Chemical Engineering 378

Science of Materials Engineering

Lecture 22

Phase Transitions, Kinetics and Microstructures

Spiritual Thought

"We don't always know the details of our future. We do not know what lies ahead. We live in a time of uncertainty. We are surrounded by challenges on all sides. Occasionally discouragement may sneak into our day; frustration may invite itself into our thinking; doubt might enter about the value of our work. In these dark moments Satan whispers in our ears that we will never be able to succeed, that the price isn't worth the effort, and that our small part will never make a difference… ***We know that God keeps His promises.*** We need to fulfill our part to receive His blessings."

-Dieter F. Uchtdorf

Advanced Materials Class

WINTER 2023

ME 557

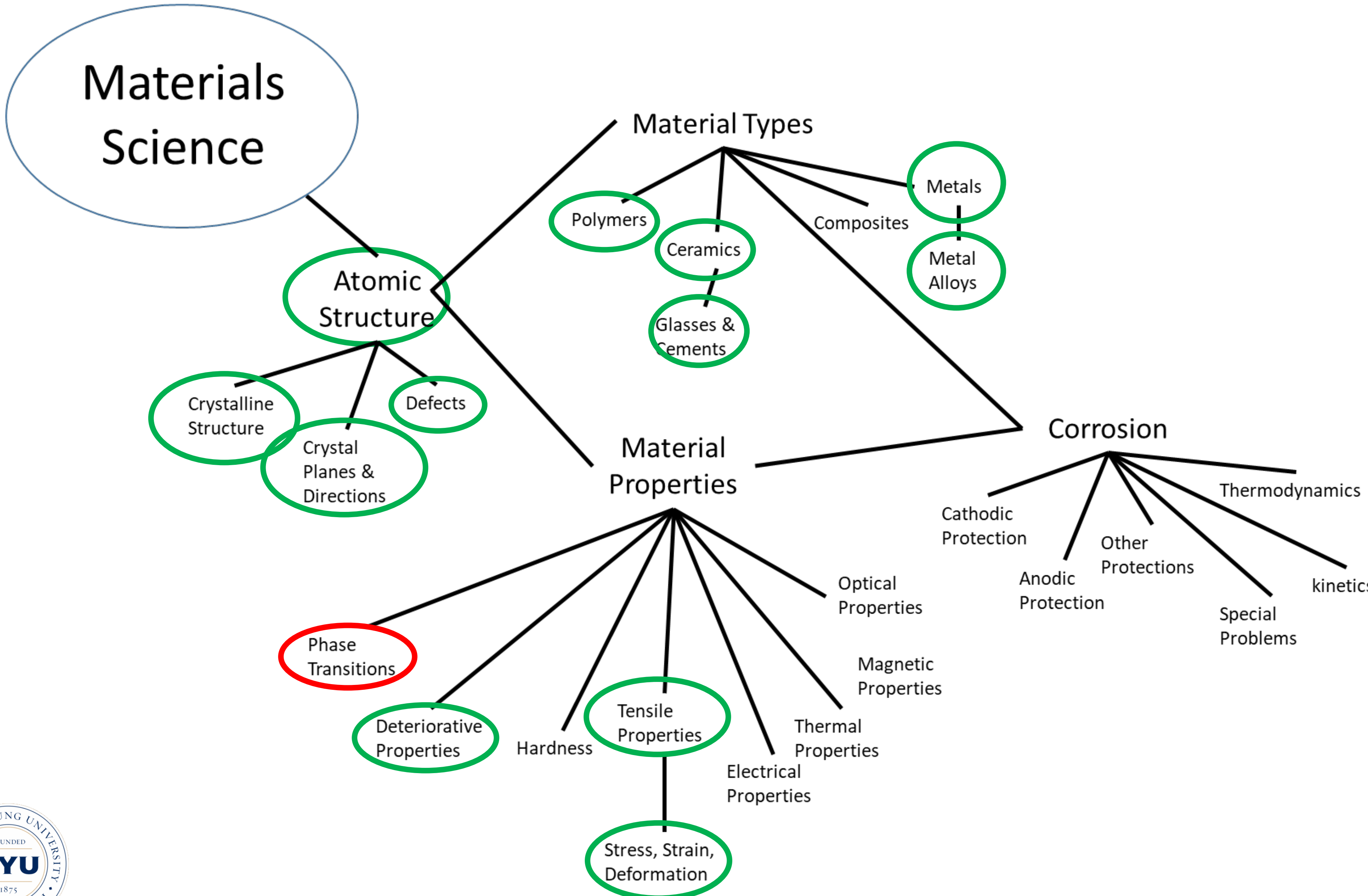
MATERIALS IN EXTREME ENVIRONMENTS

Covering the behavior of materials under extreme temperatures, radiation, corrosion, and other environments.

MON/WED/FRI

2:00 PM
CB 384

Materials Roadmap



Phase Change Timing?

https://www.youtube.com/watch?v=HLWOLVmkmKo

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)

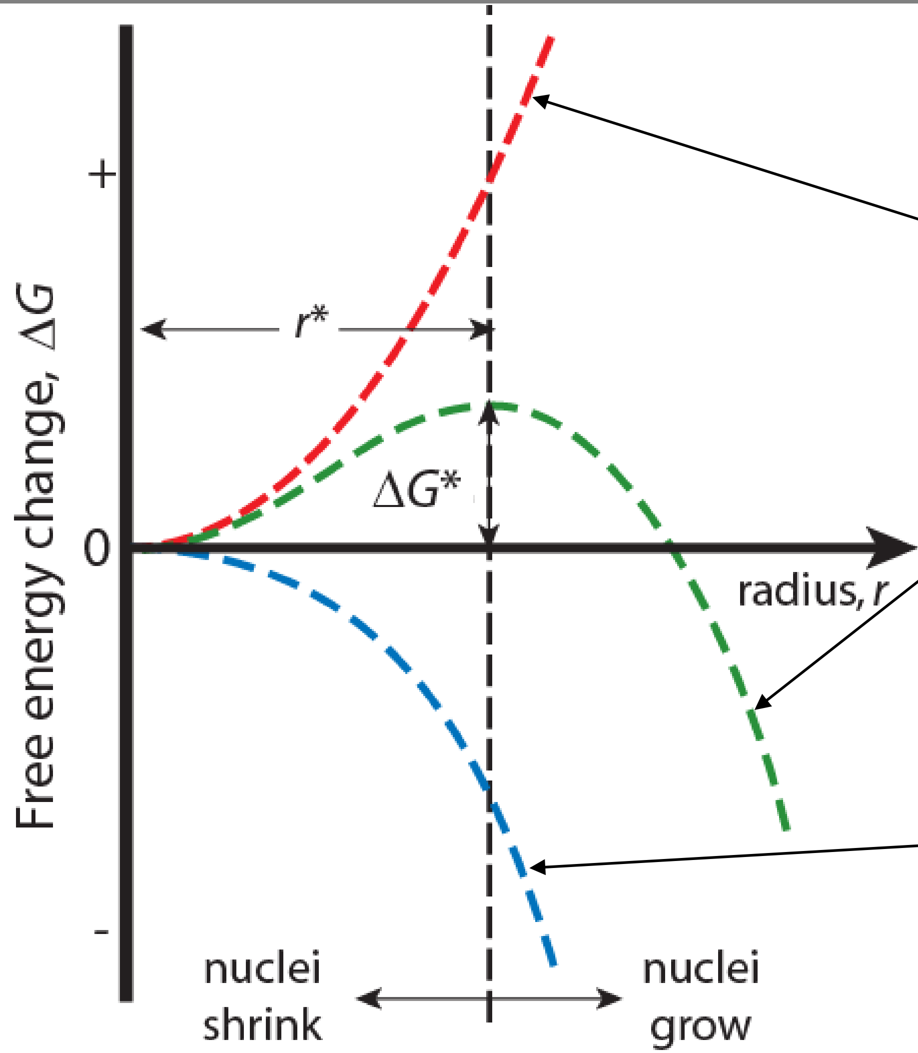
Small supercooling → slow nucleation rate - few nuclei - large crystals

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)

