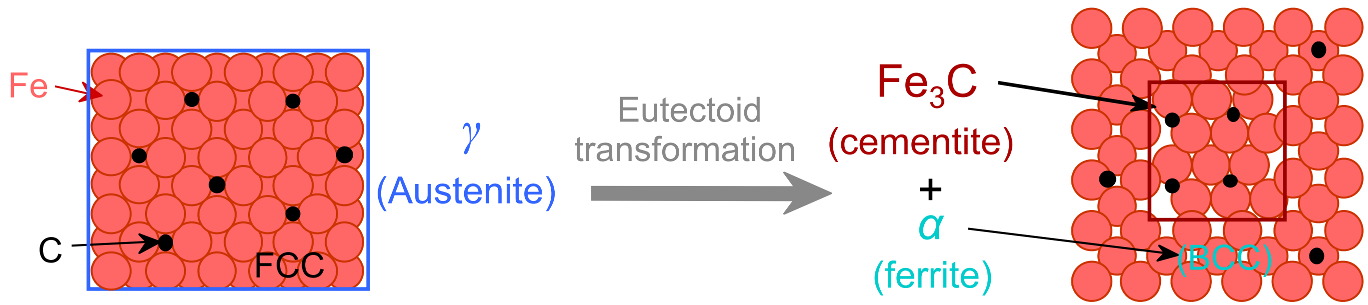
Chapter 12: Phase Transformations

ISSUES TO ADDRESS...

- Transforming one phase into another takes time.



- How does the rate of transformation depend on time and temperature ?
- Is it possible to slow down transformations so that non-equilibrium structures are formed?
- Are the mechanical properties of non-equilibrium structures more desirable than equilibrium ones?

Phase Transformations

Nucleation

- nuclei (seeds) act as templates on which crystals grow
- for nucleus to form rate of addition of atoms to nucleus must be faster than rate of loss
- once nucleated, growth proceeds until equilibrium is attained

Driving force to nucleate increases as we increase ΔT

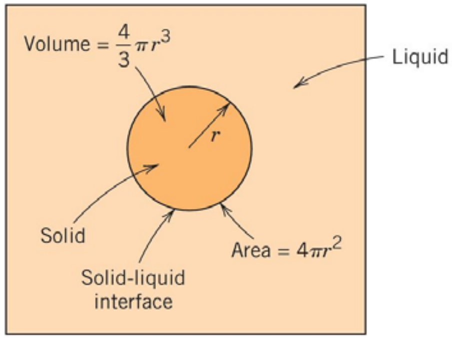
- supercooling (eutectic, eutectoid)
- superheating (peritectic)

Small supercooling → slow nucleation rate - few nuclei - large crystals

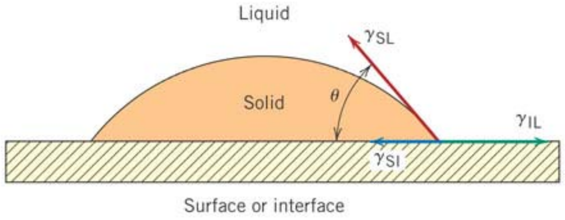
Large supercooling → rapid nucleation rate - many nuclei - small crystals

Solidification: Nucleation Types

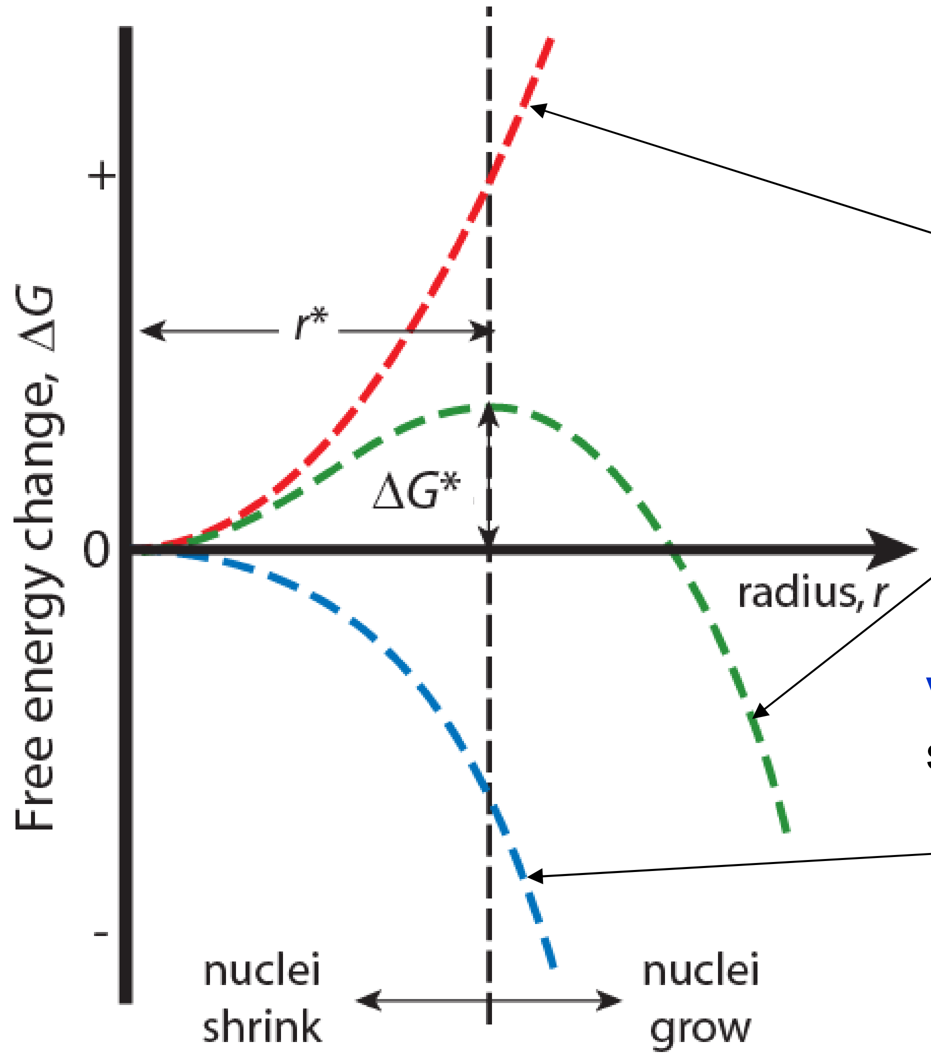
- Homogeneous nucleation
  - nuclei form in the bulk of liquid metal
  - requires considerable supercooling (typically 80-300 °C)



- Heterogeneous nucleation
  - much easier since stable “nucleating surface” is already present — e.g., mold wall, impurities in liquid phase
  - only very slight supercooling (0.1-10 ° C)



Homogeneous Nucleation & Energy Effects



Surface Free Energy- destabilizes the nuclei (it takes energy to make an interface)

$$\Delta G_S = 4\pi r^2 \gamma$$

γ = surface tension

ΔG_T = Total Free Energy
$= \Delta G_S + \Delta G_V$

Volume (Bulk) Free Energy – stabilizes the nuclei (releases energy)

$$\Delta G_V = \frac{4}{3}\pi r^3 \Delta G_v$$

$$\Delta G_v = \frac{\text{volume free energy}}{\text{unit volume}}$$

r^* = critical nucleus: for $r < r^*$ nuclei shrink; for $r > r^*$ nuclei grow (to reduce energy)

Adapted from Fig.12.2(b), *Callister & Rethwisch 9e.*

$$\frac{d\Delta G}{dr} = \frac{1}{dr}\left(\frac{4}{3}\pi r^3 \Delta G_v\right) + \frac{1}{dr}\left(4\pi r^2 \gamma\right) = 0$$

$$r^* = -\frac{2\gamma}{\Delta G_v}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v{}^2}$$

$$\Delta G_v = \Delta H_v - T\Delta S_v = \Delta H_v - T\left(\frac{\Delta H_v}{T_m}\right) = \frac{\Delta H_v\left(T_m - T\right)}{T_m} = \frac{\Delta H_v \Delta T}{T_m}$$

$$r^* = -\frac{2\gamma}{\Delta G_v} = -\frac{2\gamma T_m}{\Delta H_v \Delta T}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v{}^2} = \frac{16\pi\gamma^3 T_m^2}{3\Delta H_v^2 \Delta T^2}$$

Solidification

$$r^* = \frac{-2\gamma T_m}{\Delta H_f \Delta T}$$

r^* = critical radius

γ = surface free energy

T_m = melting temperature

ΔH_f = latent heat of solidification

$\Delta T = T_m - T$ = supercooling

Note: ΔH_f and γ are weakly dependent on ΔT

$\therefore$ r^* decreases as ΔT increases

For typical ΔT r^* ~ 10 nm

$$\Delta G^{*} = \frac{16\pi\gamma^{3}}{3\Delta G_{v}^{2}} = \frac{16\pi\gamma^{3}T_{m}^{2}}{3\Delta H_{v}^{2}\Delta T^{2}}$$

$$r^{*} = -\frac{2\gamma}{\Delta G_{v}} = -\frac{2\gamma T_{m}}{\Delta H_{v}\Delta T}$$

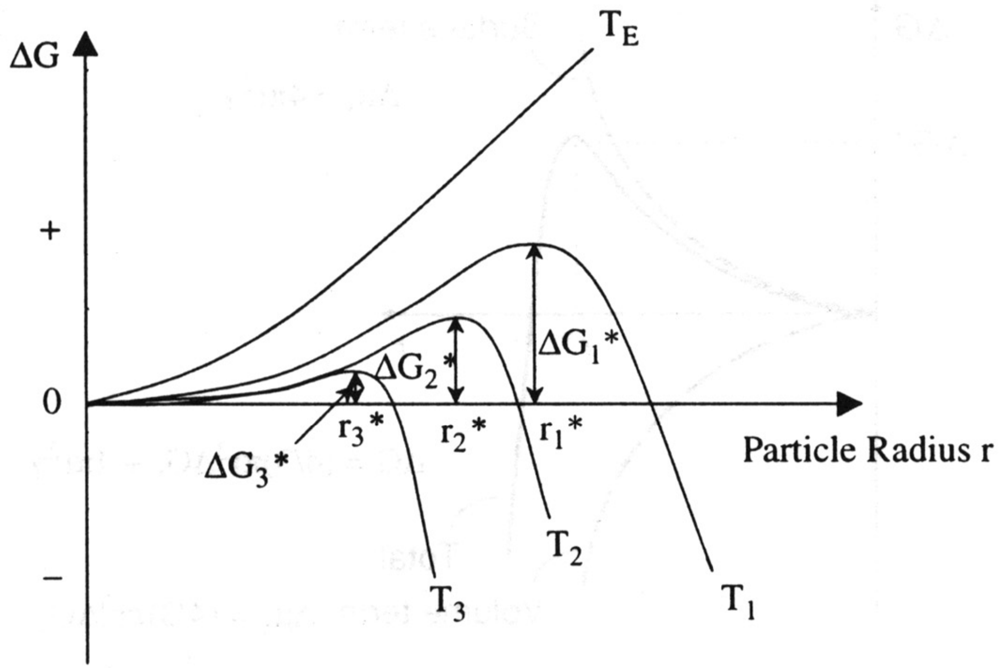


Fig. 3.3. The effect of temperature on the critical sizes and critical free energy of three spherical nuclei. Supersaturation increases with a decreasing temperature and surface energy also varies with temperature. $T_E > T_1 > T_2 > T_3$ with T_E being the equilibrium temperature.

