2009 fall

Advanced Physical Metallurgy

"Phase Equilibria in Materials"

09.01.2009

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Introduction

- **Web lecture assistance: http://eng.snu.ac.kr/lecture/index.php**
  - **All materials will be posted at the webpage.**

- **Hand out copied materials or scanned materials in web**

Text: A. PRINCE, "Alloy Phase Equilibria",
Elsevier publishing company (1966)_an out-of-printed book

References: 1) "**Phase Diagrams in Metallurgy",**
Frederick N. Rhines, McGraw-Hill Book Company, INC (19

2) "**Principles of Phase Diagrams in Materials Systems",**
Paul Gordon, McGraw-Hill Book Company, INC (1968)

3) "**Phase Transformations in Metals and Alloys",**
D.A. Porter and K.E. Eastering, Nelson thornes Ltd (2001)

Additional reading materials will be provided.

Course Goals

This course provides the fundamental concepts and advanced understandings of phase equilibria in materials, including relationship of free energy to phase diagram. The course will address some kinetic and non-equilibrium concepts and some phenomenological discussions. In particular, phase and composition determinations in ternary and quaternary systems, relationship between phase diagrams and thermodynamic data, and cooling paths during cooling of the ternary melts will be covered. This course can provide a working knowledge of how to construct and read phase diagrams and use them to solve problems involving materials and process design.

Schedule

week 1 **Introductory Thermodynamics**
week 2 **Thermodynamics of Solutions**
week 3 **Binary Phase Diagrams**: Two-phase Equilibrium
week 4 **Binary Phase Diagrams**: Three-phase Equilibrium
week 5 **Binary Phase Diagrams**: Limited Solubility in Both the Liquid and Solid State
week 6 **Binary Phase Diagrams**: Reactions in the Solid State
week 7 **Binary Phase Diagrams**: Allotropy of the Components
week 8 **Ternary Phase Diagrams**: Two-phase Equilibrium
week 9 **Ternary Phase Diagrams**: Three-phase Equilibrium
week 10 **Ternary Phase Diagrams**: Four-phase Equilibrium
week 11 **Ternary Phase Diagrams**: Intermediate Phases
week 12 **Ternary Phase Diagrams**: Liquid Immiscibility
week 13 **Ternary Phase Diagrams**: Four-phase Equilibrium Involving Allotropy of One Component
week 14 **The Association of Phase Regions**
week 15 **Quaternary Phase Diagrmas I**
week 16 **Quaternary Phase Diagrmas II**

Components of Your Grade:

1) **Exams (mid: 30% + final: 30%)**
   There will be two exams, each of which takes place in class for 2 hours. The exams will be conceptual and difficult.

2) **Reports and Presentation (20%)**
   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.

3) **Quiz (15%) and attendance (5%)**
   There will be a few short quizzes among the major exams. These will take place in class and early for 20 minutes.

REMARK: The percentage can be changed under 5%.

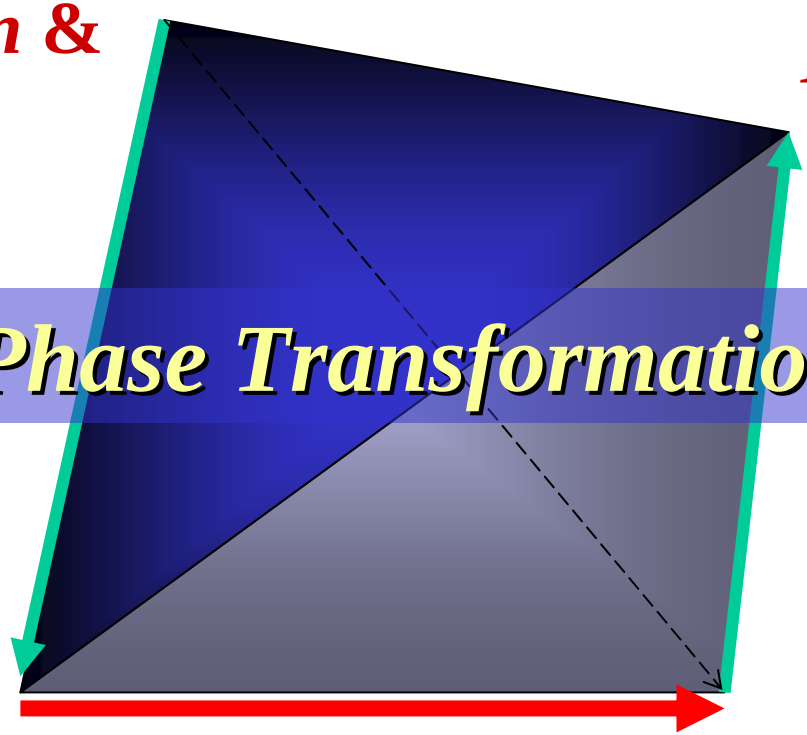
Policies and Procedures

- ***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 **Thursday,** you can get 80% credit if you turn it in on **Friday,** 50% on next**Tuesday,** 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.

Microstructure-Properties Relationships

Alloy design & Processing

Performance



Microstructure

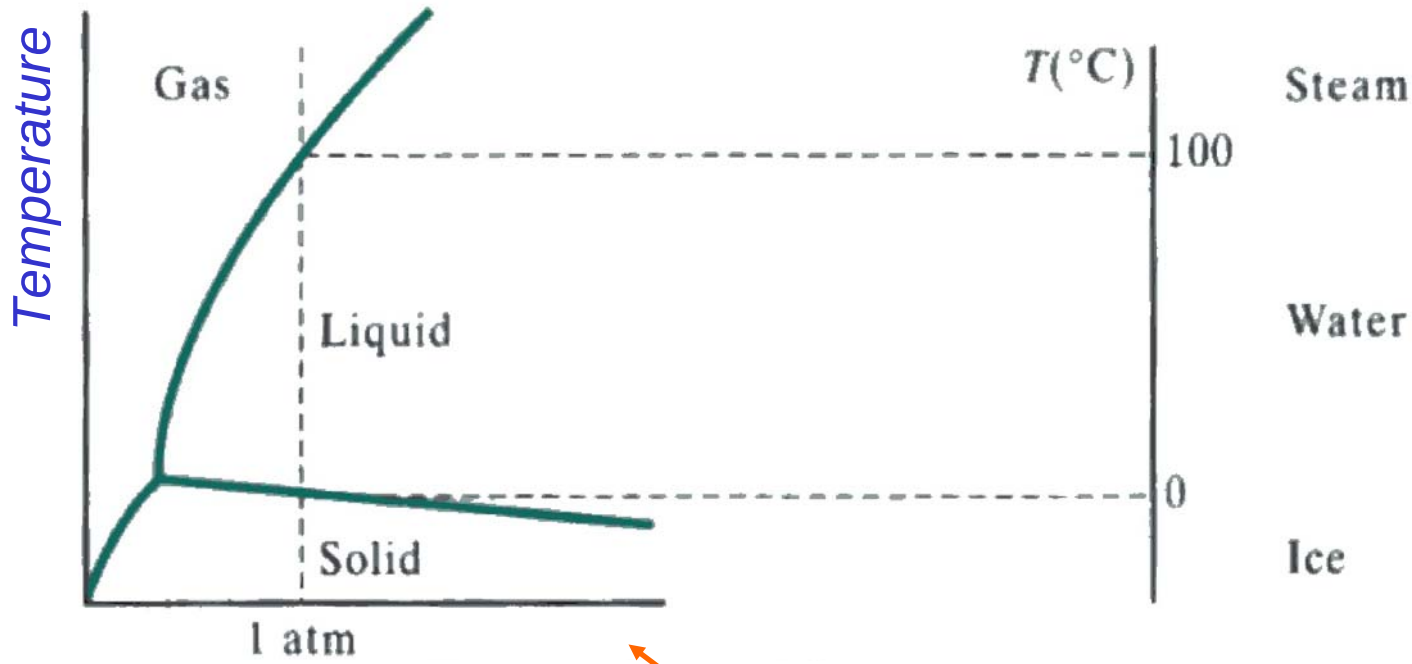
down to atomic scale

Properties

"Tailor-made Materials Design"

What is *Phase*?

A phase is a chemically and structurally homogeneous portion of the microstructure.



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

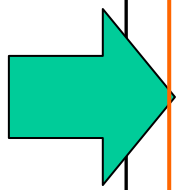
Equilibrium phase ➡ only consider Thermodynamics

Perfect Crystal **is good in many aspects, But …**

- 1) ***Imperfection*** in Metallic Materials ;

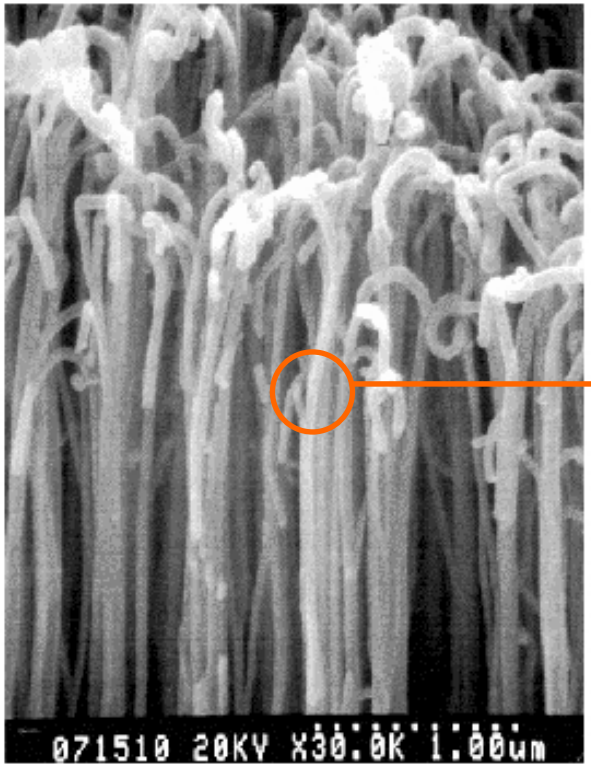
  Point defect : Vacancies,
  Impurity atoms
  Line defect : Dislocations
  Plane defect : Grain Boundaries,
  Free Surfaces
  Bulk defect : Voids, Cracks

- 2) ***Second Phase Particles*** in Matrix

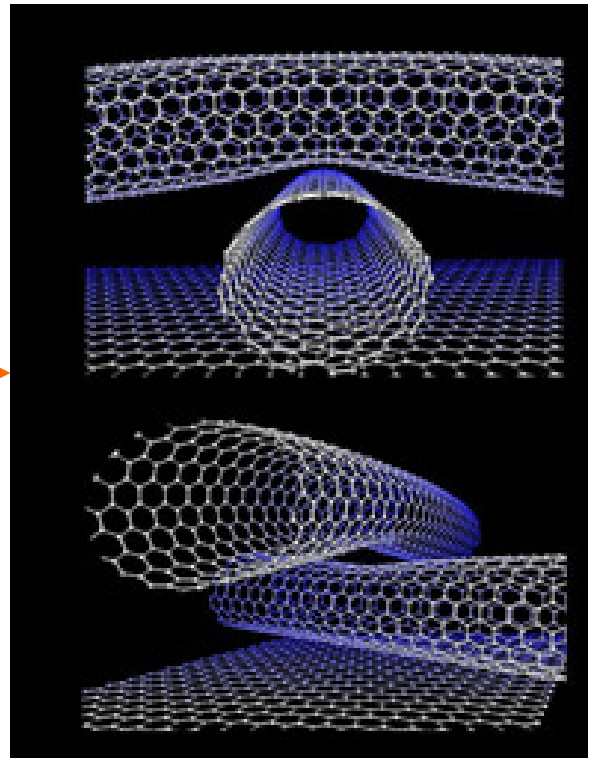


Mechanical Properties ;
Magnetic properties
Electrical properties
Etc.