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

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

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

Adapted from Fig. 10.2(b), *Callister & Rethwisch 10e.*

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

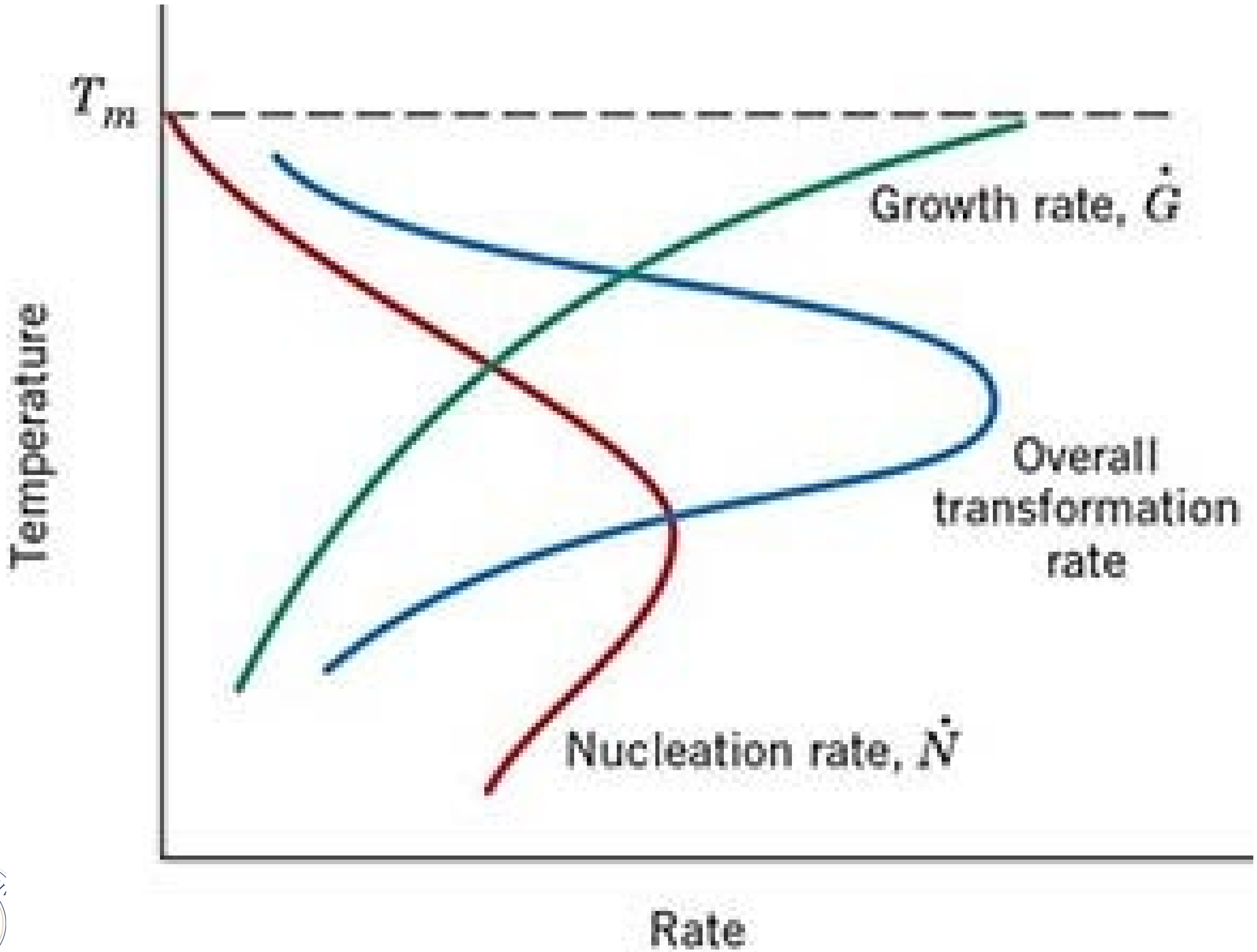
$\Delta T = T_m - T$ = supercooling

Note: ΔH_f and γ are weakly dependent on ΔT

$\therefore$ r^* decreases as ΔT increases

For typical ΔT r^* ~ 10 nm

Transformation Rate Mechanics



Rate of Phase Transformation

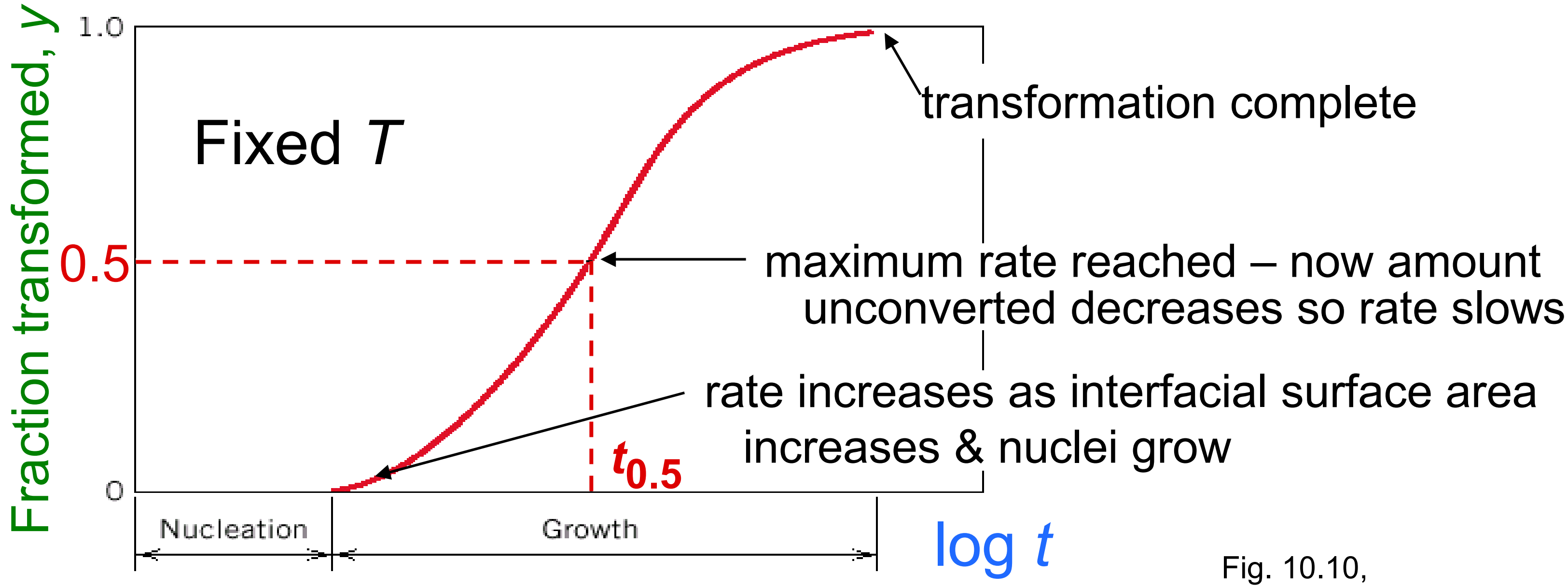


Fig. 10.10, *Callister & Rethwisch 10e.*

Avrami equation => $y = 1 - \exp(-kt^n)$

fraction transformed (y)

time (t)

– *k* & *n* are transformation specific parameters

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

Temperature Dependence of Transformation Rate

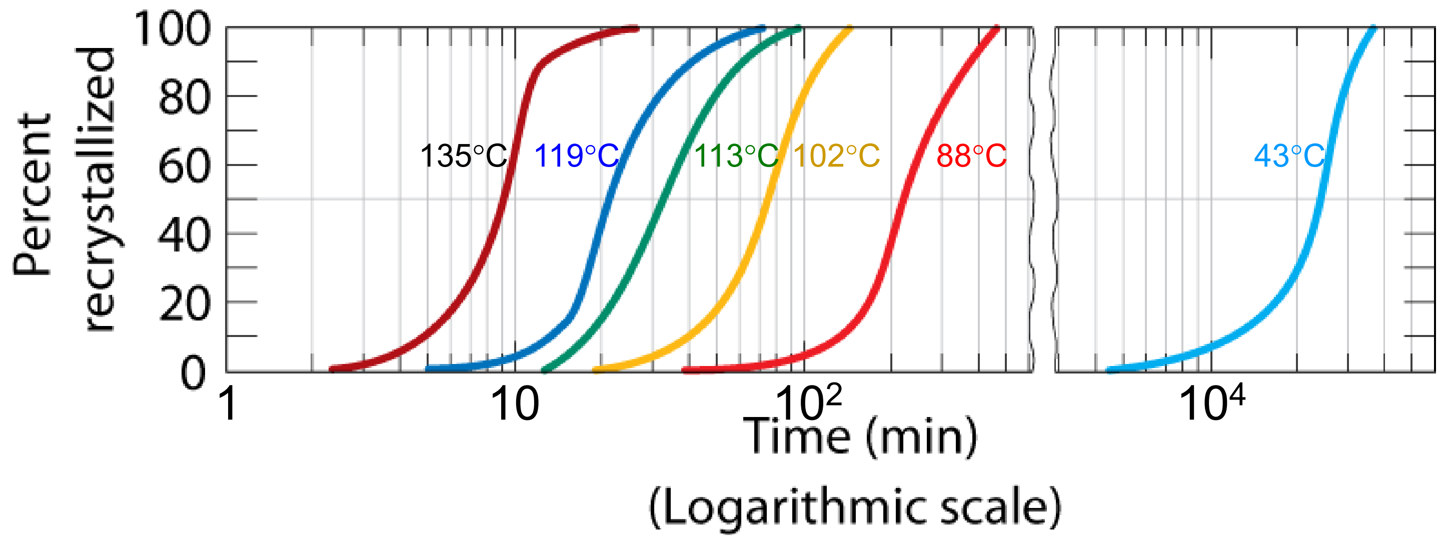


Fig. 10.11, *Callister & Rethwisch 10e.* (Reprinted with permission from *Metallurgical Transactions*, Vol. 188, 1950, a publication of The Metallurgical Society of AIME, Warrendale, PA. Adapted from B. F. Decker and D. Harker, "Recrystallization in Rolled Copper," Trans. AIME, 188, 1950, p. 888.)

