2020 Fall

Introduction to Materials Science and Engineering

11. 17. 2020

Eun Soo Park

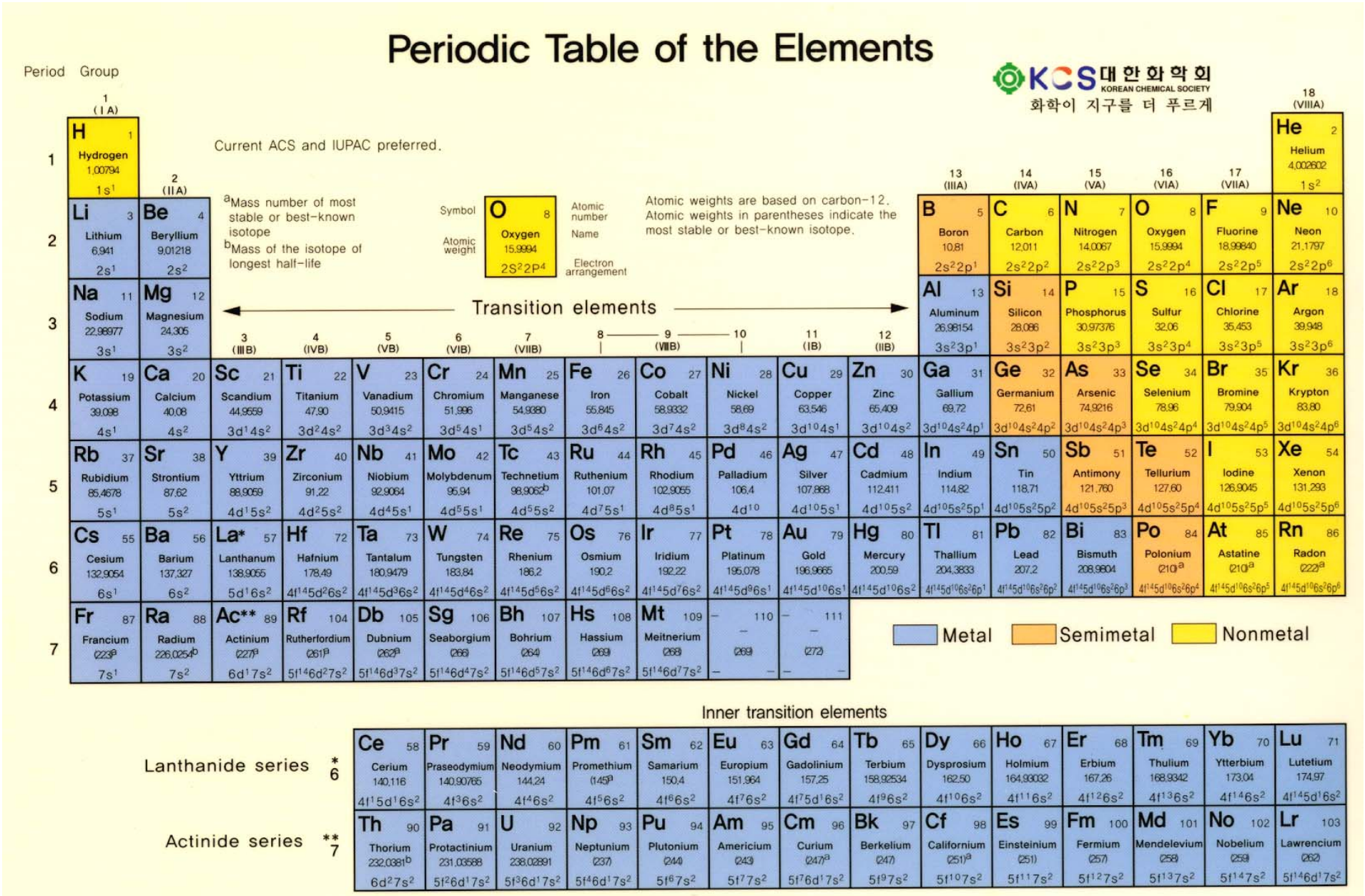
Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by appointment

Chapter 11:
Applications and Processing of Metal Alloys

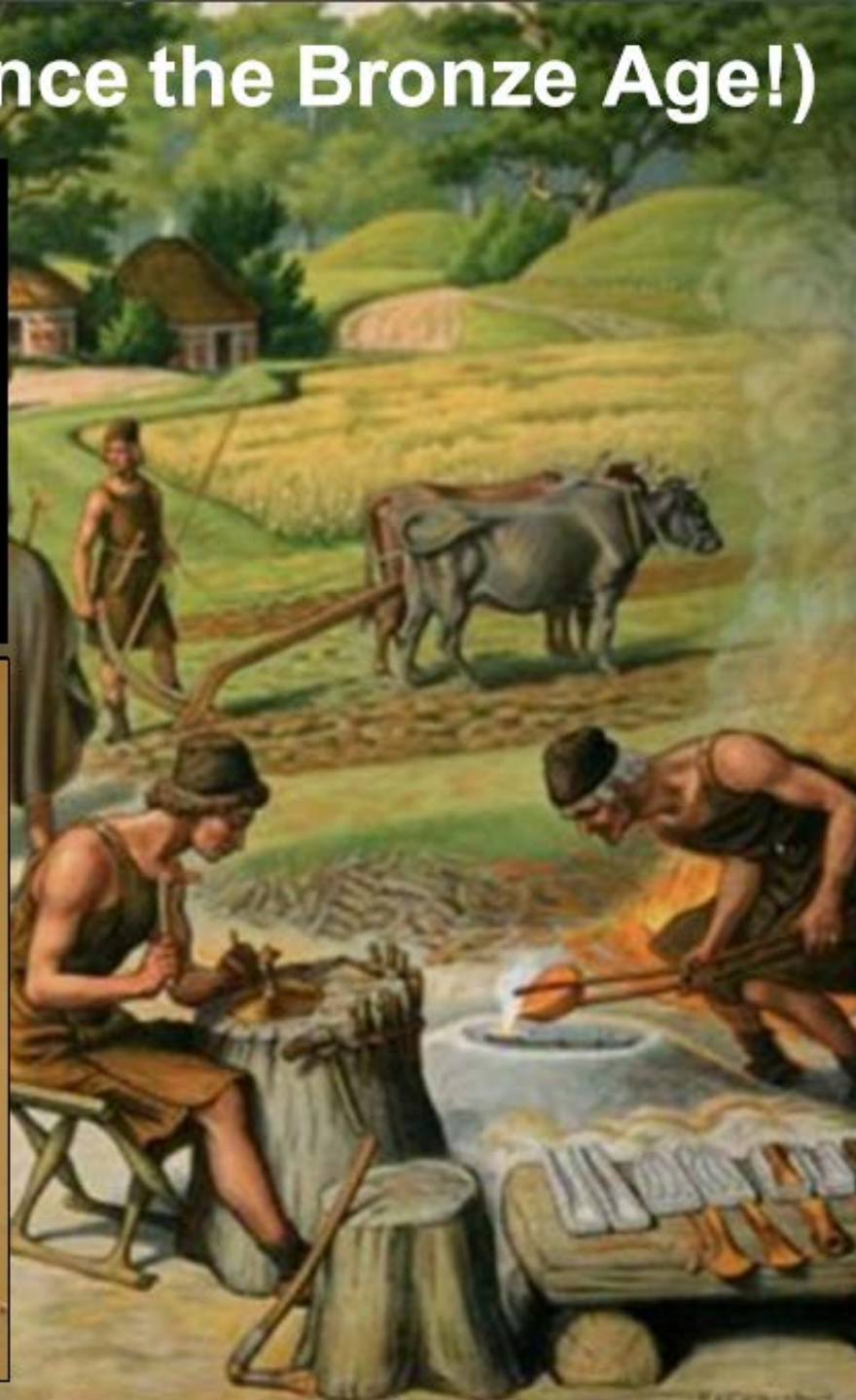
ISSUES TO ADDRESS...

- How are metal alloys classified and what are their common applications?
- What are some of the common fabrication techniques for metals?
- What heat treatment procedures are used to improve the mechanical properties of both ferrous and nonferrous alloys?

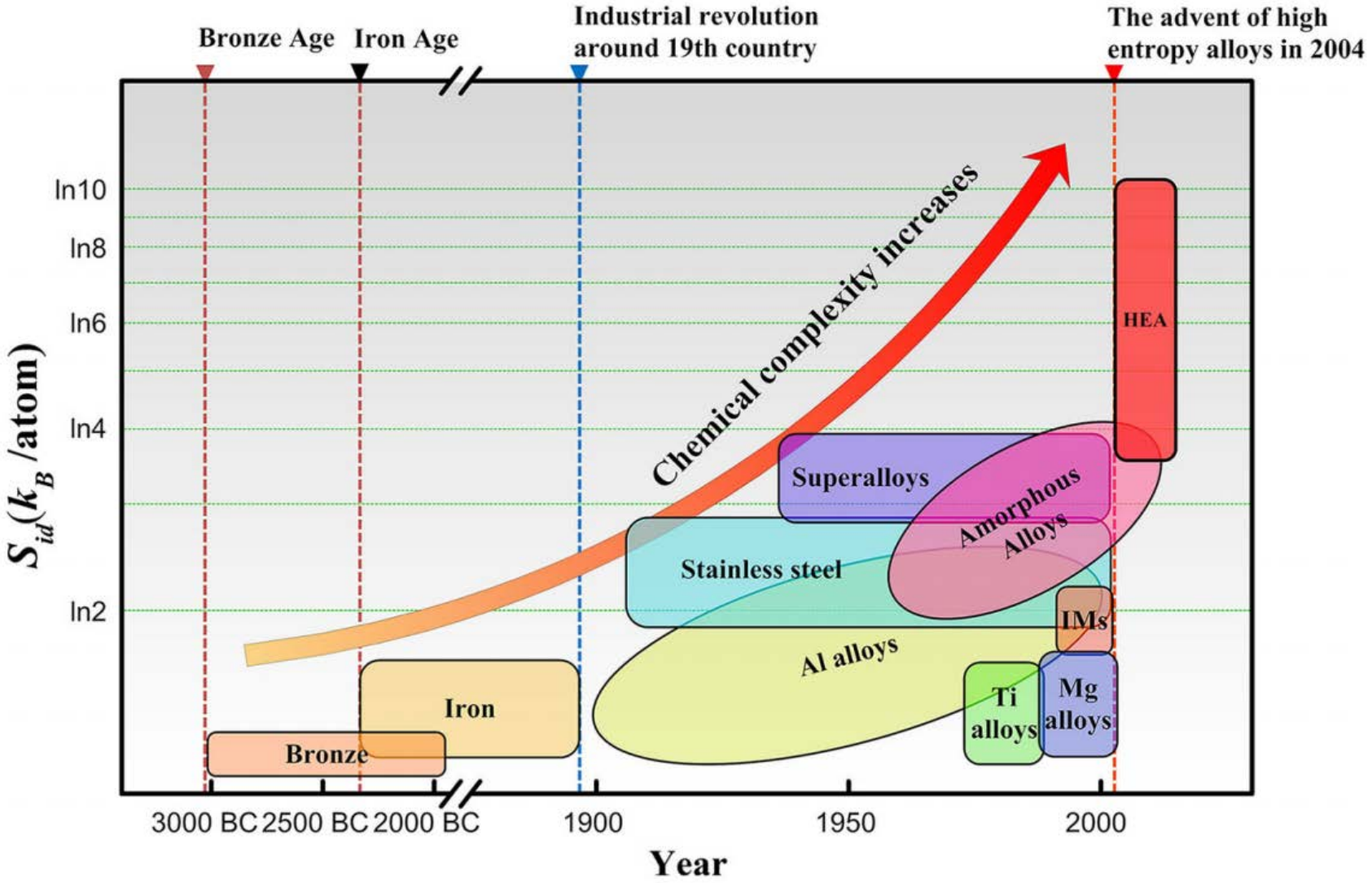
Materials Design-for-Properties : "Alloyed Pleasure"



Design-for-properties (since the Bronze Age!)

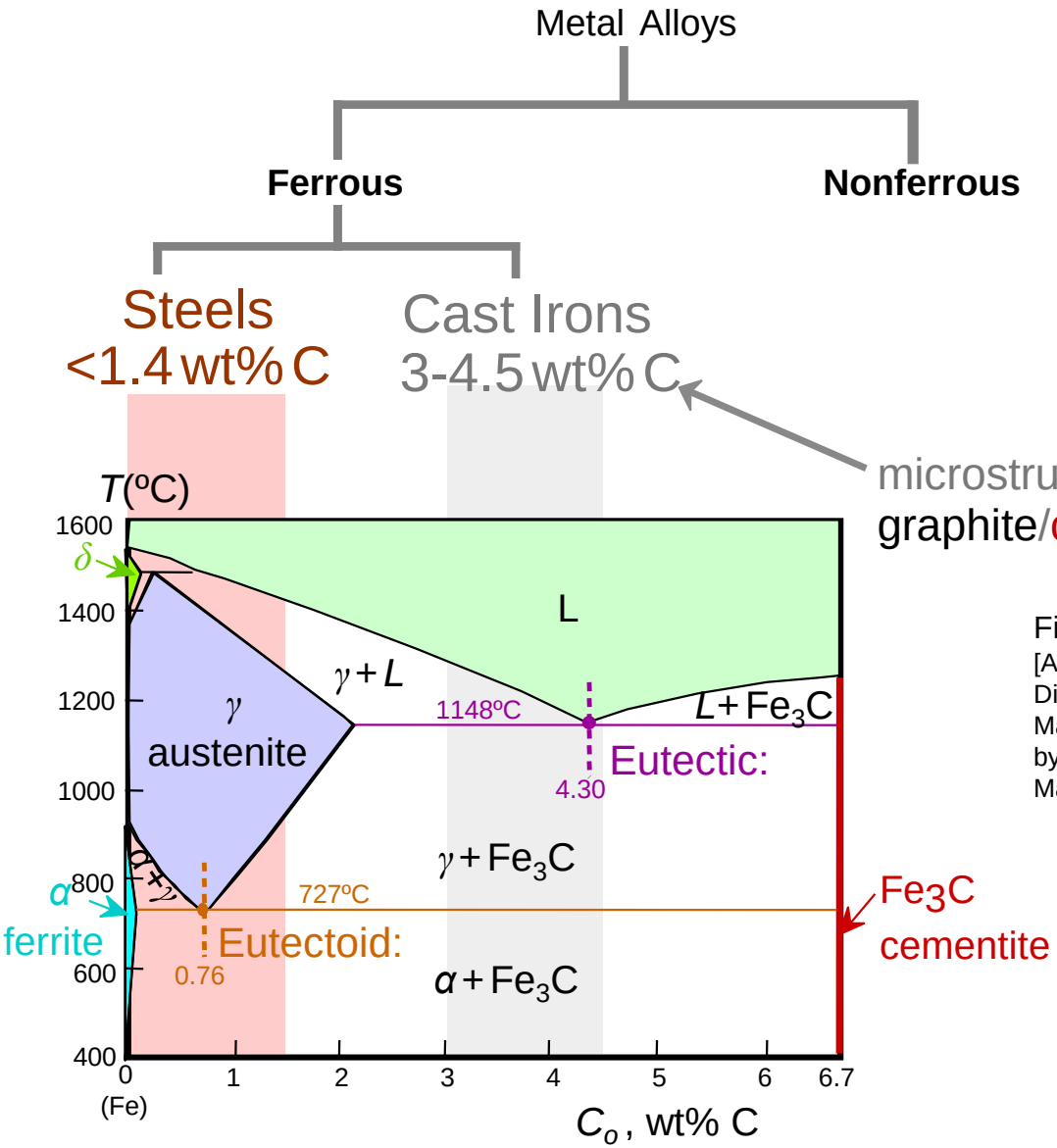


Materials Design-for-Properties : "Alloyed Pleasure"



Rising trend of alloy chemical complexity versus time. Note that ''IMs'' stands for intermetallics or metallic compounds and ''HEA'' for high-entropy alloy.

Classification of Metal Alloys

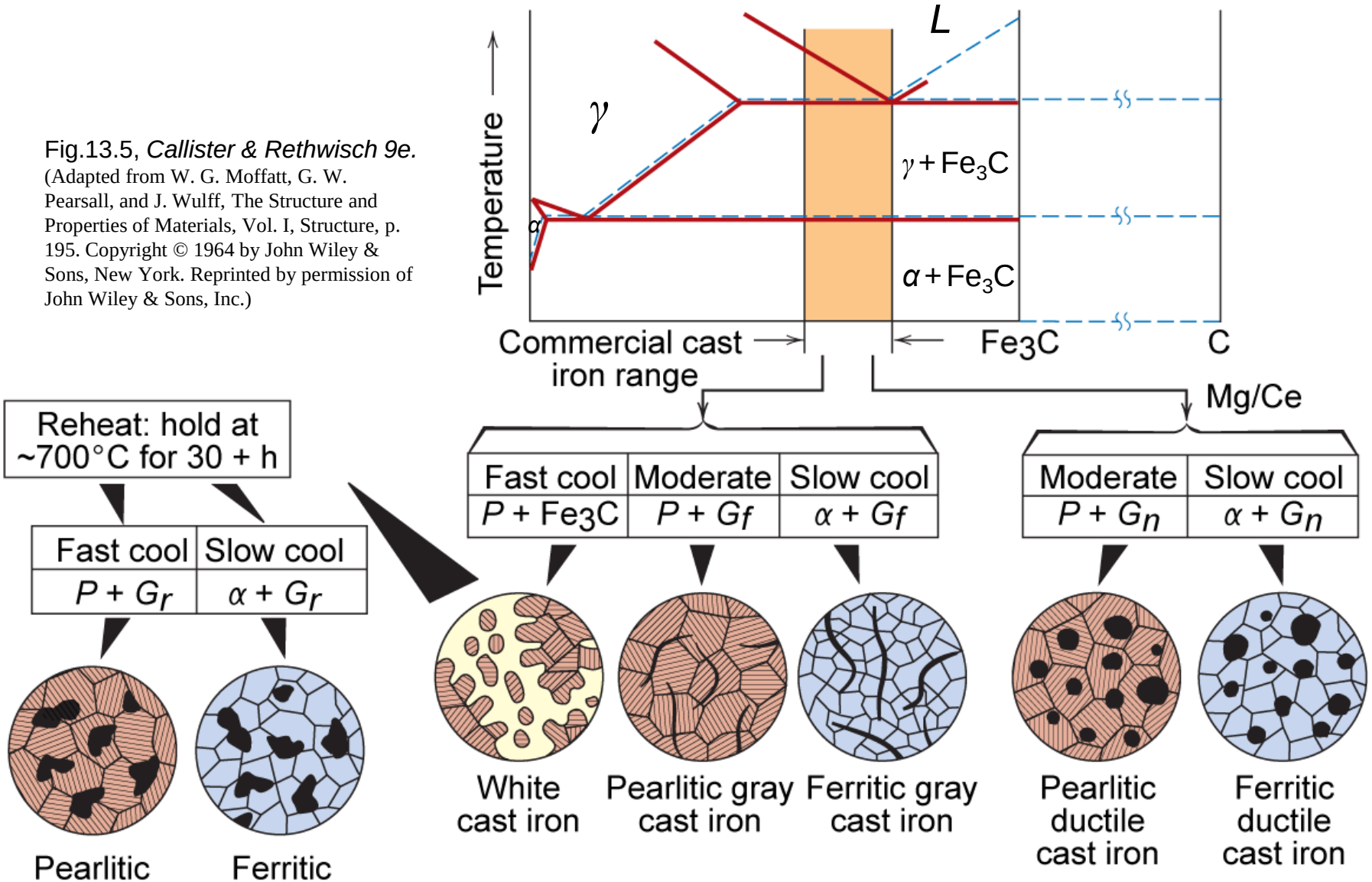


Adapted from Fig. 13.1, *Callister & Rethwisch 9e.*

Fig. 11.23, *Callister & Rethwisch 9e*. [Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

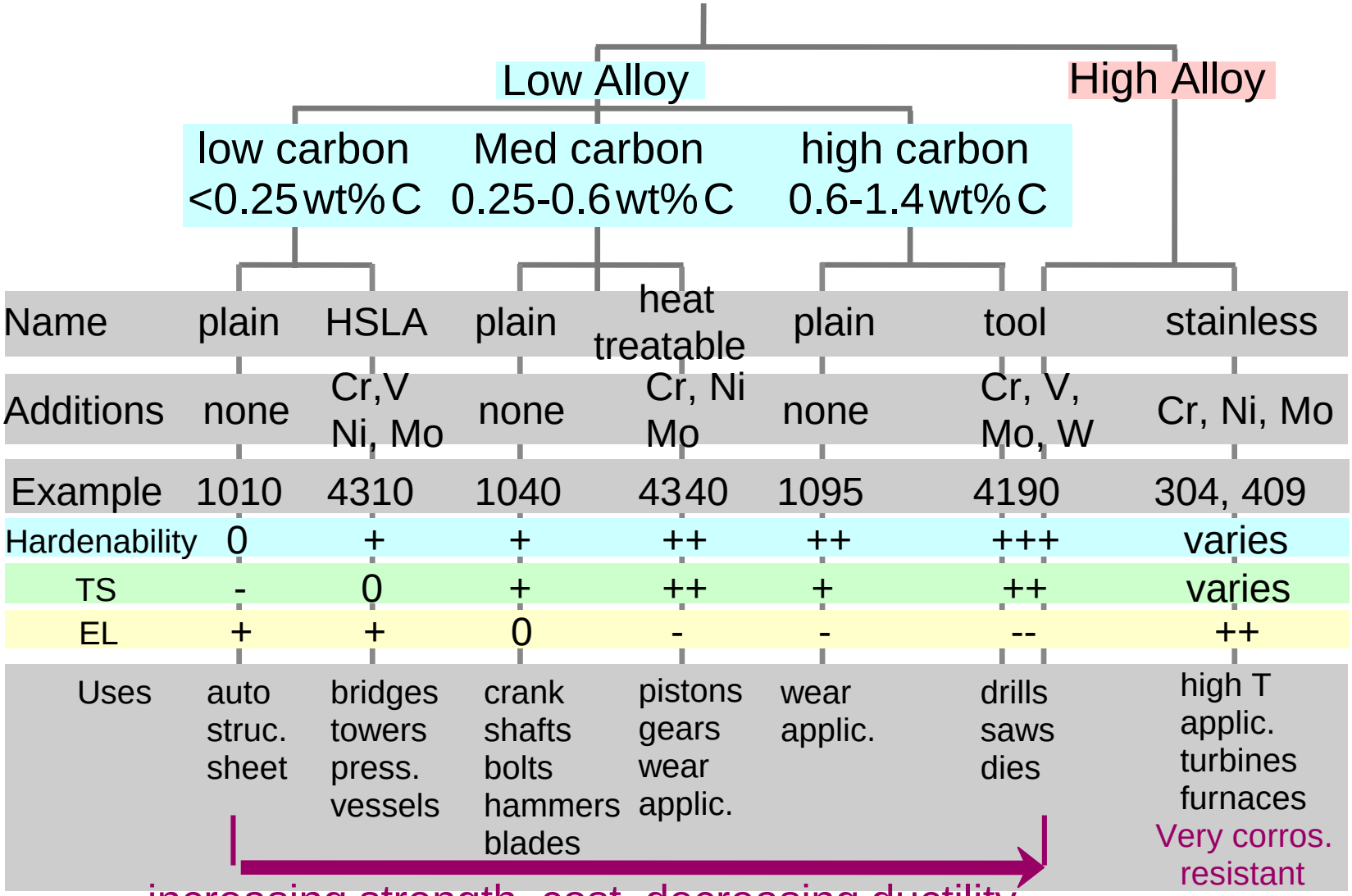
Production of Cast Irons

Fig.13.5, *Callister & Rethwisch 9e.*
(Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, The Structure and Properties of Materials, Vol. I, Structure, p. 195. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



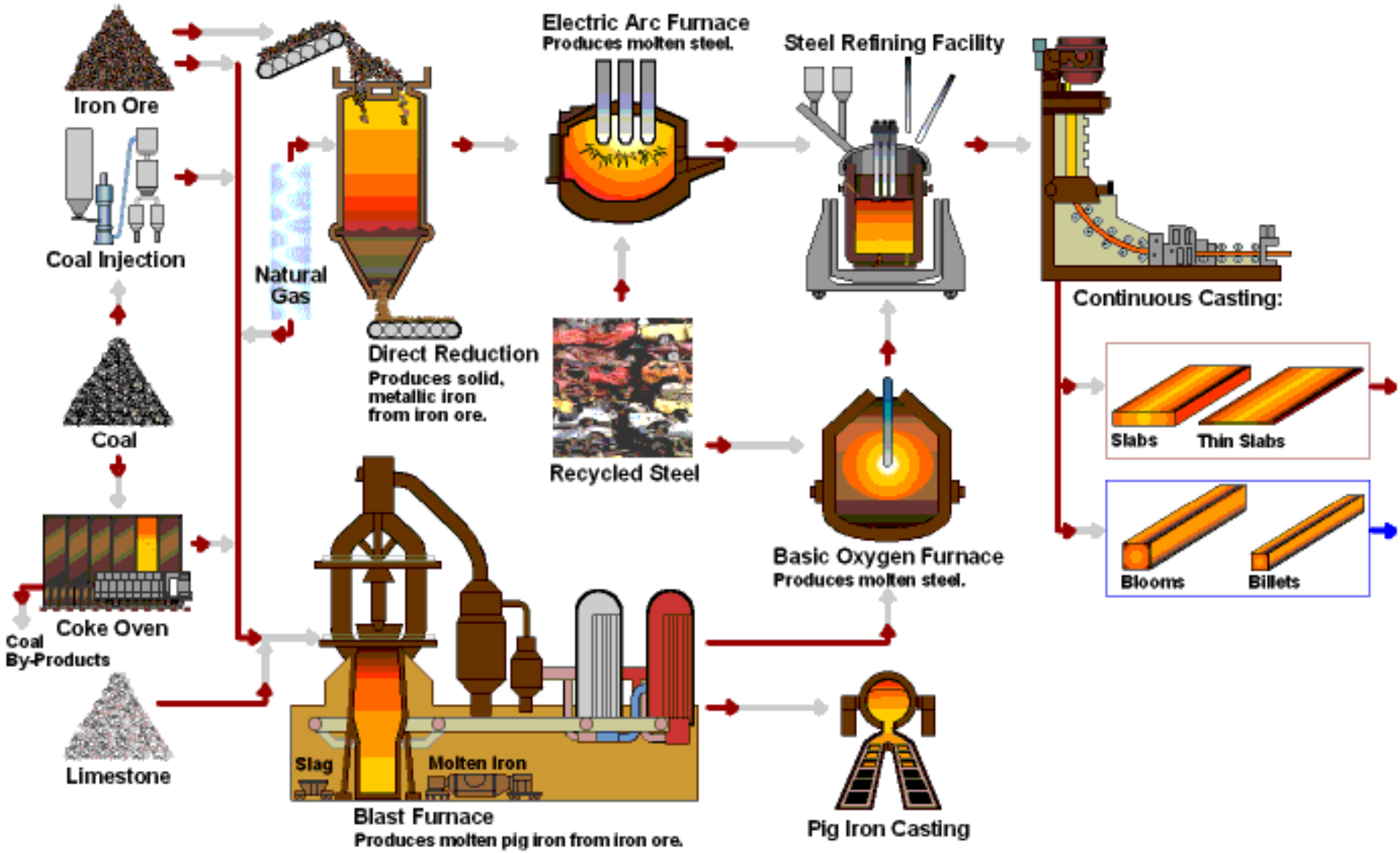
G_r (장미형 흑연), G_f (박편 흑연), G_n(구상흑연), P(펄라이트), α(페라이트)

Steels

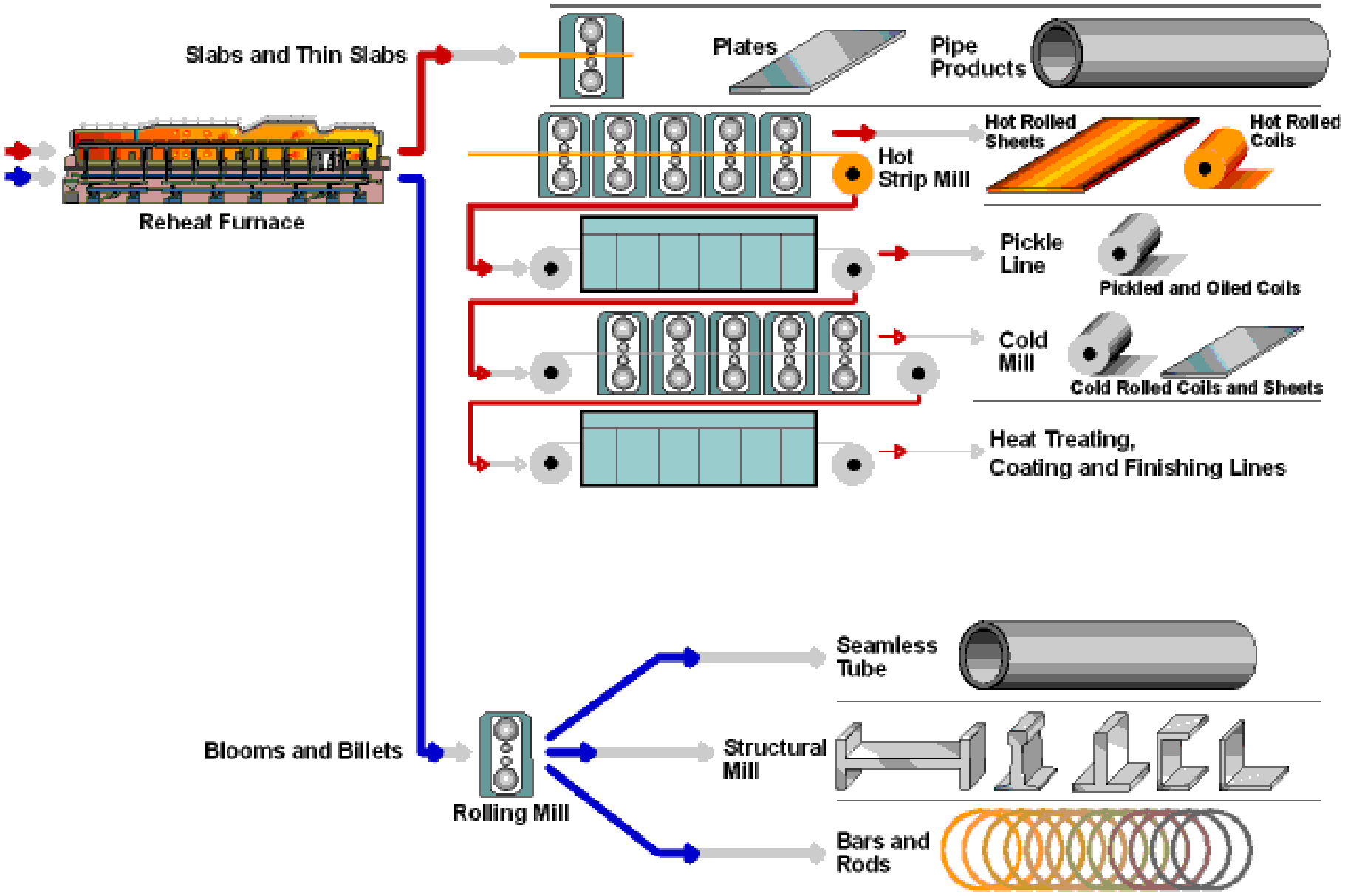


Based on data provided in Tables 13.1(b), 14.4(b), 13.3, and 13.4, *Callister & Rethwisch 9e.*

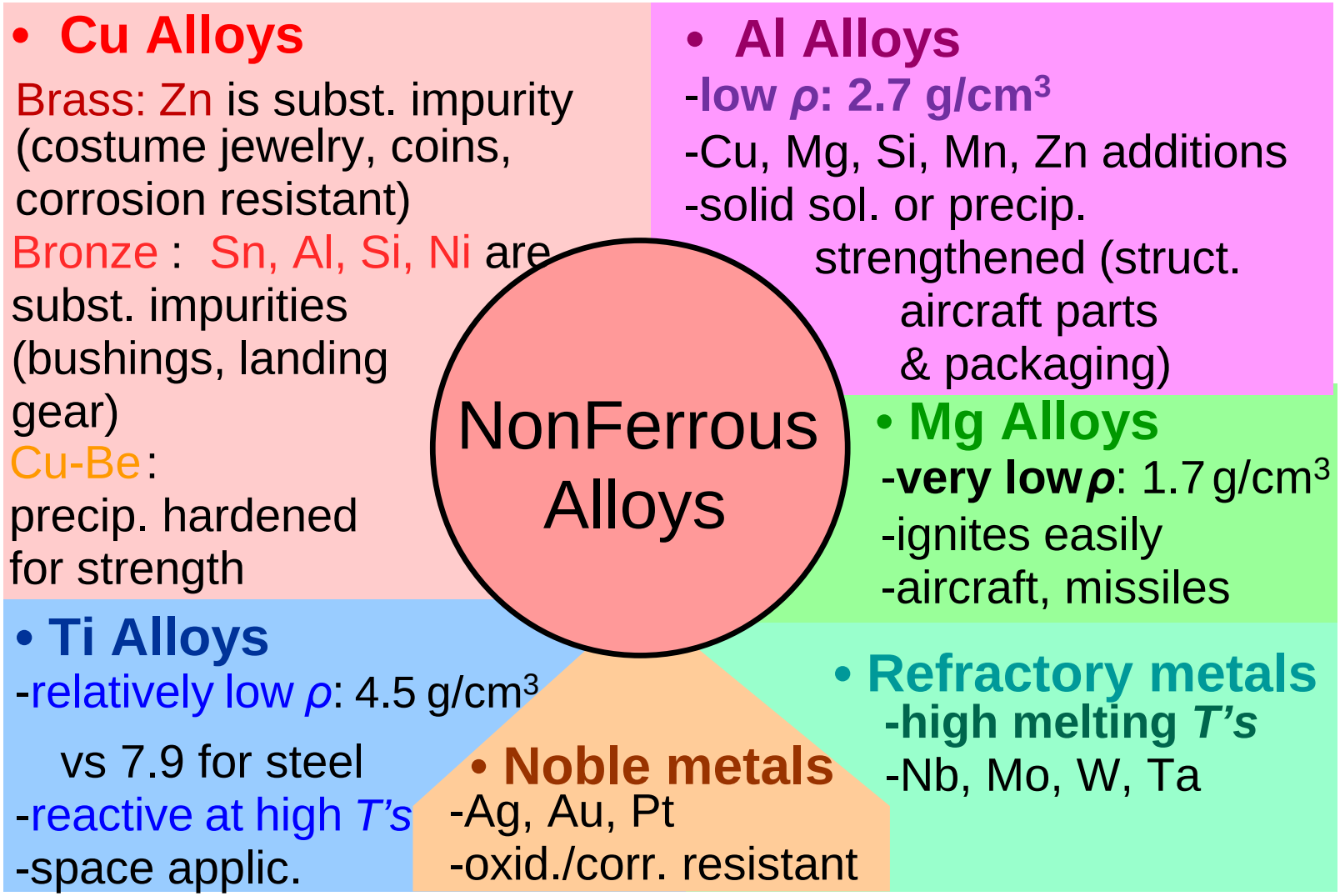
철강의 생산과정 : Iron making → Steelmaking → Rolling



철강의 생산과정 : Iron making → Steelmaking → Rolling



II. Nonferrous Alloys



Based on discussion and data provided in Chapter 13, *Callister & Rethwisch 9e.*

III. Advanced Engineering Alloys

a. Superalloys

b. Shape memory alloys

c. Quasicrytals

d. Bulk metallic glasses

e. High entropy alloys

...

