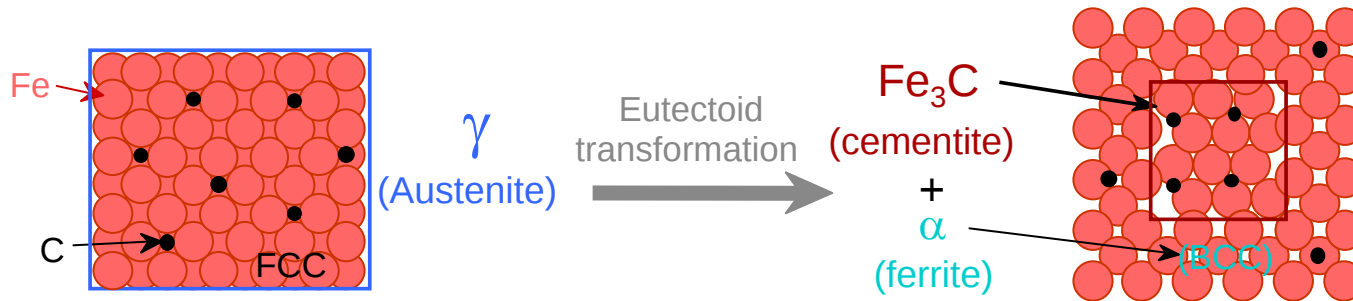


Chapter 10:

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 $\rightarrow$ slow nucleation rate - few nuclei - large crystals

Large supercooling $\rightarrow$ rapid nucleation rate - many nuclei - small crystals

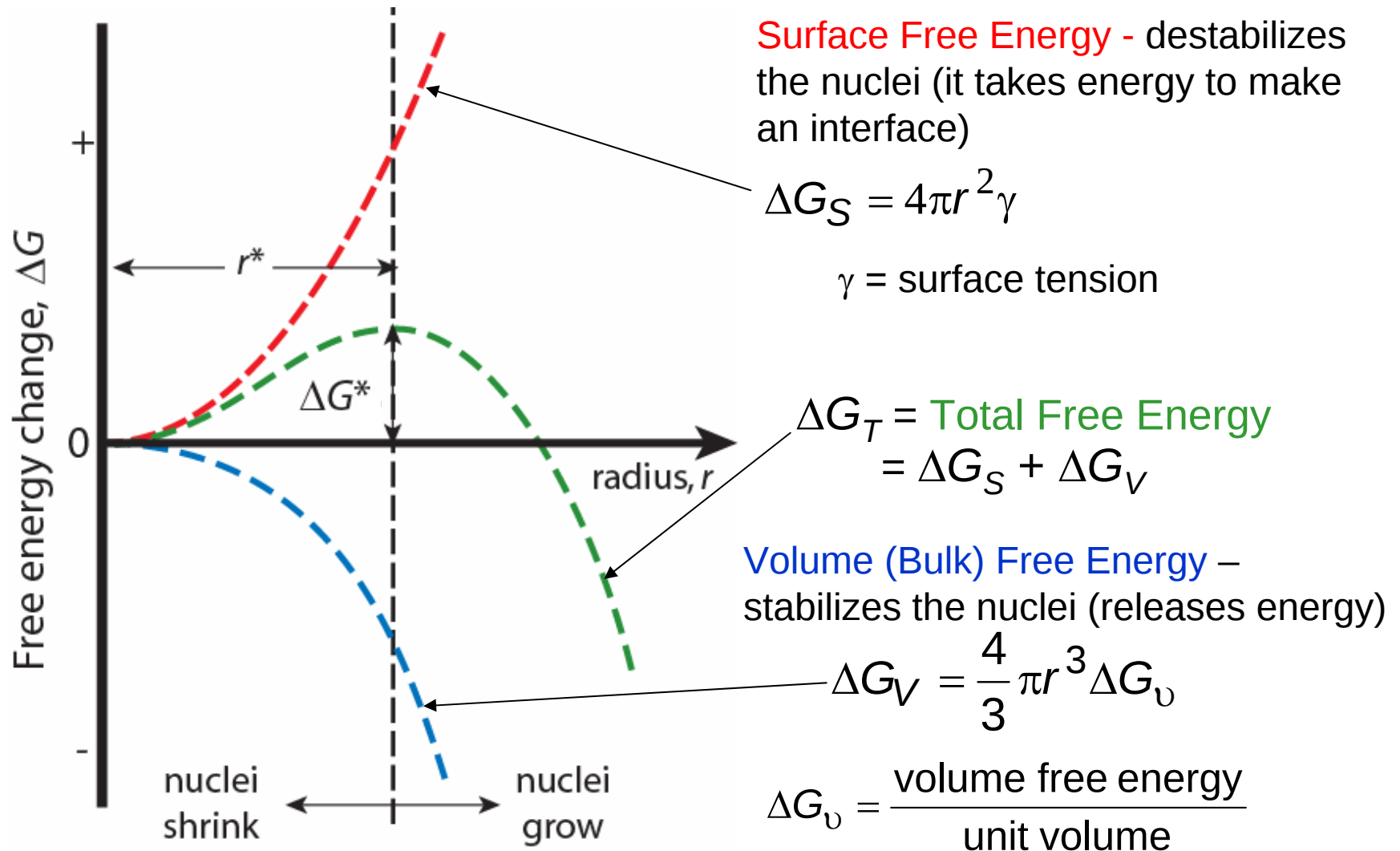


Solidification: Nucleation Types

- **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



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

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 $r^* \sim 10$ nm



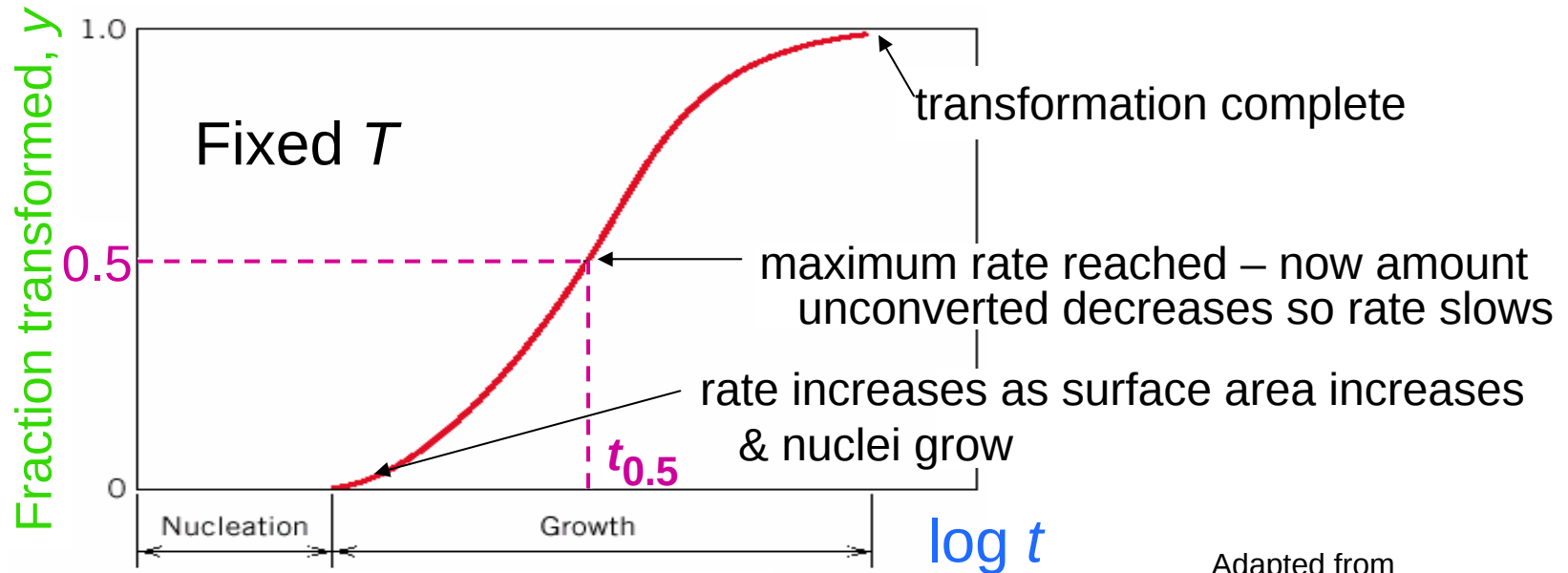
Rate of Phase Transformations

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



Adapted from
Fig. 10.10,
Callister &
Rethwisch 8e.