- 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):
- For transf. to occur, must cool to below 727° C (i.e., must “undercool”)

$\gamma \Rightarrow \alpha + Fe_3C$

0.76 wt% C

0.022 wt% C

6.7 wt% C

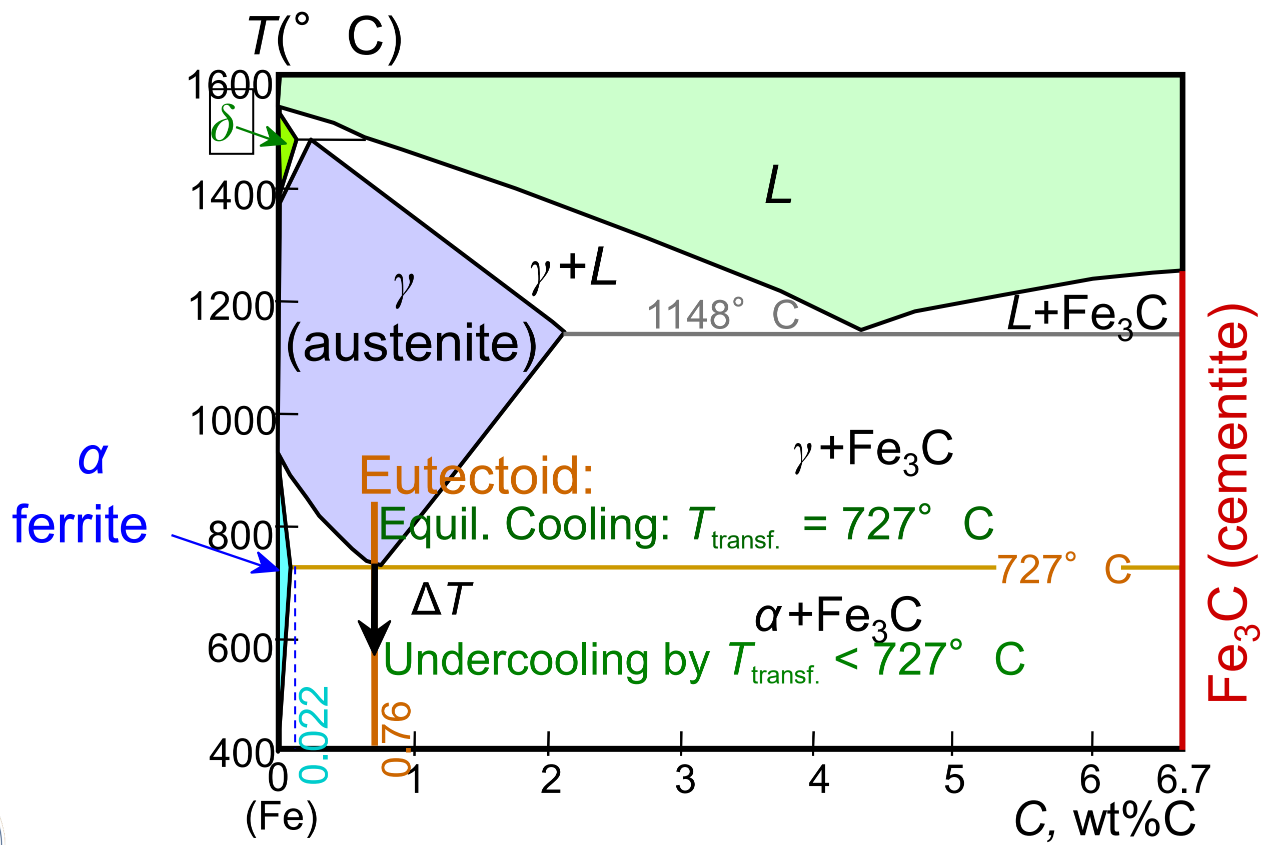
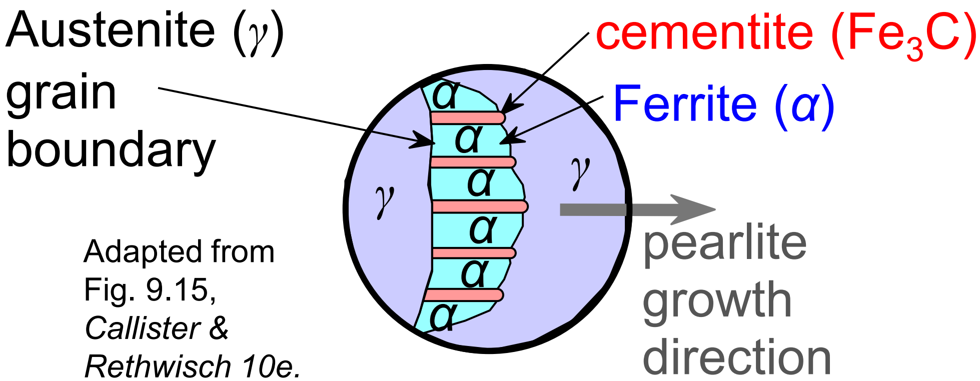


Fig. 9.24, Callister & Rethwisch 10e.
[Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

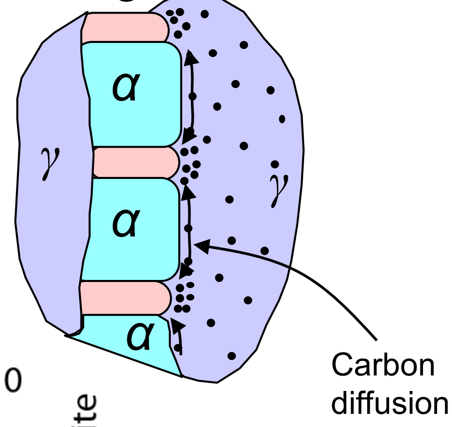
The Fe-Fe_3C Eutectoid Transformation

- Transformation of austenite to pearlite:

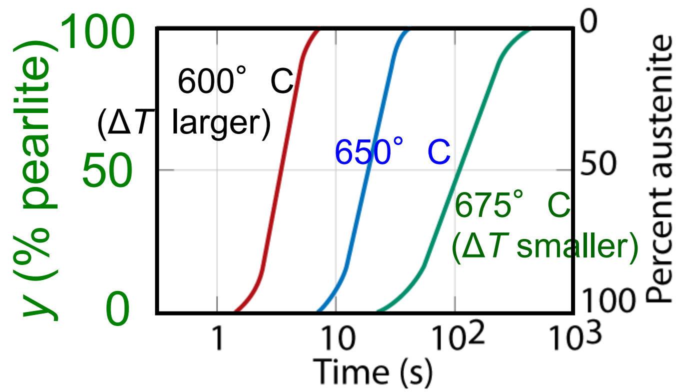


Adapted from Fig. 9.15, *Callister & Rethwisch 10e.*

Diffusion of C during transformation



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



Adapted from Fig. 10.12, *Callister & Rethwisch 10e.*

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 675ºC.

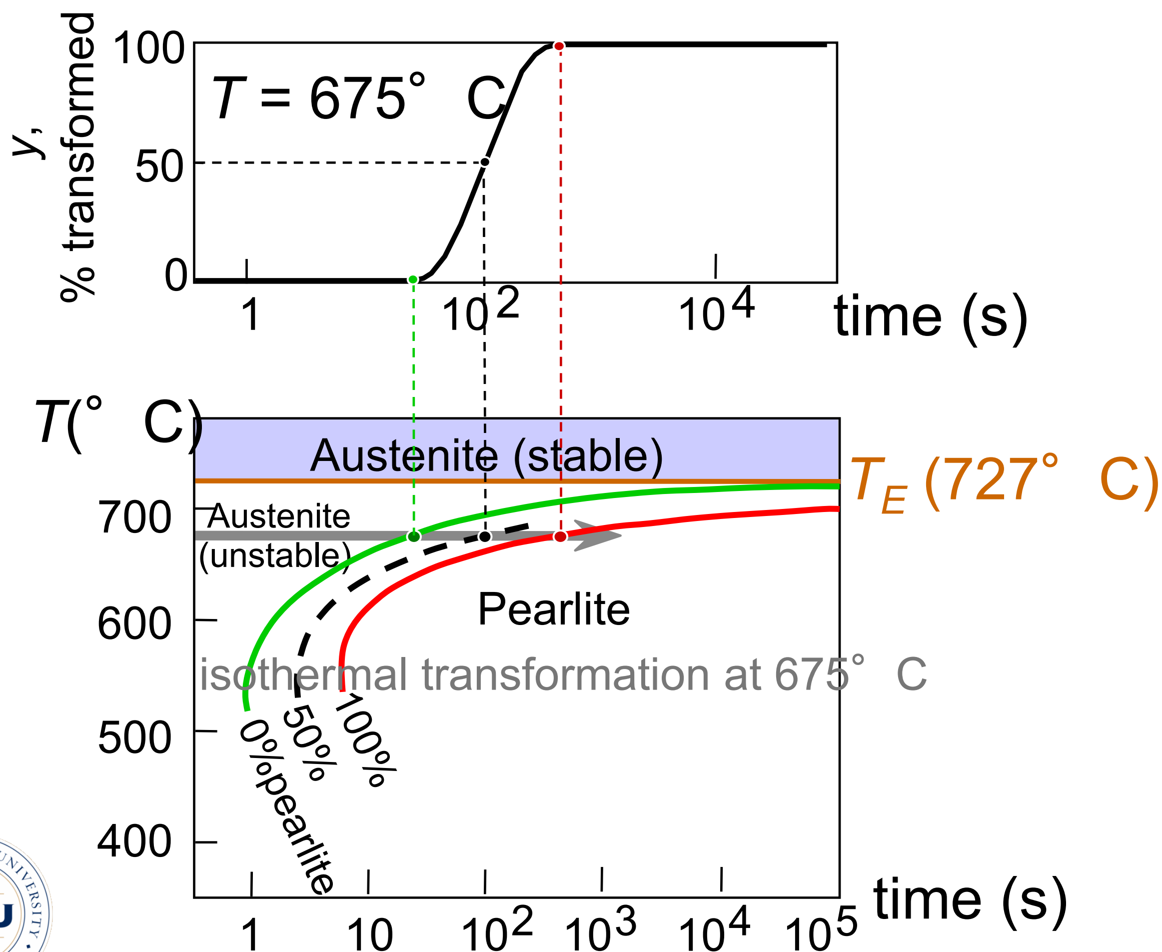


Fig. 10.13, *Callister & Rethwisch 10e.* [Adapted from H. Boyer (Editor), Atlas of Isothermal Transformation and Cooling Transformation Diagrams, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

