

**2021 Fall**

# **“Phase Transformation *in* Materials”**

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**Office hours: by an appointment**

# ***Introduction***

- **Web lecture assistance: <http://etl.snu.ac.kr>**
  - **All materials will be posted at the webpage.**
  - **text message will be sent for the important and urgent notice.**
- **실시간 비대면 Zoom 수업 중 카메라 반드시 켜 놓고 음소거 바랍니다**  
(실시간 질의 미응답 및 화상접속 없는 경우 결석처리 불이익 받을 수 있음)

**Text: “Phase Transformations in Metals and Alloys”,**

D.A. Porter and K.E. Eastering, Chapman & Hall

**Prerequisite coursework:** Materials Science and Engineering, Thermodynamics

**References: 1) “Diffusion in Solid,”** Paul G. Shewman, TMS (1989)

**2) “Physical Metallurgy Principles,”** Reed-Hill, PWS–Kent (1992)

**Additional reading materials will be provided.**

# ***Course Goals***

This course presents a unified treatment of the thermodynamics and kinetics of phase transformations from phenomenological and atomistic viewpoints. Phase transformations in condensed metal and nonmetal systems will be discussed. This course begins with reviewing the principles of thermodynamics, phase equilibria, diffusion, and crystal interfaces. The topics include absolute reaction rate theory, thermodynamics of irreversible processes, thermodynamics of surfaces and interfaces, chemical kinetics, nucleation and growth, spinodal decomposition, order-disorder transformations, diffusional transformations, martensitic transformations, coarsening, and glass transition. By the end of the semester, you will be able to understand key concepts, experimental techniques, and open questions in the transformation phenomena of various materials.

# Contents of this course\_Phase transformation

Background  
to understand  
phase  
transformation

(Ch1) Thermodynamics and Phase Diagrams

(Ch2) Diffusion: Kinetics

(Ch3) Crystal Interface and Microstructure

Representative  
Phase  
transformation

(Ch4) Solidification: Liquid  $\rightarrow$  Solid

(Ch5) Diffusional Transformations in Solid: Solid  $\rightarrow$  Solid

(Ch6) Diffusionless Transformations: Solid  $\rightarrow$  Solid

# Schedule

- week 1** Introduction to phase transformation
- week 2** Equilibrium single component system/ Binary solutions
- week 3** Binary phase diagram
- week 4** Ternary phase diagram
- week 5** Atomic mechanism of diffusion/ Interstitial diffusion
- week 6** Substitutional diffusion/ Atomic mobility/ Diffusion in alloy, **1<sup>st</sup> Exam**
- week 7** Interfacial free energy/ Solid/vapor interfaces
- week 8** Boundaries in single-phase solids/ Interphase interfaces in solids
- week 9** Interface migration
- week 10** Nucleation in pure metals
- week 11** Growth a pure solid/ Alloy solidification
- week 12** Solidification of ingots and casting, **2<sup>nd</sup> Exam**
- week 13** Nucleation/ Precipitate growth/ Precipitation in age-hardening alloys
- week 14** Various diffusional transformation in solids
- week 15** Diffusionless transformation – Martensite transformation
- week 16** **Team project presentation & Final exam**

# ***Components of Your Grade:***

## **1) Exams (1st: 25%; 2nd 25%; final: 25%)**

There will be two exams, each of which will take 2-3 hours. I will not use class time for the exams and instead will reserve separate time slots.. The exams will be conceptual and difficult.

## **2) Team project (15%)**

Course participants will organize into small groups. Topics for phase transformation will be discussed, and each group will submit a proposal and reports as well as give a final presentation.

## **3) Homework (5%) (+Incentive Homework 5%) and Attendance (5%)**

Assignments handed in after the start of class lose credit depending on the timing. If you wish, you may work together on homework assignments. But, you must hand in your own work, in your own words.

### **Remarks:**

- 1) The weight of each component above could be adjusted up to 5% based on students' performance. 2) Student who retakes this course will have their final scores adjusted downward by 5% in order to ensure fairness with other students.

\* 청강 학생들은 숙제는 안내도 되지만 반드시 시험에 참여해야 함을 미리 고지합니다! 6

# ***Policies and Procedures***

- *All homework are due by the start of class on the stated deadline.*
  - Late assignments go to my office. If I'm not around, slide it under my door and leave me an email so that I know when you turned it in.
  - You lose 20% of the full assignment value per day late. Since homework are due on **Wednesday**, you can get 80% credit if you turn it in on **Friday**, 50% on next **Wednesday**, nothing thereafter.
- *If you wish, you may work together on homework assignments. BUT, you must hand in your own work, in your own words.*
- **IMPORTANT:** *you MUST reference your sources appropriately, including texts, journals web sites, etc.*
  - Article authors, title, journal, volume, year, pages
  - Book authors, title, publisher, year, pages
  - Web address
  - etc.

Q & A



# Materials Science and Engineering

Chapter 1 Introduction

Chapter 2 Atomic Structure and Interatomic Bonding

Chapter 3 Fundamentals of Crystallography

Chapter 4 The Structure of Crystalline Solids

Chapter 5 Structure of Polymers

Chapter 6 Imperfections in Solids

Chapter 7 Diffusion

Chapter 8 Mechanical properties of Metals

Chapter 9 Dislocations and Strengthening Mechanism

Chapter 10 Failure

Chapter 11 Phase Diagrams

Chapter 12 Phase Transformations

Chapter 13 Properties and Applications of Metals

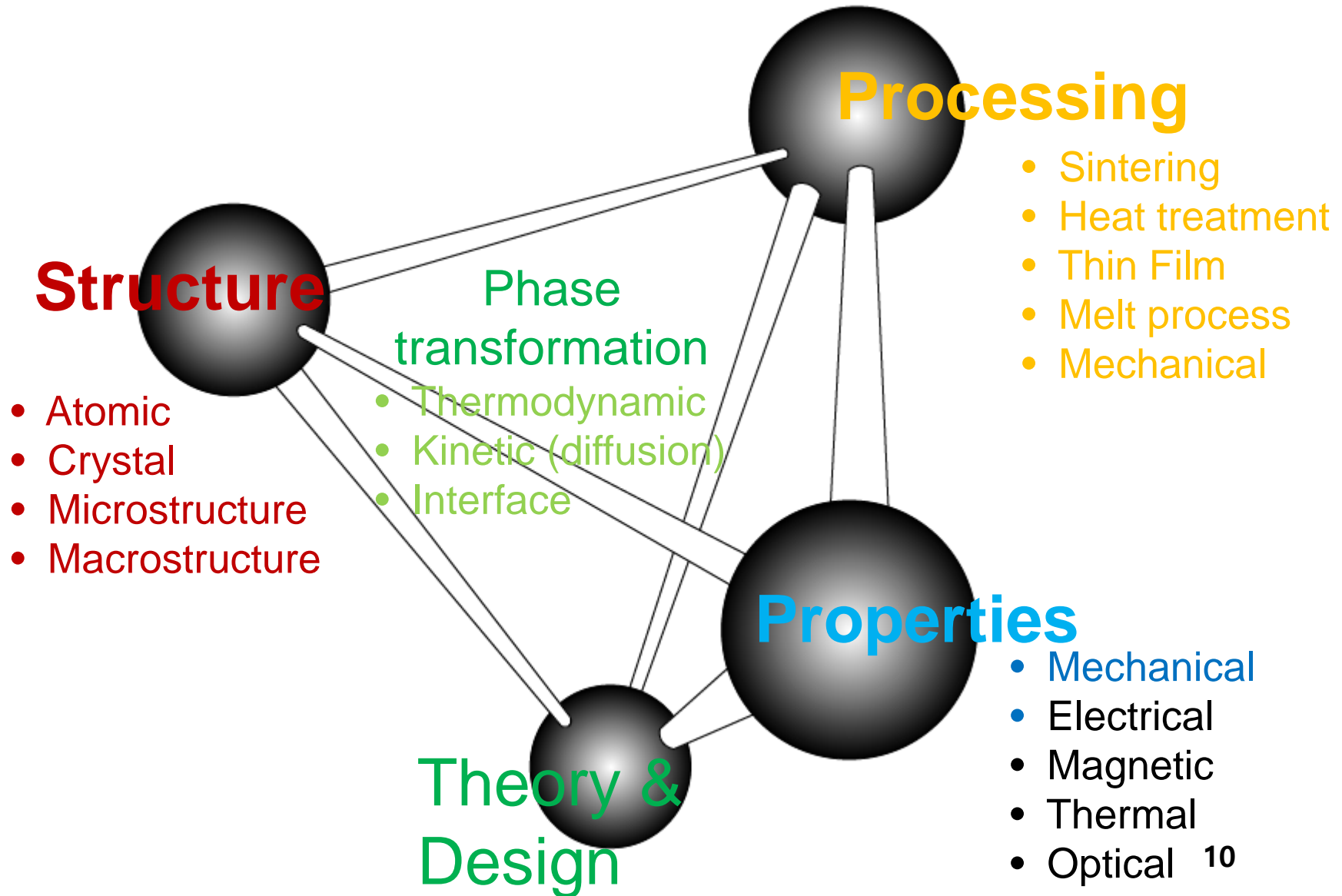
Chapter 14 Properties and Applications of Ceramics

Chapter 15 Properties and Applications of Polymers

Chapter 16 Composites Materials

Chapter 17 Fabrication and Processing of Engineering Materials

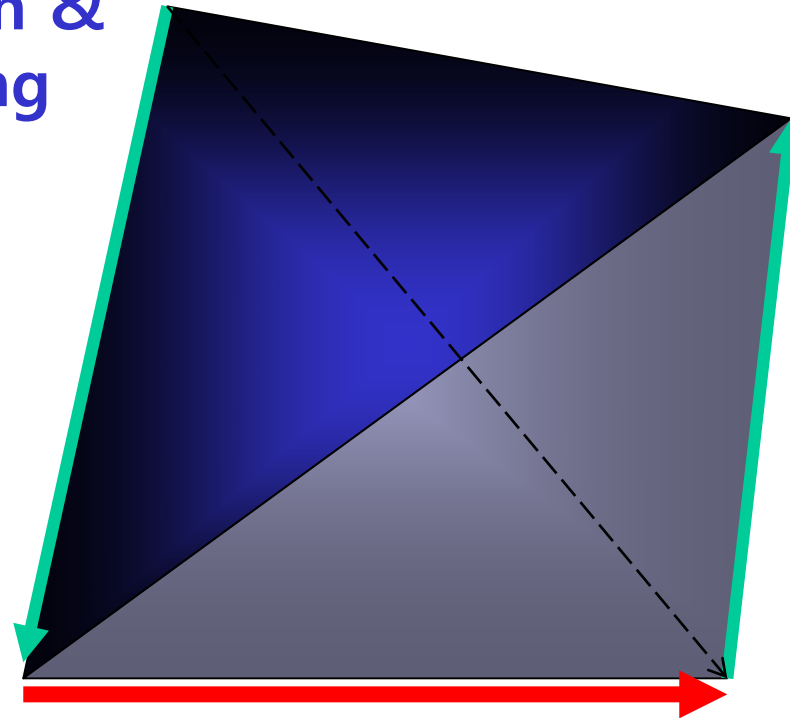
# Materials Science and Engineering



# Microstructure-Properties Relationships

Alloy design &  
Processing

Performance



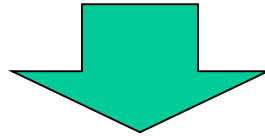
**Microstructure**  
down to atomic scale

**Properties**

*“Tailor-made Materials Design”*

Alloy design + Process control →

## ***Microstructure Control of Materials***



***Better Material Properties***

**Q1: What is alloy design?**

**“Materials selection” - Composition**

## 1) Alloy design: a. Materials selection

# One of the Most Popular Structural Materials ; **Iron-Carbon Alloy (or Steel)**



**Steel frame of building**

1) Alloy design: Materials selection → b. Change of alloy compositions

# Application of Iron-Carbon Alloy

K1 – main battle tank of Korea army



**Need of the strongest materials**

1) Alloy design: Materials selection ➡ c. Change of alloy system

# Dominant Material for Airplanes ; **Aluminum Alloy**

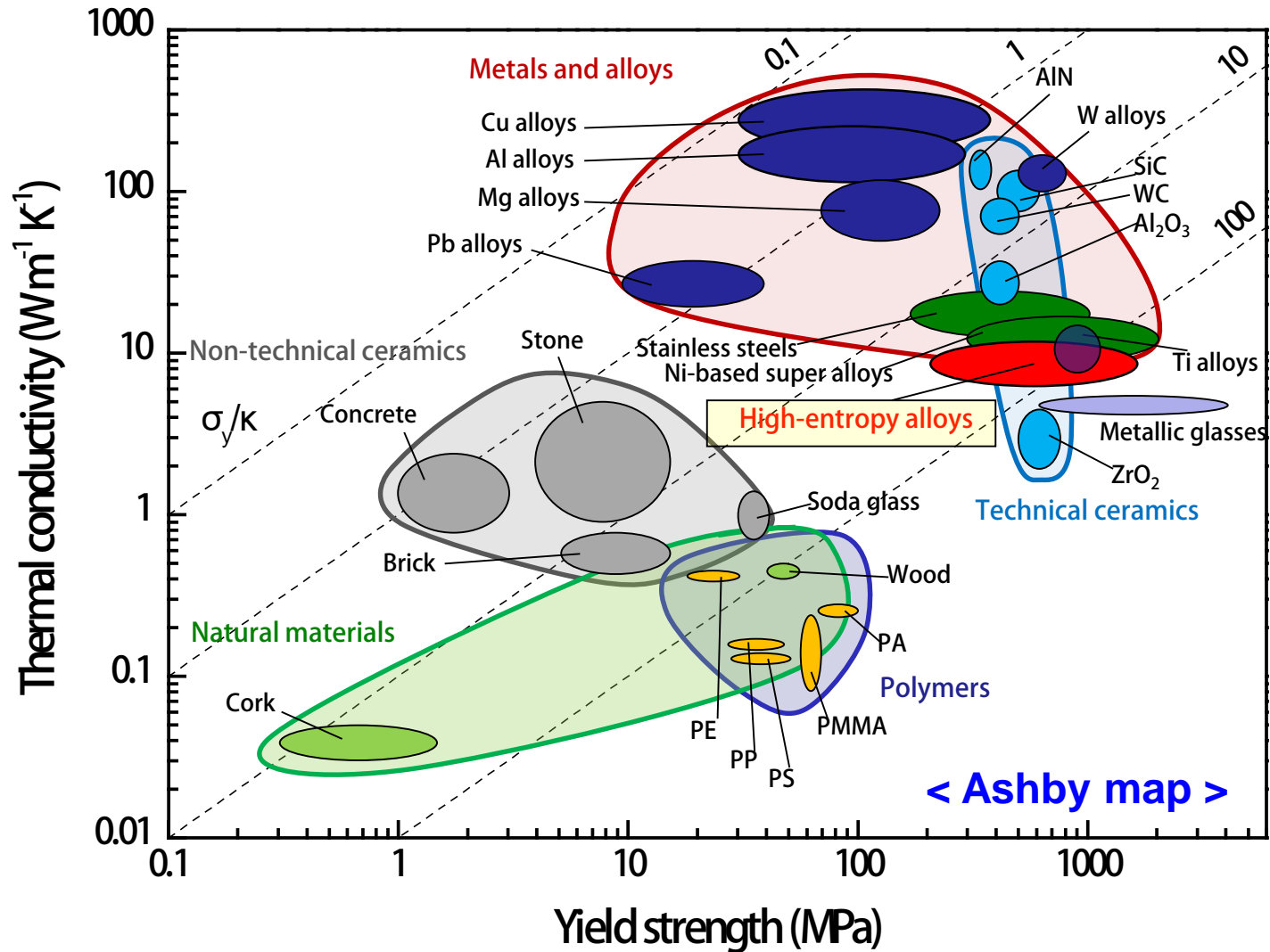
B737-800 of Korean Air



**Need of light, strong and tough material**



# 1) Alloy design: Materials selection → c. Change of alloy system

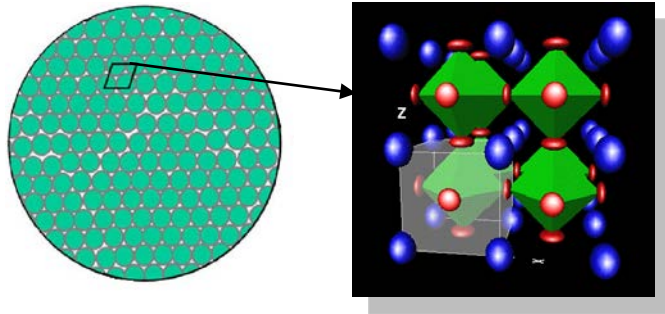
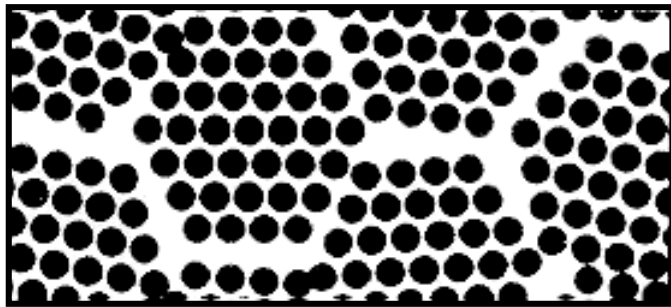


**Q2: How to classify material  
depending on the structure?**

## 2) Classification of Material depending on the structure

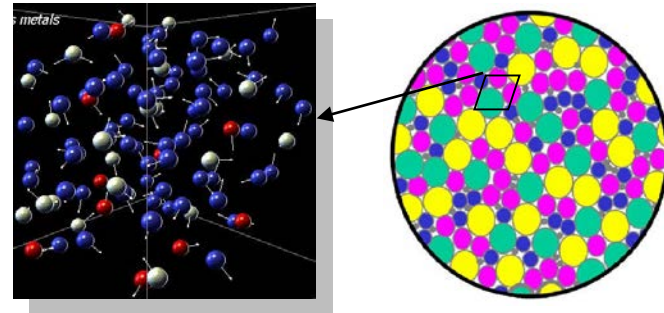
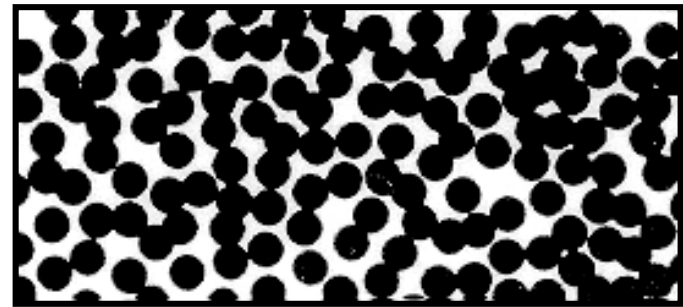
### **Structure** of crystals, liquids and glasses