Perfect Crystals without Defect



Carbon Nanotubes

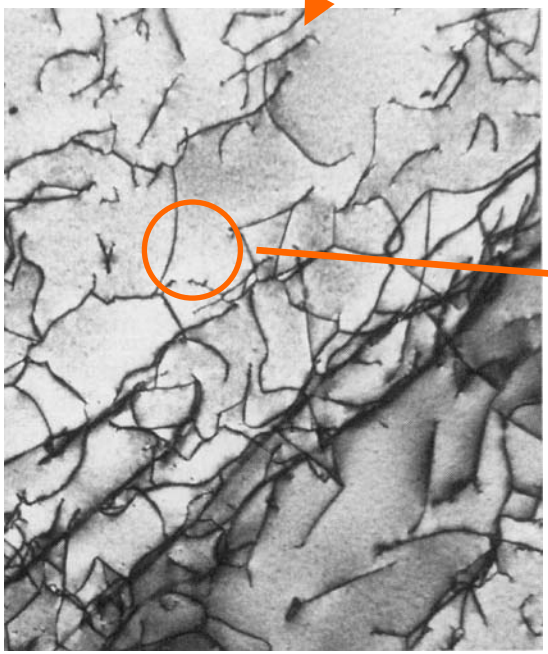


High strength, unique magnetic/electrical properties

1) *Imperfection:* Dislocations

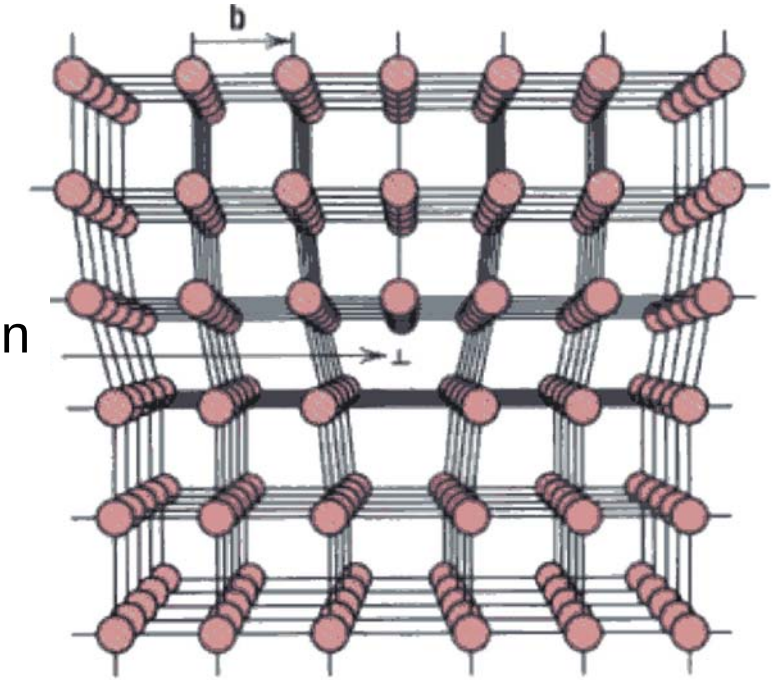
SR-71 with armor of titanium alloy

It looks perfect. But….



