The Limitation of Equilibrium Phase Diagrams

- Unable to indicate the time period required for the attainment of equilibrium
- Equilibrium conditions are maintained only if heating or cooling is carried out at extremely slow and unpractical rates.

Chapter 10: Phase Transformations

WHY STUDY PHASE TRANSFORMATION?

- The development of a set of desirable mechanical characteristics for a material often results from a phase transformation. That is wrought by **heat-treatment**.

- It is important to design a proper heat-treatment to get the desired room-temperature mechanical properties of an alloy.

- **Is it possible to develop other microstructural elements than pearlite for iron-carbon alloys?**

Phase Transformations

- Phase transformation may be wrought in metal alloy systems by varying temperature, composition, and the external pressure.

- Temperature changes by means of heat-treatments are most conveniently utilized to induce phase transformations.

- This corresponds to crossing a phase boundary on the composition-temperature phase diagram as an alloy of a given temperature is heated or cooled.

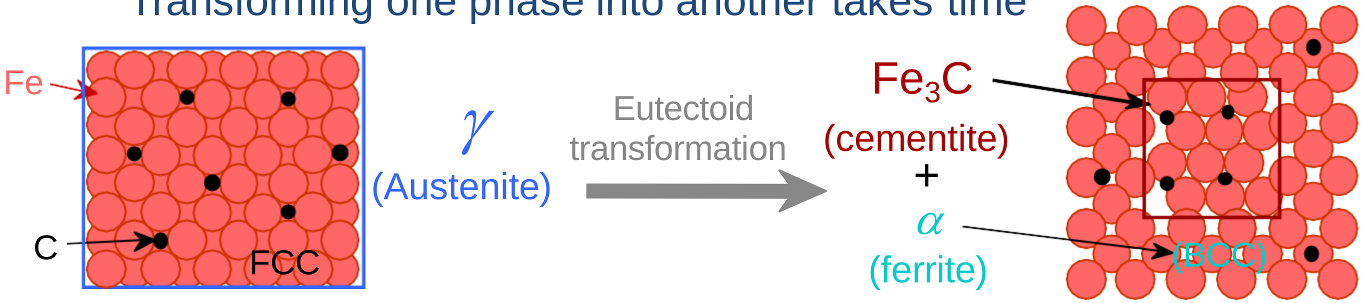
- One limitation of phase diagrams is their inability to indicate the time period required for the attainment of equilibrium.

- Equilibrium conditions are maintained only if heating or cooling is carried out at extremely slow and unpractical rates.

THE INFLUENCE OF TIME

- Why it is important to study the influence of time on phase transformation?
- How does the rate of transformation depend on time and temperature?

Transforming one phase into another takes time



Fe

C

FCC

γ

(Austenite)

Eutectoid transformation

Fe_3C

(cementite)

+

α

(ferrite)

(BCC)

- For other than equilibrium cooling, transformations are shifted to lower temperatures than indicated by the phase diagram.

- **Supercooling:** the shift to lower temperatures for cooling
- **Superheating:** the shift to higher temperatures for heating

Transformations & Undercooling

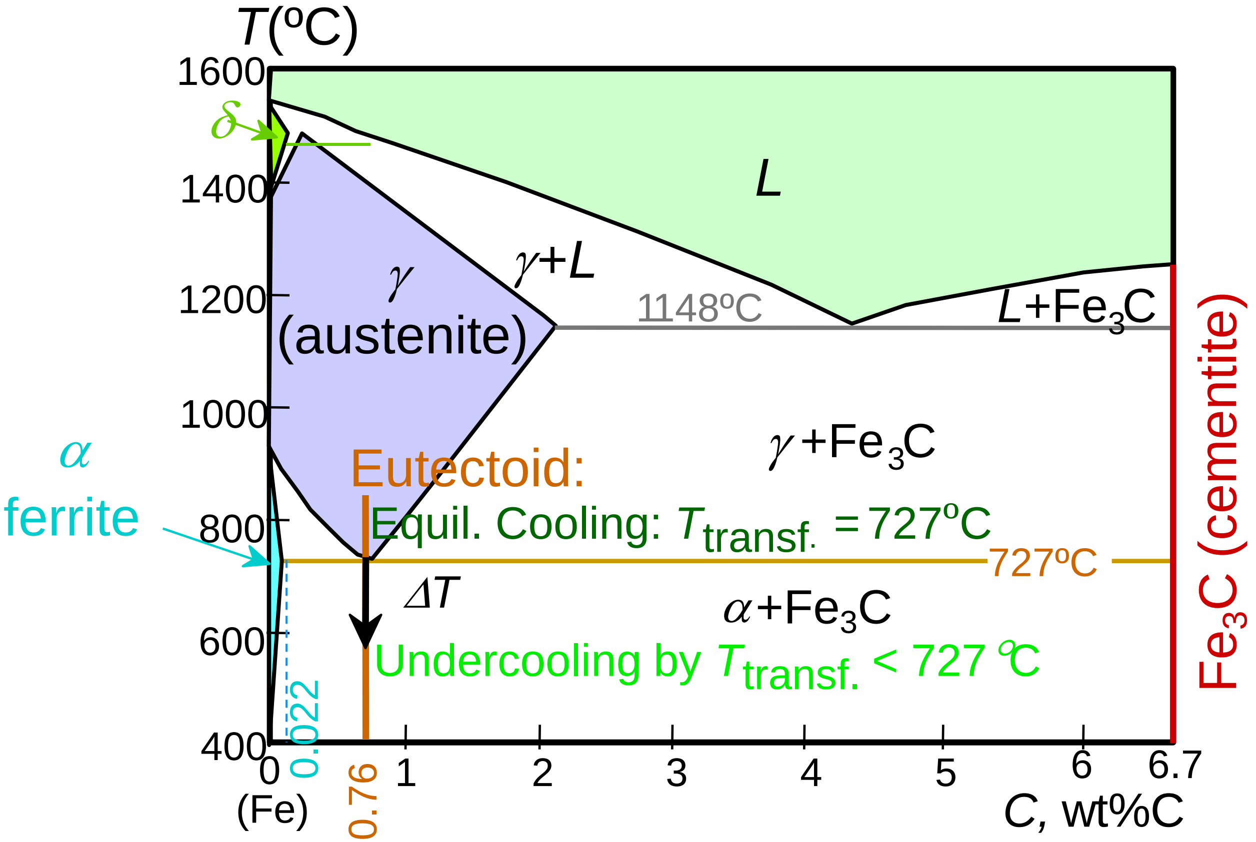
- Eutectoid transf. (Fe-Fe_3C system):
- For transf. to occur, must cool to below 727°C (i.e., must "undercool")

$$\gamma \Rightarrow \alpha + Fe_3C$$

0.76 wt% C

0.022 wt% C

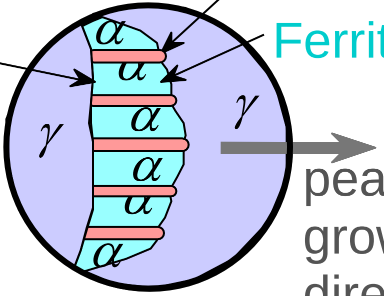
6.7 wt% C



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_3C Eutectoid Transformation

- Transformation of austenite to pearlite:



Austenite (γ) grain boundary

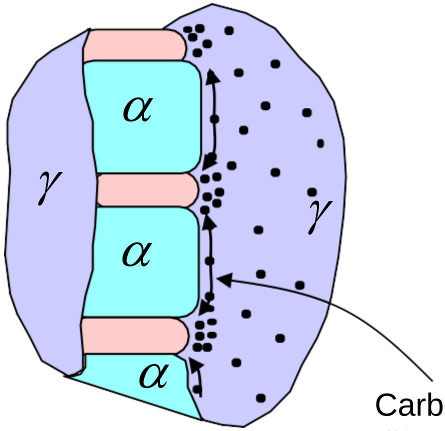
cementite (Fe_3C)

Ferrite (α)

pearlite growth direction

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

Diffusion of C during transformation

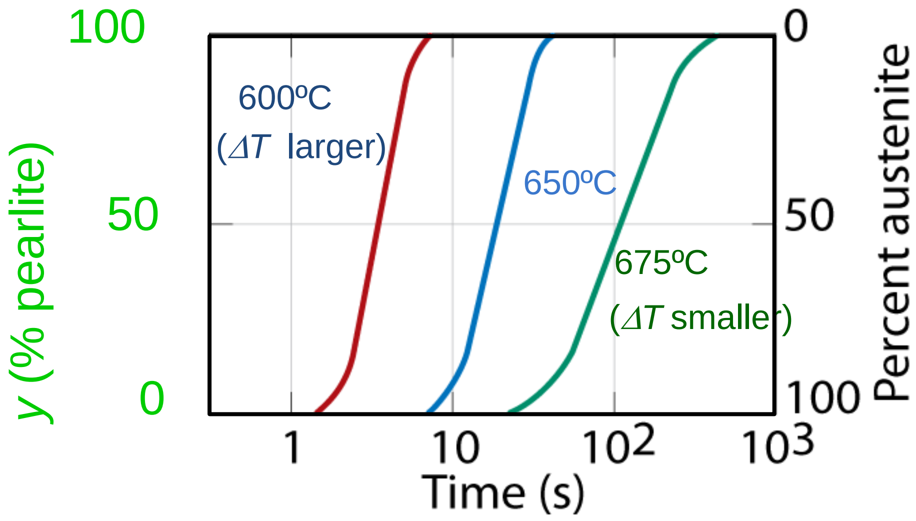


Carbon diffusion

The Fe-Fe_3C Eutectoid Transformation (cont.)

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

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



- S-shaped curves of the percentage transformation versus the logarithm of time at three different temperatures.
- For each curve, data were collected after rapidly cooling a specimen composed of 100% austenite to the temperature indicated.
- That temperature was maintained constant throughout the course of the reaction.

ISOTHERMAL TRANSFORMATION DIAGRAMS

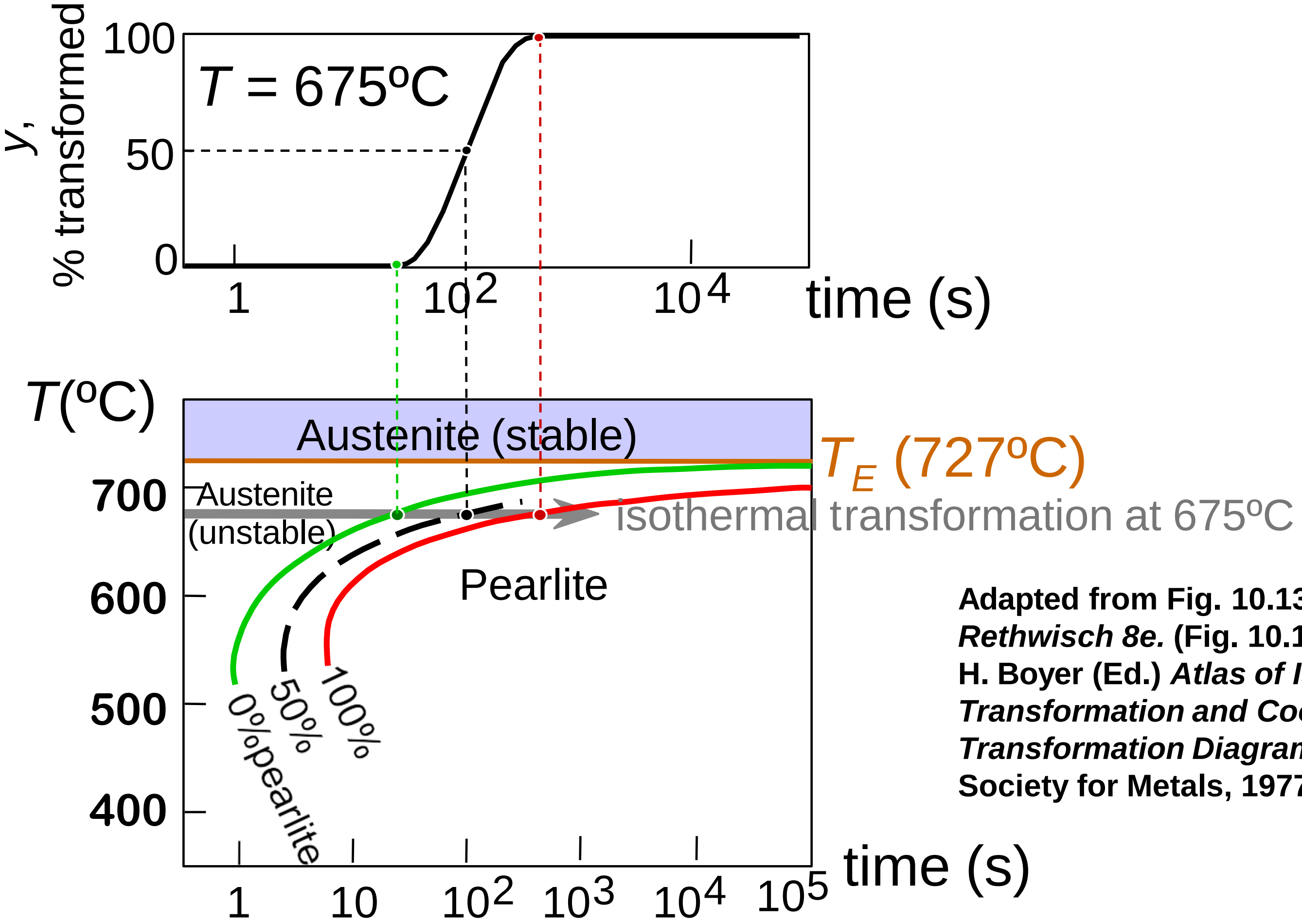
- A more convenient way of representing both the time and temperature dependence of this transformation.

- These curves were generated from a series of plots of the percentage transformations versus the logarithm of time taken over a range of temperatures (from the S-shaped curves).

