2019 Fall

Introduction to Materials Science and Engineering

11. 14. 2019

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Contents for previous class

Chapter 12. Phase Transformations

Contents_Phase transformation course

Background to understand phase transformation

- (Ch1) Thermodynamics and Phase Diagrams
- (Ch2) Diffusion: Kinetics
- (Ch3) Crystal Interface and Microstructure

Representative Phase transformation

- (Ch4) Solidification: Liquid → Solid
- (Ch5) Diffusional Transformations in Solid: Solid → Solid
- (Ch6) Diffusionless Transformations: Solid → Solid

4.1.1. Homogeneous Nucleation

Driving force for solidification

$G^L = H^L - TS^L$

$G^S = H^S - TS^S$

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

$L : \Delta H = H^L - H^S$

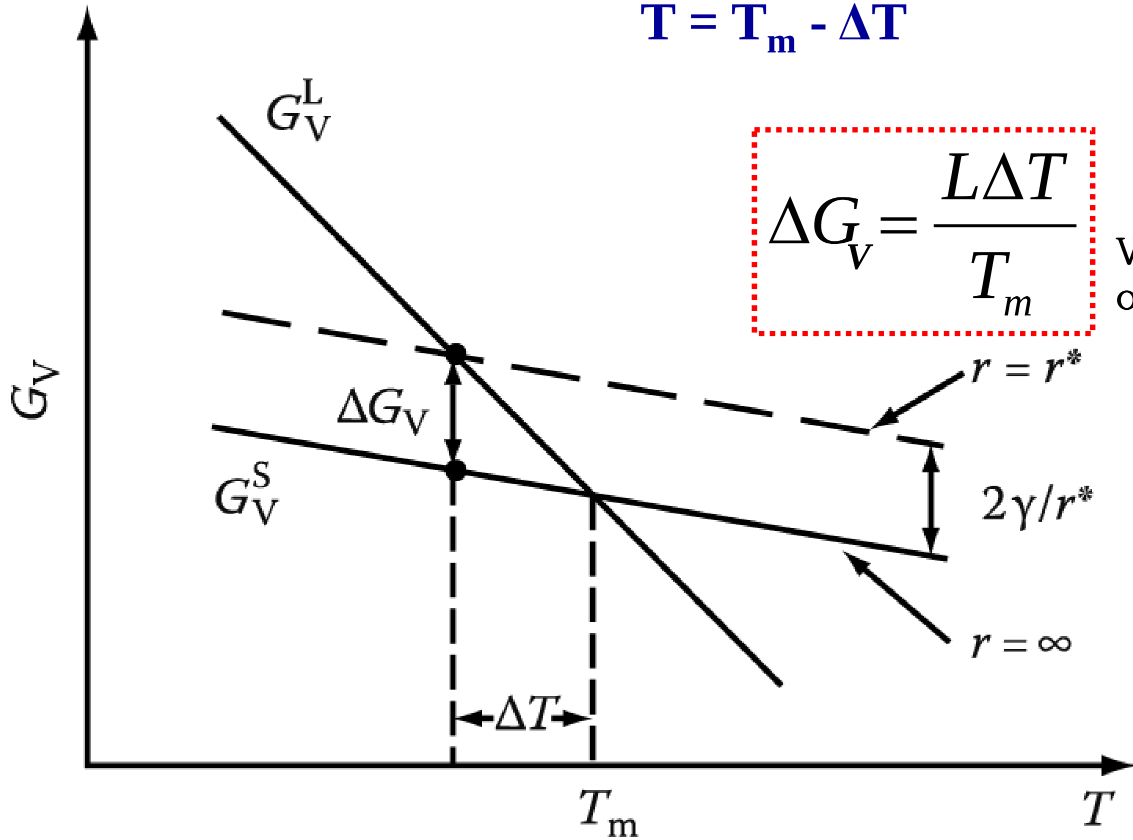
(Latent heat)

$T = T_m - \Delta T$

$\Delta G = 0 = \Delta H - T_m \Delta S$

$\Delta S = \Delta H / T_m = L / T_m$

$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$

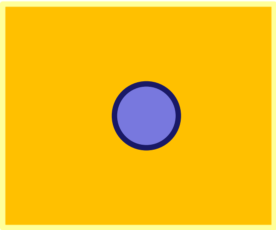


$$\Delta G_V = \frac{L\Delta T}{T_m}$$

Variation of free energy per unit volume obtained from undercooling (ΔT)

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

Liquid | T_m | Undercooled Liquid | Solid

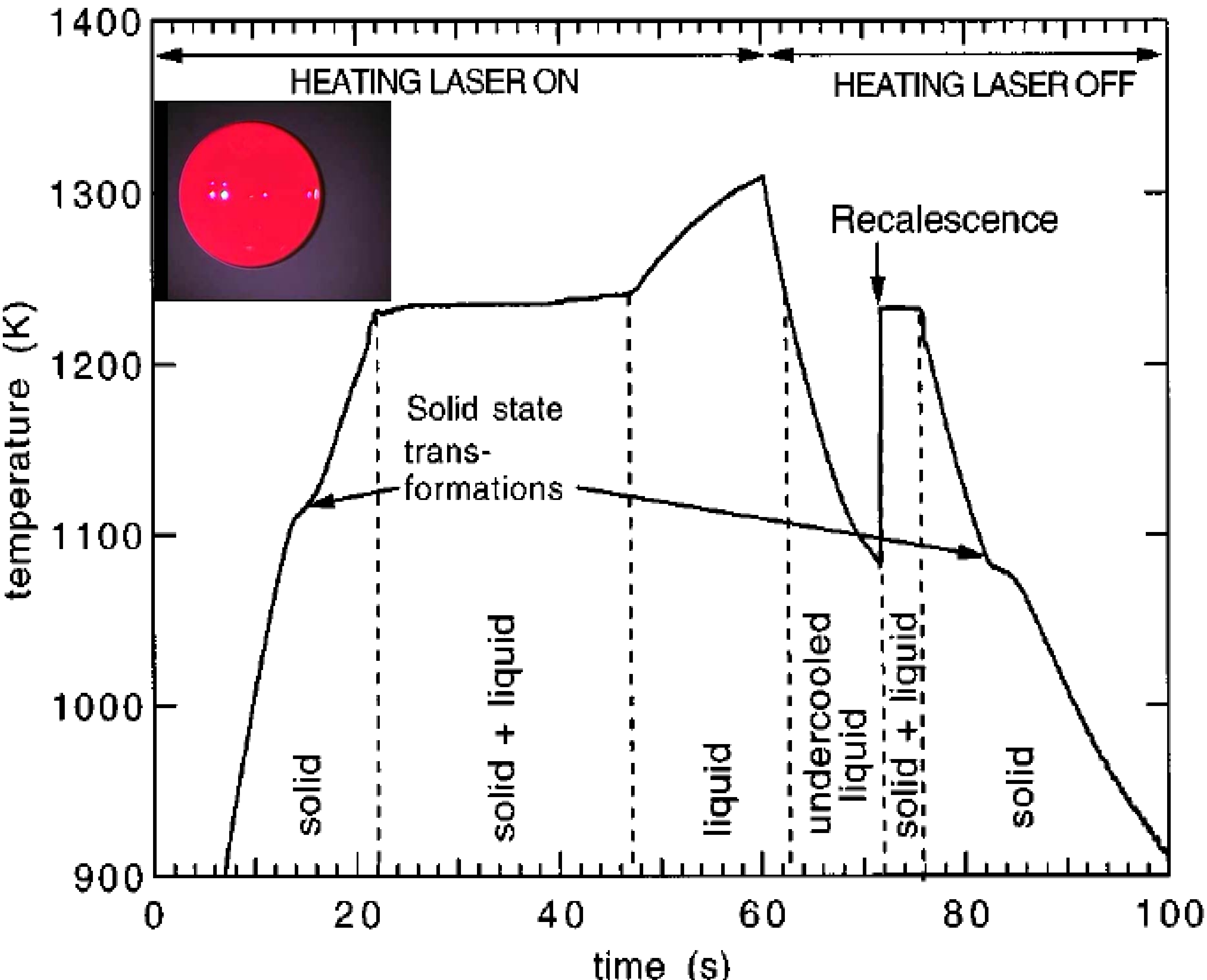
No superheating required!

- Interfacial energy ⇨ No ΔT_N

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

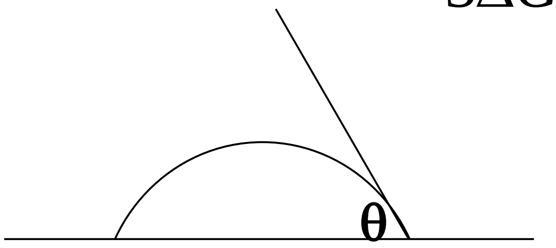
vapor

Melting: Liquid ← Solid

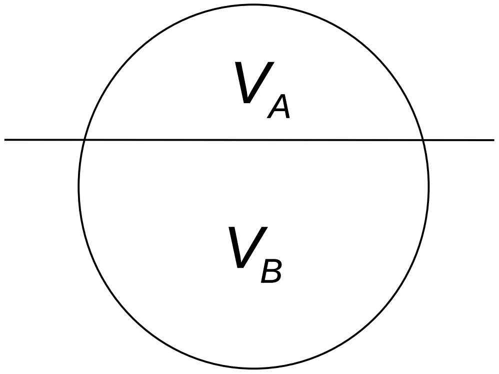

HEATING LASER ON
HEATING LASER OFF
Recalescence
Solid state
trans-
formations
solid
solid + liquid
liquid
undercooled
liquid
solid + liquid
solid
temperature (K)
time (s)
1400
1300
1200
1100
1000
900
0
20
40
60
80
100

Barrier of Heterogeneous Nucleation

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta) = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot \frac{(2-3\cos\theta+\cos^3\theta)}{4}$$



$$\Delta G_{het}^* = S(\theta)\Delta G_{\mathrm{hom}}^*$$



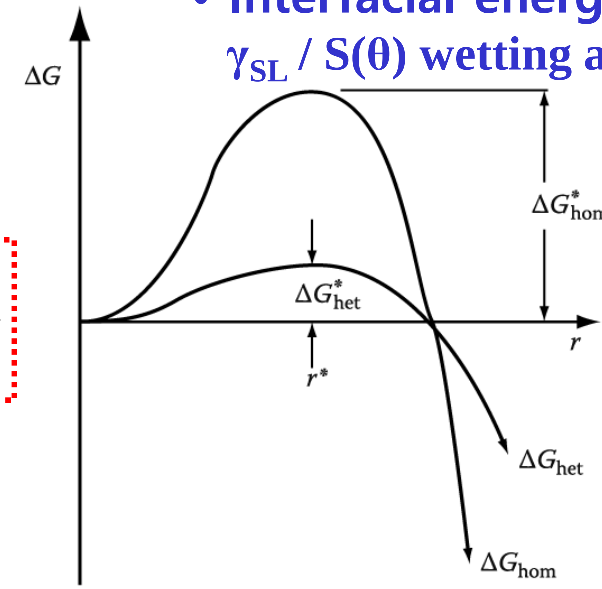
$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{2-3\cos\theta+\cos^3\theta}{4} \right)$$

$$\frac{V_A}{V_A+V_B} = \frac{2-3\cos\theta+\cos^3\theta}{4} = S(\theta)$$

How about the nucleation at the crevice or at the edge?

Solidification: Liquid ⟶ Solid

- Undercooling ΔT
- Interfacial energy
  γ_{SL} / S(θ) wetting angle



- Nucleation in Pure Metals
- Homogeneous Nucleation

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

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2}\right)\frac{1}{(\Delta T)^2}$$

r* & ΔG* ↓ as ΔT ↑

$$N_{\text{hom}} \approx f_0 C_o \exp\{-\frac{A}{(\Delta T)^2}\} \sim \frac{1}{\Delta T^2}$$

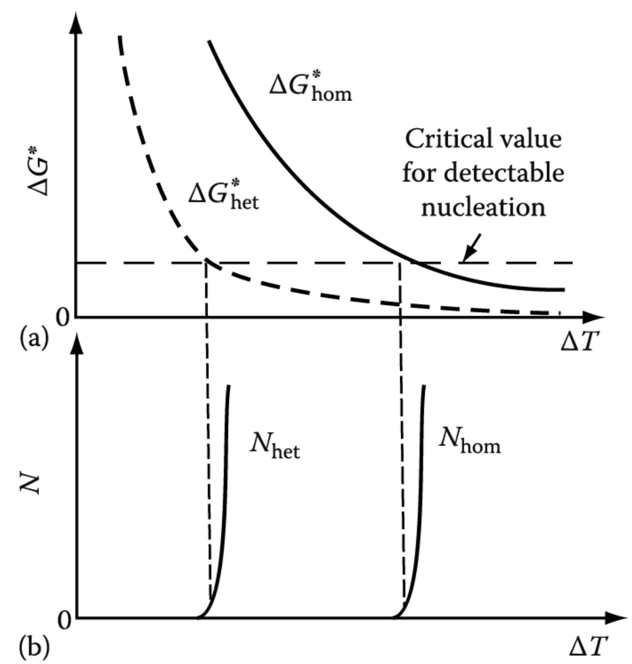
- Heterogeneous Nucleation

$$\Delta G_{het}^* = S(\theta)\Delta G_{\text{hom}}^*$$

$$\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = S(\theta)$$

- Nucleation of melting

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$ **(commonly)**



5.4 Overall Transformation Kinetics – TTT Diagram

If isothermal transformation,

The fraction of Transformation as a function of Time and Temperature

→ $f\,(t,T)$

Plot f vs log t.

- isothermal transformation
- f ~ volume fraction of β at any time; 0~1

Plot the fraction of transformation (1%, 99%) in T-log t coordinate.

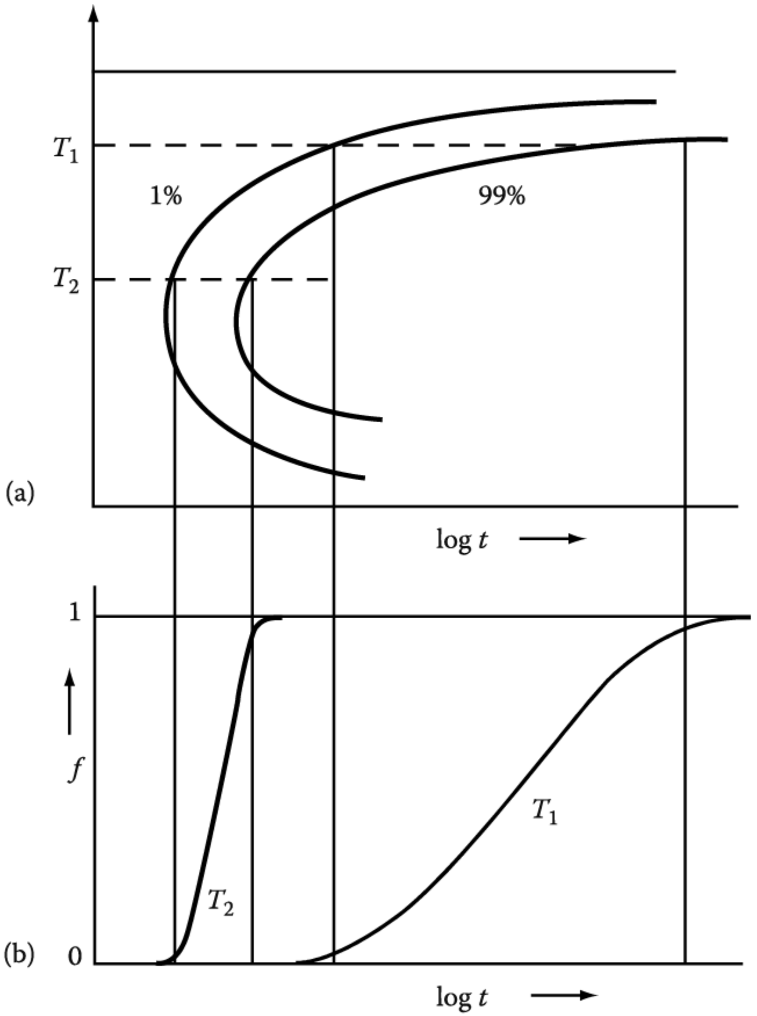


Fig. 5.23 The percentage transformation versus time for different transformation temperatures.