#### *Crystals*



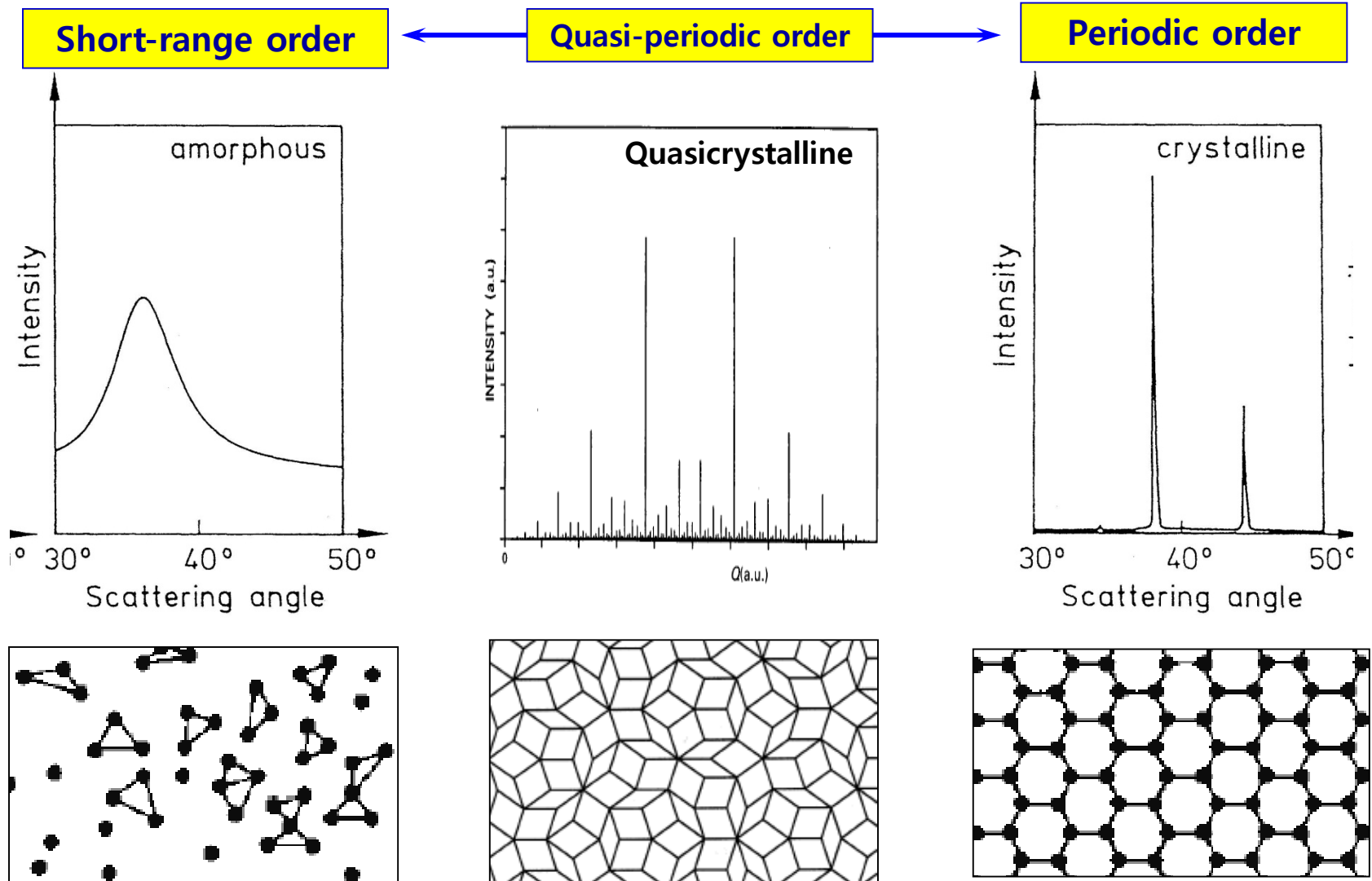
- periodic
- grain boundaries

#### *Liquids, glasses*



- amorphous = non-periodic
- no grain boundaries

# Atomic structure



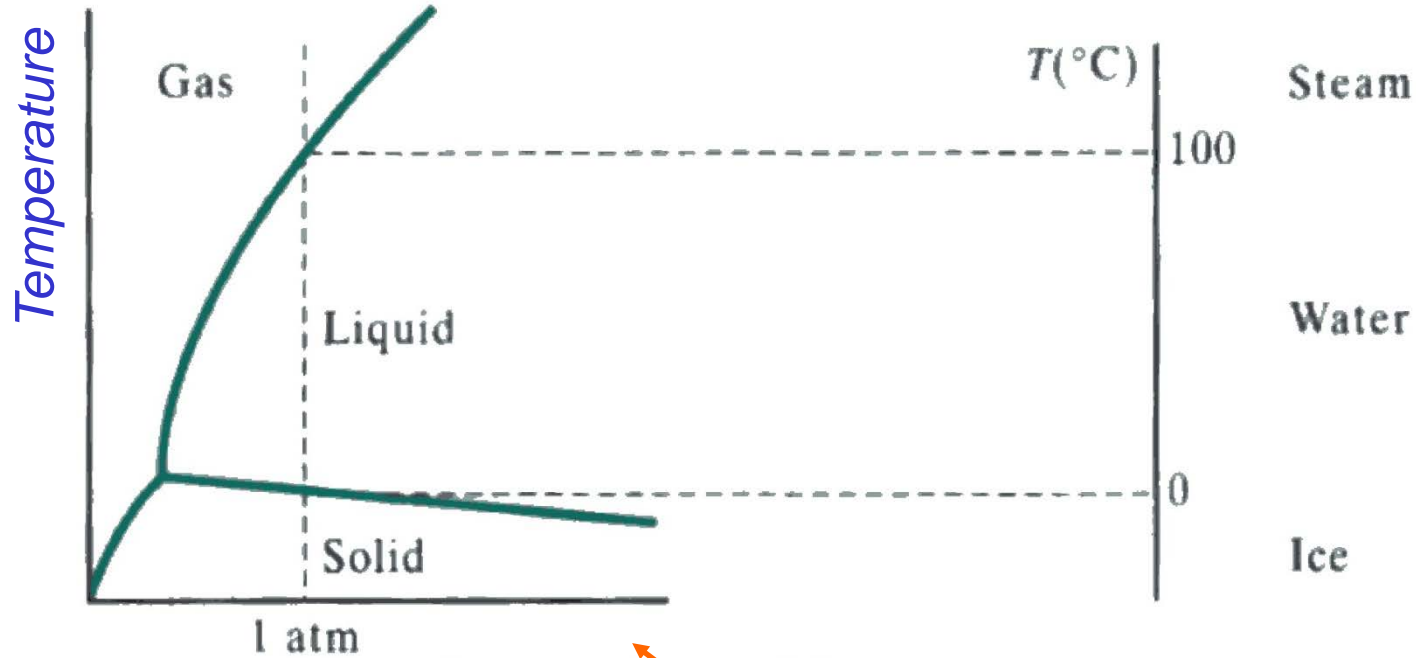
**Q3: What are phase, phase diagram  
and phase transformation?**

### 3) Microstructure control

: Equilibrium phase → Only consider Thermodynamics

#### ① What is *Phase*?

*A phase* is a chemically and structurally homogeneous portion of the microstructure.  
(structure or composition or order)



Pressure (log scale)

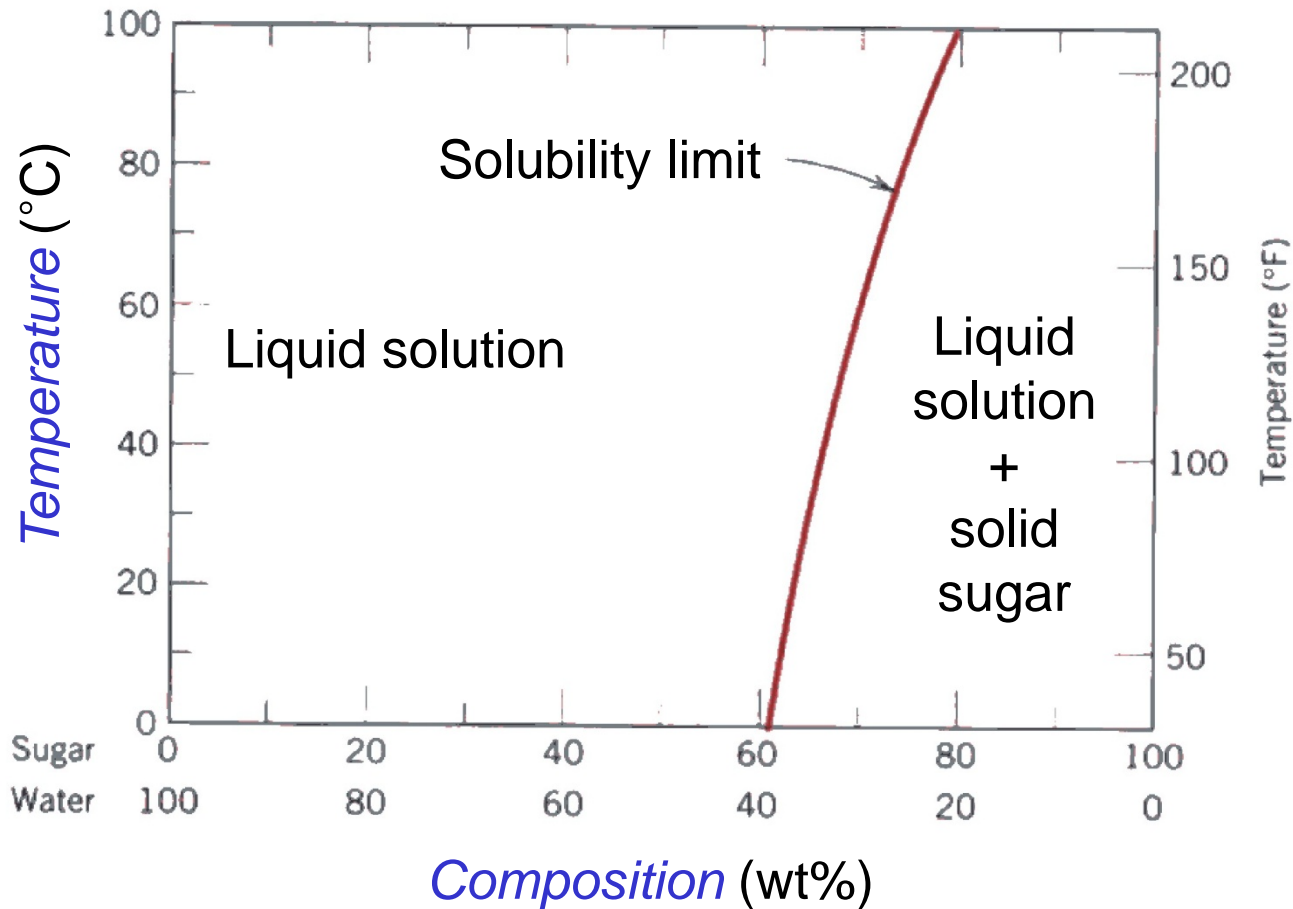
Phase diagram ;  
equilibrium phase of material 22

# Microstructure control

: Equilibrium phase → Only consider Thermodynamics

## ② *Phase Diagram* of Temperature – Composition ;

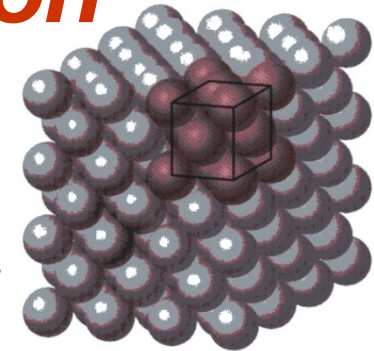
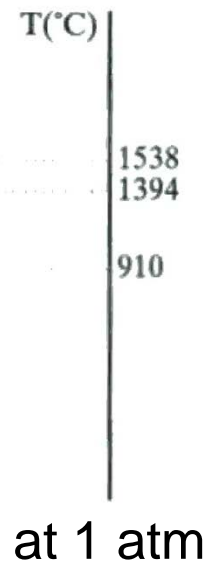
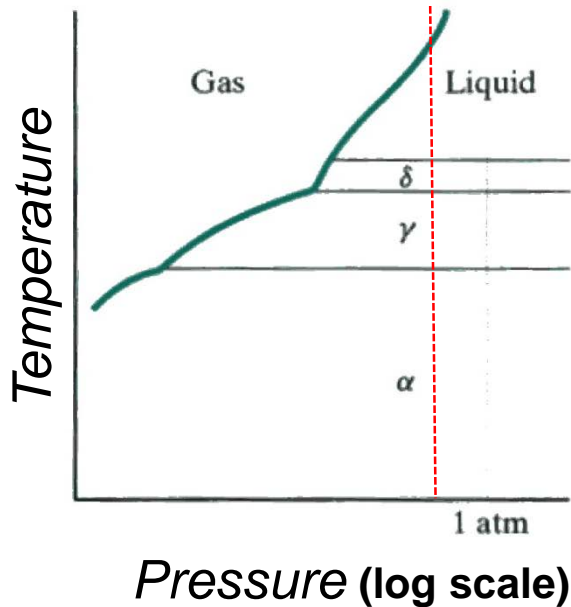
most useful in materials science & engineering



# Microstructure control

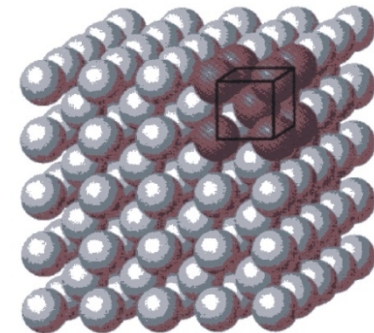
: Phase transformation → Atomic Migration

## ③ *Phase Transformation* of Iron and *Atomic Migration*



Face-Centered Cubic

↕ Atomic Migration



Body-Centered Cubic



**Q4: What is microstructure?**

## 4) What is microstructure?

**Microstructure** originally meant the **structure inside a material** that could be observed with the aid of a microscope.

In contrast to the crystals that make up materials, which can be approximated as collections of atoms in specific packing arrangements (crystal structure), **microstructure** is the **collection of defects in the materials**.

What defects are we interested in?

**Interfaces** (both grain boundaries and interphase boundaries),  
which are planar defects,

**Dislocations** (and other line defects), and

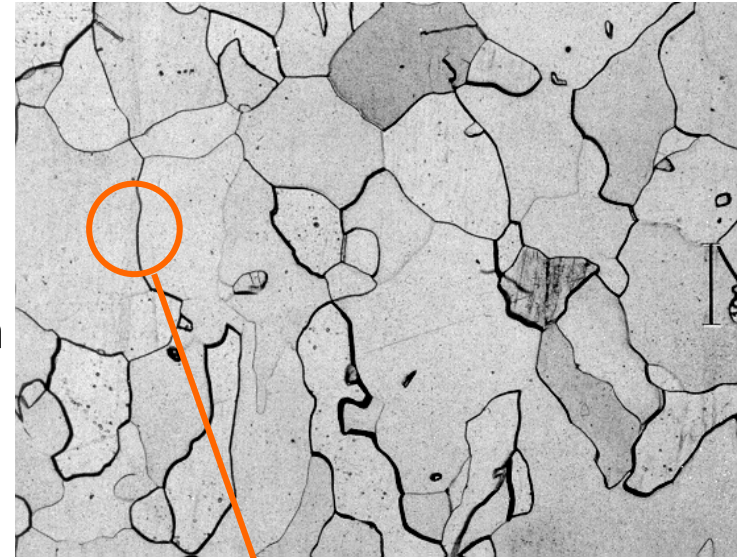
**Point defects** (such as interstitials and vacancies as well as solute atoms in solution)

# \* Imperfection: Grain Boundaries

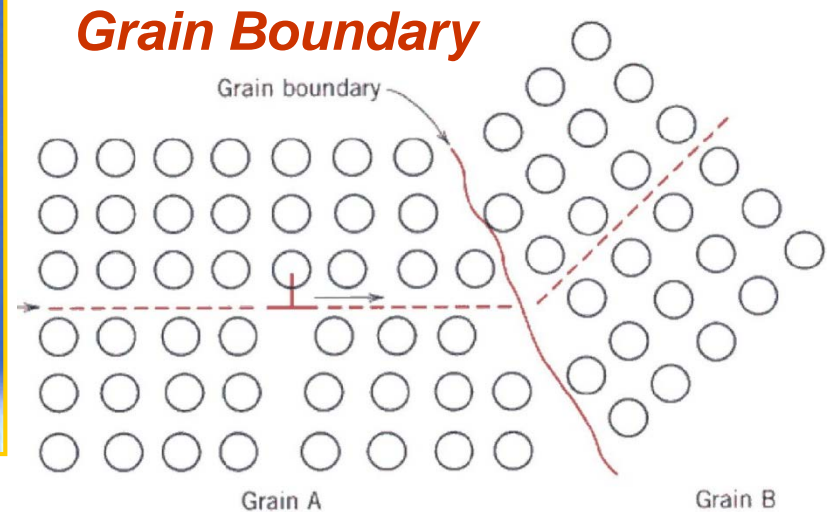
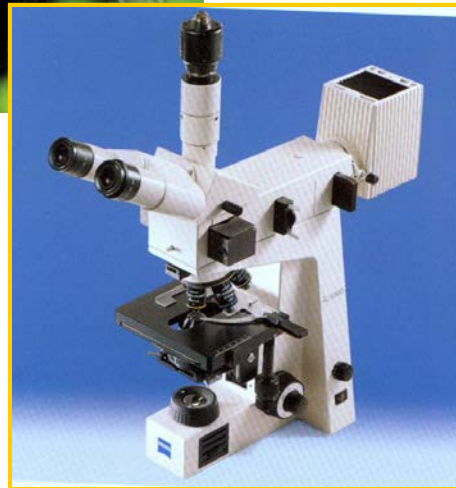
(Planer defect)



Low Carbon Steel



Optical  
Microscope

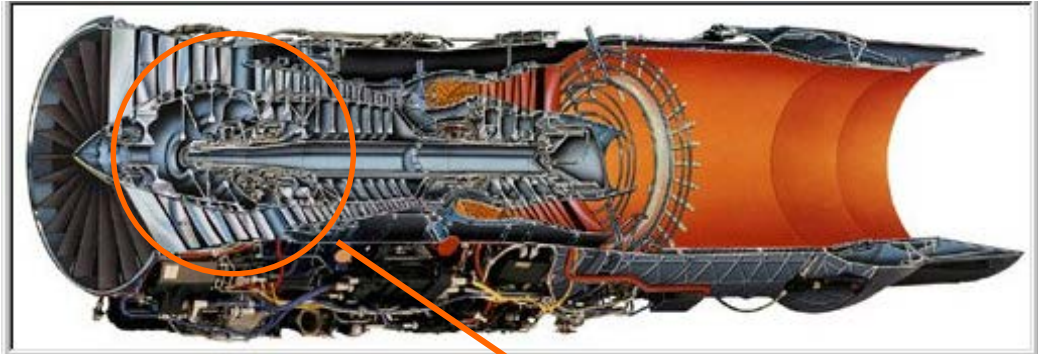


**Q5: How to control the microstructure  
by process control?**

# 5) Microstructure control

: process control after materials selection → property optimization

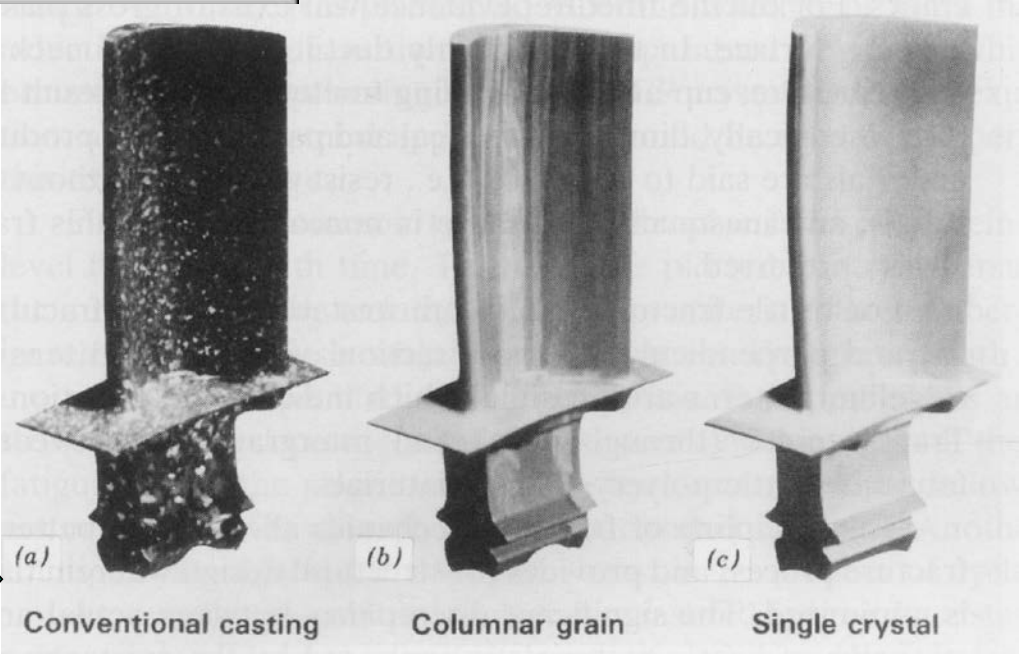
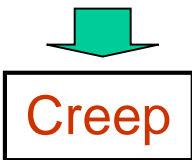
## A Example of ① Grain Boundary Engineering ; Turbine blade in Aircraft Engine