Generation of Isothermal Transformation Diagrams

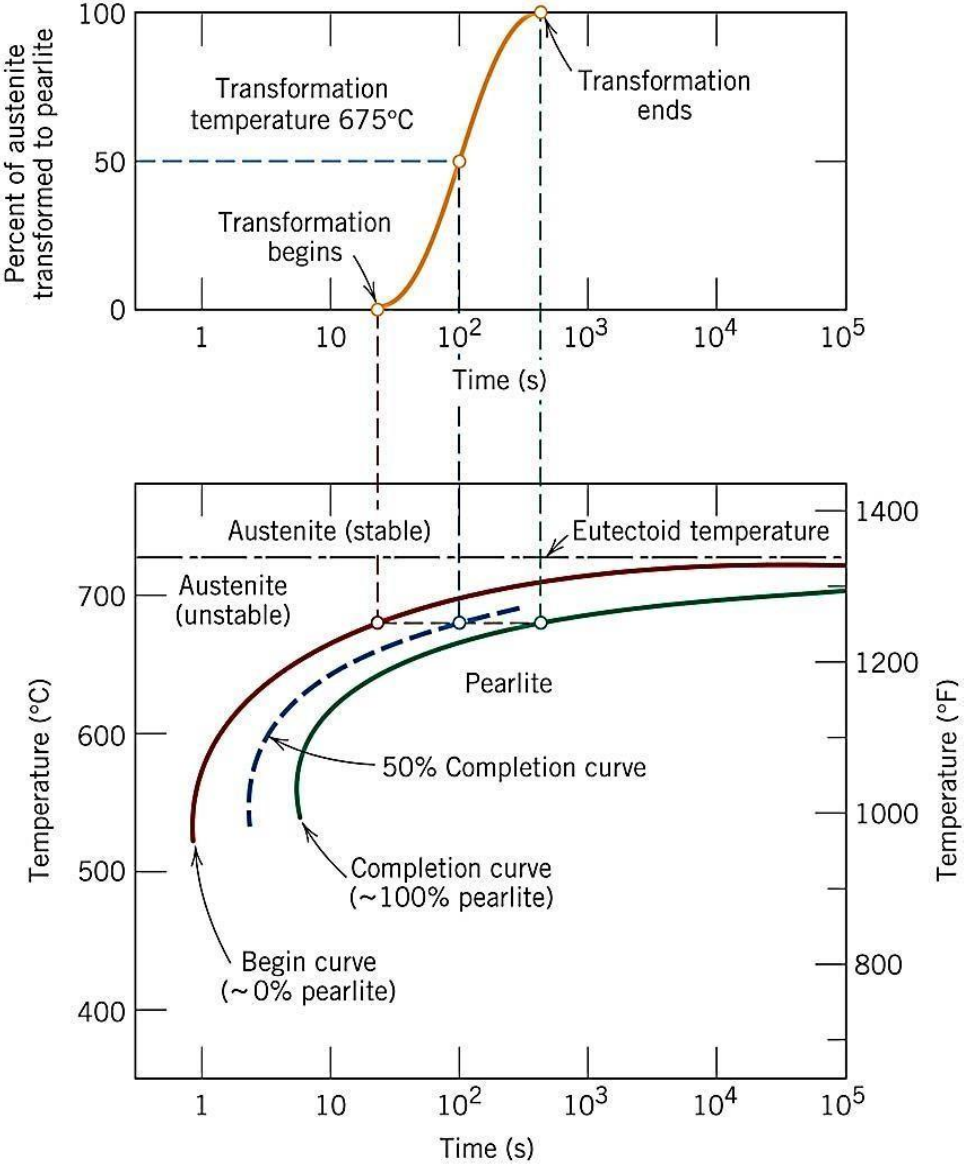
Consider:

- 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.)

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.)

ISOTHERMAL TRANSFORMATION DIAGRAMS

- The austenite-to-pearlite transformation will occur only if an alloy is supercooled to below the eutectoid

- The time necessary for the transformation to begin and then end depends on temperature.

- The start and finish curves are nearly parallel, and they approach the eutectoid line asymptotically.

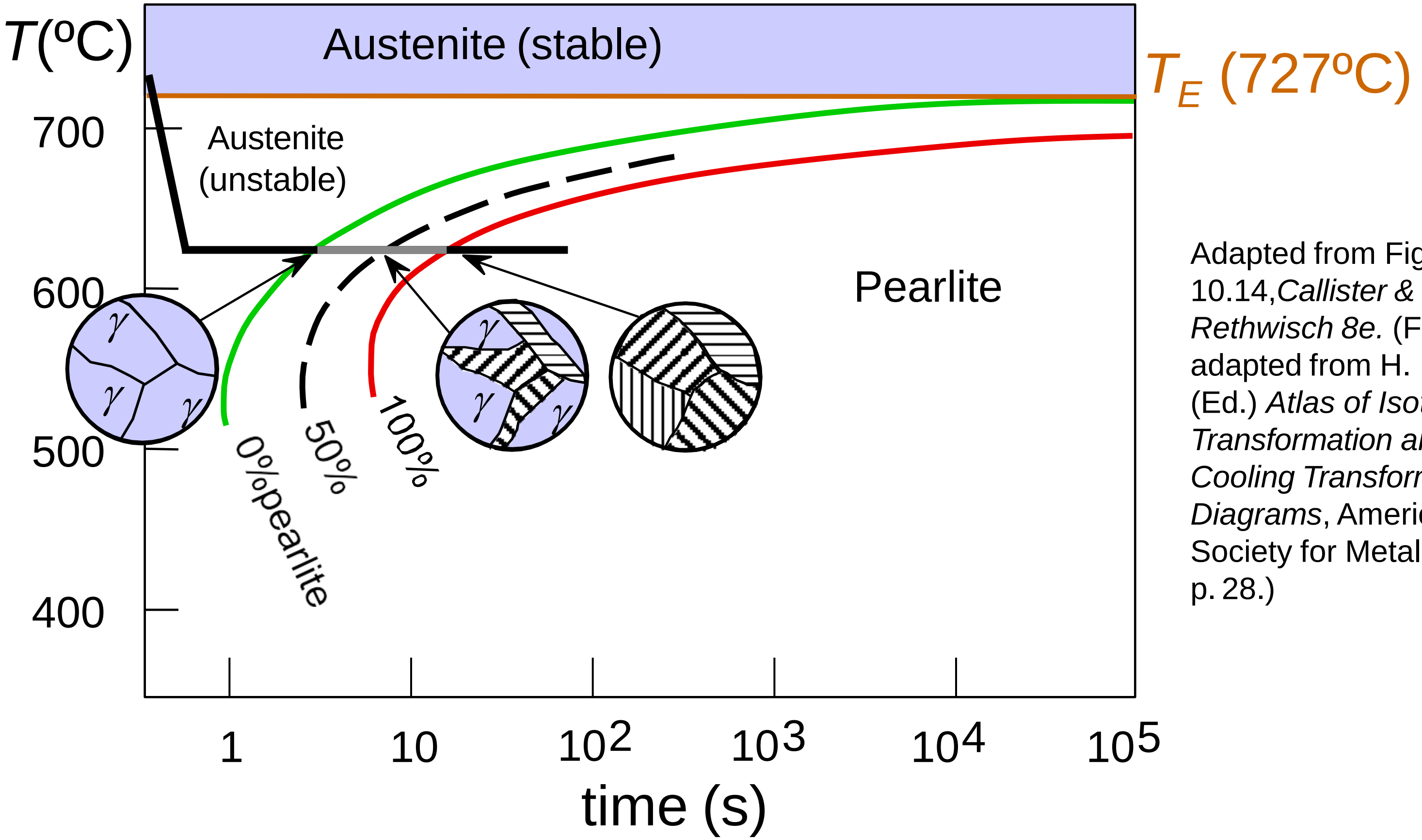
- To the left of the transformation start curve, only austenite (unstable) will be present

- To the right of the finish curve, only pearlite will exist.

- In between, the austenite is in the process of transforming to pearlite, and both microconstituents will be present.

Austenite-to-Pearlite Isothermal Transformation

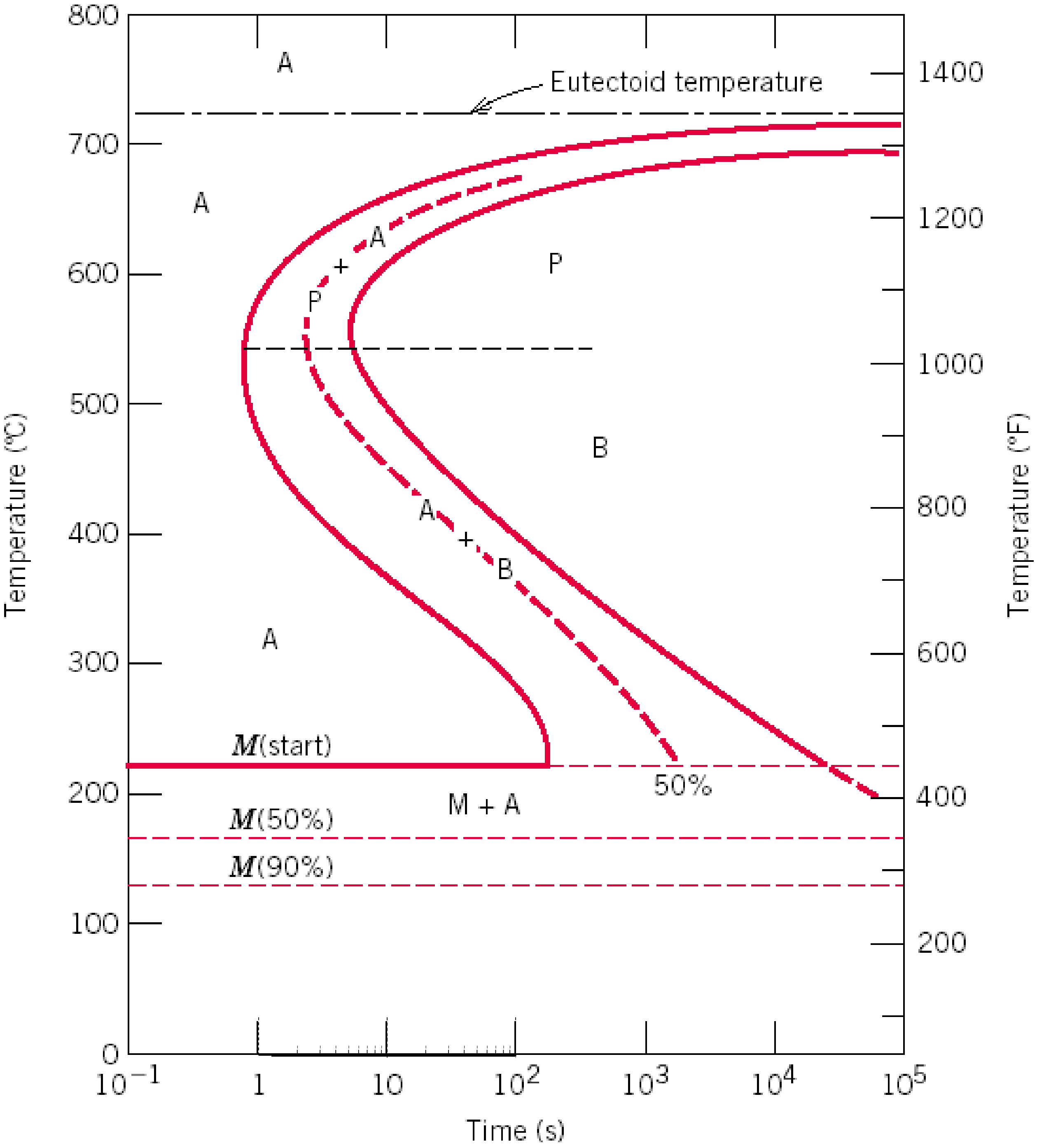
- Eutectoid composition, $C_0 = 0.76$ wt% C
- Begin at $T > 727^{o}$C
- Rapidly cool to 625ºC
- Hold T (625ºC) constant (isothermal treatment)



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.)

Austenite-to-Pearlite Isothermal Transformation (cont.)

- This plot is only valid for an iron-carbon alloy of eutectoid composition (different curves for other alloys).
- Such a plot is called **isothermal transformation diagram** or **time-temperature-transformation (T-T-T).**
- Shorter the time → higher is the rate of transformation
- For instance, at temperatures just below the eutectoid, very long times are required for the 50% transformation (i.e., the action rate is very slow).
- Coarse pearlite → formed at higher temperatures – relatively soft
- Fine pearlite → formed at lower temperatures – relatively hard



The complete TTT diagram for an iron-carbon alloy of eutectoid composition.