* Development strategy of completely new materials

a. Alloyed pleasures: Multi-metallic cocktails

b. Synthesize metastable phases

Equilibrium conditions → Non-equilibrium conditions

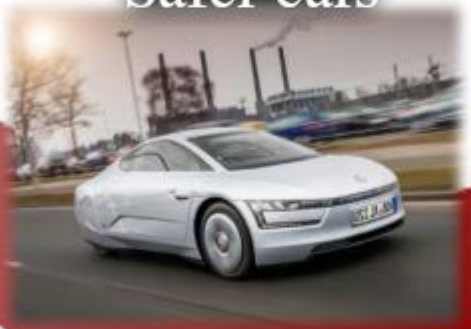
: non-equilibrium processing = "energize and quench" a material

TABLE 1.1

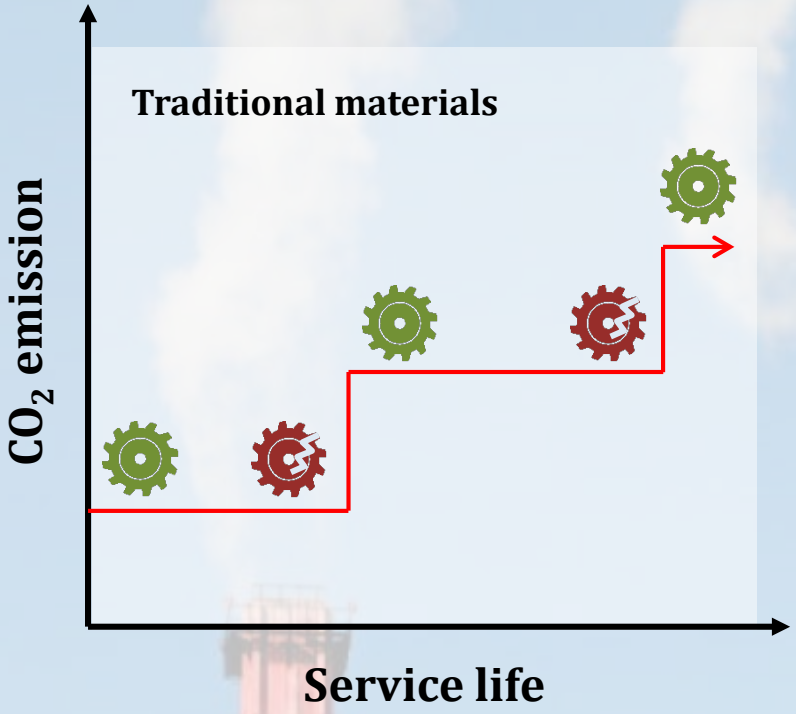
Departure from Equilibrium Achieved in Different Nonequilibrium Processing Methods

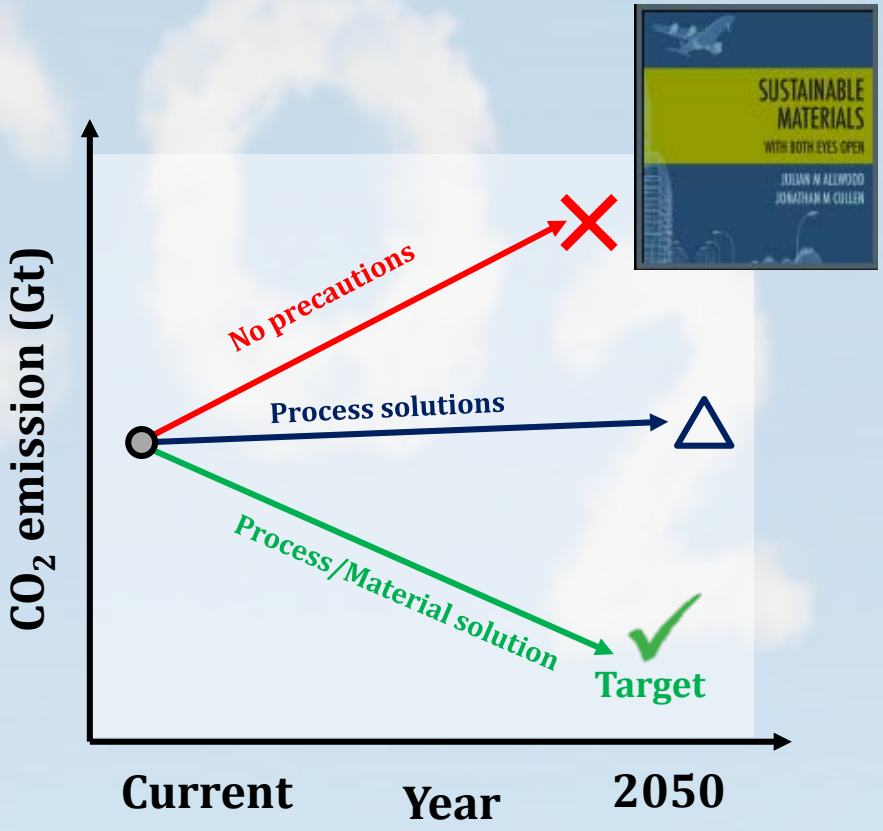
Technique	Effective Quench Rate ($K\ s^{-1}$), Ref. [25]	Maximum Departure from Equilibrium ($kJ\ mol^{-1}$)	
		Ref. [28]	Refs. [29,30]
Solid-state quench	10^3	—	16
Rapid solidification processing	10^5–10^8	2–3	24
Mechanical alloying	—	30	30
Mechanical cold work	—	—	1
Irradiation/ion implantation	10^{12}	—	30
Condensation from vapor	10^{12}	—	160

Still design-for-properties, to enable new technologies



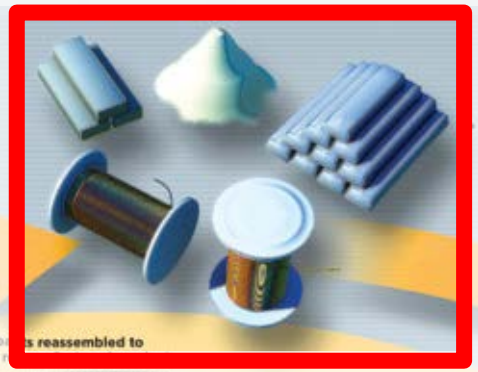
New challenges : *Less use, Extend lifetime, Reuse!*





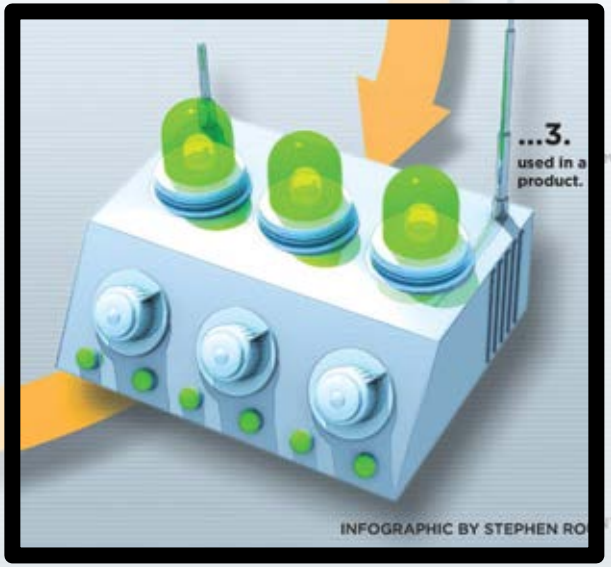
Extend lifetime, where possible, *Reuse!*

Remanufacturing : Machine design-for-reuse!



Materials design-for reuse ?

Machine design-for reuse!



Materials design for reuse

Damage process is incremental, and often local → repair opportunity

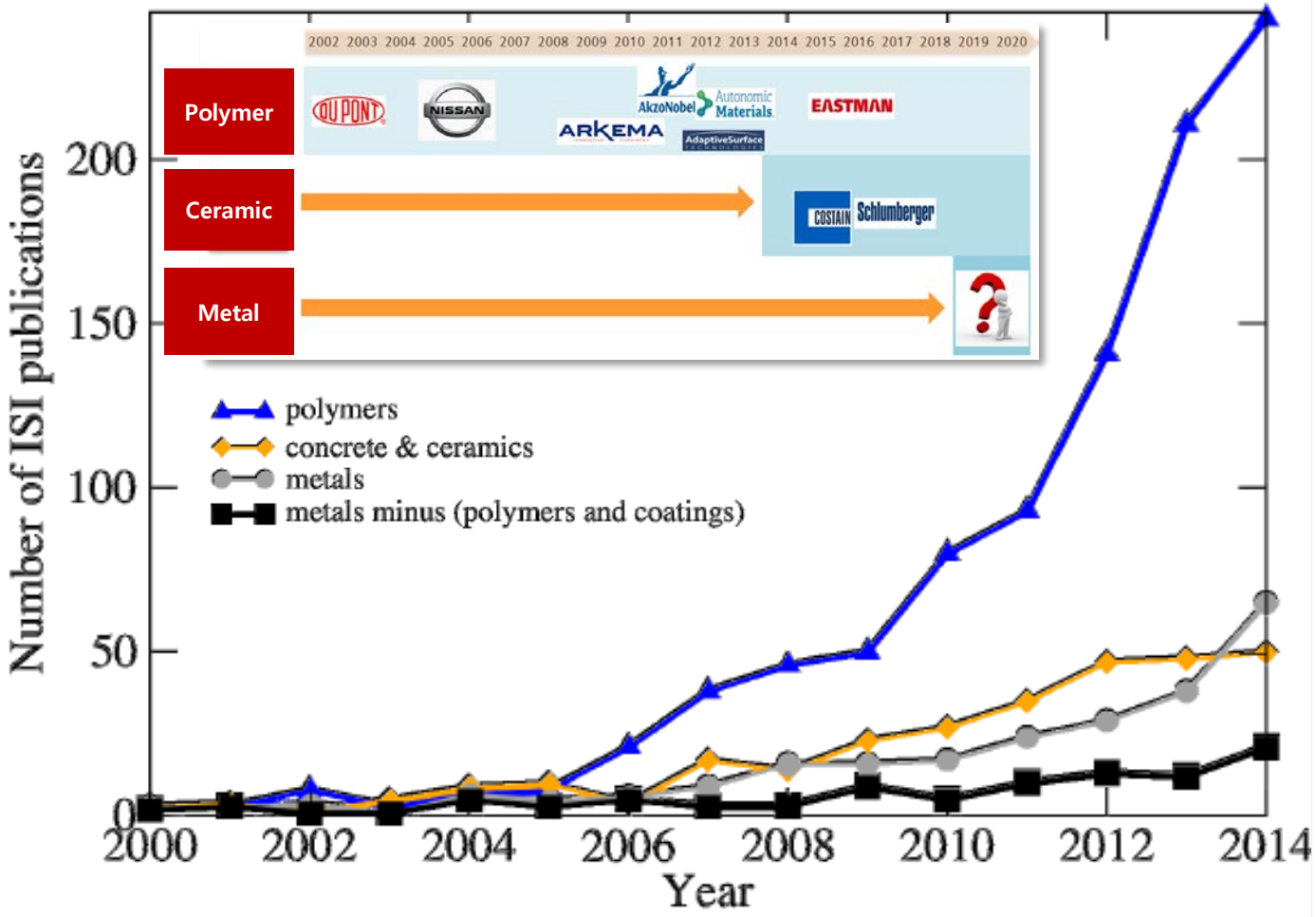
Two damage repair options possible:

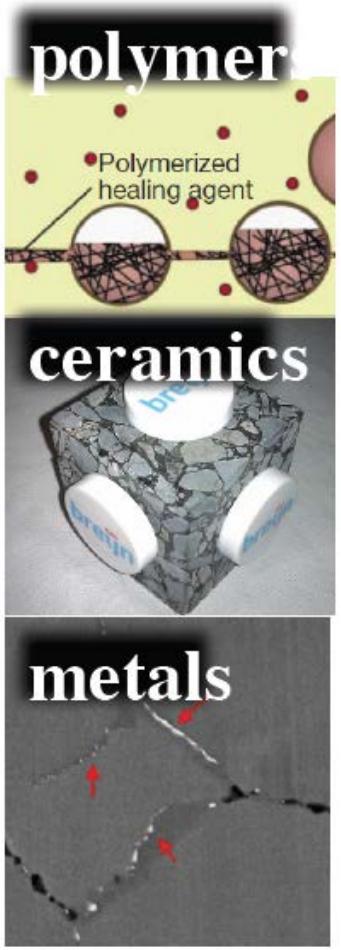
- The metal autonomously repair damage → ***Self-healing***

- Damage is repaired by an external treatment → ***Resetting***

Self Healing

New paradigm for structural material development





- **Transformation kinetics in metals are slow at room temperature!**

Commercialized self-healing polymer

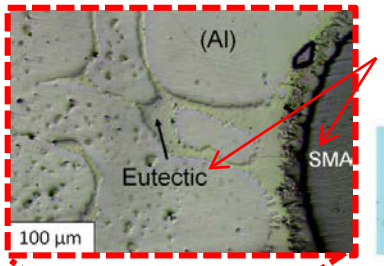
Healing agent's movement and reaction occurs even with small energy at room temperature

Self-healing metals

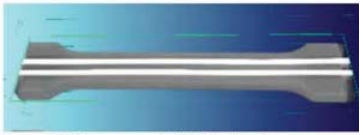
Current technical level

Prevention of microcrack propagation via healing agent

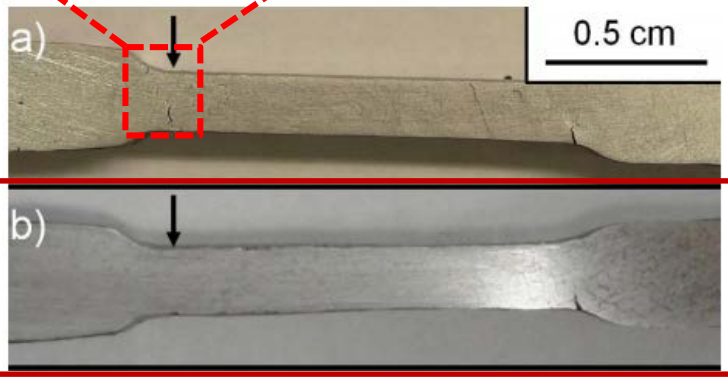
Al-3at% Si composite reinforced with 2 vol% NITI SMA wire



a. Healing agent
(ex. SMA wire etc.)



CT scan of VHP dogbone

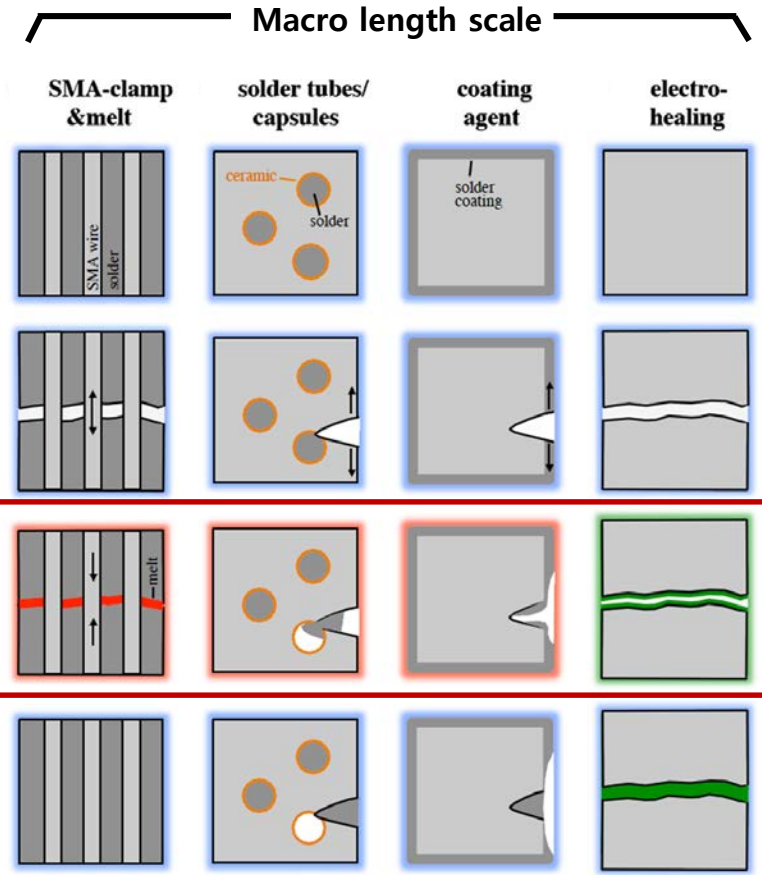


heating

b. Healing Treatment & **c. Local melting**
(ex. Aging, electro pulse etc.) (ex. Eutectic phase, Sn etc.)

➡ **Prevention of Macroscale crack propagation**

Grabowski & Tasan, Self-healing Metals (2016).

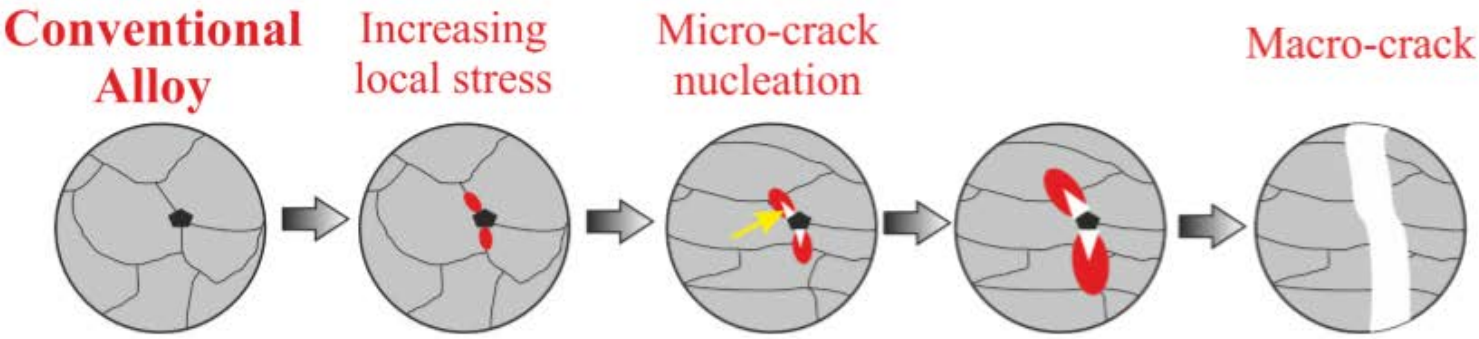


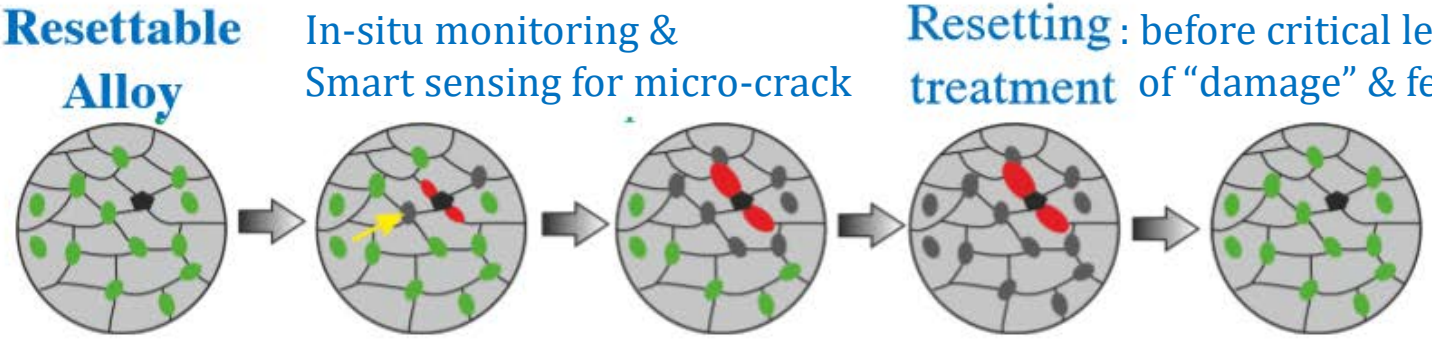
Heating or E field

For metals, restrictive thermodynamic / kinetic driving force for self-healing at RT!

Self-healing metals vs Resettable alloys

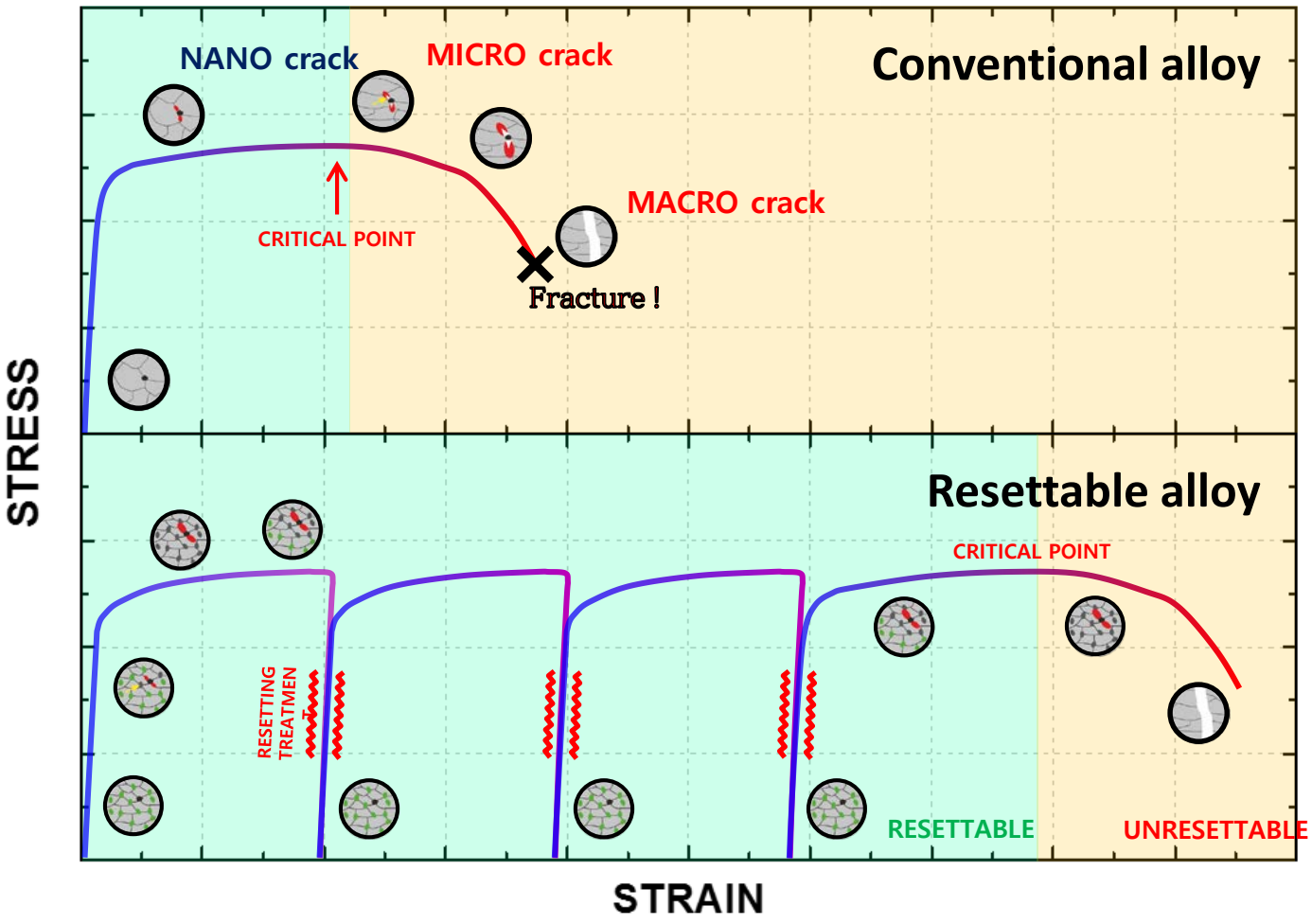
- self-healing: "*autonomic closure of micro-cracks*"
- resetting: "*non-autonomic retrieval of crack-arresting ability*"





Different failure mechanisms require different resetting strategies

New challenges : *Resettable alloys*!



Resetting treatment 를 통해 초기 미세구조로 회복 가능한 **Resettable alloy!**

Resettable Liquid Metal Harmonic Drive

Principal Investigator - 박 은 수 (서울대학교, 재료공학부)

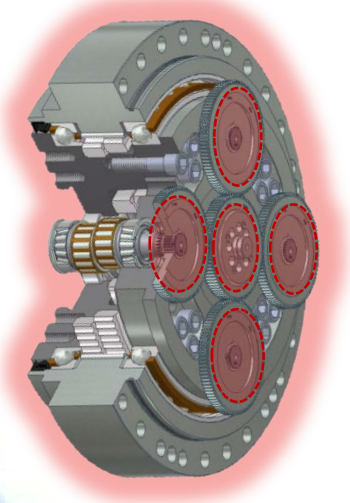
Co-Principal Investigator - 이 동 우 (성균관대학교, 기계공학부)

고품위 구동부의 핵심기술 = 감속기 : RV reducer → "하모닉 드라이브"

$$N_C = \frac{Z_I}{Z_I + Z_S} \times N_I + \frac{Z_S}{Z_I + Z_S} \times N_S$$

: 감속을 위해 최소 4 개의 기어가 맞물려
최대 200 : 1 내외의 감속비 확보 가능

Rotate vector reducer



여러 개의 기어가 동시에
작동하는 감속 시스템

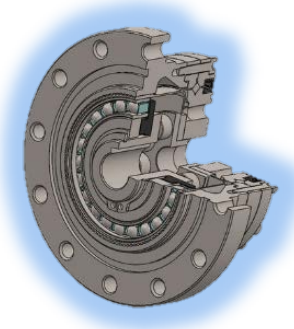
▶ 소형화 한계 !

토크 증폭 위한
Rotate Vector 감속기

$$\text{reduction ratio} = \frac{\text{flex spline teeth} - \text{circular spline teeth}}{\text{flex spline teeth}}$$

: 하나의 감속 시스템만으로 30 : 1 to 320 : 1의 감속비 확보 가능 /
Reduction ratio ∝ number of teeth

Harmonic drive



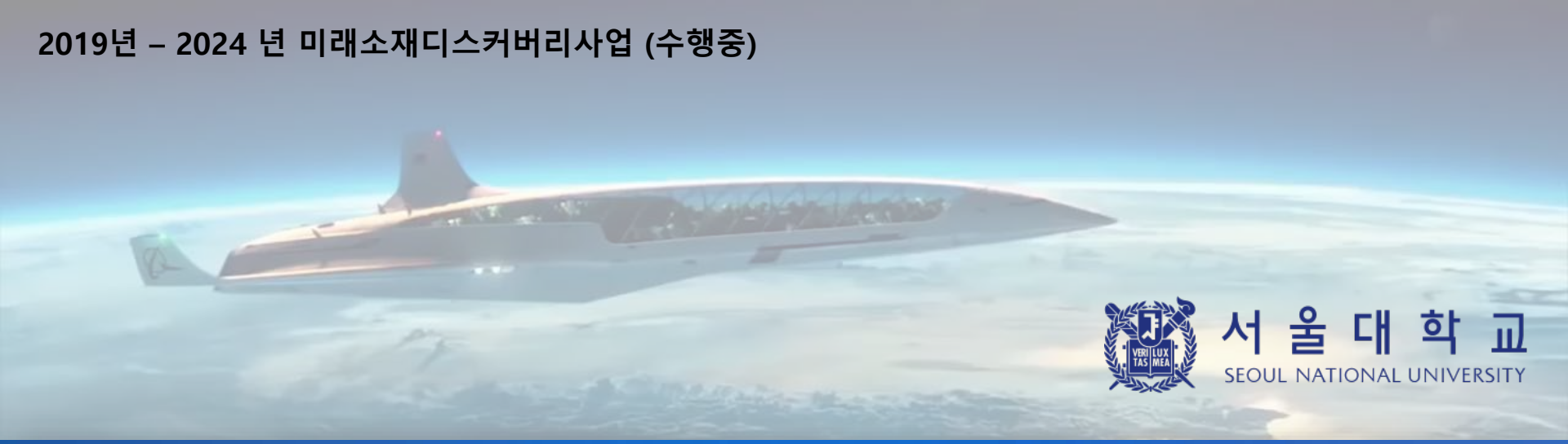
하나의 시스템에 의해
감속되는 **하모닉드라이브**

▶ 소형화/경량화

1. Single Stage
2. No Backlash
3. Higher Precision

미래 산업 성장의 핵심인 초고속 운송수단 및 에너지 신산업 개발을 위해

극한 구동환경 적용가능 구조新소재 개발 필요!



서 울 대 학 교
SEOUL NATIONAL UNIVERSITY

지능형 자가변환 기반 자가치유 센테니얼 합금 개발

연구책임자: 박은수 (서울대학교 재료공학부)

참여연구원: 고원석 (울산대학교 첨단소재공학부)
한흥남 (서울대학교 재료공학부)
김원태 (청주대학교 레이저광정보학과)
서진유 (KIST, 고온에너지재료연구센터)
김영운 (서울대학교 재료공학부)
심기동 (KAIST, 기계공학과)
김도향 (연세대학교 신소재공학부)
이동우 (성균관대학교 기계공학부)
박형기 (한국생산기술연구원)

Urgent need for mission change:

Materials design-for-"properties" & "reuse"

Materials Che*f* & Doc*tor* Academy
ESPark Research group @ SNU
http://espark.snu.ac.kr

I. Metal Fabrication

- How do we fabricate metals?
  - Blacksmith - hammer (forged)
  - Cast molten metal into mold

- Forming Operations
  - Rough stock formed to final shape

Hot working vs. Cold working

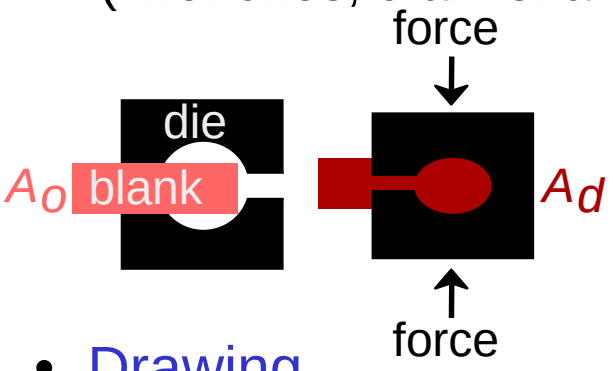
- Deformation temperature high enough for **recrystallization**
- Large deformations

- Deformation **below recrystallization temperature**
- Strain hardening occurs
- Small deformations

Metal Fabrication Methods (i)

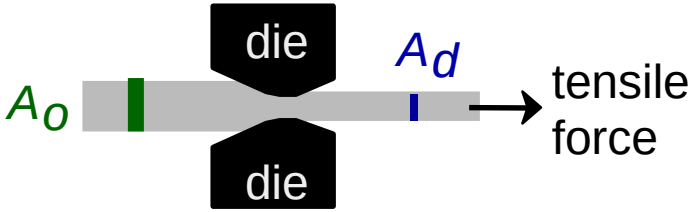
FORMING | CASTING | MISCELLANEOUS

- Forging (Hammering; Stamping)
  (wrenches, crankshafts)



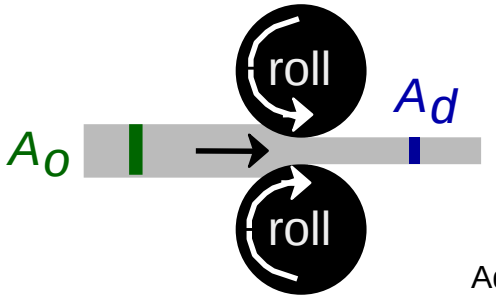
often at elev. *T*

- Drawing
  (rods, wire, tubing)

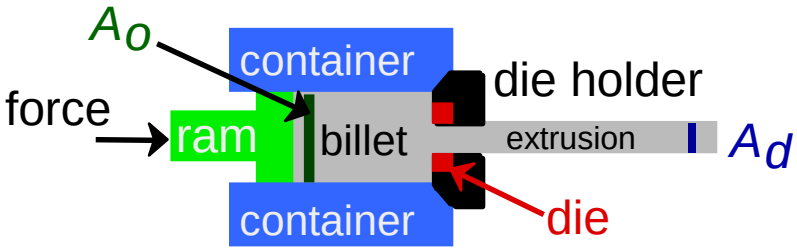


die must be well lubricated & clean

- Rolling (Hot or Cold Rolling)
  (I-beams, rails, sheet & plate)



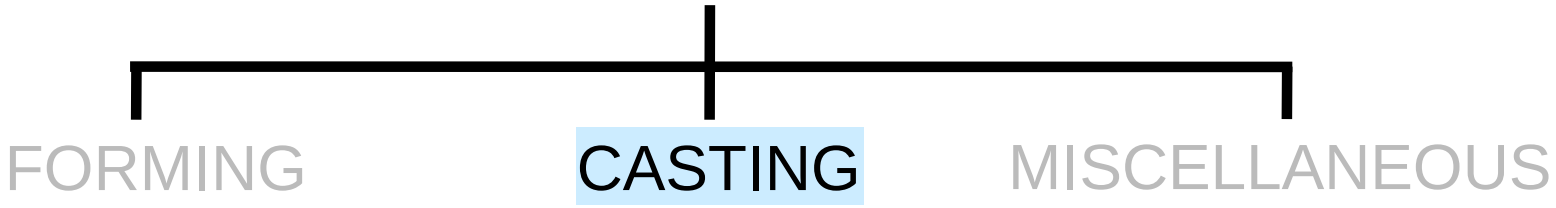
- Extrusion
  (rods, tubing)



ductile metals, e.g. Cu, Al (hot)

Adapted from Fig. 17.2, *Callister & Rethwisch 9e.*

Metal Fabrication Methods (ii)



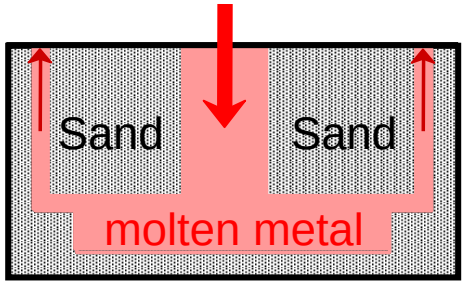
- Casting- mold is filled with molten metal
  - metal melted in furnace, perhaps alloying elements added, then cast in a mold
  - common and inexpensive
  - gives good production of shapes
  - weaker products, internal defects
  - good option for brittle materials

Metal Fabrication Methods (iii)

FORMING | CASTING | MISCELLANEOUS

- Sand Casting

  (large parts, e.g., auto engine blocks)

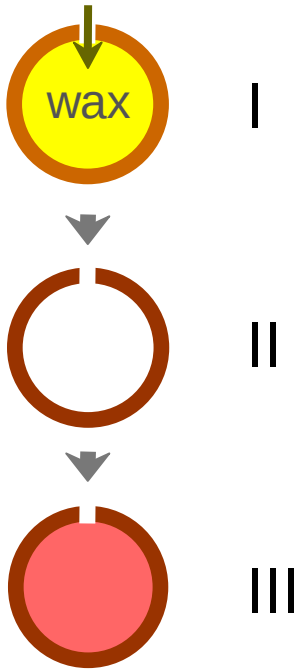


- What material will withstand T >1600˚ C and is inexpensive and easy to mold?
- Answer: sand!!!
- To create mold, pack sand around form (pattern) of desired shape

Metal Fabrication Methods (iv)

FORMING | **CASTING** | MISCELLANEOUS

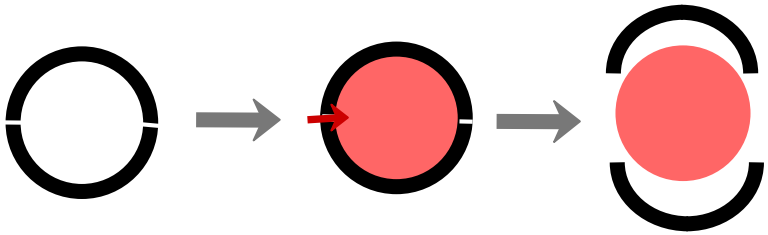
- Investment Casting (정밀주조)
  (low volume, complex shapes
  e.g., jewelry, turbine blades)
  - Stage I — Mold formed by pouring plaster of paris (석고형) around wax pattern. Plaster allowed to harden.
  - Stage II — Wax is melted and then poured from mold—hollow mold cavity remains.
  - Stage III — Molten metal is poured into mold and allowed to solidify.