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)

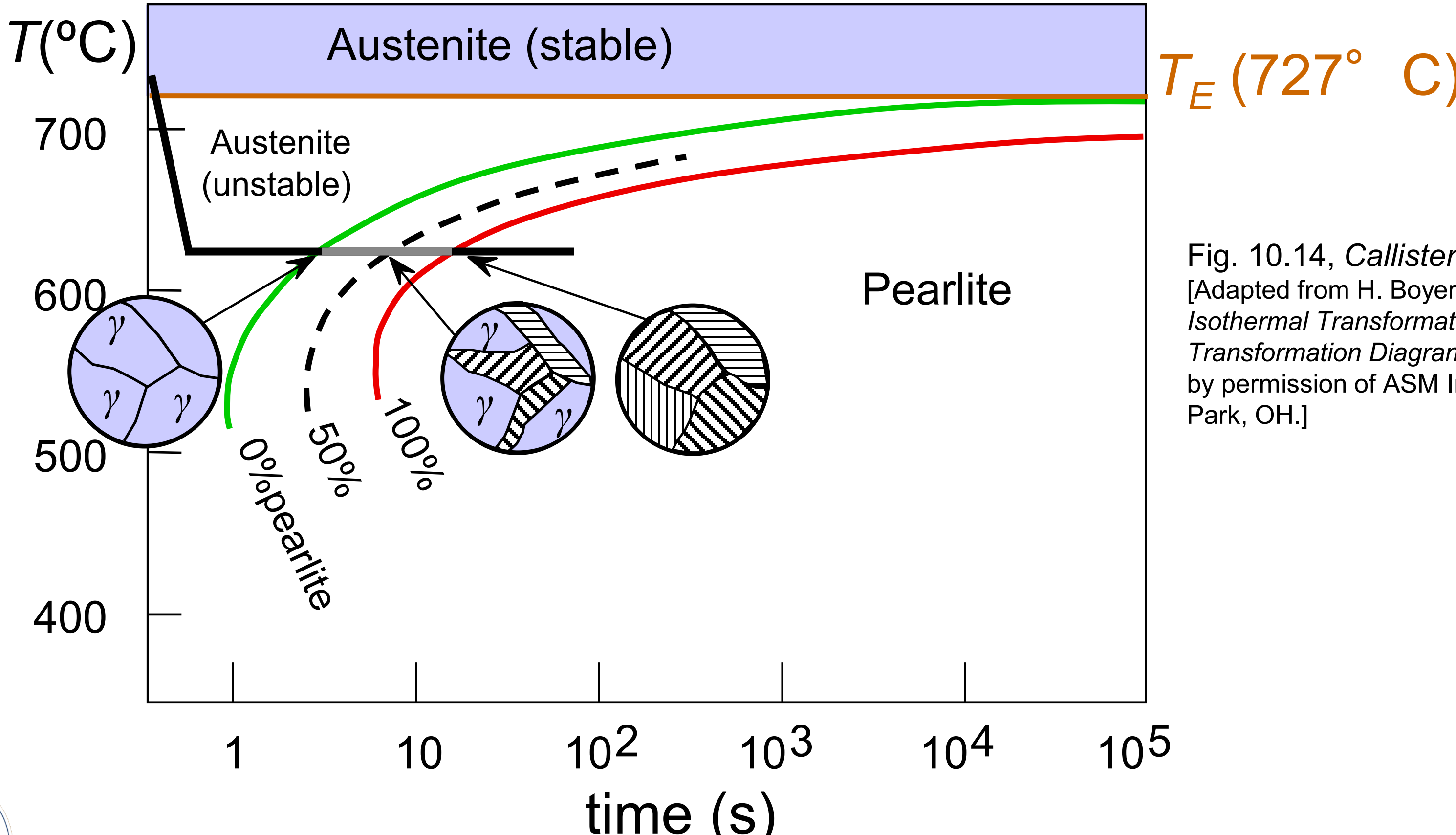


Fig. 10.14, *Callister & Rethwisch 10e.* [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Transformations Involving Noneutectoid Compositions

Consider C_0 = 1.13 wt% C

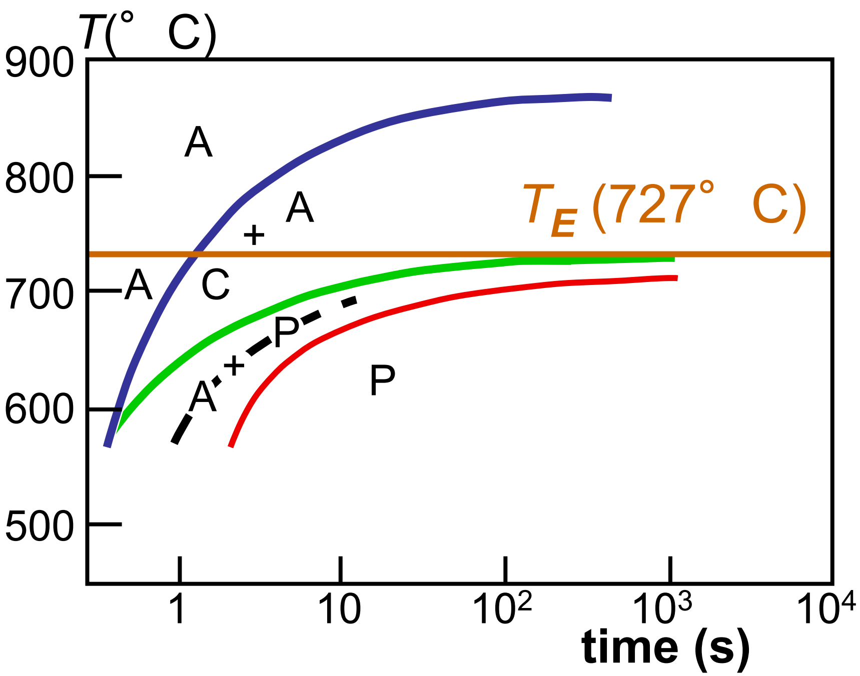


Fig. 10.16, *Callister & Rethwisch 10e.*
[Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

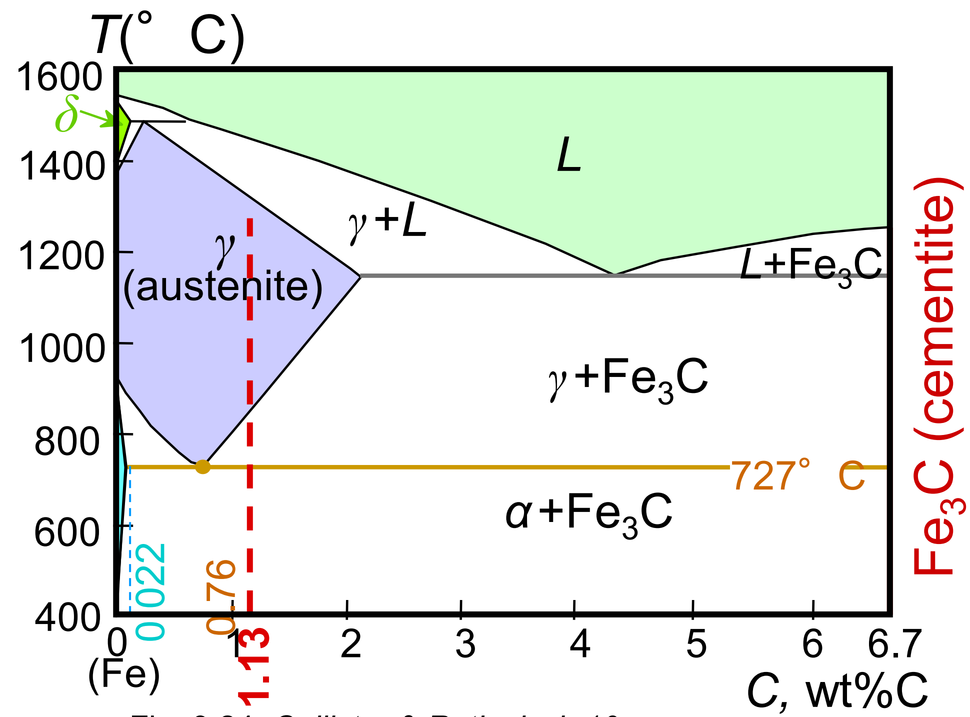
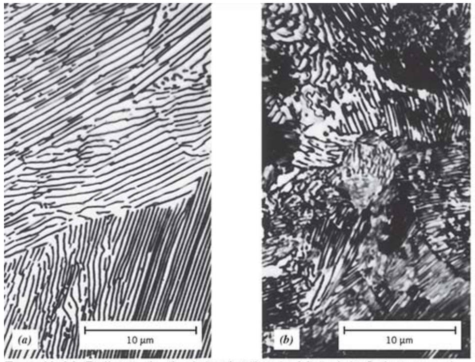


Fig. 9.24, *Callister & Rethwisch 10e.*
[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