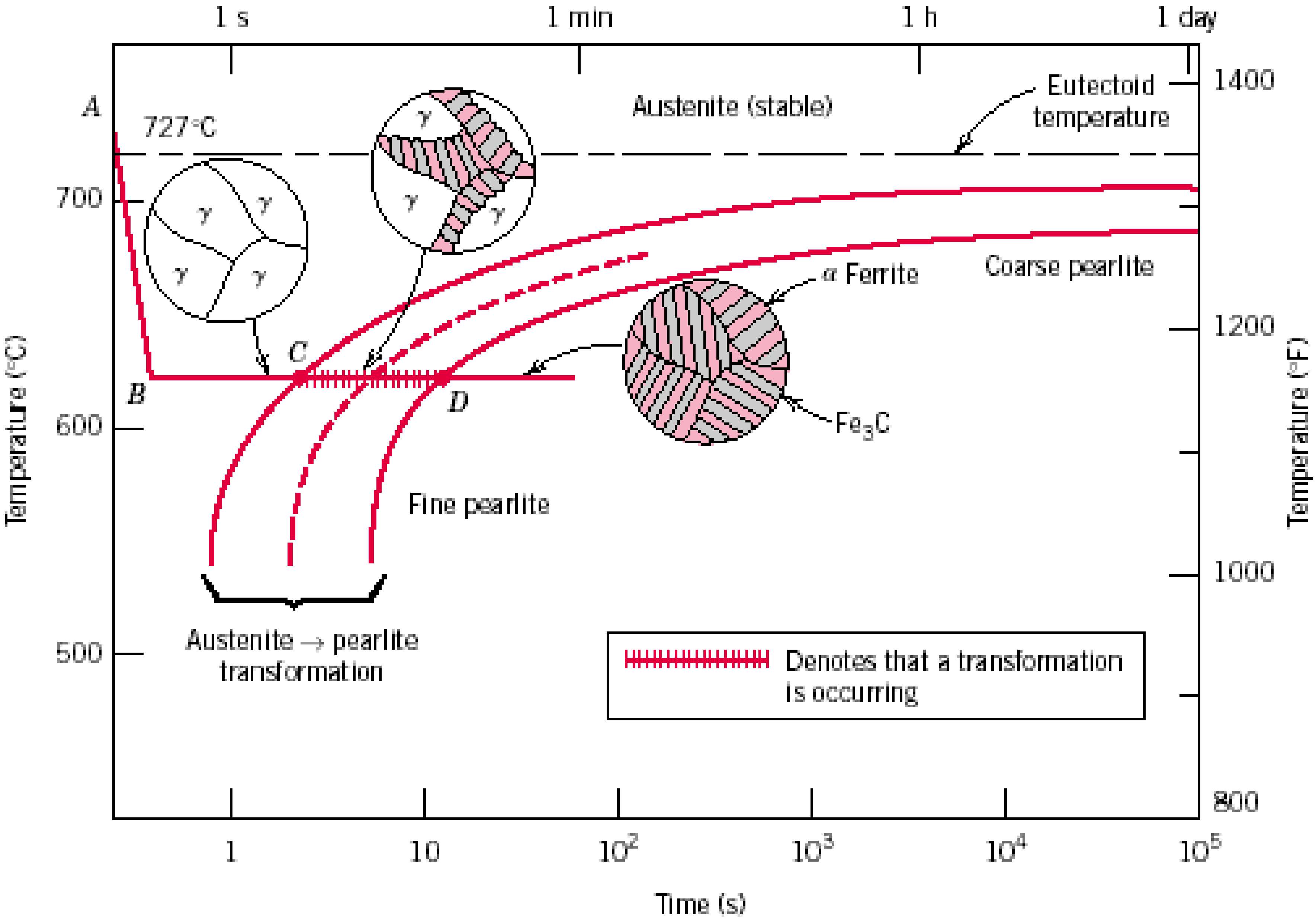
A: austenite

B: bainite

M: martensite

P: pearlite

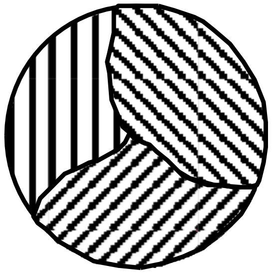
TTT Diagram for a Eutectoid Fe-C Alloy



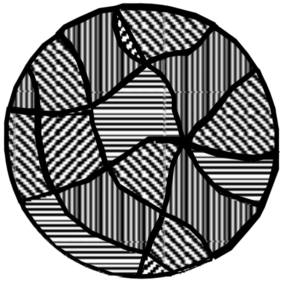
Time-Temperature-Transformation (T-T-T) Diagrams

Pearlite

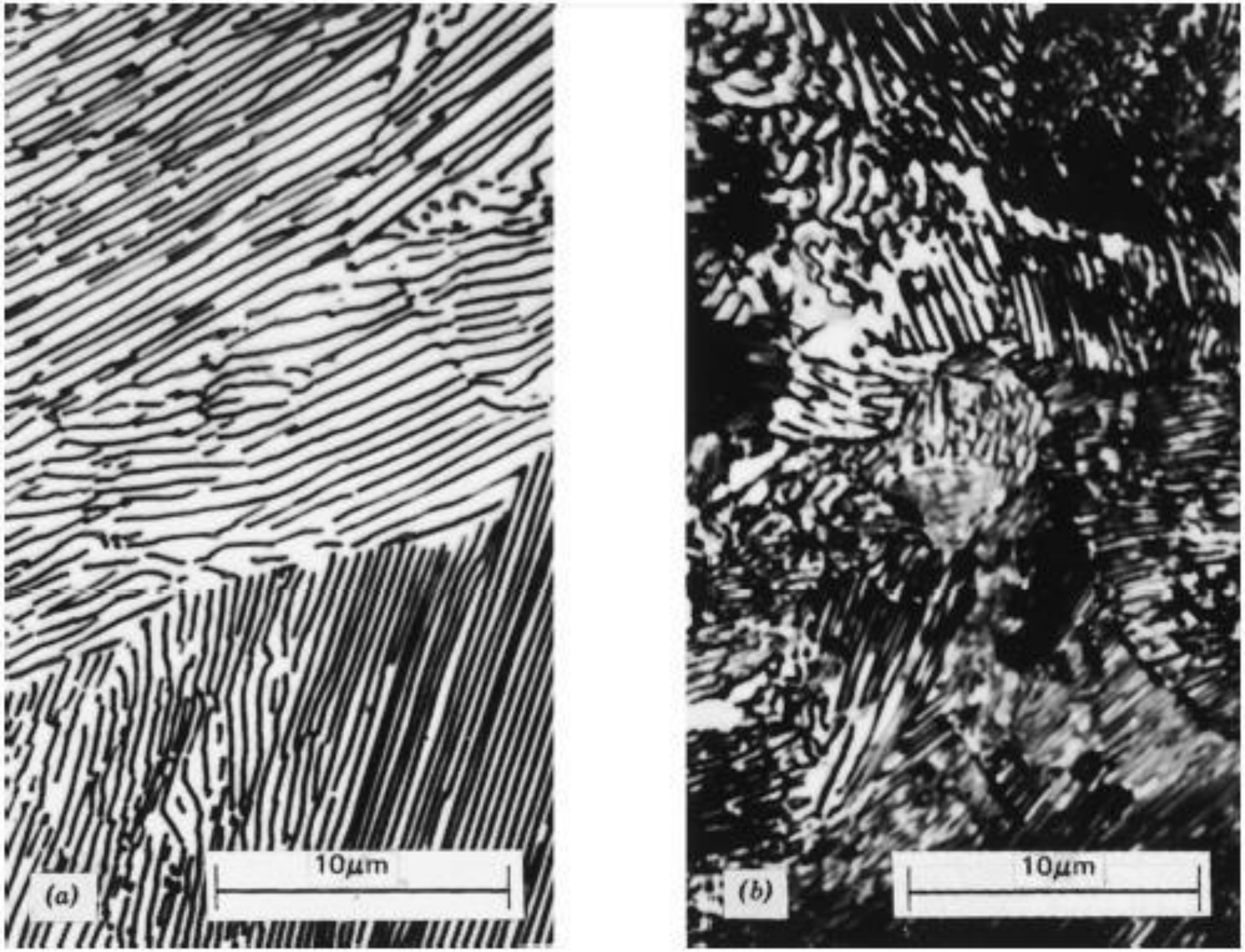
- The thickness of the ferrite/cementite layers in pearlite depends on the temperature. With decreasing temperature, the layers become progressively thinner.
  - At temperatures just below eutectoid → relatively thick layers → coarse pearlite
  - In the vicinity of 540 ℃ → relatively thin layers → fine pearlite



- Smaller ΔT: colonies are larger



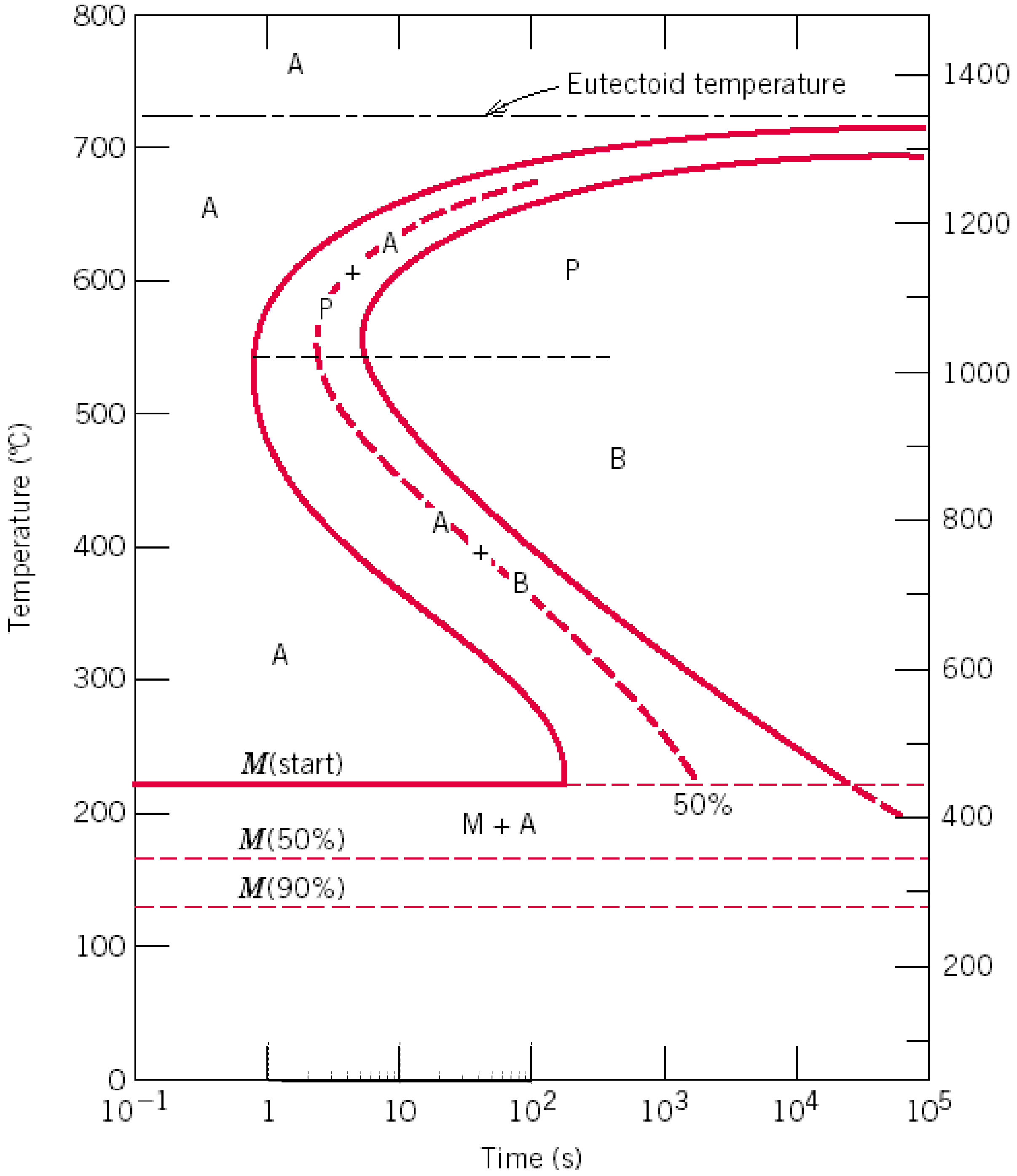
- Larger ΔT: colonies are smaller



(a) Coarse Pearlite

(b) Fine Pearlite

Photomicrographs of (a) coarse pearlite and (b) fine pearlite. 3000X.



The complete isothermal transformation diagram for an iron-carbon alloy of eutectoid composition.

A: austenite

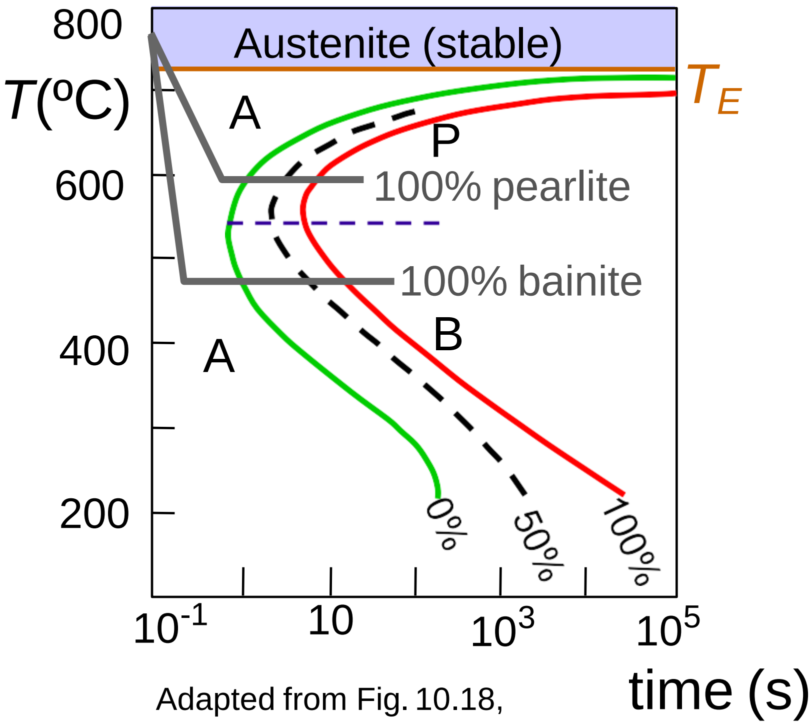
B: bainite

M: martensite

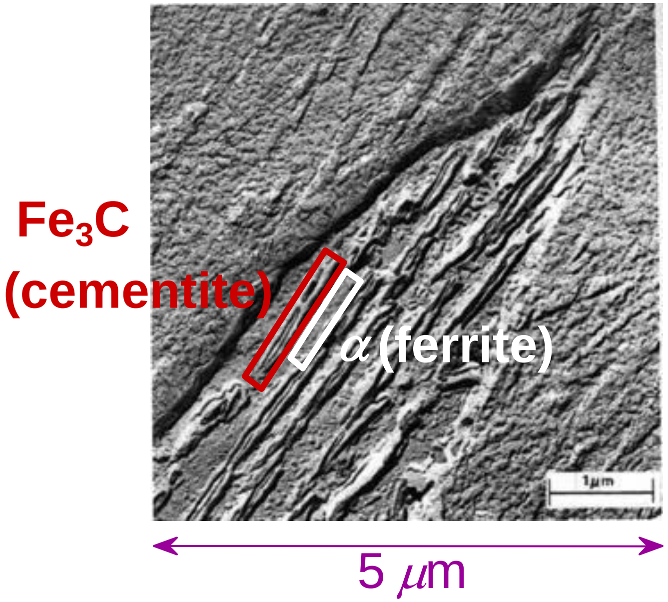
P: pearlite

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



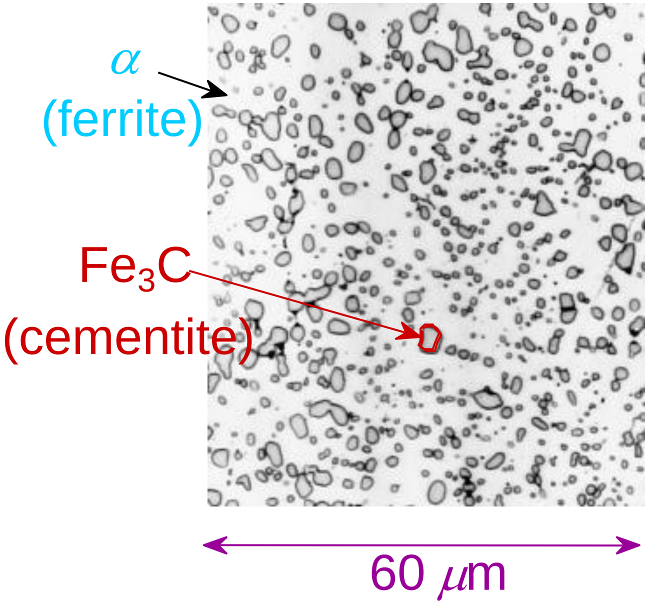
Adapted from Fig. 10.18, *Callister & Rethwisch 8e.*