Constant Nucleation Rate Conditions

- **consider impingement + repeated nucleation effects**

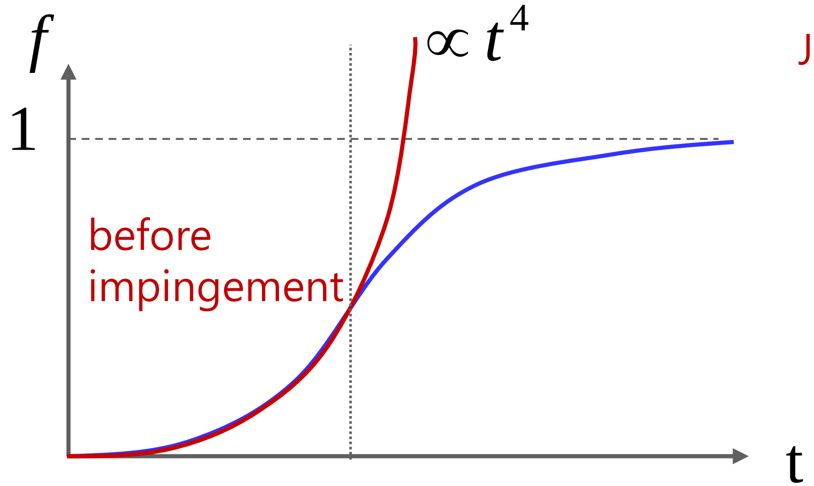
$$df = (1-f)\,df_e \longrightarrow df_e = \frac{df}{1-f}$$

$$f_e = -\ln(1-f)$$

$$f(t) = 1-\exp(-f_e(t)) = 1-\exp\left(-\frac{\pi}{3}Iv^3t^4\right)$$

* Short time:
1-exp(z)~Z (z ≪1)

* Long time:
t→∞, $f \rightarrow 1$



Johnson-Mehl-Avrami Equation

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

k: T sensitive $f(I, v)$ $\quad -\frac{\pi}{3}Iv^3$

n: 1 ~ 4 (depend on nucleation mecnanism)

Growth controlled. **Nucleation-controlled.**

If no change of nucleation mechanism during phase transformation, n is not related to T.

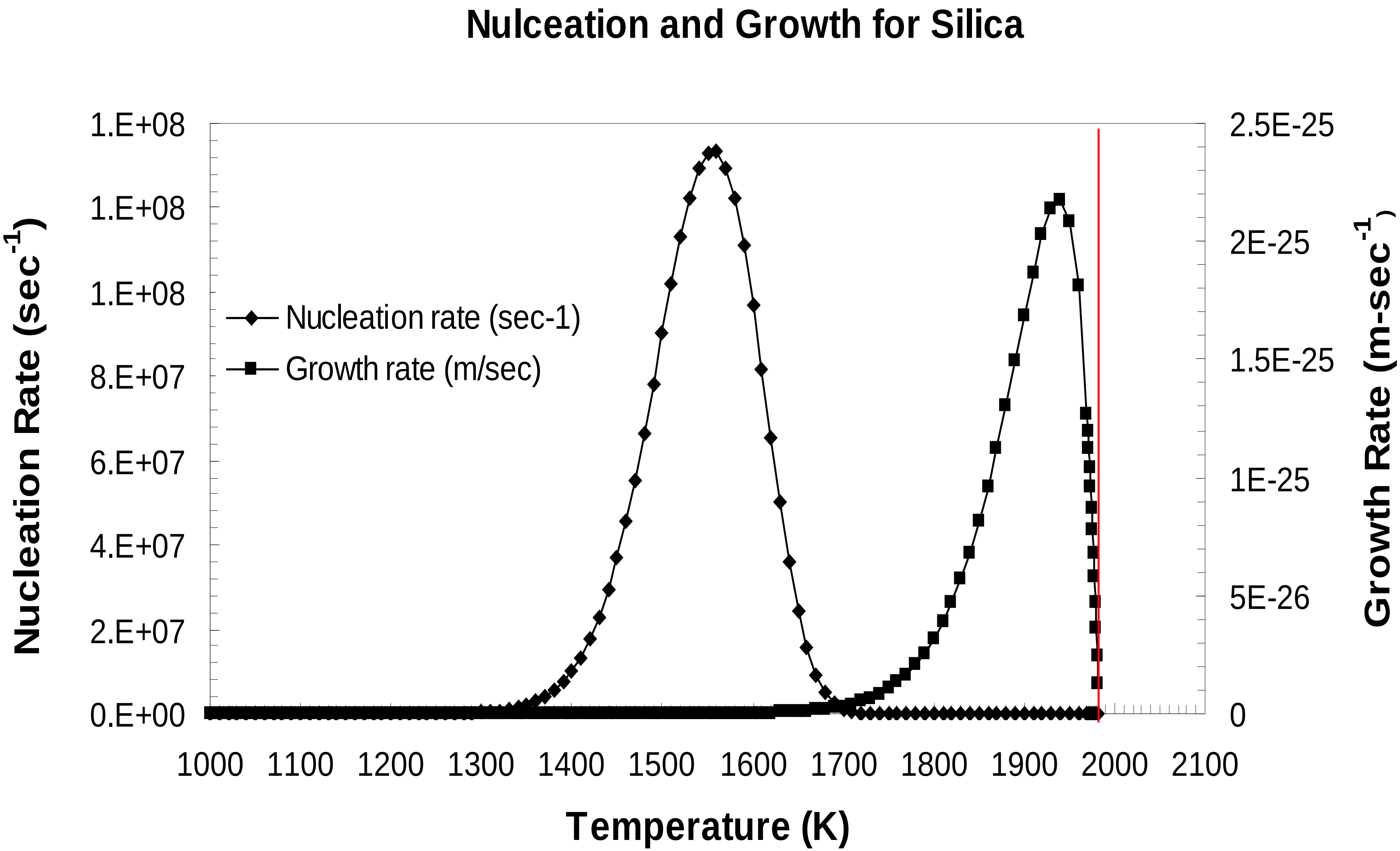
i.e. 50% transform

Exp (-0.7) = 0.5

$$kt_{0.5}^n = 0.7 \quad t_{0.5} = \frac{0.7}{k^{1/n}} \quad \xrightarrow{\frac{\pi}{3}Iv^3} \quad t_{0.5} = \frac{0.9}{N^{1/4}v^{3/4}}$$

Rapid transformations are associated with (large values of k), or (rapid nucleation and growth rates)

Nucleation and Growth Rates



Time–Temperature–Transformation Curves (TTT)

- How much time does it take at any one temperature for a given fraction of the liquid to transform (nucleate and grow) into a crystal?

- $f(t,T) \sim \pi I(T)\mu(T)^3 t^4/3$

where *f* is the fractional volume of crystals formed, typically taken to be 10^{-6}, a barely observable crystal volume.

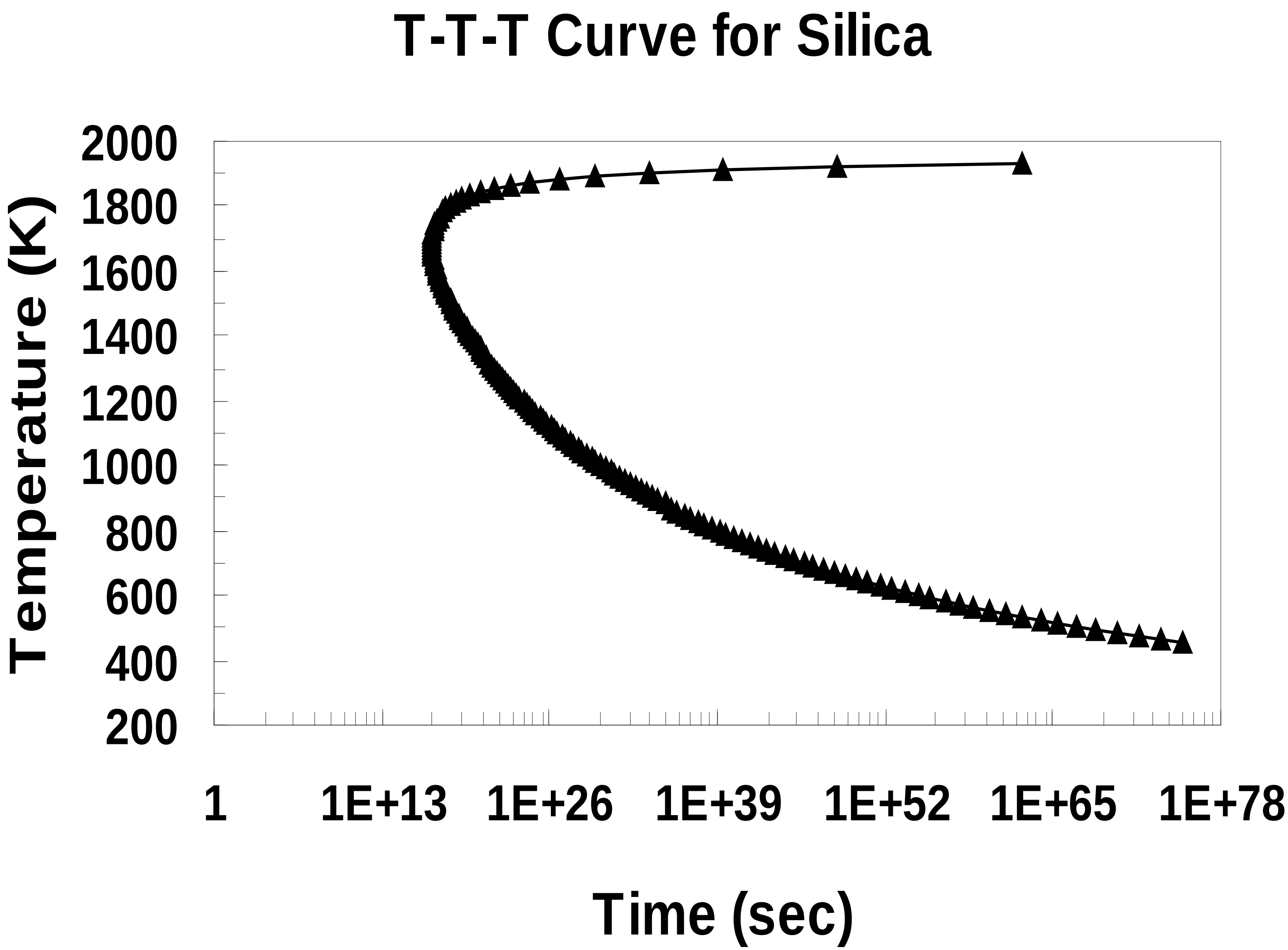
Nucleation rates

$$I = n\nu \exp\left\{\left(\frac{16\pi\Delta H_{cryst}}{81RT}\right)\left(\frac{T_m}{\Delta T}\right)^2\right\}\exp\left\{\frac{-\Delta E_D}{RT}\right\}$$

Growth rates

$$\mu(T) = \left(\frac{fRT}{3N\pi a^2\eta(T)}\right)\left(1-\exp\left[\left(\frac{\Delta H_m}{RT}\right)\left(\frac{\Delta T}{T_m}\right)\right]\right)$$

Time Transformation Curves for Silica



* Time-Temperature-Transformation diagrams

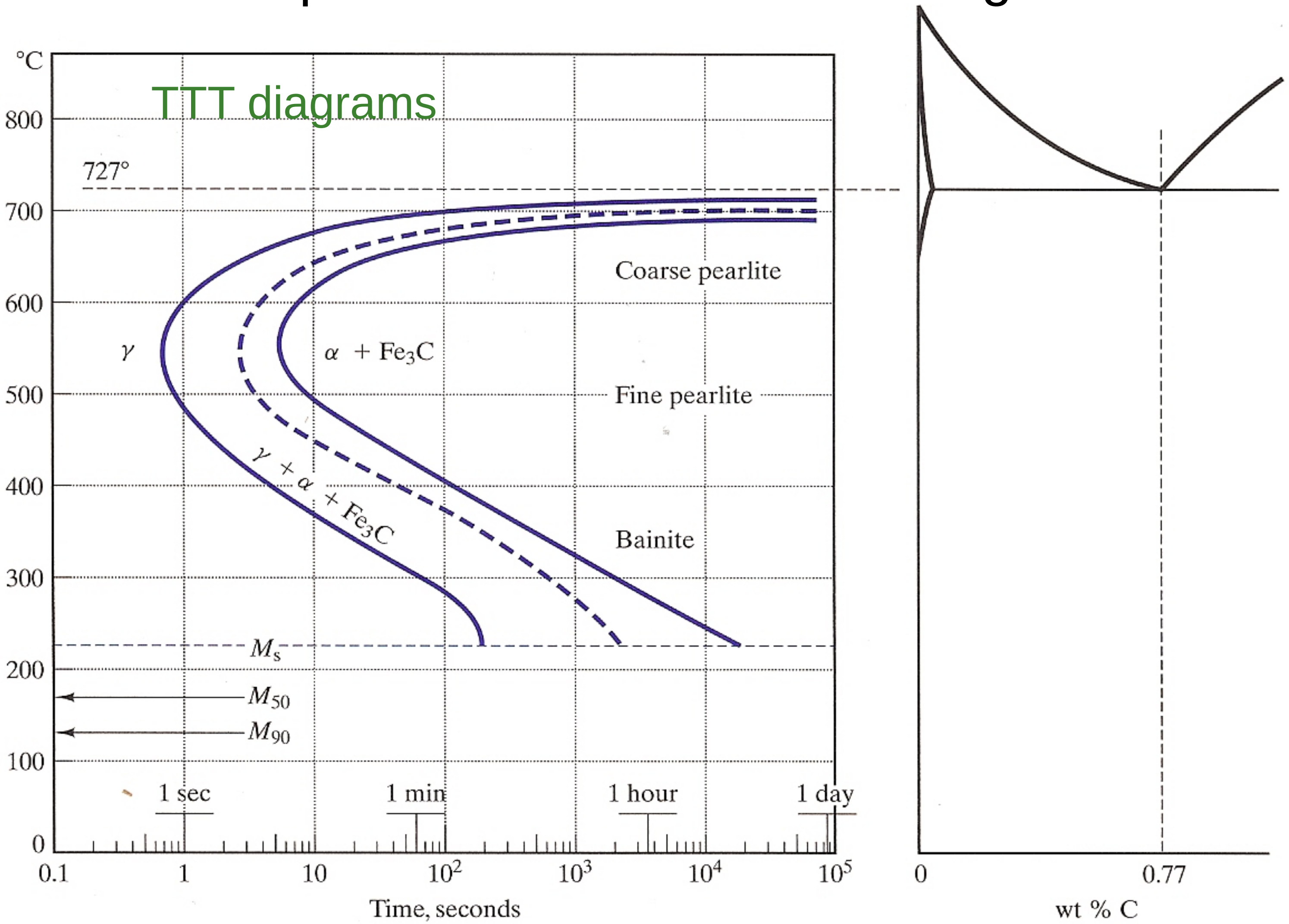


FIGURE 10.11 *A more complete TTT diagram for eutectoid steel than was given in Figure 10.7. The various stages of the time-independent (or diffusionless) martensitic transformation are shown as horizontal lines. M_s represents the start, M_{50} represents 50% transformation, and M_{90} represents 90% transformation. One hundred percent transformation to martensite is not complete until a final temperature (M_f) of −46°C.*

* Continuous Cooling Transformation diagrams

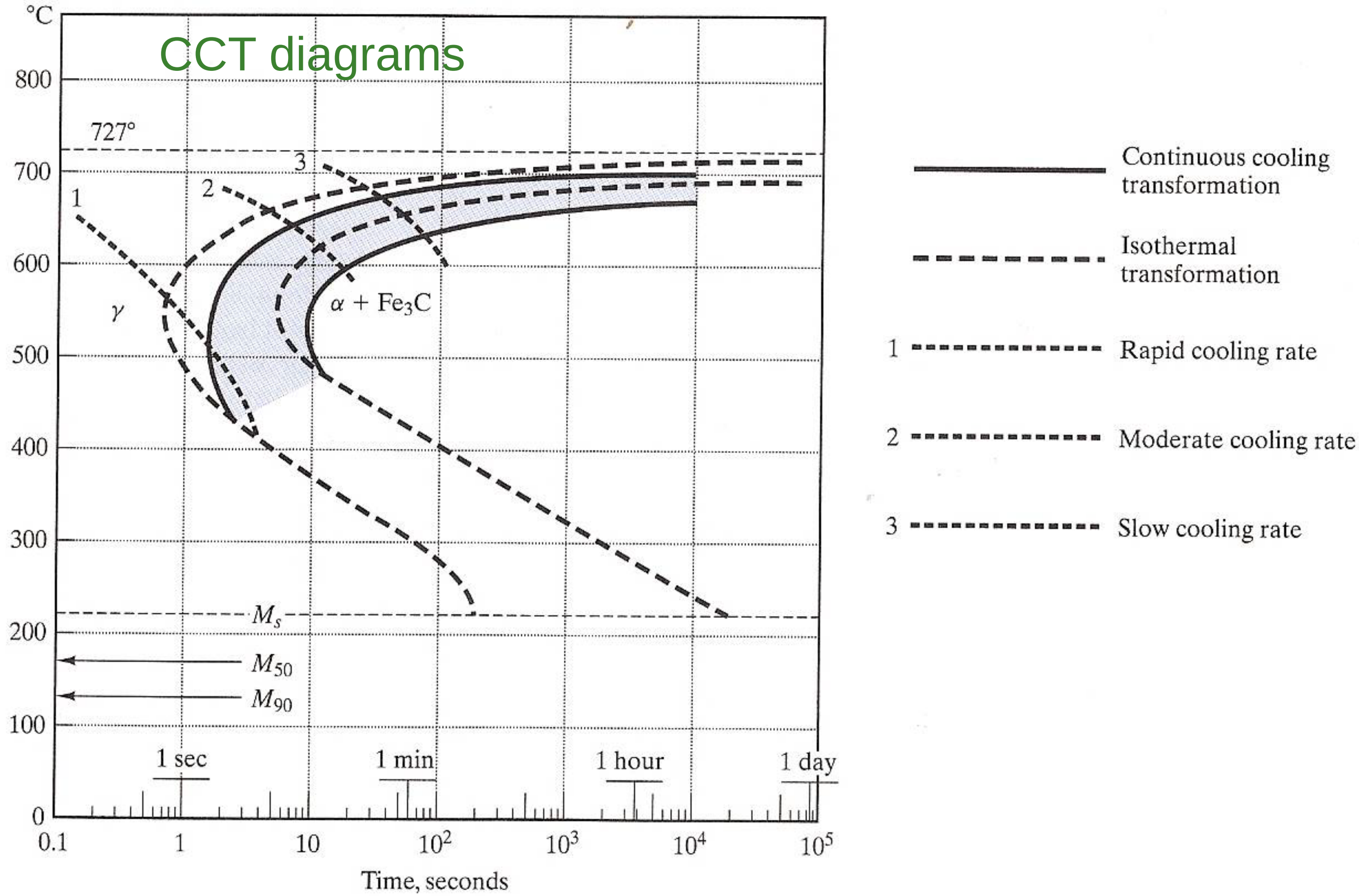


FIGURE 10.14 *A continuous cooling transformation (CCT) diagram is shown superimposed on the isothermal transformation diagram of Figure 10.11. The general effect of continuous cooling is to shift the transformation curves downward and toward the right. (After* Atlas of Isothermal Transformation and Cooling Transformation Diagrams, *American Society for Metals, Metals Park, OH, 1977.)*