F100-PW-229  
in F-16 fighting falcon

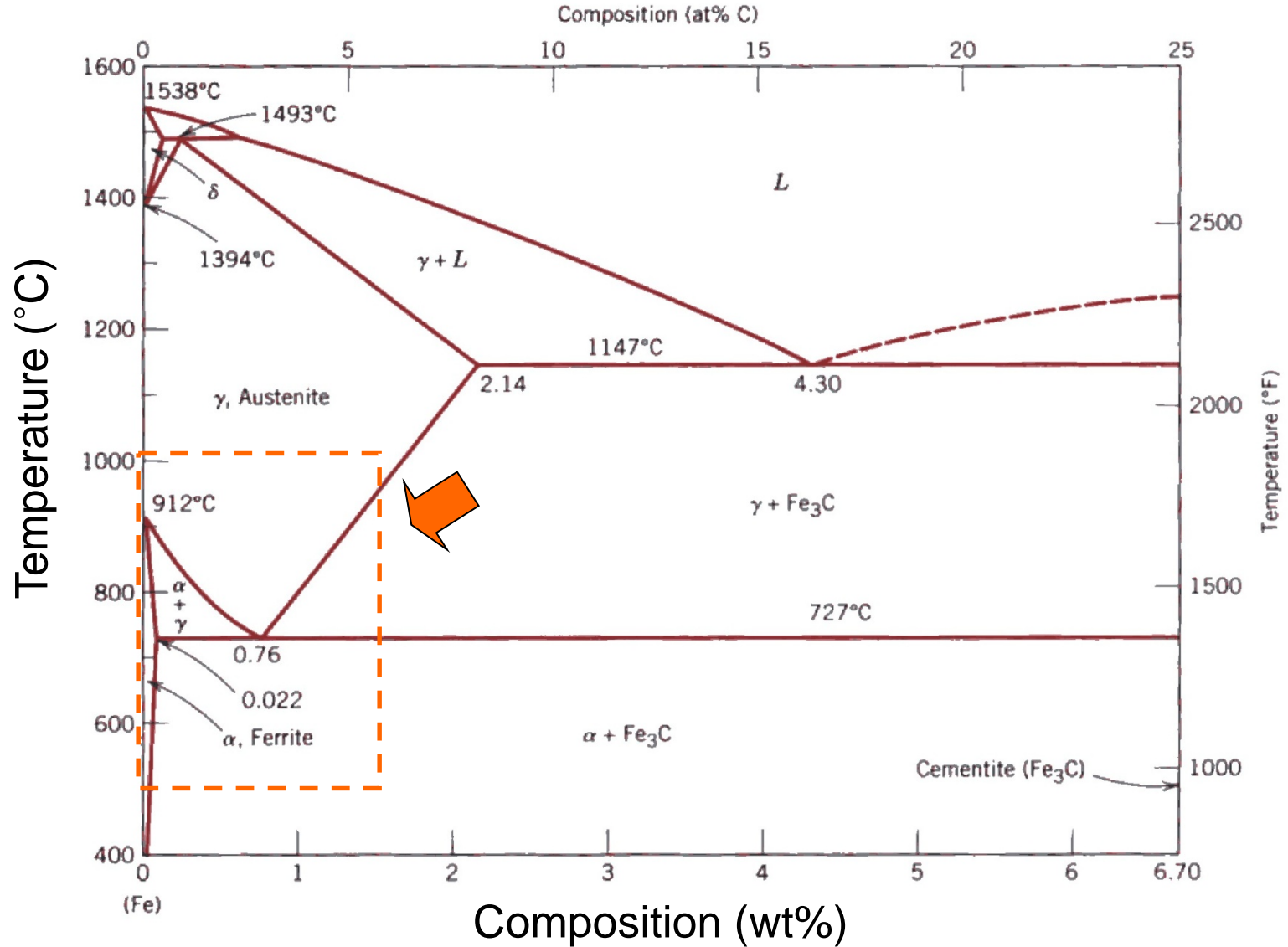
Turbine Blade

Grain boundaries  
at high Temperature ;  
Diffusion path of atoms



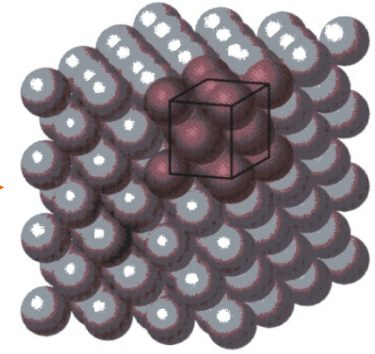
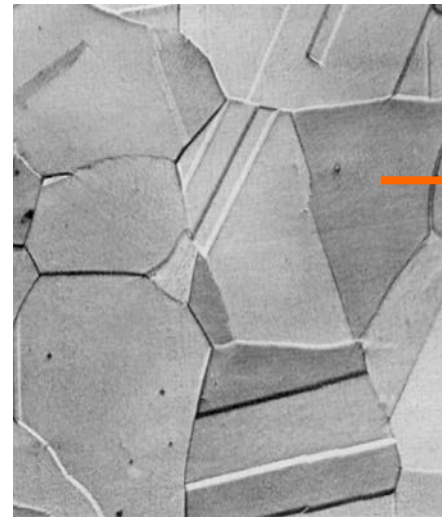
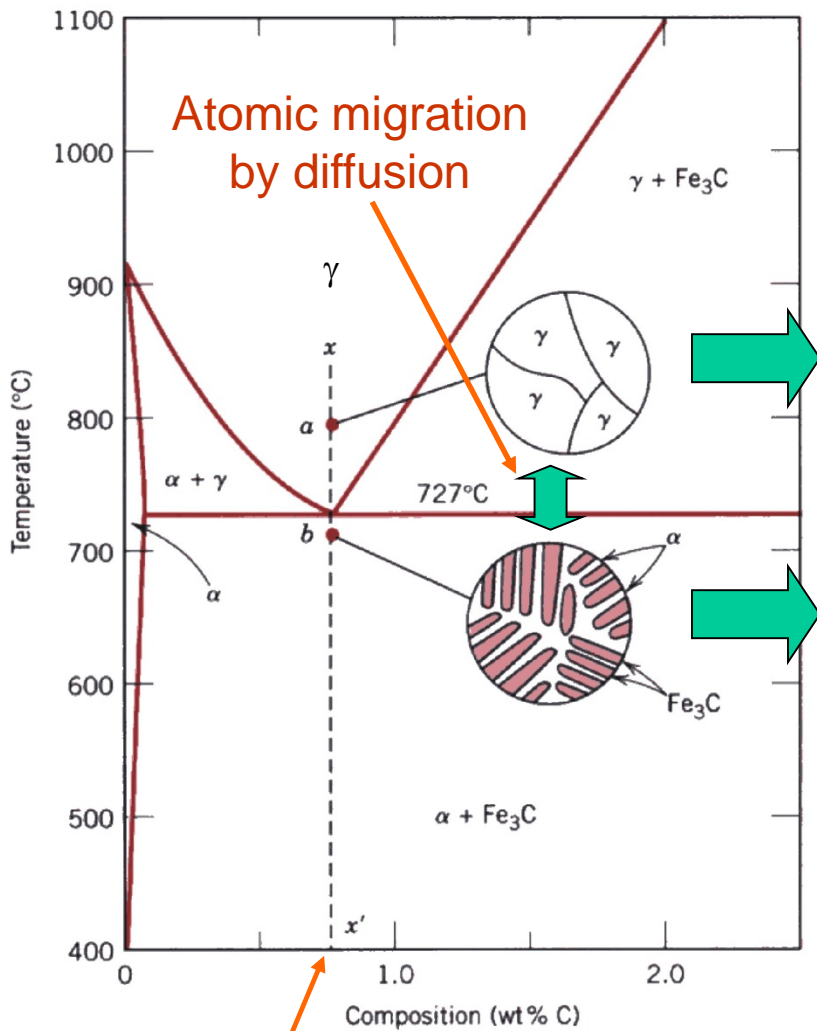
# 5) Microstructure control : ② Secondary phase control

## a. Phase Diagram of Iron–Carbon Alloy



# 5) Microstructure control : ② Secondary phase control

## b. Equilibrium Phases of Iron-Carbon Alloy



$\gamma$  phase (FCC)

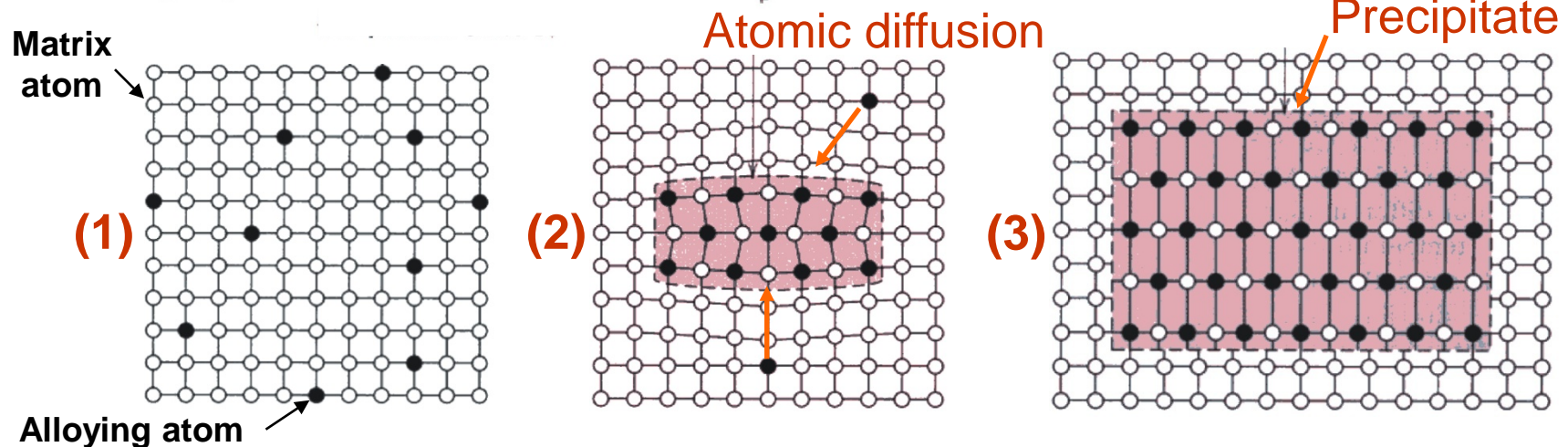
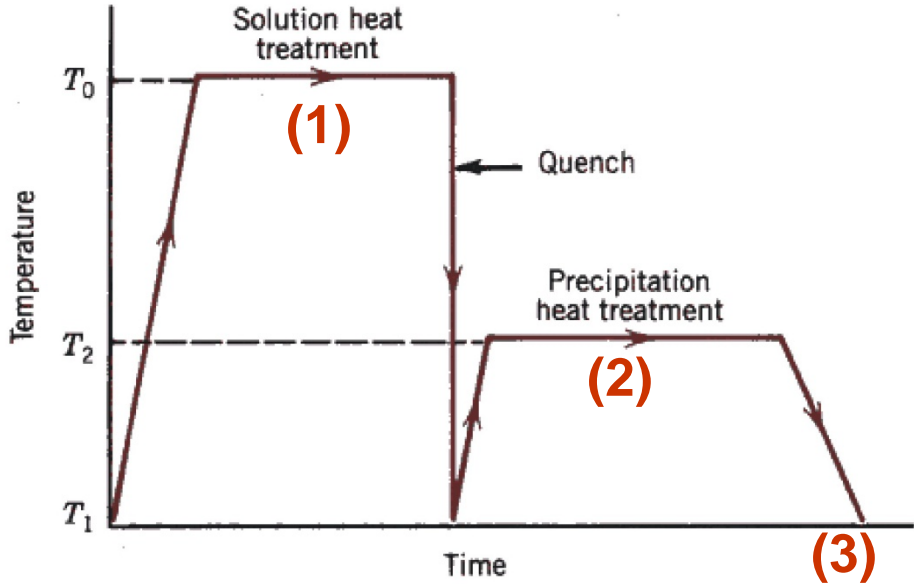
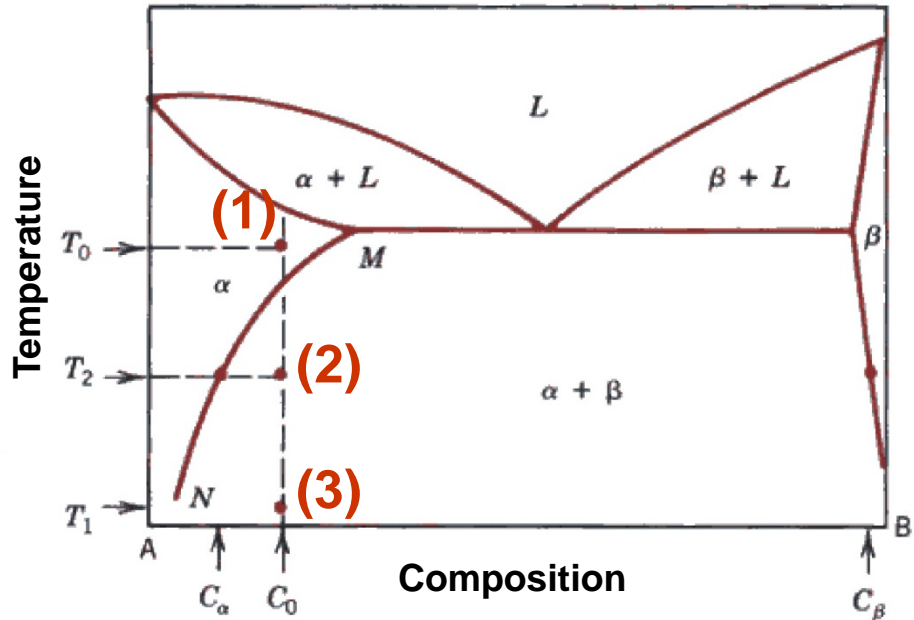


$Fe_3C$  phase

$\alpha$  phase (BCC)

# 5) Microstructure control : ② Secondary phase control

## c. Mechanism of Precipitation

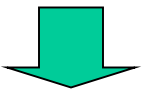




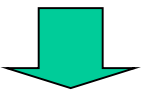
5) Microstructure control : ② Secondary phase control

***d. Effect of Second Phase Particle on Mechanical Property***

Second phase particle in matrix material

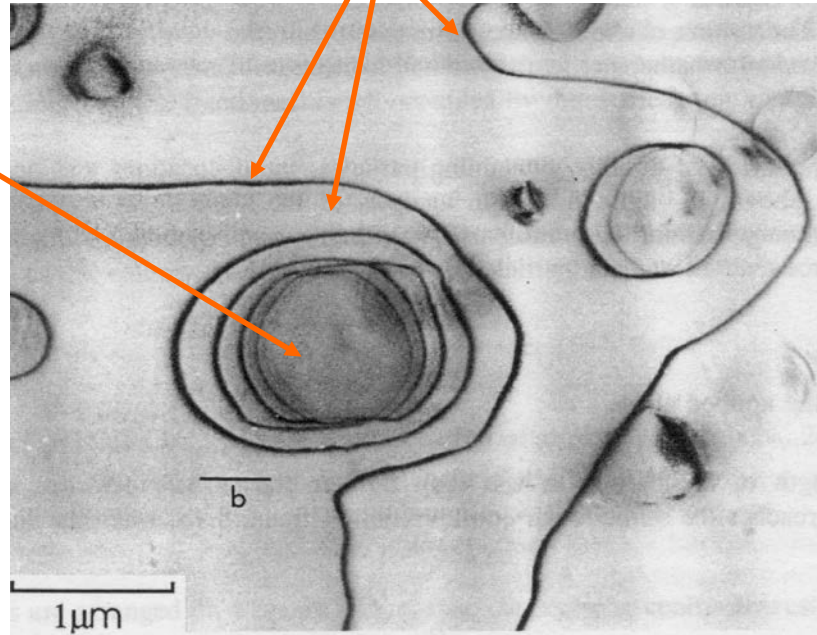


Obstacle of dislocation slip & grain growth



High strength

Dislocations

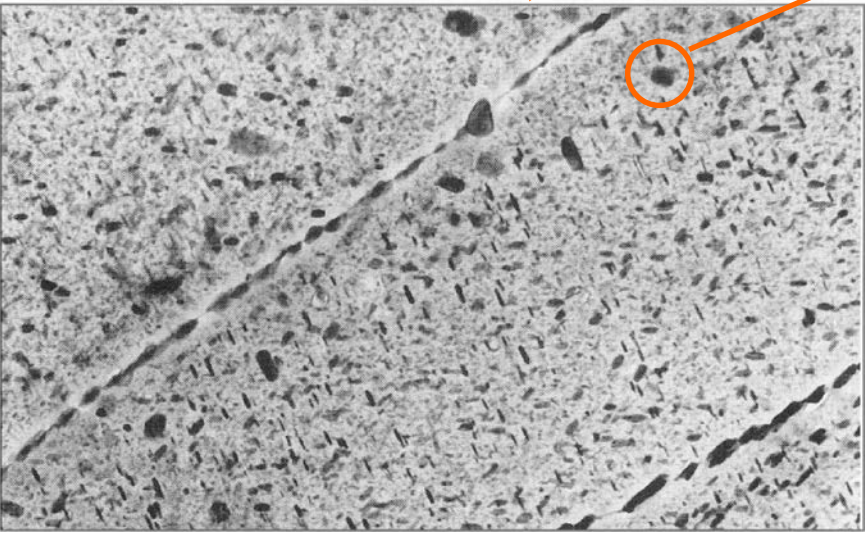


Ni<sub>3</sub>Si particles in Ni-6%Si single crystal

5) Microstructure control : ② Secondary phase control

**e. Control of Microstructures by  
Precipitation Transformation in Aluminum Alloy**

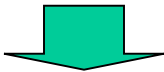
Boeing 767 by AA7150 T651 alloy



**Precipitates  
in aluminum matrix**



**Hindering dislocation slip**



**High strength**

**Q6: How to optimize microstructure  
by process control?**

## 6) Microstructure optimization by process control

### ① **Cold Work** \_압력을 가해 성형하고 인성을 증가시키는 과정

김홍도 "Smithy\_대장간"



Joseon Dynasty



Modern forging machine

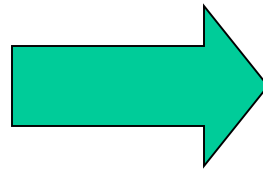
## 6) Microstructure optimization by process control

### Hardening Mechanism by Cold Working



Before cold work

Deformation  
*or*  
Cold work



Aluminum alloy

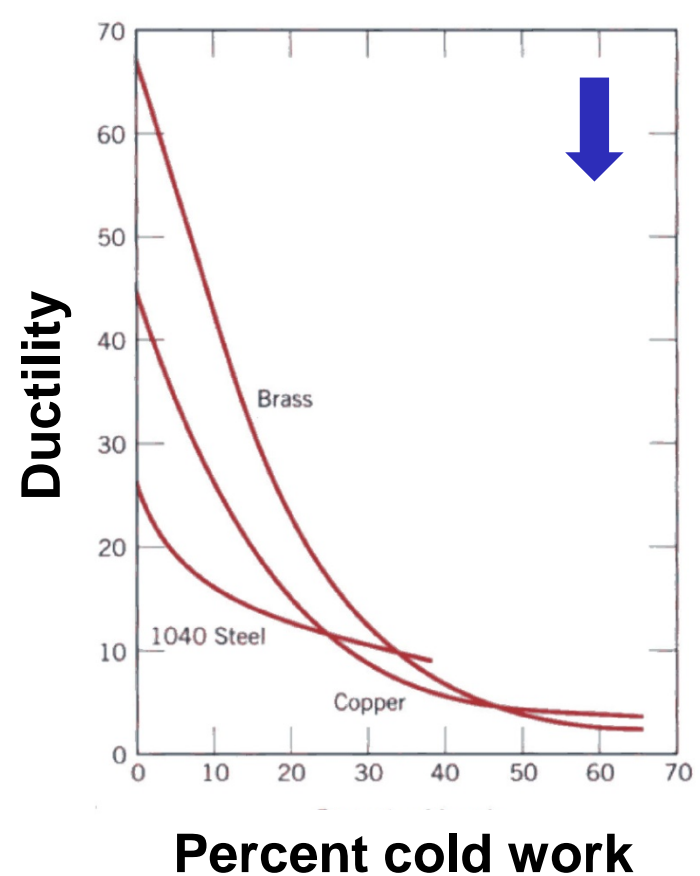
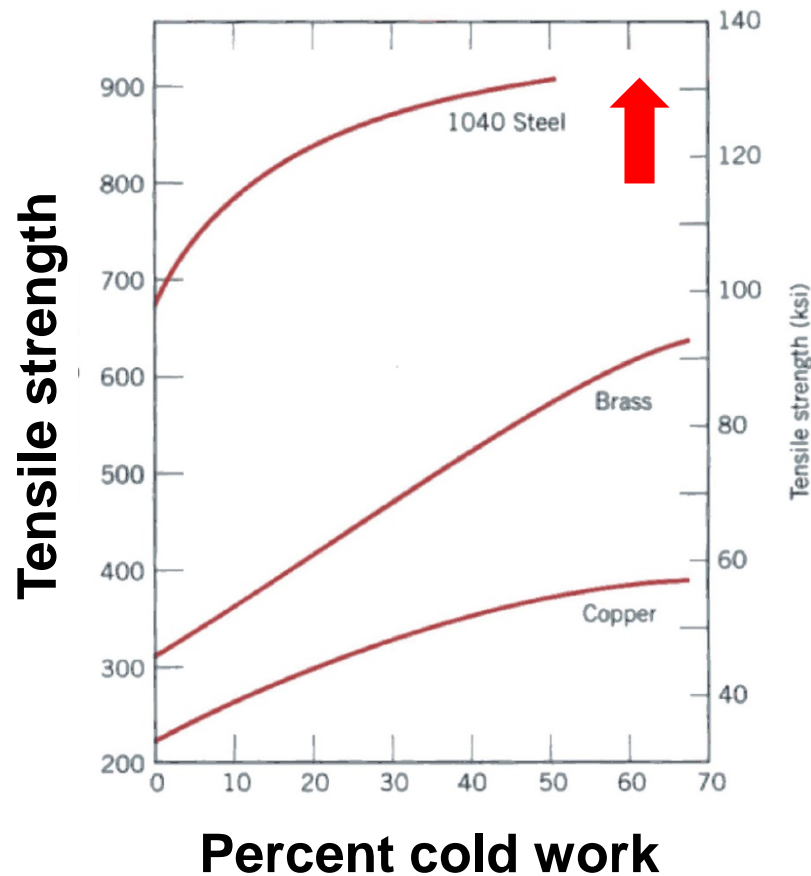


Accumulation  
of dislocations

Dislocation tangle

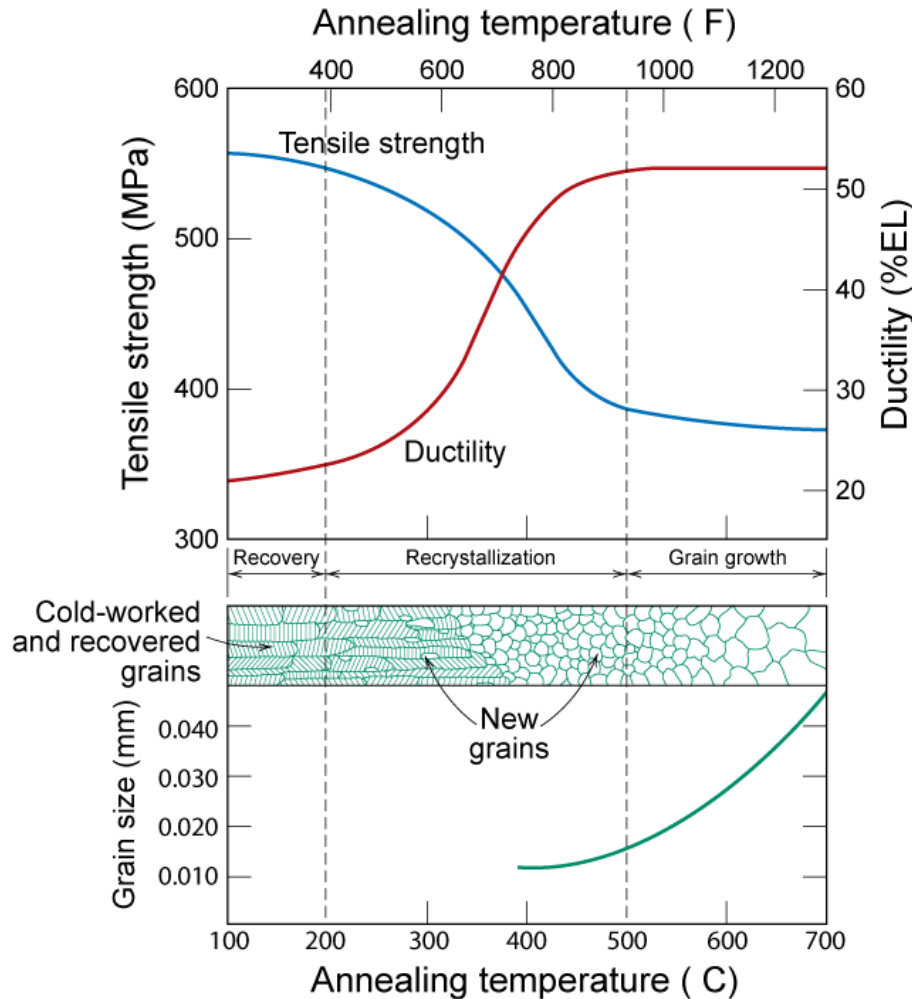
## 6) Microstructure optimization by process control

### Changes of Strength and Ductility by Cold Working



# 6) Microstructure optimization by process control

## ② Changes of Microstructure & Mechanical Properties during Annealing



Cold working → recovery → recrystallization → grain growth

내부 변형률 에너지 제거 낮은 전위밀도 (변형률이 없는) 결정립

**Q7: How to optimize material property?**

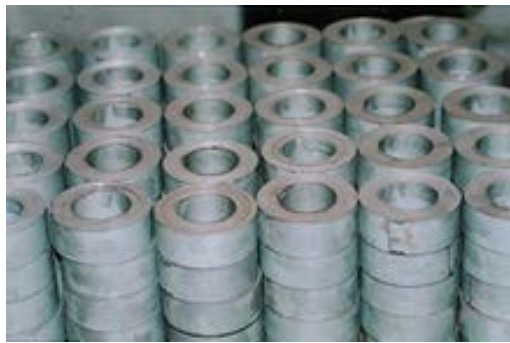
**“Alloy design + Process control”**



## 7) Alloy design + Process control → Property optimization

### e.g. Production and Application of Electrical Steel

**Hot rolling - cold rolling – 1<sup>st</sup> annealing – 2<sup>nd</sup> annealing**



**Coils**



**Stacked transformer core**

Transformer  
Motor  
Etc.