Nucleation Kinetics

The number of stable nuclei having radii greater than r*

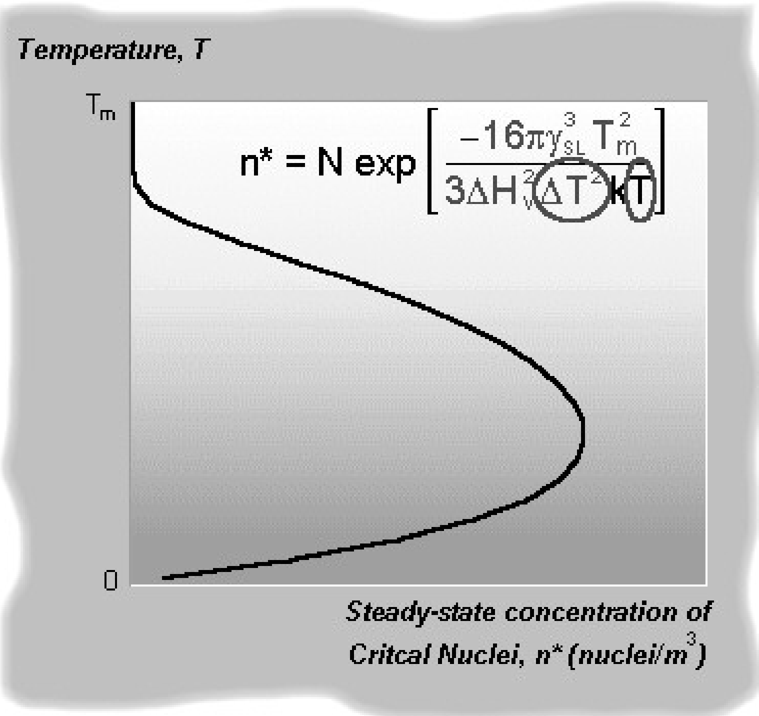
$$n^* = K_1 \, exp\left(-\frac{\Delta G^*}{kT}\right)$$

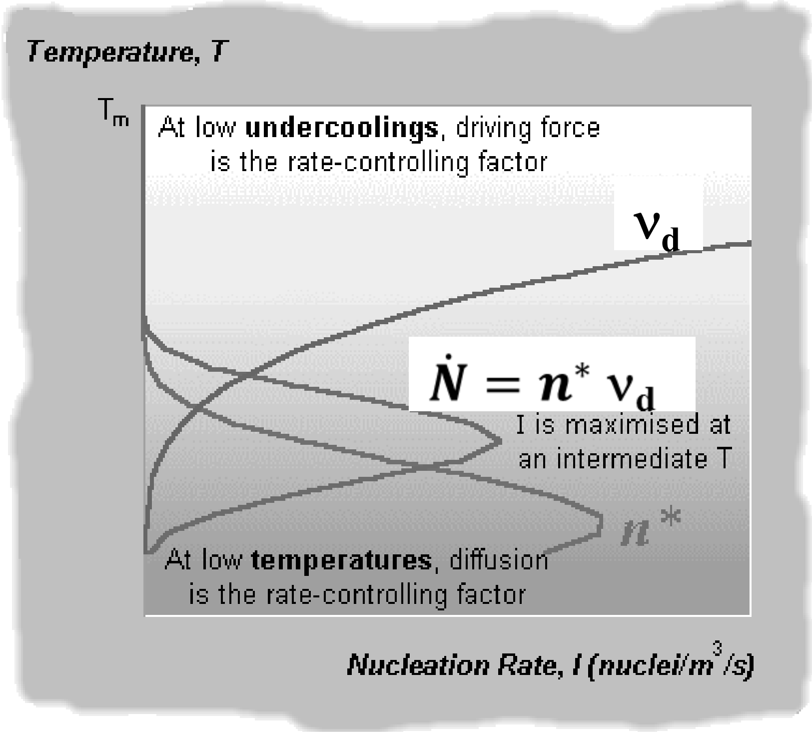
Frequency of atoms jumping to the surface of nuclei

$$\nu_d = K_2 \, exp\left(-\frac{Q_d}{kT}\right)$$

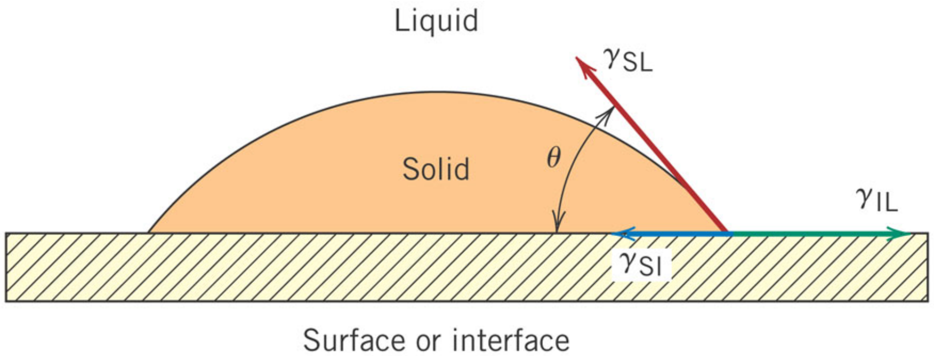
Final nucleation rate

$$\dot{N} = K_3 \, n^* \, \nu_d \, exp\left(-\frac{\Delta G^*}{kT}\right) \, exp\left(-\frac{Q_d}{kT}\right)$$





Heterogeneous Nucleation

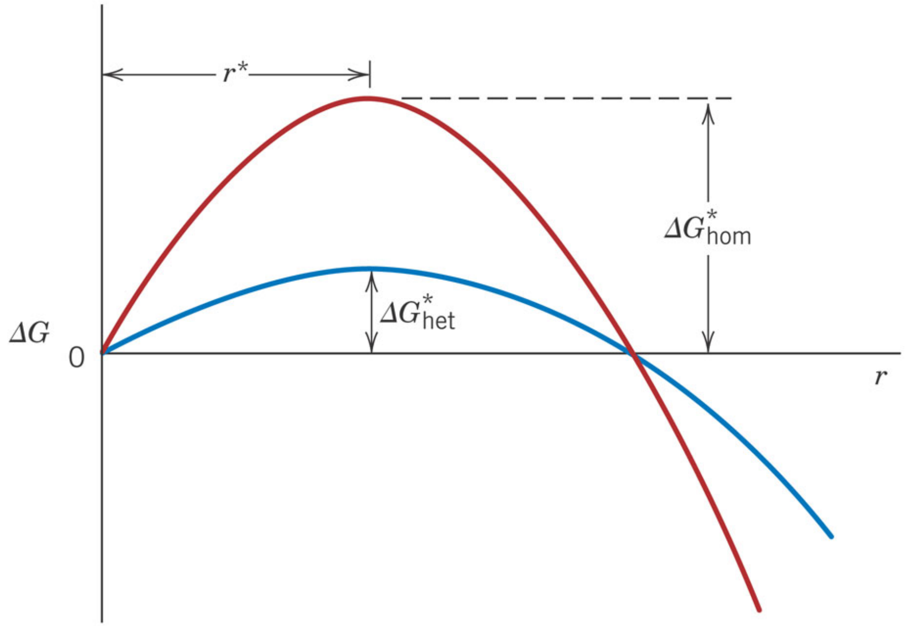


$$\gamma_{IL} = \gamma_{SI} + \gamma_{SL}\cos\theta$$

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

$$\Delta G^*_{hetero} = \left(\frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2}\right)\left(\frac{2 - 3\cos\theta + \cos^3\theta}{4}\right)$$

$$\Delta G^*_{hetero} = \Delta G^*_{homo} S(\theta)$$



Rate of Phase Transformations

Kinetics - study of reaction rates of phase transformations

- To determine reaction rate – measure degree of transformation as function of time (while holding temp constant)
  - How is degree of transformation measured?
    - X-ray diffraction – many specimens required
    - electrical conductivity measurements – on single specimen
    - measure propagation of sound waves – on single specimen

Rate of Phase Transformation

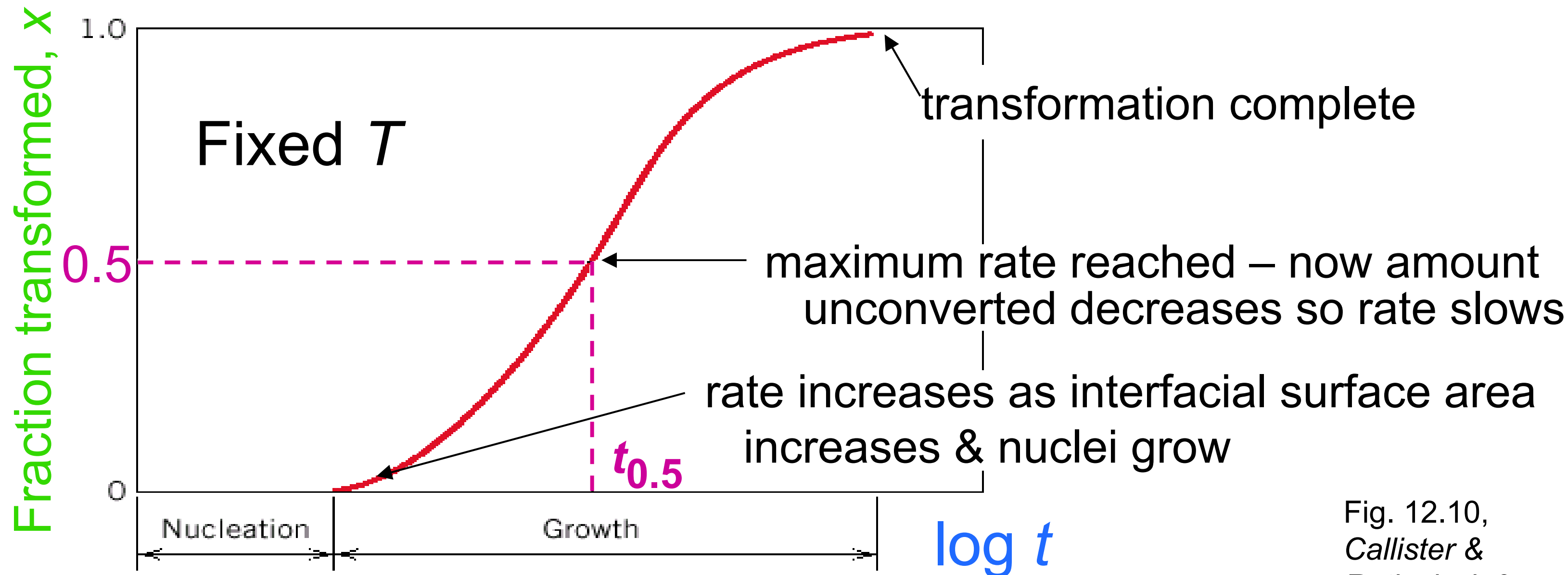


Fig. 12.10, *Callister & Rethwisch 9e.*

Jonson-Mehl-Avrami (JMA) equation => $x = 1 - \exp(-kt^n)$

fraction transformed (x) **time** (t)

K: reaction rate constant

n : Avrami exponent

By convention $rate = 1 / t_{0.5}$

Rate of Phase Transformation

The kinetics of recrystallization for some alloys obey the JMA equation and the Avrami exponent, n, is 3.1. If the fraction of recrystallized is 0.3 after 20 min, determine the rate of recrystallization.

$$x = 1 - \exp(-kt^n)$$

$$\ln(1-x) = -kt^n \qquad k = -\frac{\ln(1-x)}{t^n}$$

$$k = -\frac{\ln(1-0.3)}{(20\ min)^n} = 3.3x10^{-5}$$

$$t^n = -\frac{\ln(1-x)}{k}$$

$$t = -\left[\frac{\ln(1-x)}{k}\right]^{\frac{1}{n}}$$

$$t_{0.5} = -\left[\frac{\ln(1-0.5)}{3.3x10^{-5}}\right]^{\frac{1}{3.1}} = 24.8\ min$$

$$rate = \frac{1}{t_{0.5}} = \frac{1}{24.8\ min} = 4.0x10^{-2}\ (min)^{-1}$$

Temperature Dependence of Transformation Rate

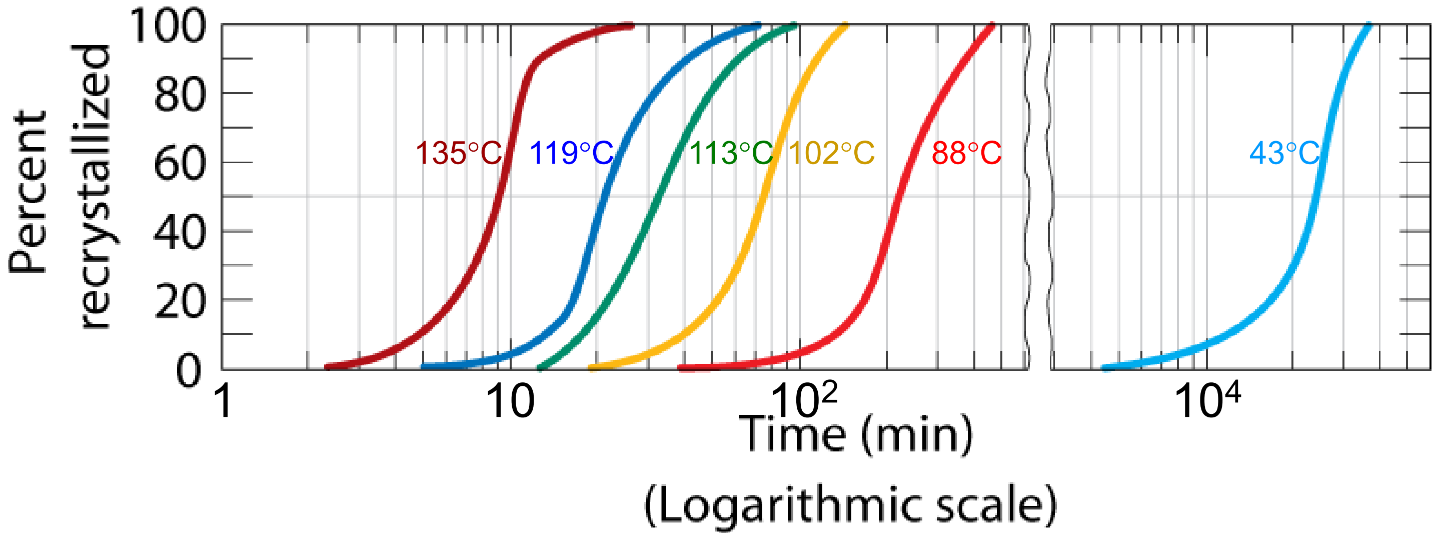


Fig. 12.11, *Callister & Rethwisch 9e.*
(Reprinted with permission from *Metallurgical Transactions*, Vol. 188, 1950, a publication of The Metallurgical Society of AIME, Warrendale, PA. Adapted from B. F. Decker and D. Harker, "Recrystallization in Rolled Copper," Trans. AIME, 188, 1950, p. 888.)