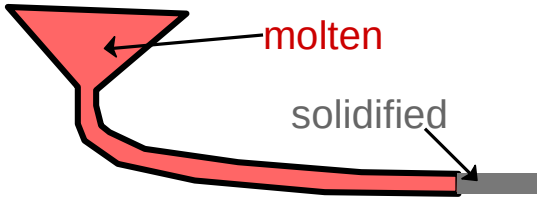
Metal Fabrication Methods (v)

FORMING | CASTING | MISCELLANEOUS

- Die Casting
  - -- high volume
  - -- for alloys having low melting temperatures, Al alloys



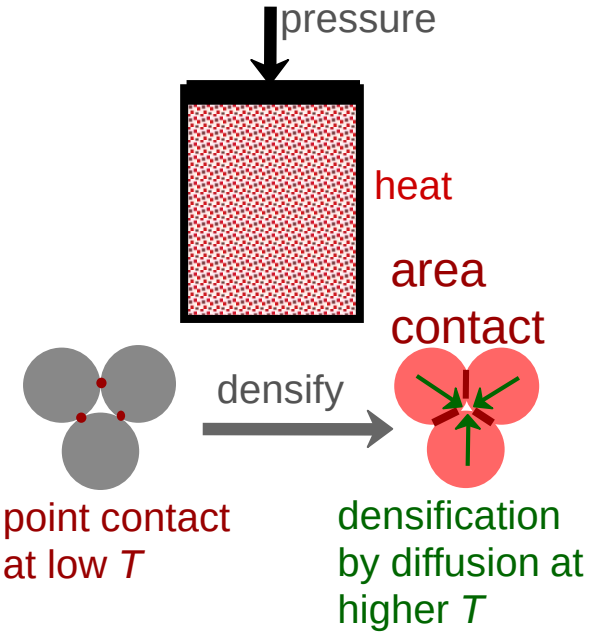
- Continuous Casting
  - -- simple shapes (e.g., rectangular slabs, cylinders)



Metal Fabrication Methods (vi)

FORMING | CASTING | MISCELLANEOUS

- Powder Metallurgy
  (metals w/low ductilities)



- Welding
  (when fabrication of one large part is impractical)

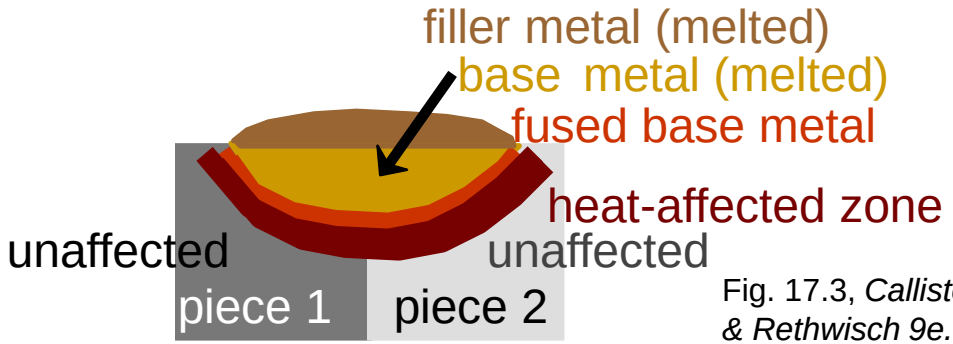


Fig. 17.3, *Callister & Rethwisch 9e.* [From *Iron Castings Handbook*, C.F. Walton and T.J. Opar (Ed.), Iron Castings Society, Des Plaines, IL,1981.]

- Heat-affected zone:
  (HAZ, region in which the microstructure has been changed).

Metal Fabrication Methods (vii)

FORMING CASTING MISCELLANEOUS

3D printing (Additive manufacturing)

- Direct Energy Deposition (DED)
- Powder Bed Fusion

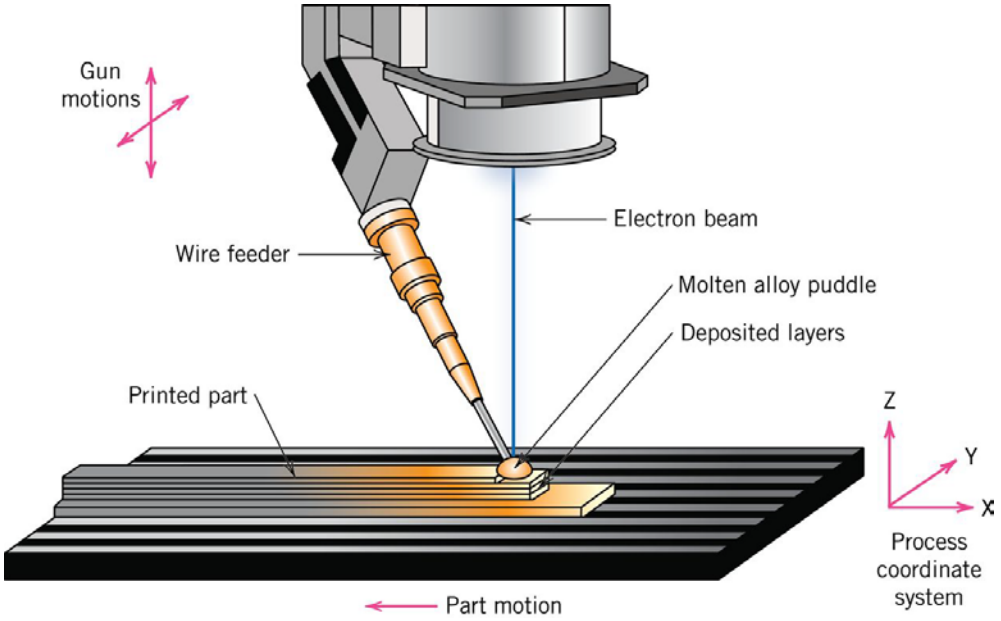


Figure 11.12 Schematic representation of the direct energy deposition 3D printing process for metals using an electron beam)

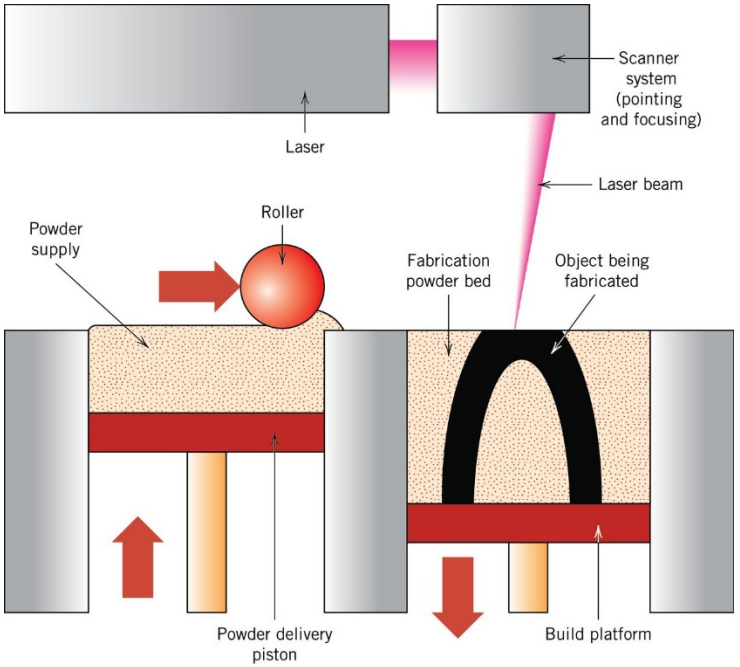
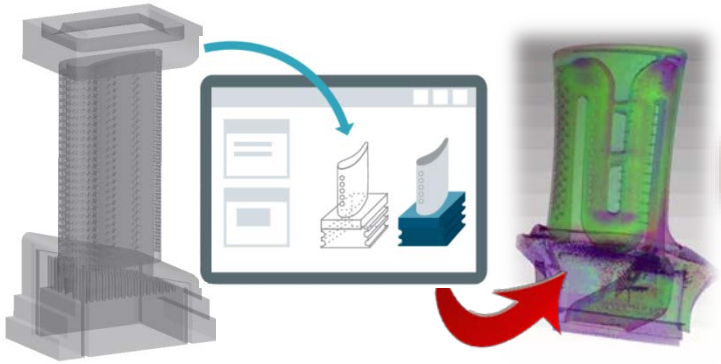


Figure 11.13 Schematic diagram that demonstrates the powder bed fusion process for 3D printing of metals

맞춤형 구조제어 직접디지털제조 공정기술

냉각효율 극대화를 위한 3차원 구조 설계

Turbine design by 3D digital modeling



Complex internal cooling channel

→ Cooling efficiency ↑

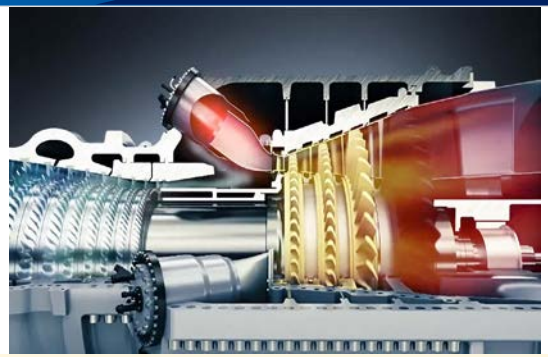
3D 프린팅 기반 직접 디지털 제조 공정기술 개발

Turbine Blade

Feedback

(Powder ↔ Laser ↔ Cooling)

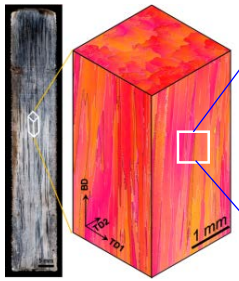
차세대 초고효율 터빈 부품화 기술 개발

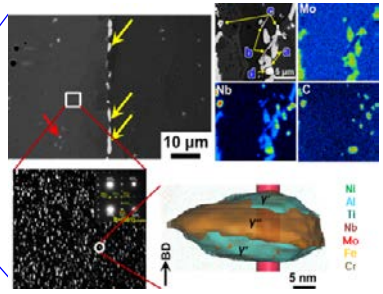


(3) 초임계 성능 구현 터빈 부품 제조

(2) 3D printing Microstructure control

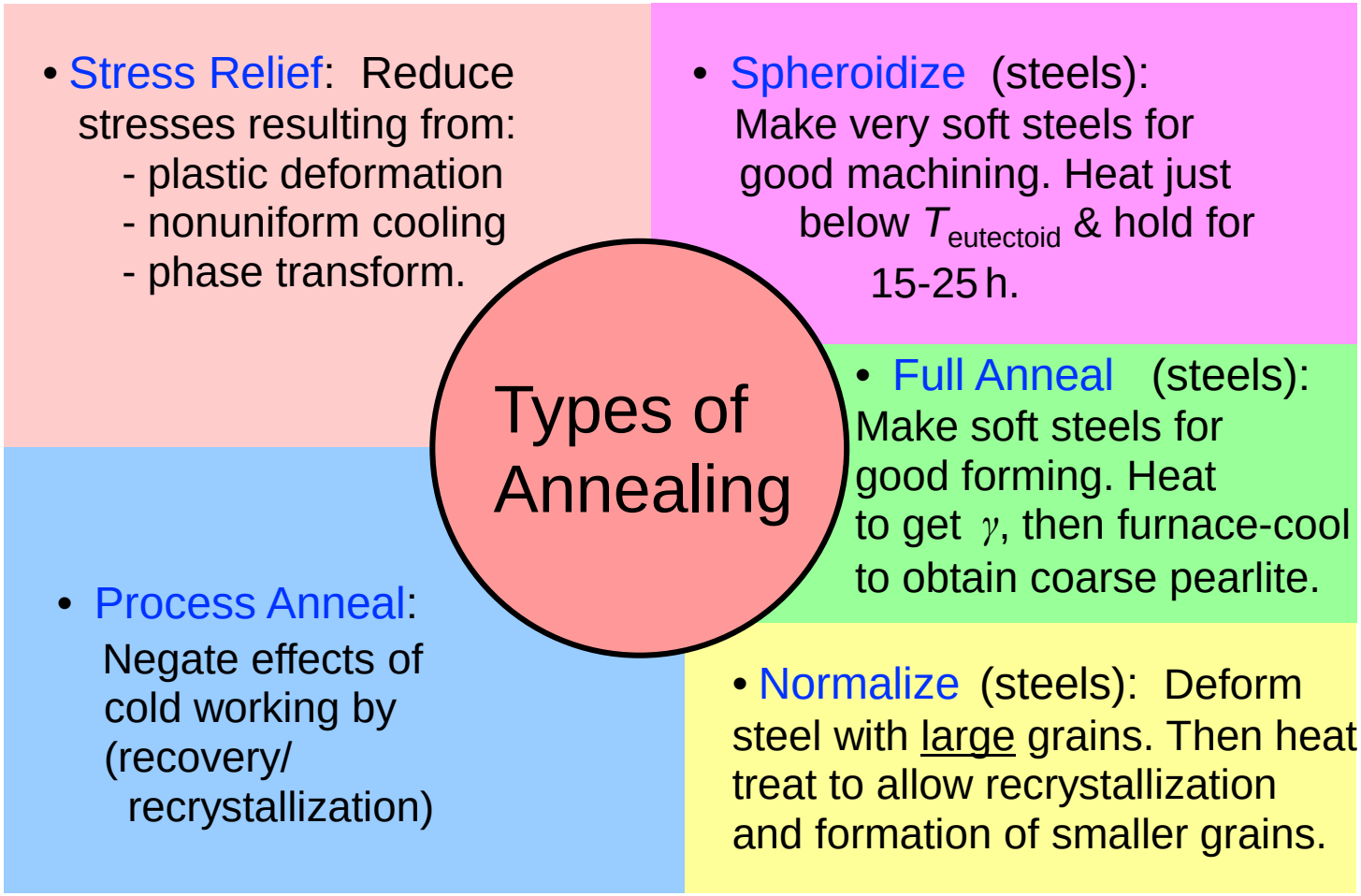
Directional solidification + Fine precipitate





Thermal Processing of Metals

Annealing: Heat to T_{anneal}, then cool slowly.



Based on discussion in Section 17.5, *Callister & Rethwisch 9e*.

Heat Treatment Temperature-Time Paths

a) Full Annealing

b) Quenching

c) Tempering (Tempered Martensite)

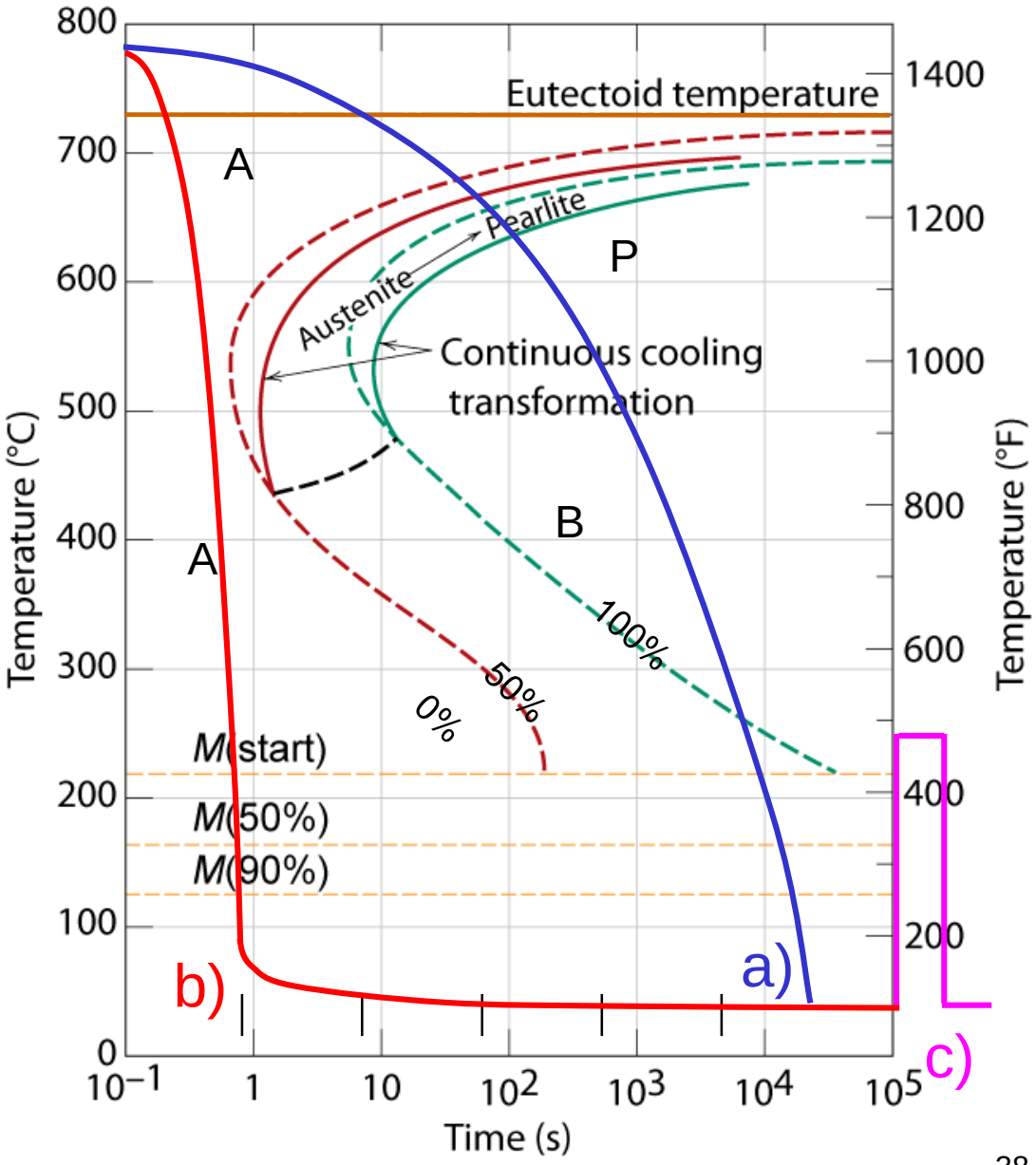


Fig. 12.25, *Callister & Rethwisch 9e*. [Adapted from H. Boyer (Editor), Atlas of Isothermal Transformation and Cooling Transformation Diagrams, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Hardenability -- Steels

- Hardenability – measure of the ability to form martensite
- Jominy end quench test used to measure hardenability.

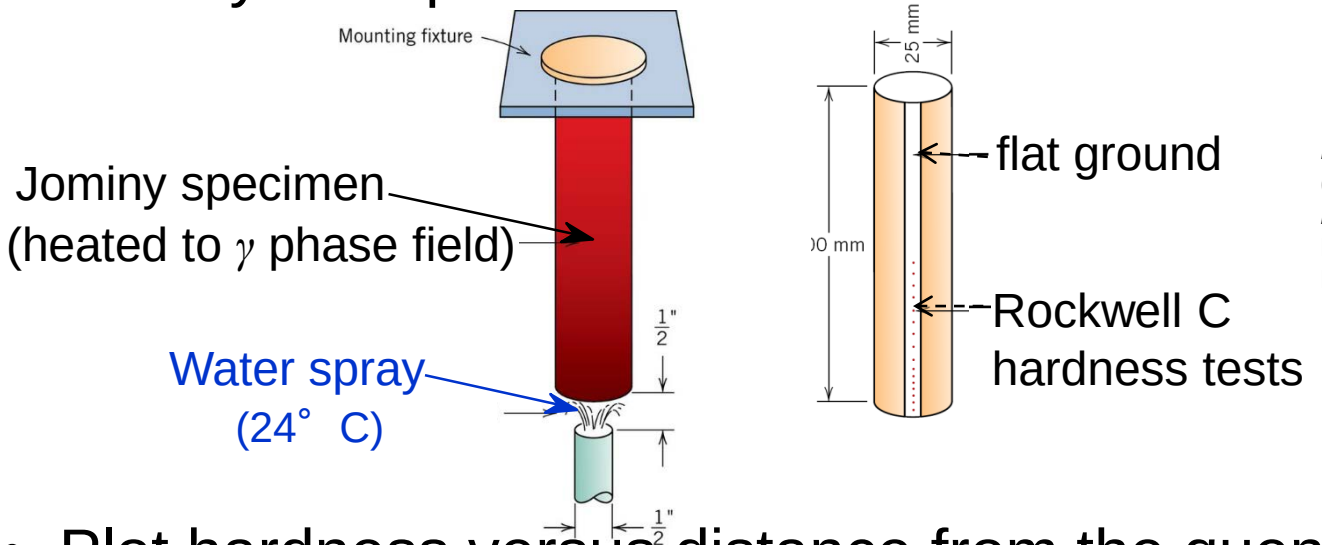


Fig. 17.5, *Callister & Rethwisch 9e*.
(Adapted from A.G. Guy, *Essentials of Materials Science*, McGraw-Hill Book Company, New York, 1978.)

- Plot hardness versus distance from the quenched end.

Fig. 17.6, *Callister & Rethwisch 9e*.

Reason Why Hardness Changes with Distance

- The cooling rate decreases with distance from quenched end.

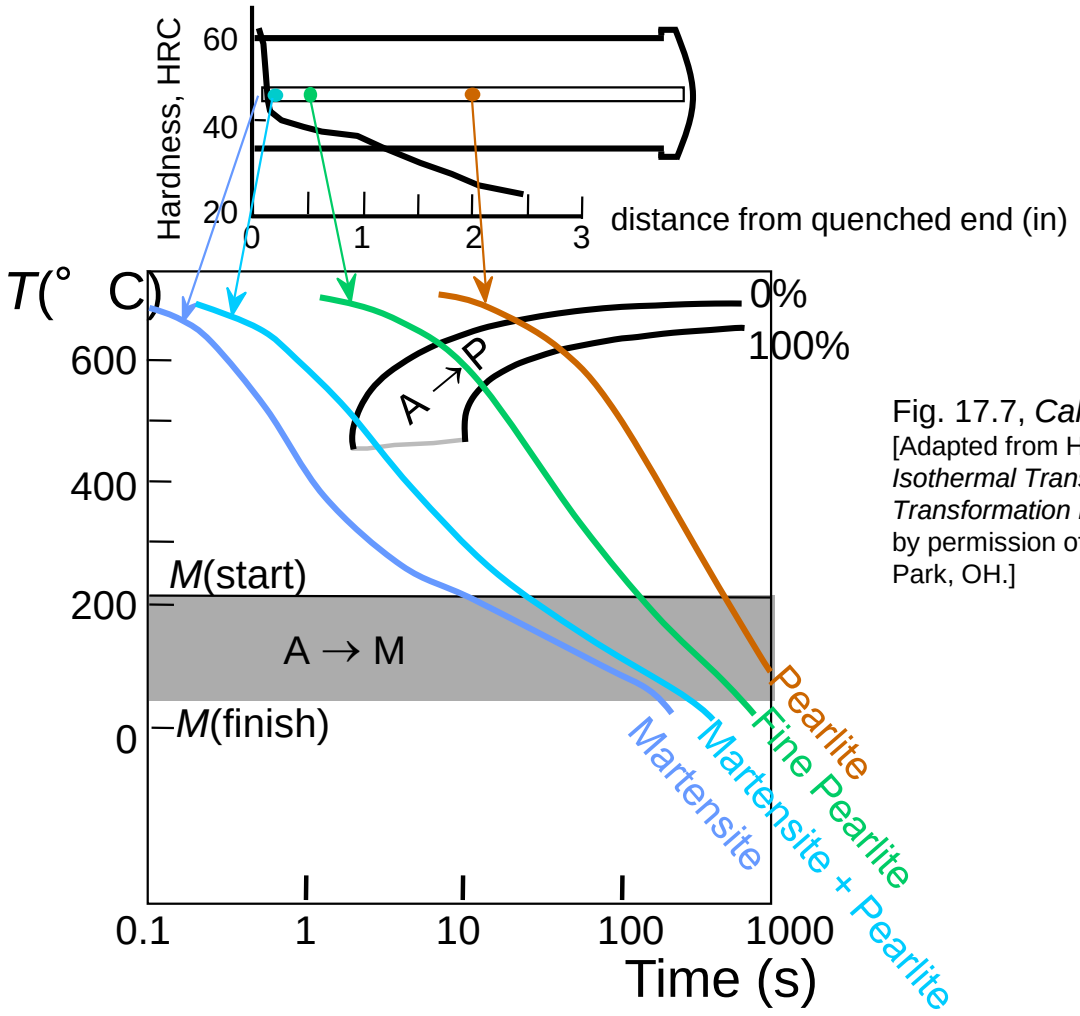


Fig. 17.7, *Callister & Rethwisch 9e*. [Adapted from H. Boyer (Ed.), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Hardenability vs Alloy Composition

- Hardenability curves for five alloys each with, C = 0.4 wt% C

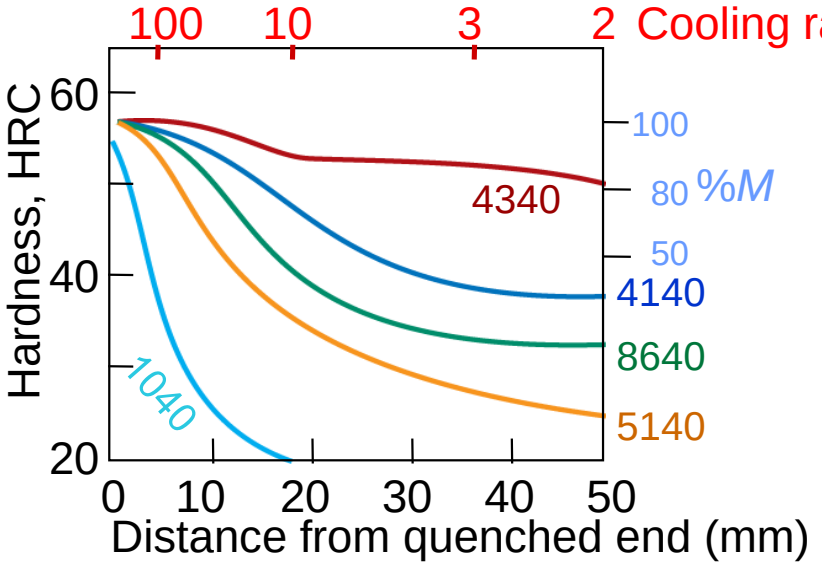
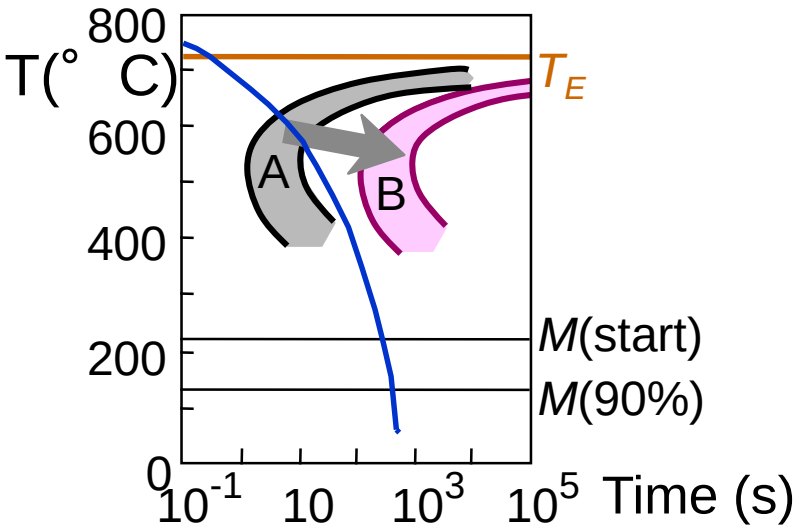


Fig. 17.8, *Callister & Rethwisch 9e*.
(Adapted from figure furnished courtesy Republic Steel Corporation.)

- "Alloy Steels" (4140, 4340, 5140, 8640)
  - -- contain Ni, Cr, Mo (0.2 to 2 wt%)
  - -- these elements shift the "nose" to longer times (from A to B)
  - -- martensite is easier to form



Influences of Quenching Medium & Specimen Geometry

- Effect of quenching medium:

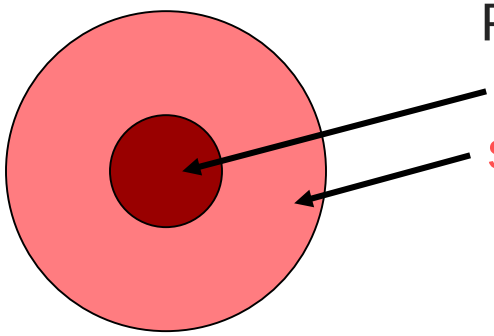
Medium	Severity of Quench	Hardness
air	low	low
oil	moderate	moderate
water	high	high

- Effect of specimen geometry:

  When surface area-to-volume ratio increases:

  -- cooling rate throughout interior increases

  -- hardness throughout interior increases



Position	Cooling rate	Hardness
center	low	low
surface	high	high

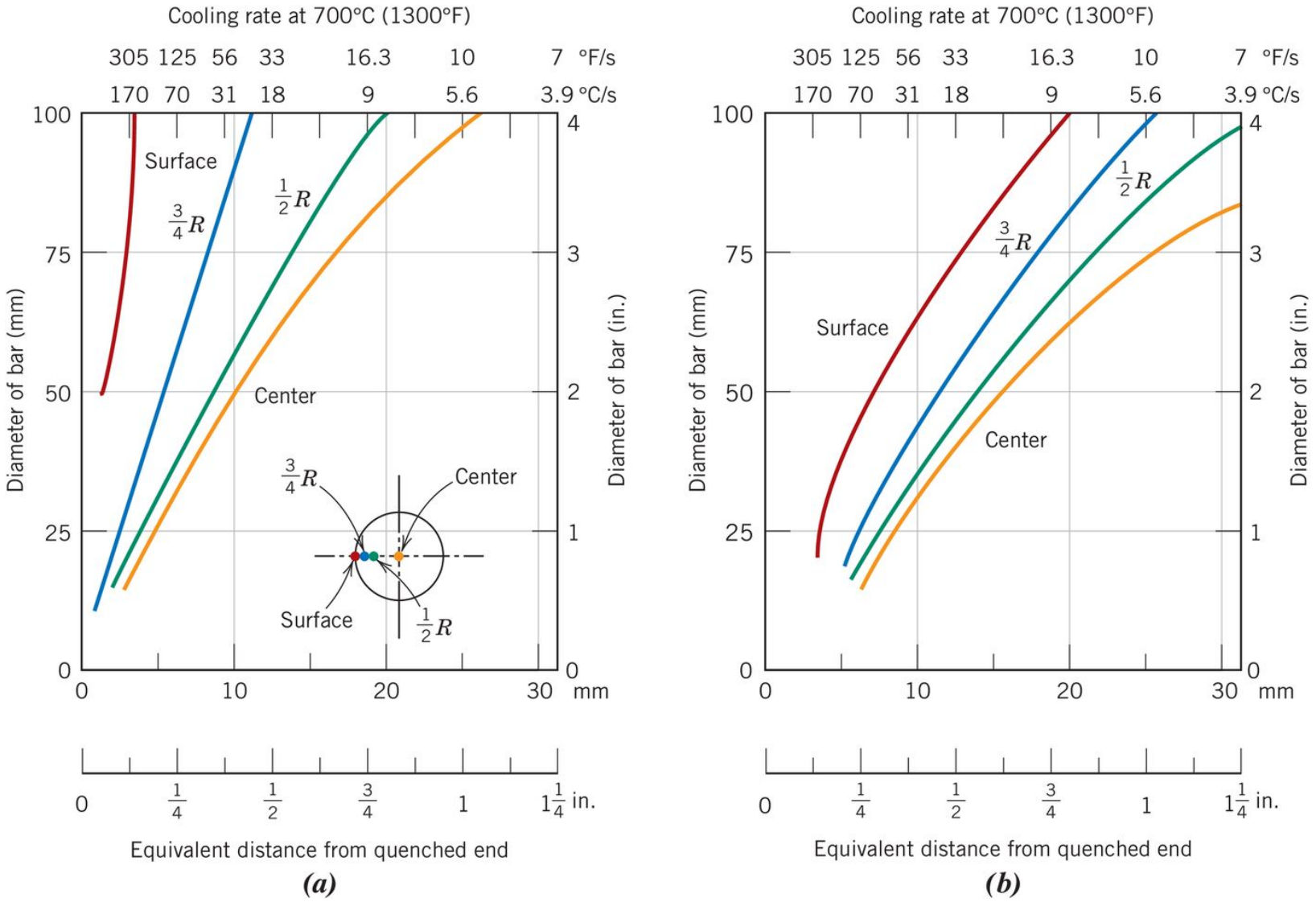


Figure 11.21 Cooling rate as a function of the diameter at the surface, the three-quarter radius (3/4R), the midradius (1/2R), and the center positions for cylindrical bars quenched in mildly agitated (a) water and (b) oil. Equivalent Jominy positions are included along the bottom axes.