**Soft magnetization property**

# Microstructural Parameters vs Properties

## Microstructural Parameters

- Grain size
- Grain shape
- Phase structure
- Composite structure
- Chemical composition (alloying)
- Crystal structure
- Defect structure (e.g. porosity)



## Properties

- Strength
- Toughness
- Formability
- Conductivity
- Corrosion Resistance
- Piezoelectric strain
- Dielectric constant
- Magnetic Permeability

Alloy design + Process control →

***Microstructure Control of Materials***



***Better Material Properties***

**Important!!!**

**8) *Understanding and Controlling*  
Phase Transformation *of* Materials**

**Q8: How to control the phase transformation?**

**“Thermodynamics + Kinetics”**

# Phase Transformation

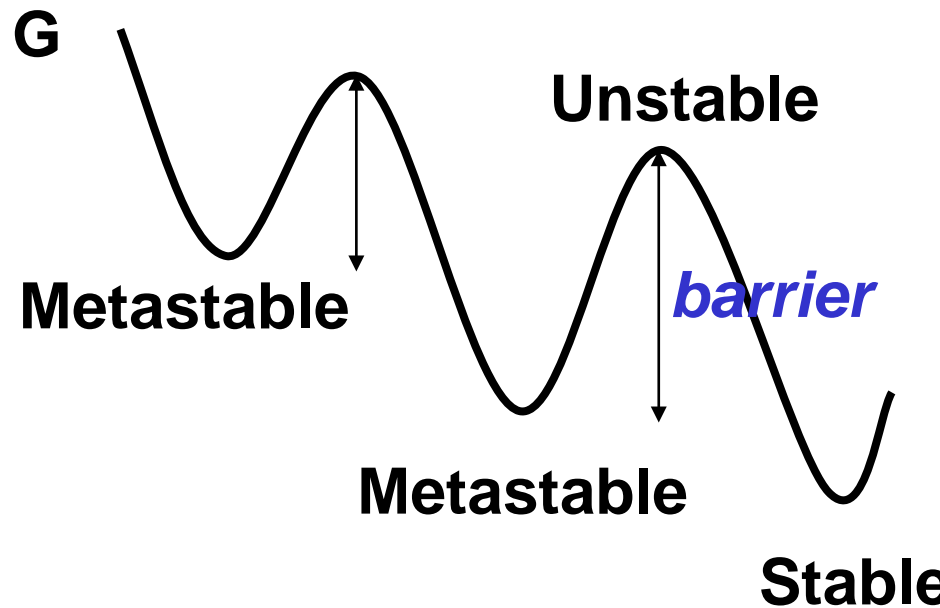
$$\Delta G = G_2 - G_1 < 0$$

Phase 1  $\rightarrow$  phase 2  $\rightarrow$

equilibrium state

structure or composition or order

Lowest possible value of Gibb's Free Energy  
No desire to change ad infinitum

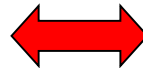


# How does thermodynamics different from kinetics?

**Thermodynamics** → **There is no time variable.**

says which process is possible or not and never says how long it will take.

The existence of a thermodynamic driving force does not mean that the reaction will necessarily occur!!!



**Allotrope (同質異像): any of two or more physical forms in which an element can exist**  
화학적 성분 같고 결정구조 다름

There is a driving force for diamond to convert to **graphite**  
but there is (huge) nucleation barrier.

How long it will take is the problem of **kinetics**.  
The **time variable** is a **key parameter**.

# Phase Transformation

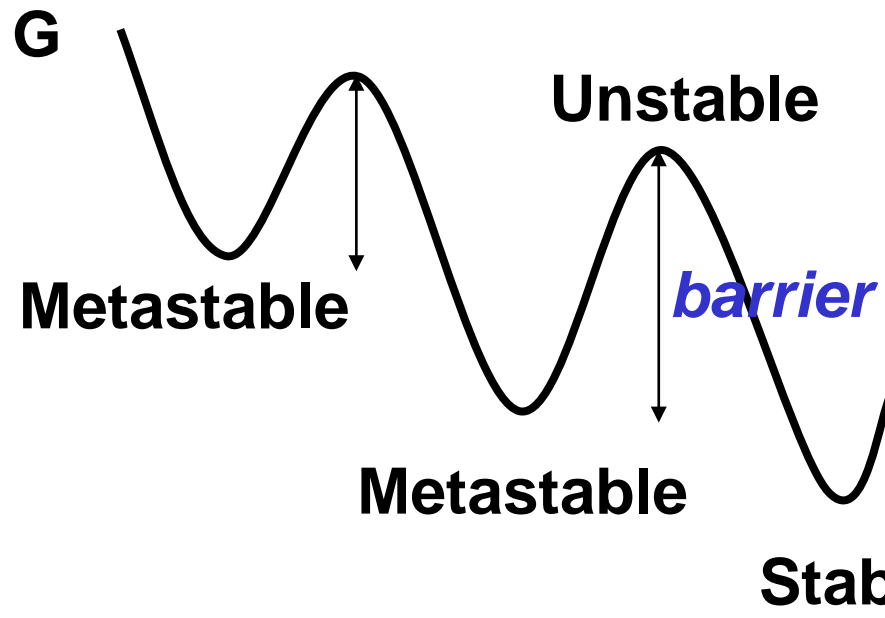
$$\Delta G = G_2 - G_1 < 0$$

Phase 1  $\rightarrow$  phase 2  $\rightarrow$

equilibrium state

structure or composition or order

Lowest possible value of Gibb's Free Energy  
No desire to change ad infinitum



$\rightarrow$  Governed by Thermodynamics & Kinetics

**Q9: What are the representative PTs?**



## 9) Representative Phase Transformation

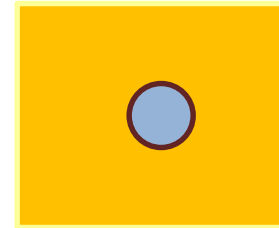
- **Solidification: Liquid  $\rightarrow$  Solid**
- **Phase transformation in Solids**
  - ① **Diffusion-controlled phase transformation ;**  
**Generally long-distance atomic migration**
    - Precipitation transformation
    - Eutectoid transformation ( **S  $\rightarrow$  S<sub>1</sub> + S<sub>2</sub>** )
    - etc.
  - ② **Diffusionless transformation ;**  
**Short-distance atomic migration**
    - Martensitic transformation

# Melting and Crystallization are **Thermodynamic Transitions**

**Solidification:** Liquid  $\rightarrow$  Solid

<Thermodynamic>

• Interfacial energy  $\Rightarrow \Delta T_N$



Liquid

$T_m$

Undercooled Liquid

Solid

No superheating required!

• Interfacial energy  $\Rightarrow$  No  $\Delta T_N$

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

**Melting:** Liquid  $\leftarrow$  Solid

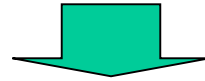
vapor



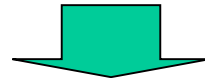
In general, wetting angle = 0  $\Rightarrow$  No superheating required!

## ① Diffusion-controlled phase transformation

**Diffusion- Controlled Phase Transformation**  
**time dependency**



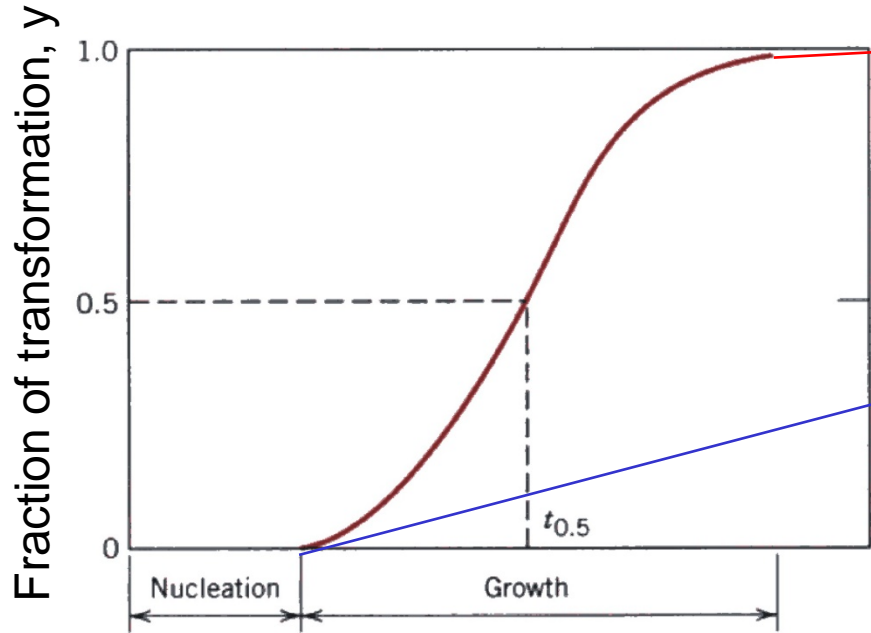
**Non-Equilibrium Phases → Equilibrium phase**



**a. Need of Controlling**  
**not only *Temperature* & *Composition***  
**but *Process conditions* (*Cooling Rate*)**

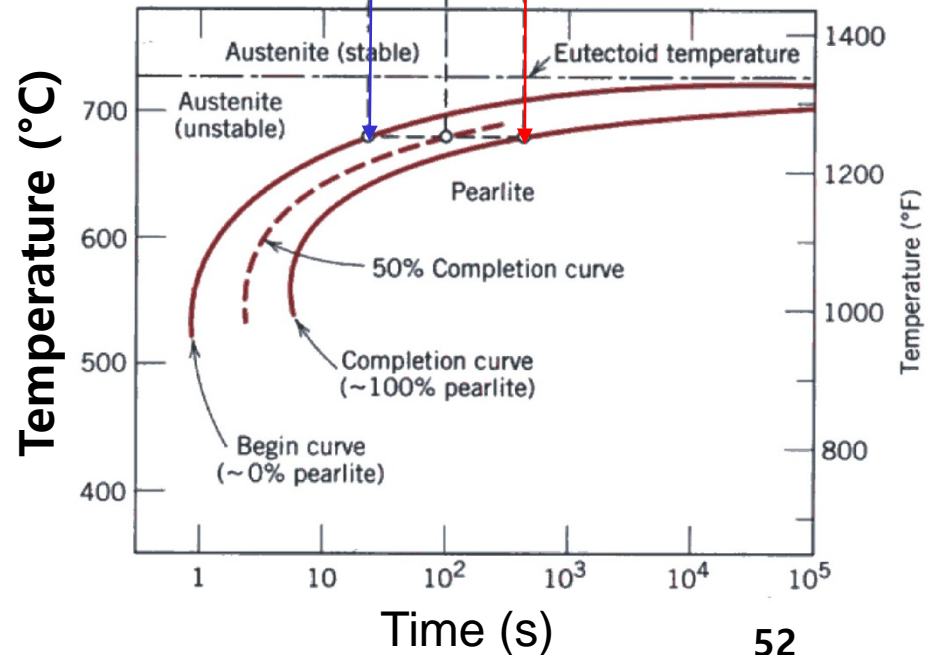
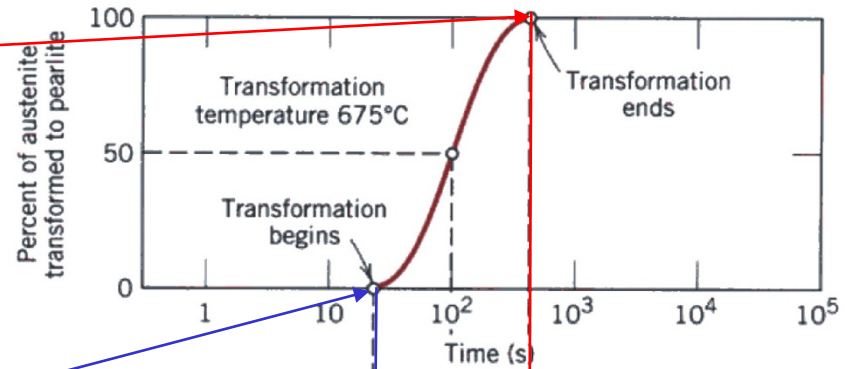
# Transformation Kinetics :

## b. Isothermal Transformation Diagram



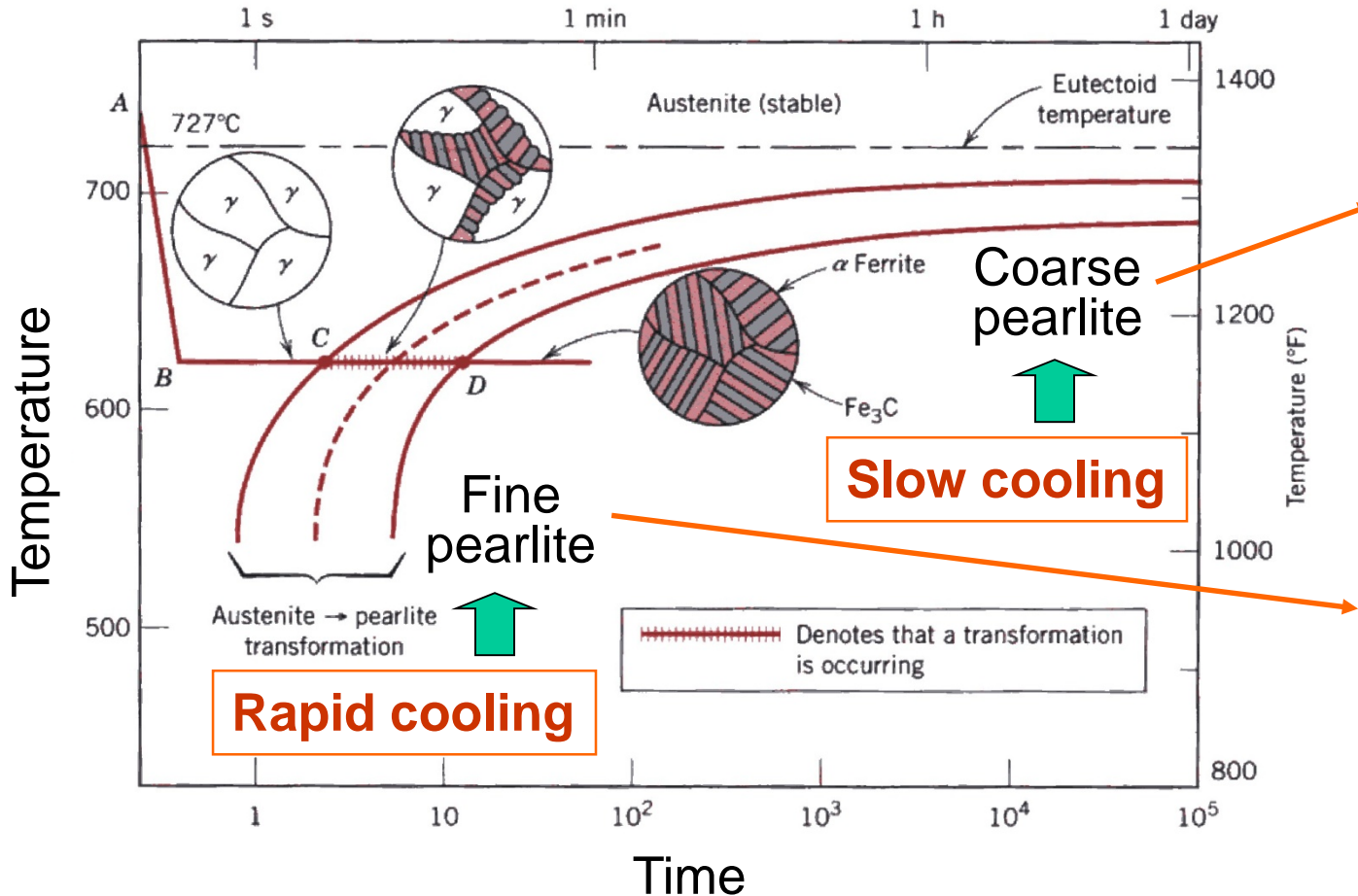
$$y = \exp(-kt^n)$$

Kinetics of diffusion-controlled solid-state transformation



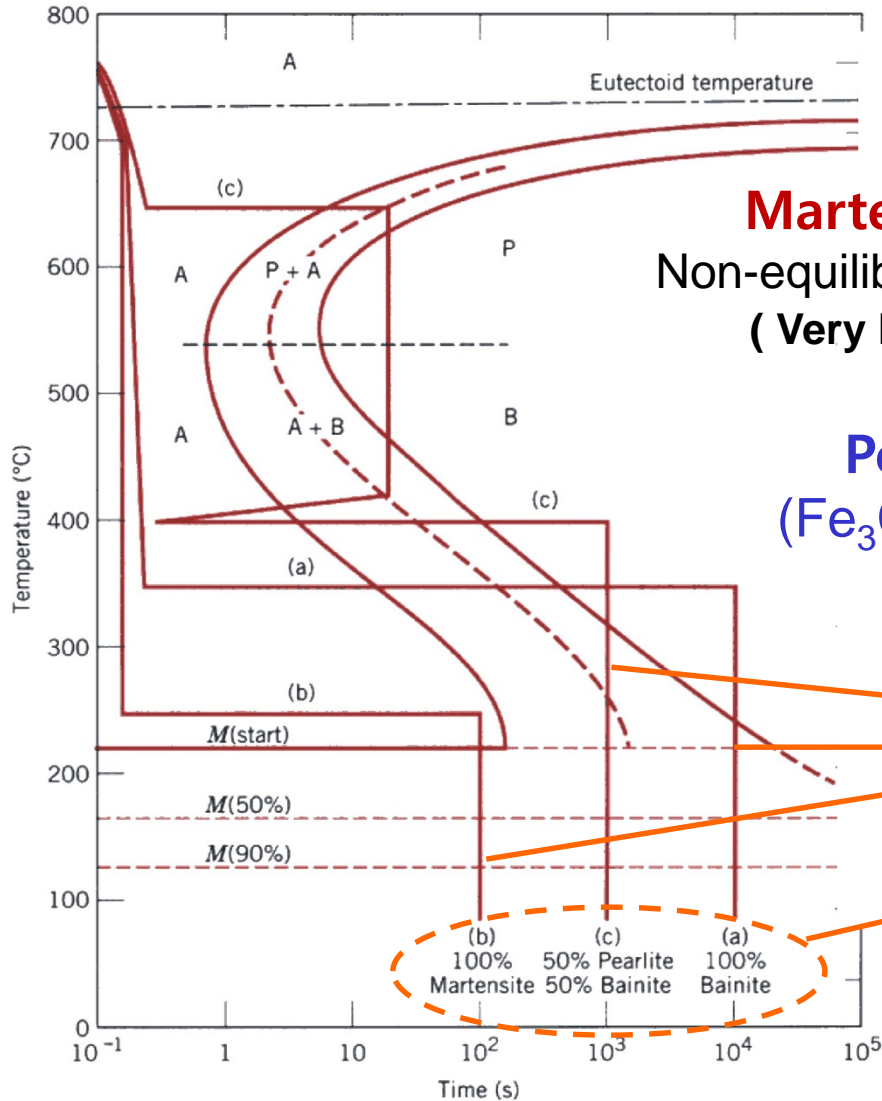
TTT diagram → Isothermal transformation diagram

# c. Isothermal Transformation Diagram of a Eutectoid Iron-Carbon Alloy



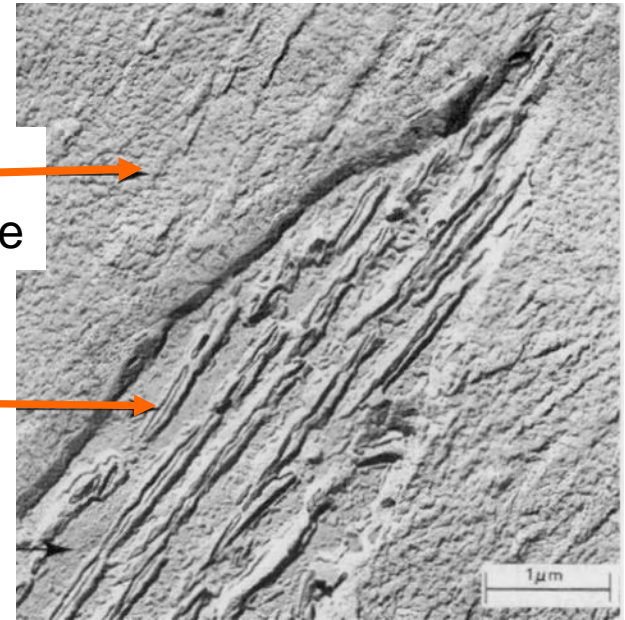
$\rightarrow$  Microstructure control by phase transformation