Hypereutectoid composition – proeutectoid cementite

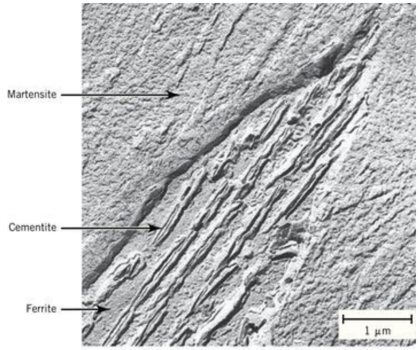
Steel Microstructures

- Pearlite – fine and course



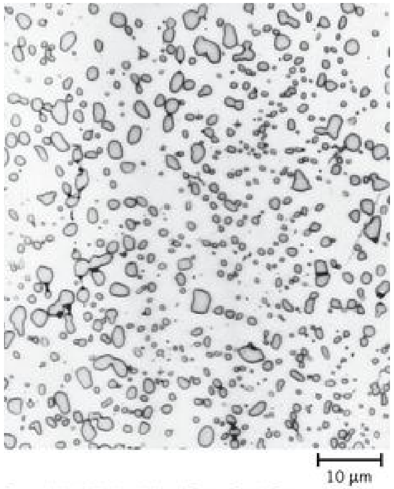
From K. M. Ralls et al., *An Introduction to Materials Science and Engineering*, p. 361. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

- Bainite



From *Metals Handbook*, Vol. 8, 8th edition, *Metallography, Structures and Phase Diagrams*, 1973. Reproduced by permission of ASM International, Materials Park, OH.

- Spherodite



Copyright 1971 by United States Steel Corporation.

- Martensite

Photomicrograph courtesy of United States Steel Corporation.

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

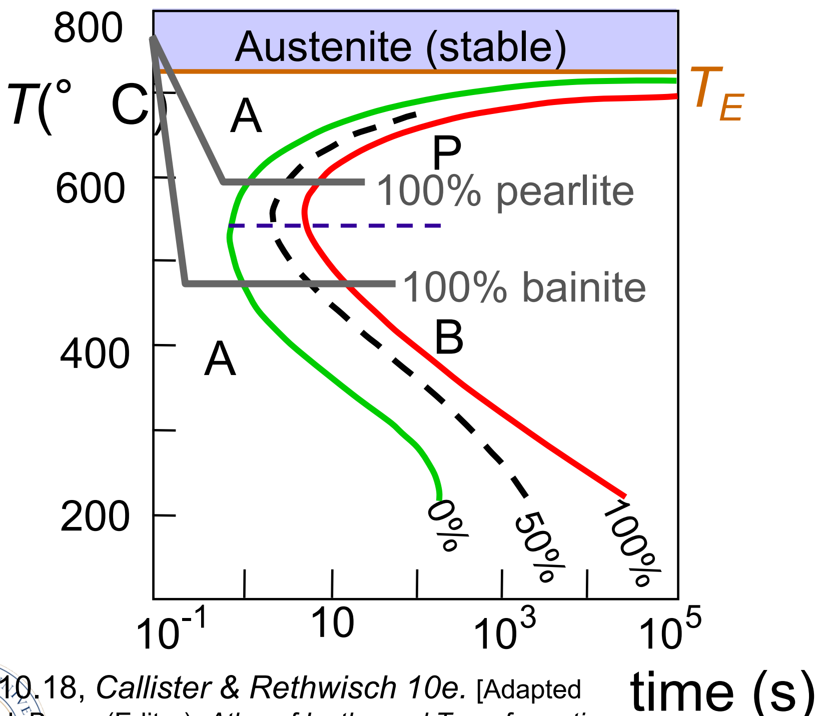


Fig. 10.18, *Callister & Rethwisch 10e.* [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

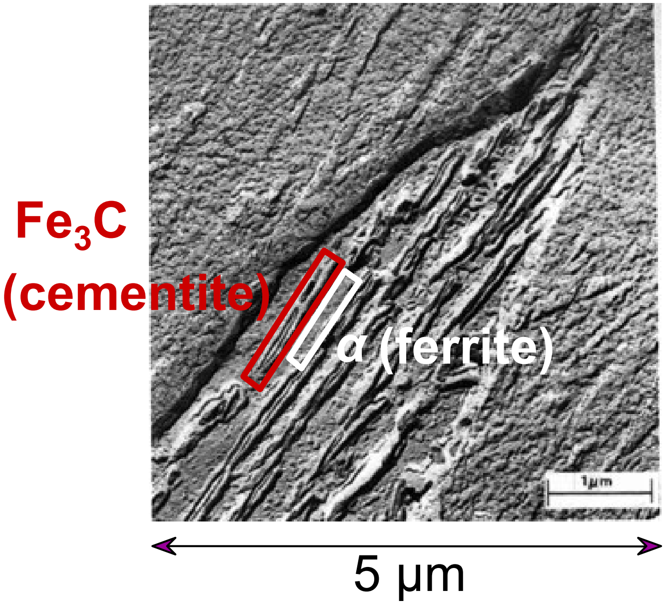


Fig. 10.17, *Callister & Rethwisch 10e.* (From *Metals Handbook*, Vol. 8, 8th edition, *Metallography, Structures and Phase Diagrams*, 1973. Reproduced by permission of ASM International, Materials Park, OH.)

Spheroidite: Another Microstructure for the $Fe\text{-}Fe_3C$ 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

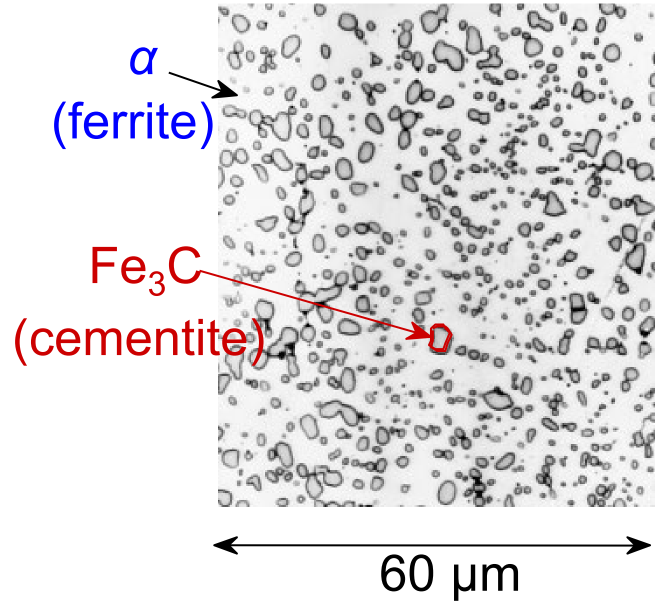
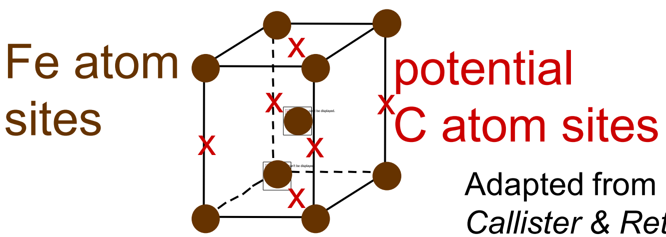


Fig. 10.19, *Callister & Rethwisch 10e.*

Martensite: A Nonequilibrium Transformation Product

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



Adapted from Fig. 10.21, *Callister & Rethwisch 10e.*

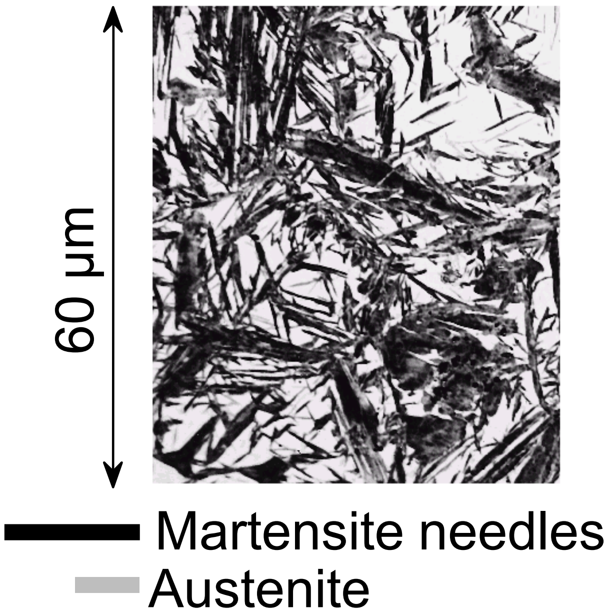
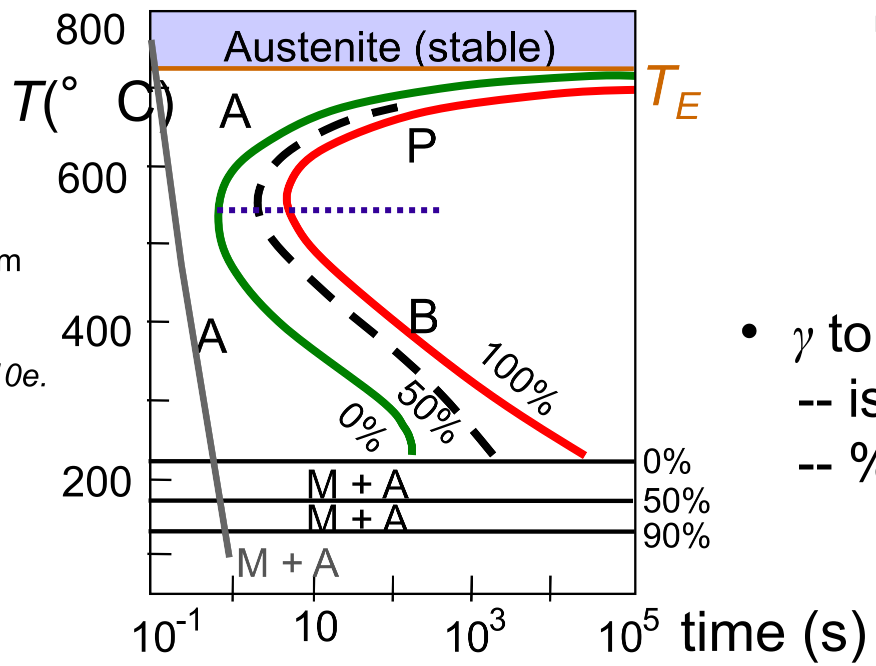


Fig. 10.21, *Callister & Rethwisch 10e.* (Courtesy United States Steel Corporation.)