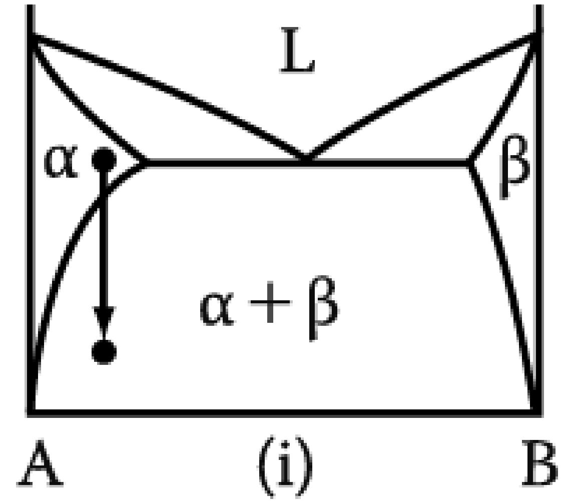
5. Diffusion Transformations in solid

: diffusional nucleation & growth

(a) Precipitation

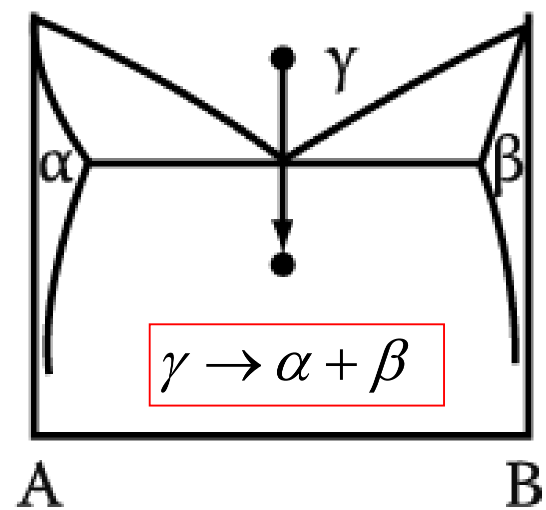
$$\alpha' \rightarrow \alpha + \beta$$

Metastable supersaturated
Solid solution



(b) Eutectoid Transformation

Composition of product phases differs from that of a parent phase.
→ long-range diffusion



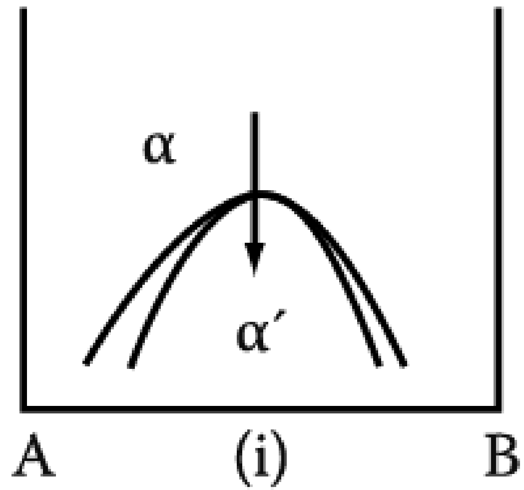
Which transformation proceeds by short-range diffusion?

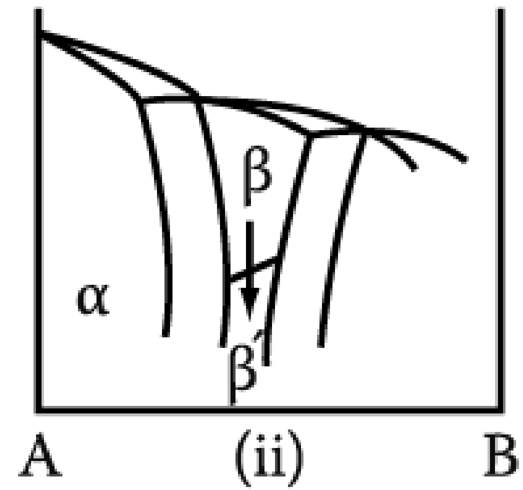
5. Diffusion Transformations in solid

(c) Order-Disorder Transformation

$$\alpha \rightarrow \alpha'$$

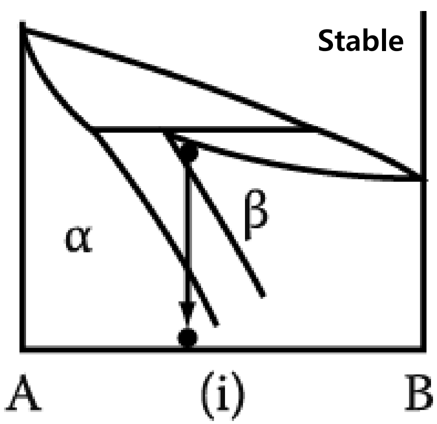
Disorder (high temp.) Order (low temp.)



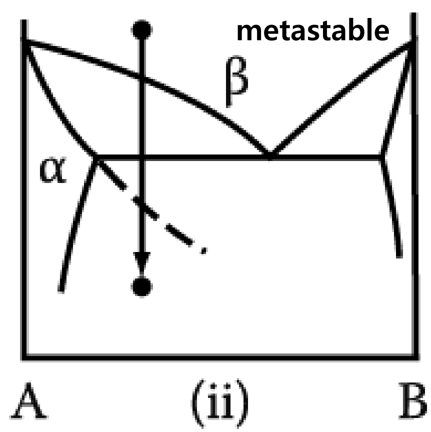


(d) Massive Transformation

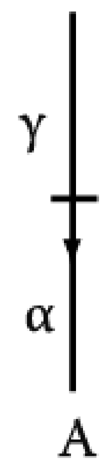
: The original phase decomposes into one or more new phases which have the same composition as the parent phase, but different crystal structures.



$$\beta \rightarrow \alpha$$



(e) Polymorphic Transformation



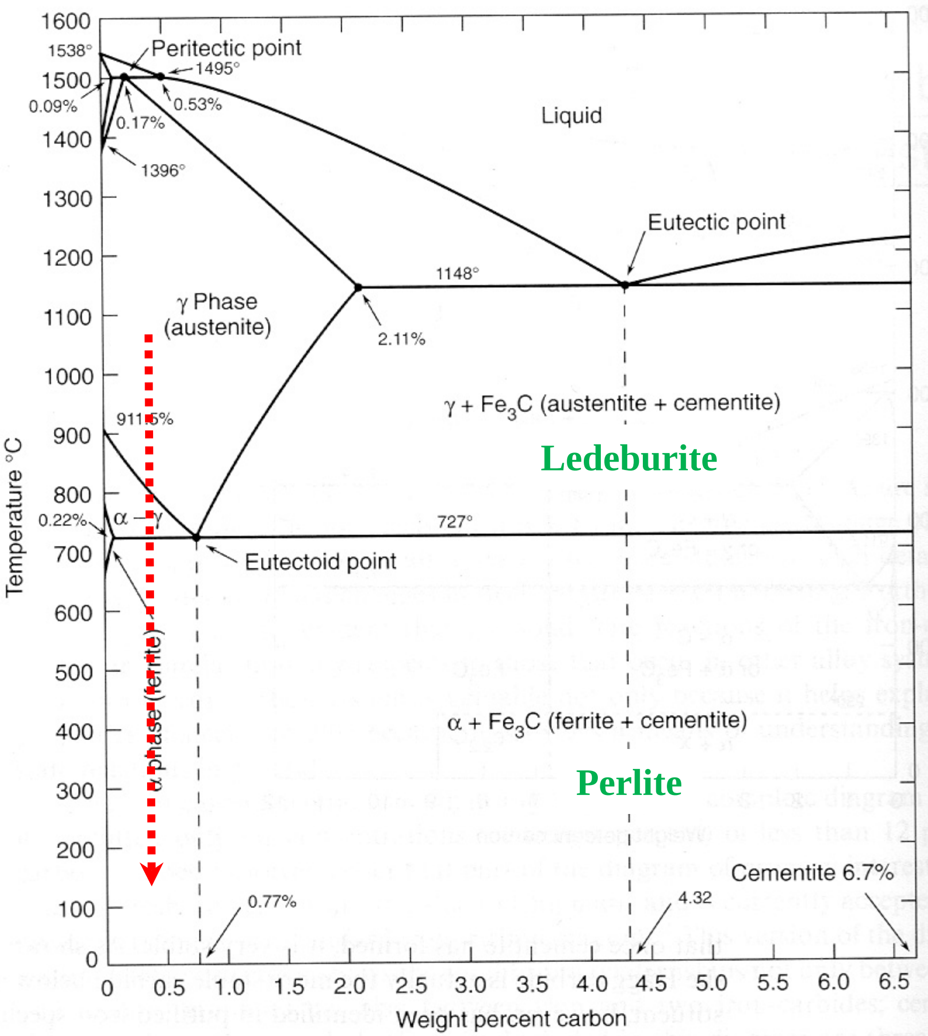
In single component systems, different crystal structures are stable over different temperature ranges.

* 철-탄소 합금에서 미세조직과 특성의 변화

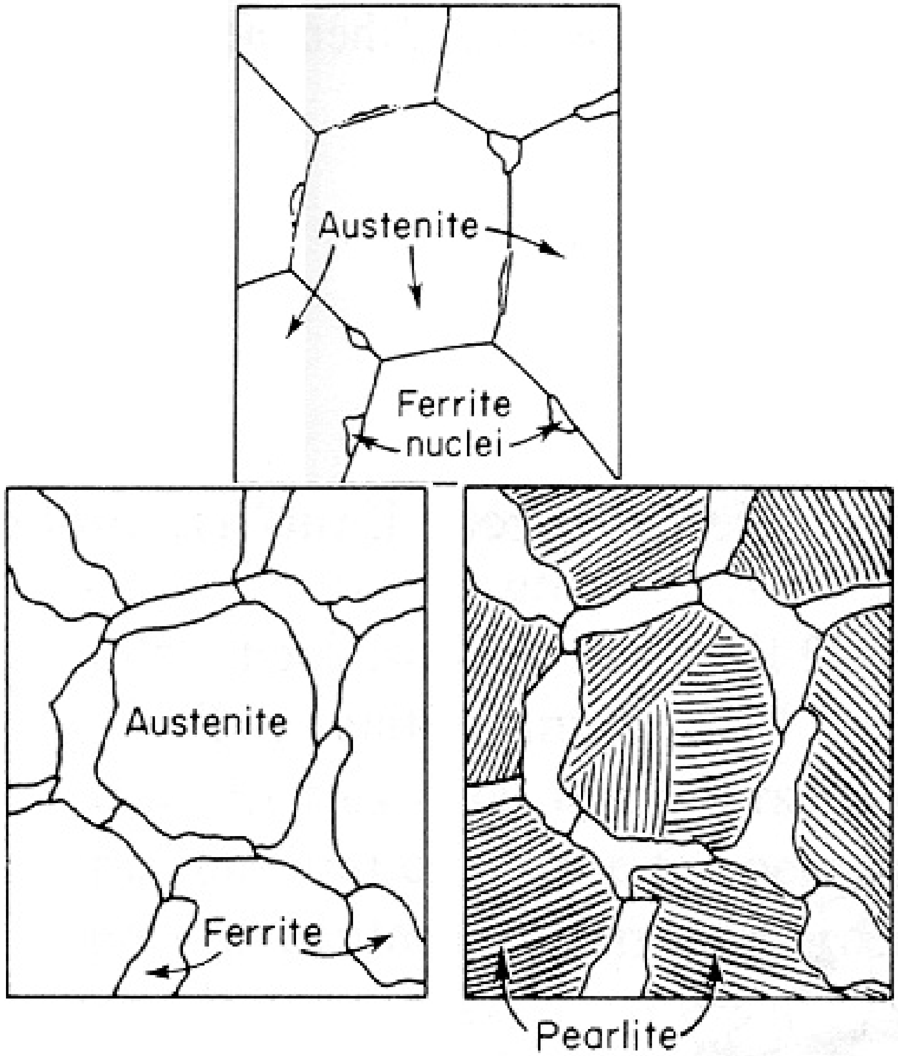
5.6. The Precipitation of Ferrite from Austenite (γ→α)

(Most important nucleation site: Grain boundary and the surface of inclusions)

The Iron-Carbon Phase Diagram



Microstructure (0.4 wt%C) evolved by slow cooling (air, furnace) ?



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 → γ; 0.022 wt% C → α; 6.7 wt% C → Fe_3C

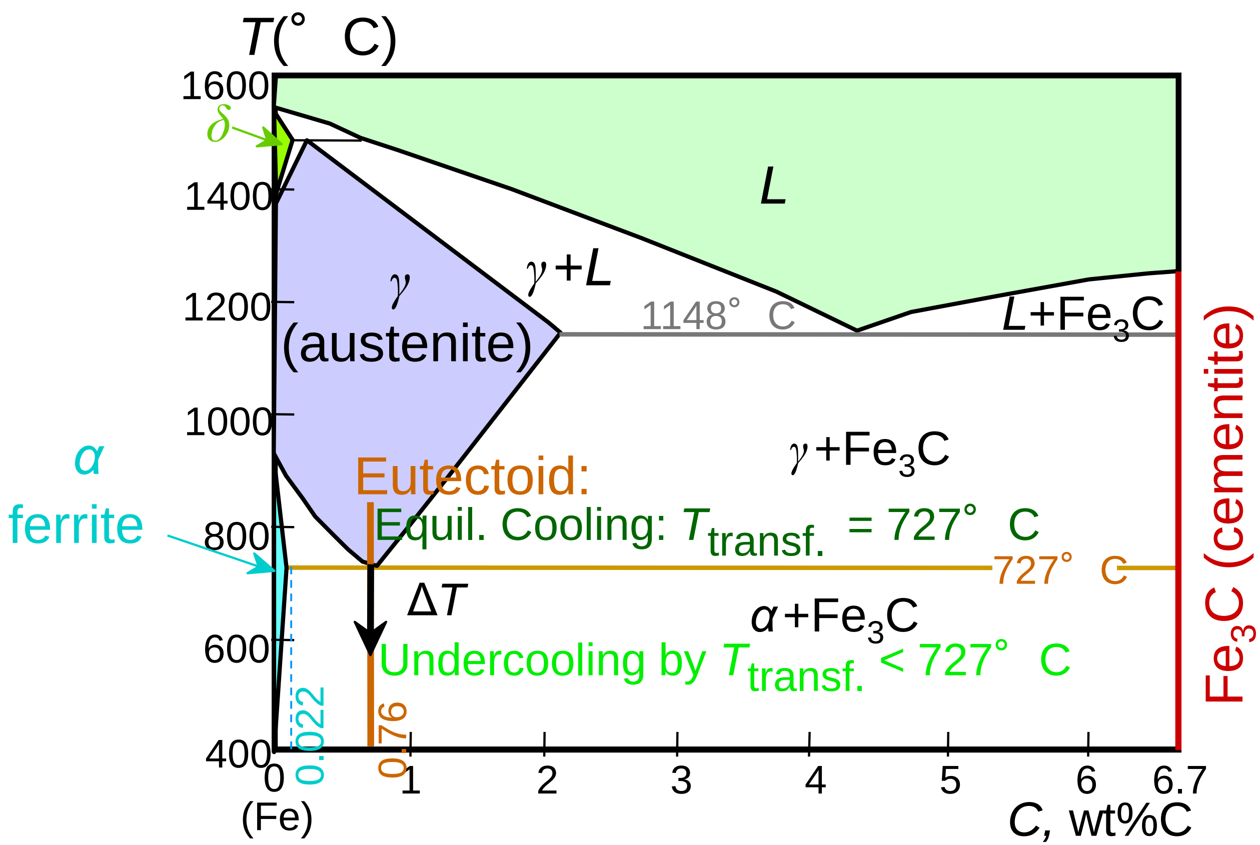
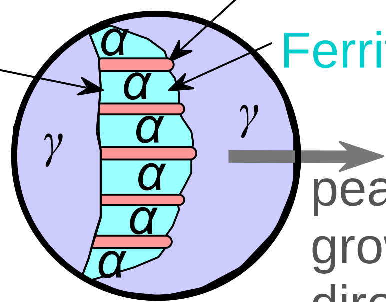


Fig. 11.23, Callister & Rethwisch 9e.
[Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

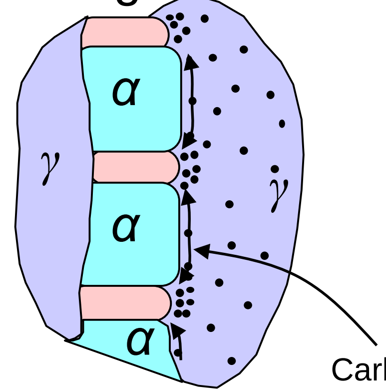
The Fe-Fe_3C Eutectoid Transformation

- Transformation of austenite to **pearlite**:

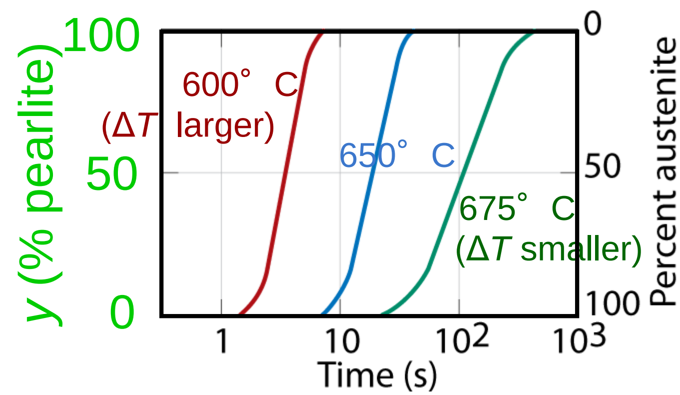


Adapted from Fig. 11.14, *Callister & Rethwisch 9e.*

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 675ºC.