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-Fe_3C System

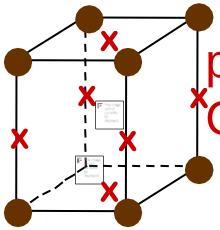
- **Spheroidite**:
  -- Fe_3C particles within an α-ferrite matrix
  -- formation requires diffusion
  -- heat bainite or pearlite at temperature just below eutectoid for long times
  -- driving force – reduction of α-ferrite/Fe_3C interfacial area



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

Martensite: A Nonequilibrium Transformation Product

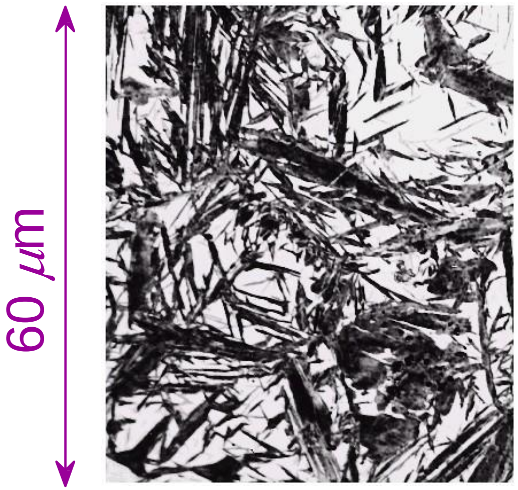
- Martensite:
  -- γ(FCC) to Martensite (BCT)



Fe atom sites

potential C atom sites

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

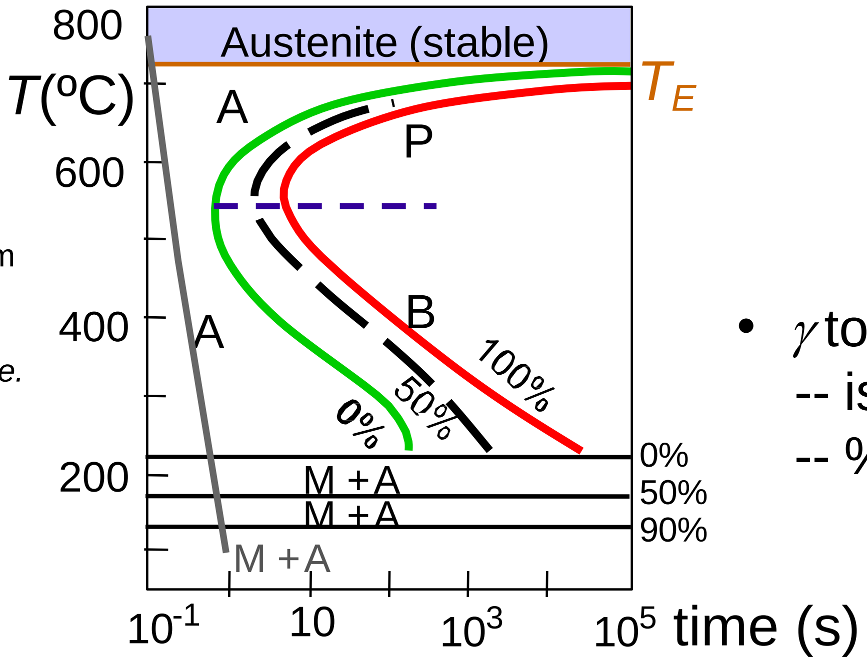


▬ Martensite needles

▬ Austenite

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

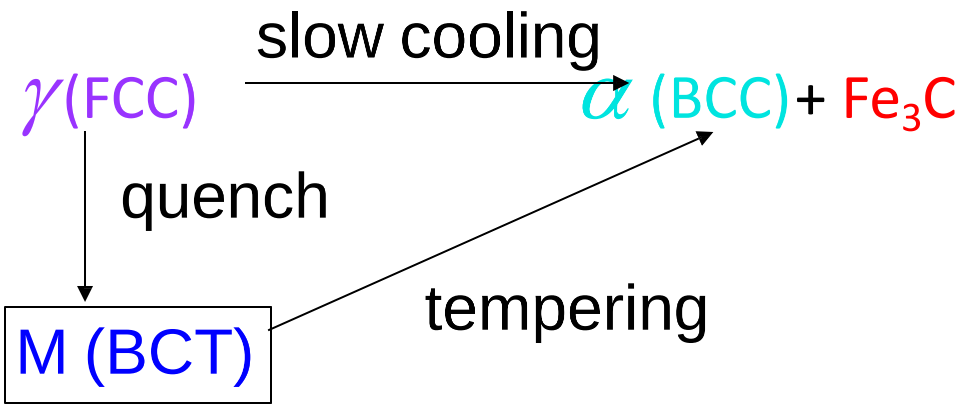
- Isothermal Transf. Diagram



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

Martensite Formation



γ(FCC)

slow cooling

α (BCC) + Fe_3C

quench

M (BCT)

tempering

Martensite (M) – single phase

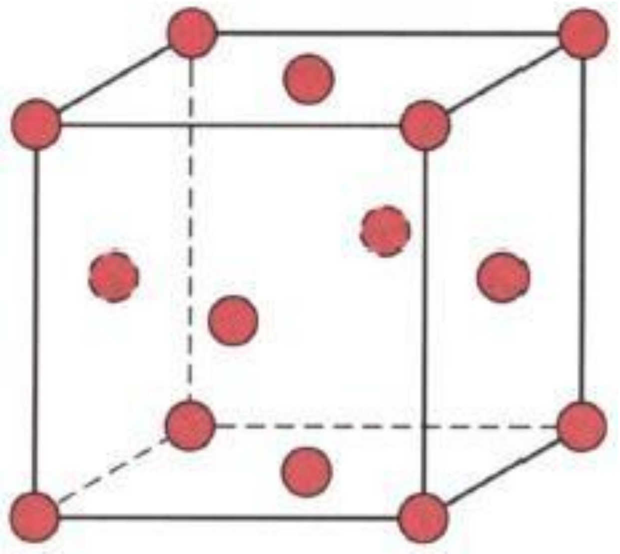
– has body centered tetragonal (BCT) crystal structure

Diffusionless transformation BCT if $C_0 > 0.15$ wt% C

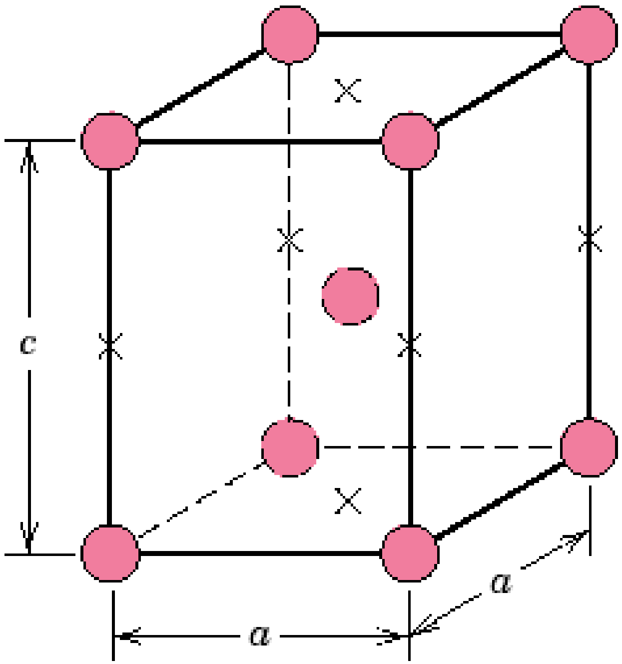
BCT → few slip planes → hard, brittle

Martensite

- Martensite is formed when austenitized Fe-C alloys are rapidly cooled (or quenched) to a relatively low temperature (in the vicinity of the ambient).
  - Non-equilibrium single phase
  - A transformation product that is competitive with pearlite
  - Transformation of FCC to BCT (body-centered tetragonal)
  - Occurs instantaneously → time-independent
  - The martensite grains nucleate and grow at a very rapid rate — the velocity of sound within the austenite matrix.



FCC Austenite
(γ phase)

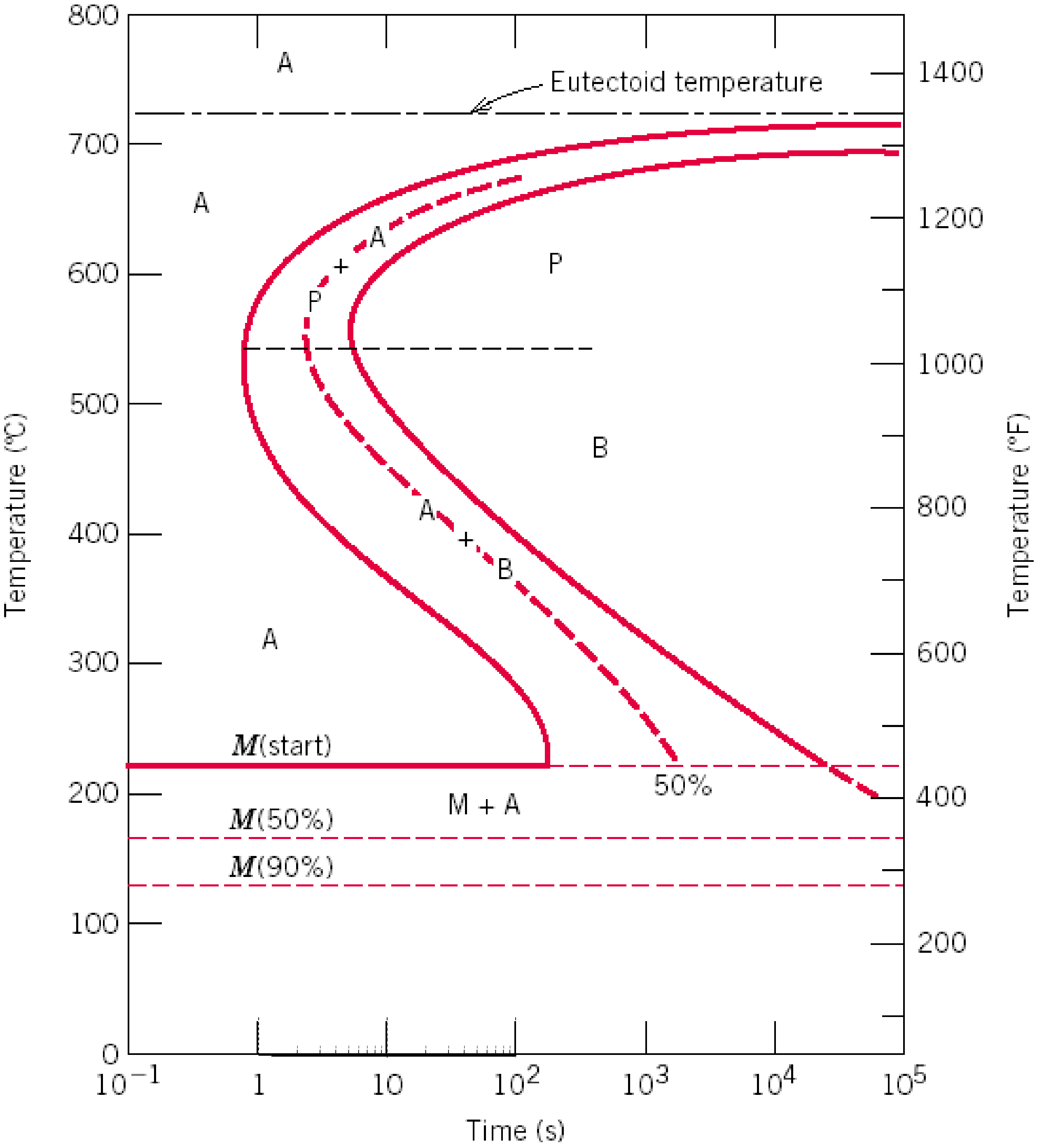


BCT Martensite
(body-centered tetragonal)

The body-centered tetragonal unit cell for martensitic steel showing iron atoms (circles) and sites that may be occupied by carbon atoms (crosses). For this tetragonal unit cell, c > a.

Lenticular or plate martensitic microstructure

Photomicrograph showing the lenticular or plate martensitic microstructure. The needle-shaped grains are the martensite phase, and the white regions are austenite that failed to transform during the rapid quench. 1220X.



The complete isothermal transformation diagram for an iron-carbon alloy of eutectoid composition.