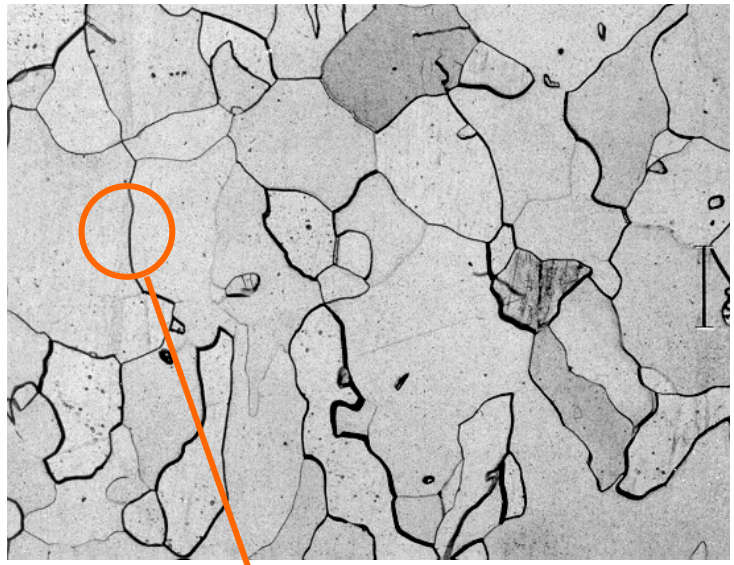
Edge Dislocation Line

Burgers vector



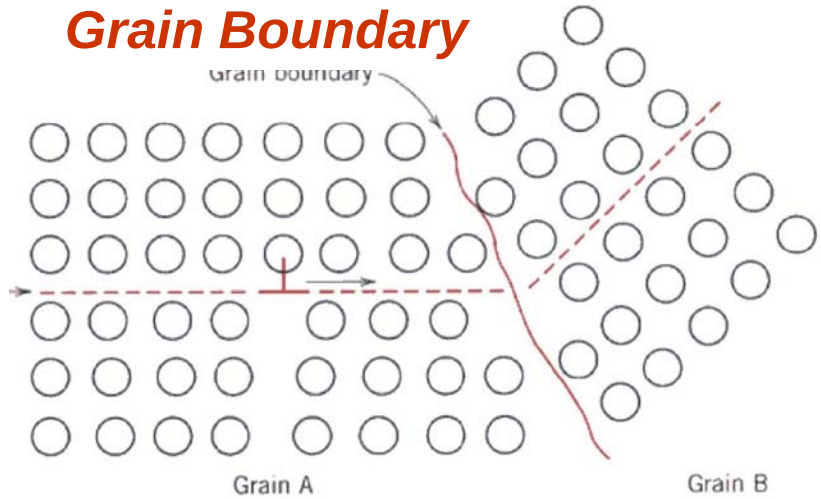
1) *Imperfection:* Grain Boundaries

Low Carbon Steel

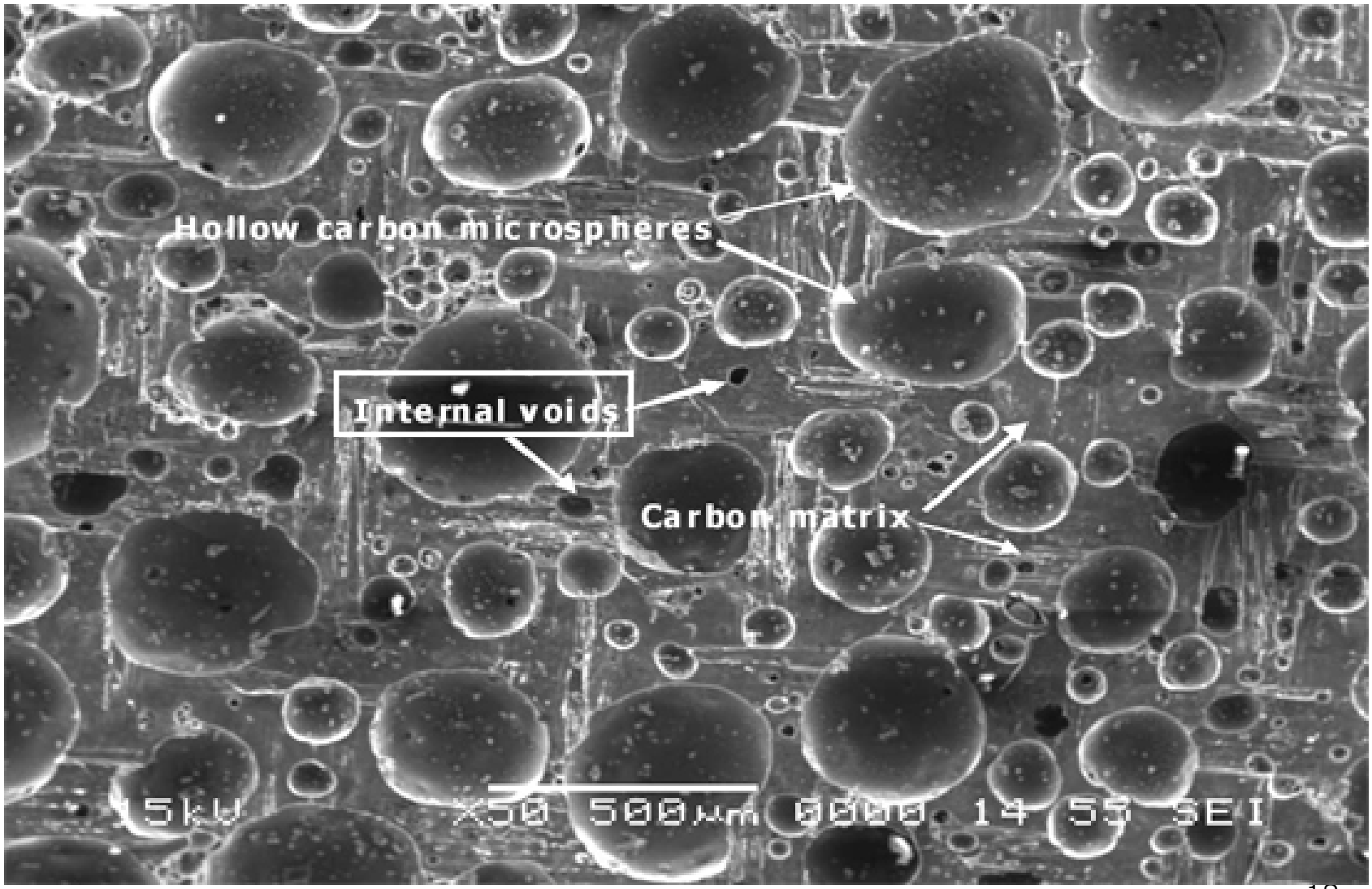


Grain Boundary

Optical Microscope

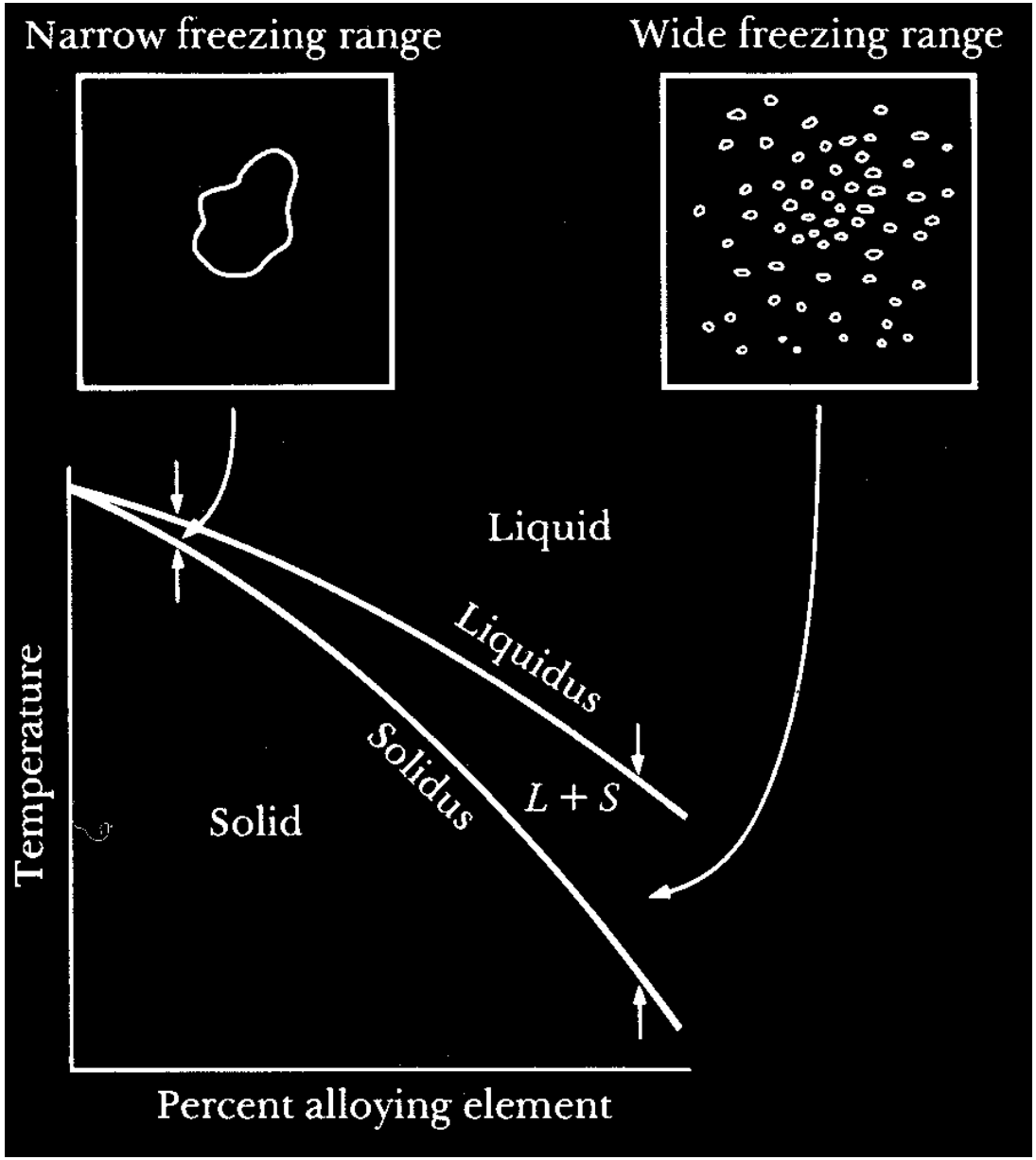


1) *Imperfection:* Voids during formation

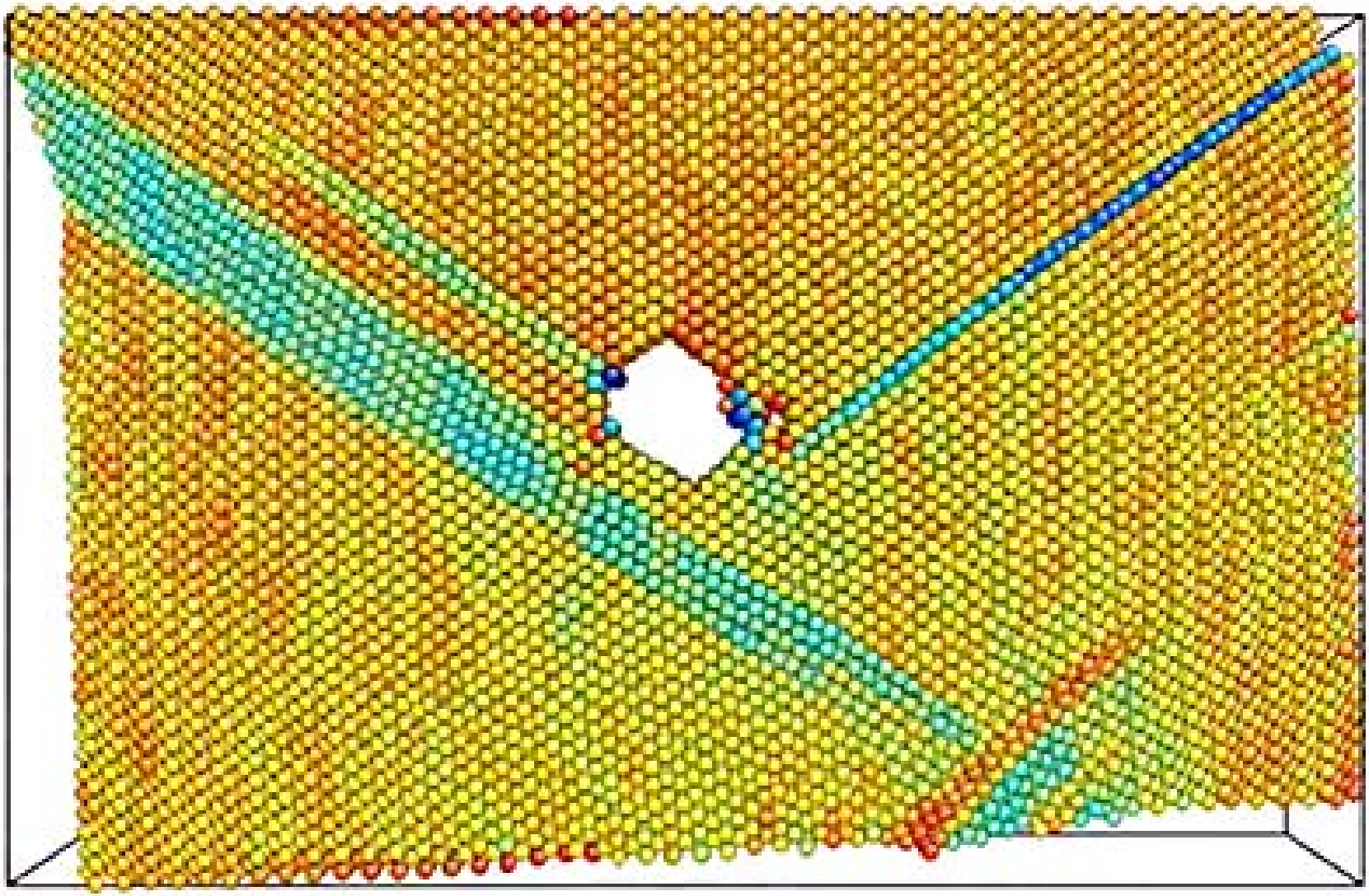


1) *Imperfection:* Voids during solidification

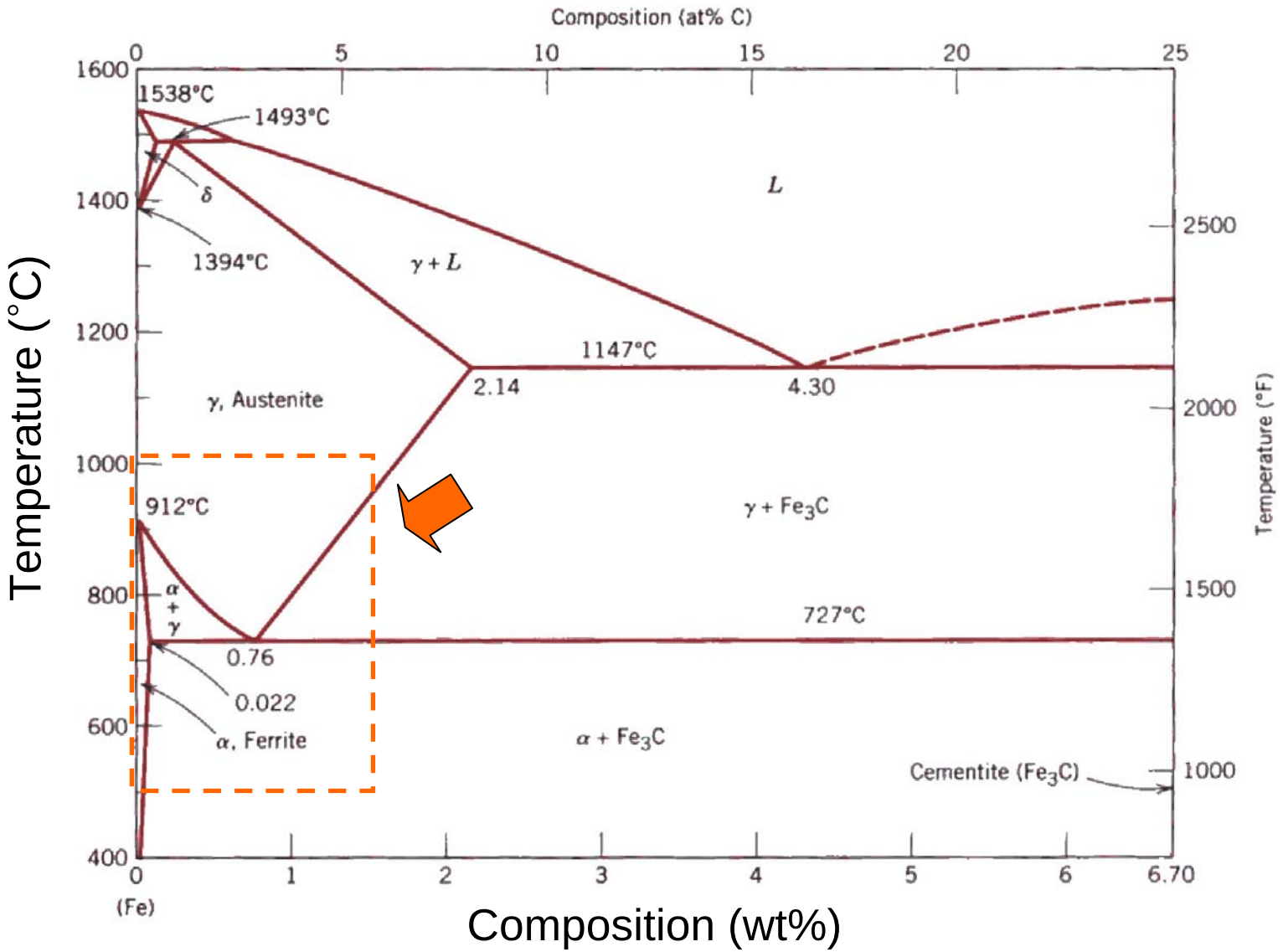
Shrinkage effect



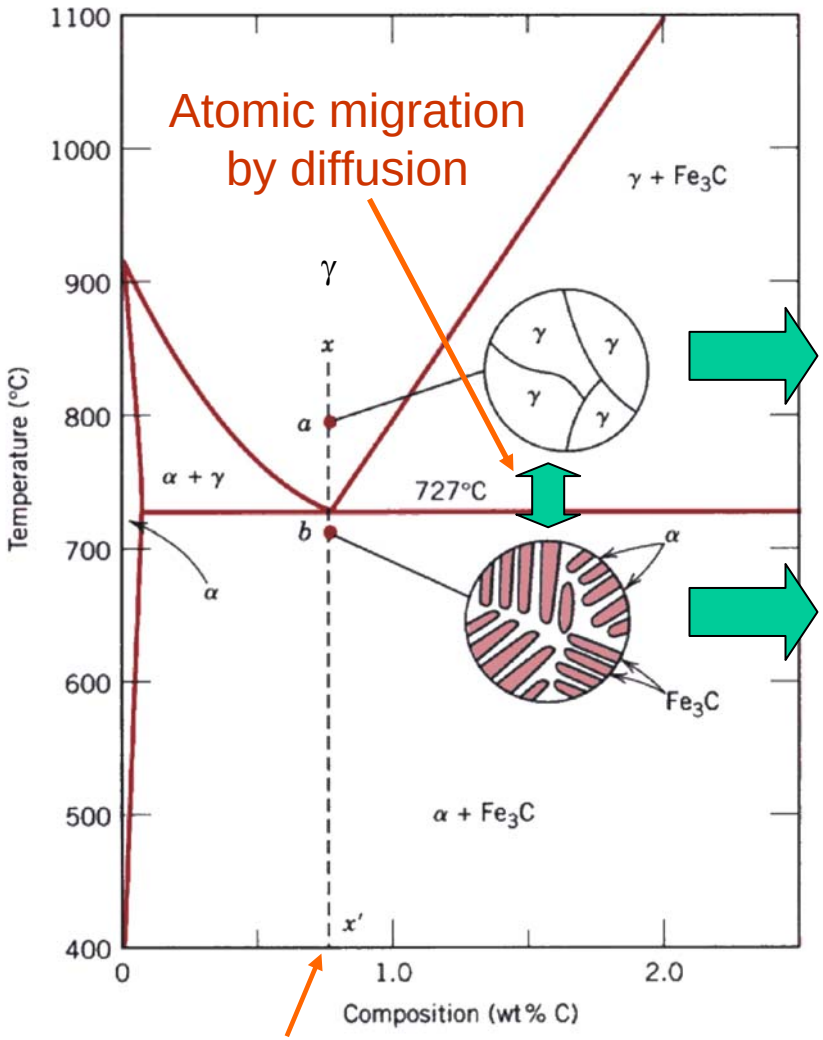
1) *Imperfection:* Voids during deformation



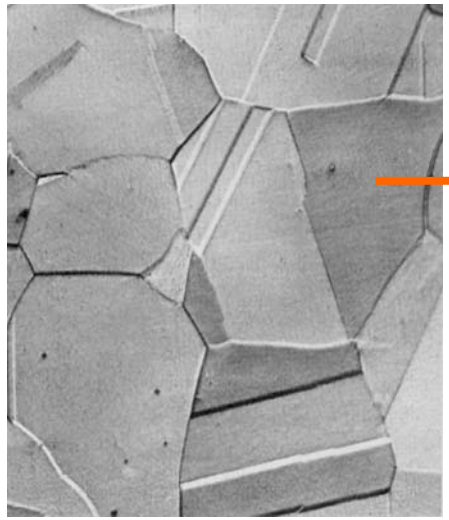
Phase Diagram of Iron–Carbon Alloy

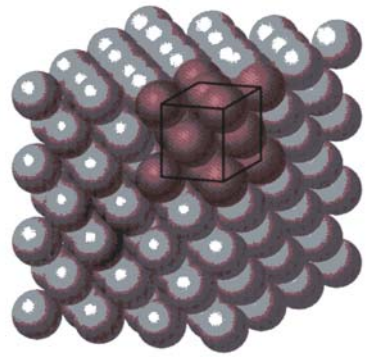


Equilibrium Phases of Iron-Carbon Alloy



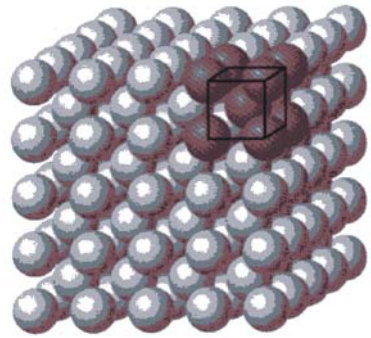
Eutectoid composition





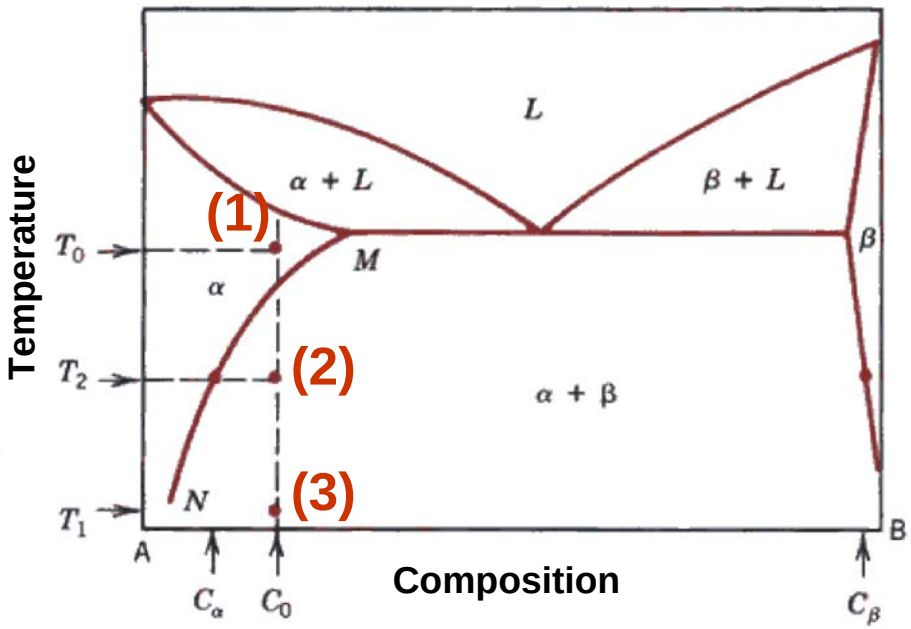
γ phase
(FCC)

