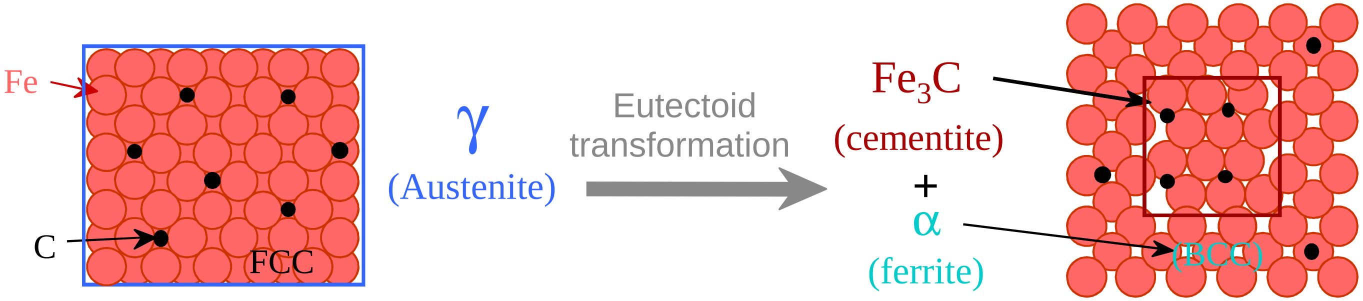
Chapter 12:
Phase Transformations

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?

Classifications of Phase Transformation

- **Small Diffusion-dependent Transformation**

  - no change in number or composition of the phases presented

  e.g., pure metal, allotropic transf., recrystallization and grain growth

- **Diffusion-dependent Transformation**

  some alteration in phase composition and in the number of phases present

  e.g., eutectoid reaction.

- **Diffusionless Transformation**

  e.g., martensitic transformation.

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 80-300ºC)
- **Heterogeneous nucleation**
  - much easier since stable “nucleating surface” is already present — e.g., mold wall, impurities in liquid phase
  - only very slight supercooling (0.1-10ºC)

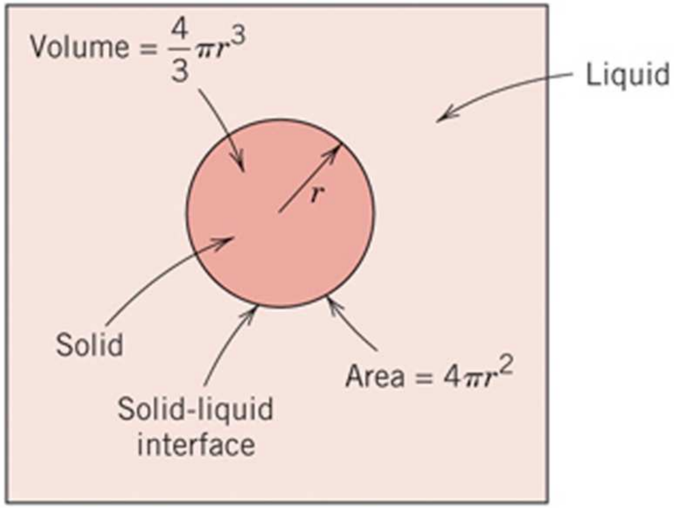
Kinetics of Phase Transformations

- The total free energy change for the system is the sum of the two factors.

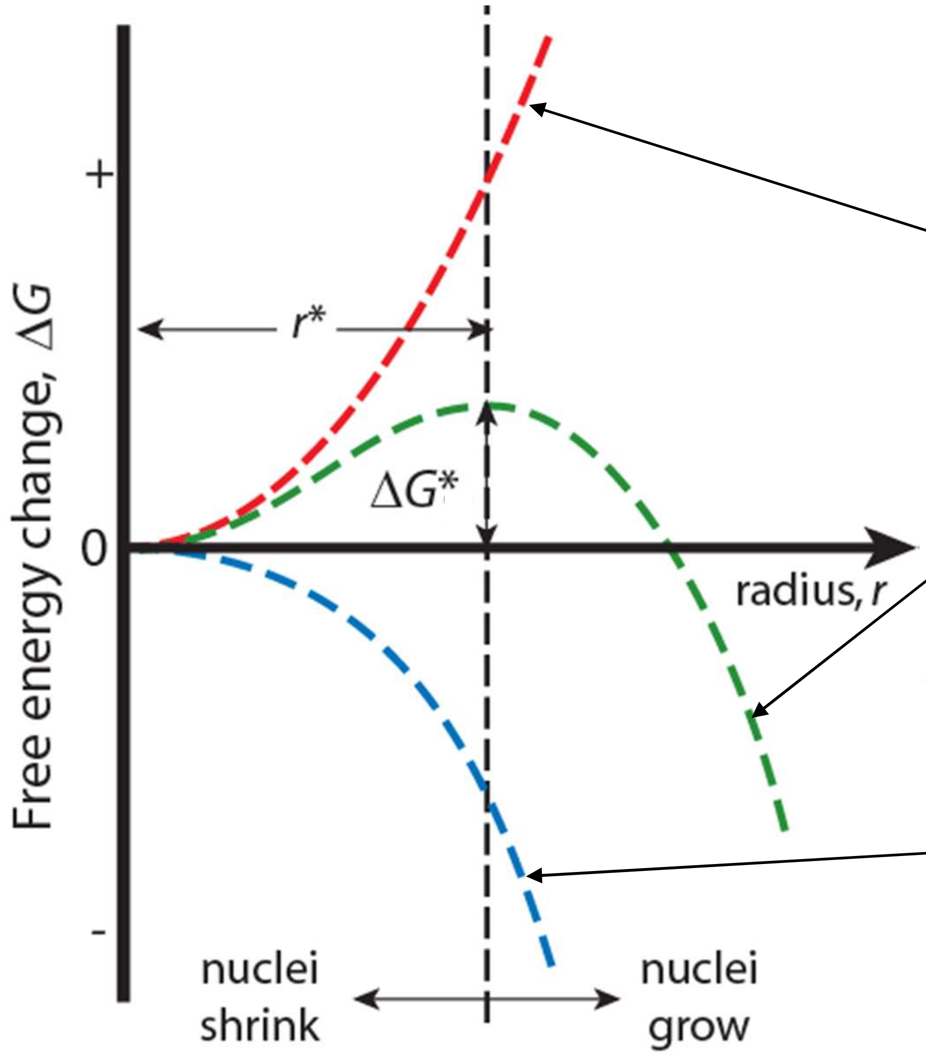
  - The volume free energy goes up as the cube of the radius

  - The surface free energy goes up as the square of the radius

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



Homogeneous Nucleation & Energy Effects



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

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

g = surface tension

$$\Delta G_T = \text{Total Free Energy} = \Delta G_S + \Delta G_V$$

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)

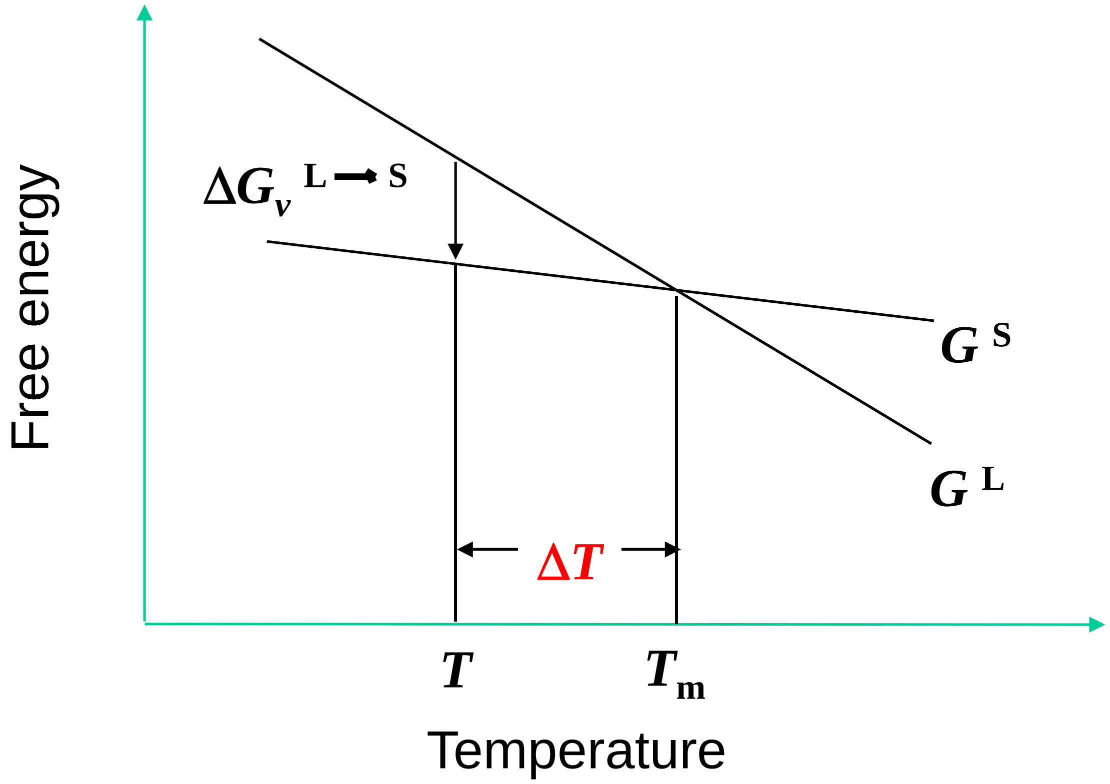
Adapted from Fig.10.2(b), *Callister & Rethwisch 8e.*

Effect of Temperature on Volume Free Energy Change (Driving Force)

$$\Delta G_v = \Delta H_f - T\Delta S = \Delta H_f (T_m - T)/T_m$$

ΔH_f : latent heat of fusion (the heat given up during solidification)

T_m : the equilibrium solidification temperature



Solidification

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

r^* = critical radius

γ = surface free energy

T_m = melting temperature

ΔH_f = latent heat of solidification

$\Delta T = T_m - T$ = supercooling

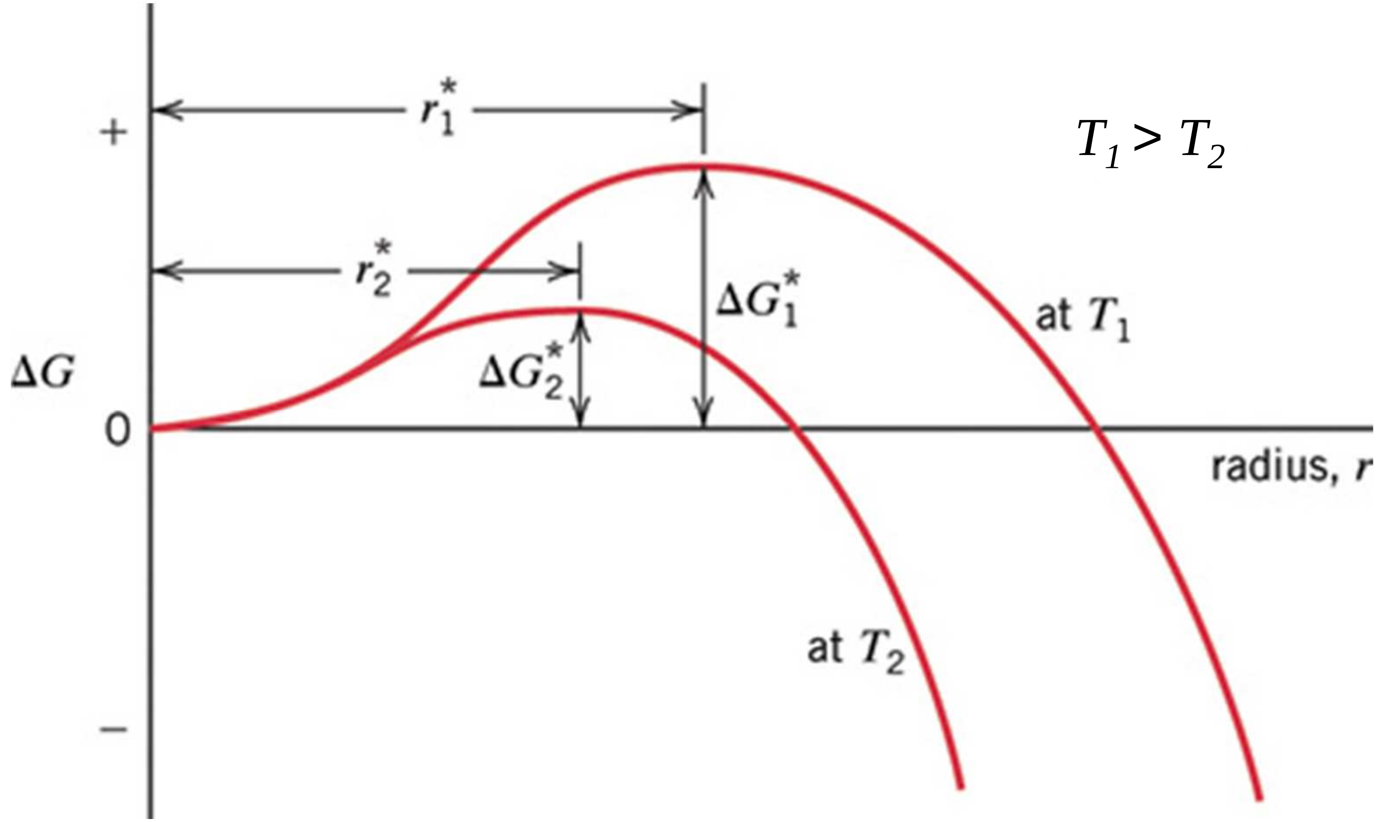
Note: ΔH_f and γ are weakly dependent on ΔT