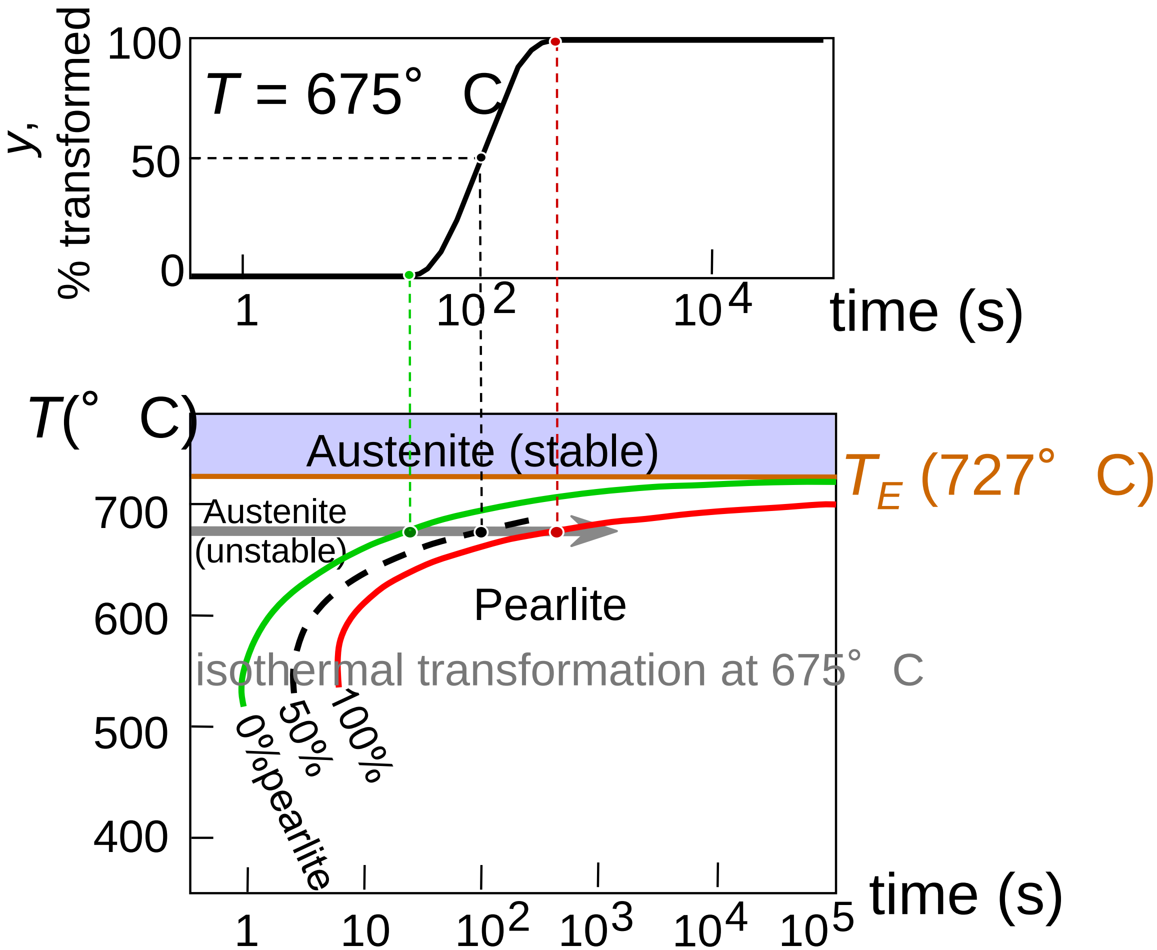


Fig. 12.13, *Callister & Rethwisch 9e.* [Adapted from H. Boyer (Editor), Atlas of Isothermal Transformation and Cooling Transformation Diagrams, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Generation of Isothermal Transformation Diagrams

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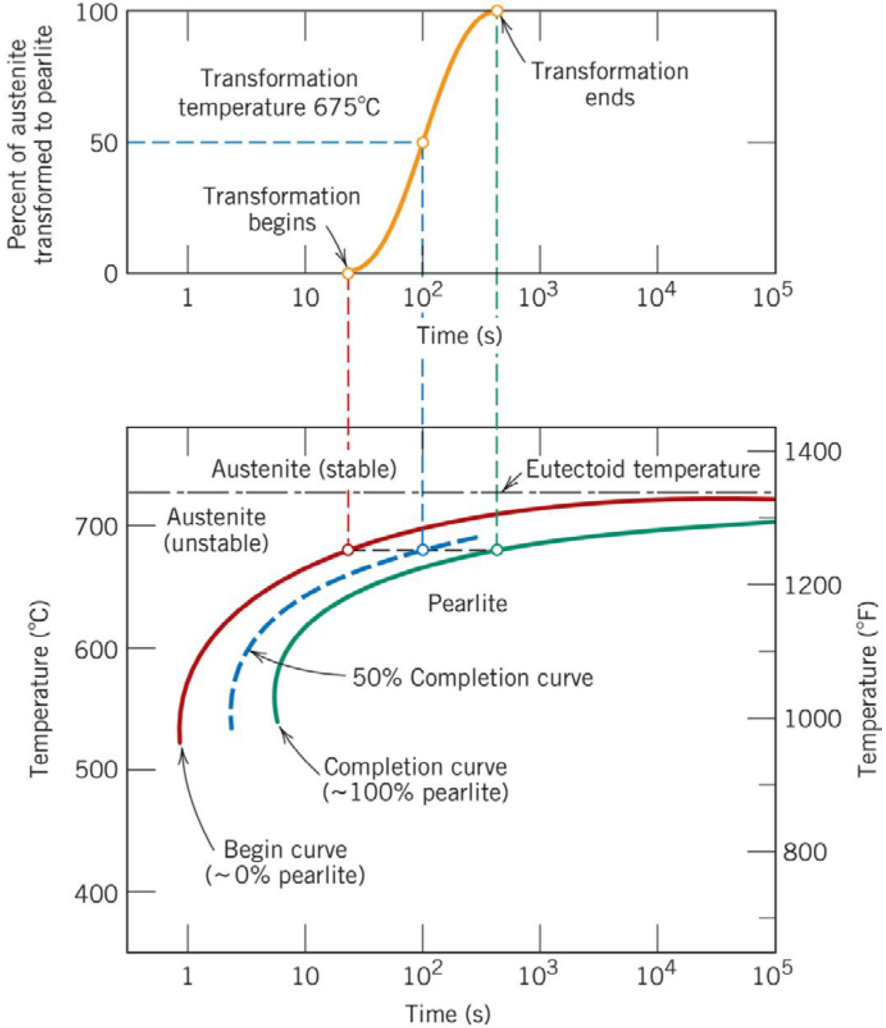

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Fig. 12.13, *Callister & Rethwisch 9e.*
[Adapted from H. Boyer (Editor), Atlas of Isothermal Transformation and Cooling Transformation Diagrams, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

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)

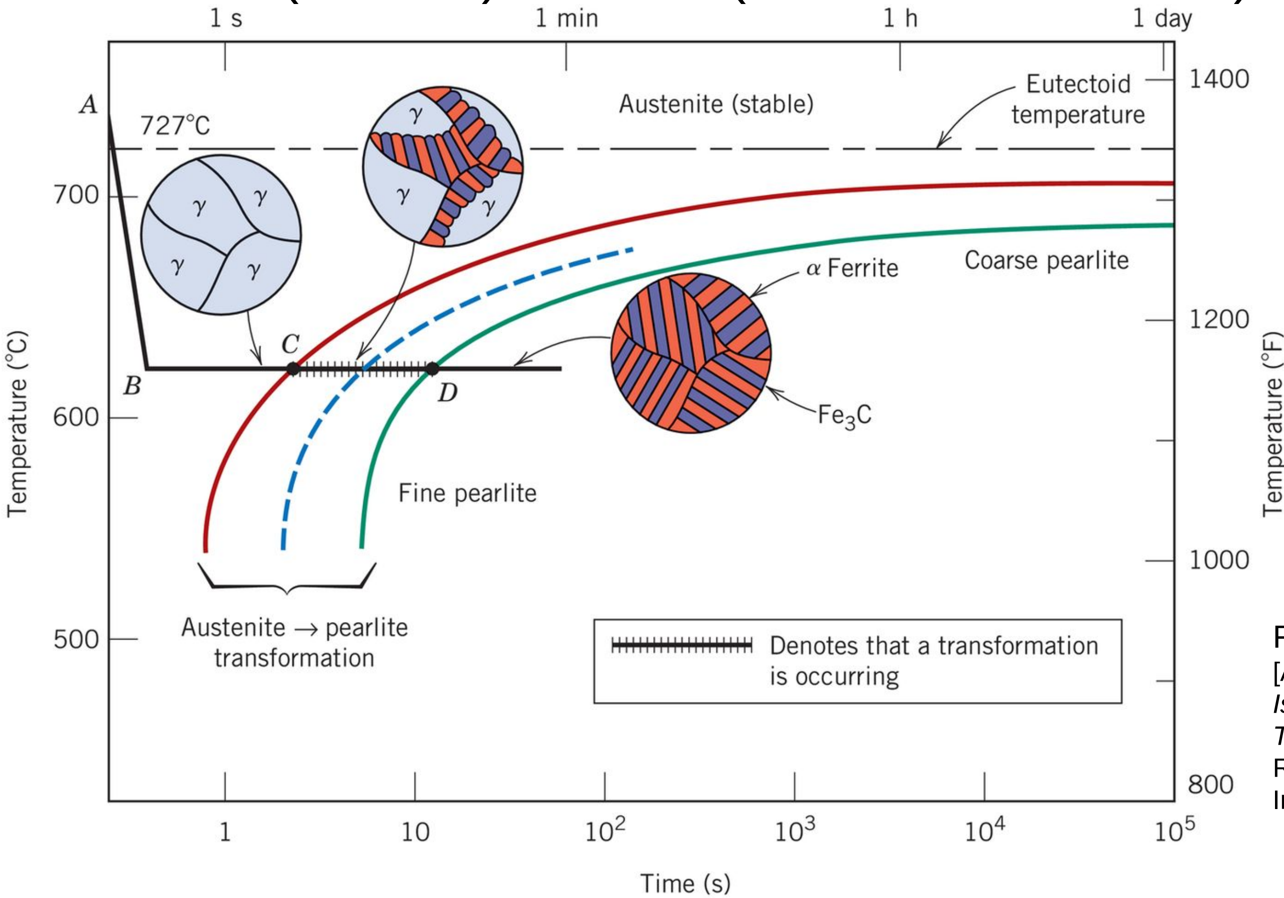

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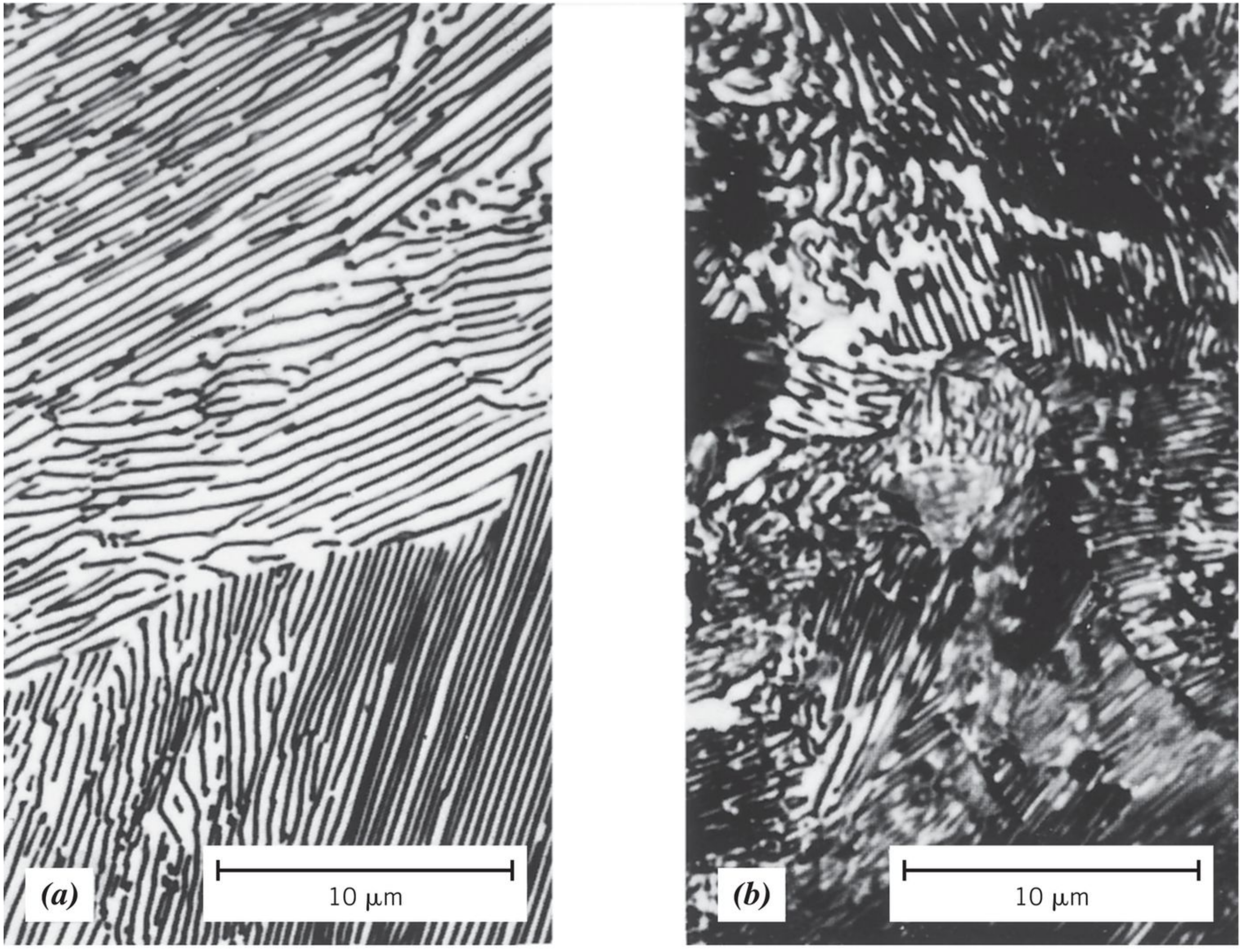
Fig. 12.14, *Callister & Rethwisch 9e.* [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Coarse perlite

Fine perlite



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.)

