed by tempering between 540 - 675˚C. Used to achieve grade 100-70-03. Hardness's as high as 255HB, increase short time fatigue strength, decreases fatigue life. Increases tensile and yield strengths at the expense of ductility.

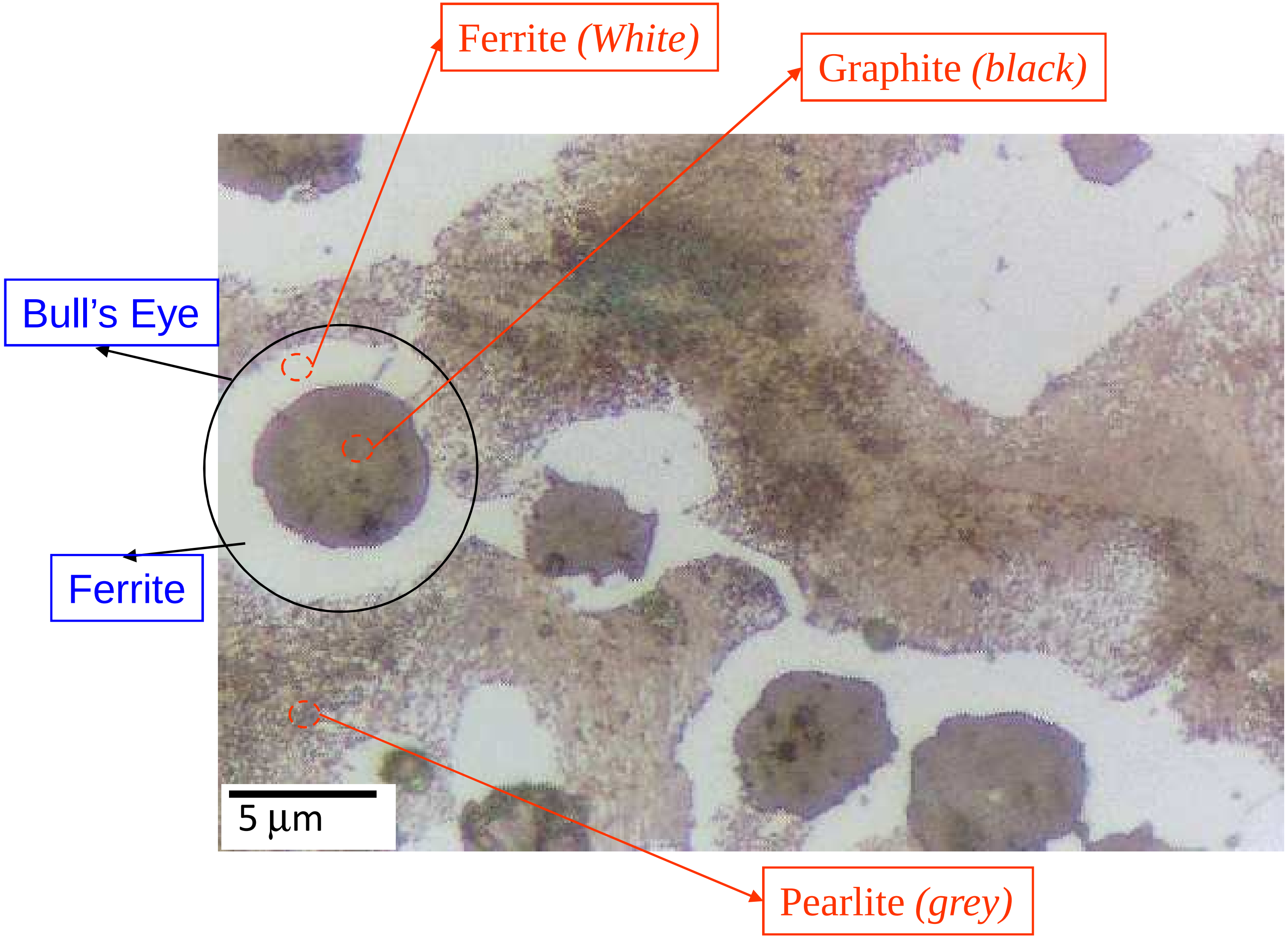


Relationship between austempering temperature and the strength and ductility of a 1.5Ni-03.Mo alloyed ductile iron. Austenitizing temperature was 900˚C.

