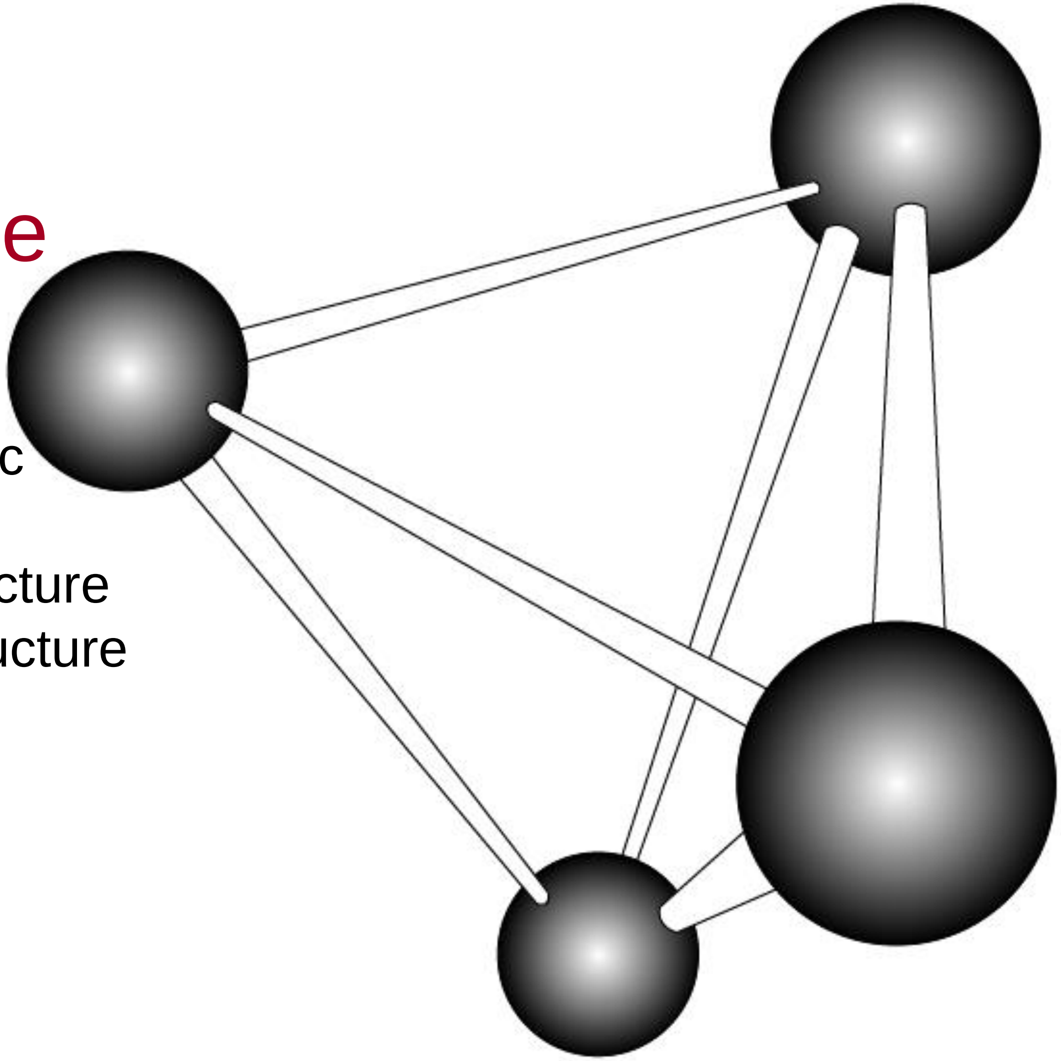
재료상변태

Phase Transformation of Materials

주영창

Nano Flexible Device Materials Lab
서울대학교 재료공학부

Materials Science and Engineering



Structure

- ✓ Subatomic
- ✓ Crystal
- ✓ Microstructure
- ✓ Macrostructure

Processing

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

Properties

- ✓ Mechanical
- ✓ Electrical
- ✓ Magnetic
- ✓ Thermal
- ✓ Optical

Performance

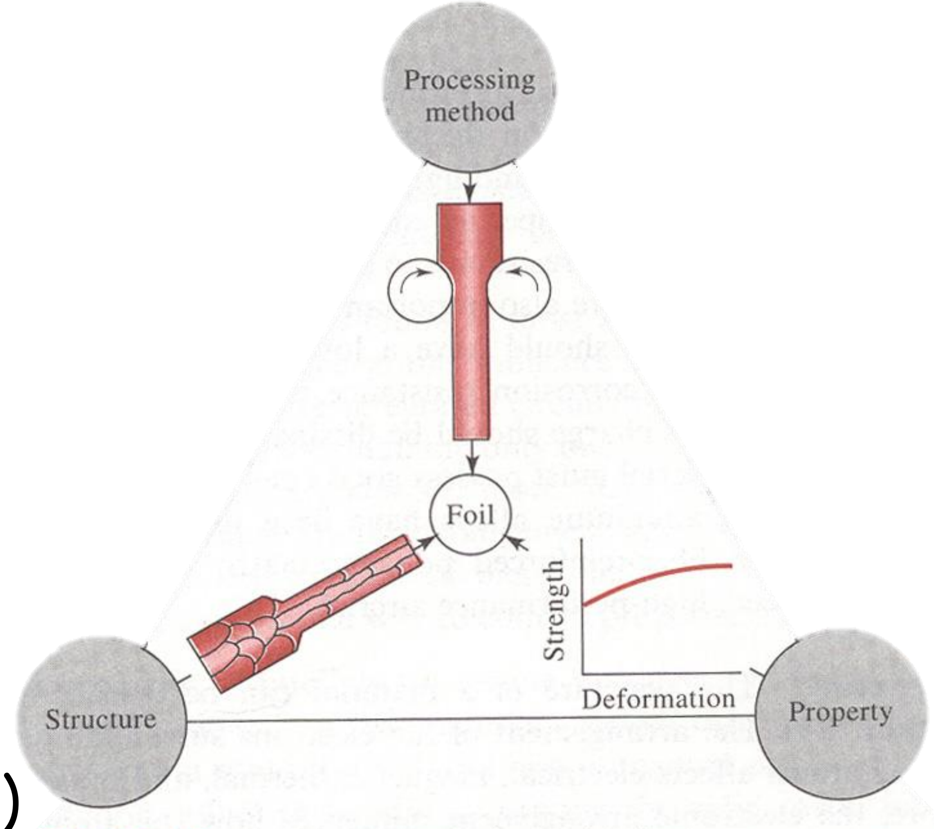
Materials Science, Materials Engineering

- **Materials Science**
  - ✓ Investigating the relationships that exist between the structures and properties of materials

- **Materials Engineering**
  - ✓ Designing or engineering the structure of a material to produce a predetermined set of properties

Materials Science and Engineering

공정(工程)



미세조직

(微細組織)

물성(物性)

FIGURE 1-8 The three-part relationship between structure, properties, and processing method. When aluminum is rolled into foil, the rolling process changes the metal's structure and increases its strength.

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

Steel frame of building

Steel house

Application of Iron-Carbon Alloy

K1 – main battle tank of Korea army

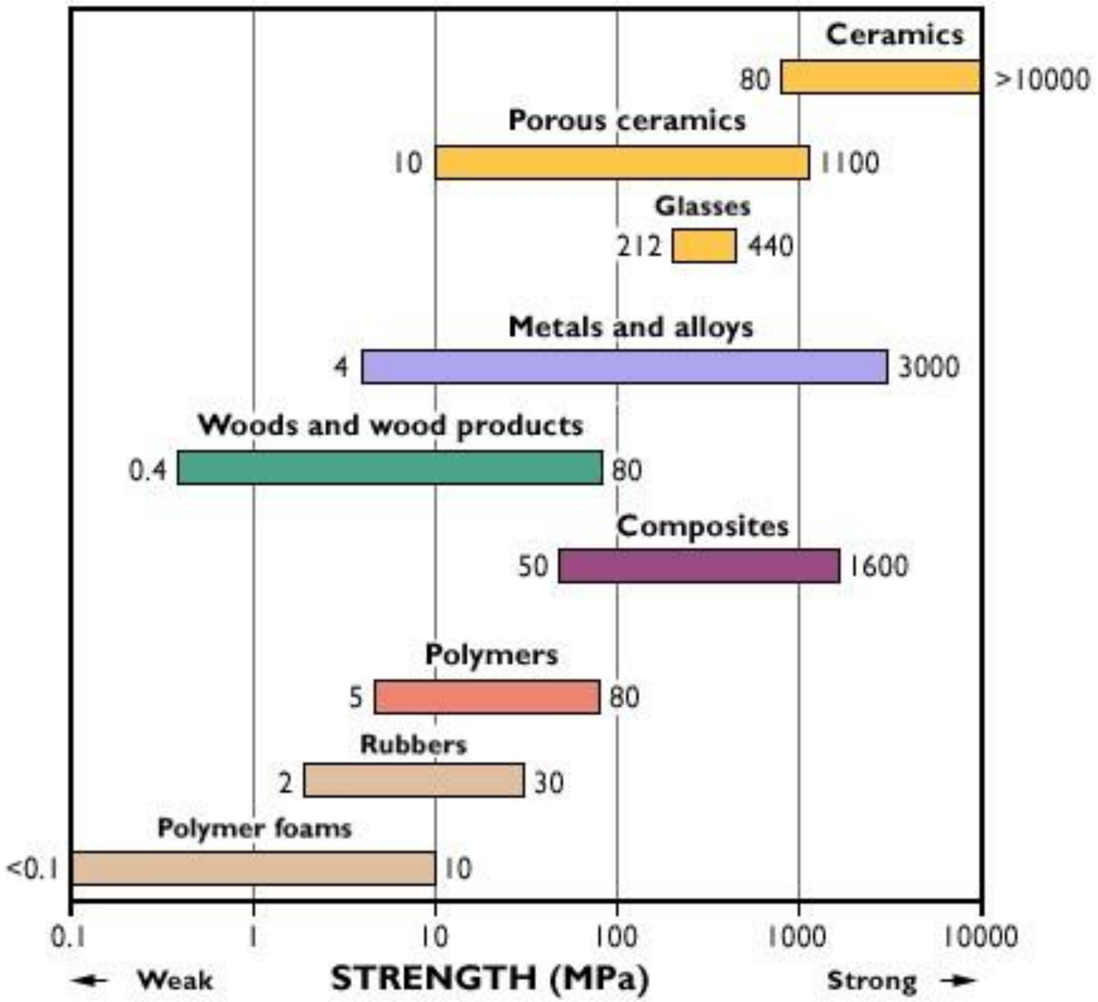
Need of the strongest materials

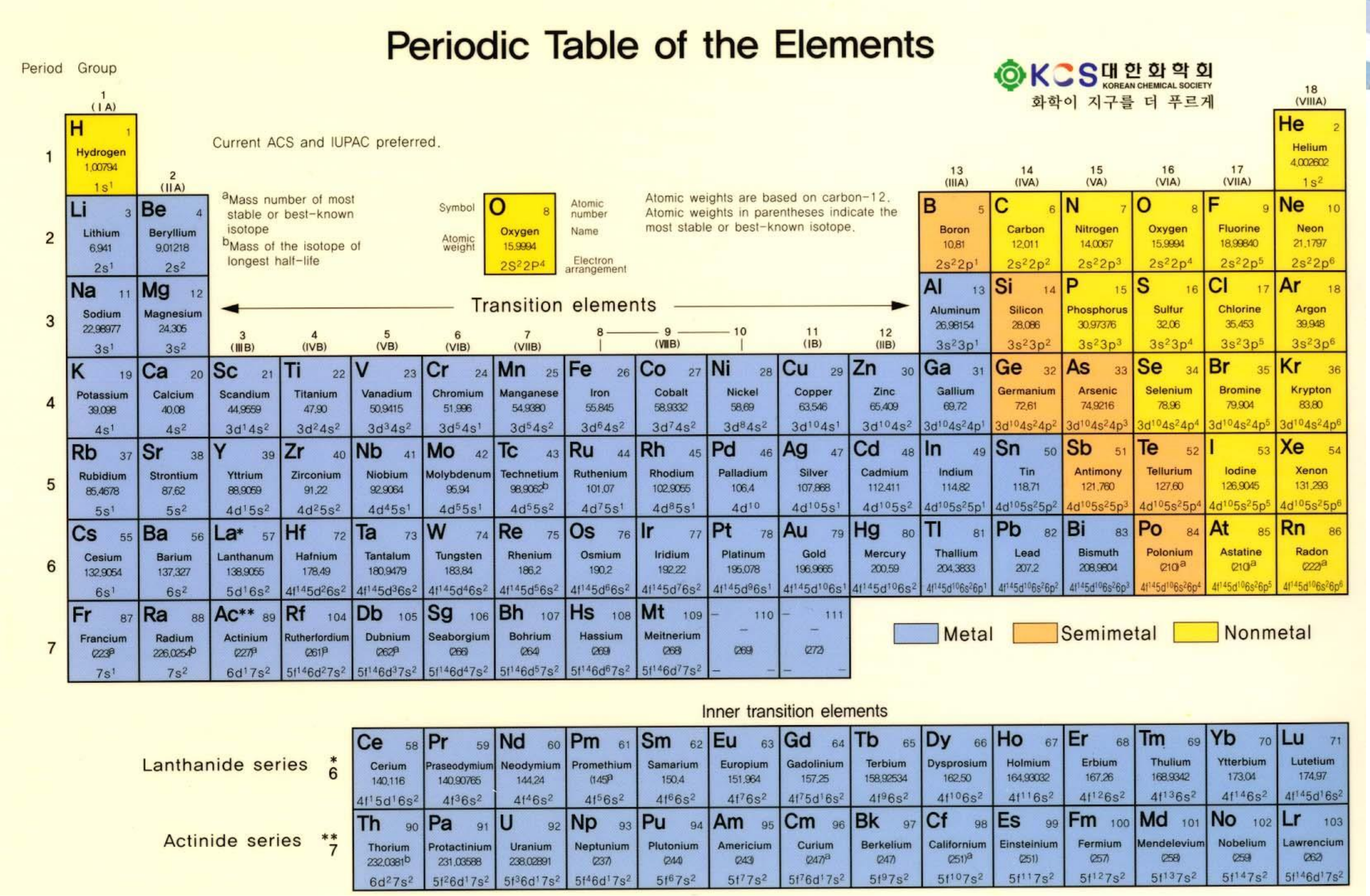
Dominant Material for Airplanes
; Aluminum Alloy

B737-800 of Korean Air

Need of light, strong and tough material

Strength of Materials





Periodic Table of the Elements

KCS 대한화학회
KOREAN CHEMICAL SOCIETY
화학이 지구를 더 푸르게

Current ACS and IUPAC preferred.

[a]Mass number of most stable or best-known isotope
[b]Mass of the isotope of longest half-life

Symbol | Atomic number | Name | Atomic weight | Electron arrangement:

Symbol	Atomic number	Name	Atomic weight	Electron arrangement
O	8	Oxygen	15.9994	$2S^22P^4$

Atomic weights are based on carbon-12. Atomic weights in parentheses indicate the most stable or best-known isotope.

← Transition elements →

Period	1 (IA)	2 (IIA)	3 (IIIB)	4 (IVB)	5 (VB)	6 (VIB)	7 (VIIB)	8	9 (VIIIB)	10	11 (IB)	12 (IIB)	13 (IIIA)	14 (IVA)	15 (VA)	16 (VIA)	17 (VIIA)	18 (VIIIA)
1	**H** 1 Hydrogen 1.00794 $1s^1$																	**He** 2 Helium 4.002602 $1s^2$
2	**Li** 3 Lithium 6.941 $2s^1$	**Be** 4 Beryllium 9.01218 $2s^2$											**B** 5 Boron 10.81 $2s^22p^1$	**C** 6 Carbon 12.011 $2s^22p^2$	**N** 7 Nitrogen 14.0067 $2s^22p^3$	**O** 8 Oxygen 15.9994 $2s^22p^4$	**F** 9 Fluorine 18.99840 $2s^22p^5$	**Ne** 10 Neon 21.1797 $2s^22p^6$
3	**Na** 11 Sodium 22.98977 $3s^1$	**Mg** 12 Magnesium 24.305 $3s^2$											**Al** 13 Aluminum 26.98154 $3s^23p^1$	**Si** 14 Silicon 28.086 $3s^23p^2$	**P** 15 Phosphorus 30.97376 $3s^23p^3$	**S** 16 Sulfur 32.06 $3s^23p^4$	**Cl** 17 Chlorine 35.453 $3s^23p^5$	**Ar** 18 Argon 39.948 $3s^23p^6$
4	**K** 19 Potassium 39.098 $4s^1$	**Ca** 20 Calcium 40.08 $4s^2$	**Sc** 21 Scandium 44.9559 $3d^14s^2$	**Ti** 22 Titanium 47.90 $3d^24s^2$	**V** 23 Vanadium 50.9415 $3d^34s^2$	**Cr** 24 Chromium 51.996 $3d^54s^1$	**Mn** 25 Manganese 54.9380 $3d^54s^2$	**Fe** 26 Iron 55.845 $3d^64s^2$	**Co** 27 Cobalt 58.9332 $3d^74s^2$	**Ni** 28 Nickel 58.69 $3d^84s^2$	**Cu** 29 Copper 63.546 $3d^{10}4s^1$	**Zn** 30 Zinc 65.409 $3d^{10}4s^2$	**Ga** 31 Gallium 69.72 $3d^{10}4s^24p^1$	**Ge** 32 Germanium 72.61 $3d^{10}4s^24p^2$	**As** 33 Arsenic 74.9216 $3d^{10}4s^24p^3$	**Se** 34 Selenium 78.96 $3d^{10}4s^24p^4$	**Br** 35 Bromine 79.904 $3d^{10}4s^24p^5$	**Kr** 36 Krypton 83.80 $3d^{10}4s^24p^6$
5	**Rb** 37 Rubidium 85.4678 $5s^1$	**Sr** 38 Strontium 87.62 $5s^2$	**Y** 39 Yttrium 88.9059 $4d^15s^2$	**Zr** 40 Zirconium 91.22 $4d^25s^2$	**Nb** 41 Niobium 92.9064 $4d^45s^1$	**Mo** 42 Molybdenum 95.94 $4d^55s^1$	**Tc** 43 Technetium 98.9062[b] $4d^55s^2$	**Ru** 44 Ruthenium 101.07 $4d^75s^1$	**Rh** 45 Rhodium 102.9055 $4d^85s^1$	**Pd** 46 Palladium 106.4 $4d^{10}$	**Ag** 47 Silver 107.868 $4d^{10}5s^1$	**Cd** 48 Cadmium 112.411 $4d^{10}5s^2$	**In** 49 Indium 114.82 $4d^{10}5s^25p^1$	**Sn** 50 Tin 118.71 $4d^{10}5s^25p^2$	**Sb** 51 Antimony 121.760 $4d^{10}5s^25p^3$	**Te** 52 Tellurium 127.60 $4d^{10}5s^25p^4$	**I** 53 Iodine 126.9045 $4d^{10}5s^25p^5$	**Xe** 54 Xenon 131.293 $4d^{10}5s^25p^6$
6	**Cs** 55 Cesium 132.9054 $6s^1$	**Ba** 56 Barium 137.327 $6s^2$	**La*** 57 Lanthanum 138.9055 $5d^16s^2$	**Hf** 72 Hafnium 178.49 $4f^{14}5d^26s^2$	**Ta** 73 Tantalum 180.9479 $4f^{14}5d^36s^2$	**W** 74 Tungsten 183.84 $4f^{14}5d^46s^2$	**Re** 75 Rhenium 186.2 $4f^{14}5d^56s^2$	**Os** 76 Osmium 190.2 $4f^{14}5d^66s^2$	**Ir** 77 Iridium 192.22 $4f^{14}5d^76s^2$	**Pt** 78 Platinum 195.078 $4f^{14}5d^96s^1$	**Au** 79 Gold 196.9665 $4f^{14}5d^{10}6s^1$	**Hg** 80 Mercury 200.59 $4f^{14}5d^{10}6s^2$	**Tl** 81 Thallium 204.3833 $4f^{14}5d^{10}6s^26p^1$	**Pb** 82 Lead 207.2 $4f^{14}5d^{10}6s^26p^2$	**Bi** 83 Bismuth 208.9804 $4f^{14}5d^{10}6s^26p^3$	**Po** 84 Polonium (210)[a] $4f^{14}5d^{10}6s^26p^4$	**At** 85 Astatine (210)[a] $4f^{14}5d^{10}6s^26p^5$	**Rn** 86 Radon (222)[a] $4f^{14}5d^{10}6s^26p^6$
7	**Fr** 87 Francium (223)[a] $7s^1$	**Ra** 88 Radium 226.0254[b] $7s^2$	**Ac**** 89 Actinium (227)[a] $6d^17s^2$	**Rf** 104 Rutherfordium (261)[a] $5f^{14}6d^27s^2$	**Db** 105 Dubnium (262)[a] $5f^{14}6d^37s^2$	**Sg** 106 Seaborgium (266) $5f^{14}6d^47s^2$	**Bh** 107 Bohrium (264) $5f^{14}6d^57s^2$	**Hs** 108 Hassium (269) $5f^{14}6d^67s^2$	**Mt** 109 Meitnerium (268) $5f^{14}6d^77s^2$	– 110 – (269) – –	– 111 – (272) – –							