$$\text{Avrami equation} \Rightarrow y = 1 - \exp(-kt^n)$$

fraction transformed time

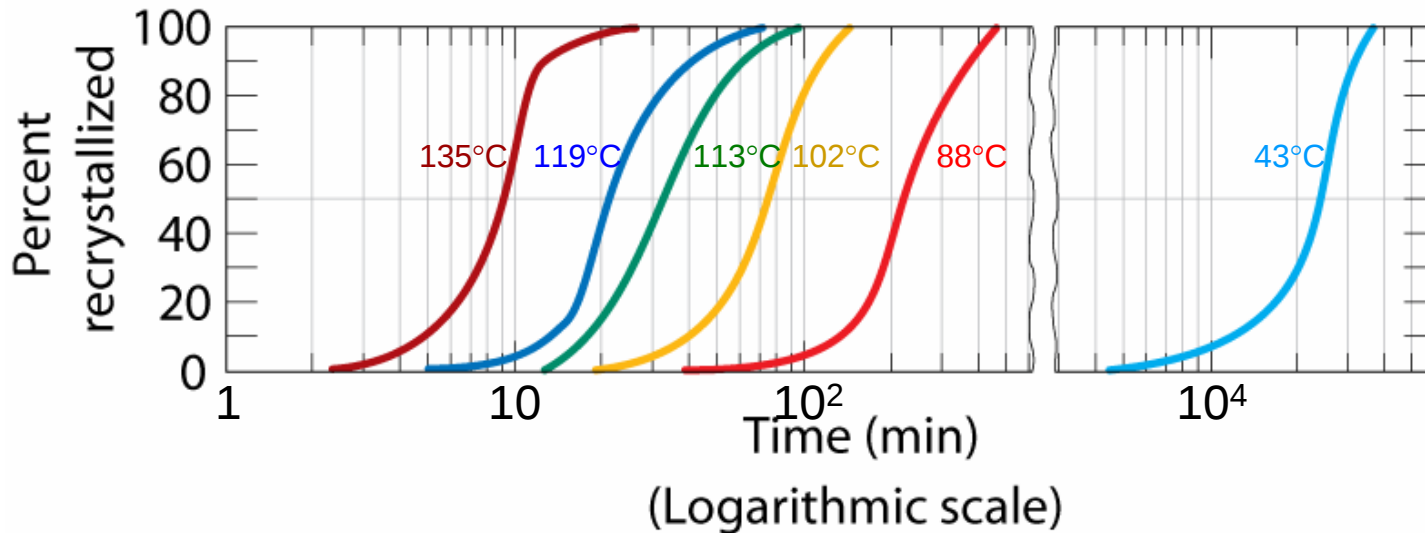
– k & n are transformation specific parameters

By convention

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



Temperature Dependence of Transformation Rate



Adapted from Fig. 10.11, *Callister & Rethwisch 8e*. (Fig. 10.11 adapted from B.F. Decker and D. Harker, "Recrystallization in Rolled Copper", *Trans AIME*, **188**, 1950, p. 888.)

- For the recrystallization of Cu, since

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

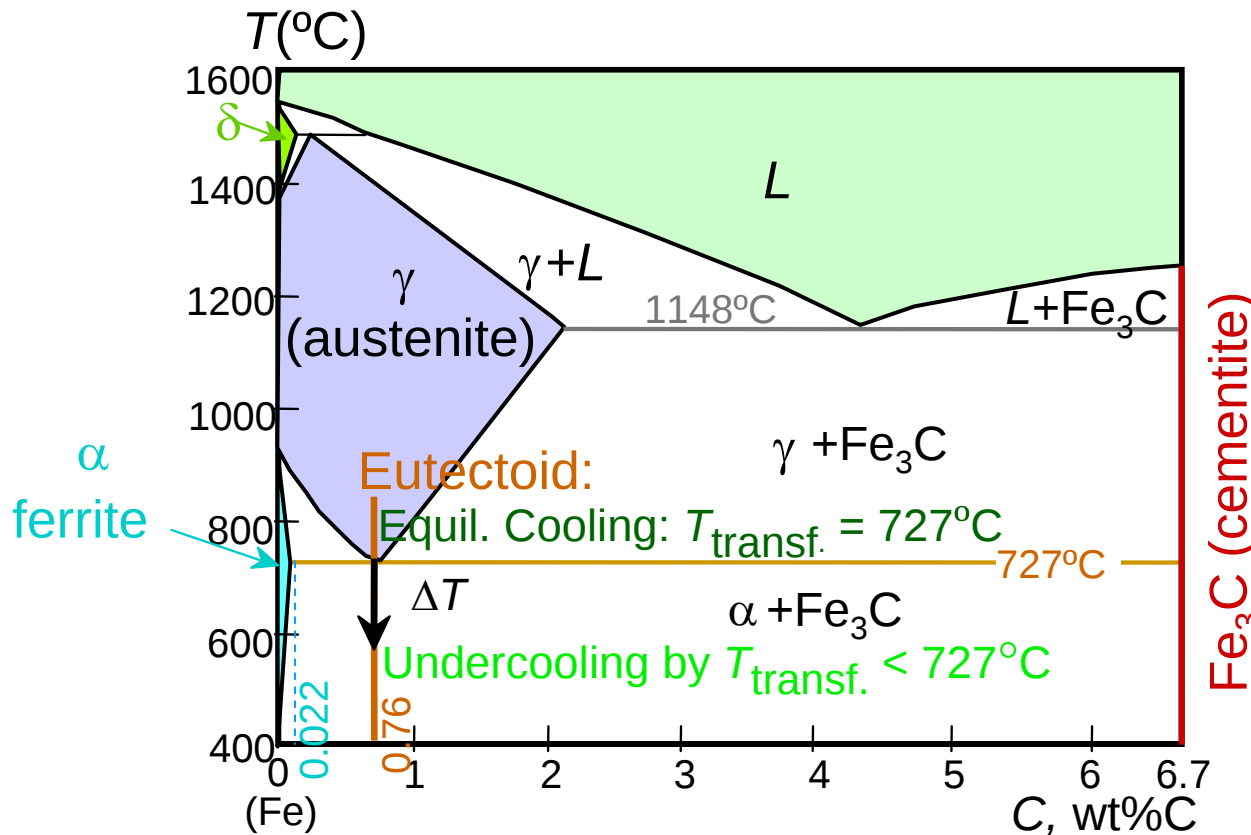
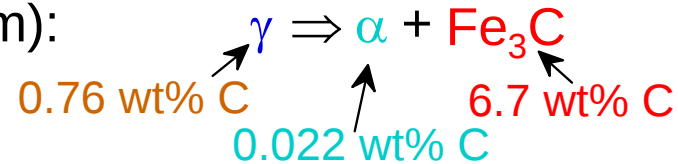
rate increases with increasing temperature

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



Transformations & Undercooling

- Eutectoid transf. (Fe-Fe₃C system):
- For transf. to occur, must cool to below 727°C (i.e., must “undercool”)

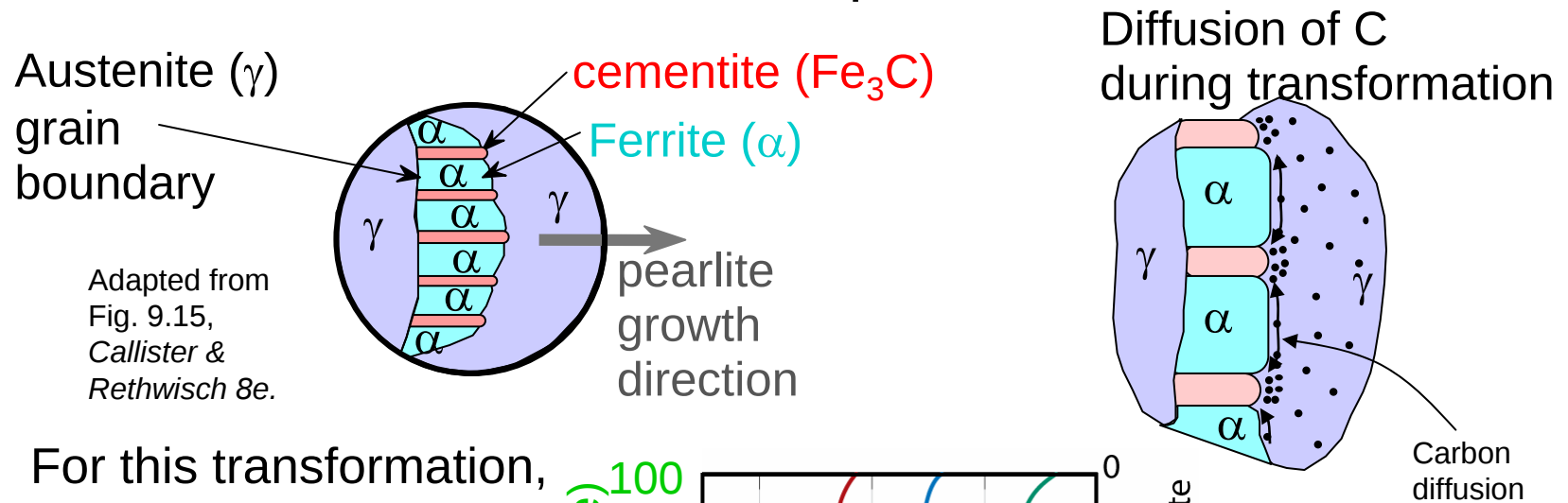


Adapted from Fig. 9.24, Callister & Rethwisch 8e. (Fig. 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)

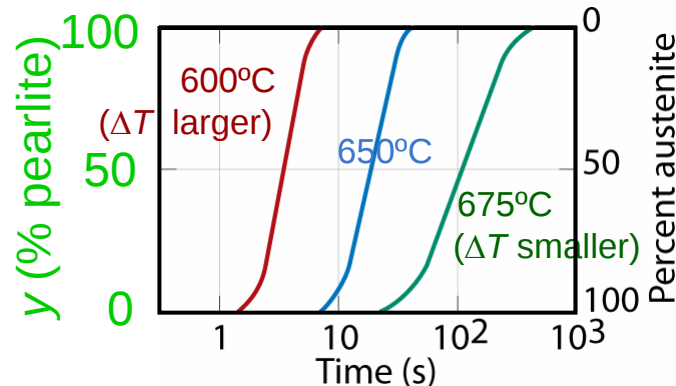


The Fe-Fe₃C Eutectoid Transformation

- Transformation of austenite to pearlite:



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



Adapted from Fig. 10.12, Callister & Rethwisch 8e.