Spheroidal Graphite (SG) iron : Heat treatment

- ☐ AUSTEMPERING: Used to achieve Austempered Ductile Iron, requires two stages. Stage 1: heating to and holding at 900˚C. Stage 2: quenching and isothermally holding at the required austempering temperature, usually in a salt bath. austempering temperatures shown in figure below.
- ☐ SURFACE HARDENING : SG iron are also flame or induction hardened. Pearlite type of SG irons are preferred for flame or induction hardening as time required for austenitizing is comparatively small. in the case pearlitic SG iron, tempering is carried out at 595-650°C for 1 hour plus 1 hour per 25 mm of section thickness to remove virtually all internal stresses before going in for flame or induction hardening.
- ☐ The possible applications of S.G Iron are very wide. The use of S.G Iron is suggested where improved properties are dictate a replacement of other material or where the use of S.G Iron will permit an improvement in the design.
- ☐ Some popular uses of S.G Iron for various engineering application are for –Support bracket for agricultural tractor, Tractor life arm, Check beam for lifting track, Mine cage guide brackets, Gear wheel and pinion blanks and brake drum, Machines worm steel, Flywheel, Thrust bearing, Frame for high speed diesel engine, Four throw crankshaft, etc.,

Spheroidal Graphite (SG) iron : Nodular cast iron



Ferrite *(White)*

Graphite *(black)*

Bull's Eye

Ferrite

Pearlite *(grey)*

Malleable Cast Iron

$$\text{White Cast Iron} \xrightarrow[\text{To Increase Ductility}]{\text{Malleabilize}} \text{Malleable Cast Iron}$$

- ☐ As we discussed earlier that cementite is actually a metastable phase. There is a tendency for cementite to decompose into iron and carbon. This tendency to form free carbon is the basis for the manufacture of malleable cast iron.
- ☐ The reaction of $Fe_3C \longrightarrow 3Fe + C$ is favored by elevated temperatures, the existence of solid nonmetallic impurities, higher carbon contents, and the presence of elements that aid the decomposition of Fe_3C.
- ☐ Categorized into 3 categories: Ferritic, Pearlitic, and Martensitic Malleable Cast Iron.
- ☐ ferritic malleable Irons require a two stage annealing cycle. first: converts primary carbides to temper Carbon.
- ☐ Second: converts Carbon dissolved in Austenite at the first-stage annealing temperature to temper Carbon and Ferrite. Consists of temper Carbon in a matrix of Ferrite. Contain a slight amount of controlled Iron.
- ☐ Pearlitic :1st stage identical to that of Ferrite. Casting is slowly cooled to approx 870˚C. When the combined Carbon content of the Austenite is reduced to about .75% the castings are air cooled. Usually air blasted to avoid the formation of ferrite around the temper Carbon particles. Then, the castings are tempered to specified time.

Malleable Cast Iron

Stage I

- (940-960)°C *(Above eutectoid temperature)*
- Competed when all Cementite → Graphite

A: Low T structure (Ferrite + Pearlite + Martensite) → (γ + Cementite)

B: Graphite nucleation at γ/Cementite interface
(rate of nucleation increased by C, Si)
(Si ↓ solubility of C in $\gamma \Rightarrow$ ↑ driving force for growth of Graphite)

C: Cementite dissolves → C joining growing Graphite plates

Time for Graphitization in Stage I

- Spacing between Cementite and Graphite →
  ↓ *spacing* ⇒ ↓ *time (obtained by faster cooling of liquid)*
- Addition of Alloying elements
  → *which increase the nucleation rate of Graphite temper nodules*
- Si ↑ ⇒ t ↓

Malleable Cast Iron

Stage II

- (720-730)°C *(Below eutectoid temperature)*
- After complete graphitization in Stage I $\rightarrow$ Further Graphitization