# d. Control of Phases by Heat Treatment



**Martensite** ;  
Non-equilibrium phase  
( Very hard )

**Pearlite**  
(Fe<sub>3</sub>C+ferrite)



**Heat Treatment** Process control

**Phase & Microstructure**

**Properties of Material**

# e. Control of Mechanical Properties by Proper Heat Treatment in Iron-Carbon Alloy



**Martensite**

Tip of needle shape grain

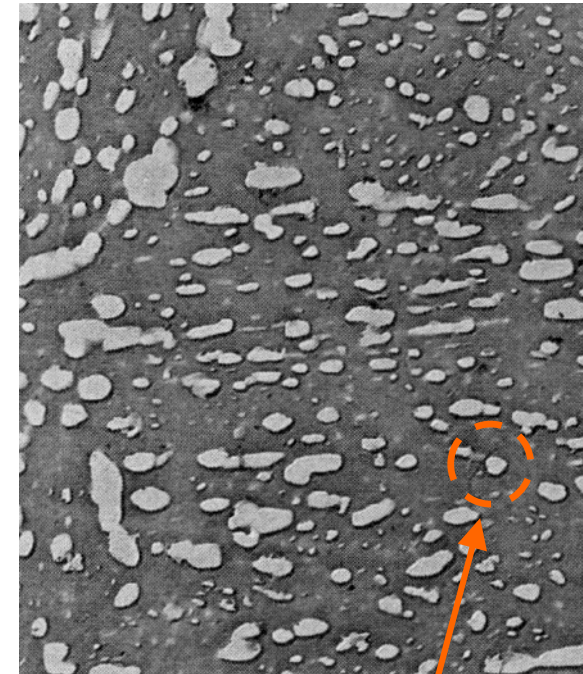
Nucleation site of fracture

Brittle

Process control



Proper heat treatment (tempering)



**Tempered martensite**

Very small & spherical shape grain

Good strength, ductility, toughness

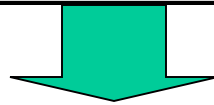
## ② Diffusionless Transformation

Individual atomic movements are less than one interatomic spacing.

e.g. a Martensitic transformation in iron-carbon alloy

**e.g. b Martensitic transformation in Ni-Ti alloy ;**

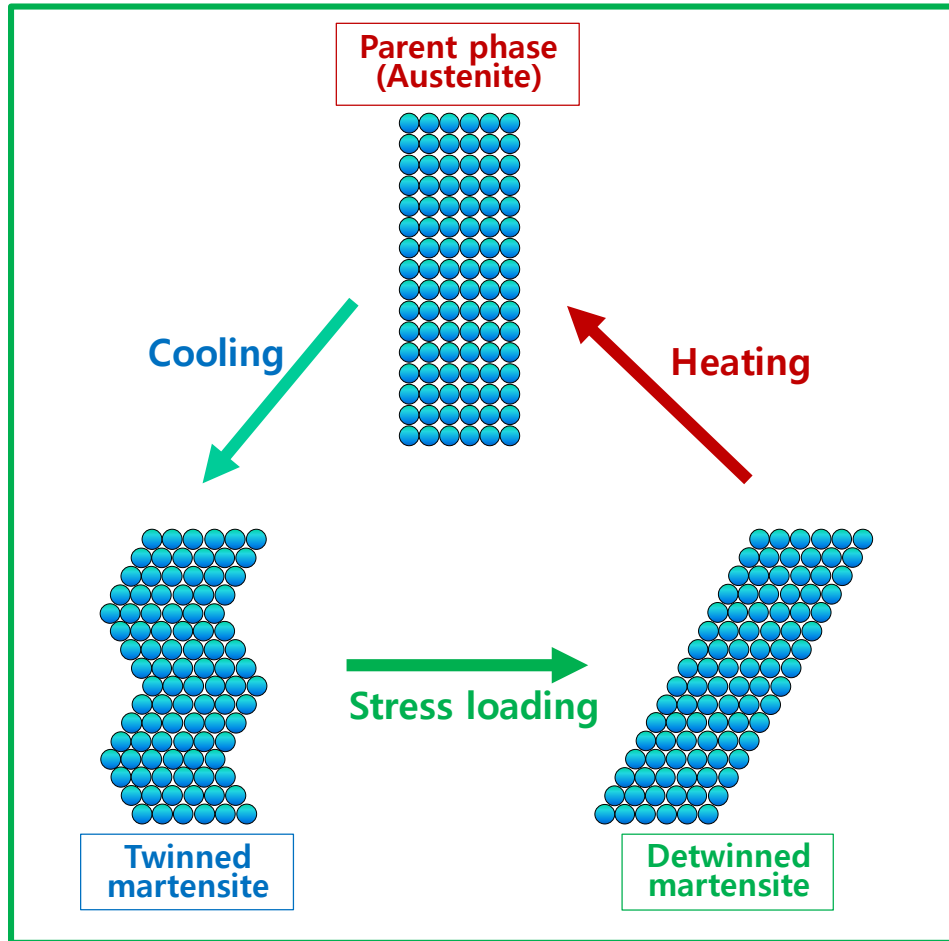
**55~55.5 wt%Ni - 44.5~45 wt%Ti (“Nitinol”)**



**Ex) Shape memory alloy**



# Principles - Shape memory process

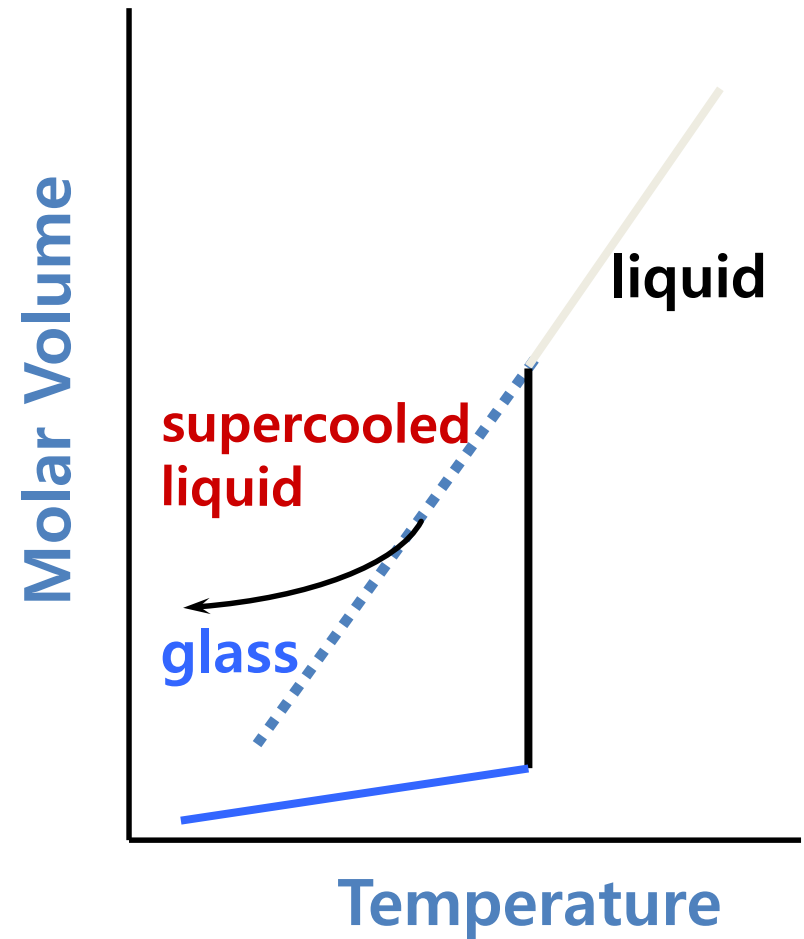


1.  $A_f$  이상의 온도로 열처리를 통해 Austenite 상에서 형상 기억
2.  $M_s$  이하의 온도로 냉각시 Twinned martensite 생성
3. 항복강도 이상의 응력을 가하면 Twin boundary의 이동에 의한 소성 변형
4.  $A_f$  이상으로 가열해주면 martensite 에서 다시 Austenite로 변태  
 → 기억된 형상으로 회복

“  $\gamma \leftrightarrow M$  transformation: Short-distance atomic migration ”

# Glass Formation is Controlled by **Kinetics**

- Glass-forming liquids are those that are able to **“by-pass” the melting point,  $T_m$**
- Liquid may have a **“high viscosity”** that makes it difficult for atoms of the liquid to diffuse (rearrange) into the crystalline structure
- Liquid maybe cooled so fast that it does **not have enough time to crystallize**
- Two time scales are present
  - **“Internal” time scale** controlled by the viscosity (bonding) of the liquid
  - **“External” timescale** controlled by the cooling rate of the liquid



# Microstructure-Properties Relationships

Alloy design &  
Processing

Performance

“Phase Transformation”

Microstructure  
down to atomic scale

Properties

*“Tailor-made Materials Design”*

**Q10: What are the contents of this course?**

# 10) Contents of this course\_Phase transformation

**Background  
to understand  
phase  
transformation**

(Ch1) Thermodynamics and Phase Diagrams

(Ch2) Diffusion: Kinetics

(Ch3) Crystal Interface and Microstructure

**Representative  
Phase  
transformation**

(Ch4) Solidification: Liquid  $\rightarrow$  Solid

(Ch5) Diffusional Transformations in Solid: Solid  $\rightarrow$  Solid

(Ch6) Diffusionless Transformations: Solid  $\rightarrow$  Solid

**2021 Fall**

# **“Phase Transformation *in* Materials”**

**09.06.2021**

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**Office hours: by an appointment**

Contents for previous class

# Microstructure-Properties Relationships

Alloy design &  
Processing

Performance

“Phase Transformation”

Microstructure  
down to atomic scale

Properties

*“Tailor-made Materials Design”*

## Contents for previous class

# Contents of this course\_Phase transformation

**Background  
to understand  
phase  
transformation**

(Ch1) Thermodynamics and Phase Diagrams

(Ch2) Diffusion: Kinetics

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**Representative  
Phase  
transformation**

(Ch4) Solidification: Liquid  $\rightarrow$  Solid

(Ch5) Diffusional Transformations in Solid: Solid  $\rightarrow$  Solid

(Ch6) Diffusionless Transformations: Solid  $\rightarrow$  Solid



# Contents for today's class I

## Chapter 1

### Thermodynamics and Phase Diagrams

- **Equilibrium**

- **Single component system**

  - Gibbs Free Energy  
as a Function of Temp. and Pressure

- **Classification of phase transition**

- **Driving force for solidification**

# **Q1: “thermodynamic equilibrium”?**

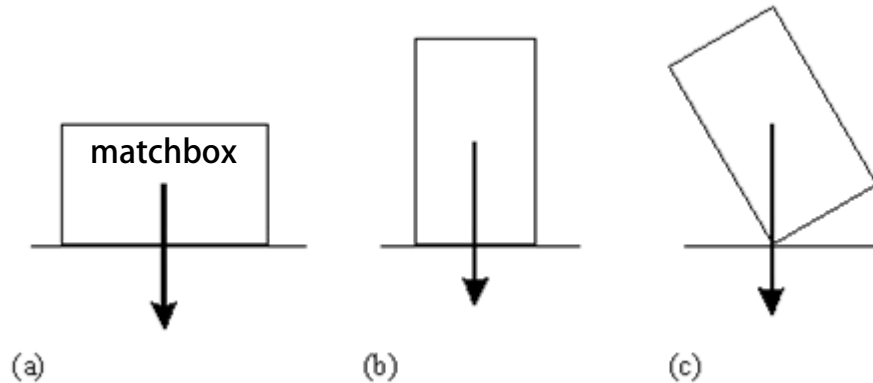
**Lowest possible value of Gibb’s Free Energy**

→ **The main use of thermodynamics in metallurgy is to allow the prediction of whether an alloy is in equilibrium.**

# Chapter 1

## Equilibrium

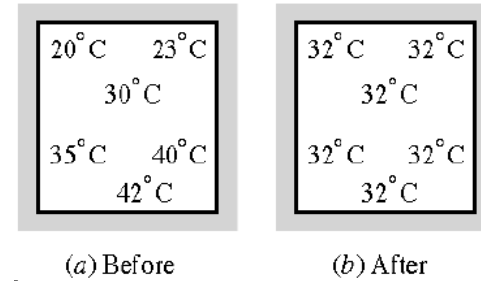
### Mechanical equilibrium



: total potential energy of the system is a minimum.

### Thermal equilibrium

: absence of temperature gradients in the system



### Chemical equilibrium

: no further reaction occurs between the reacting substances  
i.e. the forward and reverse rates of reaction are equal.

## Thermodynamic equilibrium

: the system is under mechanical, thermal and chemical equilibrium

The properties of the system-P, T, V, concentrations-do not change with time.

# Chapter 1.1

Relative Stability of a System  $\Rightarrow$  Gibbs Free Energy

$$\text{Gibbs free energy : } G = E + PV - TS = H - TS$$

**Useful when P is constrained during thermodynamic process.**

*H : Enthalpy* ; Measure of the heat content of the system

Mixture of one or more phases

$$H = E + PV$$

$$H \cong E \text{ for Condensed System}$$

**E : Internal Energy**, Kinetic + Potential Energy of a atom within the system

Kinetic Energy :

Atomic Vibration (Solid, Liquid)

Translational and Rotational Energy in liquid and gas.

Potential Energy : Interactions or Bonds between the atoms within the system

*T : The Absolute Temperature*

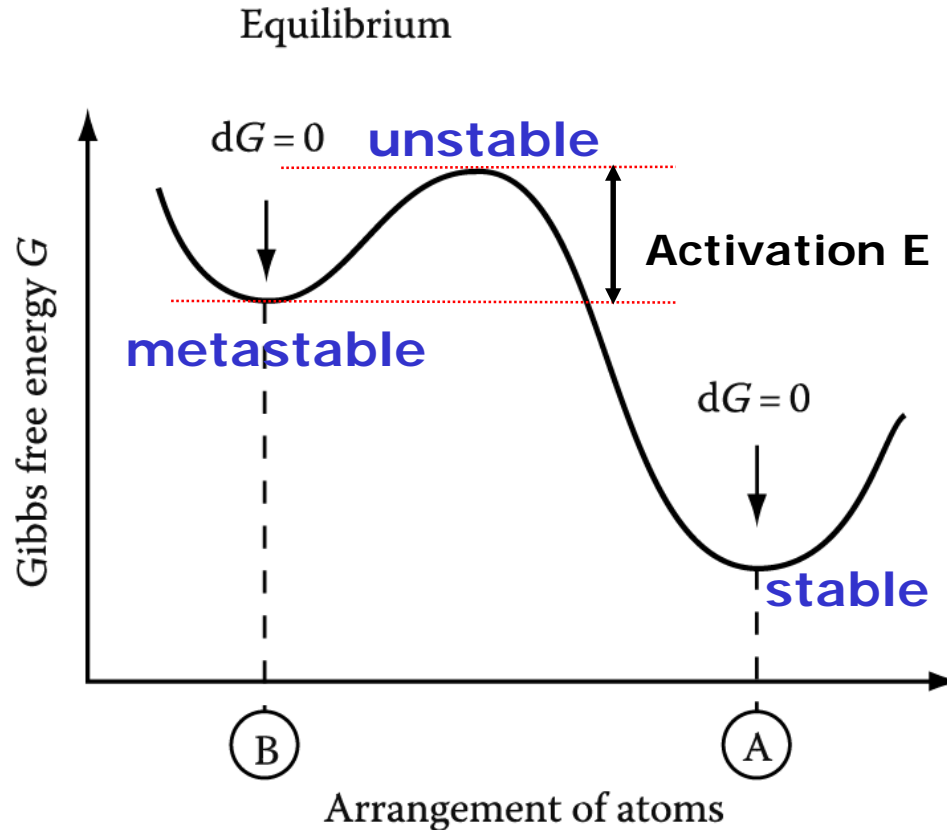
*S : Entropy*, The *Randomness* of the System

## Equilibrium

$$dG = 0$$

**Lowest possible value of Gibb's Free Energy**

No desire to change ad infinitum



Phase Transformation

$$\Delta G = G_2 - G_1 < 0$$

## **Q2: What is single component system?**

Different elements or chemical compounds

# 1.2 Single component system

One element (Al, Fe)

One type of molecule (H<sub>2</sub>O)

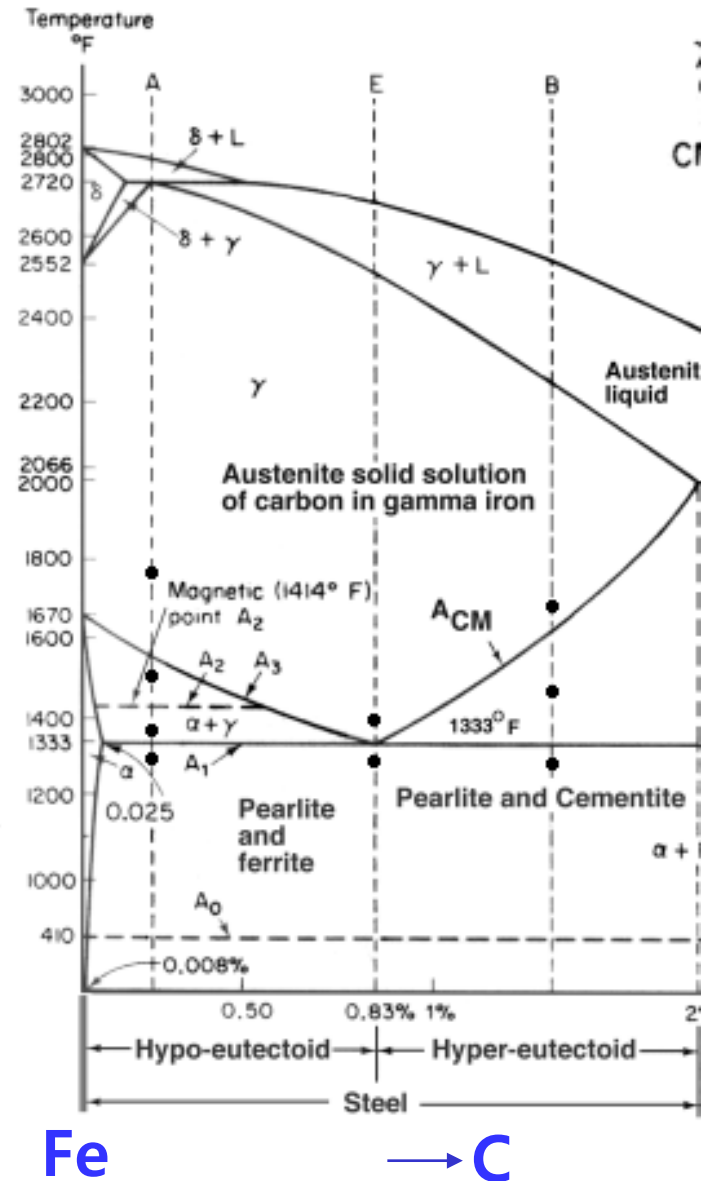
- Allotropic forms?

- How is phase stability measured?

$$G = H - TS$$



1.2.1 Gibbs Free Energy as a Function of Temp. 10



\* What is the role of temperature on equilibrium?

Q3:  $C_v$  vs.  $C_p$  ?

**Specific heat**

(the quantity of heat (in joules) required to raise the temperature of substance by 1K)  
**at constant volume VS. at constant pressure**



$$H = E + PV \longrightarrow dE = \delta Q - P \cdot dV$$

When V is constant,

$$\frac{\delta Q}{dT} = \frac{dE}{dT} + P \frac{dV}{dT} \xrightarrow{0}$$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \quad \text{or} \quad E = \int C_V dT$$

Experimentally, it is easy to keep constant P (Cp) than constant V because it is difficult to make constant V (Cv) → pressure ex) 1 atm,

When pressure is constant,

$$\begin{aligned} H \equiv E + PV &\longrightarrow dH = dE + PdV + VdP \\ &= \delta Q - \delta w + PdV + VdP \\ &= \delta Q - PdV + PdV + VdP \\ &= \delta Q + VdP \end{aligned}$$

$$dE = \delta Q - P \cdot dV$$

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

$$\rightarrow \frac{dP}{dT} = 0 \quad \text{when } P \text{ is constant}$$

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

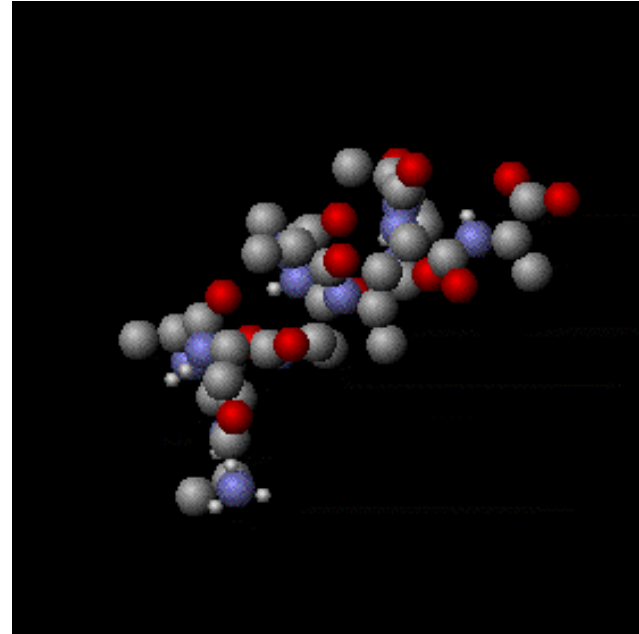
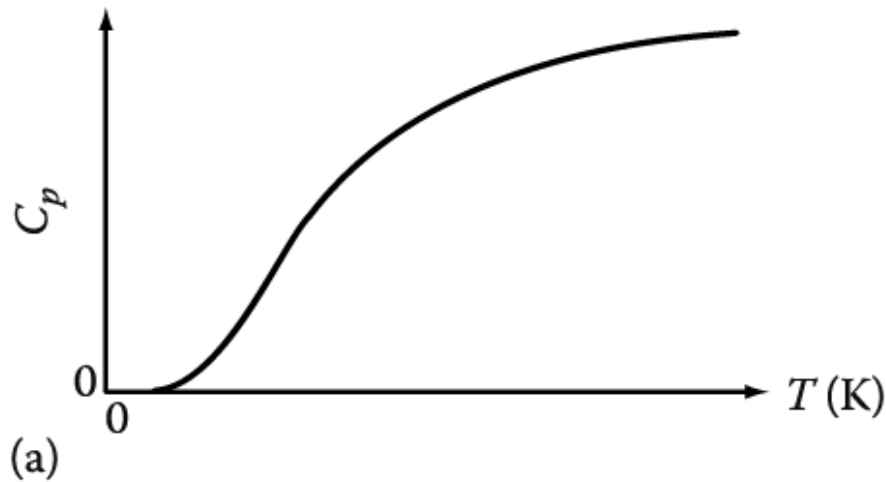
$$H = \int C_P dT$$

In alloy work one usually consider systems at constant pressure so that enthalpy changes are more important than energy changes.