- Isothermal Transf. Diagram



Adapted from Fig. 10.23, *Callister & Rethwisch 10e.*

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

Martensite Formation

$$\begin{tikzcd}[column sep=huge, row sep=large]
\gamma\ \text{(FCC)} \arrow[rr, "\text{slow cooling}"] \arrow[d, "\text{quench}"] & & \alpha\ \text{(BCC)} + Fe_3C \\
\boxed{\text{M (BCT)}} \arrow[urr, "\text{tempering}"'] & &
\end{tikzcd}$$

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

Continuous Cooling Transformation Diagrams

Conversion of isothermal transformation diagram to continuous cooling transformation diagram

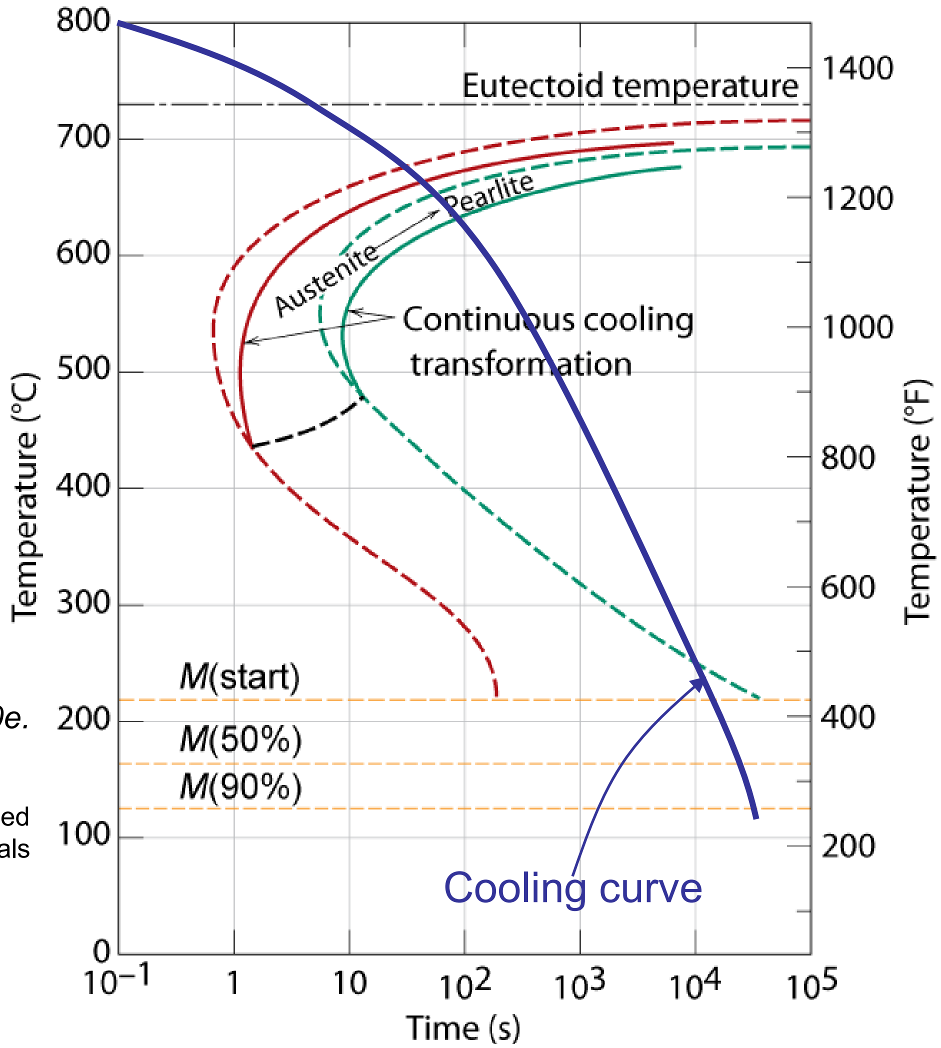


Fig. 10.26, *Callister & Rethwisch 10e.* [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

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

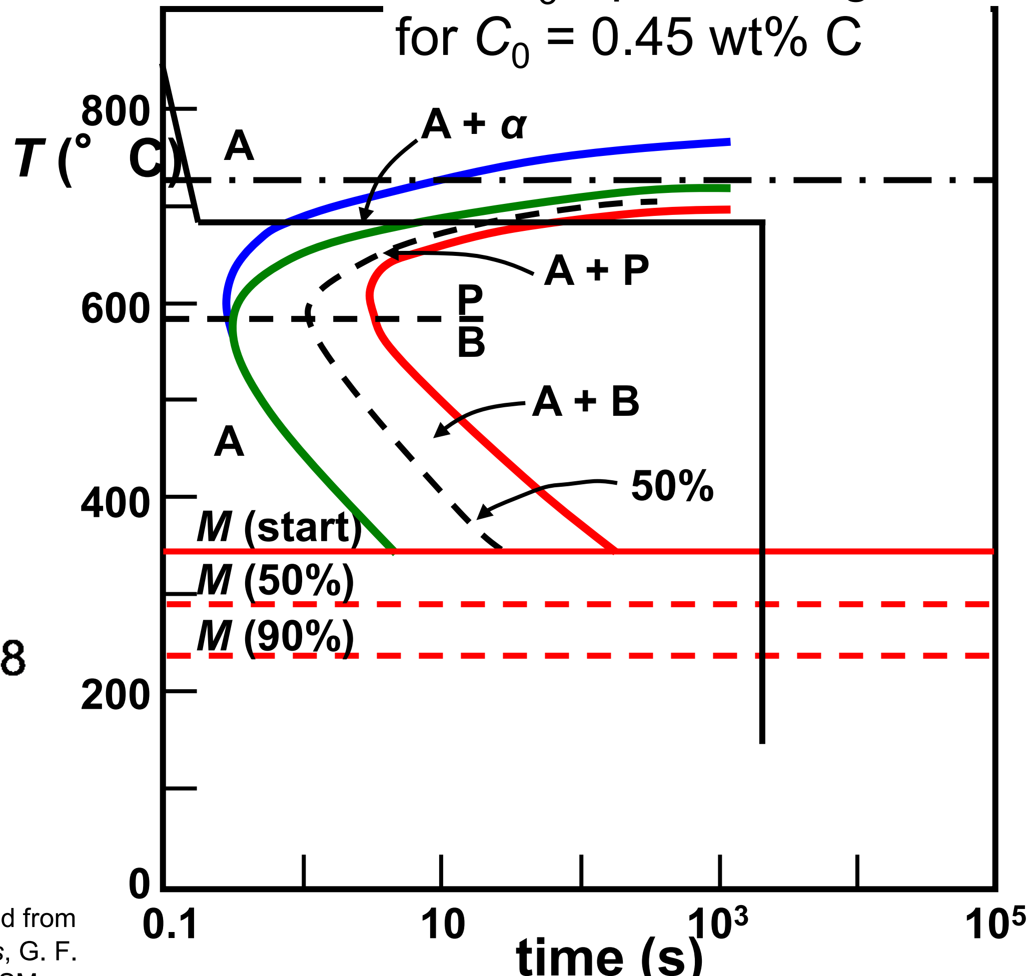


Figure 10.40, *Callister & Rethwisch 10e*. (Adapted from *Atlas of Time-Temperature Diagrams for Irons and Steels*, G. F. Vander Voort, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

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.