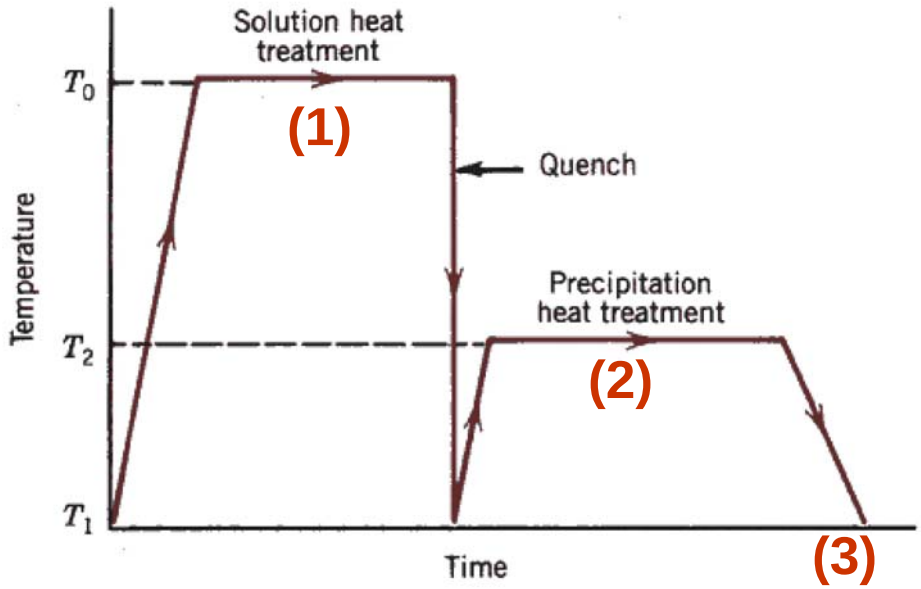
Fe_3C phase

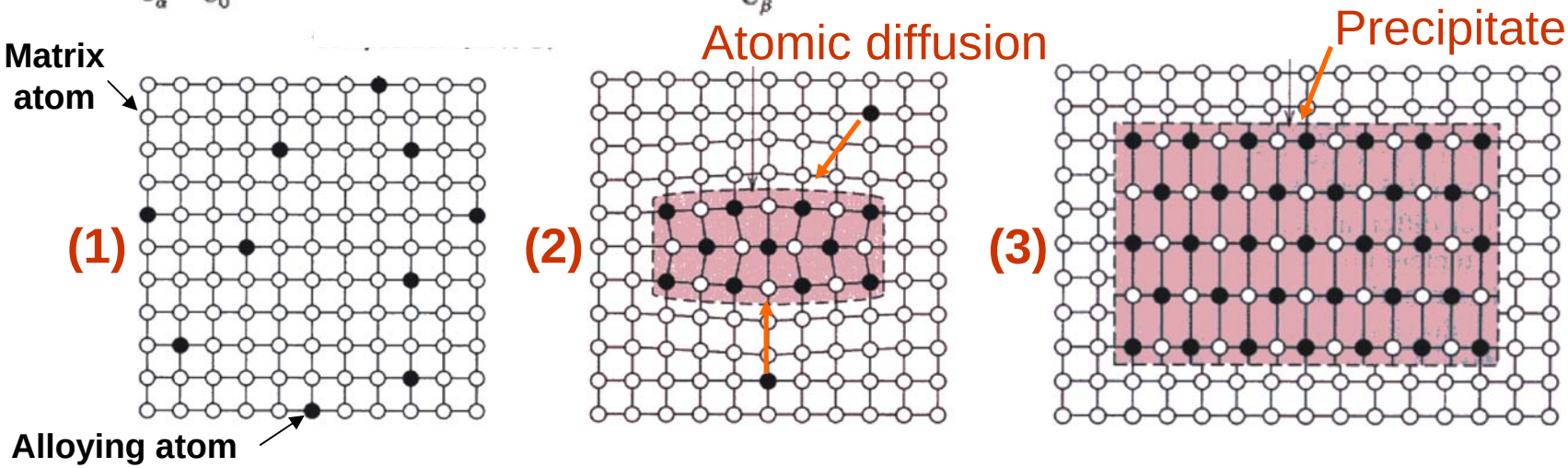


α phase
(BCC)

Mechanism of Precipitation







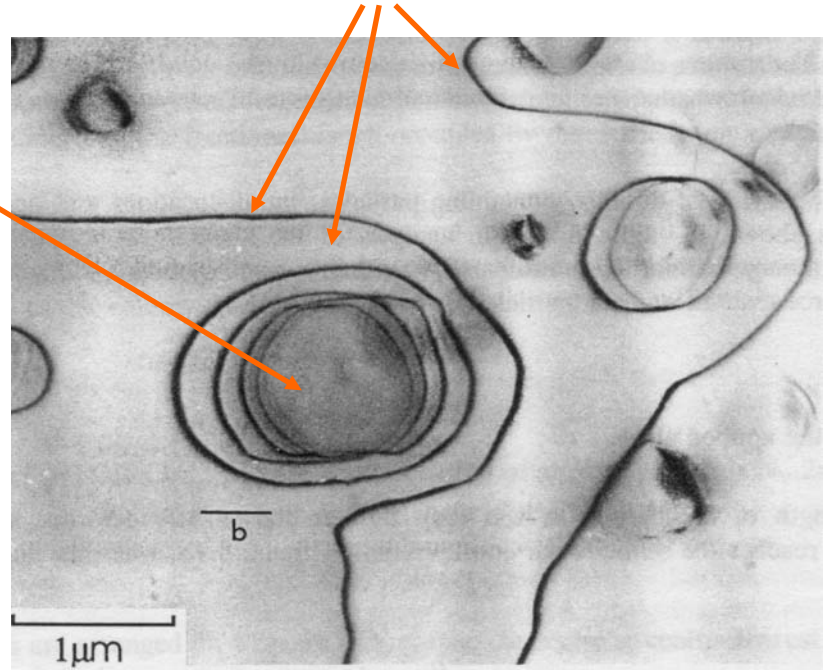
Effect of Second Phase Particle
on Mechanical Property