$C_p$ ; temperature-dependent function

$$C_p = a + bT + CT^{-2}$$

(empirical formula above room temp)



Molecules have internal structure because they are composed of atoms that have different ways of moving within molecules. Kinetic energy stored in these internal degrees of freedom contributes to a substance's specific heat capacity and not to its temperature.

**\* What is the role of temperature on equilibrium?**

**Q4: How is  $C_p$  related with H and S?**

# Draw the plots of (a) $C_p$ vs. $T$ , (b) $H$ vs. $T$ and (c) $S$ vs. $T$ .

*How is  $C_p$  related with  $H$  and  $S$ ?*

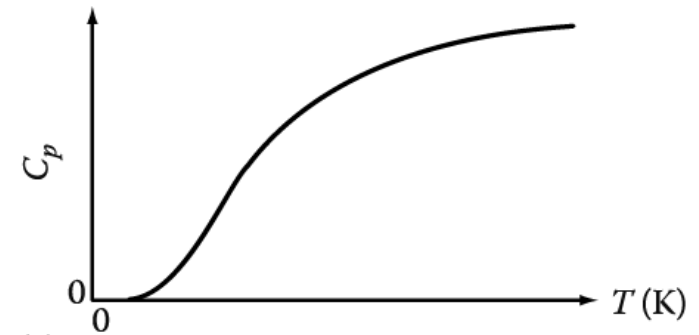
$$C_P = \left( \frac{\partial H}{\partial T} \right)_P \quad H = ? \quad H = \int_{298}^T C_P dT$$

**$H = 0$  at 298K for a pure element  
in its most stable state.**

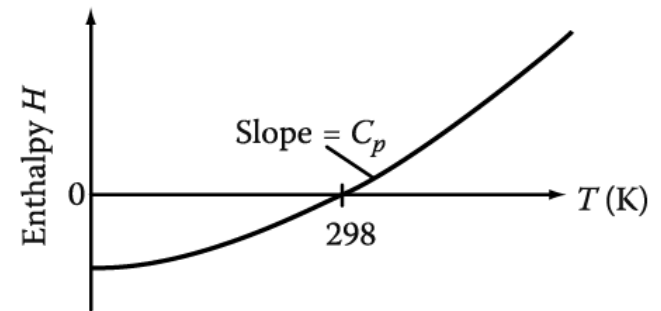
: When considering a phase transformation or a chemical reaction, the important thing is not the value of the thermodynamic function, but **the amount of change.**

Entropy :  $S = \frac{q}{T}$

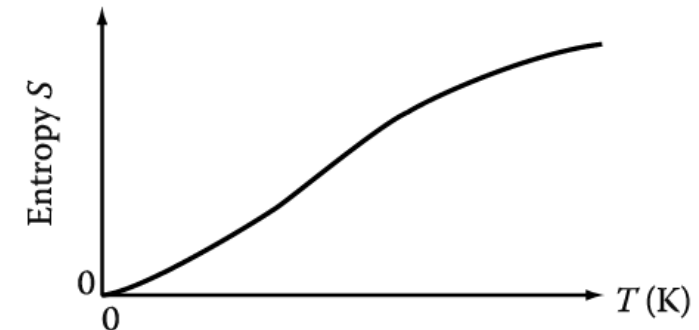
$$S = ? \quad \frac{C_P}{T} = \left( \frac{\partial S}{\partial T} \right)_P \quad S = \int_0^T \frac{C_P}{T} dT$$



(a)



(b)

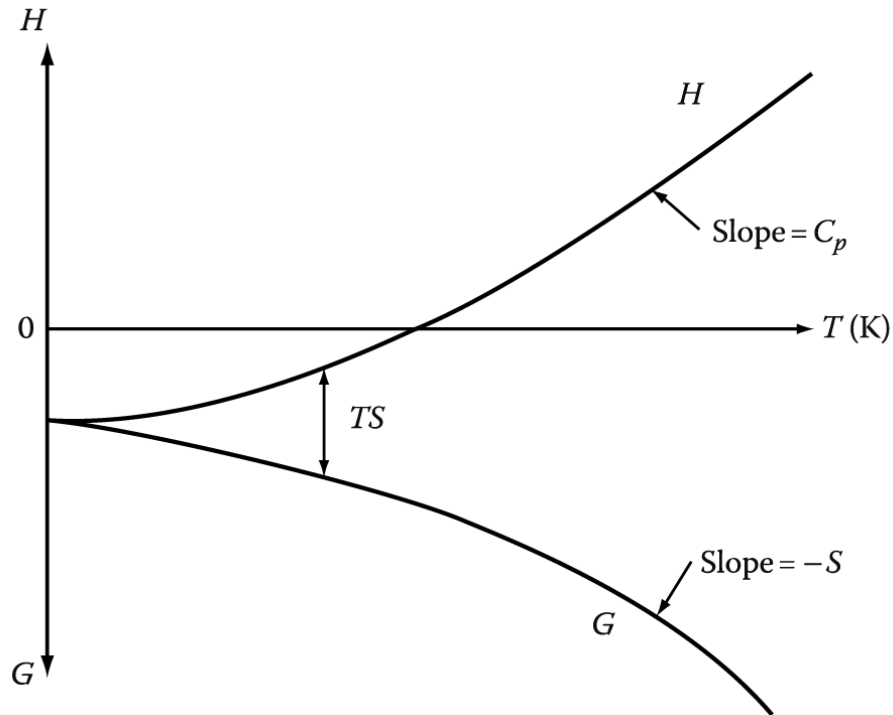


(c)

**\* What is the role of temperature on equilibrium?**

**Q5: How to draw the plots of H vs.T and G vs. T in single component system?**

# Compare the plots of H vs.T and G vs. T.



$$G = G(T, P)$$

$$dG = \left( \frac{\partial G}{\partial T} \right)_P dT + \left( \frac{\partial G}{\partial P} \right)_T dP$$

$$G = H - TS$$

$$dG = dH - d(TS) = dE + d(PV) - d(TS)$$

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

$$= VdP - SdT$$

$$\left( \frac{\partial G}{\partial T} \right)_P = -S, \quad \left( \frac{\partial G}{\partial P} \right)_T = V$$

$$dG = VdP - SdT$$

$$G(P, T) = G(P_0, T_0) + \int_{P_0}^{P_1} V(T_0, P) dP - \int_{T_0}^{T_1} S(P, T) dT$$

**\* What is the role of temperature on equilibrium?**

**Q6:  $G^S$  vs  $G^L$  as a function of temperature?**

## 1.2.1 Gibbs Free Energy as a Function of Temp.

- Which is larger,  $H^L$  or  $H^S$ ?
- $H^L > H^S$  at all temp.
- Which is larger,  $S^L$  or  $S^S$ ?
- $S^L > S^S$  at all temp.

→ Gibbs free energy of the liquid decreases more rapidly with increasing temperature than that of the solid.

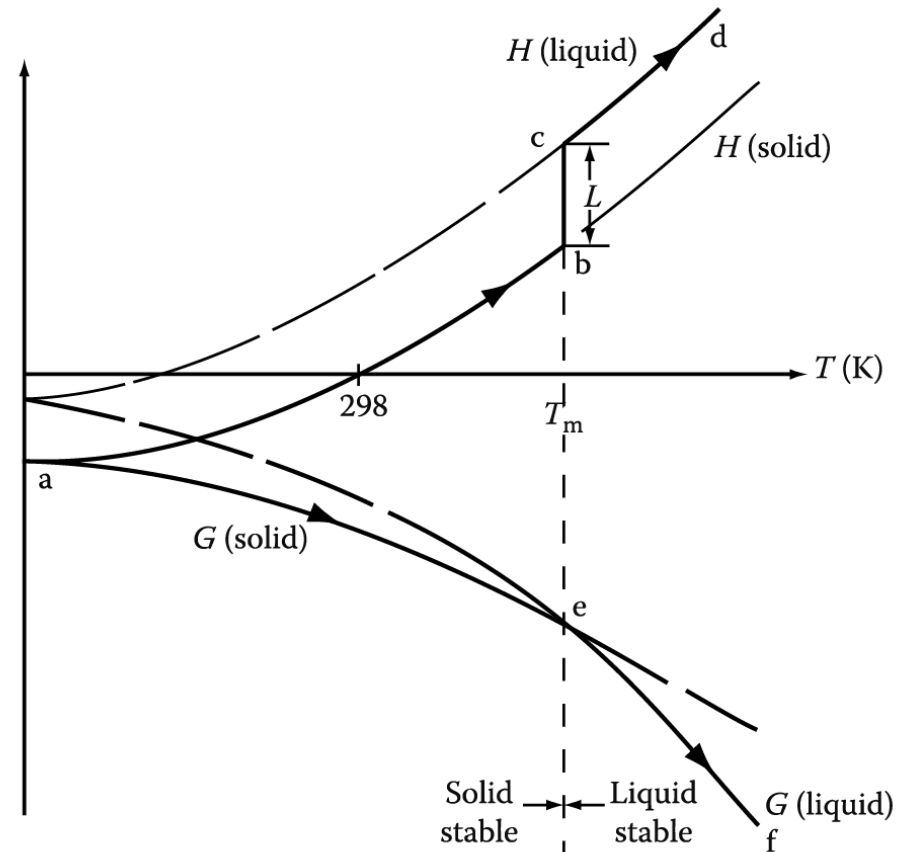


Fig. 1.4 Variation of enthalpy (H) and free energy (G) with temperature for the Solid and liquid phases of a pure metal. L is the latent heat of melting,  $T_m$  the Equilibrium melting temperature.

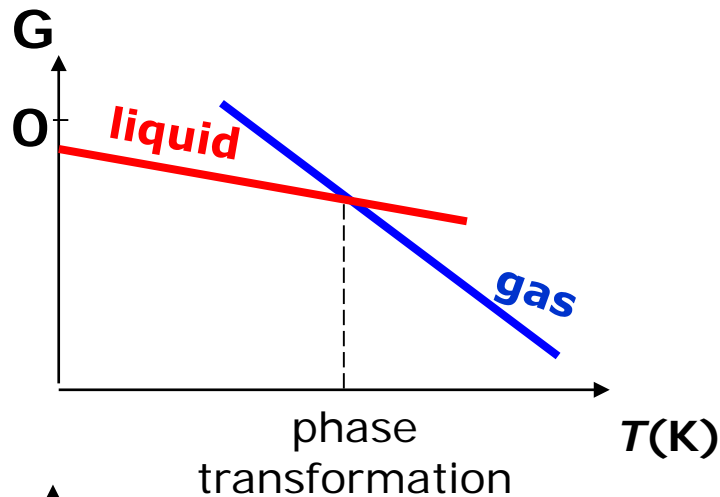
- Which is larger,  $G^L$  or  $G^S$  at low T?
- $G^L > G^S$  (at low Temp) and  $G^S > G^L$  (at high Temp)



Considering  $P, T$   $G = G(T, P)$

$$dG = VdP - SdT$$

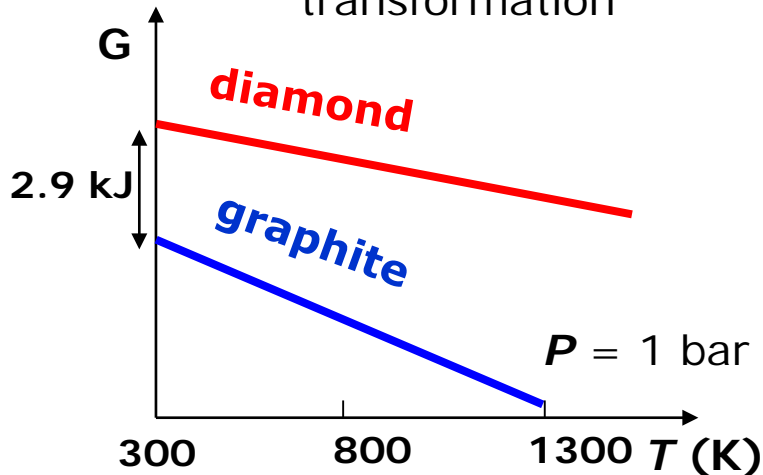
$$G(P, T) = G(P_0, T_0) + \int_{P_0}^{P_1} V(T_0, P)dP - \int_{T_0}^{T_1} S(P, T)dT$$



$$S(\text{water}) = 70 \text{ J/K}$$

$$S(\text{vapor}) = 189 \text{ J/K}$$

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



$$S(\text{graphite}) = 5.74 \text{ J/K,}$$

$$S(\text{diamond}) = 2.38 \text{ J/K,}$$

## Q7: What is the role of pressure on equilibrium?

$$* \textit{Clausius-Clapeyron Relation} : \left( \frac{dP}{dT} \right)_{eq} = \frac{\Delta H}{T_{eq} \Delta V}$$

(applies to all coexistence curves)

## 1.2.2 Pressure Effects

**When the two phases with different molar volumes are in equilibrium, if the pressure changes, the equilibrium temperature T should also change with pressure.**

If  $\alpha$  &  $\beta$  phase are equilibrium,

$$dG^\alpha = V^\alpha dP - S^\alpha dT$$

$$dG^\beta = V^\beta dP - S^\beta dT$$

At equilibrium,

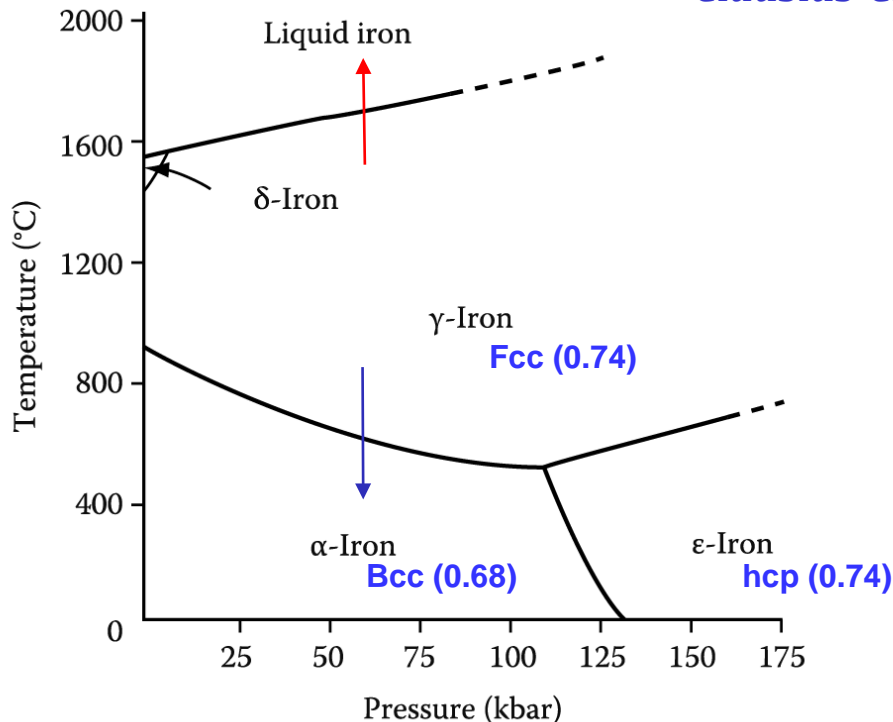
$$dG^\alpha = dG^\beta$$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{S^\beta - S^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S}{\Delta V}$$

Here,  $\Delta S = \frac{\Delta H}{T_{eq}}$

**\* Clausius-Clapeyron Relation :** 
$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq} \Delta V}$$

(applies to all coexistence curves)



For,  $\gamma \rightarrow$  liquid;  $\Delta V (+)$ ,  $\Delta H(+)$

$$\left(\frac{dP}{dT}\right) = \frac{\Delta H}{T_{eq} \Delta V} > 0$$

For,  $\alpha \rightarrow \gamma$  ;  $\Delta V (-)$ ,  $\Delta H(+)$

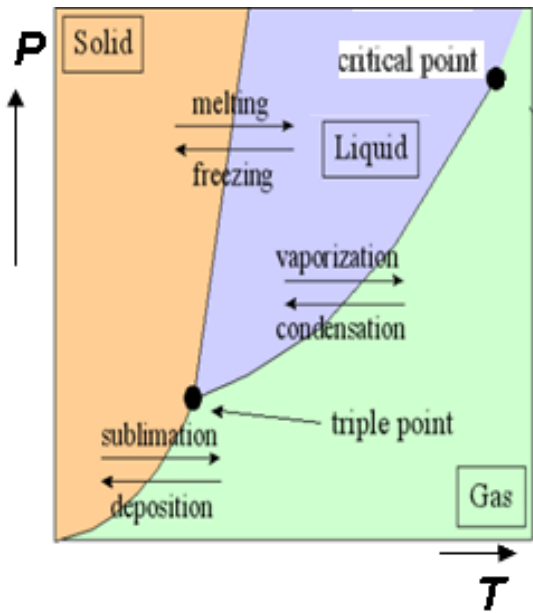
$$\left(\frac{dP}{dT}\right) = \frac{\Delta H}{T_{eq} \Delta V} < 0$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Fig. 1.5 Effect of pressure on the equilibrium phase diagram for pure iron

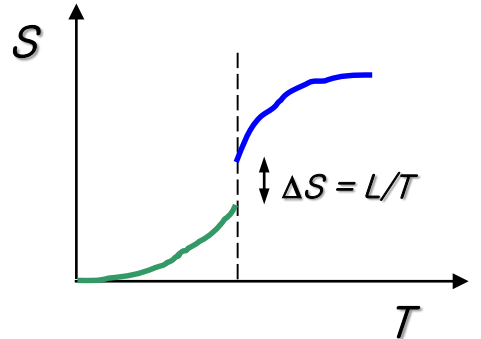
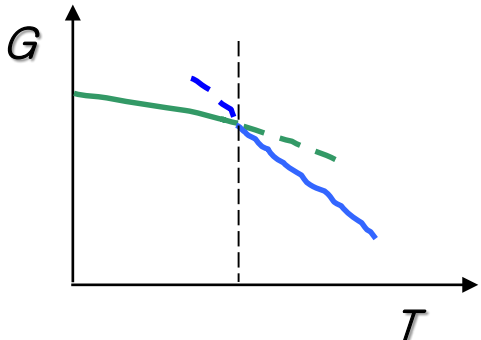
**Q8: How to classify phase transition?**

**“First order transition” vs “Second order transition”**

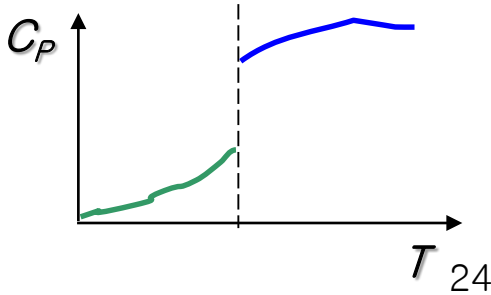


# The First-Order Transition

Latent heat  
Energy barrier  
Discontinuous entropy, heat capacity



$$C_P = T \left( \frac{\partial S}{\partial T} \right)_{P,N}$$



• First Order Phase Transition at  $T_T$ :

- $G$  is **continuous** at  $T_T$
- First derivatives of  $G$  ( $V, S, H$ ) are **discontinuous** at  $T_T$

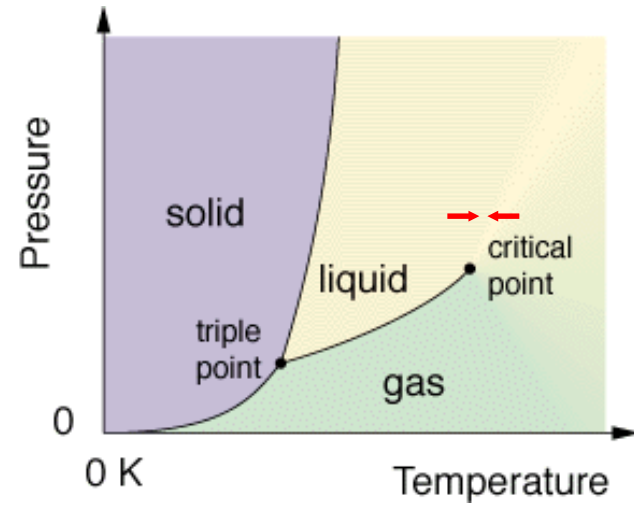
$$V = \left( \frac{\partial G}{\partial P} \right)_T \quad S = - \left( \frac{\partial G}{\partial T} \right)_P \quad H = G - T \left( \frac{\partial G}{\partial T} \right)_P$$

- Second derivatives of  $G$  ( $\alpha, \beta, C_p$ ) are **discontinuous** at  $T_T$

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P \quad \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \beta = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

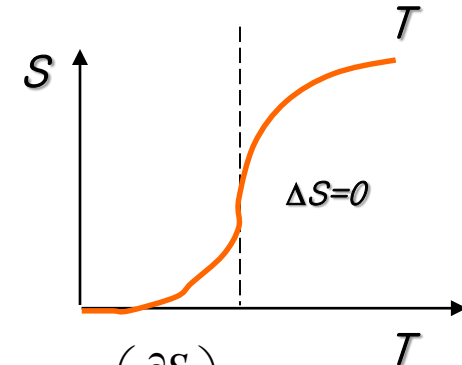
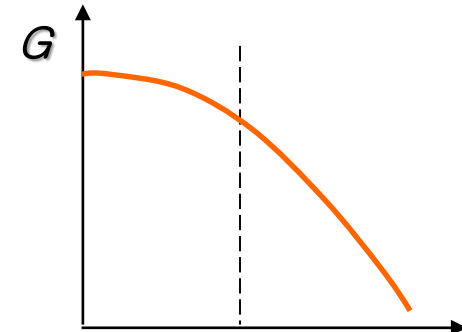
- **Examples:** Vaporization, Condensation, Fusion, Crystallization, Sublimation.