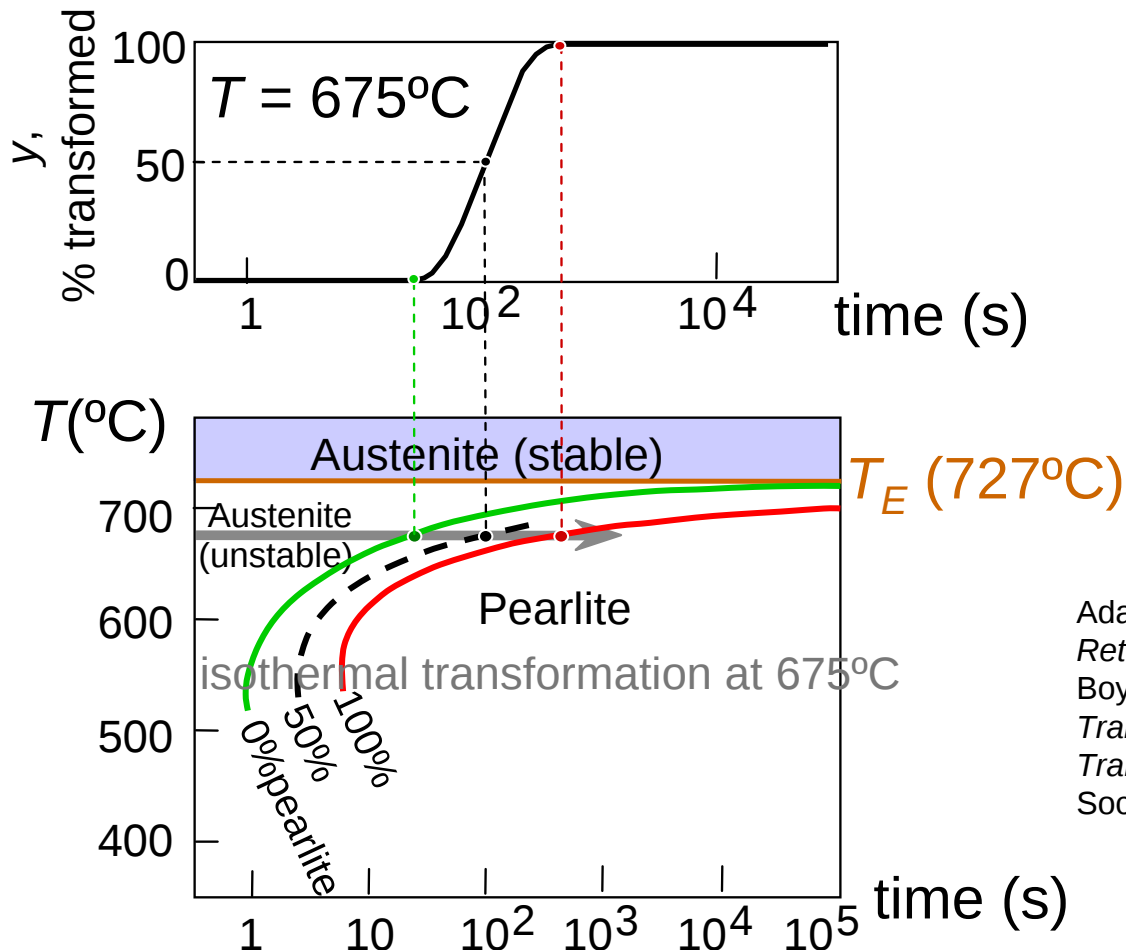
Coarse pearlite → formed at higher temperatures – relatively soft

Fine pearlite → formed at lower temperatures – relatively hard

Generation of Isothermal Transformation Diagrams

Consider:

- The Fe-Fe₃C system, for $C_0 = 0.76$ wt% C
- A transformation temperature of 675°C.

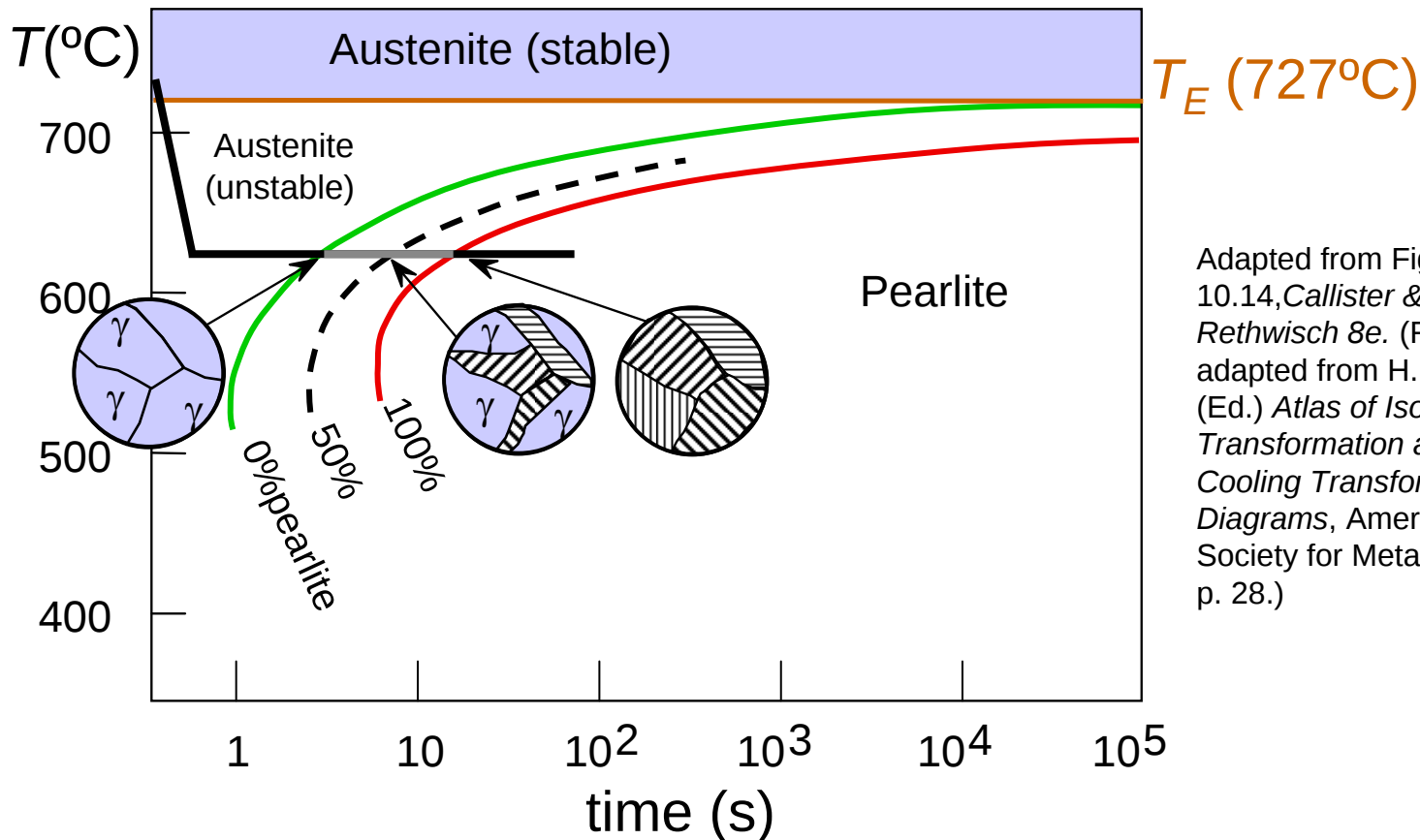


Adapted from Fig. 10.13, Callister & Rethwisch 8e. (Fig. 10.13 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1977, p. 369.)