Second phase particle in matrix material

Obstacle of dislocation slip & grain growth

High strength

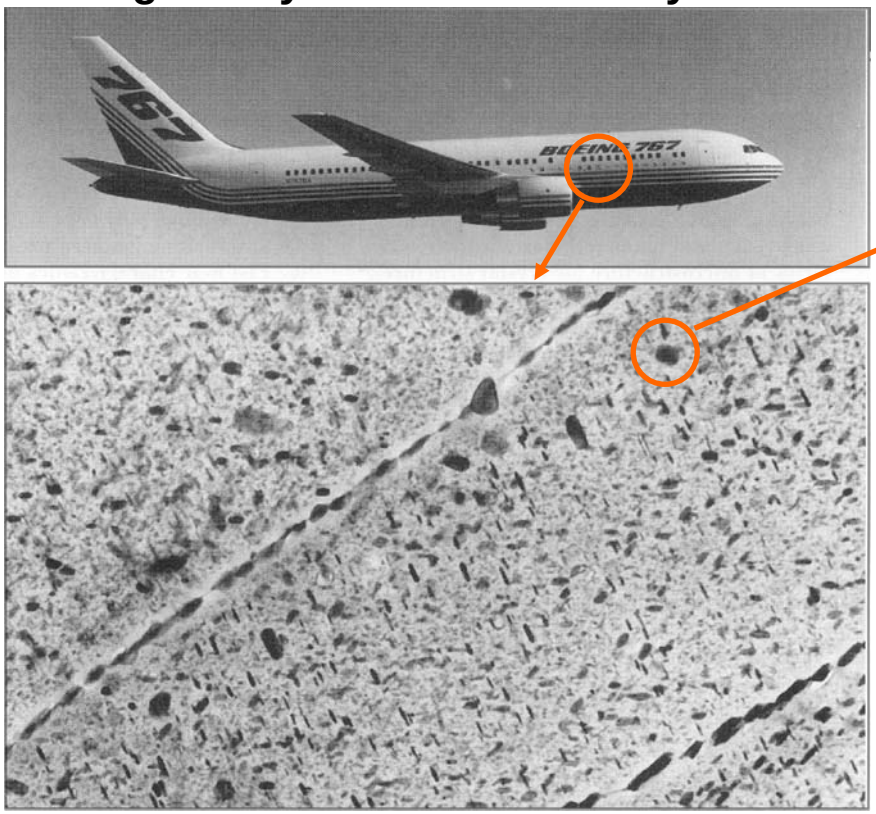
Dislocations



Ni_3Si particles in Ni-6%Si single crystal

Control of Microstructures by
Precipitation Transformation in Aluminum Alloy

Boeing 767 by AA7150 T651 alloy



Precipitates in aluminum matrix

Hindering dislocation slip

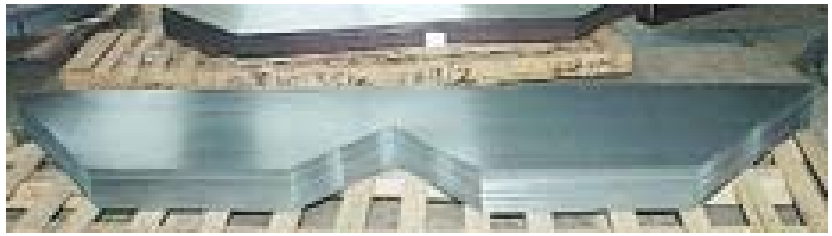
High strength

Alloy design + process control ➡ optimization of property

Production and Application of Electrical Steel

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

Coils



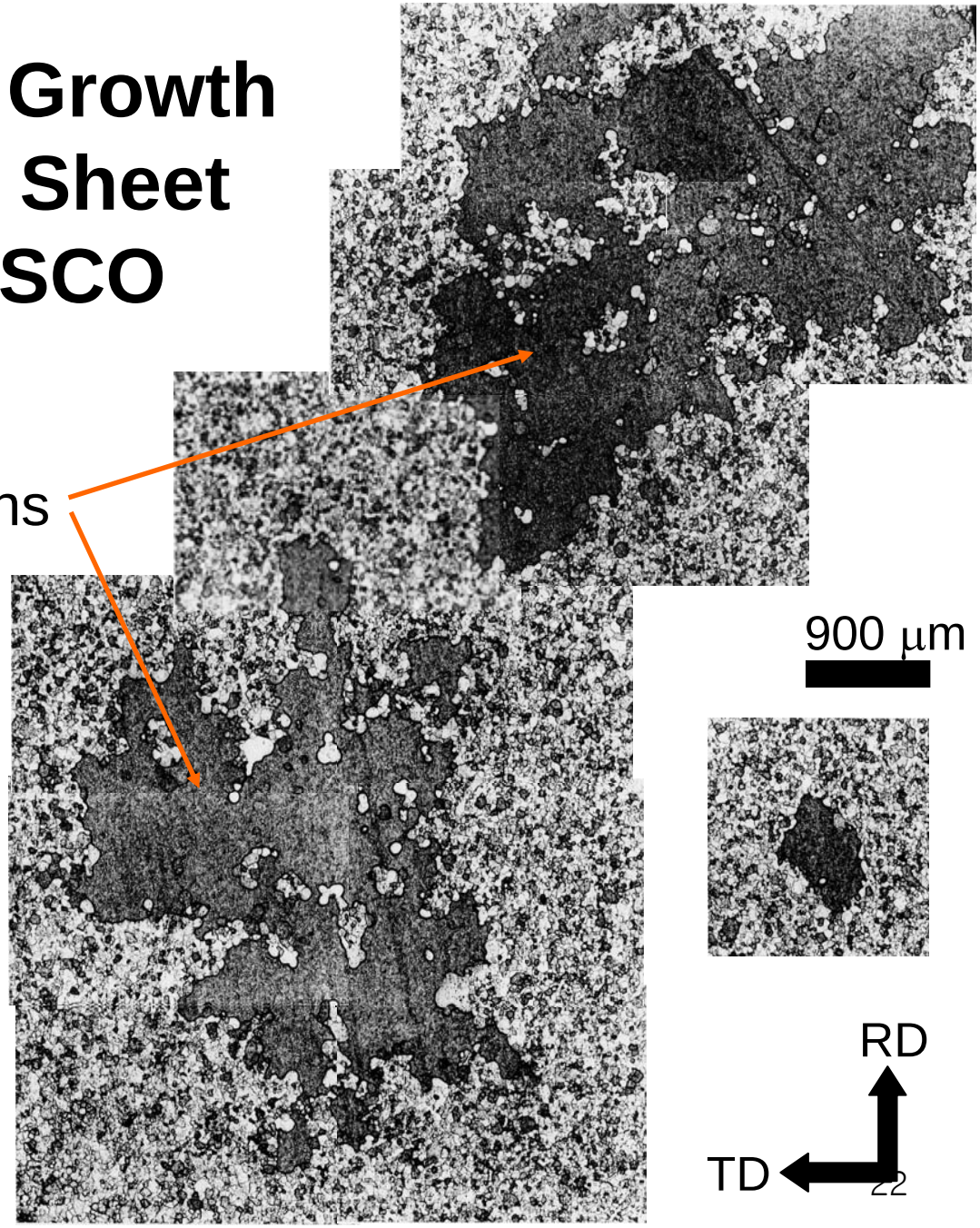
Stacked transformer core

Transformer
Motor
Etc.

Soft magnetization property

Abnormal Grain Growth In Fe-3%Si Steel Sheet produced by POSCO

Abnormally grown grains with Goss texture

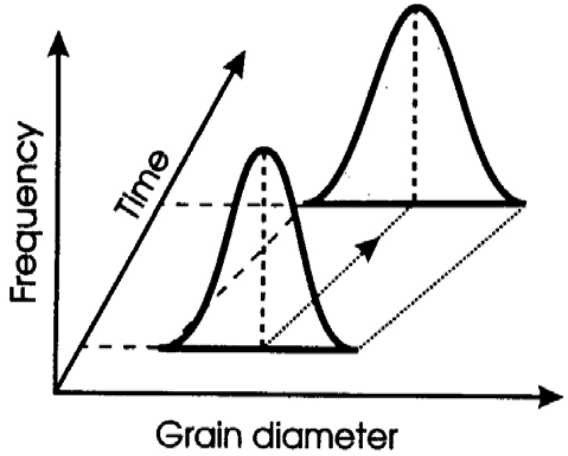


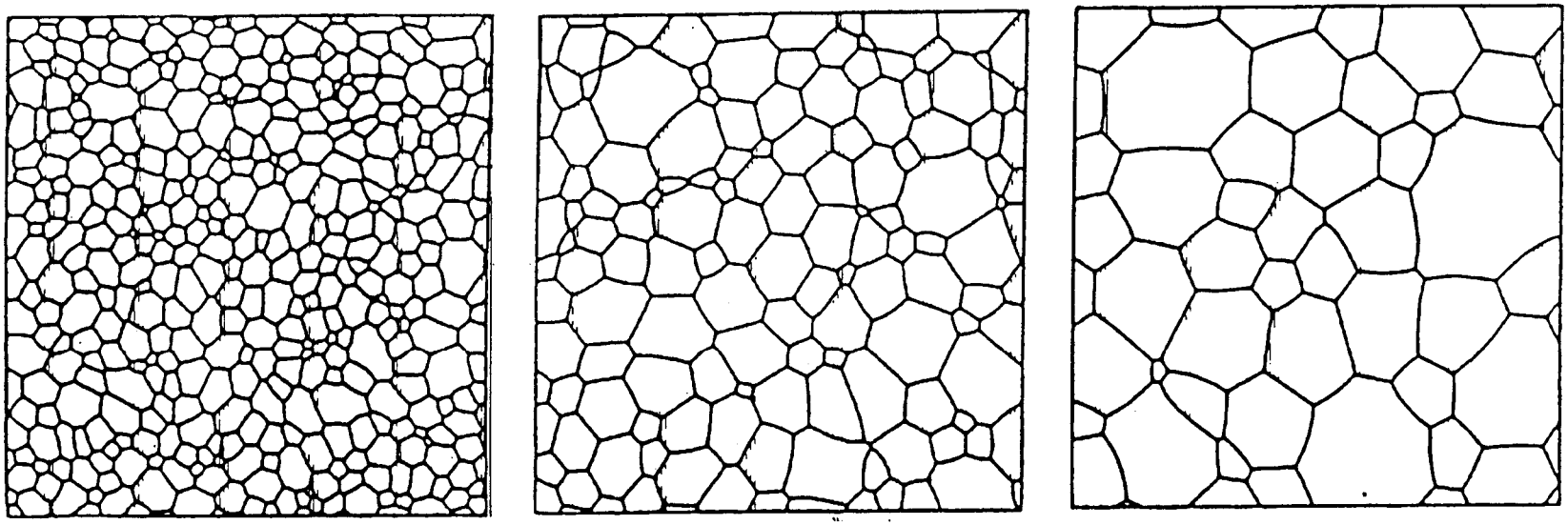
Control of grain growth

Control of magnetic property

Normal Grain Growth

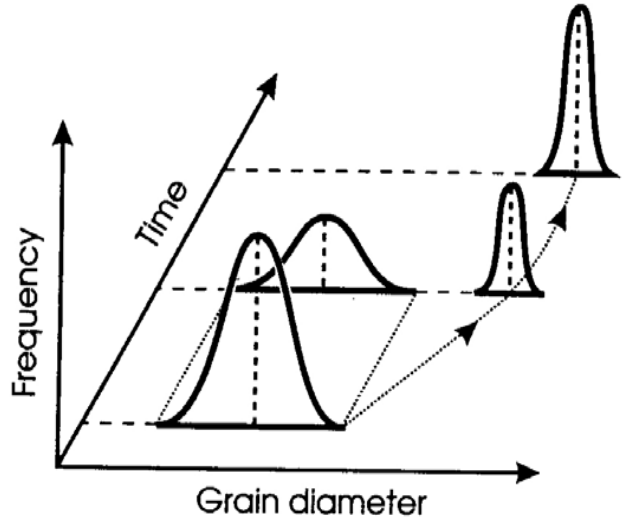
- Grain boundary moves to reduce area and total energy
- Large grain grow, small grains shrink
- Average grain size increases
- Little change of size distribution



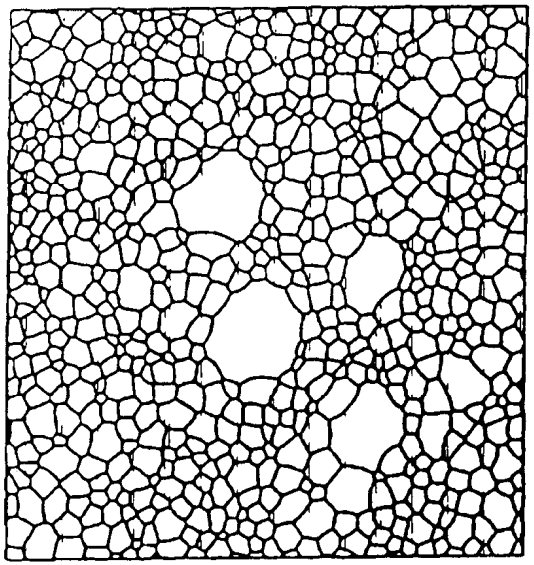


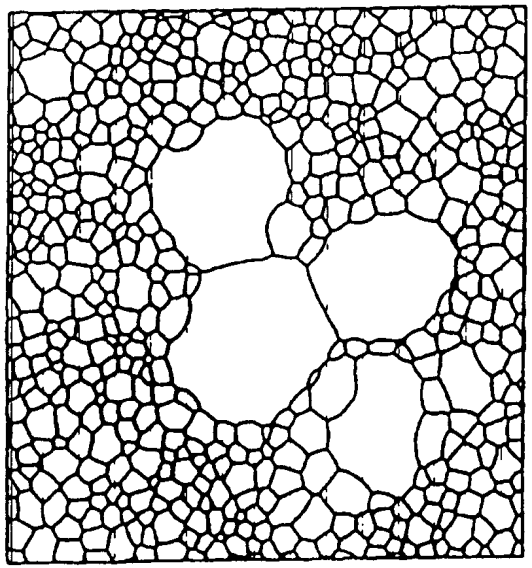
Abnormal Grain Growth

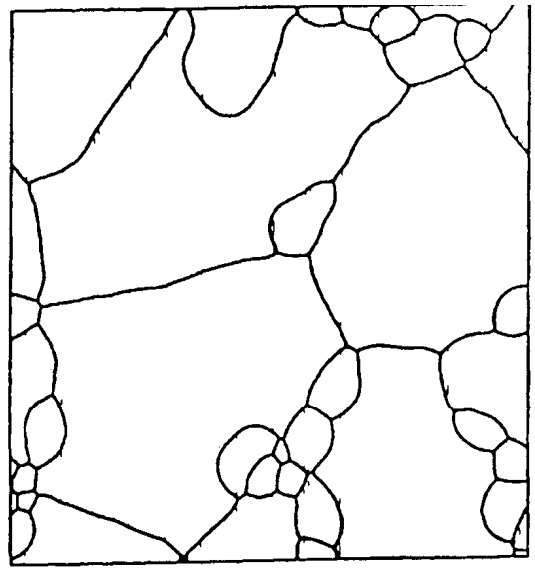
- **Discontinuous growth of a few selected grains**
  - Local breaking of pinning by precipitates
  - Anisotropy of grain boundary mobility
  - Anisotropy of surface & grain boundary energy
  - Selective segregation of impurity atoms
  - Inhomogeneity of strain energy



- **Bimodal Size distribution**







Abnormal Grain Growth
= discontinuous grain growth or secondary recrystallization

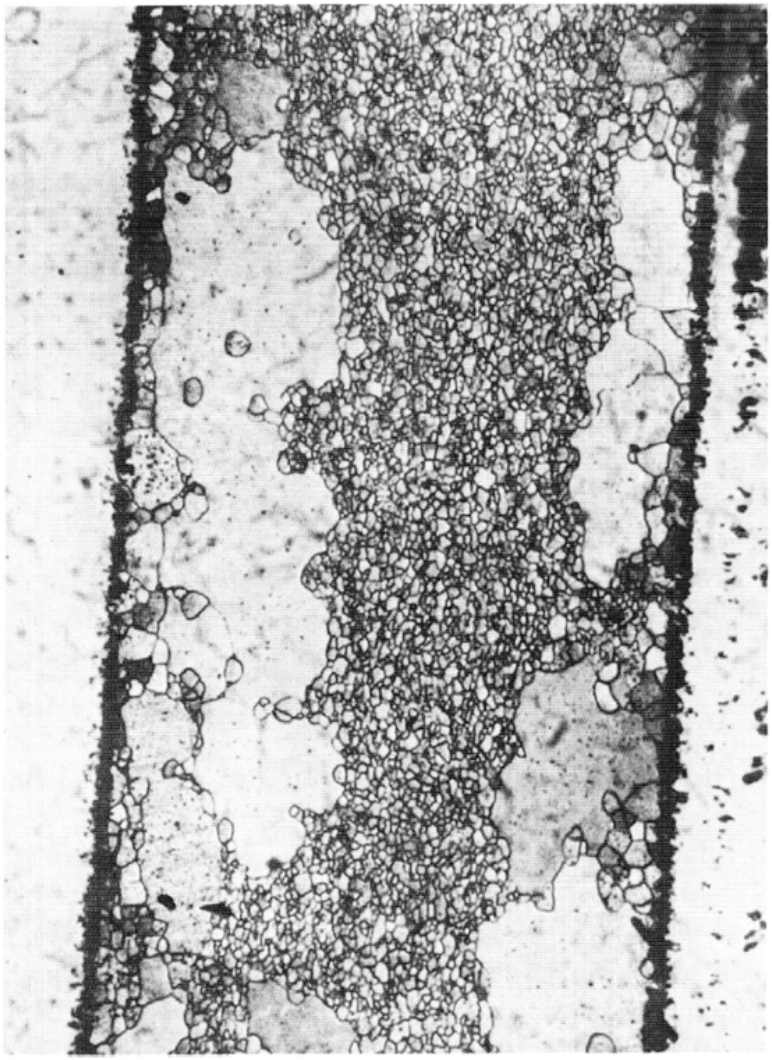


Figure 5.87 Optical micrograph showing abnormal grain growth in a fine grain steel containing 0.4 wt% carbon. The matrix grains are prevented from growing by a fine dispersion of carbide particles that are not revealed. Magnification ×135. (After Gawne and Higgins 1971. Courtesy of the Metals Society.)