# The Second Order Transition

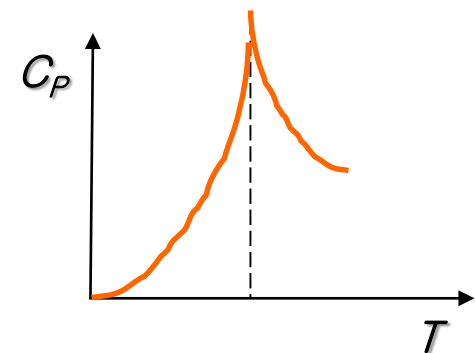


No Latent heat  
Continuous entropy

Second-order transition



$$C_P = T \left( \frac{\partial S}{\partial T} \right)_{P,N} \rightarrow \infty$$



## • Second Order Phase Transition at $T_T$ :

–  $G$  is **continuous** at  $T_T$

– First derivatives of  $G$  ( $V$ ,  $S$ ,  $H$ ) are **continuous** at  $T_T$

$$V = \left( \frac{\partial G}{\partial P} \right)_T \quad S = - \left( \frac{\partial G}{\partial T} \right)_P \quad H = G - T \left( \frac{\partial G}{\partial T} \right)_P$$

– Second derivatives of  $G$  ( $\alpha$ ,  $\beta$ ,  $C_p$ ) are **discontinuous** at  $T_T$

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P \quad \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \beta = \frac{-1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

– **Examples:** Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

**Q9: What is the driving force for  
“Solidification: Liquid → Solid”?**

## 1.2.3 Driving force for solidification

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

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

$$\Delta G = \Delta H - T \Delta S$$

$$L : \Delta H = H^L - H^S$$

(Latent heat)

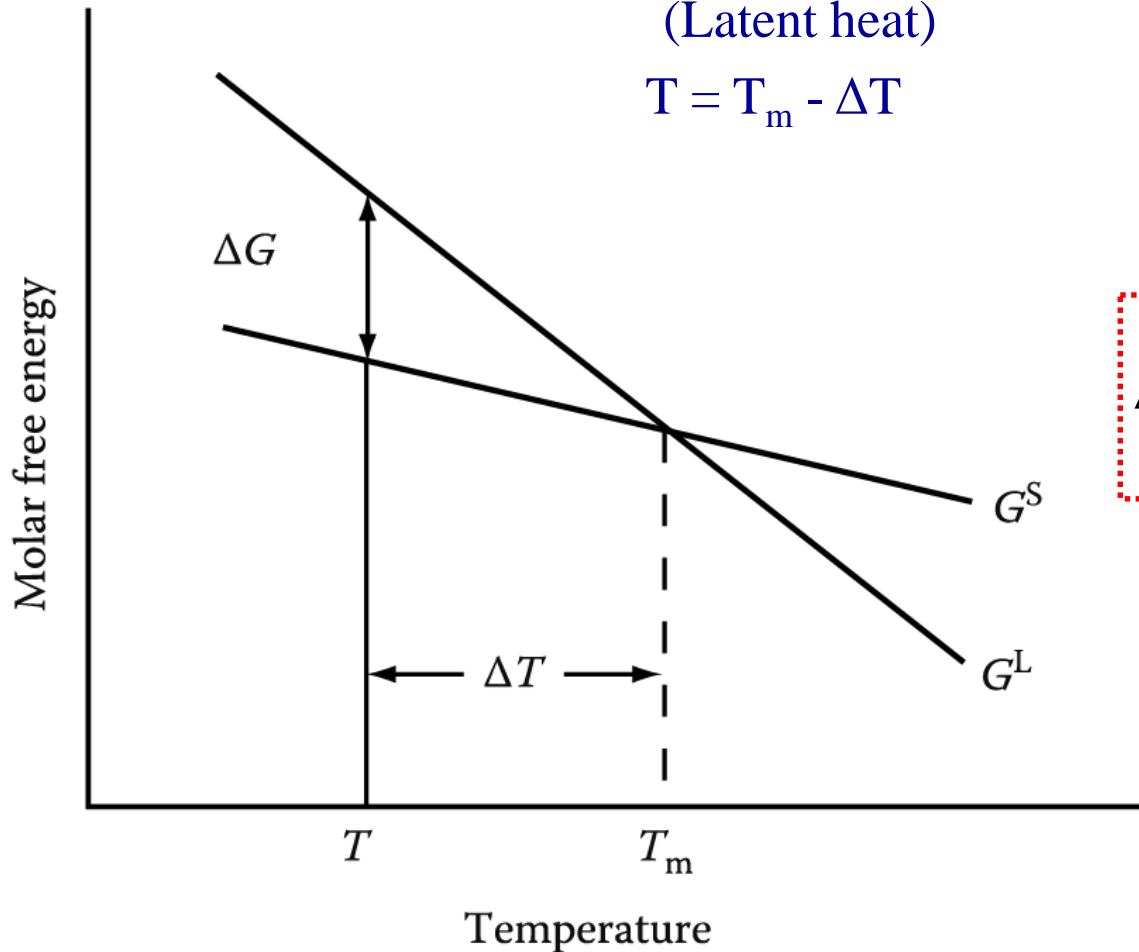
$$T = T_m - \Delta T$$

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

$$\Delta S = \Delta H / T_m = L / T_m$$

$$\Delta G = L - T(L/T_m) \approx (L\Delta T) / T_m$$

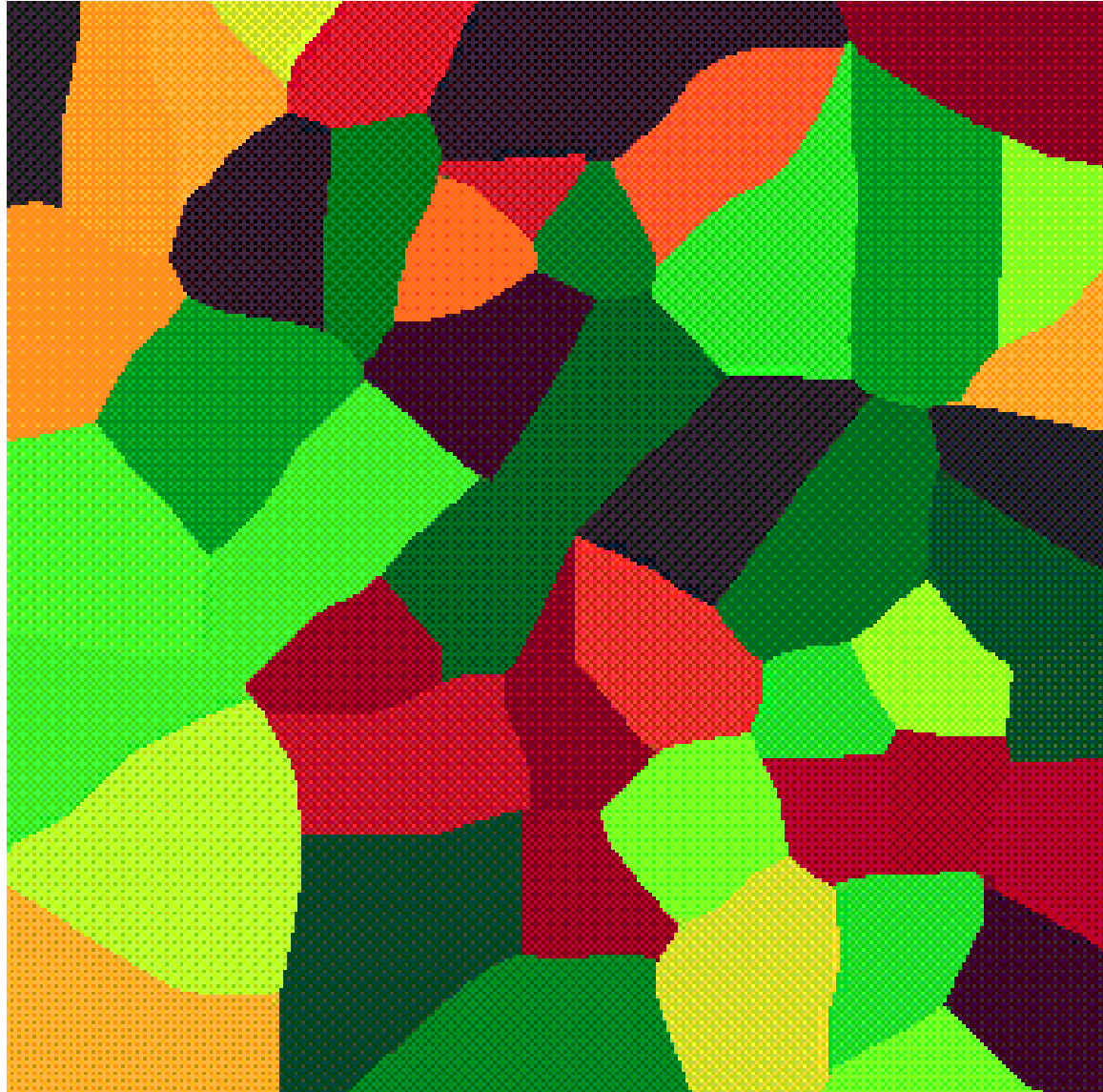
(eq. 1.17)



$$\Delta G = \frac{L\Delta T}{T_m}$$

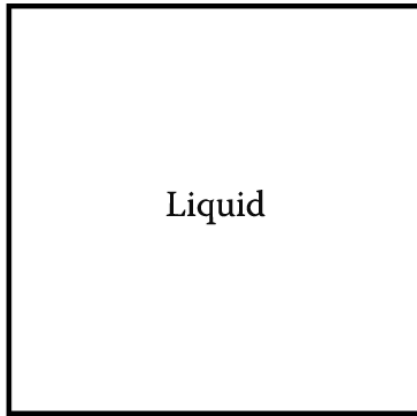


4. Solidification: Liquid  $\longrightarrow$  Solid



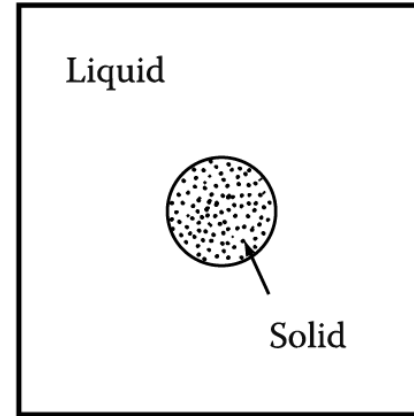
4 Fold Anisotropic Surface Energy/2 Fold Kinetics, Many Seeds

## 4.1.1. Homogeneous Nucleation



(a)  $G_1$

$$G_1 = (V_S + V_L)G_V^L$$



(b)  $G_2 = G_1 + \Delta G$

$$G_2 = V_S G_V^S + V_L G_V^L + A_{SL} \gamma_{SL}$$

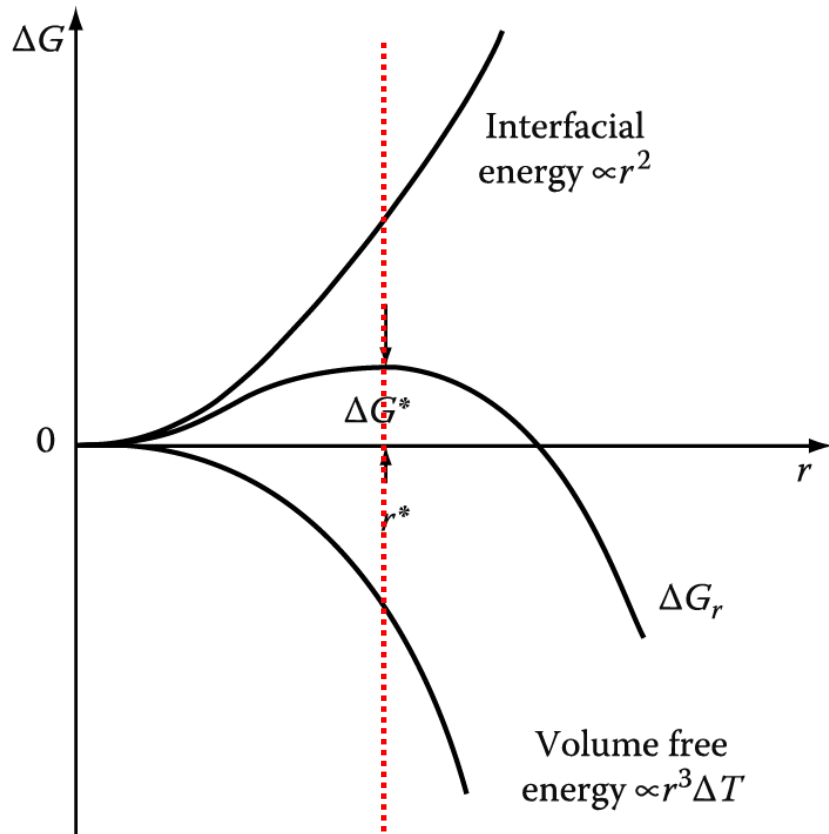
$G_V^S, G_V^L$  : free energies per unit volume

$$\Delta G = G_2 - G_1 = -V_S (G_V^L - G_V^S) + A_{SL} \gamma_{SL}$$

for spherical nuclei (isotropic) of radius :  $r$

$$\Delta G_r = -\frac{4}{3} \pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

# 4.1.1. Homogeneous Nucleation



**Unstable equilibrium**

Fig. 4.2 The free energy change associated with homogeneous nucleation of a sphere of radius  $r$ .

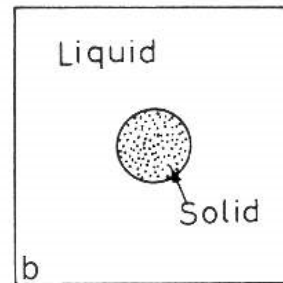
**Why  $r^*$  is not defined by  $\Delta G_r = 0$ ?**

$r < r^*$  : **unstable** (lower free E by reduce size)

$r > r^*$  : **stable** (lower free E by increase size)

$r^*$  : **critical nucleus size**

$r^*$   $\longrightarrow$   **$dG=0$**

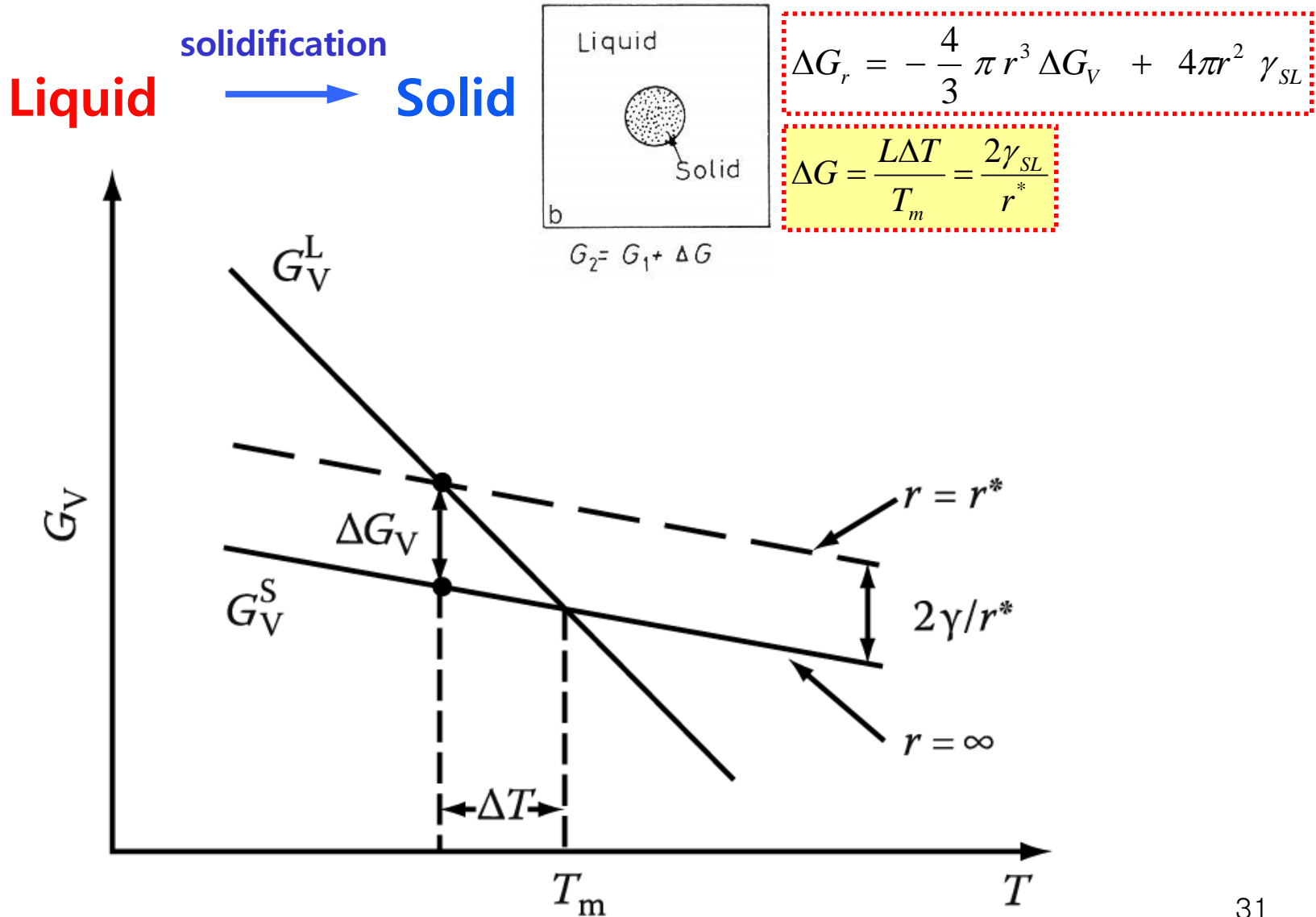


$$G_2 = G_1 + \Delta G$$

$$\Delta G_r = -\frac{4}{3} \pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

$$\Delta G^* = \frac{2\gamma_{SL}}{r^*}$$

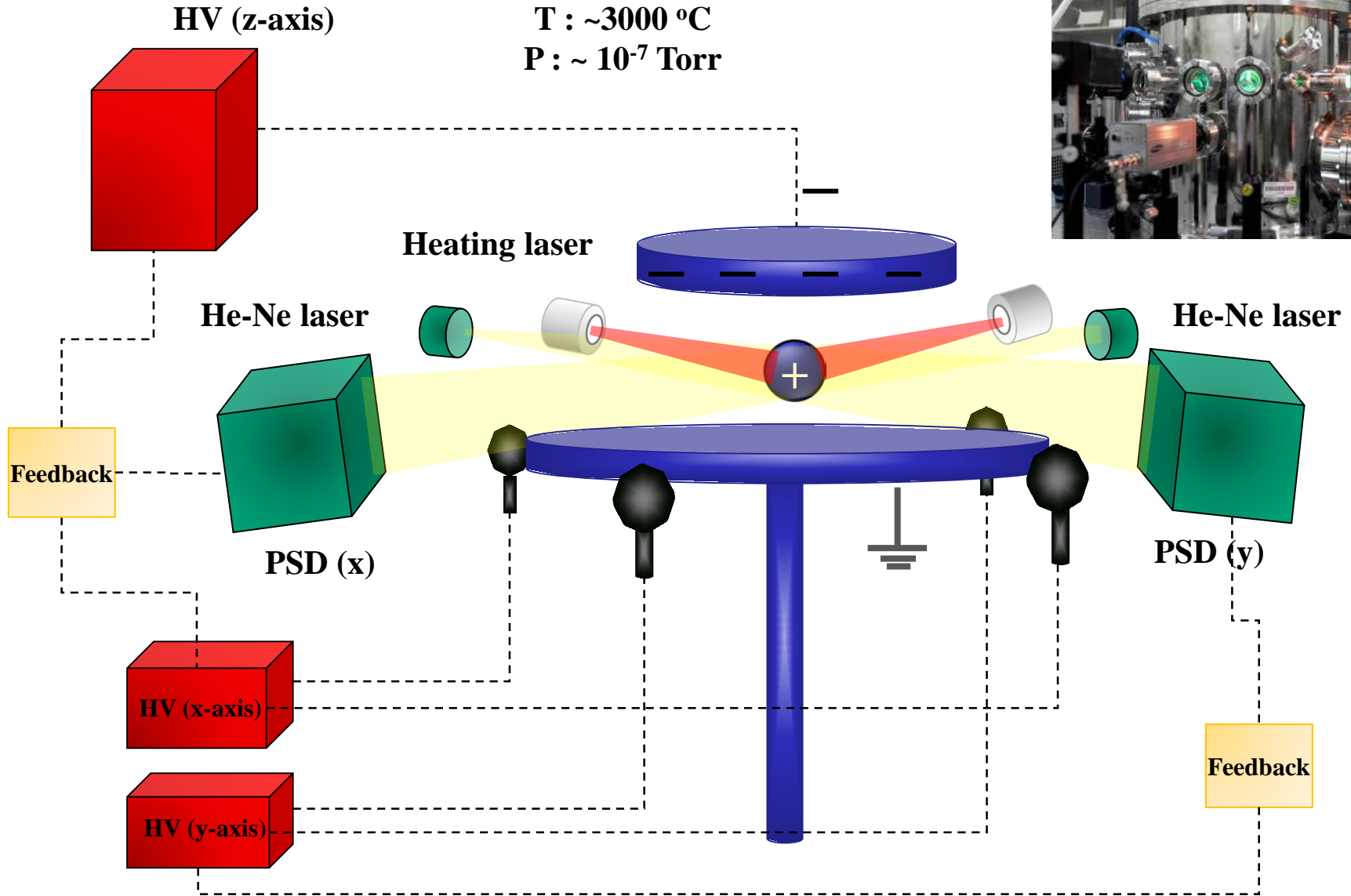
## 1.2.3 Driving force for solidification