Transformations Involving noneutectoid compositions

Consider C_0 = 1.13 wt% C

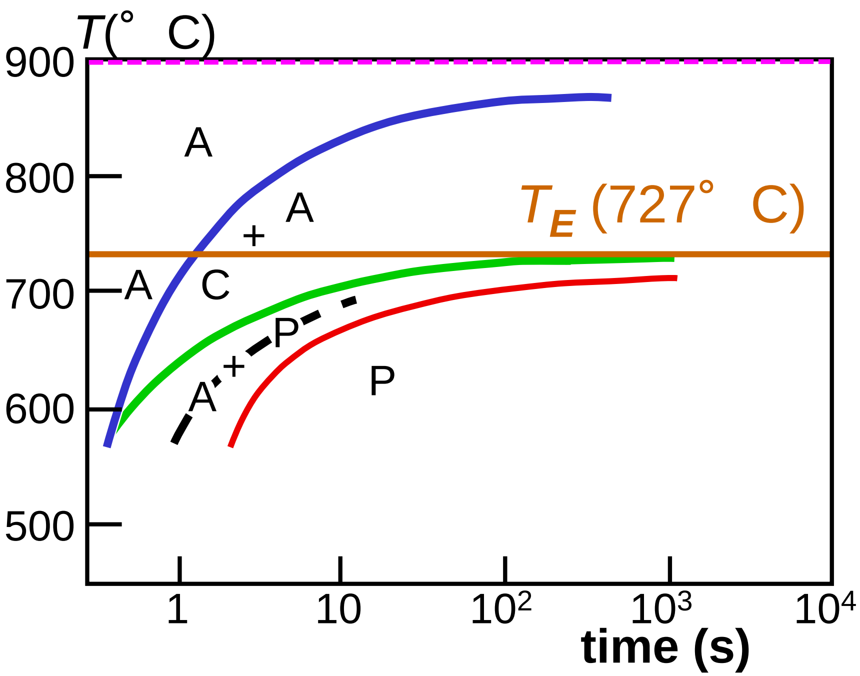


Fig. 12.16, *Callister & Rethwisch 9e.*
[Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

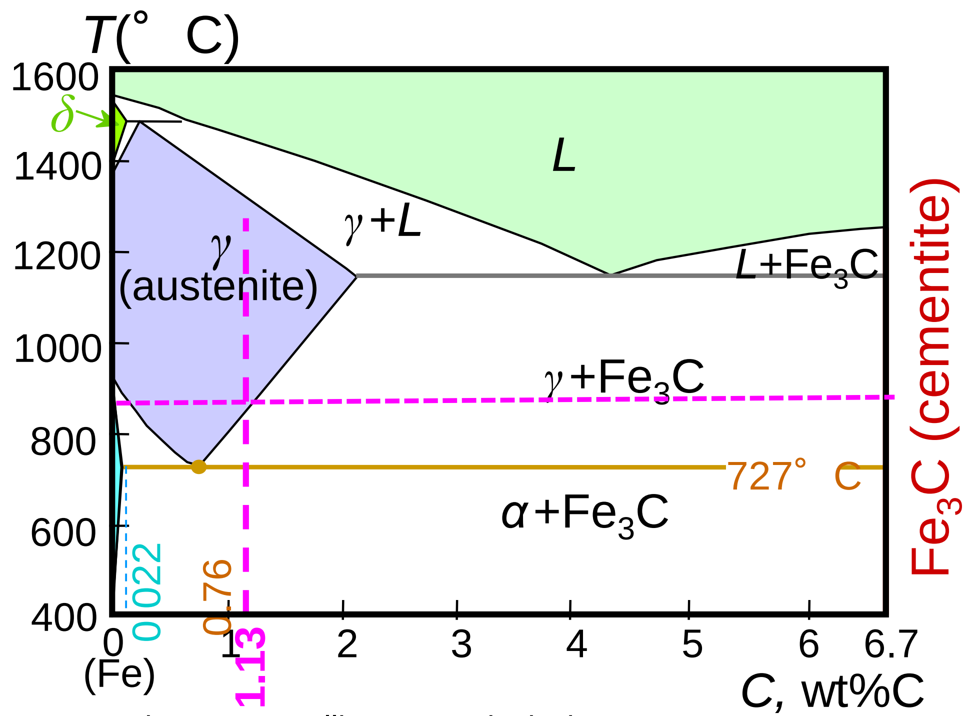


Fig. 11.23, Callister & Rethwisch 9e.
[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

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

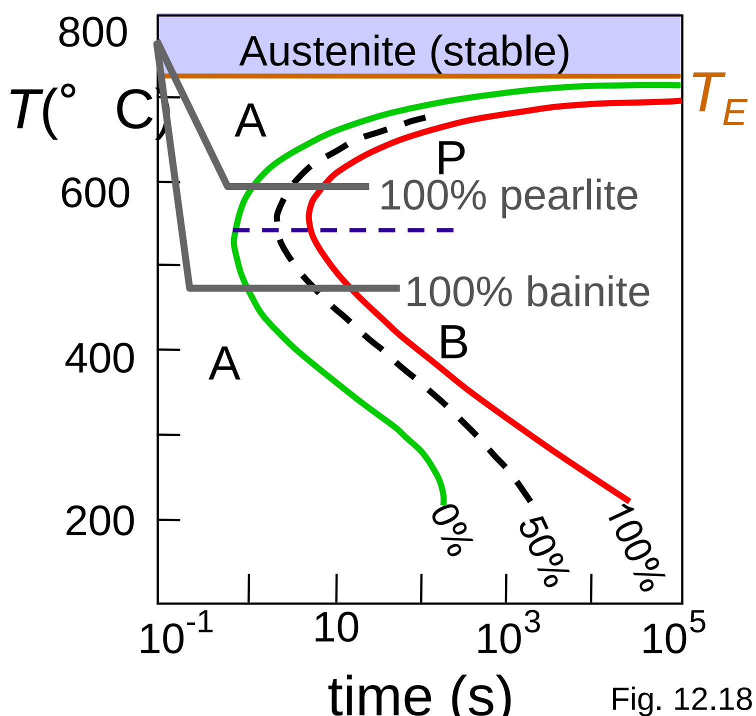


Fig. 12.18, *Callister & Rethwisch 9e.* [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

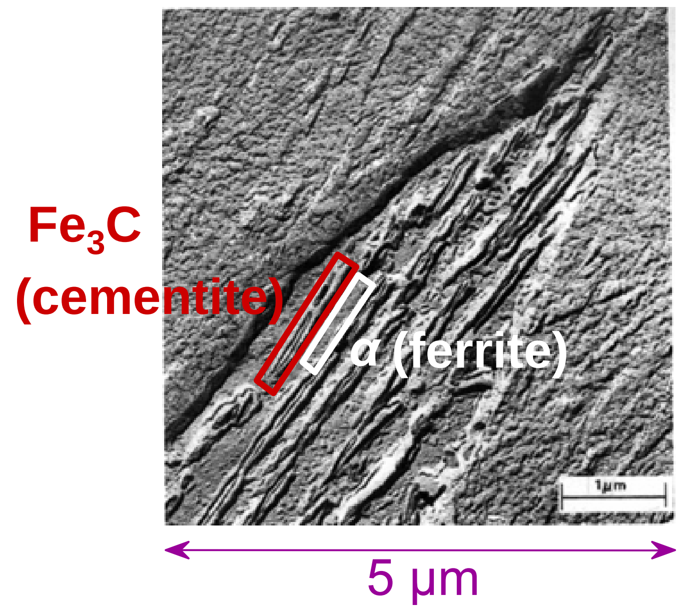


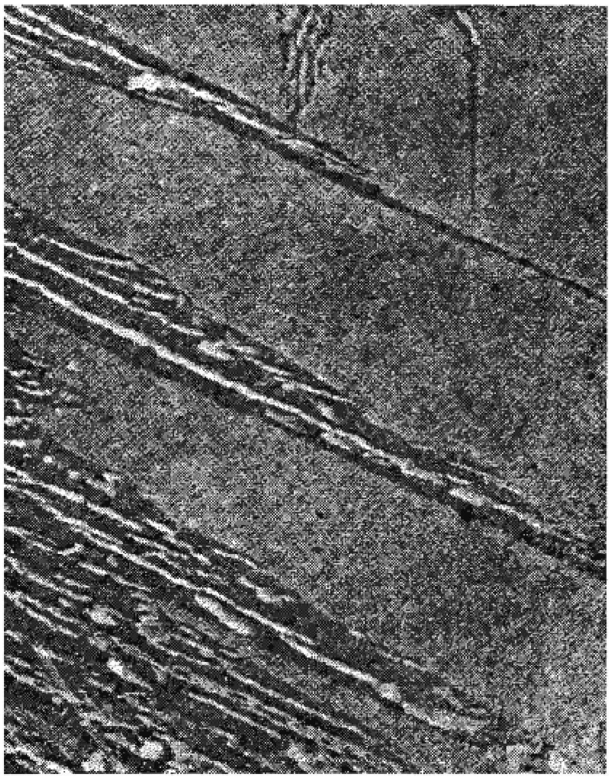
Fig. 12.17, *Callister & Rethwisch 9e.* (From *Metals Handbook*, Vol. 8, 8th edition, *Metallography, Structures and Phase Diagrams*, 1973. Reproduced by permission of ASM International, Materials Park, OH.)

5.8.2 Bainite Transformation

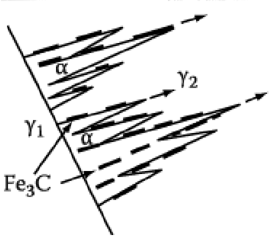
The microstructure of bainite depends mainly on the temperature at which it forms.

Upper Banite in medium-carbon steel

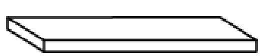
At high temp. 350 ~ 550°C, ferrite laths, K-S relationship, similar to Widmanstäten plates



(a)



(b)



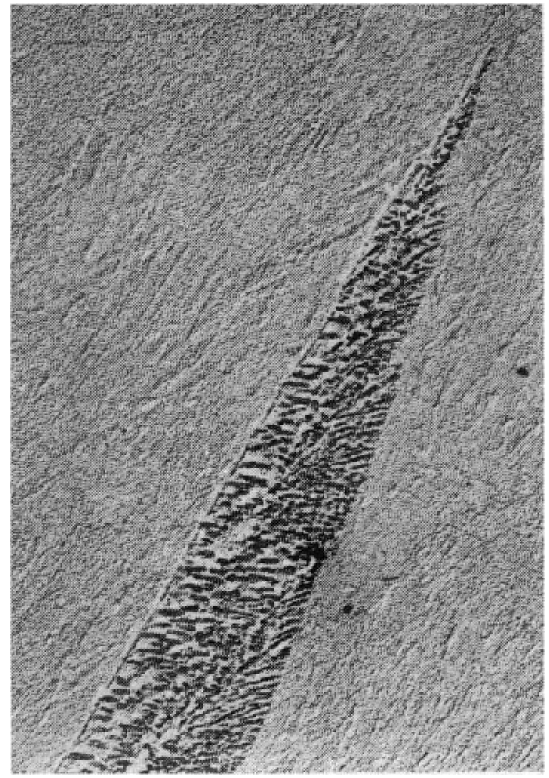
(c)

(b) Schematic of growth mechanism. Widmanstatten ferrite laths growth into γ_2. Cementite plates nucleate in carbon-enriched austenite.

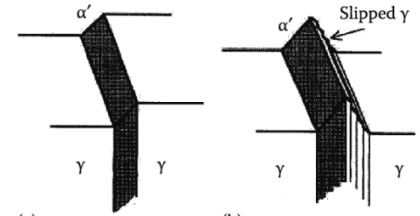
Lower Bainite in 0.69wt% C low-alloy steel

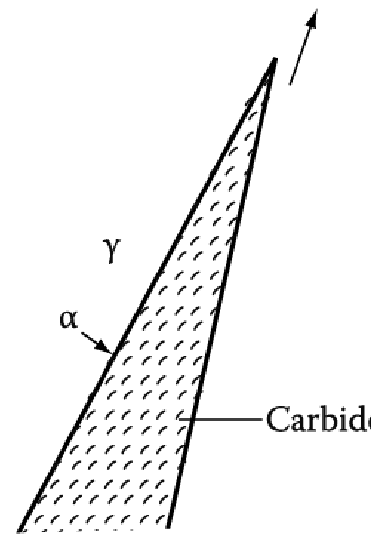
At sufficiently low temp. laths → plates

Carbide dispersion becomes much finer, rather like in tempered M.



(a)





(b)

Surface tilts by bainite trans. like M trans.
Due to Shear mechanism/ordered military manner

(b) A possible growth mechanism. α/γ interface advances as fast as carbides precipitate at interface thereby removing the excess carbon in front of the α.

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

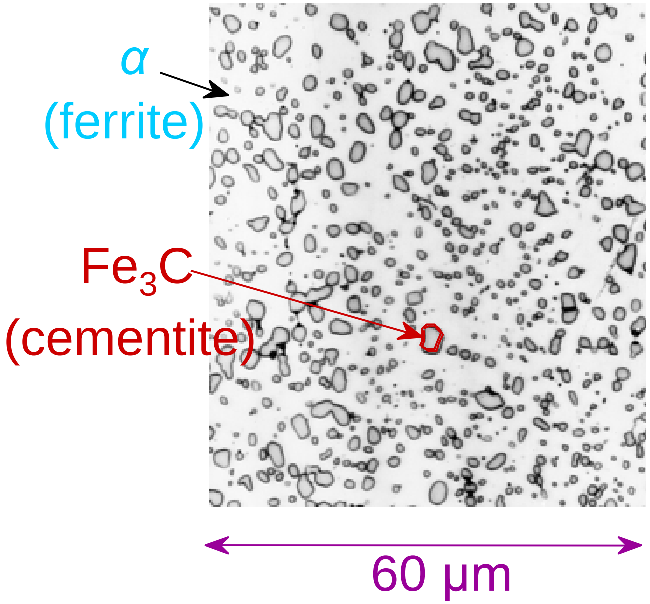
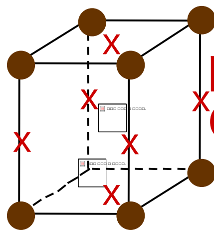


Fig. 12.19, *Callister & Rethwisch 9e.*
(Copyright United States Steel Corporation, 1971.)

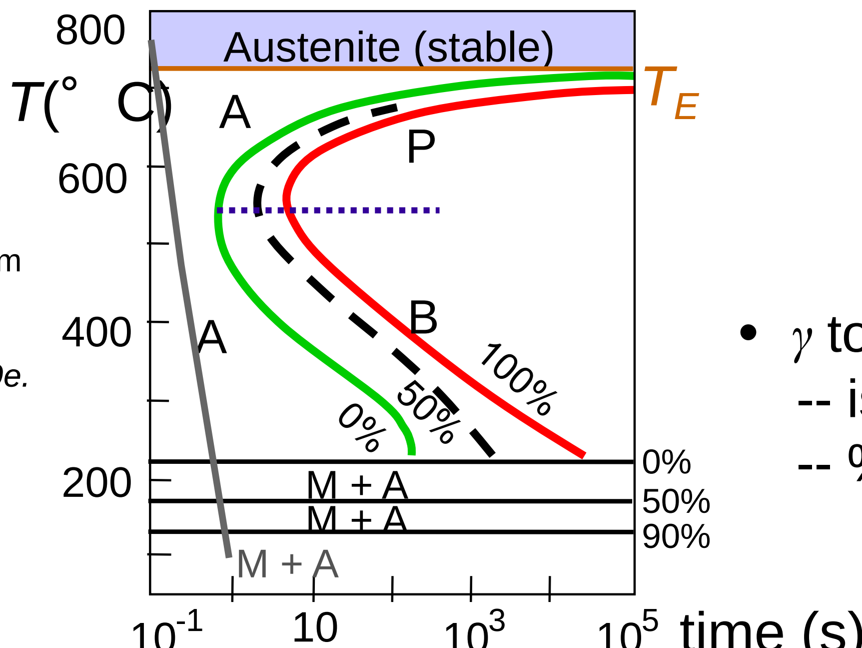
Martensite: A Nonequilibrium Transformation Product

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



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

- Isothermal Transf. Diagram



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

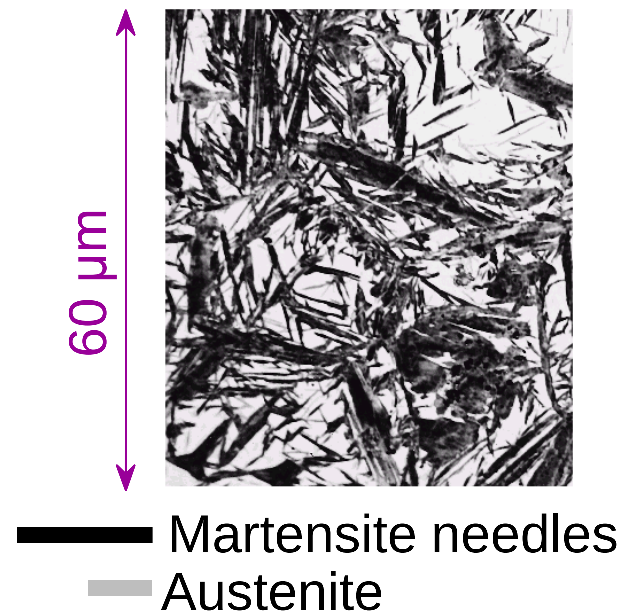
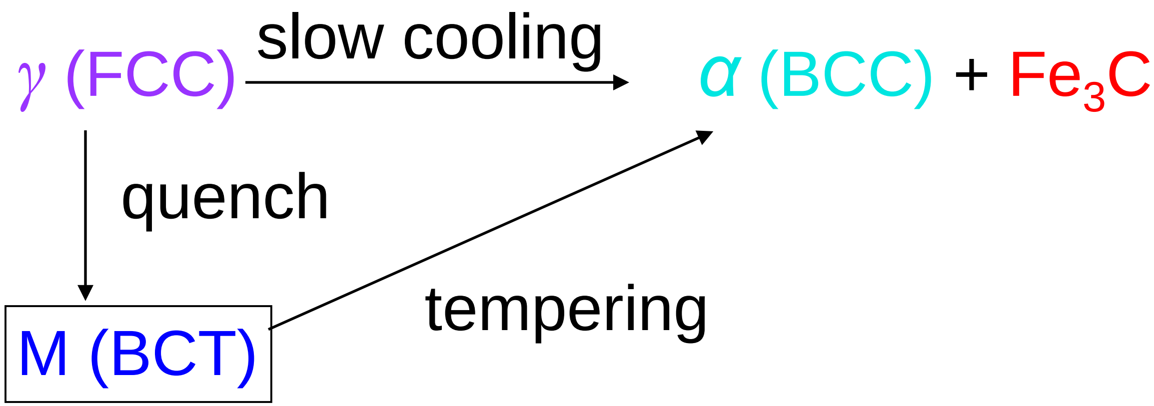


Fig. 12.21, *Callister & Rethwisch 9e.*
(Courtesy United States Steel Corporation.)