- For the recrystallization of Cu, since

$$rate = 1/t_{0.5}$$

  rate increases with increasing temperature

- Rate often so slow that attainment of equilibrium state not possible!

Transformations & Undercooling

- Eutectoid transf. (Fe-Fe_3C system): $\gamma \Rightarrow \alpha + Fe_3C$
  - γ: 0.76 wt% C
  - α: 0.022 wt% C
  - Fe_3C: 6.7 wt% C
- For transf. to occur, must cool to below 727 °C (i.e., must "undercool")

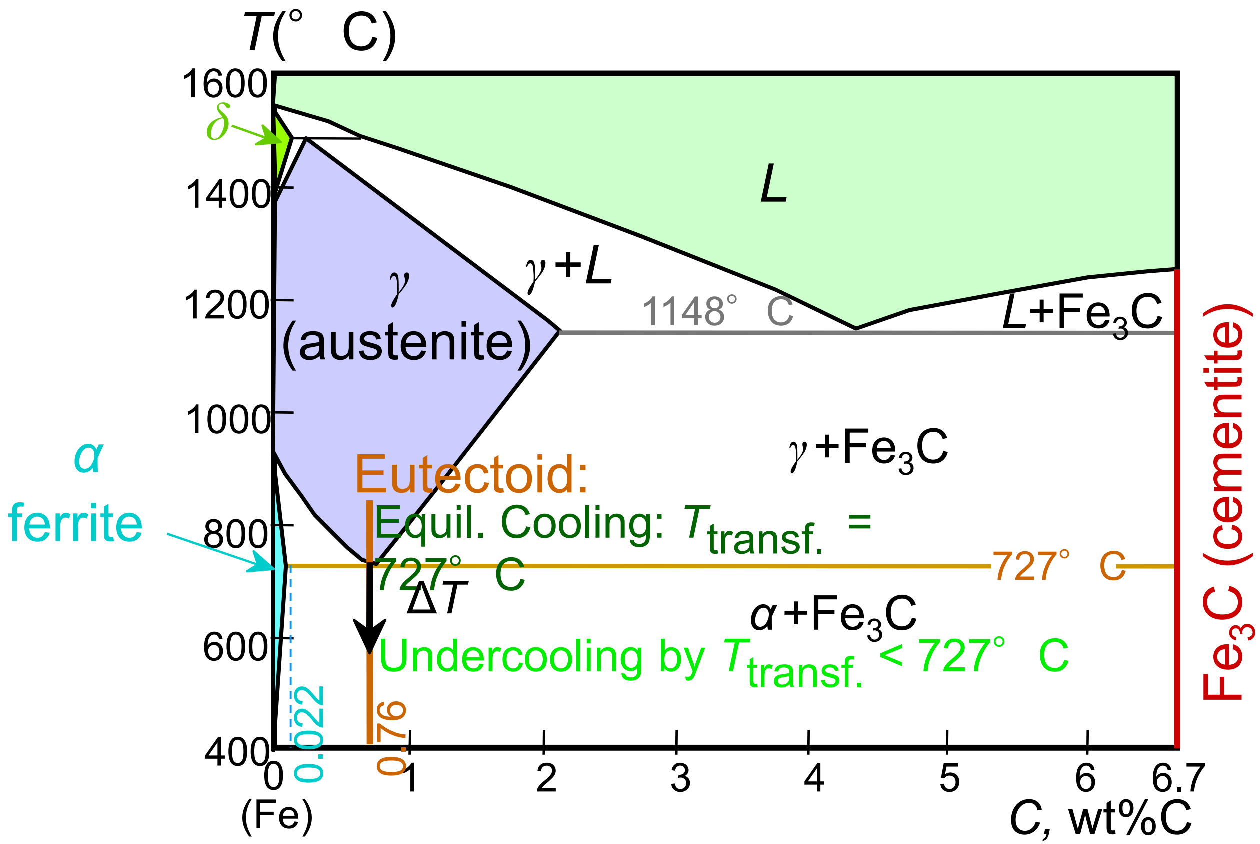
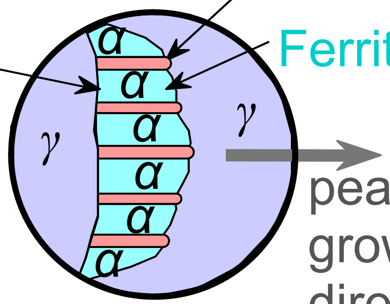


Fig. 11.23, Callister & Rethwisch 9e.
[Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

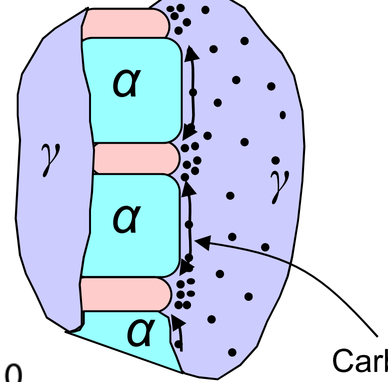
The Fe-Fe_3C Eutectoid Transformation

- Transformation of austenite to pearlite:

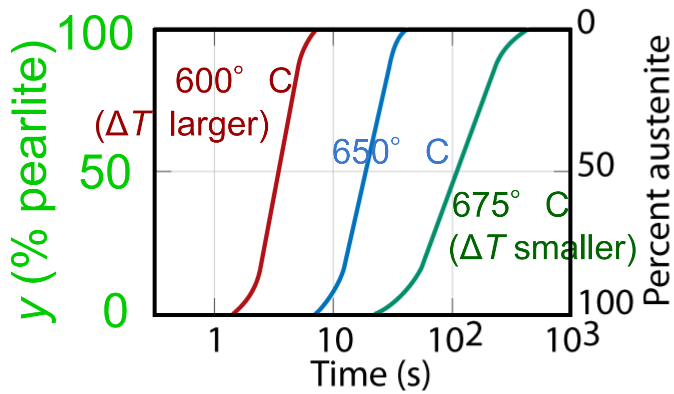


Adapted from Fig. 11.14, *Callister & Rethwisch 9e.*

Diffusion of C during transformation



- For this transformation, rate increases with [$T_{eutectoid}$ – T] (i.e., ΔT).



Adapted from Fig. 12.12, *Callister & Rethwisch 9e.*

Coarse pearlite → formed at higher temperatures – relatively soft

Fine pearlite → formed at lower temperatures – relatively hard

Generation of Isothermal Transformation Diagrams

Consider:

- The Fe-Fe_3C system, for C_0 = 0.76 wt% C
- A transformation temperature of 675 ºC.

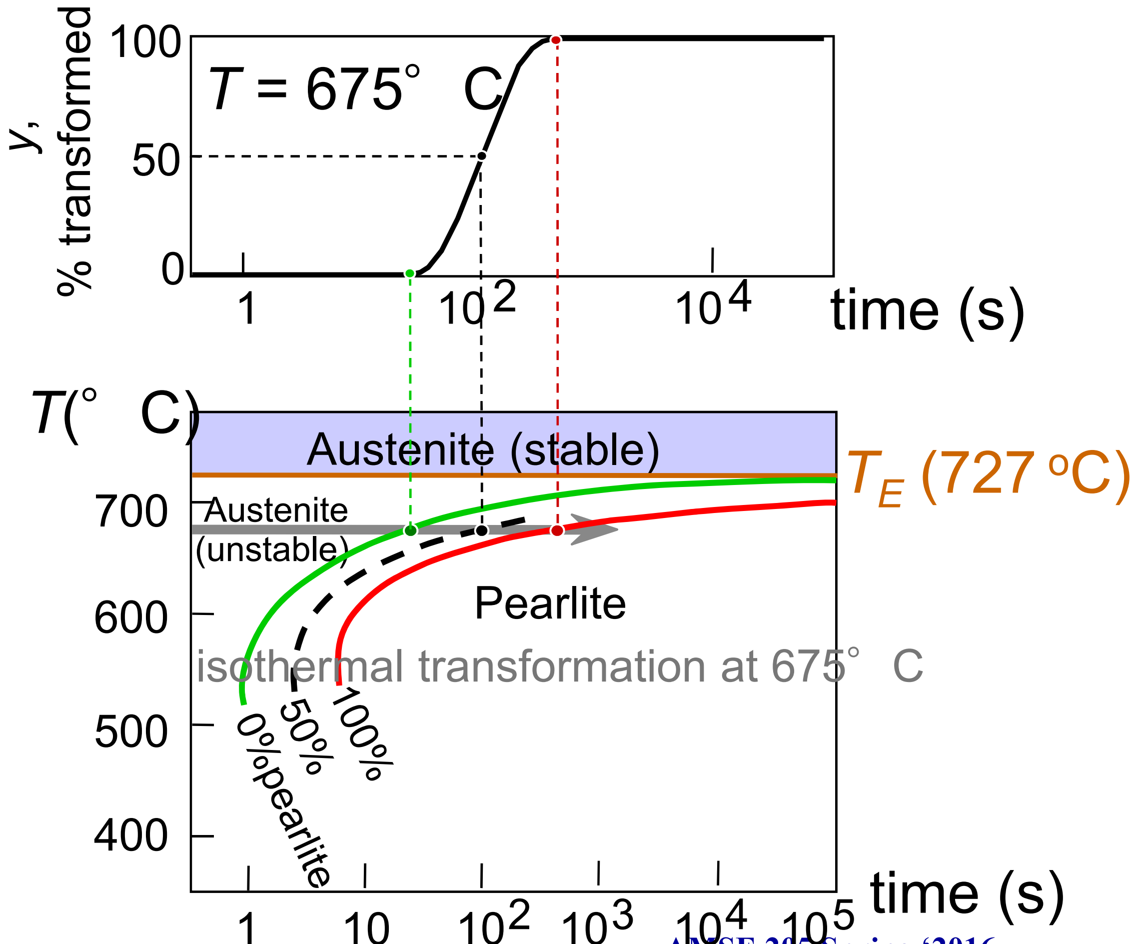


Fig. 12.13, *Callister & Rethwisch 9e.* [Adapted from H. Boyer (Editor), Atlas of Isothermal Transformation and Cooling Transformation Diagrams, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Austenite-to-Pearlite Isothermal Transformation

- Eutectoid composition, C_0 = 0.76 wt% C
- Begin at T > 727° C
- Rapidly cool to 625 °C
- Hold T (625 °C) constant (isothermal treatment)