🟦 Metal 🟧 Semimetal 🟨 Nonmetal

Inner transition elements

Lanthanide series *6	**Ce** 58 Cerium 140.116 $4f^15d^16s^2$	**Pr** 59 Praseodymium 140.90765 $4f^36s^2$	**Nd** 60 Neodymium 144.24 $4f^46s^2$	**Pm** 61 Promethium (145)[a] $4f^56s^2$	**Sm** 62 Samarium 150.4 $4f^66s^2$	**Eu** 63 Europium 151.964 $4f^76s^2$	**Gd** 64 Gadolinium 157.25 $4f^75d^16s^2$	**Tb** 65 Terbium 158.92534 $4f^96s^2$	**Dy** 66 Dysprosium 162.50 $4f^{10}6s^2$	**Ho** 67 Holmium 164.93032 $4f^{11}6s^2$	**Er** 68 Erbium 167.26 $4f^{12}6s^2$	**Tm** 69 Thulium 168.9342 $4f^{13}6s^2$	**Yb** 70 Ytterbium 173.04 $4f^{14}6s^2$	**Lu** 71 Lutetium 174.97 $4f^{14}5d^16s^2$
Actinide series **7	**Th** 90 Thorium 232.0381[b] $6d^27s^2$	**Pa** 91 Protactinium 231.03588 $5f^26d^17s^2$	**U** 92 Uranium 238.02891 $5f^36d^17s^2$	**Np** 93 Neptunium (237) $5f^46d^17s^2$	**Pu** 94 Plutonium (244) $5f^67s^2$	**Am** 95 Americium (243) $5f^77s^2$	**Cm** 96 Curium (247)[a] $5f^76d^17s^2$	**Bk** 97 Berkelium (247) $5f^97s^2$	**Cf** 98 Californium (251)[a] $5f^{10}7s^2$	**Es** 99 Einsteinium (251) $5f^{11}7s^2$	**Fm** 100 Fermium (257) $5f^{12}7s^2$	**Md** 101 Mendelevium (258) $5f^{13}7s^2$	**No** 102 Nobelium (259) $5f^{14}7s^2$	**Lr** 103 Lawrencium (262) $5f^{14}6d^17s^2$

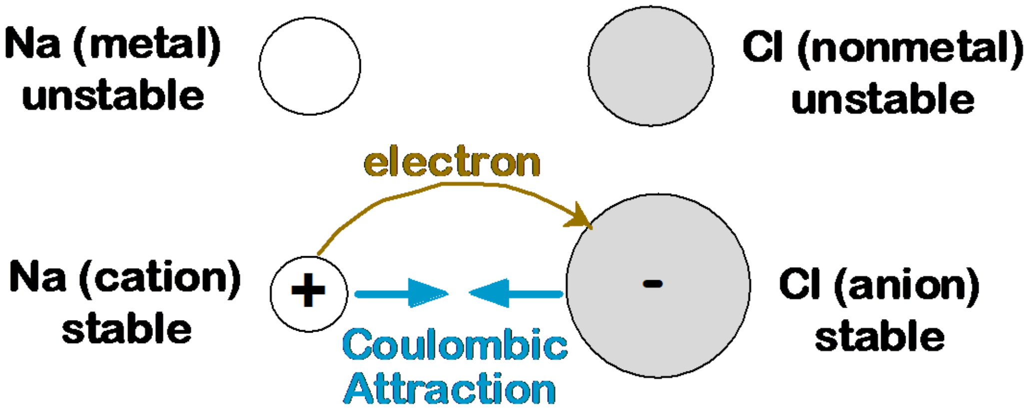
Bonding

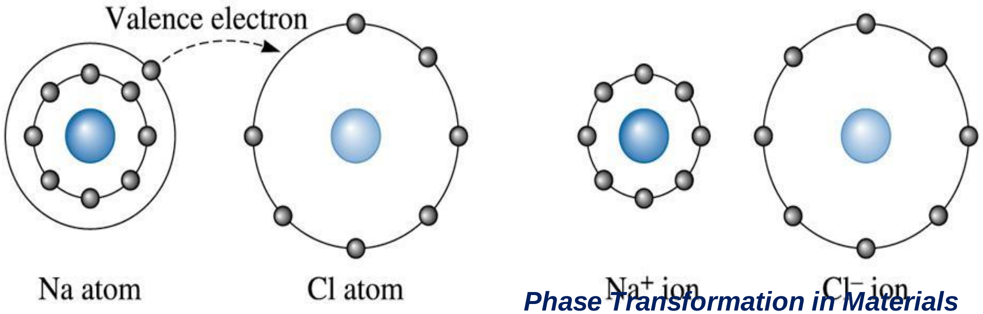
- **primary bonding**
  - ✓ ionic bonding
  - ✓ covalent bonding
  - ✓ metallic bonding

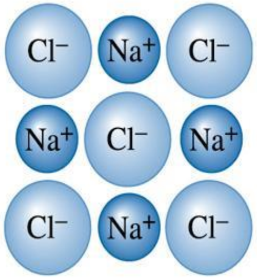
- **secondary bonding**
  - ✓ van der Waals
  - ✓ hydrogen bonding

Ionic Bonding

- Occurs between + and - ions
- Requires electron transfer
- Large difference in electronegativity required
- An ionic bond is created between two unlike atoms with different electronegativities
- When sodium donates its valence electron to chlorine, each becomes an ion; attraction occurs, and the ionic bond is formed

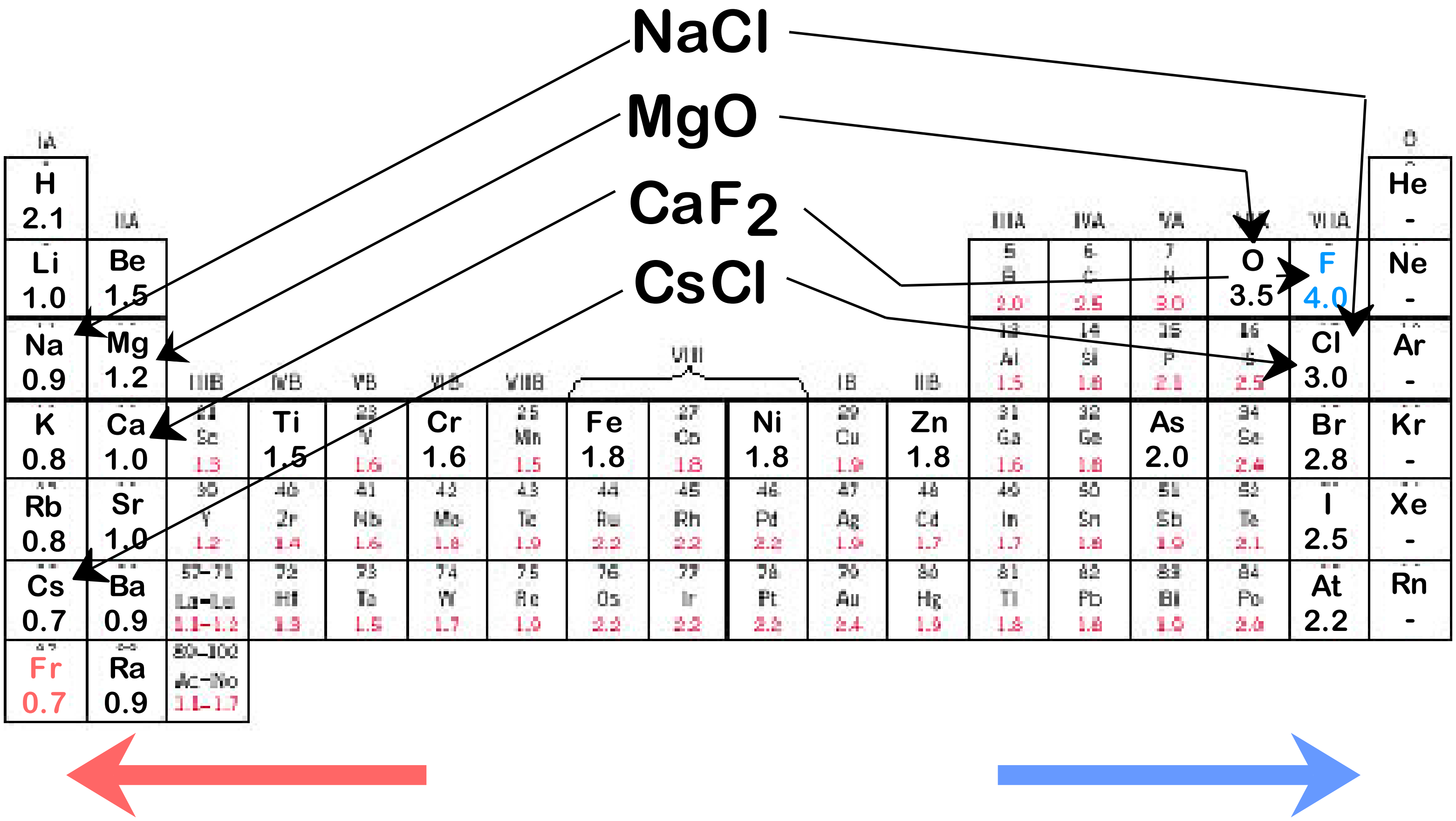






Example : Ionic Bonding

- Predominant bonding in **Ceramics**

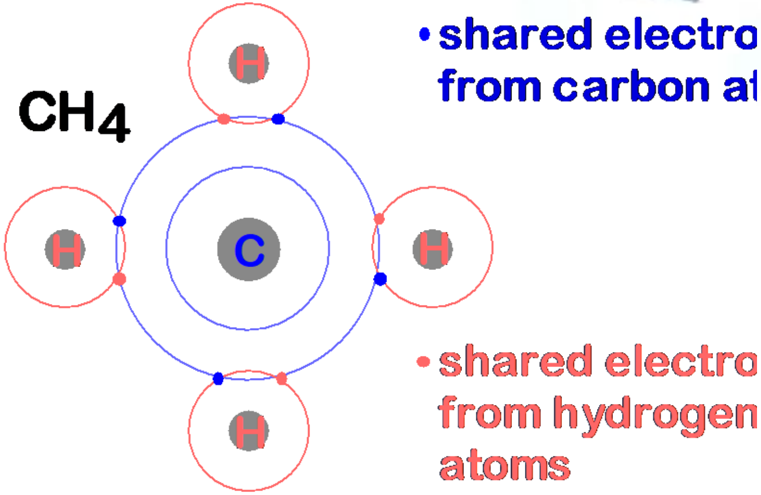


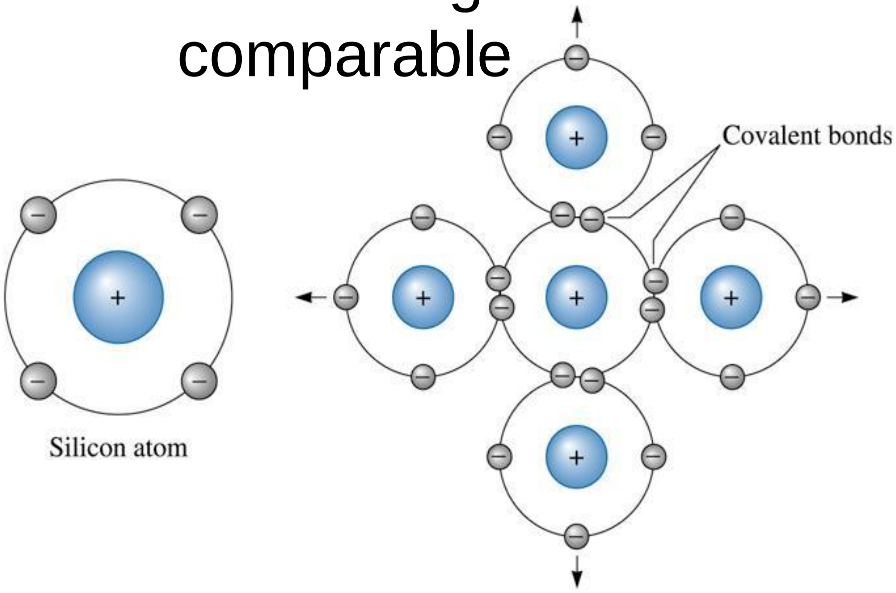
Give up electrons

Acquire electrons

Covalent Bonding

- **Requires shared electrons**
- **Example: CH_4**
  - ✓ C: has 4 valence e, needs 4 more
  - ✓ H: has 1 valence e, needs 1 more
  - ✓ Electronegativities are comparable



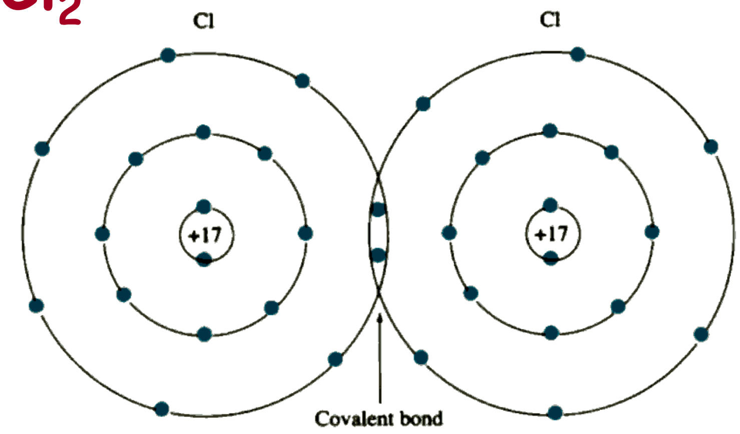


Covalent bonding requires that electrons be shared between atoms in such a way that each atom has its outer *sp* orbital filled. In Si, with a valence of four, four covalent bonds must be formed.