A: austenite

B: bainite

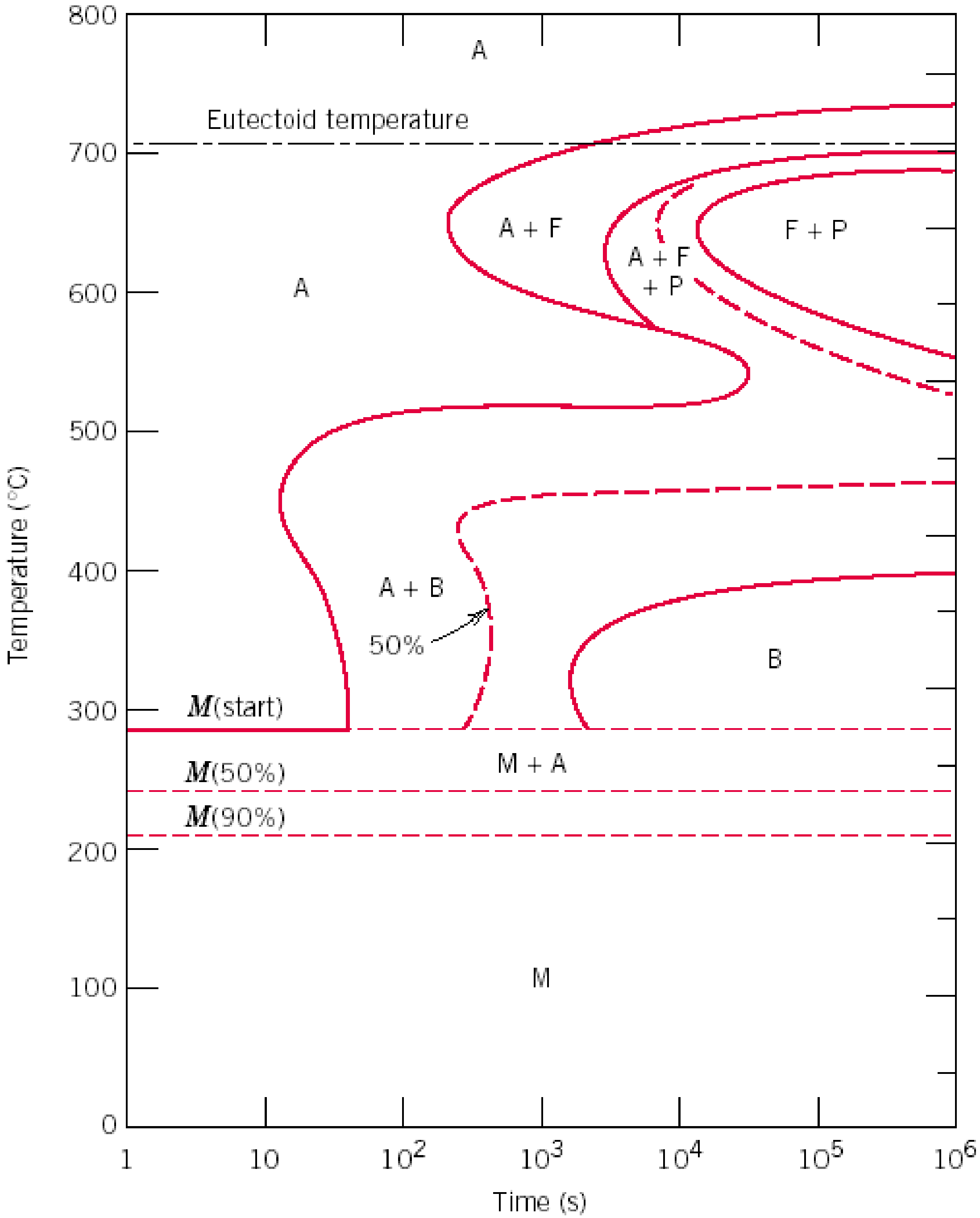
M: martensite

P: pearlite

The Martensitic Transformation

Since the martensitic transformation is instantaneous, it is not depicted in this diagram like the pearlitic reaction.

- **The beginning of this transformation is represented by a horizontal line designated M(start).**
- **Two other horizontal and dashed lines, labeled M(50%) and M(90%), indicate percentages of the austenite-to-martensite transformation.**
- **The temperatures at which these lines are located vary with alloy composition; the temperatures must be relatively low.**
- **The horizontal and linear character of these lines indicates that the martensitic transformation is independent of time; it is a function only of the temperature to which the alloy is quenched.**



Effects of alloying elements

The presence of alloying elements other than carbon (e.g., Cr, Ni, Mo, and W) may cause significant changes in the positions/shapes of the curves in the isothermal transformation diagrams.

TTT diagram for an alloy steel (type 4340):

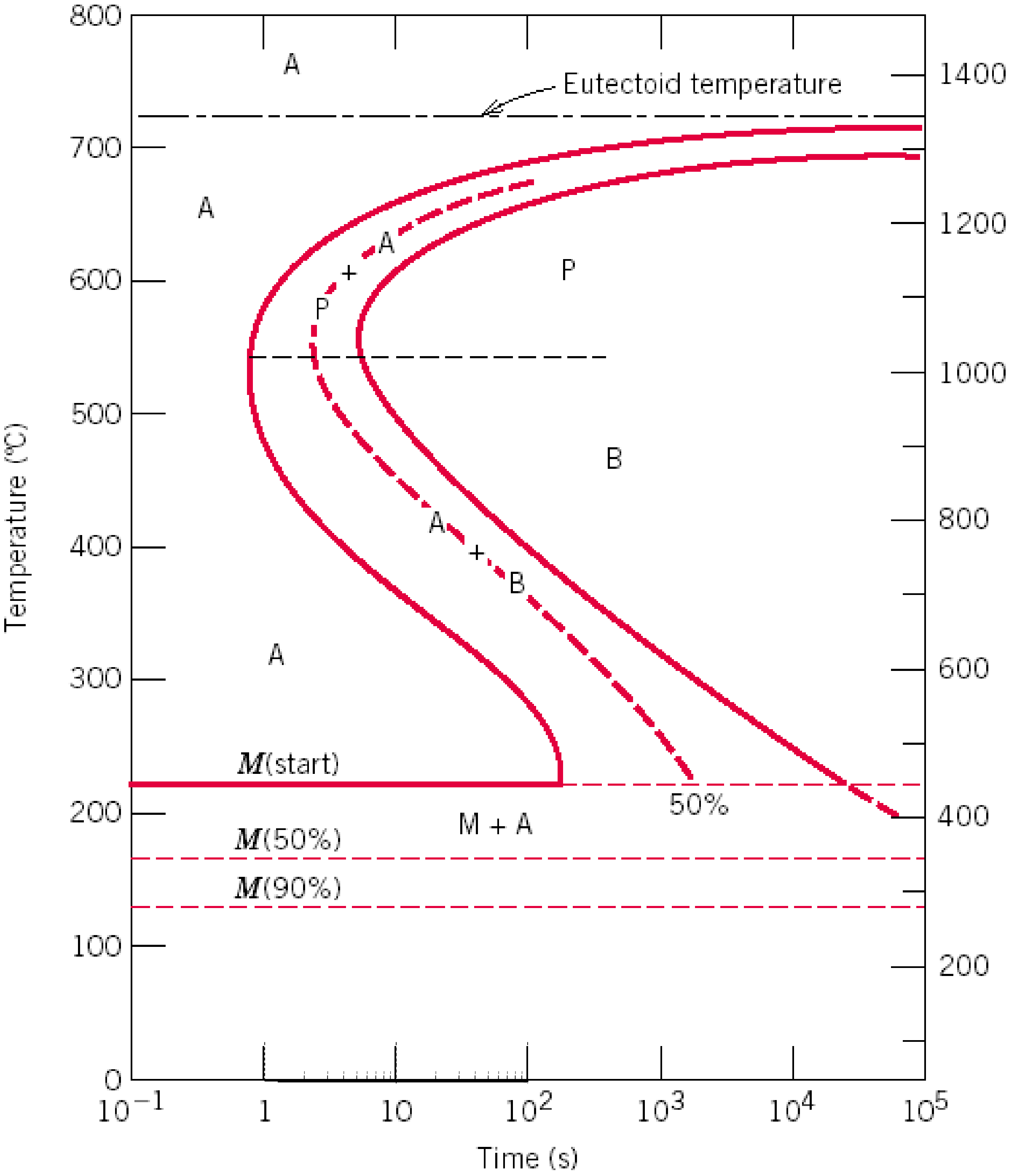
A, austenite;

B, bainite;

P, pearlite;

M, martensite;

F, proeutectoid ferrite.



The complete isothermal transformation diagram for an iron-carbon alloy of eutectoid composition.

A: austenite

B: bainite

M: martensite

P: pearlite

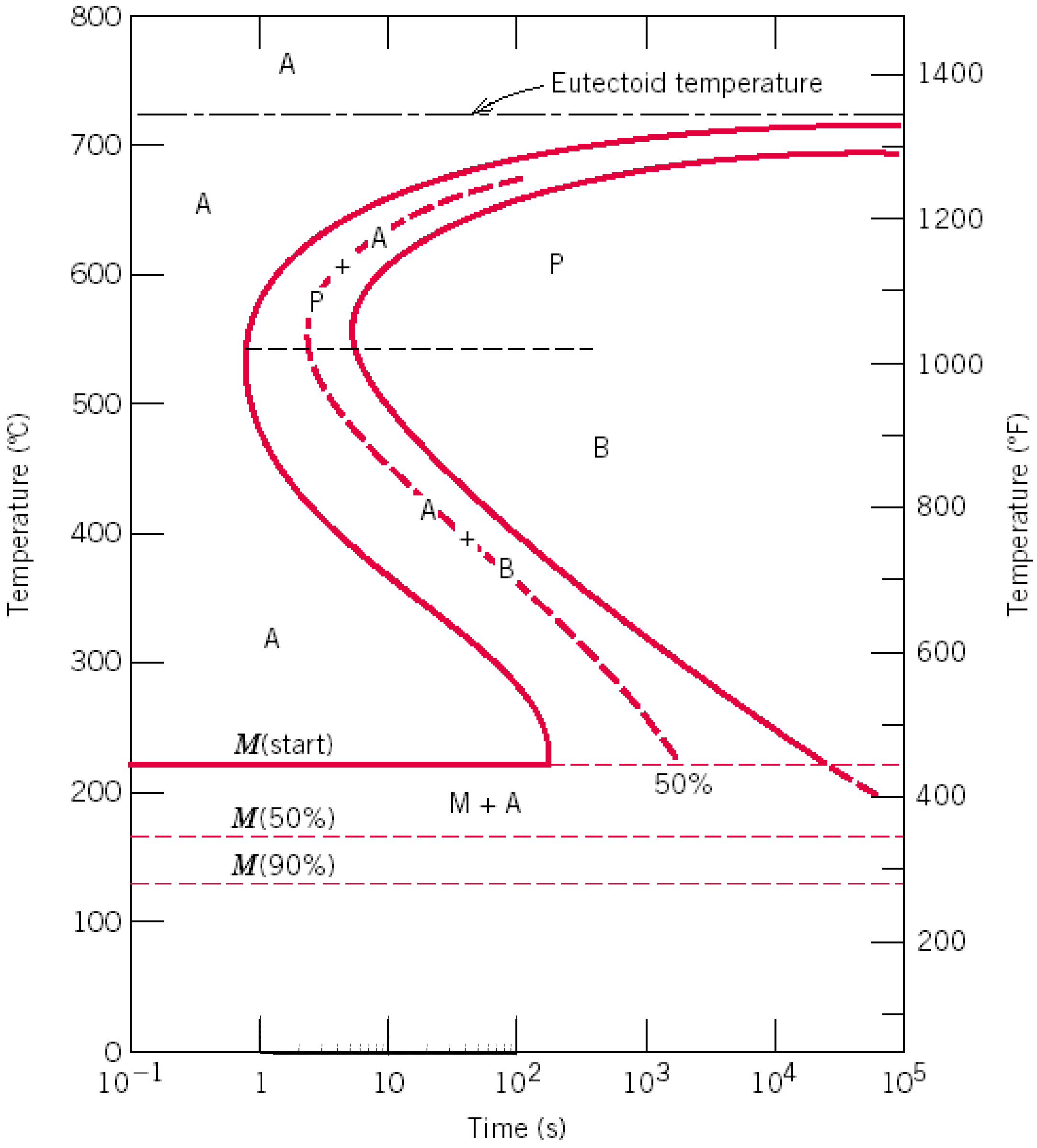
Example Problem

Using the isothermal transformation diagram for an iron-carbon alloy of eutectoid composition, specify the nature of the final microstructure of a small specimen that has been subjected to the <u>following time-temperature treatments</u>.

The specimen begins at 760° C and that it has been held at this temperature long enough to have achieved a <u>complete and homogeneous austenitic structure</u>.