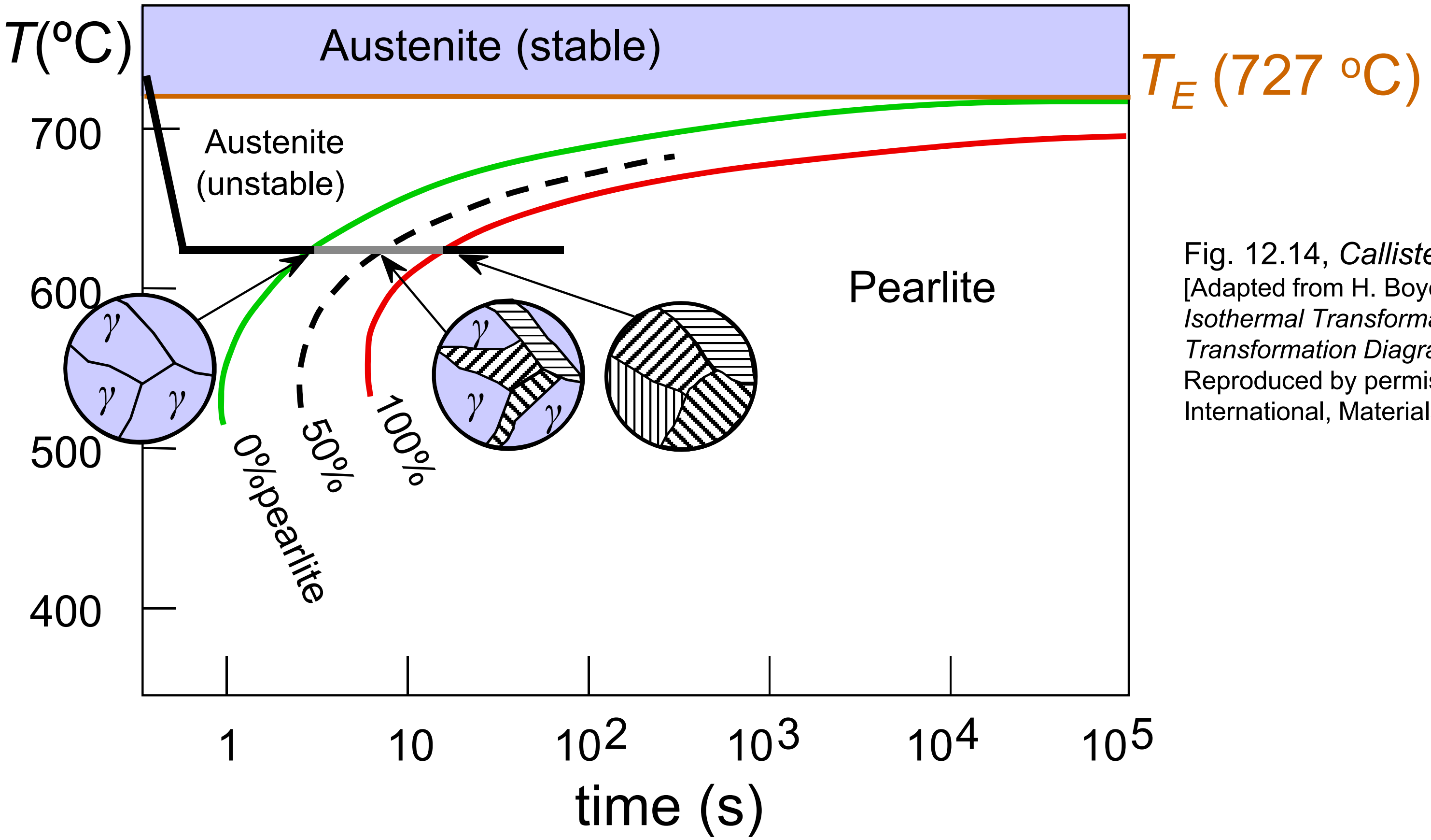


Fig. 12.14, *Callister & Rethwisch 9e.*
[Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Transformations Involving Noneutectoid Compositions

Consider C_0 = 1.13 wt% C

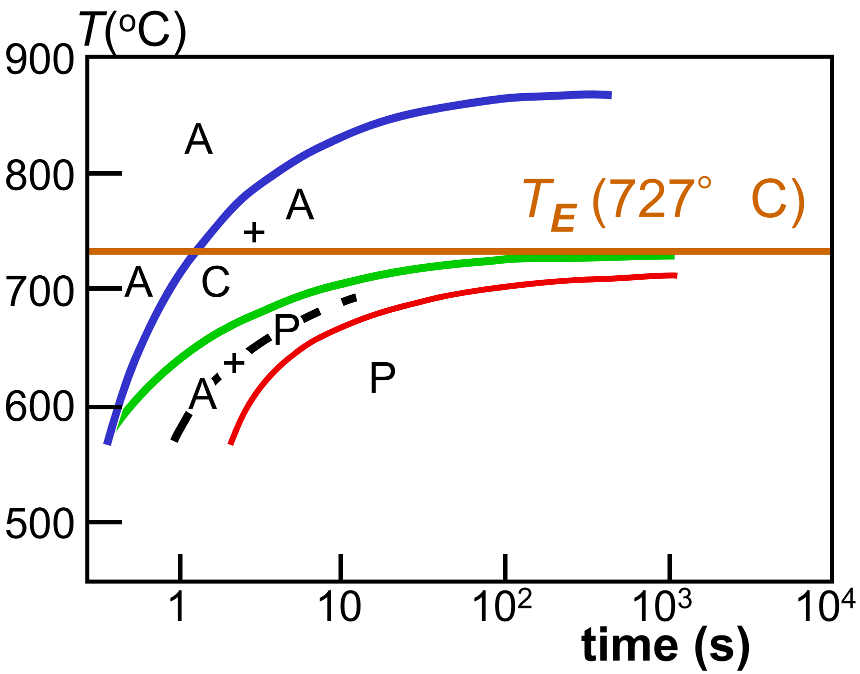


Fig. 12.16, *Callister & Rethwisch 9e.*
[Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

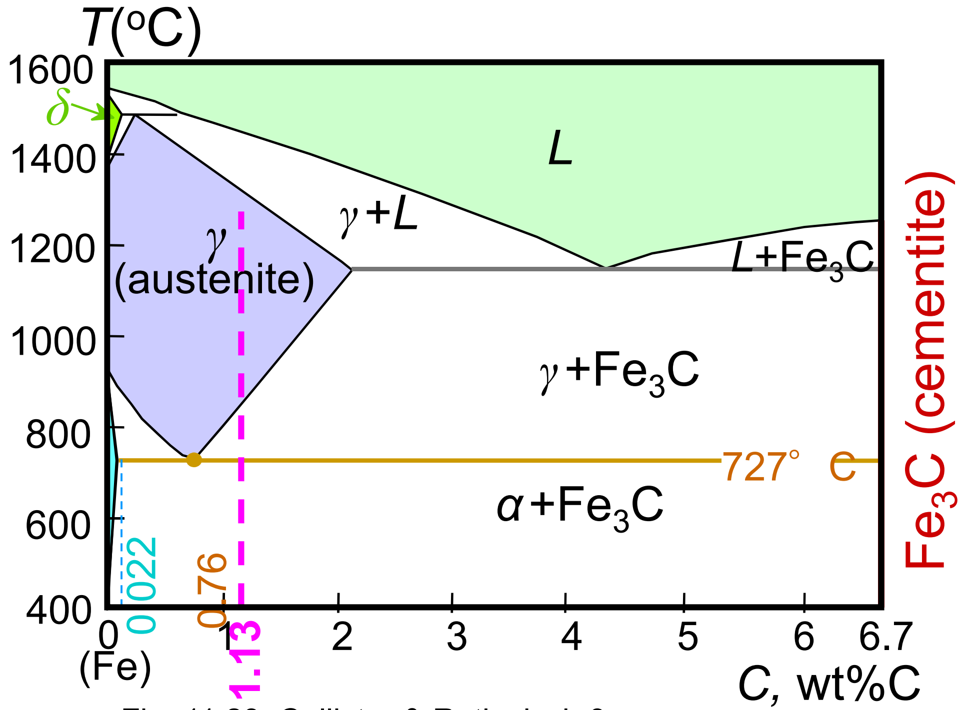


Fig. 11.23, Callister & Rethwisch 9e.
[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

Hypereutectoid composition – proeutectoid cementite

Bainite: Another Fe-Fe_3C Transformation Product

- Bainite:
  -- elongated Fe_3C particles in α-ferrite matrix
  -- diffusion controlled
- Isothermal Transf. Diagram, C_0 = 0.76 wt% C

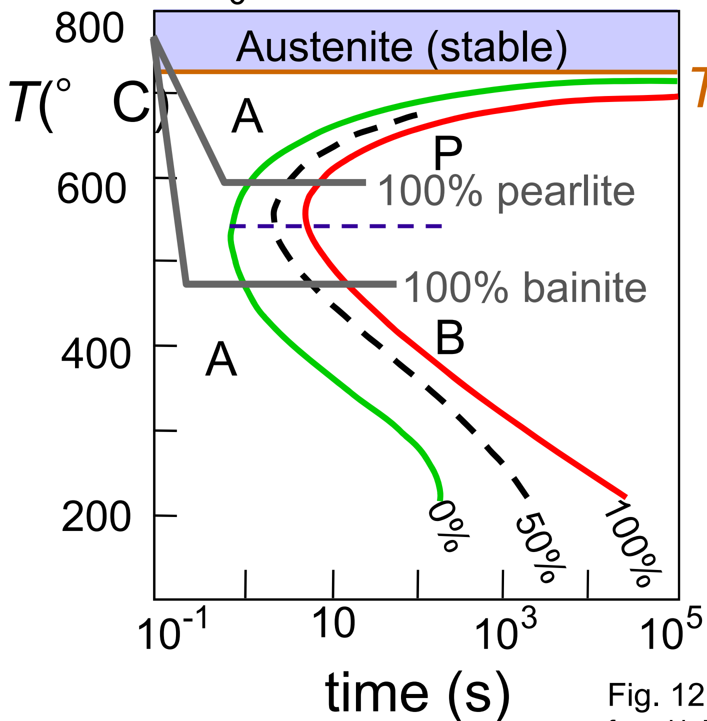


Fig. 12.18, *Callister & Rethwisch 9e.* [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

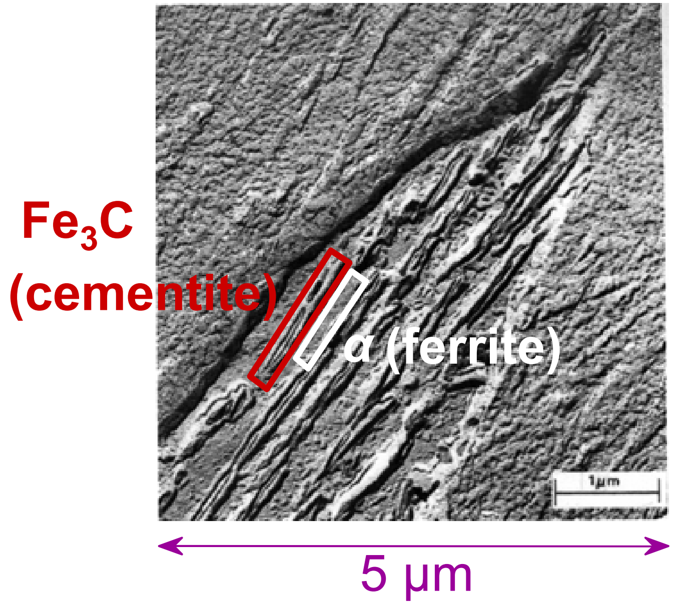


Fig. 12.17, *Callister & Rethwisch 9e.* (From *Metals Handbook*, Vol. 8, 8th edition, *Metallography, Structures and Phase Diagrams*, 1973. Reproduced by permission of ASM International, Materials Park, OH.)

Spheroidite: Another Microstructure for the Fe-Fe_3C System

- Spheroidite:
  -- Fe_3C particles within an α-ferrite matrix
  -- formation requires diffusion
  -- heat bainite or pearlite at temperature just below eutectoid for long times
  -- driving force – reduction of α-ferrite/Fe_3C interfacial area

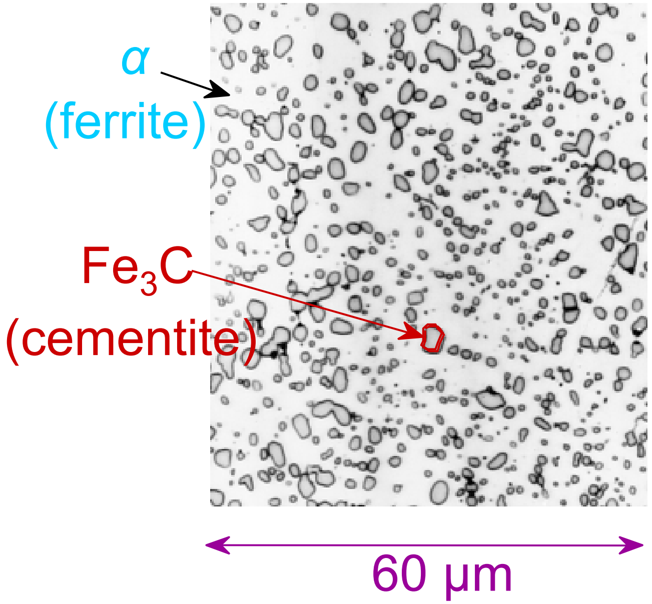
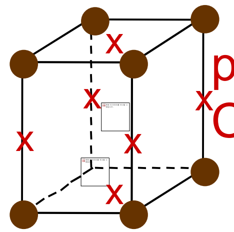


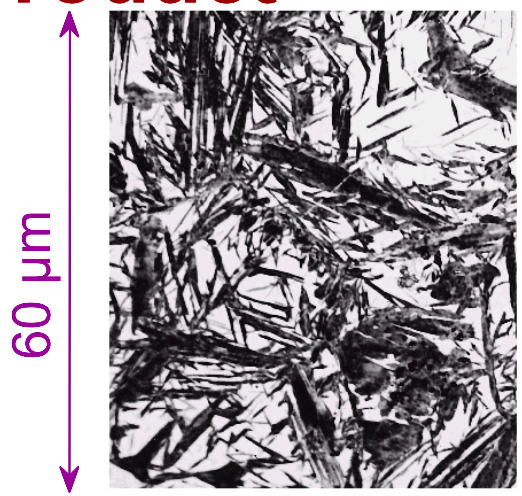
Fig. 12.19, *Callister & Rethwisch 9e.*
(Copyright United States Steel Corporation, 1971.)