❑ Slow cool to the lower temperature such that γ does not form Cementite

❑ C diffuses through γ to Graphite temper nodules
(called Ferritizing Anneal)

❑ *Full* Anneal in Ferrite + Graphite two phase region

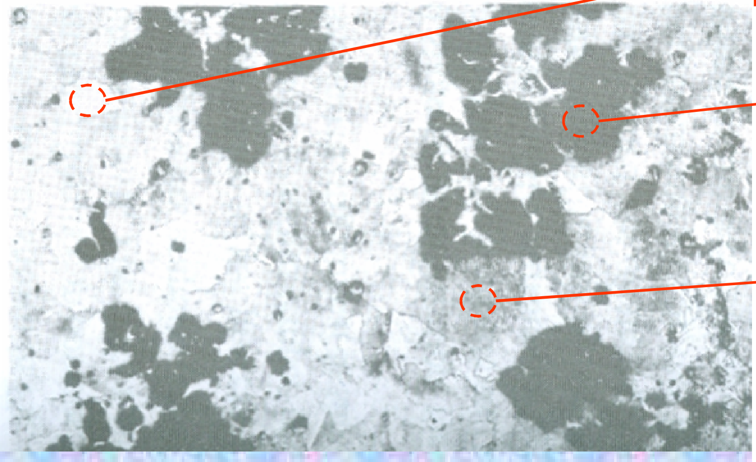
❑ *Partial* Anneal *(Insufficient time in Stage II Graphitization)*
$\gamma \rightarrow$ Ferrite is partial and the remaining γ transforms to Pearlite
$\Rightarrow \gamma \rightarrow$ Pearlite + Ferrite + Graphite

❑ If quench after Stage I $\Rightarrow \gamma \rightarrow$ Martensite *(+ Retained Austenite(RA))*
(Graphite temper nodules are present in a matrix of Martensite and RA)

$$\mathrm{Fe_3C\ (WCI)} \xrightarrow[\text{2 stage heat treatment}]{>48\,hrs} \text{Graphite Temper Nodules (Malleable Iron)}$$

