2023 Fall

“Phase Transformation *in* Materials”

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Introduction

- **Web lecture assistance:** https://myetl.snu.ac.kr/courses/249368

  - All materials will be posted at the webpage.

  - text message will be sent for the important and urgent notice.

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 equilibriums, 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 → Solid
- (Ch5) Diffusional Transformations in Solid: Solid → Solid
- (Ch6) Diffusionless Transformations: Solid → 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, 1st Exam
week 7	Interfacial free energy/ Solid/vapor interfaces
week 8	Boundaries in single-phase solids/ Interphase interfaces in solids
week 9	Interface migration, **Mid-term**
week 10	Nucleation in pure metals
week 11	Growth a pure solid/ Alloy solidification
week 12	Solidification of ingots and casting, 2nd 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 (Mid-term: 35%, Final exam: 45%)**(1st: 25%; 2nd 25%; final: 30%)

   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 (10%)**

   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!

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.

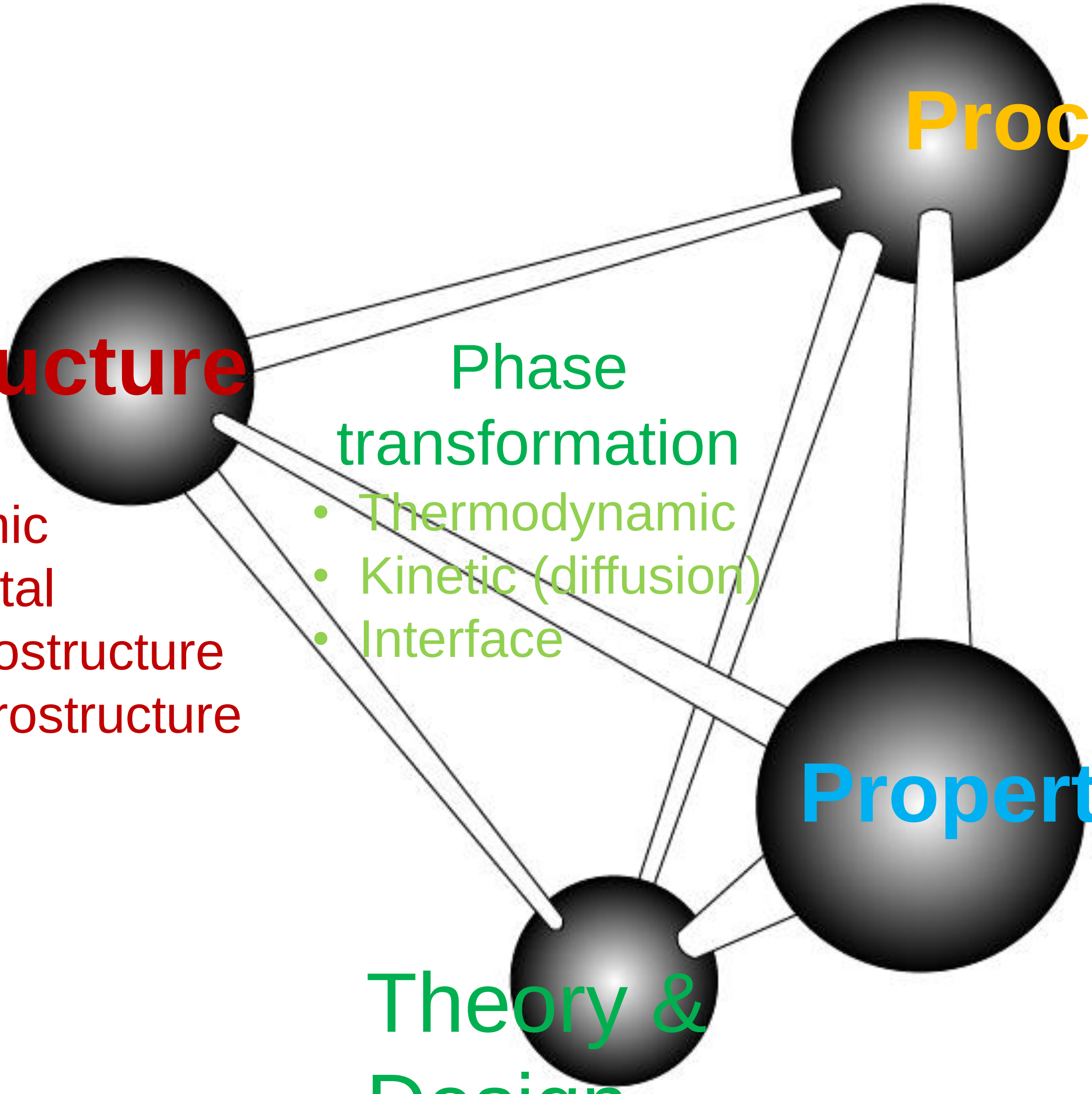
- ***If you wish, you may work together on homework assignments. BUT, you must hand in your own work, in your own words.***

- **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

Materials Science and Engineering



Processing

- Sintering
- Heat treatment
- Thin Film
- Melt process
- Mechanical

Structure

- Atomic
- Crystal
- Microstructure
- Macrostructure

Phase transformation

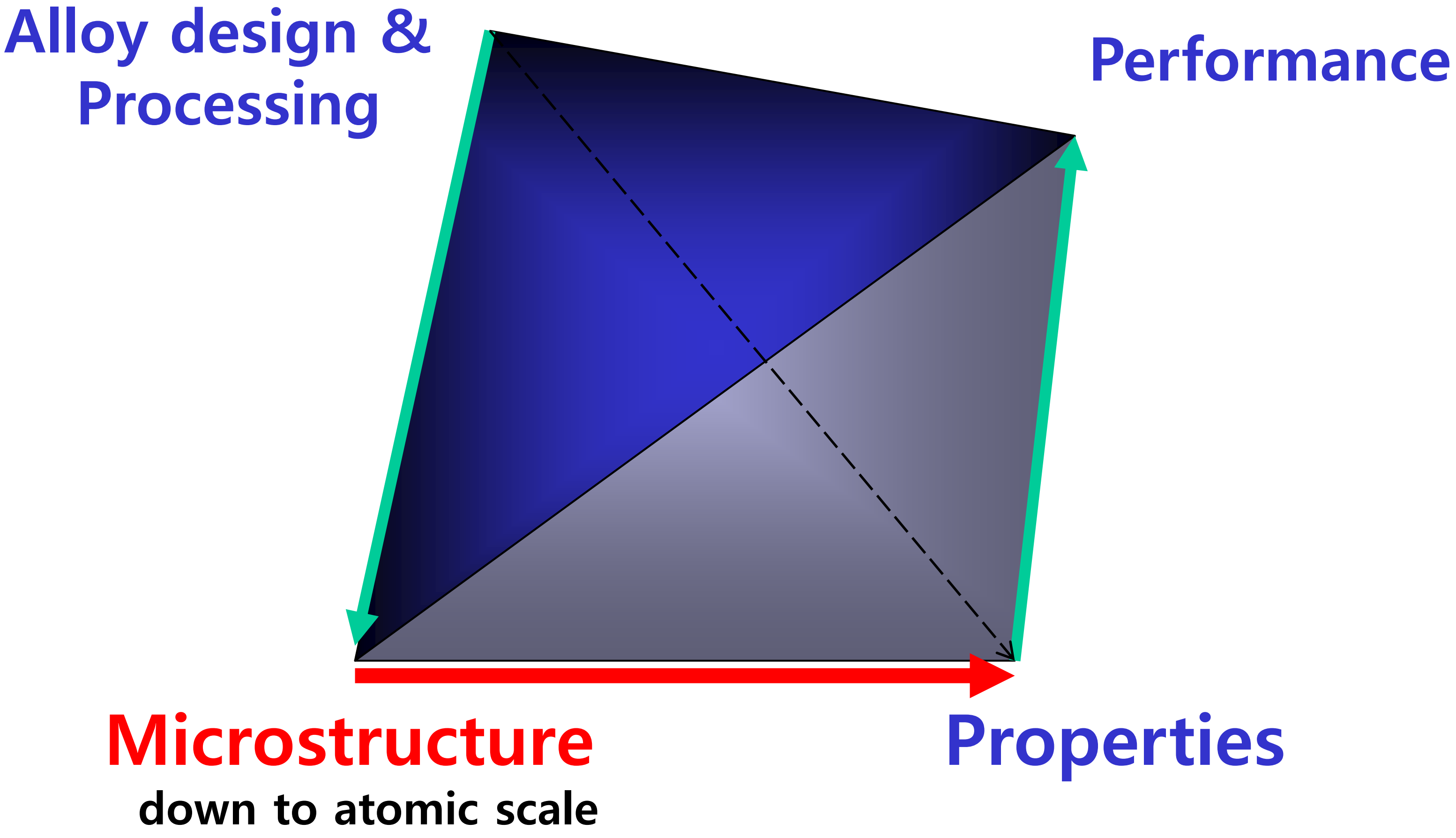
- Thermodynamic
- Kinetic (diffusion)
- Interface

Properties

- Mechanical
- Electrical
- Magnetic
- Thermal
- Optical

Theory & Design

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

Application of Iron-Carbon Alloy

K1 – main battle tank of Korea army

Need of the strongest materials

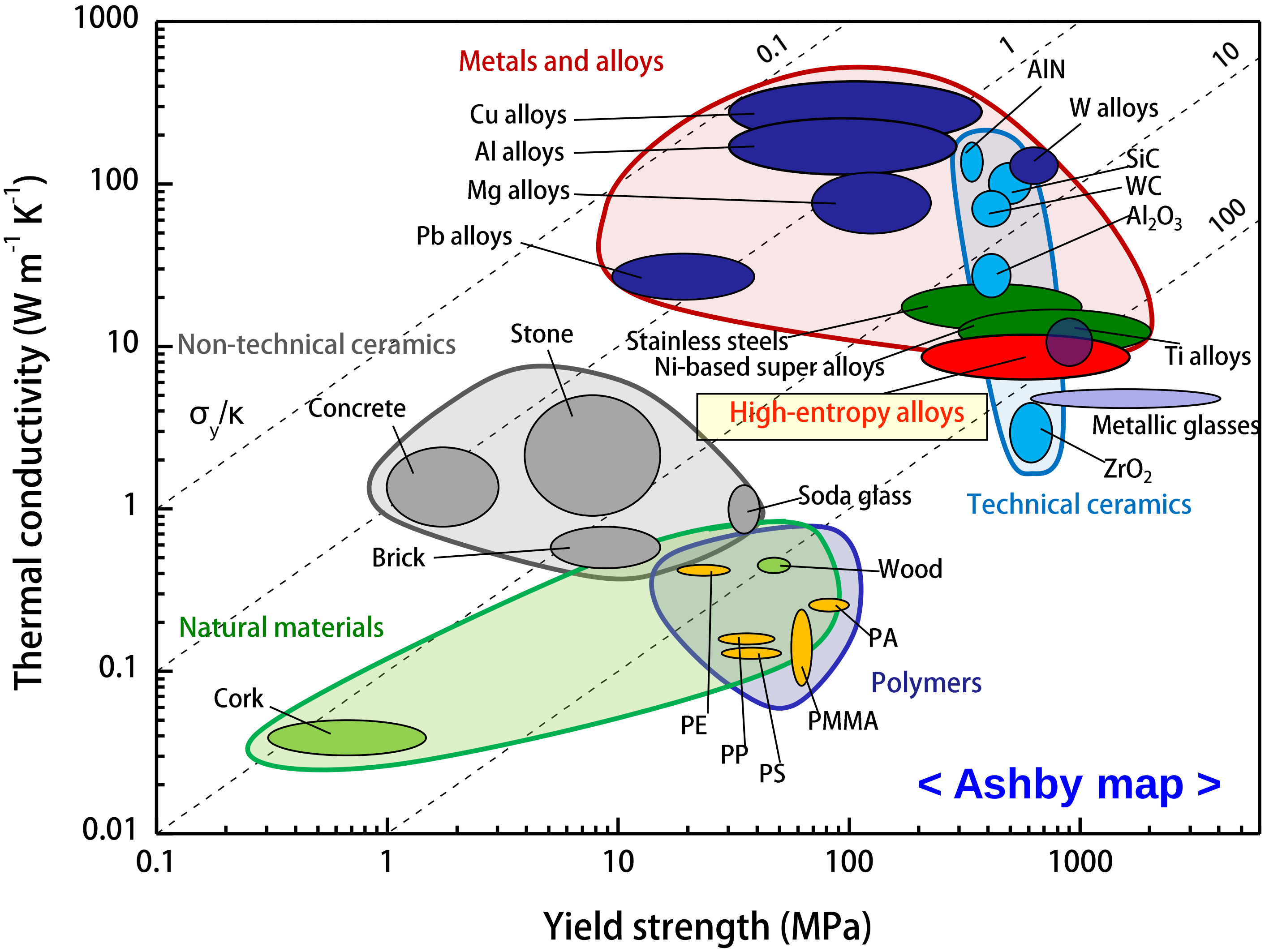
1) Alloy design: Materials selection ➡ c. Change of alloy system

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



< Ashby map >

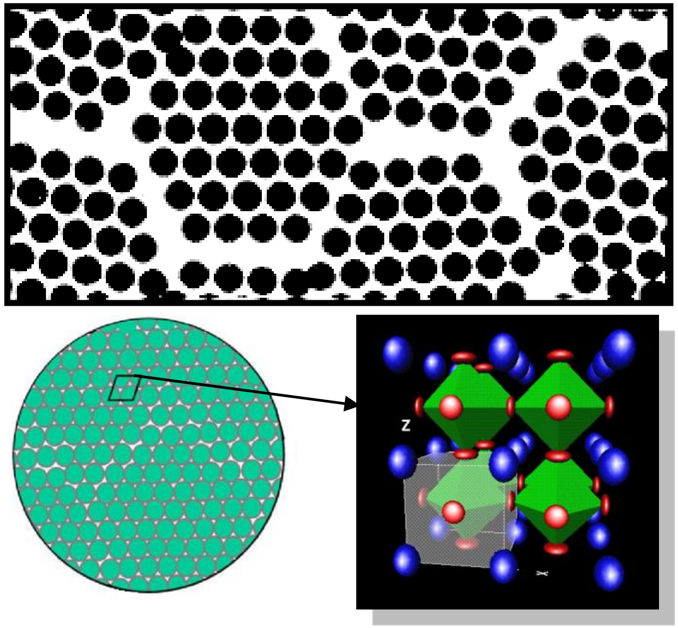
Q2: How to classify material depending on the structure?

2) Classification of Material depending on the structure

Atomic

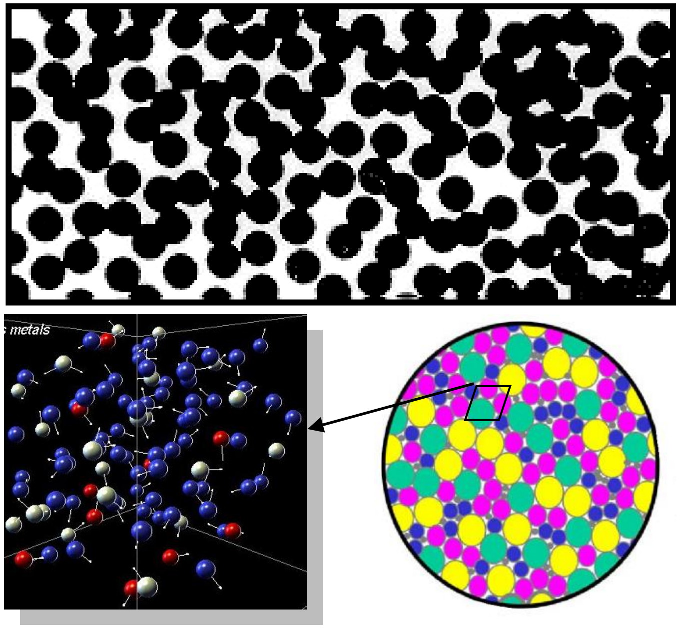
Structure *of crystals, liquids and glasses*

Crystals



- **periodic**
- **grain boundaries**

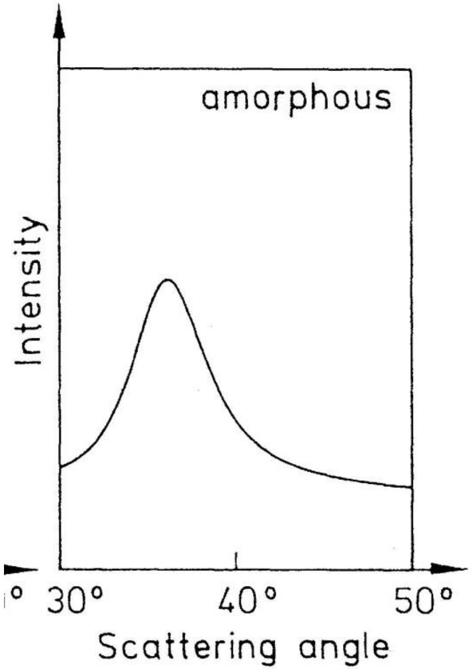
Liquids, glasses

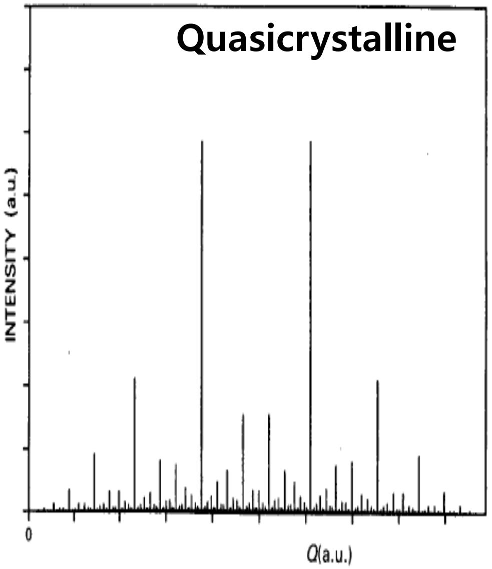


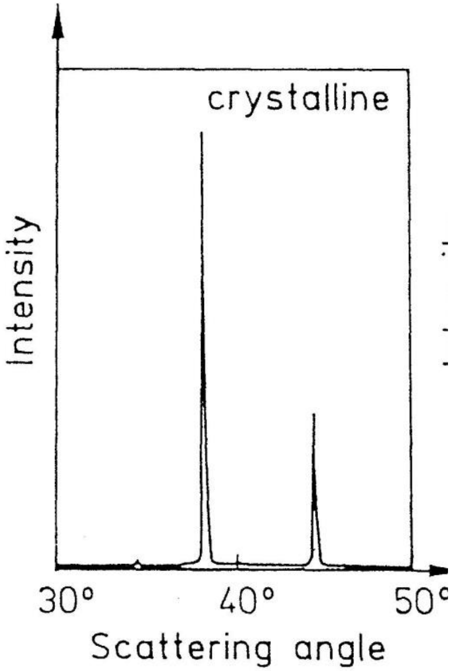
- **amorphous = non-periodic**
- **no grain boundaries**

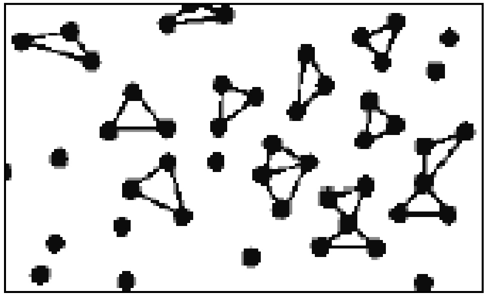
Atomic structure

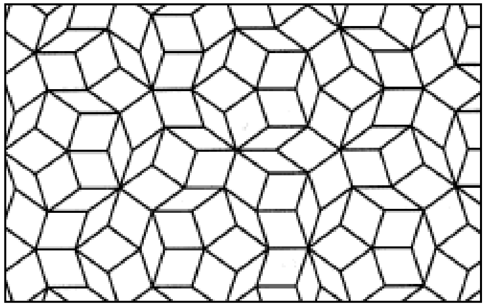
Short-range order ← **Quasi-periodic order** → **Periodic order**

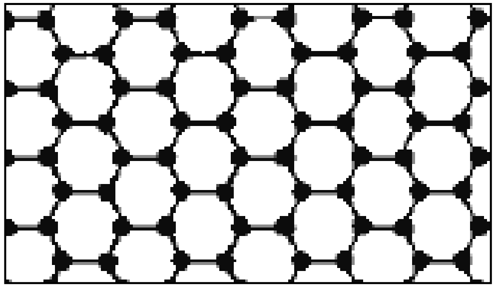












Q3: What are phase, phase diagram and phase transformation?