- 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

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.

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

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

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

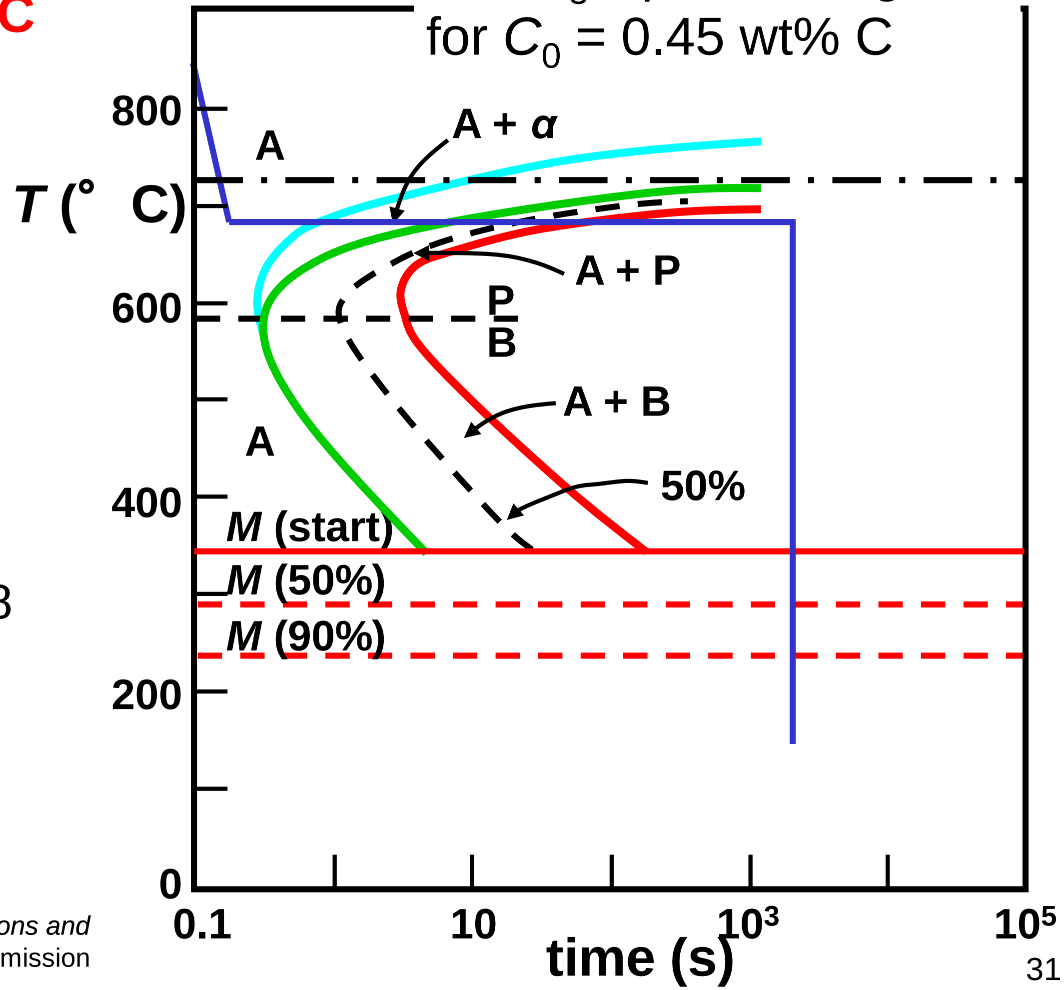


Figure 12.39, *Callister & Rethwisch 9e*.
(Adapted from *Atlas of Time-Temperature Diagrams for Irons and Steels*, G. F. Vander Voort, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

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.

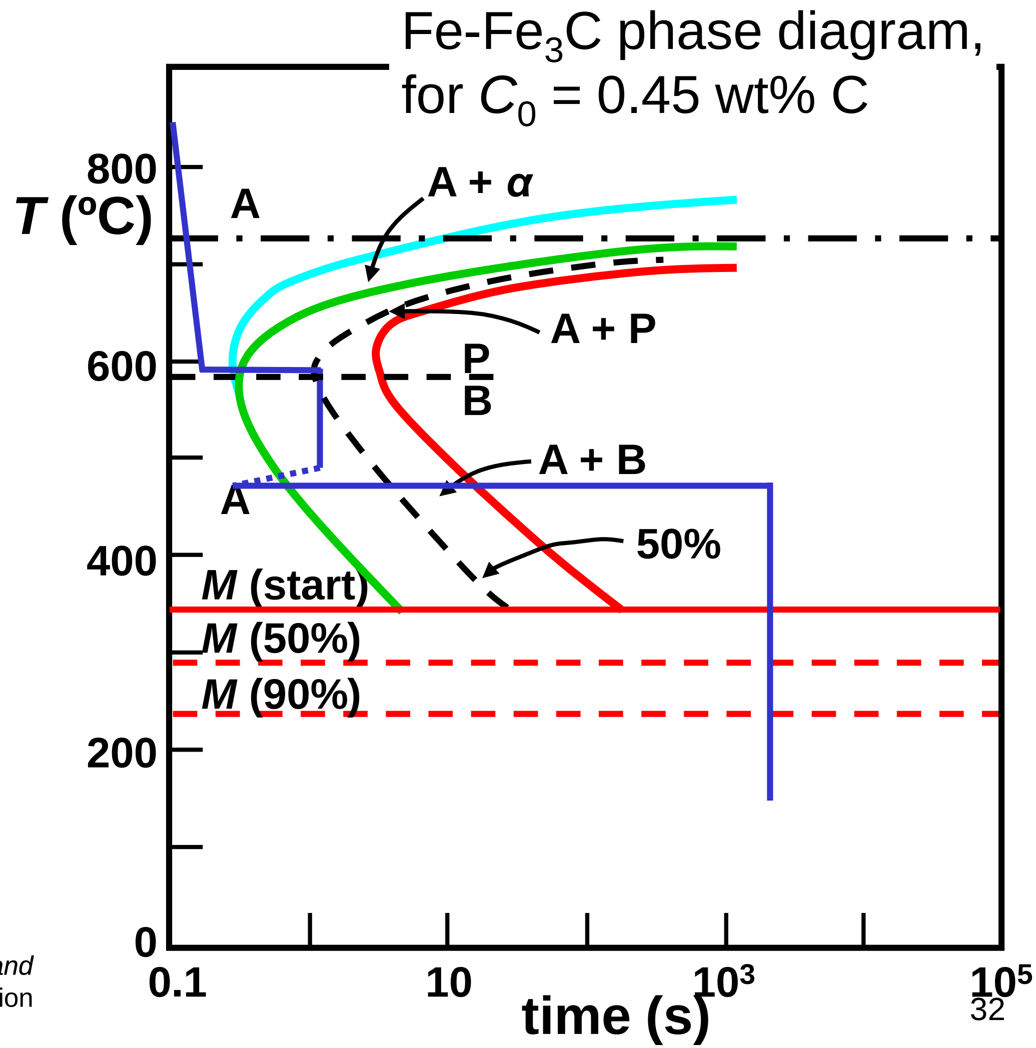


Figure 12.39, *Callister & Rethwisch 9e*.
(Adapted from *Atlas of Time-Temperature Diagrams for Irons and Steels*, G. F. Vander Voort, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

Solution to Part (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

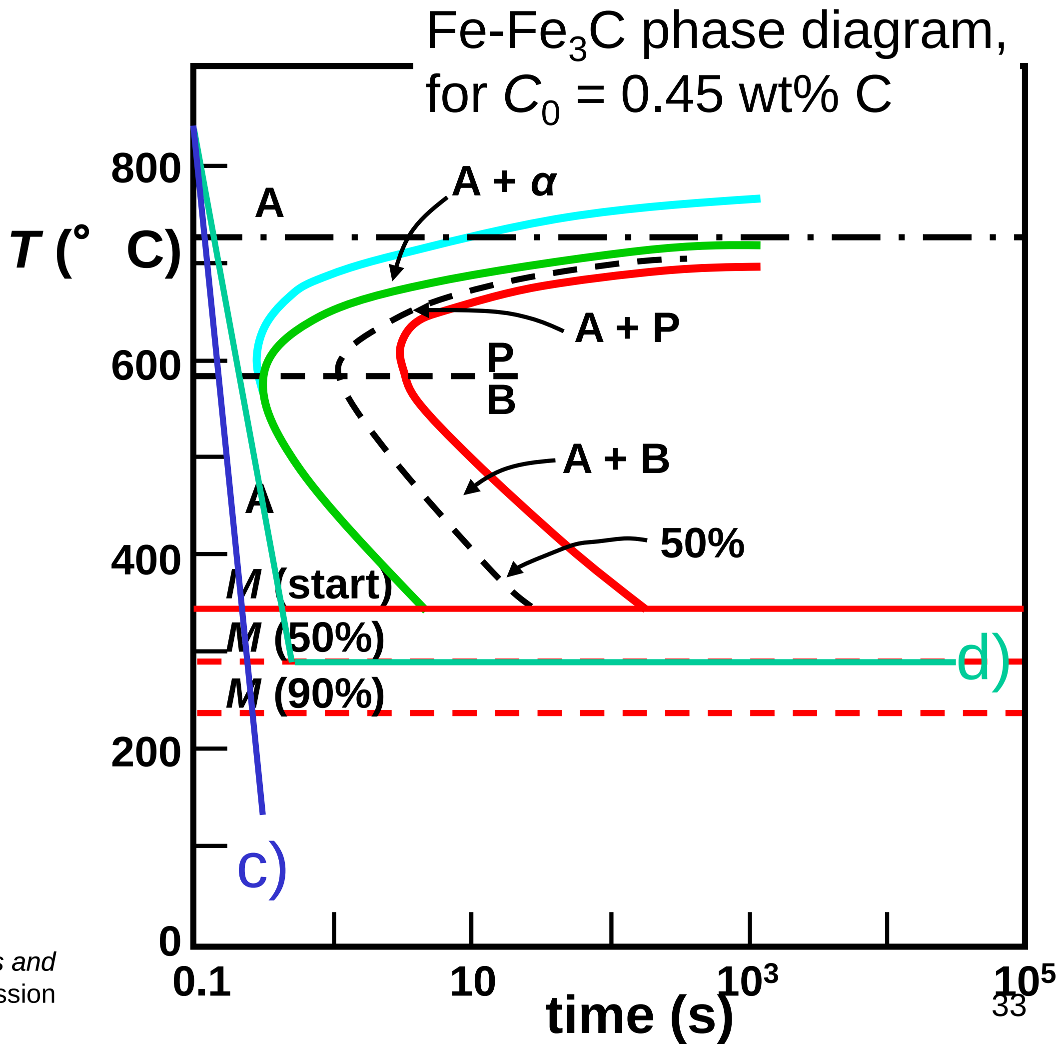


Figure 12.39, *Callister & Rethwisch 9e*.
(Adapted from *Atlas of Time-Temperature Diagrams for Irons and Steels*, G. F. Vander Voort, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

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)

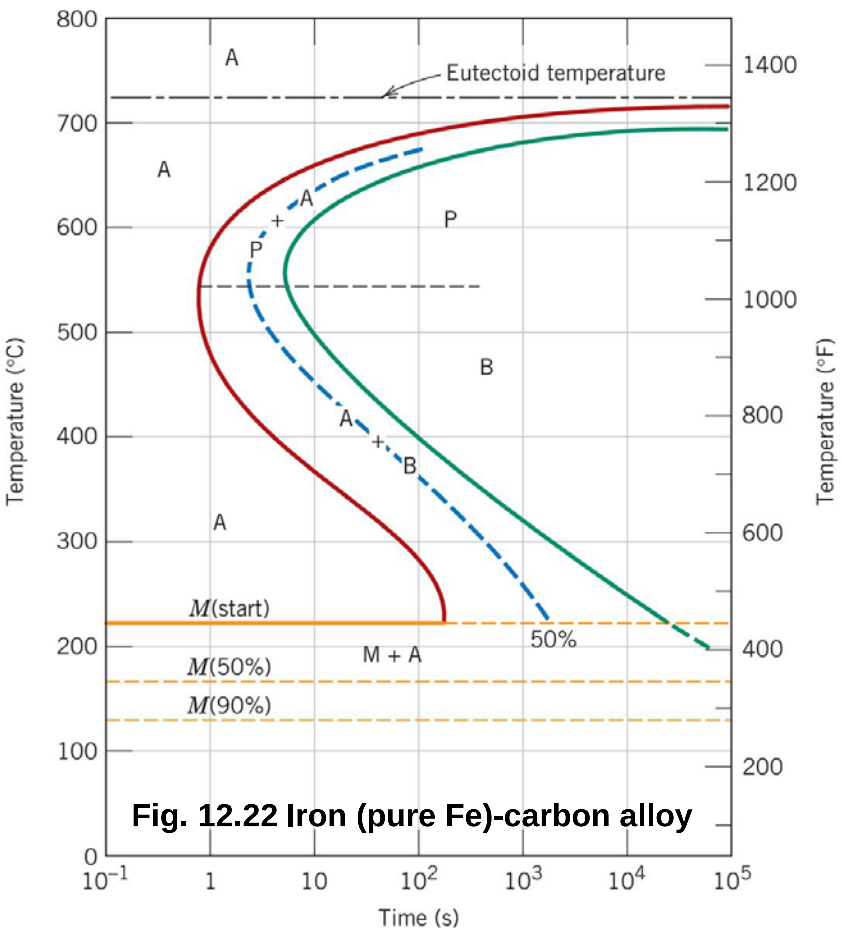


Fig. 12.22 Iron (pure Fe)-carbon alloy

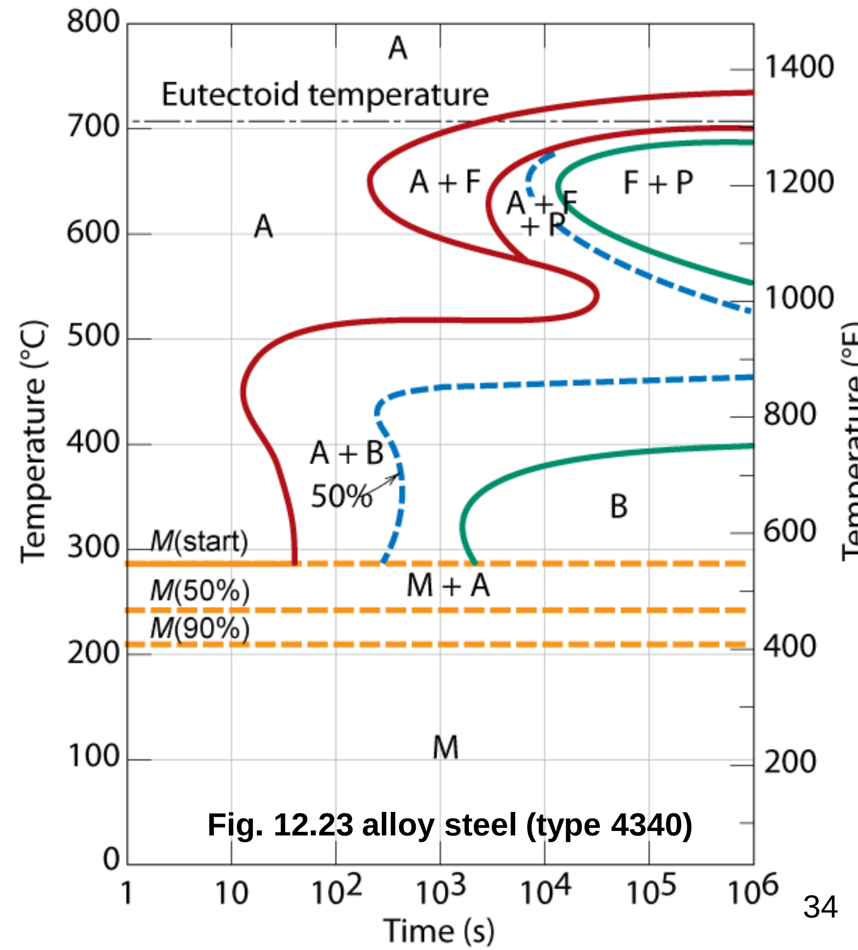


Fig. 12.23 alloy steel (type 4340)

Continuous Cooling Transformation Diagrams

Conversion of isothermal transformation diagram to continuous cooling transformation diagram

(TTT vs CCT diagram)

