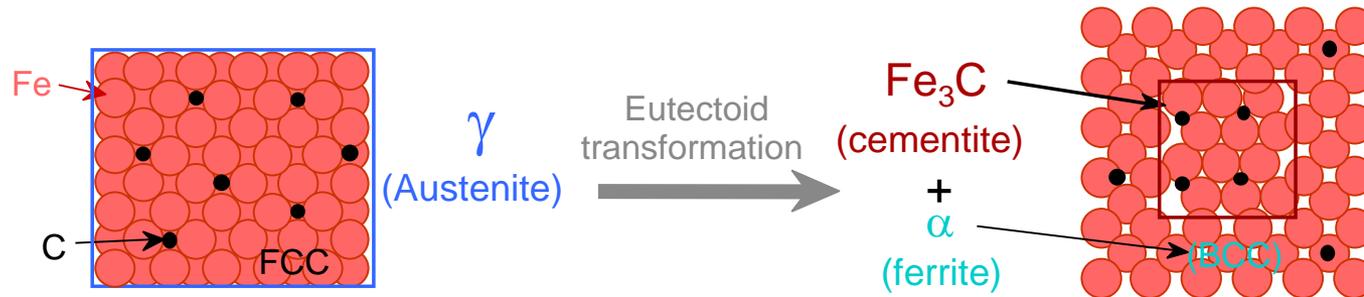


Chapter 10: Phase Transformations

ISSUES TO ADDRESS...

- Transforming one phase into another takes time.

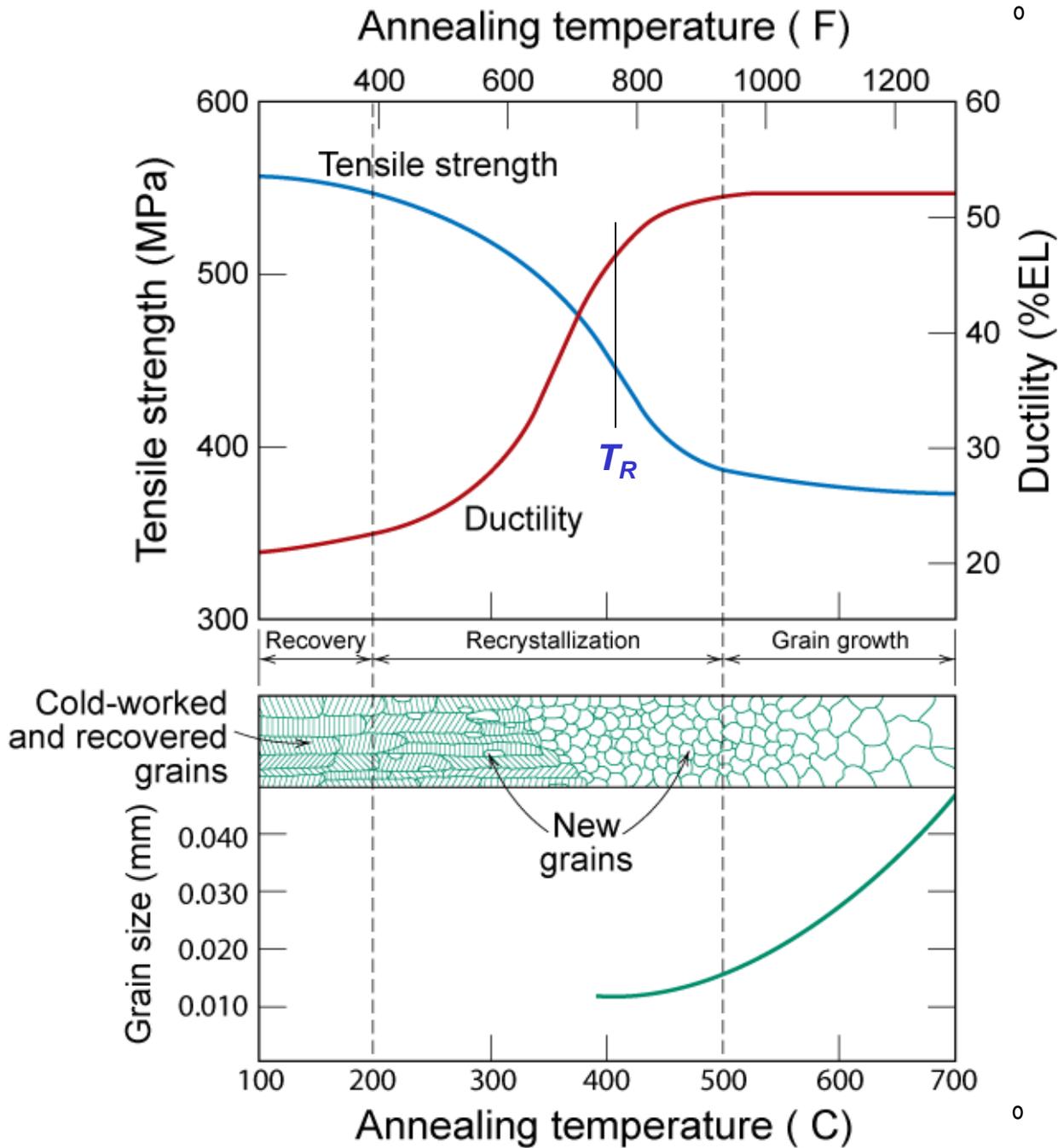


- How does the rate of transformation depend on time and T ?
- How can we slow down the transformation so that we can engineer non-equilibrium structures?
- Are the mechanical properties of non-equilibrium structures better?

Phase transformation

- Takes time (transformation rates: kinetics).
 - Involves movement/rearrangement of atoms.
 - Usually involves changes in microstructure
1. “Simple” diffusion-dependent transformation: **no change in number of compositions of phases present (e.g. solidification of pure elemental metals, allotropic transformation, recrystallization, grain growth).**
 2. Diffusion-dependent transformation: **transformation with alteration in phase composition and, often, with changes in number of phases present (e.g. eutectoid reaction).**
 3. Diffusionless transformation: **e.g. rapid T quenching to “trap” metastable phases.**





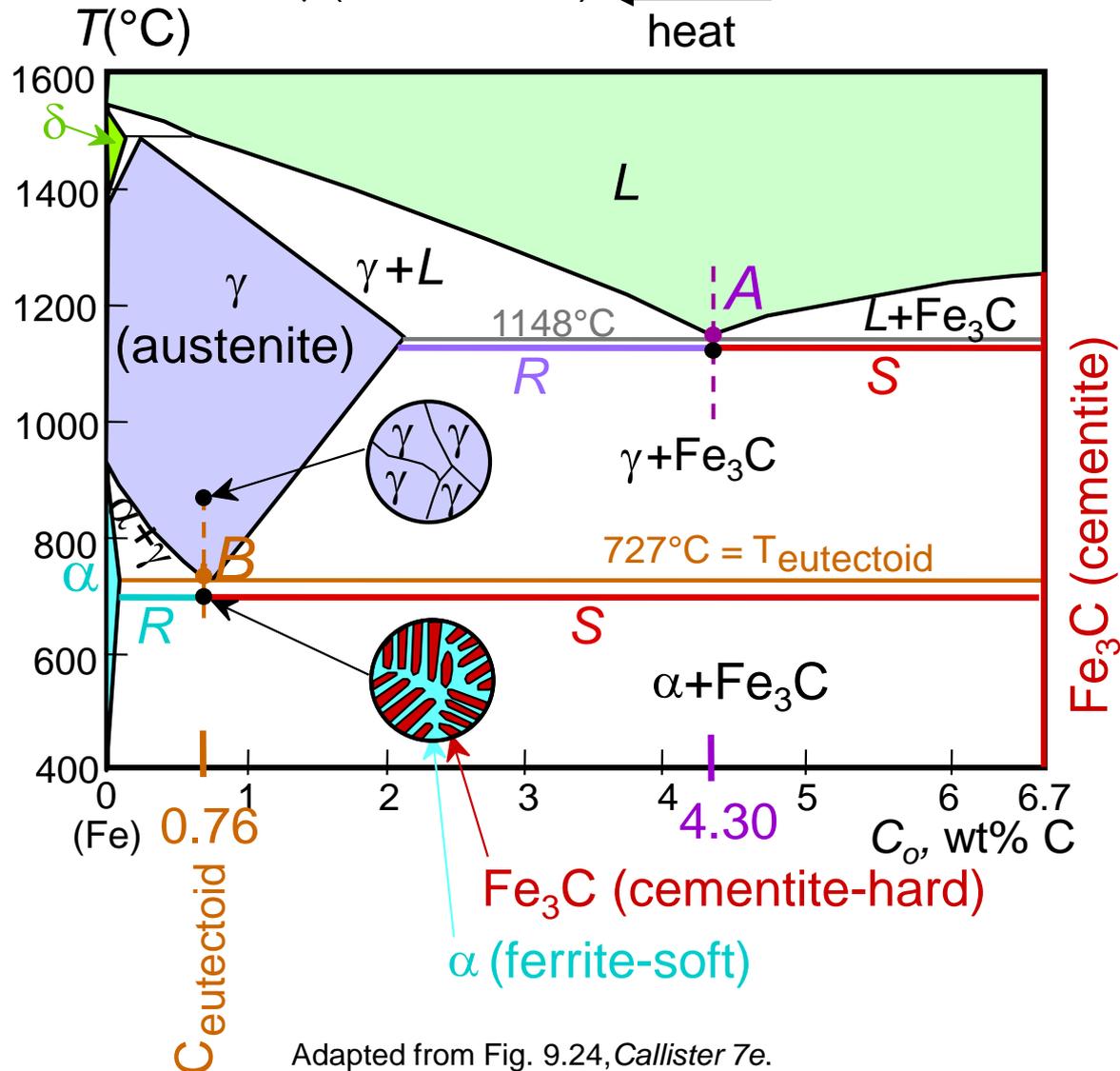
T_R = recrystallization temperature

Adapted from Fig. 7.22, Callister 7e. The influence of annealing T on the tensile strength and ductility of a brass alloy.



Iron-Carbon Phase Diagram

Eutectoid cooling:



Adapted from Fig. 9.24, Callister 7e.



Phase Transformations

Nucleation

- nuclei (seeds) act as template to grow crystals
- for nucleus to form rate of addition of atoms to nucleus must be faster than rate of loss
- once nucleated, grow until reach equilibrium

Driving force to nucleate increases as we increase ΔT

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

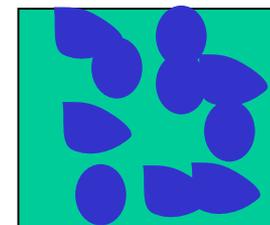
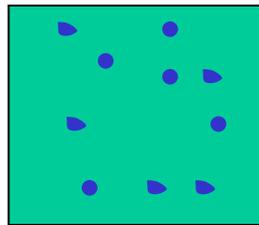
Small supercooling \rightarrow few nuclei - large crystals

Large supercooling \rightarrow rapid nucleation - many nuclei,
small crystals



Solidification: Nucleation Processes

- **Homogeneous nucleation**
 - nuclei form in the bulk of liquid metal
 - requires supercooling (typically 80-300°C max)
- **Heterogeneous nucleation**
 - much easier since stable “nucleus” is already present
 - Could be wall of mold or impurities in the liquid phase
 - allows solidification with only 0.1-10°C supercooling



Phase 1 (e.g. liquid)

Nucleation of 2nd phase

Chapter 10 - 6
Growth



Homogeneous Nucleation

Thermodynamic parameters:

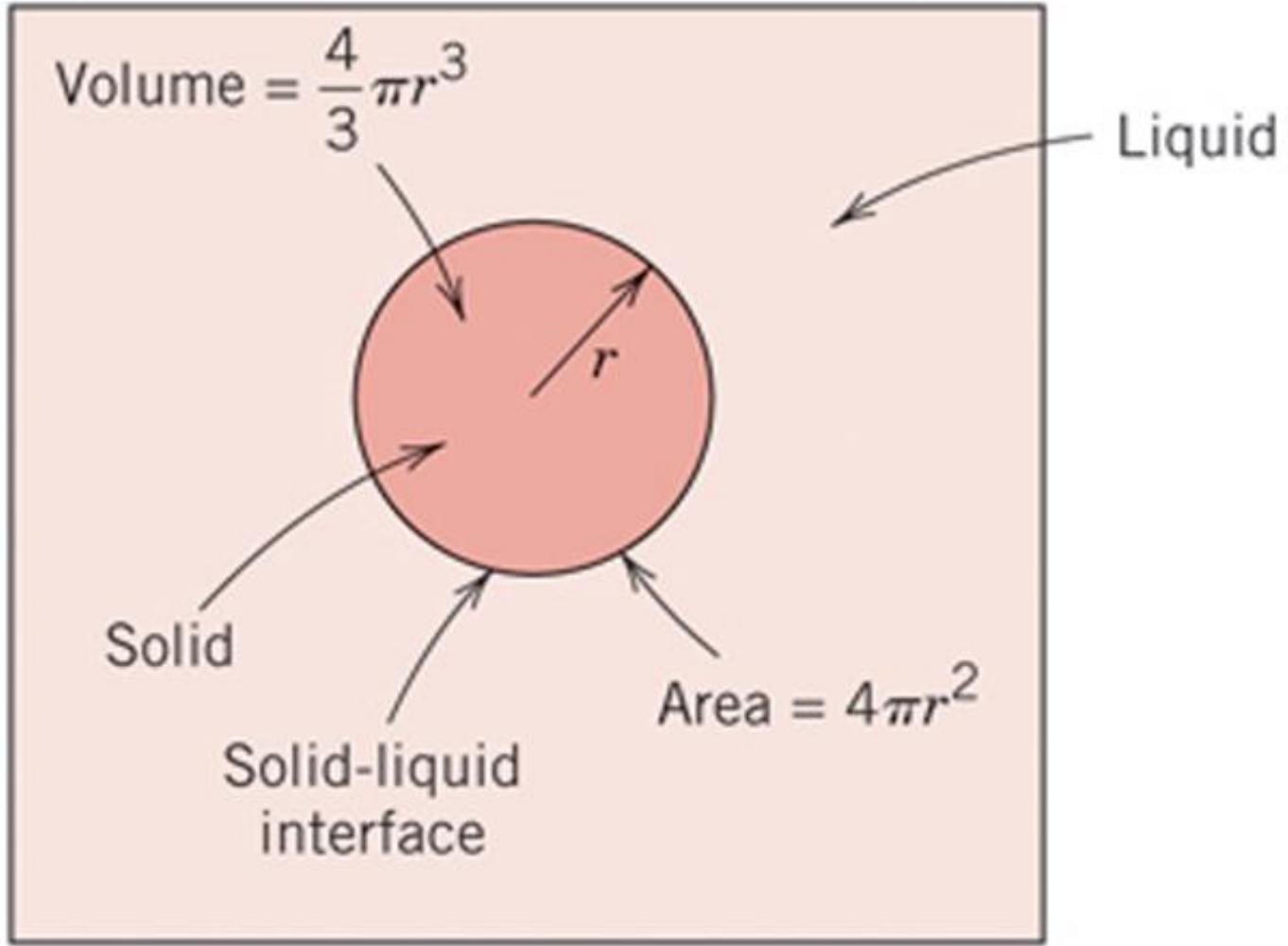
- Free energy G (or Gibbs free energy)
- Enthalpy H : internal energy of the system and the product of its volume multiplied by the pressure
- Entropy S : randomness or disorder of the atoms or molecules

ΔG is important---a phase transformation will occur spontaneously only when ΔG has a negative value.

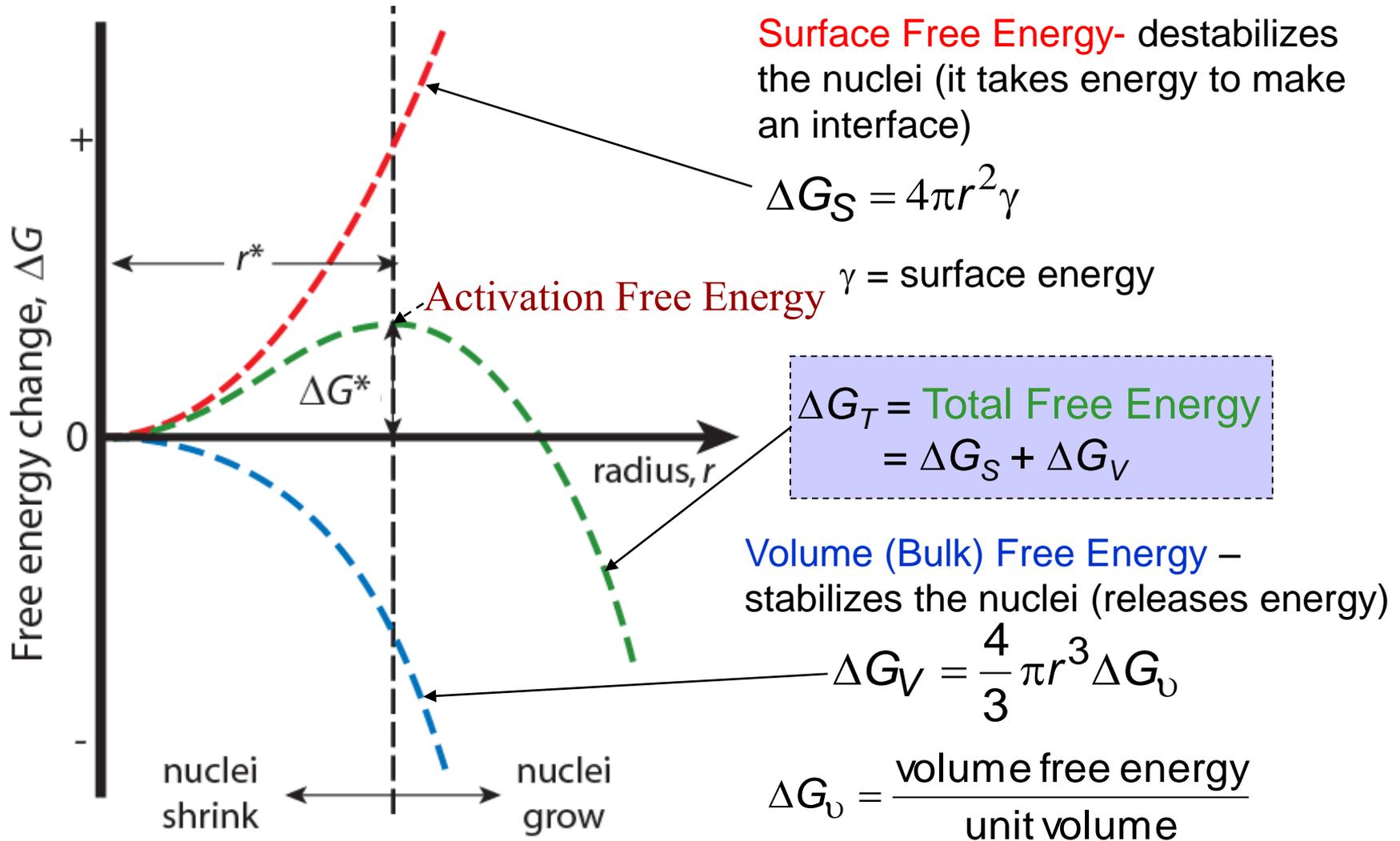
$$\Delta G = \Delta H - T\Delta S$$



Homogeneous Nucleation



Homogeneous Nucleation & Energy Effects



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



Kinetics of solid state reactions

Critical nucleus size (r_c) and the activation energy (ΔG^*)

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Take the derivative and set equal to zero to find max.

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

$$r_c = -\frac{2\gamma}{\Delta G_v}$$

Substitution in to overall ΔG equation

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



The volume free energy change is the driving force for the solidification transformation

Kinetics of solid state reactions

In terms of latent heat of fusion ΔH_f (i.e. energy release upon solidification):

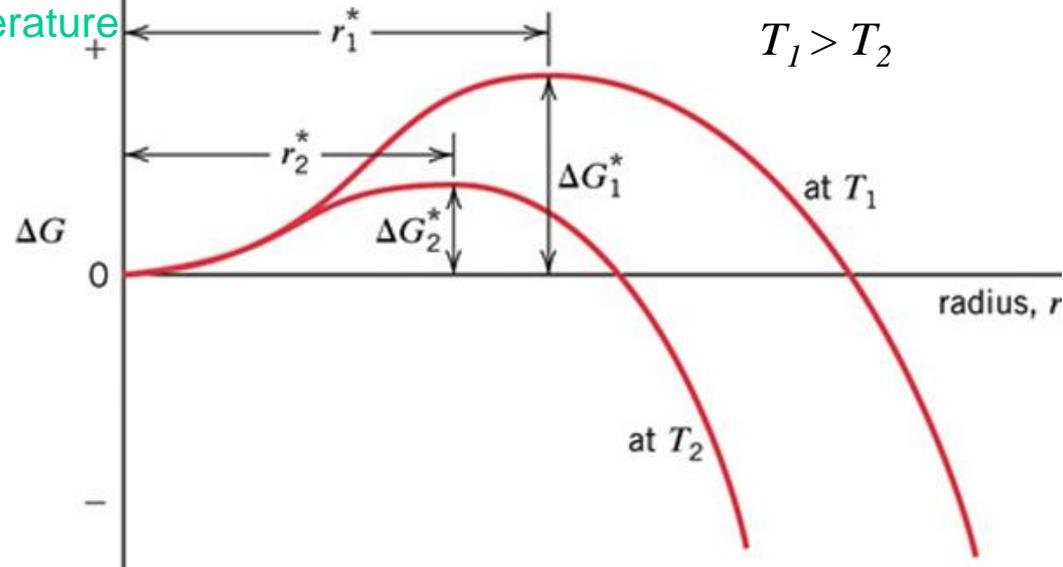
$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m}$$

Tells us how ΔG_v changes with temperature
 Equilibrium solidification temperature

With this definition, we then have:

$$r_c = -\frac{2\gamma}{\Delta H_f} \left(\frac{T_m}{T_m - T} \right)$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta H_f^2} \left(\frac{T_m}{T_m - T} \right)^2$$



As T decreases both r_c and ΔG^* become smaller

Number of stable nuclei: $n^* \propto \exp\left(-\frac{\Delta G^*}{kT}\right)$



LIQUID INSTABILITY at LOWER TEMPERATURES



Solidification

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

r^* = critical radius

γ = surface free energy

T_m = melting temperature

ΔH_S = latent heat of solidification

$\Delta T = T_m - T$ = supercooling

Note: ΔH_S = strong function of ΔT

γ = weak function of ΔT

$\therefore r^*$ decreases as ΔT increases

For typical ΔT r^* ca. 100Å

Kinetics of solid state reactions

We also need to consider diffusion:

- Faster diffusion leads to more collisions between atoms.
- More collisions means higher probability of atoms sticking to each other.

Recall diffusion $D = D_o \exp\left(-\frac{Q_d}{kT}\right)$

Then, the frequency of atoms sticking together is directly related to diffusion:

Frequency of attachment: $v_d \propto \exp\left(-\frac{Q_d}{kT}\right)$



Kinetics of solid state reactions

Combining liquid instability and diffusion effects together:

Rate of Nucleation (units: nuclei per unit volume per second)

$$\frac{dN}{dt} = Kn^*v_d = K' \left[\exp\left(-\frac{\Delta G^*}{kT}\right) \exp\left(-\frac{Q_d}{kT}\right) \right]$$

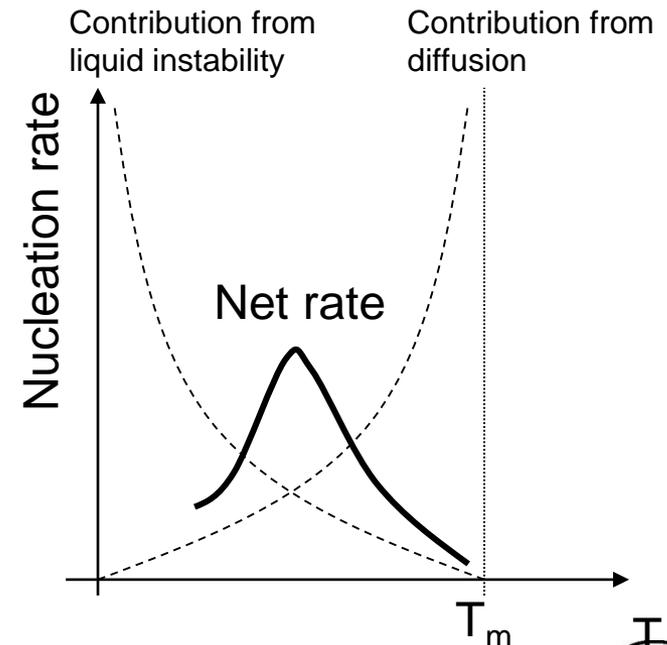
$$n^* \propto \exp\left(-\frac{\Delta G^*}{kT}\right)$$

Liquid instability



$$v_d \propto \exp\left(-\frac{Q_d}{kT}\right)$$

Diffusion



Example problem: critical radius and activation energy for nucleation

- A) If pure liquid gold is cooled to 230°C below its melting point, calculate the critical radius and the activation energy. Values for the latent heat of fusion and surface free energy are $-1.16 \times 10^9 \text{ J/m}^3$ and 0.132 J/m^2 , respectively.

$$r_c = -\frac{2\gamma}{\Delta H_f} \left(\frac{T_m}{T_m - T} \right)$$

$$1.32 \text{ nm}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta H_f^2} \left(\frac{T_m}{T_m - T} \right)^2$$

$$9.64 \times 10^{-19} \text{ J}$$

- B) Calculate the number of atoms per nucleus of this critical size. Au is FCC with $a = 0.413 \text{ nm}$.

$$\# \text{ unit cells/particle} = \frac{\text{critical nucleus volume}}{\text{unit cell volume}} = \frac{\frac{4}{3}\pi r^*{}^3}{a^3} = 137$$