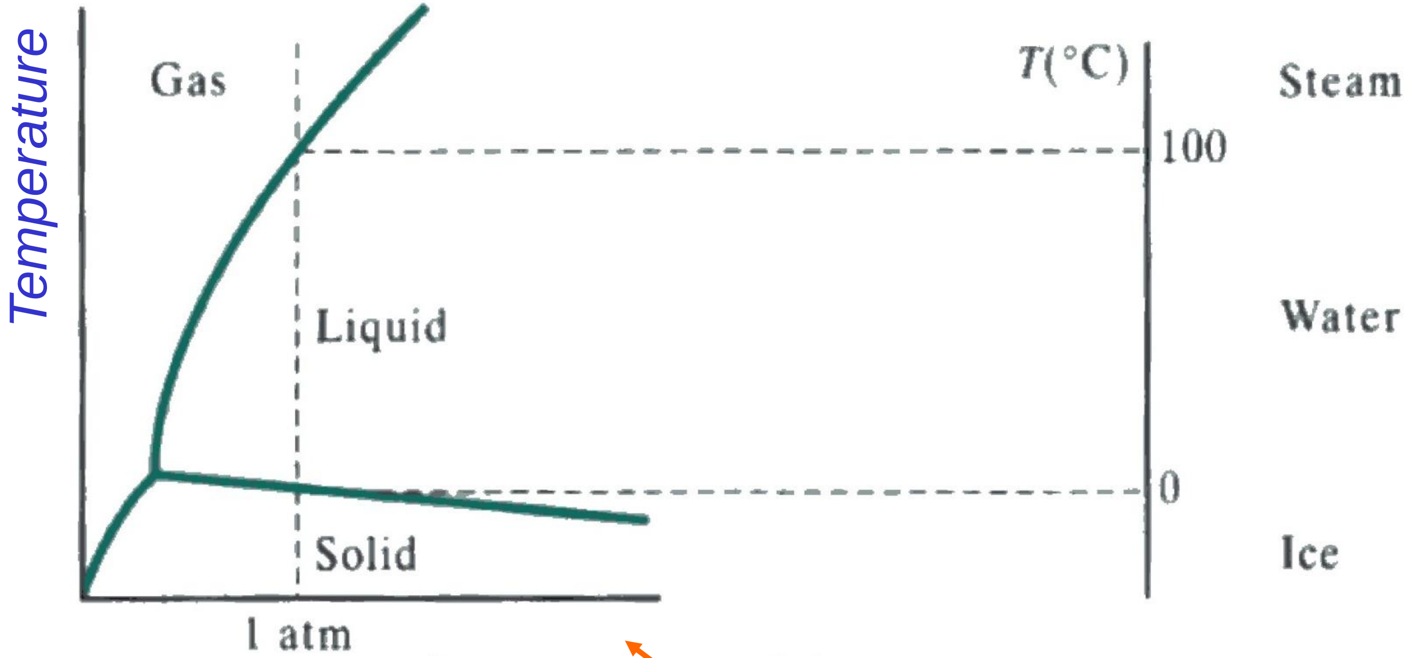
3) Microstructure control

: 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)



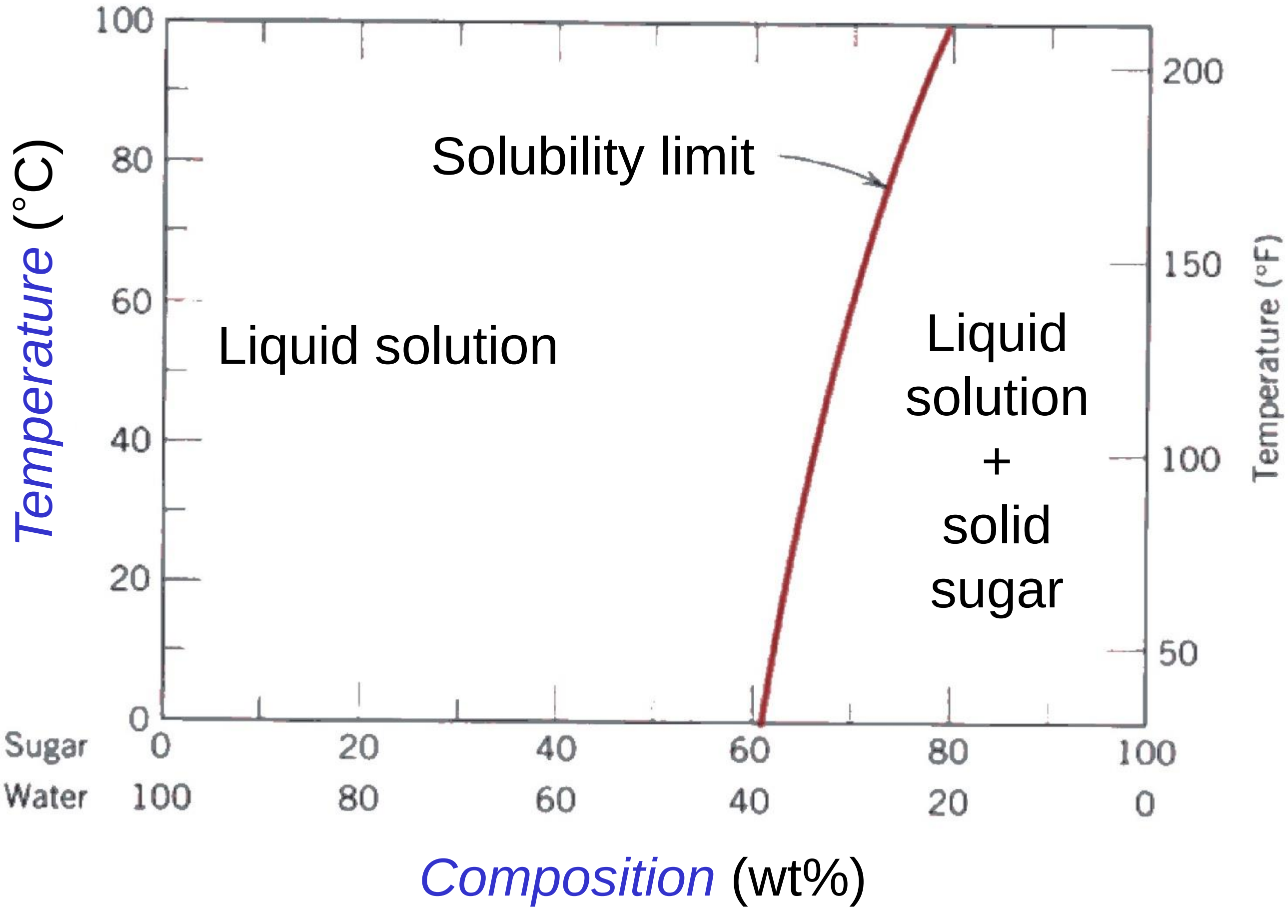
Phase diagram ;
<u>equilibrium phase</u> of material

Microstructure control

: Equilibrium phase ➡ Only consider Thermodynamics

② *Phase Diagram* of Temperature – Composition ;

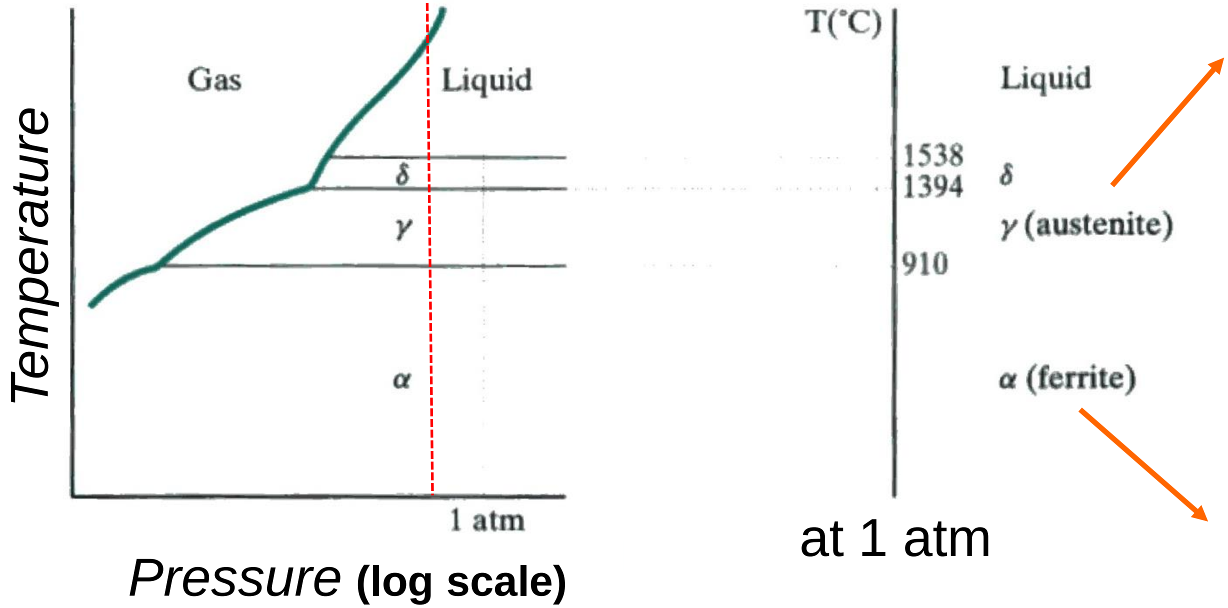
most useful in materials science & engineering

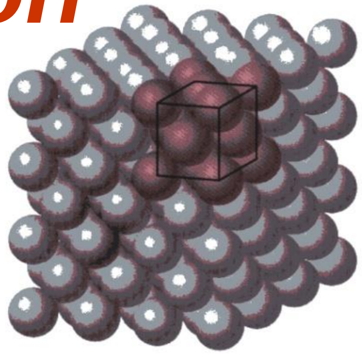


Microstructure control

: Phase transformation ➡ Atomic Migration

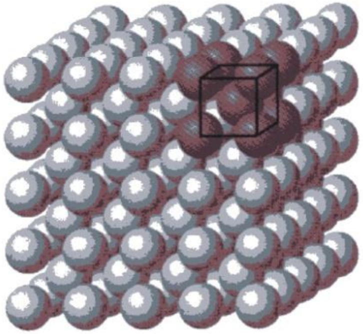
③ *Phase Transformation* of Iron and *Atomic Migration*





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?

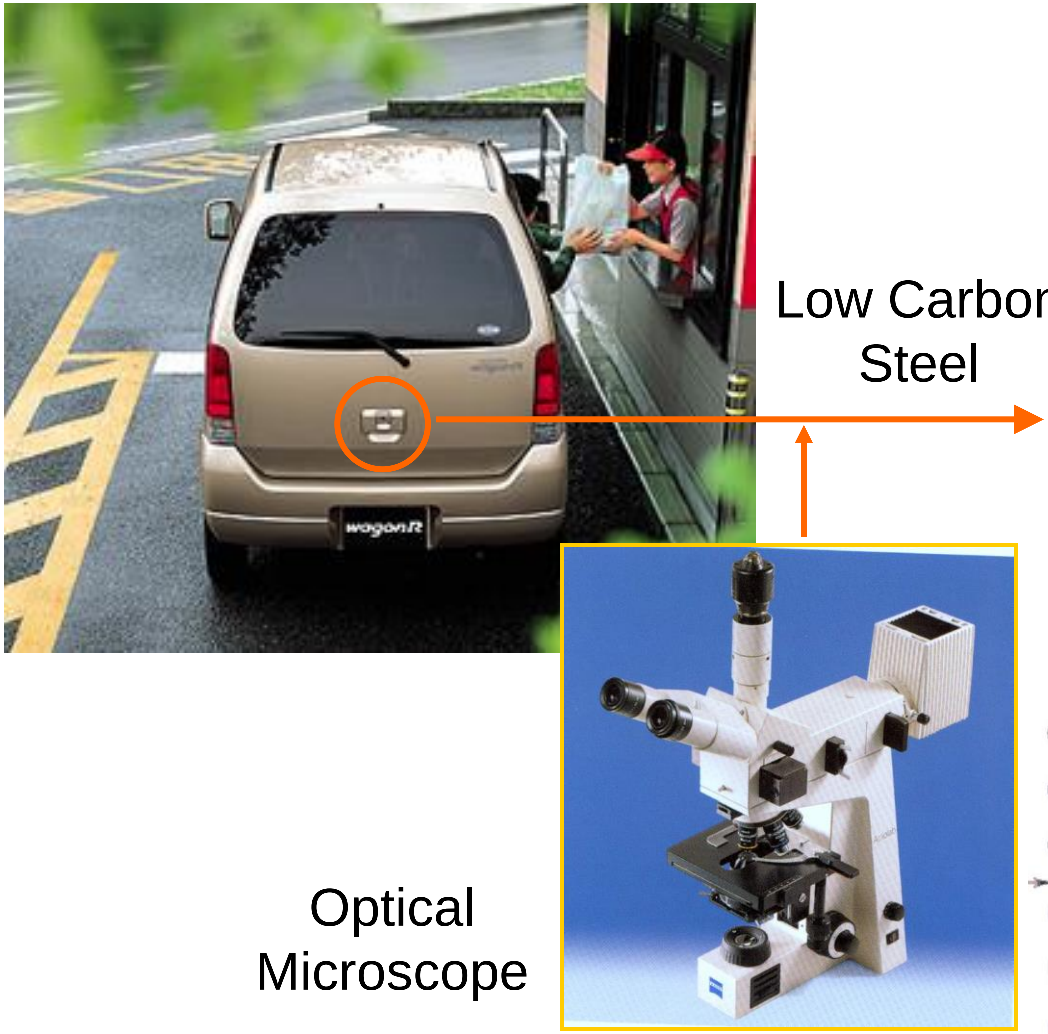
Interfaces (both grain boundaries and interphase boundaries), which are planar defects,

Dislocations (and other line defects), and

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

* *Imperfection:* Grain Boundaries

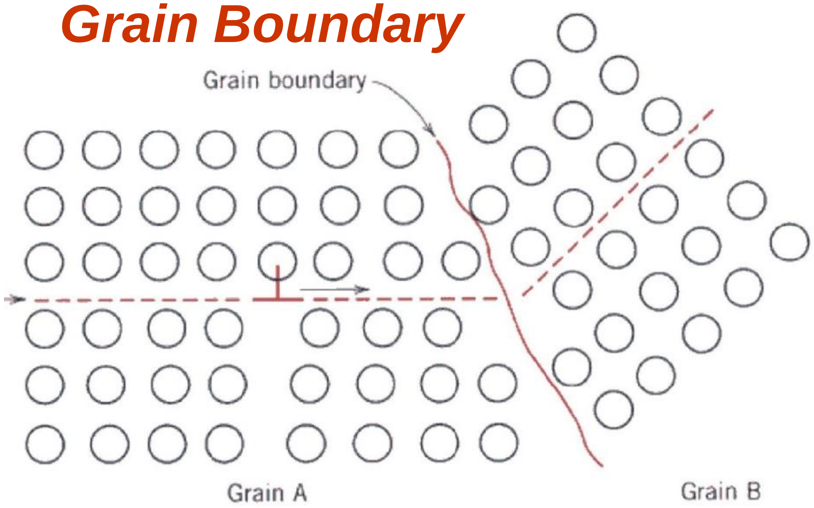
(Planer defect)



Low Carbon Steel

Optical Microscope

Grain Boundary

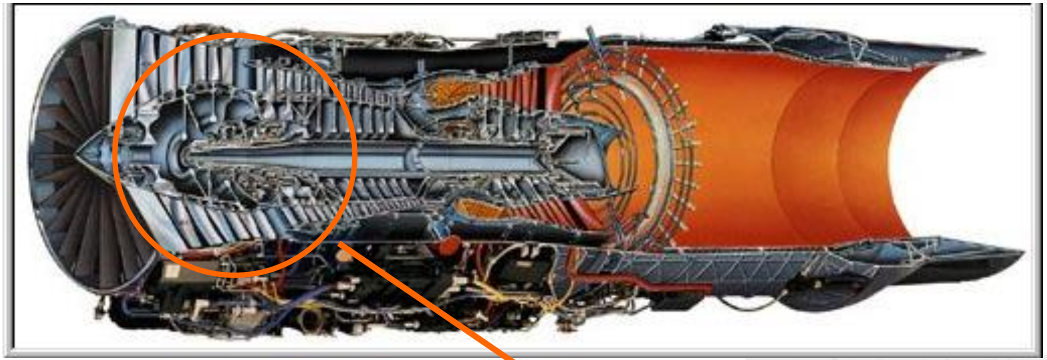


Q5: How to control the microstructure by process control?