Martensite: A Nonequilibrium Transformation Product

- Martensite:
  -- γ(FCC) to Martensite (BCT)



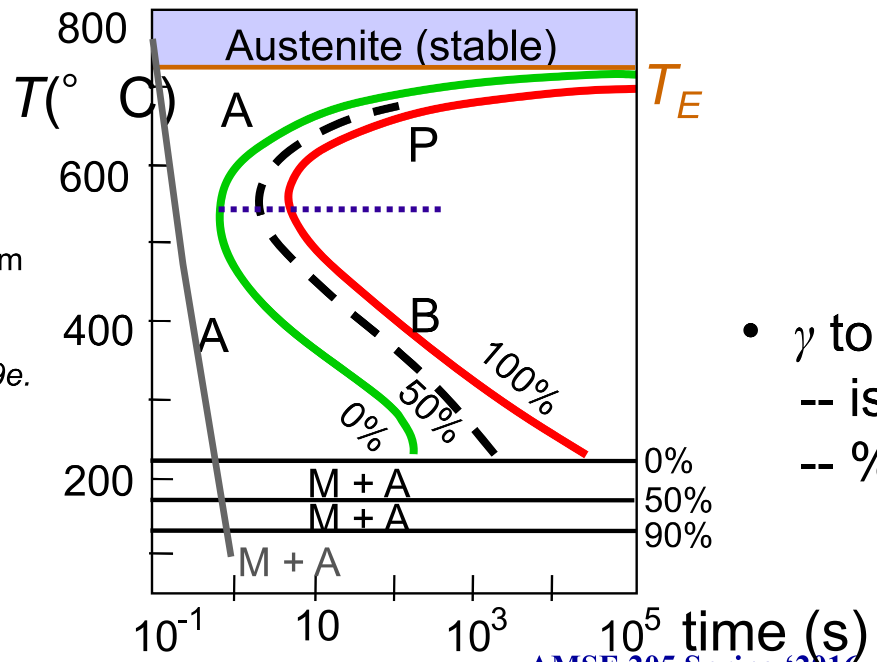
Adapted from Fig. 12.20, *Callister & Rethwisch 9e.*



Martensite needles
Austenite

Fig. 12.21, *Callister & Rethwisch 9e.*
(Courtesy United States Steel Corporation.)

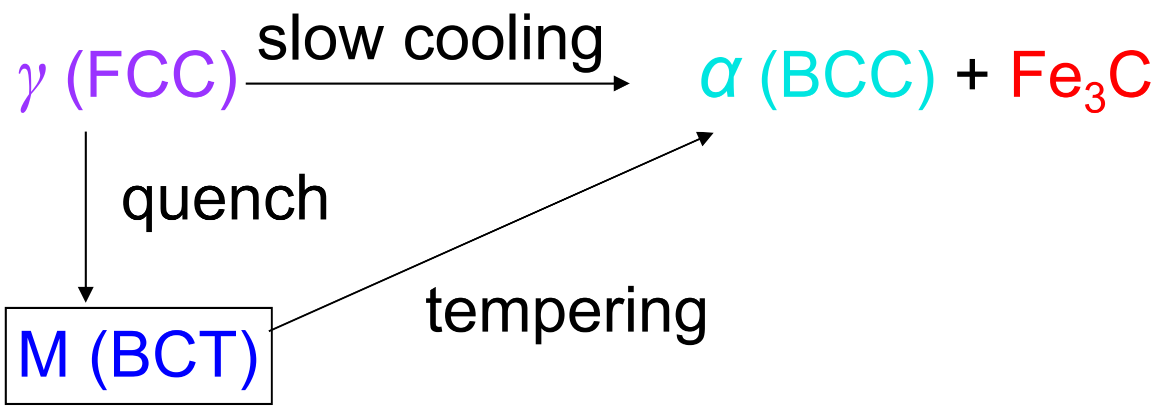
- Isothermal Transf. Diagram



Adapted from Fig. 12.22, *Callister & Rethwisch 9e.*

- γ to martensite (M) transformation.
  -- is rapid! (diffusionless)
  -- % transformation depends only on T to which rapidly cooled

Martensite Formation



Martensite (M) – single phase

– has body centered tetragonal (BCT) crystal structure

Diffusionless transformation   BCT if C_0 > 0.15 wt% C

BCT → few slip planes → hard, brittle

Phase Transformations of Alloys

Effect of adding other elements

Change transition temp.

Cr, Ni, Mo, Si, Mn

retard $\gamma \rightarrow \alpha + Fe_3C$ reaction (and formation of pearlite, bainite)

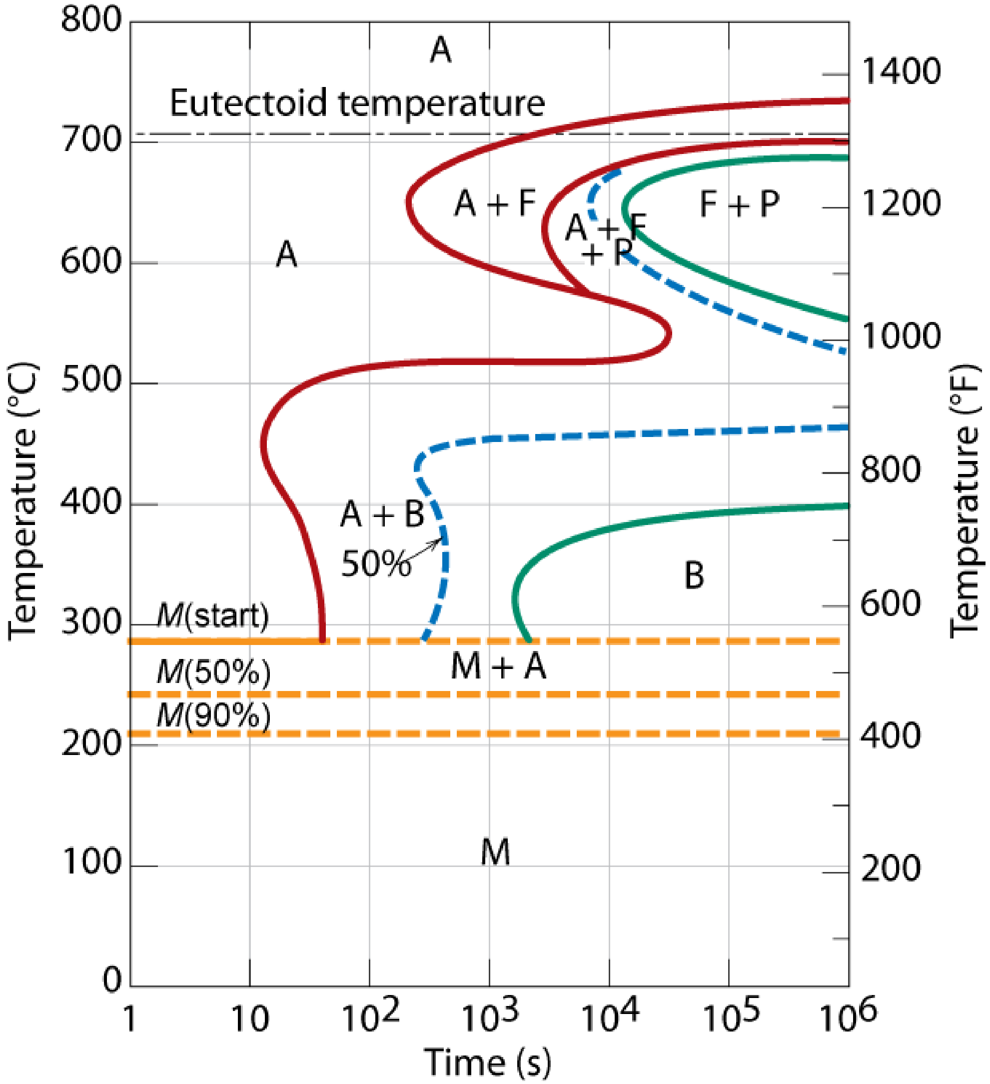


Fig. 12.23, *Callister & Rethwisch 9e.* [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Continuous Cooling Transformation Diagrams

Conversion of isothermal transformation diagram to continuous cooling transformation diagram

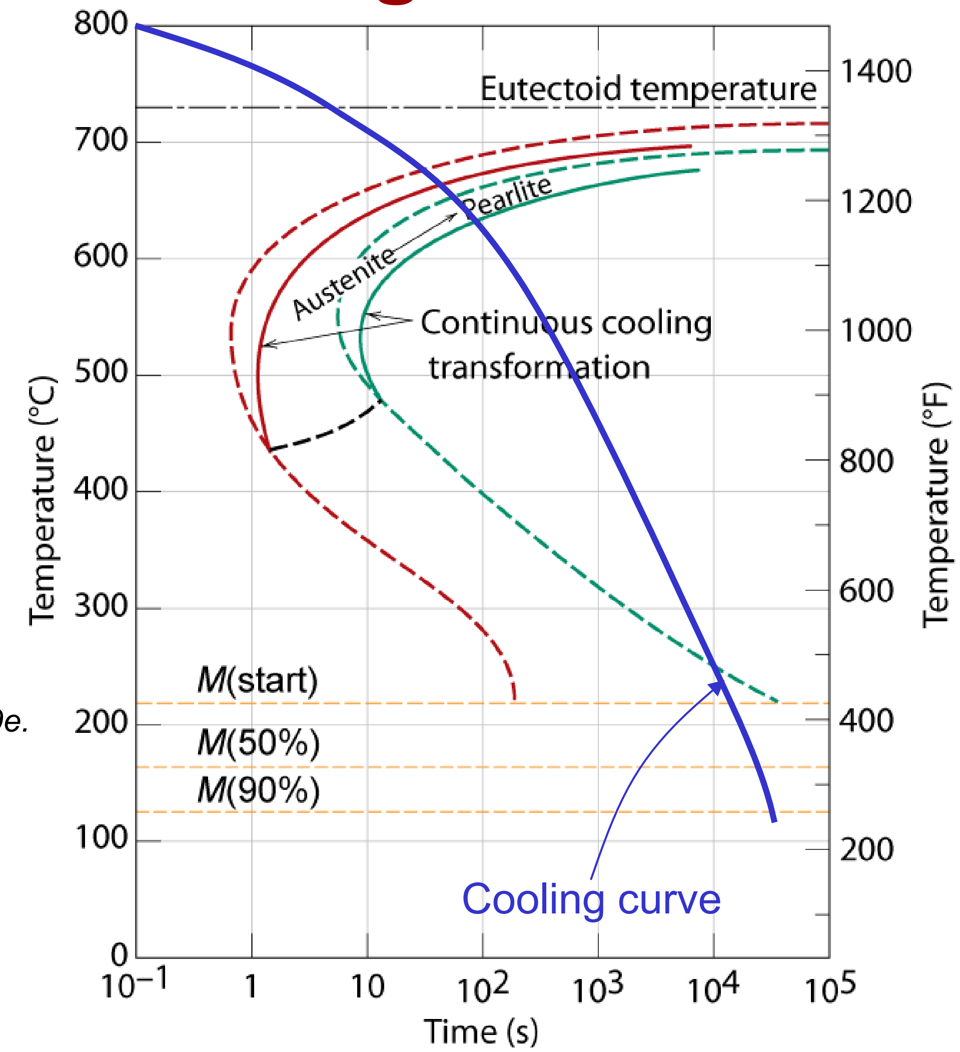


Fig. 12.25, *Callister & Rethwisch 9e.*
[Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Isothermal Heat Treatment Example Problems

On the isothermal transformation diagram for a 0.45 wt% C, Fe-C alloy, sketch and label the time-temperature paths to produce the following microstructures:

a) 42% proeutectoid ferrite and 58% coarse pearlite
b) 50% fine pearlite and 50% bainite
c) 100% martensite
d) 50% martensite and 50% austenite

Solution to Part (a) of Example Problem

a) 42% proeutectoid ferrite and 58% coarse pearlite

Isothermally treat at ~ 680° C

-- all austenite transforms to proeutectoid α and coarse pearlite.