$\therefore$ r^* decreases as ΔT increases

For typical ΔT $r^* \sim 10$ nm

Influence of Increasing Undercooling

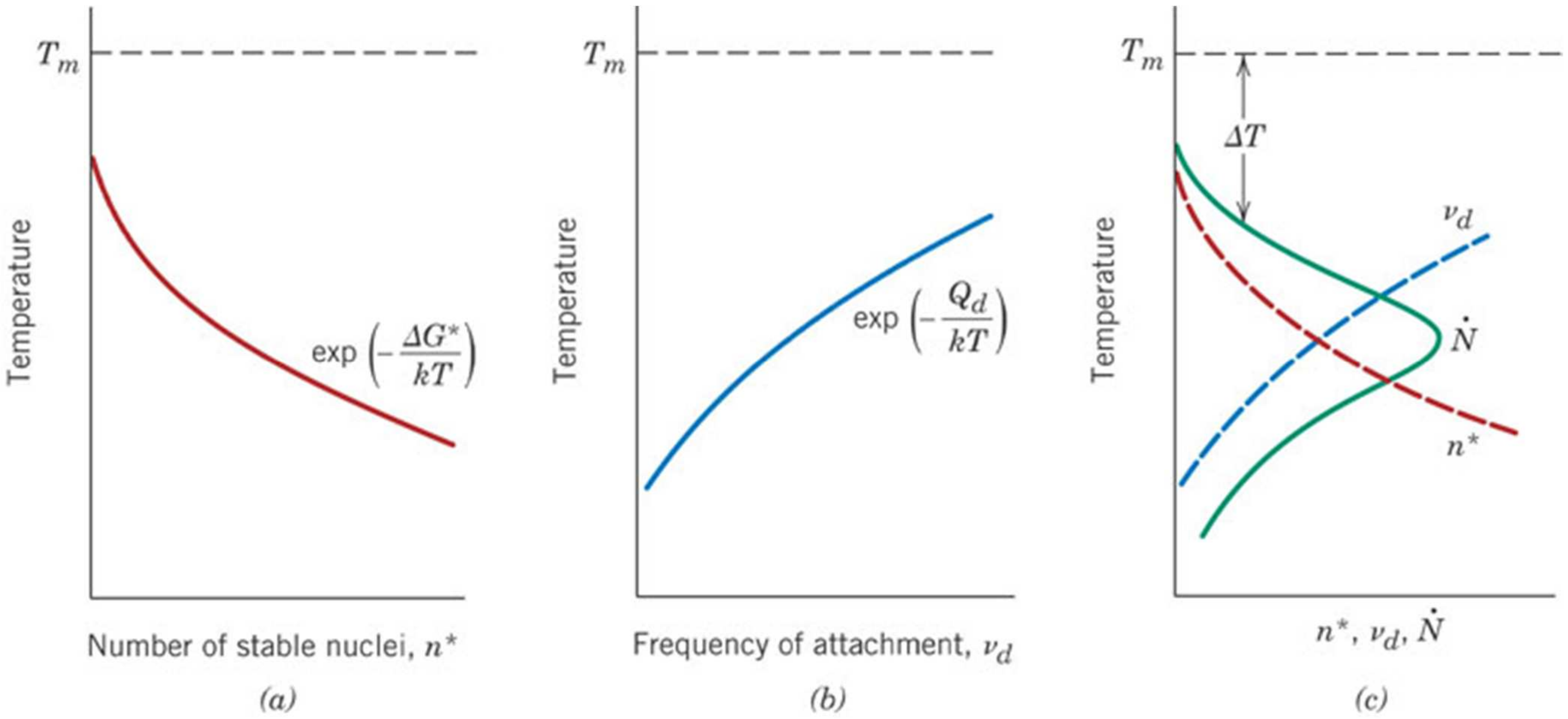
$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\cdot\left(\frac{1}{T_m - T}\right),\ \ \Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\cdot\frac{1}{(T_m - T)^2}$$



$T_1 > T_2$

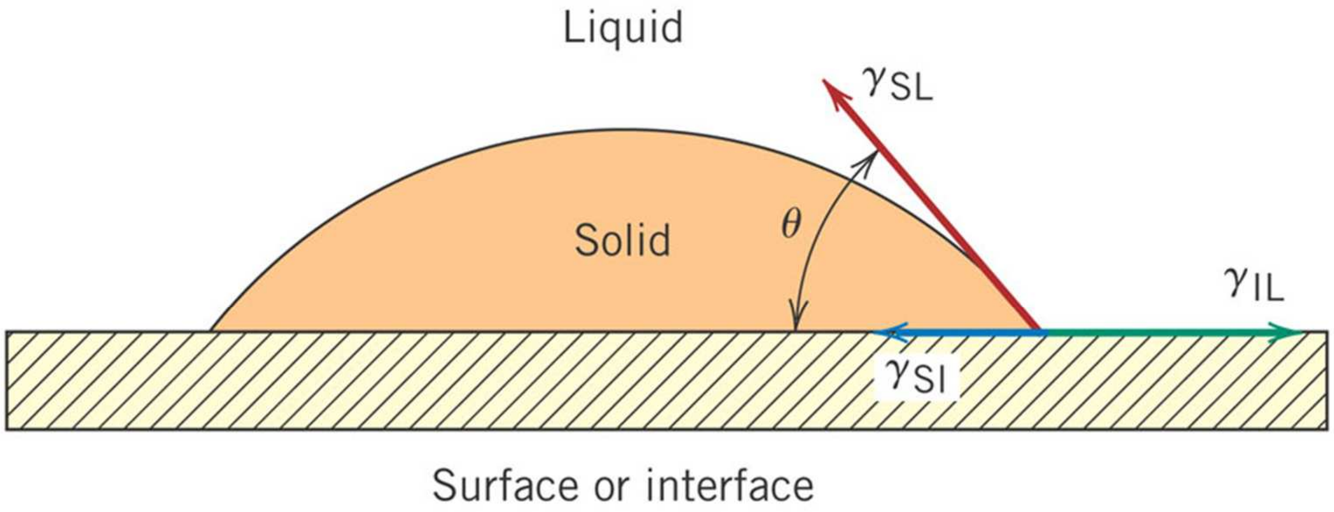
Free-energy-versus-embryo/nucleus-radius curves for two different temperatures.

Nucleation rate v.s. Temperature



Heterogeneous Nucleation

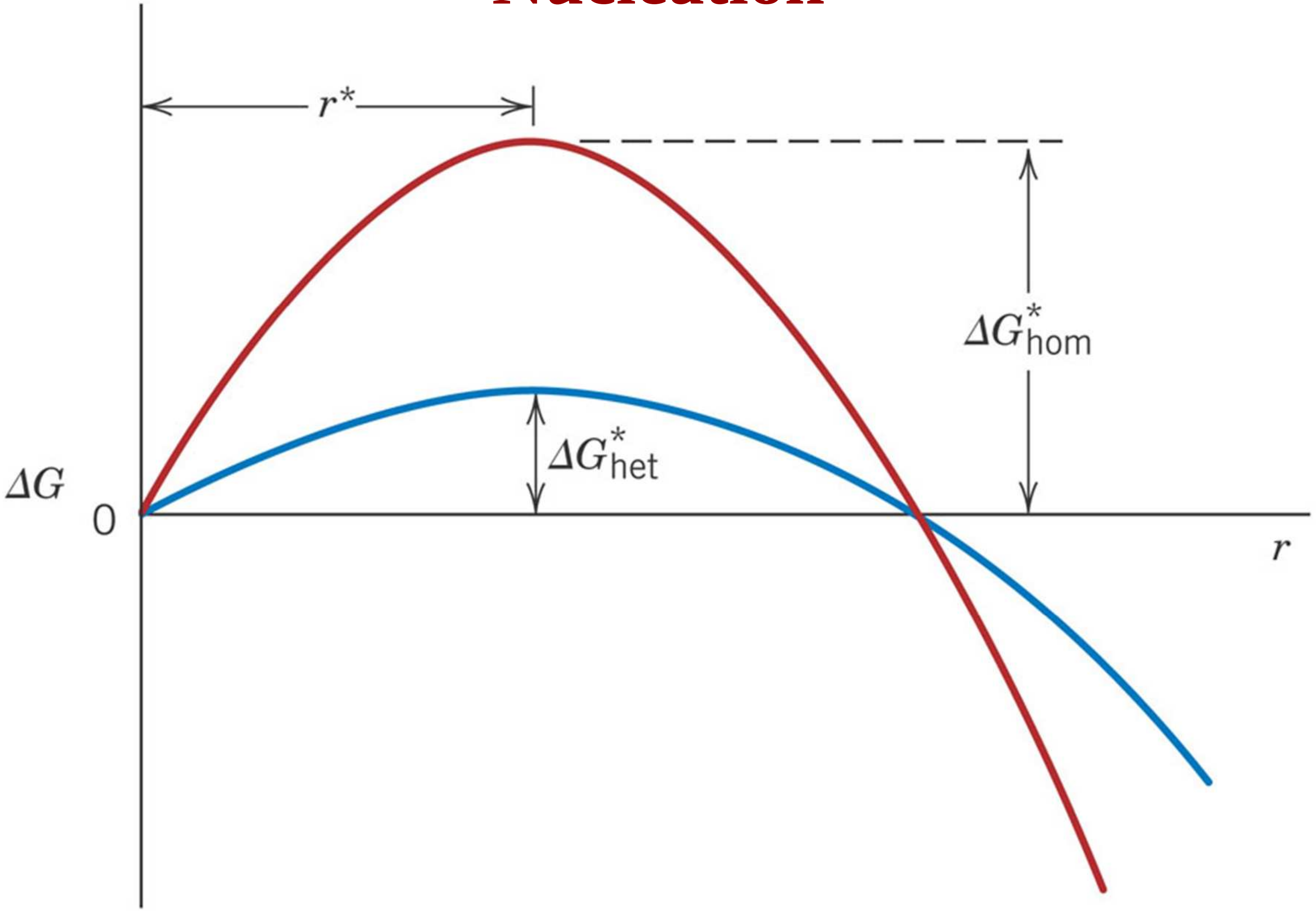
$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right) \cdot \left(\frac{1}{T_m - T}\right), \quad \Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right) \cdot \frac{1}{(T_m - T)^2}$$