5) Microstructure control

: process control after materials selection → property optimization

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



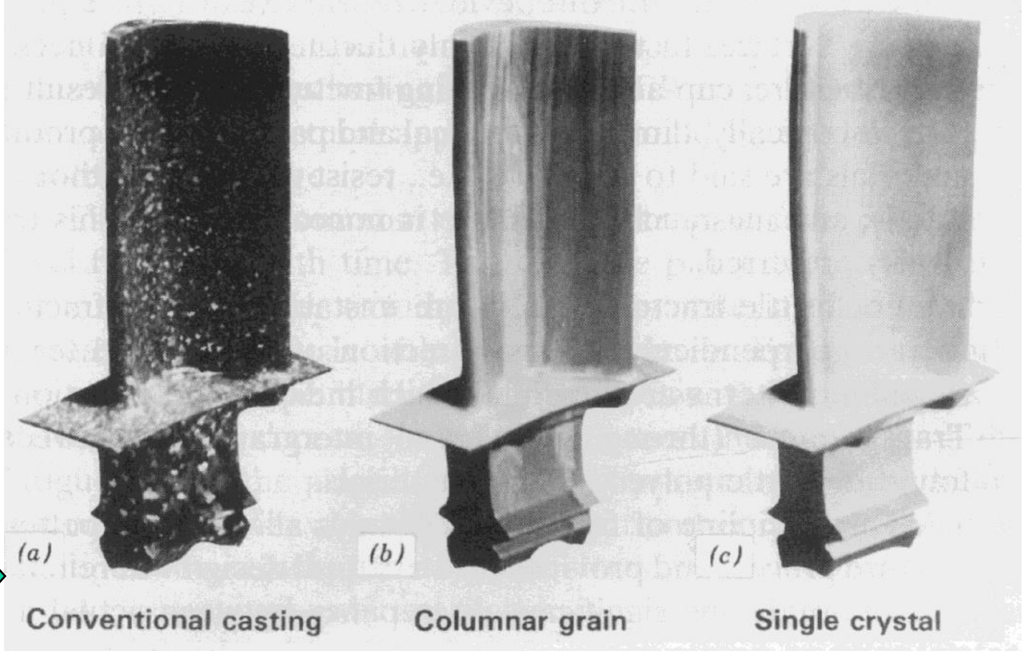
F100-PW-229
in F-16 fighting falcon

Turbine Blade

Grain boundaries
at high Temperature ;
Diffusion path of atoms

Creep

Reducing grain boundaries



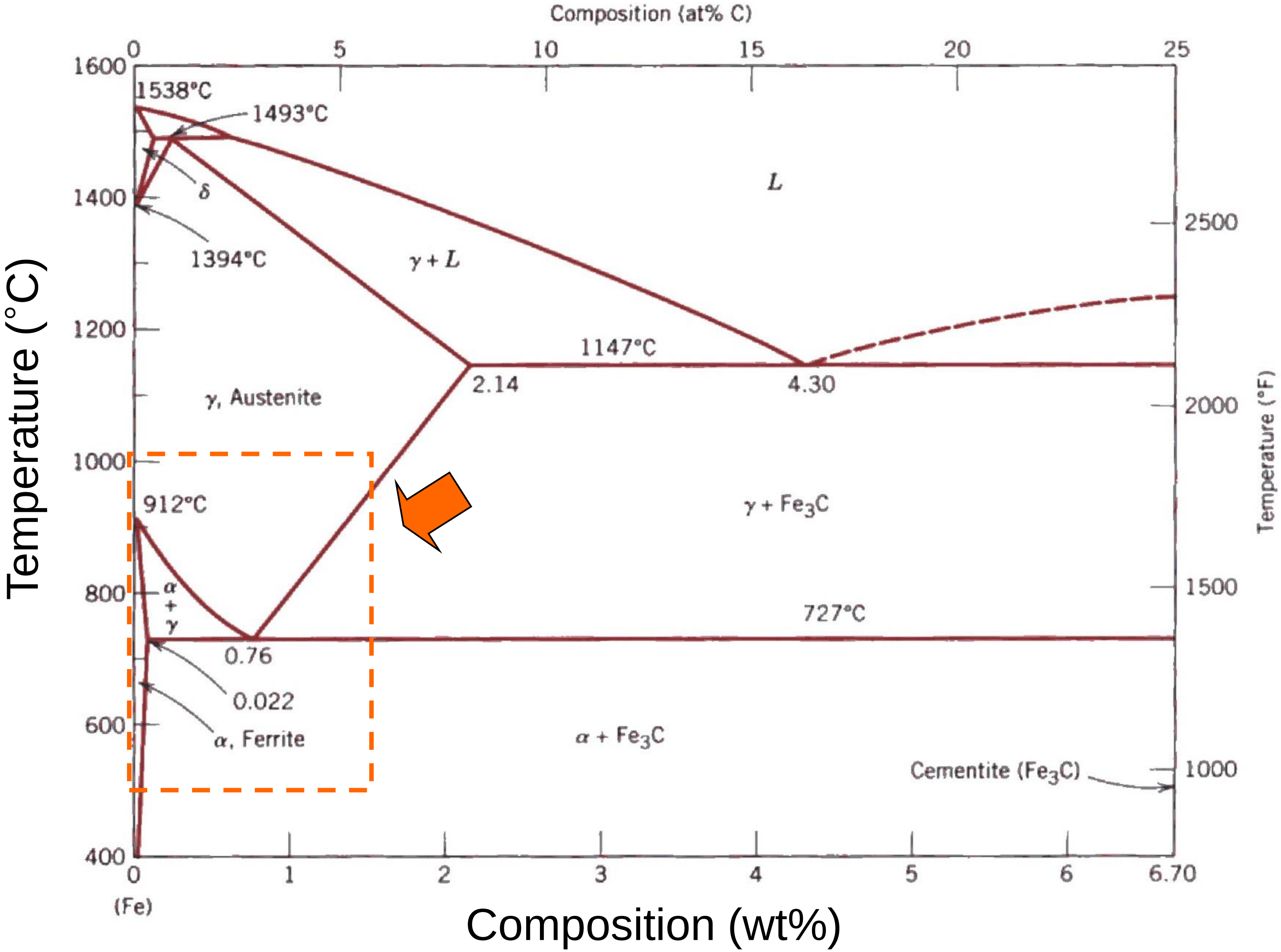
Conventional casting

Columnar grain

Single crystal

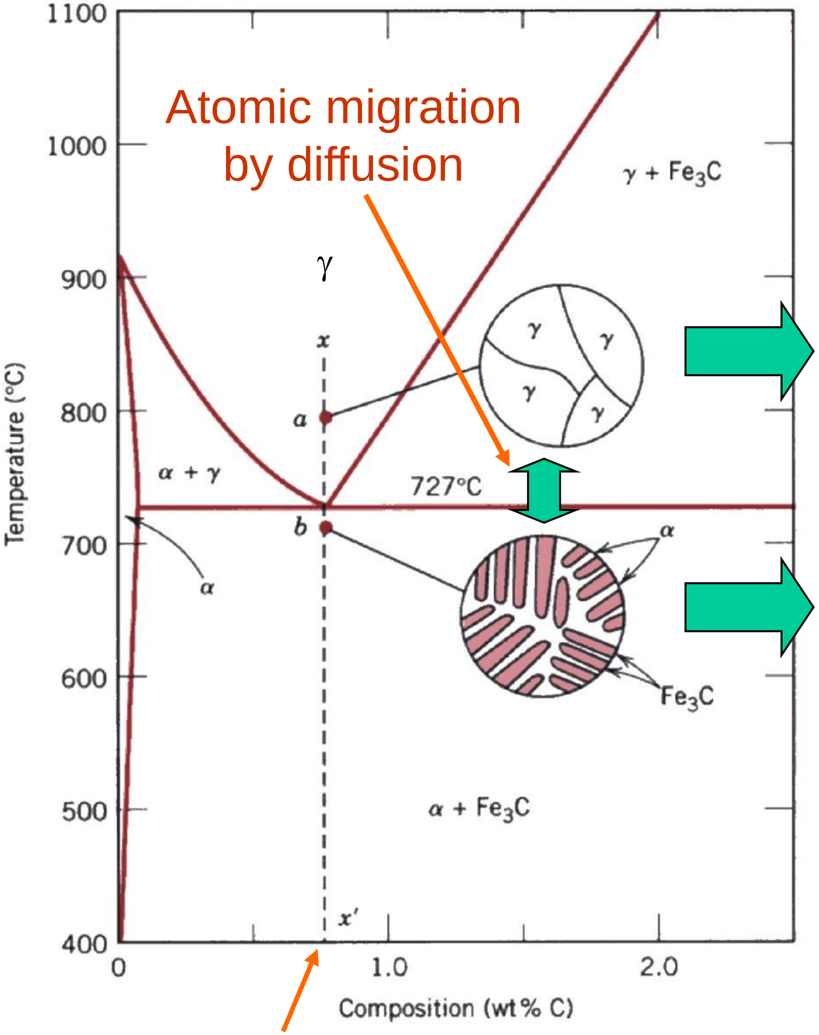
5) Microstructure control : ② Secondary phase control

a. Phase Diagram of Iron–Carbon Alloy



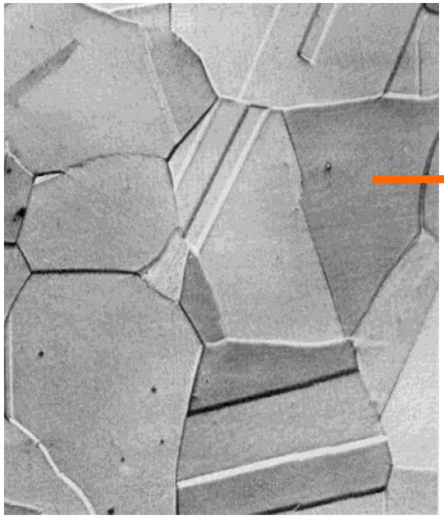
5) Microstructure control : ② Secondary phase control

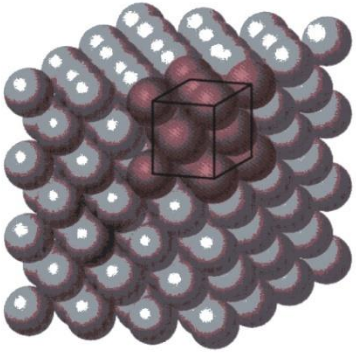
b. Equilibrium Phases of Iron-Carbon Alloy



Atomic migration by diffusion

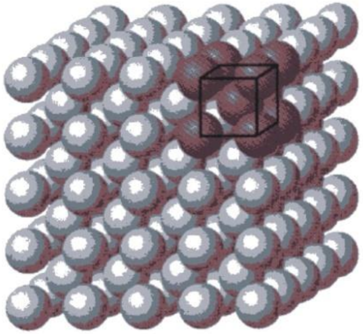
Eutectoid composition





γ phase (FCC)

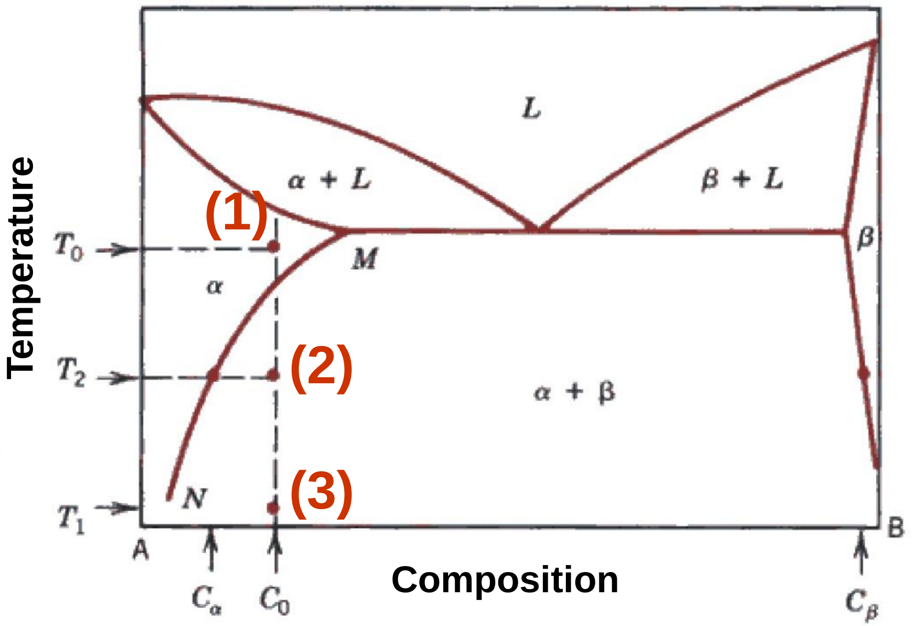
Fe$_3$C phase

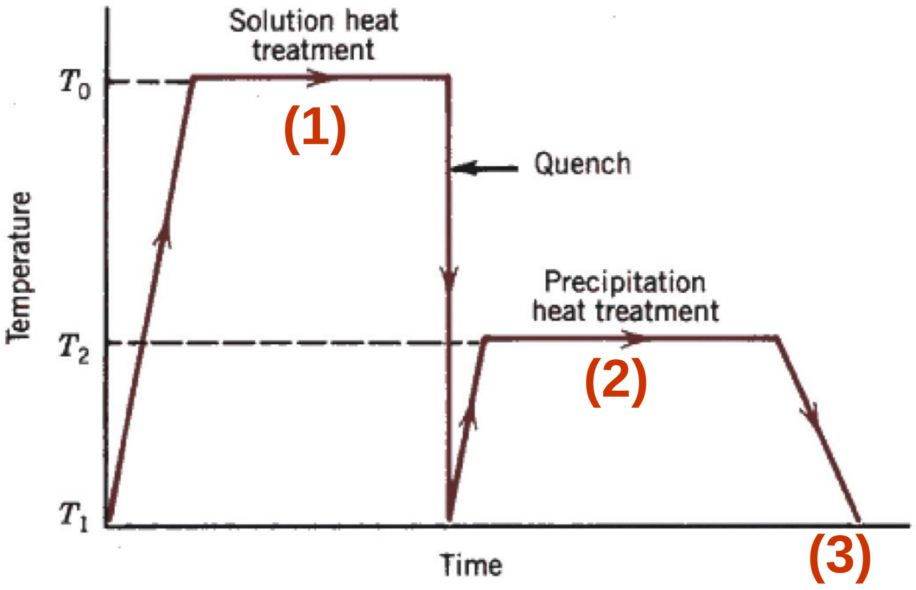


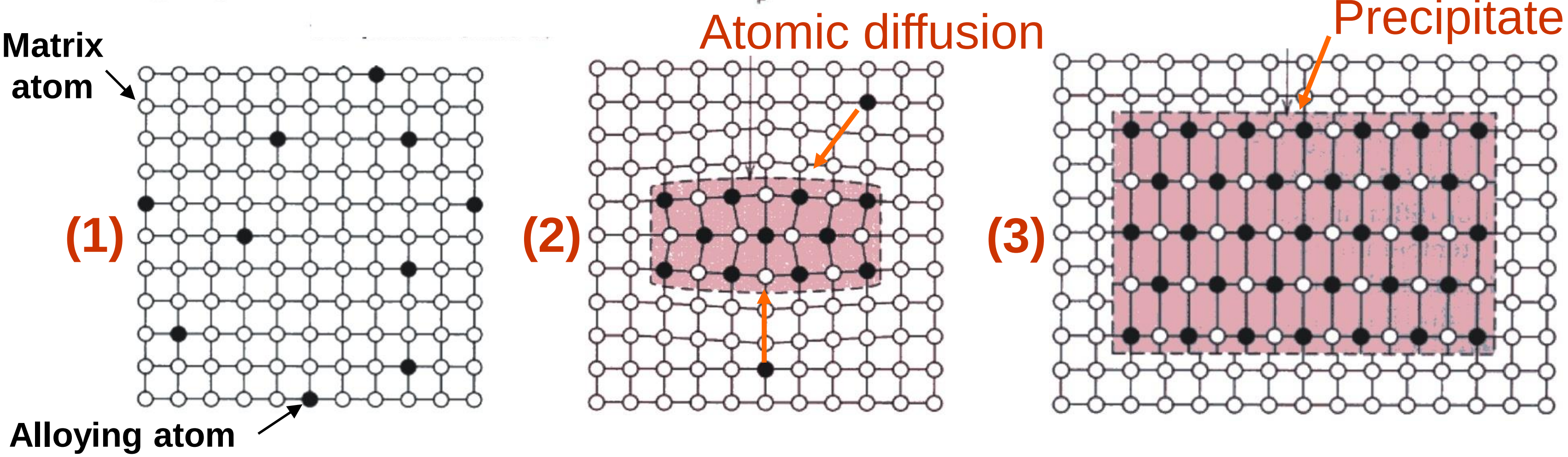
α phase (BCC)

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

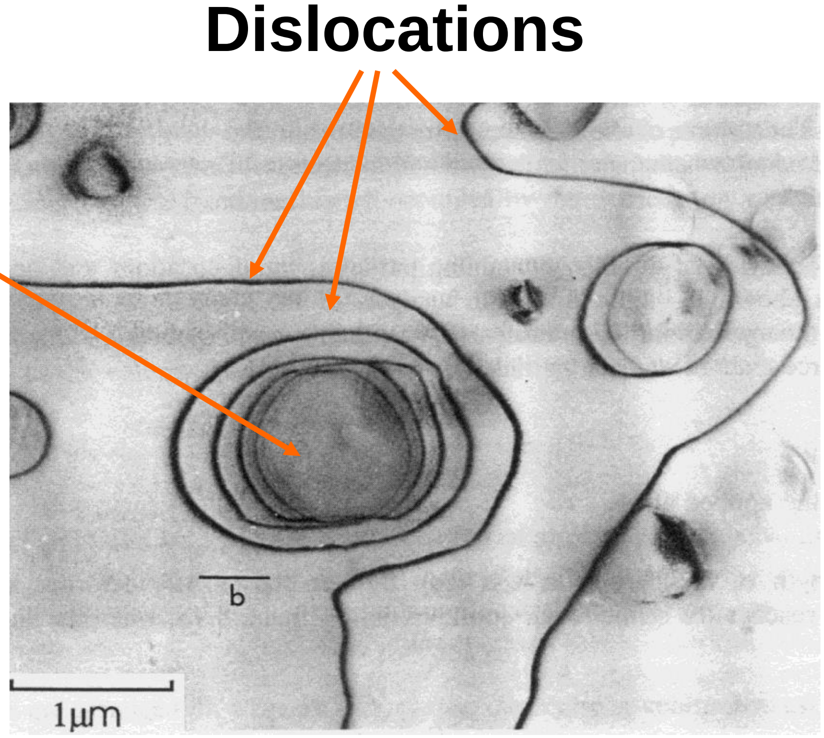
Second phase particle in matrix material

↓

Obstacle of dislocation slip & grain growth

↓

High strength

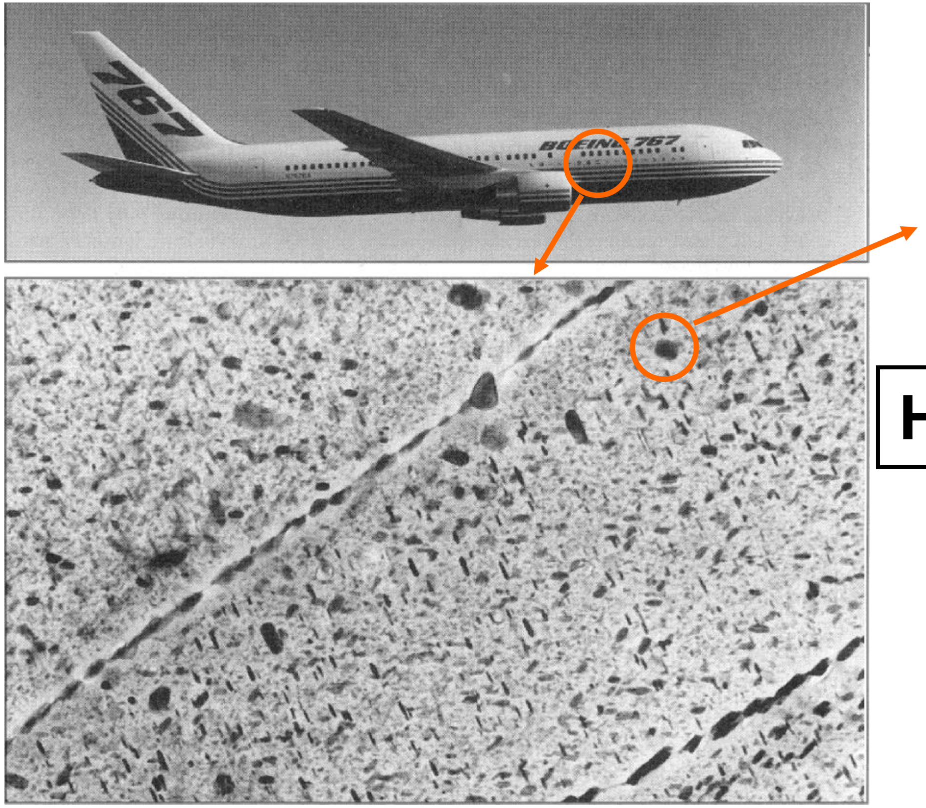


Ni$_3$Si particles in Ni-6%Si single crystal

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

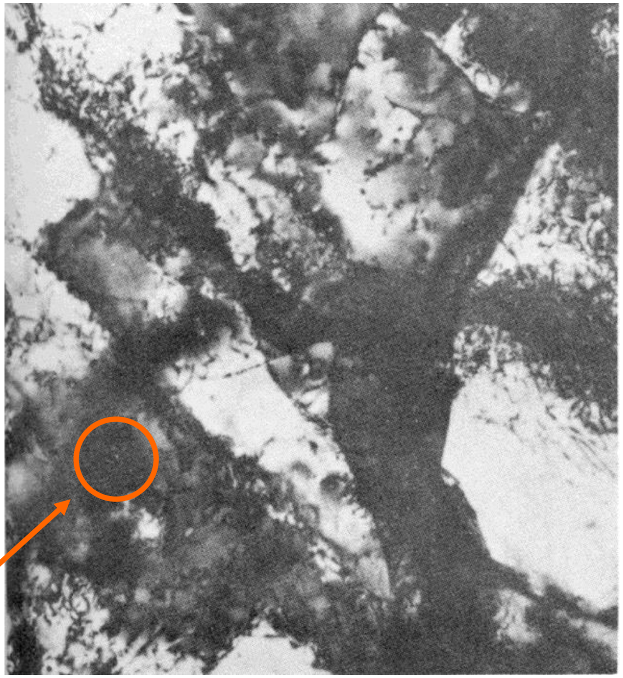
6) Microstructure optimization by process control