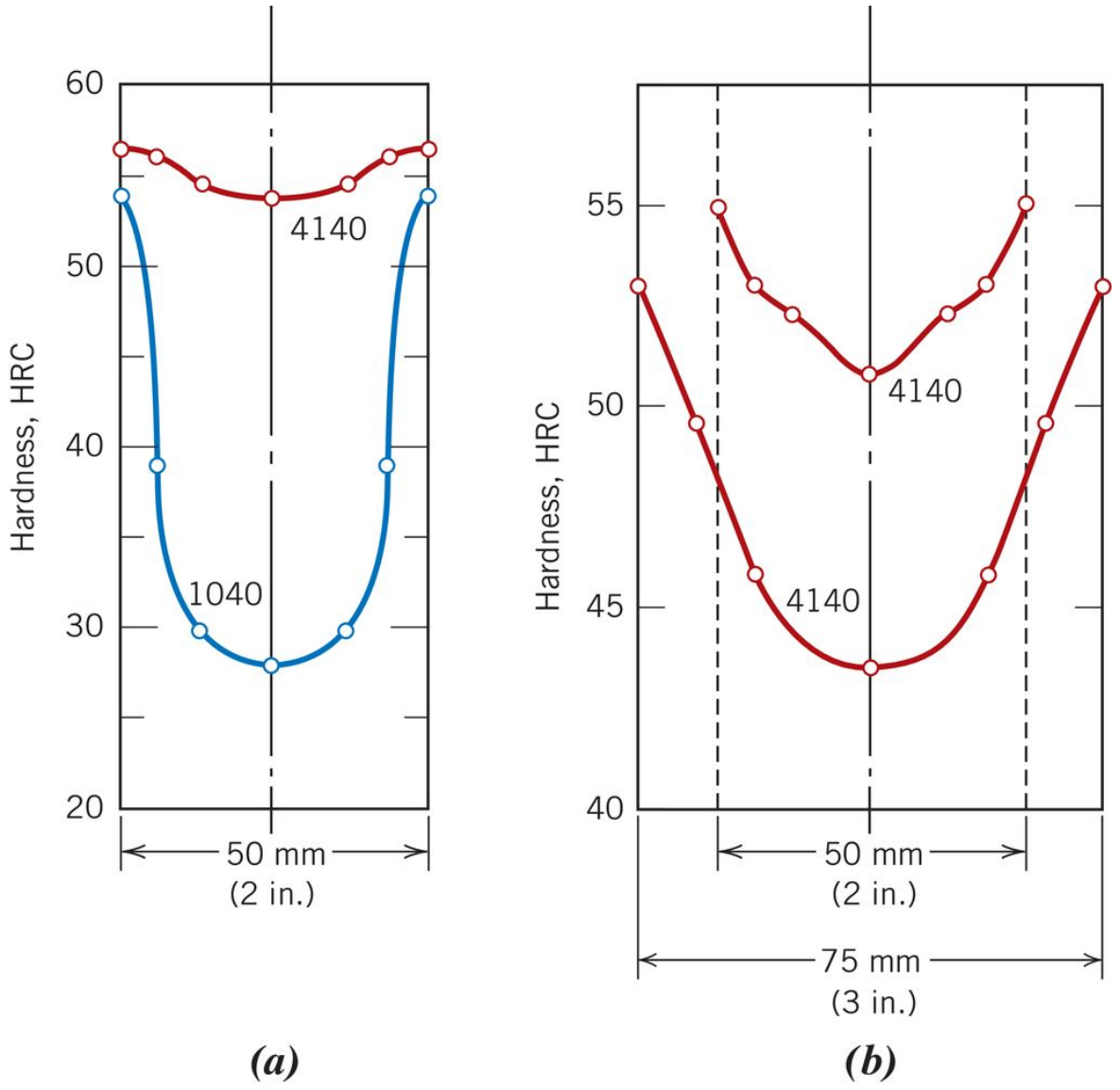


Figure 11.22 Radial hardness profiles for (a) 50-mm- (2 in.) diameter cylindrical 1040 and 4140 steel specimens quenched in mildly agitated water, and (b) 50- and 75-mm- (2 and 3 in.) diameter cylindrical specimens of 4140 steel quenched in mildly agitated oil.

Precipitation Hardening

- Particles impede dislocation motion.
- Ex: Al-Cu system
- Procedure:
  - -- Pt A: solution heat treat (get α solid solution)
  - -- Pt B: quench to room temp. (retain α solid solution)
  - -- Pt C: reheat to nucleate small θ particles within α phase.
- Other alloys that precipitation harden:
  - Cu-Be
  - Cu-Sn
  - Mg-Al

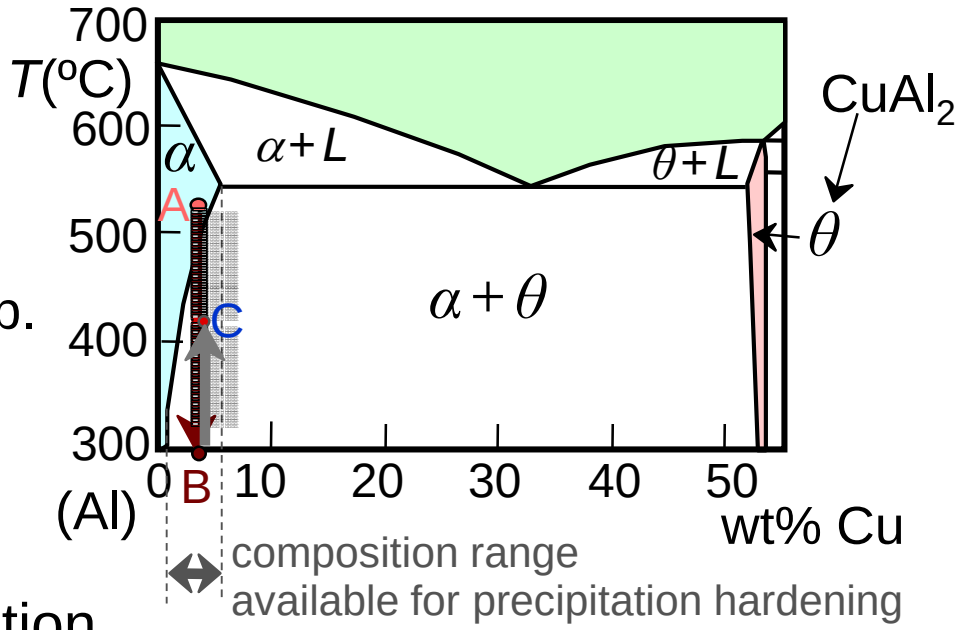
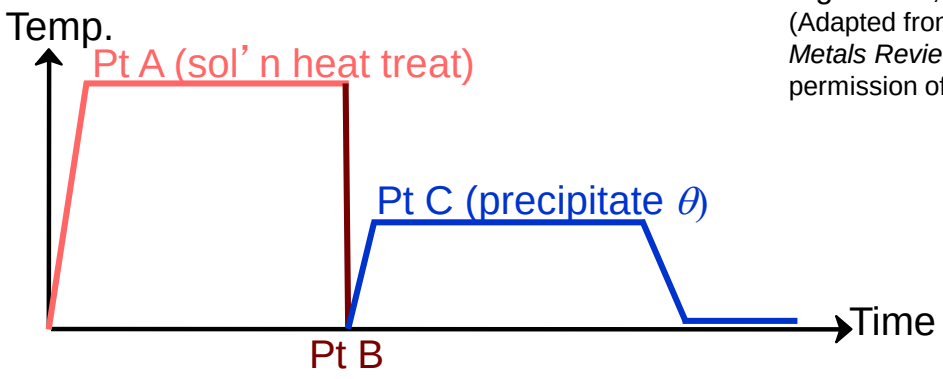


Fig. 17.18, *Callister & Rethwisch 9e*. (Adapted from J.L. Murray, *International Metals Review* **30**, p.5, 1985. Reprinted by permission of ASM International.)



Adapted from Fig. 17.16, *Callister & Rethwisch 9e*.

Precipitation Hardening_age hardening

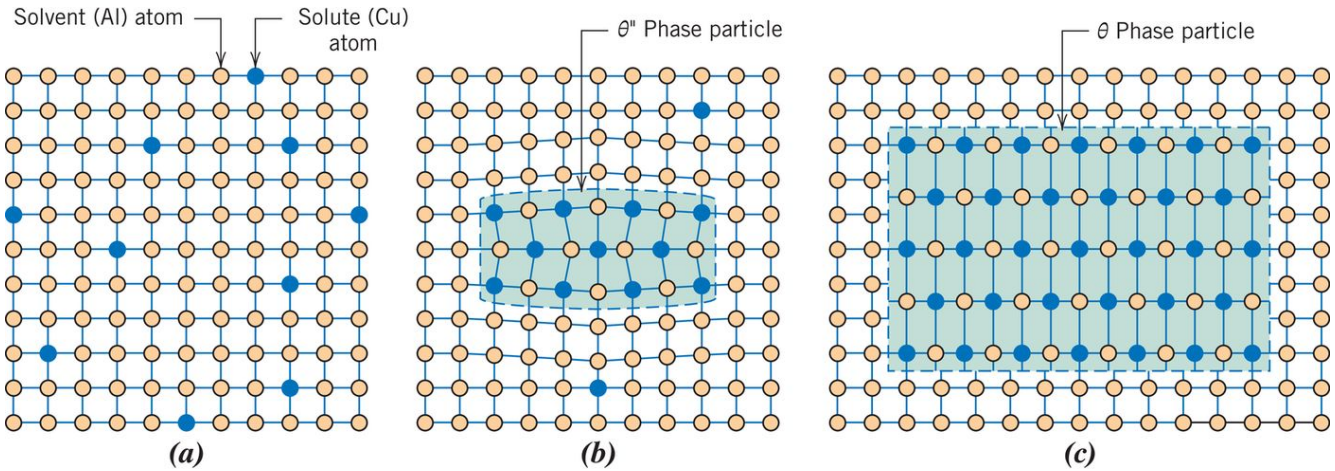


Figure 11.30 Schematic depiction of several stages in the formation of the equilibrium precipitate (Θ) phase. (a) A super-saturated α solid solution. (b) A transition, Θ", precipitate phase. (c) The equilibrium Θ phase, within the α-matrix phase

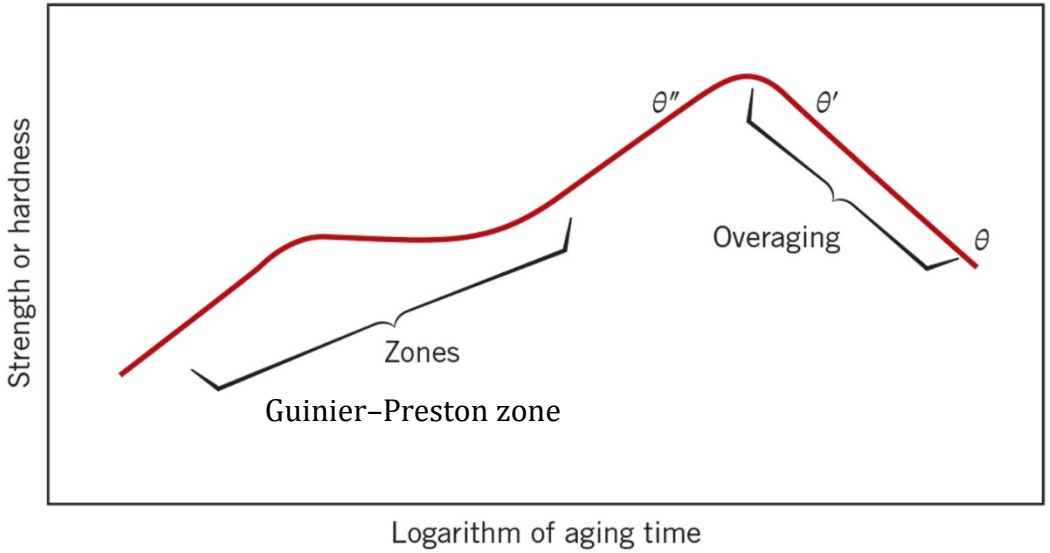
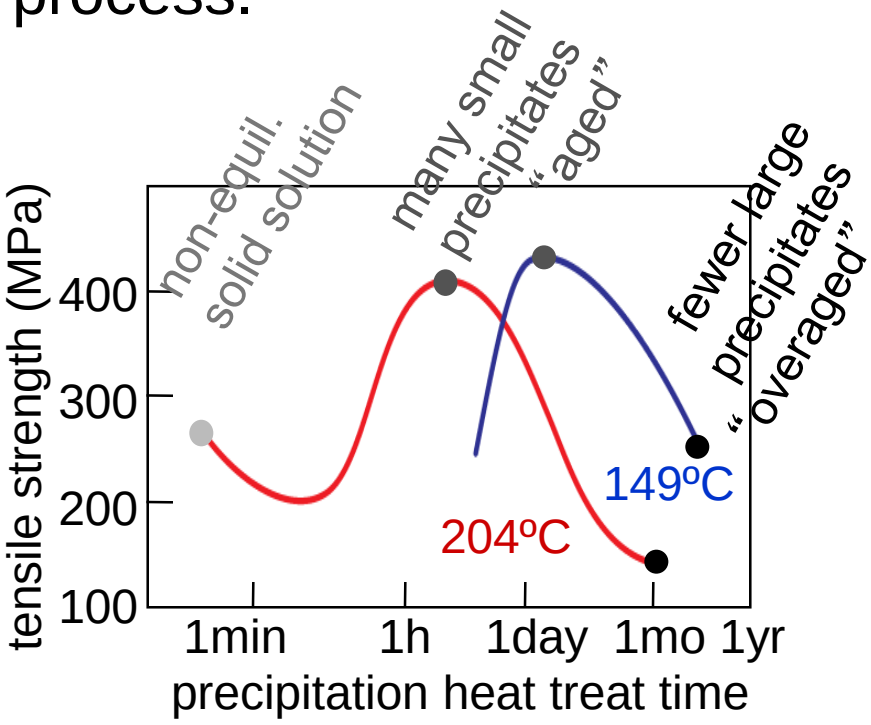


Figure 11.28 Schematic diagram showing strength and hardness as a function of the logarithm of aging time at constant temperature during the precipitation heat treatment.

Influence of Precipitation Heat Treatment on *TS*, %*EL*

- 2014 Al Alloy:
- Maxima on *TS* curves.
- Increasing *T* accelerates process.
- Minima on %*EL* curves.



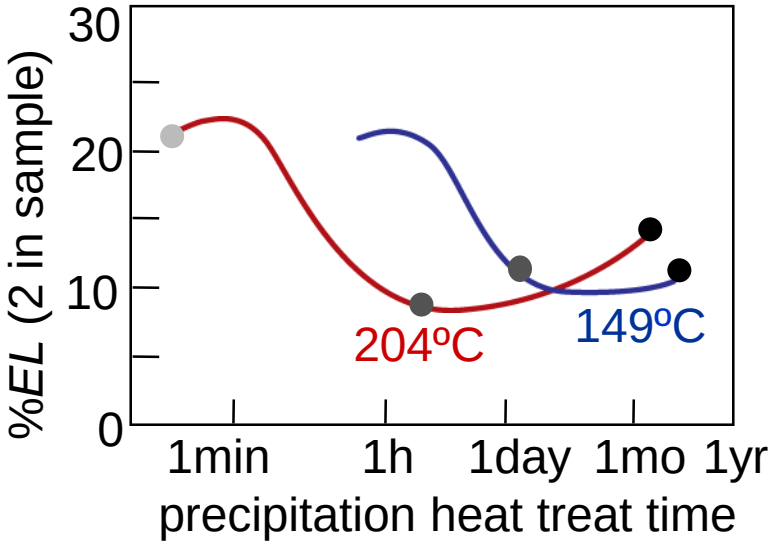


Fig. 17.21, *Callister & Rethwisch 9e*. [Adapted from *Metals Handbook: Properties and Selection: Nonferrous Alloys and Pure Metals*, Vol. 2, 9th ed., H. Baker (Managing Ed.), 1979. Reproduced by permission of ASM International, Materials Park, OH.]

Summary

- Ferrous alloys: steels and cast irons
- Non-ferrous alloys:
  -- Cu, Al, Ti, and Mg alloys; refractory alloys; and noble metals.
- Advanced engineering alloys

-- Superalloy, SMA, BMG, Quasicrystal, HEA, etc.

- Metal fabrication techniques:
  -- forming, casting, miscellaneous, additive manufacturing.
- Hardenability of metals
  -- measure of ability of a steel to be heat treated.
  -- increases with alloy content.
- Precipitation hardening
  --hardening, strengthening due to formation of
  precipitate particles.
  --Al, Mg alloys precipitation hardenable.

2020 Fall

Introduction to Materials Science and Engineering

11. 19. 2020

Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by appointment

Chapter 11:
Applications and Processing of Metal Alloys

- Ferrous alloys: steels and cast irons
- Non-ferrous alloys:
  -- Cu, Al, Ti, and Mg alloys; refractory alloys; and noble metals.
- Advanced engineering alloys
  -- Superalloy, SMA, BMG, Quasicrystal, HEA, etc.

- Metal fabrication techniques:
  -- forming, casting, miscellaneous, additive manufacturing.
- Hardenability of metals
  -- measure of ability of a steel to be heat treated.
  -- increases with alloy content.
- Precipitation hardening
  --hardening, strengthening due to formation of
  precipitate particles.
  --Al, Mg alloys precipitation hardenable.

Precipitation Hardening

- Particles impede dislocation motion.
- Ex: Al-Cu system
- Procedure:
  - -- Pt A: solution heat treat (get α solid solution)
  - -- Pt B: quench to room temp. (retain α solid solution)
  - -- Pt C: reheat to nucleate small θ particles within α phase.
- Other alloys that precipitation harden:
  - Cu-Be
  - Cu-Sn
  - Mg-Al

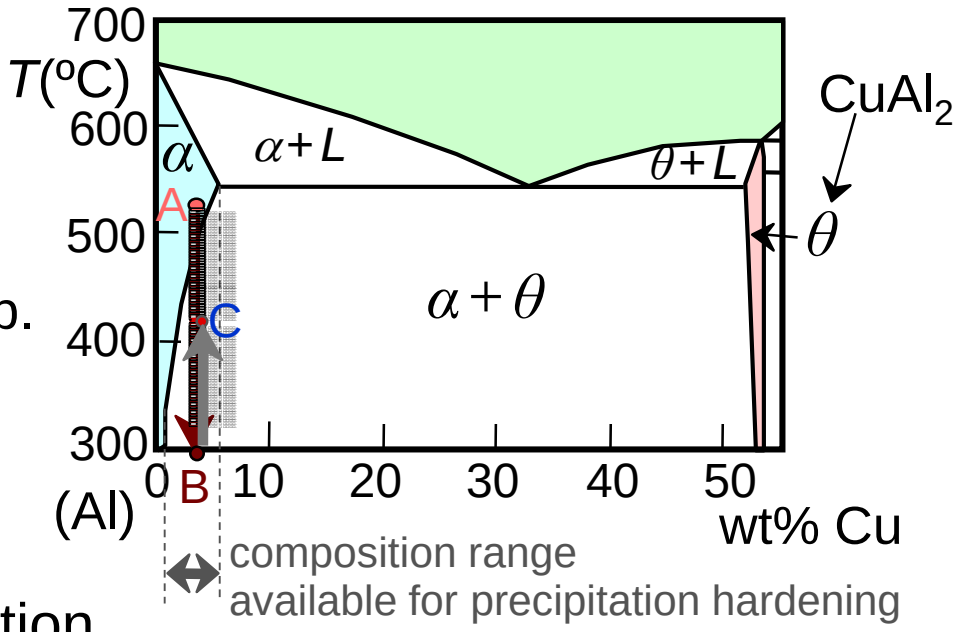
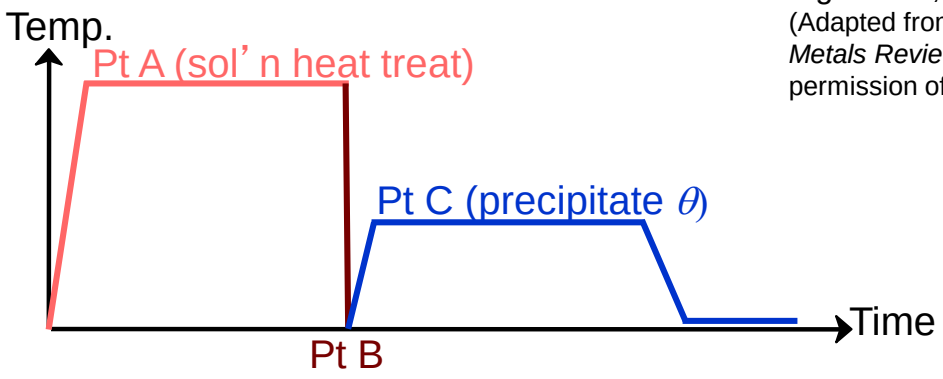


Fig. 17.18, *Callister & Rethwisch 9e*. (Adapted from J.L. Murray, *International Metals Review* **30**, p.5, 1985. Reprinted by permission of ASM International.)



Adapted from Fig. 17.16, *Callister & Rethwisch 9e*.

Precipitation Hardening_age hardening

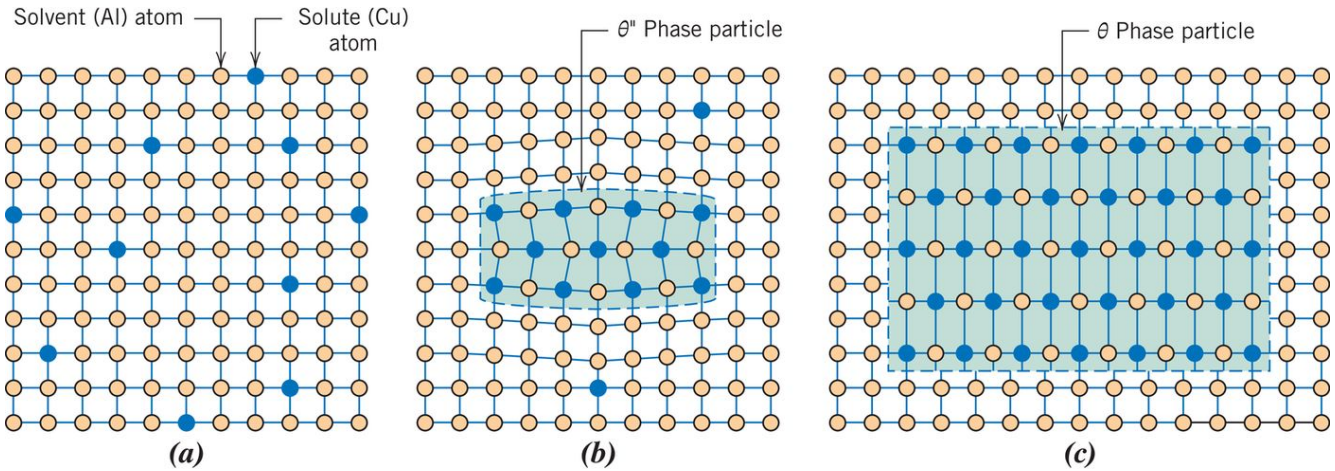


Figure 11.30 Schematic depiction of several stages in the formation of the equilibrium precipitate (Θ) phase. (a) A super-saturated α solid solution. (b) A transition, Θ", precipitate phase. (c) The equilibrium Θ phase, within the α-matrix phase

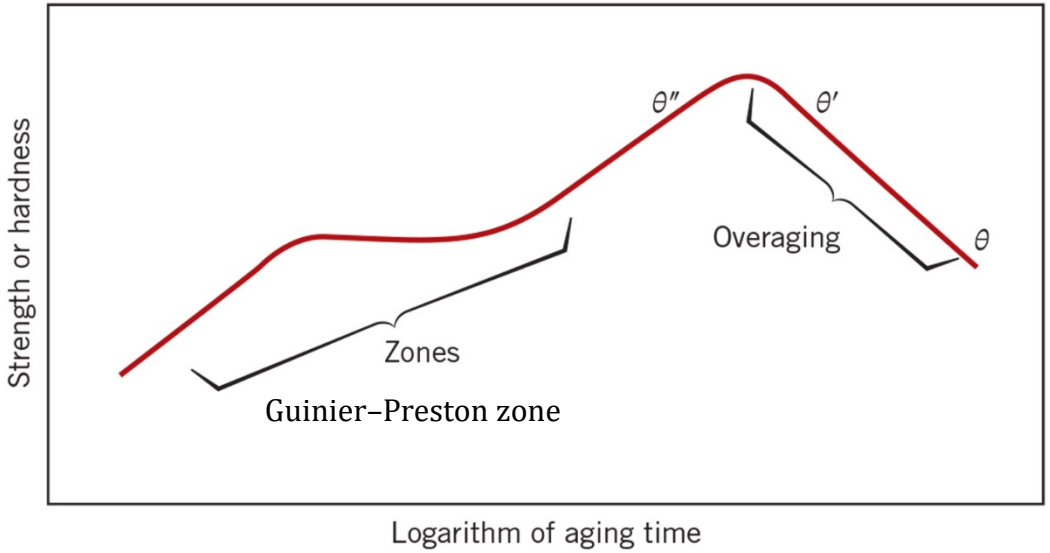
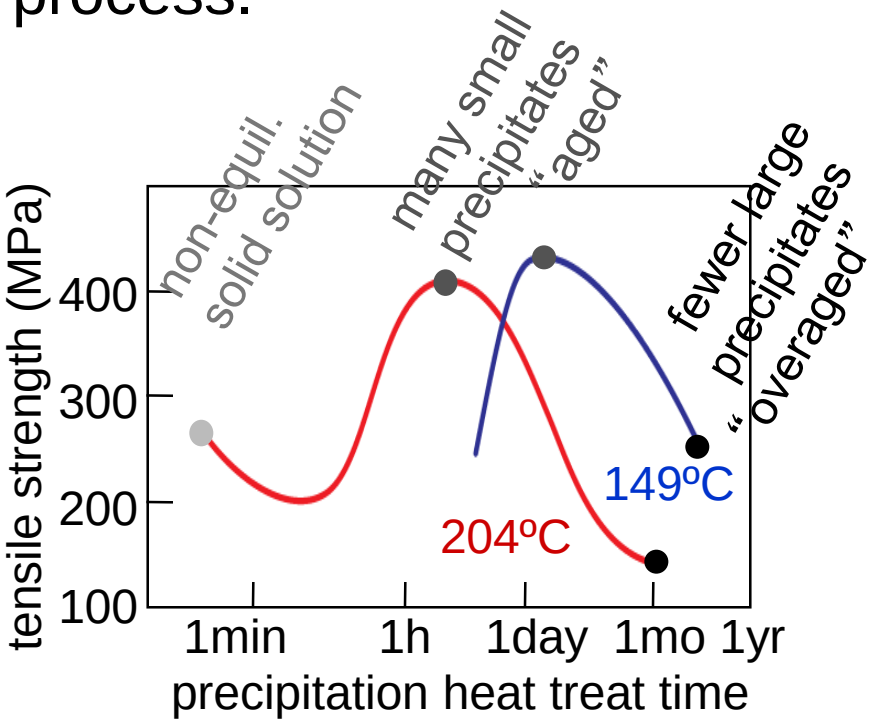


Figure 11.28 Schematic diagram showing strength and hardness as a function of the logarithm of aging time at constant temperature during the precipitation heat treatment.

Influence of Precipitation Heat Treatment on *TS*, %*EL*

- 2014 Al Alloy:
- Maxima on *TS* curves.
- Increasing *T* accelerates process.
- Minima on %*EL* curves.



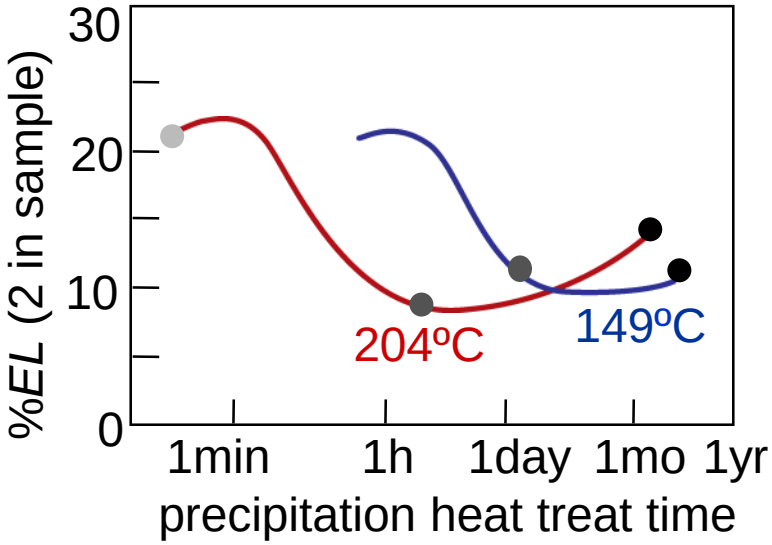


Fig. 17.21, *Callister & Rethwisch 9e*. [Adapted from *Metals Handbook: Properties and Selection: Nonferrous Alloys and Pure Metals*, Vol. 2, 9th ed., H. Baker (Managing Ed.), 1979. Reproduced by permission of ASM International, Materials Park, OH.]

Chapter 12: Structures & Properties of Ceramics

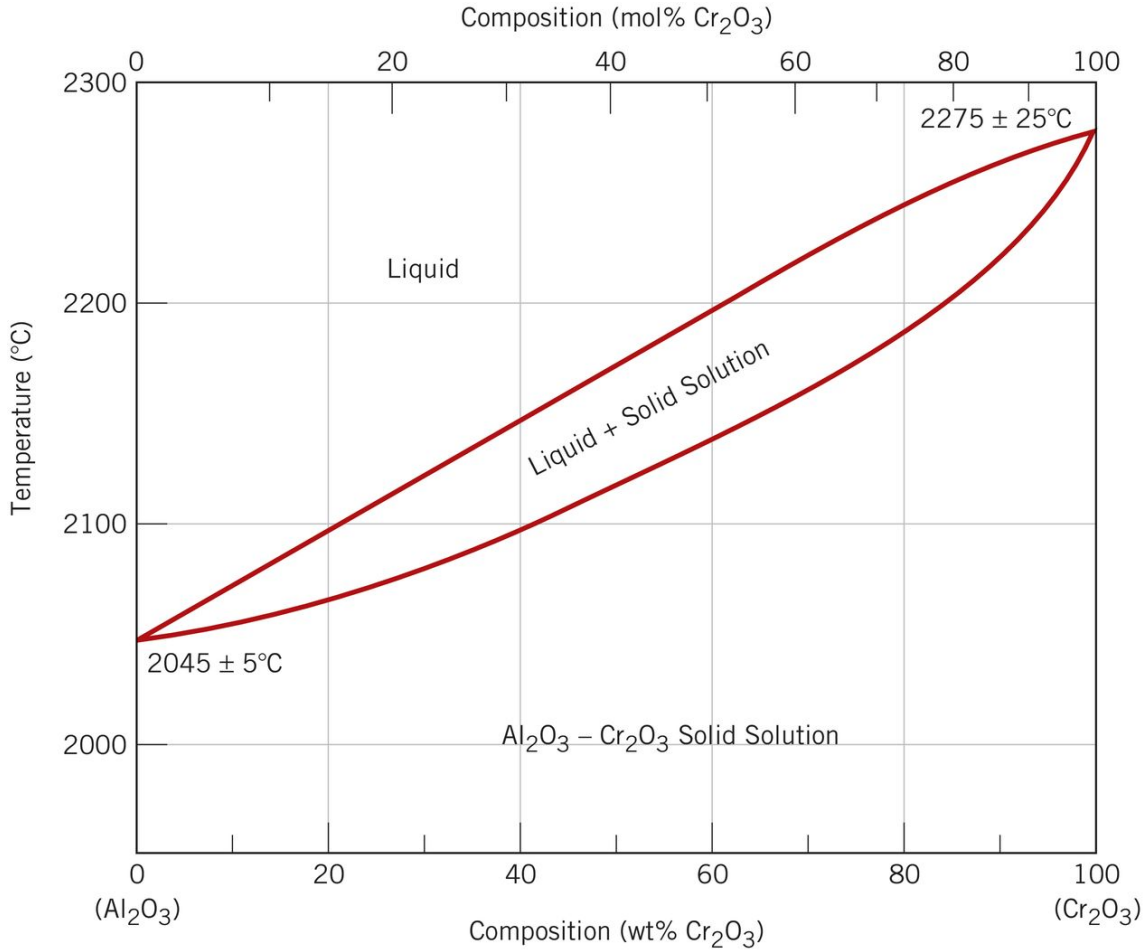
ISSUES TO ADDRESS...

Ceramics Structures **Lecture note 6: 41-71 pages 참고**

- How do the crystal structures of ceramic materials differ from those for metals?
- How do point defects in ceramics differ from those defects found in metals?
- How are impurities accommodated in the ceramic lattice?
- In what ways are ceramic phase diagrams different from phase diagrams for metals?
- How are the mechanical properties of ceramics measured, and how do they differ from those for metals?

I. Ceramic Phase Diagrams

a. Al_2O_3- Ca_2O_3diagram: complete solid solution

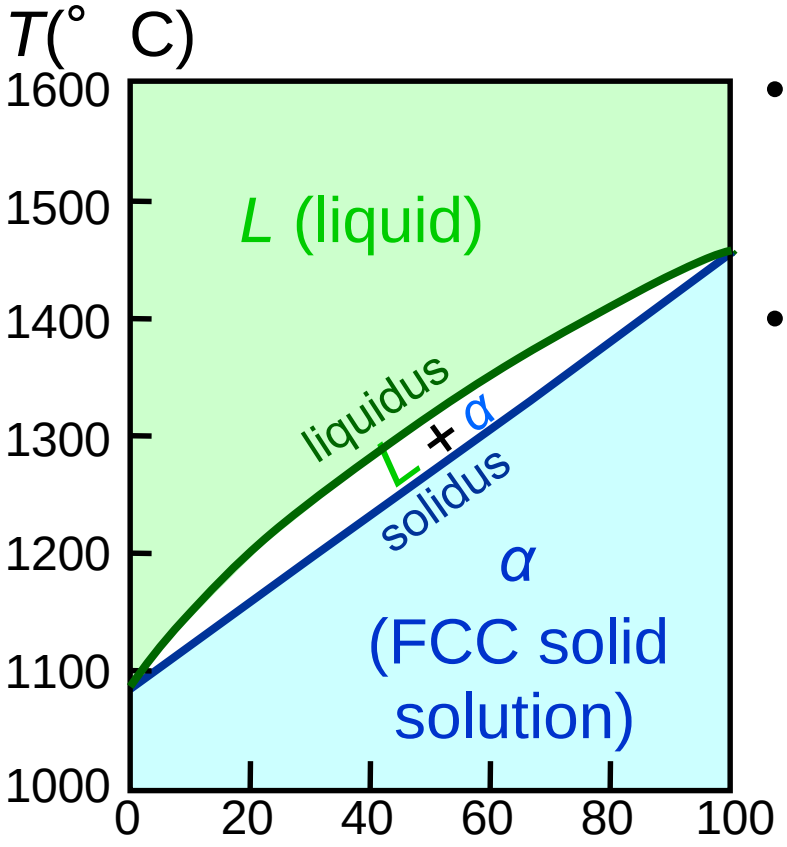


Adapted from E. N. Bunting, "Phase Equilibria in the System Cr2O3–Al2O3," Bur. Standards J. Research, 6, 1931, p. 948.

Isomorphous Binary Phase Diagram

- Indicate phases as a function of *T*, *C*, and *P*.
- For this course:
  - binary systems: just 2 components (Cu and Ni).
  - independent variables: *T* and *C* (*P* = 1 atm is almost always used).