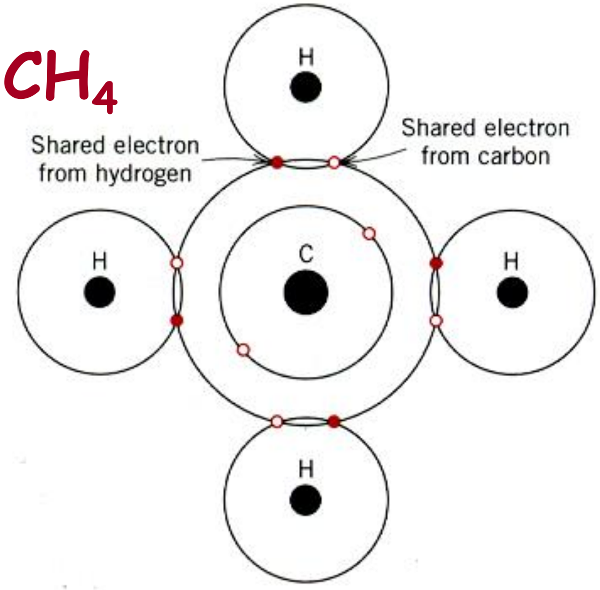
Covalent Bonding

- ❖ **Electron sharing**
- ❖ **Directional**

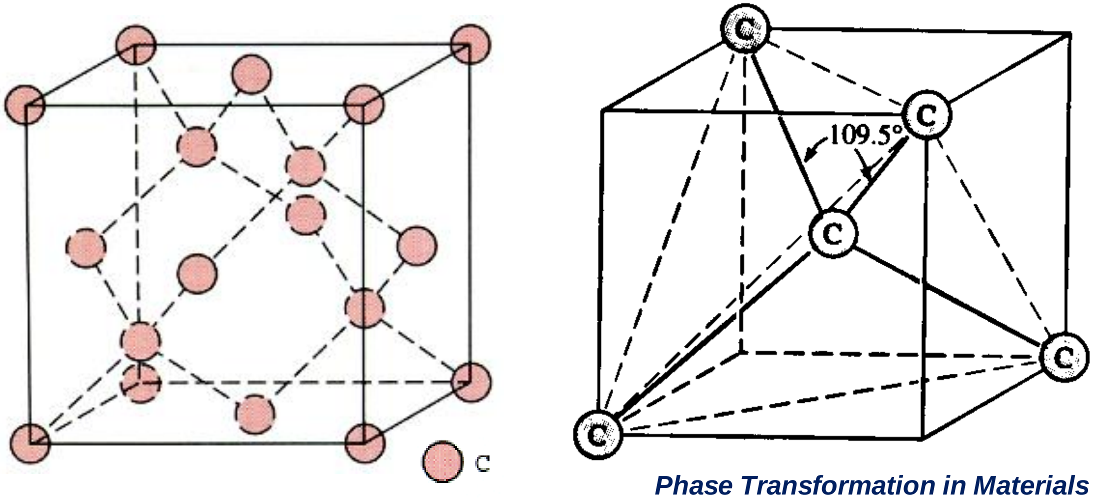
Cl_2



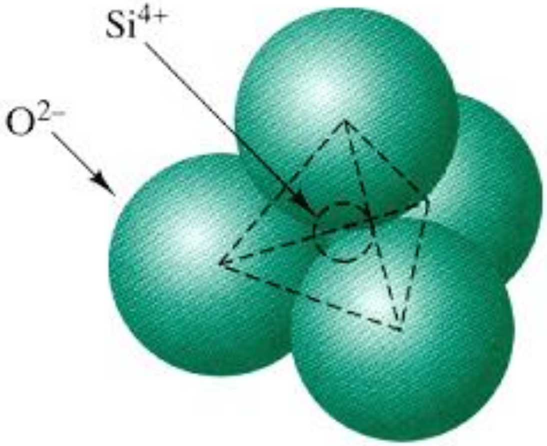
CH_4



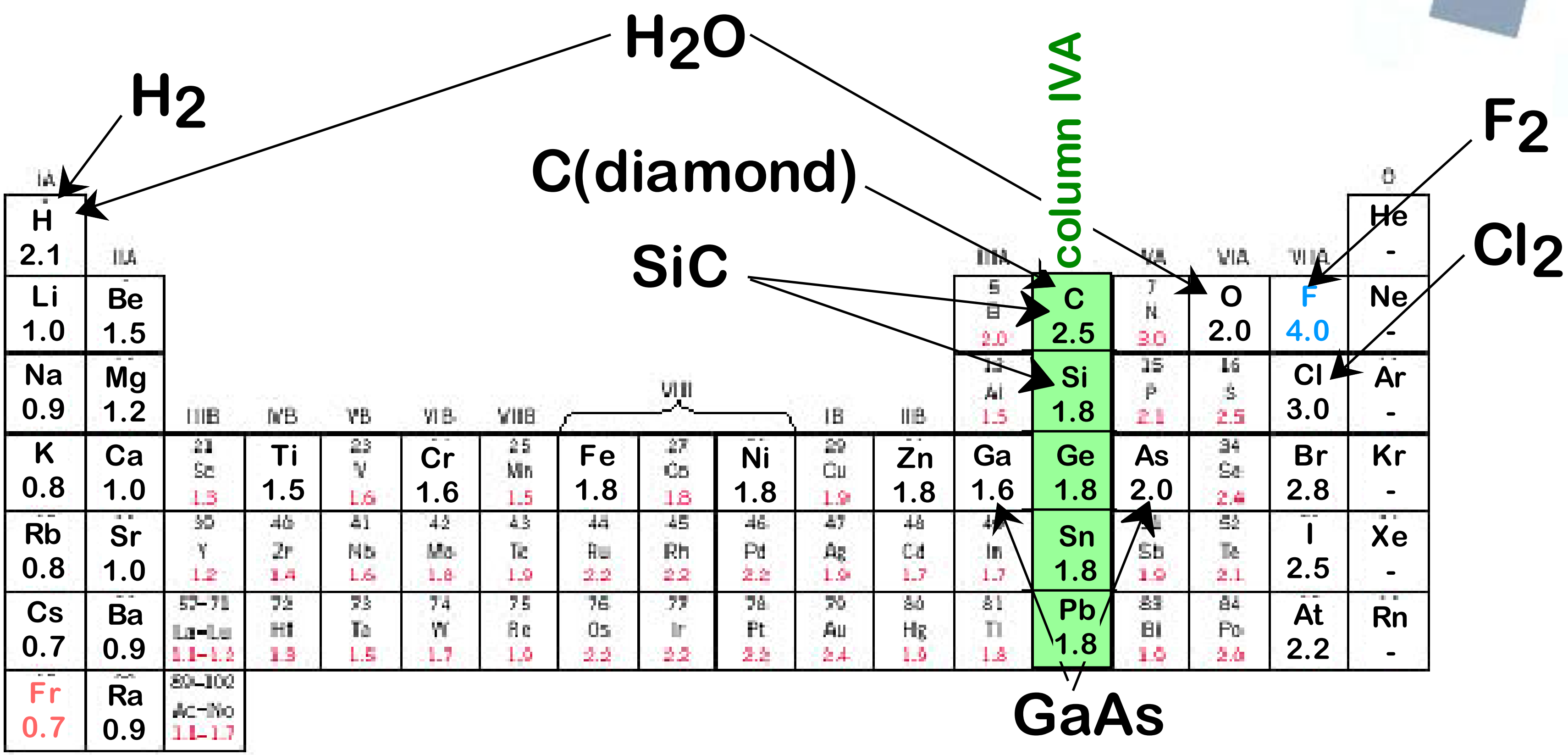
diamond



SiO_4^{2-}

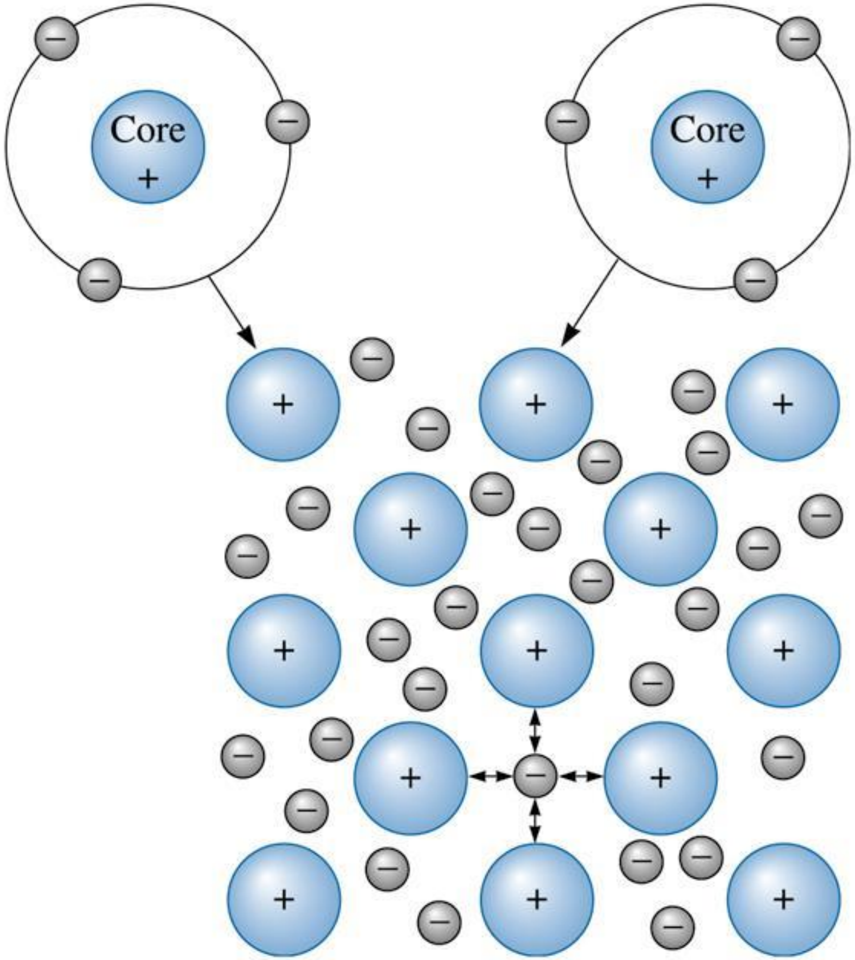


Example : Covalent Bonding



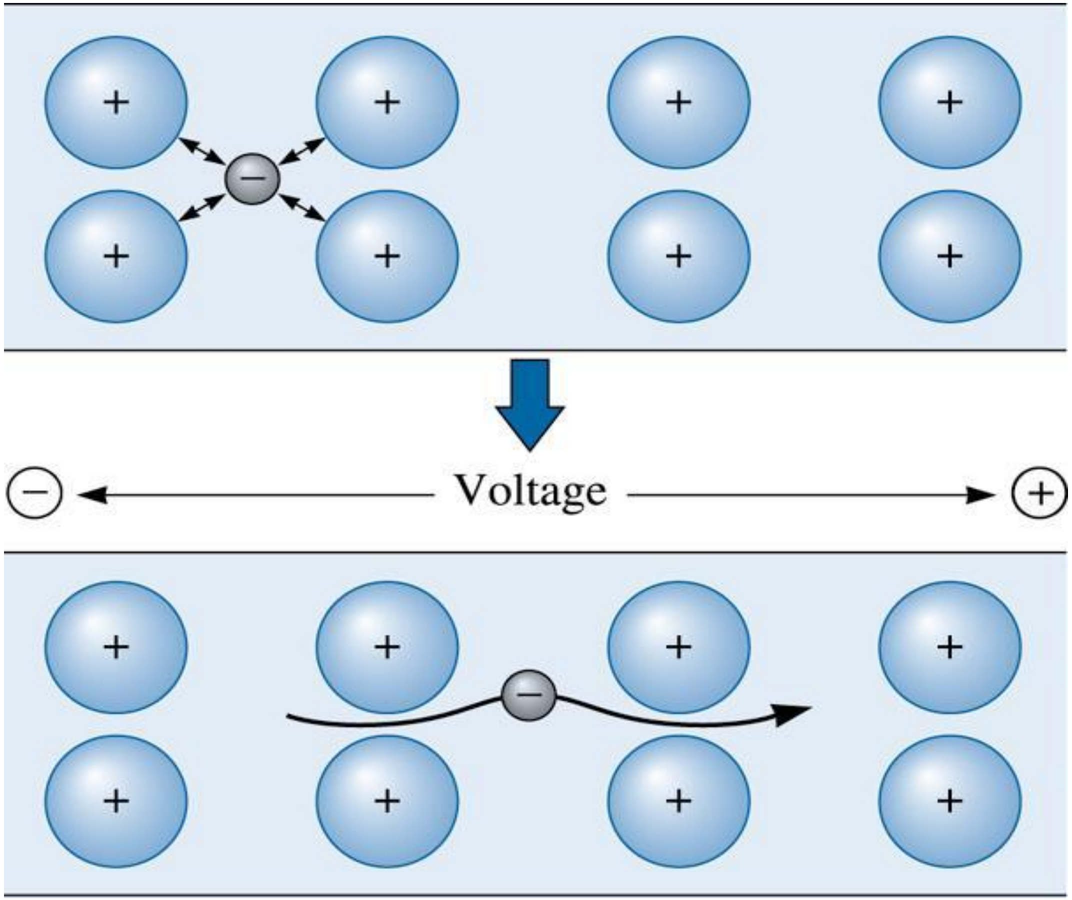
- molecules with **nonmetals**
- molecules with **metals** and **nonmetals**
- elemental solids
- compound solids (about **column IVA**)

Metallic Bonding



- The metallic bond forms when atoms give up their valence electrons, which then form an electron sea.
- The positively charged atom cores are bonded by mutual attraction to the negatively charged electrons.

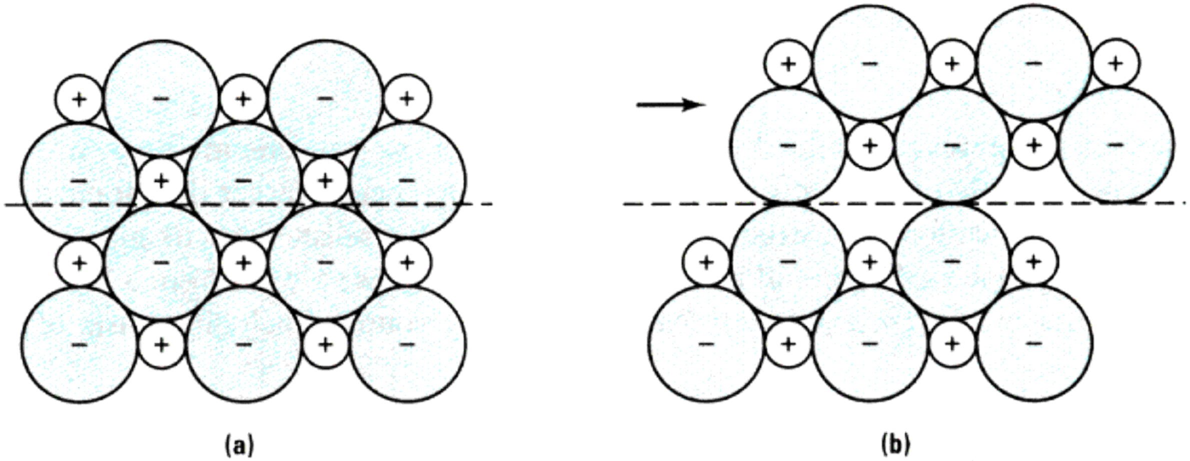
Metallic Bonding



- When voltage is applied to a metal, the electrons in the electron sea can easily move and carry a current.

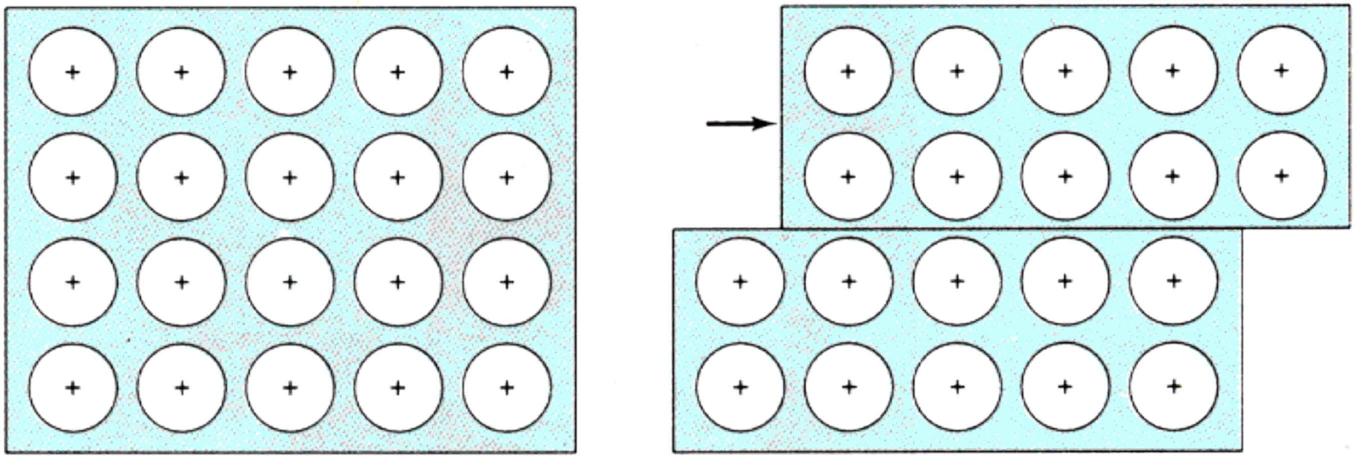
Metallic Bonding

❖ **mechanical property**



Ionic bonding

brittle

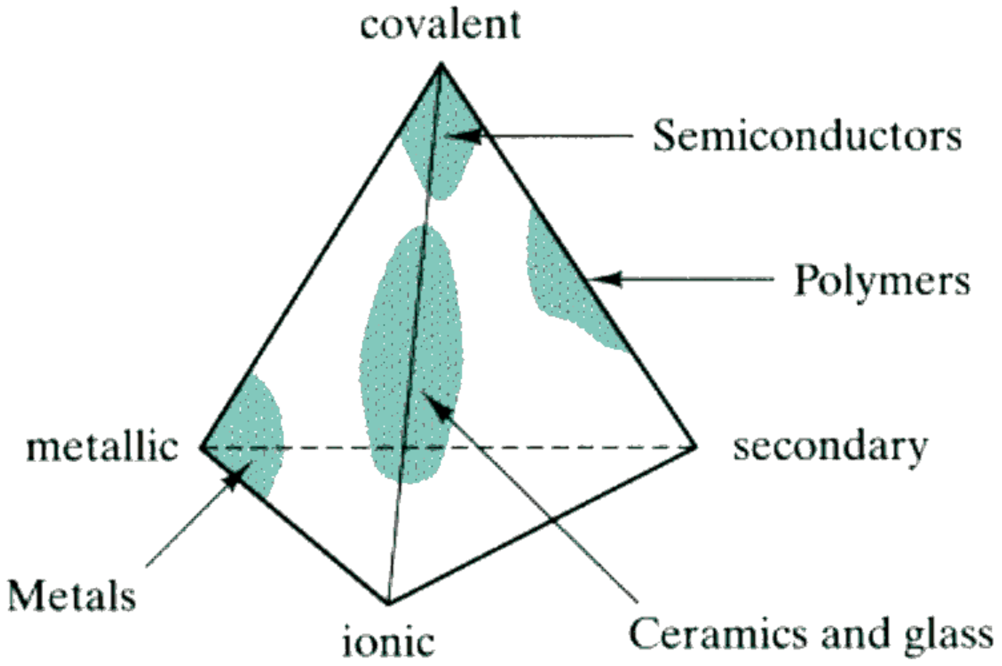


Metallic bonding

ductile

Materials-Bonding Classification

Material type	Bonding character	Example
Metal	Metallic	Iron (Fe) and the ferrous alloys
Ceramics and glasses	Ionic/covalent	Silica (SiO_2): crystalline and noncrystalline
Polymers	Covalent and secondary	Polyethylene $\left(C_2H_4 \right)_n$
Semiconductors	Covalent or covalent/ionic	Silicon (Si) or cadmium sulfide (CdS)



Materials and Packing

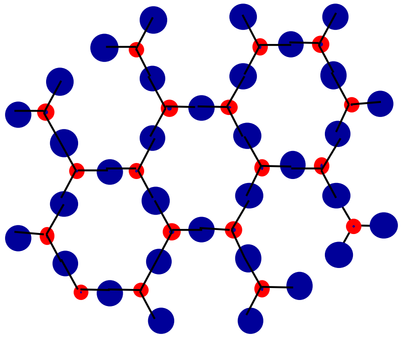
1. **Crystalline** materials

- ✓ atoms pack in periodic, 3D arrays
- ✓ typical of: - metals
  - many ceramics
  - some polymers

2. **Noncrystalline** materials...

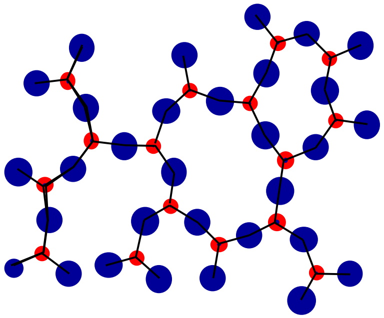
- ✓ atoms have no periodic packing
- ✓ occurs for: - complex structures
  - rapid cooling

❖ **"Amorphous" = Noncrystalline**



crystalline SiO_2

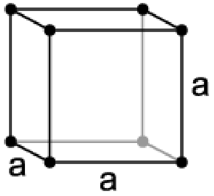
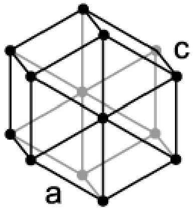
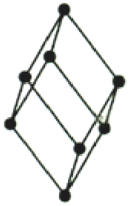
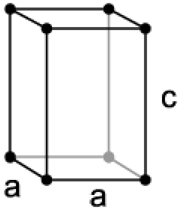
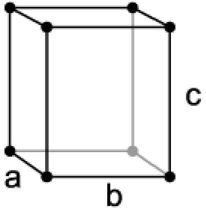
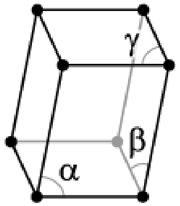
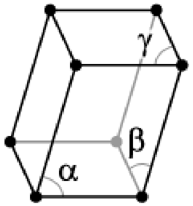
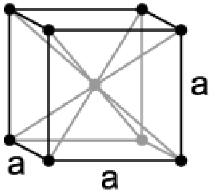
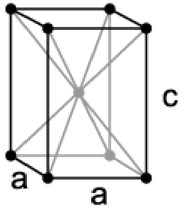
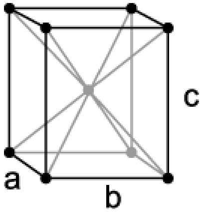
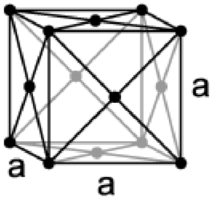
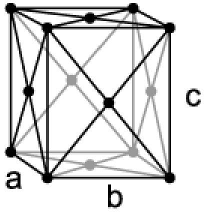
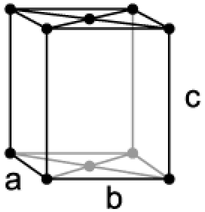
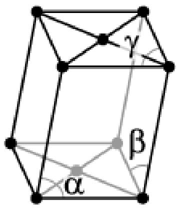
Si • ● Oxygen



noncrystalline SiO_2

Unit cell

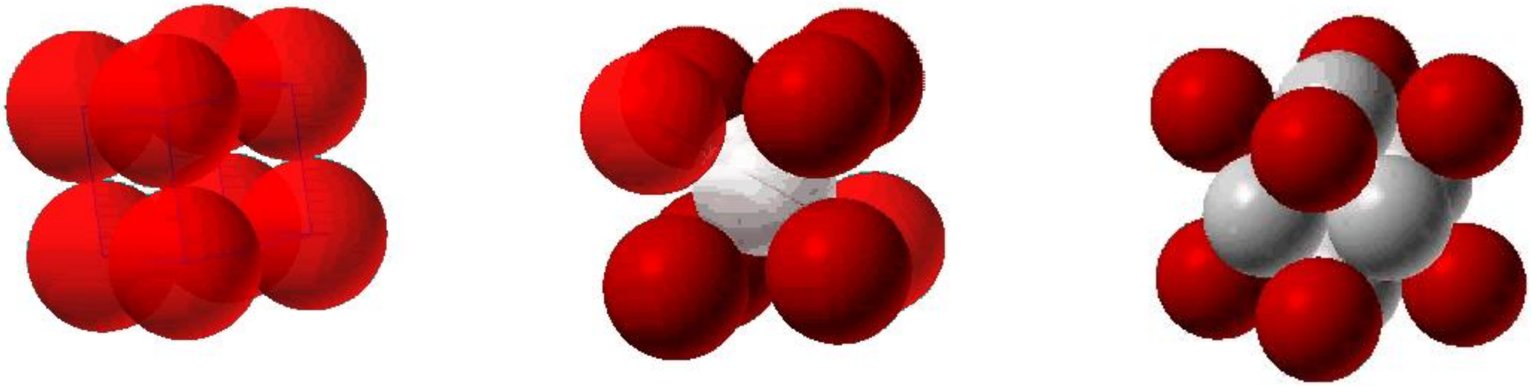
- **14 Bravais Lattice - Only 14 different types of unit cells are required to describe all lattices using symmetry**

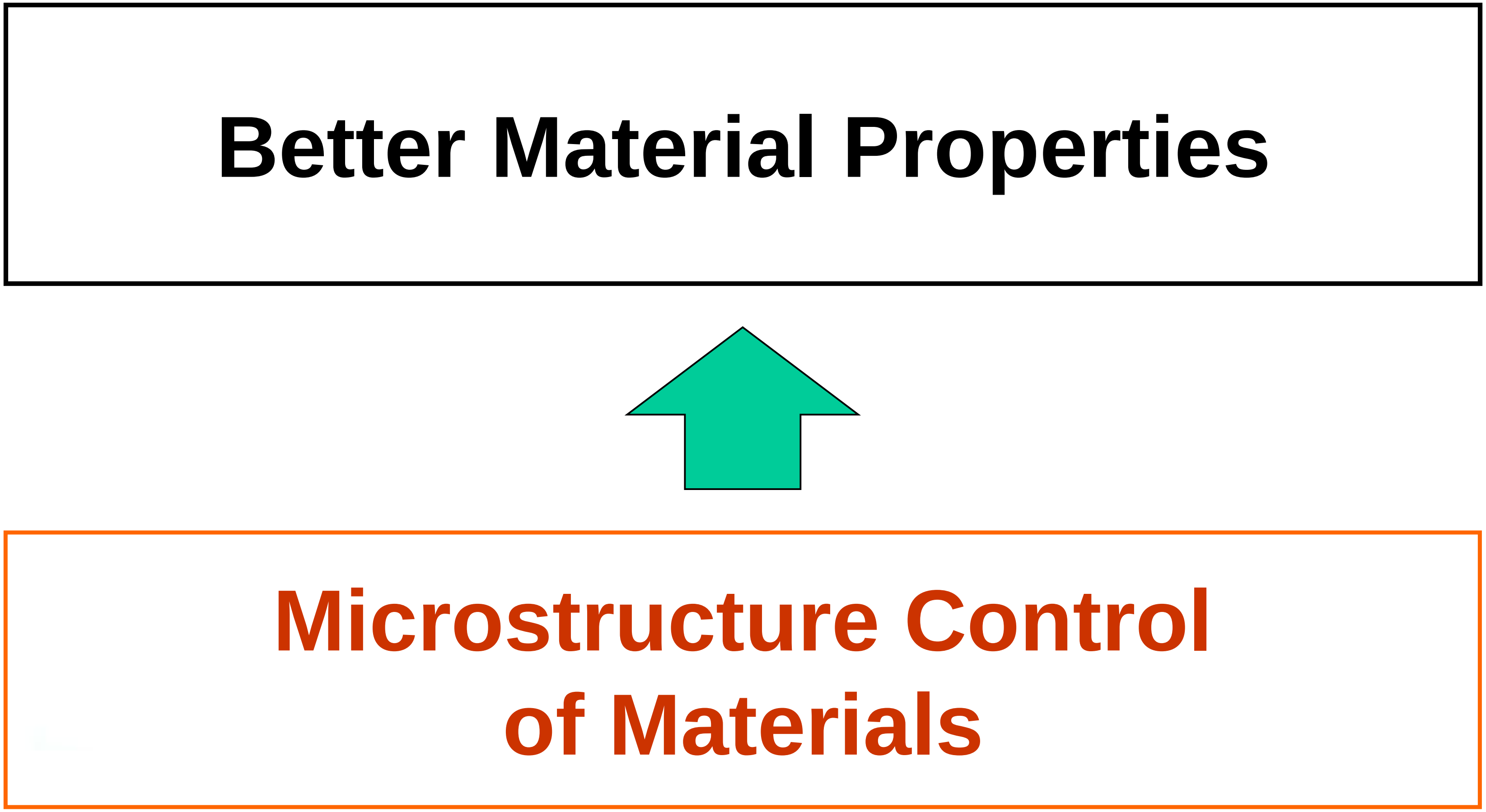
	cubic	hexagonal	rhombohedral (trigonal)	tetragonal	orthorhombic	monoclinic	triclinic
P							
I							
F							
C							

Metallic crystal system

TABLE 3-2 ■ *Crystal structure characteristics of some metals*

Structure	a_0 versus r	Atoms per Cell	Coordination Number	Packing Factor	Examples
Simple cubic (SC)	$a_0 = 2r$	1	6	0.52	Polonium (Po), α-Mn
Body-centered cubic	$a_0 = 4r/\sqrt{3}$	2	8	0.68	Fe, Ti, W, Mo, Nb, Ta, K, Na, V, Zr, Cr
Face-centered cubic	$a_0 = 4r/\sqrt{2}$	4	12	0.74	Fe, Cu, Au, Pt, Ag, Pb, Ni
Hexagonal close-packed	$a_0 = 2r$ $c_0 \approx 1.633a_0$	2	12	0.74	Ti, Mg, Zn, Be, Co, Zr, Cd





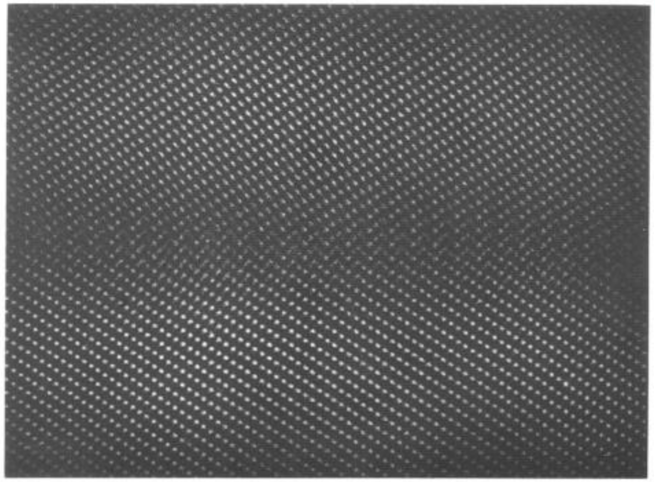
Better Material Properties

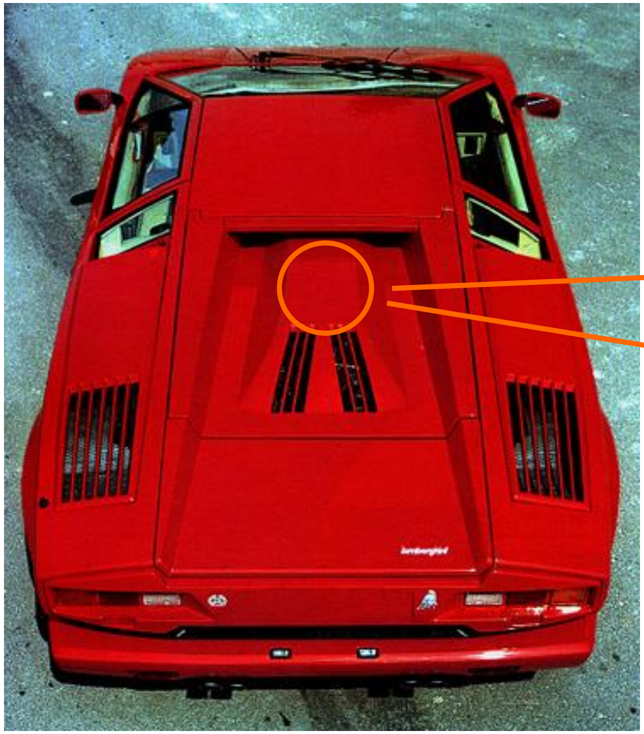
Microstructure Control of Materials

What is Microstructure in Materials Science?