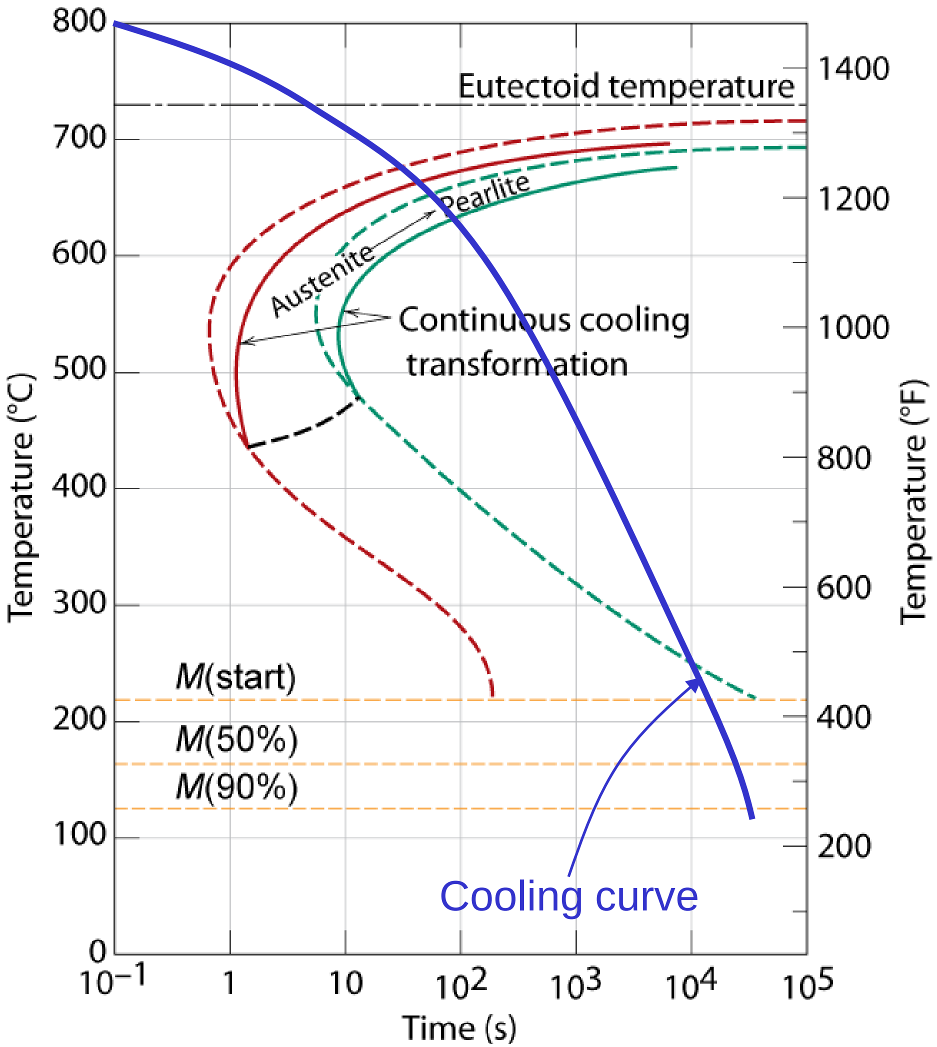


Fig. 12.25, *Callister & Rethwisch 9e.*
[Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

그림 12.26 공석 조성을 갖는 철-탄소 합금의 연속 냉각 변태도 위에 그려진 적당한 급랭과 서냉온도 곡선

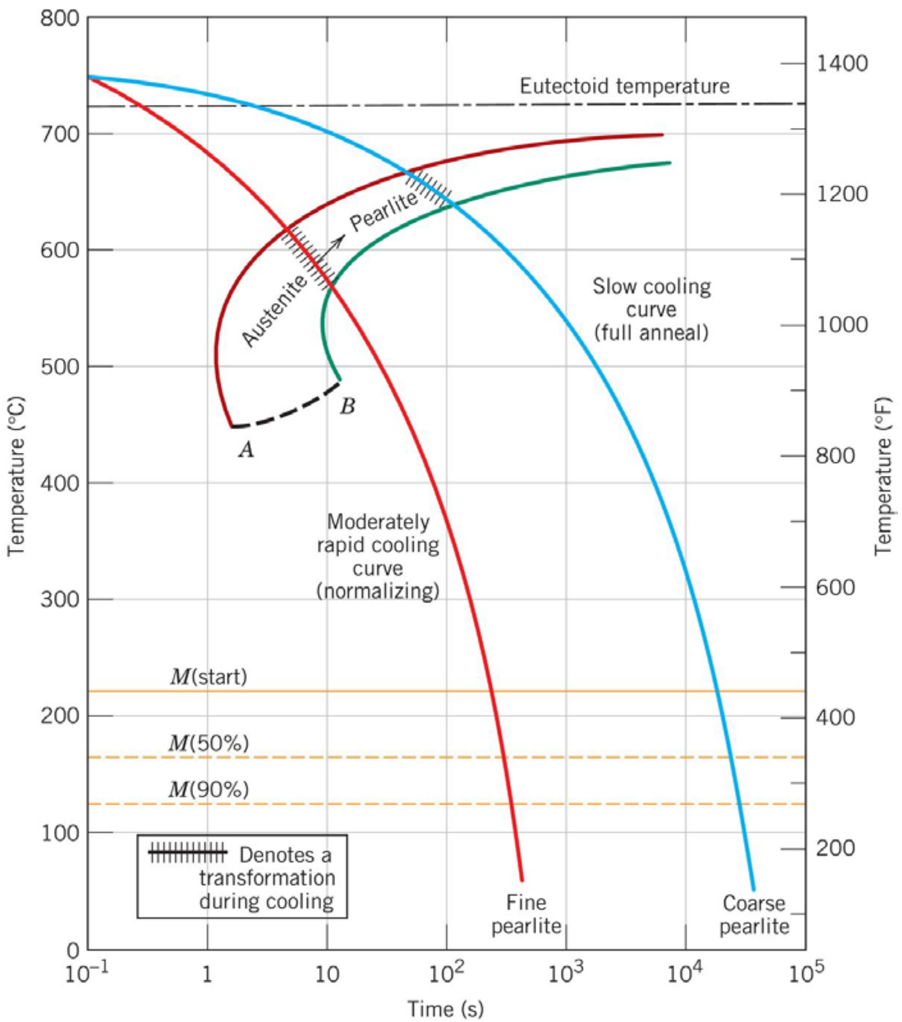


그림 12.27 공석 조성의 철-탄소 합금의 연속 냉각 변태도와 냉각 곡선. 냉각 중에 일어나는 변태에 따른 최종 미세조직 변화를 볼 수 있다.

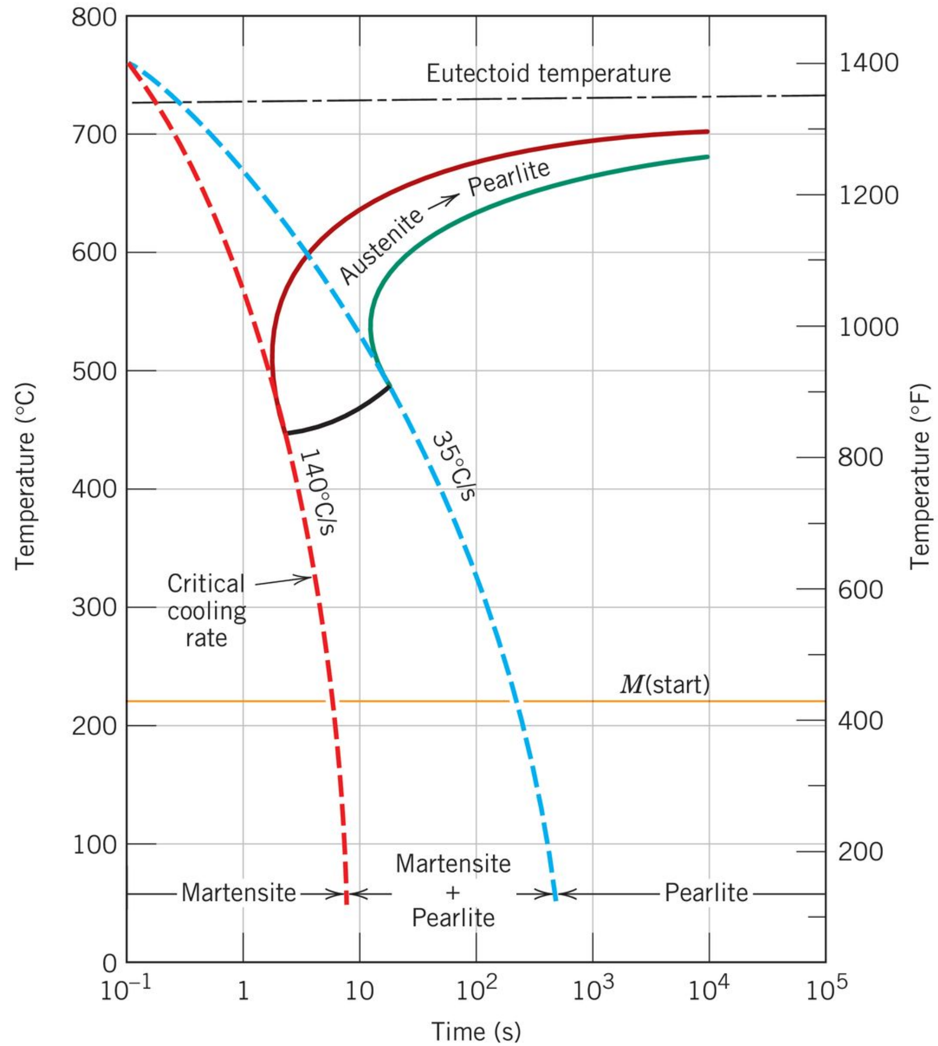
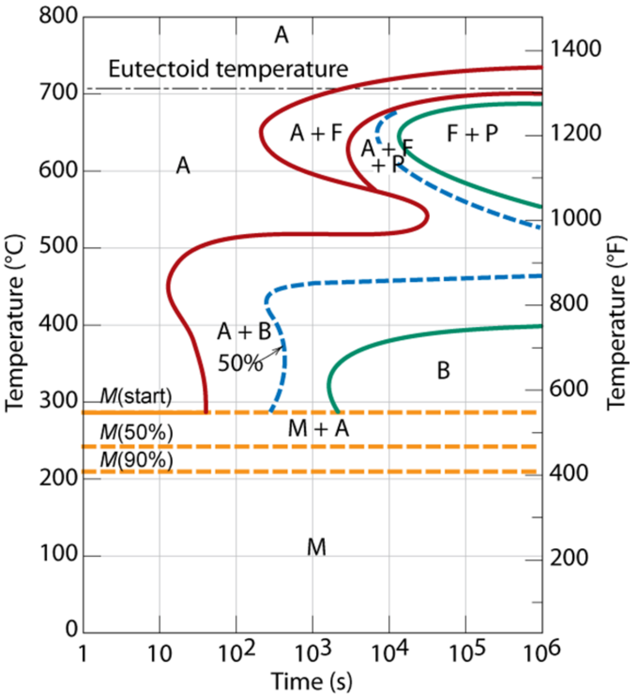
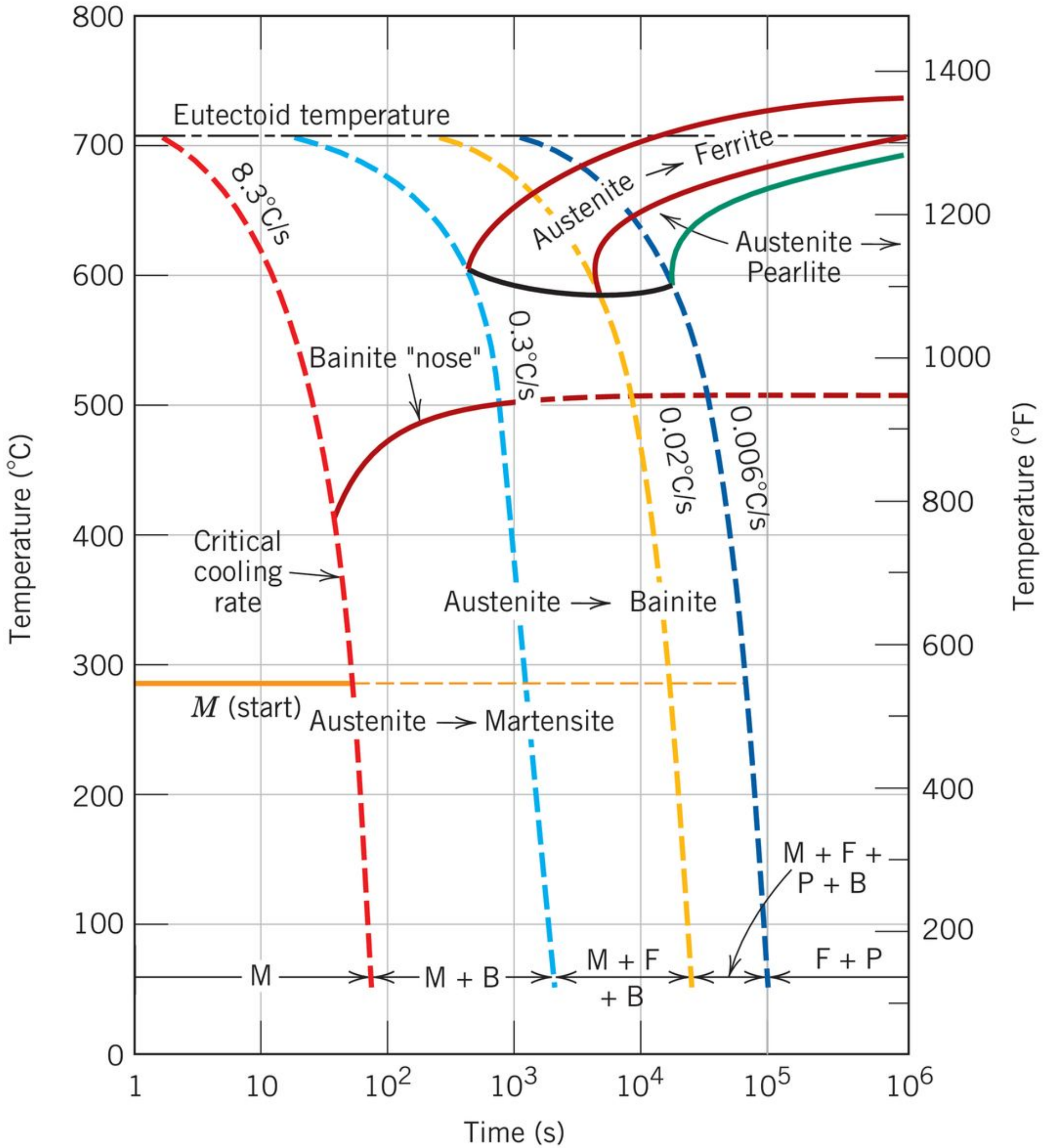


그림 12.27

4030 합금강의 연속 냉각 변태도와 여러 조건의 냉각 곡선. 냉각 중에 일어나는 변태에 따른 최종 미세조직의 변화를 볼 수 있다.





Adapted from H. E. McGannon (Editor), The Making, Shaping and Treating of Steel, 9th edition, United States Steel Corporation, Pittsburgh, 1971, p. 1096.

Mechanical Props: a. Influence of C Content

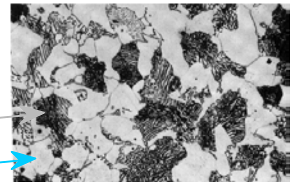
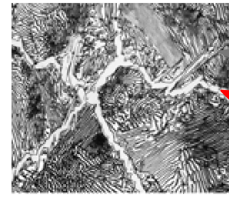


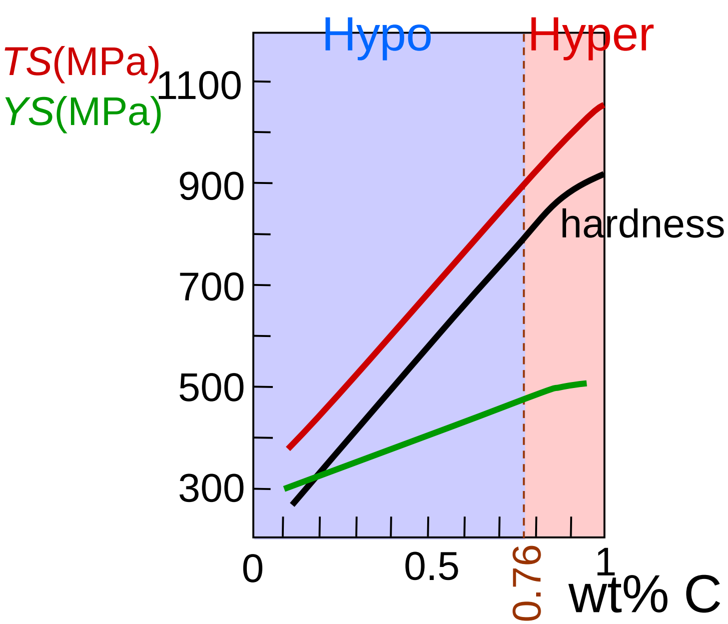
Fig. 11.29, *Callister & Rethwisch 9e.*
(Courtesy of Republic Steel Corporation.)

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.)