Phase Diagram for Cu-Ni system

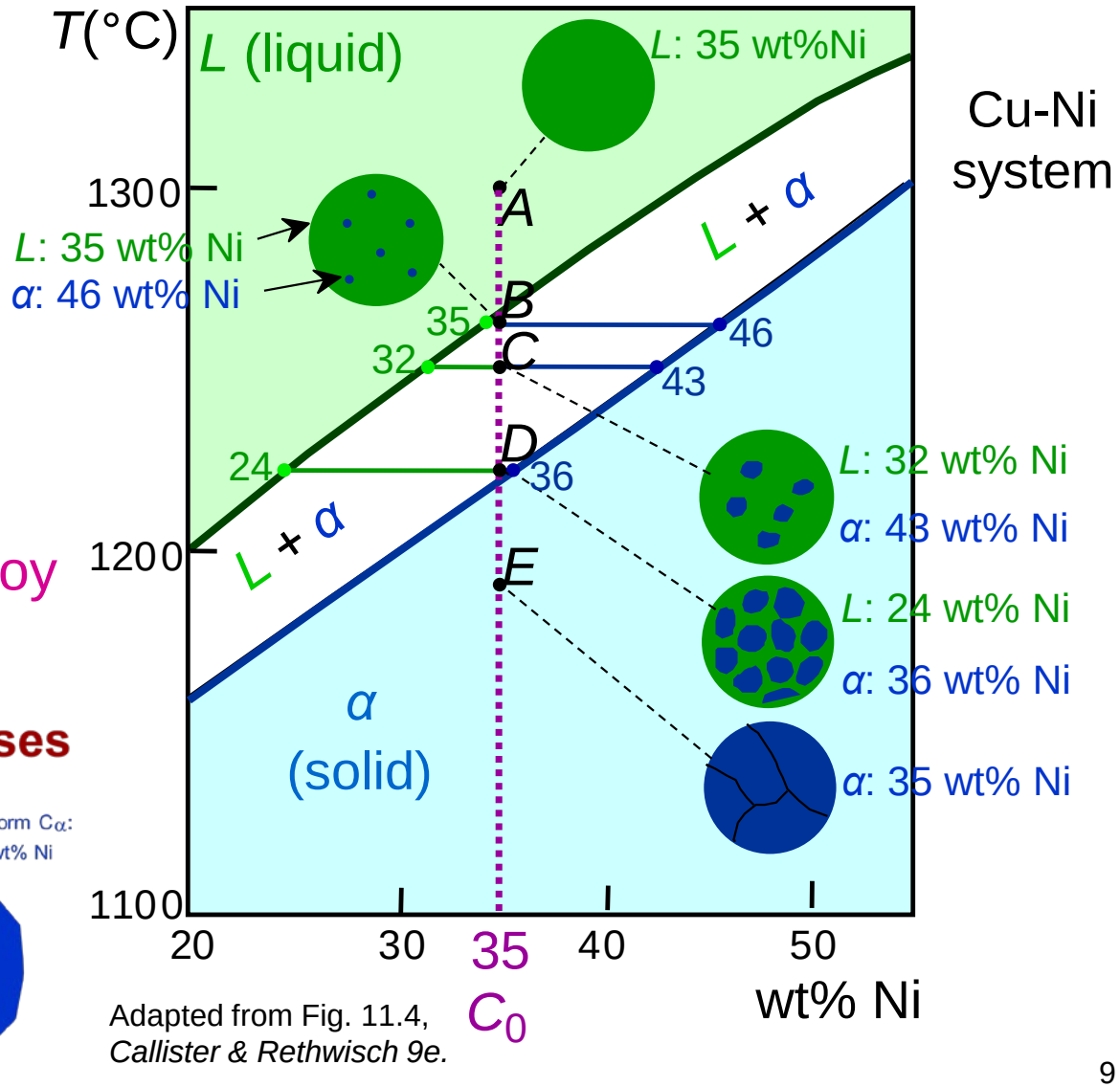


- 2 phases:
  - *L* (liquid)
  - *α* (FCC solid solution)
- 3 different phase fields:
  - *L*
  - *L* + *α*
  - *α*

Fig. 11.3(a), *Callister & Rethwisch 9e.* (Adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

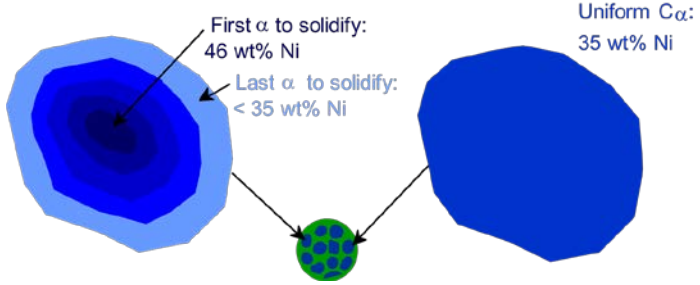
Cooling of a Cu-Ni Alloy

- Phase diagram: Cu-Ni system.
- Consider microstuctural changes that accompany the cooling of a C_0 = 35 wt% Ni alloy



Adapted from Fig. 11.4, *Callister & Rethwisch 9e.*

- Cored vs Equilibrium Phases



Ceramic Phase Diagrams

b. MgO-Al_2O_3 diagram: Eutectic system

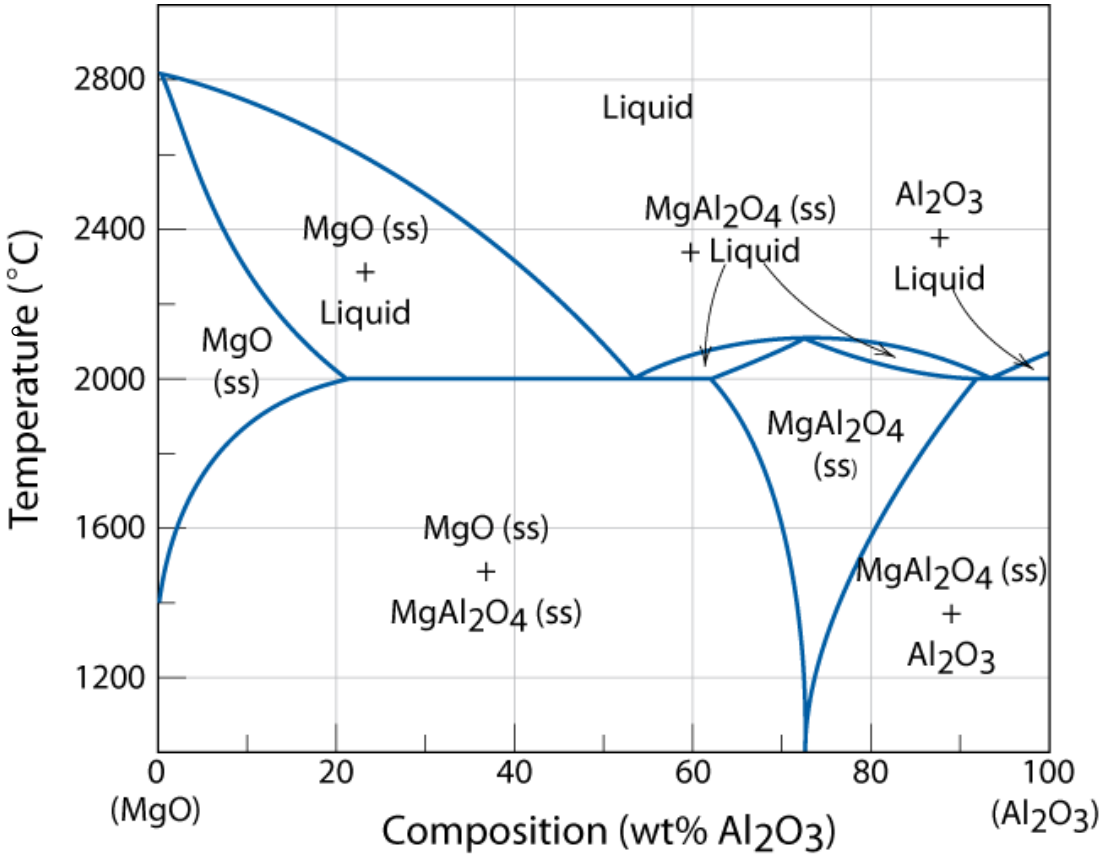


Fig. 14.2, Callister & Rethwisch 9e.
[Adapted from B. Hallstedt, "Thermodynamic Assessment of the System MgO–Al_2O_3," J. Am. Ceram. Soc., 75[6], 1502 (1992). Reprinted by permission of the American Ceramic Society.]

$MgAl_2O_4$ (or MgO-Al_2O_3) Spinel: 중간상 - 고용체

Eutectic Systems

- For alloy of composition $C_0 = C_E$
- Result: Eutectic microstructure (lamellar structure)
  -- alternating layers (lamellae) of α and β phases.

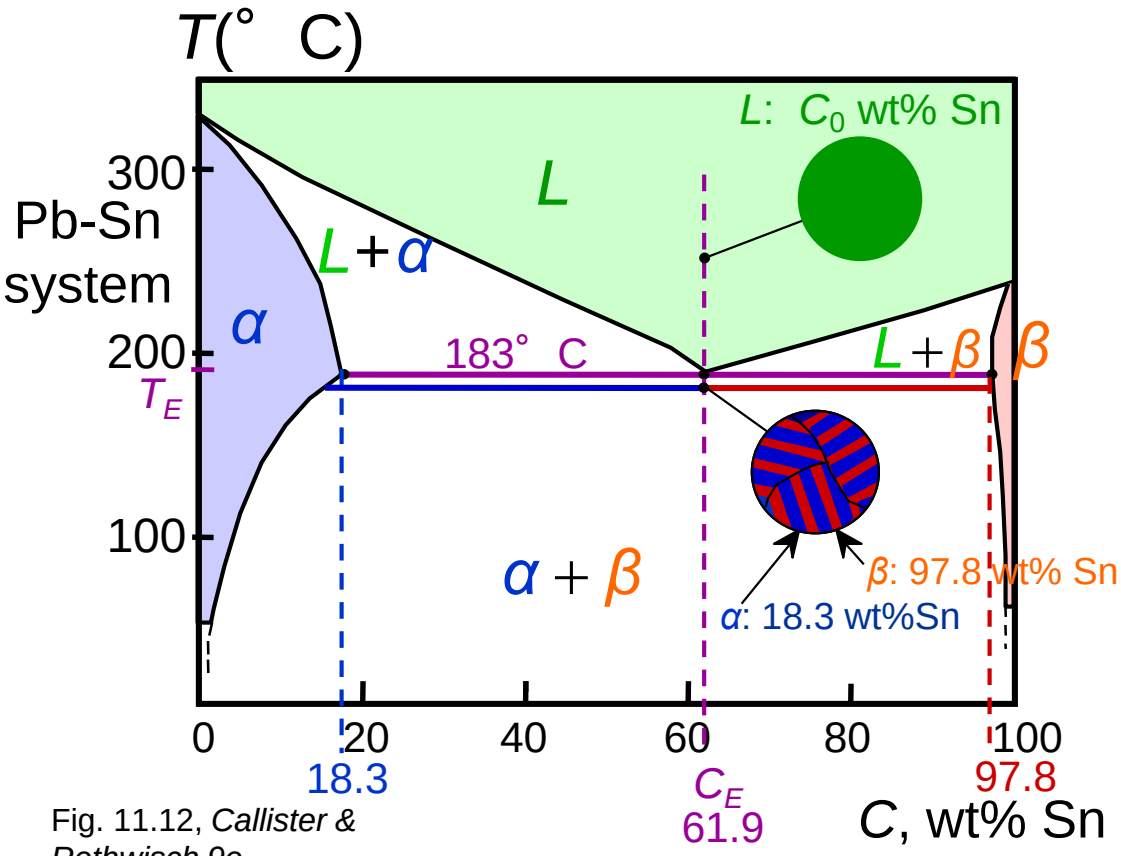


Fig. 11.12, *Callister & Rethwisch 9e.*

Micrograph of Pb-Sn eutectic microstructure

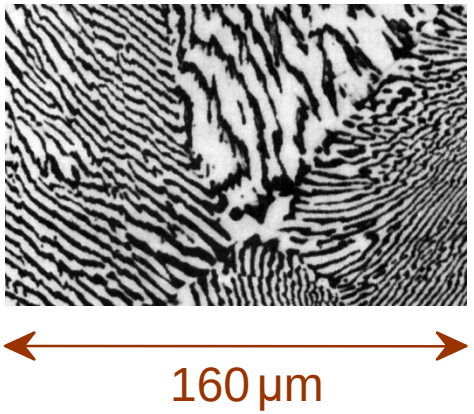


Fig. 11.13, *Callister & Rethwisch 9e.*
(From *Metals Handbook*, 9th edition, Vol. 9, *Metallography and Microstructures*, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

Ceramic Phase Diagrams

c. ZrO_2-CaO diagram: Eutectic system

T ↔ M 커다란 부피변화
: 재료내 균열 야기

→ CaO 첨가

→ Cubic phase 안정화

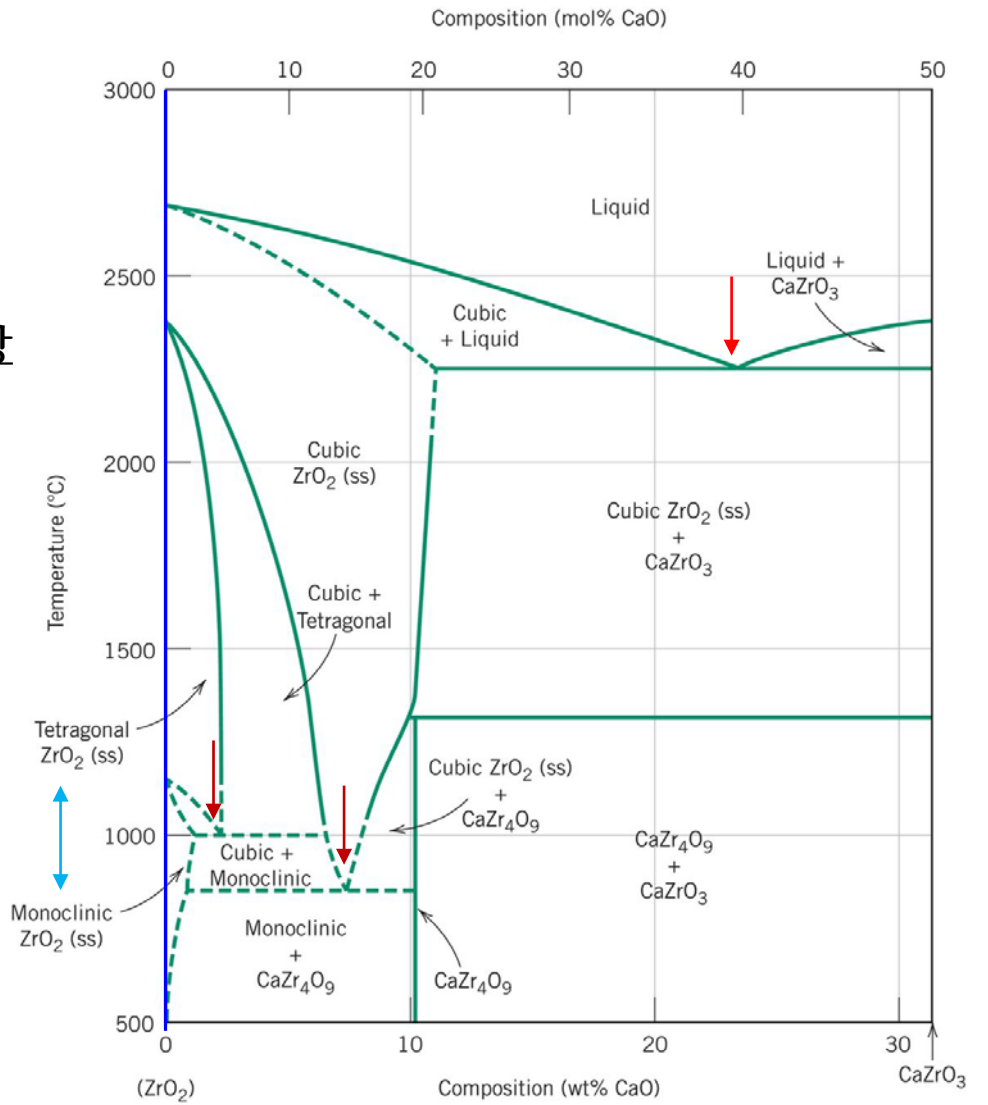
→ Cubic + Tetragonal 상 공존 냉각 조건에 따라 상온에서도 유지되도록 함

→ 취성이 작은 안정화 지르코니아 (Partially stabilized Zirconia, PSZ) 형성

→ Y_2O_3, MgO 도 안정화제

→ 함량 증가시 Cubic이 상온까지 안정화

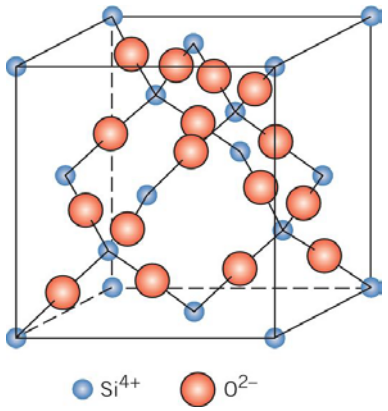
→ 완전 안정화 지르코니아



Adapted from V. S. Stubican and S. P. Ray, "Phase Equilibria and Ordering in the System ZrO2–CaO," J. Am. Ceram. Soc., 60[11–12] 535 (1977). Reprinted by permission of the American Ceramic Society.

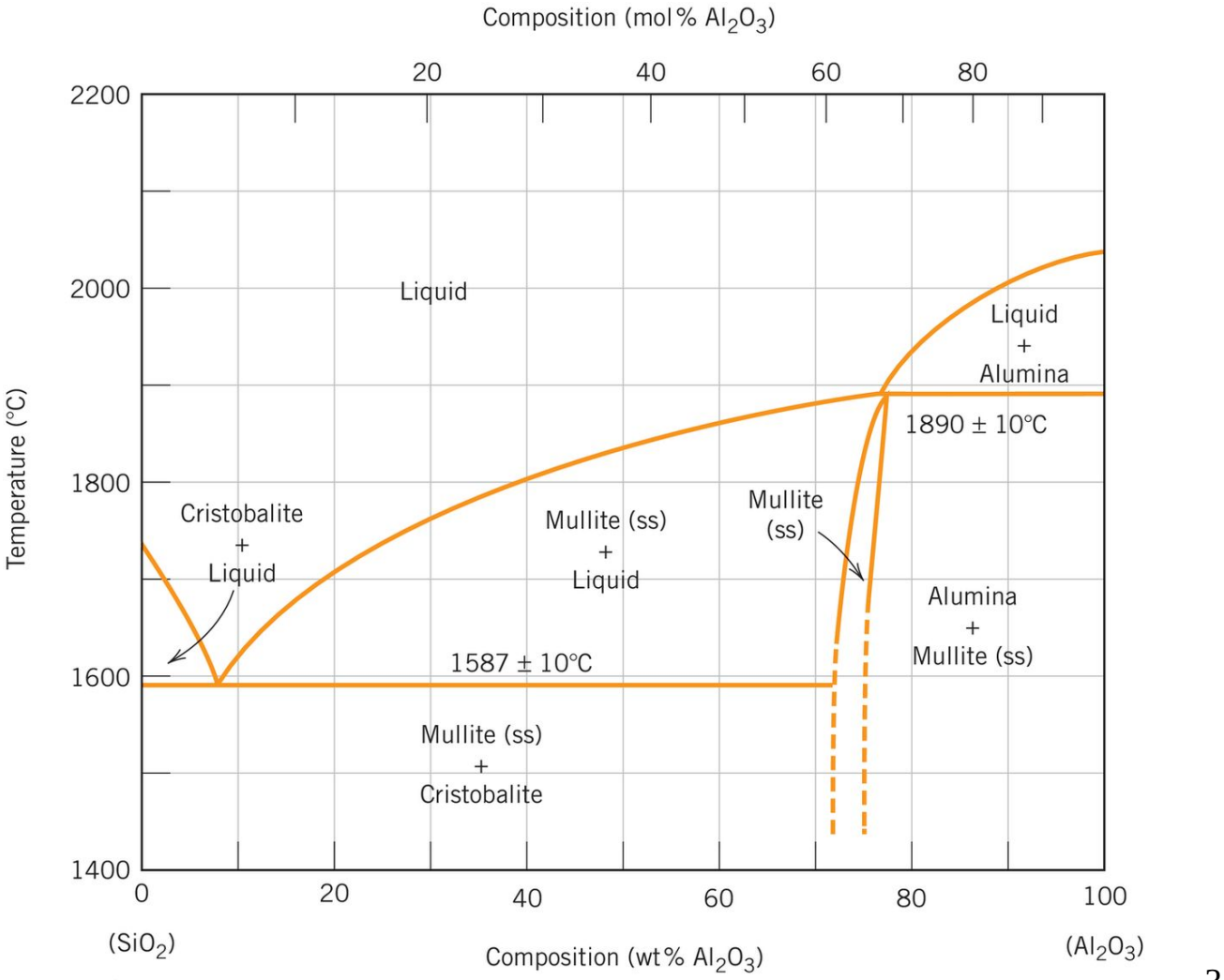
Ceramic Phase Diagrams

d. SiO_2-Al_2O_3 diagram: 대표적 내화세라믹 재료



Cristobalite
Figure 4.11

Mullite
$3Al_2O_3$-$2SiO_2$



Adapted from F. J. Klug, S. Prochazka, and R. H. Doremus, "Alumina–Silica Phase Diagram in the Mullite Region," J. Am. Ceram. Soc., 70[10], 758 (1987). Reprinted by permission of the American Ceramic Society.

II. Mechanical Properties

12.8 세라믹의 취성파괴

Ceramic materials are **more brittle** than metals.

: 재료의 파괴시 에너지 흡수가 거의 없이 **취성파괴**를 일으킴

Why is this so?

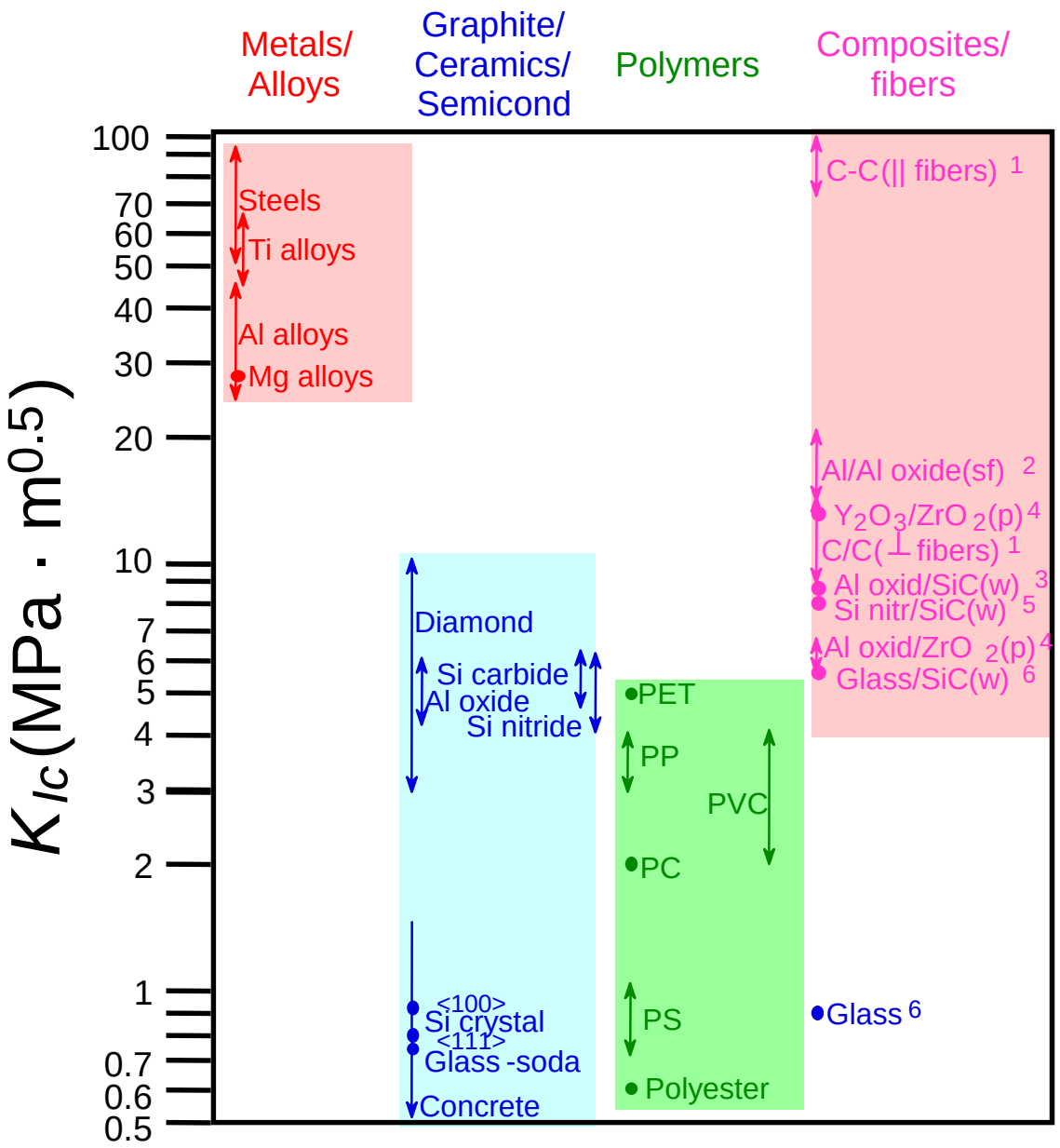
- Consider **mechanism of deformation**
  - **In crystalline, by dislocation motion**
  - In highly ionic solids, dislocation motion is difficult
    - few slip systems
    - resistance to motion of ions of like charge (e.g., anions) past one another

Fracture Toughness

균열이 존재할 때 취성 파괴에 대한 재료의 저항 정도 나타냄

$$K_c = Y\sigma\sqrt{\pi a}$$

$$(= MPa\sqrt{m})$$



대체로 얇은 판에 있어 K_c값은 시편 두께에 따라 변한다. 시편의 두께가 균열 크기보다 매우 크면 K_c 값은 시편 두께의 영향을 받지 않으며, 이를 **평면 변형률(plane strain) 상태**라고 한다. 이러한 두꺼운 시편에서의 **K_c값을 평면 변형률 파괴 인성(plane strain fracture toughness) K_{Ic}**라 함.

Based on data in Table B5, *Callister 7e*.

$$K_c = Y\sigma\sqrt{\pi a}$$
$$(= MPa\sqrt{m})$$

* 우측항 값이 K_{Ic} 보다 작아도 어떤 환경의 정적 응력하에서 세라믹 재료 파괴

= Static Fatigue or delayed fracture

→대기 중 습기의 영향으로 균열 선단에서
응력부식 파괴가 발생

→정적 피로 강도 표시는 (응력 + 시간)

* **세라믹 재료의 파괴강도** 왼쪽과 같은
분포를 나타냄_결함의 존재확률로 설명

단, 압축 응력에서는 결함에 의해 응력
증폭의 효과가 없어 세라믹에서의
강도가 인장에서보다 압축이 10배정도 큼

→ 세라믹의 파괴강도는 표면에 잔류 압축
응력을 부가하여 상당히 증가시킬 수 있음
열 템퍼링 (Thermal tempering)

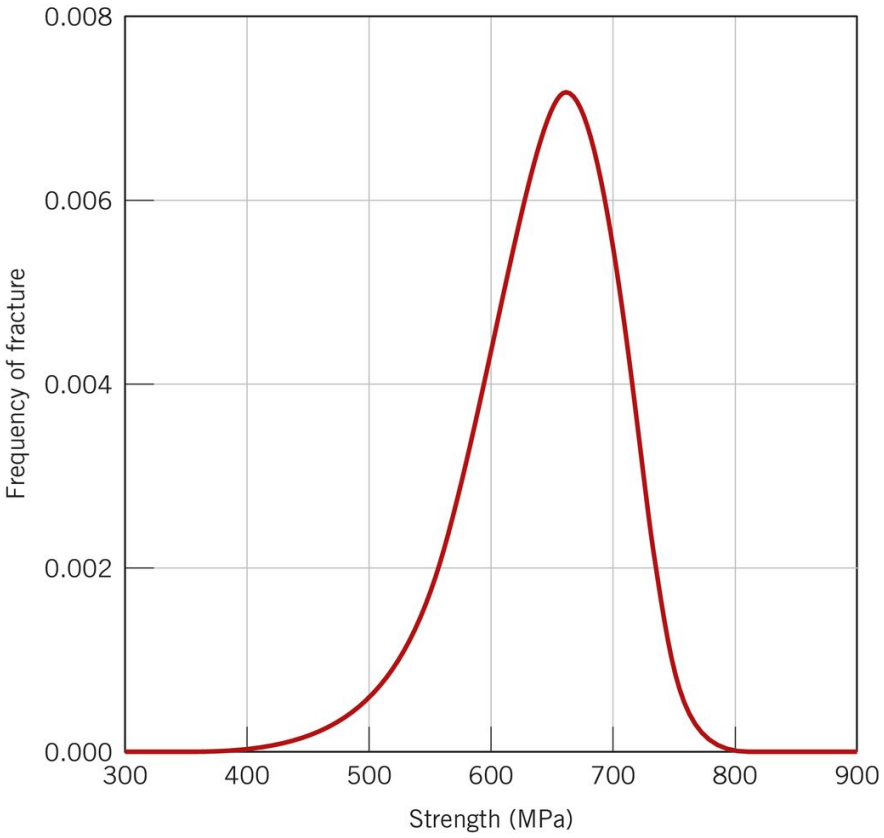
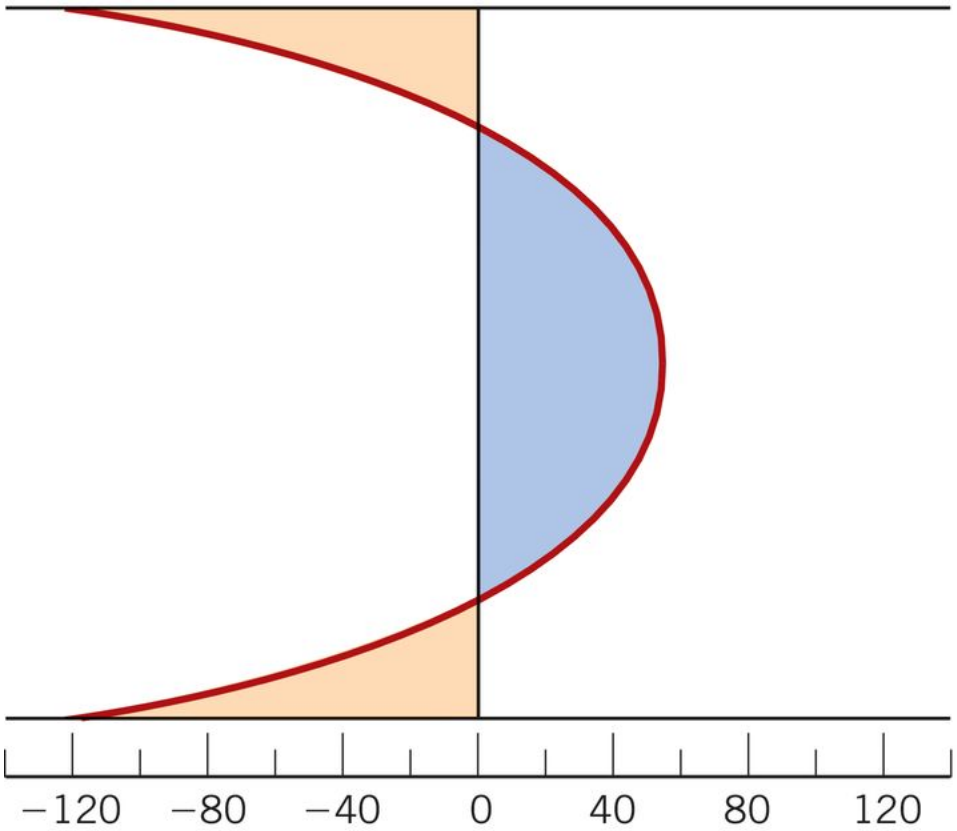


Figure 14.5 질화규소 재료에서 측정된 파괴강도의 분포 빈도

* 유리판 단면의 상온 잔류응력 분포

: 공기 제트나 기름욕 (oil bath) 내에서 상온까지 냉각
표면과 내부의 냉각 속도가 상이하기 때문에 잔류응력 발생



From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, Introduction to Ceramics, 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

* 세라믹의 파면

a. 균열의 기원 및 형상

균열이 생성되고
전파하는 동안에
균열 전파가 가속되어
임계 속도 [또는 종착 속도
Terminal speed)]에 도달시
(유리의 경우, 음속의 ½)
균열은 가지를 치게 되는데
(분기, branching)
이 과정이 반복되어
균열 군이 생성됨

균열이 분기되는 정도는
인가된 응력에 따라 증가

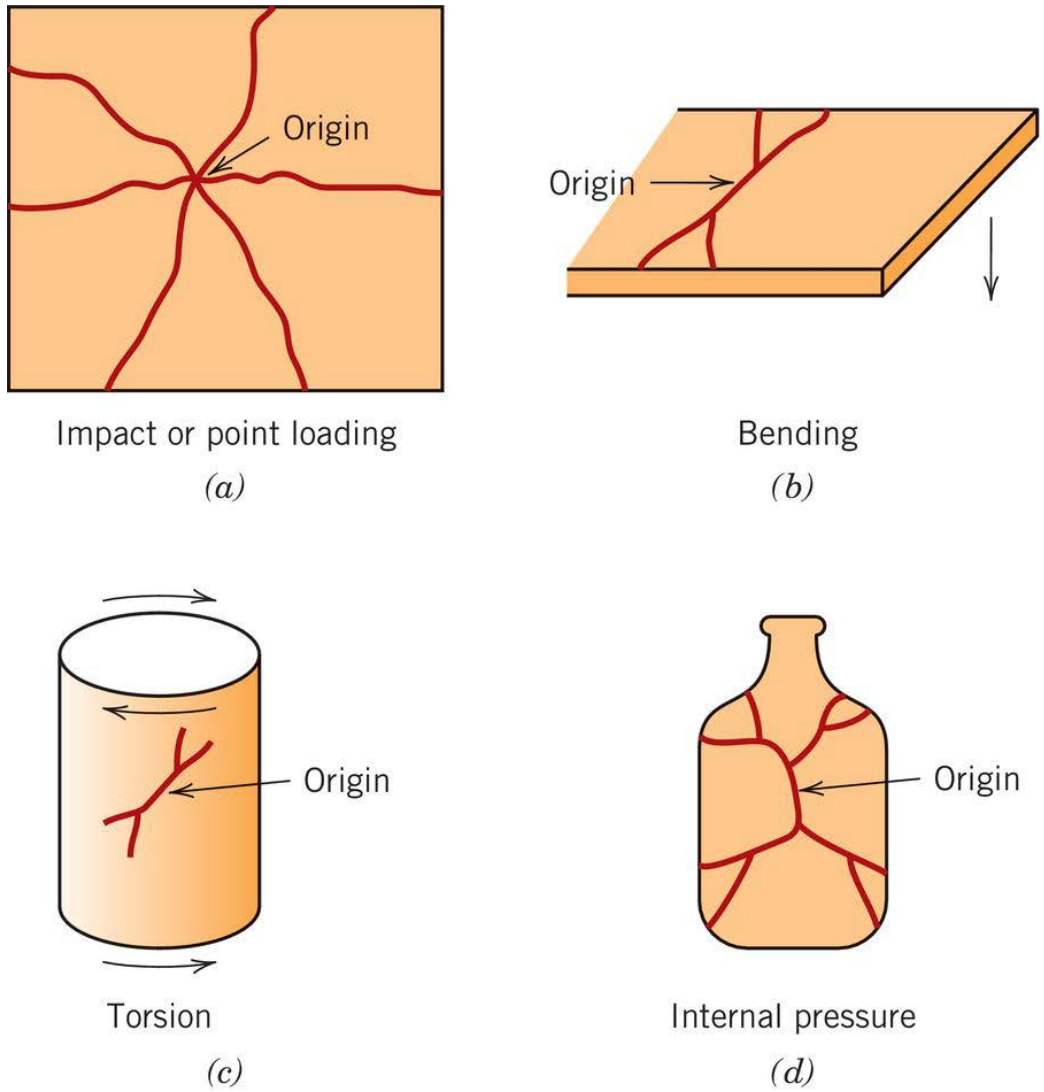


Figure 14.6 취성 세라믹에서 일반적인 네 종류의 하중 인가 조건에서 인가된 응력 패턴에 따른 생성되는 **균열의 기원 및 형상의 모식도**

* 세라믹의 파면

b. 파단면 (Fractography)

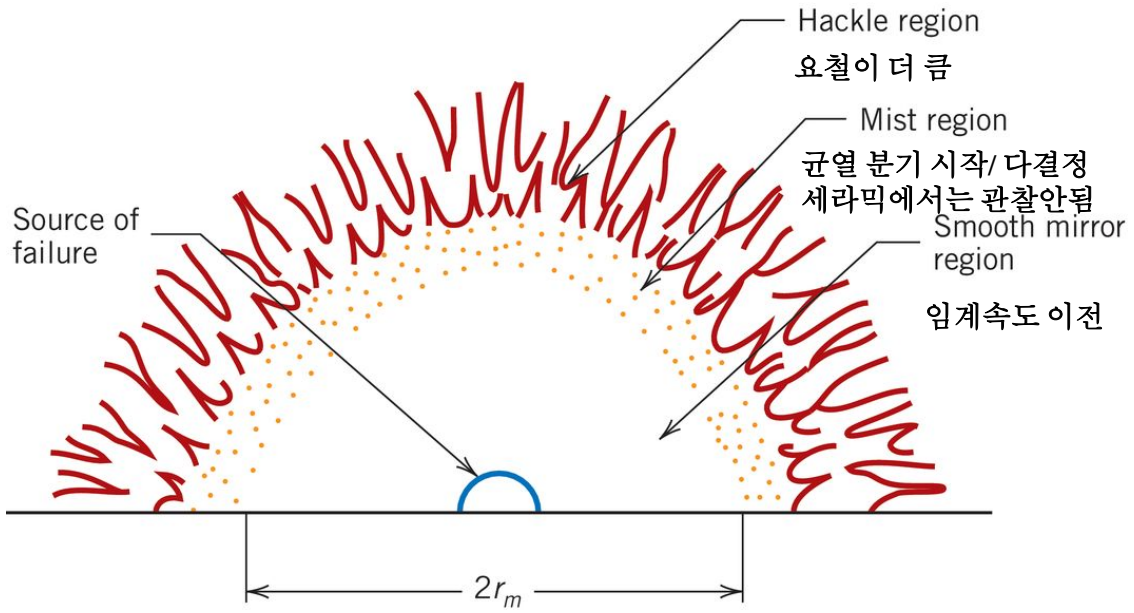
균열이 전파하는 동안
재료의 미세구조, 응력,
발생된 탄성파 등과
상호작용을 하며
파단면에 특정한 특징을 유발

파괴 응력값 (σ_f)

$$\sigma_f \propto \frac{1}{r_m^{0.5}}$$

응력 증가↑→가속도↑→r_m↓

Figure 12.28 취성 세라믹의 파단면상에서 관찰되는 일반적인 특징 모식도



Adapted from J. J. Mecholsky, R. W. Rice, and S. W. Freiman, "Prediction of Fracture Energy and Flaw Size in Glasses from Measurements of Mirror Size," J. Am. Ceram. Soc., 57[10] 440 (1974). Reprinted with permission of The American Ceramic Society, www.ceramics.org. Copyright 1974. All rights reserved.