4 atoms/unit cell.....**548** atoms/critical nucleus



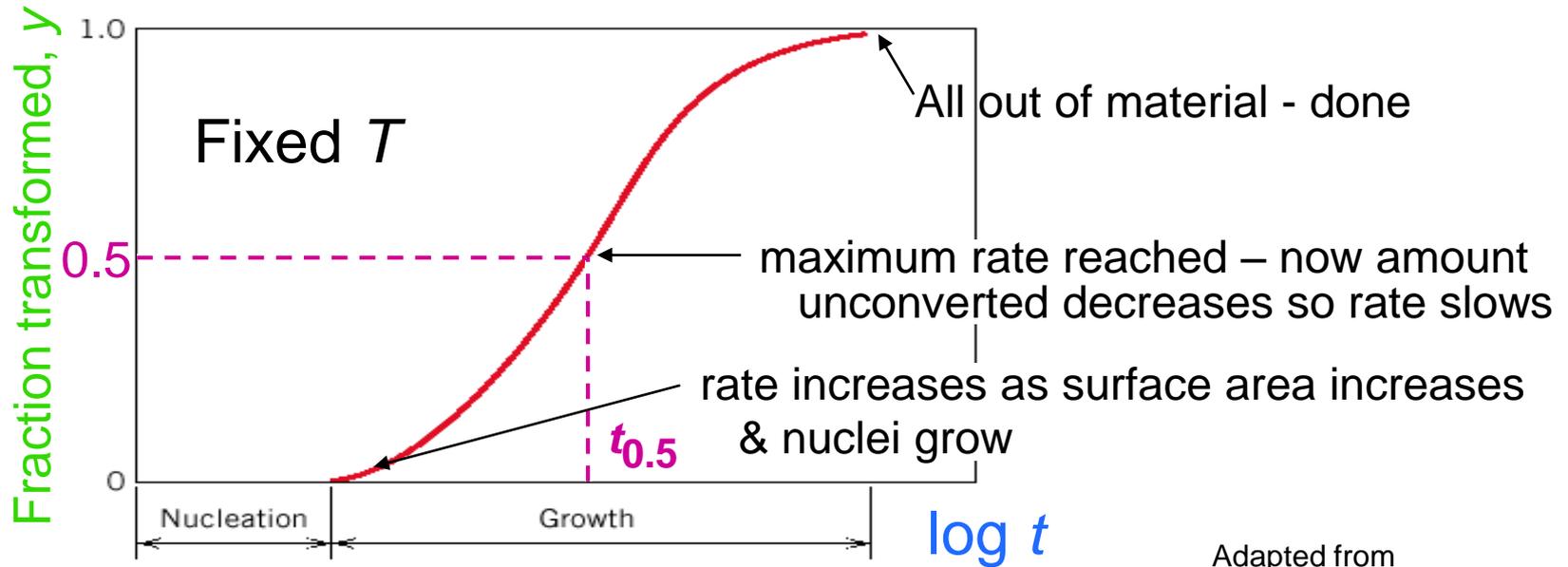
Rate of Phase Transformations

Kinetics – time dependence of nucleation, growth and transformation rates.

- Hold temperature constant & measure transformation vs. time
 - **How is transformation measured?**
 - microscopic examination
 - X-ray diffraction – have to do many samples
 - electrical conductivity – follow one sample
 - sound waves – one sample



Rate of Phase Transformation



Adapted from
Fig. 10.10,
Callister 7e.

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

fraction transformed **time**

– k & n fit for specific sample

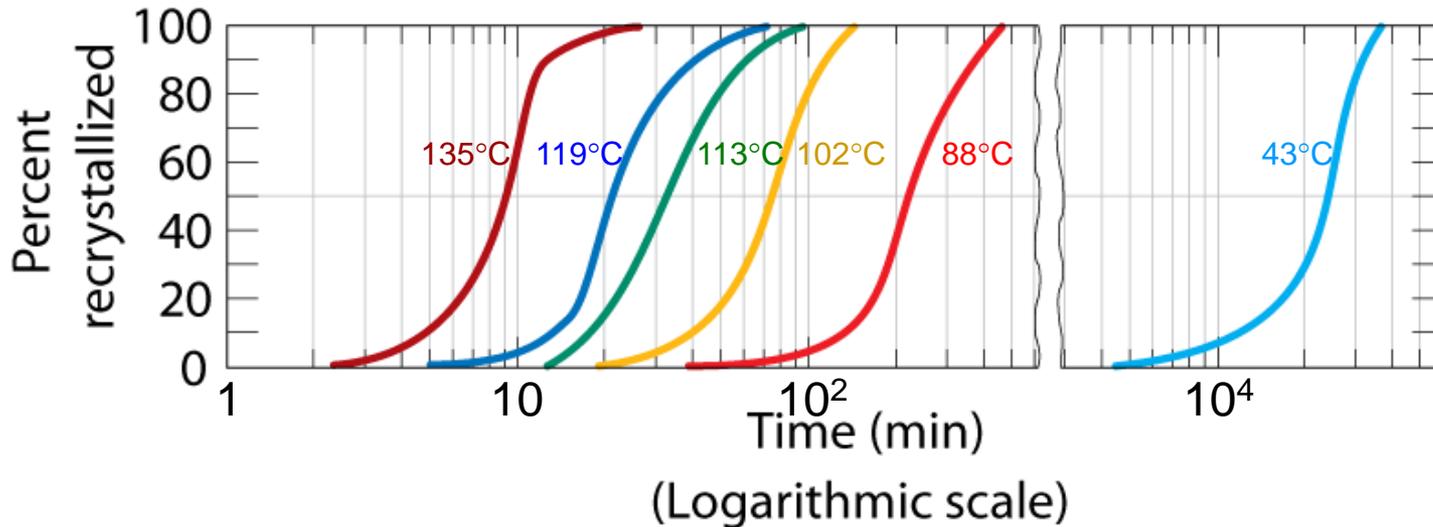
By convention

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



Rate of Phase Transformations

Cu



Adapted from Fig. 10.11, *Callister 7e*. (Fig. 10.11 adapted from B.F. Decker and D. Harker, "Recrystallization in Rolled Copper", *Trans AIME*, **188**, 1950, p. 888.)

- In general, rate increases as $T \uparrow$

$$r = 1/t_{0.5} = A e^{-Q/RT}$$

- R = gas constant
- T = temperature (K)
- A = preexponential factor
- Q = activation energy

Arrhenius
expression

- r often small: equilibrium not possible!



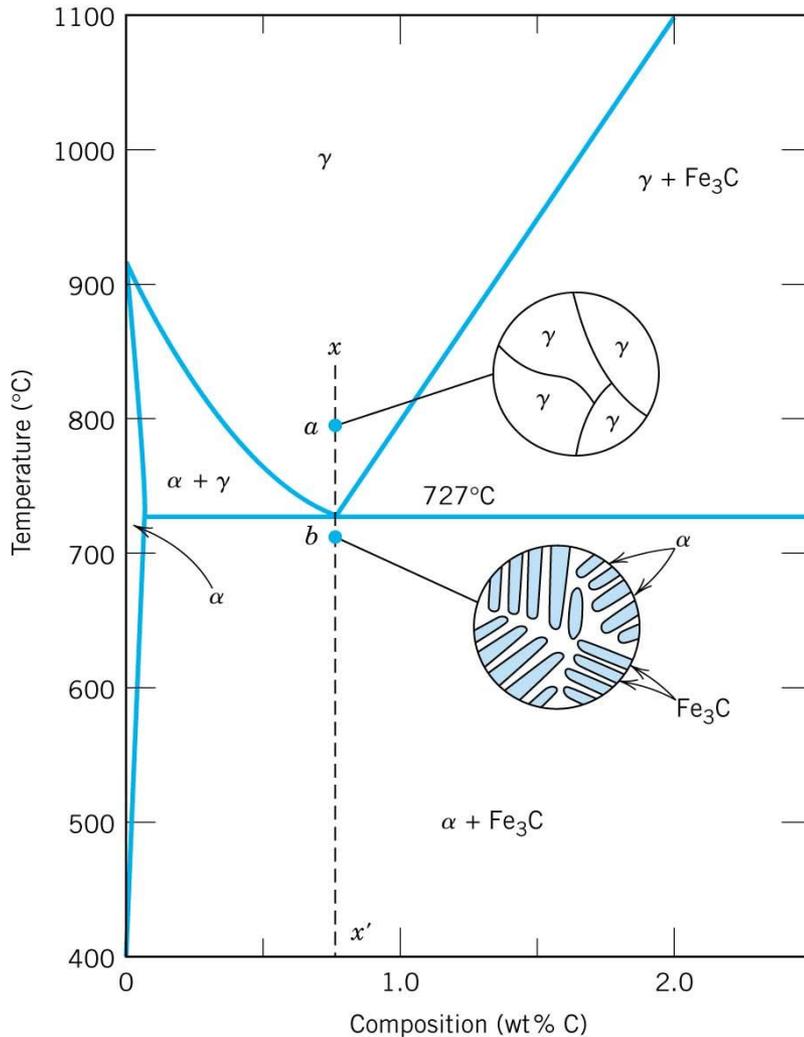
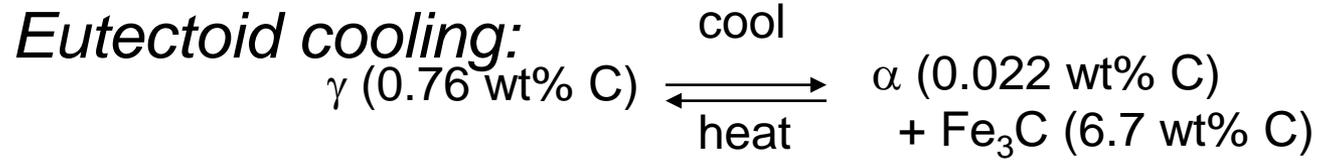


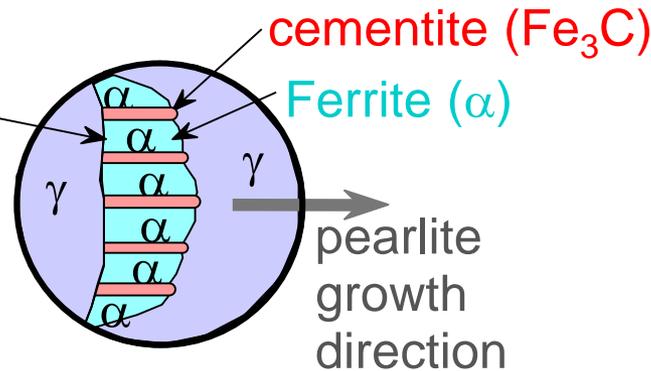
FIGURE 9.23 Schematic representations of the microstructures for an iron-carbon alloy of eutectoid composition (0.76 wt% C) above and below the eutectoid temperature.



Eutectoid Transformation Rate

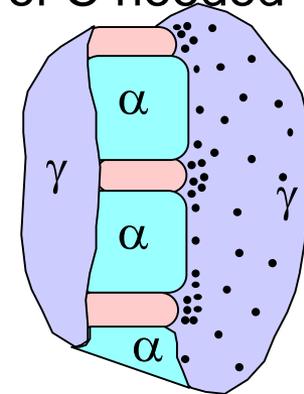
- Growth of pearlite from austenite:

Austenite (γ)
grain
boundary

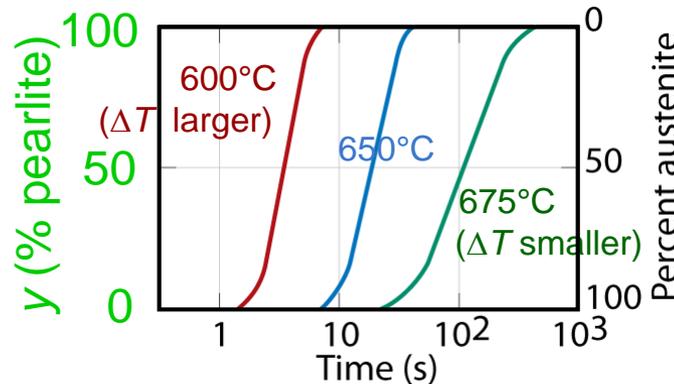


Adapted from
Fig. 9.15,
Callister 7e.

Diffusive flow
of C needed



- Recrystallization rate increases with ΔT .

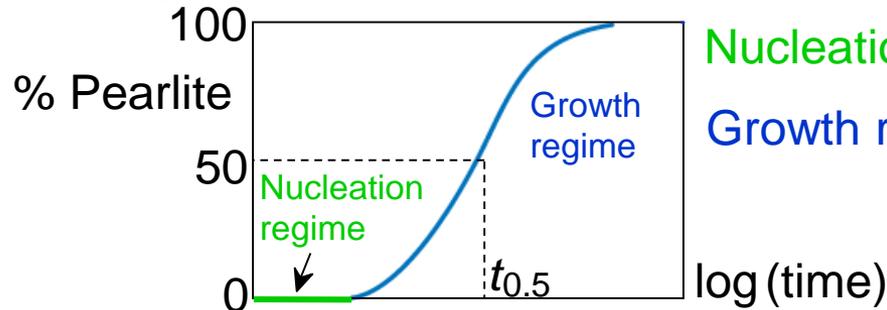


Adapted from
Fig. 10.12,
Callister 7e.