Malleable Cast Iron

Pearlitic Matrix



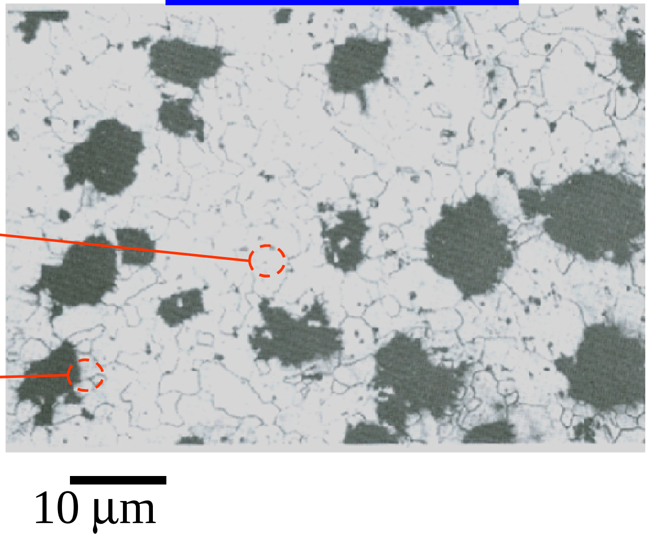
Ferrite *(White)*

Graphite *(black)*

Pearlite *(grey)*

Partially Malleabilized Iron
→ Incomplete Ferritizing Anneal

Ferritic Matrix



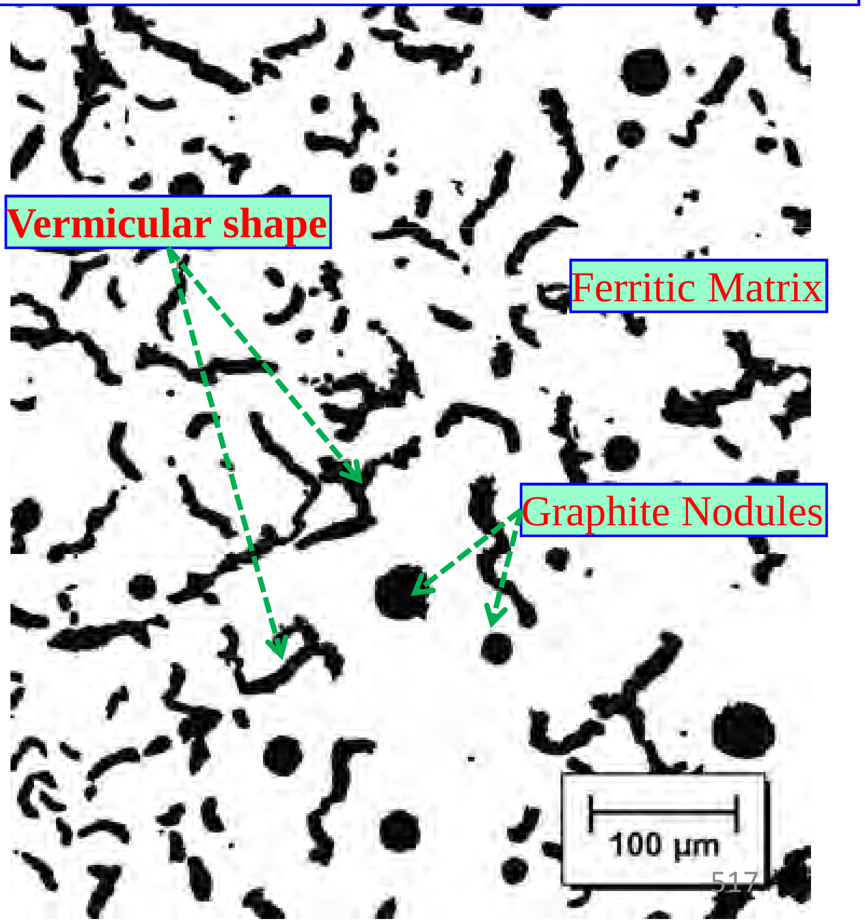
Ferrite *(White)*

Graphite *(black)*

Fully Malleabilized Iron
→Complete Ferritizing Anneal

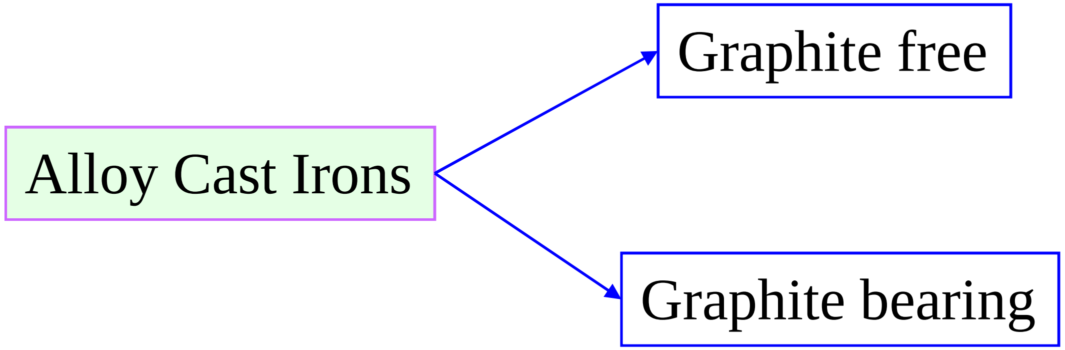
Compacted graphite Cast Iron

- A relatively recent addition to the family of cast irons is *compacted graphite (CGI).*
- Micro structurally, the graphite in CGI alloys has a worm-like (or vermicular) shape; a typical CGI microstructure. In a sense, this microstructure is intermediate between that of gray iron and ductile iron and, in fact, some of the graphite (less than 20%) may be as nodules.
- The chemistries of CGIs are more complex than for the other cast iron types; compositions of Mg, Ce and other additives must be controlled so as to produce a microstructure that consists of the worm-like graphite particles, while at the same time limiting the degree of graphite nodularity, and preventing the formation of graphite flakes. Furthermore, depending on heat treatment, the matrix phase will be pearlite and/or ferrite.
- CGI are now being used in a number of important applications – these include: diesel engine blocks, exhaust manifolds, gearbox housings, brake discs for high speed trains and flywheels.