Materials ;
Assemblage of Atoms

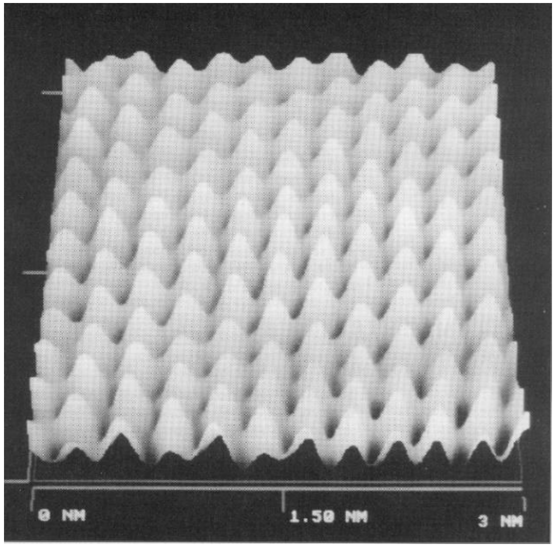
Transmission Electron Microscope





Lamborghini - Countach

Atomic Force Microscope



Perfect Crystal is Good in many aspects, But…

☐ Imperfection in Metallic Materials ;

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

☐ Second Phase Particles in Matrix

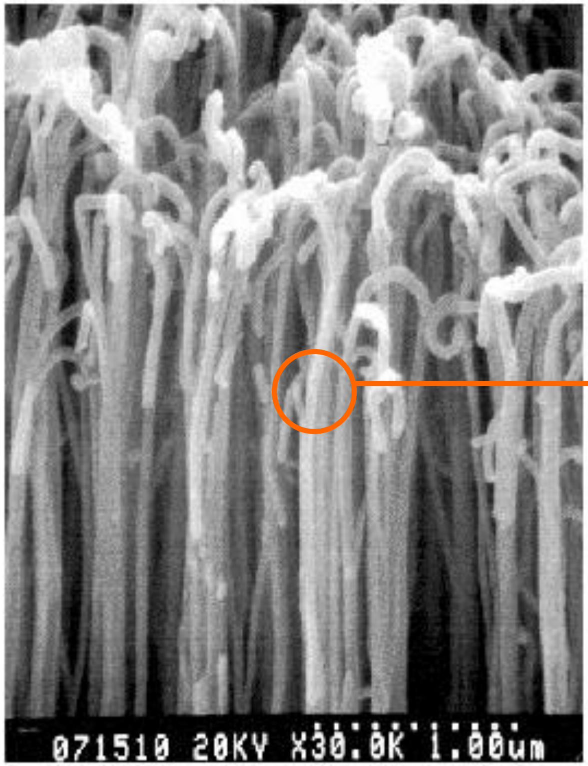
Mechanical Properties ;

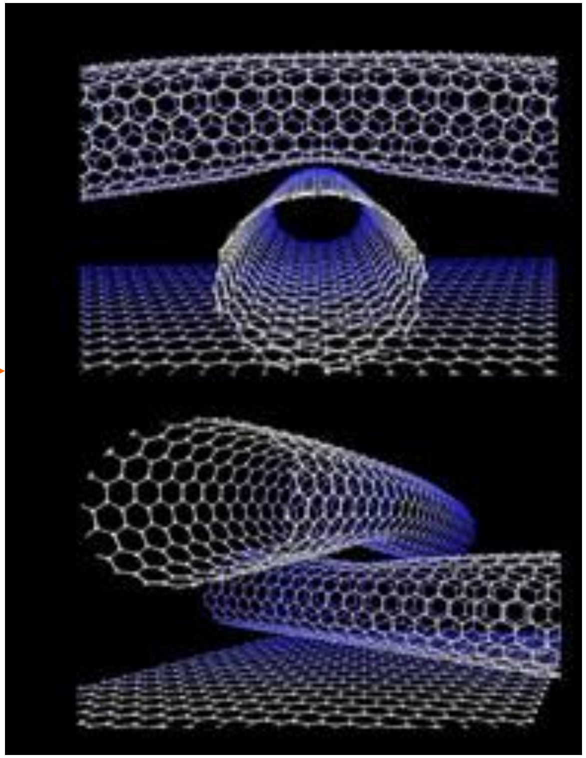
Magnetic properties

Electrical properties

Etc.

Perfect Crystals without Defect

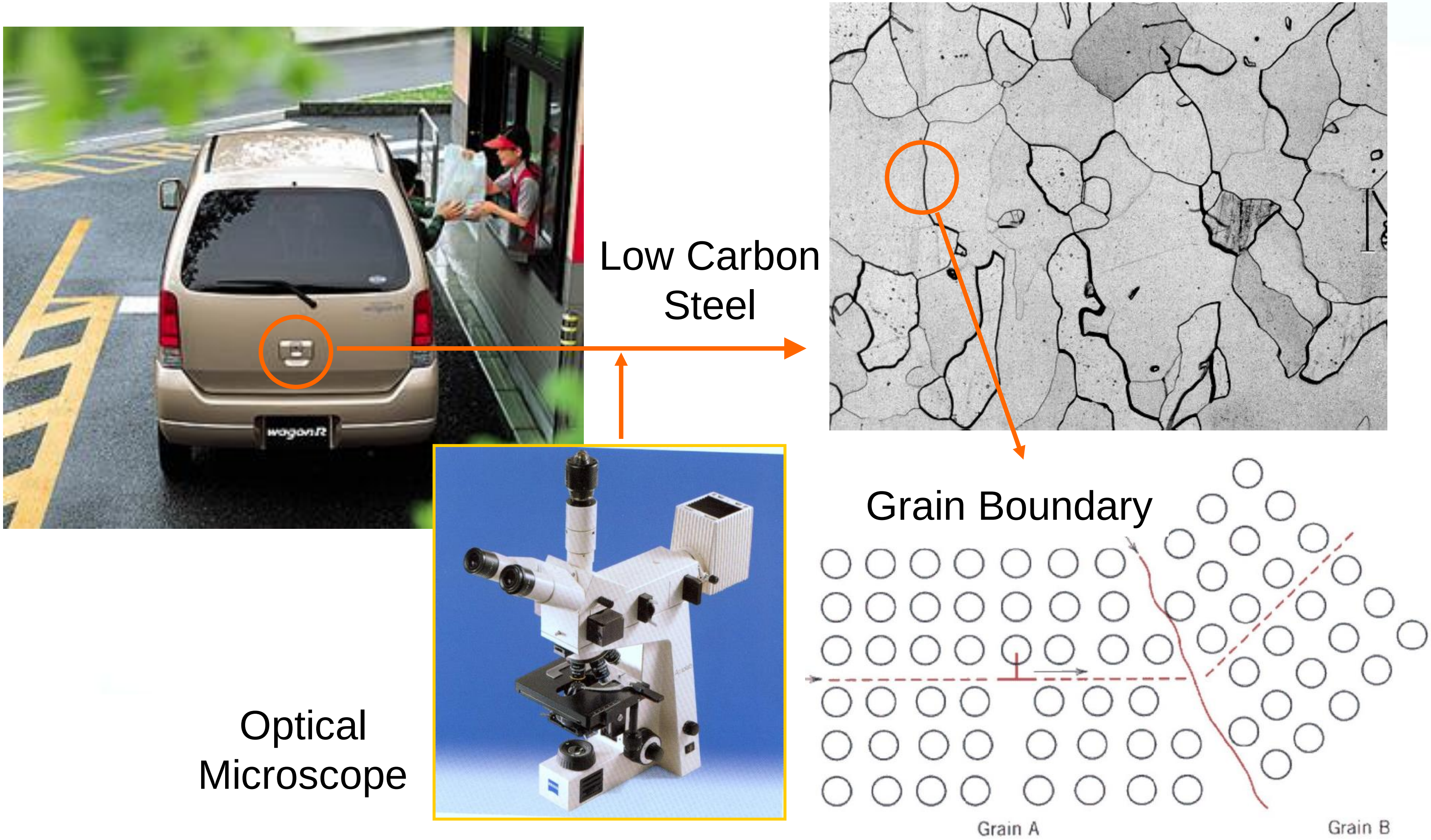




Carbon
Nanotubes

High strength, unique magnetic/electrical properties

Grain Boundaries



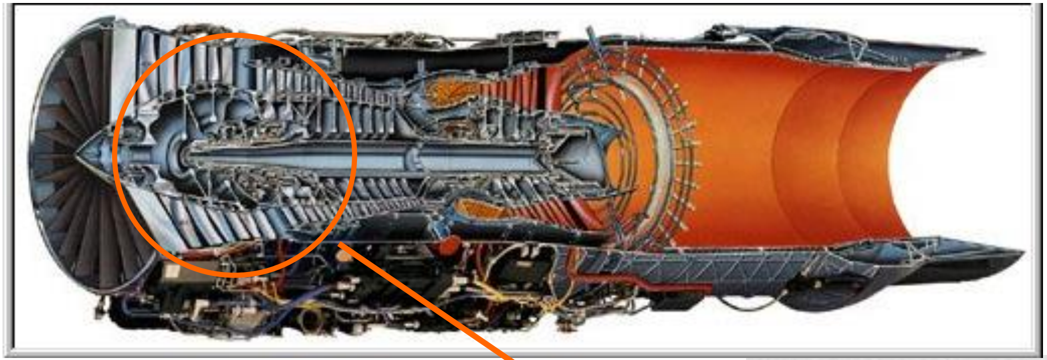
Low Carbon Steel

Grain Boundary

Optical Microscope

A Example of Grain Boundary Engineering

❖ Turbine Blade in Aircraft Engine



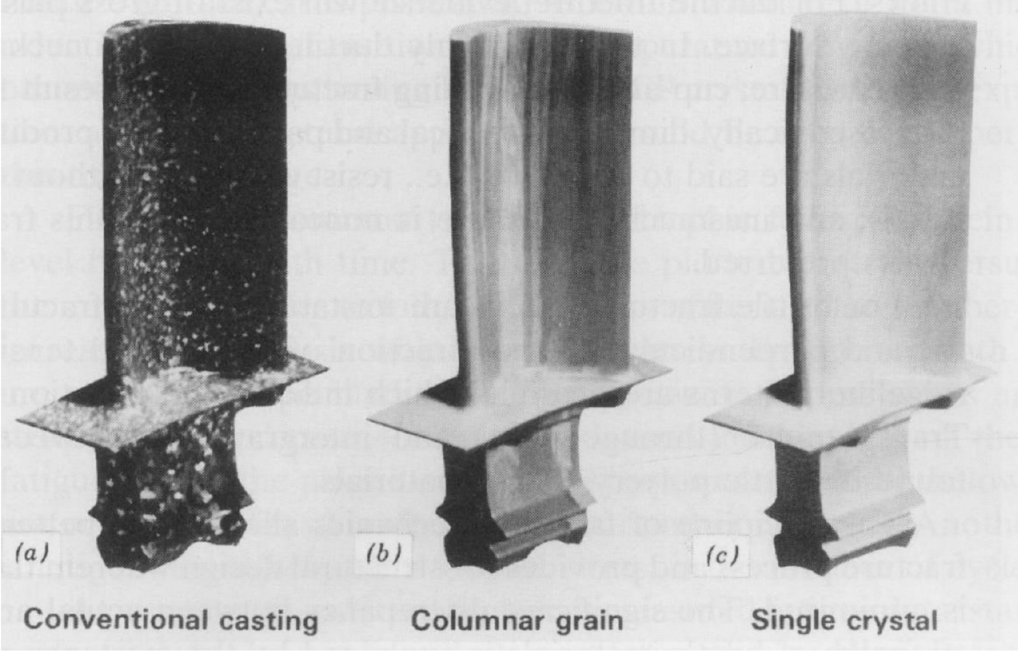
F100-PW-229
in F-16 fighting falcon

Turbine Blade

Grain boundaries
at high Temperature ;
Diffusion path of atoms

Creep

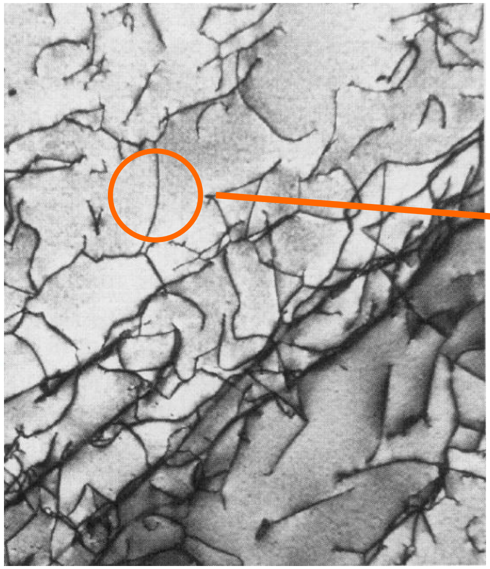
Reducing grain boundaries


(a) Conventional casting
(b) Columnar grain
(c) Single crystal

Dislocations

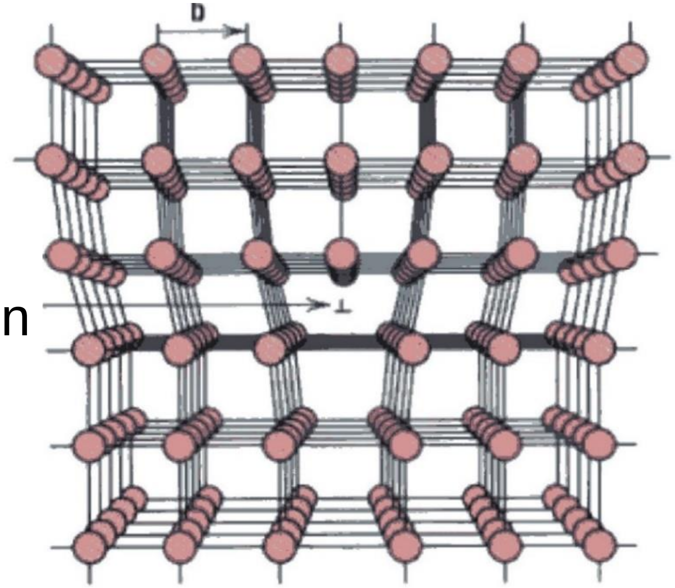
SR-71
with armor of
titanium alloy

It looks perfect.
But….



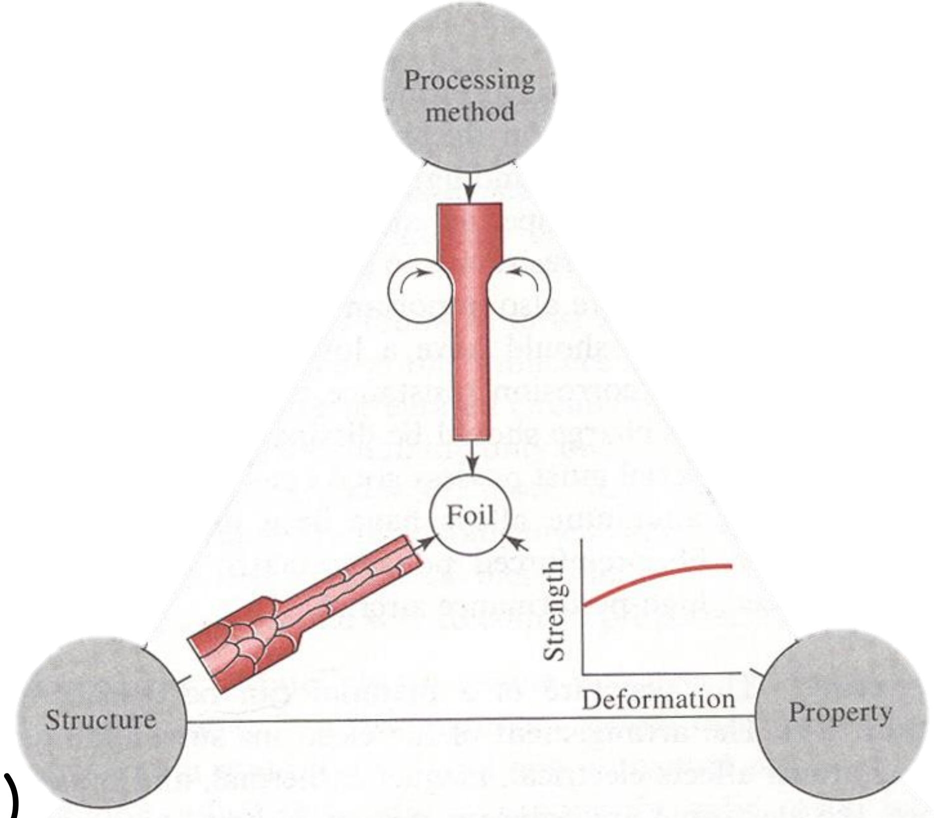
Edge
Dislocation
Line

Burgers vector



Materials Science and Engineering

공정(工程)



미세조직

(微細組織)

물성(物性)

FIGURE 1-8 The three-part relationship between structure, properties, and processing method. When aluminum is rolled into foil, the rolling process changes the metal's structure and increases its strength.

Control of Microstructures ;Cold Work

김홍도
“대장간”