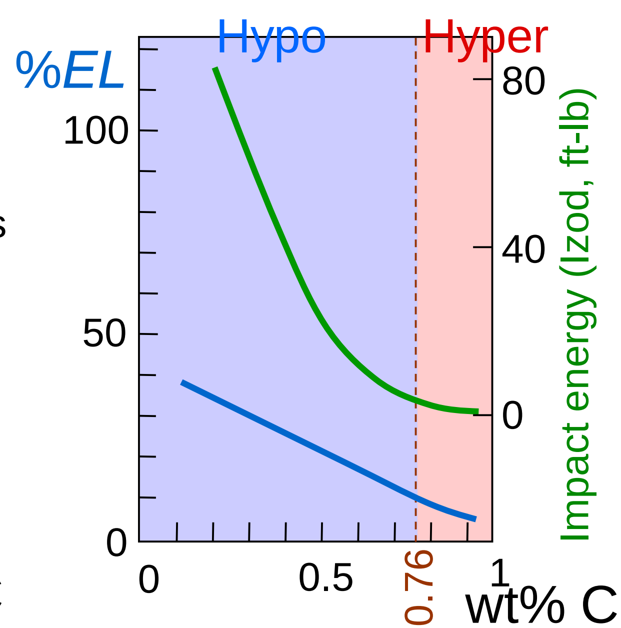
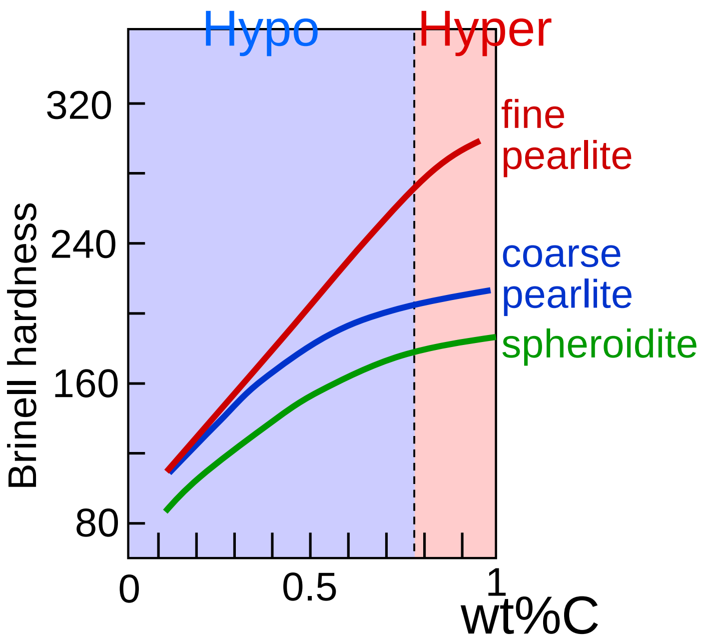


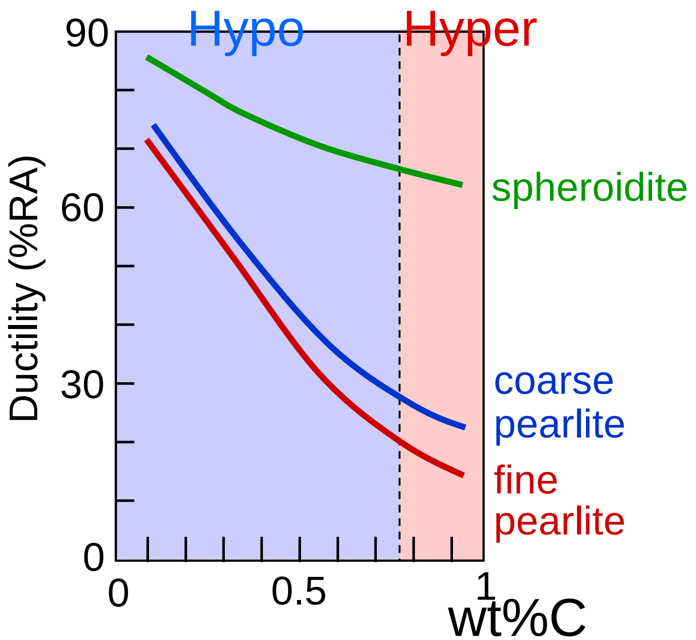
Fig. 12.29, *Callister & Rethwisch 9e.*
[Data taken from *Metals Handbook: Heat Treating*, Vol. 4, 9th edition, V. Masseria (Managing Editor), 1981. Reproduced by permission of ASM International, Materials Park, OH.]

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

Mechanical Props:

b. 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:

c. Fine Pearlite vs. Martensite

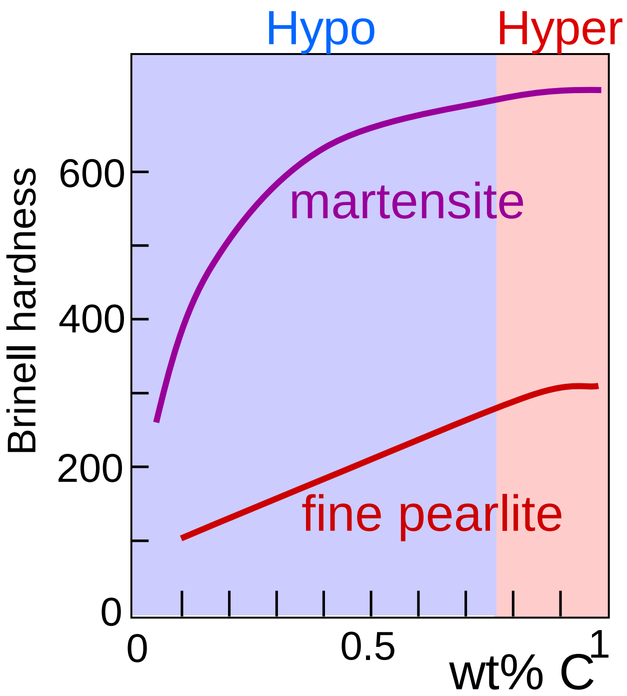


Fig. 12.32, *Callister & Rethwisch 9e.*
(Adapted from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, 1939; and R. A. Grange, C. R. Hribal, and L. F. Porter, *Metall. Trans.* A, Vol. 8A. Reproduced by permission of ASM International, Materials Park, OH.)

- **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

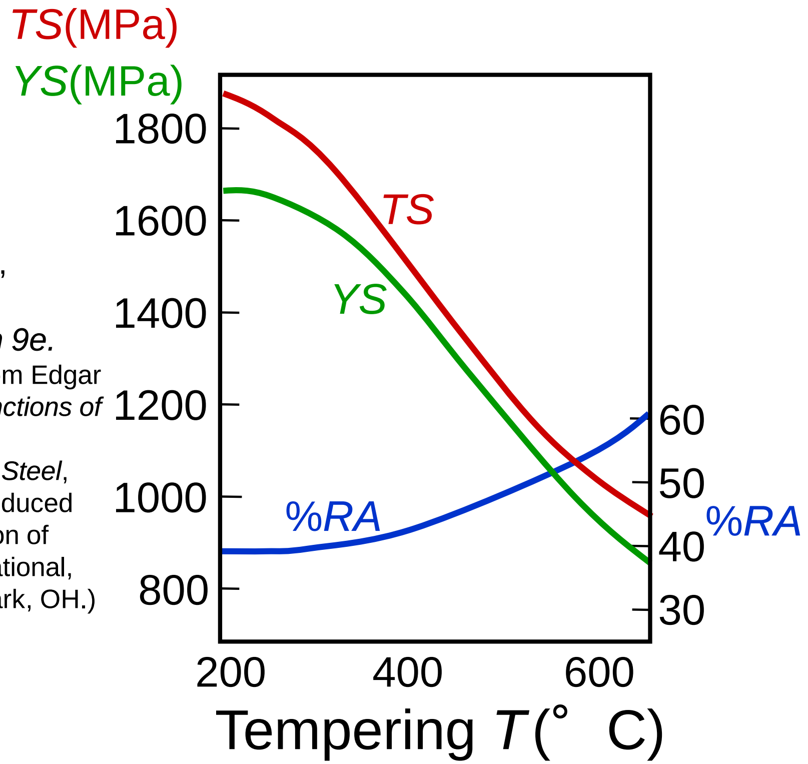


Fig. 12.34, *Callister & Rethwisch 9e.* (Adapted from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, 1939. Reproduced by permission of ASM International, Materials Park, OH.)

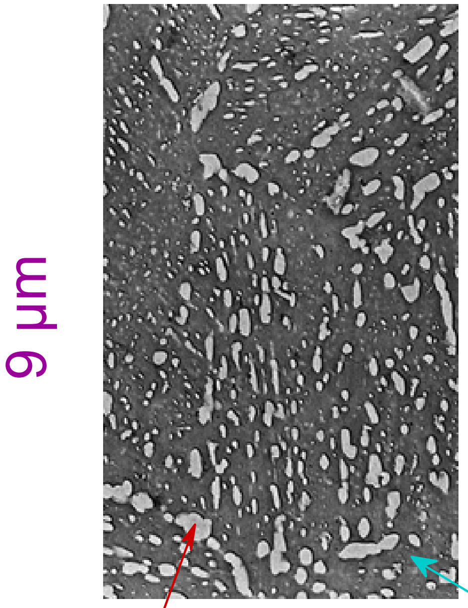
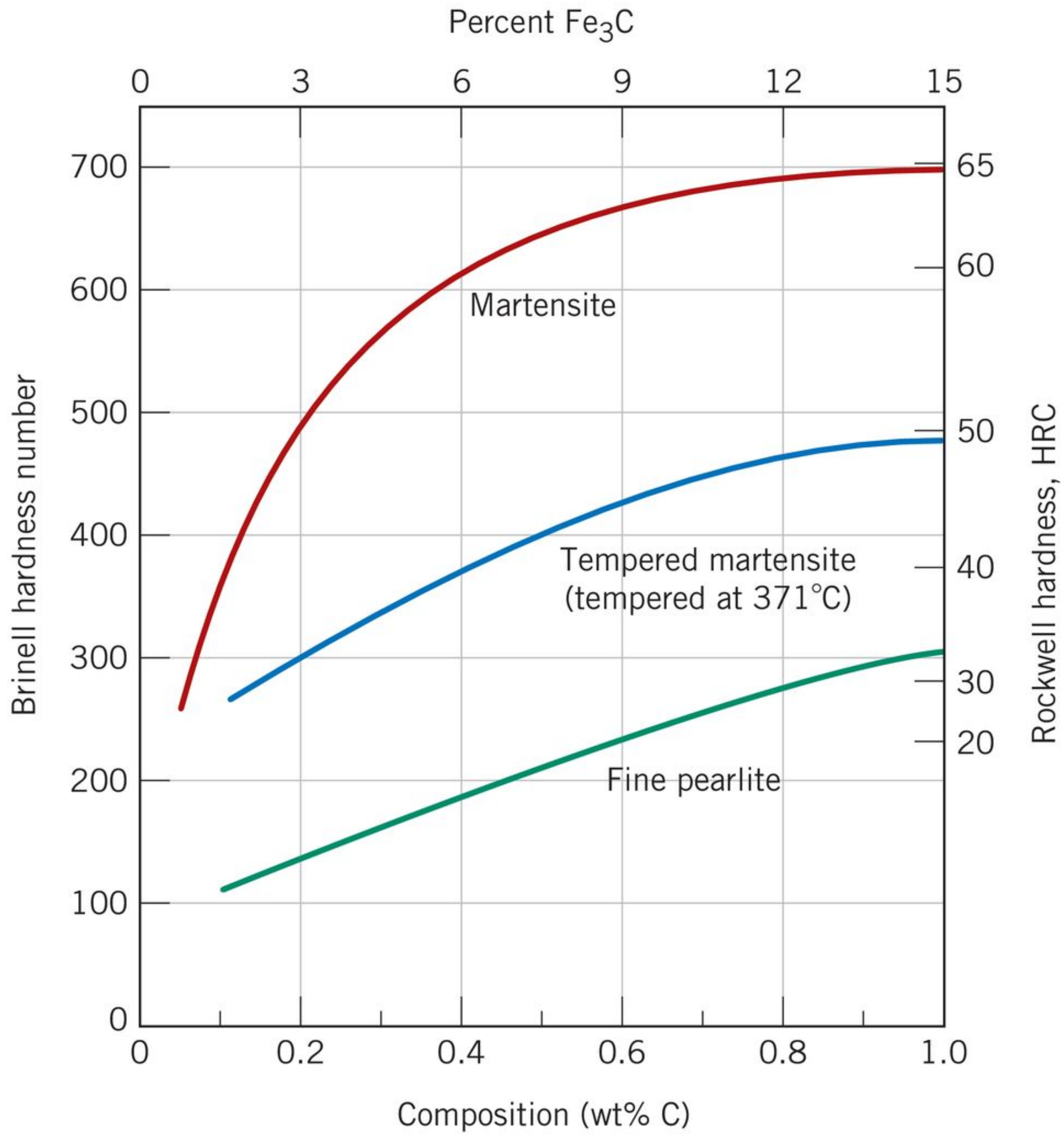


Figure 12.33, *Callister & Rethwisch 9e.* (Copyright 1971 by United States Steel Corporation.)

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

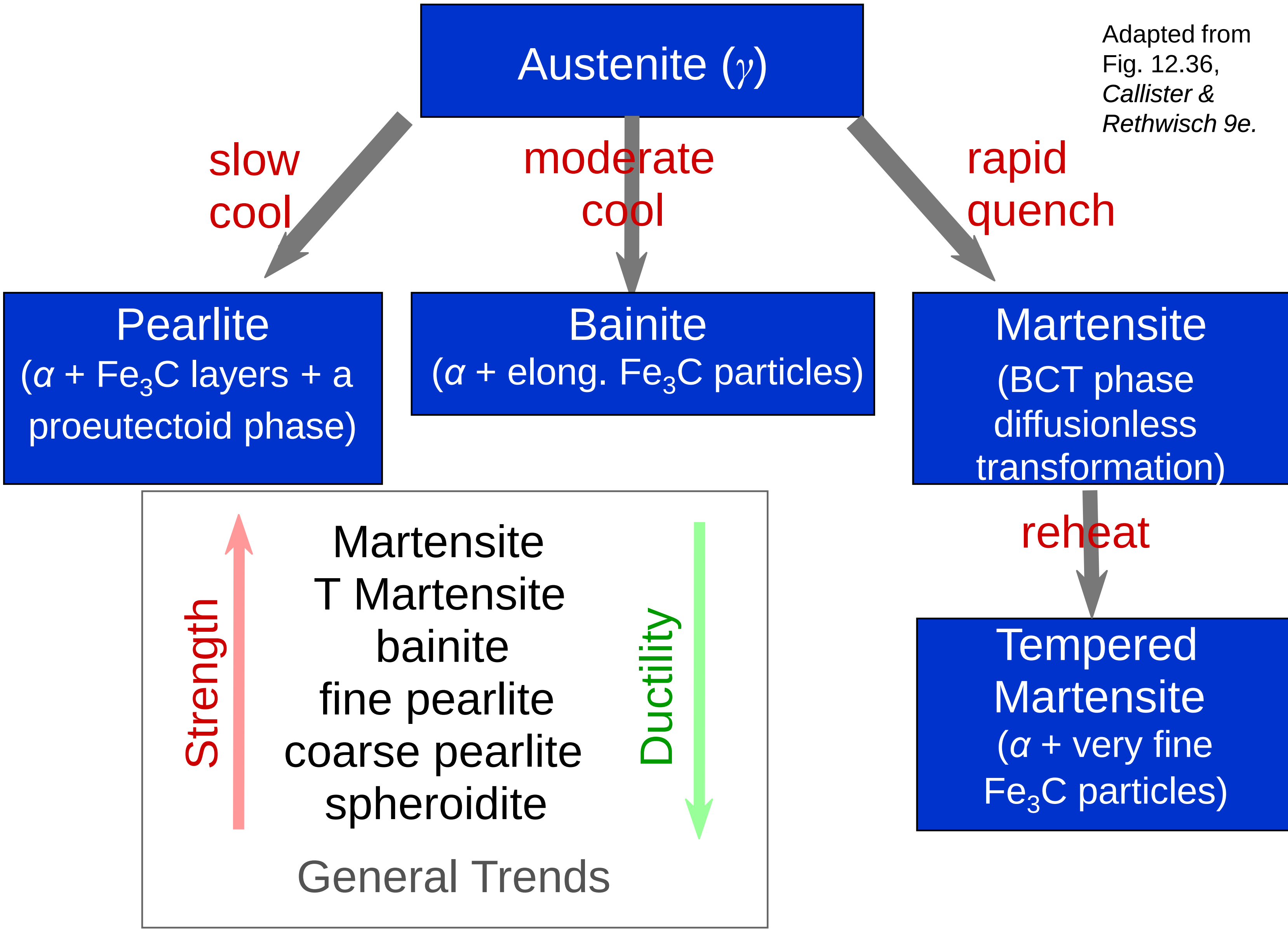
그림 12.32

순 탄소 마텐자이트강, 템퍼링된 마텐자이트강 [371°C 템버링], 펄라이트 강의 탄소농도에 따른 상온 경도값



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.

Summary of Possible Transformations in Fe-C binary phase diagram



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

11월 19일과 11월 21일 휴강

Homework 1: 8장 / 9장/ 10장 예제문제

Homework 2: 아래 내용 Summary
Chapter 13 Nonferrous Alloys (pp. 445 – 457)
Chapter 14 Types and Applications of Ceramics (pp. 475 – 491)
Chapter 15 Polymer Types (pp. 520 -532)

Incentive Homework 1: 관심있는 Advanced Engineering Materials
하나 정해서 5 pages 이내 정리

Incentive Homework 2 : 서울대학교 재료공학부 진학이유와
앞으로의 포부-"자기자신에게 보내는 편지"