Hardening Mechanism by Cold Working

Before cold work

Deformation
or
Cold work

Aluminum alloy

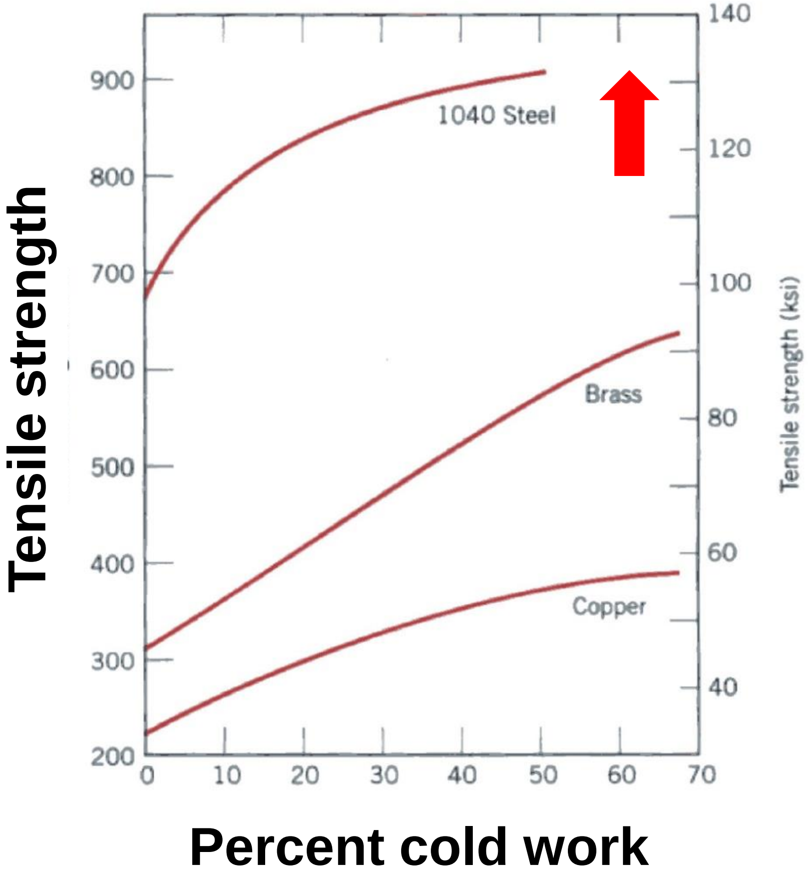


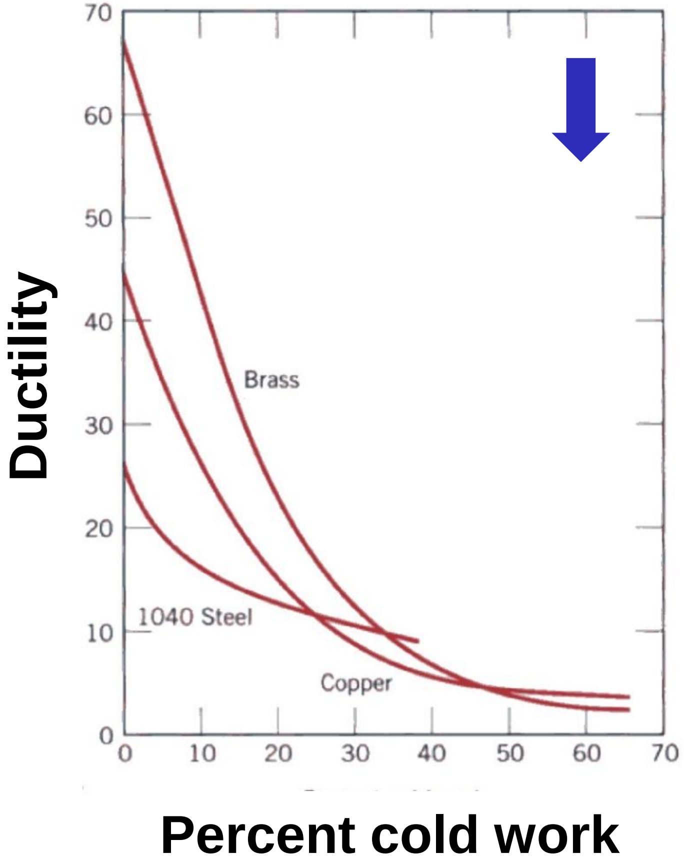
Dislocation tangle

Accumulation of dislocations

6) Microstructure optimization by process control

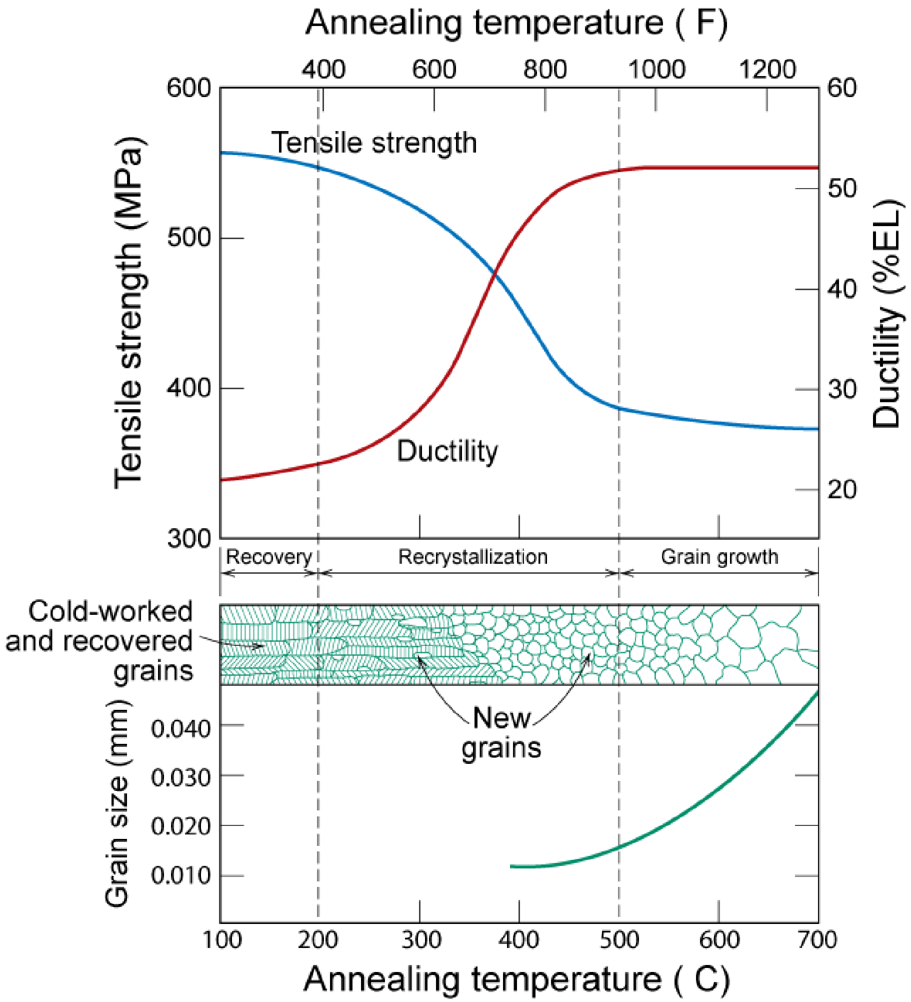
Changes of Strength and Ductility by Cold Working





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

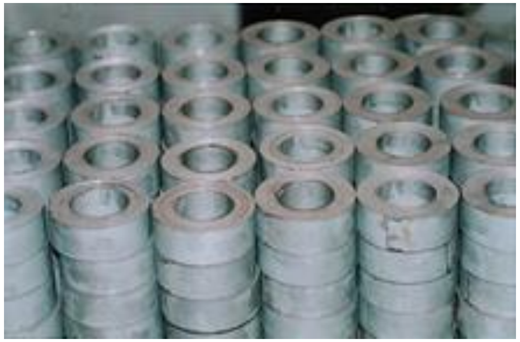
Q7: How to optimize material property?

“Alloy design + Process control”

7) Alloy design + Process control ➡ Property optimization

e.g. Production and Application of Electrical Steel

Hot rolling - cold rolling – 1st annealing – 2nd 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

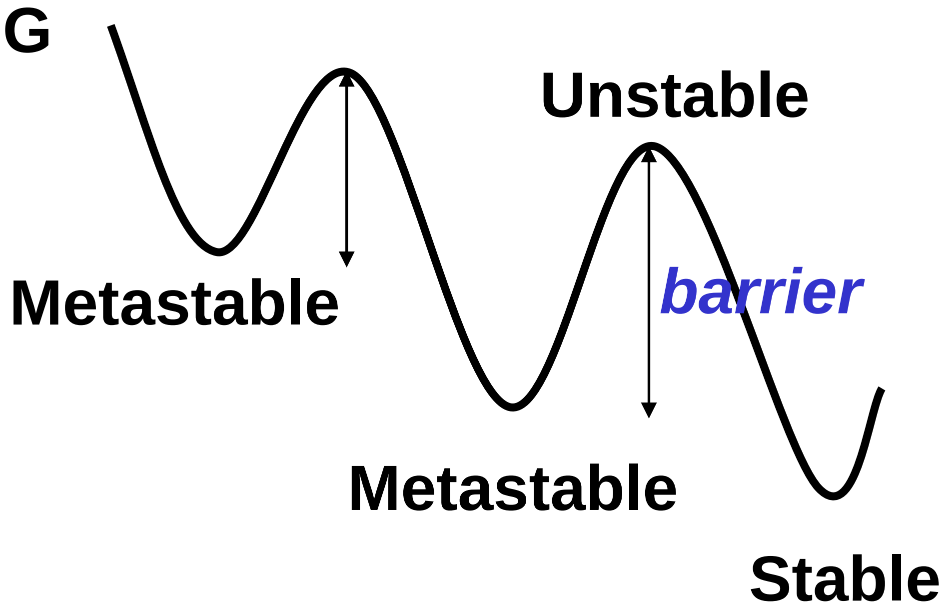
$$\boxed{\Delta G = G_2 - G_1 < 0}$$

Phase 1 → phase 2 ➡ **equilibrium state**

structure or **composition** or **order**

Lowest possible value of Gibb's Free Energy

No desire to change ad infinitum



$$\boxed{dG = 0}$$

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

화학성분 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

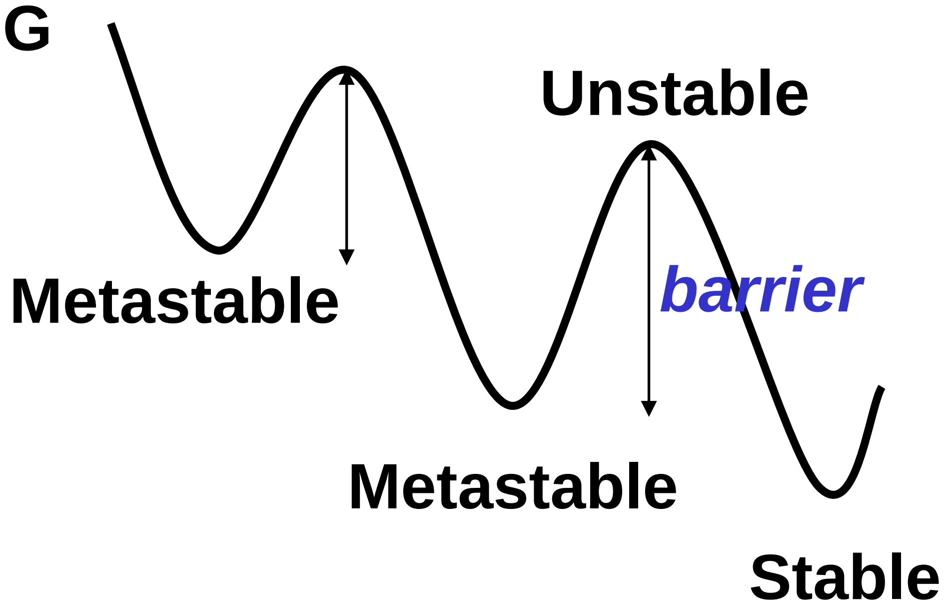
$$\boxed{\Delta G = G_2 - G_1 < 0}$$

Phase 1 → phase 2 ➡ **equilibrium state**

structure or **composition** or **order**

Lowest possible value of Gibb's Free Energy

No desire to change ad infinitum



$$\boxed{dG = 0}$$

➡ **Governed by Thermodynamics & Kinetics**

Q9: What are the representative PTs?

9) Representative Phase Transformation

- **Solidification: Liquid ⟹ Solid**
- **Phase transformation in Solids**

① Diffusion-controlled phase transformation ;

Generally long-distance atomic migration

- Precipitation transformation
- Eutectoid transformation ($\mathbf{S} \Rightarrow \mathbf{S_1} + \mathbf{S_2}$)
- etc.

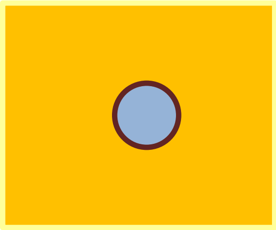
② Diffusionless transformation ;

Short-distance atomic migration

- Martensitic transformation

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

Liquid T_m Undercooled Liquid Solid

No superheating required!

- Interfacial energy ⇨ No ΔT_N

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

Melting: Liquid ← Solid

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

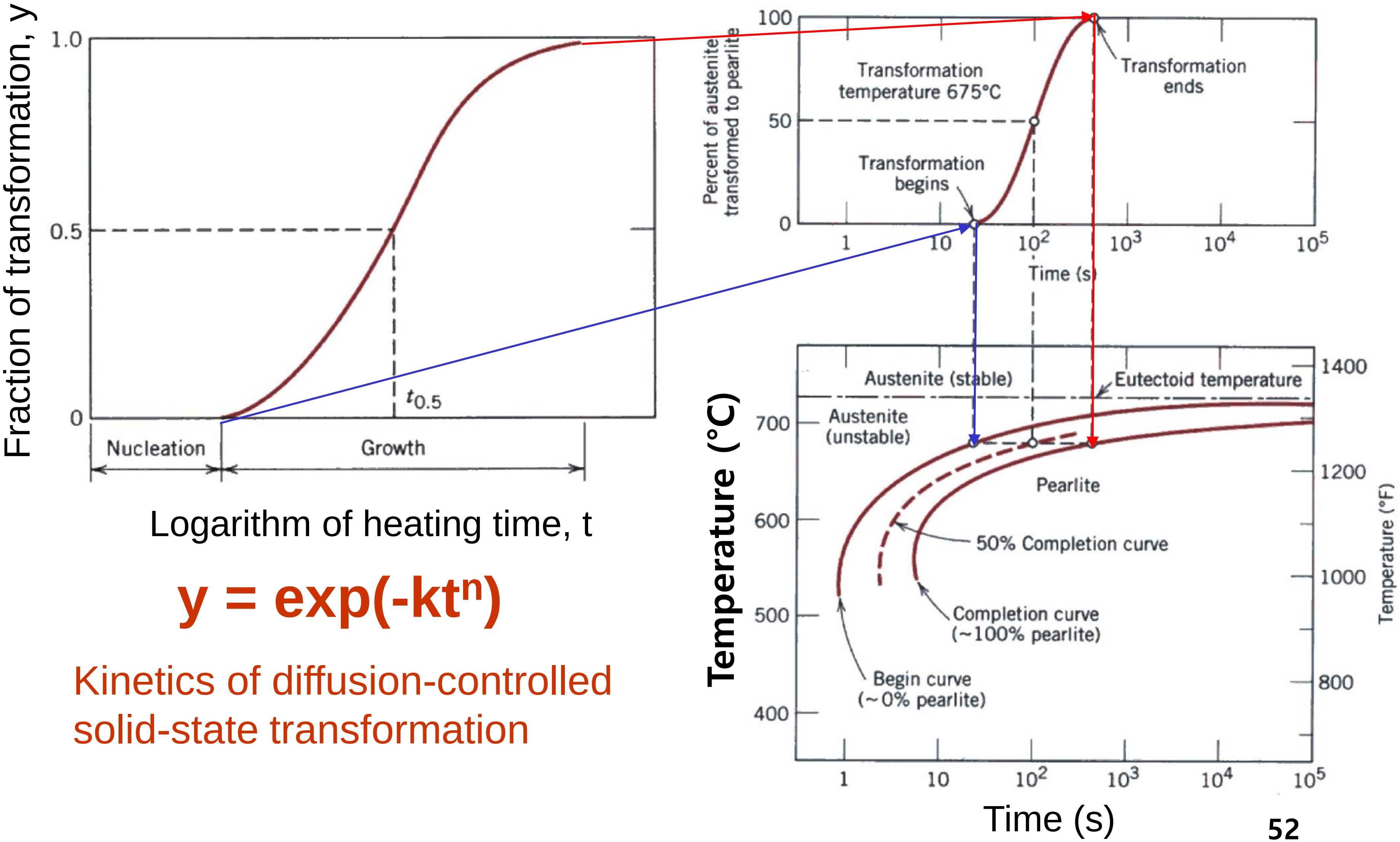
① Diffusion-controlled phase transformation

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



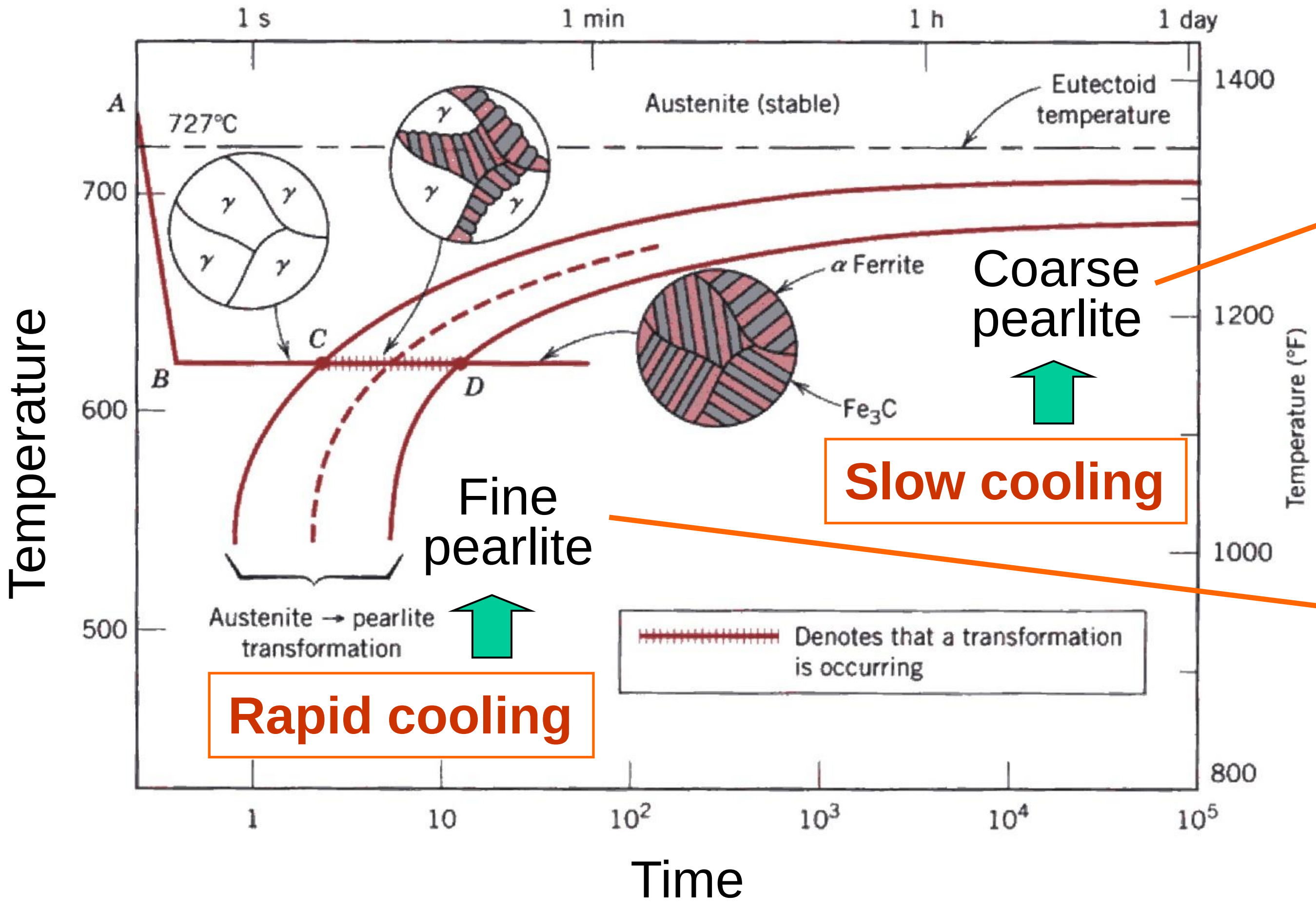
$$y = \exp(-kt^n)$$

Kinetics of diffusion-controlled solid-state transformation

TTT diagram ➡ **Isothermal transformation diagram**

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

γ Austenite ⇨ **α Ferrite + Fe_3C graphite**



Coarse pearlite

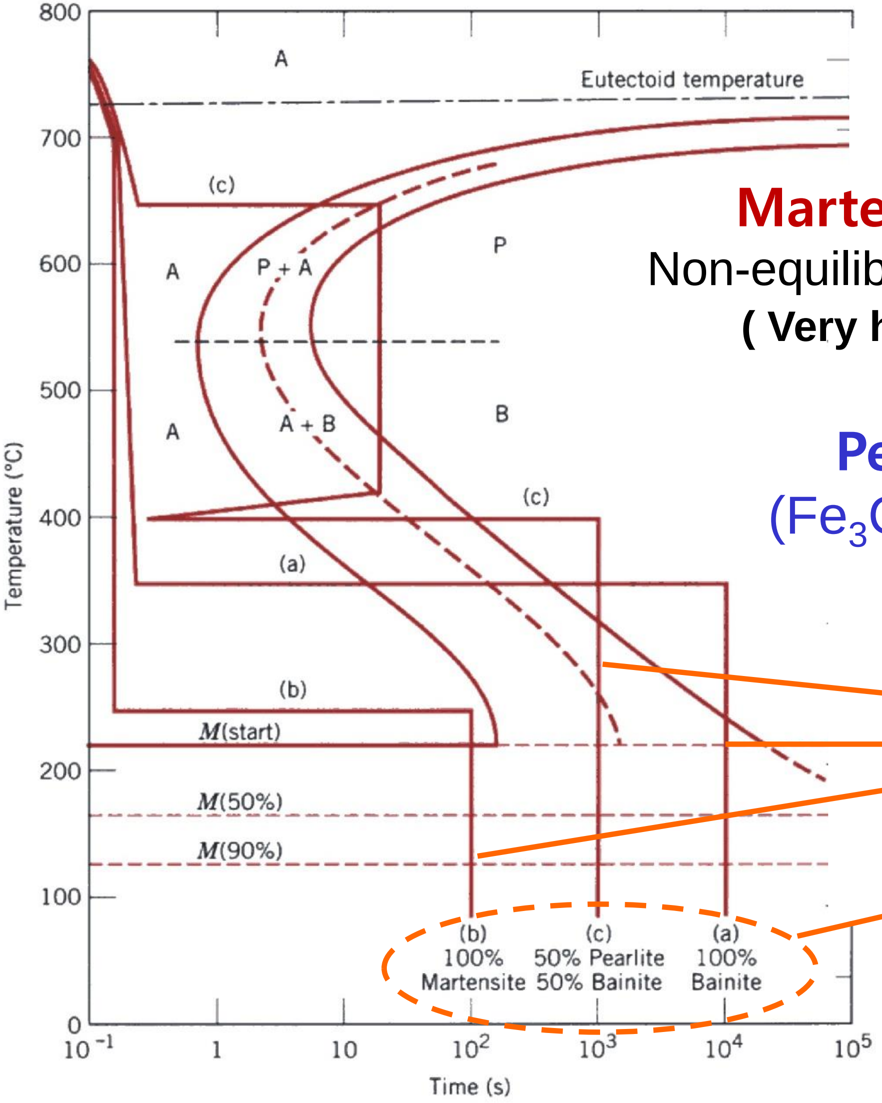
Slow cooling

Fine pearlite

Rapid cooling

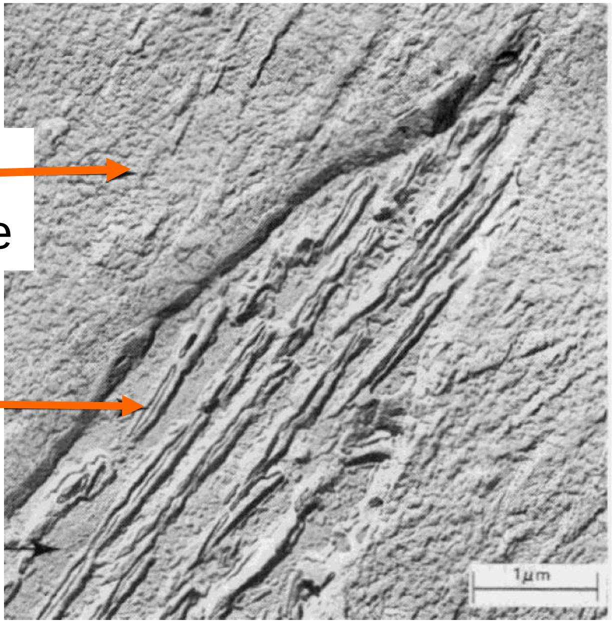
➡ **Microstructure control by phase transformation**

d. Control of Phases by Heat Treatment



Martensite ;
Non-equilibrium phase
(Very hard)

Pearlite
(Fe_3C+ferrite)



Heat Treatment

Process
control

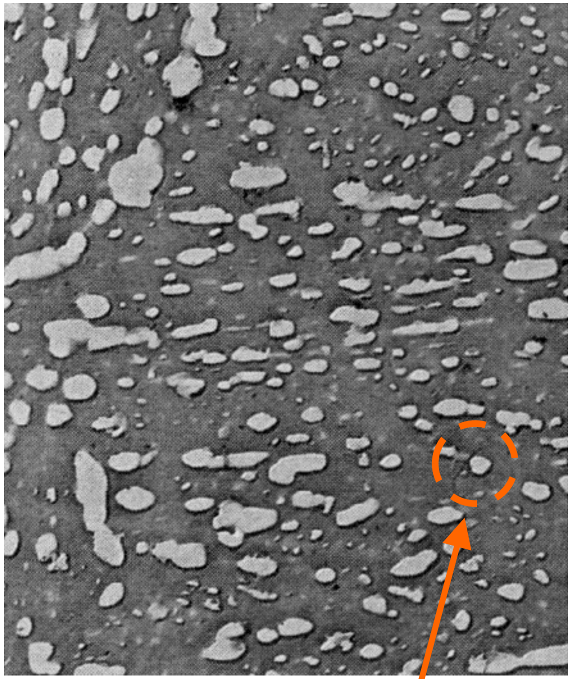
Phase & Microstructure

Properties of Material

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

Process control

Proper heat treatment (tempering)



Martensite

- Tip of needle shape grain
- Nucleation site of fracture
- Brittle

Tempered martensite

- Very small & spherical shape grain
- Good strength, ductility, toughness

② Diffusionless Transformation

Individual atomic movements are less than one interatomic spacing.