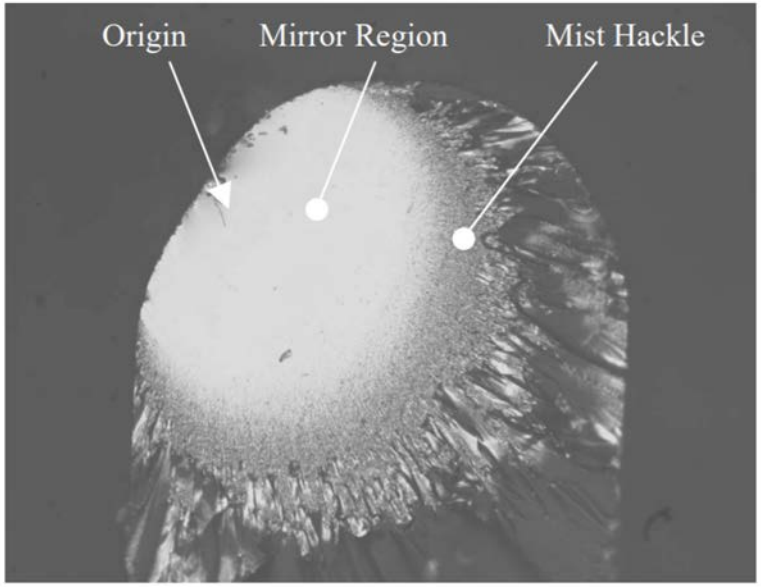
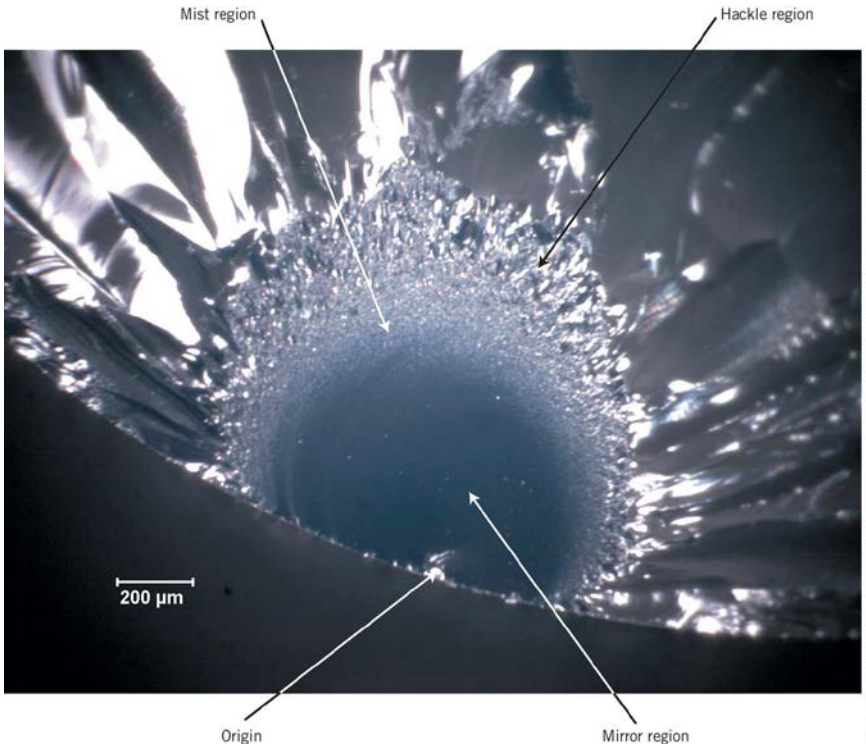


Fig. 6 Fracture surface around origin. Origin is surrounded with mirror region, which is covered with mist Hackle mark. Failure stress can be estimated using radius of the mirror region.

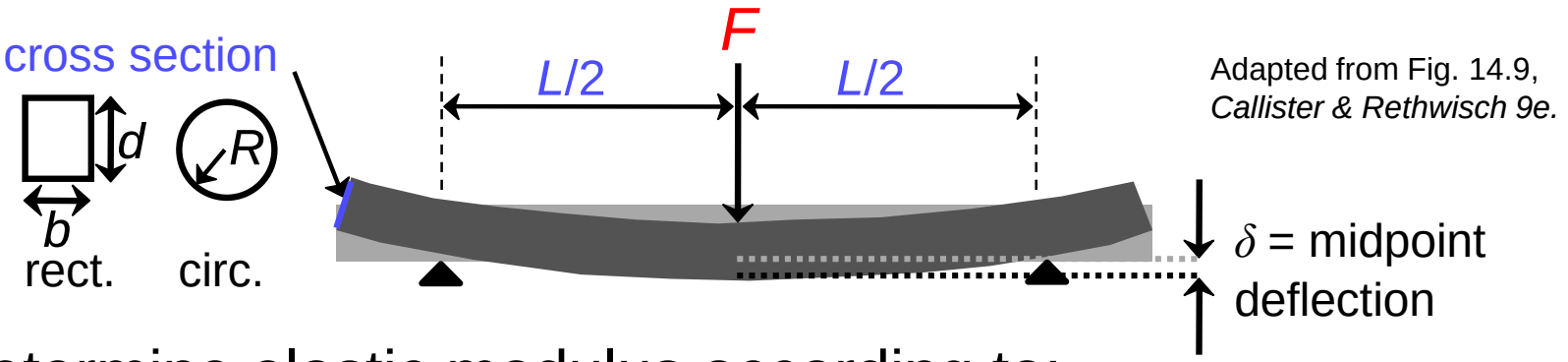


: 응력 분포 및 균열의 전파방향에 대한 정보제공

아크 형상 파단시 생성되는 탄성(음)파와 균열 선단과 상호작용으로 발생

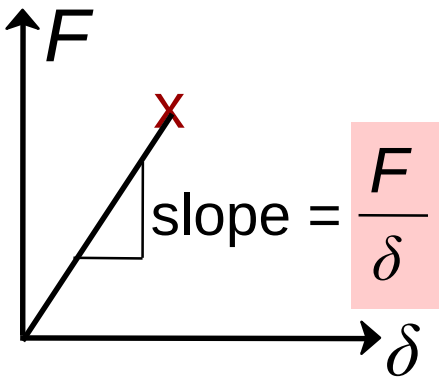
Flexural Tests – Measurement of Elastic Modulus

- Room *T* behavior is usually elastic, with brittle failure.
- 3-Point Bend Testing often used.
  -- tensile tests are difficult for brittle materials.



Adapted from Fig. 14.9, *Callister & Rethwisch 9e.*

- Determine elastic modulus according to:



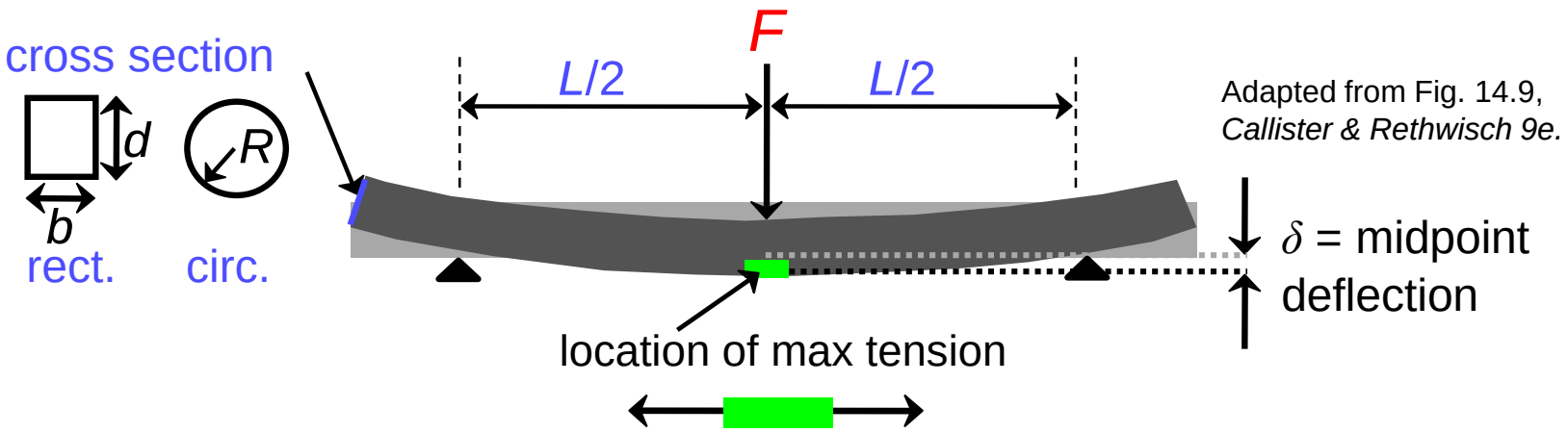
linear-elastic behavior

$$E = \frac{F}{\delta}\frac{L^3}{4bd^3}$$ (rect. cross section)

$$E = \frac{F}{\delta}\frac{L^3}{12\pi R^4}$$ (circ. cross section)

Flexural Tests – Measurement of Flexural Strength

- 3-point bend test to measure room-*T* flexural strength.



- Flexural strength:

$$\sigma_{fs} = \frac{3F_f L}{2bd^2} \quad \text{(rect. cross section)}$$

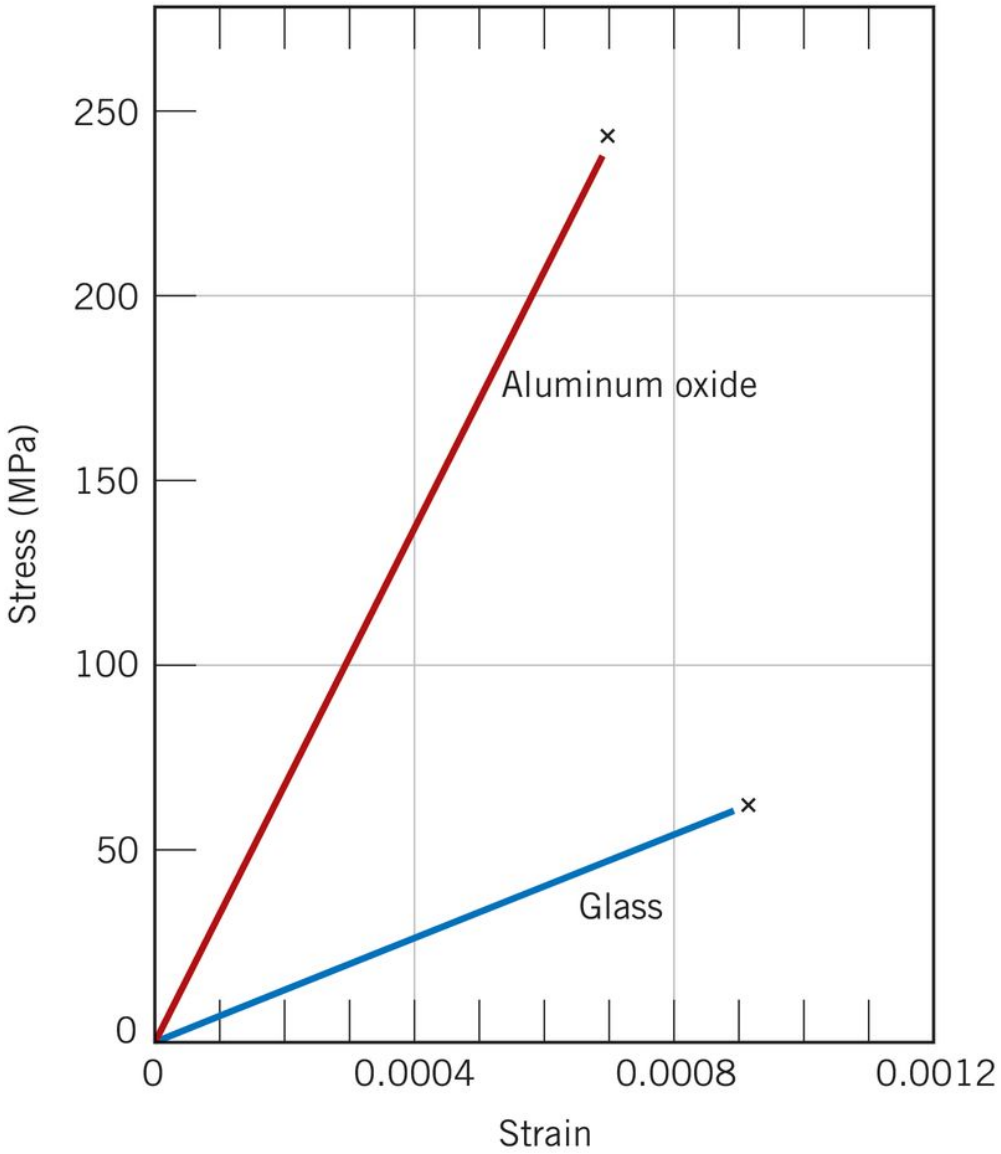
$$\sigma_{fs} = \frac{F_f L}{\pi R^3} \quad \text{(circ. cross section)}$$

- Typical values:

Material	σ_{fs} (MPa)	E(GPa)
Si nitride	250-1000	304
Si carbide	100-820	345
Al oxide	275-700	393
glass (soda-lime)	69	69

Data from Table 14.1, *Callister & Rethwisch 9e.*

Figure 12.31 알루미나와 유리의 응력 변형률 거동_ 탄성거동
세라믹의 탄성계수 = **70 ~ 500 GPa** 범위 금속보다 약간 높음



12.10 소성변형기구

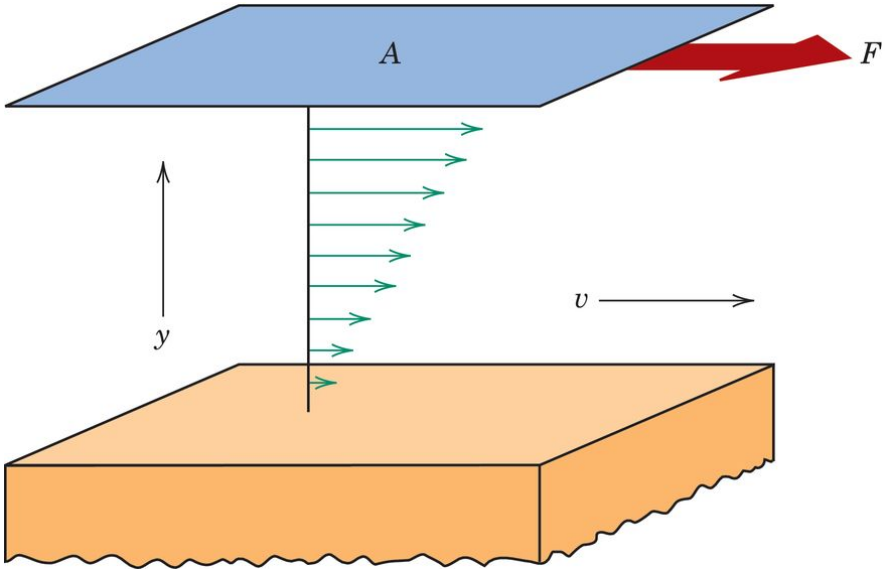
Consider mechanism of deformation

In crystalline ceramic, by dislocation motion

In non-crystalline ceramic, by viscous flow

Viscosity (η): 비정질 재료의 변형에 대한 저항

$$\eta = \frac{\tau}{dv/dy} = \frac{F/A}{dv/dy}$$



단위: P (poise) or Pa·s

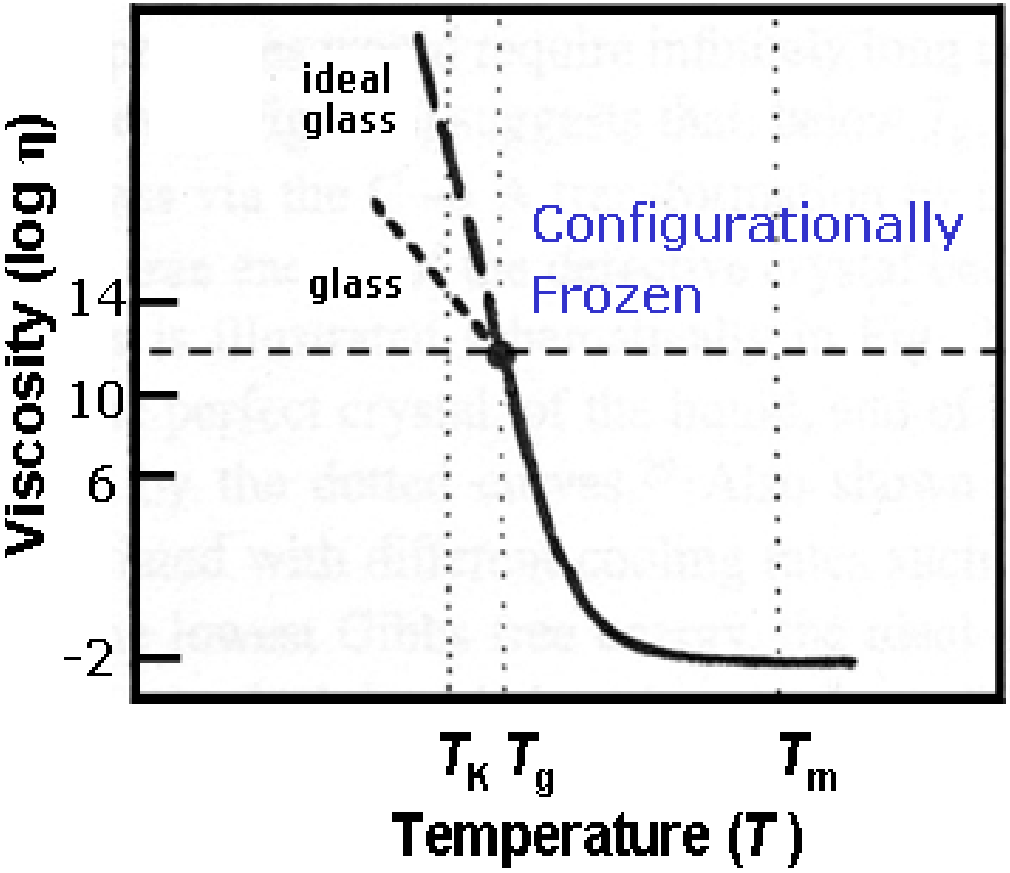
1P=1dyne·s/cm^2, 1 Pa·s=1N·s/m^2

10 P (poise) = 1 Pa·s

Figure 14.11 가해진 전단응력에 대한 액체와 유리의 점성유동의 모식도

Glass : undercooled liquid with high viscosity

The higher the structural relaxation, the closer it moves toward a "true" glass.



A solid is a materials whose viscosity exceeds $10^{14.6}$ centiPoise (10^{12} Pa s)

cf) liquid ~*10^{-2} poise*

12.11 기타 기계적 고려사항

a. **탄성계수**의 기공도 의존성: $E = E_0(1 - 1.9P + 0.9P^2)$

P (기공의 부피분율)↑ → E ↓

b. 기공 분율이 **굴곡 강도**에 미치는 영향: $\sigma_{fs} = \sigma_0 \exp(-nP)$

기공은 (1) 하중이 가해지는 면적을 감소시킴 (2) 응력집중자 역할

P 가 파단 계수를 지수함수적으로 감소시킴 ex) 10% 기공, 강도 50%이상 감소

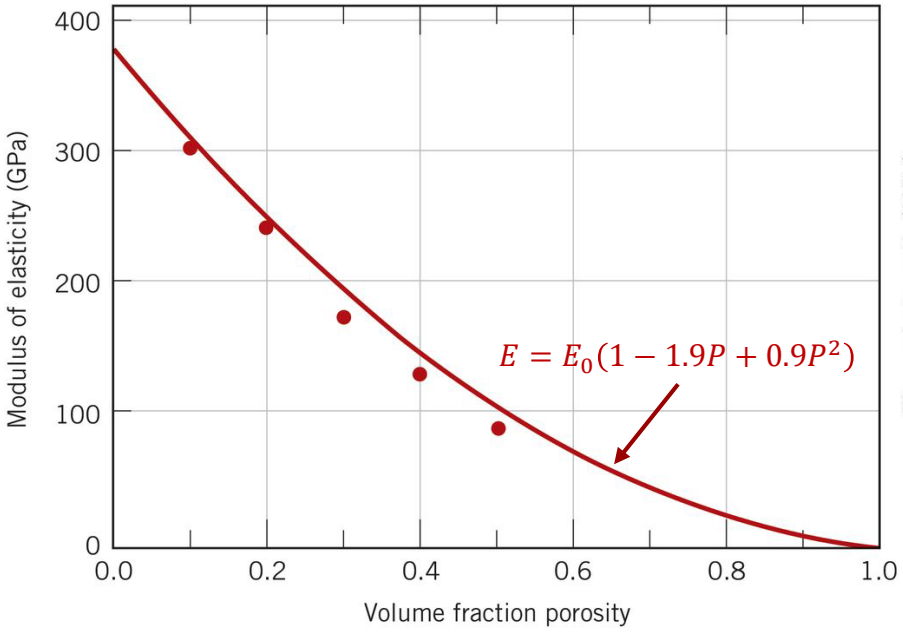


Figure 14.12

상온에서 알루미나의 탄성 계수에 미치는 기공의 영향

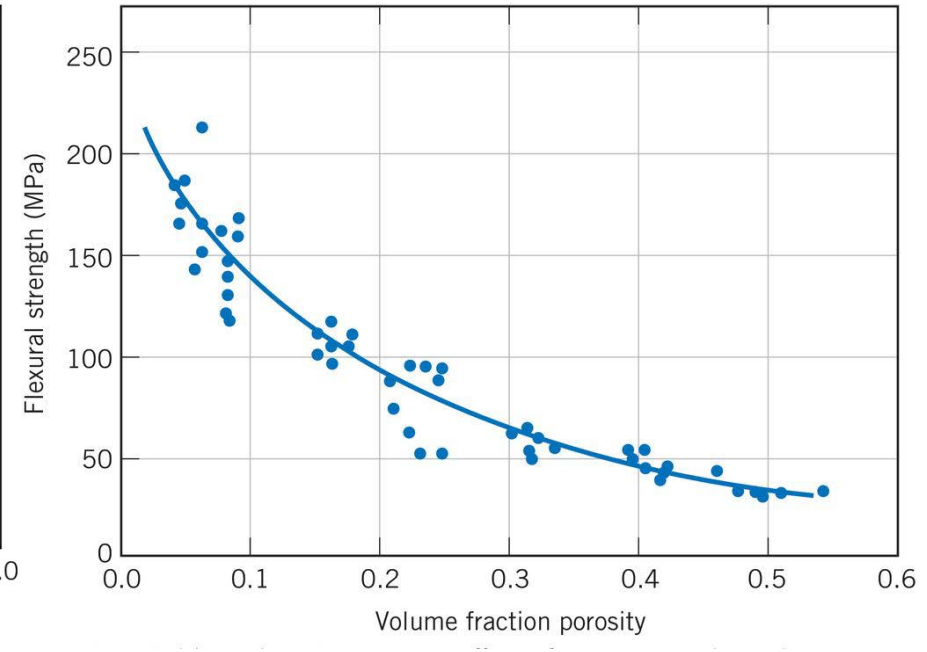


Figure 14.13

상온에서 알루미나의 굴곡강도에 미치는 기공의 영향

c. 경도 : 경도가 가장 높은 재료들이 세라믹 재료에 속함

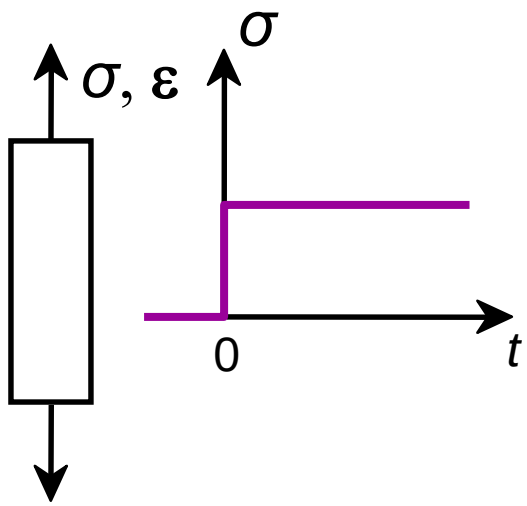
- 세라믹 재료는 압입시 쉽게 균열이 발생하여 정확한 경도를 측정하기 어려움
  따라서, 균열을 심하게 유발하는 구형 압입자 [로크웰 Rockwell 경도 시험기와 브린넬 Brinell 경도시험기]가 사용되지 않고, 피라미드형 압입자인 비커스 Vickers 와 누프 Knoop 법 (취성이 매우 심한 경우)이 주로 사용됨.

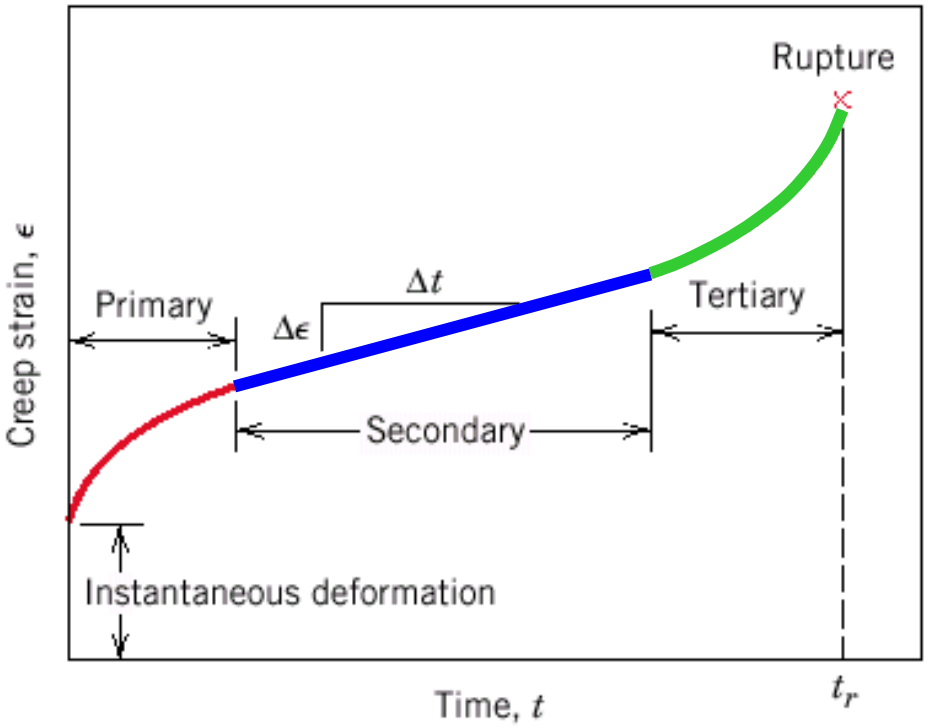
Table 14.2 Vickers (and Knoop) Hardnesses for Eight Ceramic Materials

Material	*Vickers Hardness (GPa)*	*Knoop Hardness (GPa)*	*Comments*
Diamond (carbon)	130	103	Single crystal, (100) face
Boron carbide (B_4C)	44.2	—	Polycrystalline, sintered
Aluminum oxide (Al_2O_3)	26.5	—	Polycrystalline, sintered, 99.7% pure
Silicon carbide (SiC)	25.4	19.8	Polycrystalline, reaction bonded, sintered
Tungsten carbide (WC)	22.1	—	Fused
Silicon nitride (Si_3N_4)	16.0	17.2	Polycrystalline, hot pressed
Zirconia (ZrO_2) (partially stabilized)	11.7	—	Polycrystalline, 9 mol% Y_2O_3
Soda-lime glass	6.1	—	

Creep

Sample deformation at a constant stress (σ) vs. time





Primary Creep: slope (creep rate) decreases with time.

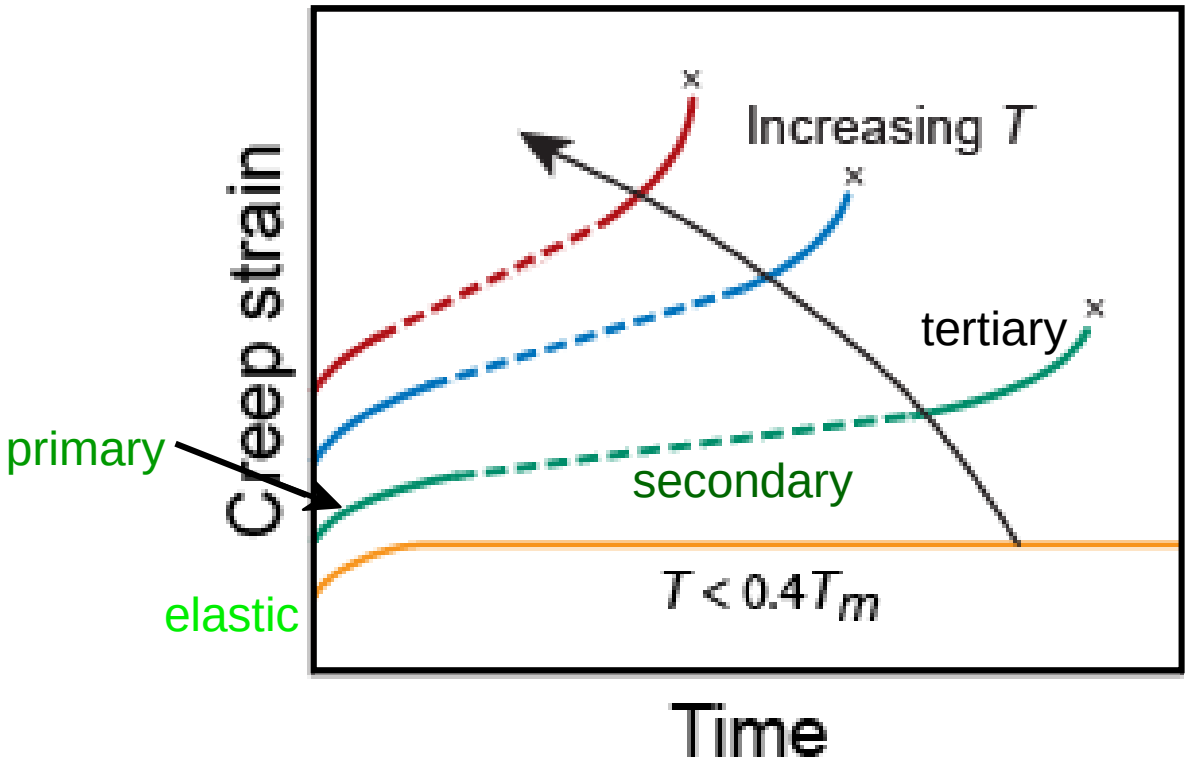
Secondary Creep: steady-state i.e., constant slope ($\Delta \varepsilon / \Delta t$).

Tertiary Creep: slope (creep rate) increases with time, i.e. acceleration of rate.

Adapted from Fig. 10.29, *Callister & Rethwisch 9e.*

Creep: Temperature Dependence

- Occurs at elevated temperature, $T > 0.4\,T_m$ (in K)



Figs. 10.30, *Callister & Rethwisch 9e.*

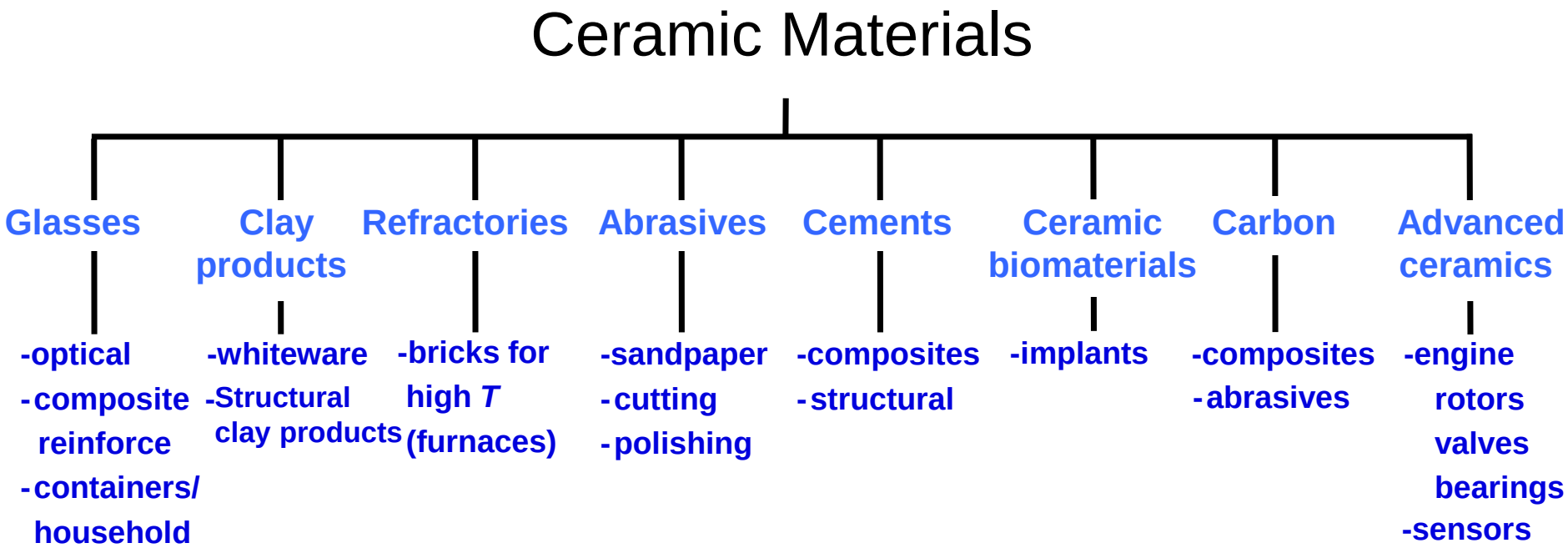
d. 세라믹 재료의 크리프는 T_m이 금속보다 상대적으로 커서 좀더 높은 온도에서 발생

Chapter 13: Applications and Processing of Ceramics

ISSUES TO ADDRESS...