Austenite-to-Pearlite Isothermal Transformation

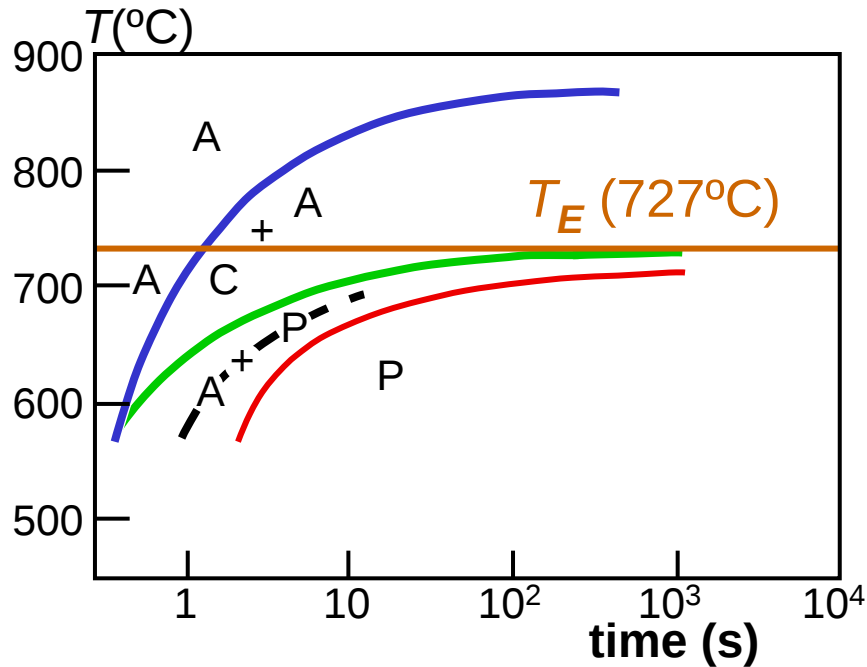
- Eutectoid composition, $C_0 = 0.76 \text{ wt\% C}$
- Begin at $T > 727^\circ\text{C}$
- Rapidly cool to 625°C
- Hold T (625°C) constant (isothermal treatment)



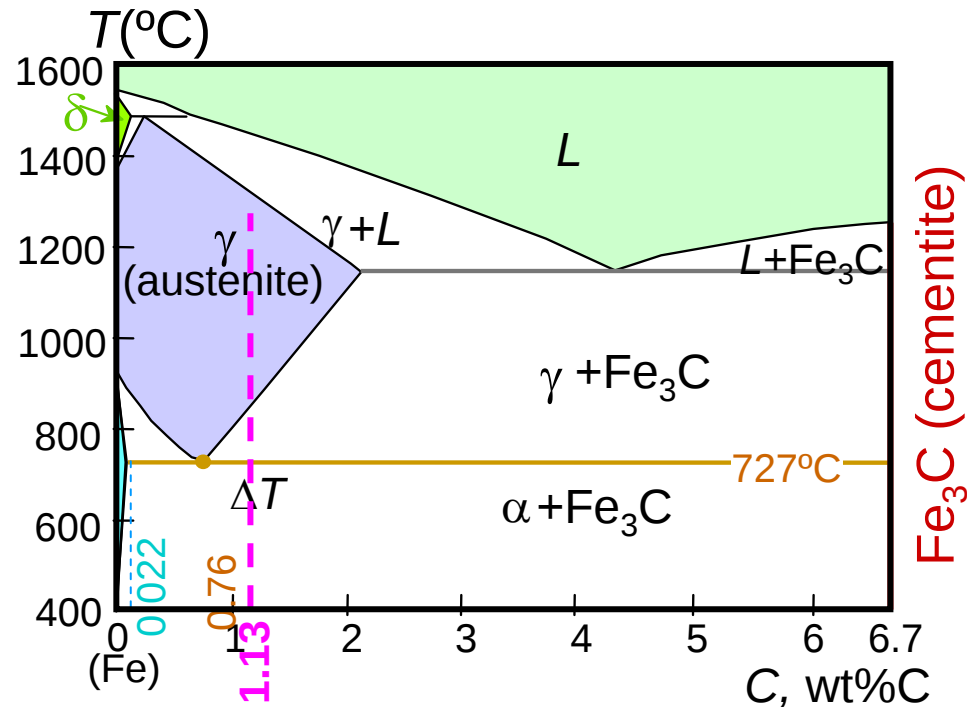
Adapted from Fig. 10.14, Callister & Rethwisch 8e. (Fig. 10.14 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1997, p. 28.)

Transformations Involving Noneutectoid Compositions

Consider $C_0 = 1.13 \text{ wt\% C}$



Adapted from Fig. 10.16,
Callister & Rethwisch 8e.



Adapted from Fig. 9.24,
Callister & Rethwisch 8e.

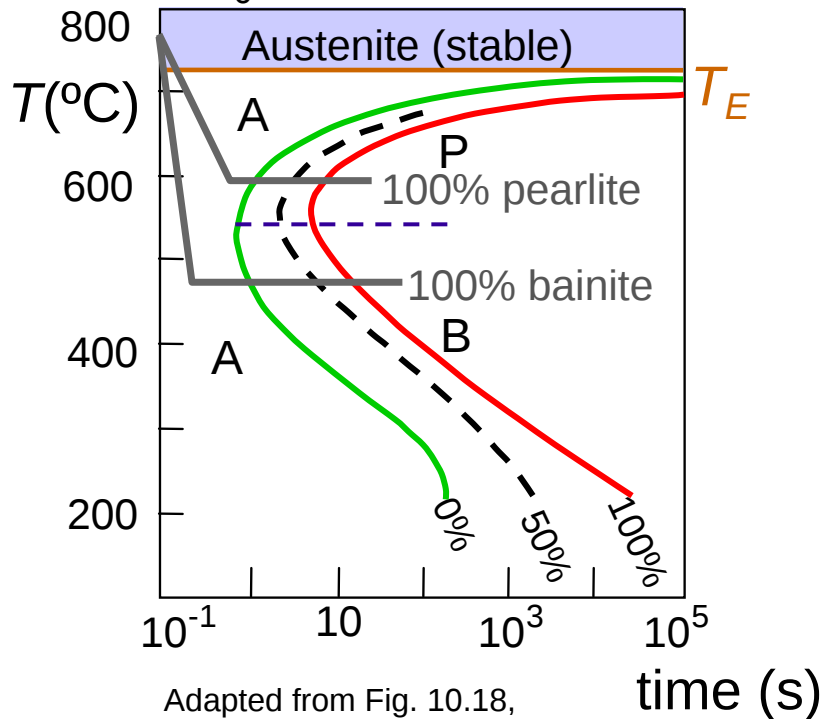
Hypereutectoid composition – proeutectoid cementite



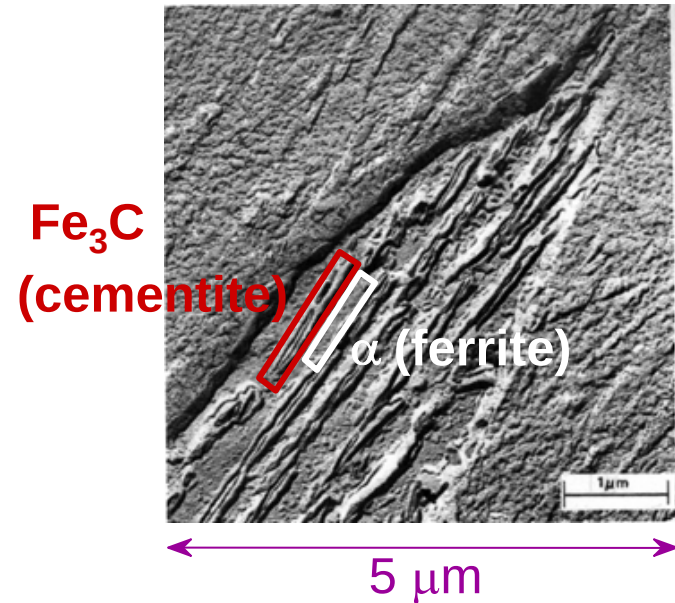
Bainite: Another Fe-Fe₃C Transformation Product

- Bainite:
 - elongated Fe₃C particles in α -ferrite matrix
 - diffusion controlled

- Isothermal Transf. Diagram, $C_0 = 0.76 \text{ wt\% C}$



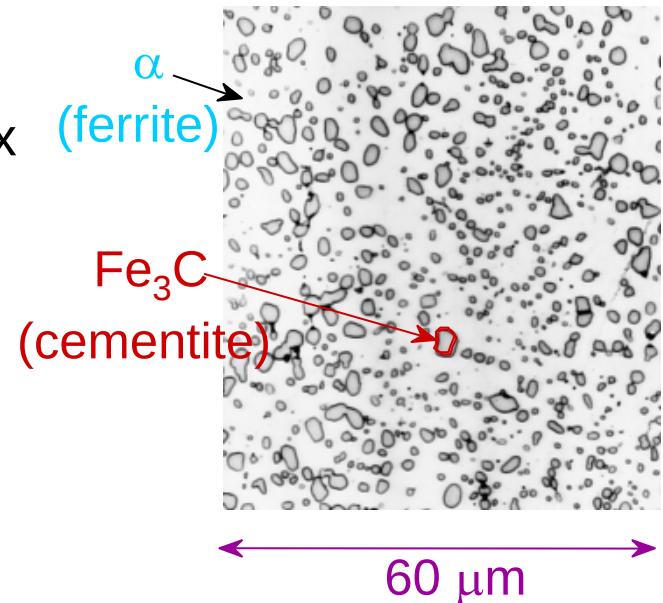
Adapted from Fig. 10.18,
Callister & Rethwisch 8e.



Adapted from Fig. 10.17, Callister & Rethwisch 8e. (Fig. 10.17 from *Metals Handbook*, 8th ed., Vol. 8, *Metallography, Structures, and Phase Diagrams*, American Society for Metals, Materials Park, OH, 1973.)