Course pearlite \rightarrow formed at higher T - softer
Fine pearlite \rightarrow formed at low T - harder

Nucleation and Growth

- Reaction rate is a result of nucleation and growth of crystals.

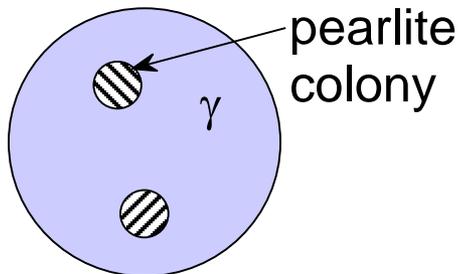


Nucleation rate increases with ΔT

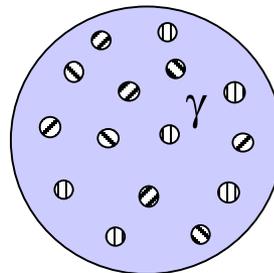
Growth rate increases with T

Adapted from
Fig. 10.10, Callister 7e.

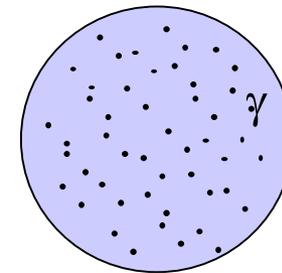
- Examples:



T just below T_E
Nucleation rate low
Growth rate high



T moderately below T_E
Nucleation rate med
Growth rate med.



T way below T_E
Nucleation rate high
Growth rate low

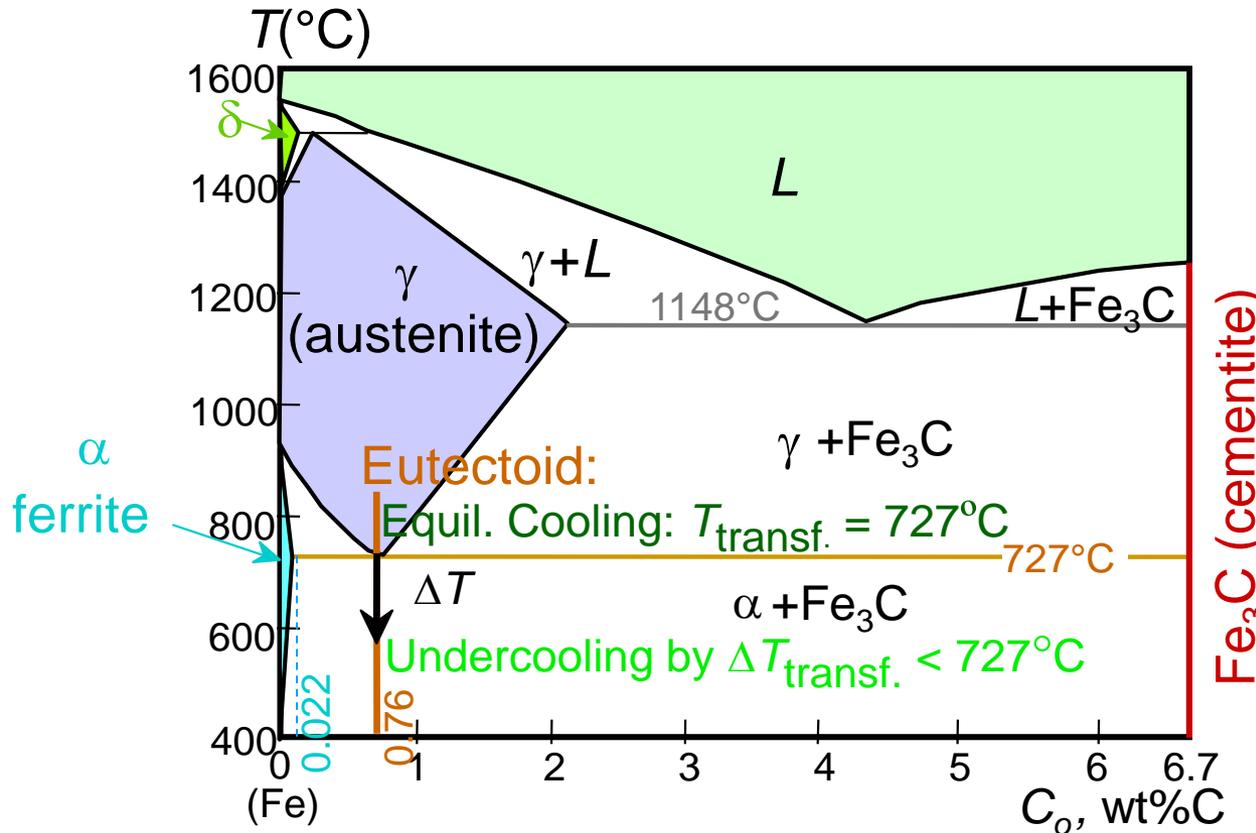
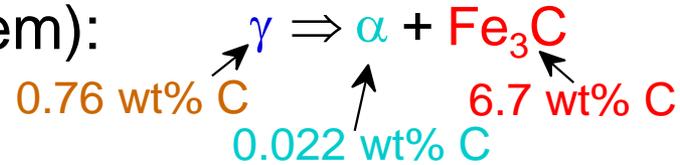
Transformations & Undercooling

- Eutectoid transf. (Fe-C System):

- Can make it occur at:

...727°C (cool it slowly)

...below 727°C (“undercool” it!)



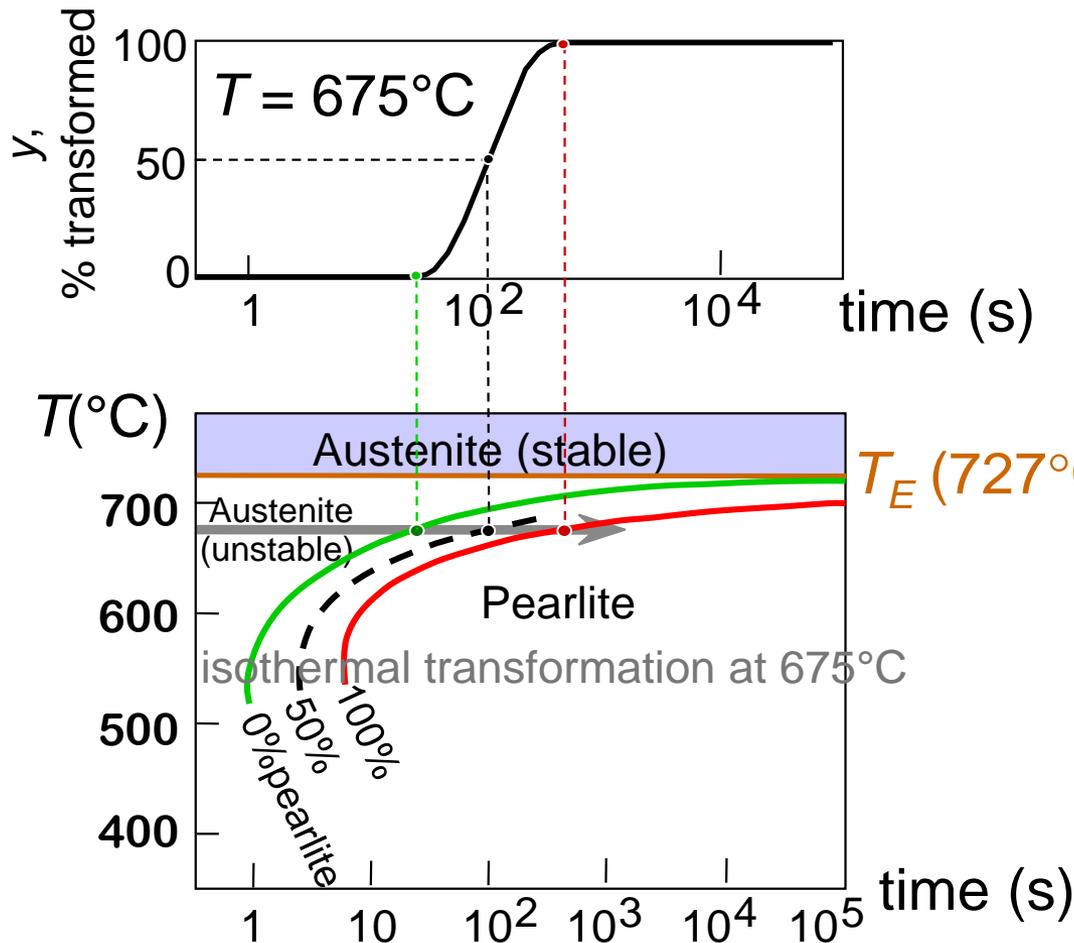
Adapted from Fig. 9.24, Callister 7e. (Fig. 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)



Isothermal Transformation Diagrams

T-T-T plots

- Fe-C system, $C_o = 0.76 \text{ wt\% C}$
- Transformation at $T = 675^\circ\text{C}$. T: hold constant



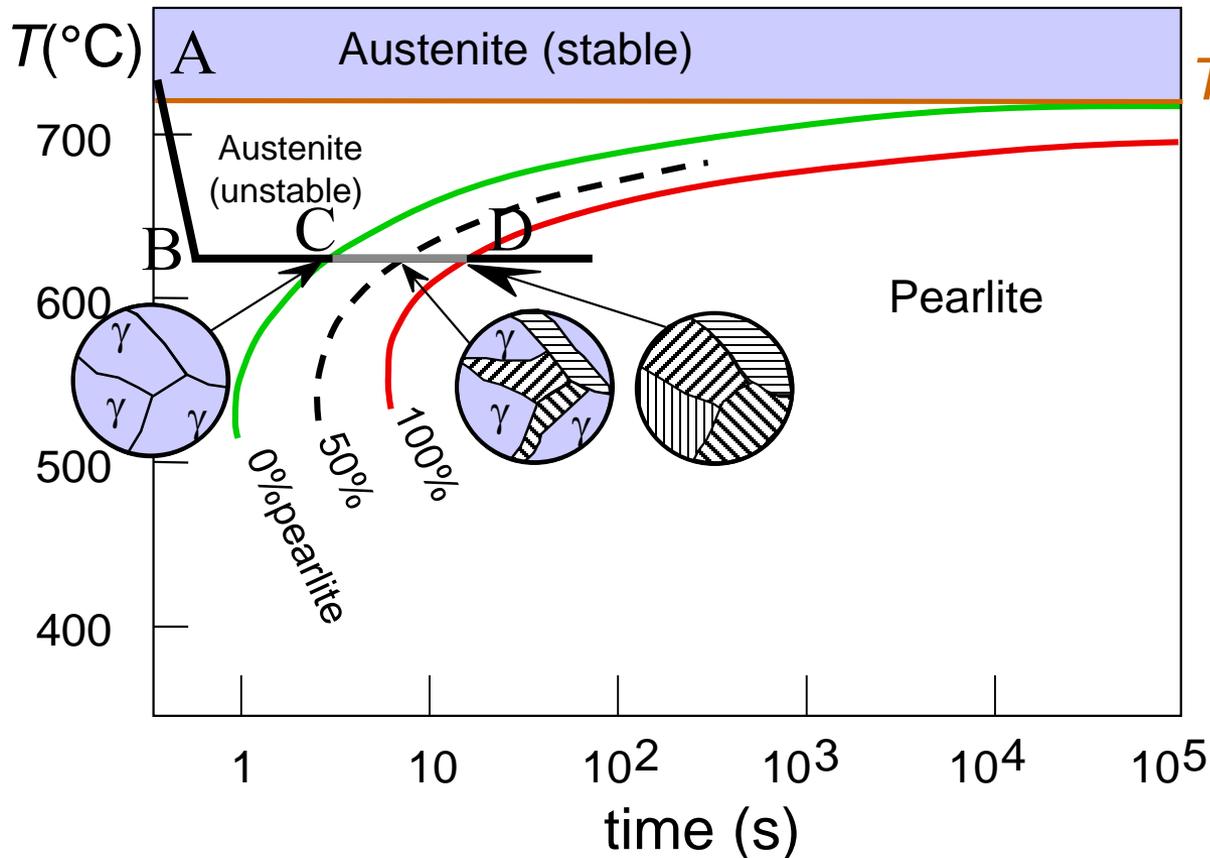
Only for Fe-C alloy of eutectoid composition

Adapted from Fig. 10.13, Callister 7e. (Fig. 10.13 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1977, p. 369.)



Effect of Cooling History in Fe-C System

- Eutectoid composition, $C_o = 0.76 \text{ wt\% C}$
- Begin at $T > 727^\circ\text{C}$
- Rapidly cool to 625°C and hold isothermally.



Adapted from Fig. 10.14, *Callister 7e*.
(Fig. 10.14 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1997, p. 28.)