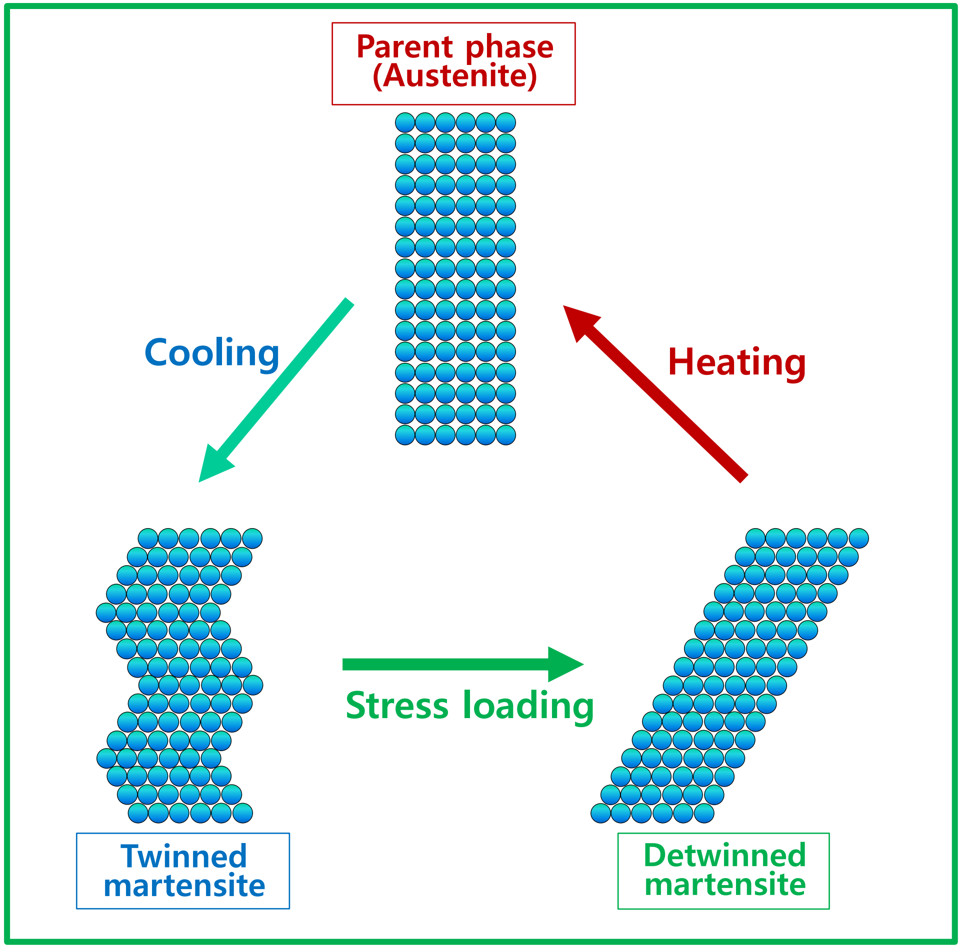
e.g. a Martensitic transformation in iron-carbon alloy

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

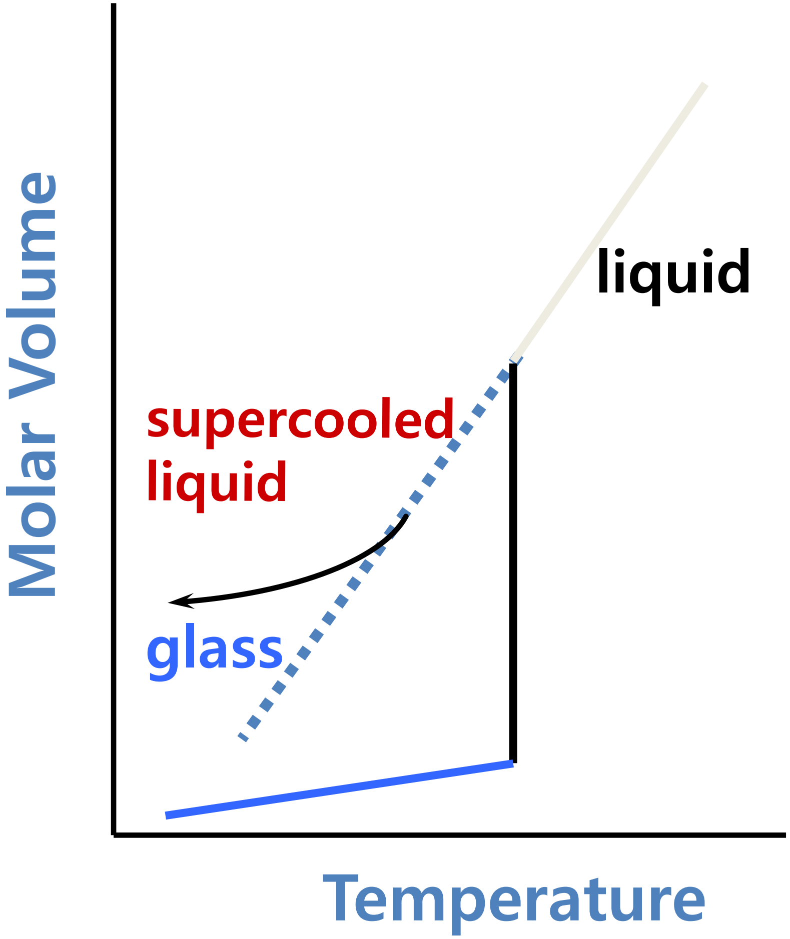
3. 항복강도 이상의 응력을 가하면 Twin boundary의 이동에 의한 소성 변형

4. A_f 이상으로 가열해주면 martensite 에서 다시 Austenite로 변태
➡ 기억된 형상으로 회복

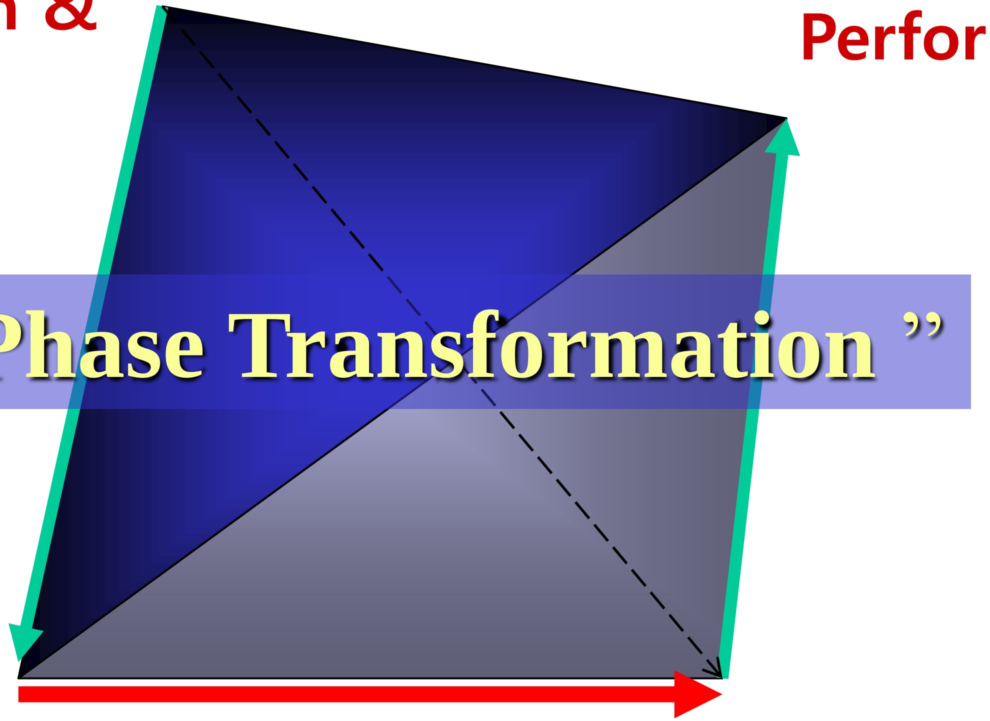
“ $\gamma \leftrightarrow M$ transformation: Short-distance atomic migration ”

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 → Solid
- (Ch5) Diffusional Transformations in Solid: Solid → Solid
- (Ch6) Diffusionless Transformations: Solid → Solid

2023 Fall

“Phase Transformation *in* Materials”

09.06.2023

Eun Soo Park

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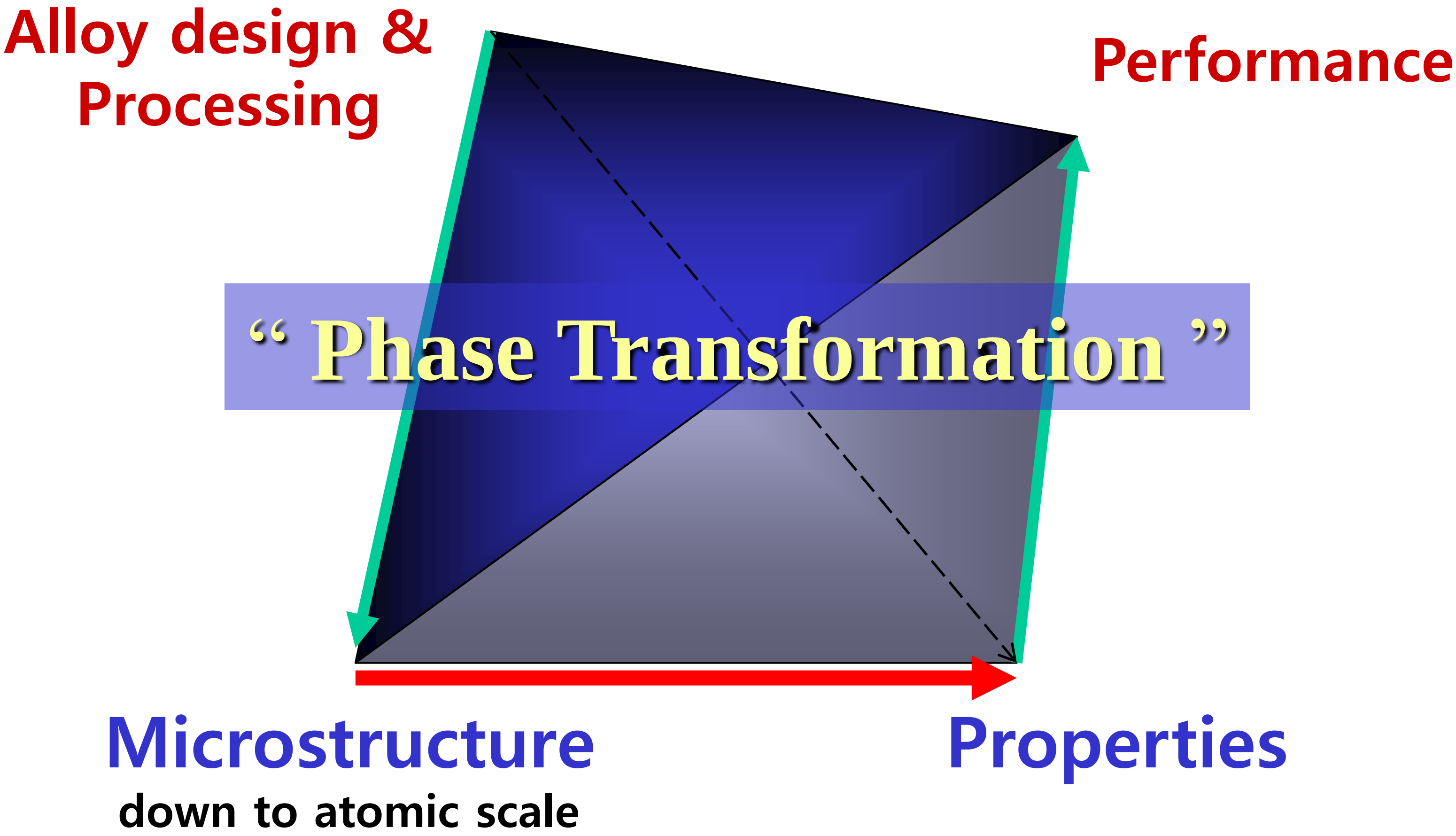
Contents for previous class

Microstructure-Properties Relationships



Alloy design &
Processing

Performance

“ Phase Transformation ”

Microstructure
down to atomic scale

Properties

“Tailor-made Materials Design”

Contents of this course_Phase transformation

Background to understand phase transformation

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- (Ch5) Diffusional Transformations in Solid: Solid → Solid
- (Ch6) Diffusionless Transformations: Solid → Solid

Contents for today's class I

Chapter 1

Thermondynamics 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

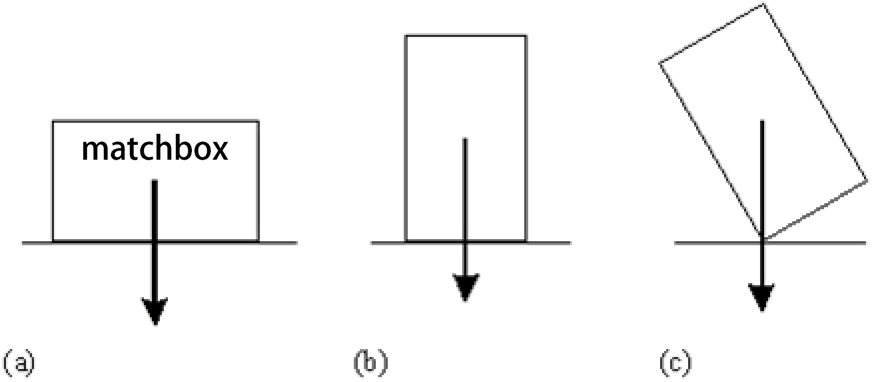
Q1: “thermodynamic equilibrium”?

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.

Equilibrium

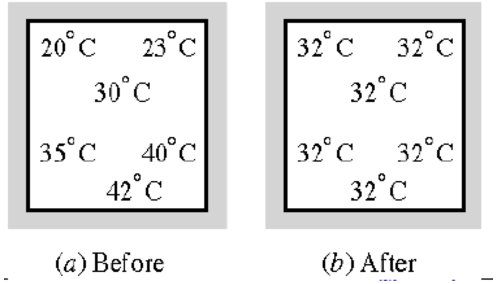
Mechanical equilibrium



: total potential energy of the system is a minimum.

Thermal equilibrium

: absence of temperature gradients in the system



(*a*) Before (*b*) After

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.

Relative Stability of a System ➡ Gibbs Free Energy

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

$$H = E + PV$$

$$H \cong E \quad \textit{for Condensed System}$$

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

$$\boxed{dG = 0}$$

Lowest possible value of Gibb's Free Energy

No desire to change ad infinitum

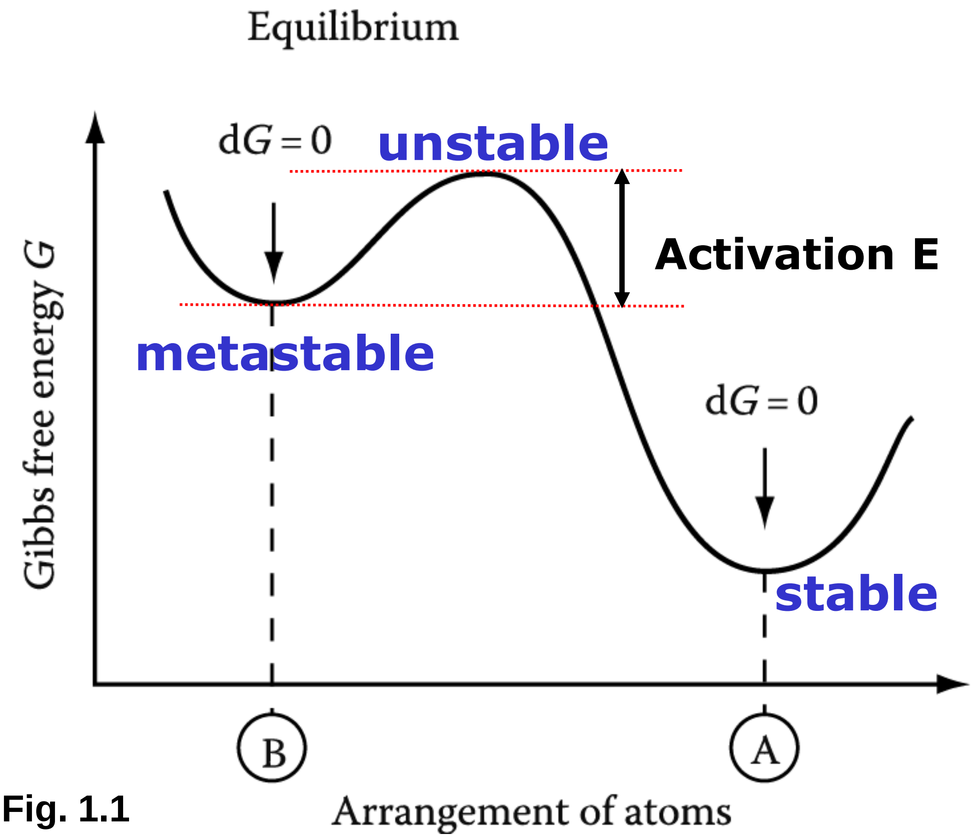


Fig. 1.1

Phase Transformation

$$\boxed{\Delta G = G_2 - G_1 < 0}$$

Q2: What is single component system?

Different elements or chemical compounds

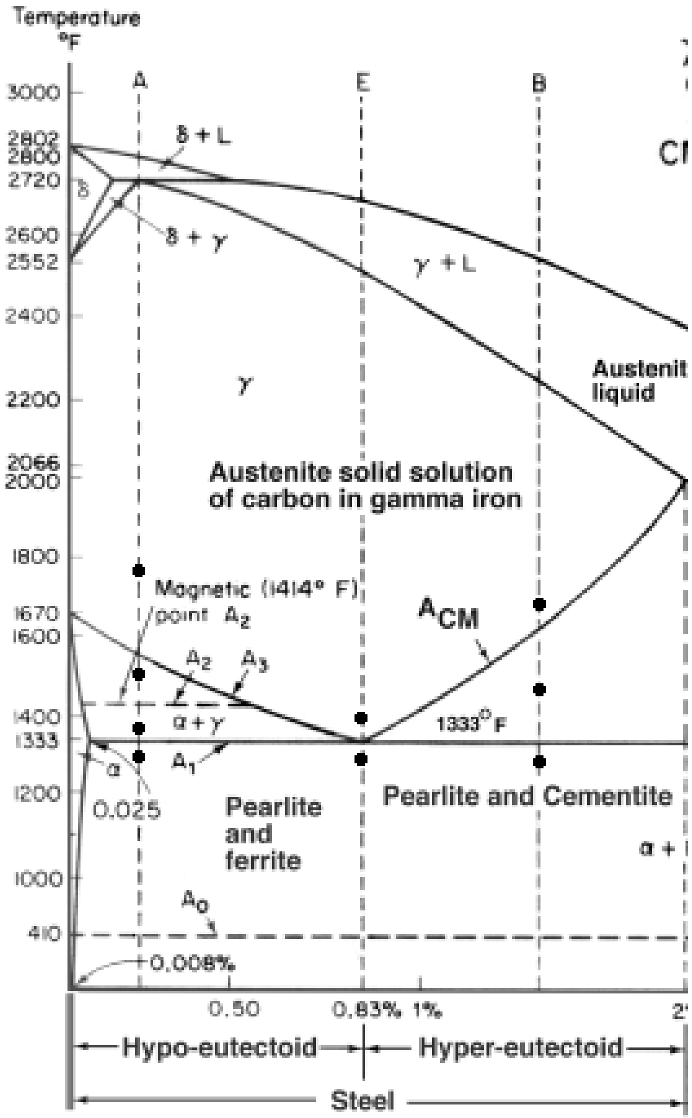
1.2 Single component system

One element (Al, Fe)

One type of molecule (H_2O)

- Allotropic forms?