(a)Rapidly cool to 250° C, hold for 100s, and quench to room temperature

(b)Rapidly cool to 600° C, hold for 10^4 s, and quench to room temperature

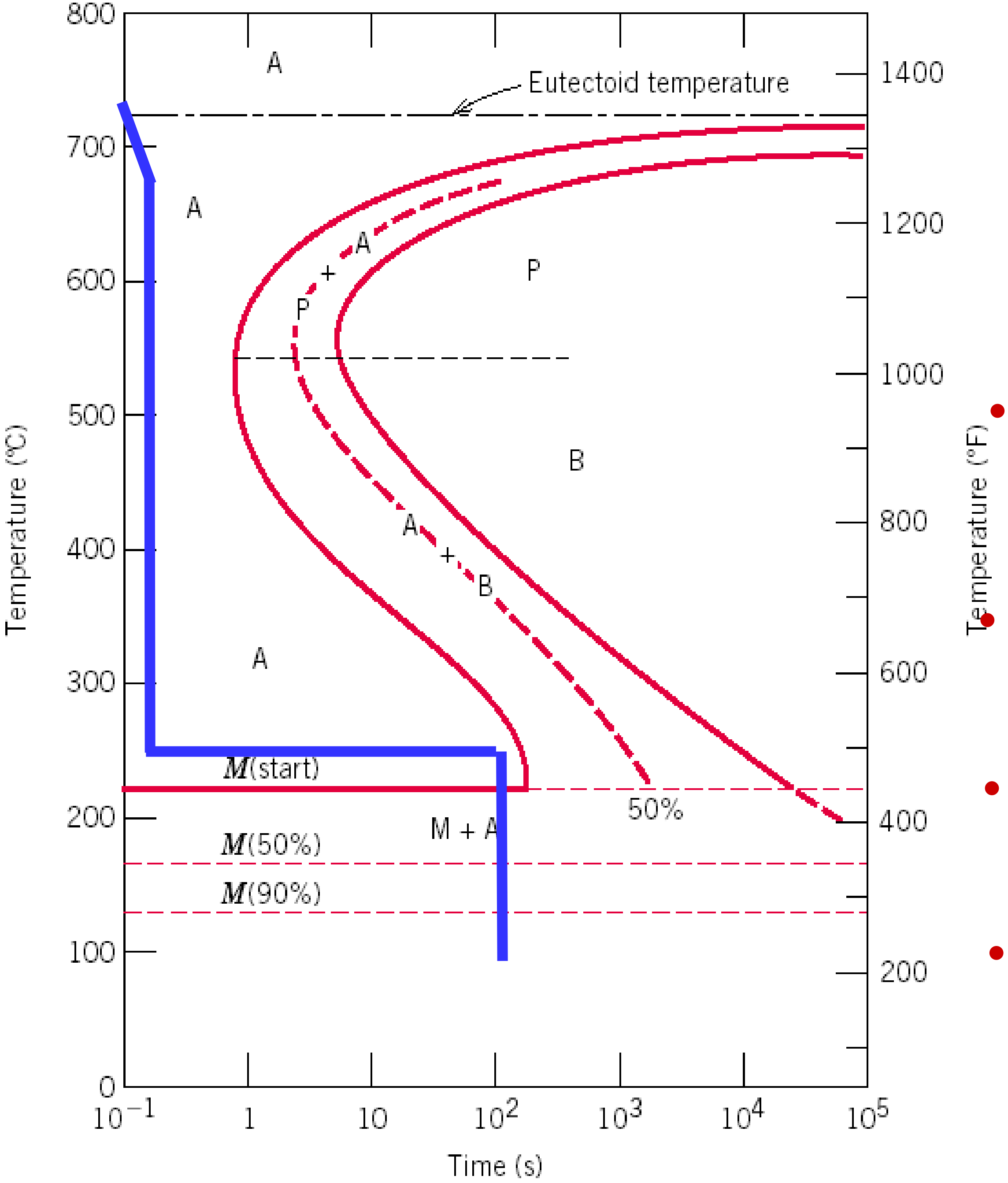


Example Problem

(a)Rapidly cool to 250° C, hold for 100s, and quench to room temperature

(b)Rapidly cool to 600° C, hold for 10^4 s, and quench to room temperature

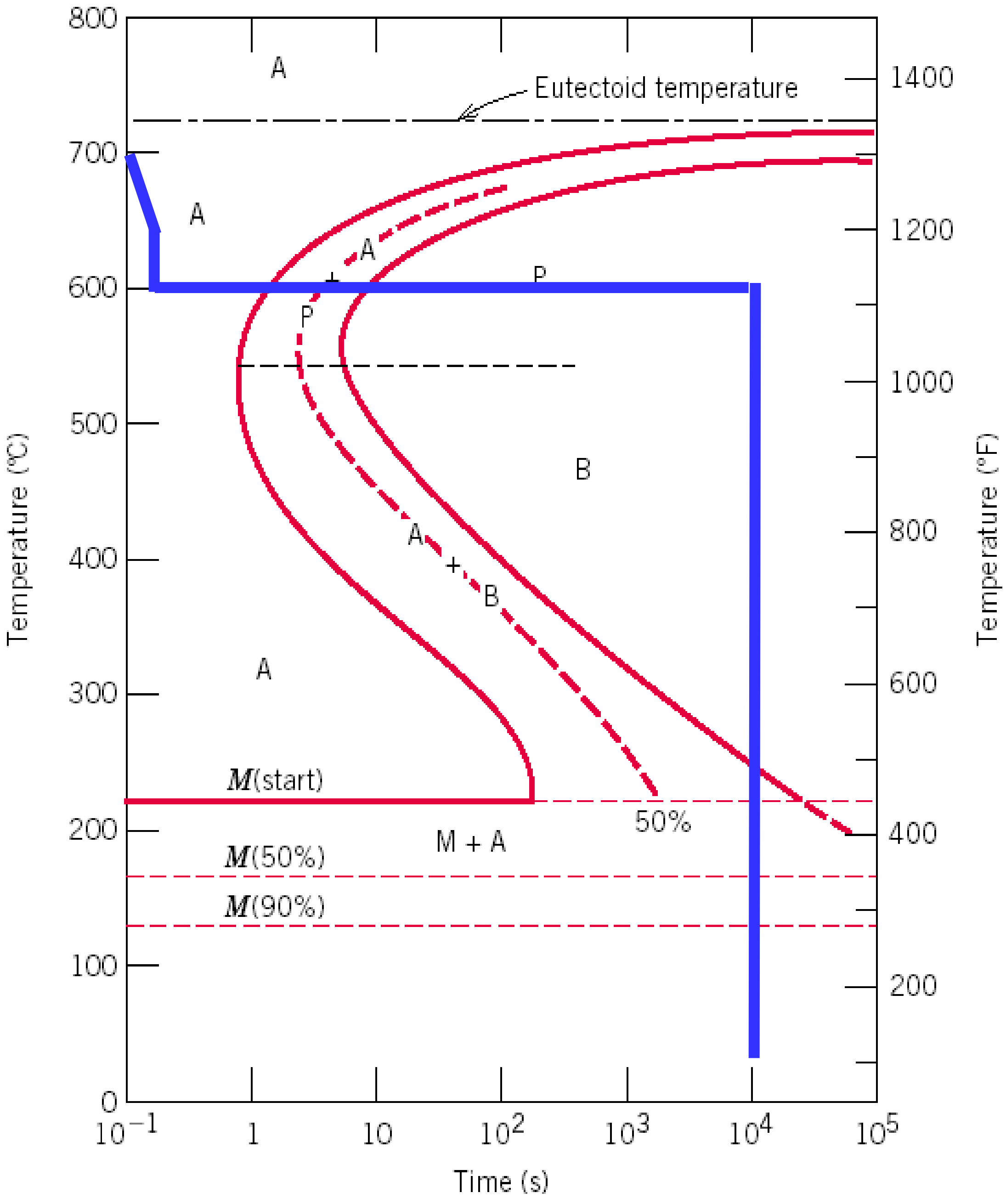
The time-temperature-transformation diagram for an iron-carbon alloy of eutectoid composition and the isothermal heat treatments



Example Problem

(a) Rapidly cool to 250° C, hold for 100s, and quench to room temperature

- At 760° C: in the austenite region (*γ*)—100% austenite
- Rapidly cool from 760° C to 250° C: 100% austenite
- Hold for 100 seconds at 250° C: 100% austenite
- Quench to room temp.: 100% martensite



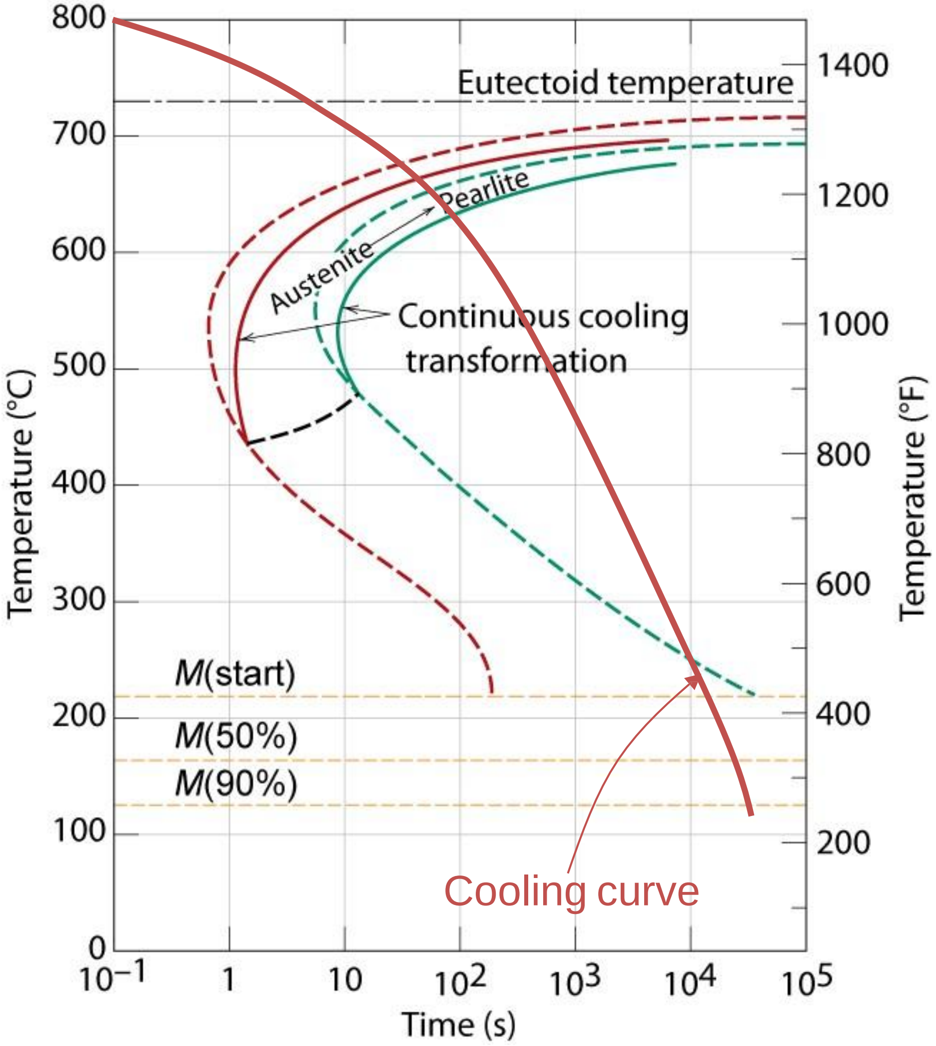
Example Problem

(b) Rapidly cool to 600° C, hold for 10^4 s, and cool to room temperature

- At 760° C: in the austenite region (γ)—100% austenite
- Rapidly cool from 760° C to 600° C: 100% austenite
- Hold for 10^4 s at 250° C: 100% pearlite
- Quench to room temp.: 100% pearlite

Continuous Cooling Transformation Diagrams

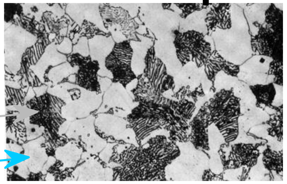
Conversion of isothermal transformation diagram to continuous cooling transformation diagram



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

Mechanical Props: Influence of C Content

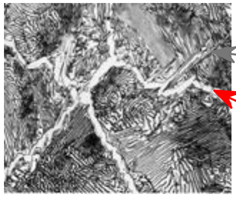
Pearlite (med)
ferrite (soft)



$C_0 < 0.76$ wt% C

Hypoeutectoid

Adapted from Fig. 9.30, *Callister & Rethwisch 8e.*

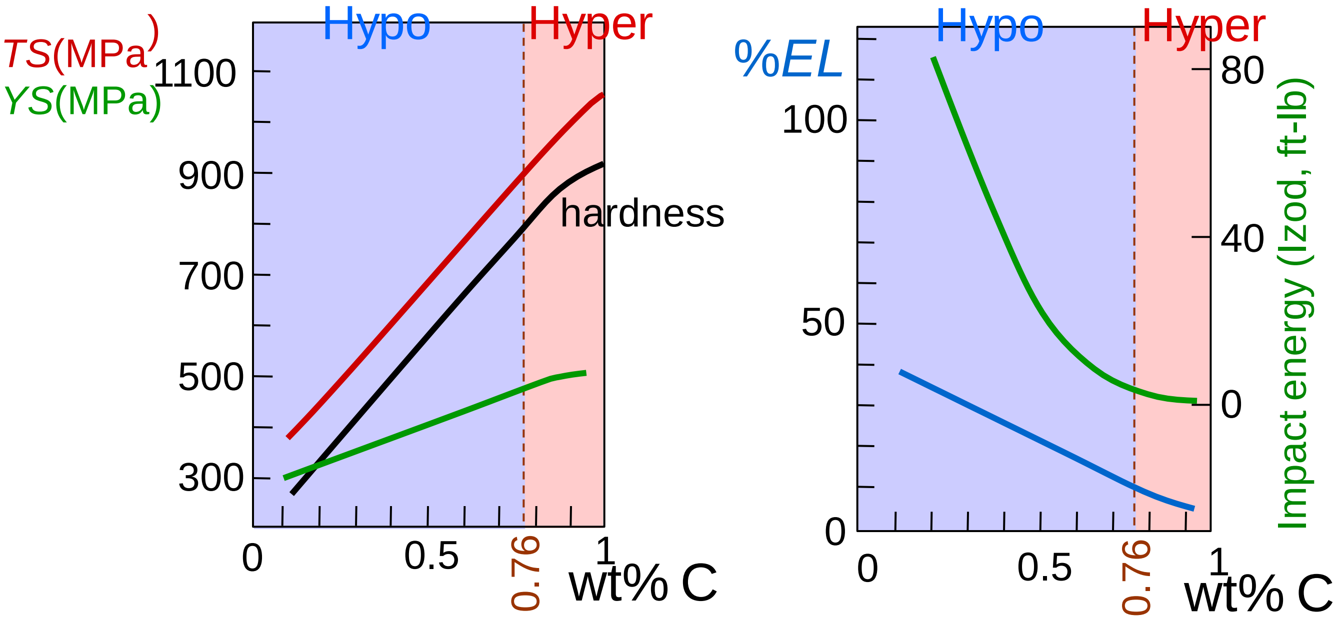


Pearlite (med)
Cementite (hard)