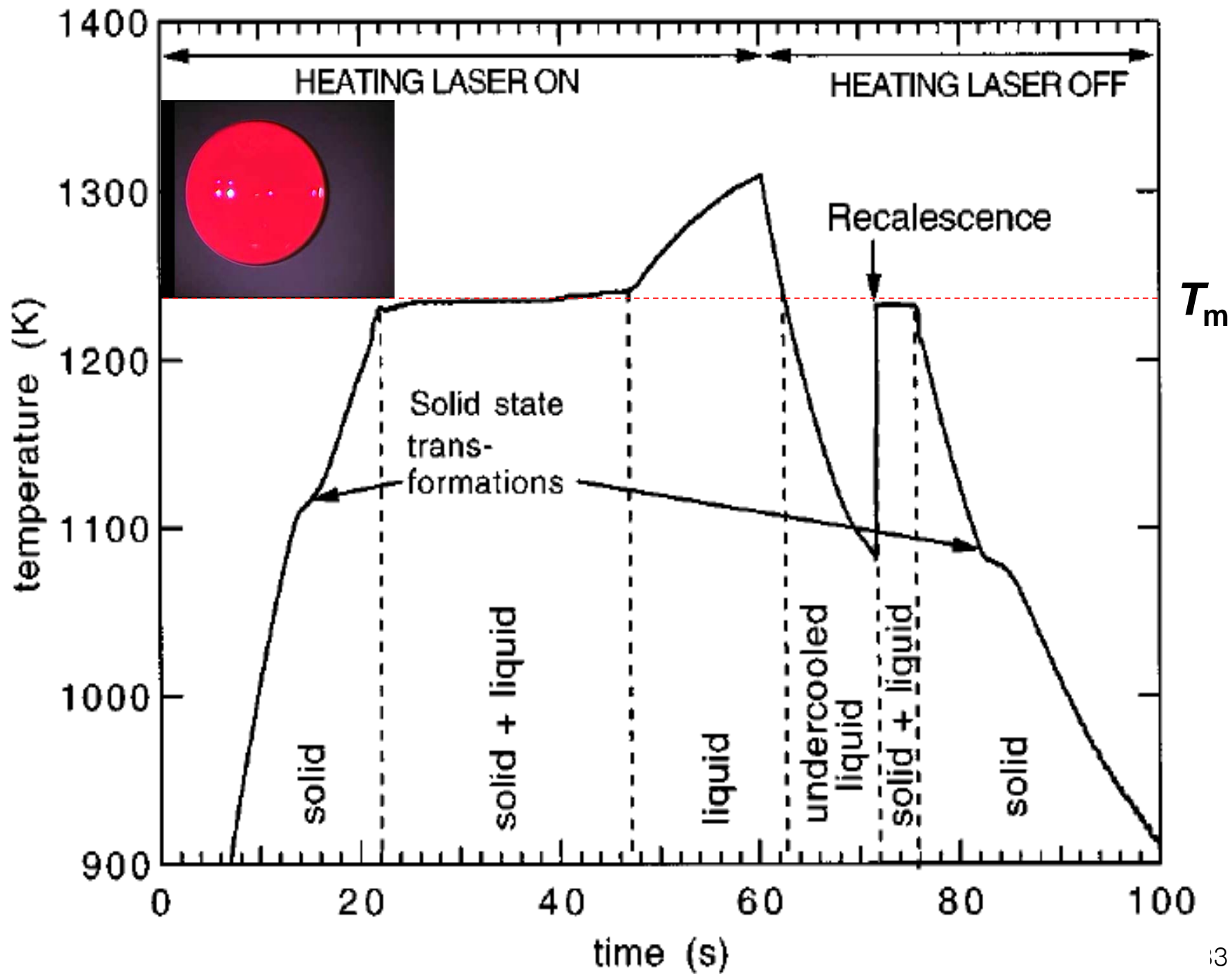


# Electrostatic levitation in KRISS

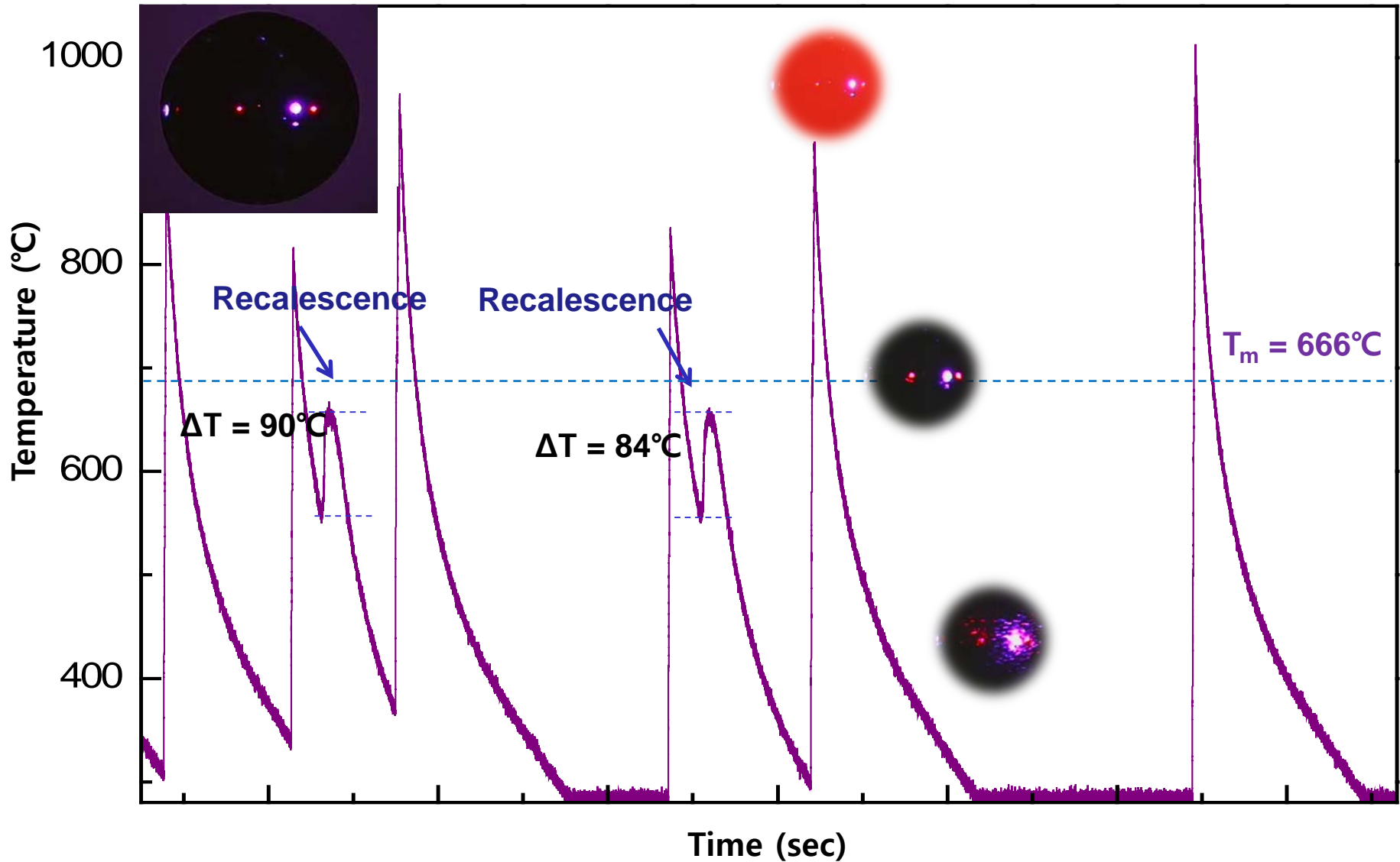
HV (z-axis)

T : ~3000 °C  
P : ~ 10<sup>-7</sup> Torr





# Cyclic cooling curves of $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$



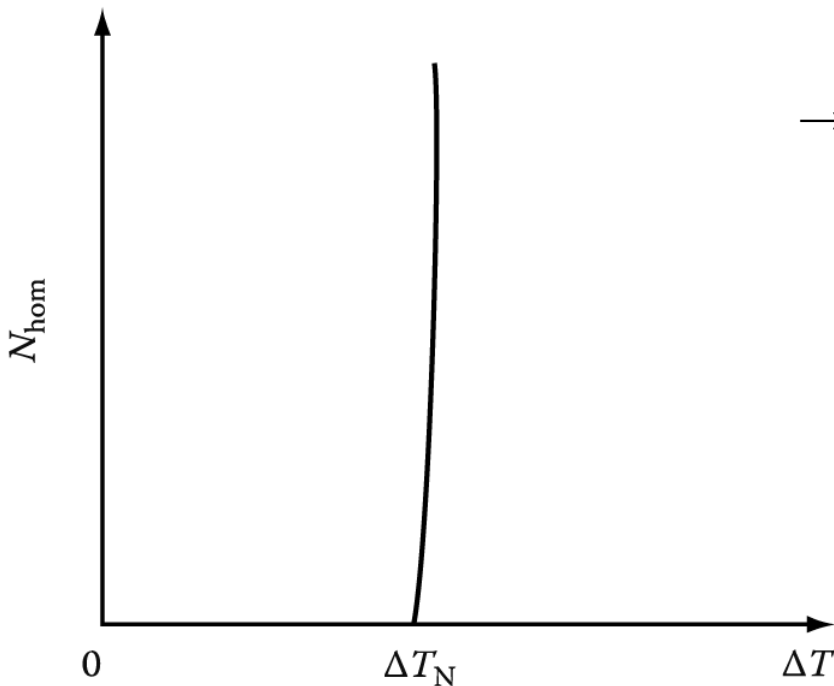
## \* The homogeneous nucleation rate - kinetics

$$I = \frac{nkT}{h} \exp\left(-\frac{G_A}{kT}\right) \exp\left(-\frac{16\pi\sigma_{SL}^3 T_E^2}{3L^2(\Delta T)^2 kT}\right)$$

: insensitive to Temp.

How do we define nucleation temperature,  $\Delta T_N$  ?

$$N_{\text{hom}} \sim \frac{1}{\Delta T^2}$$



→ critical value for detectable nucleation

- critical supersaturation ratio

- critical driving force

- critical supercooling

→ for most metals,  $\Delta T_N \sim 0.2 T_m$  (i.e.  $\sim 200\text{K}$ )

The homogeneous nucleation rate as a function of undercooling  $\Delta T$ .  $\Delta T_N$  is **the critical undercooling** for homogeneous nucleation.



## \* Relationship between Maximum Supercoolings and $T_m$

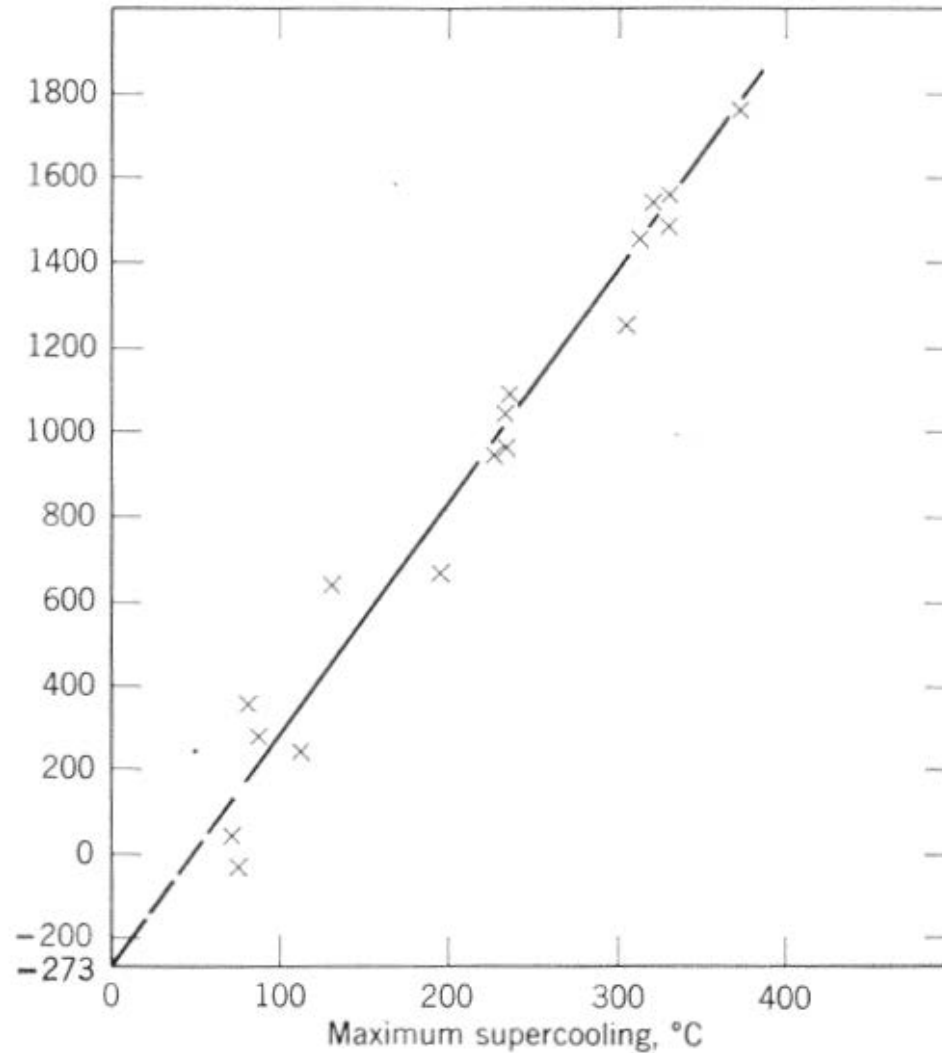


Fig. 3.7. Maximum supercooling as a function of melting point. (From *Thermodynamics in Physical Metallurgy*, American Society for Metals, Cleveland, 1911, p. 11.)

# Solidification: Liquid $\longrightarrow$ Solid

- casting & welding
- single crystal growth
- directional solidification
- rapid solidification

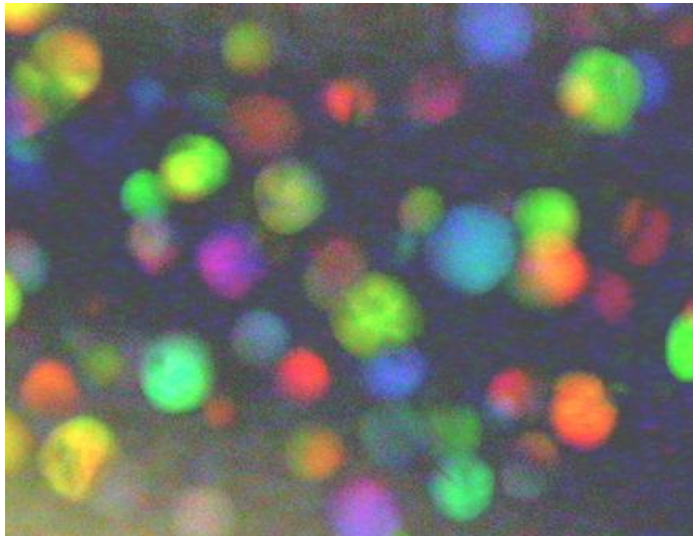
## Nucleation in Pure Metals

$$T_m : G_L = G_S$$

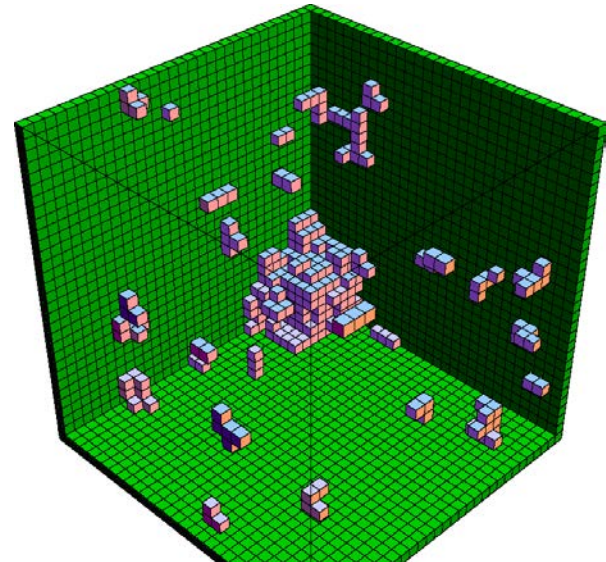
- Undercooling (supercooling) for nucleation: 250 K  $\sim$  1 K

<Types of nucleation>

- Homogeneous nucleation



- Heterogeneous nucleation



**Q10: What is the driving force for  
“Melting: Solid → Liquid”?**

# \* Driving force for melting

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

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

$$\Delta G = \Delta H - T \Delta S$$

$$L : \Delta H = H^L - H^S$$

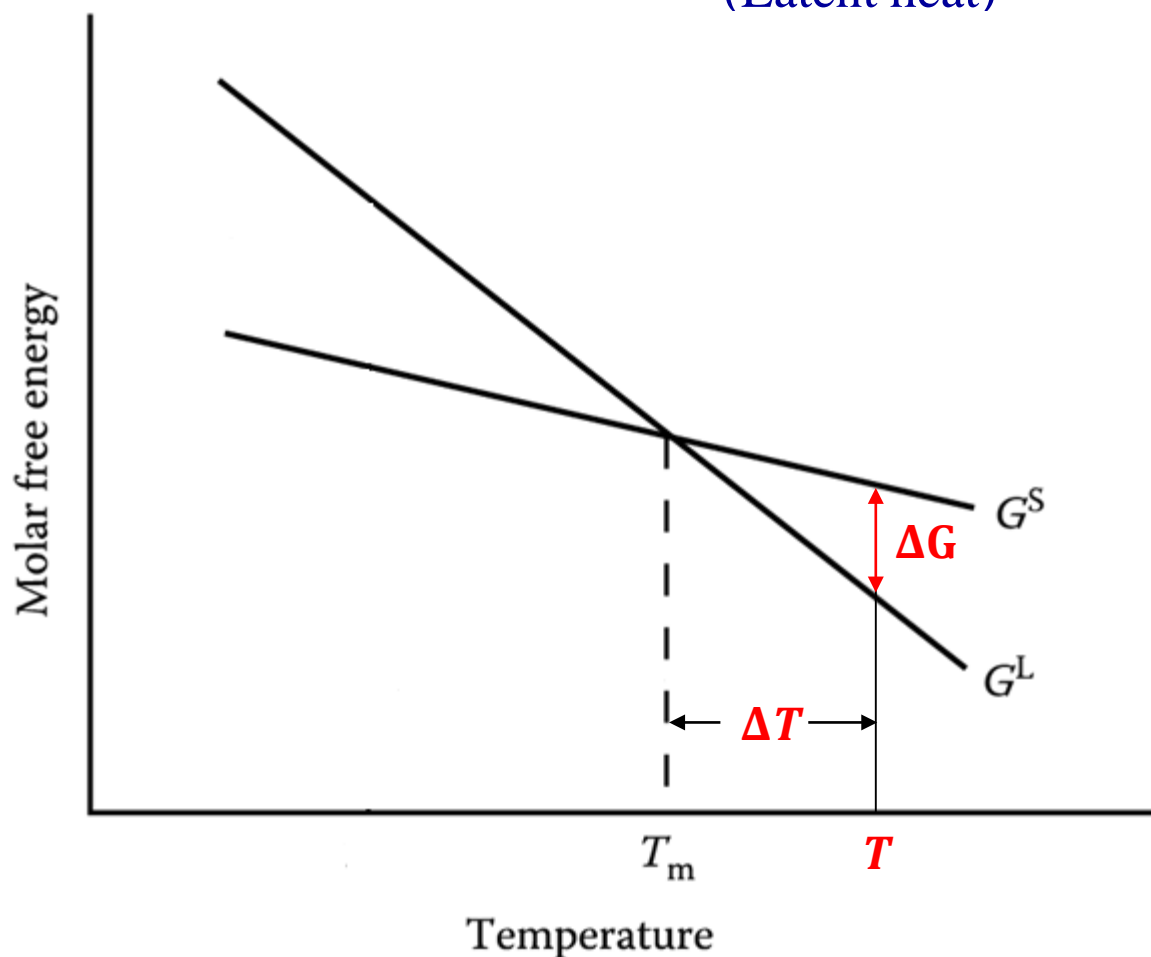
(Latent heat)

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

$$\Delta S = \Delta H / T_m = L / T_m$$

$$\Delta G = L - T(L/T_m) \approx (L\Delta T) / T_m$$

(eq. 1.17)



$$\Delta G = \frac{L\Delta T}{T_m}$$

# Nucleation of melting

Although nucleation during solidification usually requires some undercooling, melting invariably occurs at the equilibrium melting temperature even at relatively high rates of heating.

Why?

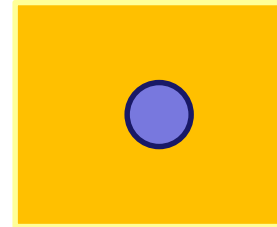
$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV} \quad (\text{commonly})$$



In general, wetting angle = 0 → No superheating required!

# Melting and Crystallization are Thermodynamic Transitions

**Solidification:** Liquid  $\rightarrow$  Solid



<Thermodynamic>

- Interfacial energy  $\Rightarrow \Delta T_N$

Liquid

$T_m$  Undercooled Liquid

Solid

No superheating required!

- Interfacial energy  $\Rightarrow$  No  $\Delta T_N$

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

**Melting:** Liquid  $\leftarrow$  Solid



# Chapter 1

## Thermodynamics and Phase Diagrams

- **Equilibrium**  $dG = 0$  Phase Transformation  
 $\Delta G = G_2 - G_1 < 0$

Lowest possible value of G

*No desire to change ad infinitum*

- **Single component system**

Gibbs Free Energy as a Function of **Temp.** and **Pressure**

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq}\Delta V}$$

*Clausius-Clapeyron Relation*

- **Classification of phase transition**

First order transition: **CDD**/Second order transition: **CCD**

- **Driving force for solidification**

$$\Delta G = \frac{L\Delta T}{T_m}$$