- How is phase stability measured?



Fe

⟶ C

$$G = H - TS$$

1.2.1 Gibbs Free Energy as a Function of Temp.

* 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

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

When V is constant,

$$\frac{\delta Q}{dT} = \frac{dE}{dT} + P\cancelto{0}{\frac{dV}{dT}} \qquad C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \qquad \boxed{C_V = \left(\frac{\partial E}{\partial T}\right)_V \quad \text{or} \quad E = \int C_V \, dT}$$

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,

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

$$\boxed{dE = \delta Q - P \cdot dV}$$

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

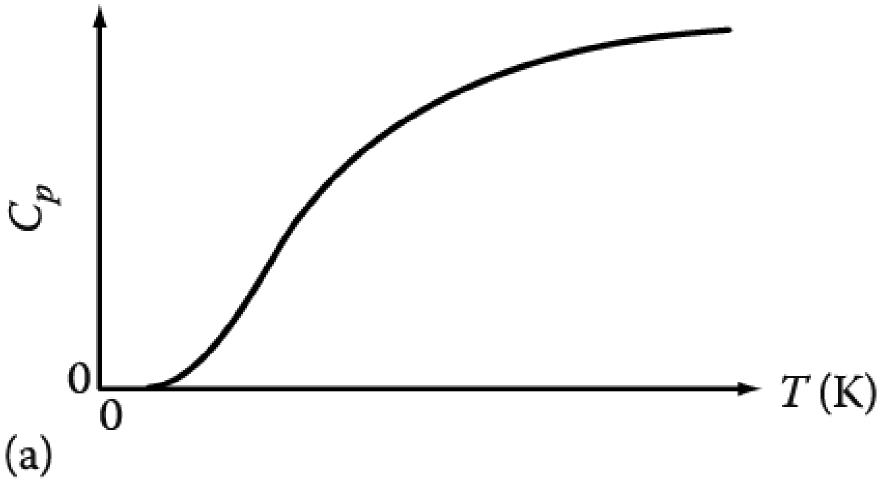
➡ $$\frac{dP}{dT} = 0 \ \text{ when } P \text{ is constant} \qquad \boxed{\left(\frac{dH}{dT}\right)_P = \left(\frac{\delta Q}{dT}\right)_P = C_P} \qquad \boxed{H = \int C_p \, dT}$$

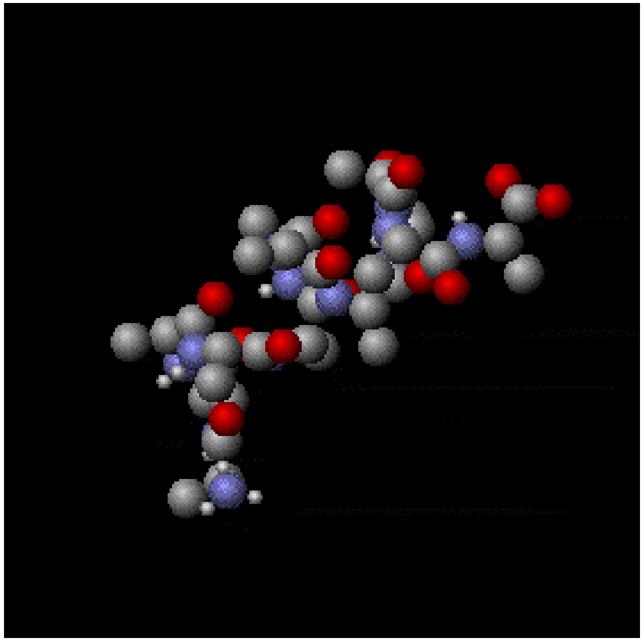
In alloy work one usually consider systems at constant pressure so that enthalpy changes are more important then energy changes.

C_P ; tempeature-dependent function

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

(empirical formula above room temp)





Molecules have <u>internal structure</u> because they are composed of atoms that have different ways of moving within molecules. Kinetic energy stored in these *<u>internal degrees of freedom</u>* 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?

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

H = ?

$$H = \int_{298}^{T} C_P dT$$

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.

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

S = ?

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

$$S = \int_{0}^{T} \frac{C_P}{T} dT$$

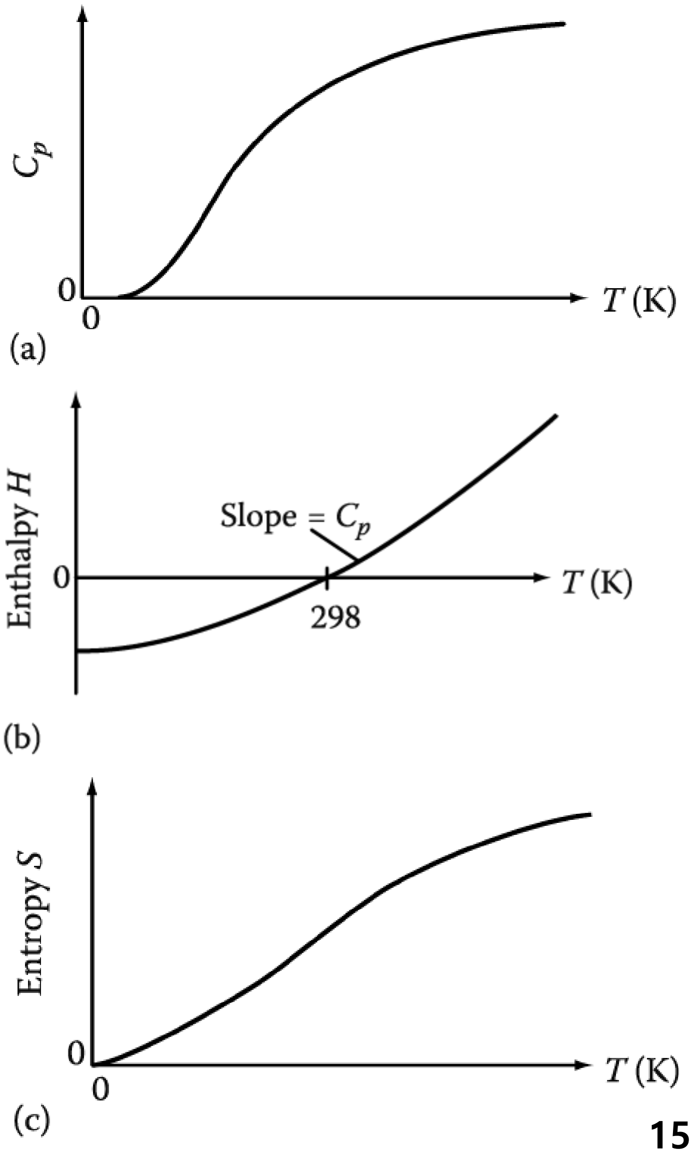


Fig. 1.2

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.

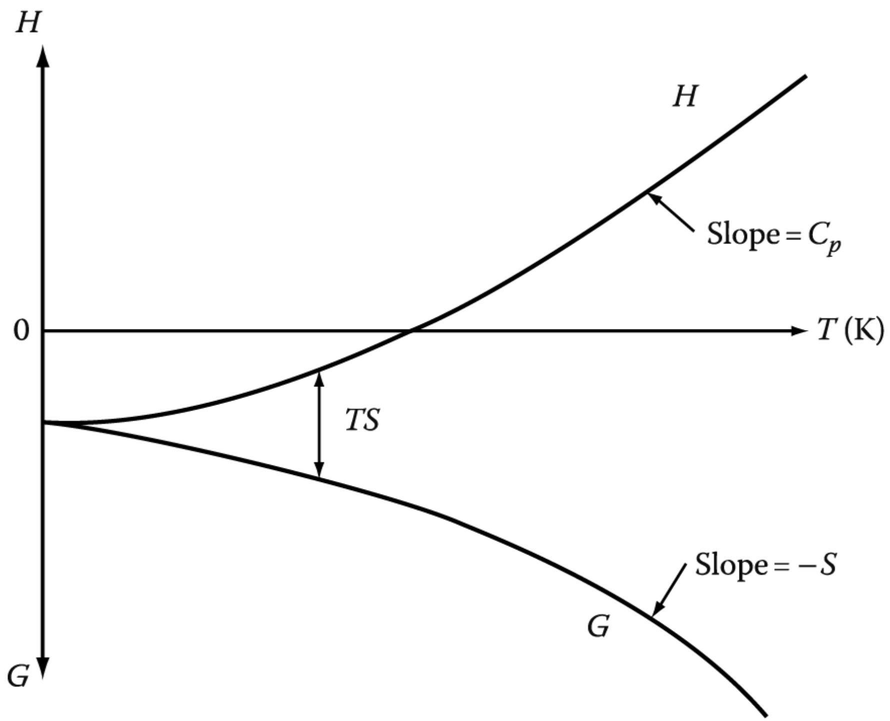


Fig. 1.3

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

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

$$G = H - TS$$

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

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

$$= VdP - SdT$$

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

$$dG = VdP - SdT$$

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

* 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 <u>decreases more rapidly</u> with increasing temperature than that of the solid.

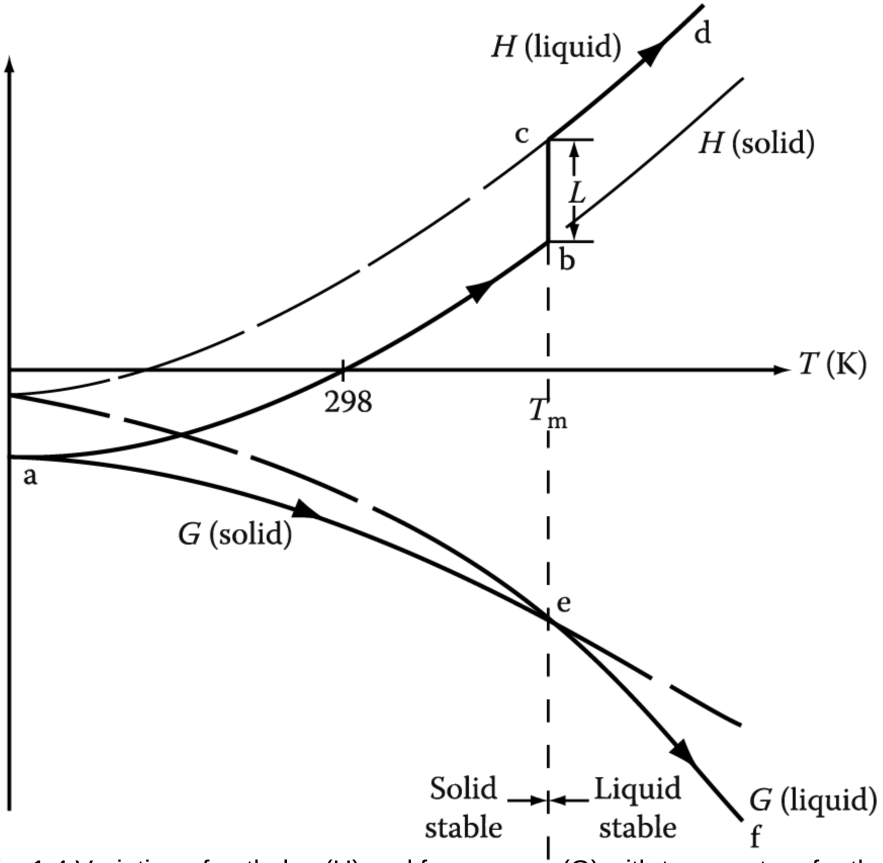


Fig. 1.4 Variation of enthalpy (H) and free energy (G) with temperature for the Solid and liquid phases of a pure metal. L is the latent heat of melting, Tm the Equilibrium melting temperature.

Fig. 1.4

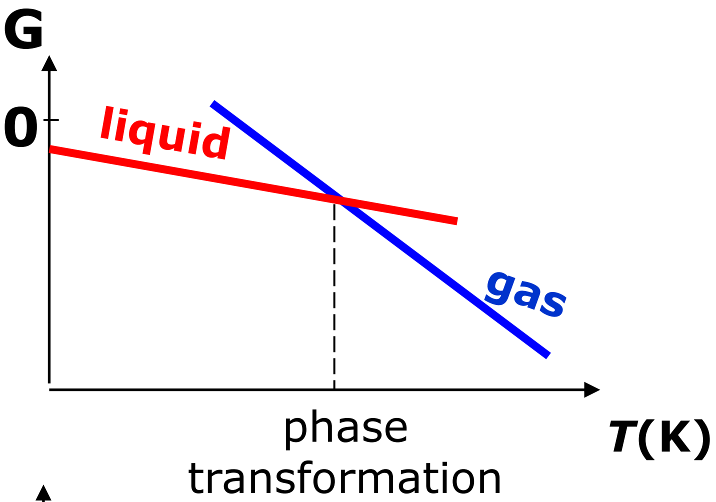
- **Which is larger, G^L or G^S at low T?**
- **$G^L > G^S$ (at low Temp) and $G^S > G^L$ (at high Temp)**

Considering P, T

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

$$dG = VdP - SdT$$

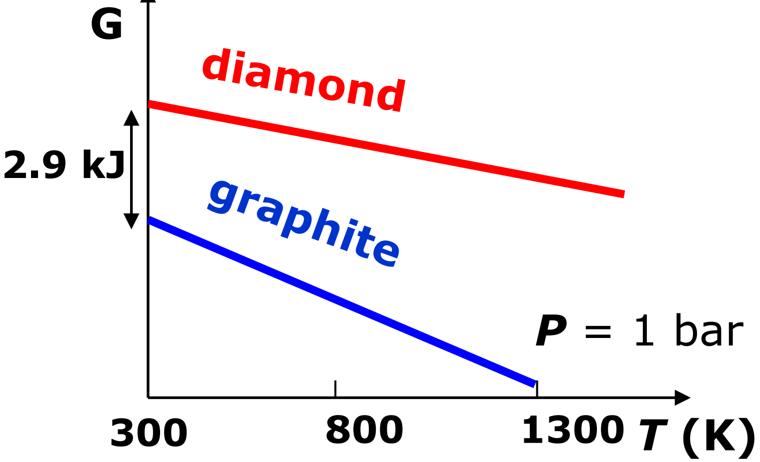
$$G(P,T) = G(P_0,T_0) + \int_{P0}^{P1} V(T_0,P)dP - \int_{T0}^{T1} S(P,T)dT$$



S(water) = 70 J/K

S(vapor) = 189 J/K

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



S(graphite) = 5.74 J/K,
S(diamond) = 2.38 J/K,

Q7: What is the role of pressure on equilibrium?

*** 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 α & β 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)

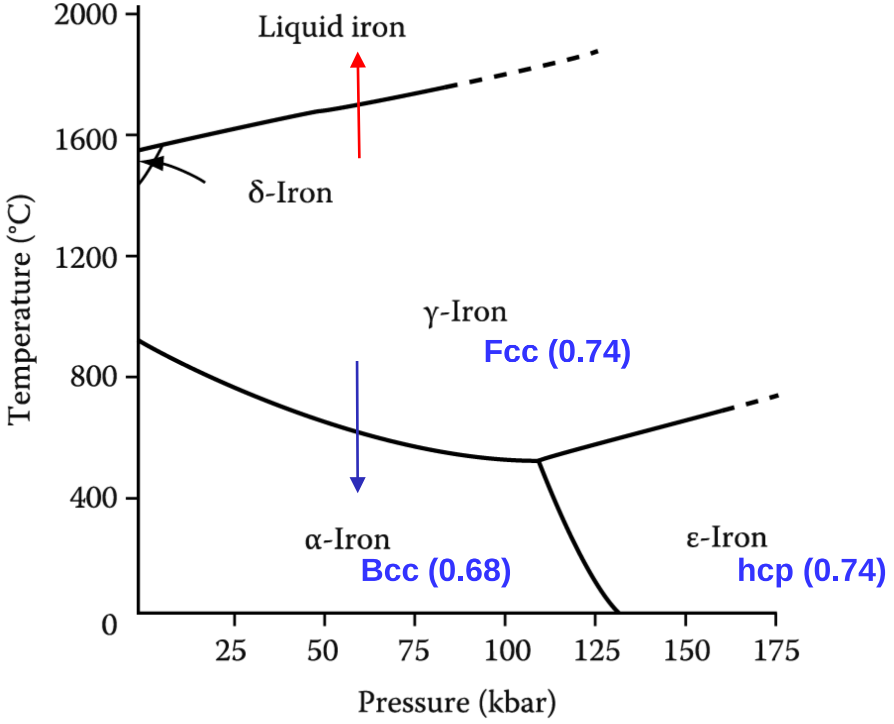


Fig. 1.5 Effect of pressure on the equilibrium phase diagram for pure iron

For, γ →liquid; ΔV (+), ΔH(+)

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

For, α→γ ; ΔV (-), ΔH(+)

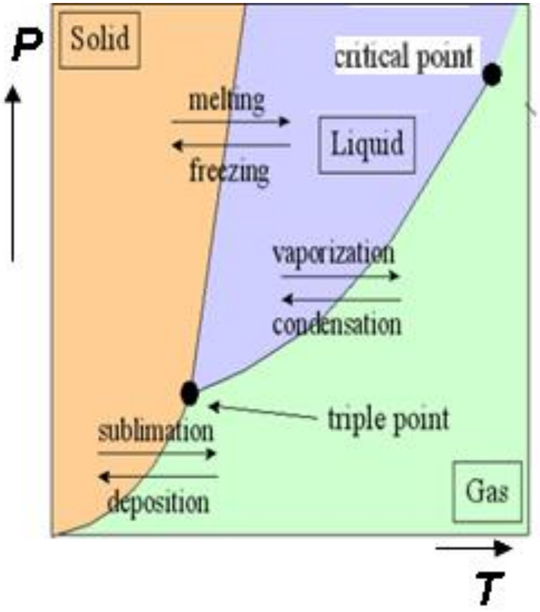
$$\left(\frac{dP}{dT}\right) = \frac{\Delta H}{T_{eq}\Delta V} < 0$$

$$\boxed{\left(\frac{\partial G}{\partial P}\right)_{T} = V}$$

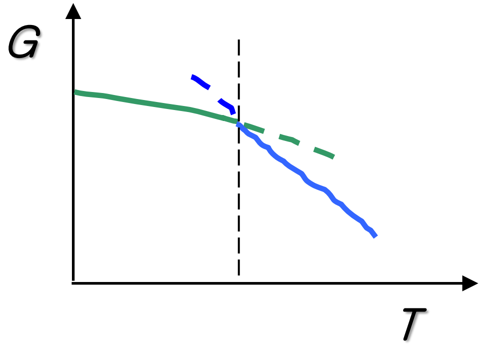
Q8: How to classify phase transition?