$$W_{pearlite} = \frac{C_0 - 0.022}{0.76 - 0.022}$$

$$= \frac{0.45 - 0.022}{0.76 - 0.022} = 0.58$$

$$W_{\alpha'} = 1 - 0.58 = 0.42$$

Fe-Fe_3C phase diagram, for C_0 = 0.45 wt% C

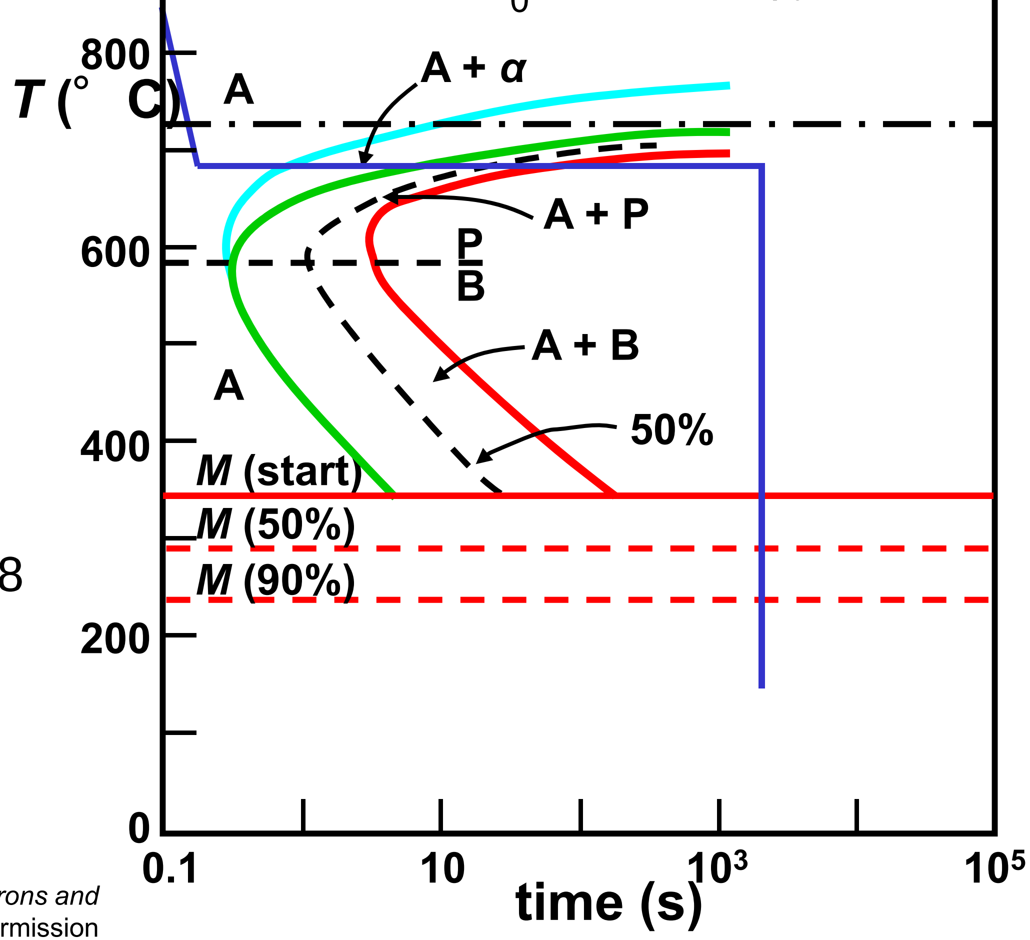


Figure 12.39, *Callister & Rethwisch 9e.* (Adapted from *Atlas of Time-Temperature Diagrams for Irons and Steels*, G. F. Vander Voort, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

Solution to Part (b) of Example Problem

b) 50% fine pearlite and 50% bainite

Isothermally treat at ~ 590° C
– 50% of austenite transforms to fine pearlite.

Then isothermally treat at ~ 470° C
– all remaining austenite transforms to bainite.

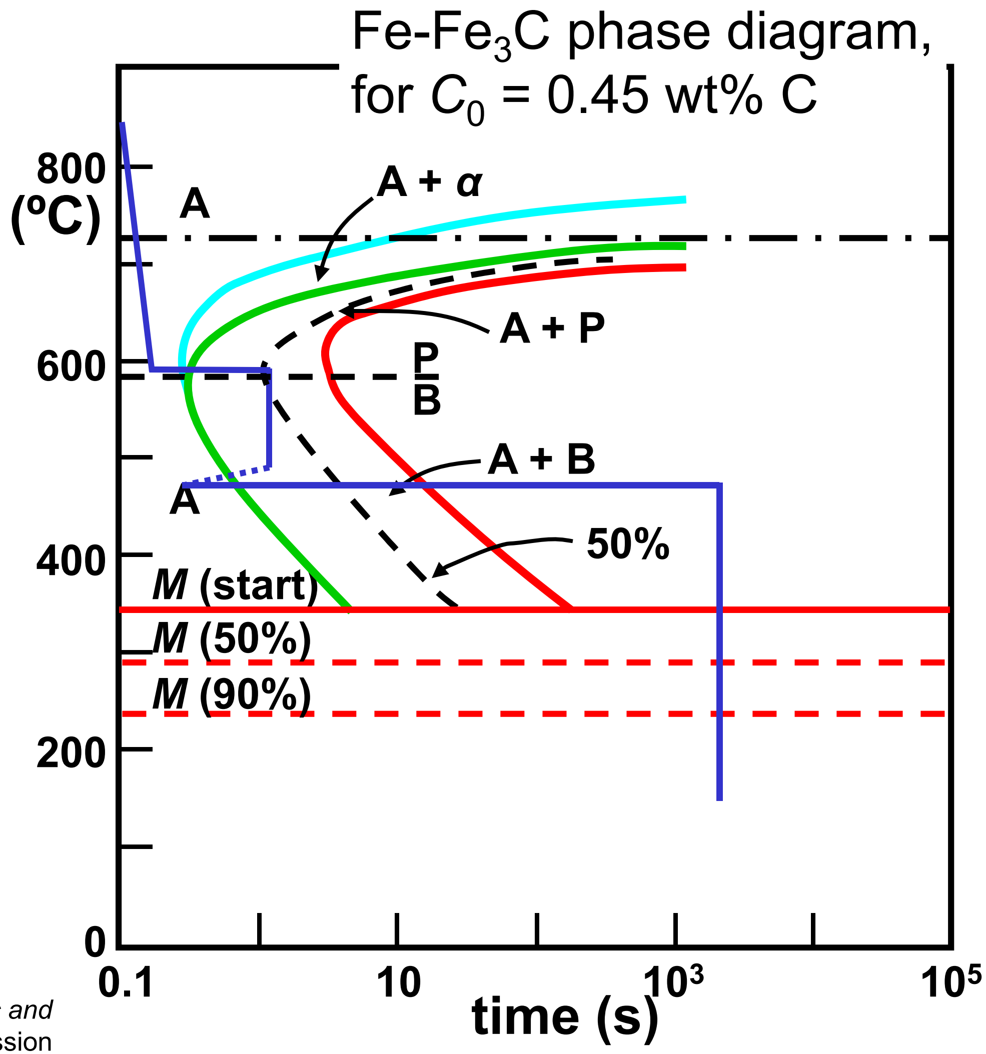


Figure 12.39, *Callister & Rethwisch 9e*.
(Adapted from *Atlas of Time-Temperature Diagrams for Irons and Steels*, G. F. Vander Voort, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

Solutions to Parts (c) & (d) of Example Problem

c) 100% martensite – rapidly quench to room temperature

d) 50% martensite & 50% austenite

-- rapidly quench to ~ 290° C, hold at this temperature

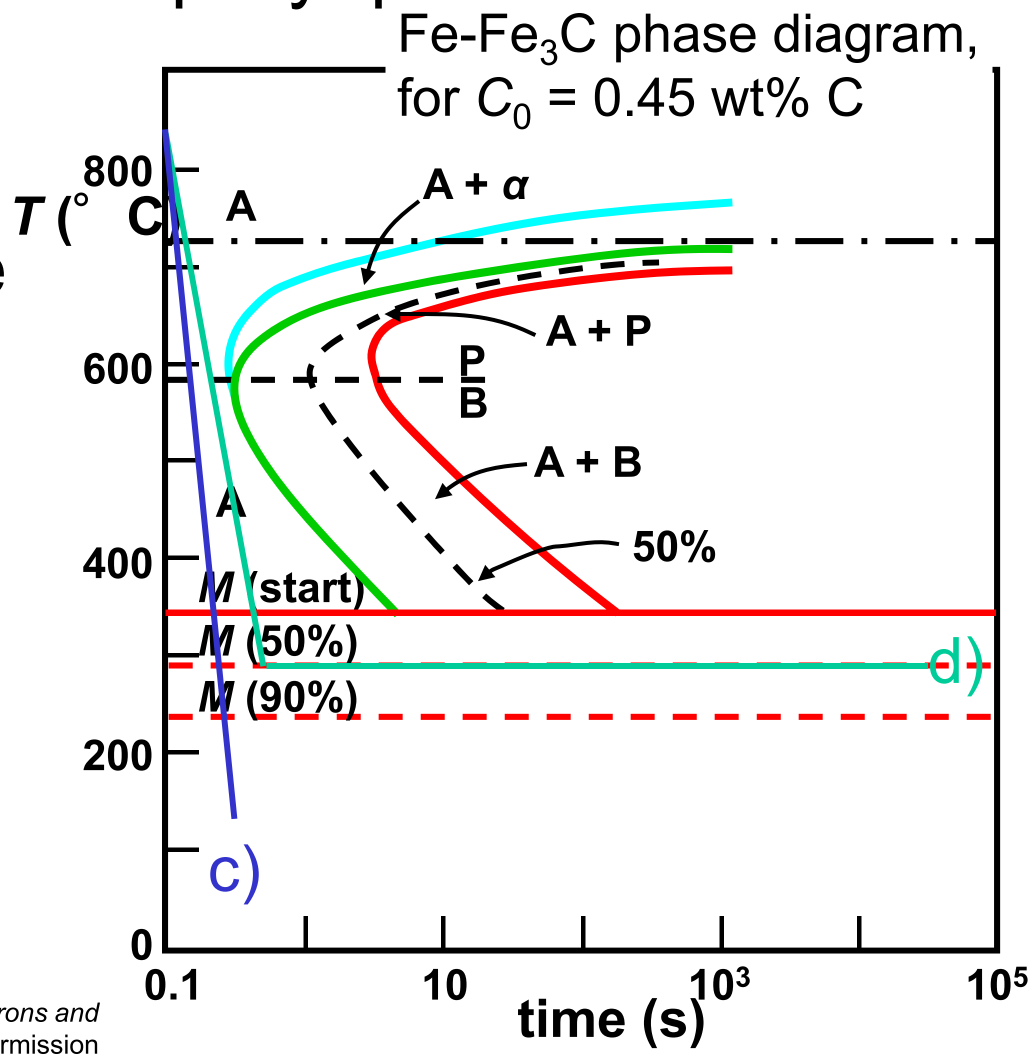


Figure 12.39, *Callister & Rethwisch 9e*.
(Adapted from *Atlas of Time-Temperature Diagrams for Irons and Steels*, G. F. Vander Voort, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

Mechanical Props: Influence of C Content

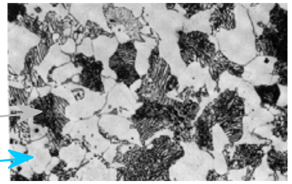
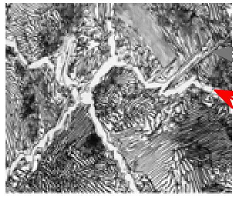


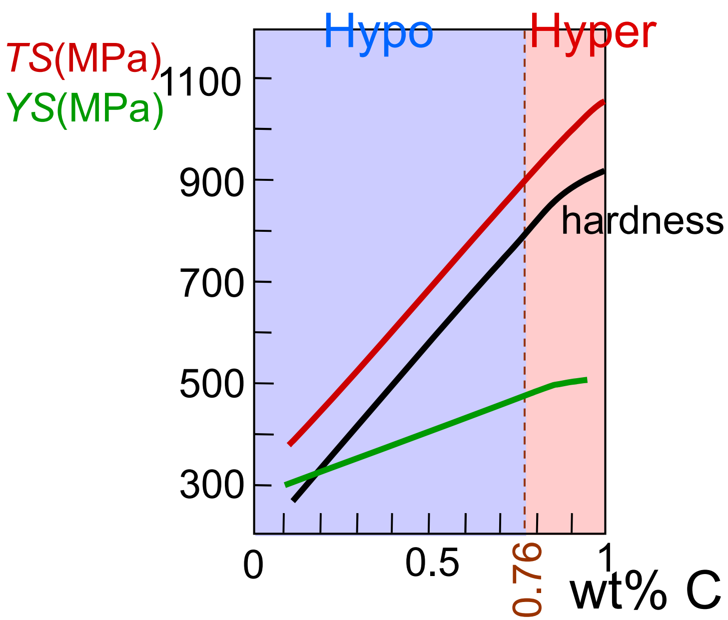
Fig. 11.29, *Callister & Rethwisch 9e.*
(Courtesy of Republic Steel Corporation.)