- How do we classify ceramics?
- What are some applications of ceramics?
- How is processing of ceramics different than for metals?

III. Classification of Ceramics

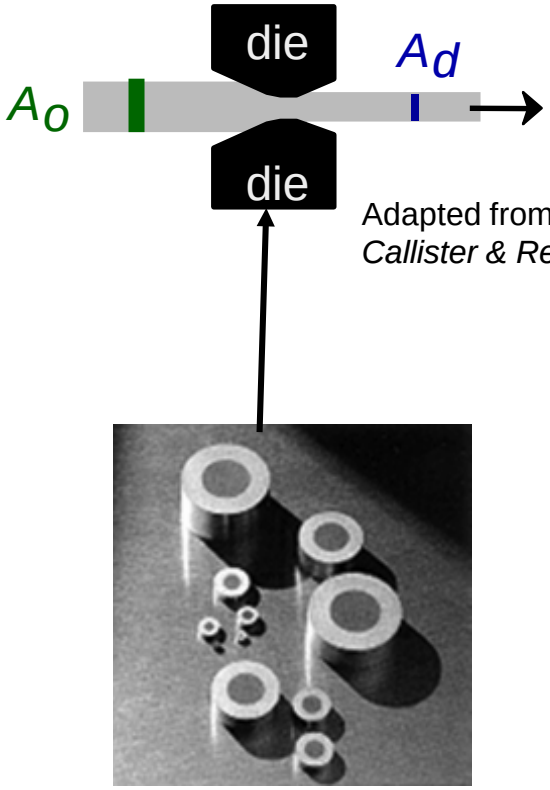


Adapted from Fig. 13.1 and discussion in Sections 13.2-10, *Callister & Rethwisch 10e.*

Figure 13.1 용도에 따라 분류한 세라믹 재료

Ceramics Application: Die Blanks

- Die blanks:
  -- Need wear resistant properties!
- Die surface:
  -- 4 μm polycrystalline diamond particles that are sintered onto a cemented tungsten carbide substrate.
  -- polycrystalline diamond gives uniform hardness in all directions to reduce wear.



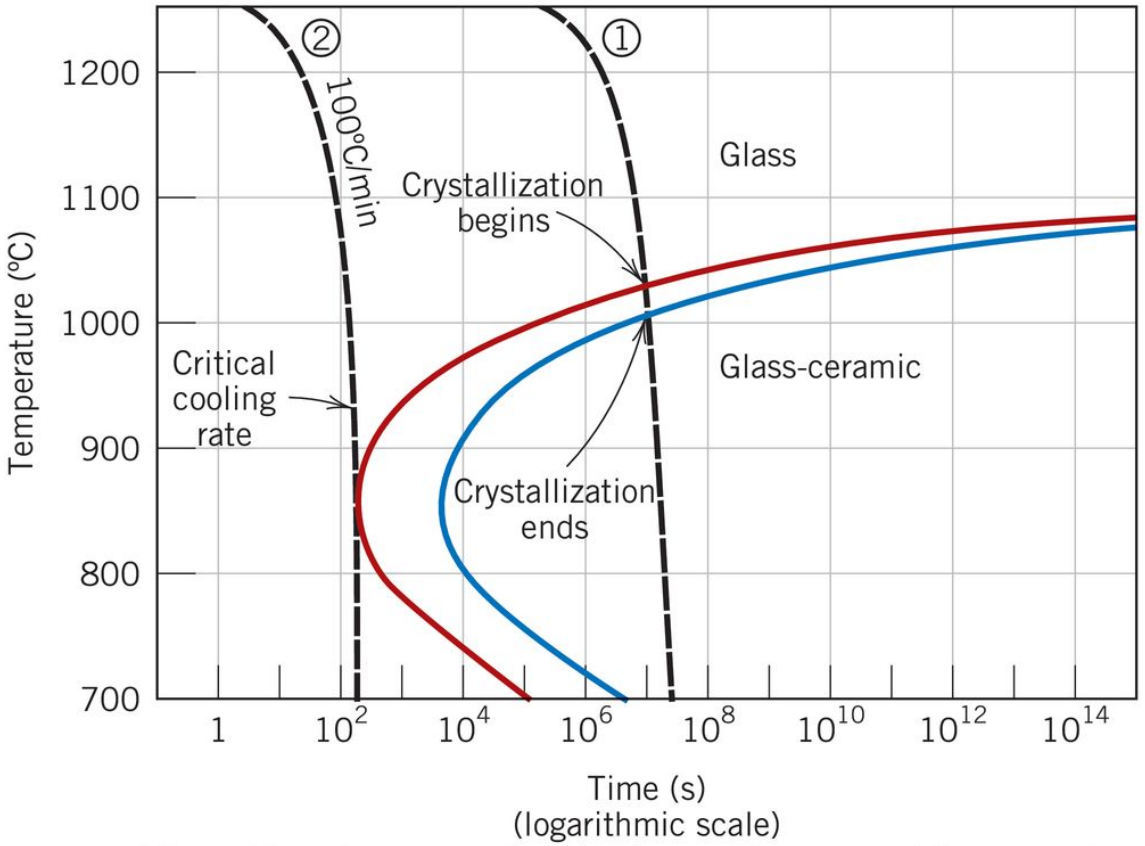
Adapted from Fig. 11.9(d), *Callister & Rethwisch 10e.*

Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.

a. Glass (유리): SiO_2 (Silicate) + CaO, Na_2O, K_2O 및 Al_2O_3 등 포함

Glass-ceramic:
다결정 재료

대부분 유리질의 핵생성 촉진을 위해 핵 생성제 (대부분 산화 티탄) 첨가 → C curve 왼쪽으로 이동



Reprinted from Glass: Science and Technology, Vol. 1, D. R. Uhlmann and N. J. Kreidl (Editors), "The Formation of Glasses," p. 22, copyright 1983, with permission from Elsevier.

Figure 14.15 루나 유리의 결정화 반응에 대한 연속냉각 변태곡선

b. 점토 제품: Structural clay products (벽돌, 타일, 하수구 파이프 등)과 Whitewares (백자=도자기, 식기, 접시, 화장실 도기 등)

c. 내화물 (Refractory ceramic):

(1) 가혹한 분위기하 불활성상태 유지, (2) 고온에서 용융되거나 분해되지 않음, (3) 열차폐 가능

Table 14.4 Compositions of Five Common Ceramic Refractory Materials

	Composition (wt%)							Apparent Porosity (%)
Refractory Type	Al_2O_3	SiO_2	MgO	Cr_2O_3	Fe_2O_3	CaO	TiO_2	
Fireclay	25–45	70–50	0–1		0–1	0–1	1–2	10–25
High-alumina fireclay	90–50	10–45	0–1		0–1	0–1	1–4	18–25
Silica	0.2	96.3	0.6			2.2		25
Periclase	1.0	3.0	90.0	0.3	3.0	2.5		22
Periclase–chrome ore	9.0	5.0	73.0	8.2	2.0	2.2		21

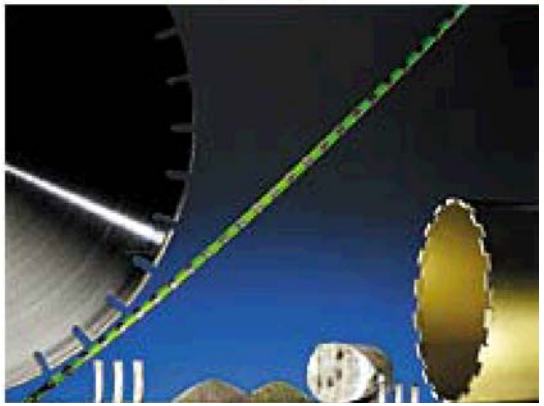
Source: From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

d. 연마재 (Abrasive ceramic):

상대적으로 연한재료를 마무, 연마, 절삭하는데 사용
인조 또는 천연 다이아몬드 (비쌈), 탄화규소, WC, 산화 알루미늄, 실리카 모래

- Cutting tools:
  -- for grinding glass, tungsten, carbide, ceramics
  -- for cutting Si wafers
  -- for oil drilling

oil drill bits

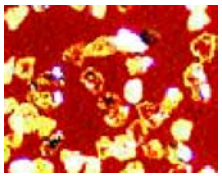


blades

* manufactured single crystal or polycrystalline diamonds in a metal or resin matrix.

Single crystal diamonds

* polycrystalline diamonds resharpen by microfracturing along cleavage planes.



polycrystalline diamonds in a resin matrix.

- Sandpaper 등 코팅된 연마재 혹은 기름과 물에 혼합된 연마재 등

e. 시멘트 (cement): 포틀랜드 시멘트, 석고 (수성), 석회석 (비수성) _
재료성분 중 일부가 결합제로 작용 → 화학적으로 결합

f. **탄소재료**: 탄소의 동질이상체 (다이아몬드, 흑연, 탄소섬유)

Table 14.5 Properties of Diamond, Graphite, and Carbon (for Fibers)

	Material			
		Graphite		
Property	***Diamond***	***In-Plane***	***Out-of-Plane***	***Carbon (Fibers)***
Density (g/cm^3)	3.51	2.26		1.78–2.15
Modulus of elasticity (GPa)	700–1200	350	36.5	230–725[a]
Strength (MPa)	1050	2500	—	1500–4500[a]
Thermal Conductivity (W/m·K)	2000–2500	1960	6.0	11–70[a]
Coefficient, Thermal Expansion ($10^{-6}\ K^{-1}$)	0.11–1.2	−1	+29	−0.5–−0.6[a] 7–10[b]
Electrical Resistivity (Ω·m)	10^{11}–10^{14}	1.4×10^{-5}	1×10^{-2}	9.5×10^{-6}–17×10^{-6}

[a]Longitudinal fiber direction.

[b]Transverse (radial) fiber direction.

g. Advanced Ceramics:

세라믹의 독특한 전기적, 자기적, 광학정 성질 활용
→ 내연기관, 터빈 엔진, 전자패키징, 절단용구 그리고
에너지 변환 저장 및 발전에 사용 (제18, 20, 21장 참고)

Ex. (1) Materials for Automobile Engines

- Advantages:
  - Operate at high temperatures – high efficiencies
  - Low frictional losses
  - Operate without a cooling system
  - Lower weights than current engines
- Disadvantages:
  - Ceramic materials are brittle
  - Difficult to remove internal voids (that weaken structures)
  - Ceramic parts are difficult to form and machine

- Potential candidate materials: Si_3N_4, SiC, & ZrO_2
- Possible engine parts: engine block & piston coatings

(2) Ceramics Application: Sensors

- Example: ZrO_2 as an oxygen sensor
- Principle: Increase diffusion rate of oxygen to produce rapid response of sensor signal to change in oxygen concentration
- Approach:

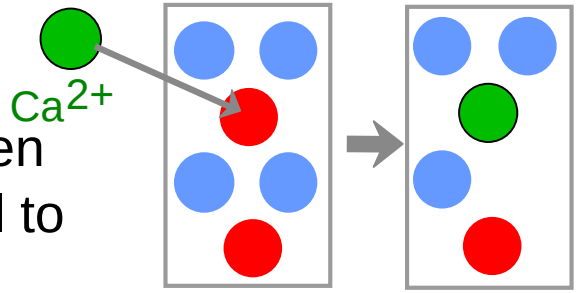
  Add Ca impurity to ZrO_2:

  -- increases O^{2-} vacancies

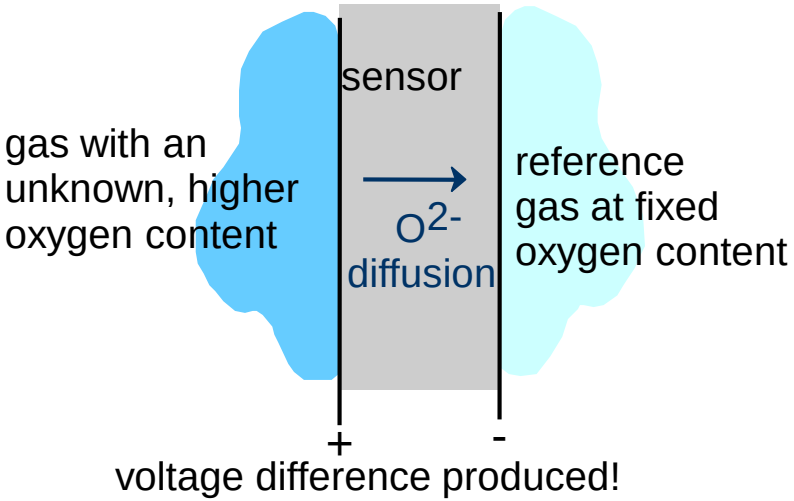
  -- increases O^{2-} diffusion rate
- Operation:

  -- voltage difference produced when O^{2-} ions diffuse from the external surface through the sensor to the reference gas surface.

  -- magnitude of voltage difference $\propto$ partial pressure of oxygen at the external surface



A substituting Ca^{2+} ion removes a Zr^{4+} ion and an O^{2-} ion.



(3) Ceramics Application: Refractories

- Materials to be used at high temperatures (e.g., in high temperature furnaces).
- Consider the Silica (SiO_2) - Alumina (Al_2O_3) system.
- Silica refractories - silica rich - small additions of alumina depress melting temperature (phase diagram):

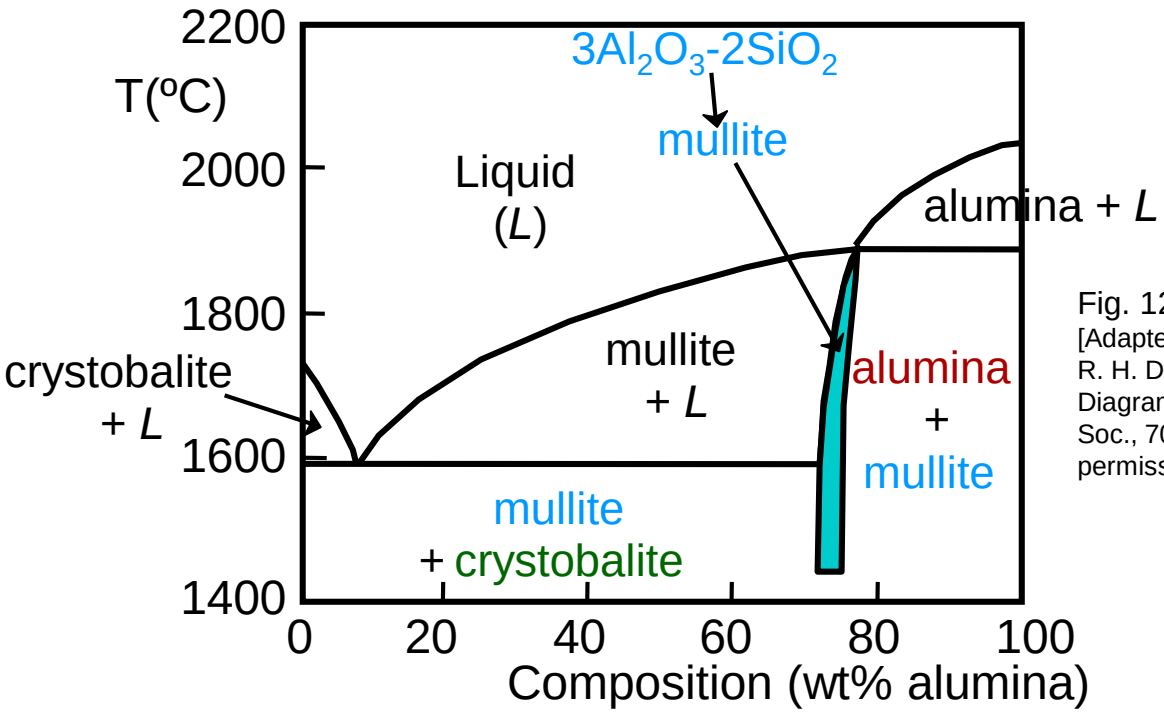


Fig. 12.25, *Callister & Rethwisch 10e.* [Adapted from F. J. Klug, S. Prochazka, and R. H. Doremus, "Alumina–Silica Phase Diagram in the Mullite Region," J. Am. Ceram. Soc., 70[10], 1987, p.758. Reprinted by permission of the American Ceramic Society.]

(4) Nanocarbons

- Fullerenes – spherical cluster of 60 carbon atoms, C_{60}
  - Like a soccer ball
- Carbon nanotubes – sheet of graphite rolled into a tube
  - Ends capped with fullerene hemispheres
- Graphene – single-atomic-layer of graphite
  - composed of hexagonally sp^2 bonded carbon atoms

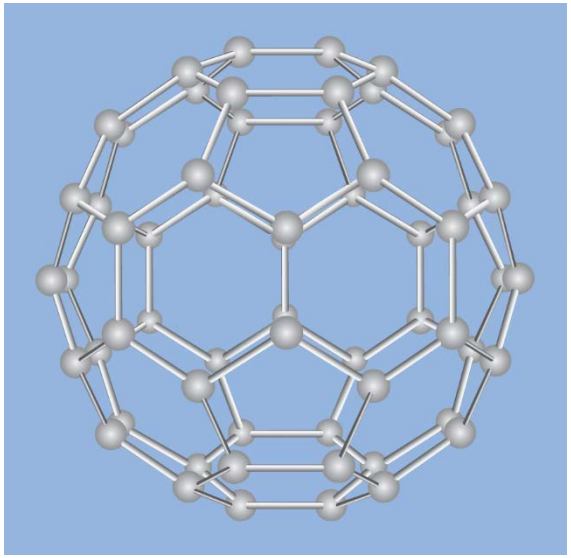


Fig. 14.20, *Callister & Rethwisch 9e.*

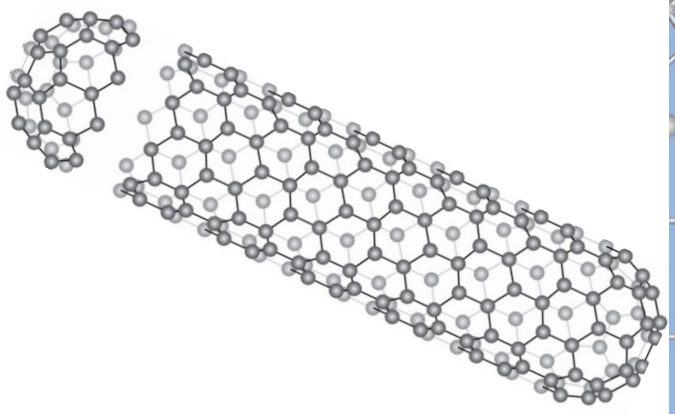


Fig. 12.19, *Callister & Rethwisch 8e.*

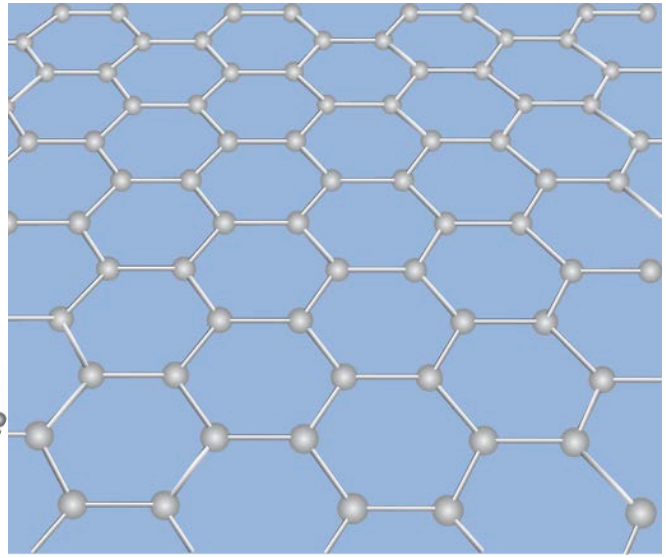


Fig. 14.22, *Callister & Rethwisch 9e.*

IV. Fabrication and Processing of Ceramics

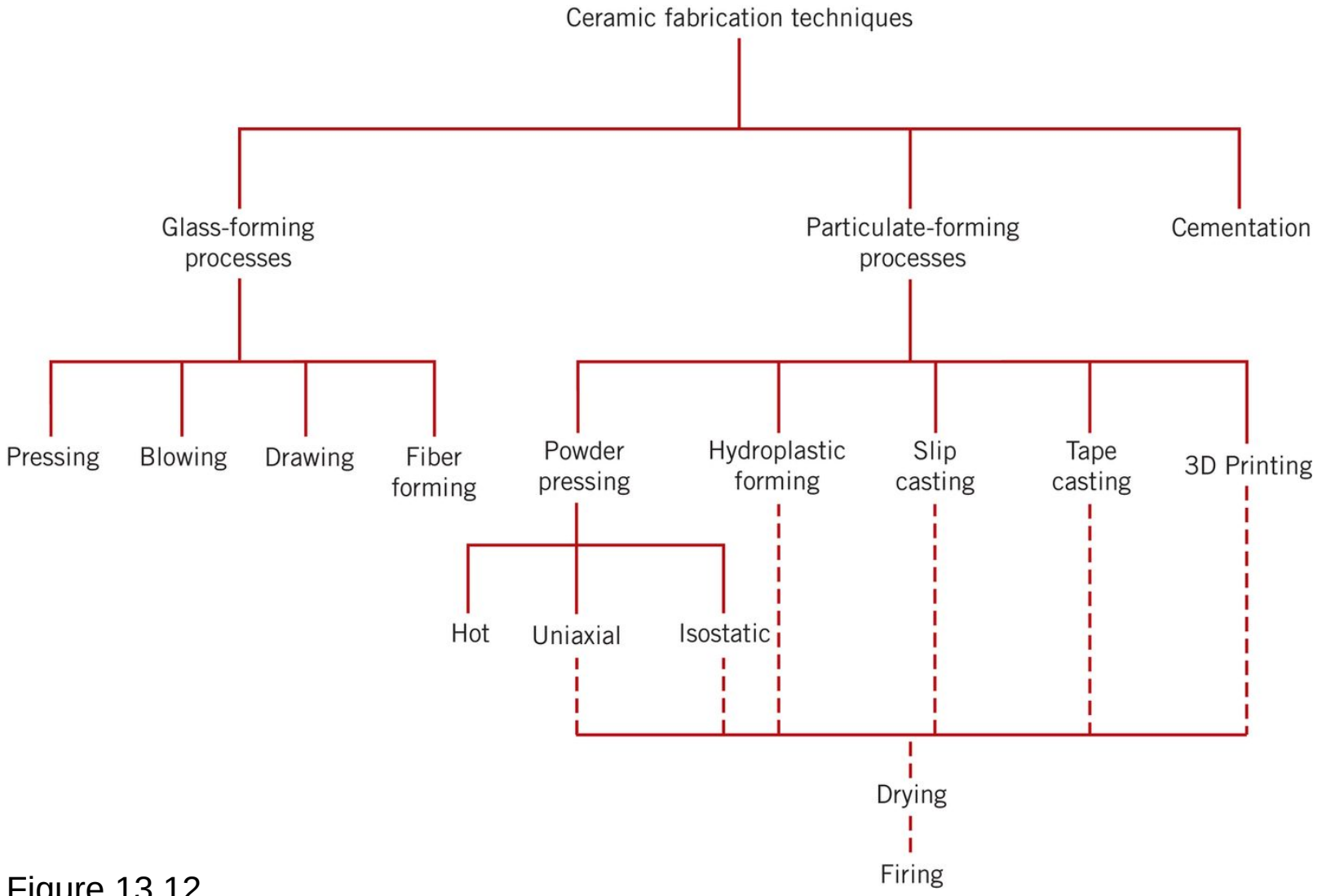
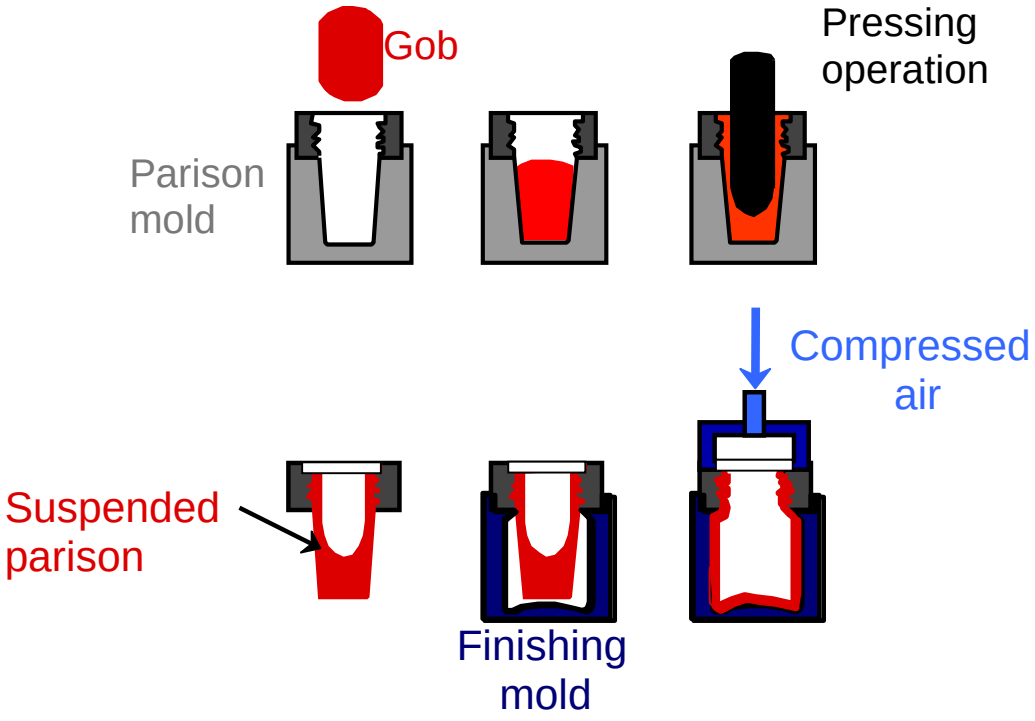


Figure 13.12
A classification scheme for the ceramic-forming techniques discussed in this chapter.

Ceramic Fabrication Methods (i)

GLASS FORMING | PARTICULATE FORMING | CEMENTATION

- Blowing of Glass Bottles:



- Pressing: plates, cheap glasses
  - -- glass formed by application of pressure
  - -- mold is steel with graphite lining
- Fiber drawing:

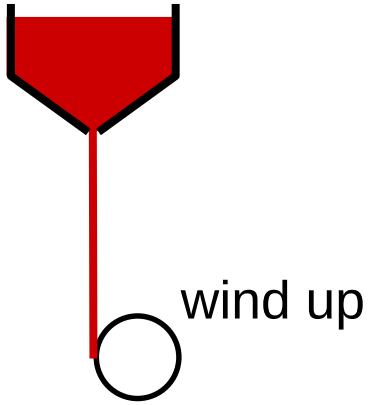
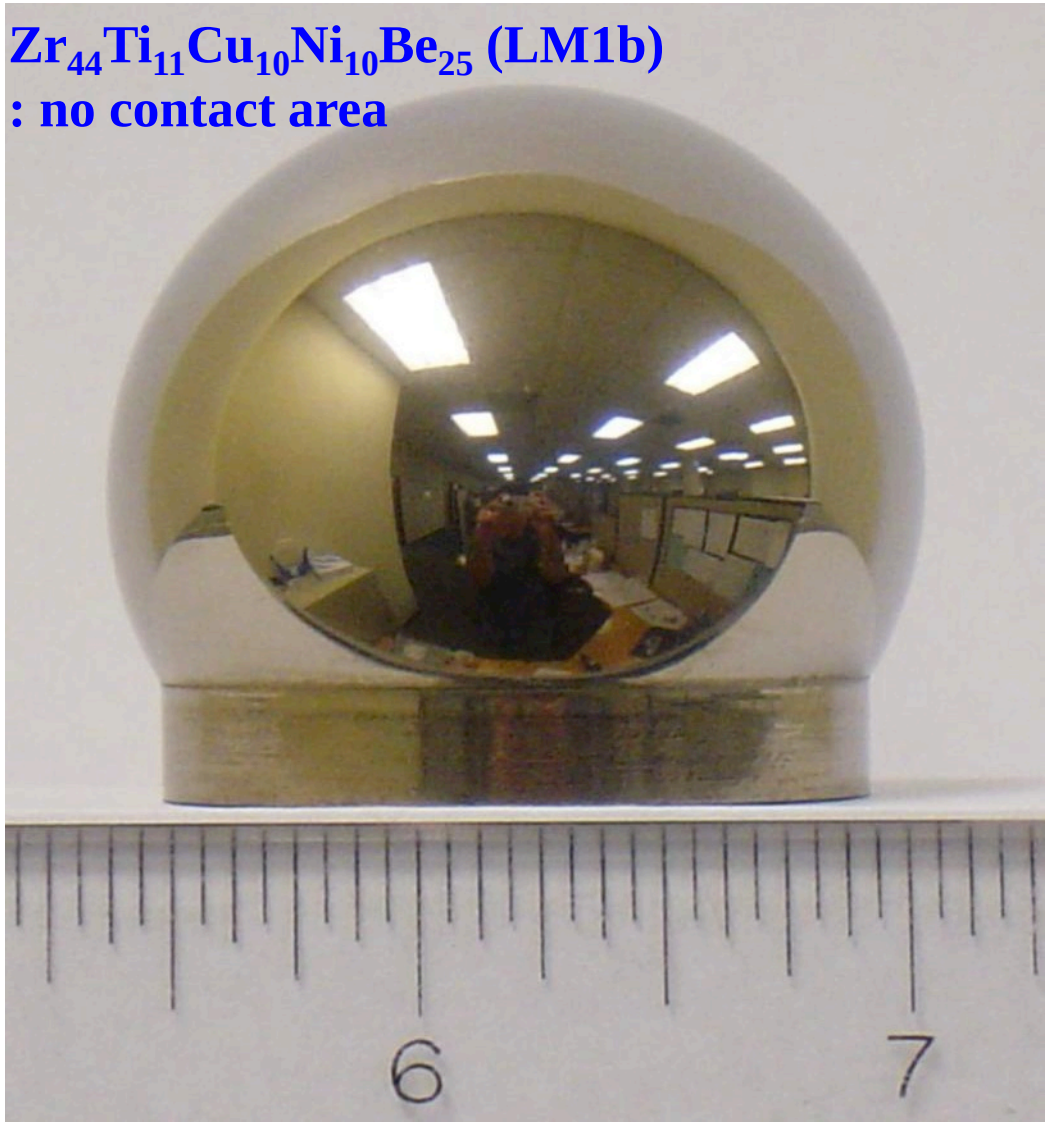
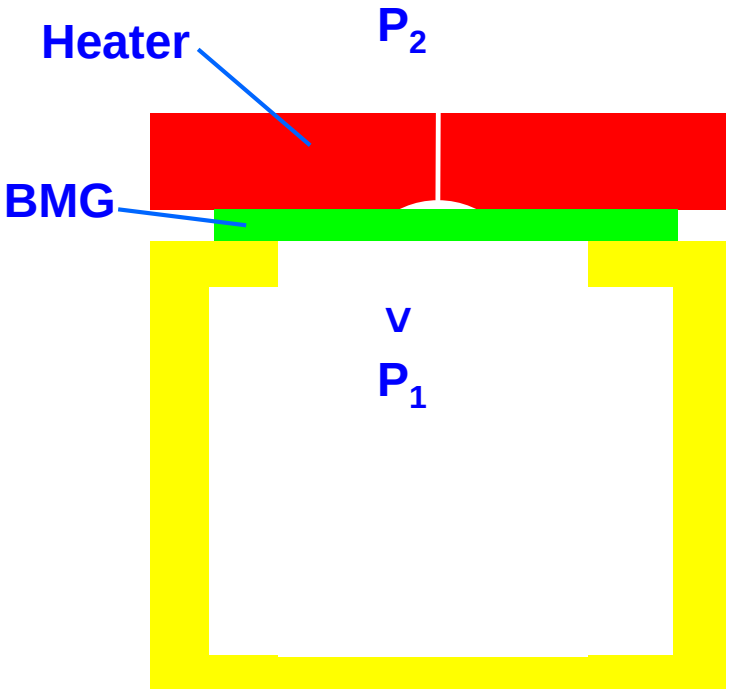


Fig. 13.15, *Callister & Rethwisch 10e*. (Adapted from C.J. Phillips, *Glass: The Miracle Maker*. Reproduced by permission of Pittman Publishing Ltd., London.)

Glassblowers in the US in 1908

BLOW-MOLDING: easy forming!



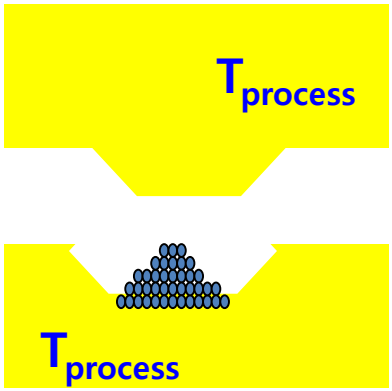


10^5 Pa, 400% strain

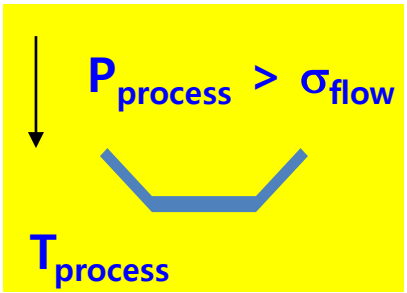
T=460° C, t =40 sec

J. Schroers, T. Nguyen, A. Peker, N. Paton, R. V. Curtis, Scripta Materialia, 57, 341 (2007)

TPF-based Compression Molding : No size limitation!