“First order transition” vs “Second order transition”

The First-Order Transition



Latent heat
Energy barrier
Discontinuous entropy, heat capacity



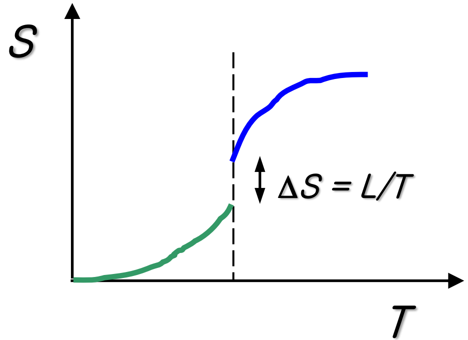
- First Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are discontinuous at T_T

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

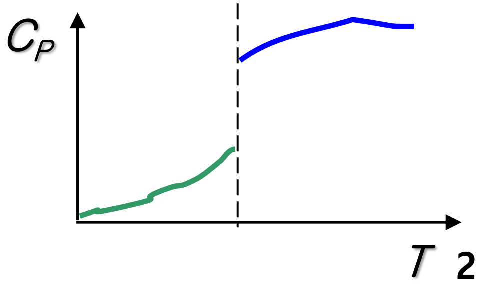
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

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

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

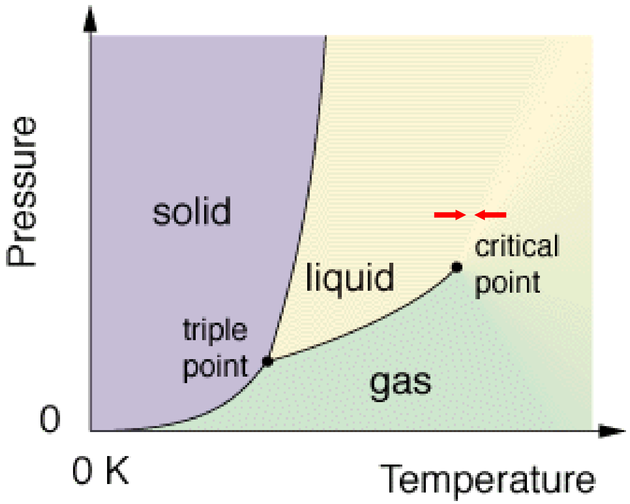


$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$



The Second Order Transition

No Latent heat
Continuous entropy



- 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

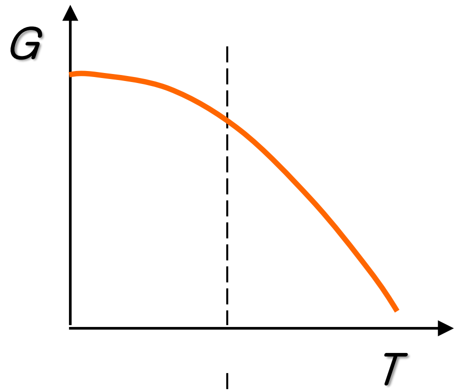
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

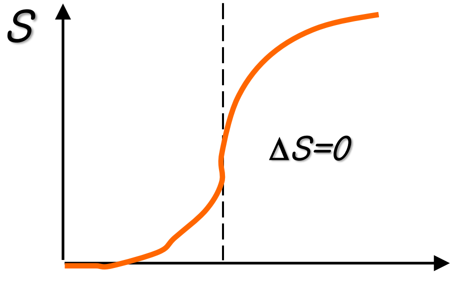
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

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

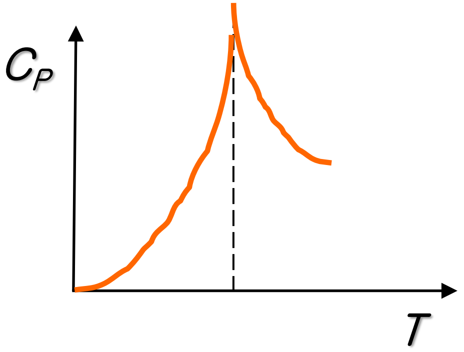
  - Examples: Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

Second-order transition





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



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)

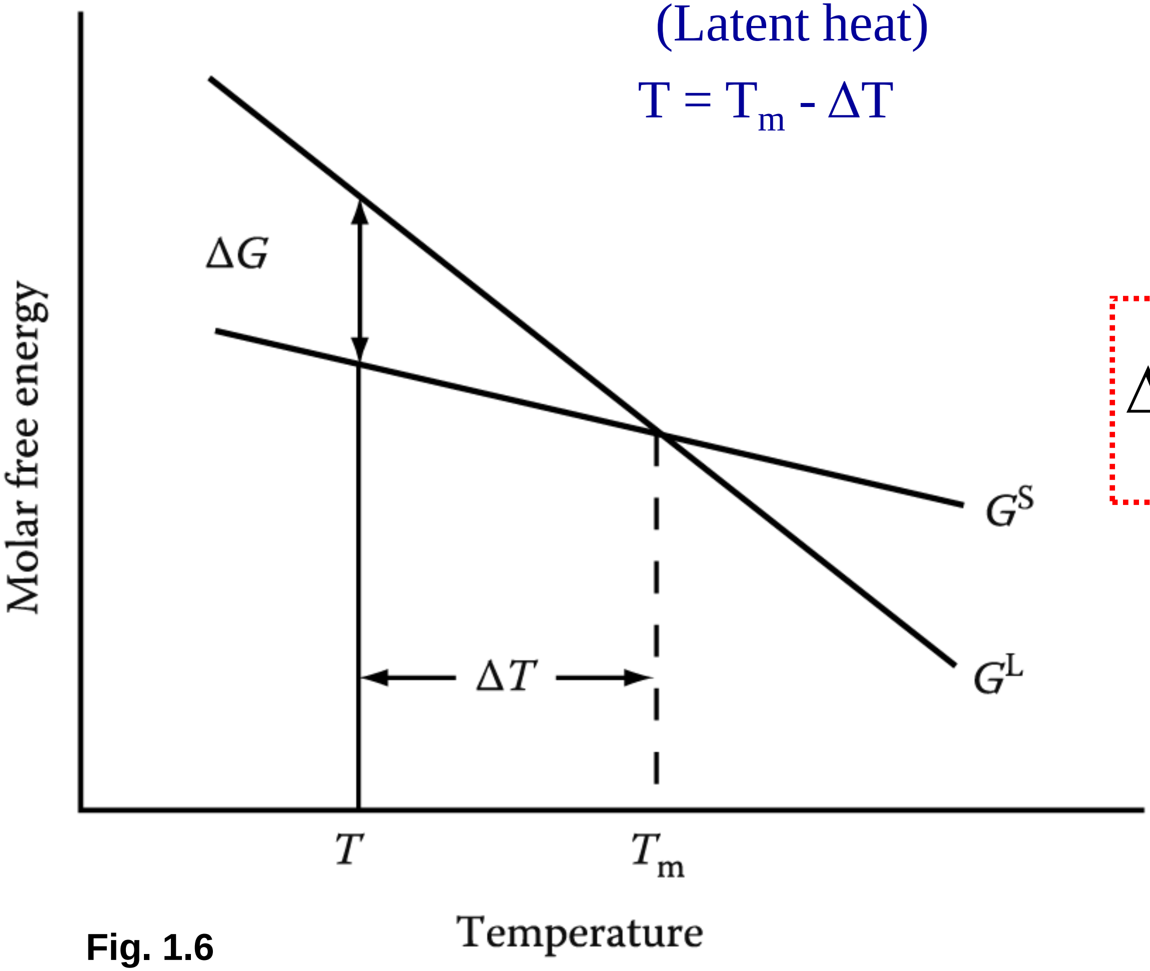
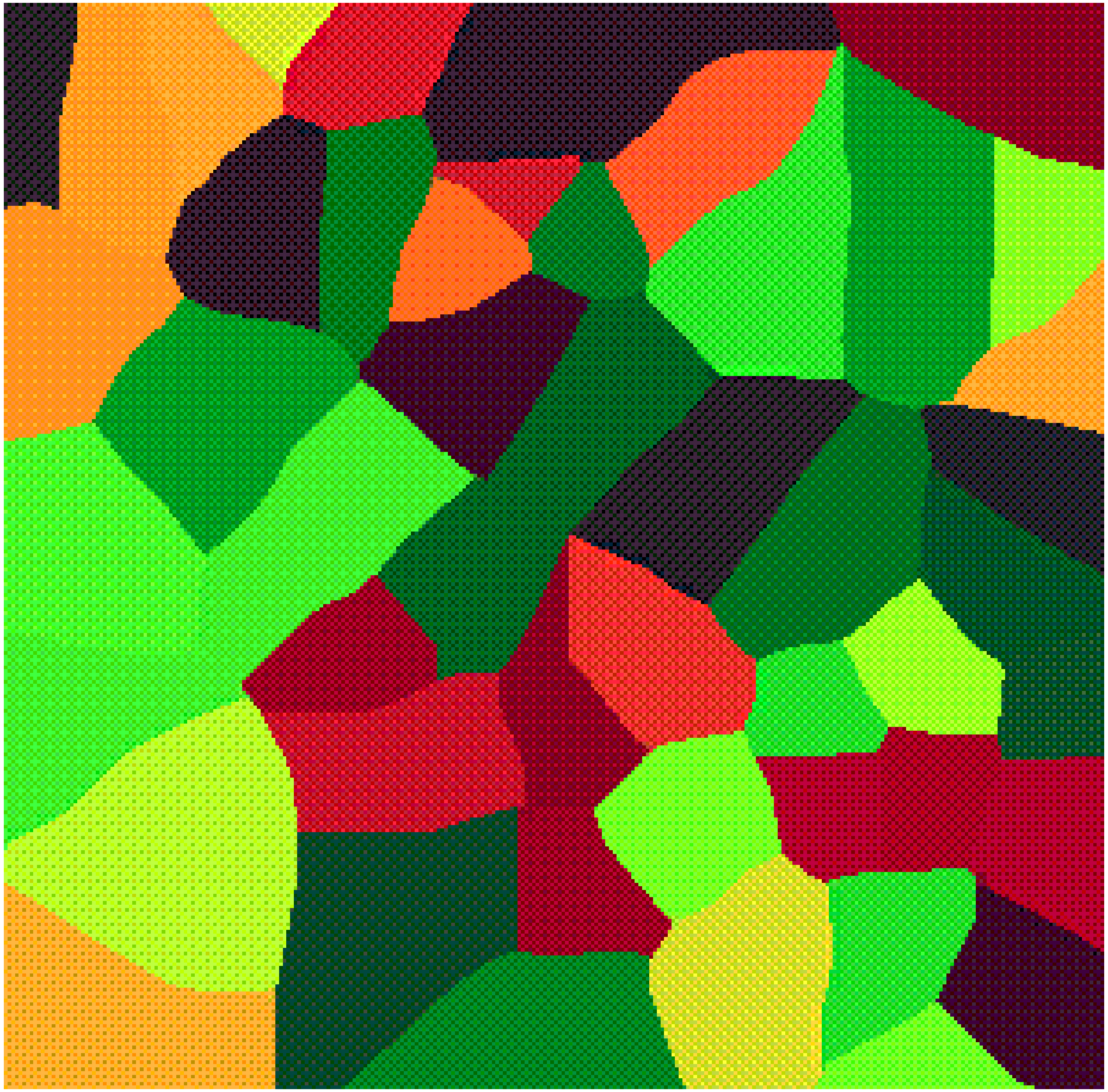


Fig. 1.6

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

4. Solidification: Liquid ⟶ Solid



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

4.1.1. Homogeneous Nucleation

Fig. 4.1 (a) G_1 (b) $G_2 = G_1 + \Delta G$

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

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

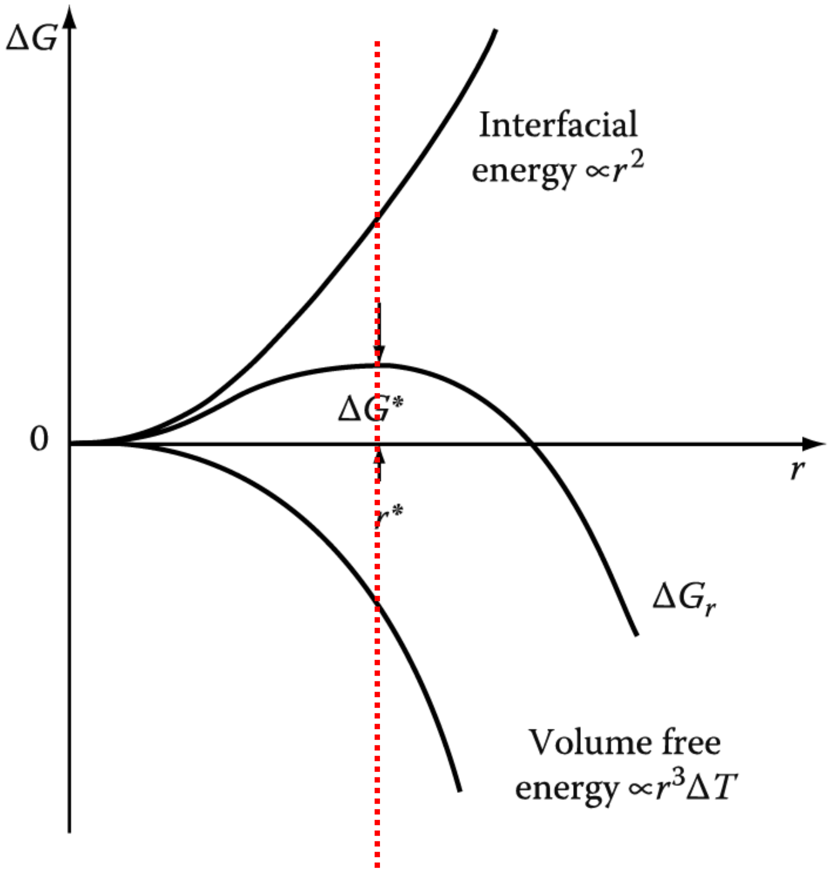
G_V^S, G_V^L **: free energies per unit volume**

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

for spherical nuclei (isotropic) of radius : r

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

4.1.1. Homogeneous Nucleation



Unstable equilibrium

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

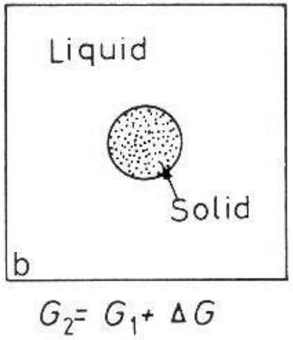
Why r^* is not defined by $\Delta G_r = 0$?

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

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

r^* **: critical nucleus size**

r^* ⟹ **dG=0**

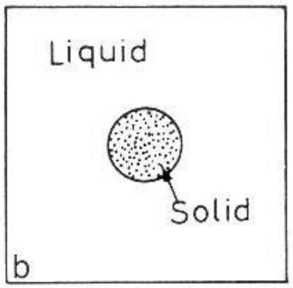


$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

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

1.2.3 Driving force for solidification

Liquid $\xrightarrow{\text{solidification}}$ **Solid**



$G_2 = G_1 + \Delta G$

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

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

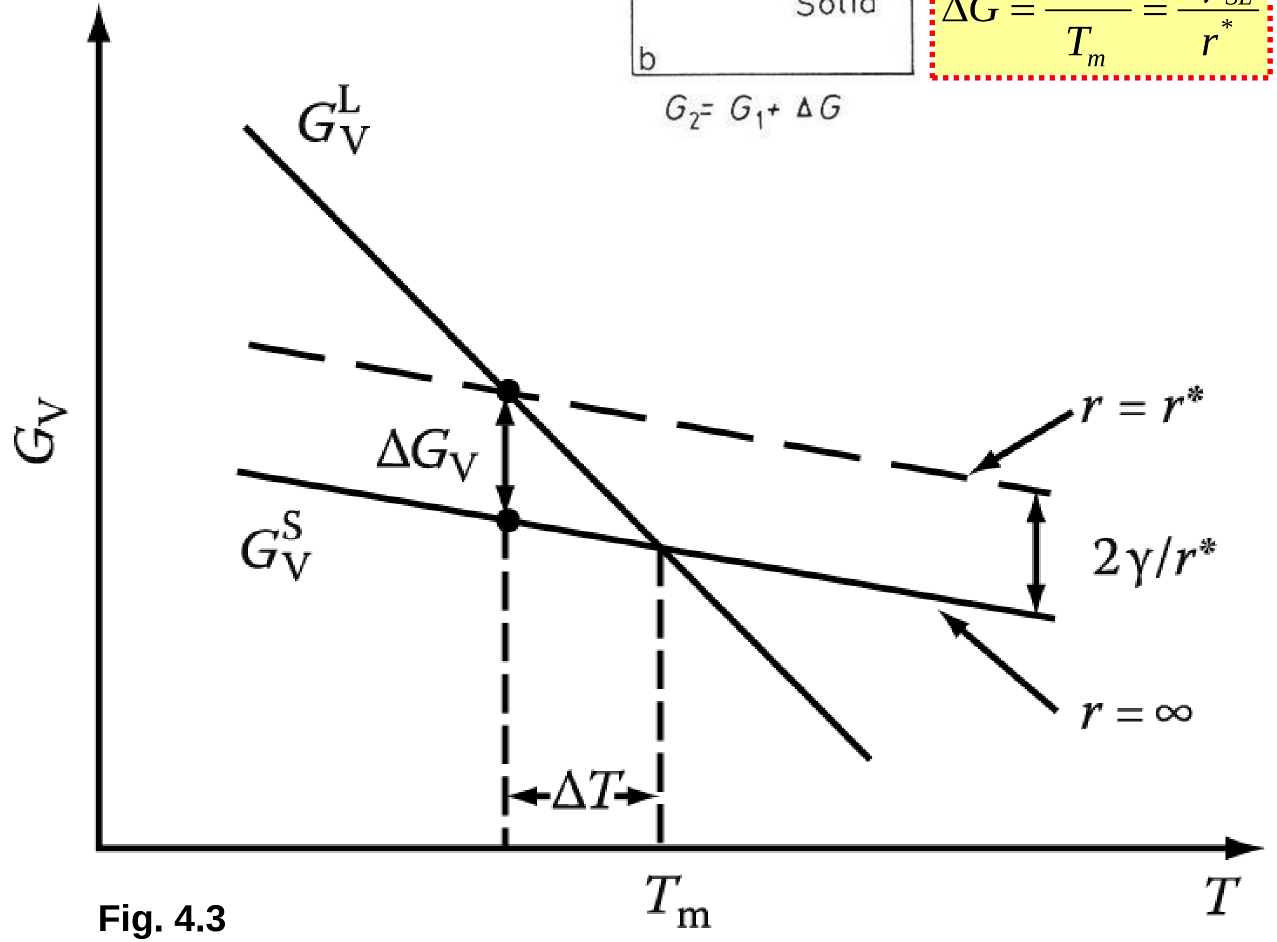
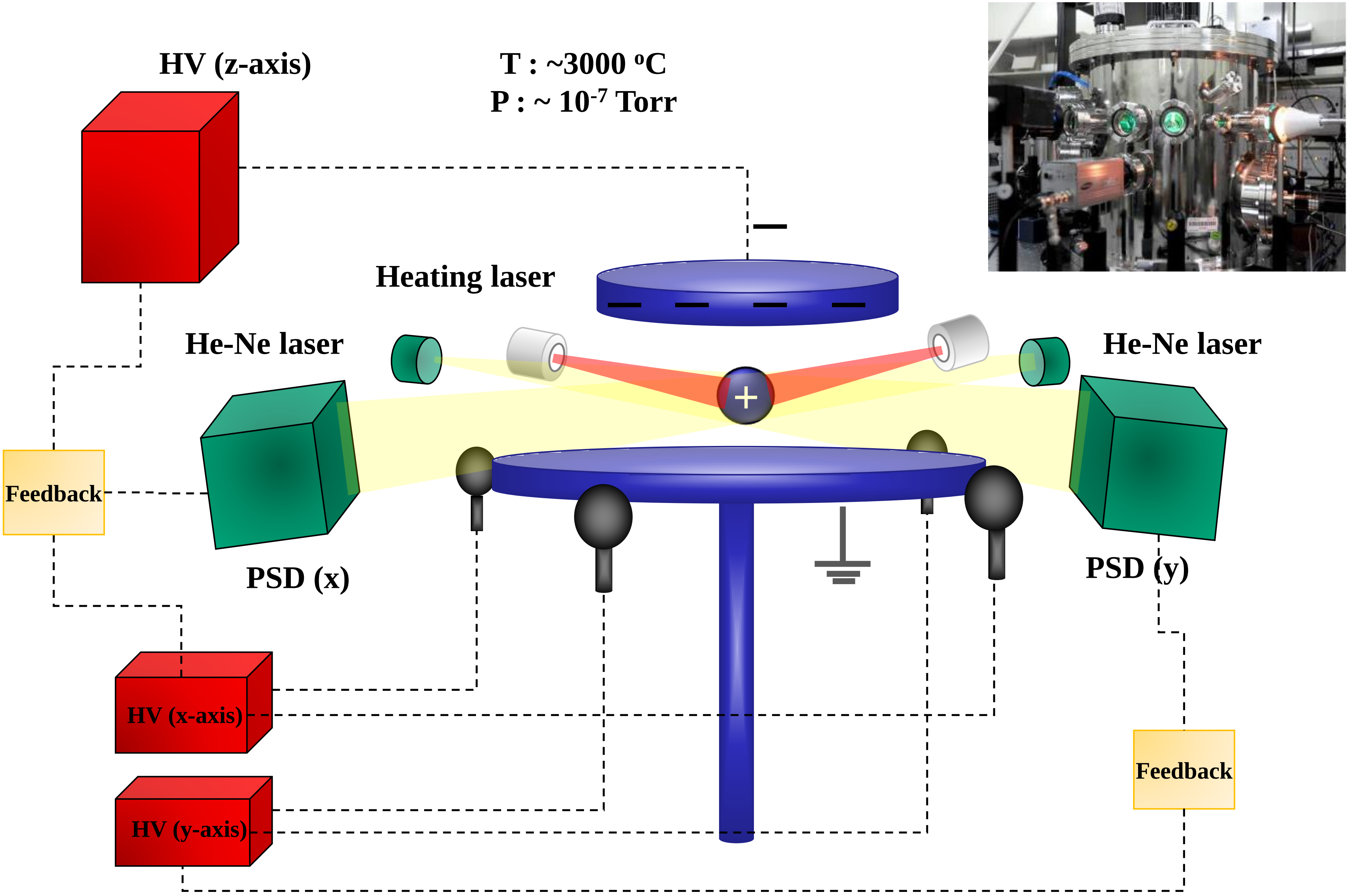


Fig. 4.3

Electrostatic levitation in KRISS



HV (z-axis)