Spheroidite: Another Microstructure for the Fe-Fe₃C System

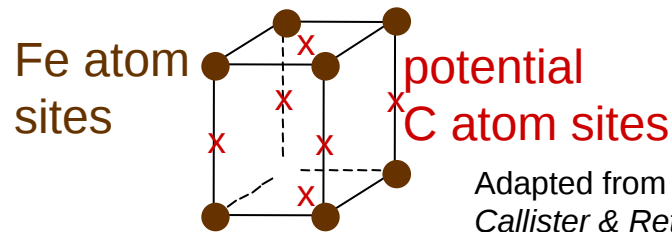
- Spheroidite:
 - Fe₃C particles within an α -ferrite matrix
 - formation requires diffusion
 - heat bainite or pearlite at temperature just below eutectoid for long times
 - driving force – reduction of α -ferrite/Fe₃C interfacial area



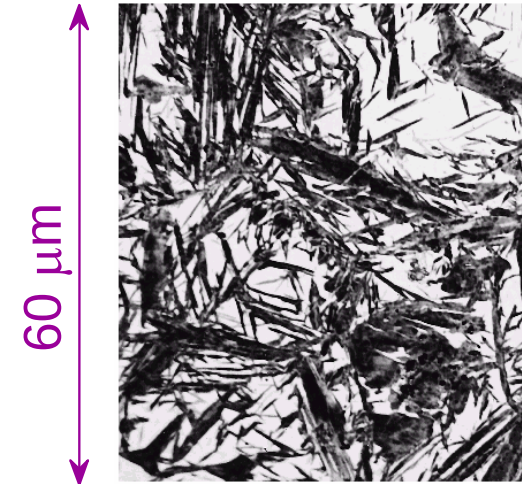
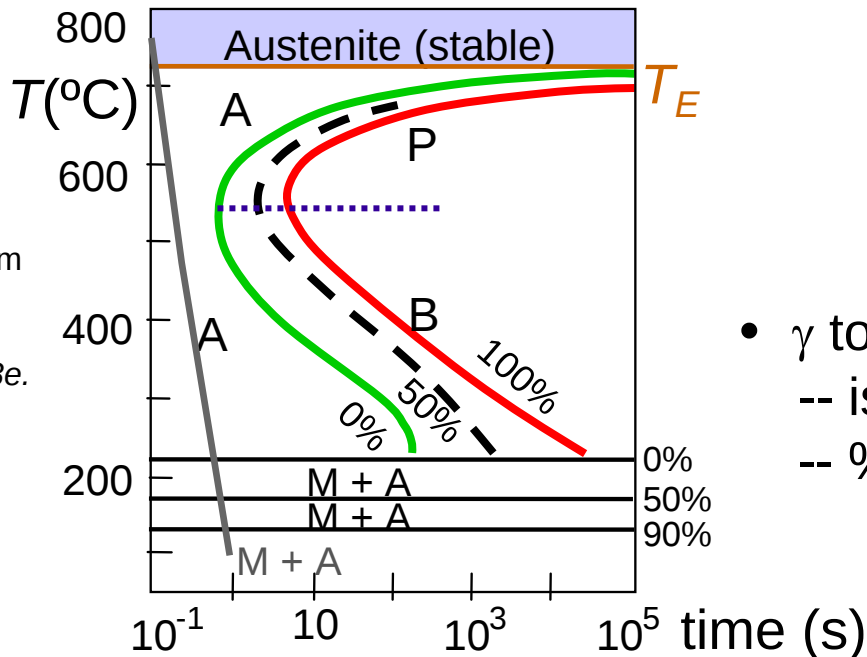
Adapted from Fig. 10.19, *Callister & Rethwisch 8e*. (Fig. 10.19 copyright United States Steel Corporation, 1971.)

Martensite: A Nonequilibrium Transformation Product

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



- Isothermal Transf. Diagram

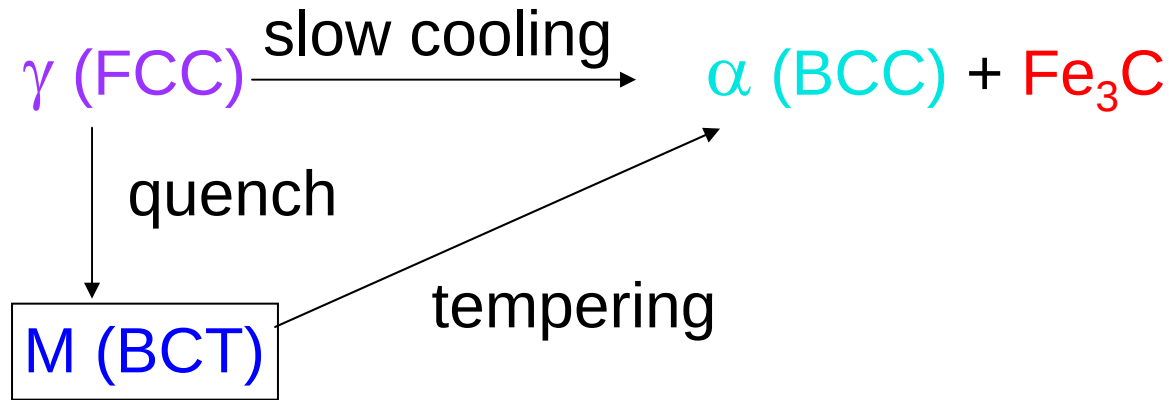


— Martensite needles
— Austenite

Adapted from Fig. 10.21, Callister & Rethwisch 8e. (Fig. 10.21 courtesy United States Steel Corporation.)

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

Martensite Formation



Martensite (M) – single phase
– has body centered tetragonal (BCT)
crystal structure

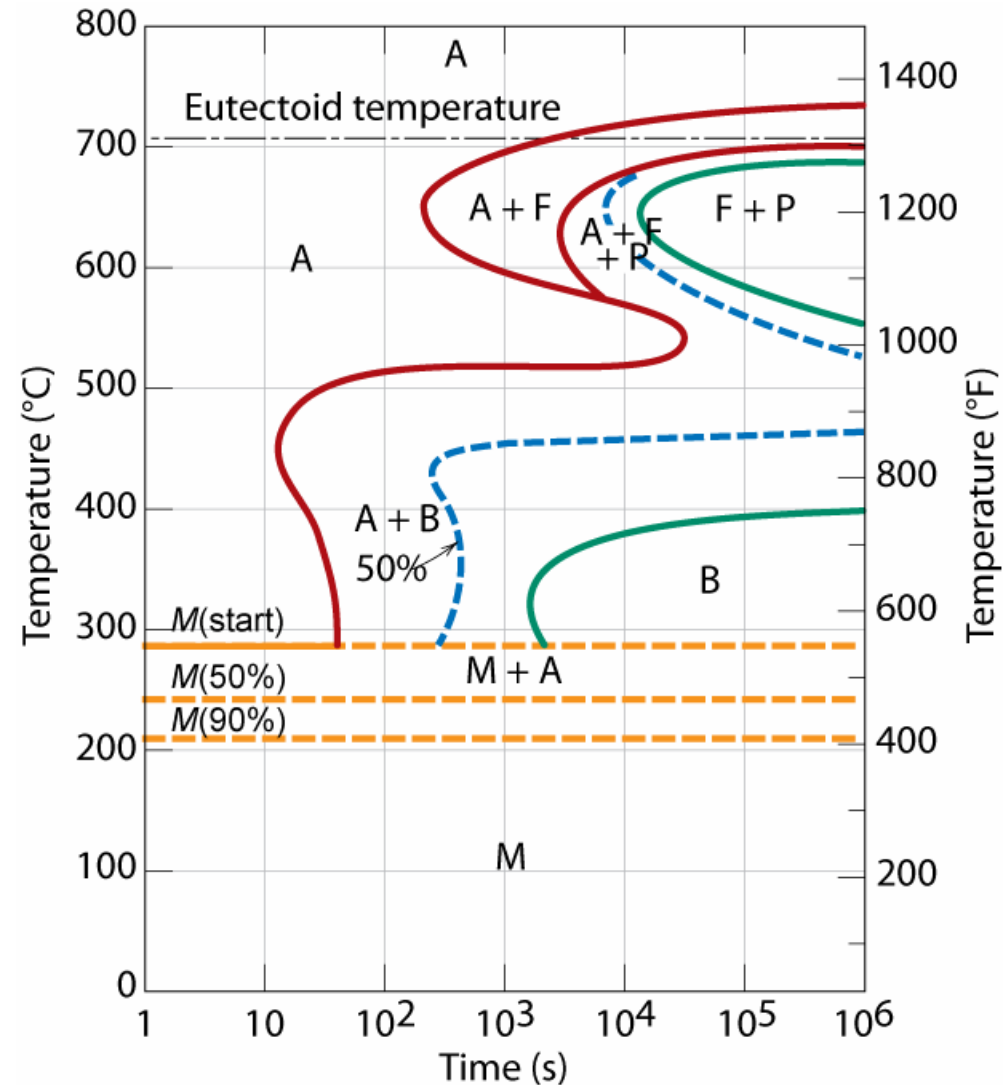
Diffusionless transformation BCT if $C_0 > 0.15$ wt% C
BCT $\rightarrow$ few slip planes $\rightarrow$ hard, brittle

Phase Transformations of Alloys

Effect of adding other elements
Change transition temp.