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

$$\Delta G_{het} = \Delta G_{hom} \times S(\theta)$$

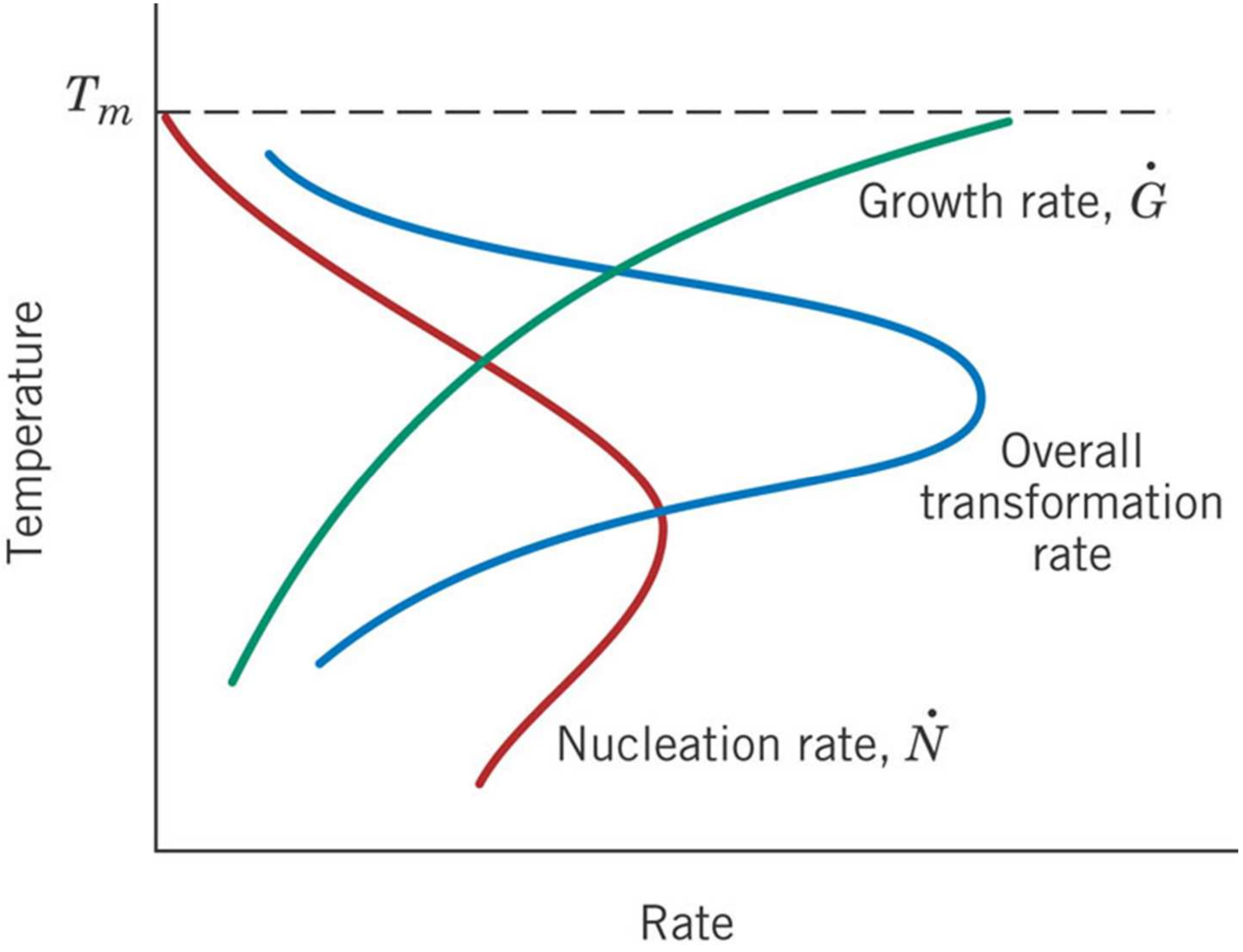
Homogeneous v.s Heterogeneous Nucleation



Overall Transformation Rate

Growth

Particle growth occurs by atomic diffusion



Rate of Phase Transformations

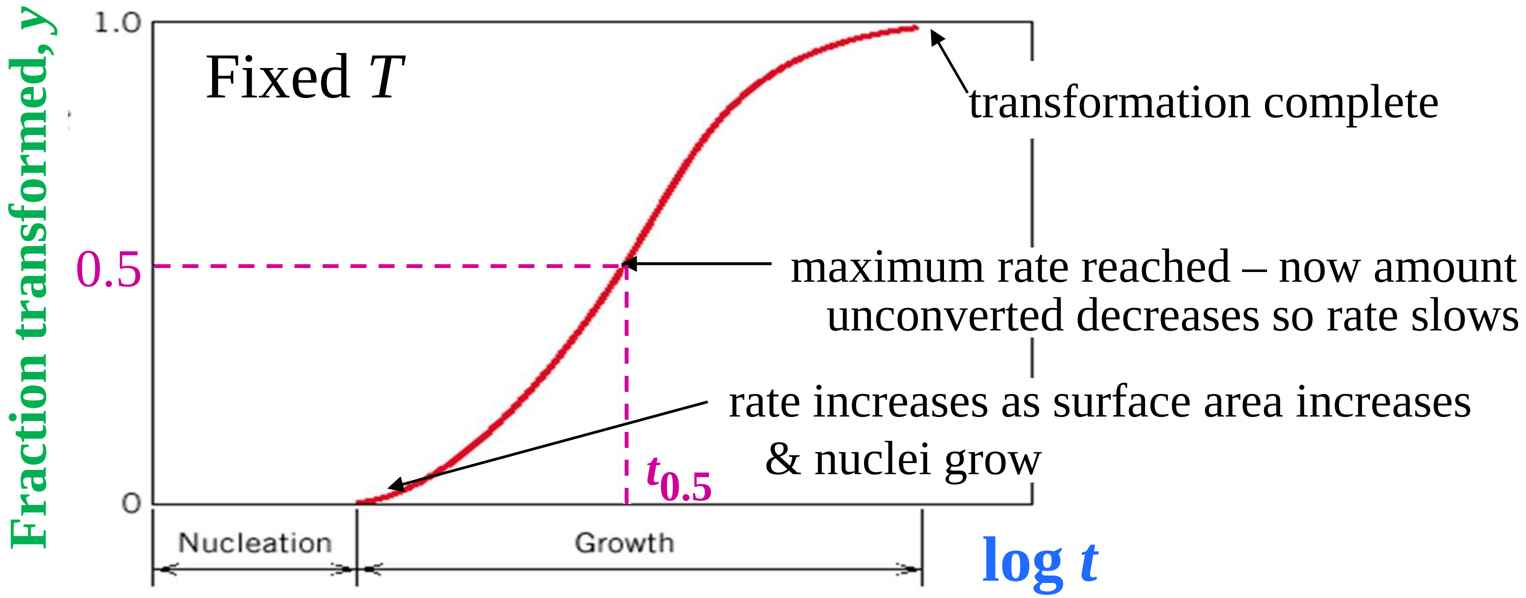
Kinetics - study of reaction rates of phase transformations

- 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



transformation complete

maximum rate reached – now amount unconverted decreases so rate slows

rate increases as surface area increases & nuclei grow

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

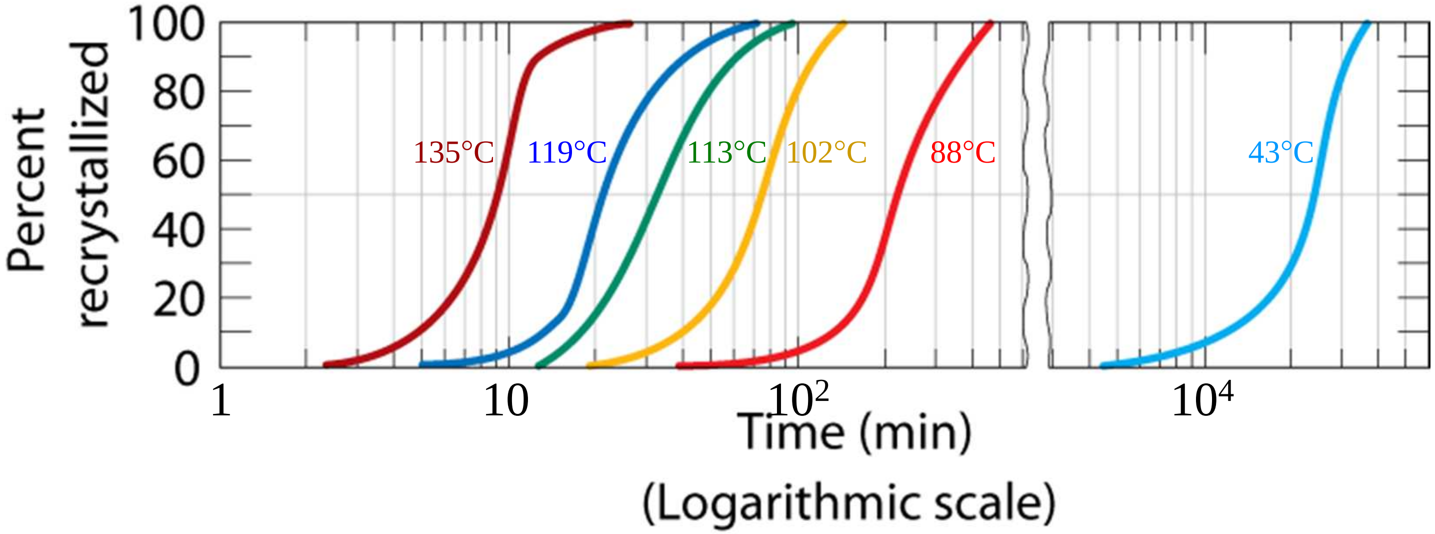
Avrami equation => $y = 1 - \exp(-kt^n)$

fraction transformed — **time**

- $\boldsymbol{k}$ & $\boldsymbol{n}$ are transformation specific parameters

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

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

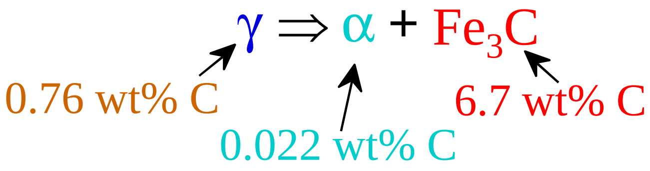
$$rate = 1/t_{0.5}$$

rate increases with increasing temperature

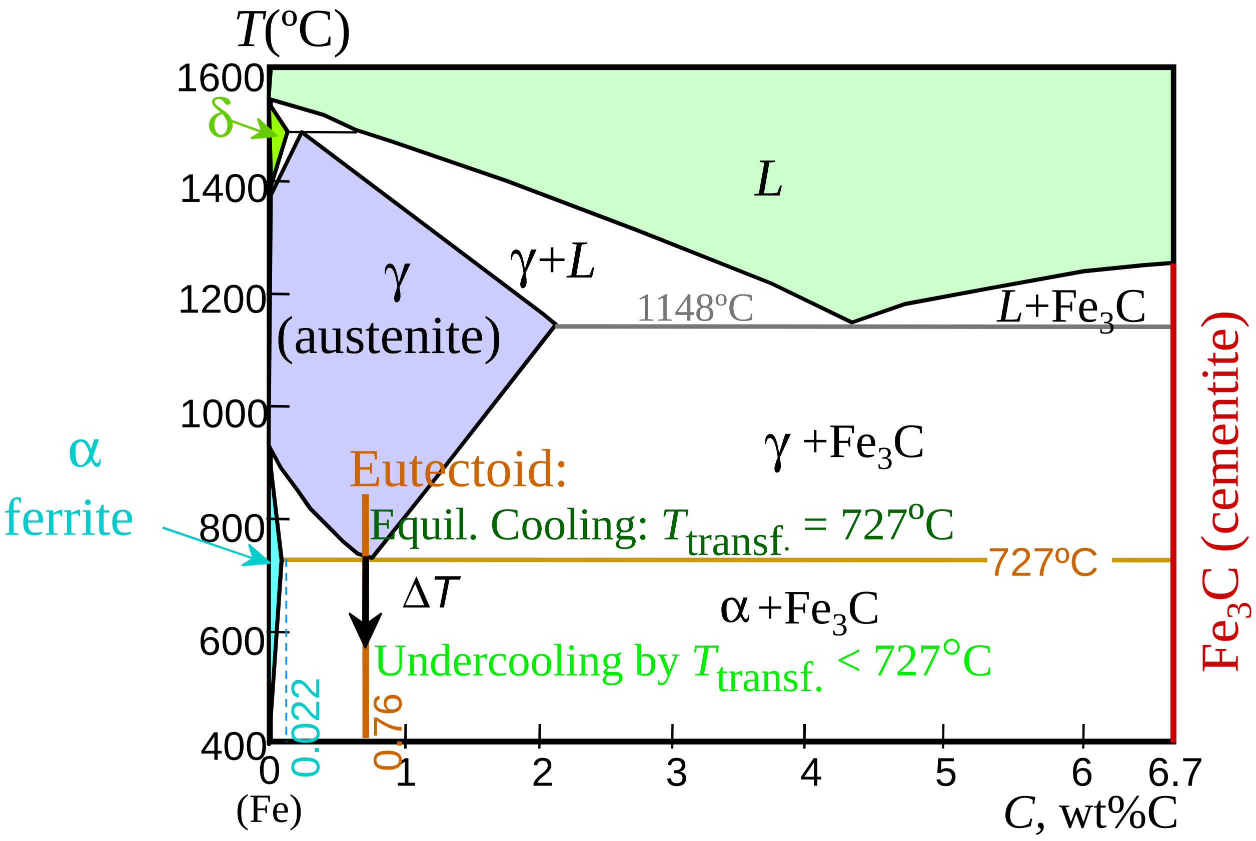
- Rate often so slow that attainment of equilibrium state not possible!