Alloy Cast Iron

- Cr, Mn, Si, Ni, Al
- ↑ the range of microstructures
- Beneficial effect on many properties
  - ↑ high temperature oxidation resistance
  - ↑ corrosion resistance in acidic environments
  - ↑ wear/abaration resistance


Alloy Cast Irons

Graphite free

Graphite bearing

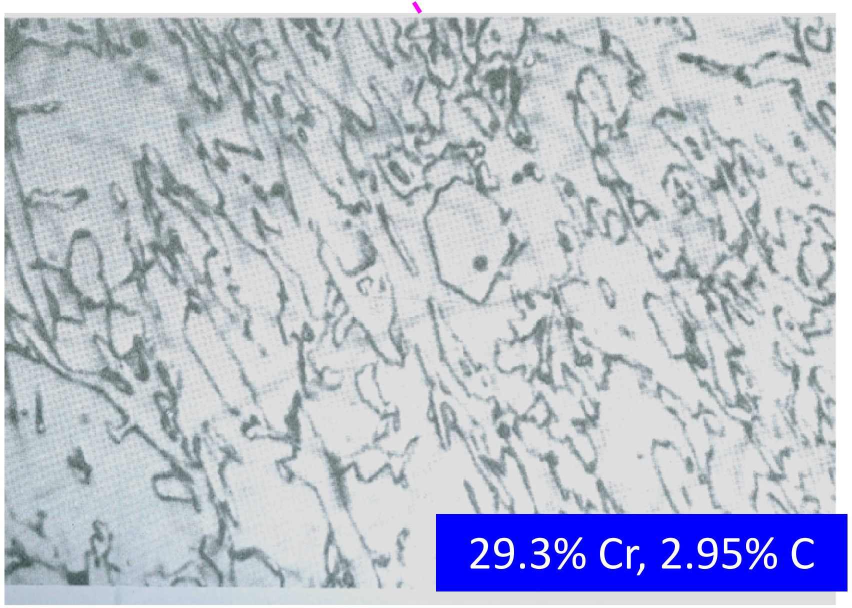
Chromium addition (12-35 wt %)

- Excellent resistance to oxidation at high temperatures
- High Cr Cast Irons are of 3 types:

❑ 12-28 % Cr ➢ matrix of Martensite + dispersed carbide

❑ 29-34 % Cr ➢ matrix of Ferrite + dispersion of alloy carbides $[(Cr,Fe)_{23}C_6, (Cr,Fe)_7C_3]$

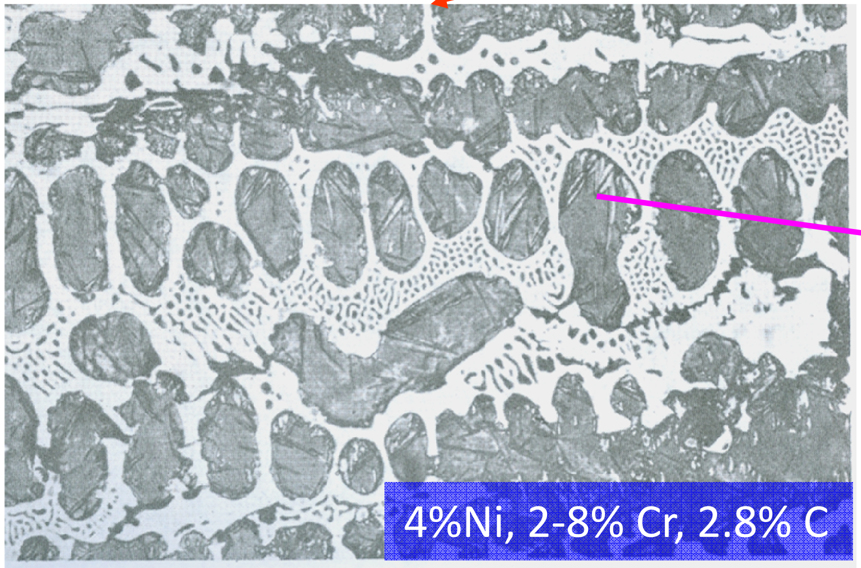
❑ 15-30 % Cr + 10-15 % Ni ➢ stable γ + carbides $[(Cr,Fe)_{23}C_6, (Cr,Fe)_7C_3]$
Ni stabilizes Austenite structure