조선시대

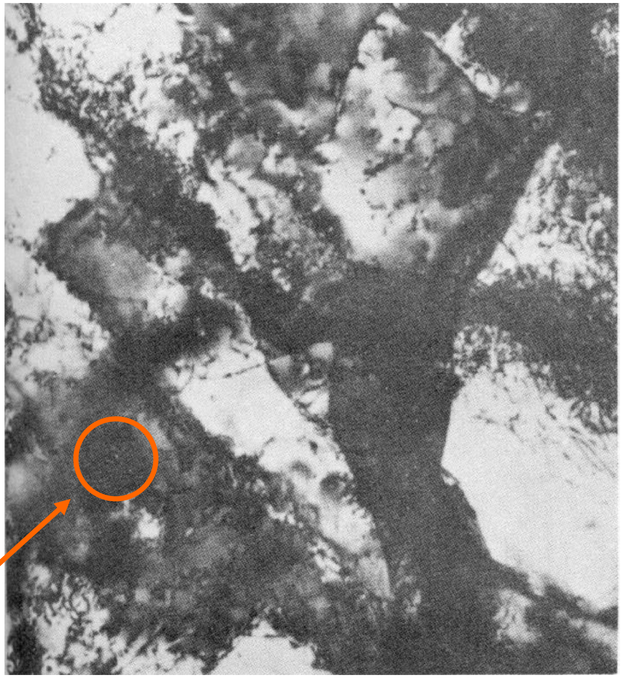
현대의 단조기

Hardening Mechanism by Cold Working

Before cold work

Deformation
or
Cold work

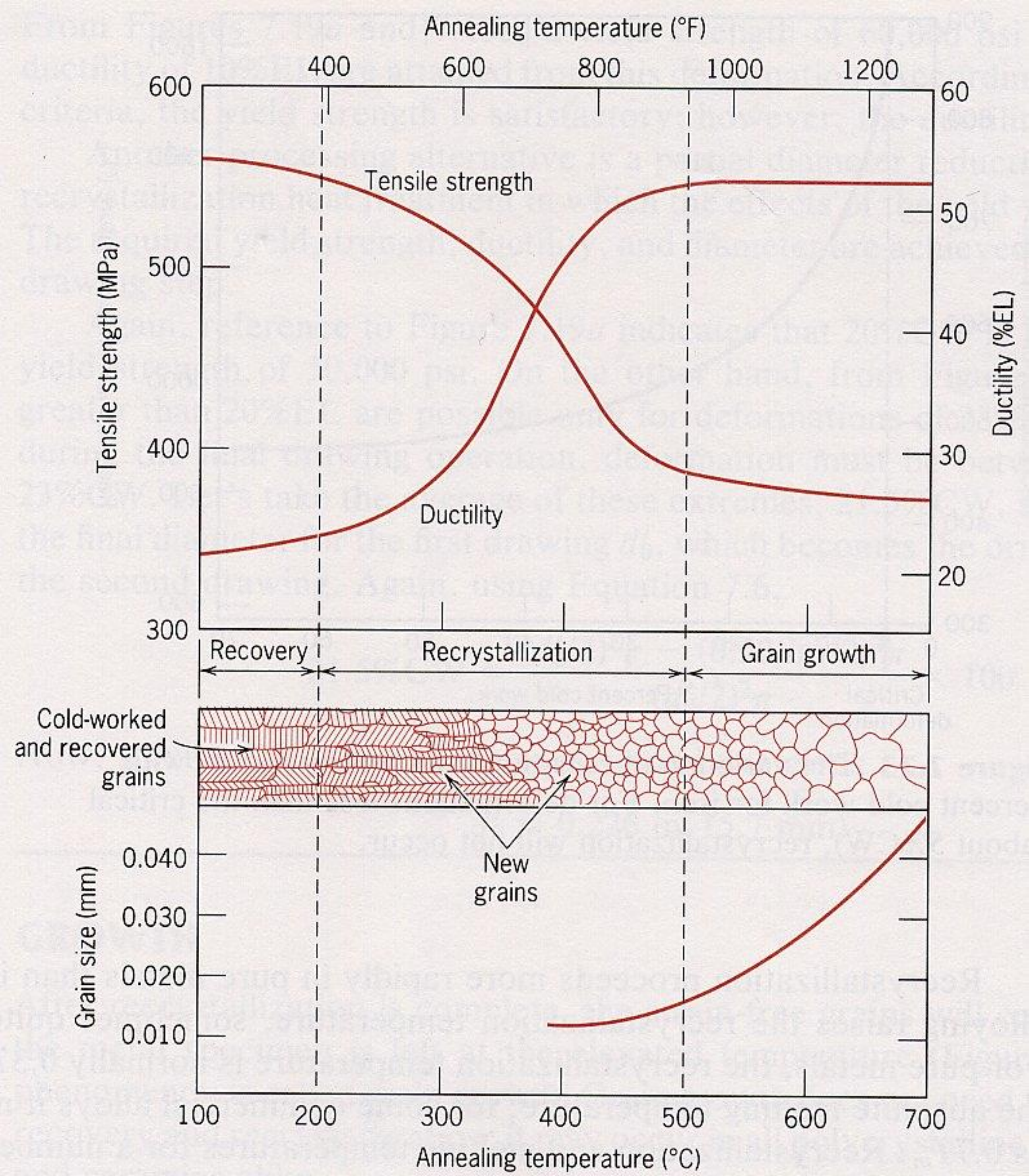
Aluminum alloy



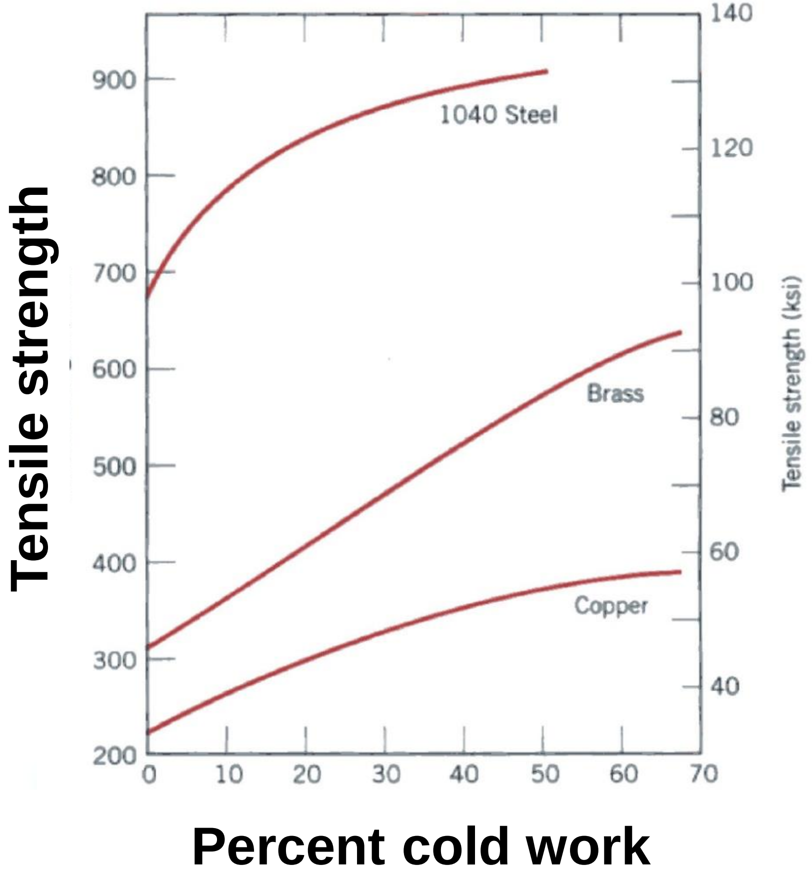
Accumulation of dislocations

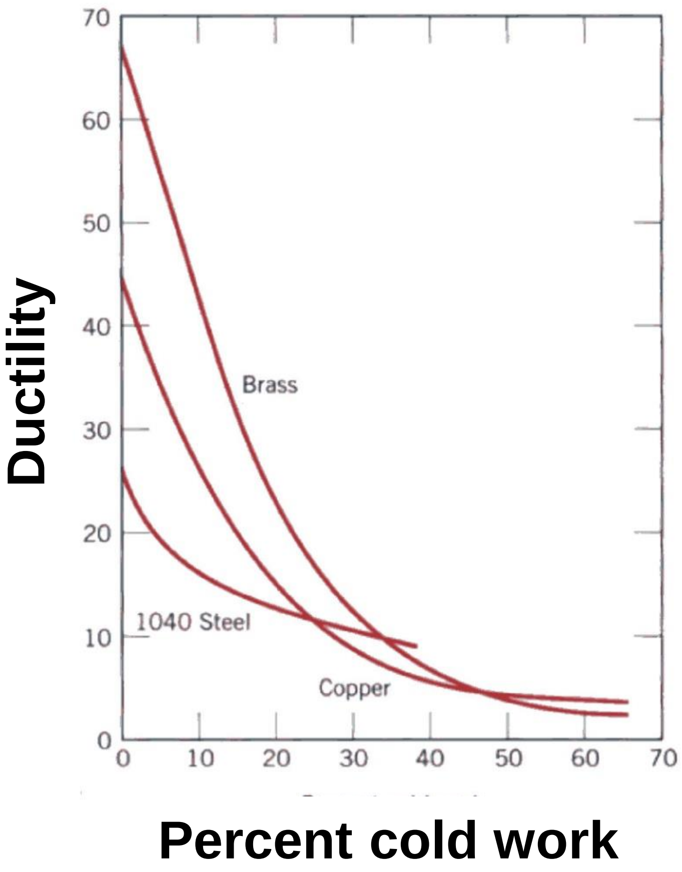
Dislocation tangle

Changes of Microstructure & Mechanical Properties during Annealing



Changes of Strength and Ductility by Cold Working





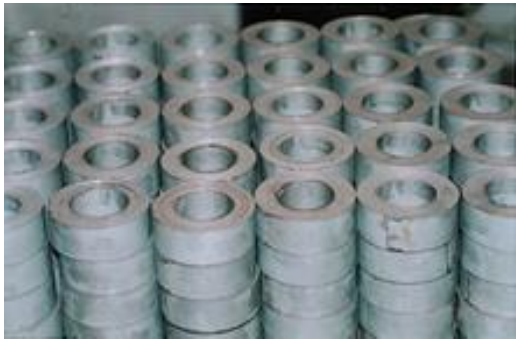
전자석 만들기

- 준비물: 대못(콘크리트 못 안됩니다.) 에나멜선 3~4m, A4용지, 알코올램프
  - ✓ 맨처음 나무젓자락에 대못이 들어가도록 구멍을 끓은 후 사진처럼 알코올램프에 못을 달궈줍니다.
    - 못을 달구는 이유는 강철 대못을 연철로 만드는 과정입니다.
  - ✓ 정확하게 못을 달구는 것만이 아니고 못을 뜨겁게 달군 후에 천천히 식혀주는 과정이 중요합니다.
    - 이 과정은 강철 대못을 연철 대못으로 만들어 주는 것입니다
  - ✓ 달구는 과정에서 못에 있던 탄소성분이 날라가면서 연철로 변하는 것이죠 ^^

- 강철대못으로 만들어도 자석처럼 작동을 합니다.
  - ✓ 하지만!!! 전기를 끊어 주어도 계속 자성을 띄는게 문제죠 ^^ 즉 영구 자석이 되어버립니다.
- 전자석이라 하면 전기를 흘려줄때만 자석이 되어야 합니다.

Production and Application of Electrical Steel

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



Coils

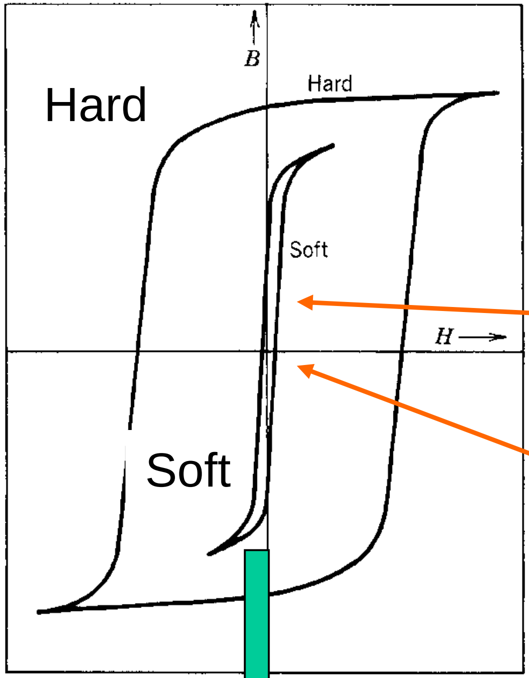
Stacked transformer core

Transformer
Motor
Etc.

Soft magnetization property

Control of Magnetic property of Fe-3% Si Steel Sheet

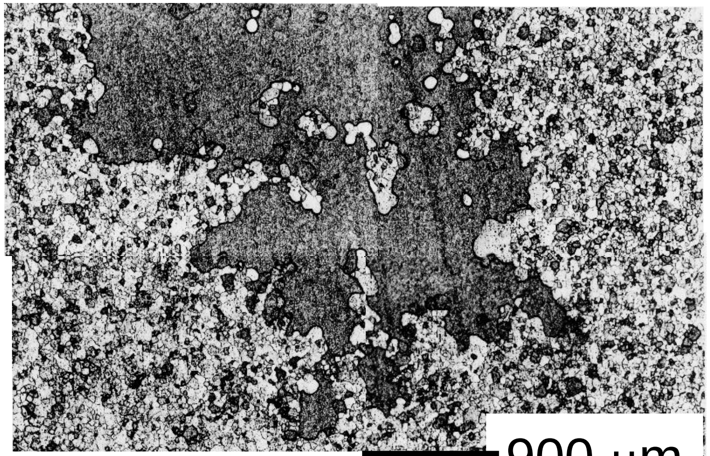
Magnetization curves for
soft and hard magnetic materials



Hard

Soft

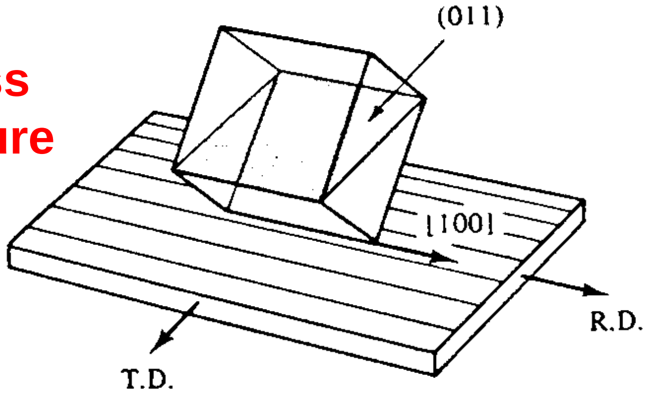
Transformer



900 μm

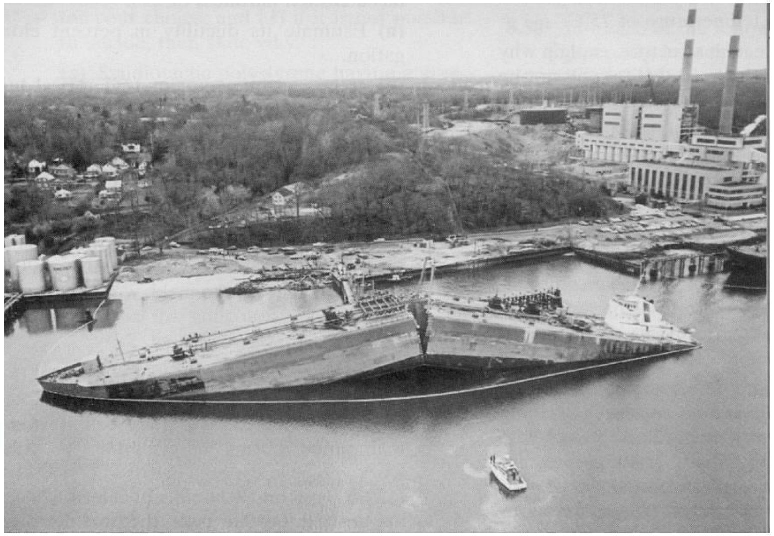
Abnormal grain growth

Goss Texture



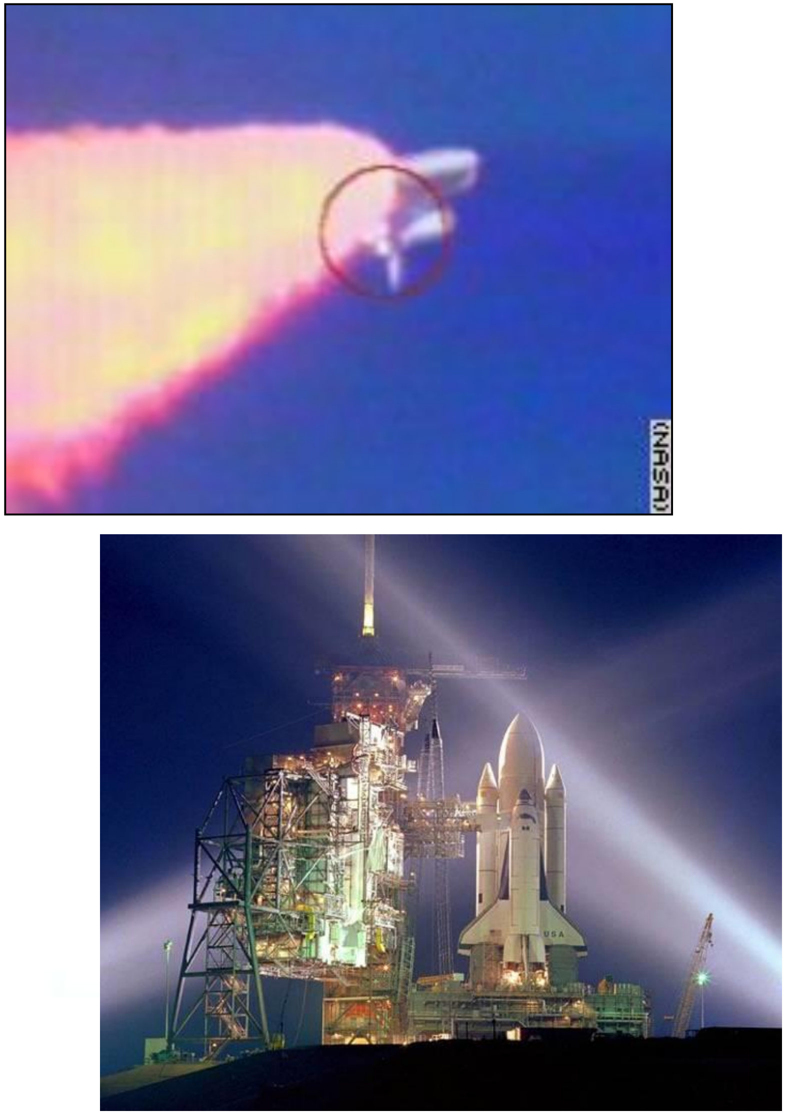
Using of Materials with Improper Microstructure

Failures

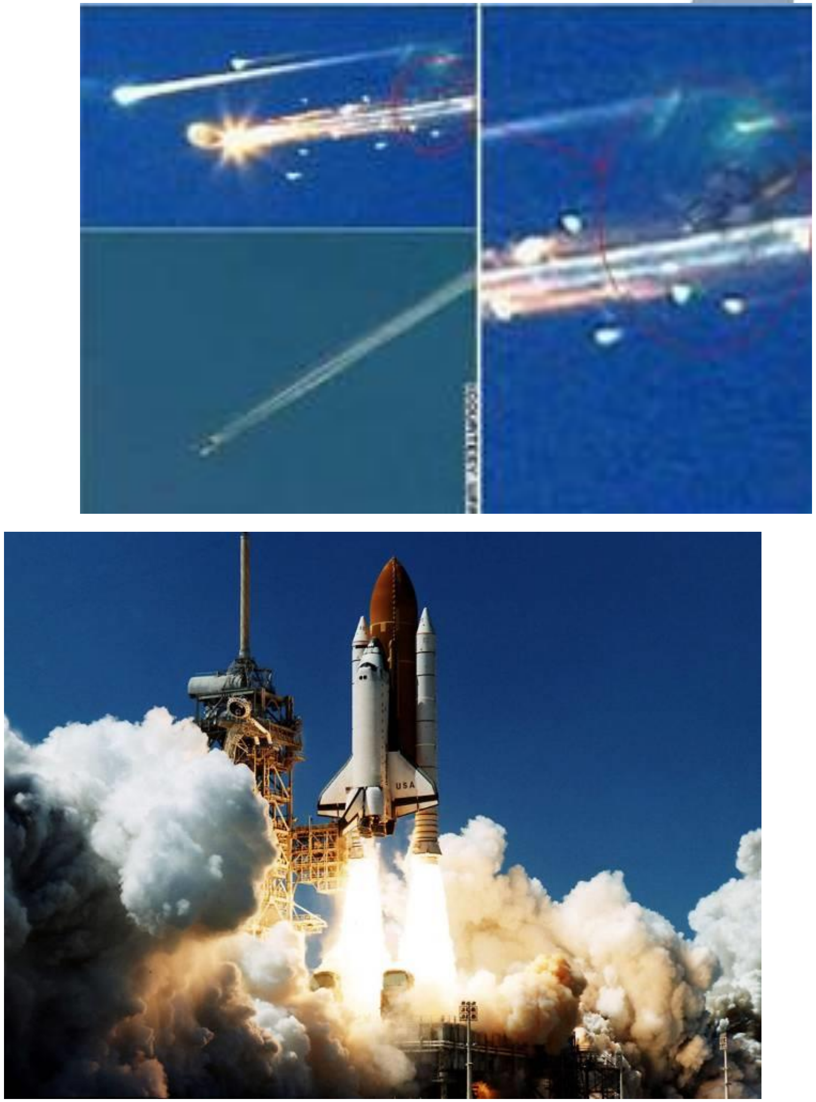


Oil tanker
fractured in a brittle manner

성수대교 붕괴 (1994.10.21)



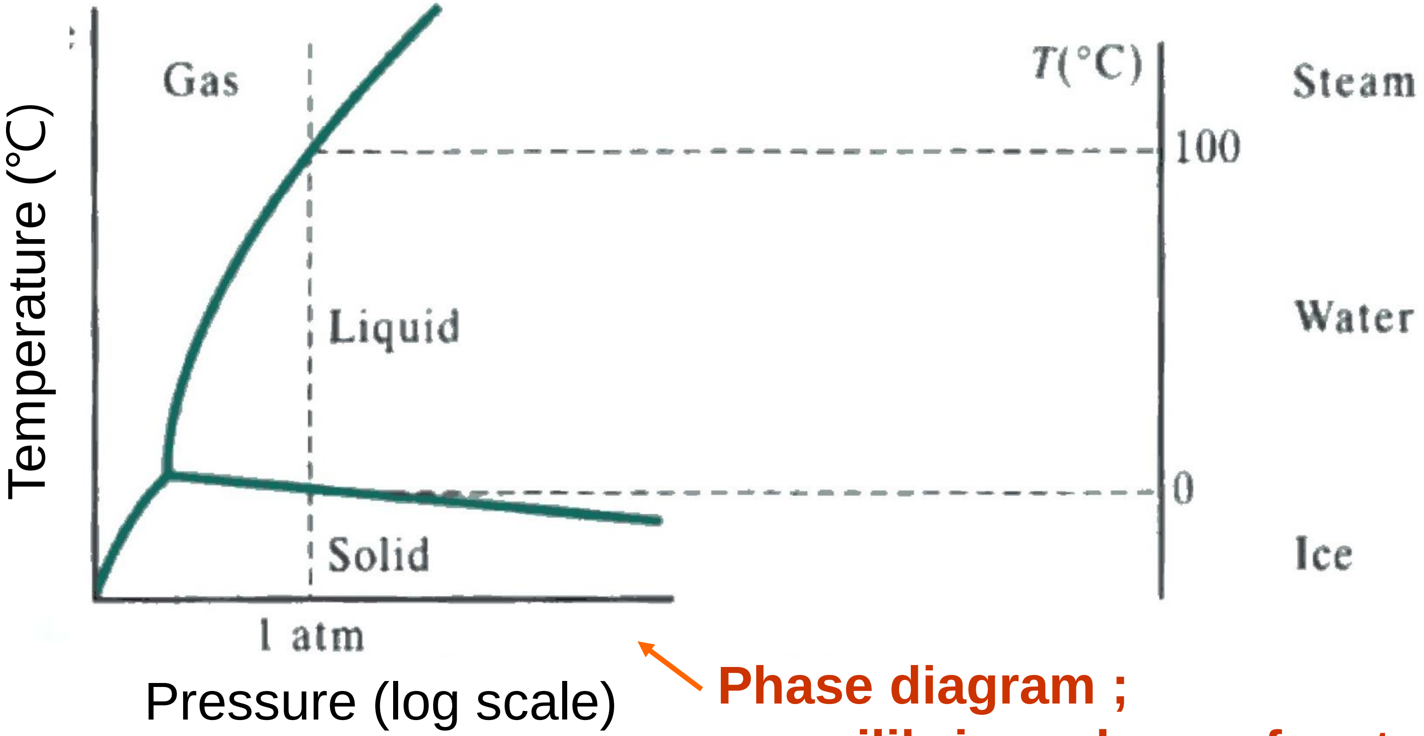
챌린저호 (1986)



컬럼비아호 (2003)

What is Phase?