$C_0 < 0.76$ wt% C
Hypoeutectoid



$C_0 > 0.76$ wt% C
Hypereutectoid

Fig. 11.32, *Callister & Rethwisch 9e.*
(Copyright 1971 by United States Steel Corporation.)



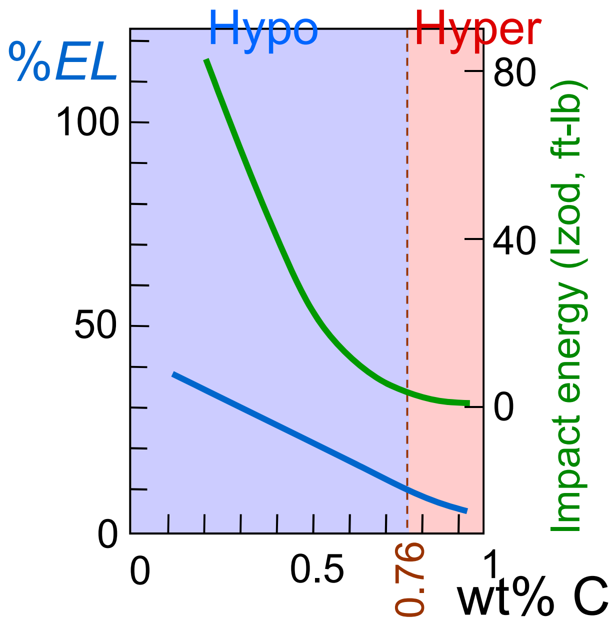
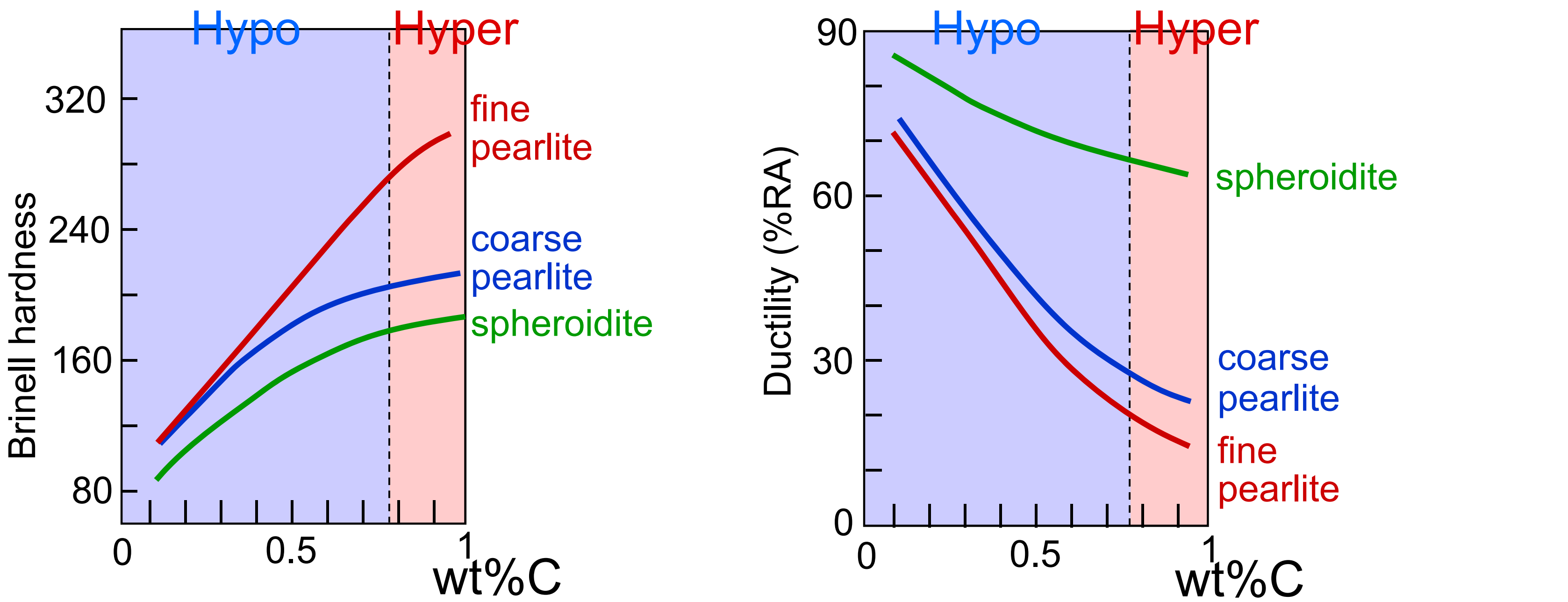


Fig. 12.29, *Callister & Rethwisch 9e.*
[Data taken from *Metals Handbook: Heat Treating*, Vol. 4, 9th edition, V. Masseria (Managing Editor), 1981. Reproduced by permission of ASM International, Materials Park, OH.]

- Increase C content: *TS* and *YS* increase, *%EL* decreases

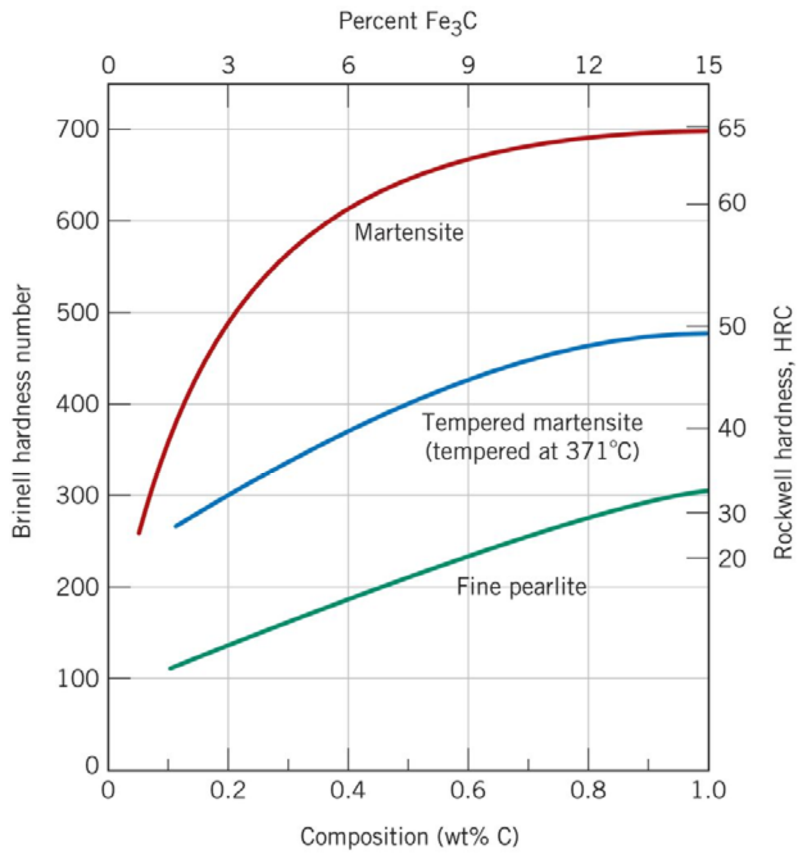
Mechanical Props: Fine Pearlite vs. Coarse Pearlite vs. Spheroidite



- Hardness: fine > coarse > spheroidite
- %RA: fine < coarse < spheroidite

Fig. 12.30, *Callister & Rethwisch 9e.*
[Data taken from *Metals Handbook: Heat Treating*, Vol. 4, 9th edition, V. Masseria (Managing Editor), 1981. Reproduced by permission of ASM International, Materials Park, OH.]

Mechanical Props: Fine Pearlite vs. Martensite



Adapted from Edgar C. Bain, Functions of the Alloying Elements in Steel, 1939; and R. A. Grange, C. R. Hribal, and L. F. Porter, Metall. Trans. A, Vol. 8A. Reproduced by permission of ASM International, Materials Park, OH.

- Hardness: fine pearlite << martensite.

Tempered Martensite

Heat treat martensite to form tempered martensite

- tempered martensite less brittle than martensite
- tempering reduces internal stresses caused by quenching

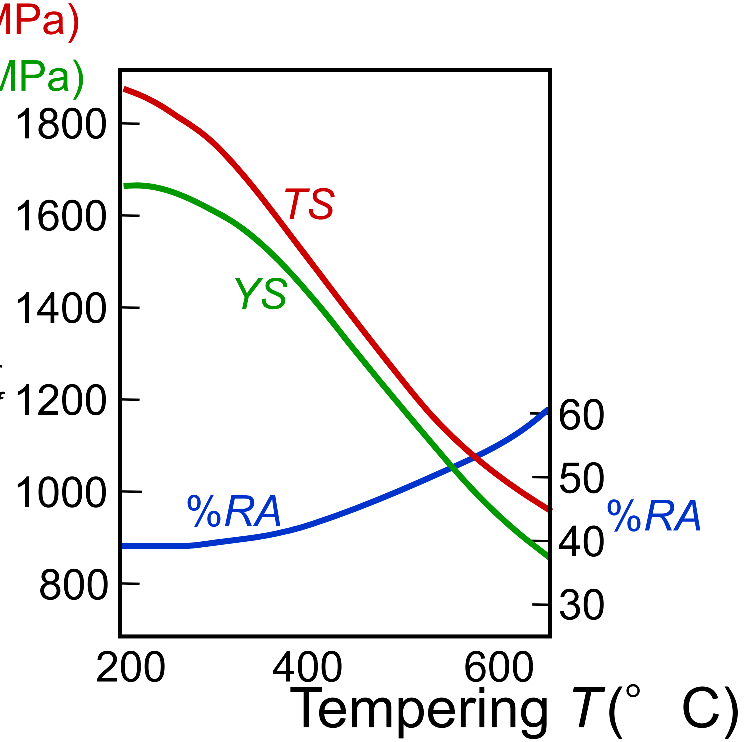


Fig. 12.34, *Callister & Rethwisch 9e.* (Adapted from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, 1939. Reproduced by permission of ASM International, Materials Park, OH.)

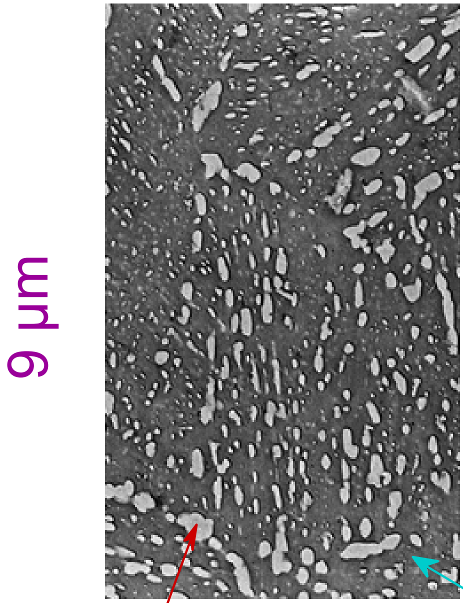
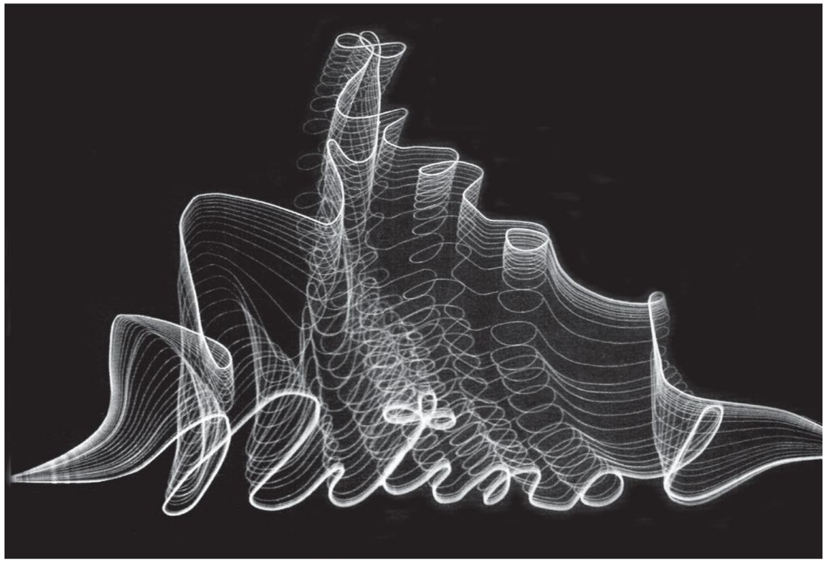