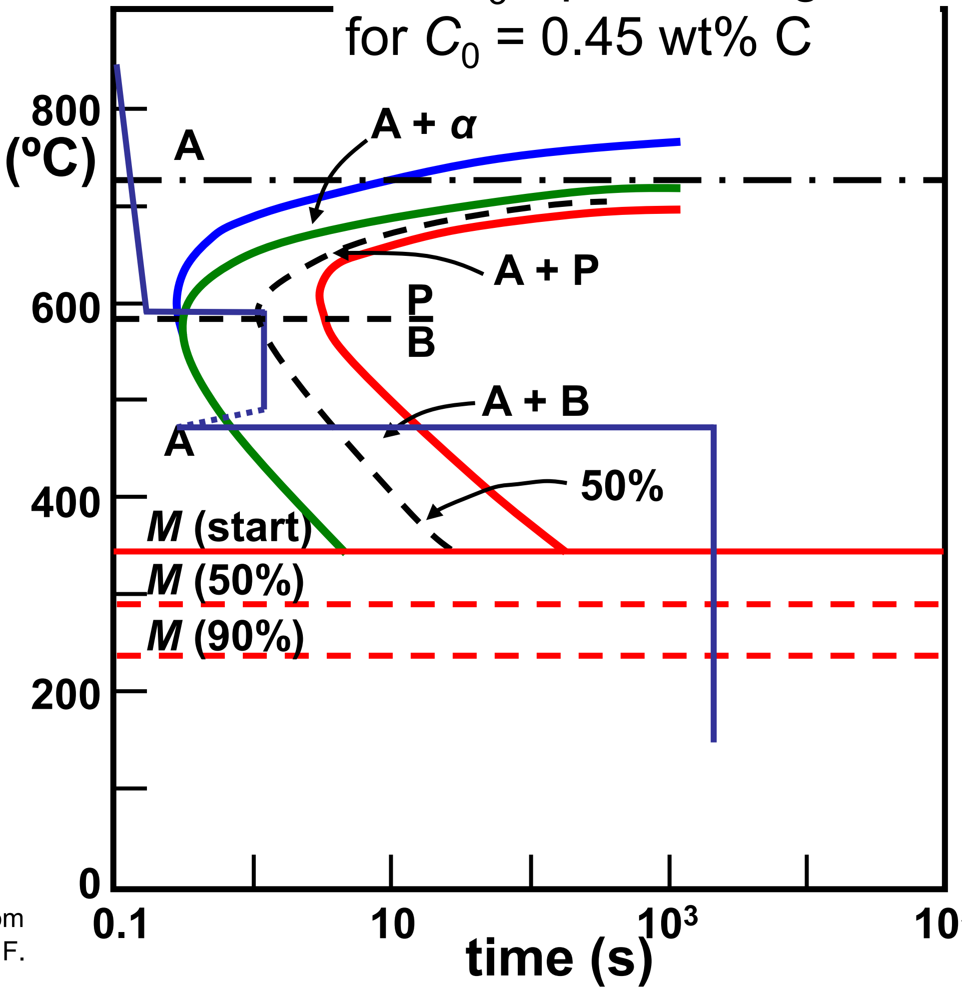


Figure 10.40, *Callister & Rethwisch 10e*. (Adapted from *Atlas of Time-Temperature Diagrams for Irons and Steels*, G. F. Vander Voort, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

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

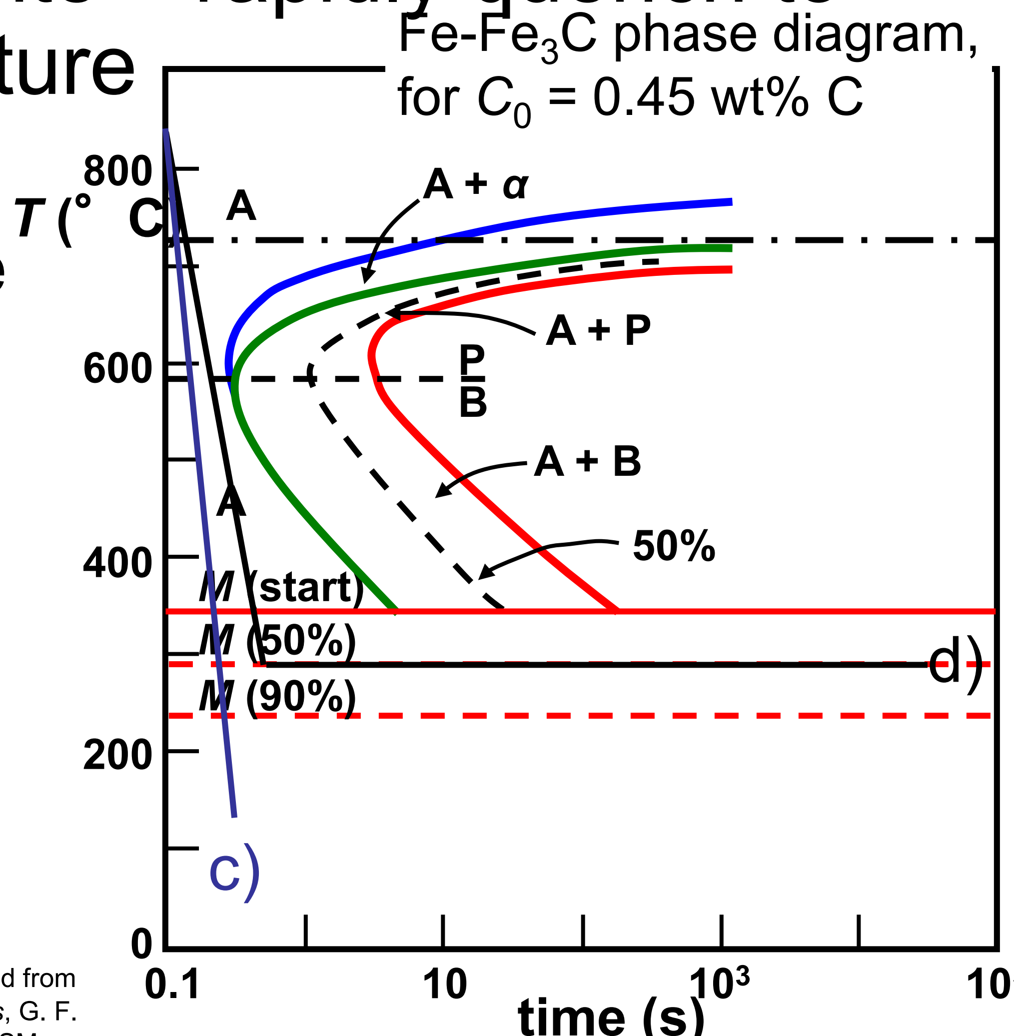


Figure 10.40, *Callister & Rethwisch 10e*. (Adapted from *Atlas of Time-Temperature Diagrams for Irons and Steels*, G. F. Vander Voort, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

Mechanical Props: Influence of C Content

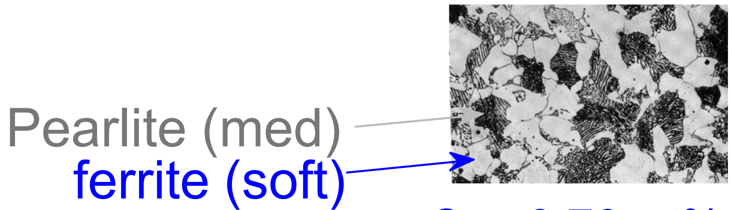
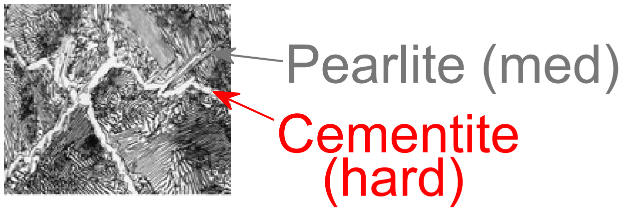


Fig. 9.30, *Callister & Rethwisch 10e.*
(Courtesy of Republic Steel Corporation.)

$C_0 < 0.76$ wt% C

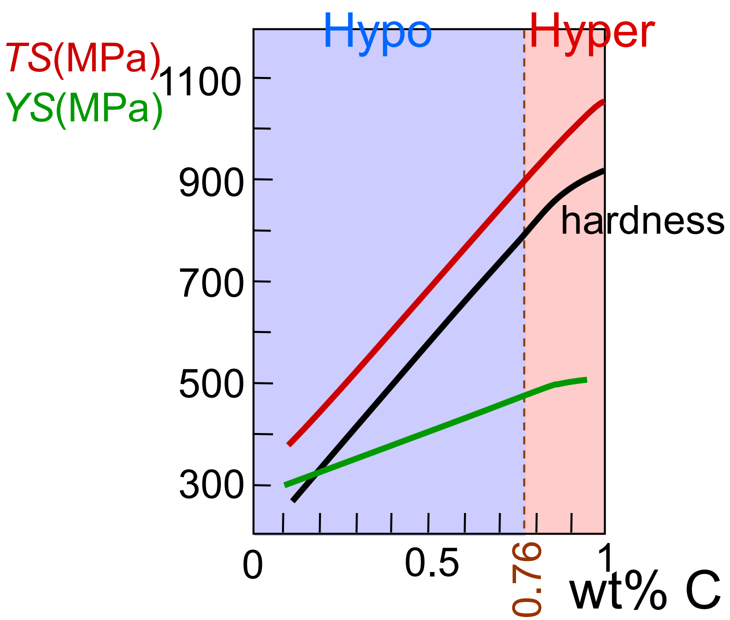
Hypoeutectoid



$C_0 > 0.76$ wt% C

Hypereutectoid

Fig. 9.33, *Callister & Rethwisch 10e.*
(Copyright 1971 by United States Steel Corporation.)