29.3% Cr, 2.95% C

Nickel Hard Cast Iron

- ❑ Stabilizes Austenitic structure
- ❑ ↑ Graphitization *(suppresses the formation of carbides)*
- ❑ (Cr counteracts this tendency of Ni for graphitization)
- ❑ ↓ Carbon content in Eutectic
- ❑ Moves nose of TTT diagram to higher times ⇒ easy formation of Martensite
- ❑ Carbide formation in presence of Cr increases the hardness of the eutectic structure → Ni Hard Cast Irons (4%Ni, 2-8% Cr, 2.8% C)



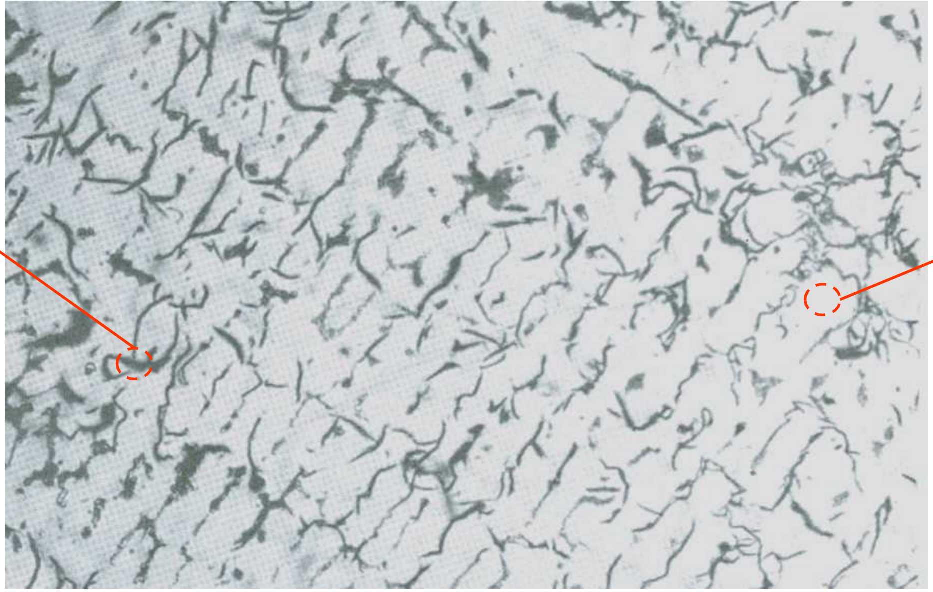
Good abrasion resistance

Needles of Martensite

Transformation sequence
- ➢ Crystallization of primary γ
- ➢ Eutectic liquid → γ + alloy carbide
- ➢ γ → Martensite