$C_0 > 0.76$ wt% C

Hypereutectoid

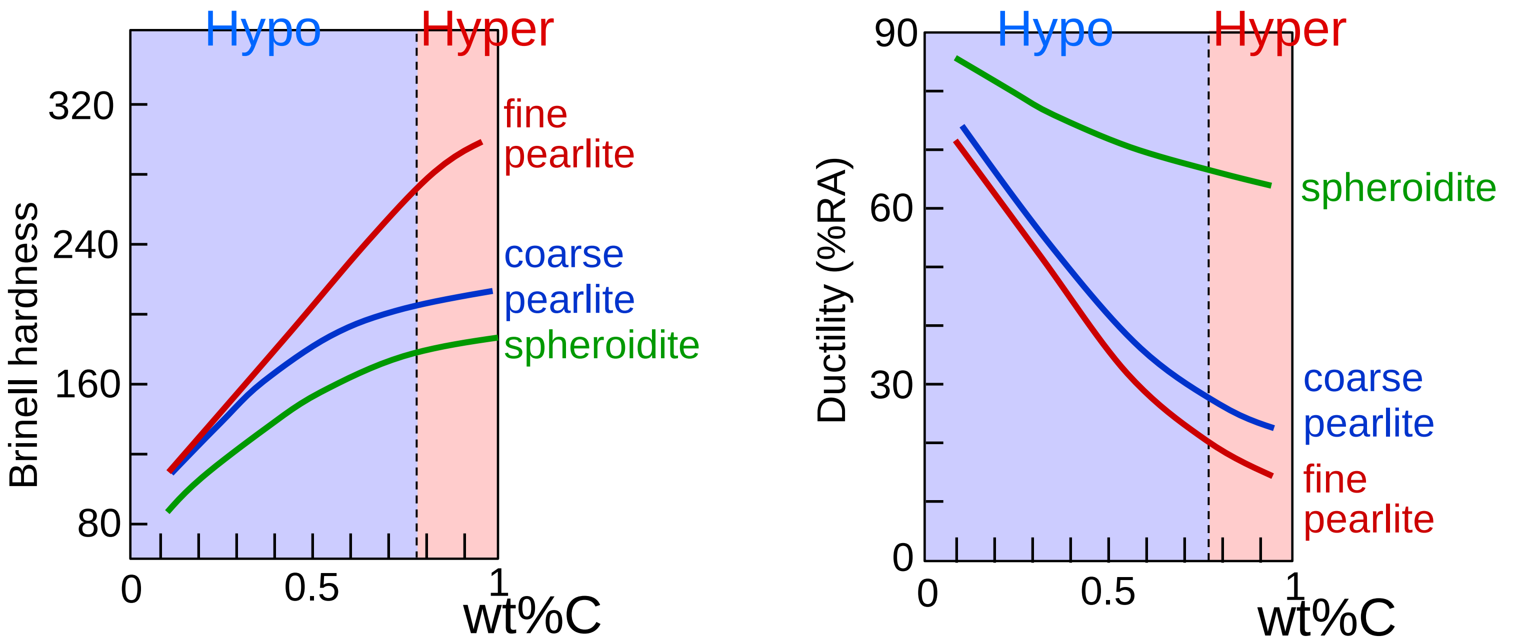
Adapted from Fig. 9.33, *Callister & Rethwisch 8e.*



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

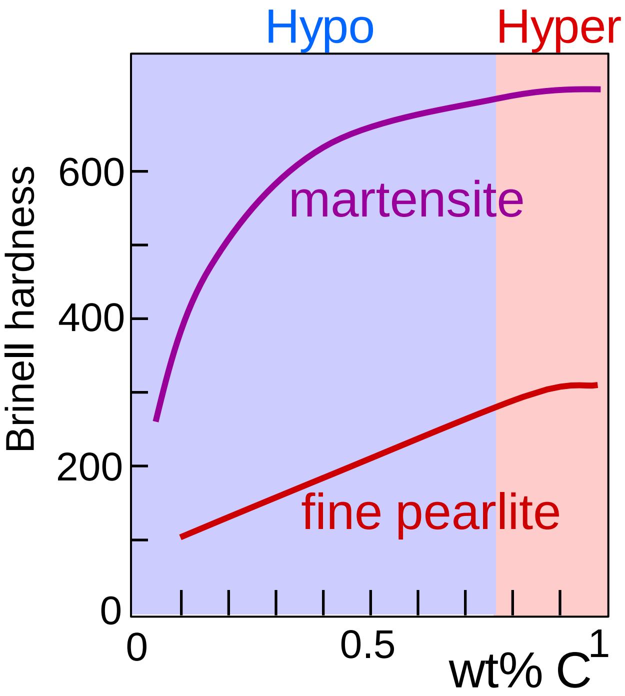
Mechanical Props: Fine Pearlite vs. Coarse Pearlite vs. Spheroidite



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.)

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

Mechanical Props: Fine Pearlite vs. Martensite



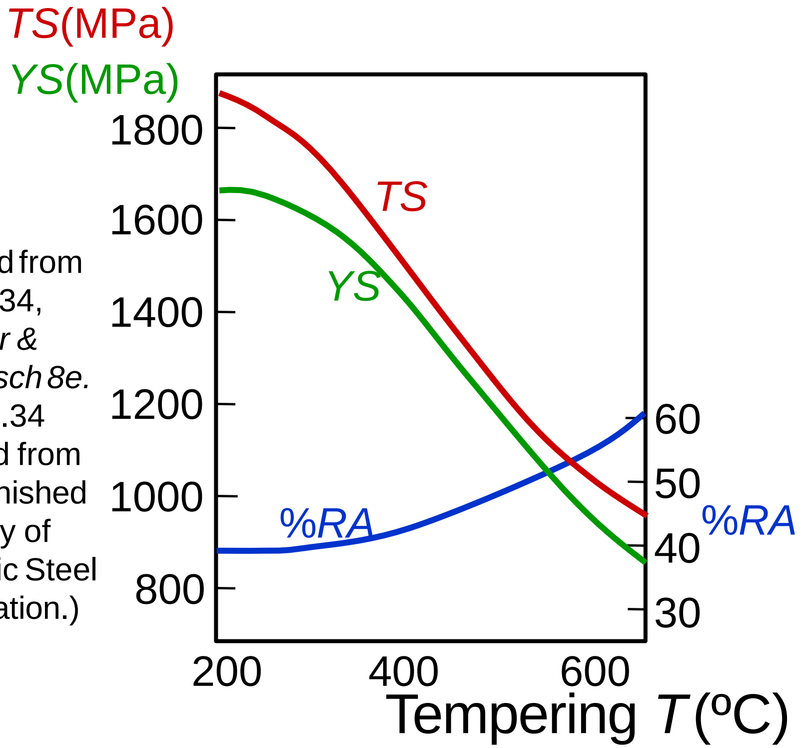
Adapted from Fig. 10.32, *Callister & Rethwisch 8e.* (Fig. 10.32 adapted from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 36; and R.A. Grange, C.R. Hribal, and L.F. Porter, *Metall. Trans. A*, Vol. 8A, p. 1776.)

- Hardness: fine pearlite << martensite.

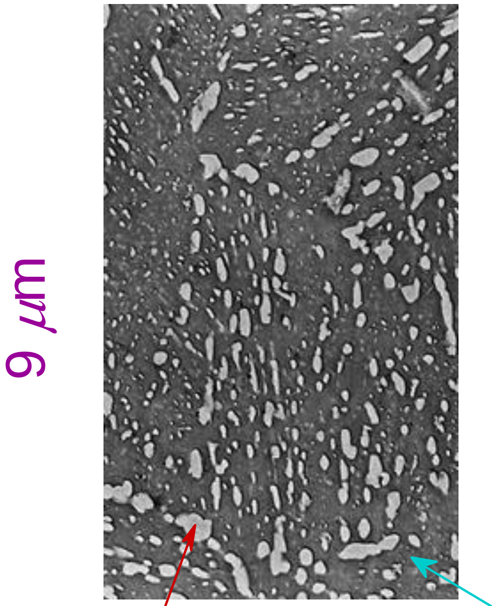
Tempered Martensite

Heat treat martensite to form tempered martensite

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



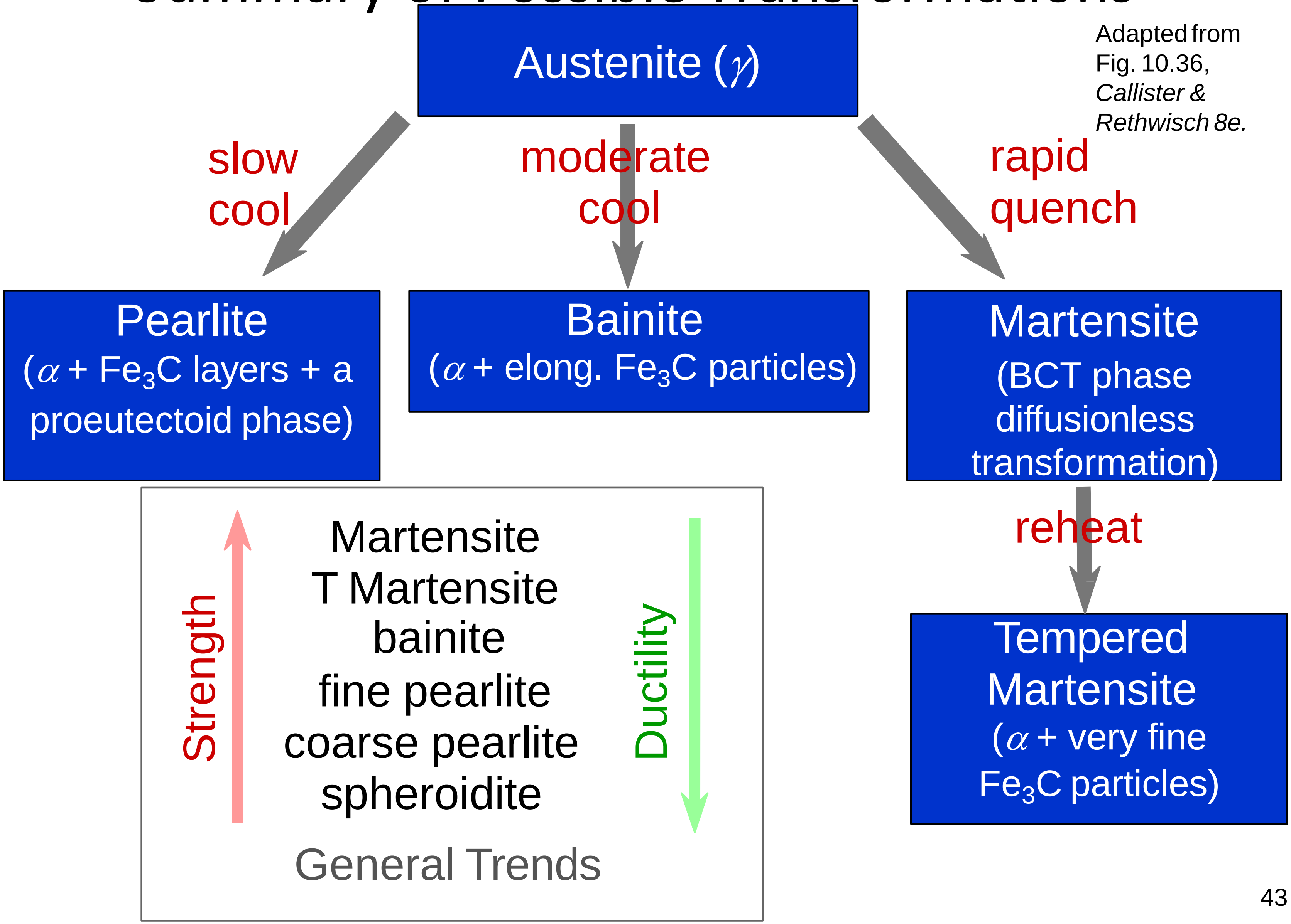
Adapted from Fig. 10.34, *Callister & Rethwisch 8e.* (Fig. 10.34 adapted from Fig. furnished courtesy of Republic Steel Corporation.)



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.*

Austenite (γ)

slow cool

Pearlite
(α + Fe_3C layers + a proeutectoid phase)

moderate cool

Bainite
(α + elong. Fe_3C particles)

rapid quench

Martensite
(BCT phase diffusionless transformation)

reheat

Tempered Martensite
(α + very fine Fe_3C particles)

Strength

Martensite
T Martensite
bainite
fine pearlite
coarse pearlite
spheroidite

Ductility

General Trends

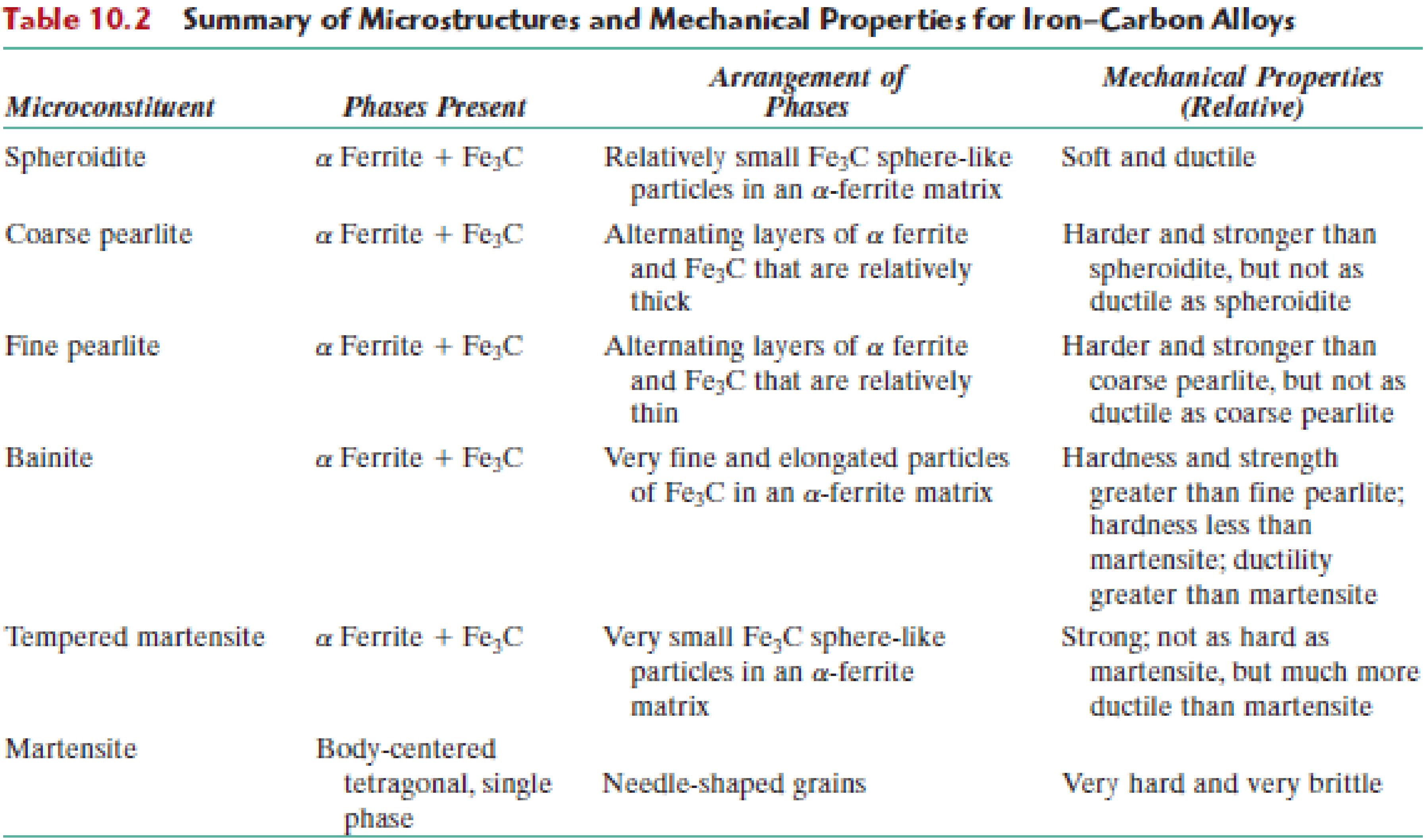


Table 10.2 Summary of Microstructures and Mechanical Properties for Iron–Carbon Alloys