Transformations & Undercooling

- Eutectoid transf. (Fe-Fe_3C system):
- For transf. to occur, must cool to below 727°C (i.e., must "undercool")



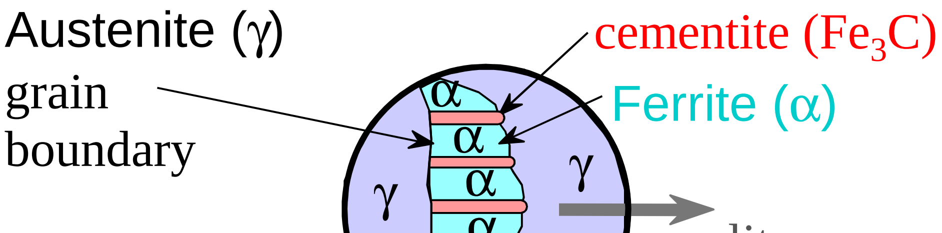
$\gamma \Rightarrow \alpha + Fe_3C$



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.)

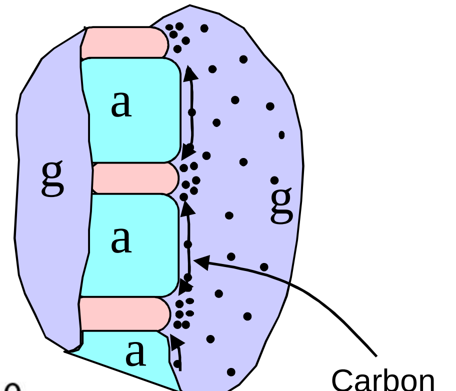
The Fe-Fe$_3$C Eutectoid Transformation

- Transformation of austenite to pearlite:

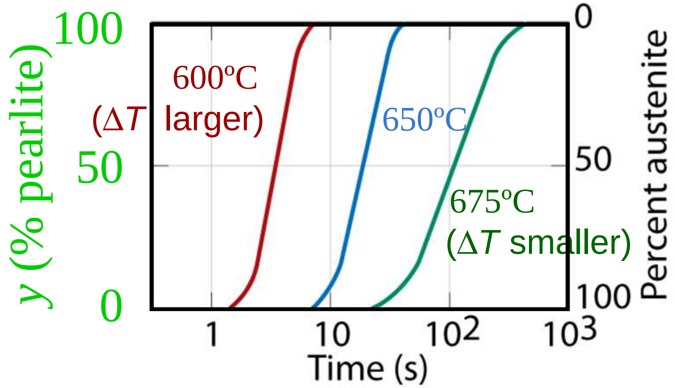


Adapted from Fig. 9.15, *Callister & Rethwisch 8e.*

Diffusion of C during transformation



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



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

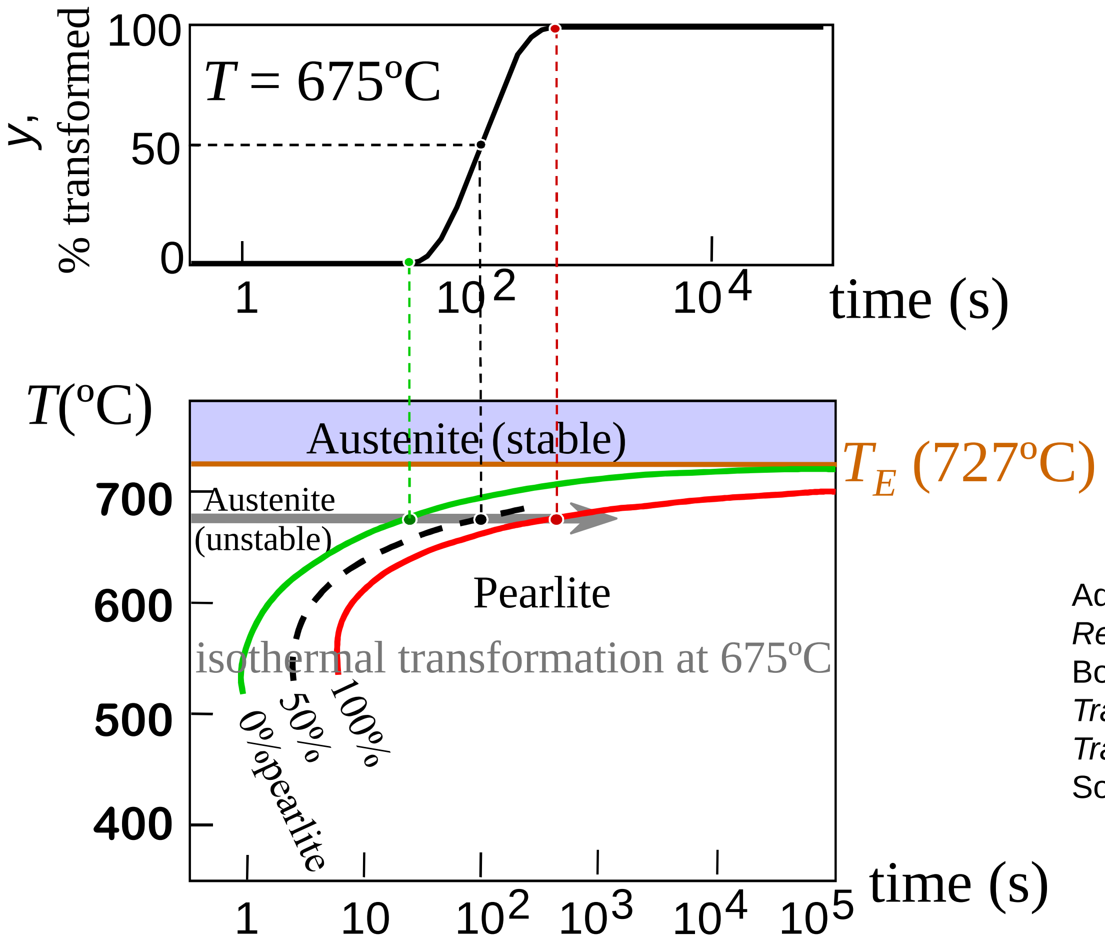
Coarse pearlite → formed at **higher** temperatures – relatively soft

Fine pearlite → formed at lower temperatures – relatively hard

Generation of Isothermal Transformation Diagrams

Consider:

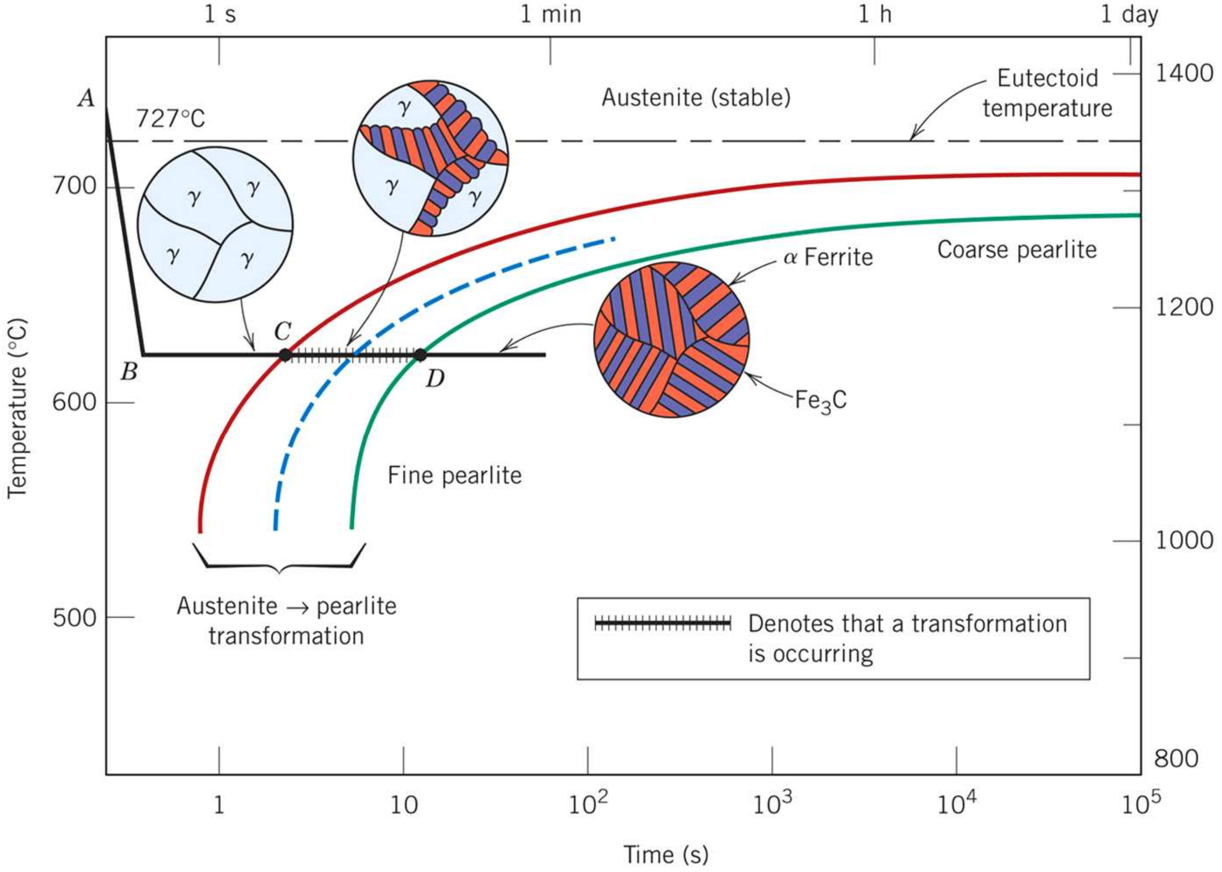
- The Fe-Fe_3C system, for C_0 = 0.76 wt% C
- A transformation temperature of 675ºC.