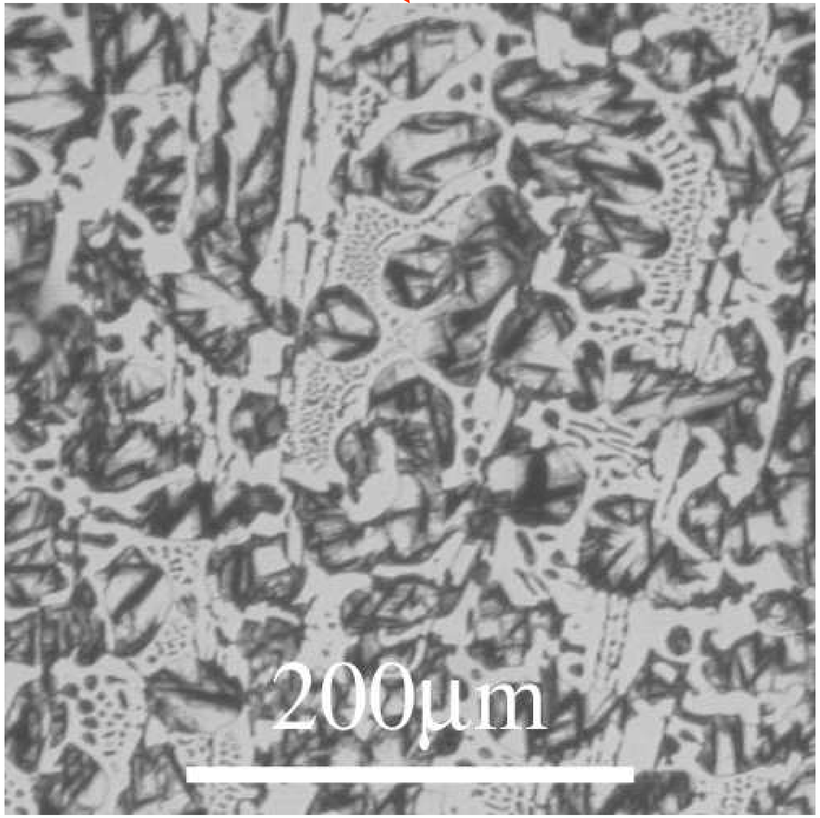
Nickel Resist Cast Iron

- Ni Resist Iron: 15-30% Ni + small amount of Cr:
- ❑ Austenitic Dendrites + Graphite plates/flakes + interdendritic carbides due to presence of Cr
- ❑ Resistant to oxidation (used in chemical processing plants, sea water, oil handling operations…)



Silicon (Silal) Cast Iron

- Silal Iron (trade name): Alloy CI with 5% Si
- ☐ Si allows solidification to occur over larger temperature range → promotes graphitization
- ☐ Forms surface film of iron silicate → resistant to acid corrosion



Some other types of Cast Irons

Chilled Cast Iron

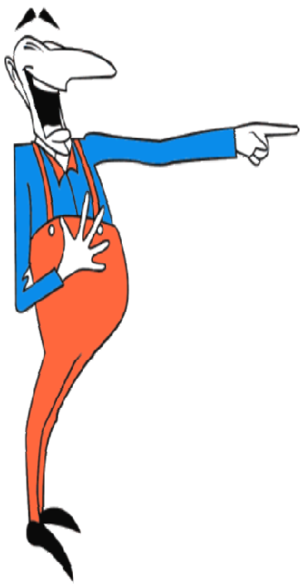
- *Chilled –iron castings are made by casting the molten metal against a metal chiller, resulting in a surface of white cast iron. This hard, abrasion-resistant white iron surface or case is backed up by a softer gray iron core.*
- *This case-core structure is obtained by careful control of the overall alloy composition and adjustment of the cooling rate.*