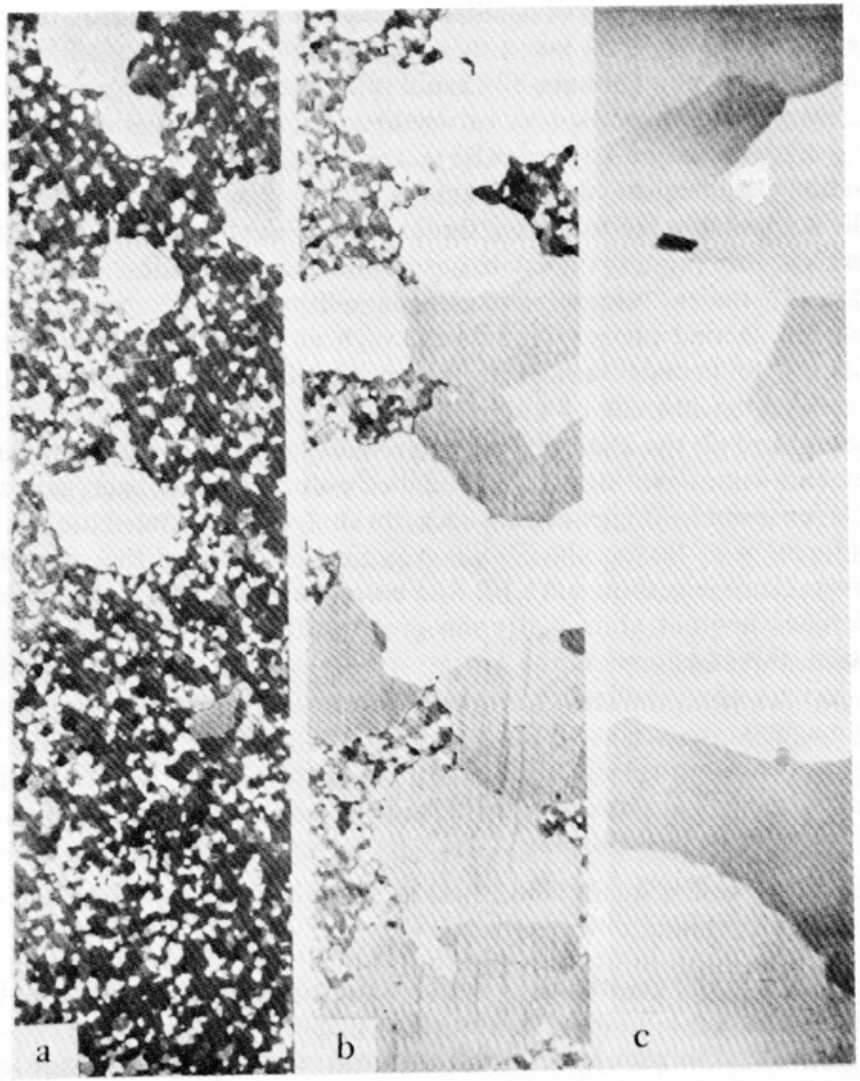


Fig. 5.48. Evidence for the preferential formation of (110)[001]-oriented grains by secondary recrystallization in 5% Si–Fe (Graham [1969]).

Important!!!

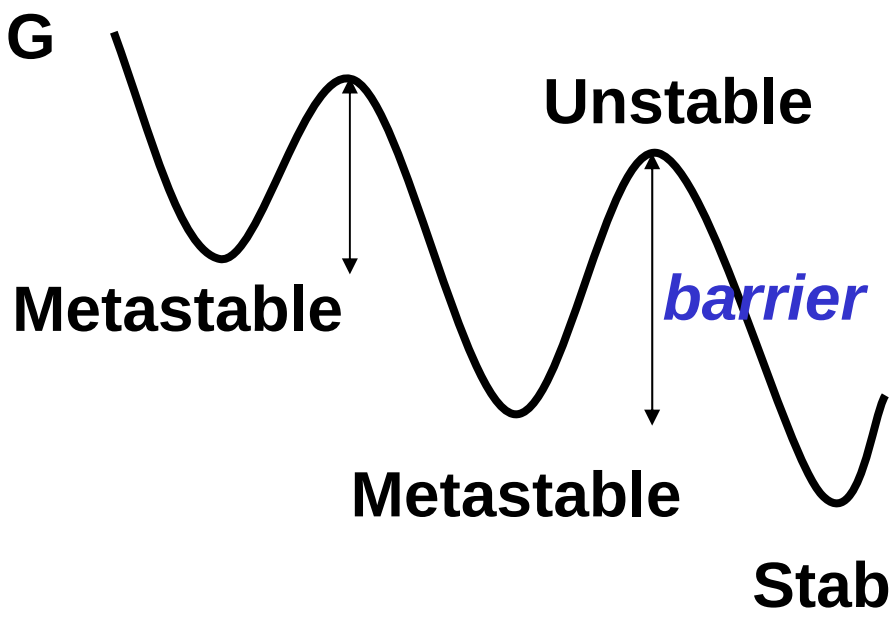
Understanding* and *Controlling

Phase Transformation of Materials

Phase Transformation

Change to another phase ➡ metastable state

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



➡ **Thermodynamics & Kinetics**

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!!!

Polymorphism (同質異像): same comp. & different form or crystal structure

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

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

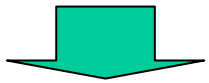
1) Diffusion-controlled phase transformation ;
Generally long-distance atomic migration

- Precipitation transformation
- Eutectoid transformation (**S ⇨ S_1 + S_2**)
- etc.

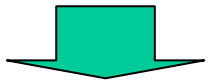
2) Diffusionless transformation ;
Short-distance atomic migration

- Martensitic transformation

1) Time-Dependency of Diffusion-Controlled Phase Transformation

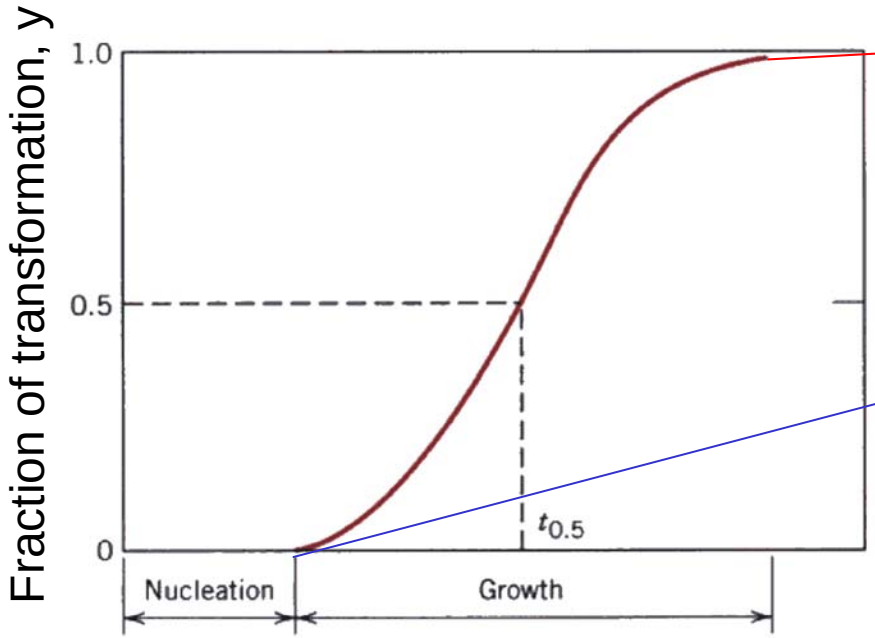


Non-Equilibrium Phases



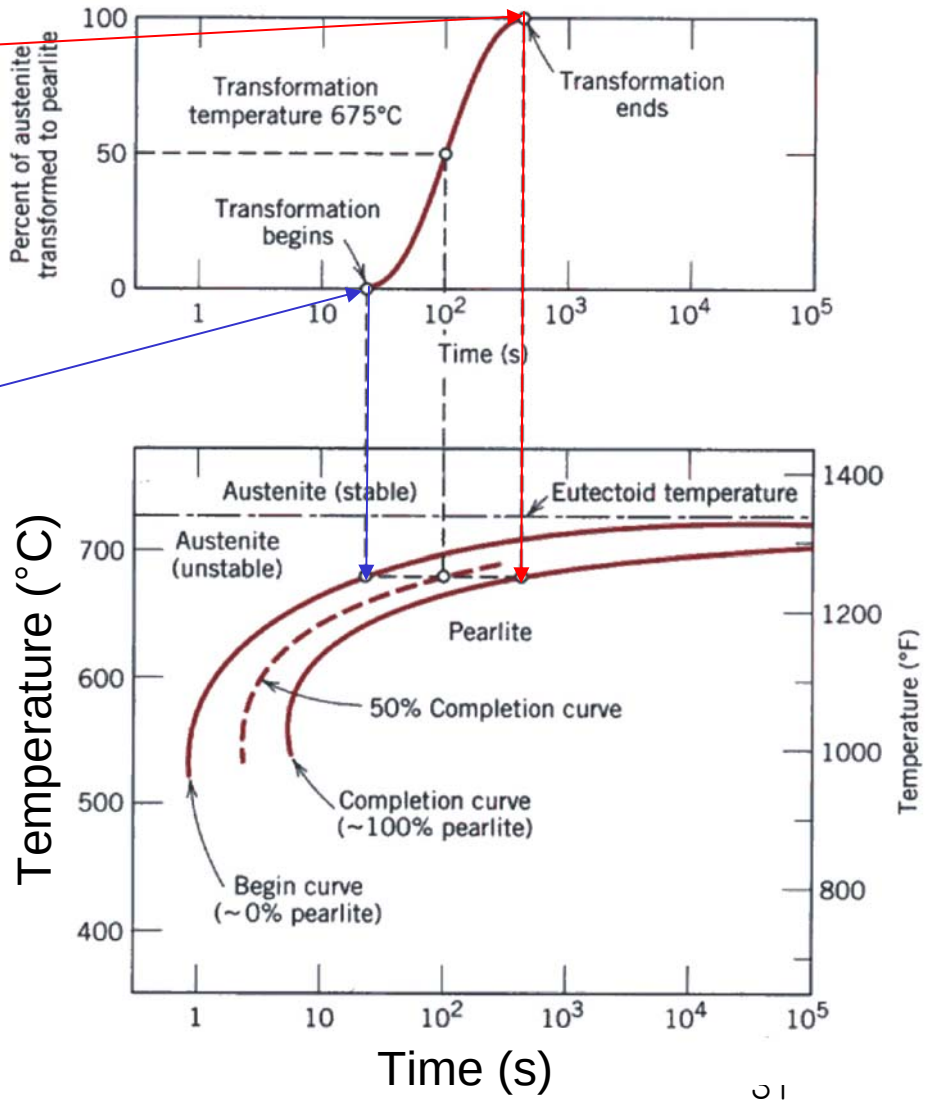
Need of Controlling
not only *Temperature* & *Composition*
but *Process conditions* (Cooling Rate)