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

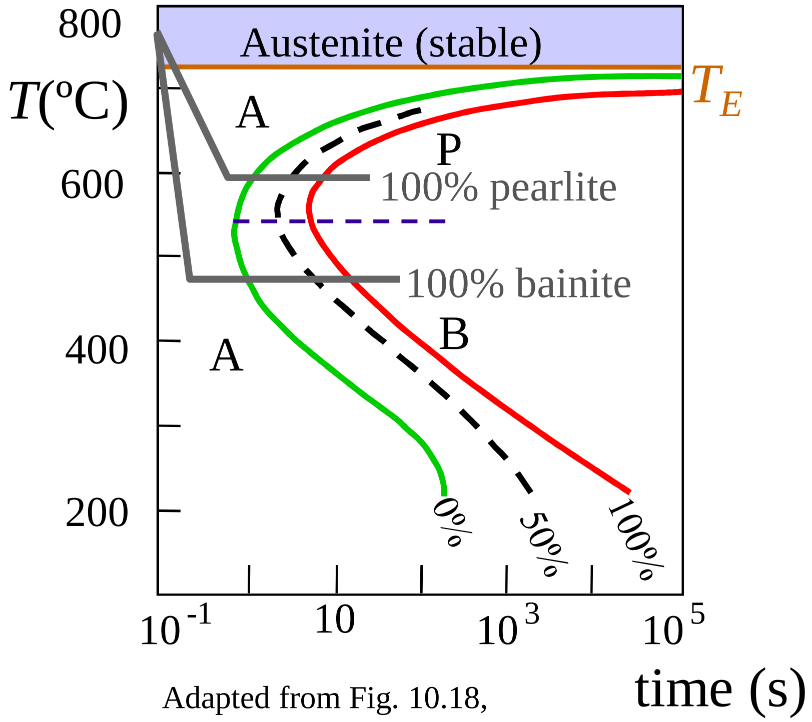
- Eutectoid composition, C_0 = 0.76 wt% C
- Begin at T > 727ºC
- Rapidly cool to 625ºC
- Hold T (625ºC) constant (isothermal treatment)



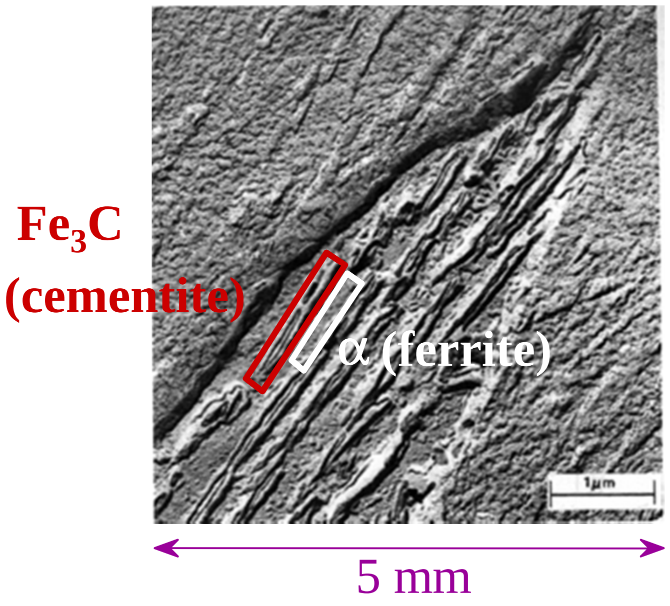
Adapted from Fig. 10.14,*Callister & Rethwisch 8e.* (Fig. 10.14 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1997, p. 28.)

Bainite: Another Fe-Fe$_3$C Transformation Product

- Bainite:
  - -- elongated Fe$_3$C particles in a-ferrite matrix
  - -- diffusion controlled
- Isothermal Transf. Diagram, C_0 = 0.76 wt% C

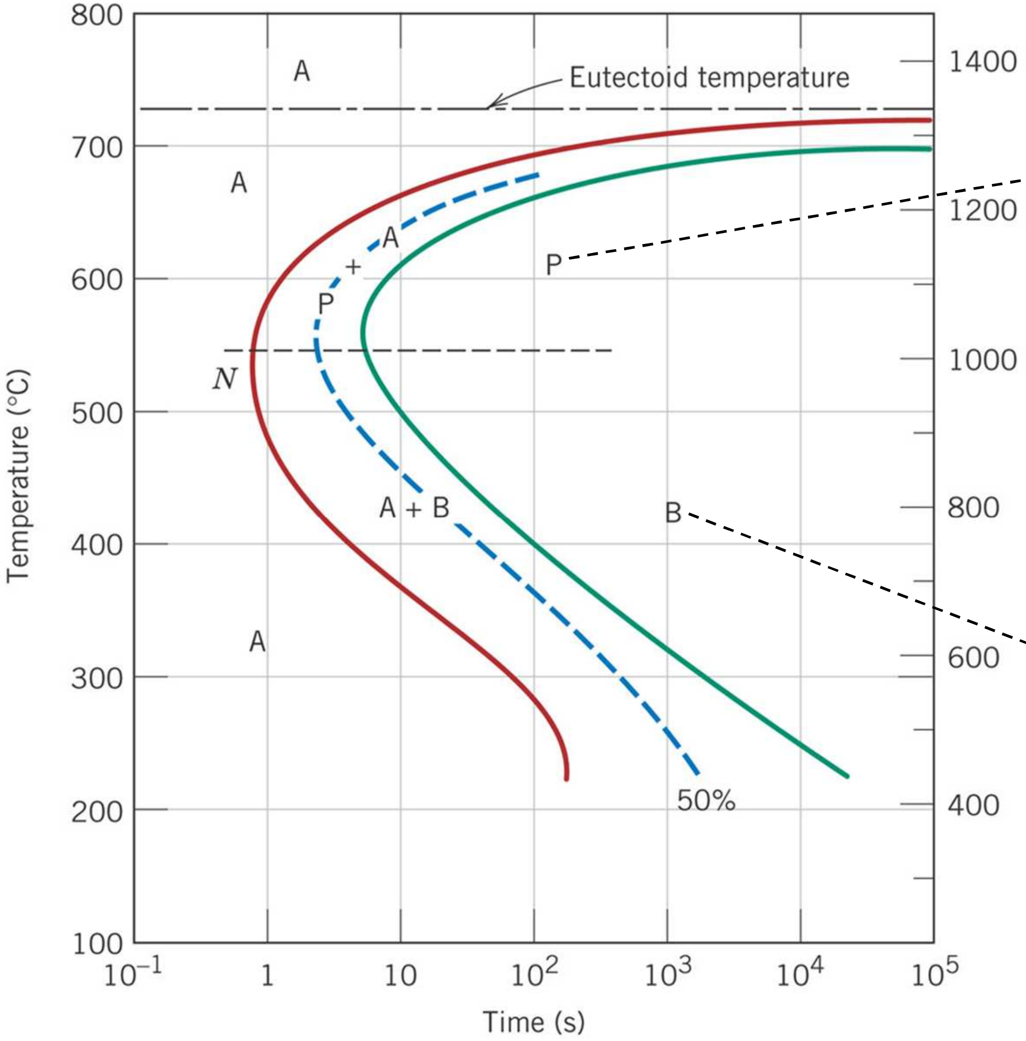


Adapted from Fig. 10.18, *Callister & Rethwisch 8e.*



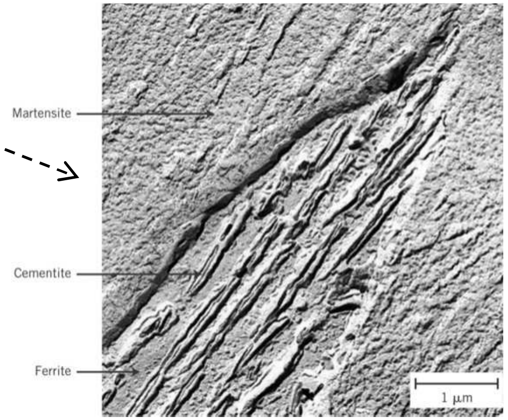
Adapted from Fig. 10.17, *Callister & Rethwisch 8e.* (Fig. 10.17 from *Metals Handbook*, 8th ed., Vol. 8, *Metallography, Structures, and Phase Diagrams*, American Society for Metals, Materials Park, OH, 1973.)

Isothermal Transformation Diagram for Fe-C alloy of eutectoid composition



Pearlite is coarser

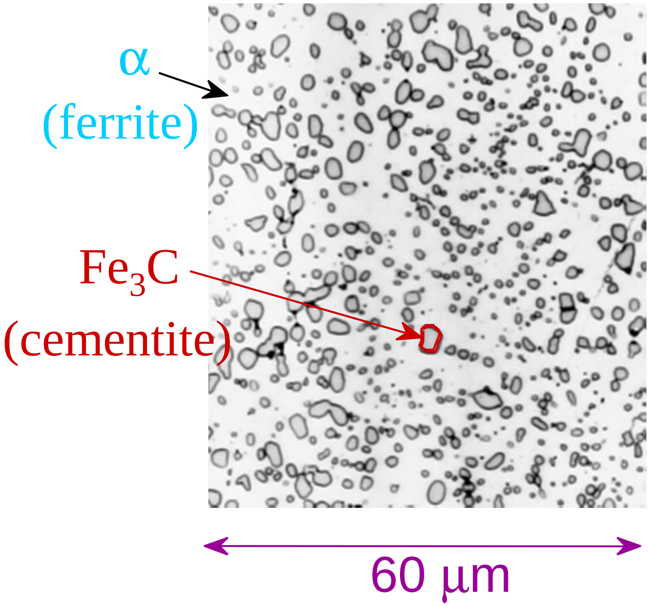
Pearlite is finer



Bainite

Spheroidite: Another Microstructure for the Fe-Fe_3C System

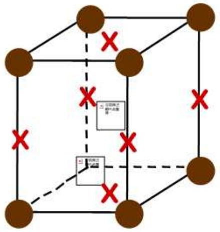
- **Spheroidite (球化鐵)**:
  - -- Fe3C particles within an a-ferrite matrix
  - -- formation requires diffusion
  - -- heat bainite or pearlite at temperature just below eutectoid for long times
  - -- driving force – reduction of α-ferrite/Fe_3C interfacial area



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)