Cr, Ni, Mo, Si, Mn

retard $\gamma \rightarrow \alpha + \text{Fe}_3\text{C}$
reaction (and formation of
pearlite, bainite)



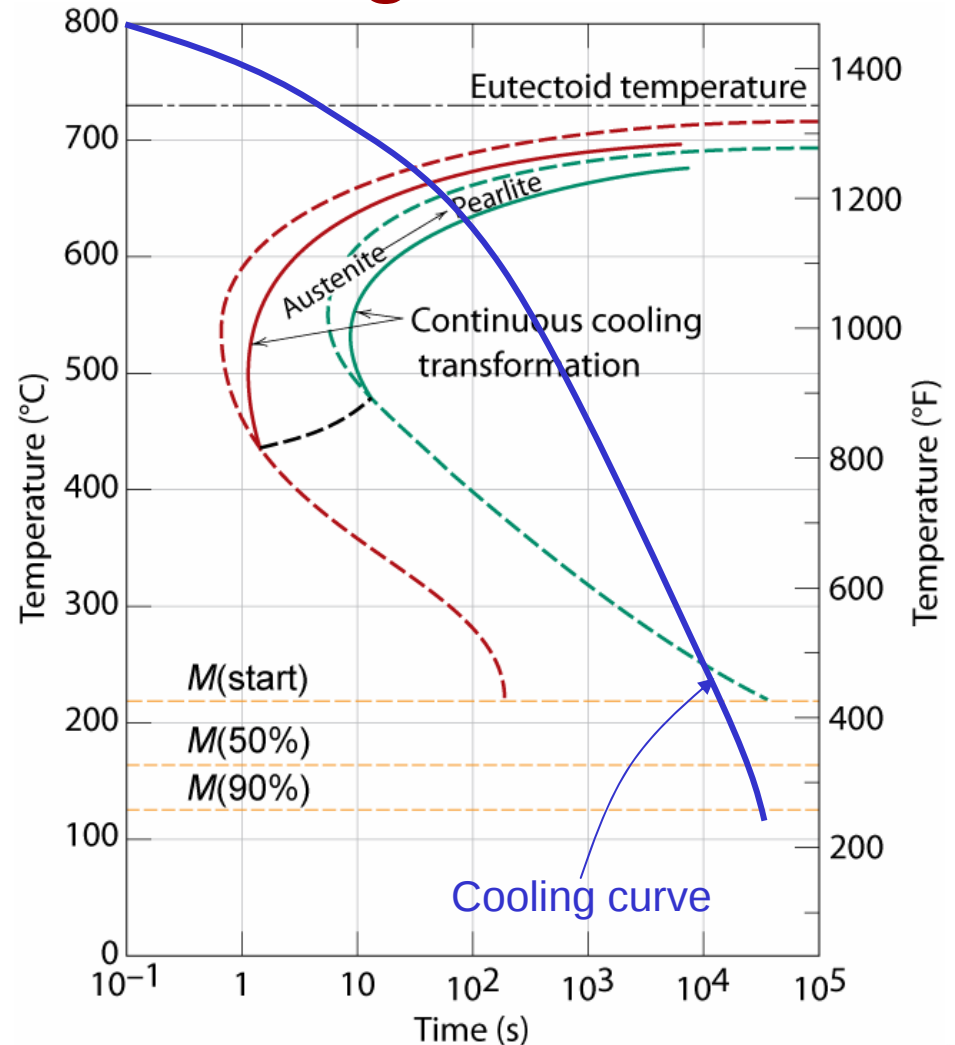
Adapted from Fig. 10.23,
Callister & Rethwisch 8e.



Continuous Cooling Transformation Diagrams

Conversion of isothermal transformation diagram to continuous cooling transformation diagram

Adapted from Fig. 10.25,
Callister & Rethwisch 8e.



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

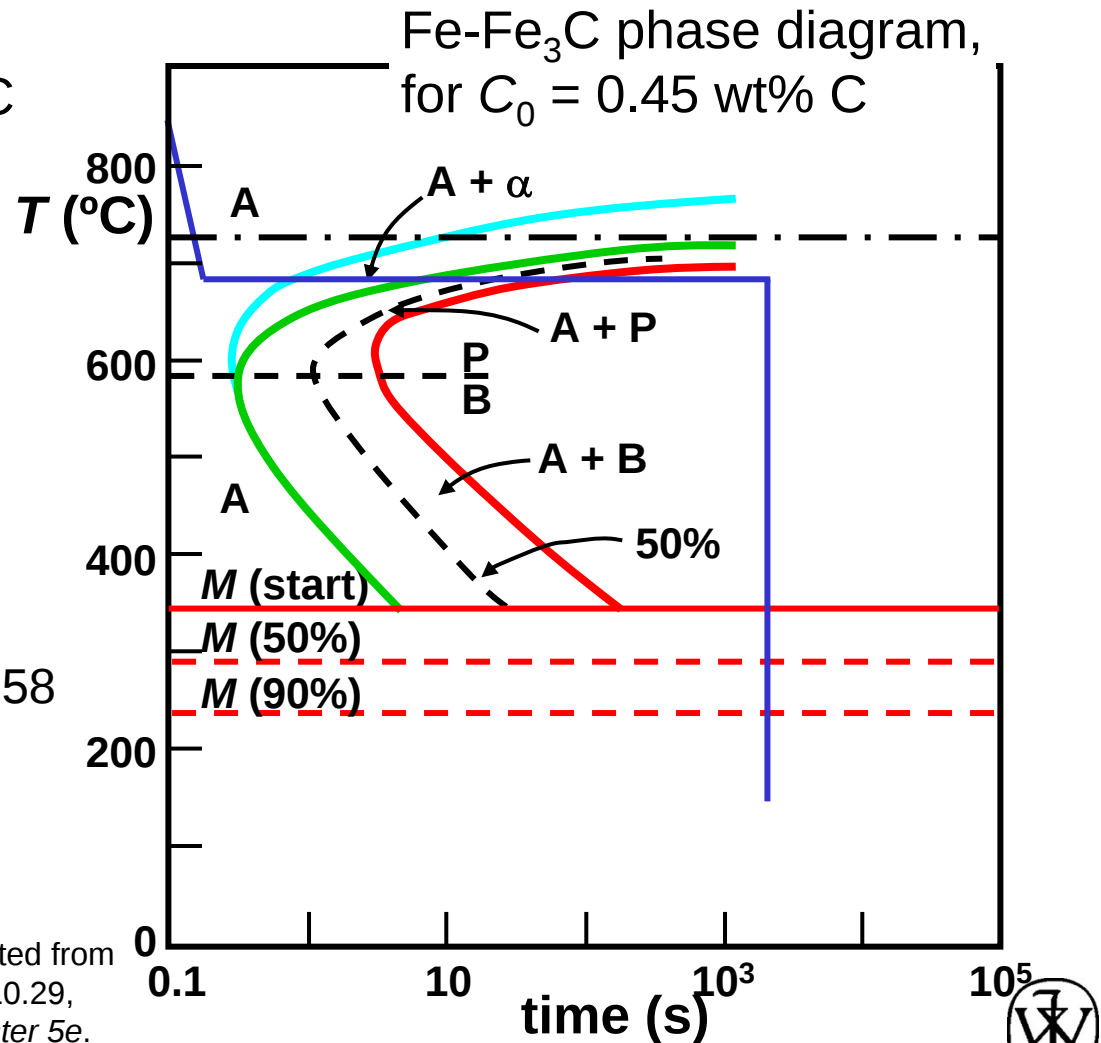
Isothermally treat at $\sim 680^\circ\text{C}$

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

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

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

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



Adapted from
Fig. 10.29,
Callister 5e.

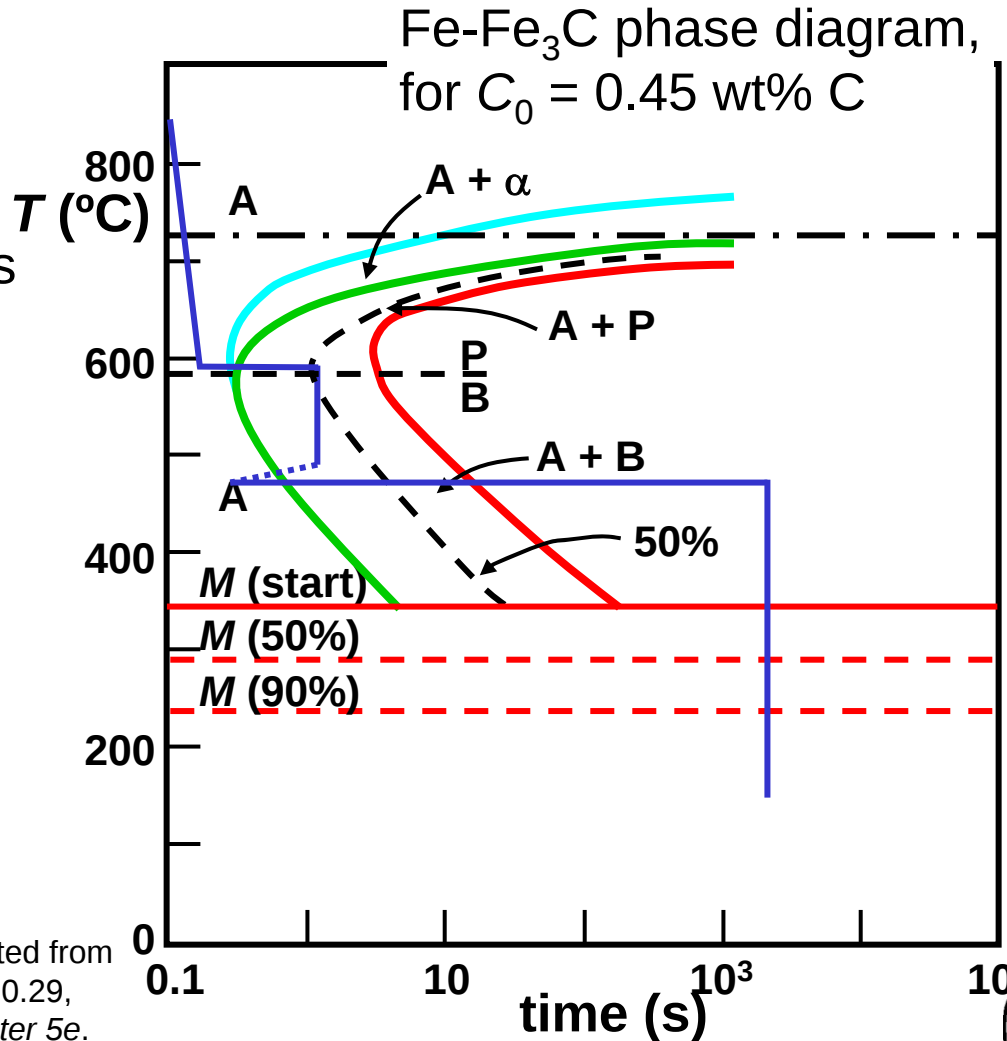


Solution to Part (b) of Example Problem

b) 50% fine pearlite and 50% bainite

Isothermally treat at $\sim 590^\circ\text{C}$
– 50% of austenite transforms
to fine pearlite.