Pearlite

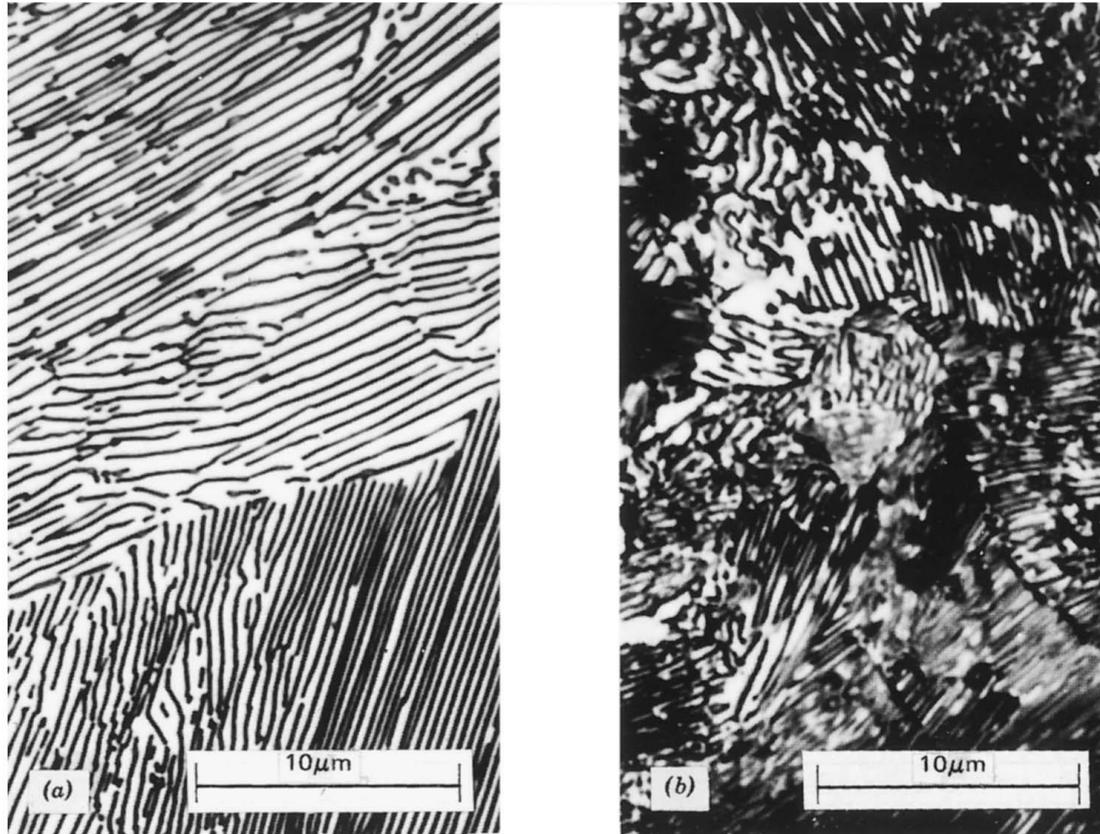


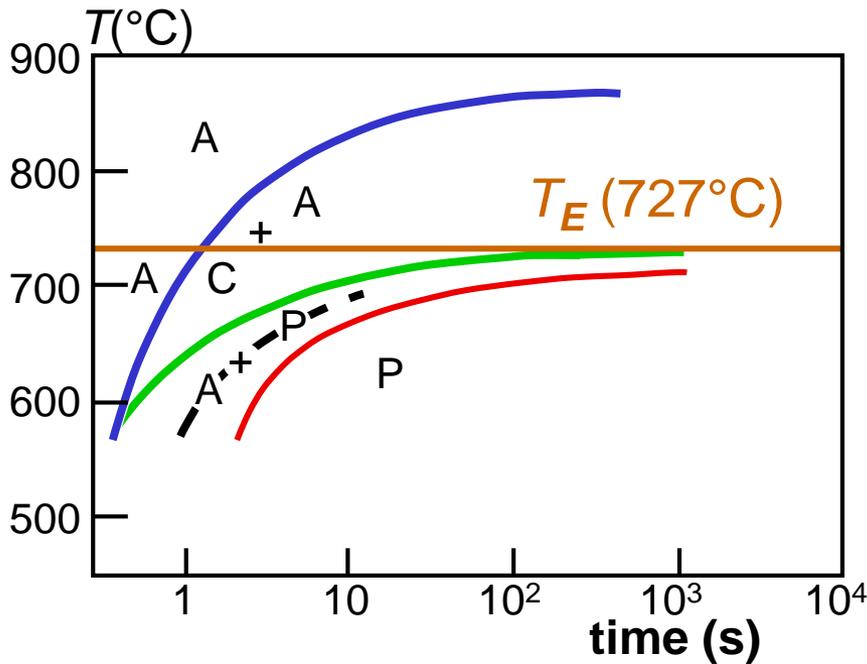
FIGURE 10.6 Photomicrographs of (a) coarse pearlite and (b) fine pearlite. 3000 \times . (From K. M. Ralls et al., *An Introduction to Materials Science and Engineering*, p. 361. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Coarse (quenched to higher T)

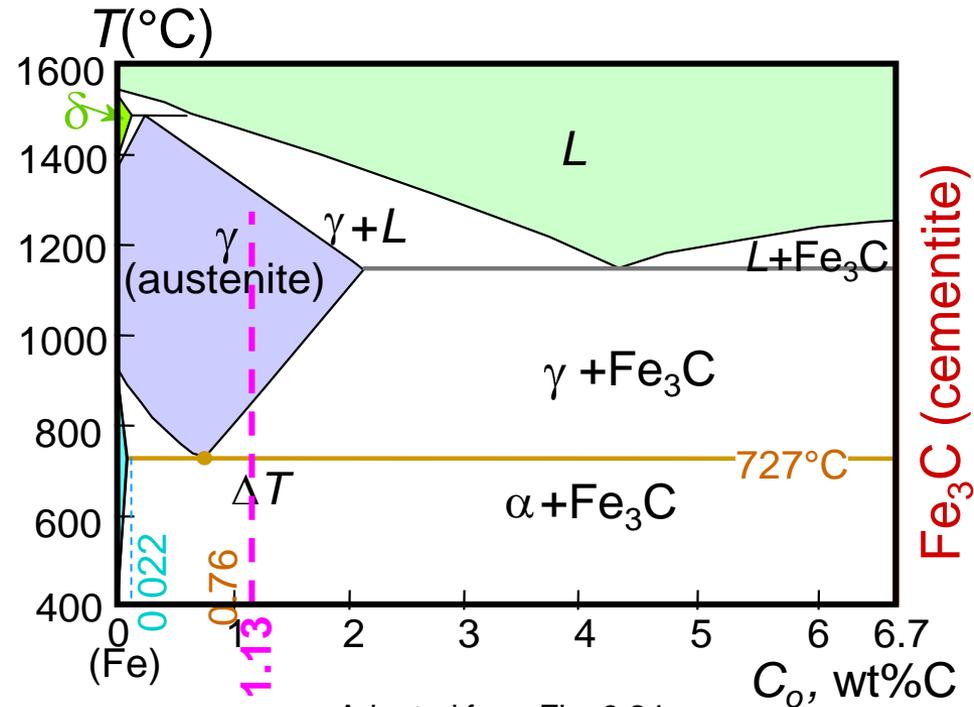
Fine (quenched to lower T)

Transformations with Proeutectoid Materials

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



Adapted from Fig. 10.16, Callister 7e.

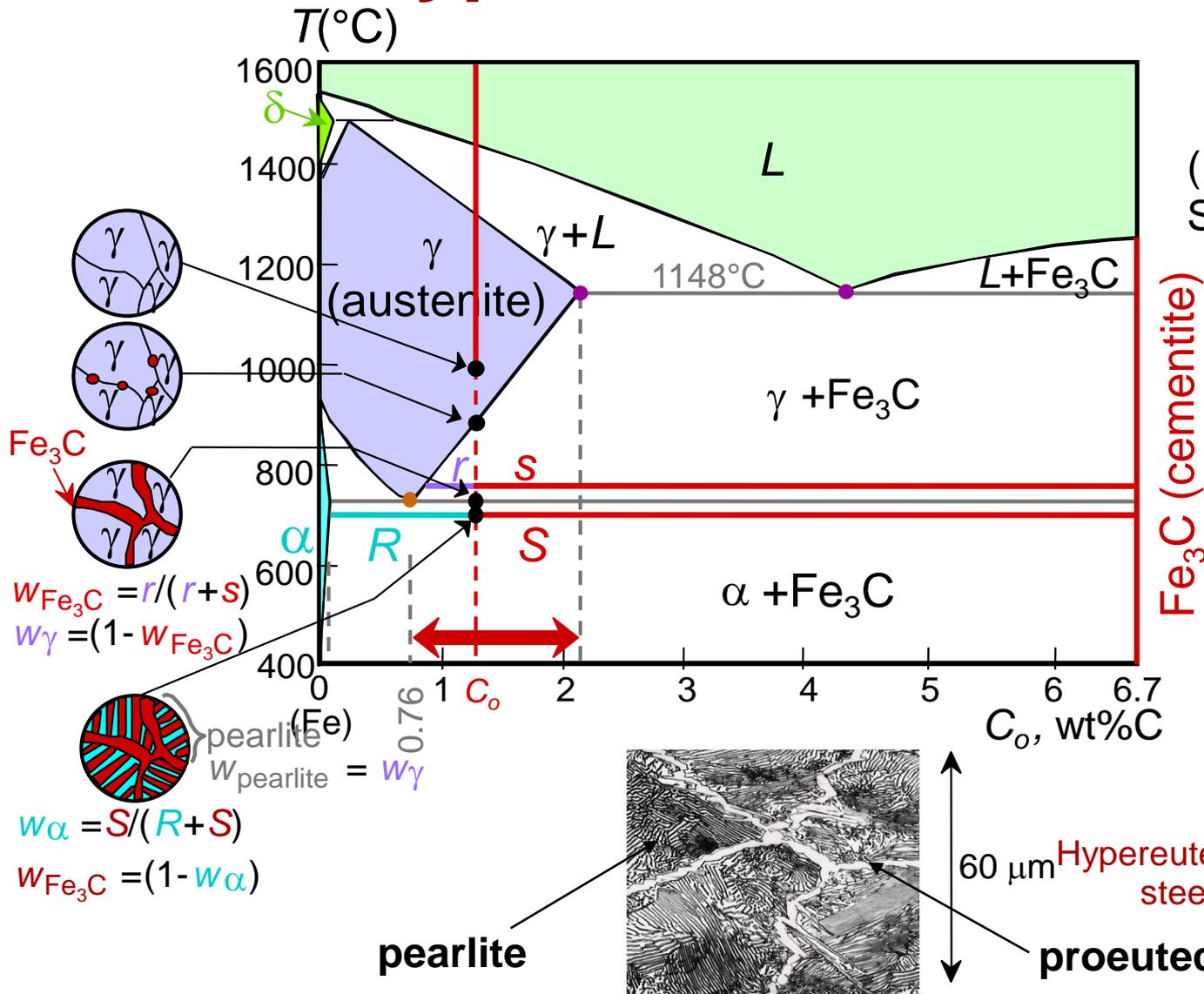


Adapted from Fig. 9.24, Callister 7e.

Hypereutectoid composition – proeutectoid cementite



Hypereutectoid Steel



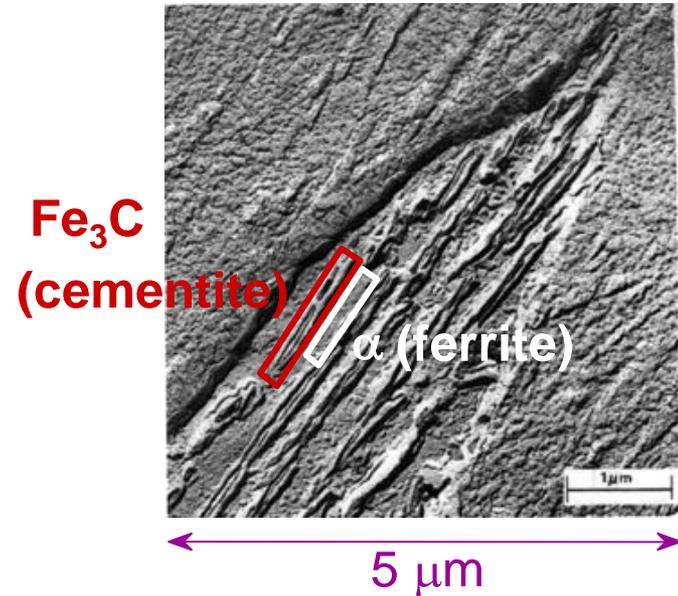
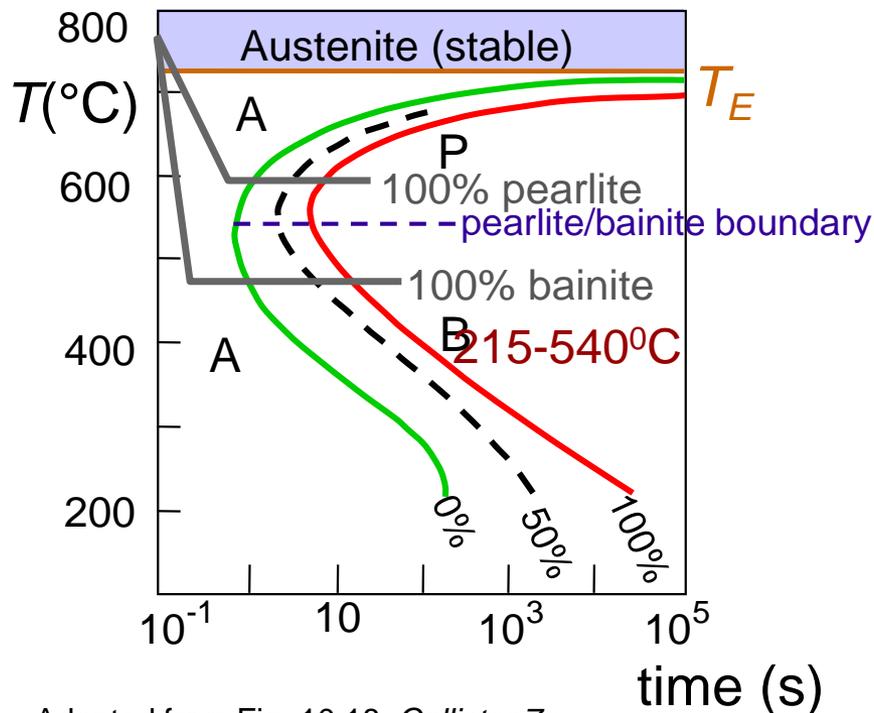
Adapted from Fig. 9.33, *Callister 7e*.