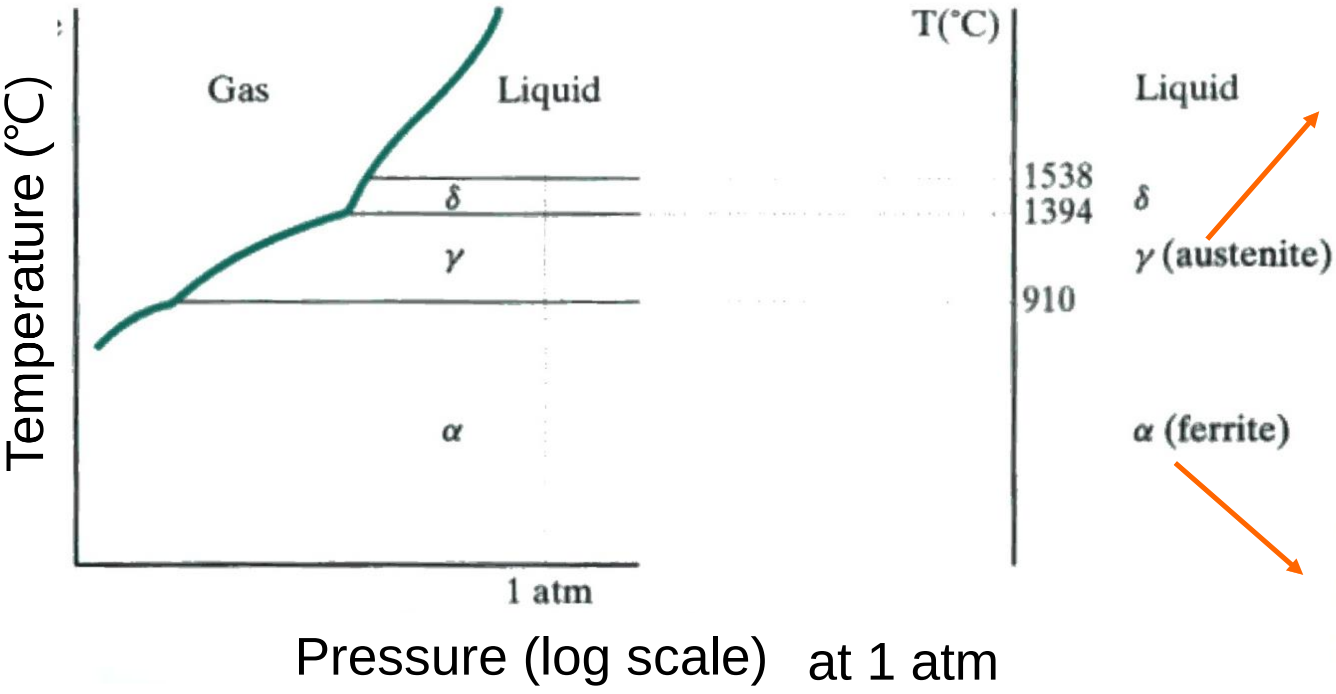
- A phase is a chemically and structurally homogeneous portion of the microstructure.

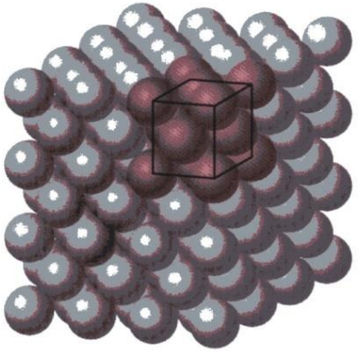


Phase diagram ;
equilibrium phase of material

Phase Transformation of Iron and Atomic Migration

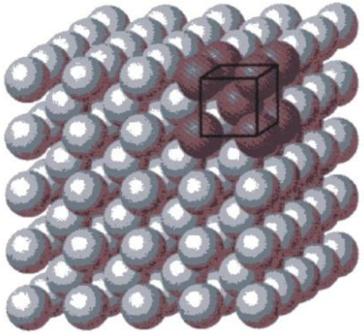
Iron





Face-Centered Cubic

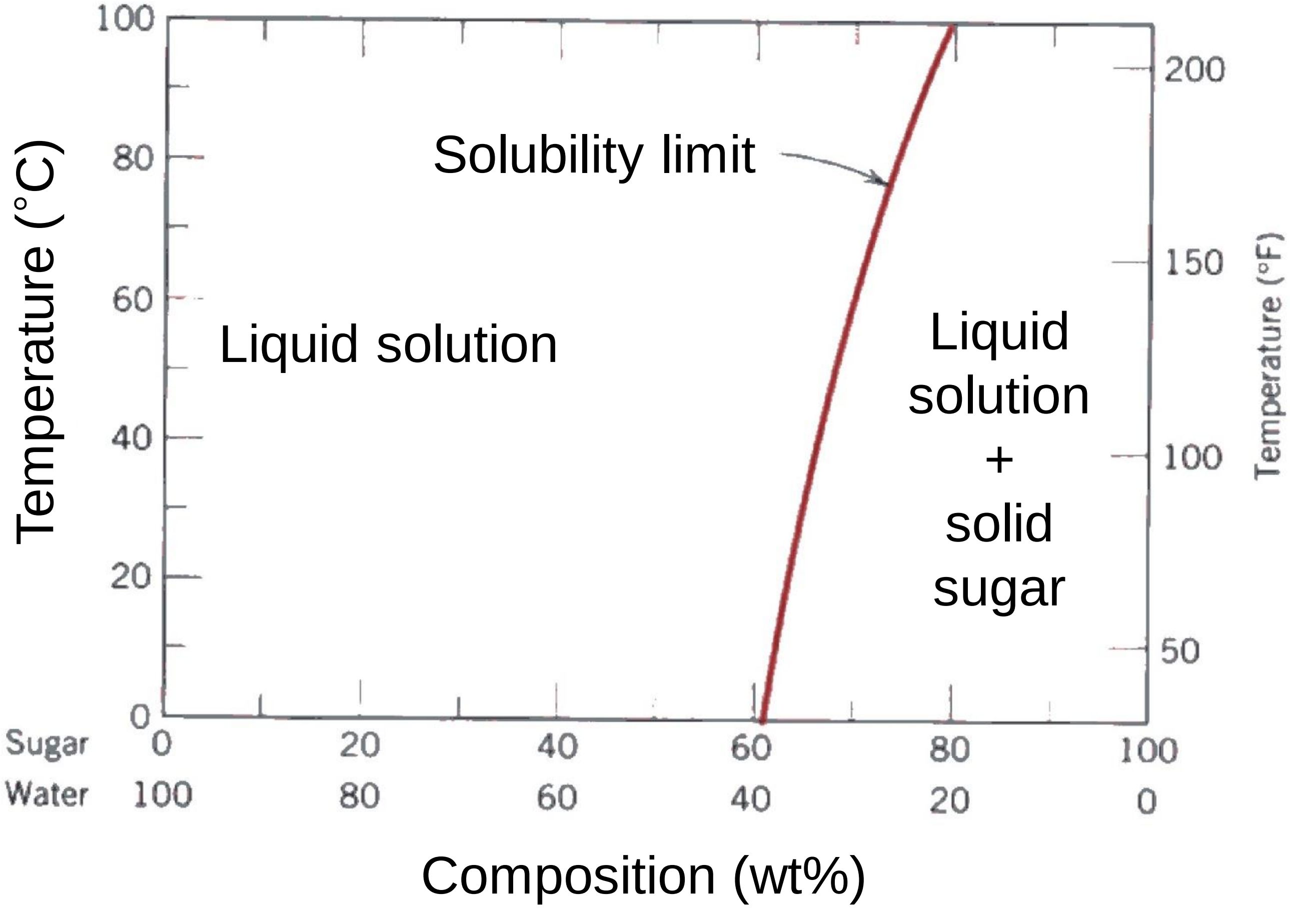
Atomic Migration



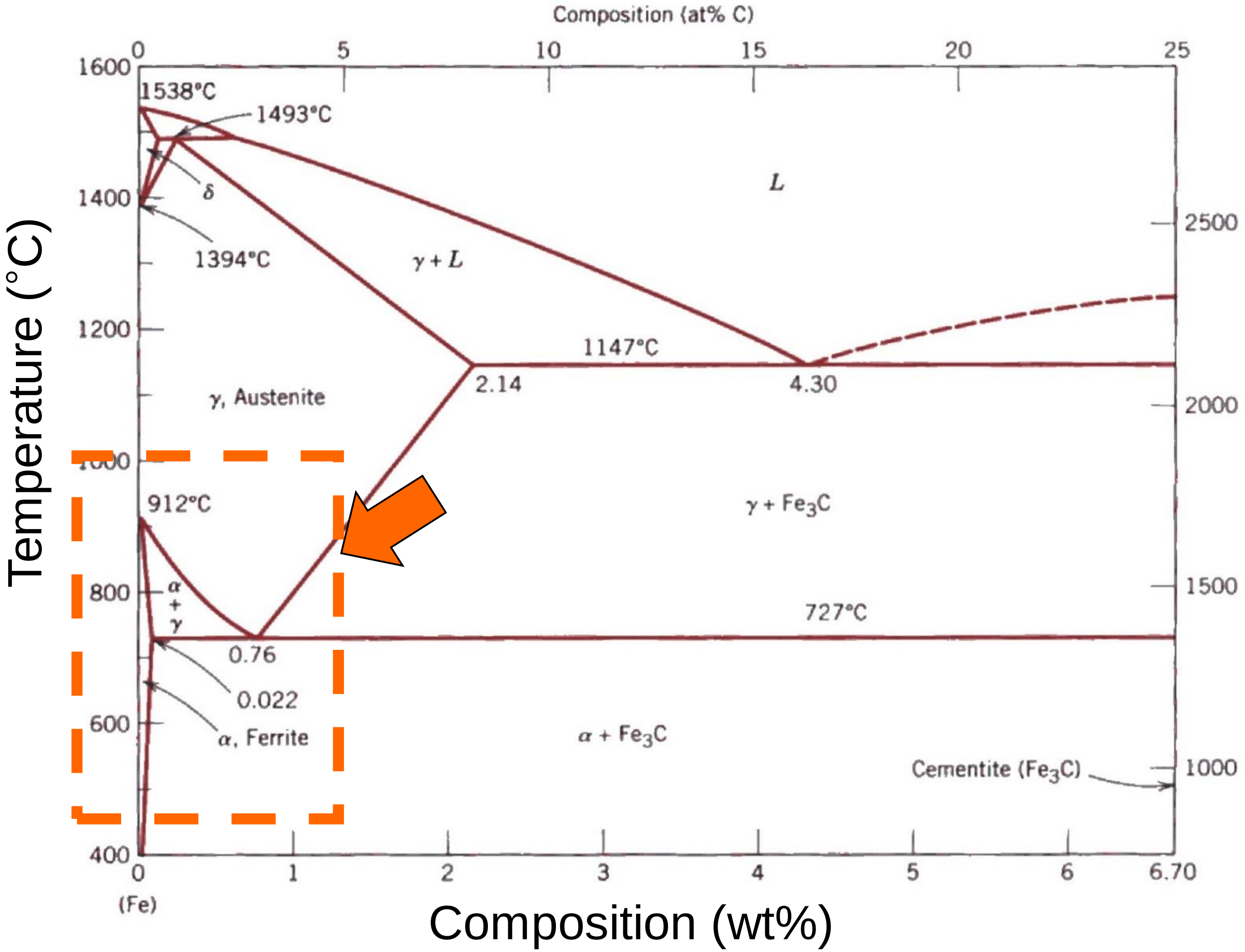
Body-Centered Cubic

Phase Diagram of Temperature – Composition ;

More useful in materials science & engineering

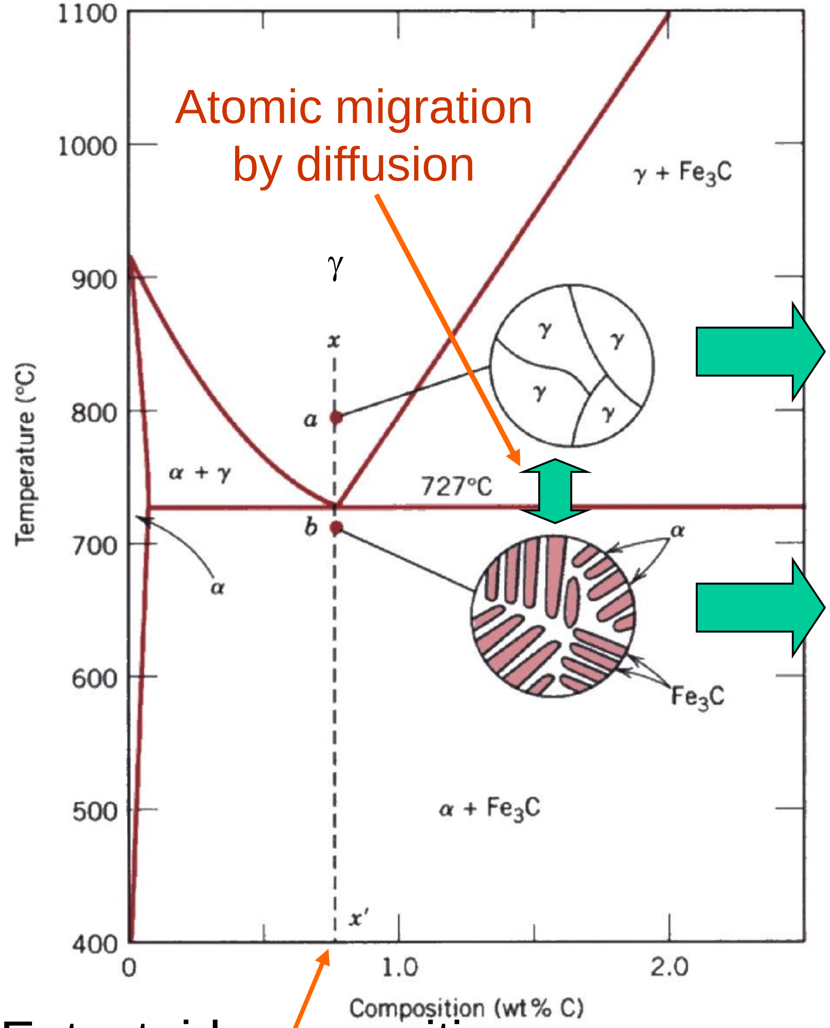


Phase Diagram of Iron–Carbon Alloy

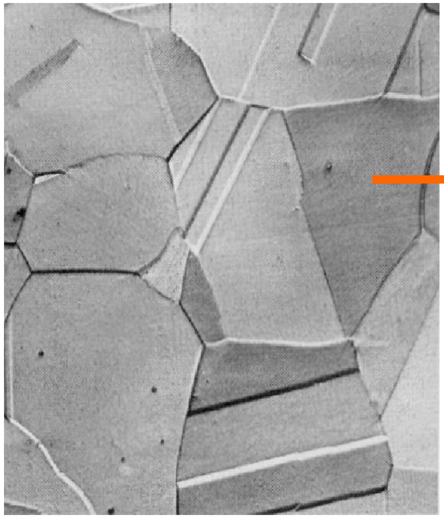


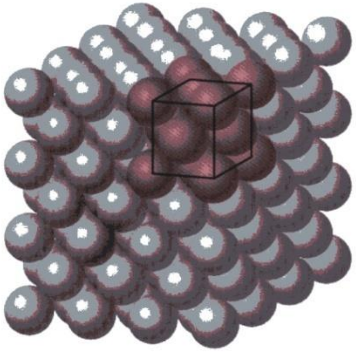
Equilibrium Phases of Iron-Carbon Alloy

Atomic migration by diffusion



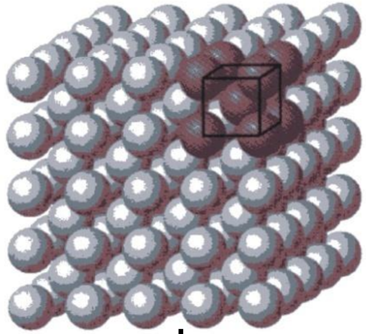
Eutectoid composition





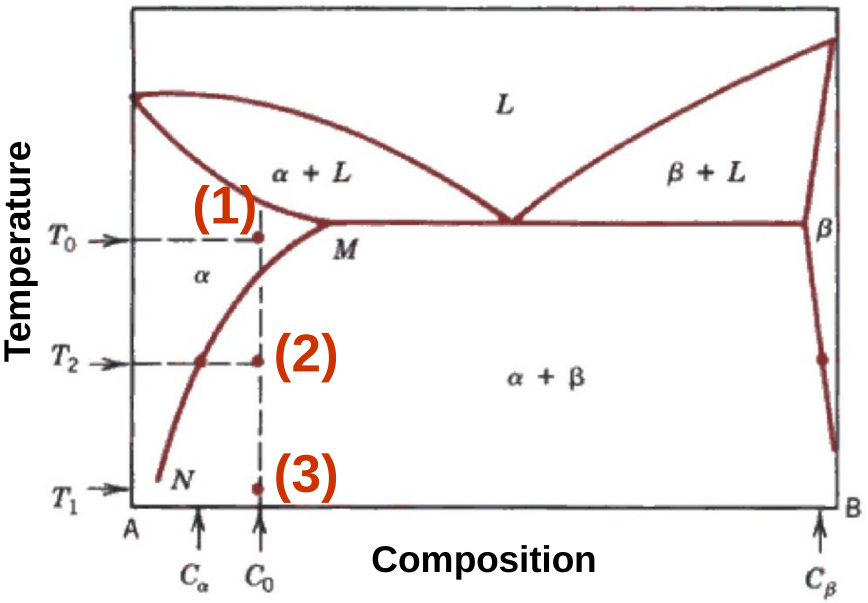
γ phase (FCC)

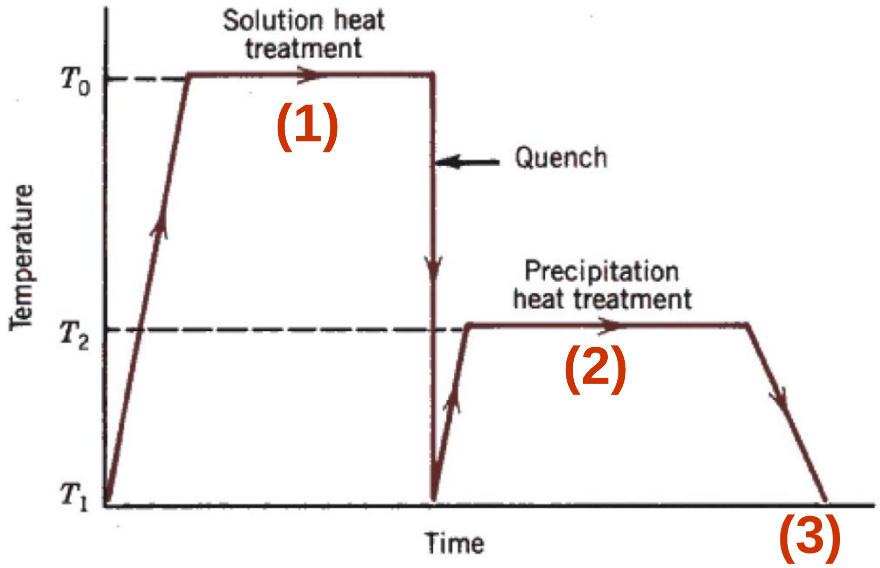
Fe_3C phase

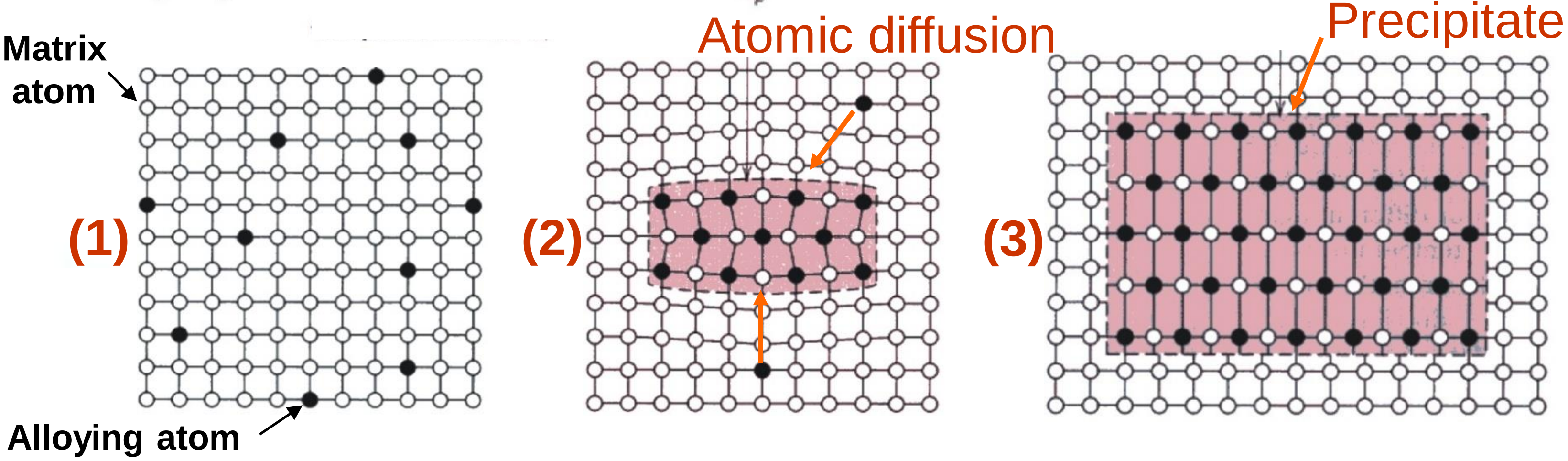


α phase (BCC)

Mechanism of Precipitation







Effect of Second Phase particle on Mechanical Property

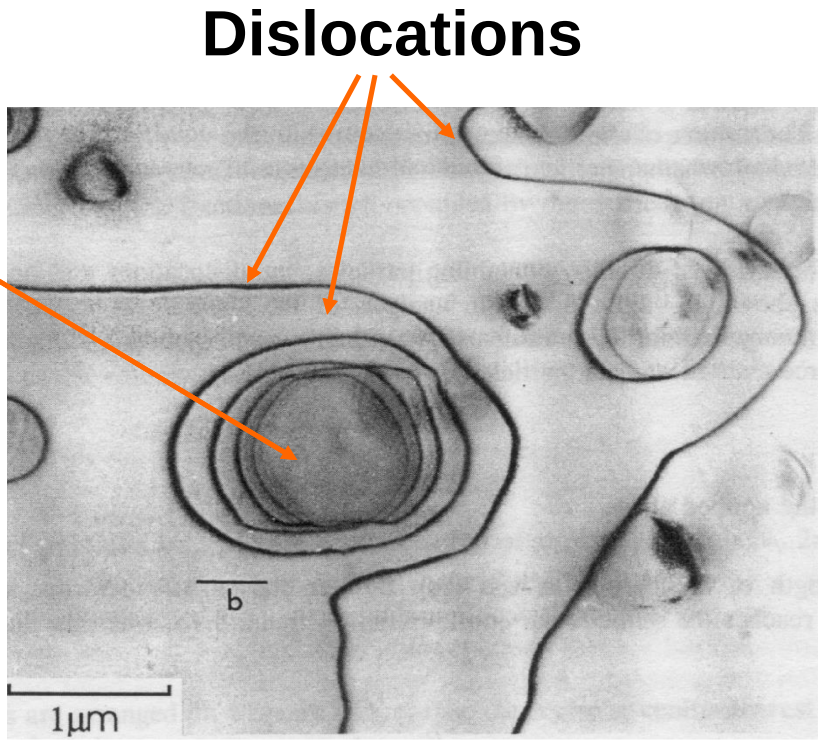
Second phase particle in matrix material