Transformation Kinetics and Isothermal Transformation Diagram



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

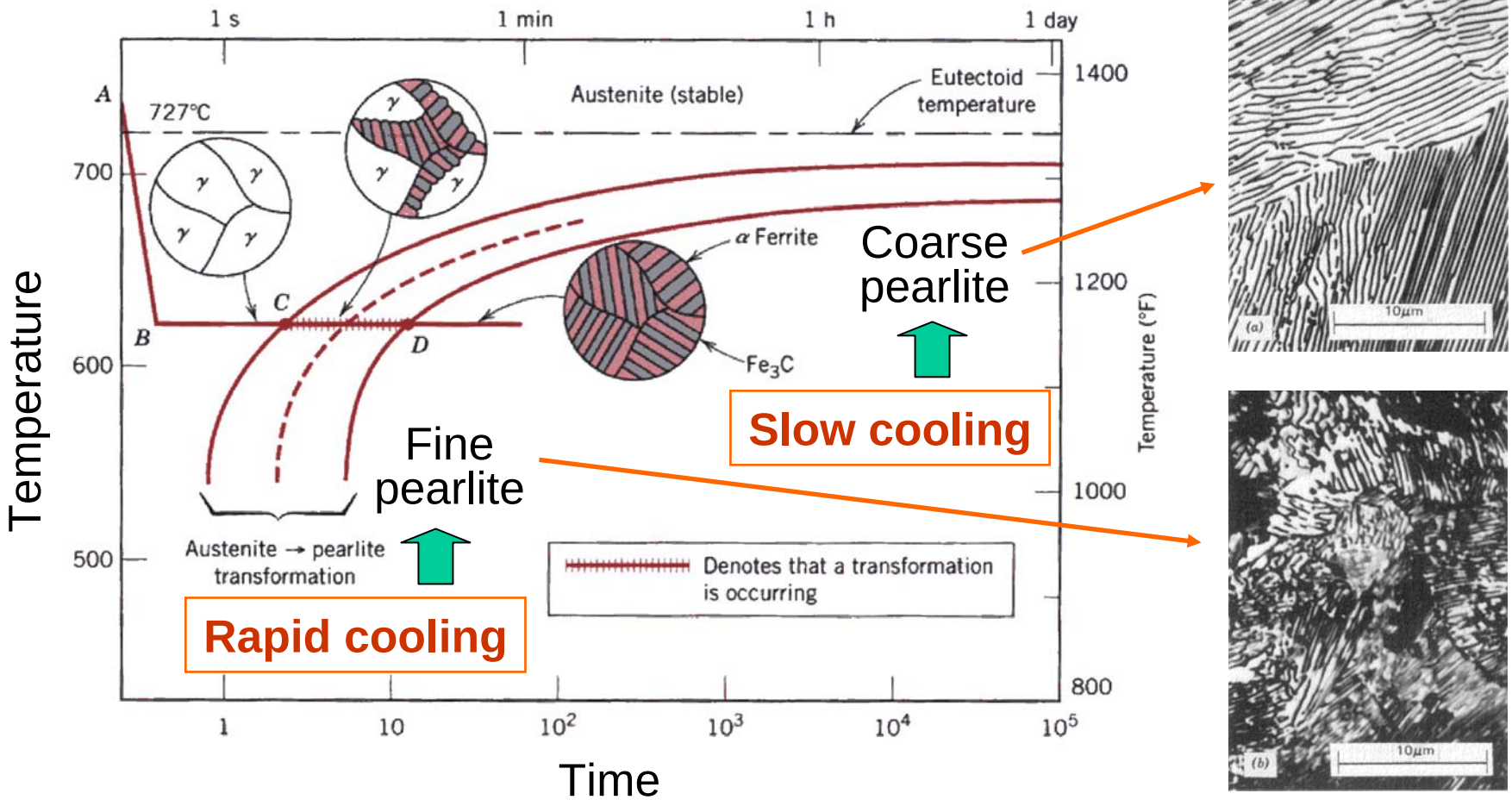
Kinetics of diffusion-controlled solid-state transformation



TTT diagram ➡ Isothermal transformation diagram

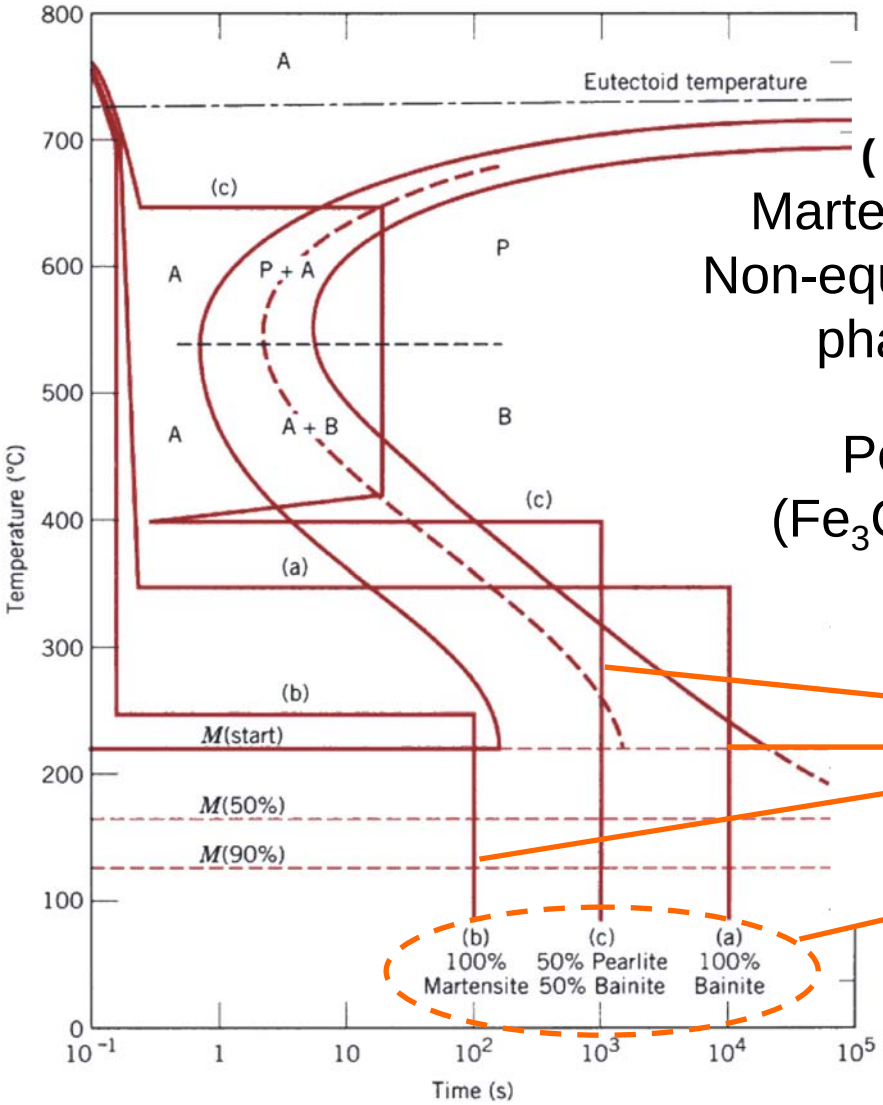
Isothermal Transformation Diagram of a Eutectoid Iron-Carbon Alloy

γ Austenite → α Ferrite + Fe_3C graphite



➡ **Tailoring of *microstructure***

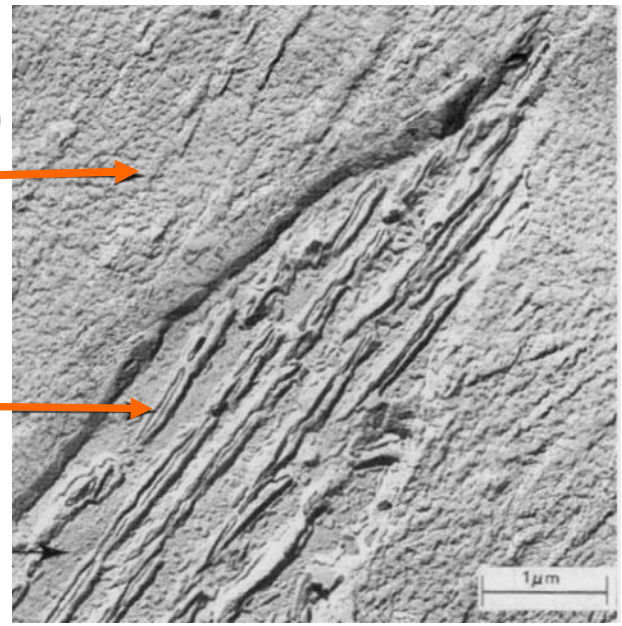
Control of Phases by Heat Treatment



(Very hard)

Martensite ;
Non-equilibrium phase

Pearlite
(Fe_3C+ferrite)



Heat Treatment

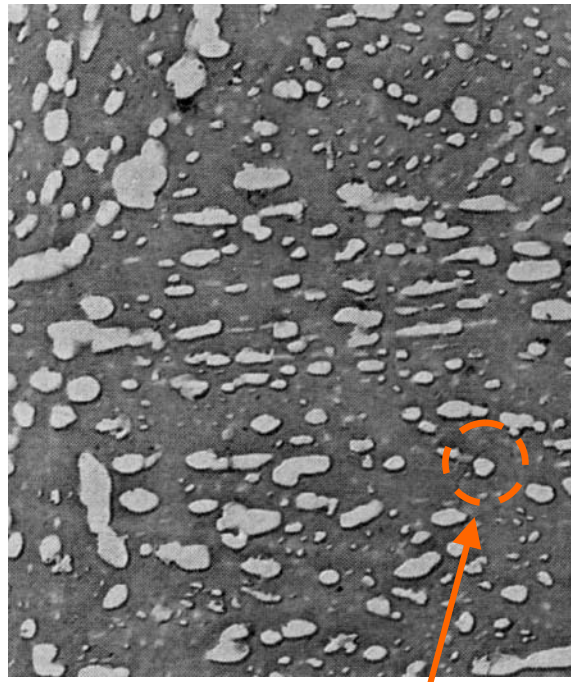
Phase & Microstructure

Properties of Material

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

공정조절

Proper heat treatment (tempering)



Martensite

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

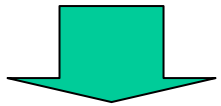
Tempered martensite

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

2) Diffusionless Transformation

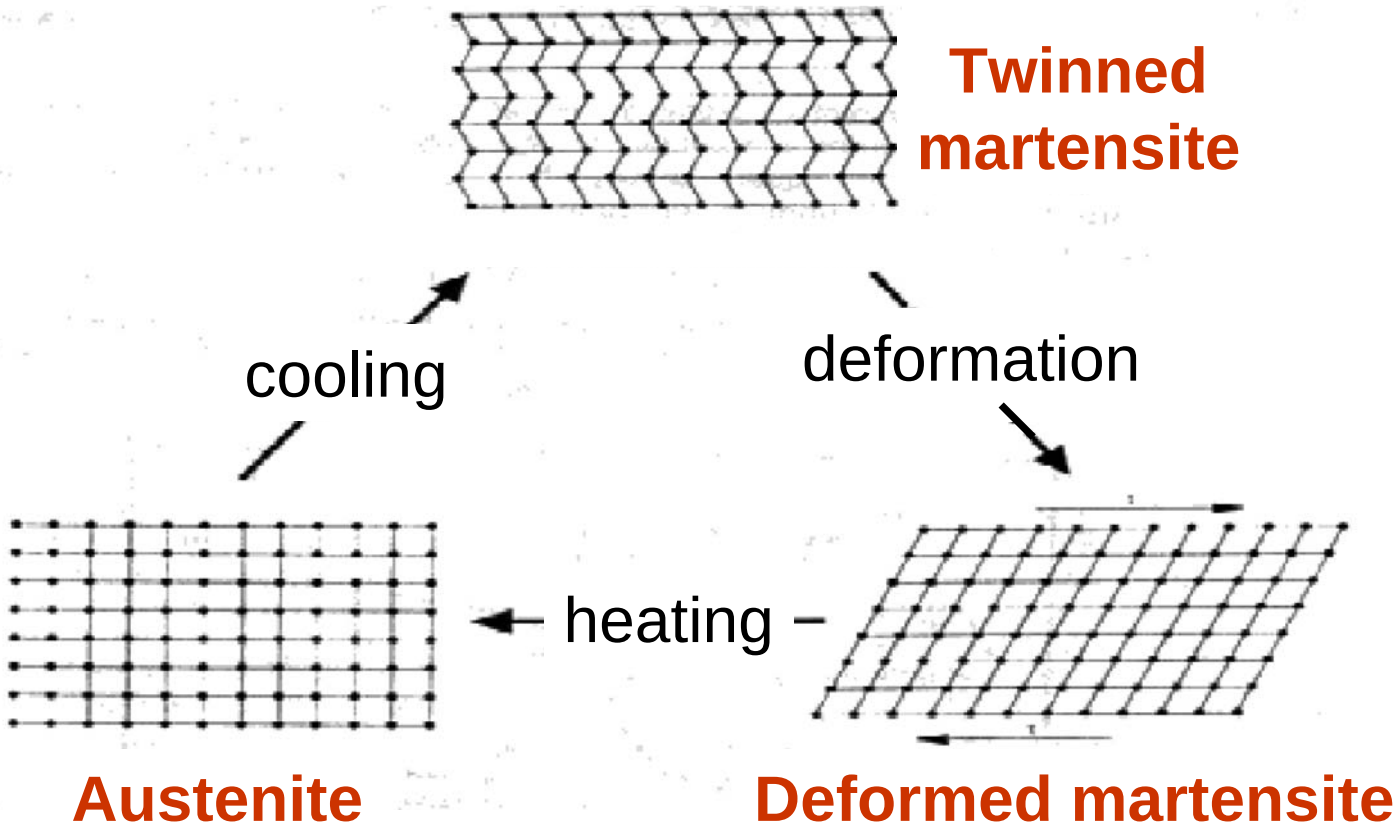
Martensitic transformation in iron-carbon alloy