Then isothermally treat
at $\sim 470^\circ\text{C}$
– all remaining austenite
transforms to bainite.

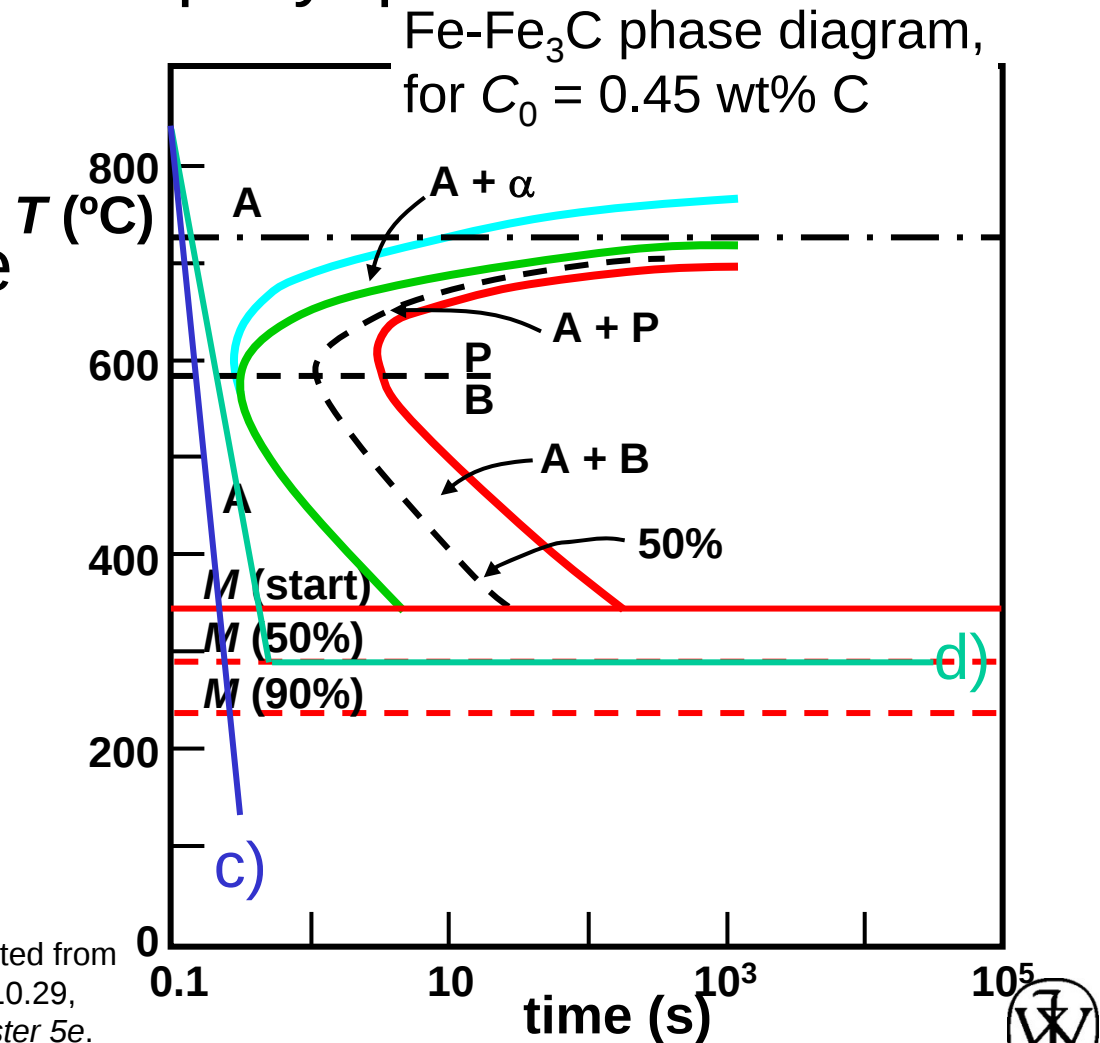


Solutions to Parts (c) & (d) of Example Problem

c) 100% martensite – rapidly quench to room temperature

d) 50% martensite & 50% austenite

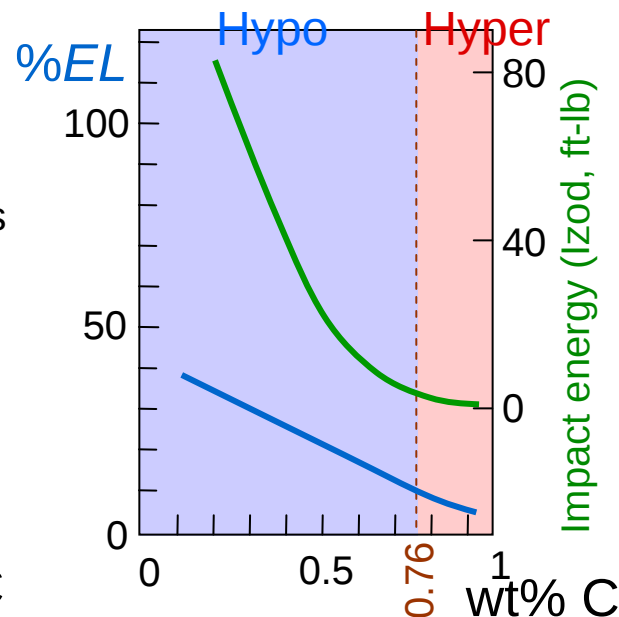
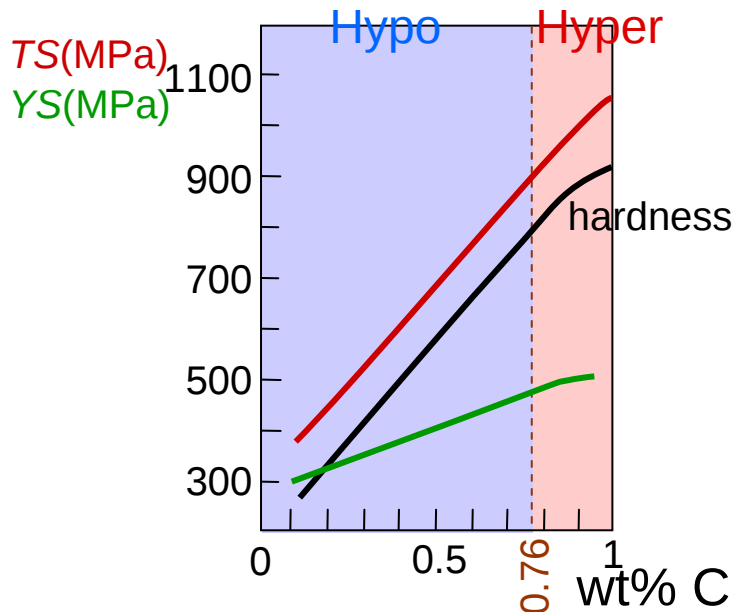
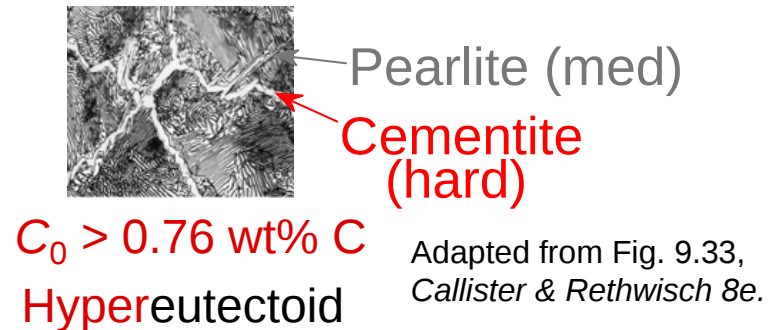
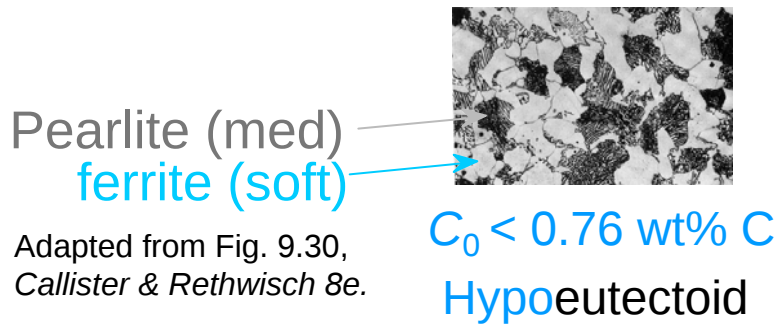
-- rapidly quench to ~ 290°C, hold at this temperature



Adapted from
Fig. 10.29,
Callister 5e.