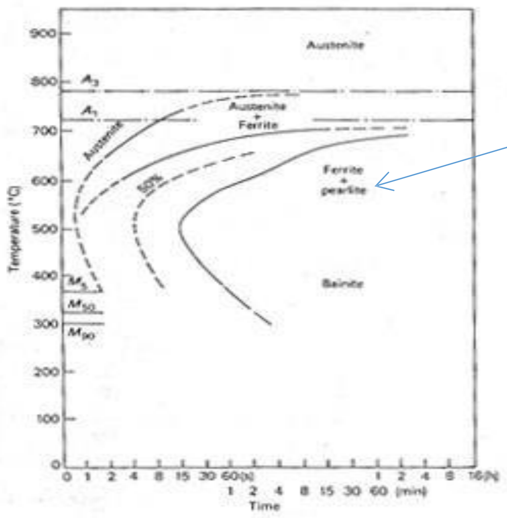
Microconstituent	*Phases Present*	*Arrangement of Phases*	*Mechanical Properties (Relative)*
Spheroidite	α Ferrite + Fe_3C	Relatively small Fe_3C sphere-like particles in an α-ferrite matrix	Soft and ductile
Coarse pearlite	α Ferrite + Fe_3C	Alternating layers of α ferrite and Fe_3C that are relatively thick	Harder and stronger than spheroidite, but not as ductile as spheroidite
Fine pearlite	α Ferrite + Fe_3C	Alternating layers of α ferrite and Fe_3C that are relatively thin	Harder and stronger than coarse pearlite, but not as ductile as coarse pearlite
Bainite	α Ferrite + Fe_3C	Very fine and elongated particles of Fe_3C in an α-ferrite matrix	Hardness and strength greater than fine pearlite; hardness less than martensite; ductility greater than martensite
Tempered martensite	α Ferrite + Fe_3C	Very small Fe_3C sphere-like particles in an α-ferrite matrix	Strong; not as hard as martensite, but much more ductile than martensite
Martensite	Body-centered tetragonal, single phase	Needle-shaped grains	Very hard and very brittle

Hardenability

- We have seen the advantage of getting martensite, M. We can temper it, getting TM with the best combination of ductility and strength.
- But the problem is this: getting M in depth, instead of just on the surface. We want a steel where Pearlite formation is relatively sluggish so we can get it to the cooler regions where M forms.
- The ability to get M (martensite) in depth for low cooling rates is called
  hardenability.
- Plain carbon steels have poor hardenability.

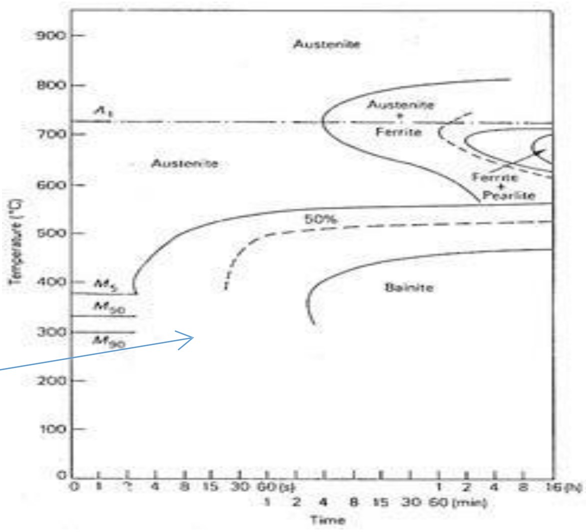
Factors Which Improve Hardenability

- 1. Austenitic Grain size. The Pearlite will have an easier time forming if there is a lot of g.b. area. Hence, having a large austenitic grain size improves hardenability.
- 2. Adding alloys of various kinds. This impedes the $\gamma \rightarrow$ P reaction.



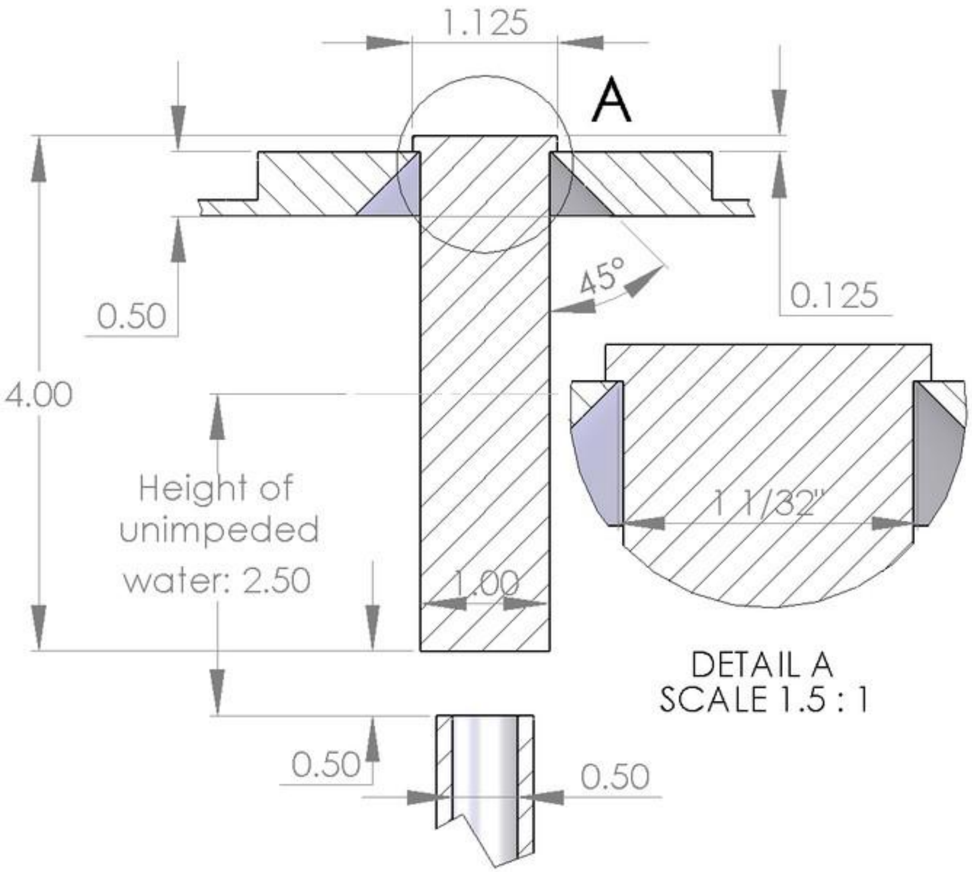
TTT diagram of a molybdenum steel 0.4C 0.2Mo

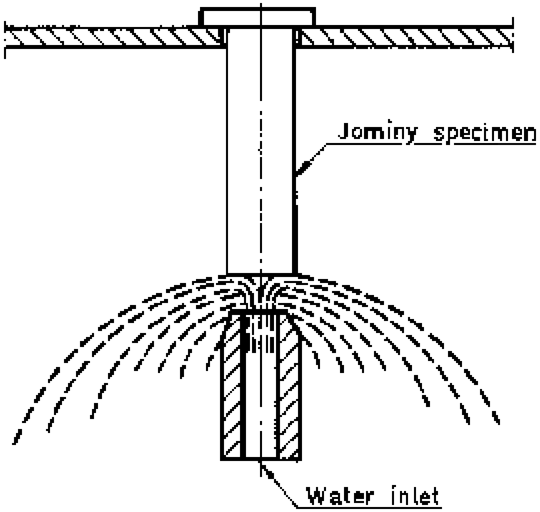
After Adding 2.0% Mo



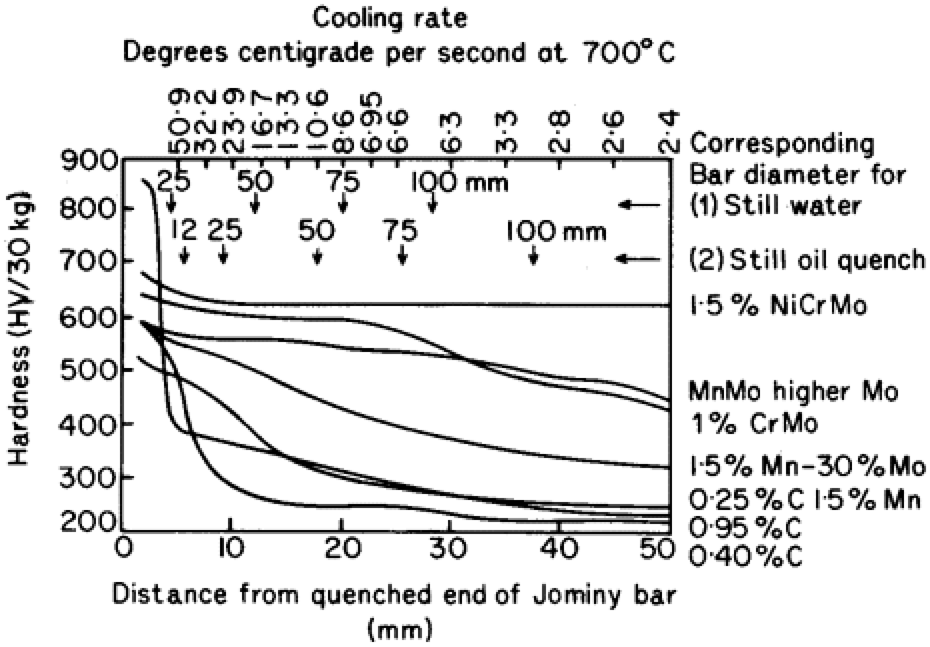
Jominy Test for Hardenability

- Hardenability not the same as hardness!





The Result is Presented in a Curve

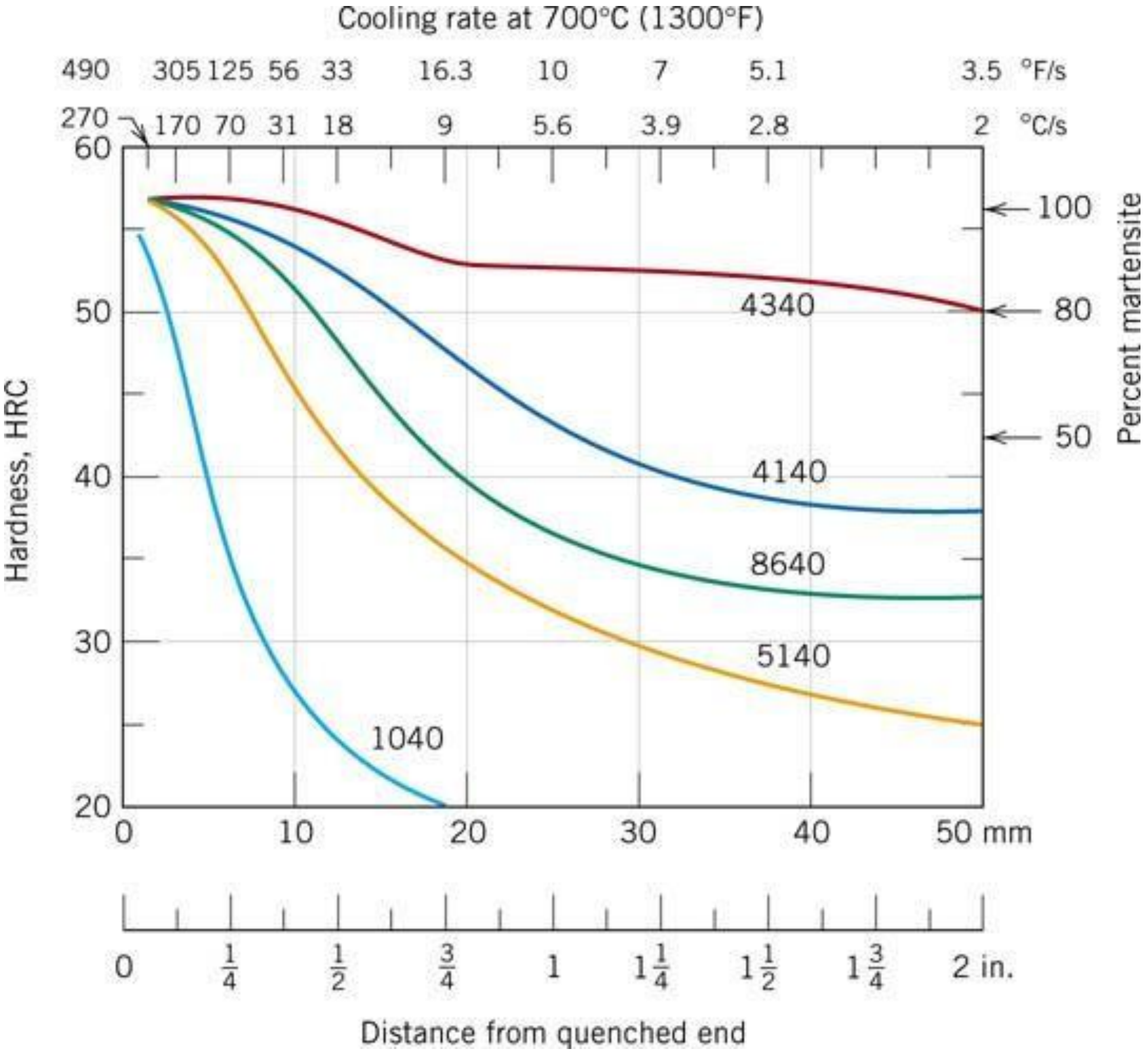


Rank steels in order of hardenability.

Note:

1. Distance from quenched end corresponds to a cooling rate, and a bar diameter
2. Notice that some steels drop off more than others at low cooling rates. Less hardenability!

Alloying and Hardenability



Carbon and Hardenability