Non-Equilibrium Transformation

Products: Fe-C

- **Bainite:**
 - α lathes (strips) with long rods of Fe_3C
 - diffusion controlled.
- Isothermal Transf. Diagram



(Adapted from Fig. 10.17, Callister, 7e. (Fig. 10.17 from *Metals Handbook*, 8th ed., Vol. 8, *Metallography, Structures, and Phase Diagrams*, American Society for Metals, Materials Park, OH, 1973.)

Adapted from Fig. 10.18, Callister 7e.

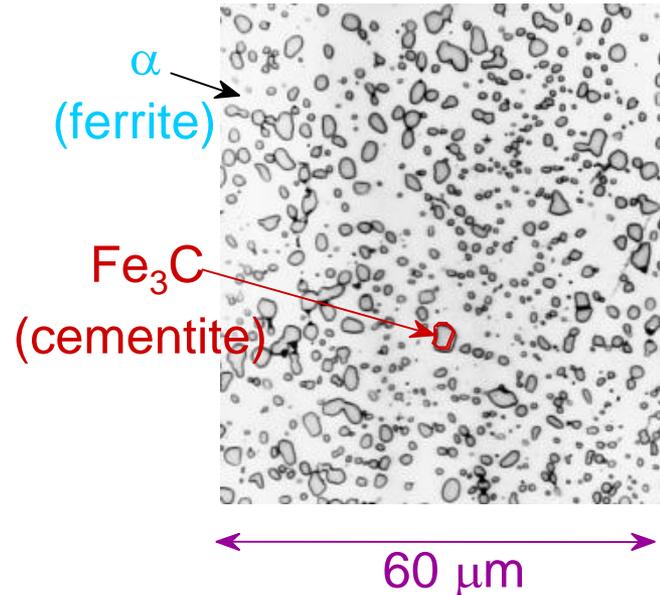
(Fig. 10.18 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1997, p. 28.)



Spheroidite: Fe-C System

- **Spheroidite:**
 - α grains with spherical Fe_3C
 - diffusion dependent.
 - heat bainite or pearlite for long times
 - reduces interfacial area (driving force)

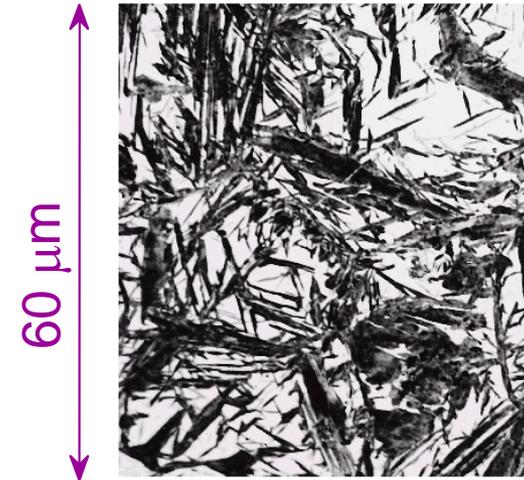
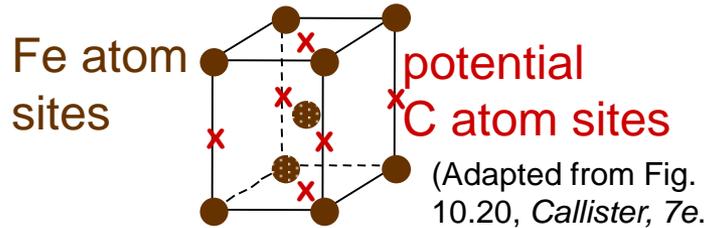
For example: 700°C, 18-24h



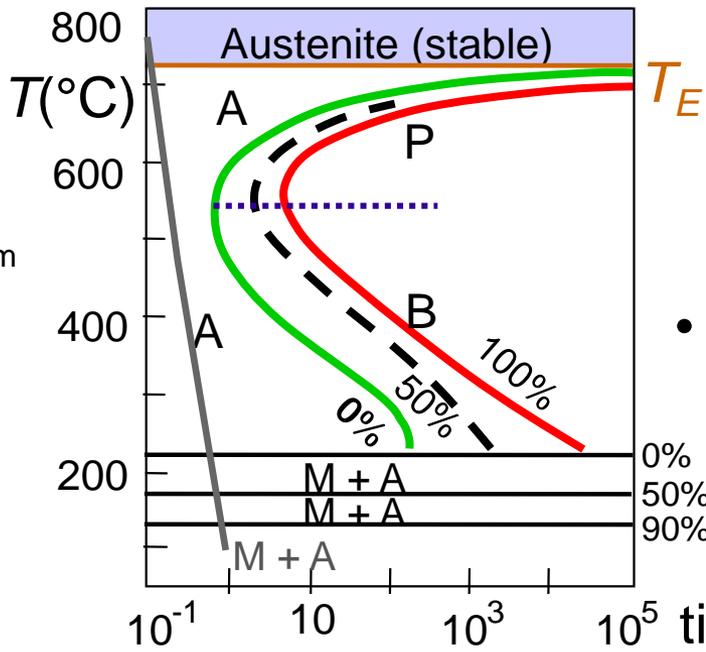
(Adapted from Fig. 10.19, *Callister, 7e.*
(Fig. 10.19 copyright United States
Steel Corporation, 1971.)

Martensite: Fe-C System

- **Martensite:**
 -- γ (FCC) to Martensite (BCT)
 (involves single atom jumps)



- Isothermal Transf. Diagram



Adapted from Fig. 10.22, Callister 7e.

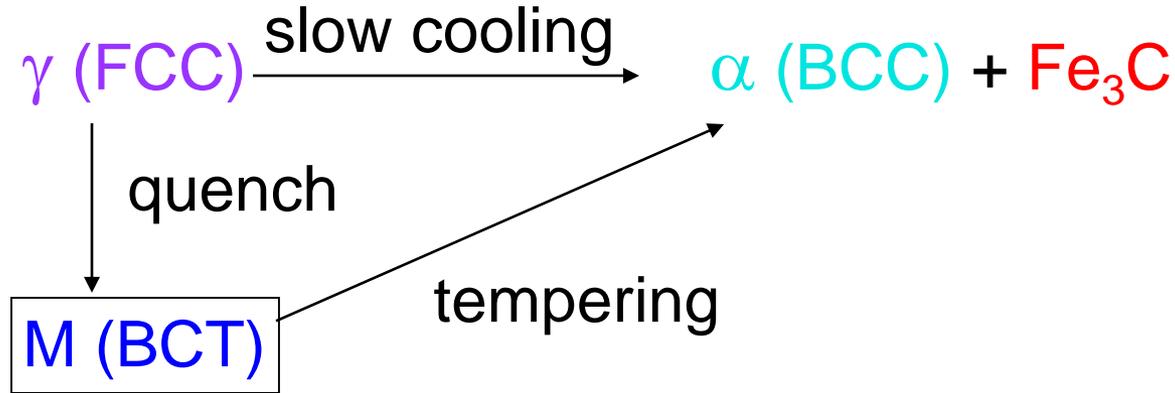
— Martensite needles
 — Austenite

(Adapted from Fig. 10.21, Callister, 7e.
 (Fig. 10.21 courtesy United States Steel Corporation.)

- γ to M transformation..
 -- is rapid! Diffusionless transformation
 -- % transf. depends on T only.



Martensite Formation



M = martensite is body centered tetragonal (BCT)

Diffusionless transformation BCT if $C > 0.15$ wt%

BCT \rightarrow few slip planes \rightarrow hard, brittle



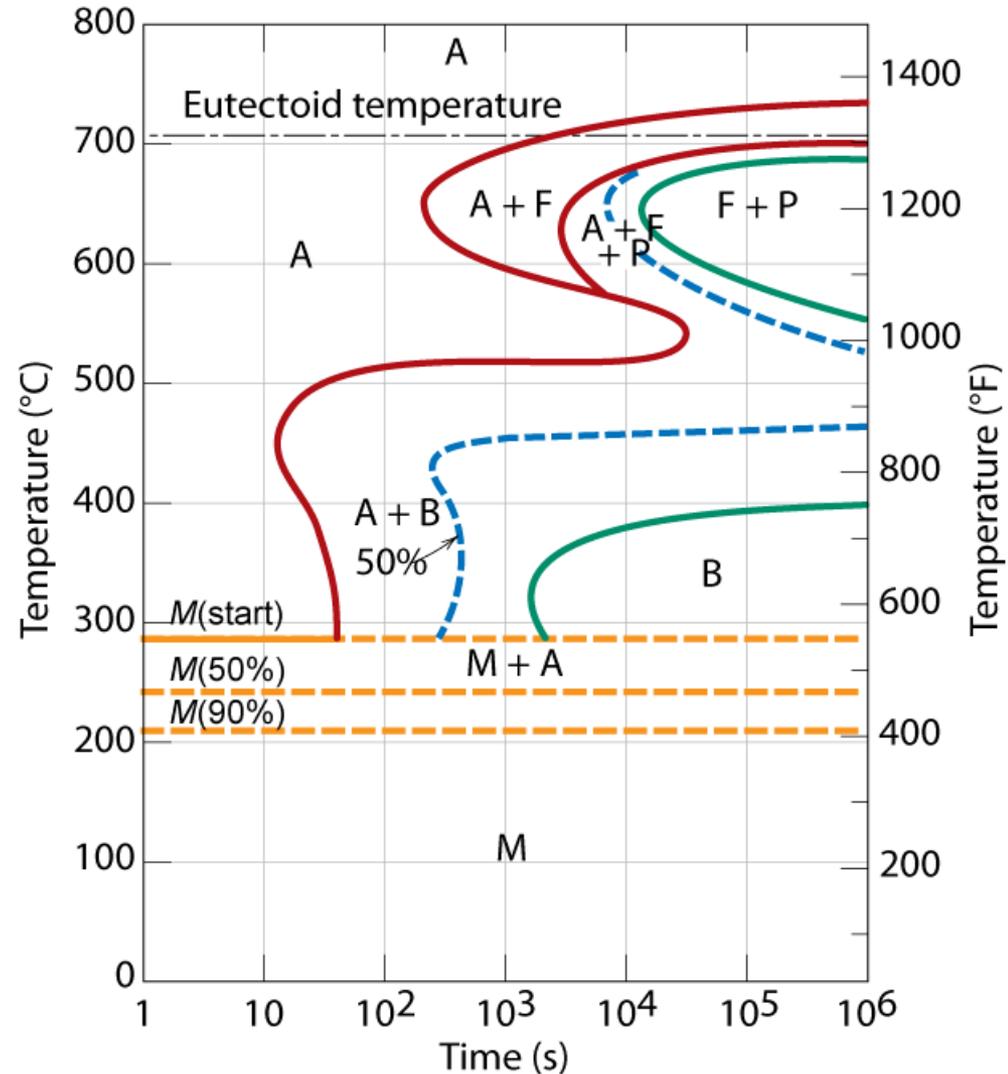
Phase Transformations of Alloys

Effect of adding other elements
Change transition temp.

Cr, Ni, Mo, Si, Mn

retard $\gamma \rightarrow \alpha + \text{Fe}_3\text{C}$
transformation

- Plain carbon steels
- Alloy steels



Adapted from Fig. 10.23, *Callister 7e*.