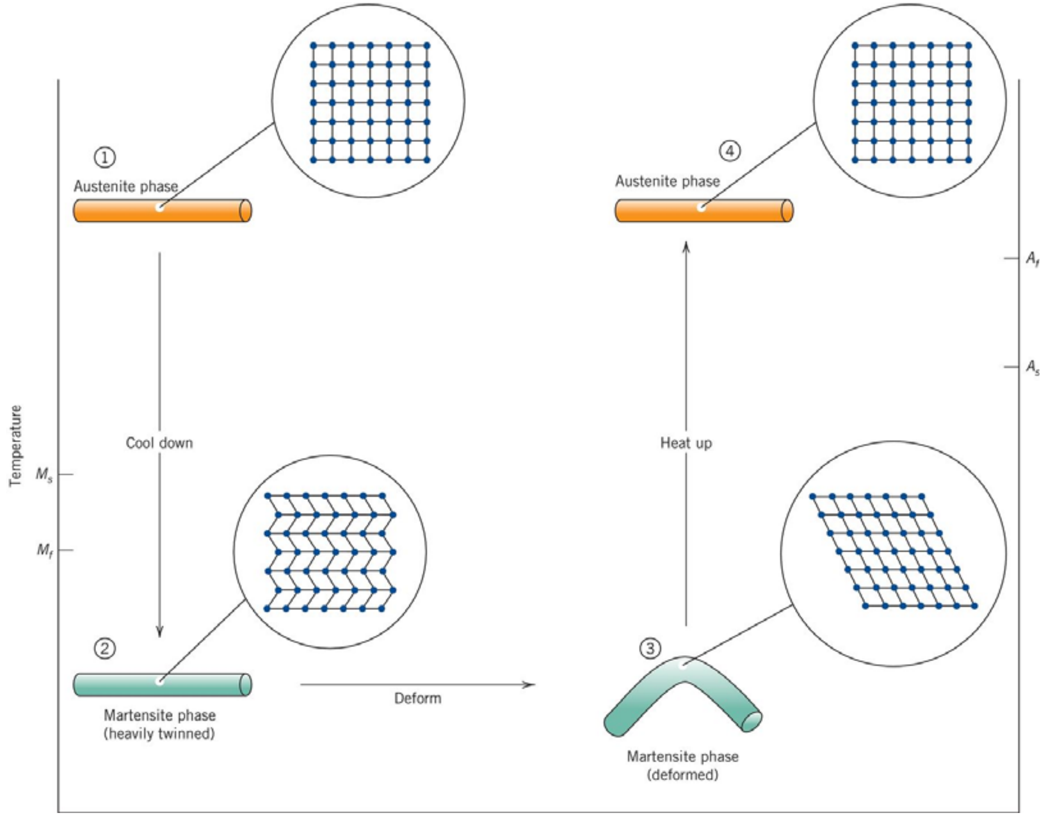
Figure 12.33, *Callister & Rethwisch 9e.* (Copyright 1971 by United States Steel Corporation.)

- tempering produces extremely small Fe_3C particles surrounded by α.
- tempering decreases *TS*, *YS* but increases %RA

Shape Memory Alloy
Nitinol: (Ni-Ti Naval Ordnance Laboratory)



Photograph courtesy the Naval Surface Warfare Center (previously the Naval Ordnance Laboratory



Shape Memory Effect

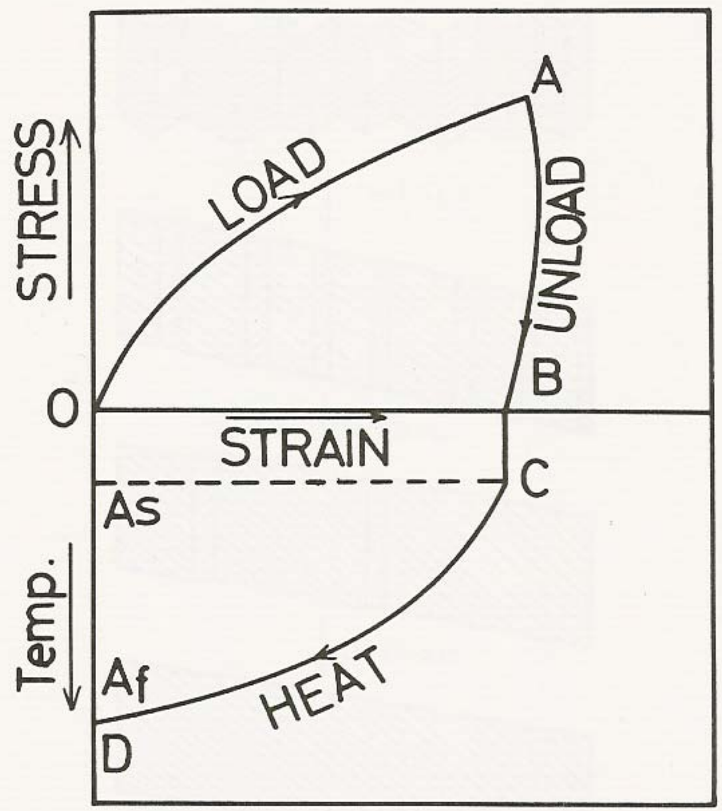


Fig. 1. The schematic illustration of shape memory effect.

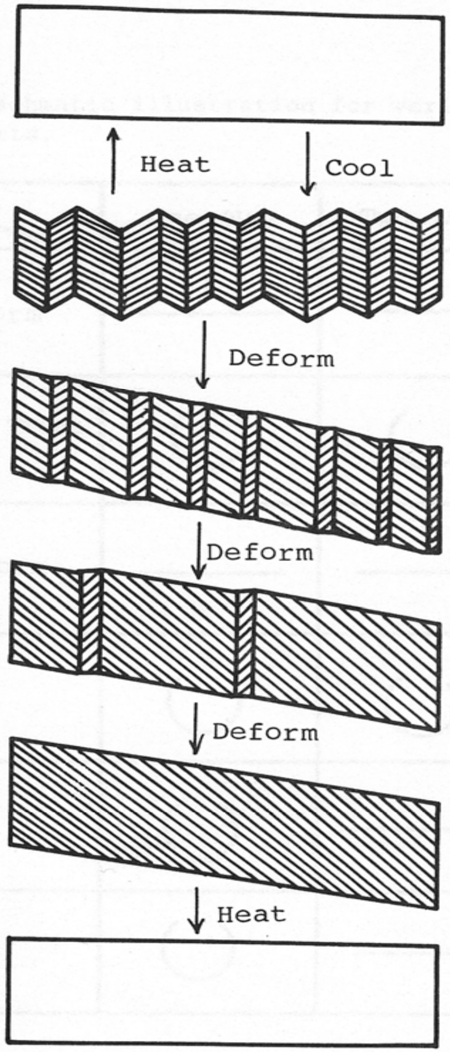


Fig. 2. The schematic illustration of shape memory effect mechanism.

Pseudo Elasticity (Super Elasticity)

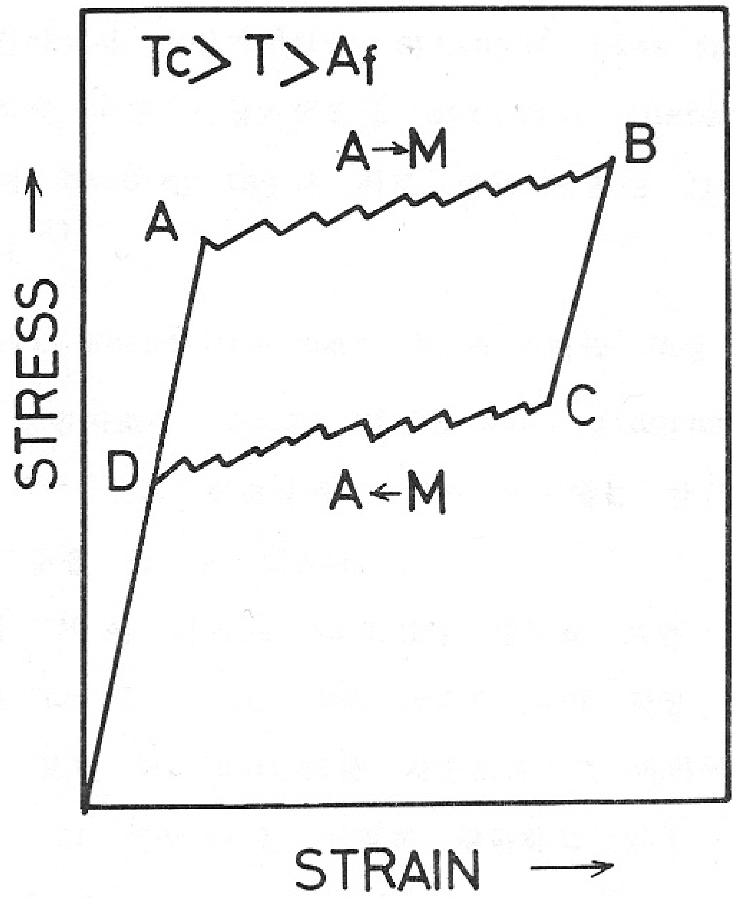
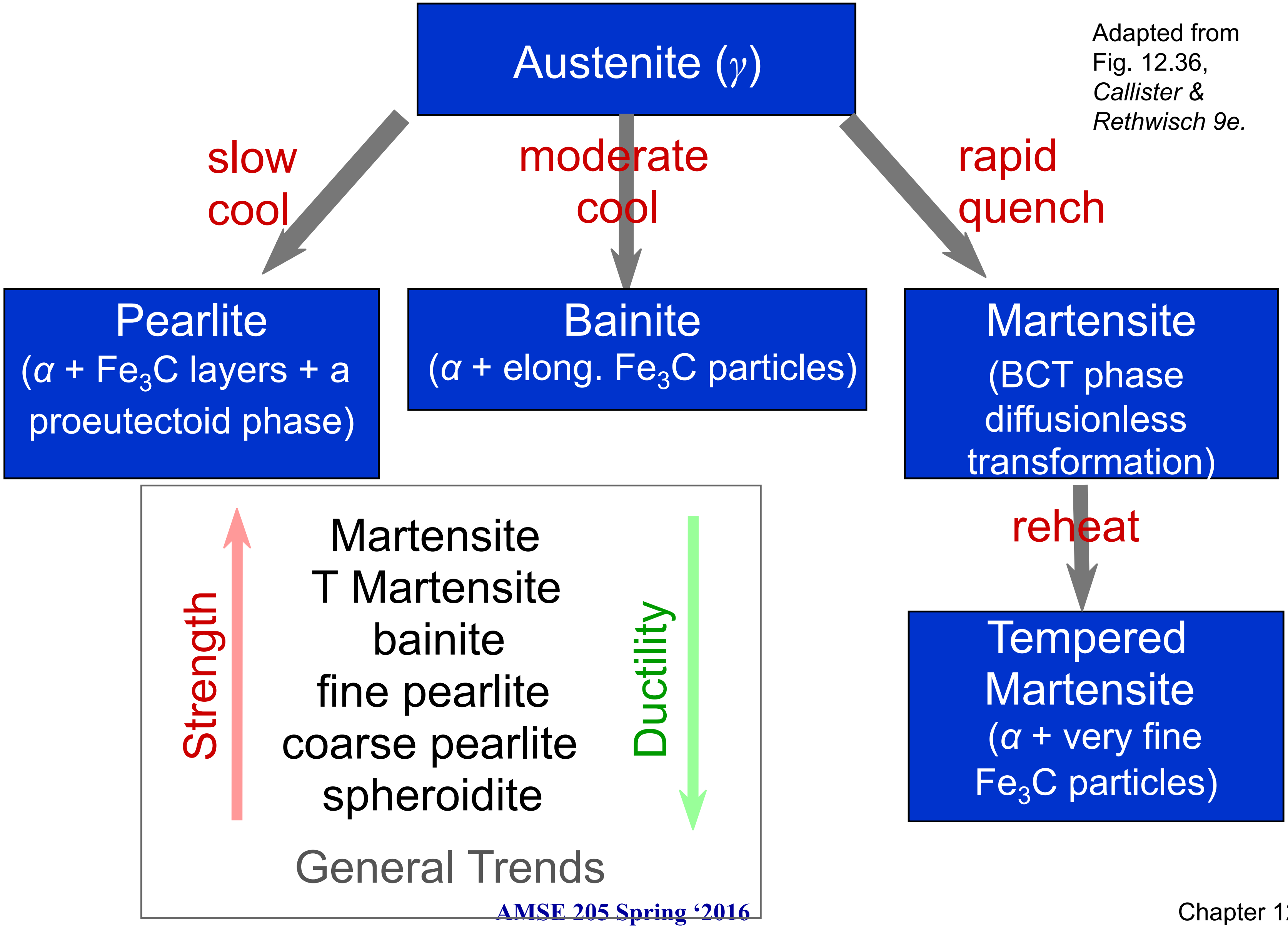


Fig. 3. The schematic illustration of pseudoelastic effect.

Summary of Possible Transformations



Adapted from Fig. 12.36, *Callister & Rethwisch 9e.*