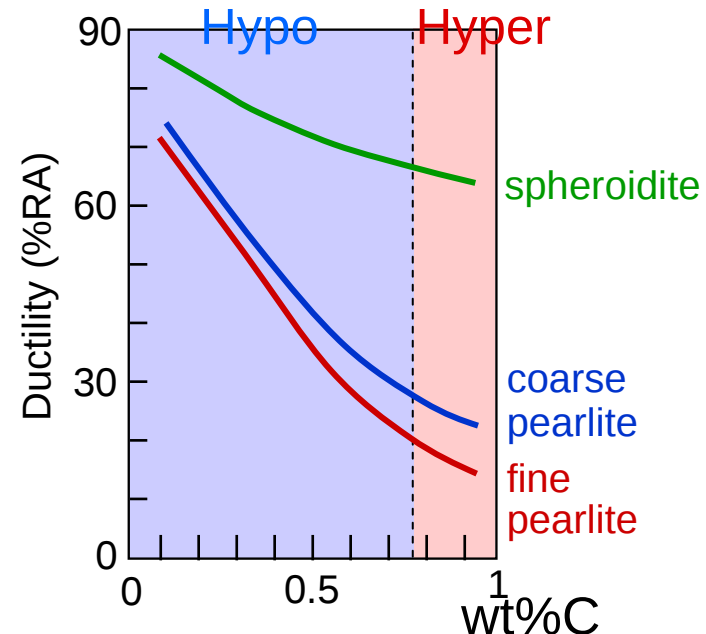
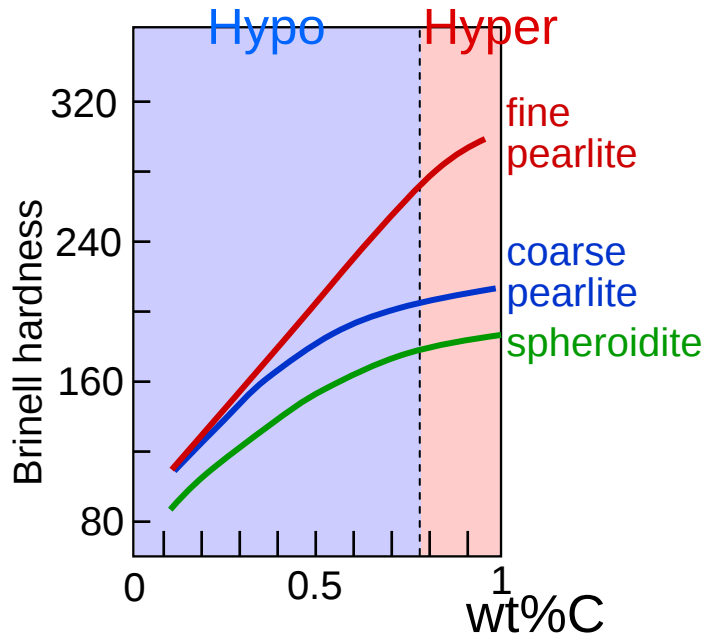
Mechanical Props: Influence of C Content



Adapted from Fig. 10.29, Callister & Rethwisch 8e. (Fig. 10.29 based on data from *Metals Handbook: Heat Treating*, Vol. 4, 9th ed., V. Masseria (Managing Ed.), American Society for Metals, 1981, p. 9.)

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

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

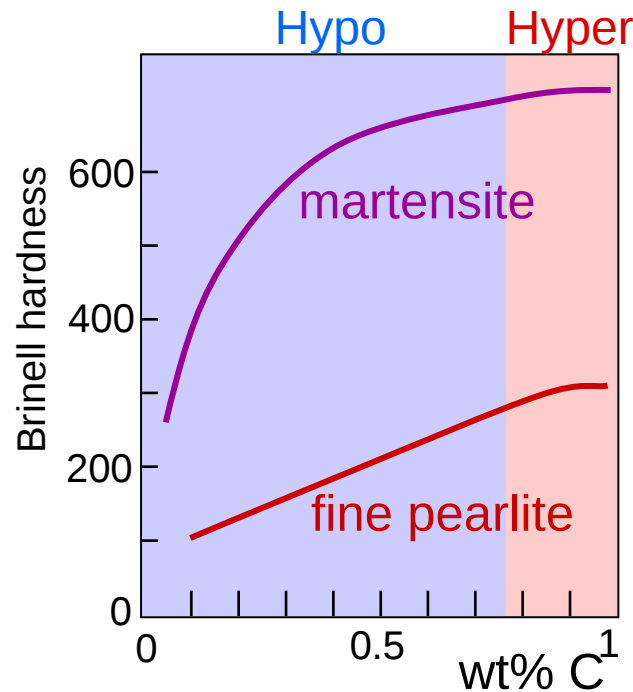


- Hardness: fine > coarse > spheroidite
- %RA: fine < coarse < spheroidite

Adapted from Fig. 10.30, *Callister & Rethwisch 8e*. (Fig. 10.30 based on data from *Metals Handbook: Heat Treating*, Vol. 4, 9th ed., V. Masseria (Managing Ed.), American Society for Metals, 1981, pp. 9 and 17.)



Mechanical Props: Fine Pearlite vs. Martensite



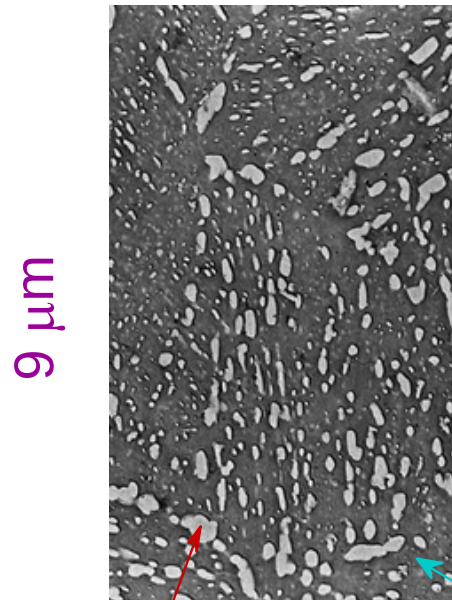
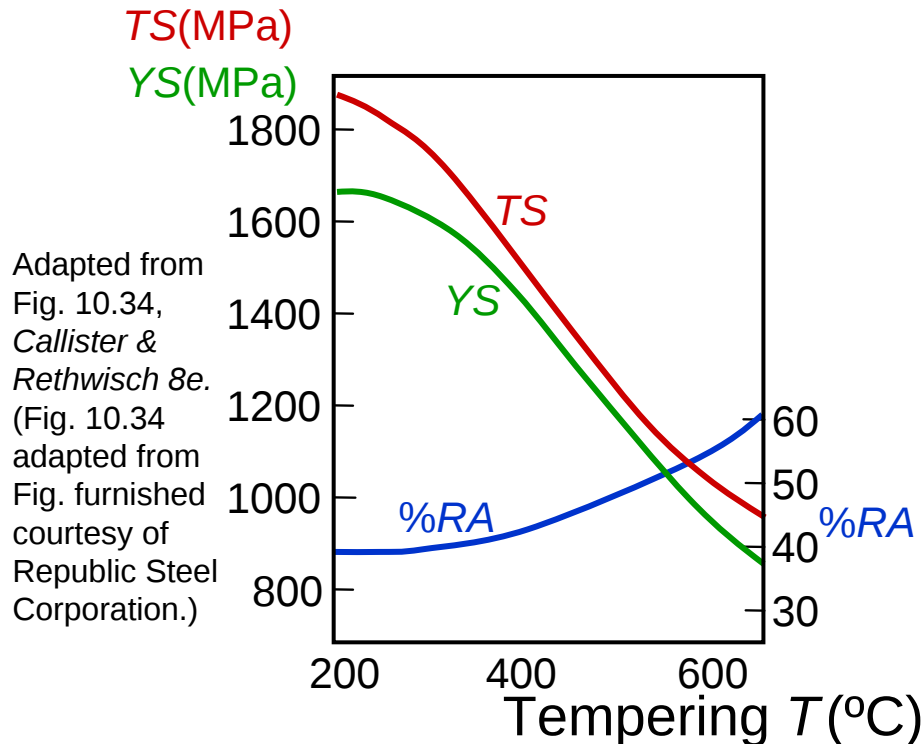
Adapted from Fig. 10.32, *Callister & Rethwisch 8e*. (Fig. 10.32 adapted from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 36; and R.A. Grange, C.R. Hribal, and L.F. Porter, *Metall. Trans. A*, Vol. 8A, p. 1776.)

- 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



Adapted from Fig. 10.33, Callister & Rethwisch 8e. (Fig. 10.33 copyright by United States Steel Corporation, 1971.)

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

Summary of Possible Transformations

Adapted from
Fig. 10.36,
Callister &
Rethwisch 8e.