↓

Obstacle of dislocation slip & grain growth

↓

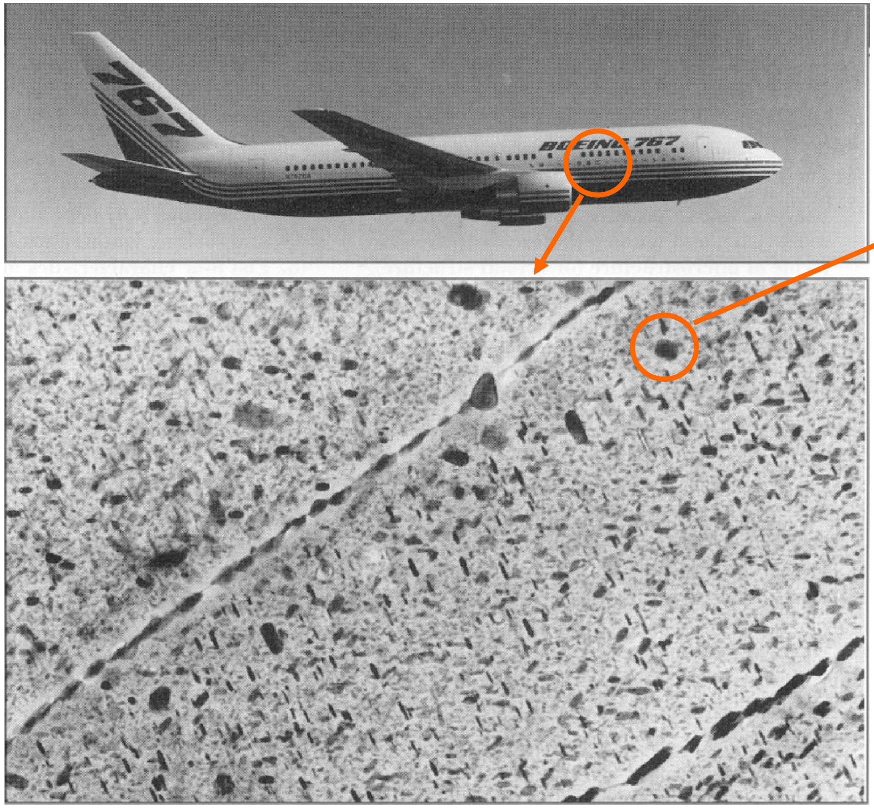
High strength



Ni$_3$Si 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

↓

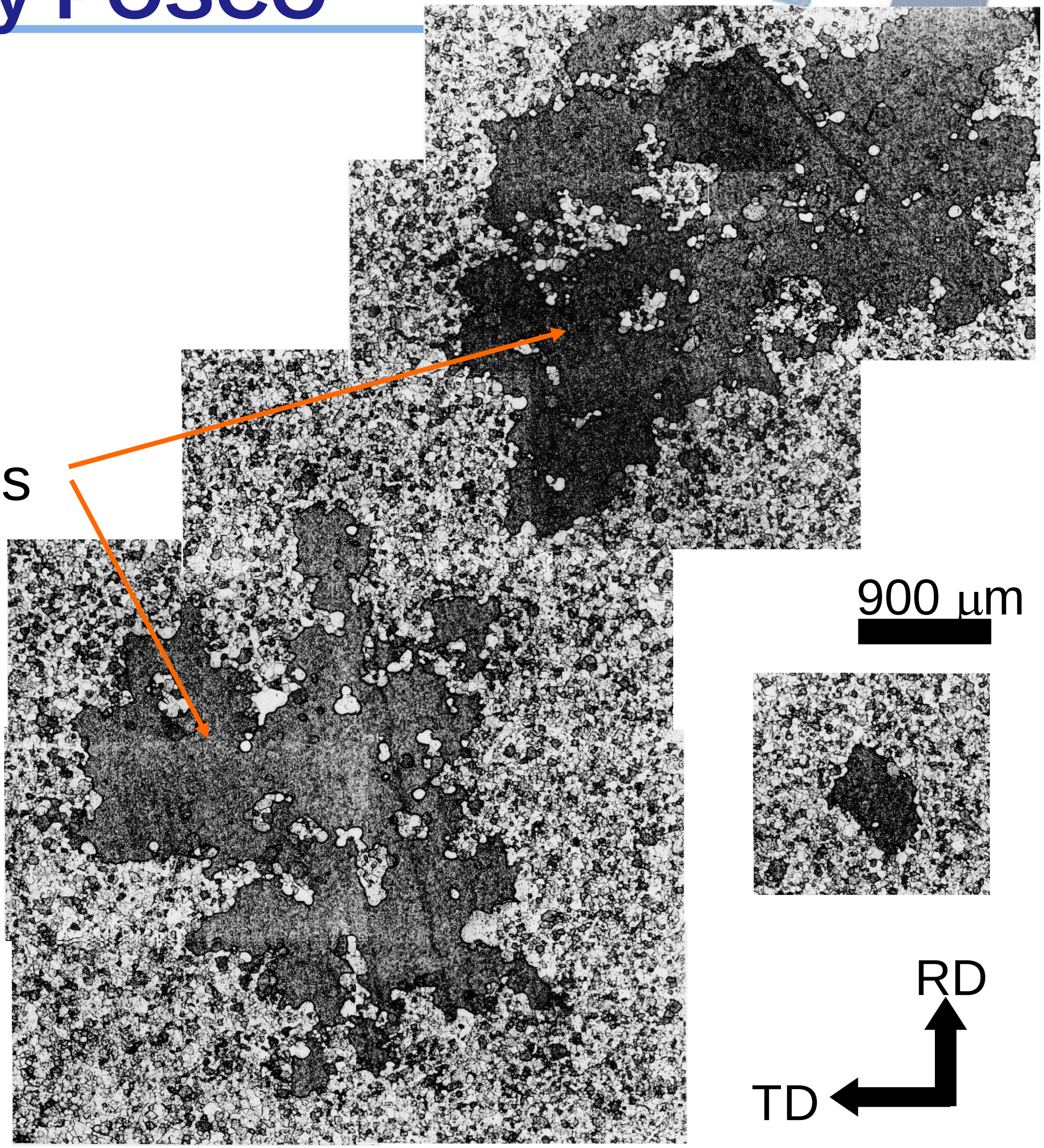
Hindering dislocation slip

↓

High strength

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

Abnormally grown grains with Goss texture

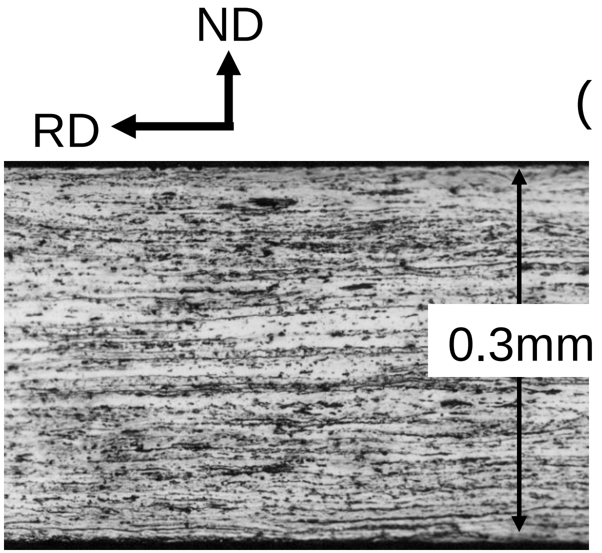


Control of grain growth

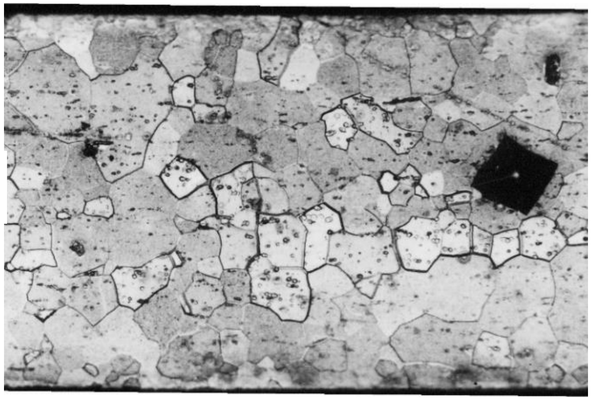
Control of magnetic property

Observations of Grain Structure & Second – phase particles using optical microscope

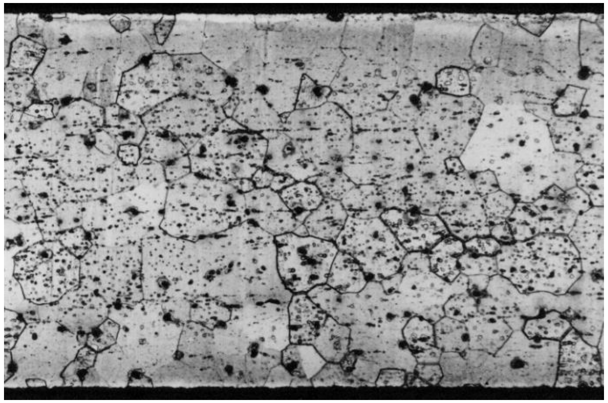
(longitudinal-sectional view)



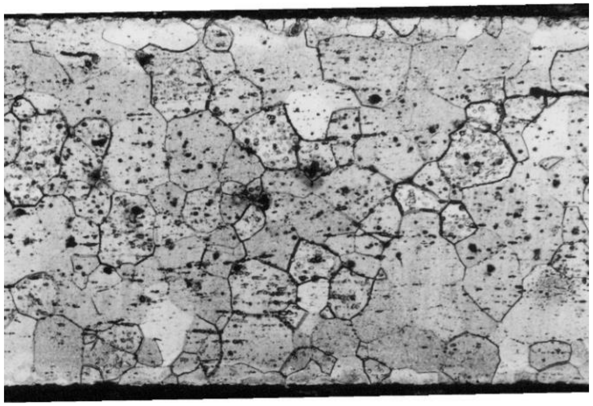
Deformed matrix

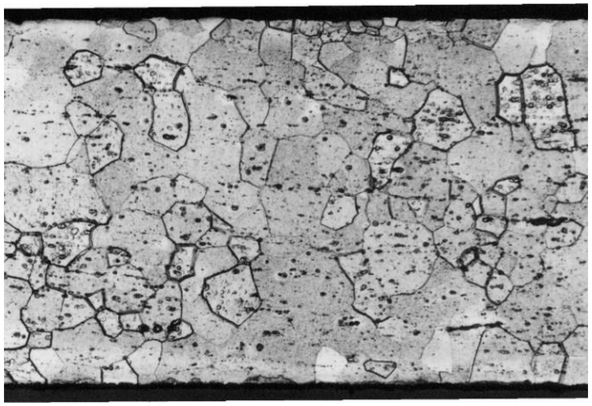


Primary recrystallized (860°C)

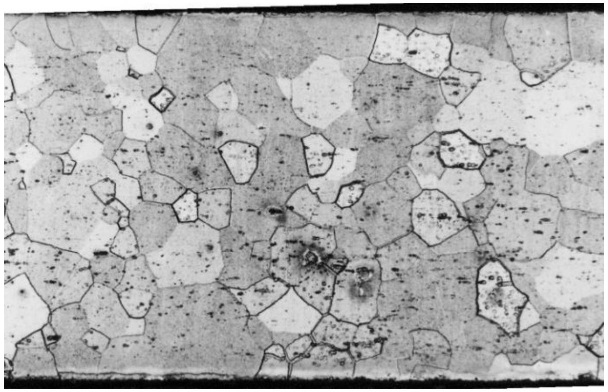


900°C



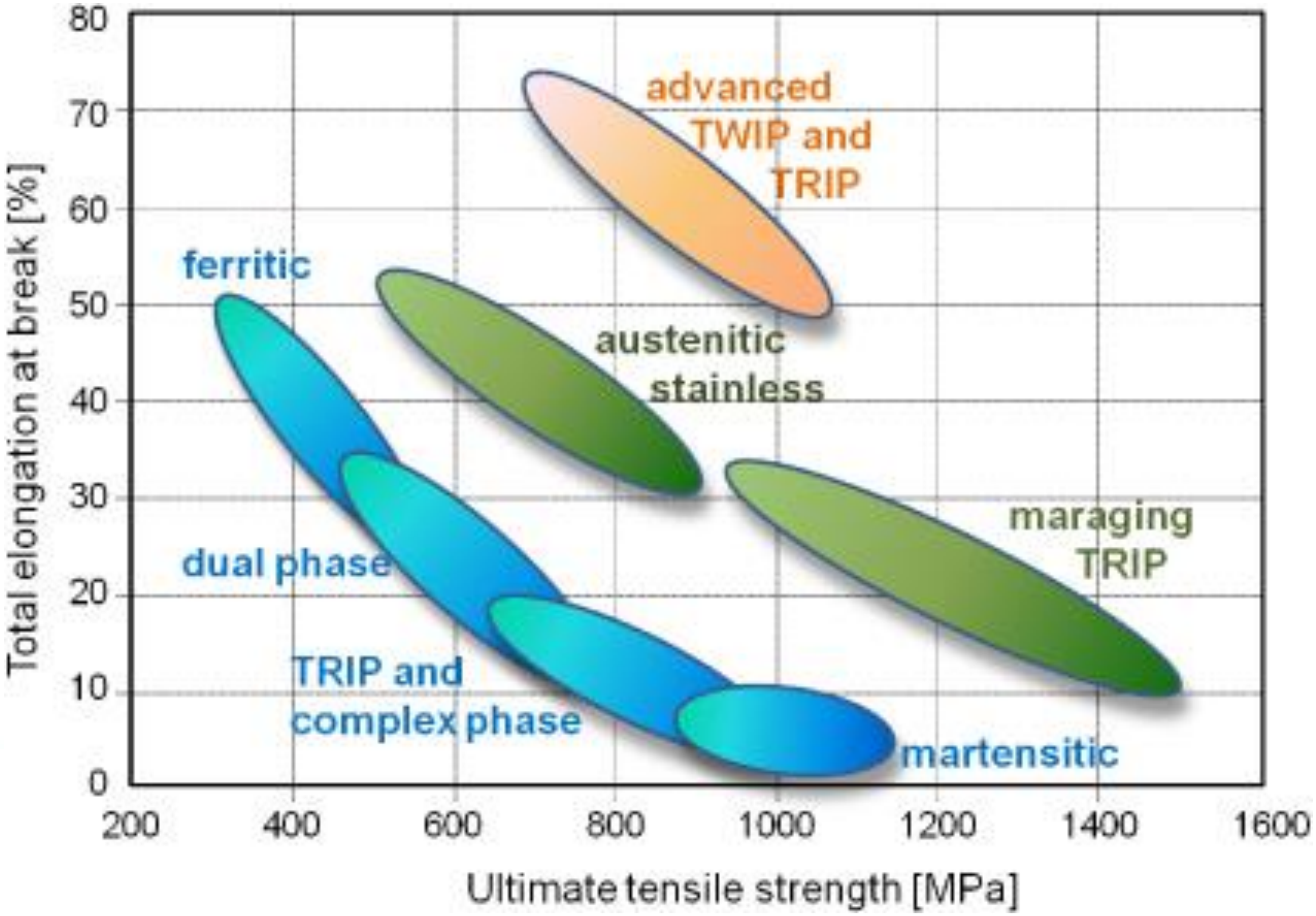


1000°C



1050°C

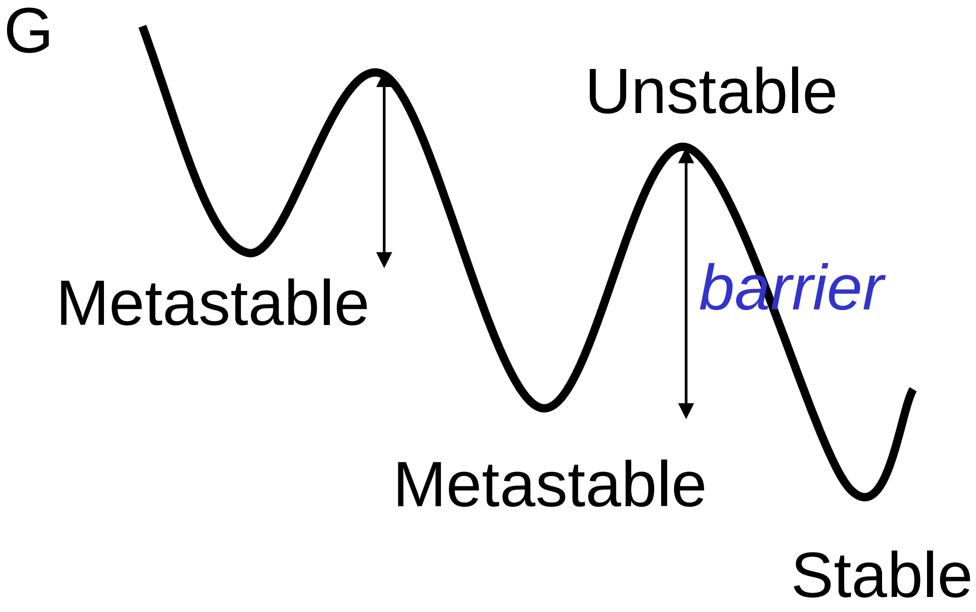
Advanced Steels: TRIP / TWIP (transition/twinning-induced plasticity)



Understanding and Controlling Phase Transformation of Materials

Phase Transformation

- **Thermodynamics**
- **Kinetics**



Types of Phase Transformations

- ❖ **Diffusion- controlled phase transformation**
  - ✓ Generally long- distance atomic migration
    - Precipitation transformation
    - Eutectoid transformation
    - Etc

- ❖ **Diffusion less transformation**
  - ✓ Short- distance atomic migration
  - ✓ Martensitic transformation

Time-Dependency of Diffusion-Controlled Phase Transformation

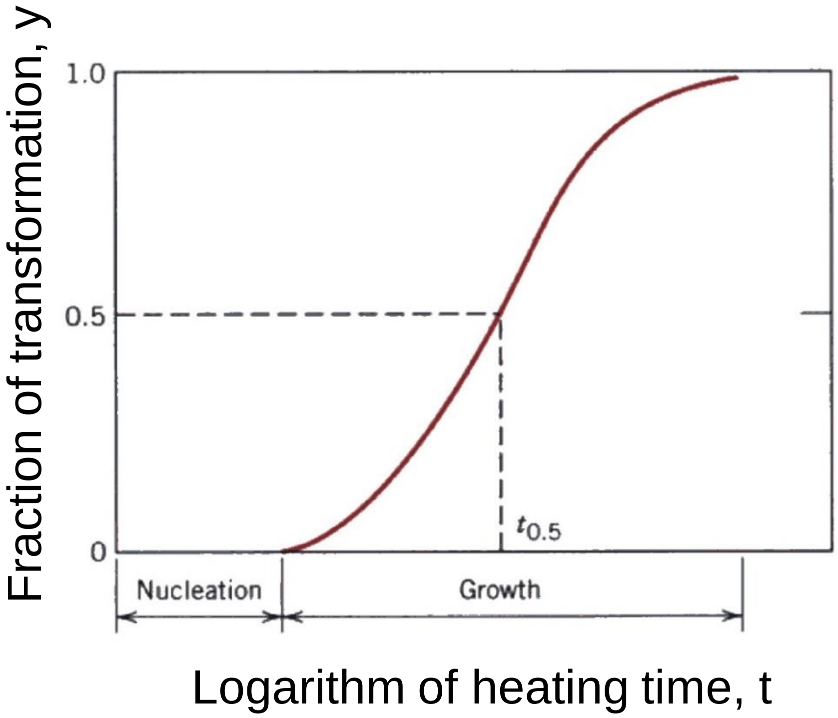
↓

Non-Equilibrium Phases

↓

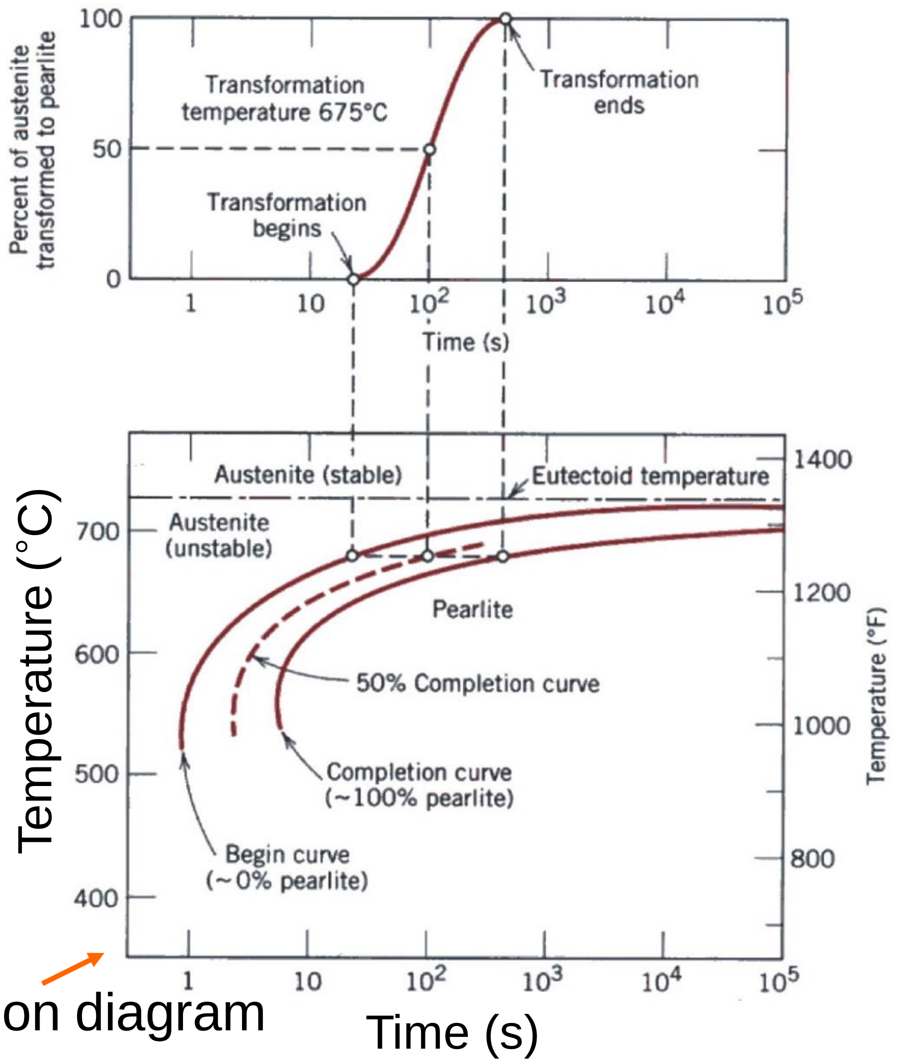
Need of Controlling
not only Temperature & Composition
but Cooling Rate