Martensitic transformation in Ni-Ti alloy ;
55~55.5wt%Ni-44.5~45wt%Ti (“Nitinol”)



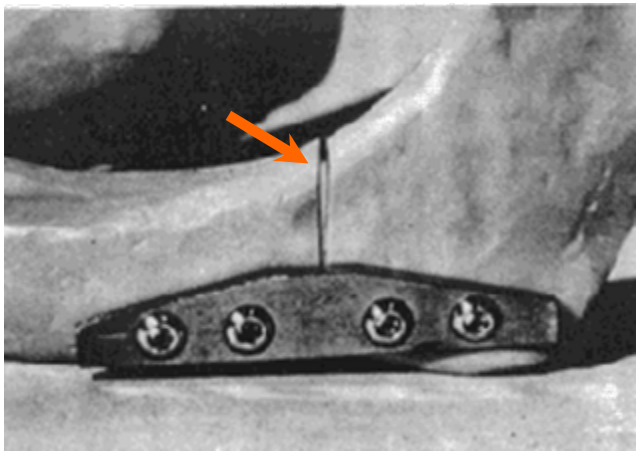
Ex) Shape memory alloy

Change of Atomic Array during Martensitic Transformation in Ni-Ti Alloy

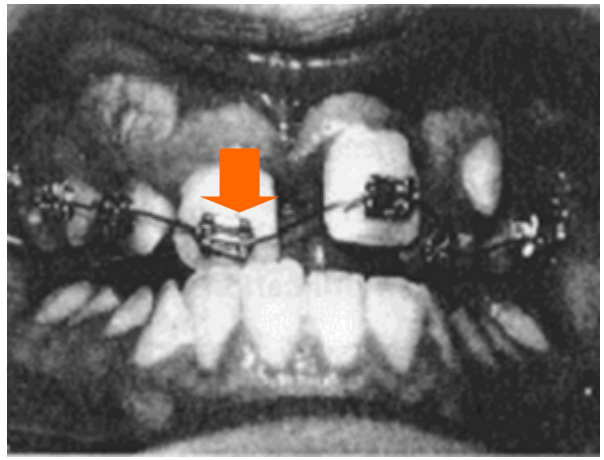


“ Short-distance atomic migration ”

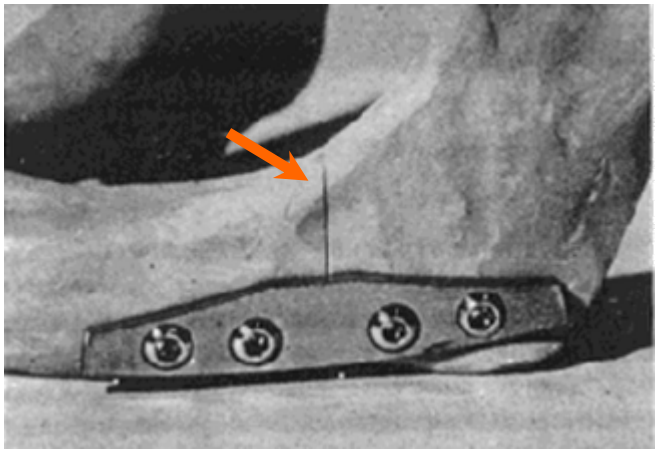
Medical Applications of Shape Memory Alloys



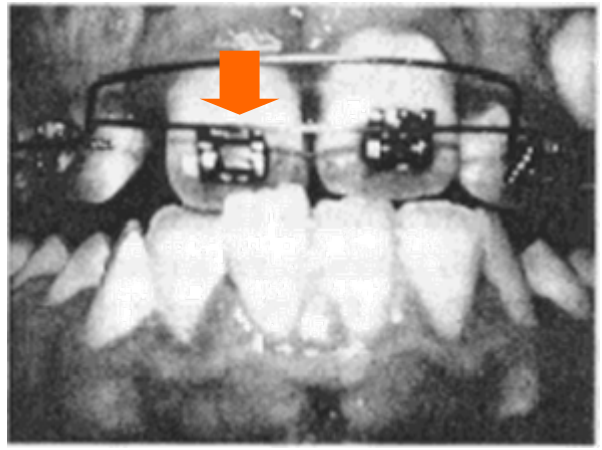
heating



After 3 weeks



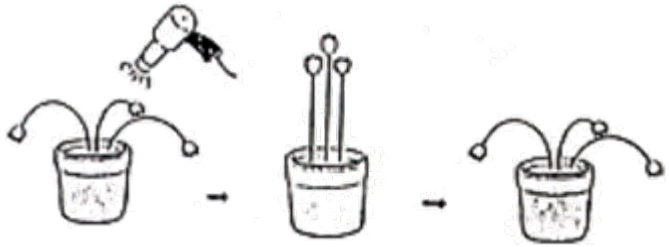
Bond-bonding staple



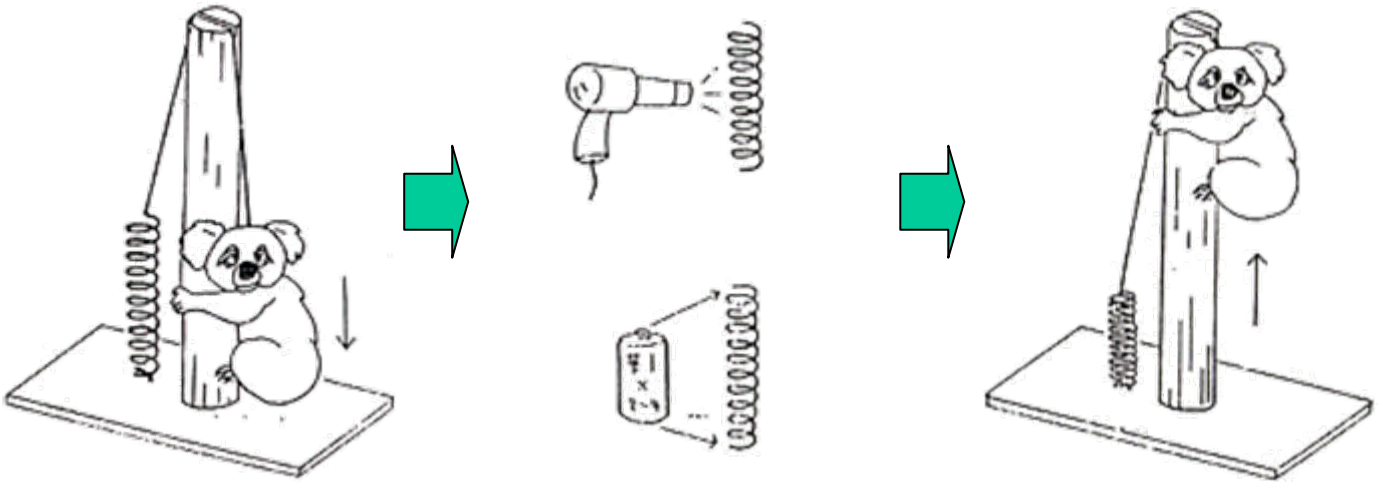
Wire for tooth-correction

Shape Memory Alloy's applications can be used in many ways depends on the use of YOUR IDEAS.

Magic flower

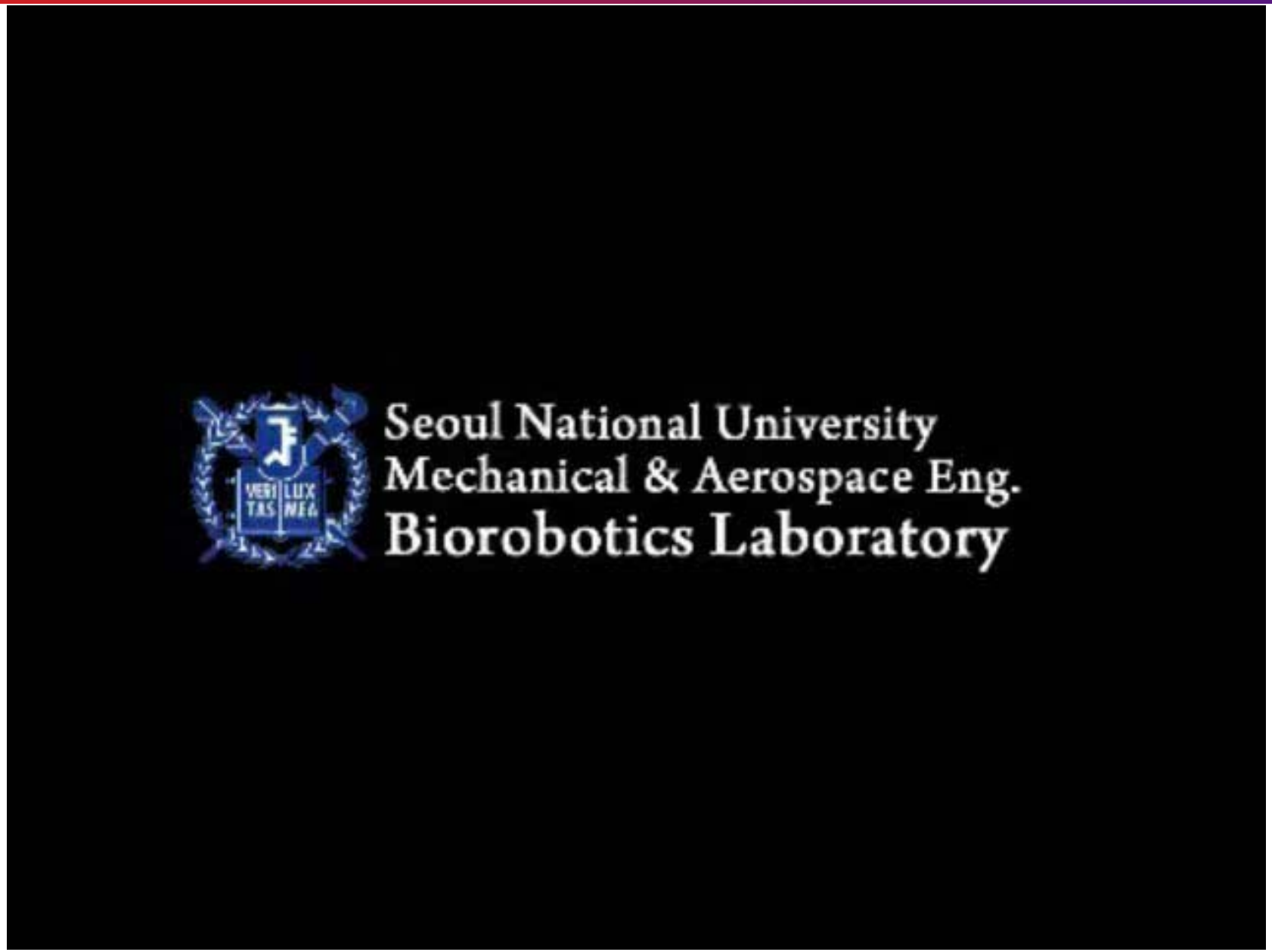


Magic spring (climb koala)



YOU Tube

Application of Shape Memory Alloys



Contents in Phase Transformation

Basic concept for understanding Phase Transformation

- (Ch1) Thermodynamics and Phase Diagram
- (Ch2) Diffusion: Kinetics
- (Ch3) Crystal Interface and Microstructure

Representative Phase Transformation

- (Ch4) Solidification: Liquid → Solid
- (Ch5) Diffusional Transformations in Solids: Solid → Solid
- (Ch6) Diffusionless Transformations: Solid → Solid

Phase Equilibria in Materials

Thermodynamics

Phase diagrams

Binary, Ternary, Quarternary

Solidification

2009년 9월

일	월	화	수	목	금	토
		1	2	3	4	5
6	7	8	9	10	11	12
13	14	15	16	17	18	19
20	21	22	23	24	25	26
27	28	29	30			