Cooling Curve

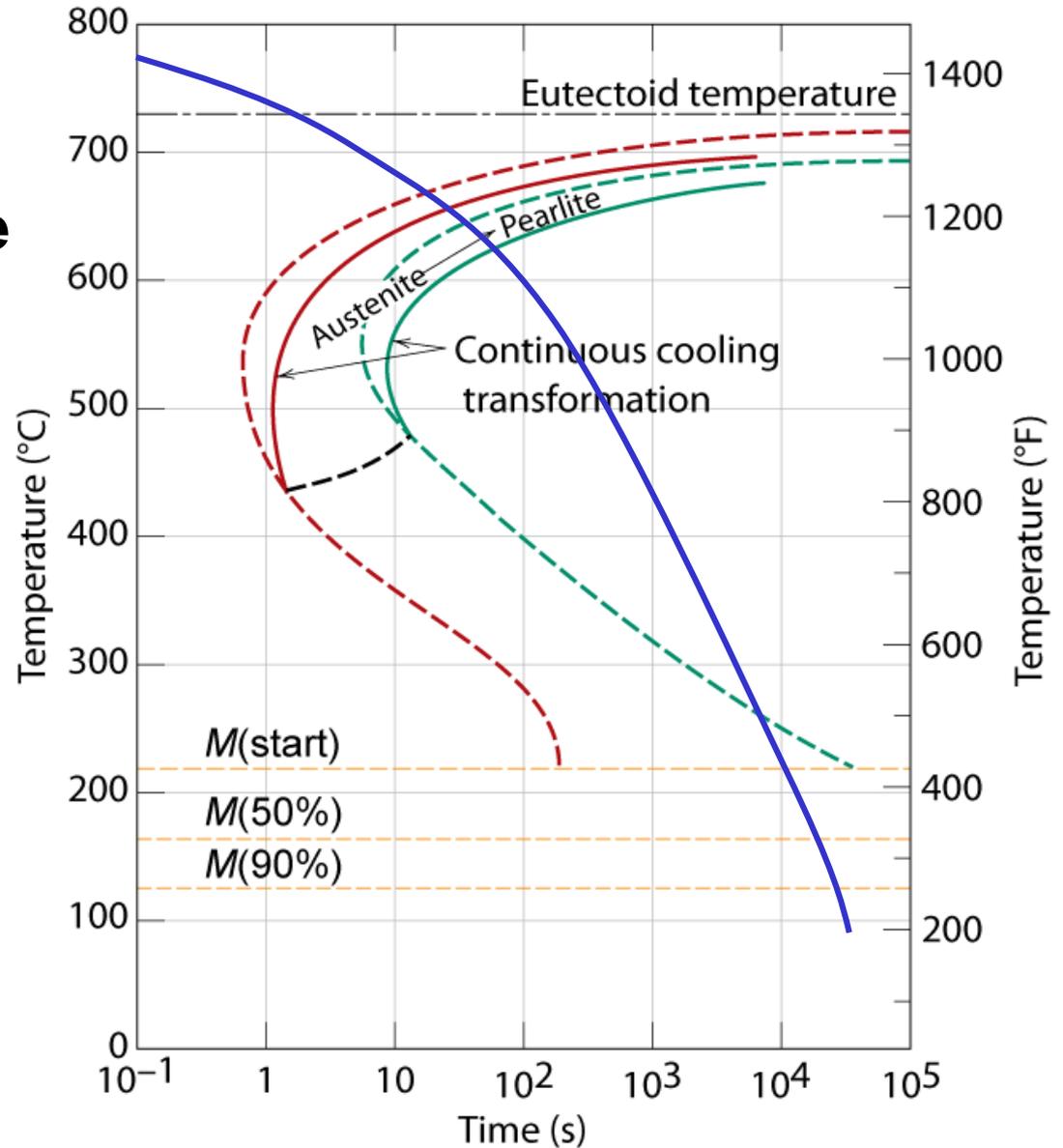
plot temp vs. time

Isothermal heat treatment is not the most practical to conduct



Continuous cooling

Adapted from Fig. 10.25, Callister 7e.



Dynamic Phase Transformations

On the isothermal transformation diagram for 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

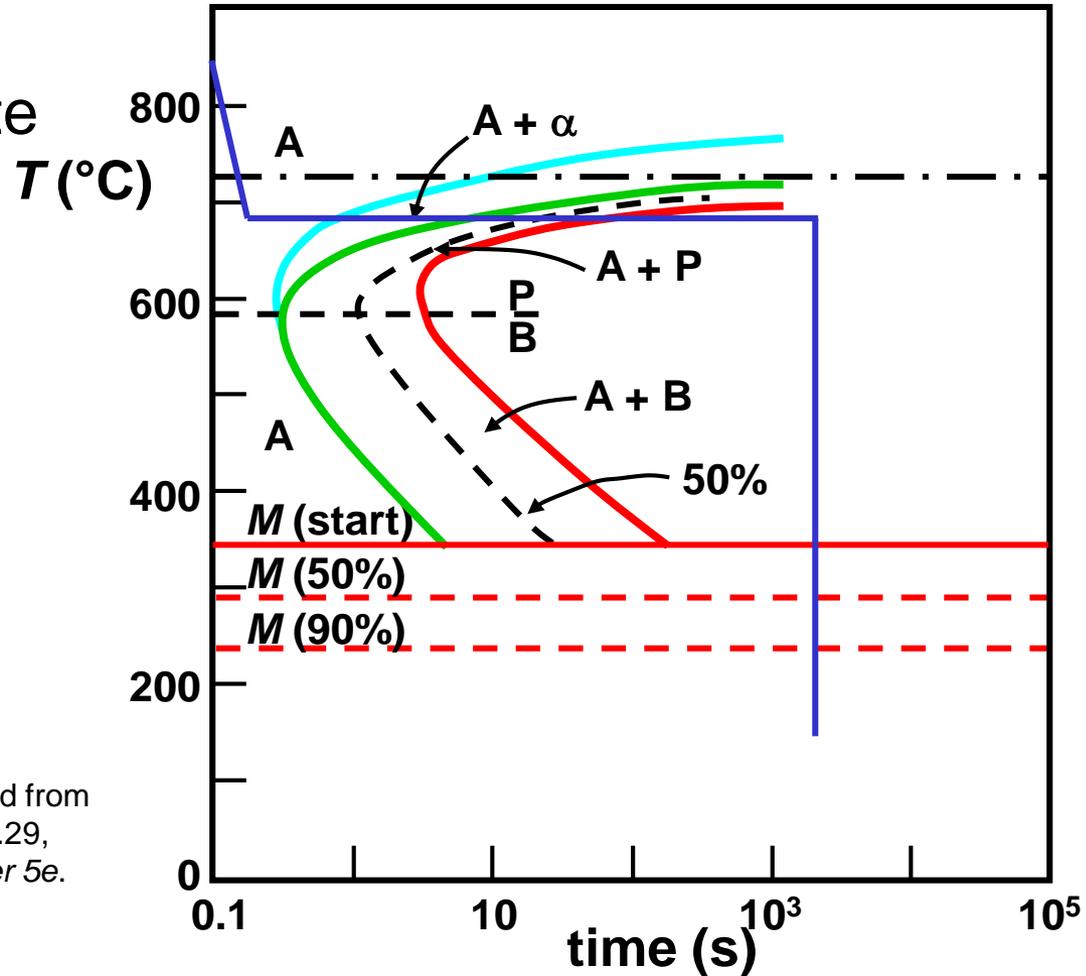


Example Problem for $C_o = 0.45 \text{ wt\%}$

a) 42% proeutectoid ferrite and 58% coarse pearlite

first make ferrite
then pearlite

course pearlite
∴ higher T



Adapted from
Fig. 10.29,
Callister 5e.

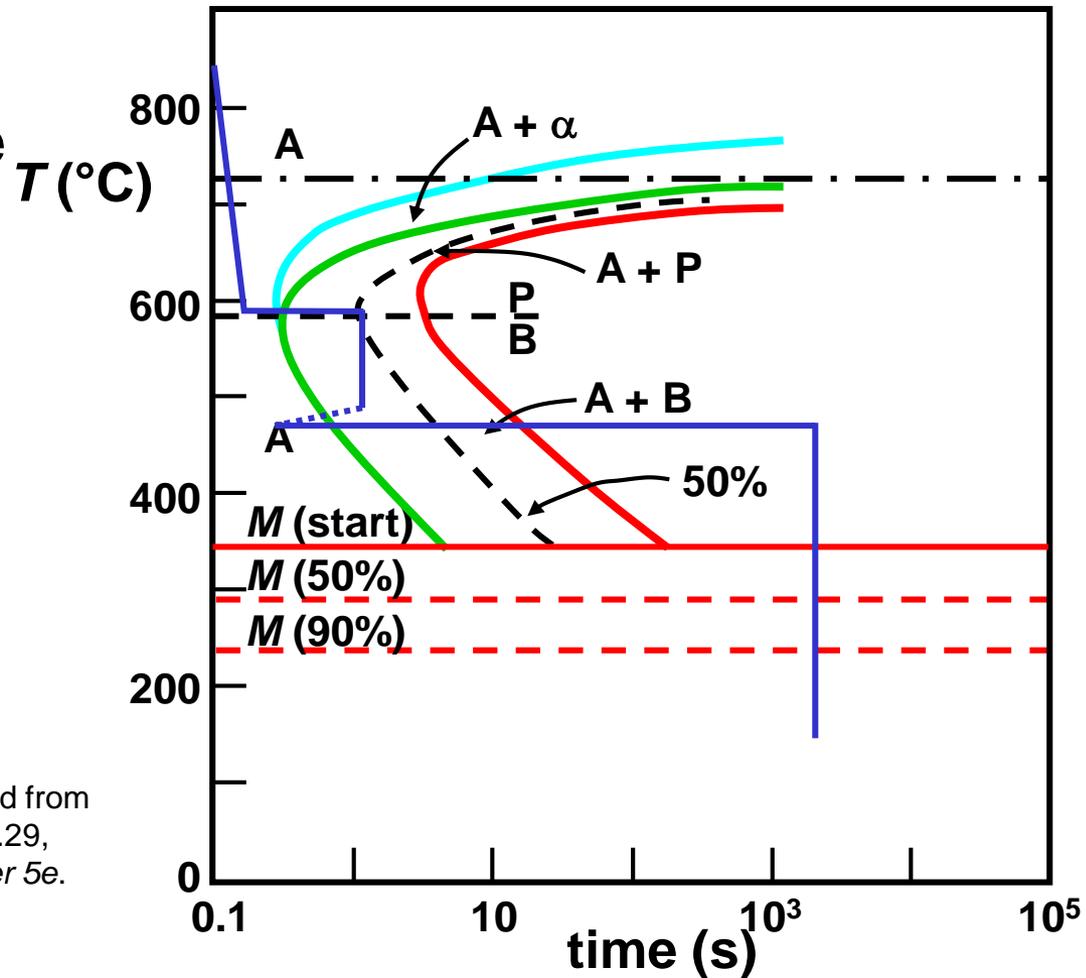


Example Problem for $C_o = 0.45 \text{ wt}\%$

b) 50% fine pearlite and 50% bainite

first make pearlite
then bainite

fine pearlite
 \therefore lower T

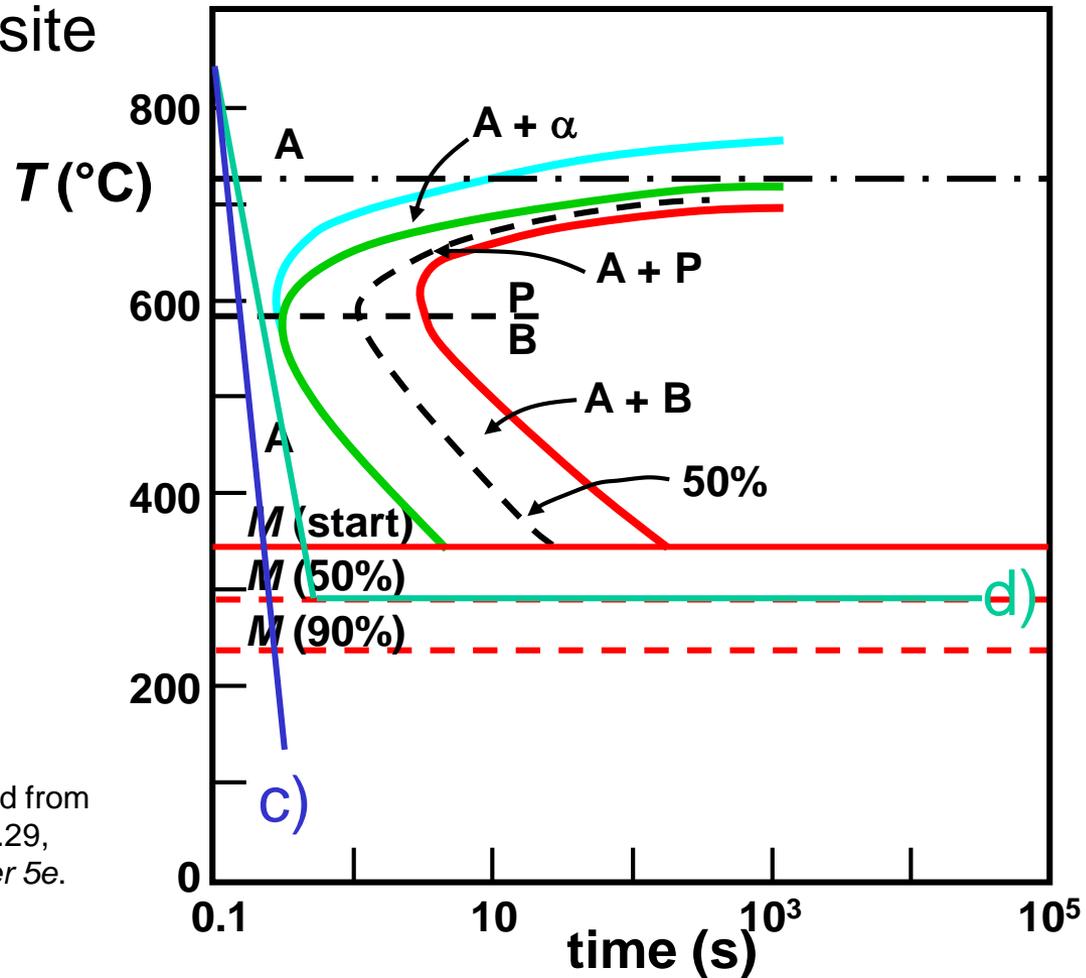


Adapted from
Fig. 10.29,
Callister 5e.



Example Problem for $C_o = 0.45 \text{ wt}\%$

- c) 100 % martensite – quench = rapid cool
- d) 50 % martensite
and 50 % austenite



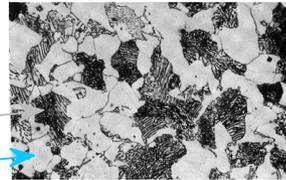
Adapted from
Fig. 10.29,
Callister 5e.



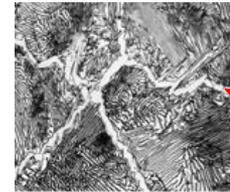
Mechanical Prop: Fe-C System (1)

- Effect of wt% C

Pearlite (med)
ferrite (soft)



$C_o < 0.76 \text{ wt\% C}$
Hypoeutectoid

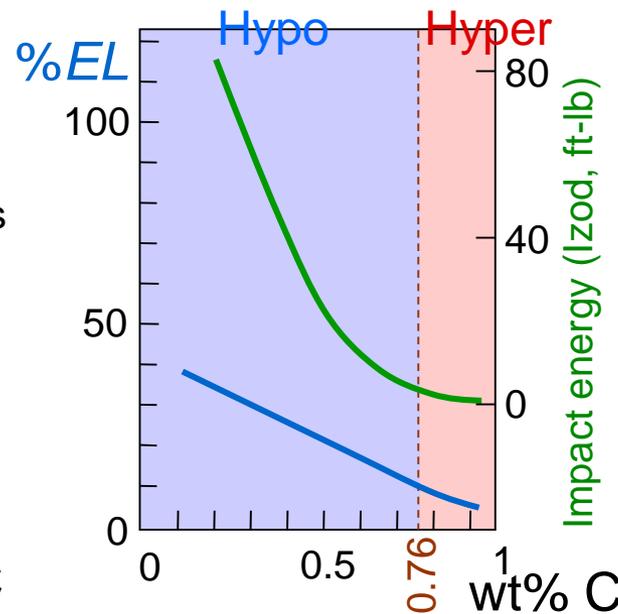
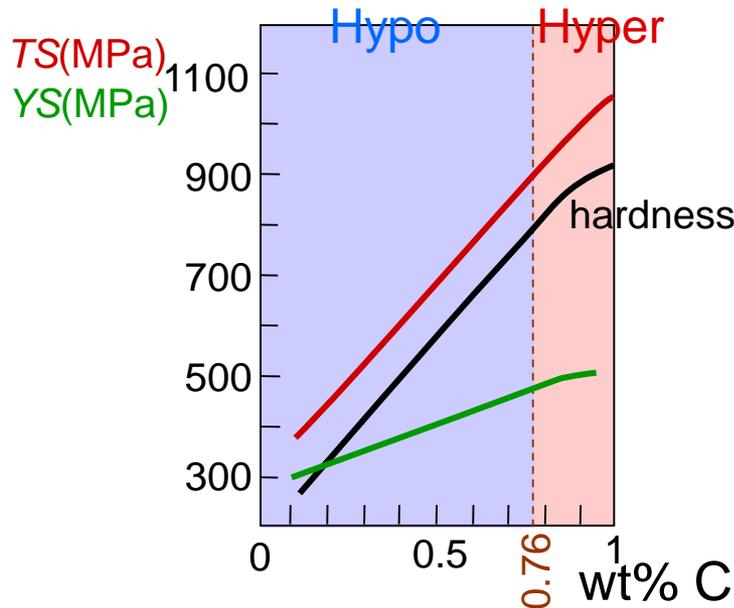


Pearlite (med)
Cementite (hard)

$C_o > 0.76 \text{ wt\% C}$
Hypereutectoid

Adapted from Fig. 9.30, *Callister 7e*. (Fig. 9.30 courtesy Republic Steel Corporation.)

Adapted from Fig. 9.33, *Callister 7e*. (Fig. 9.33 copyright 1971 by United States Steel Corporation.)



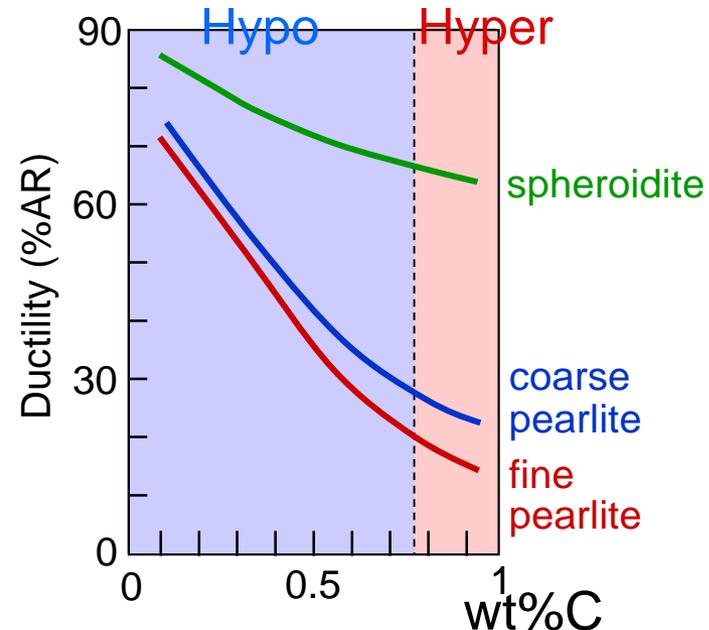
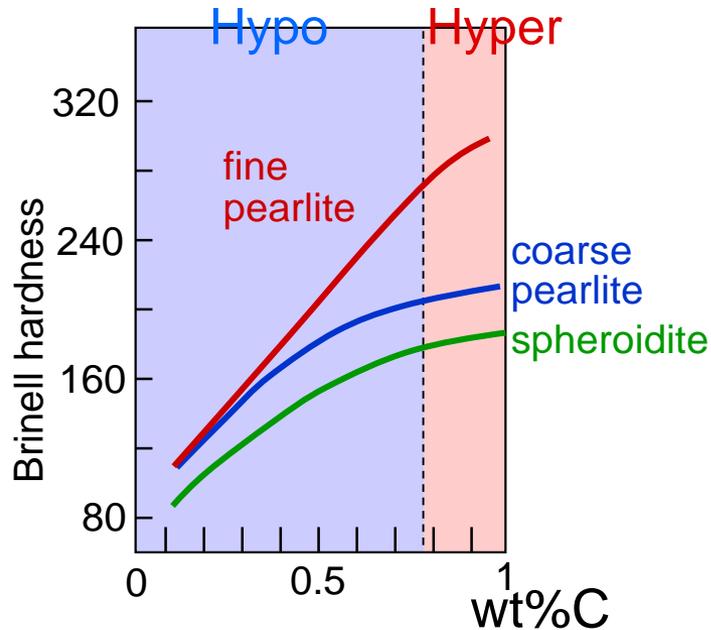
Adapted from Fig. 10.29, *Callister 7e*. (Fig. 10.29 based on data from *Metals Handbook: Heat Treating*, Vol. 4, 9th ed., V. Masseria (Managing Ed.), American Society for Metals, 1981, p. 9.)

- More wt% C: TS and YS increase, %EL decreases.



Mechanical Prop: Fe-C System (2)

- Fine vs coarse pearlite vs spheroidite



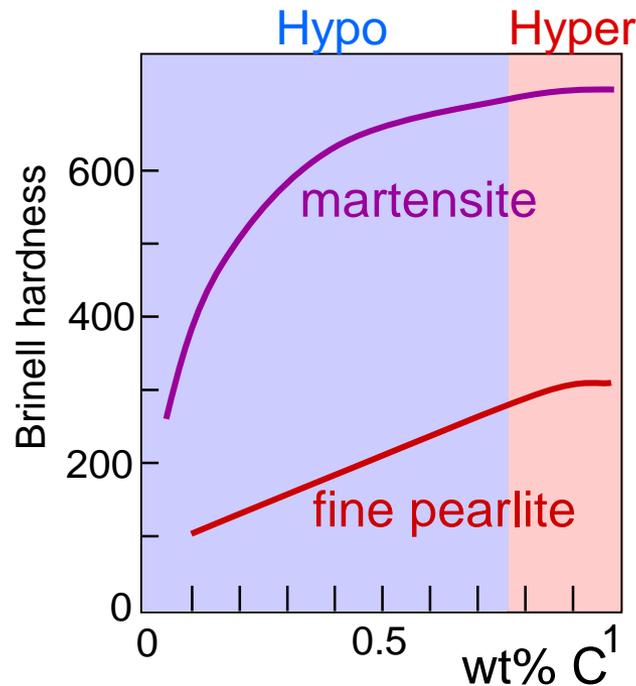
- Hardness: fine > coarse > spheroidite
- %RA: fine < coarse < spheroidite

Adapted from Fig. 10.30, *Callister 7e*.
(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 Prop: Fe-C System (3)

- Fine Pearlite vs Martensite:



Adapted from Fig. 10.32, *Callister 7e*. (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.)

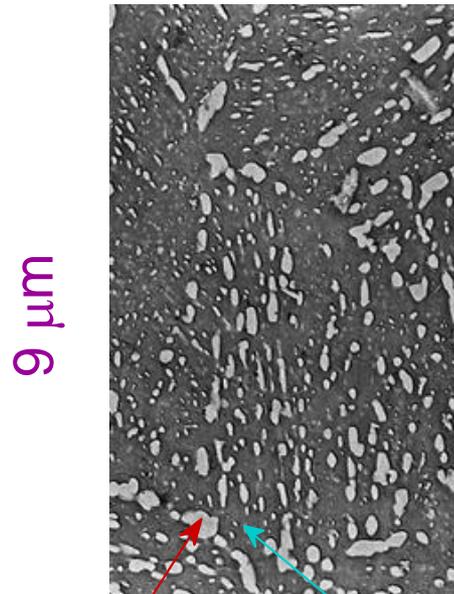
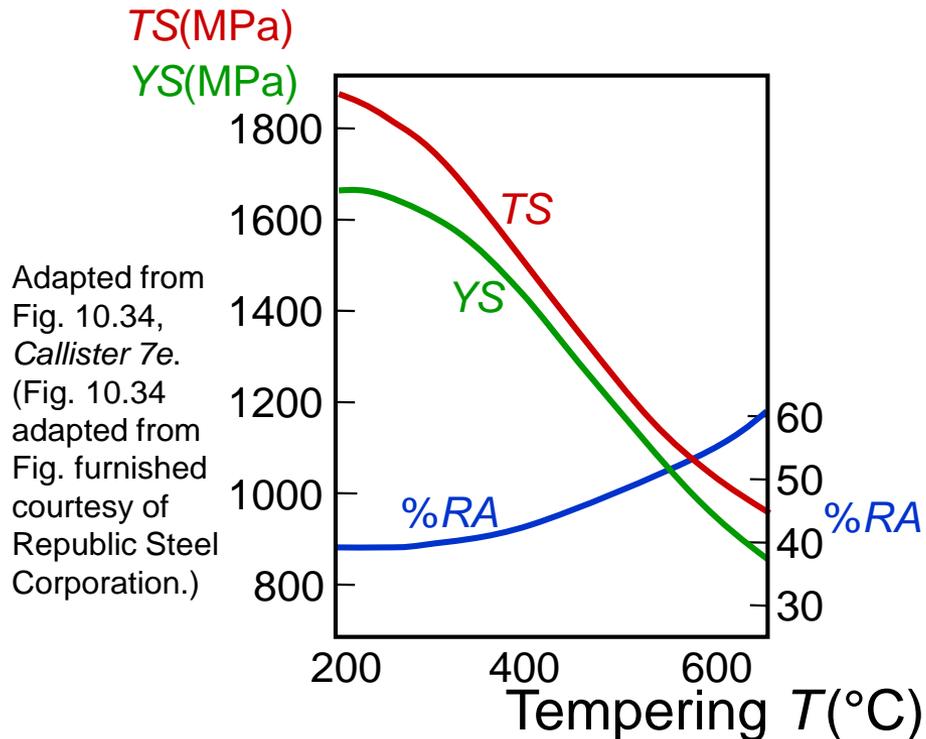
- Hardness: fine pearlite \ll martensite.

Martensite: not related to microstructure, rather to the effectiveness of the interstitial carbon atoms in hindering dislocation motion, and the relatively few slip systems for BCT structure.



Tempering Martensite

- reduces brittleness of martensite,
- reduces internal stress caused by quenching.



Adapted from Fig. 10.33, *Callister 7e*. (Fig. 10.33 copyright by United States Steel Corporation, 1971.)

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

Summary: Processing Options

Adapted from
Fig. 10.36,
Callister 7e.