T : ~3000 °C
P : ~ 10^{-7} Torr

Heating laser

He-Ne laser

He-Ne laser

Feedback

PSD (x)

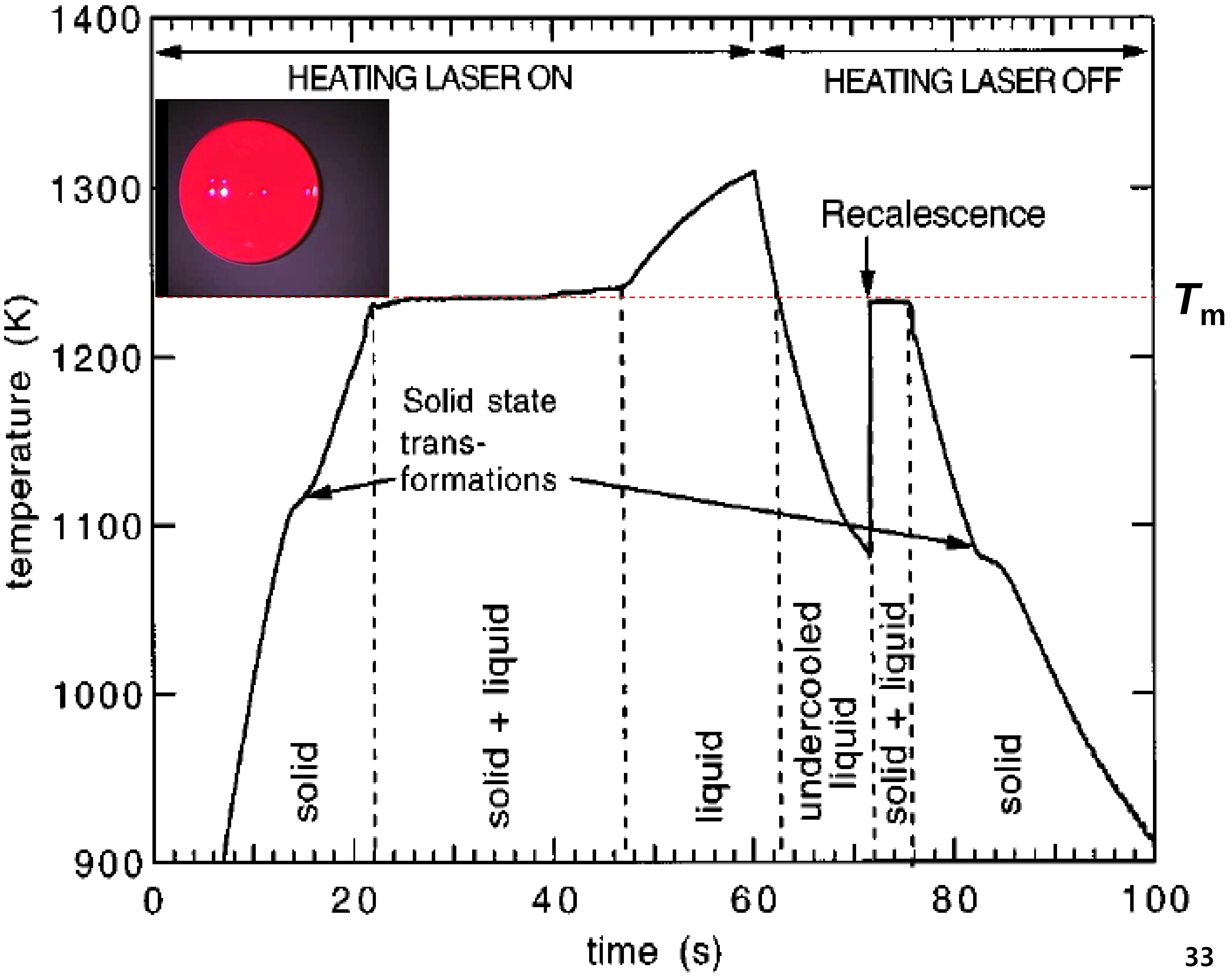
PSD (y)

HV (x-axis)

HV (y-axis)

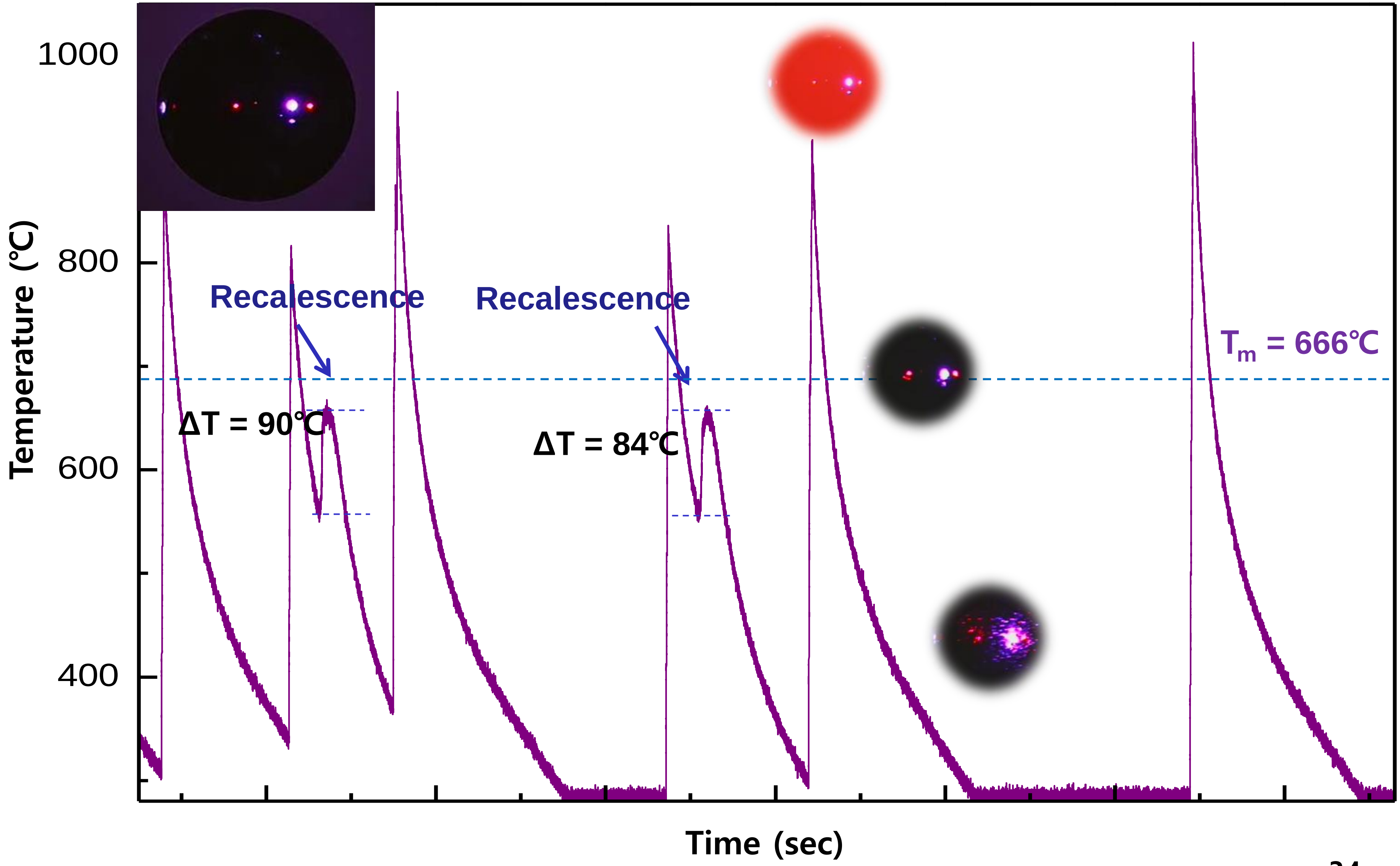
Feedback

KRISS material : Dr. G.W.Lee



1400
1300
1200
1100
1000
900
temperature (K)
0
20
40
60
80
100
time (s)
HEATING LASER ON
HEATING LASER OFF
Recalescence
T_m
Solid state trans-formations
solid
solid + liquid
liquid
undercooled liquid
solid + liquid
solid

Cyclic cooling curves of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$



* The homogeneous nucleation rate - kinetics

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

: insensitive to Temp.

How do we define nucleation temperature, ΔT_N ?

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

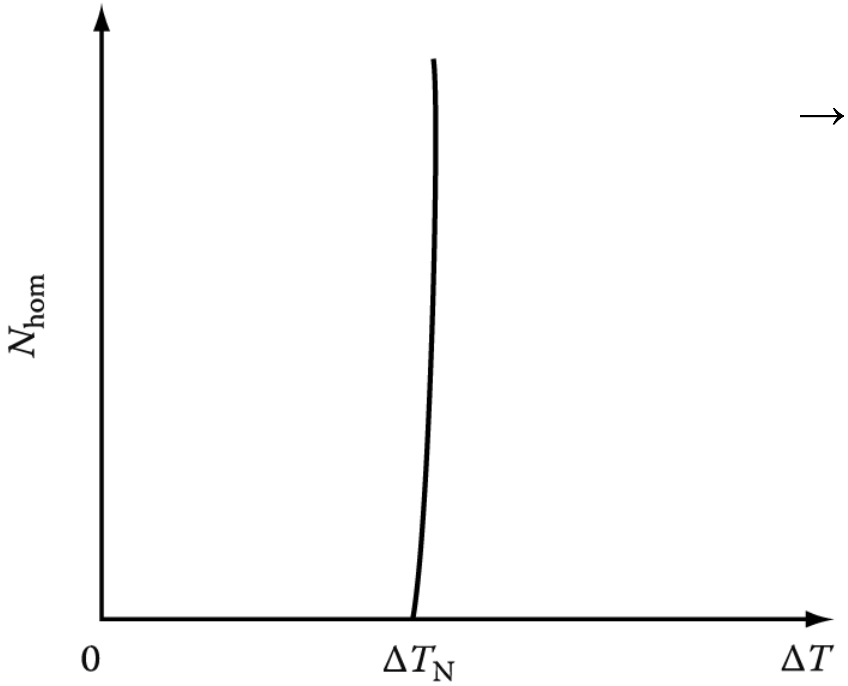


Fig. 4.6

→ **critical value for detectable nucleation**

- critical supersaturation ratio

- critical driving force

- critical supercooling

→ **for most metals, ΔT_N~0.2 T_m (i.e. ~200K)**

The homogeneous nucleation rate as a function of undercooling ΔT. ΔT_N is the critical undercooling for homogeneous nucleation.

* Relationship between Maximum Supercoolings and T_m

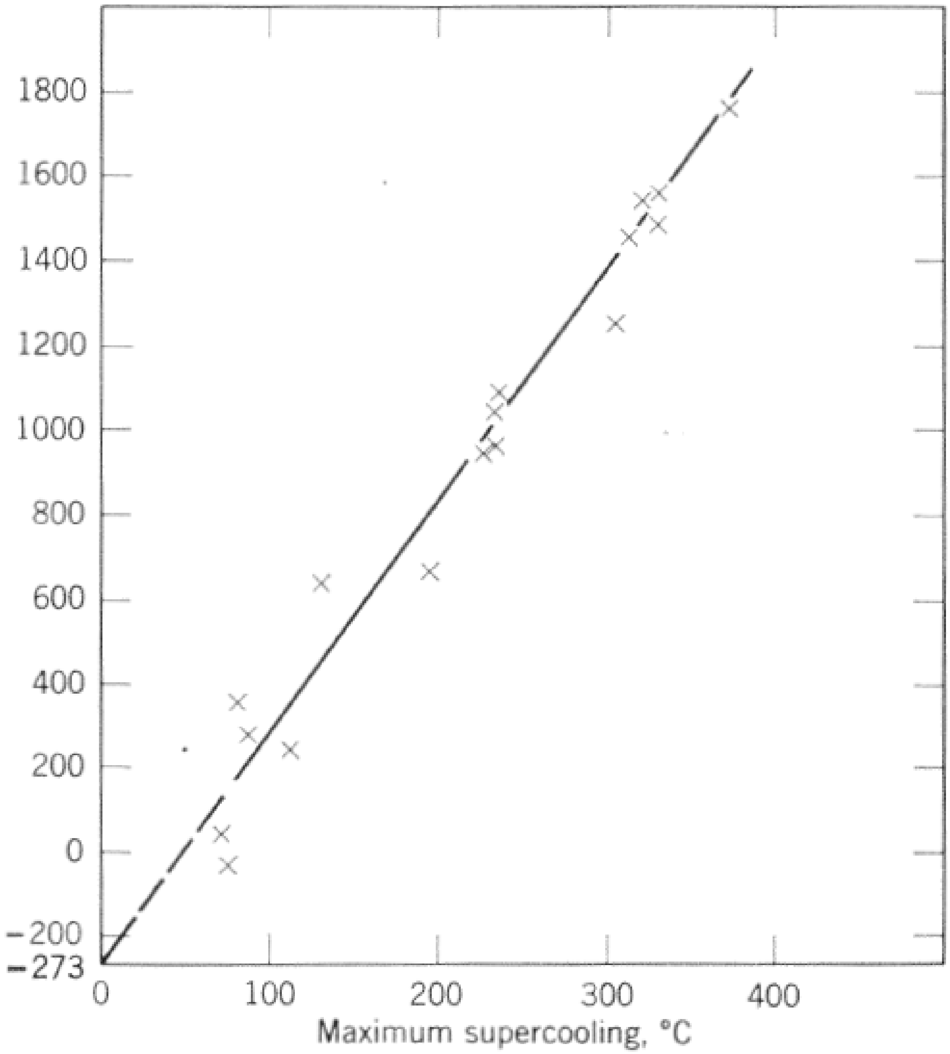


Fig. 3.7. Maximum supercooling as a function of melting point. (From *Thermodynamics in Physical Metallurgy*, American Society for Metals, Cleveland, 1911, p. 11.)

Solidification: Liquid $\longrightarrow$ Solid

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

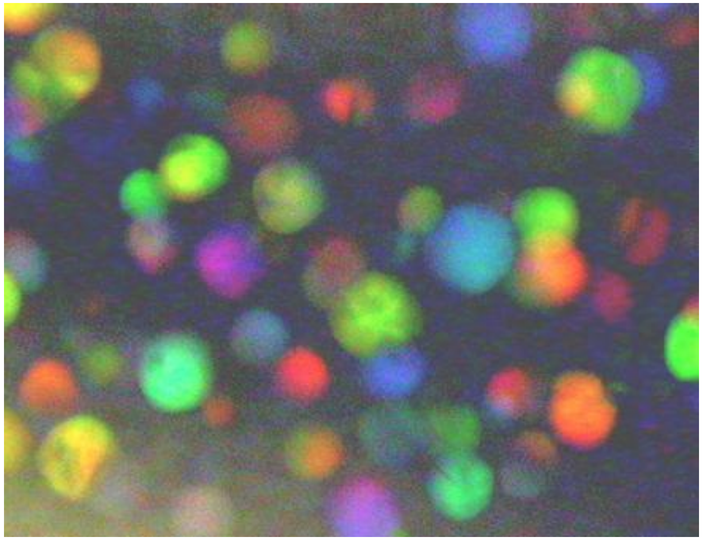
Nucleation in Pure Metals

T_m : $G_L = G_S$

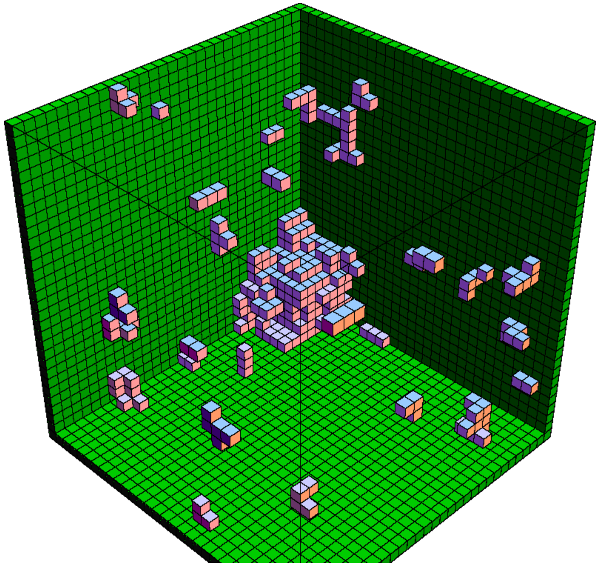
- Undercooling (supercooling) for nucleation: 250 K ~ 1 K

<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)

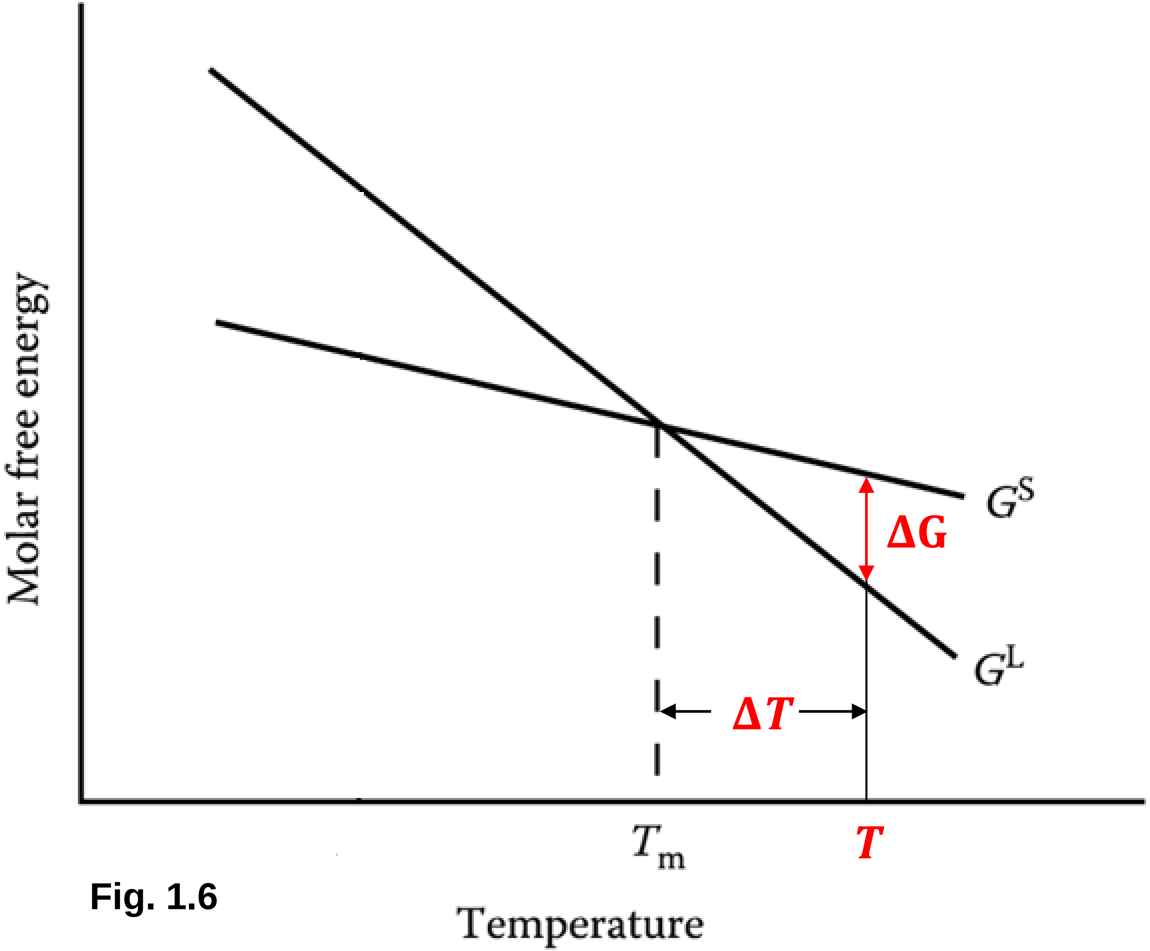


Fig. 1.6

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

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.

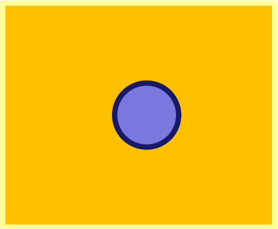
Why?

$$\boxed{\gamma_{SL} + \gamma_{LV} < \gamma_{SV}}$$ **(commonly)**

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

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

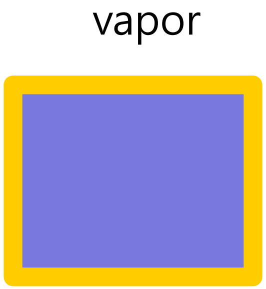
- Interfacial energy ⇨ ΔT_N

No superheating required!

- Interfacial energy ⇨ No ΔT_N

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

Melting: Liquid ← Solid



Contents for today's class

Chapter 1

Thermondynamics and Phase Diagrams

Phase Transformation

- Equilibrium_

$$\boxed{dG = 0}$$

$$\boxed{\Delta G = G_2 - G_1 < 0}$$

Lowest possible value of G

No desire to change ad infinitum

- Single component system

Gibbs Free Energy as a Function of Temp. and Pressure

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

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

Clausius-Clapeyron Relation

- Classification of phase transition

First order transition: CDD/Second order transition: CCD

- Driving force for solidification

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