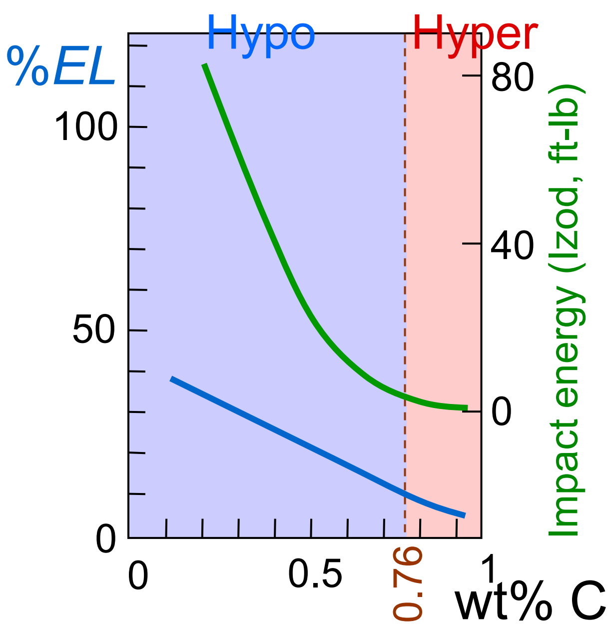
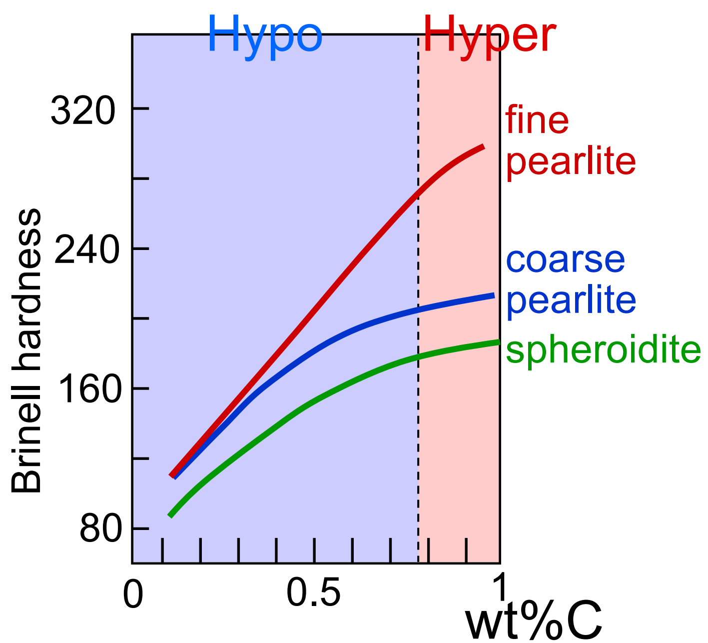


Fig. 10.30, *Callister & Rethwisch 10e.*
[Data taken from *Metals Handbook: Heat Treating*, Vol. 4, 9th edition, V. Masseria (Managing Editor), 1981. Reproduced by permission of ASM International, Materials Park, OH.]

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

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



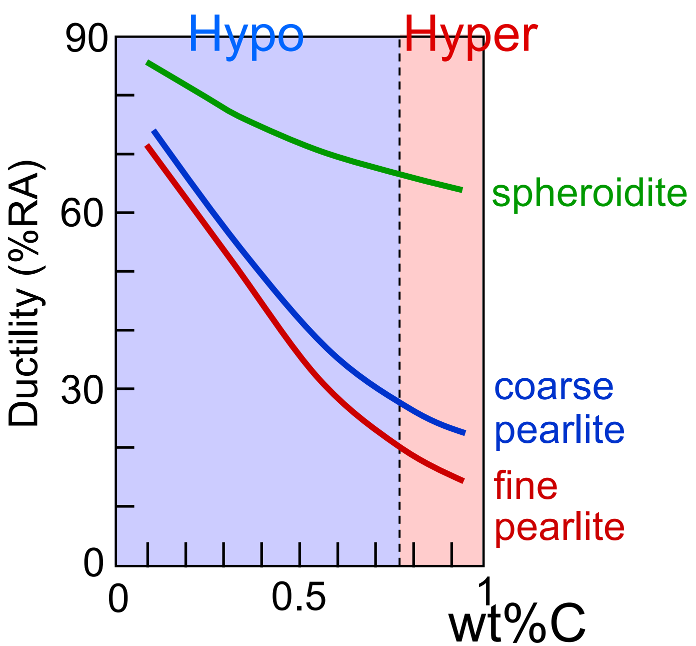


Fig. 10.31, *Callister & Rethwisch 10e.* [Data taken from *Metals Handbook: Heat Treating*, Vol. 4, 9th edition, V. Masseria (Managing Editor), 1981. Reproduced by permission of ASM International, Materials Park, OH.]

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

Mechanical Props: Fine Pearlite vs. Martensite

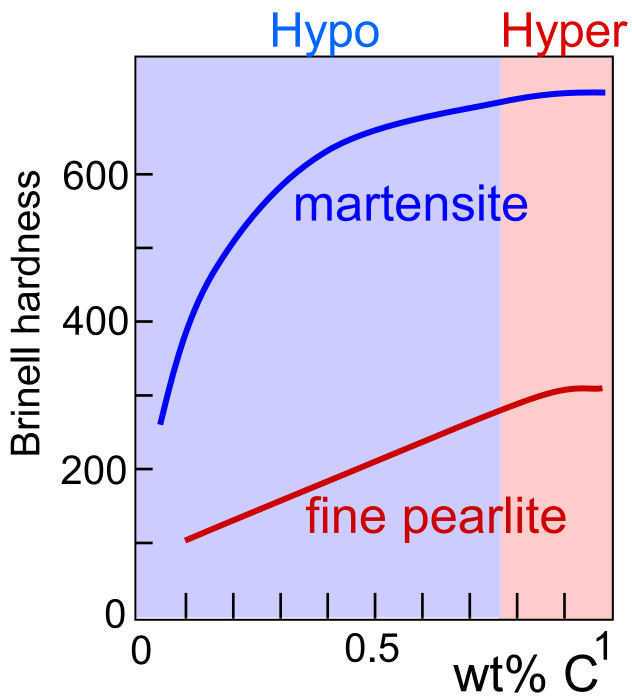


Fig. 10.33, *Callister & Rethwisch 10e.* (Adapted from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, 1939; and R. A. Grange, C. R. Hribal, and L. F. Porter, *Metall. Trans.* A, Vol. 8A. Reproduced by permission of ASM International, Materials Park, OH.)

- 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

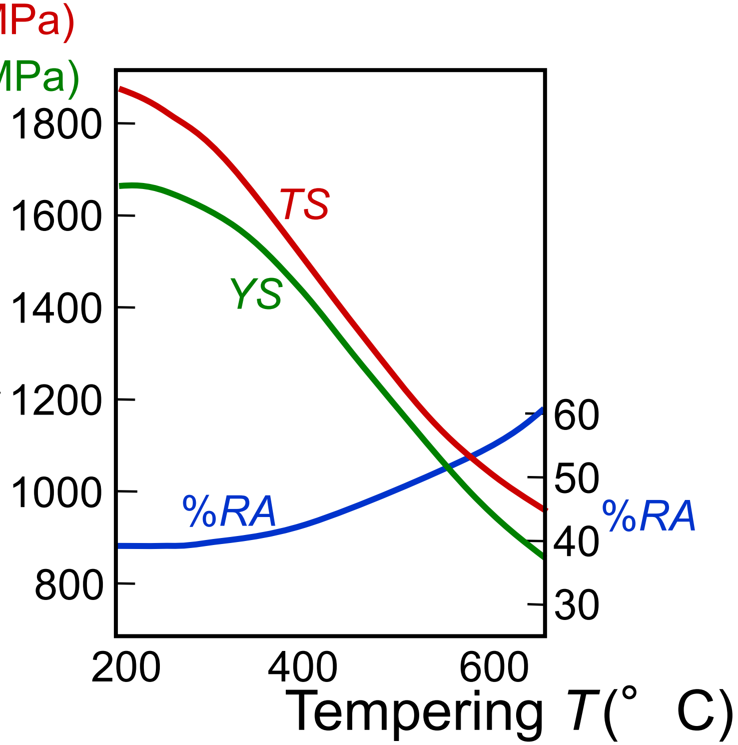


Fig. 10.35, *Callister & Rethwisch 10e.* (Adapted from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, 1939. Reproduced by permission of ASM International, Materials Park, OH.)

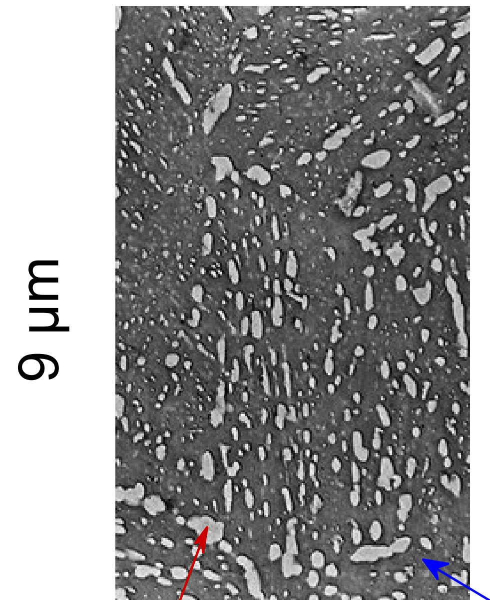


Figure 10.34, *Callister & Rethwisch 10e.* (Copyright 1971 by United States Steel Corporation.)

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

Summary of Possible Transformations

Adapted from Fig. 10.37, *Callister & Rethwisch 10e.*

Austenite (γ)

slow cool → **Pearlite** (α + Fe_3C layers + a proeutectoid phase)

moderate cool → **Bainite** (α + elong. Fe_3C particles)

rapid quench → **Martensite** (BCT phase diffusionless transformation)

reheat → **Tempered Martensite** (α + very fine Fe_3C particles)

Strength ↑ / Ductility ↓

Martensite
T Martensite
bainite
fine pearlite
coarse pearlite
spheroidite

General Trends