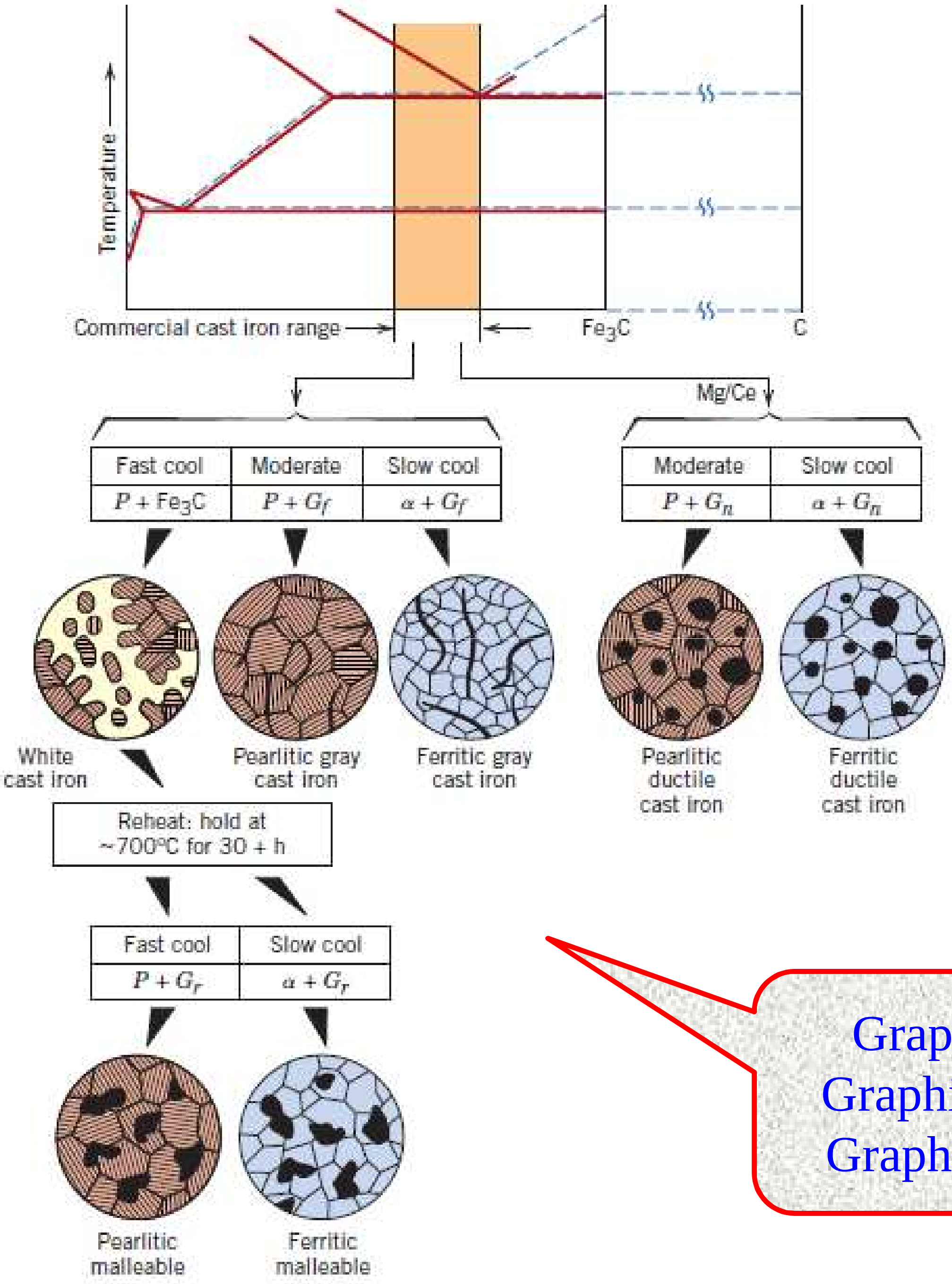
Mottled Cast Iron

- *Solidifying at a rate with extremes between those for chilled and gray irons, thus exhibiting micro structural and metallurgical characteristics of both*

High-Alloy Graphitic Irons

- *Produced with microstructures consisting of both flake and nodule structures. Mainly utilized for applications requiring a combination of high strength and corrosion resistance.*





Summary

Graphite flake - G_f
Graphite nodules - G_n
Graphite rosettes - G_r

Questions?

1. Compare the processes of ferritizing annealing and graphitizing annealing
2. How hardening and tempering is carried out for gray cast irons?
3. What heat treatment would you recommend for malleable cast iron and why?
4. What do you undesrstand by malleabilizing of cast irons?
5. Discuss the heat treatment procedures adopted for S.G. iron castings.
6. How austempering is achieved in S.G. iron castings? What are the possible applications of austempered S.G. iron?
7. Assume that a C clamp is to made of cast iron. Select a suitable a type of cast iron and explain the reasons for the selection.
8. On the basis of microstructure, briefly explain why gray iron is brittle and weak in tension.
9. Compare gray, malleable, nodular and white cast irons with respect to (a) composition and heat treatment, (b) microstructure, and (c) mechanical characteristics.
10. Discuss the influence of the following elements on the structure and properties of cast iron. (i) Si (ii) Mn (iii) S and (iv) P

THANK YOU...!