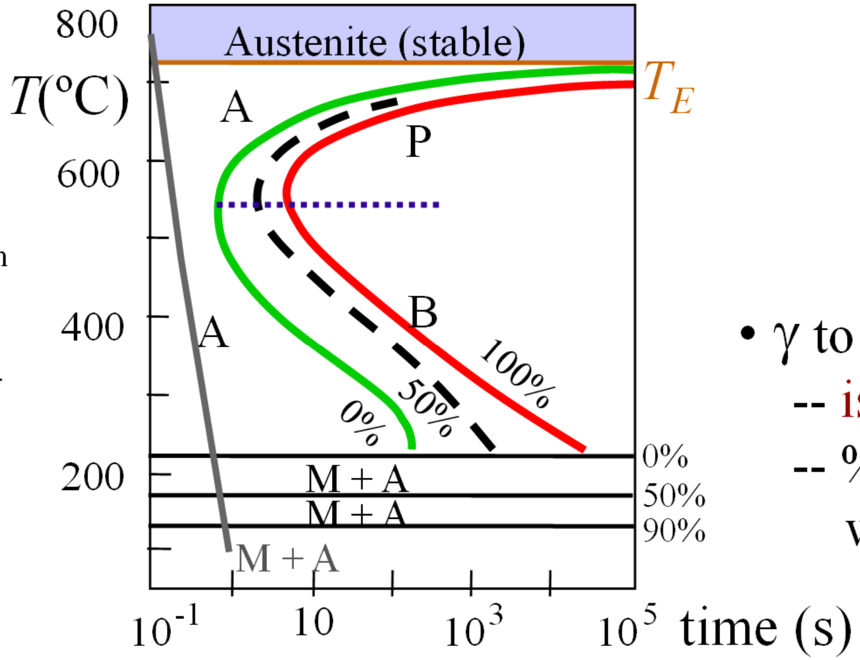


Adapted from Fig. 10.20, *Callister & Rethwisch 8e.*

▬ Martensite needles
▬ Austenite

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

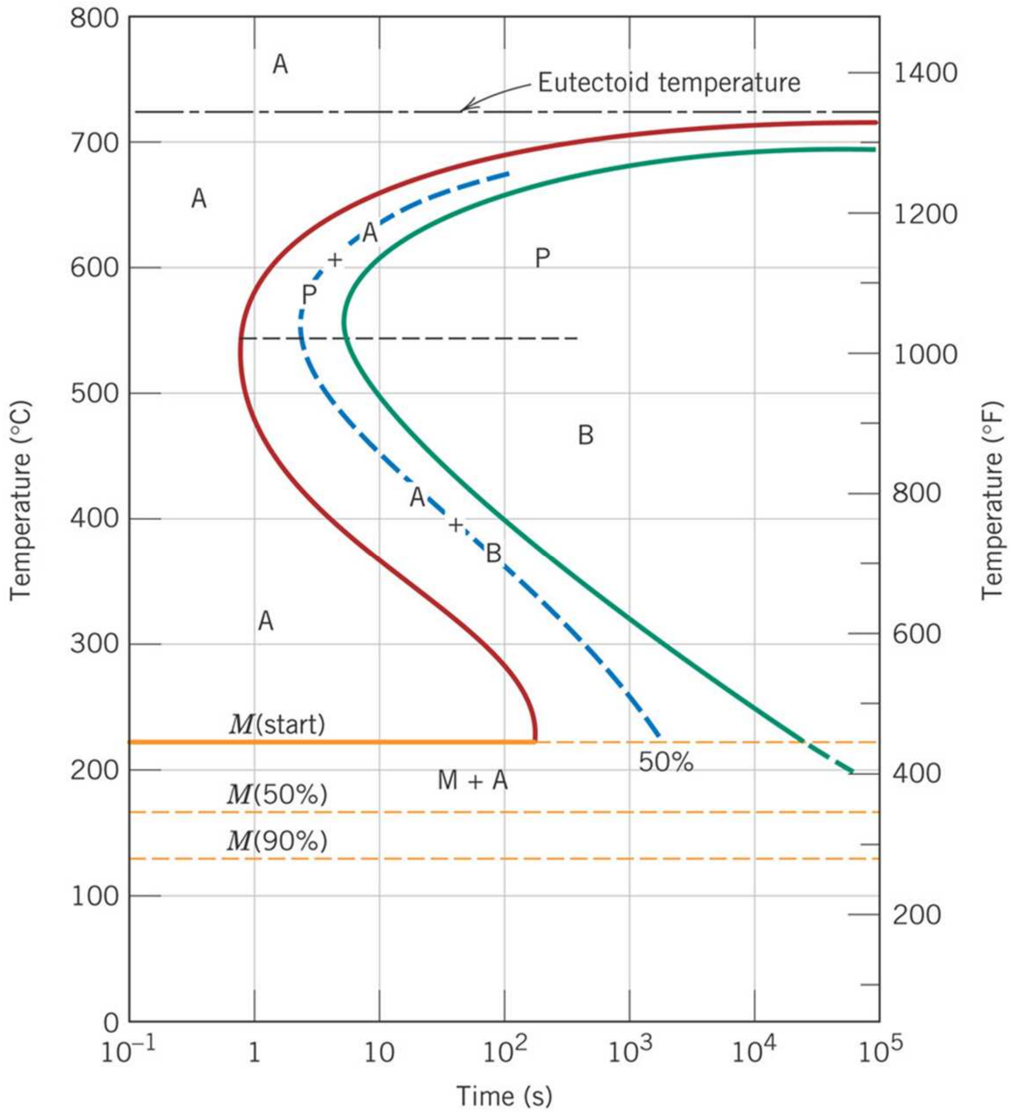
- Isothermal Transf. Diagram



Adapted from Fig. 10.22, *Callister & Rethwisch 8e.*

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

The Complete Isothermal Transformation Diagram for Fe-C alloy



Phase Transformations of Alloys

Effect of adding other elements

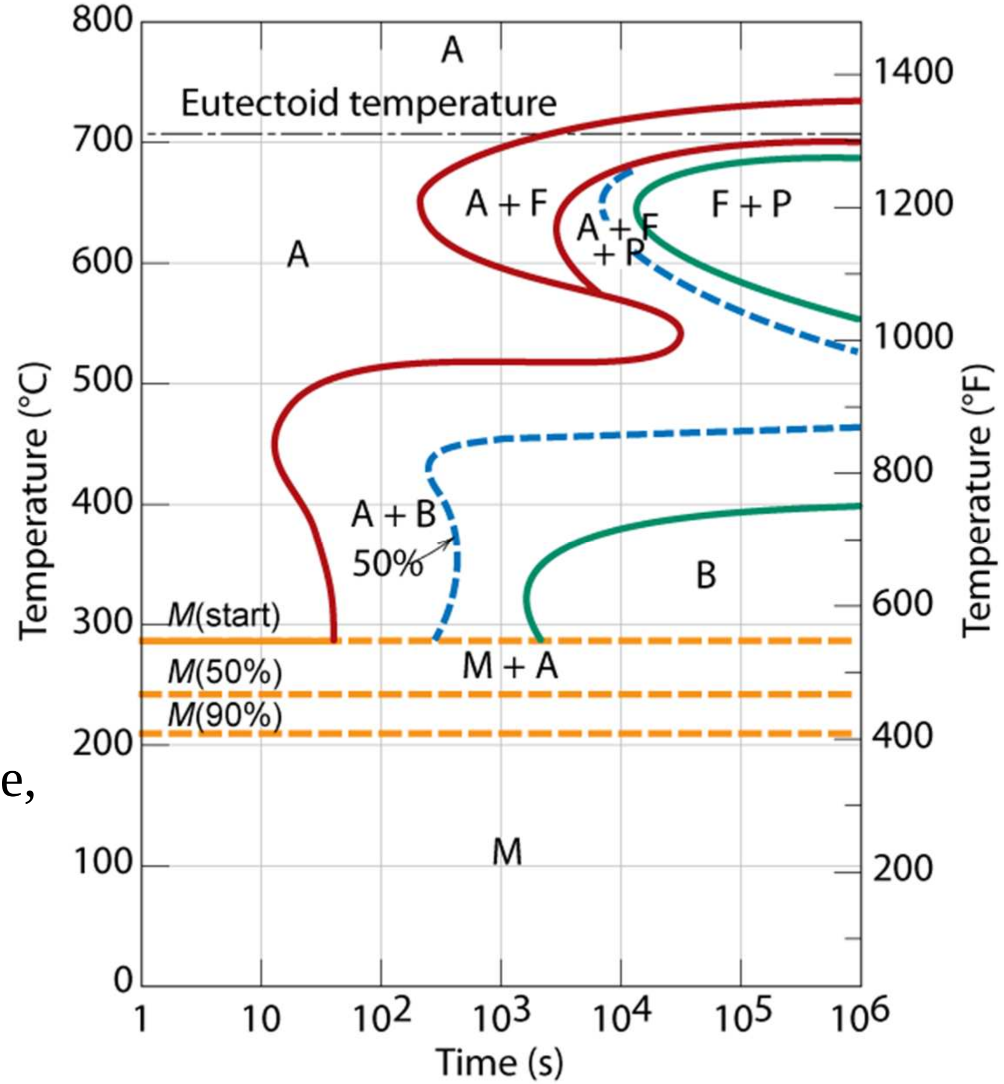
Change transition temp.

Cr, Ni, Mo, Si, Mn

retard $\gamma \rightarrow \alpha + Fe_3C$

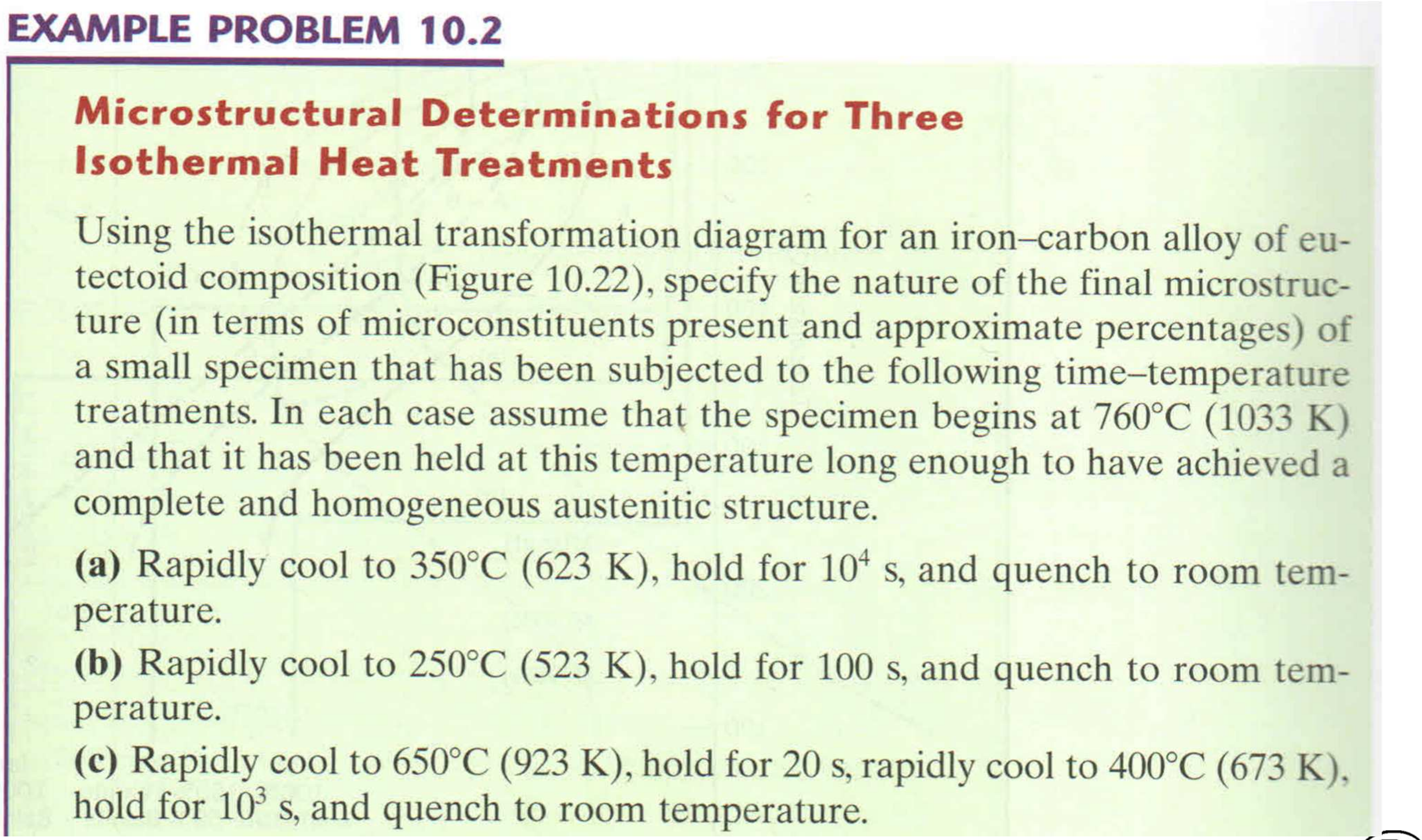
reaction (and formation of pearlite,

bainite)