$T_g < T_{process} < T_x$



$T_{process} < t_{cryst}$

J. Schroers, JOM, 57, 34 (2005)

Sheet Glass Forming

- Sheet forming – continuous casting
  - sheets are formed by floating the molten glass on a pool of molten tin

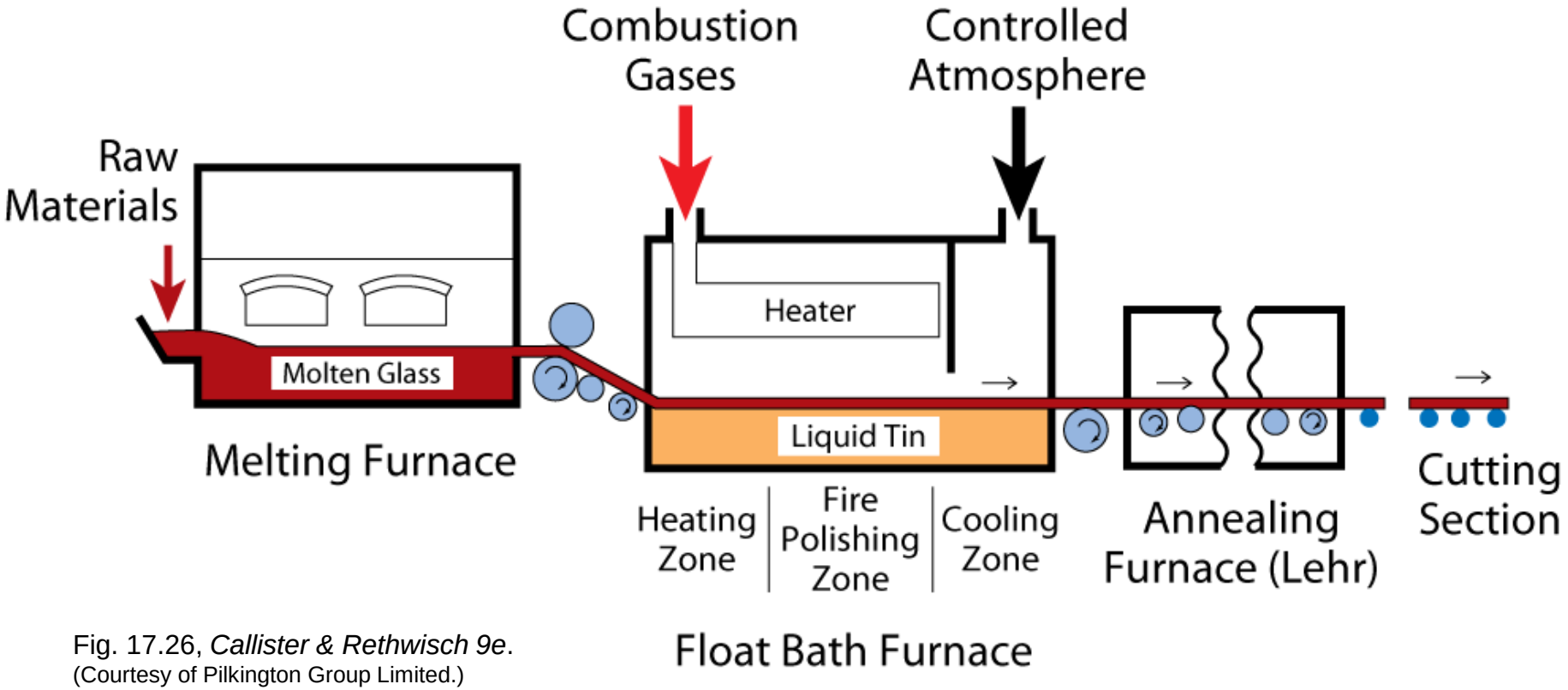
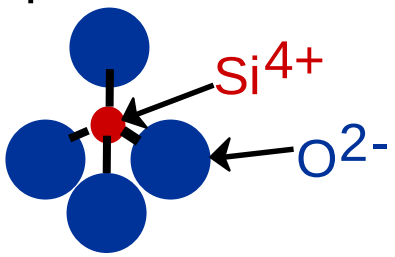


Fig. 17.26, *Callister & Rethwisch 9e*.
(Courtesy of Pilkington Group Limited.)

Glass Structure

- Basic Unit:

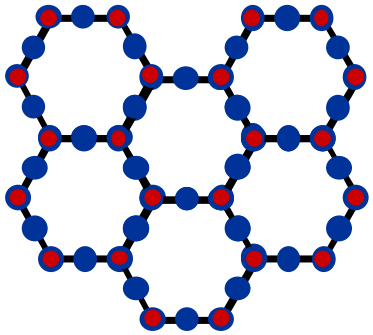
SiO_4^{4-} tetrahedron

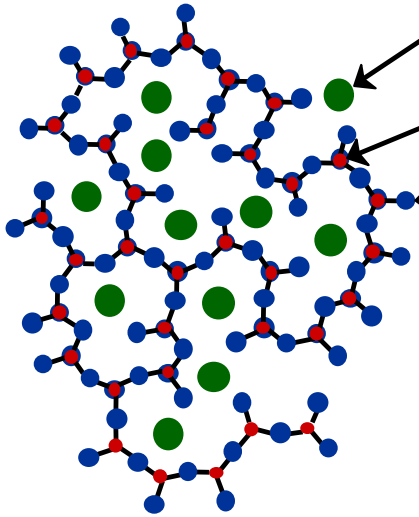


Glass is noncrystalline (amorphous)

- Fused silica is SiO_2 to which no impurities have been added
- Other common glasses contain impurity ions such as Na^+, Ca^{2+}, Al^{3+}, and B^{3+}

- Quartz is crystalline SiO_2:



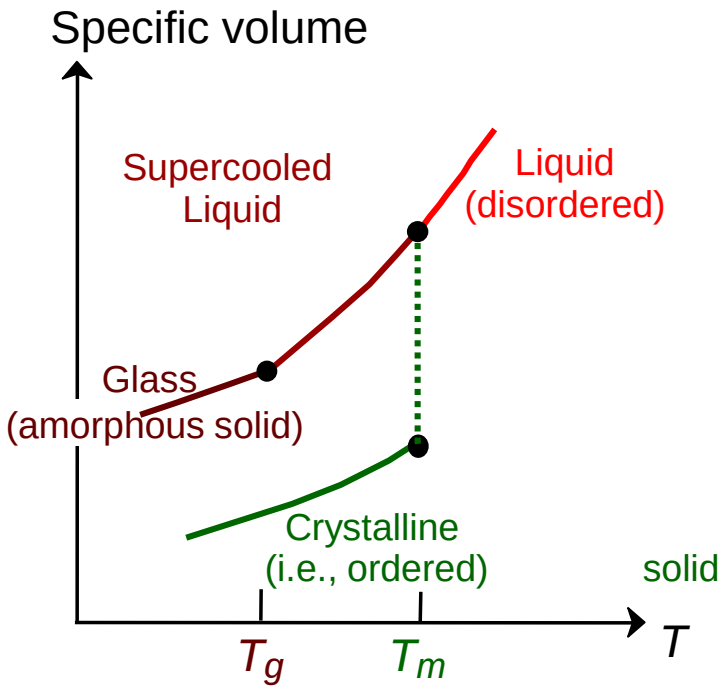


(soda glass)

Adapted from Fig. 12.11, *Callister & Rethwisch 10e*.

Glass Properties

- Specific volume ($1/\rho$) vs Temperature (T):



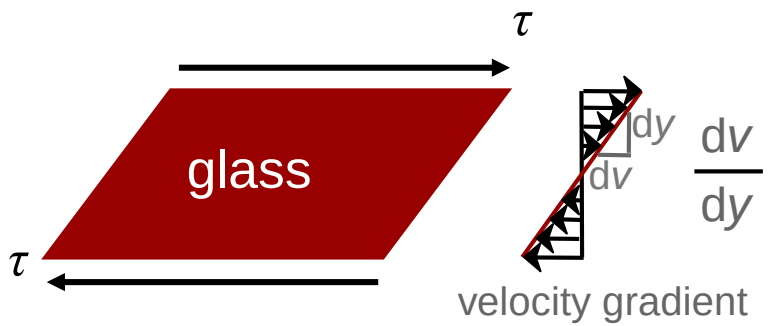
Adapted from Fig. 13.13, *Callister & Rethwisch 10e*.

- Crystalline materials:
  -- crystallize at melting temp, T_m
  -- have abrupt change in spec. vol. at T_m

- Glasses:
  -- do not crystallize
  -- change in slope in spec. vol. curve at glass transition temperature, T_g
  -- transparent - no grain boundaries to scatter light

Glass Properties: Viscosity

- Viscosity, η:
  -- relates shear stress (τ) and velocity gradient *(dv/dy):*



$$\eta = \frac{\tau}{dv / dy}$$

η has units of (Pa-s)

Log Glass Viscosity vs. Temperature

- Viscosity decreases with *T*

- soda-lime glass: 70% SiO_2 balance Na_2O (soda) & CaO (lime)
- borosilicate (Pyrex): 13% B_2O_3, 3.5% Na_2O, 2.5% Al_2O_3
- Vycor: 96% SiO_2, 4% B_2O_3
- fused silica: > 99.5 wt% SiO_2

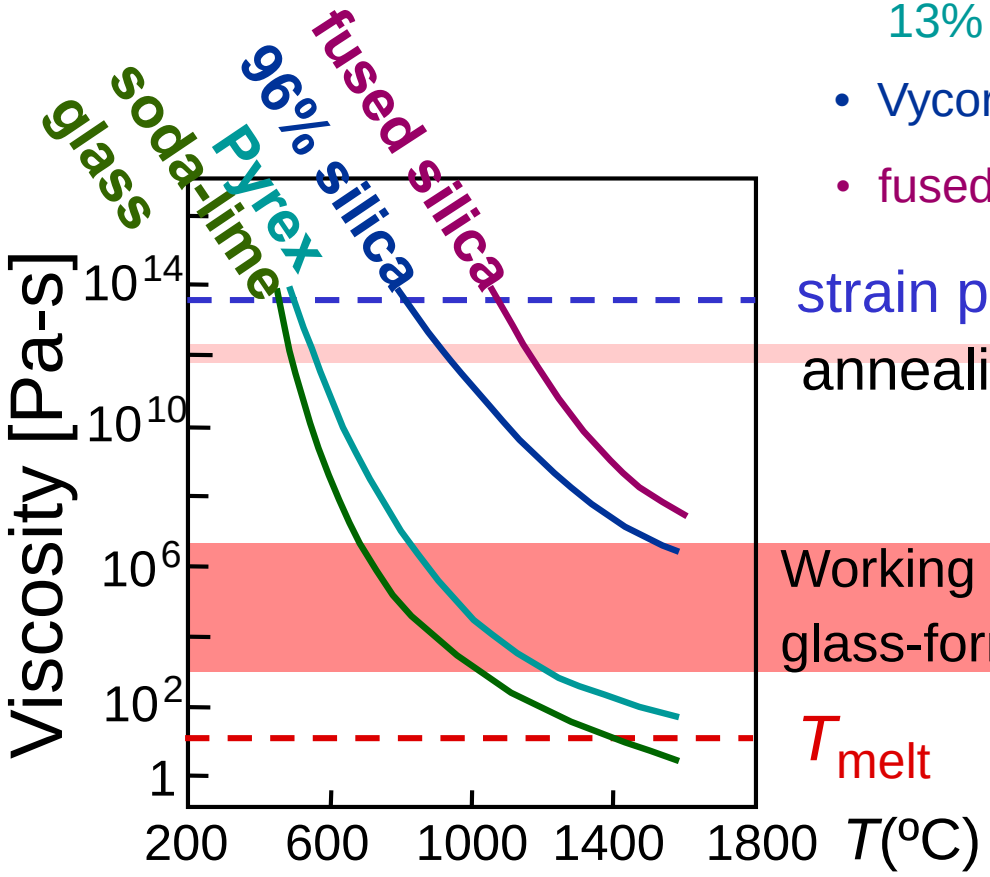
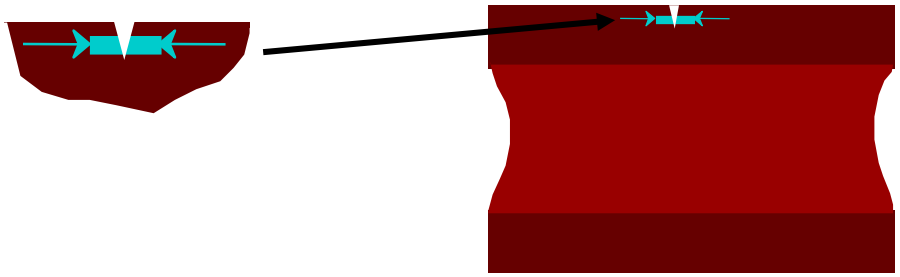


Fig. 13.14, *Callister & Rethwisch 10e*. (From E.B. Shand, *Engineering Glass*, Modern Materials, Vol. 6, Academic Press, New York, 1968, p. 262.)

Heat Treating Glass

- Annealing:
  -- removes internal stresses caused by uneven cooling.
- Tempering:
  -- puts surface of glass part into compression
  -- suppresses growth of cracks from surface scratches.
  -- sequence:

-- Result: surface crack growth is suppressed.



Ceramic Fabrication Methods (iia)

GLASS FORMING | **PARTICULATE FORMING** | CEMENTATION

Hydroplastic forming:

- Mill (grind) and screen constituents: desired particle size
- Extrude this mass (e.g., into a brick)

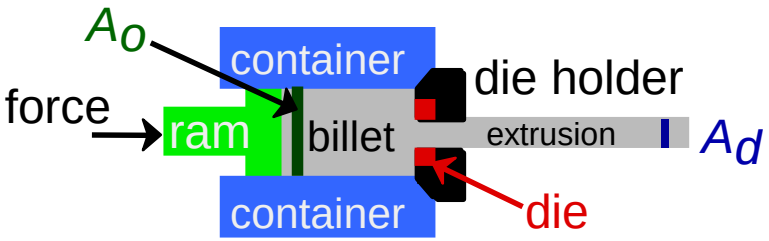


Fig. 17.2 (c), *Callister & Rethwisch 9e*.

- Dry and fire the formed piece

Ceramic Fabrication Methods (iia)

GLASS FORMING | **PARTICULATE FORMING** | CEMENTATION

Slip casting:

- Mill (grind) and screen constituents: desired particle size
- Mix with water and other constituents to form slip
- Slip casting operation

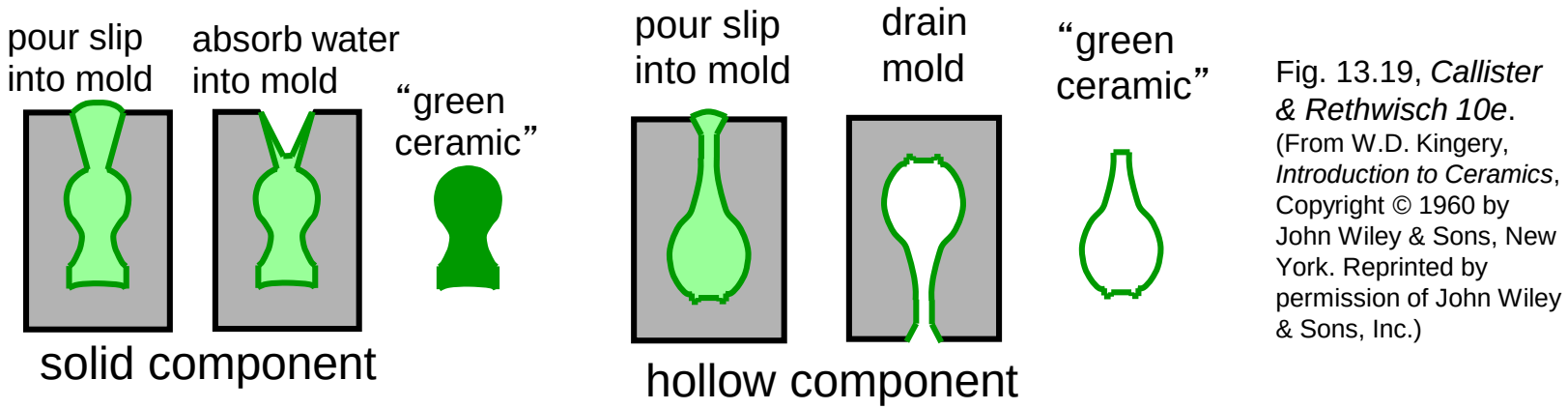


Fig. 13.19, *Callister & Rethwisch 10e*. (From W.D. Kingery, *Introduction to Ceramics*, Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

- Dry and fire the cast piece

슬립 주조[법](鑄造[法]): 석고로 만든 주형(거푸집)에 이장(泥漿)을 부어 넣어서 만드는 도기 제조법.
(도자기 제조에 쓰이는 고체 입자의 현탁액(懸濁液)

Typical Porcelain Composition

(50%) 1. Clay

(25%) 2. Filler – e.g. quartz (finely ground)

(25%) 3. Fluxing agent (Feldspar)

-- aluminosilicates plus K^+, Na^+, Ca^+

-- upon firing - forms low-melting-temp. glass

Hydroplasticity of Clay

- Clay is inexpensive
- When water is added to clay
  -- water molecules fit in between layered sheets
  -- reduces degree of van der Waals bonding
  -- when external forces applied – clay particles free to move past one another – becomes hydroplastic

- Structure of Kaolinite Clay:

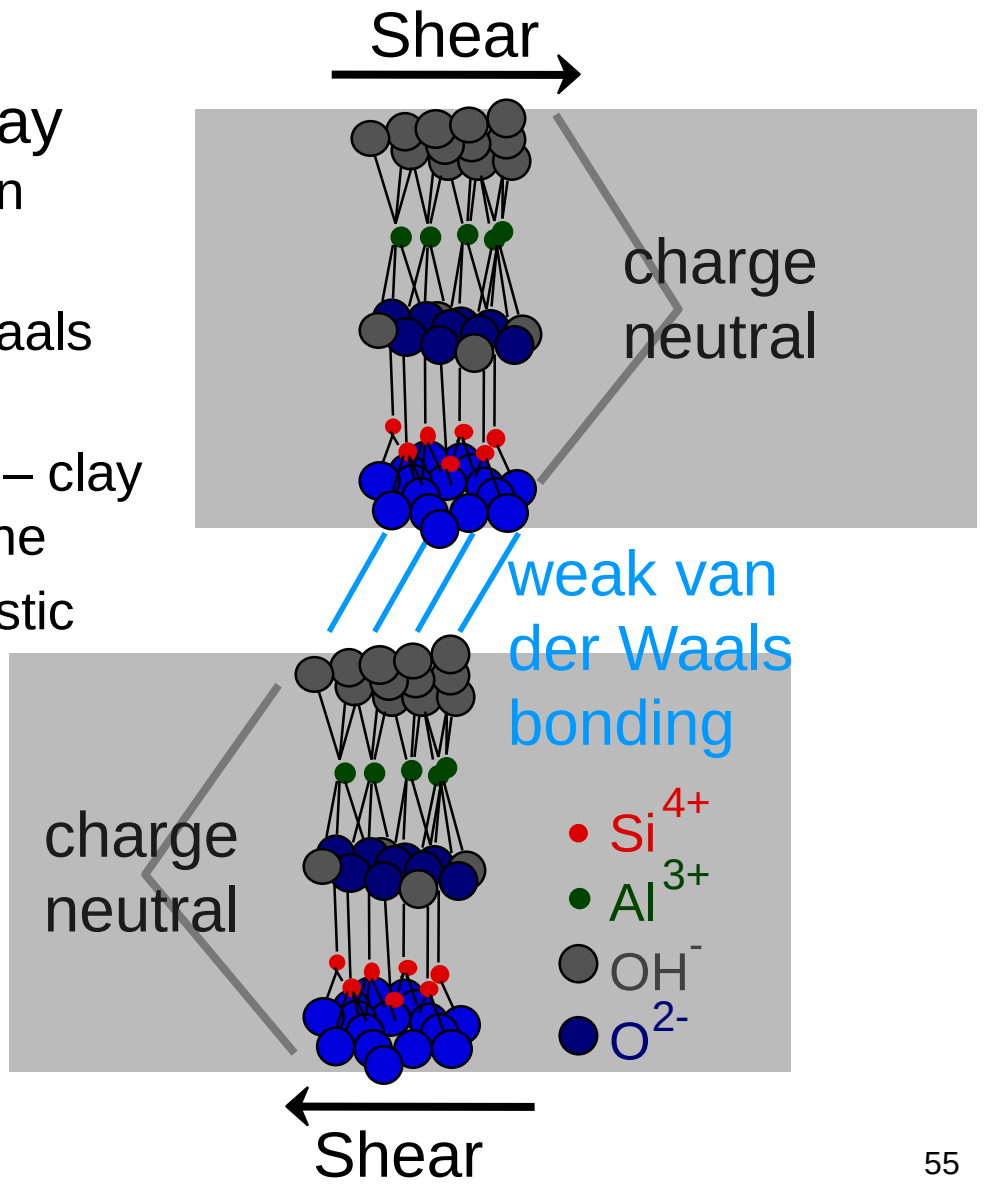
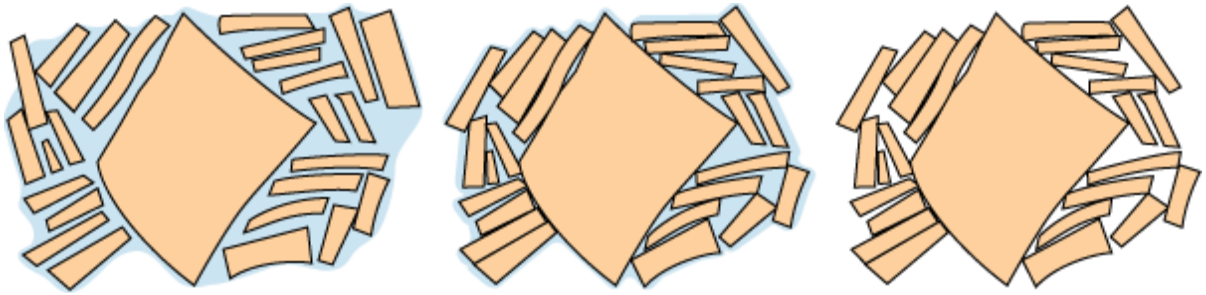


Fig. 12.14, *Callister & Rethwisch 10e*. [Adapted from W.E. Hauth, "Crystal Chemistry of Ceramics", *American Ceramic Society Bulletin*, Vol. 30 (4), 1951, p. 140.]

Drying and Firing

- Drying: as water is removed - interparticle spacings decrease – shrinkage .



wet body partially dry completely dry

Fig. 13.20, *Callister & Rethwisch 10e*. (From W.D. Kingery, *Introduction to Ceramics*, Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Drying too fast causes sample to warp or crack due to non-uniform shrinkage

- Firing:
  -- heat treatment between 900-1400°C
  -- vitrification: liquid glass forms from clay and flux – flows between SiO_2 particles. (Flux lowers melting temperature).

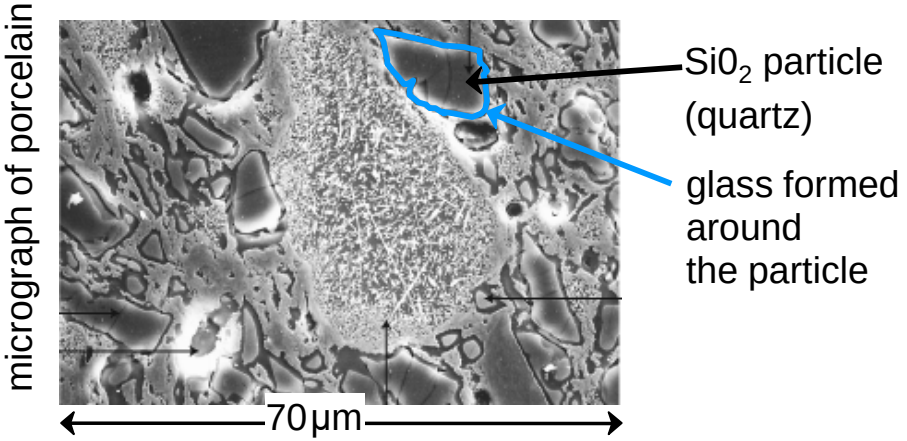
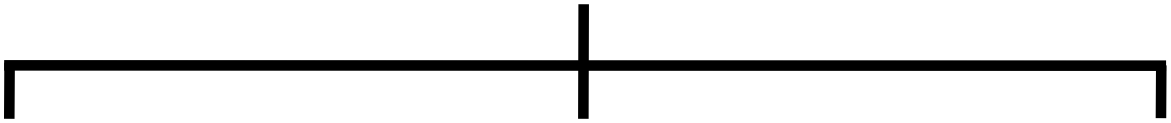


Fig. 13.21, *Callister & Rethwisch 10e*. (Courtesy H.G. Brinkies, Swinburne University of Technology, Hawthorn Campus, Hawthorn, Victoria, Australia.)

Ceramic Fabrication Methods (iib)



GLASS FORMING | **PARTICULATE FORMING** | CEMENTATION

a. Powder Pressing: used for both clay and non-clay compositions.

- Powder (plus binder) compacted by pressure in a mold
  -- Uniaxial compression - compacted in single direction
  -- Isostatic (hydrostatic) compression - pressure applied by fluid - powder in rubber envelope
  -- Hot pressing - pressure + heat

a. Powder pressing_Sintering

Sintering occurs during firing of a piece that has been powder pressed

-- powder particles coalesce and reduction of pore size

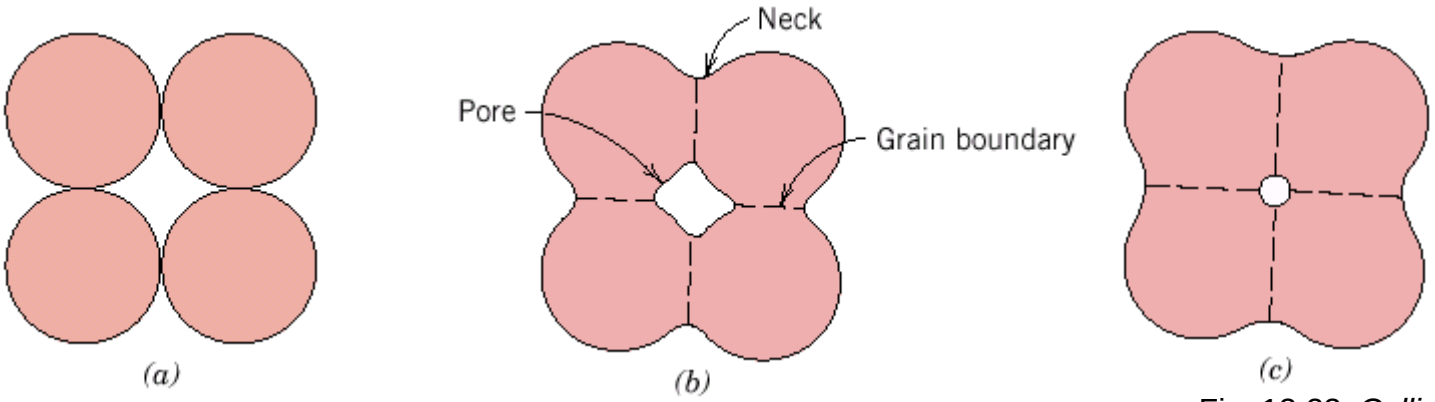


Fig. 13.23, *Callister & Rethwisch 10e*.

Aluminum oxide powder:

-- sintered at 1700°C
for 6 minutes.

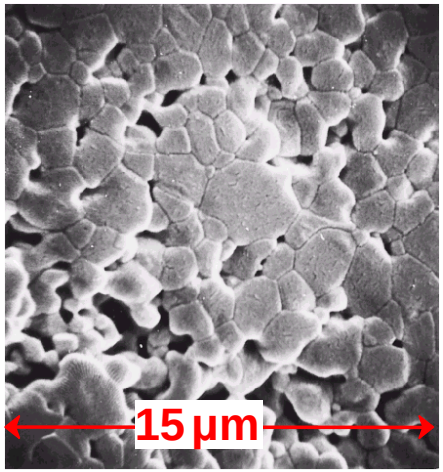


Fig. 13.24, *Callister & Rethwisch 10e*. (From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, Introduction to Ceramics, 2nd edition, p. 483. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

b. Tape Casting

- Thin sheets of green ceramic cast as flexible tape
- Used for integrated circuits and capacitors
- Slip = suspended ceramic particles + organic liquid (contains binders, plasticizers)

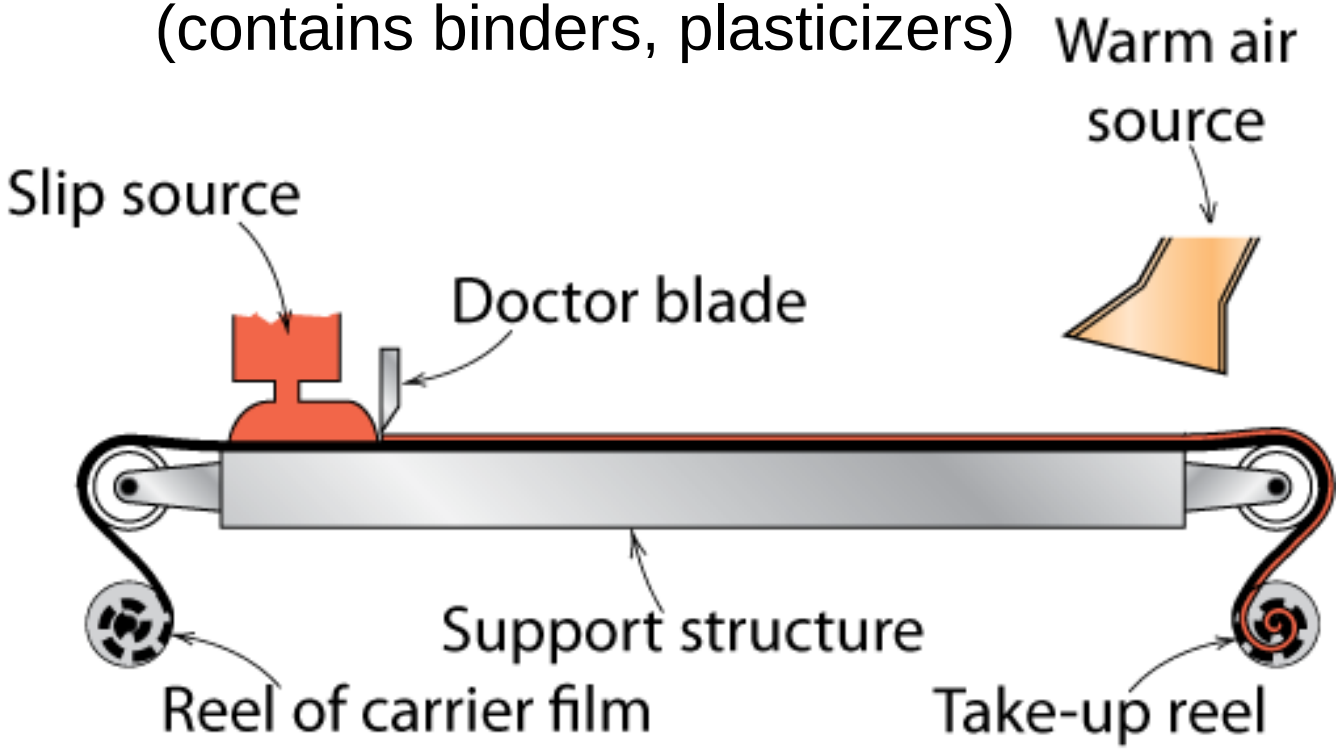


Fig. 13.25, *Callister & Rethwisch 10e*.

c. 3D printing of Ceramic Materials

- Powder Bed Fusion

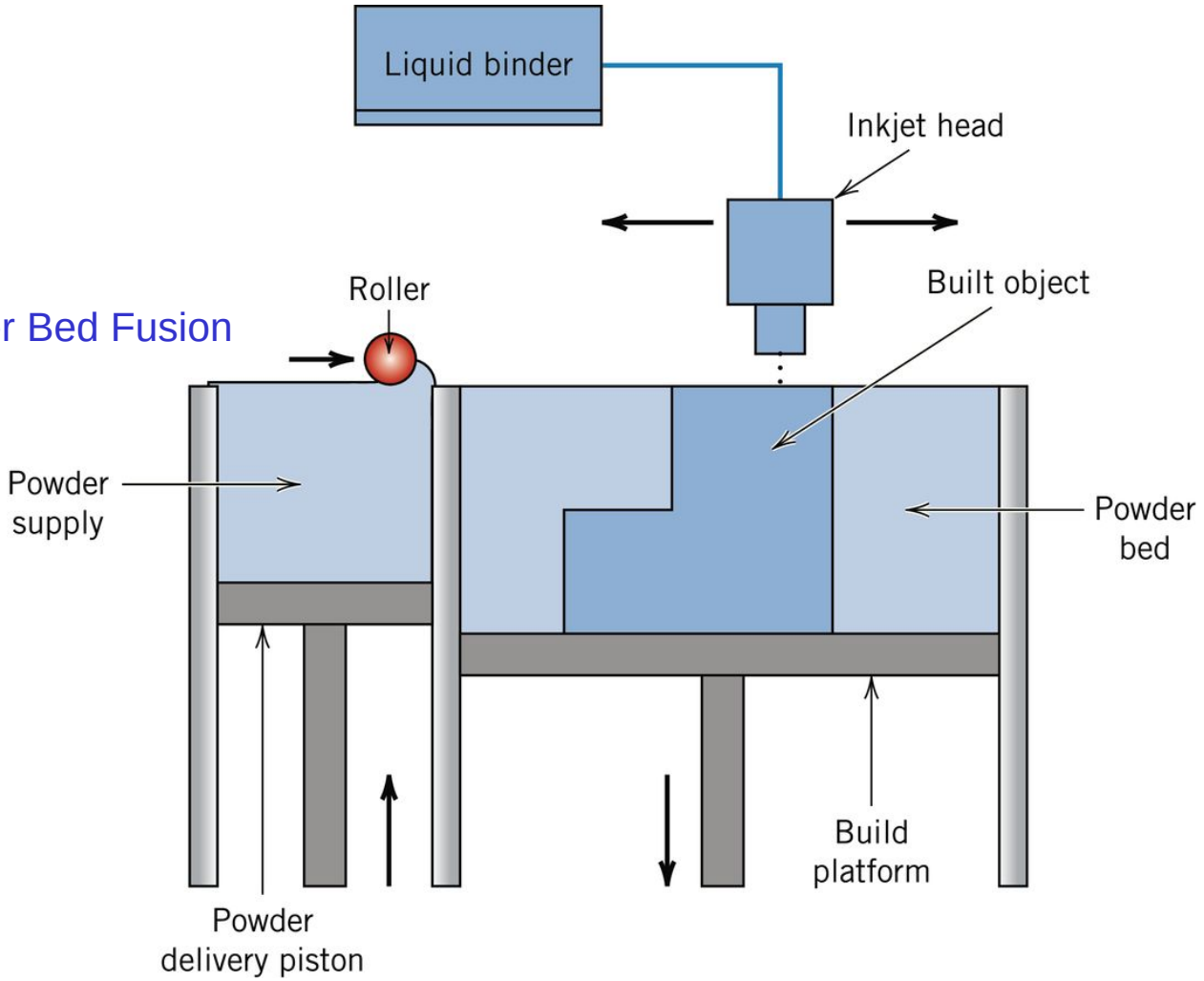
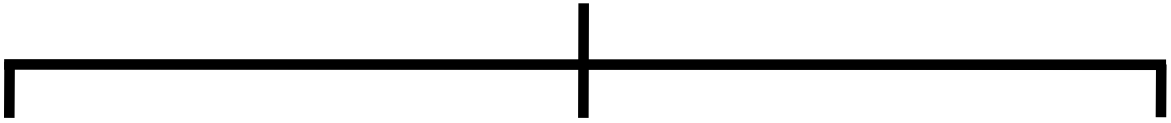


Figure 13.26 Schematic representation of the ceramic jet 3D printing technique.

Ceramic Fabrication Methods (iii)



GLASS FORMING | PARTICULATE FORMING | CEMENTATION

- Hardening of a paste – paste formed by mixing cement material with water
- Formation of rigid structures having varied and complex shapes
- Hardening process – hydration (complex chemical reactions involving water and cement particles)
- Portland cement – production of:
  -- mix clay and lime-bearing minerals
  -- calcine (heat to 1400°C)
  -- grind into fine powder

Summary

- Room-temperature mechanical behavior – flexural tests
  -- linear-elastic; measurement of elastic modulus
  -- brittle fracture; measurement of flexural modulus
- Categories of ceramics:
  -- glasses
  -- refractories
  -- advanced ceramics
  -- clay products
  -- cements
- Ceramic Fabrication techniques:
  -- glass forming (pressing, blowing, fiber drawing).
  -- particulate forming (hydroplastic forming, slip casting, powder pressing, tape casting)
  -- cementation
- Heat treating procedures
  -- glasses—annealing, tempering
  -- particulate formed pieces—drying, firing (sintering)