Transformation Kinetics and Isothermal Transformation Diagram



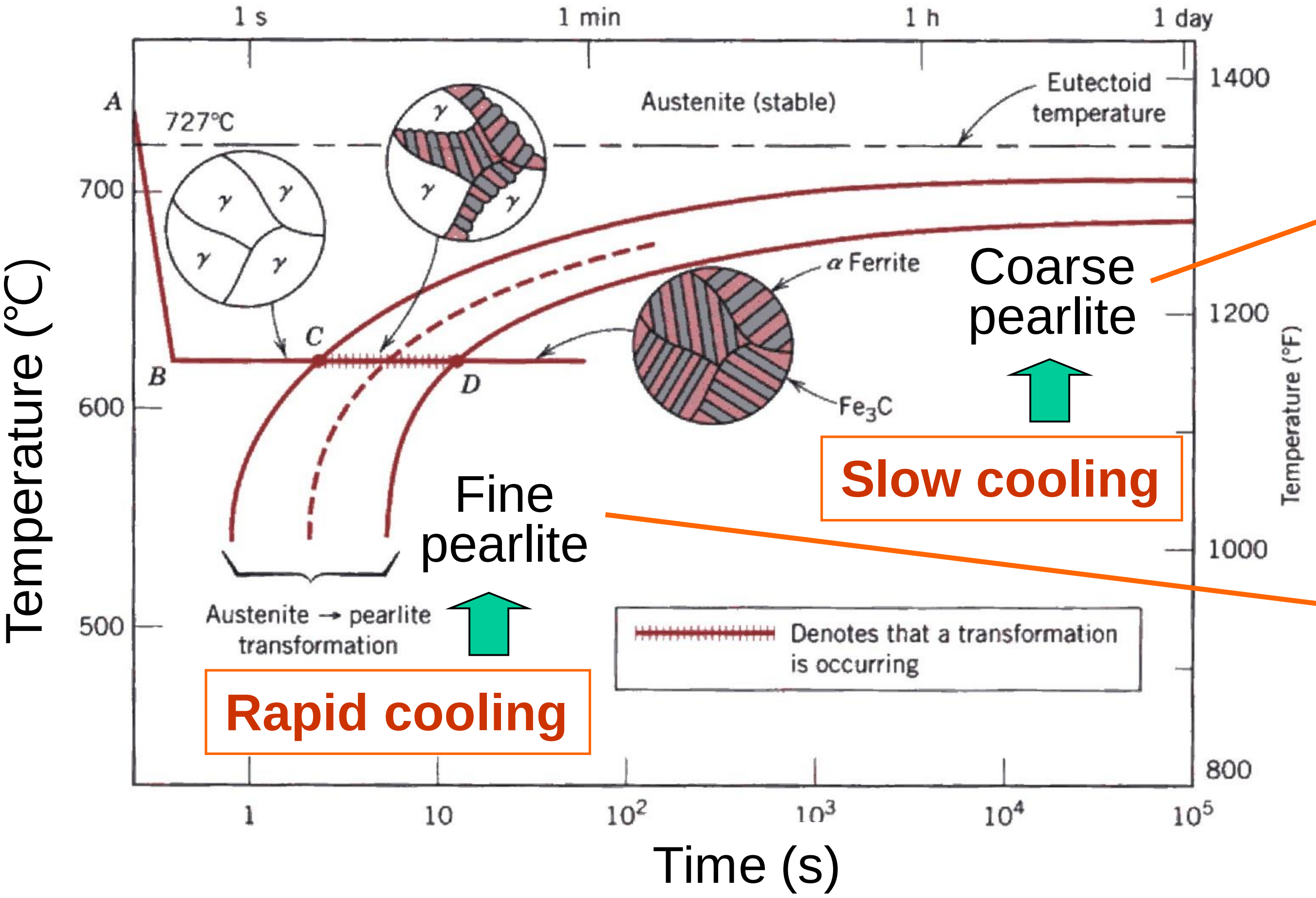
$y = \exp(-kt^n)$

Kinetics of diffusion-controlled solid-state transformation



Isothermal transformation diagram

Isothermal Transformation Diagram of a Eutectoid Iron-Carbon Alloy



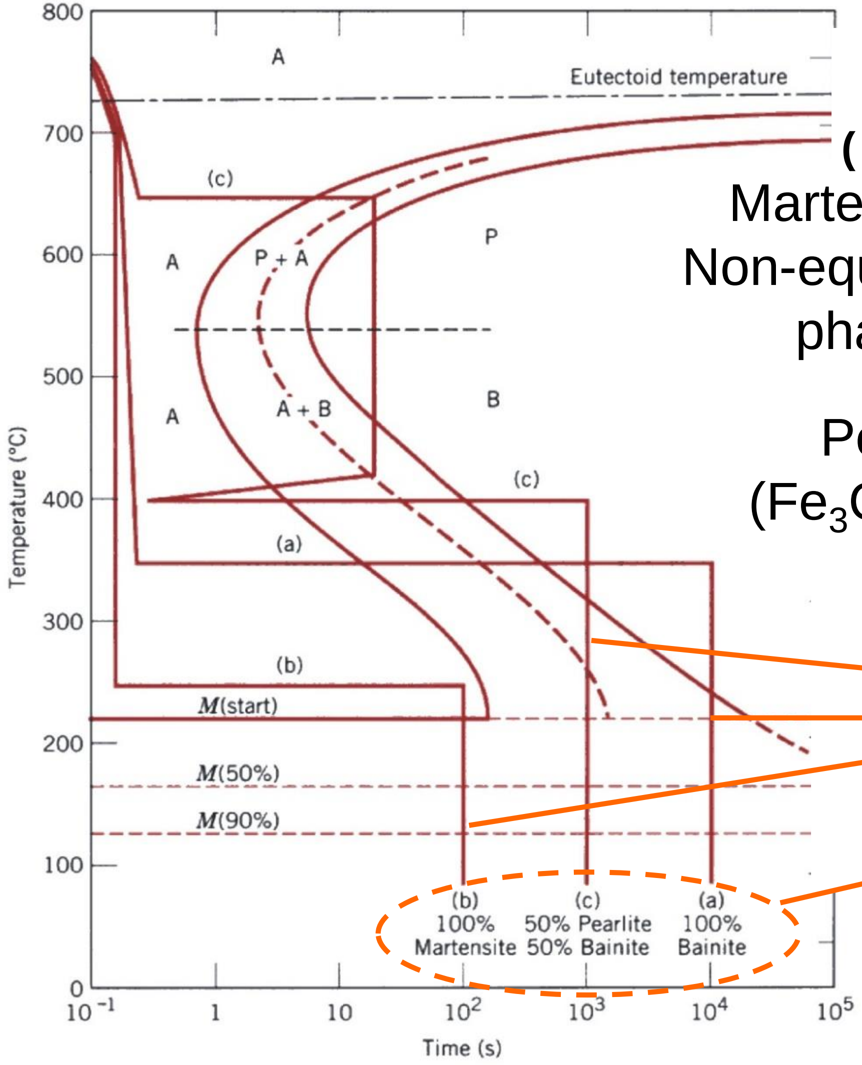
Coarse pearlite

Slow cooling

Fine pearlite

Rapid cooling

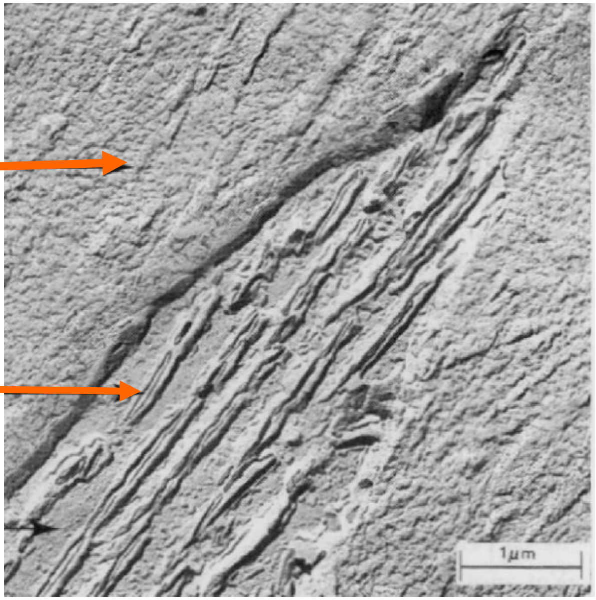
Control of Phases by Heat Treatment



(Very hard)

Martensite ;
Non-equilibrium
phase

Pearlite
(Fe_3C+ferrite)



Heat Treatment

Phase & Microstructure

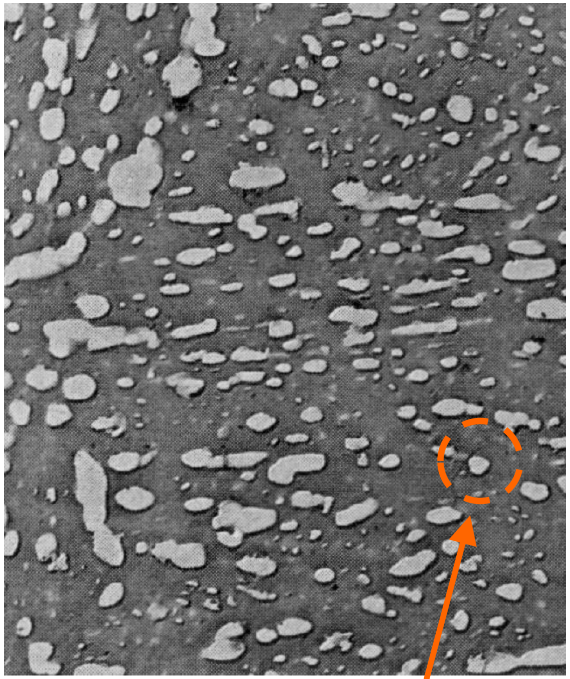
Properties of Material

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

Martensite

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

Proper heat treatment (tempering)



Tempered martensite

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

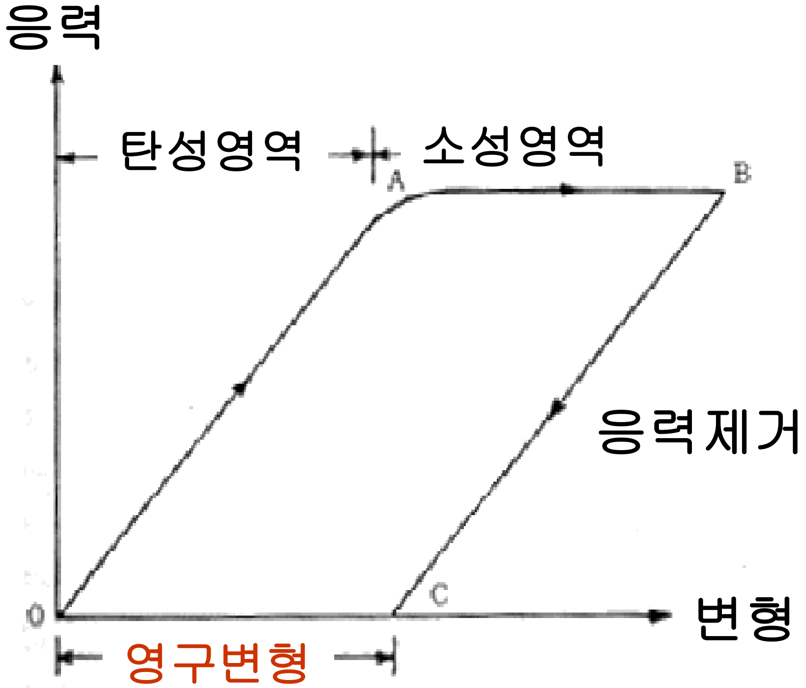
Diffusionless Transformation

Martensitic transformation in iron-carbon alloy

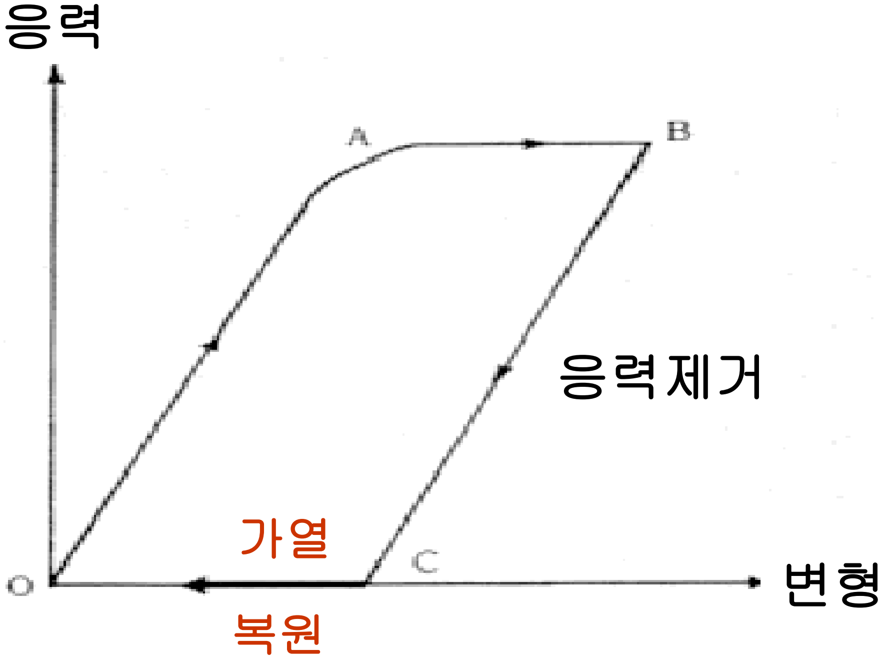
Martensitic transformation in Ni-Ti alloy ;
55~55.5wt%Ni-44.5~45wt%Ti (“Nitinol”)

Shape memory alloy

Difference of Deformation Behavior between Conventional Metals and Shape Memory Alloys

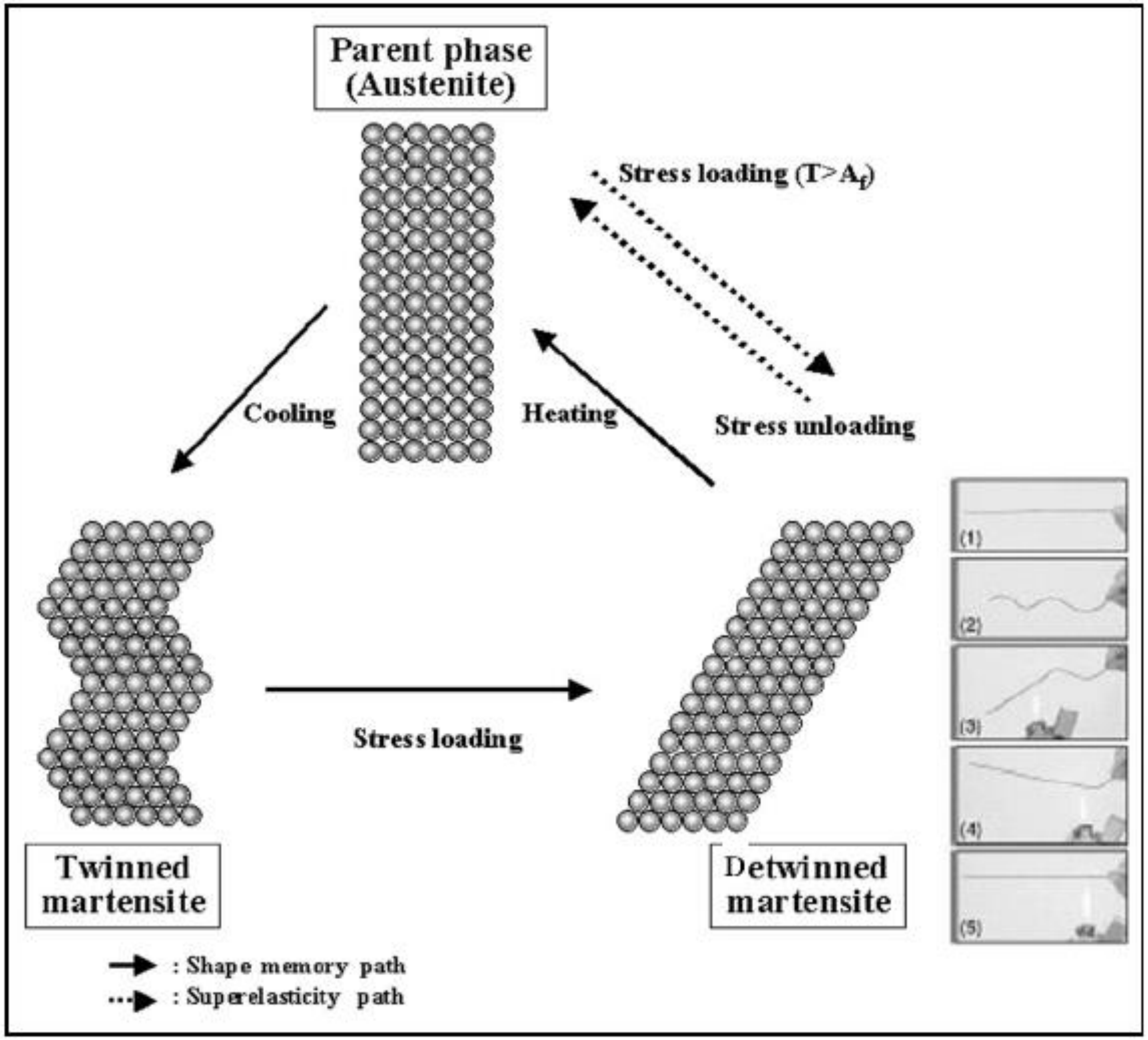


일반금속의 응력-변형 곡선

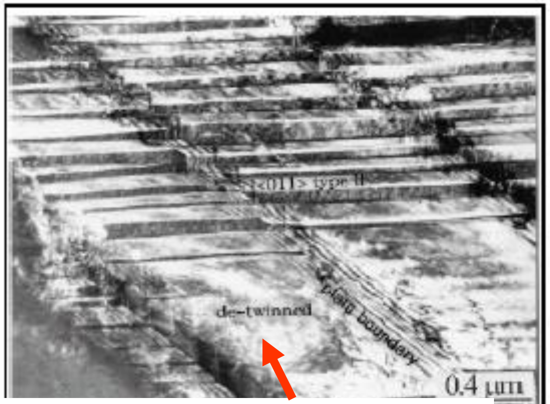


형상기억 합금의 응력-변형 곡선

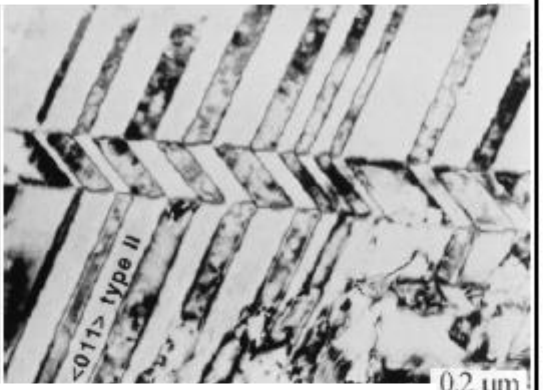
Principle of Shape Memory Alloys



Ni-Ti alloys



Detwinned martensite



Twinned martensite

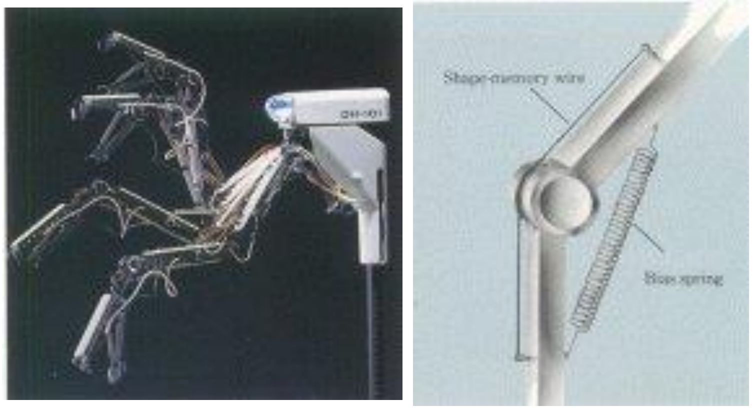
Y. Liu, Z. Xie et al, Scripta Materialia, 1999

Applications of Shape Memory Effect & Super-elasticity

형상기억합금으로 밸브를
개폐하는 커피메이커

물의 온도를 항상 일정하게
유지시켜주는 형상기억온수밸브

인체와의 접촉성이 좋고
외력에 의한 변형이 없는 안경테



로봇의 관절부위에 사용되어진
형상기억합금 작동소자

Ti-Ni형상기억합금을
이용한 휴대폰 안테나

Contents in Phase Transformation

- **Thermodynamics (Ch1)**
- **Kinetics- Diffusion (Ch2)**
- **Microstructure- Interface, Grain structure (Ch3)**
- **Liquid → Solid (Ch4)**
- **Solid → Solid (Diffusional) (Ch5)**
- **Solid → Solid (Diffusionless) (Ch6)**