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

Isothermal Heat Treatment Example Problems



EXAMPLE PROBLEM 10.2

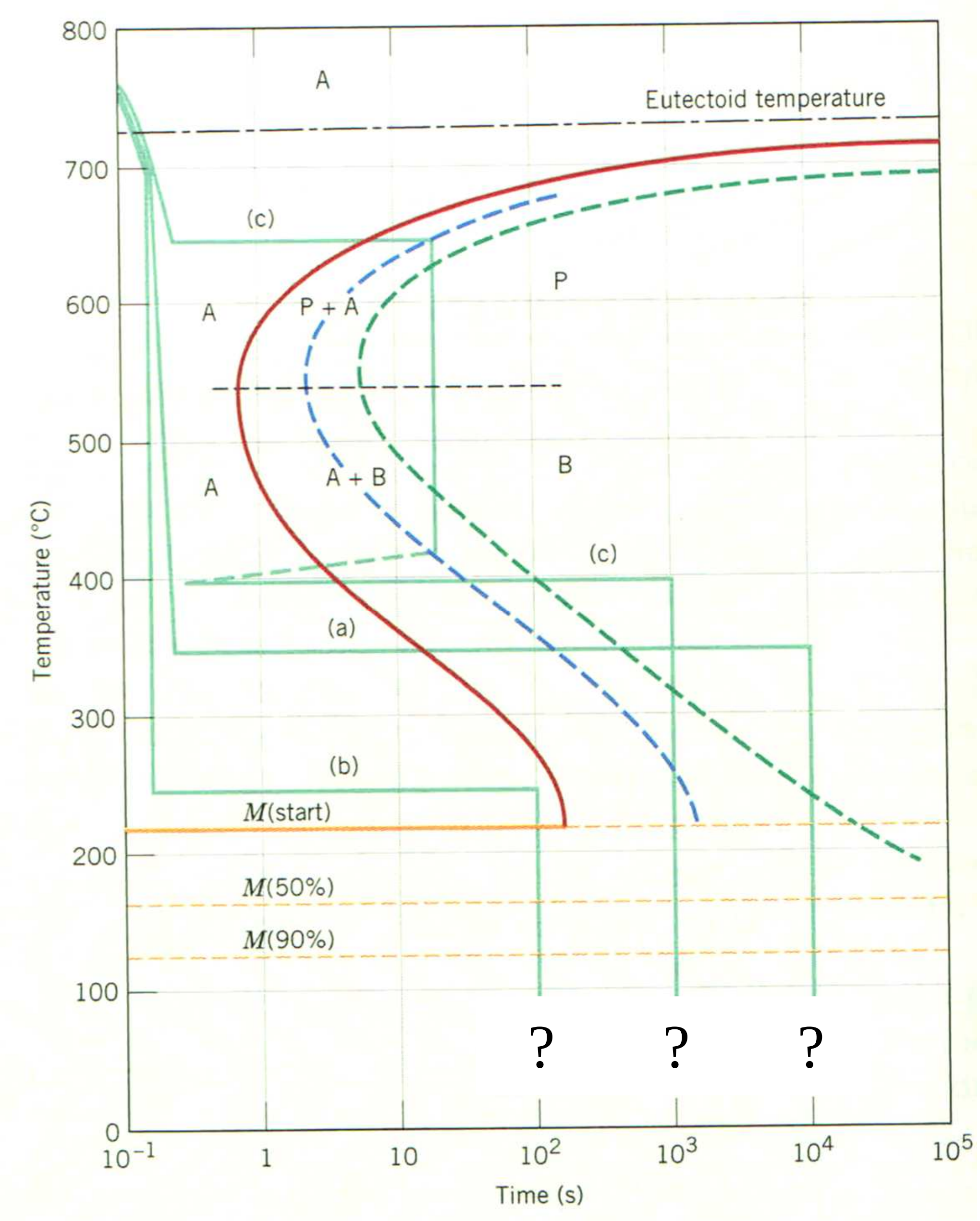
Microstructural Determinations for Three Isothermal Heat Treatments

Using the isothermal transformation diagram for an iron–carbon alloy of eutectoid composition (Figure 10.22), specify the nature of the final microstructure (in terms of microconstituents present and approximate percentages) of a small specimen that has been subjected to the following time–temperature treatments. In each case assume that the specimen begins at 760°C (1033 K) and that it has been held at this temperature long enough to have achieved a complete and homogeneous austenitic structure.

(a) Rapidly cool to 350°C (623 K), hold for 10^4 s, and quench to room temperature.

(b) Rapidly cool to 250°C (523 K), hold for 100 s, and quench to room temperature.

(c) Rapidly cool to 650°C (923 K), hold for 20 s, rapidly cool to 400°C (673 K), hold for 10^3 s, and quench to room temperature.



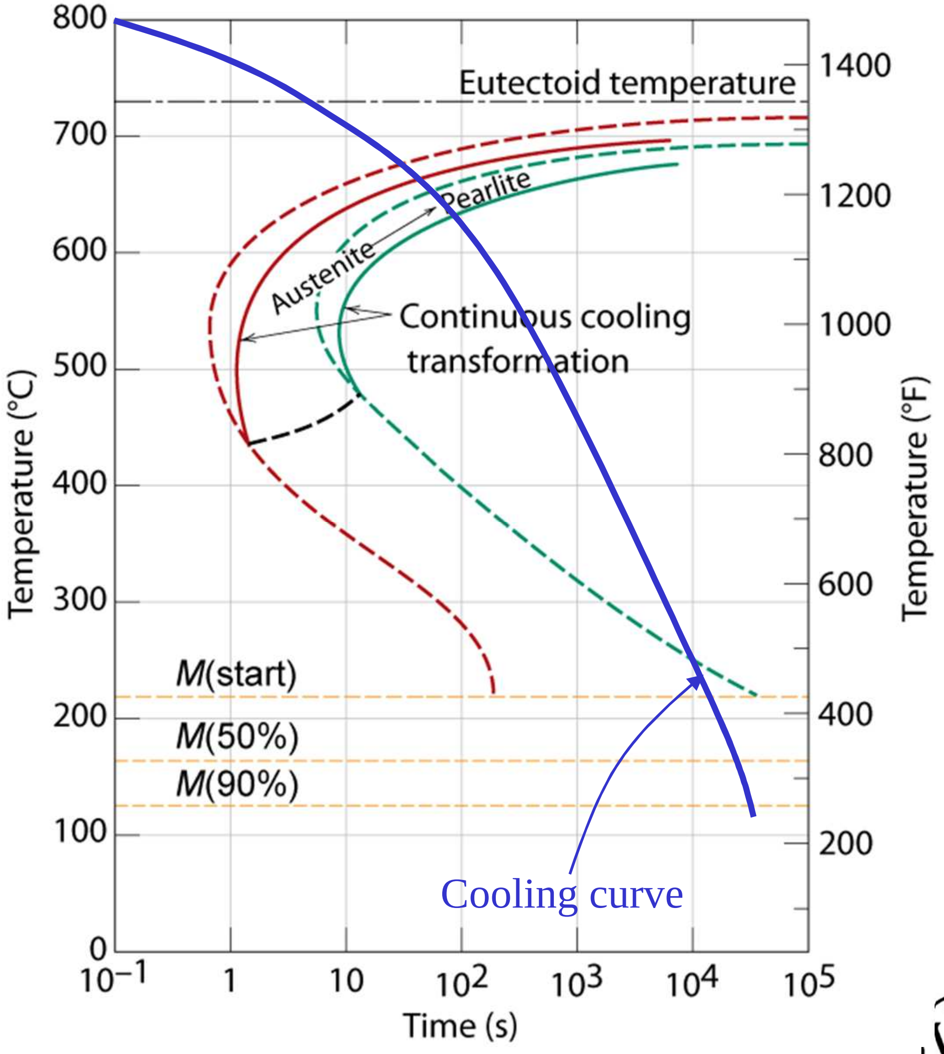
(a) 100% bainite

(b) 100% martensite

(c) 50% pearlite
50% bainite

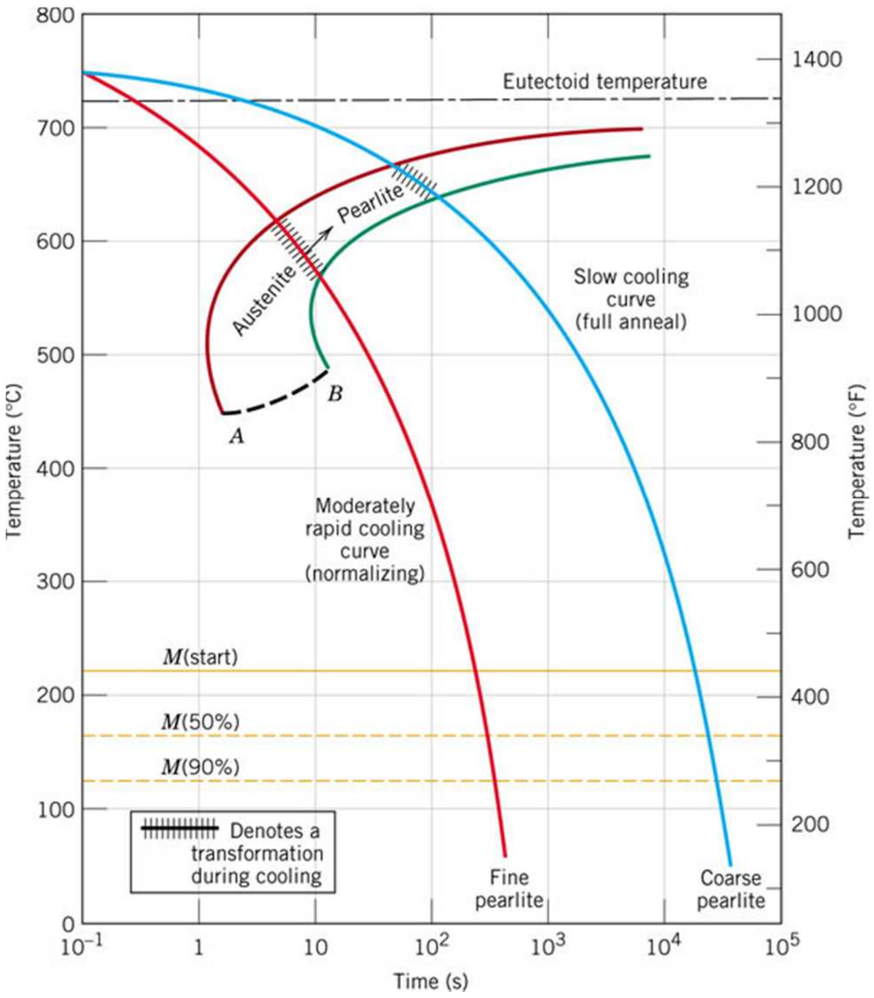
Continuous Cooling Transformation (CCT) Diagrams

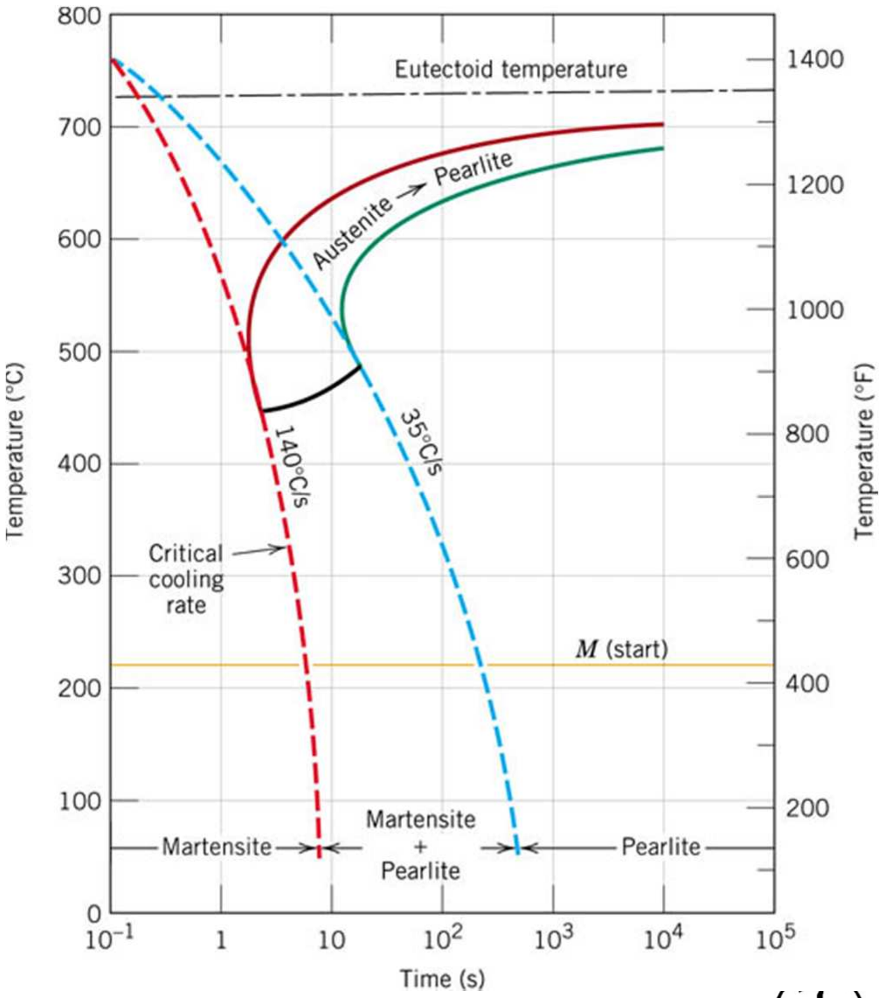
Conversion of isothermal transformation diagram to continuous cooling transformation diagram



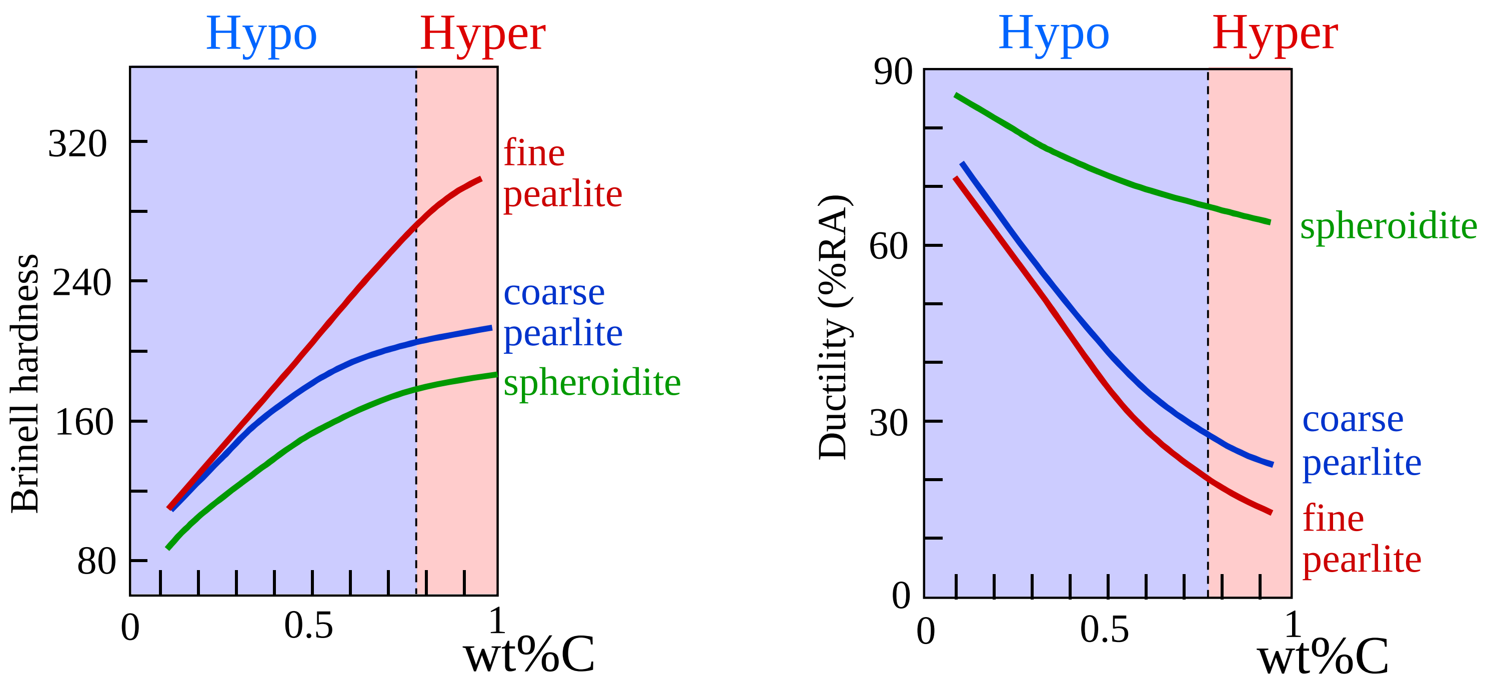
Adapted from Fig. 10.25, *Callister & Rethwisch 8e.*

Continuous Cooling Transformation Diagrams





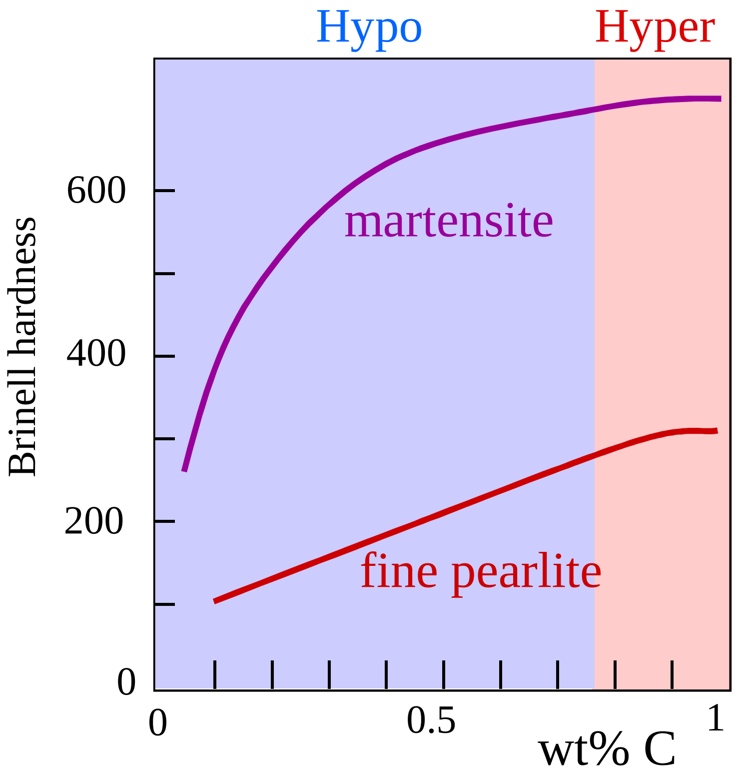
Mechanical Props: Fine Pearlite vs. Coarse Pearlite vs. Spheroidite



• 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.)

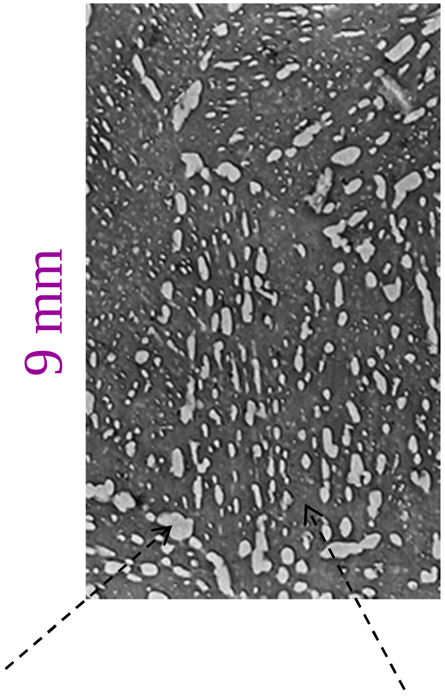
- Hardness: fine pearlite << martensite.

Tempered Martensite

Heat treat martensite to form tempered martensite

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

$$\begin{tikzcd}
\gamma\ \text{(FCC)} \arrow[r, "\text{slow cooling}"] \arrow[d, "\text{quench}"] & \alpha\ \text{(BCC)} + Fe_3C \\
\boxed{\text{M (BCT)}} \arrow[ur, "\text{Tempering}" below, "(250\sim650℃)"' below] &
\end{tikzcd}$$



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

304 Stainless Steel

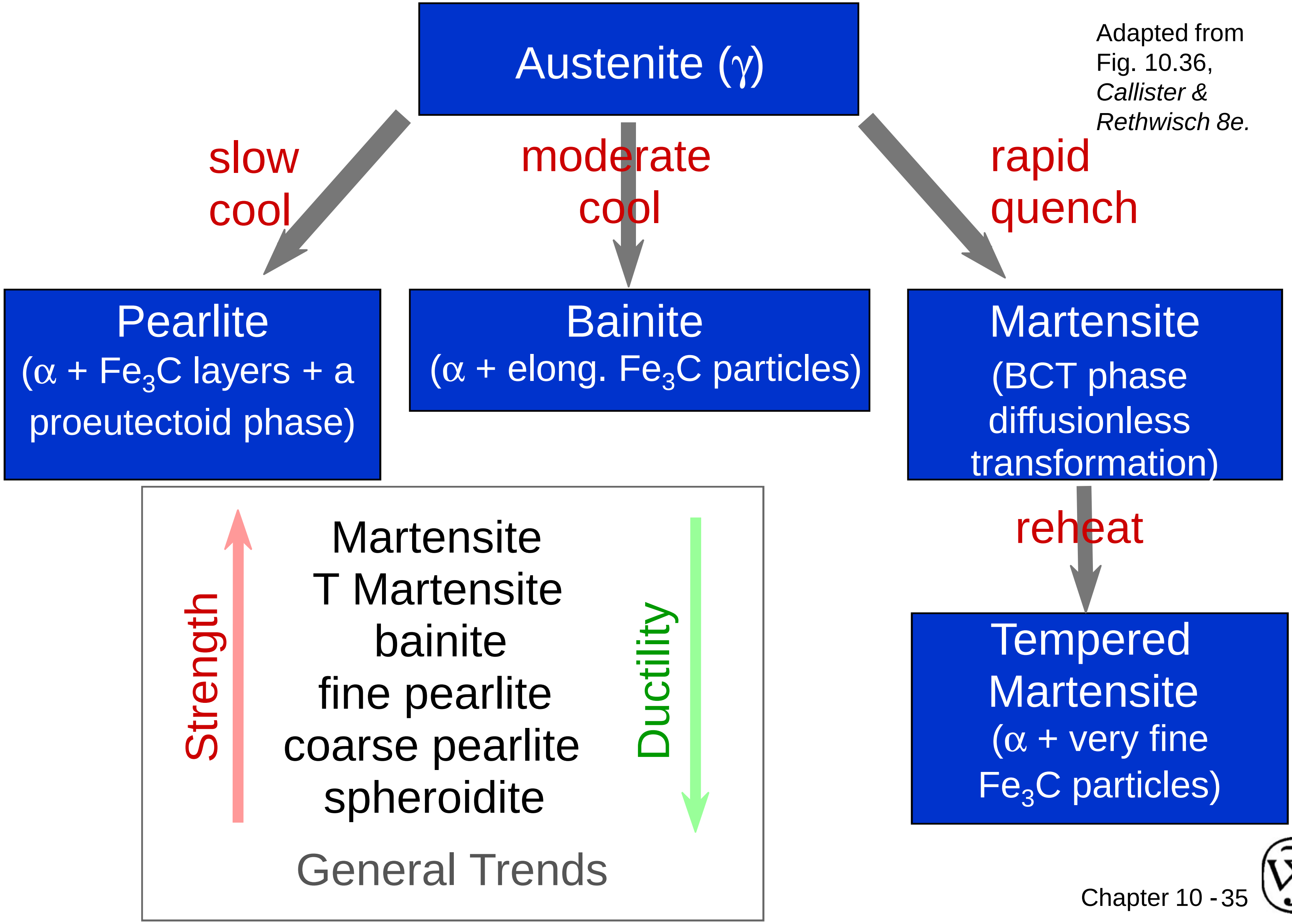
本商品規格品 名：鍋寶超真空保溫杯
型 號：SVC-5090C
材 質：瓶身／高級不銹鋼
上蓋／耐熱PP(聚丙烯.耐熱135℃)
滿水容量：500c.c.
保溫容量：470c.c.
重 量：約315g
產 地：中國

http://24h.pchome.com.tw/prod/DMAG08-A82679903

http://iguang.tw/groupbuy/crazymike/product/18219.html

http://www.momoshop.com.tw/category/DgrpCategory.jsp?d_code=1716800219

Summary of Possible Transformations



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

Austenite (γ)

slow cool

moderate cool

rapid quench

Pearlite (α + Fe_3C layers + a proeutectoid phase)

Bainite (α + elong. Fe_3C particles)

Martensite (BCT phase diffusionless transformation)

reheat

Tempered Martensite (α + very fine Fe_3C particles)

Strength

Martensite
T Martensite
bainite
fine pearlite
coarse pearlite
spheroidite

Ductility

General Trends

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: