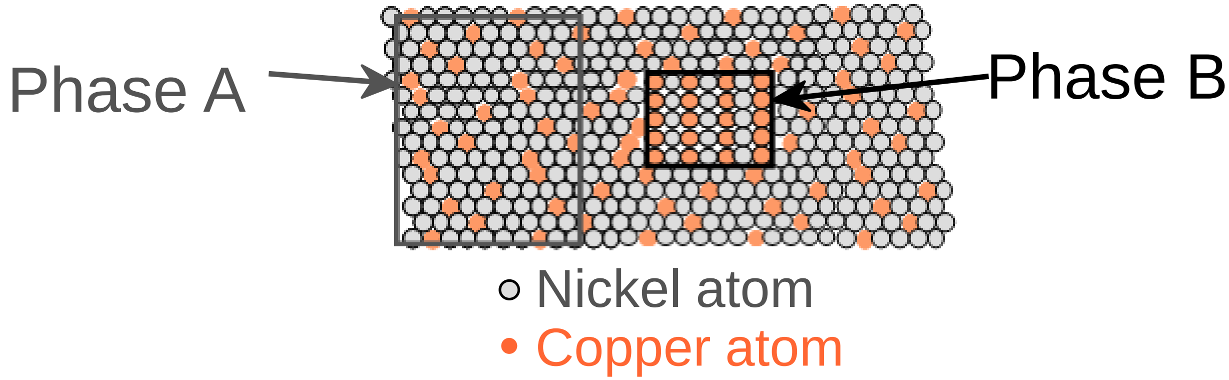
PHASE TRANSFORMATIONS AND PHASE DIAGRAMS

ISSUES TO ADDRESS...

- When we combine two elements...
  what is the resulting equilibrium state?
- In particular, if we specify...
  -- the composition (e.g., wt% Cu - wt% Ni), and
  -- the temperature (*T*)

then...
  How many phases form?
  What is the composition of each phase?
  What is the amount of each phase?

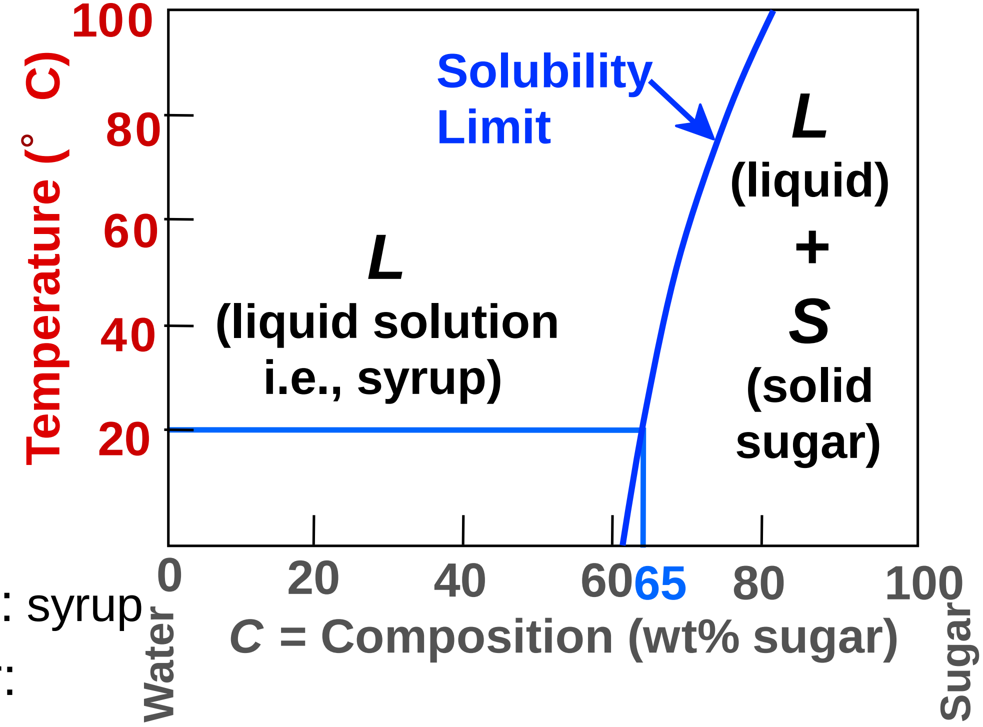


Phase Equilibria: Solubility Limit

- Solution – solid, liquid, or gas solutions, single phase
- Mixture – more than one phase

- Solubility Limit:
  Maximum concentration for which only a single phase solution exists.

Sugar/Water Phase Diagram



Question: What is the solubility limit for sugar in water at 20°C?

Answer: 65 wt% sugar.

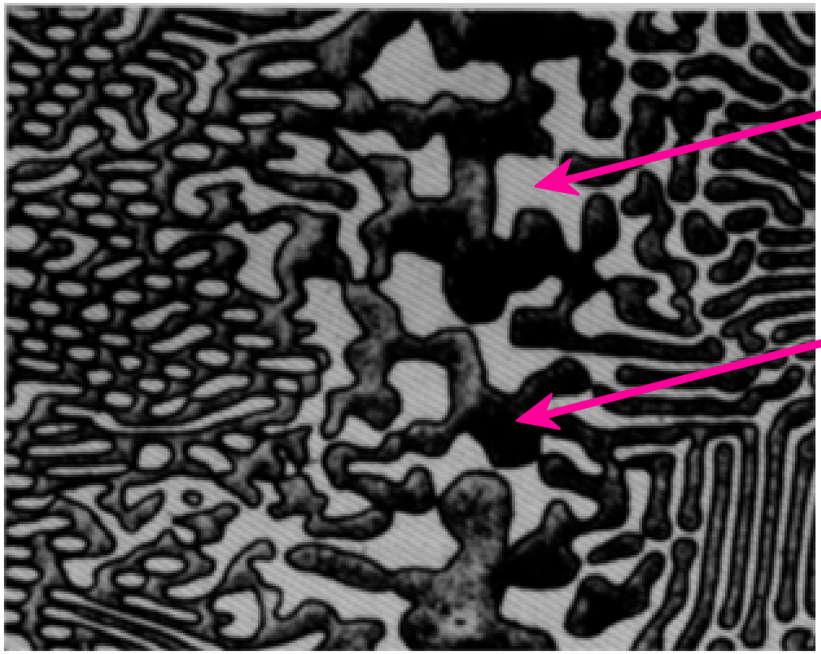
At 20°C, if C < 65 wt% sugar: syrup

At 20°C, if C > 65 wt% sugar: syrup + sugar

Components and Phases

- Components:
  The elements or compounds which are present in the alloy
  (e.g., Al and Cu)
- Phases:
  The physically and chemically distinct material regions
  that form (e.g., α and β).

Aluminum-
Copper
Alloy



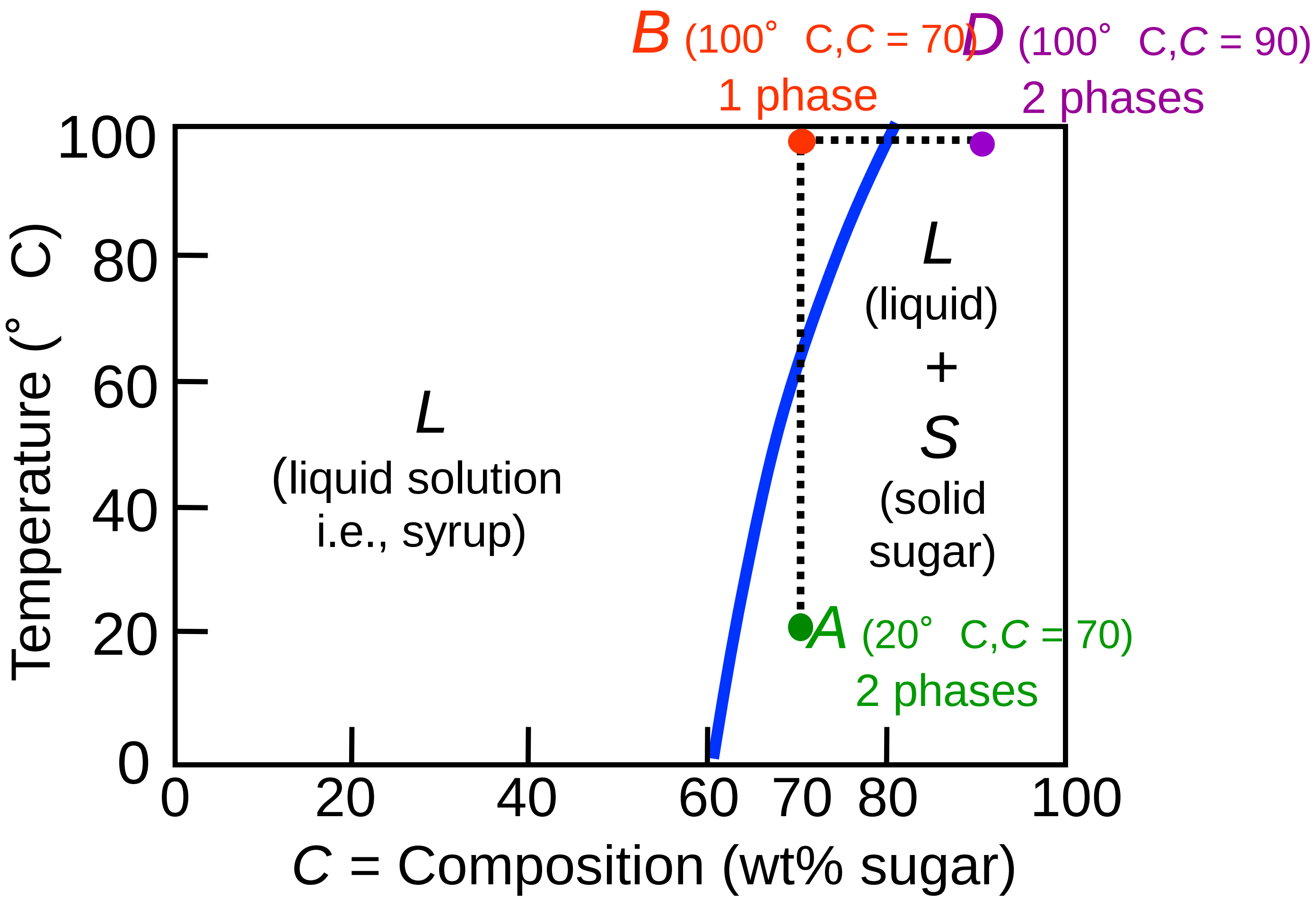
β (lighter phase)

α (darker phase)

Effect of Temperature & Composition

- Altering *T* can change # of phases: path *A* to *B*.
- Altering *C* can change # of phases: path *B* to *D*.

water-
sugar
system



Criteria for Solid Solubility

Simple system (e.g., Ni-Cu solution)

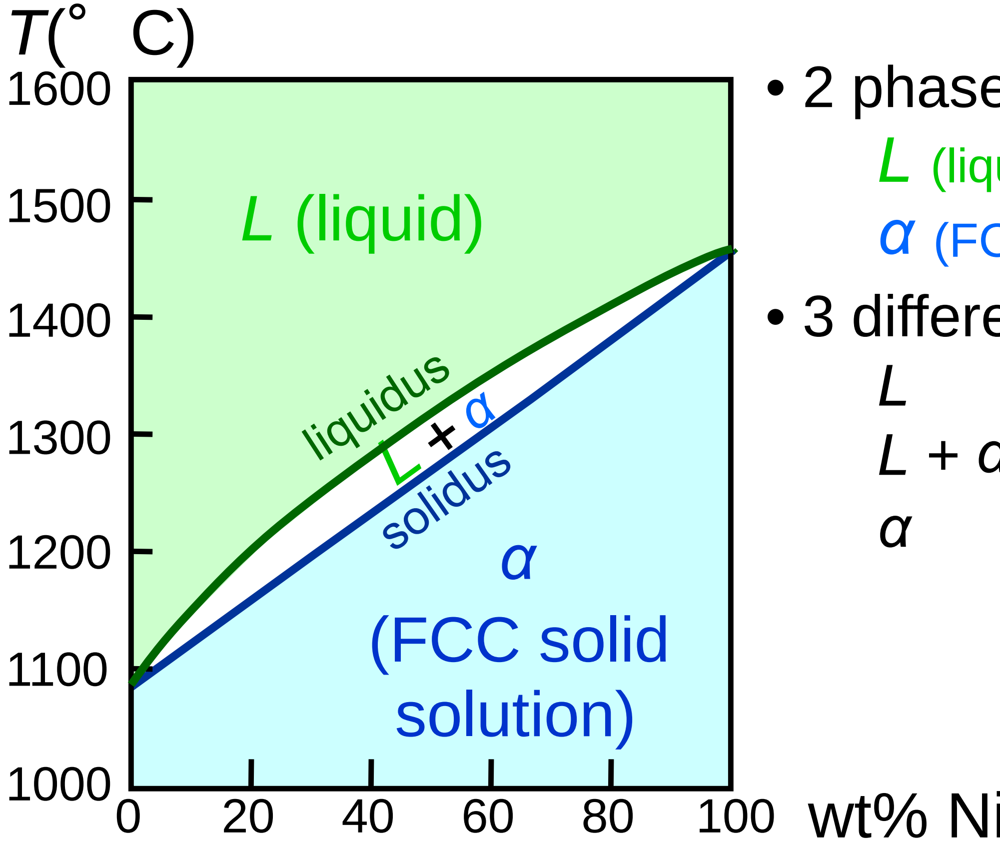
	Crystal Structure	electroneg	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- Both have the same crystal structure (FCC) and have similar electronegativities and atomic radii (W. Hume – Rothery rules) suggesting high mutual solubility.
- Ni and Cu are totally soluble in one another for all proportions.

Phase Diagrams

- Indicate phases as a function of *T*, *C*, and *P*.
- For this course:
  - binary systems: just 2 components.
  - independent variables: *T* and *C* (*P* = 1 atm is almost always used).

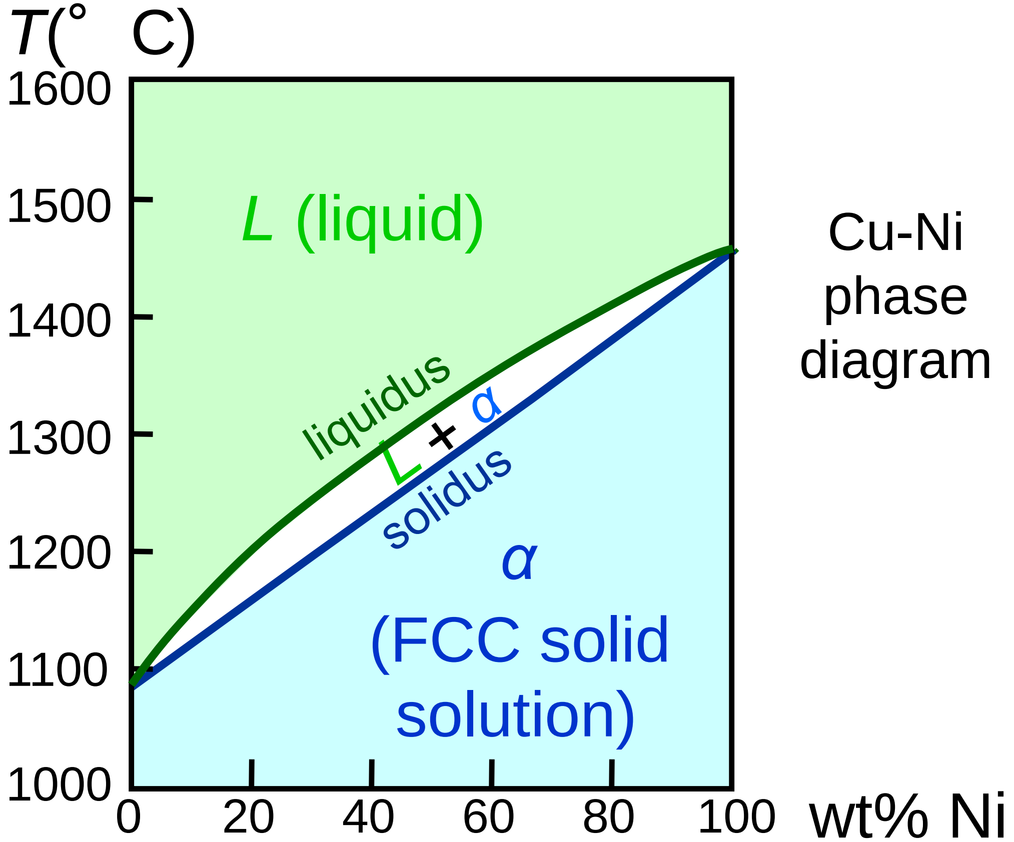
Phase Diagram for Cu-Ni system



- 2 phases:
  - *L* (liquid)
  - α (FCC solid solution)
- 3 different phase fields:
  - *L*
  - *L* + α
  - α

Isomorphous Binary Phase Diagram

- Phase diagram:
  Cu-Ni system.
- System is:
  -- binary
  i.e., 2 components:
  Cu and Ni.
  -- isomorphous
  i.e., complete
  solubility of one
  component in
  another; α phase
  field extends from
  0 to 100 wt% Ni.



Cu-Ni
phase
diagram

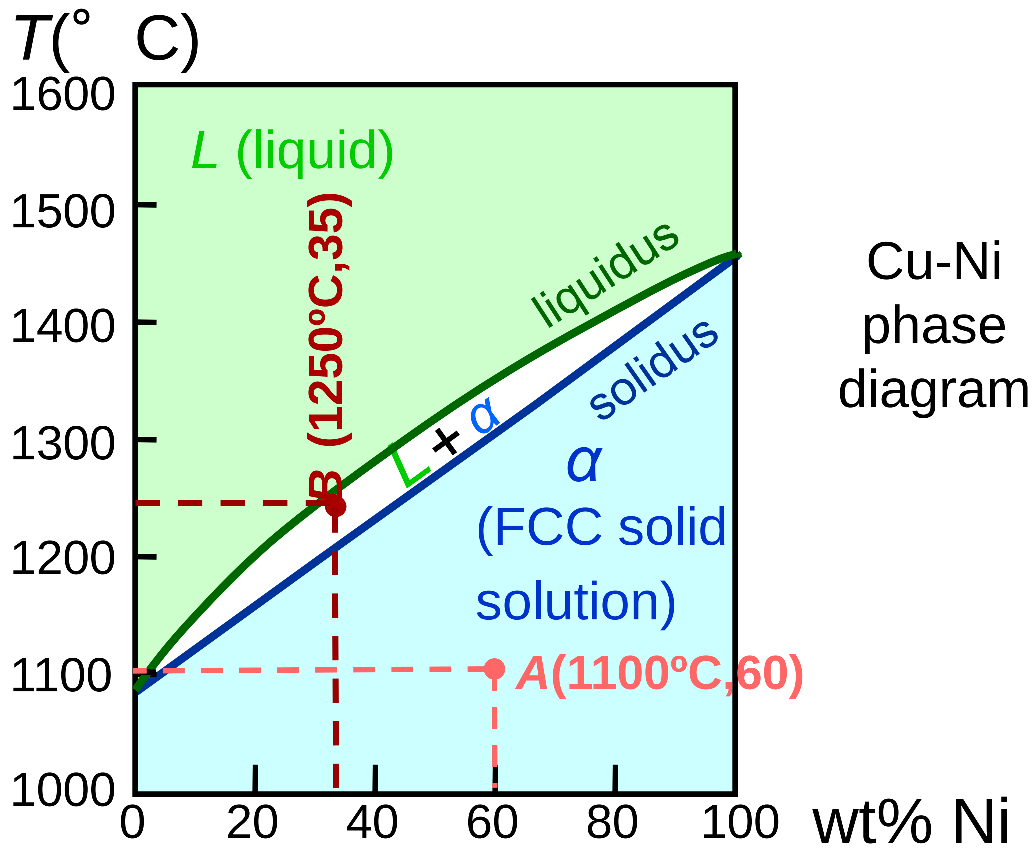
Phase Diagrams:
Determination of phase(s) present

- Rule 1: If we know T and C_o, then we know:
  - -- which phase(s) is (are) present.

- Examples:

  A(1100°C, 60 wt% Ni):
  1 phase: α

  B(1250°C, 35 wt% Ni):
  2 phases: $L + \alpha$



Cu-Ni phase diagram

Phase Diagrams:
Determination of phase compositions

- Rule 2: If we know T and C_0, then we can determine:
  -- the composition of each phase.

- Examples:

  Consider C_0 = 35 wt% Ni

  At T_A = 1320° C:

  Only Liquid (L) present

  $C_L = C_0$ (= 35 wt% Ni)

  At T_D = 1190° C:

  Only Solid (α) present

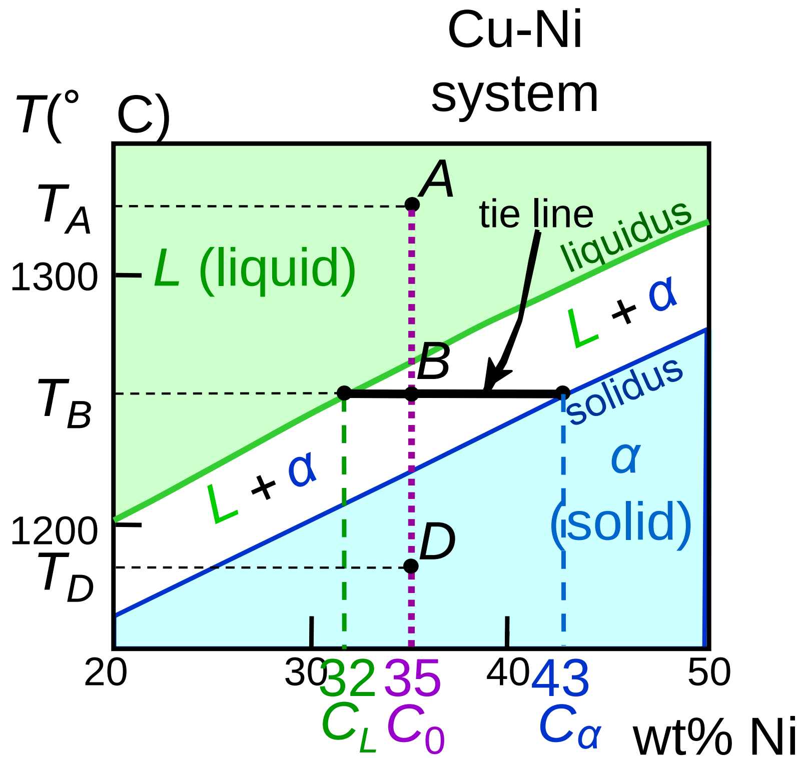
  $C_\alpha = C_0$ (= 35 wt% Ni)

  At T_B = 1250° C:

  Both α and L present

  $C_L = C_{\text{liquidus}}$ (= 32 wt% Ni)

  $C_\alpha = C_{\text{solidus}}$ (= 43 wt% Ni)



Phase Diagrams:
Determination of phase weight fractions

- Rule 3: If we know T and C_0, then can determine:
  -- the weight fraction of each phase.
- Examples:

Consider C_0 = 35 wt% Ni

At T_A : Only Liquid (L) present

W_L = 1.00, W_α = 0

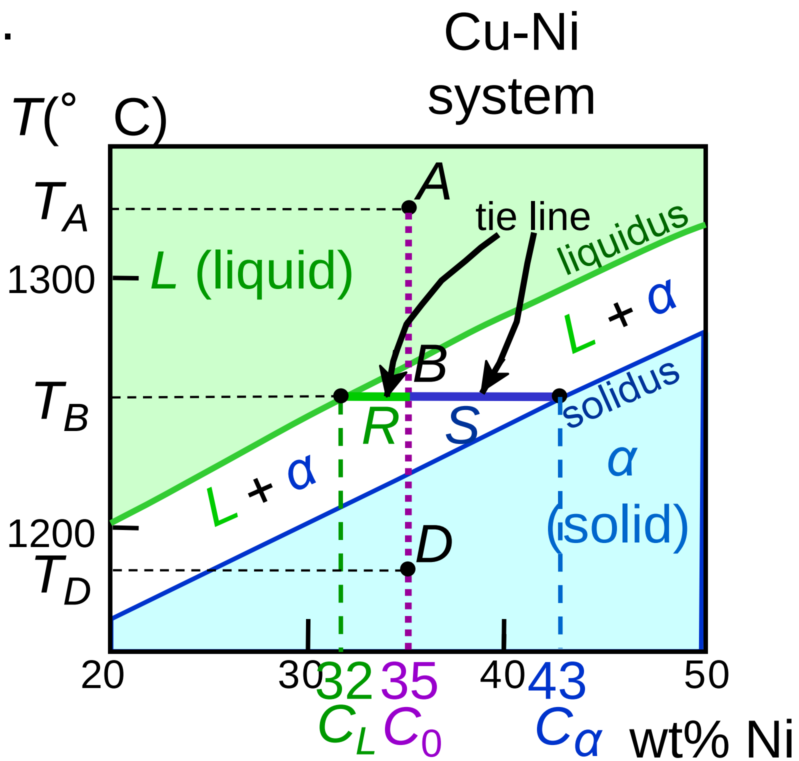
At T_D : Only Solid (α) present

W_L = 0, W_α = 1.00

At T_B : Both α and L present

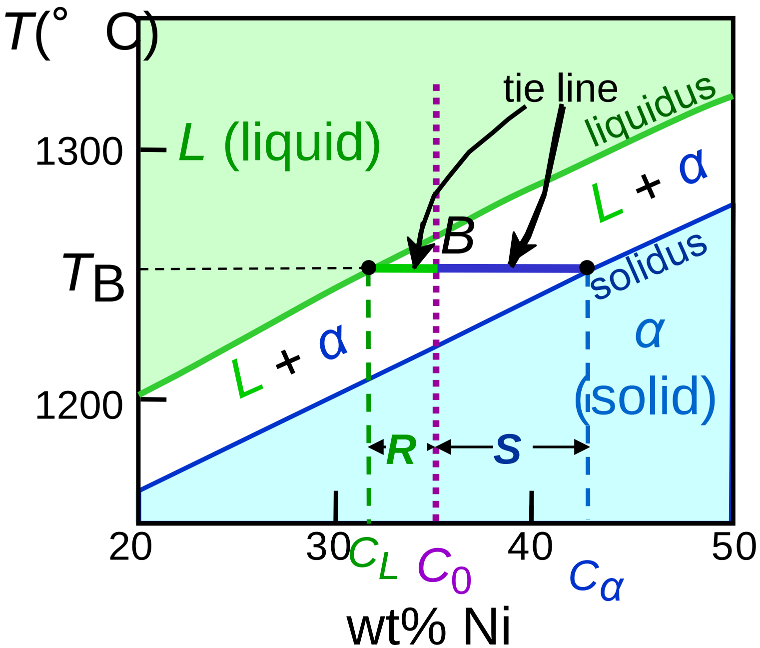
$$W_L = \frac{S}{R+S} = \frac{43-35}{43-32} = 0.73$$

$$W_\alpha = \frac{R}{R+S} = 0.27$$



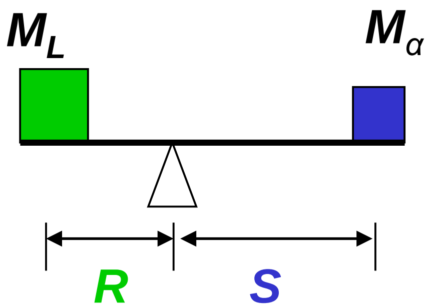
The Lever Rule

- Tie line – connects the phases in equilibrium with each other – also sometimes called an isotherm



What fraction of each phase?

Think of the tie line as a lever (teeter-totter)



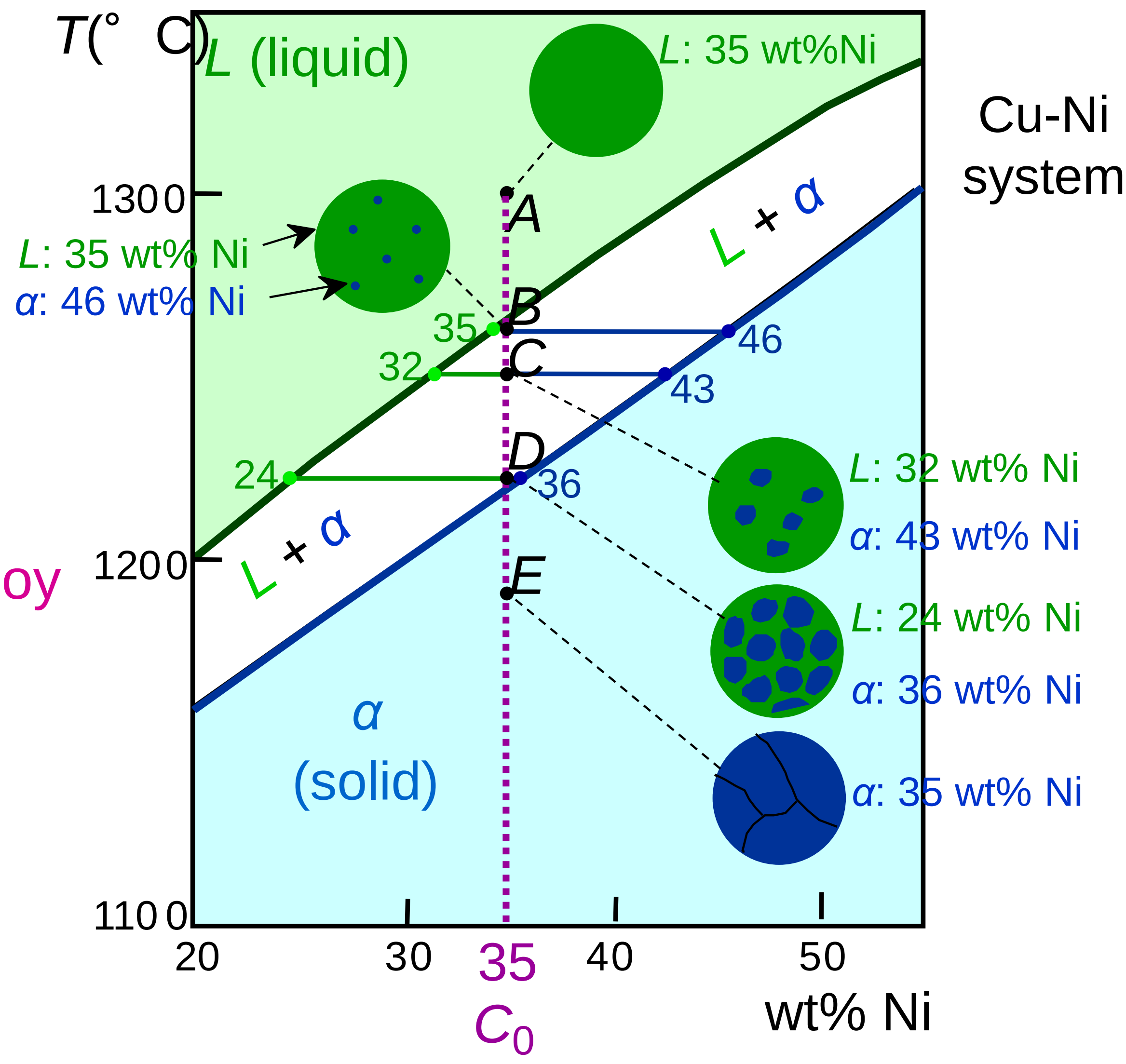
$$M_\alpha \times S = M_L \times R$$

$$W_L = \frac{M_L}{M_L + M_\alpha} = \frac{S}{R+S} = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

$$W_\alpha = \frac{R}{R+S} = \frac{C_0 - C_L}{C_\alpha - C_L}$$

Ex: Cooling of a Cu-Ni Alloy

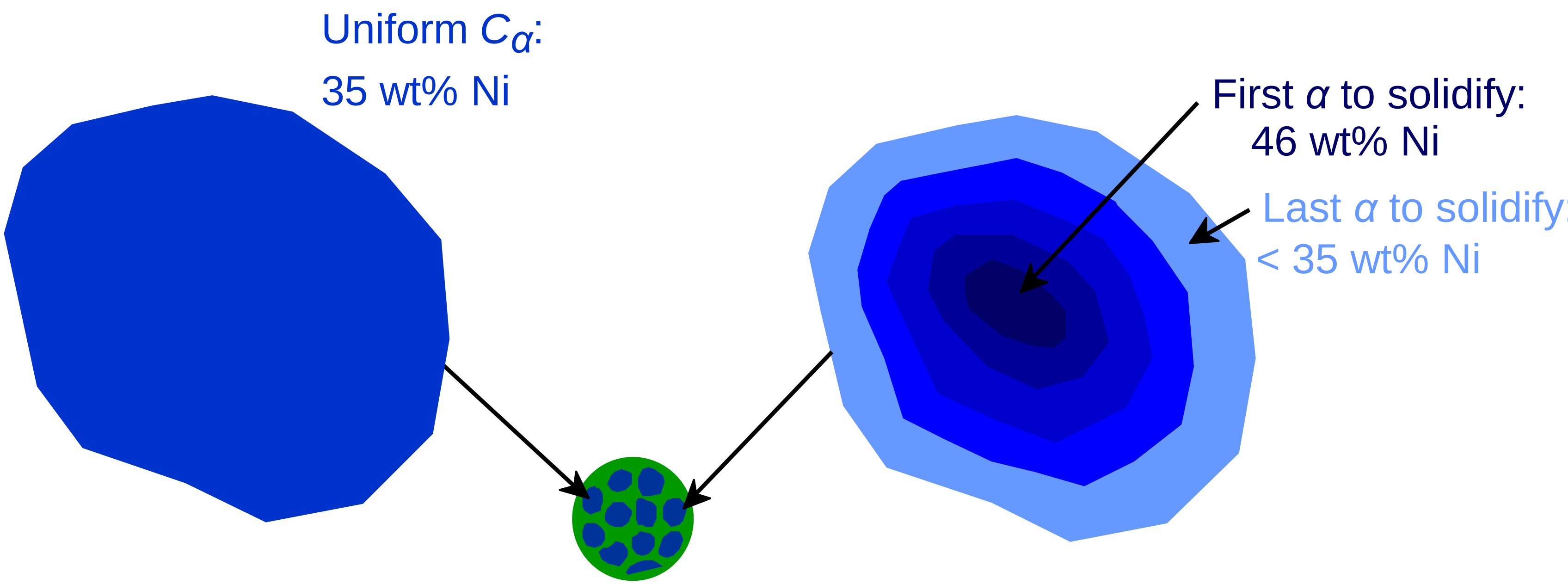
- Phase diagram: Cu-Ni system.
- Consider microstuctural changes that accompany the cooling of a C_0 = 35 wt% Ni alloy



Cored vs Equilibrium Structures

- C_α changes as we solidify.
- Cu-Ni case: First α to solidify has C_α = 46 wt% Ni.
  Last α to solidify has C_α = 35 wt% Ni.

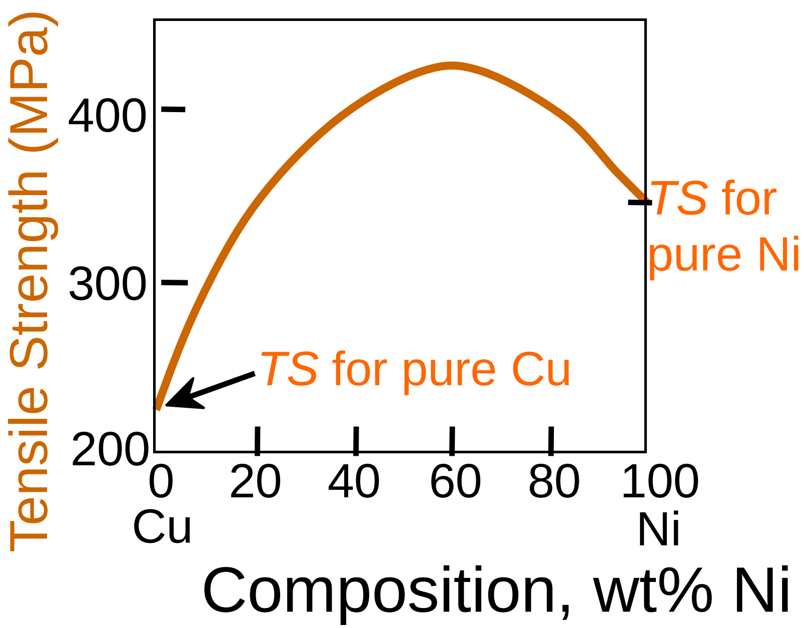
- Slow rate of cooling:
  Equilibrium structure
- Fast rate of cooling:
  Cored structure



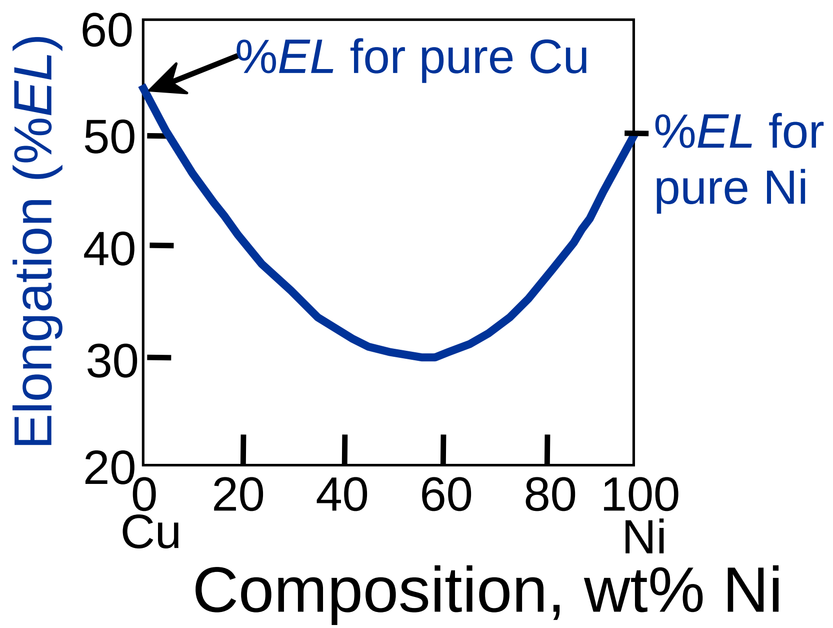
Mechanical Properties: Cu-Ni System

- Effect of solid solution strengthening on:

-- Tensile strength (*TS*)



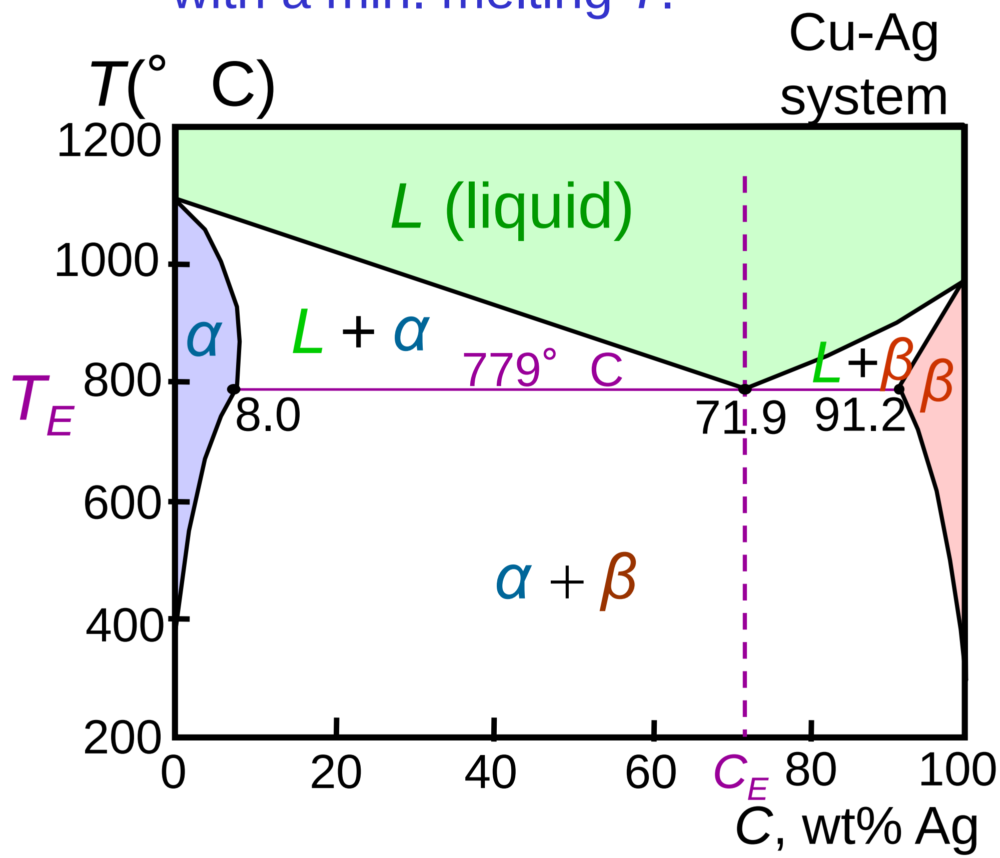
-- Ductility (%*EL*)



Binary-Eutectic Systems

2 components

has a special composition with a min. melting *T*.



Ex.: Cu-Ag system

- 3 single phase regions (L, α, β)
- Limited solubility:
  - α: mostly Cu
  - β: mostly Ag
- T_E : No liquid below T_E
- C_E : Composition at temperature T_E
- **Eutectic reaction**

$$L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

$$L(71.9\text{ wt\% Ag}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(8.0\text{ wt\% Ag}) + \beta(91.2\text{ wt\% Ag})$$

EX 1: Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 150°C, determine:
  -- the phases present

Answer: $\alpha + \beta$

-- the phase compositions

Answer: C_α = 11 wt% Sn
C_β = 99 wt% Sn

-- the relative amount of each phase

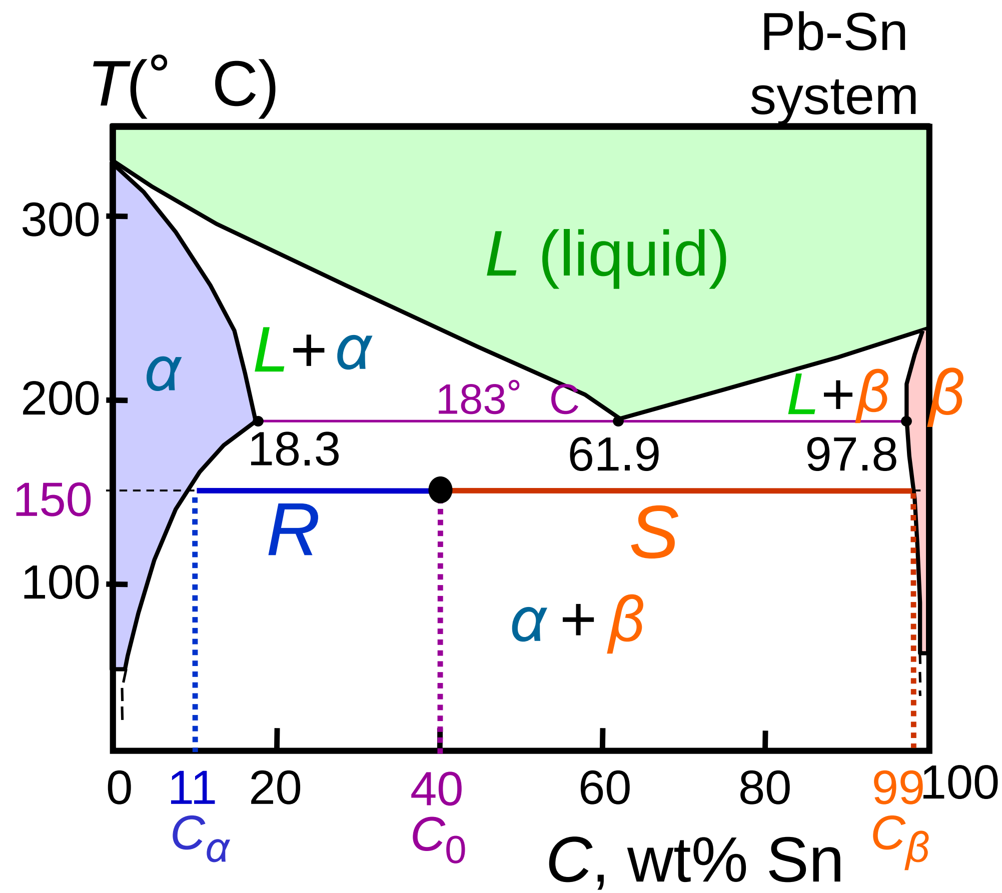
Answer:

$$W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_0}{C_\beta - C_\alpha}$$

$$= \frac{99 - 40}{99 - 11} = \frac{59}{88} = 0.67$$

$$W_\beta = \frac{R}{R+S} = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha}$$

$$= \frac{40 - 11}{99 - 11} = \frac{29}{88} = 0.33$$



EX 2: Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 220°C, determine:
  - -- the phases present:

Answer: $\alpha + L$

-- the phase compositions

Answer: C_α = 17 wt% Sn
C_L = 46 wt% Sn

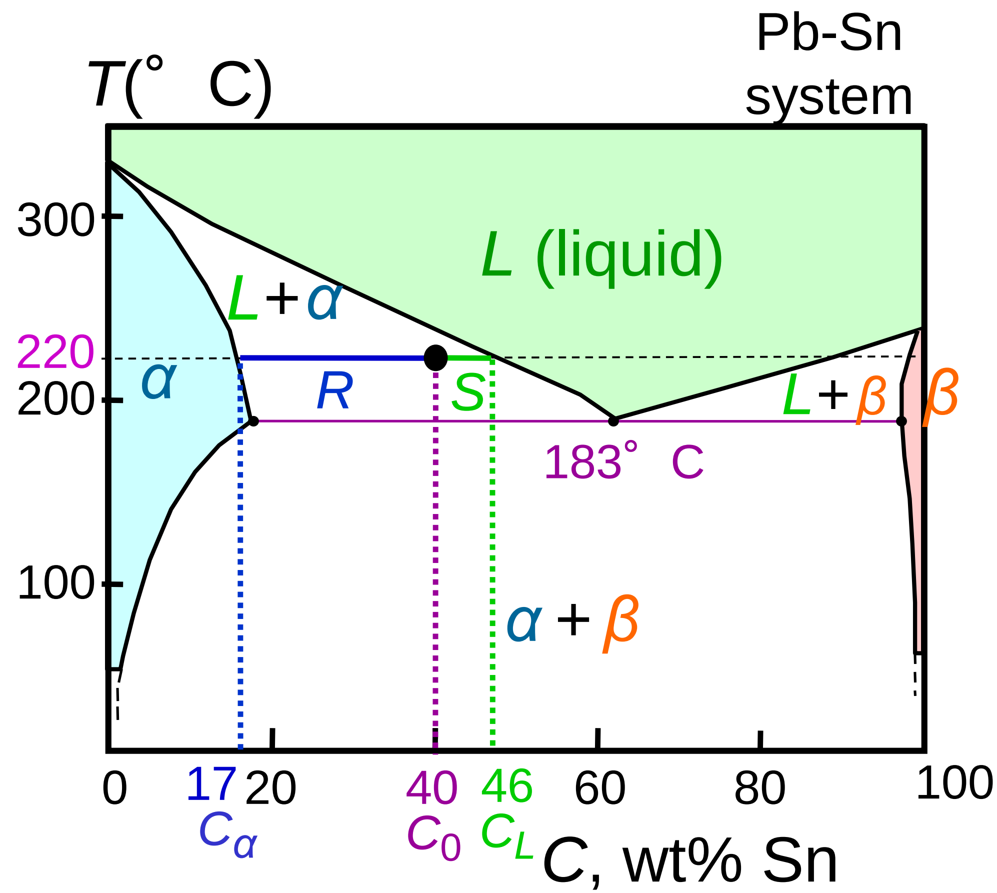
-- the relative amount of each phase

Answer:

$$W_\alpha = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17}$$

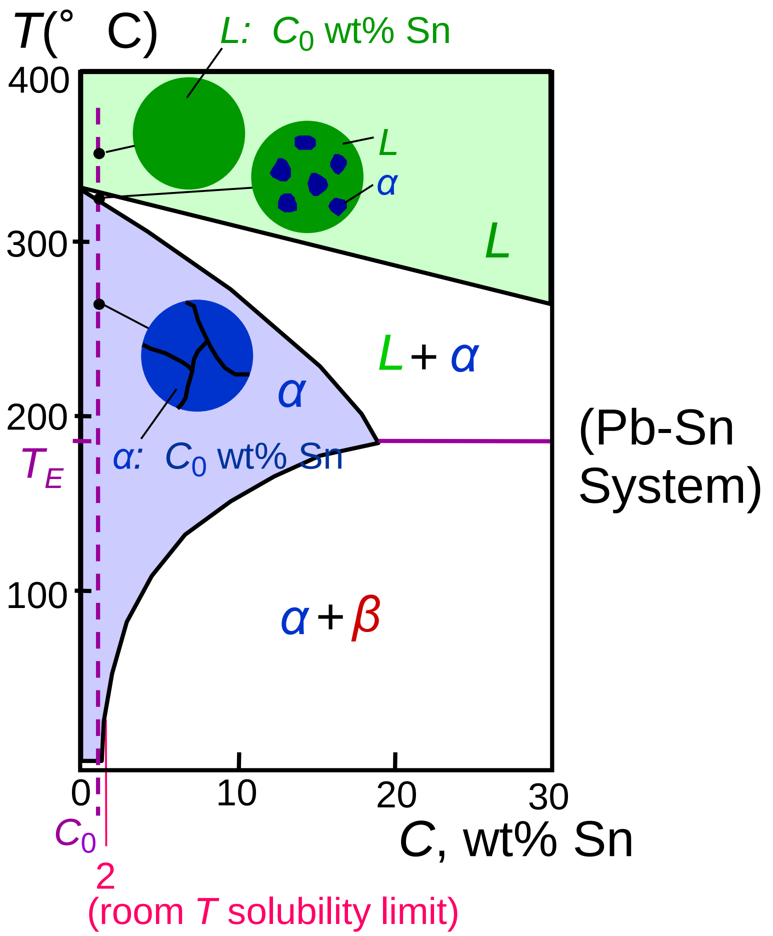
$$= \frac{6}{29} = 0.21$$

$$W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 0.79$$



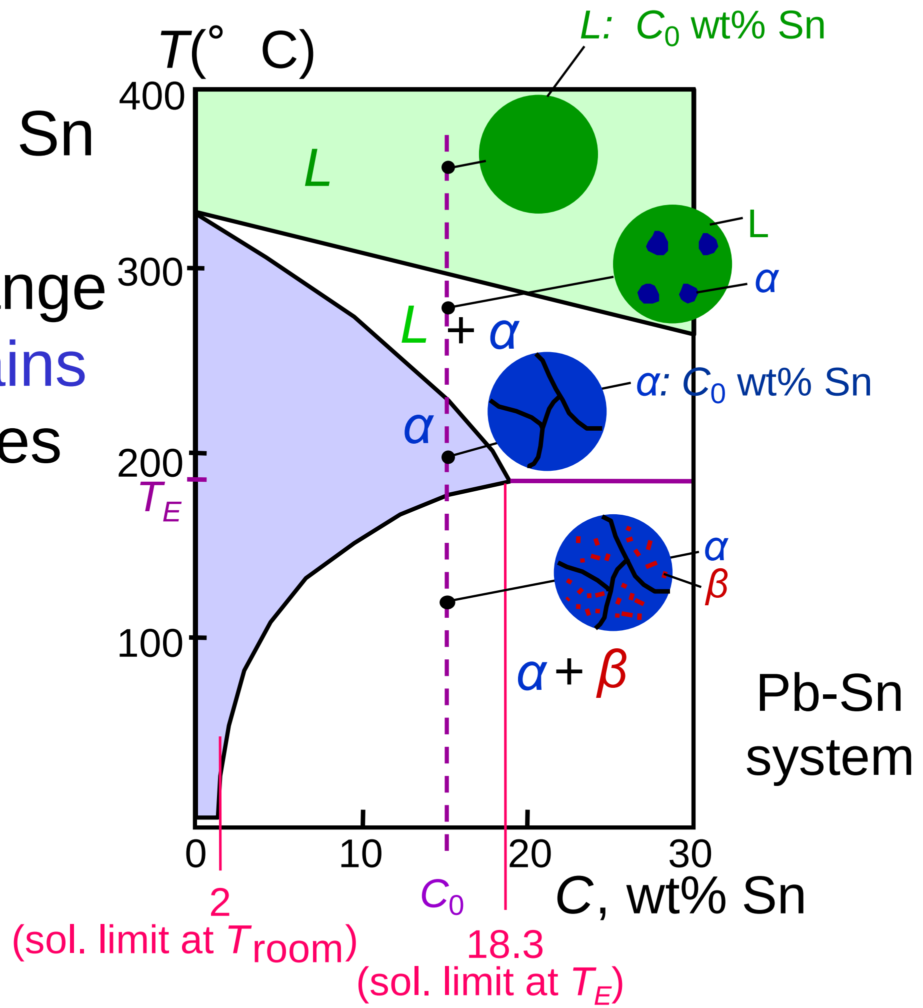
Microstructural Developments in Eutectic Systems I

- For alloys for which
  C_0 < 2 wt% Sn
- Result: at room temperature
  -- polycrystalline with grains of
  α phase having
  composition C_0



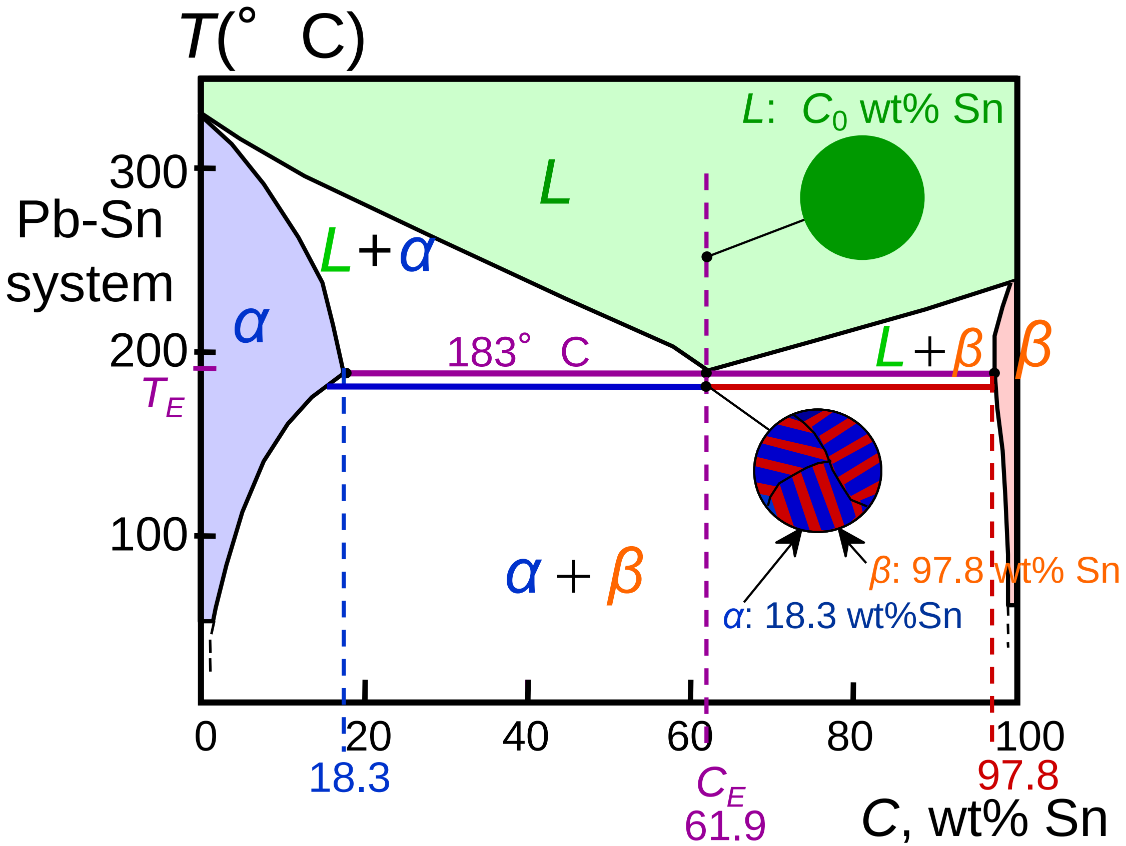
Microstructural Developments in Eutectic Systems II

- For alloys for which
  2 wt% Sn < C_0 < 18.3 wt% Sn
- Result:
  at temperatures in $\alpha + \beta$ range
  -- polycrystalline with α grains
  and small β-phase particles

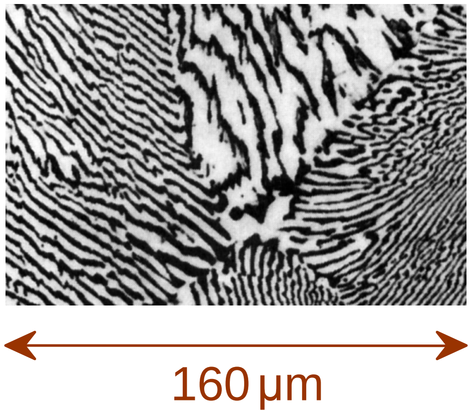


Microstructural Developments in Eutectic Systems III

- For alloy of composition $C_0 = C_E$
- Result: Eutectic microstructure (lamellar structure)
  -- alternating layers (lamellae) of α and β phases.

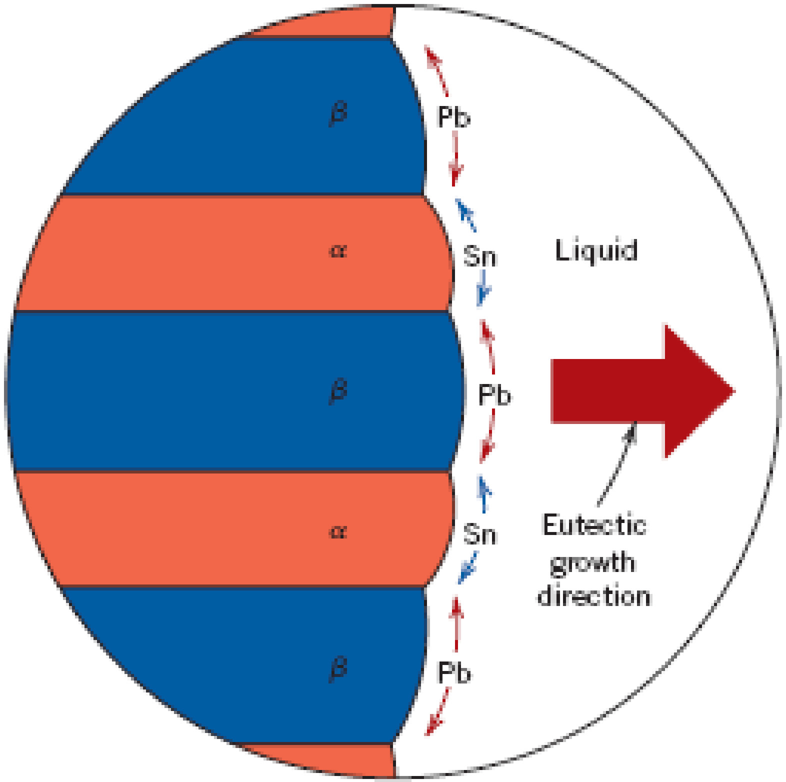


Micrograph of Pb-Sn eutectic microstructure



Callister & Rethwisch 9e.
(From *Metals Handbook*, 9th edition, Vol. 9, *Metallography and Microstructures*, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

Lamellar Eutectic Structure



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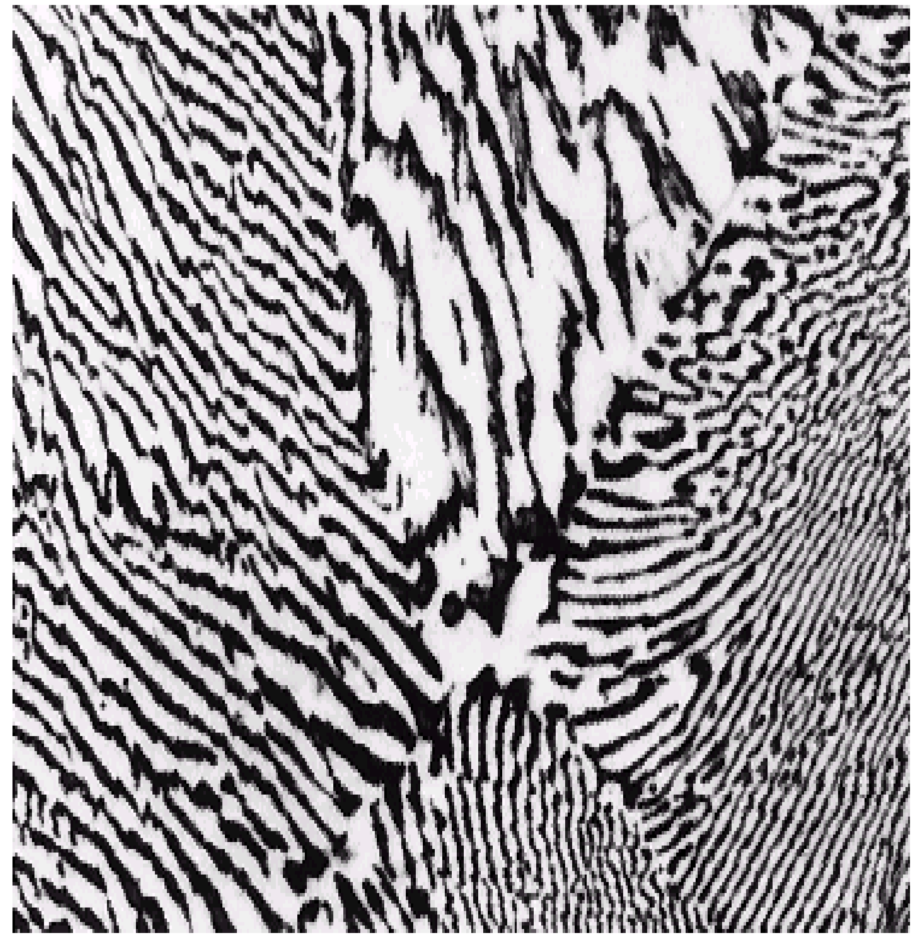
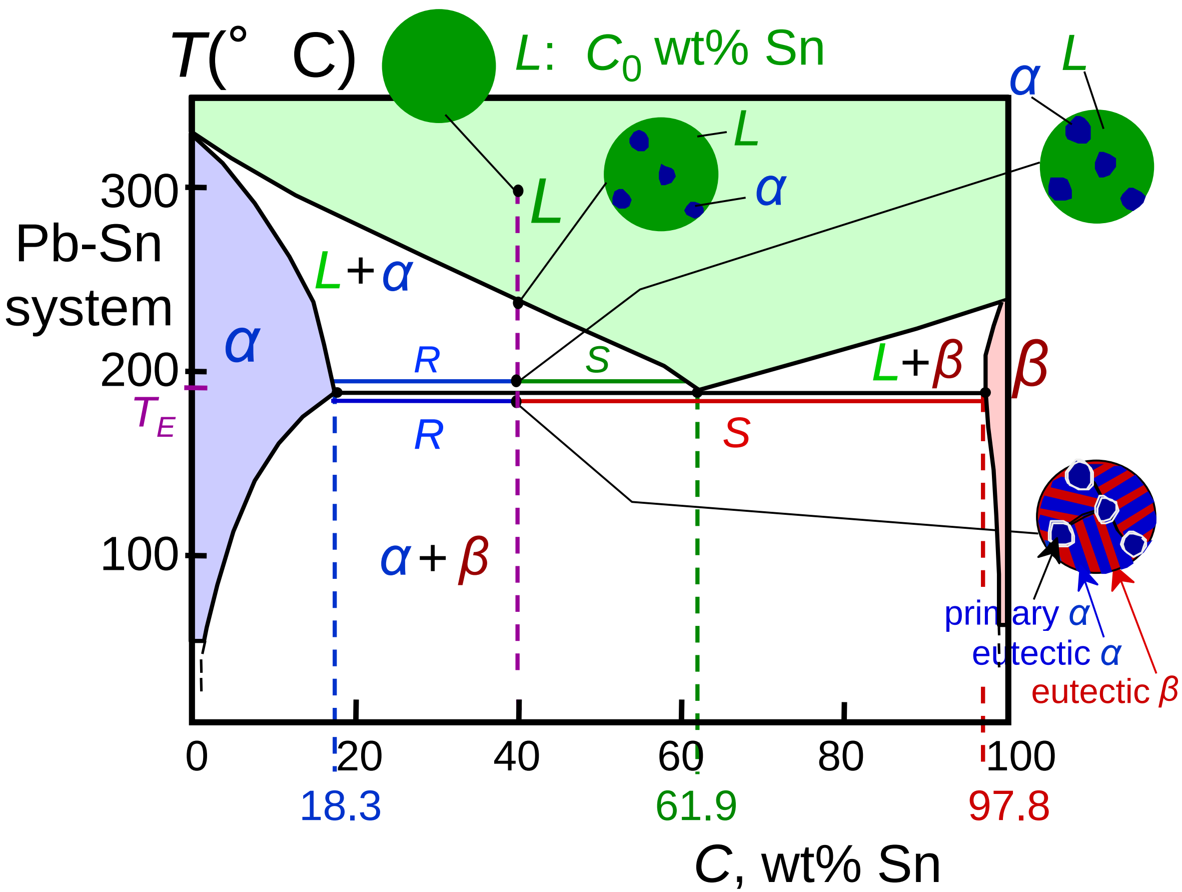


Microstructural Developments in Eutectic Systems IV

- For alloys for which 18.3 wt% Sn < C_0 < 61.9 wt% Sn
- Result: α phase particles and a eutectic microconstituent



- Just above T_E:

  $C_\alpha = 18.3$ wt% Sn

  $C_L = 61.9$ wt% Sn

  $$W_\alpha = \frac{S}{R+S} = 0.50$$

  $$W_L = (1 - W_\alpha) = 0.50$$

- Just below T_E:

  $C_\alpha = 18.3$ wt% Sn

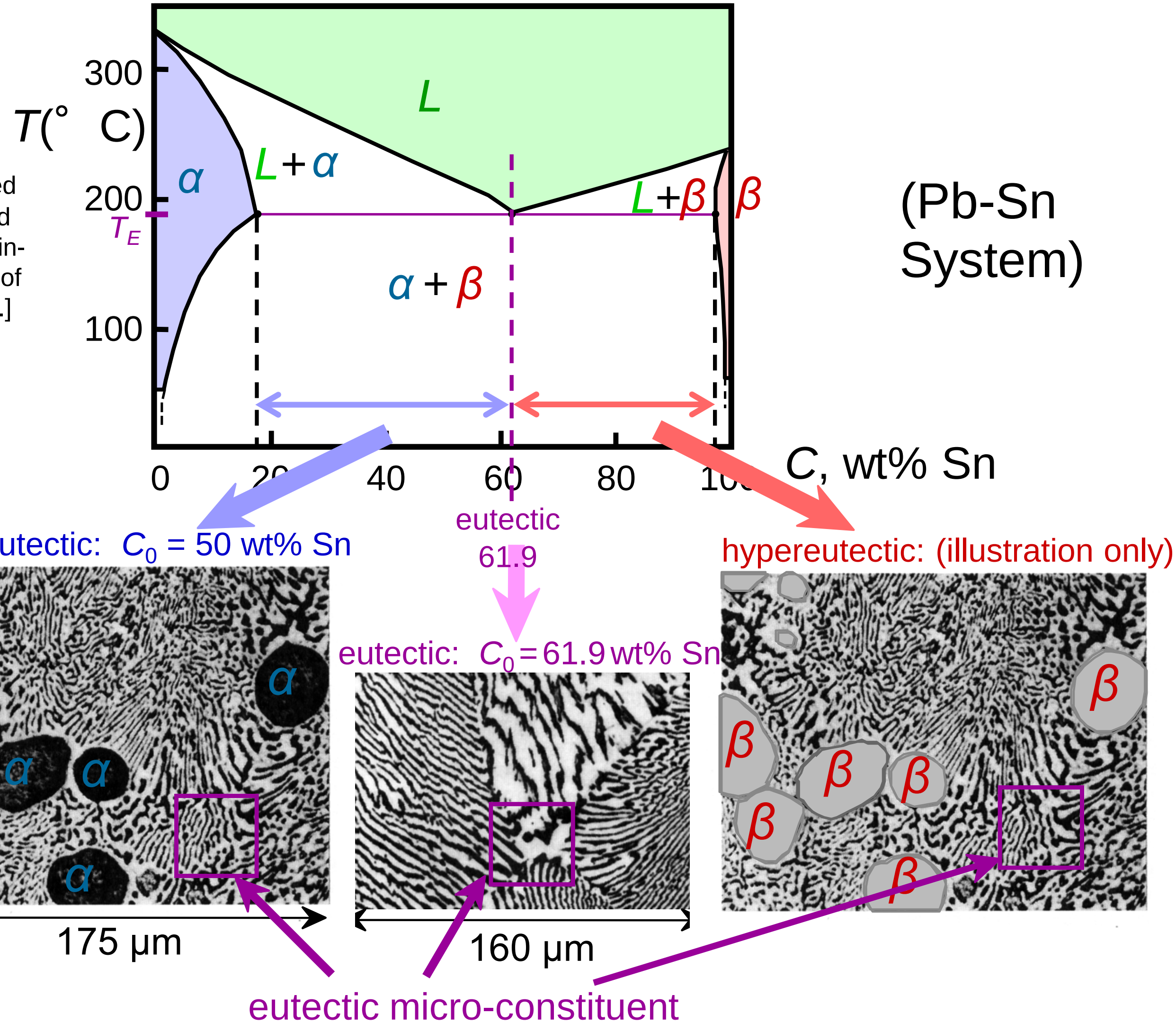
  $C_\beta = 97.8$ wt% Sn

  $$W_\alpha = \frac{S}{R+S} = 0.73$$

  $$W_\beta = 0.27$$

Hypoeutectic & Hypereutectic

Callister & Rethwisch 9e. [Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]



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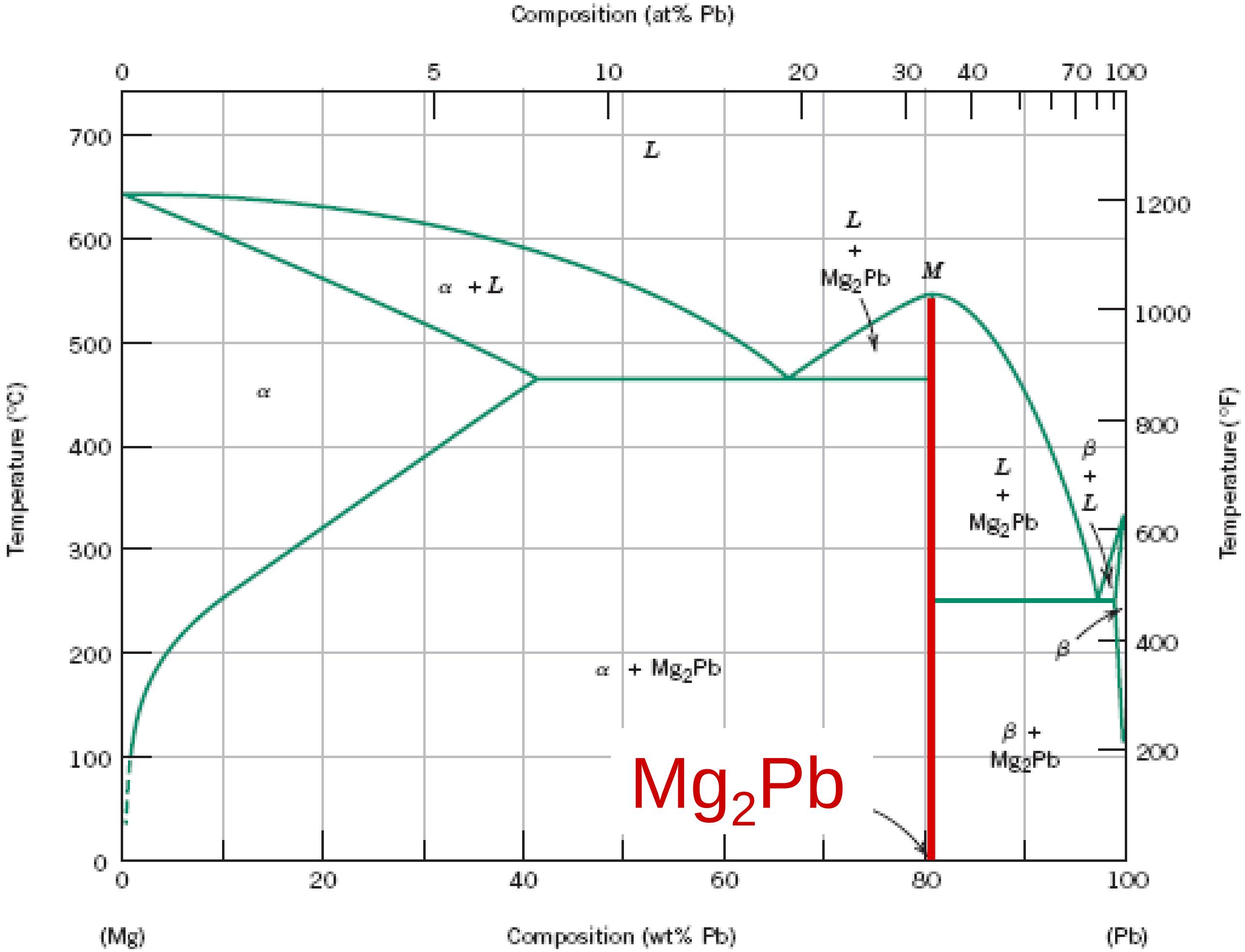
Intermetallic Compounds



[Adapted from *Phase Diagrams of Binary Magnesium Alloys*, A. A. Nayeb-Hashemi and J. B. Clark (Editors), 1988. Reprinted by permission of ASM International, Materials Park, OH.]

Note: intermetallic compound exists as a line on the diagram - not an area - because of stoichiometry (i.e. composition of a compound is a fixed value).

Eutectic, Eutectoid, & Peritectic

- Eutectic - liquid transforms to two solid phases

  $L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + \beta$ (For Pb-Sn, 183° C, 61.9 wt% Sn)

- Eutectoid – one solid phase transforms to two other solid phases

  $S_2 \rightleftharpoons S_1 + S_3$

  intermetallic compound - cementite

  $\gamma \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + Fe_3C$ (For Fe-C, 727° C, 0.76 wt% C)

- Peritectic - liquid and one solid phase transform to a second solid phase

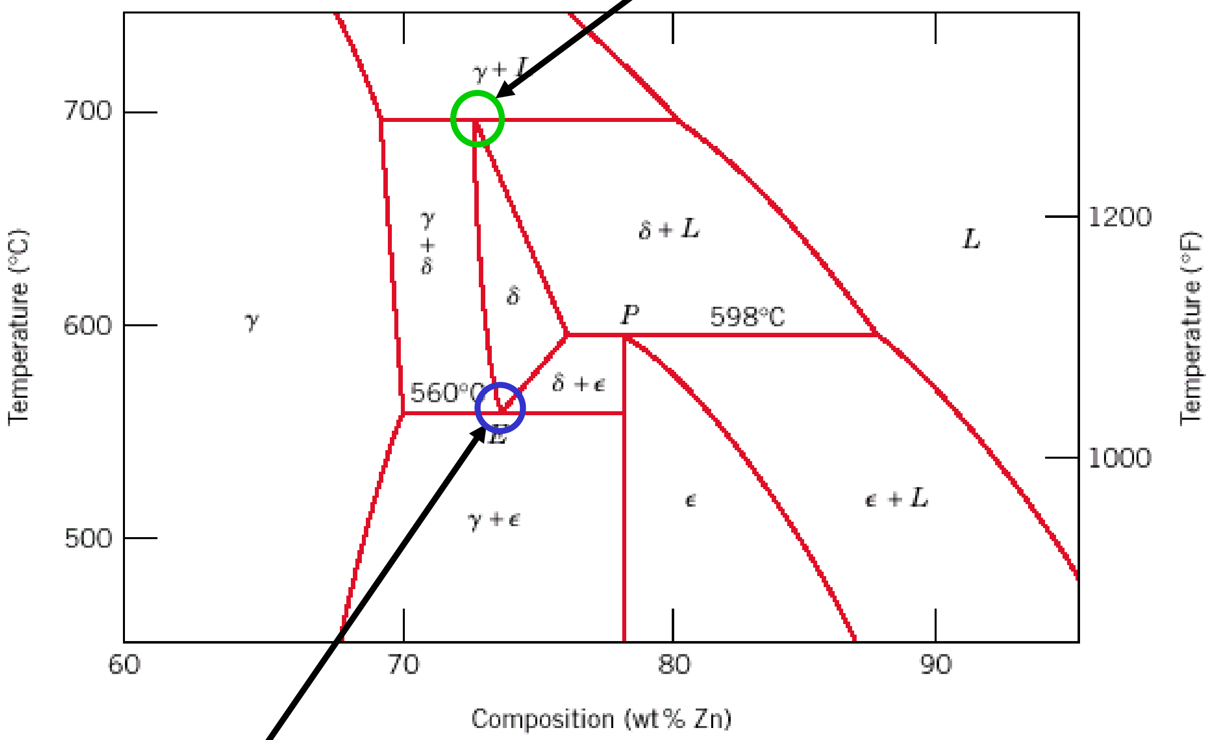
  $S_1 + L \rightleftharpoons S_2$

  $\delta + L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \gamma$ (For Fe-C, 1493° C, 0.16 wt% C)

Eutectoid & Peritectic

Peritectic transformation $\gamma + L \rightleftharpoons \delta$

Cu-Zn Phase diagram

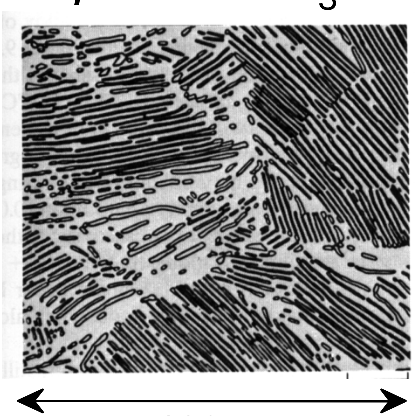


[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 2, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

Eutectoid transformation $\delta \rightleftharpoons \gamma + \epsilon$

Iron-Carbon (Fe-C) Phase Diagram

- 2 important points
  - Eutectic (*A*): $L \Rightarrow \gamma + Fe_3C$
  - Eutectoid (*B*): $\gamma \Rightarrow \alpha + Fe_3C$



Result: Pearlite = alternating layers of α and Fe_3C phases

Fig. 9.27, *Callister & Rethwisch 9e.*
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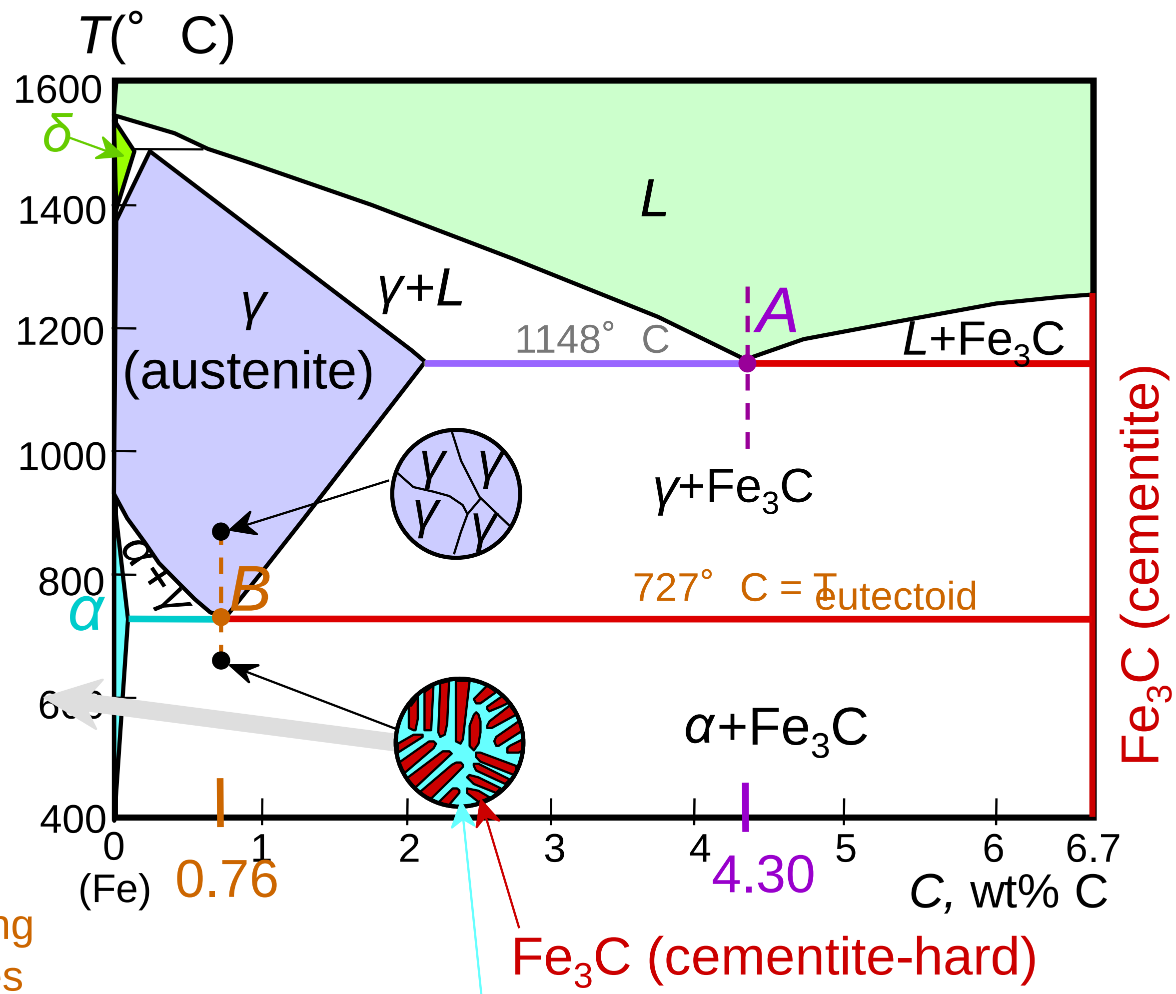
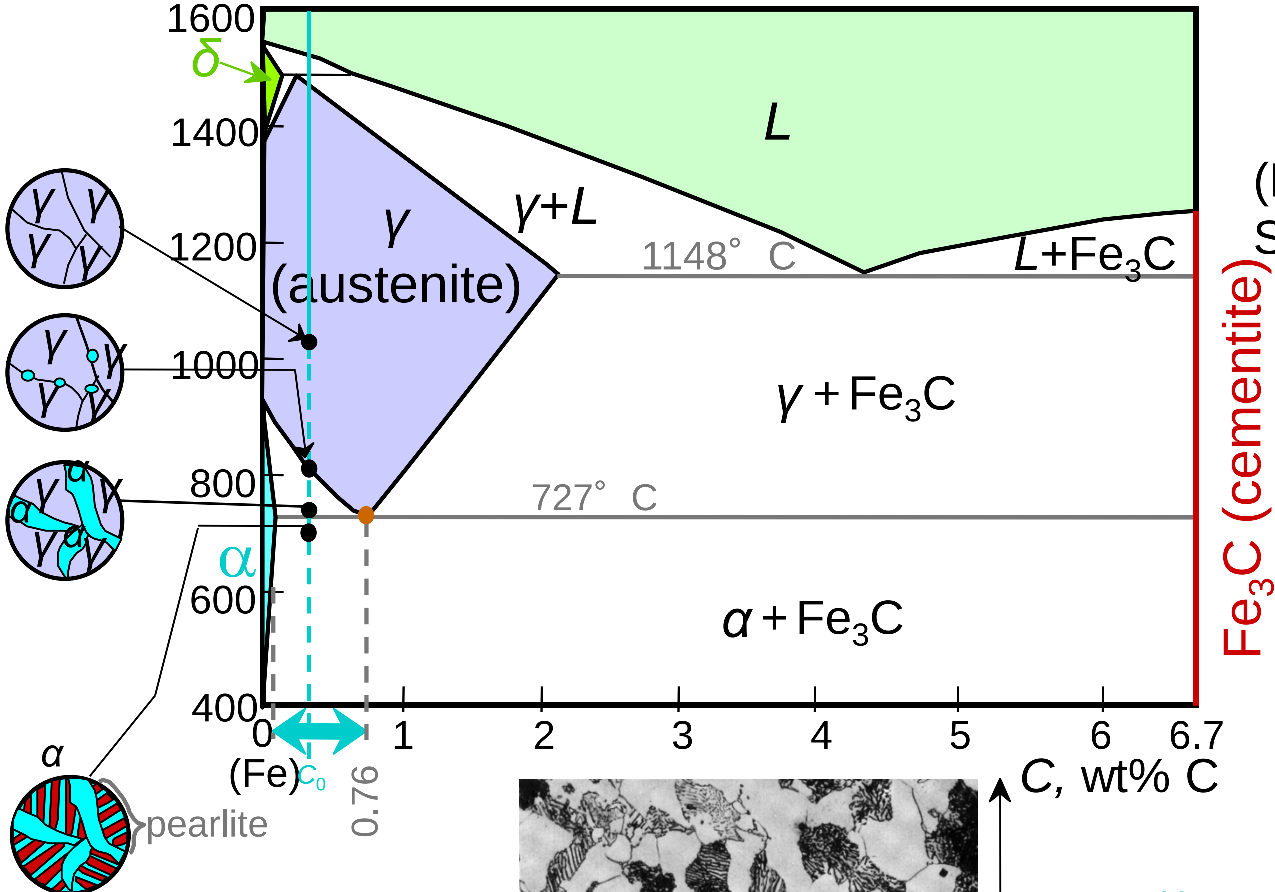


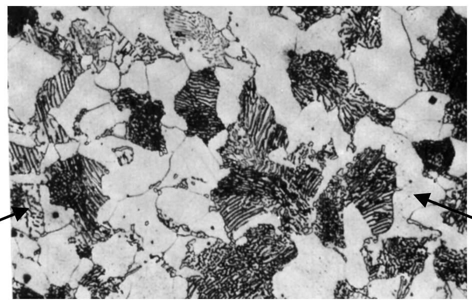
Fig. 9.24, *Callister & Rethwisch 9e.*
[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

Hypoeutectoid Steel

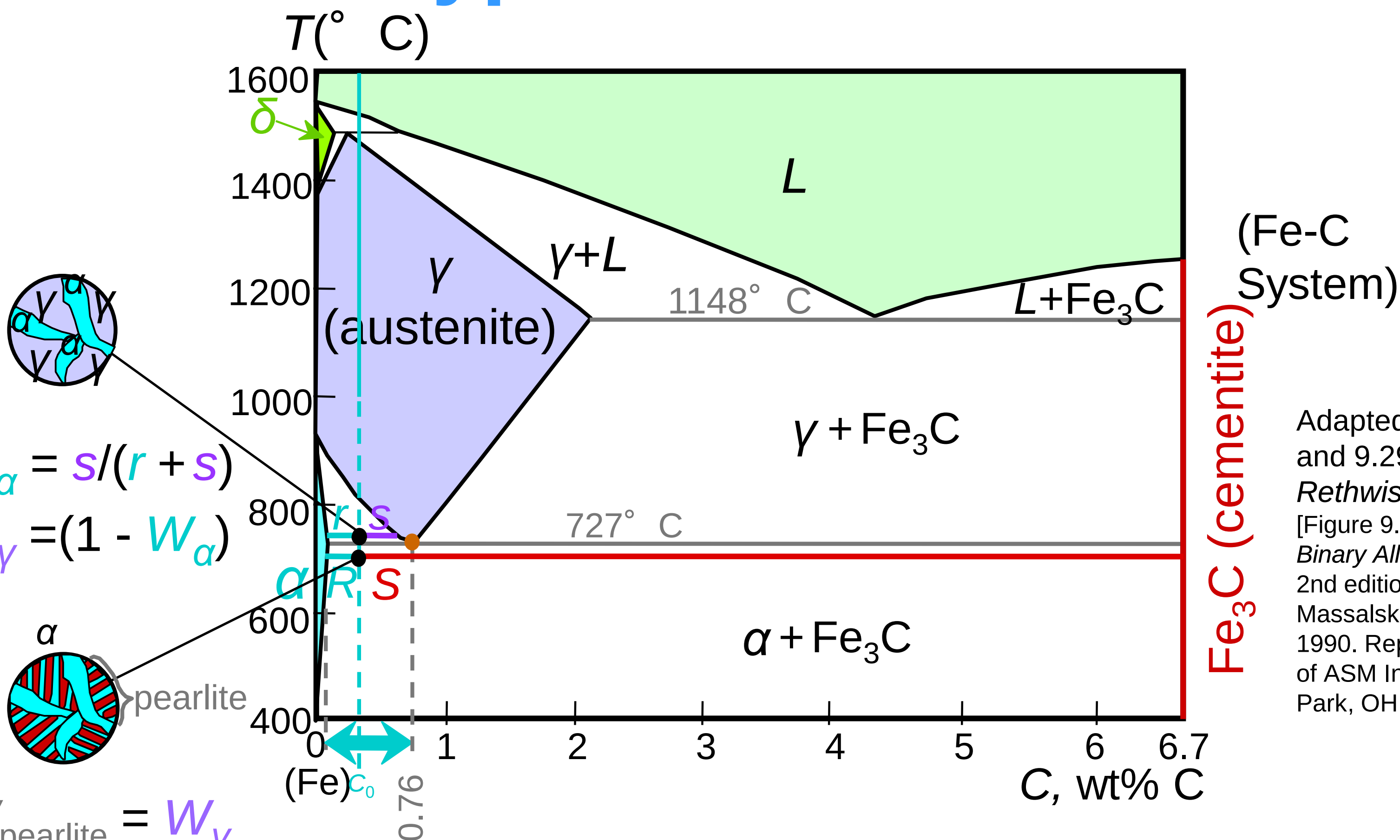


(Fe-C System)

[Figure 9.24 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.]



Hypoeutectoid Steel



$W_{\alpha} = s/(r+s)$

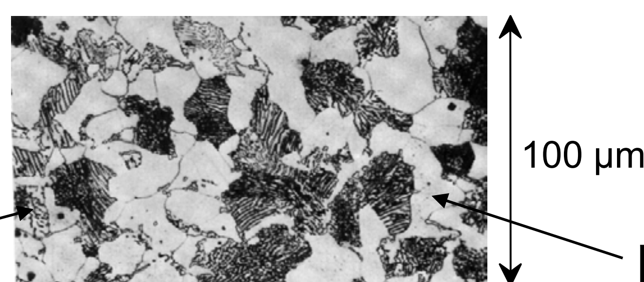
$W_{\gamma} = (1 - W_{\alpha})$

$W_{pearlite} = W_{\gamma}$

$W_{\alpha'} = S/(R+S)$

$W_{Fe_3C} = (1 - W_{\alpha'})$

Adapted from Figs. 9.24 and 9.29, *Callister & Rethwisch 9e.* [Figure 9.24 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.]

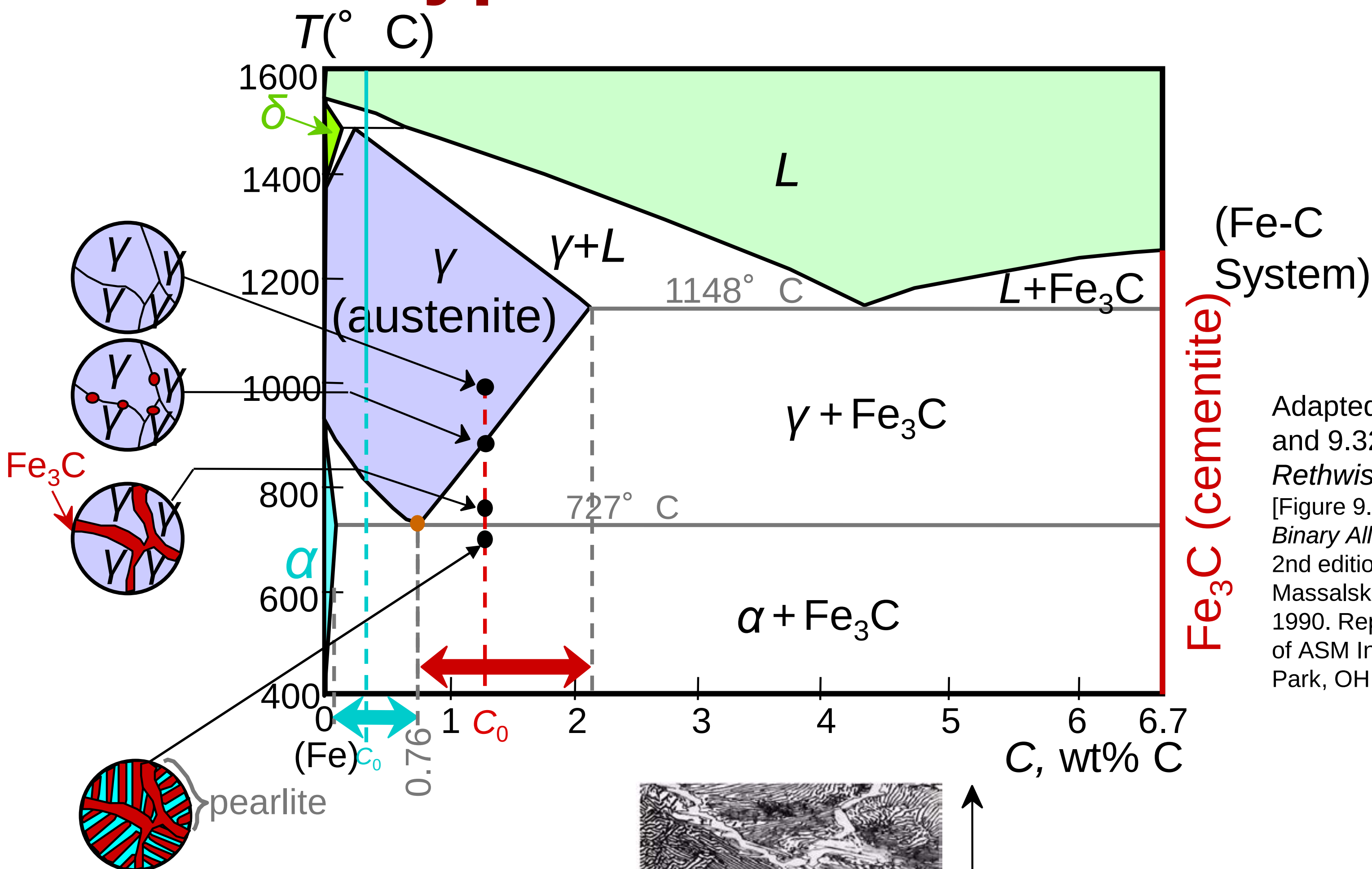


pearlite

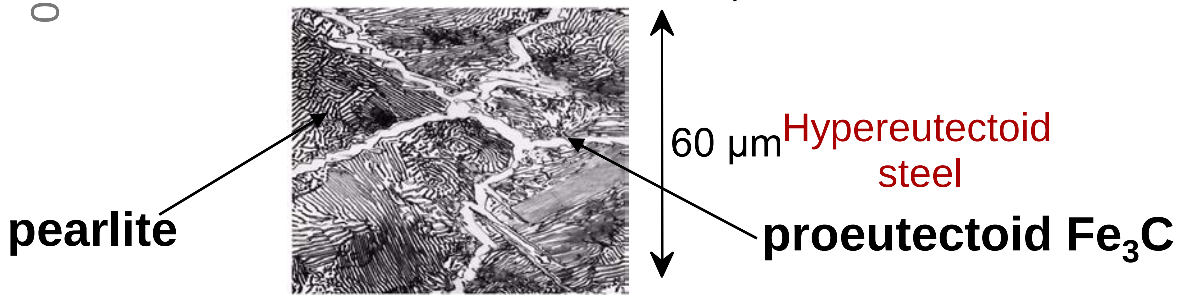
proeutectoid ferrite

Hypoeutectoid steel

Hypereutectoid Steel



Adapted from Figs. 9.24 and 9.32, *Callister & Rethwisch 9e.*
[Figure 9.24 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.]



Adapted from Fig. 9.33, *Callister & Rethwisch 9e*.
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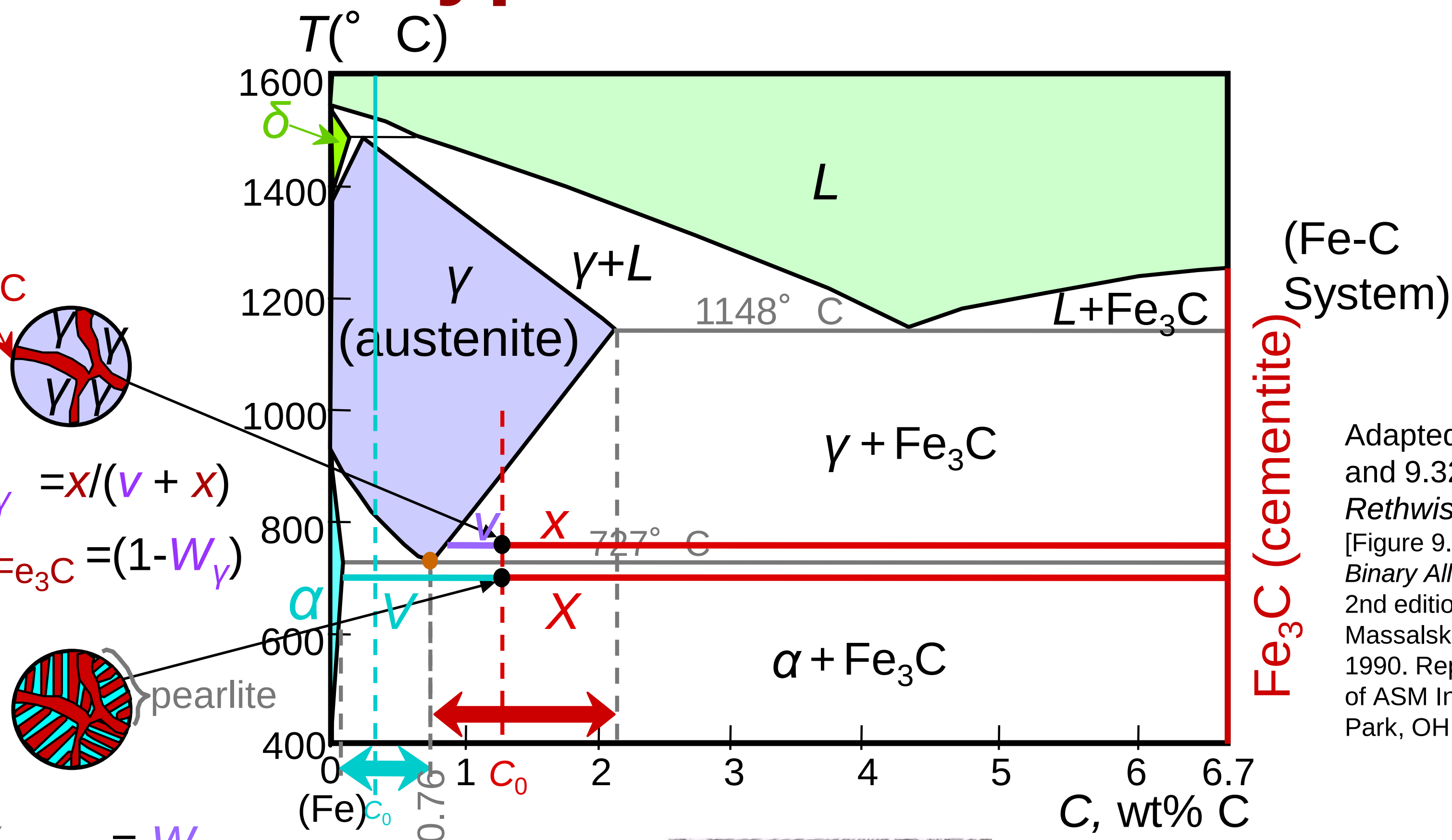
Hypereutectoid Steel



Adapted from Figs. 9.24 and 9.32, *Callister & Rethwisch 9e.* [Figure 9.24 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.]

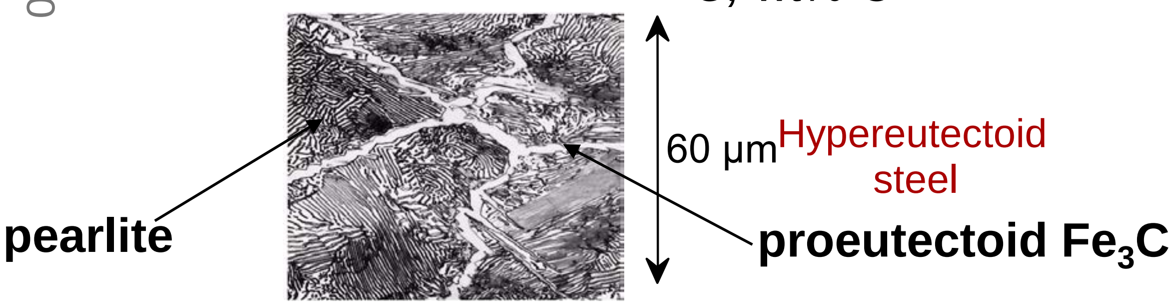
$W_{\gamma} = x/(v + x)$

$W_{Fe_3C} = (1 - W_{\gamma})$

$W_{pearlite} = W_{\gamma}$

$W_{\alpha} = X/(V + X)$

$W_{Fe_3C'} = (1 - W_{\alpha})$



Adapted from Fig. 9.33, *Callister & Rethwisch 9e.*
(Copyright 1971 by United States Steel Corporation.)

Example Problem

For a 99.6 wt% Fe-0.40 wt% C steel at a temperature just below the eutectoid, determine the following:

a) The compositions of Fe_3C and ferrite (α).

b) The amount of cementite (in grams) that forms in 100 g of steel.

c) The amounts of pearlite and proeutectoid ferrite (α) in the 100 g.

Solution to Example Problem

a) Using the *RS* tie line just below the eutectoid

C_α = 0.022 wt% C
C_{Fe_3C} = 6.70 wt% C

b) Using the lever rule with the tie line shown

$$W_{Fe_3C} = \frac{R}{R+S} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha}$$

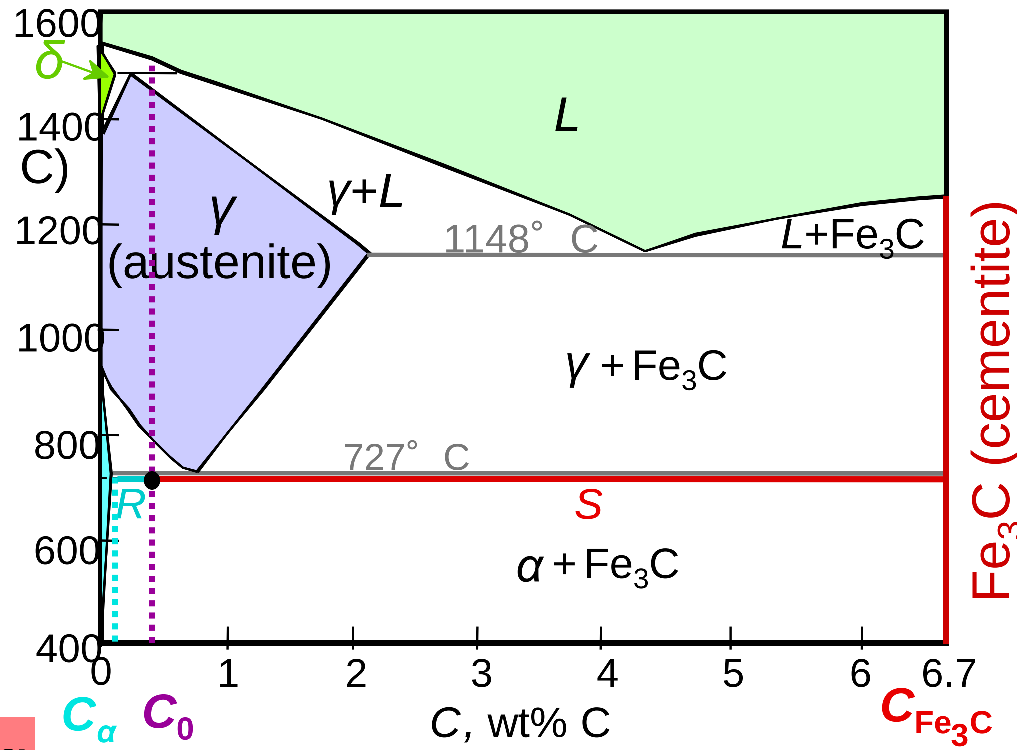
$$= \frac{0.40 - 0.022}{6.70 - 0.022} = 0.057$$

Amount of Fe_3C in 100 g

= (100 g)W_{Fe_3C}

= (100 g)(0.057) = 5.7 g

Fig. 9.24, *Callister & Rethwisch 9e.*
[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.]



Solution to Example Problem (cont.)

c) Using the *VX* tie line just above the eutectoid and realizing that

C_0 = 0.40 wt% C
C_α = 0.022 wt% C
$C_{pearlite}$ = C_γ = 0.76 wt% C

$$W_{pearlite} = \frac{V}{V+X} = \frac{C_0 - C_\alpha}{C_\gamma - C_\alpha}$$

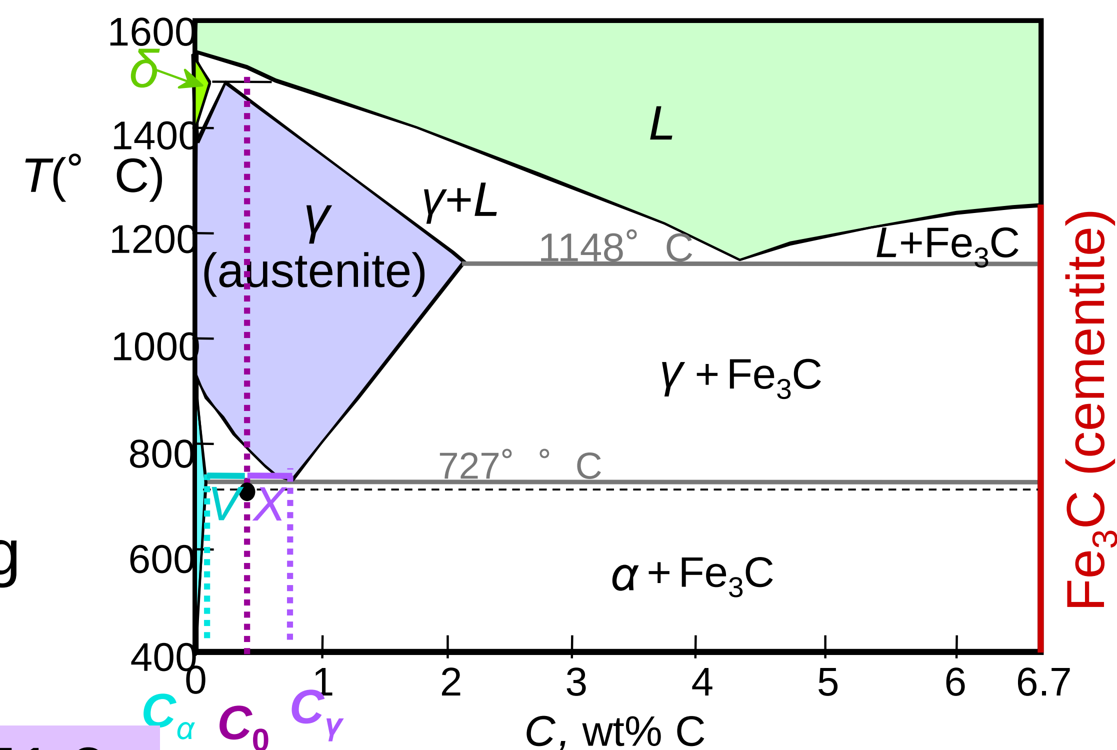
$$= \frac{0.40 - 0.022}{0.76 - 0.022} = 0.512$$

Amount of pearlite in 100 g

= (100 g)$W_{pearlite}$

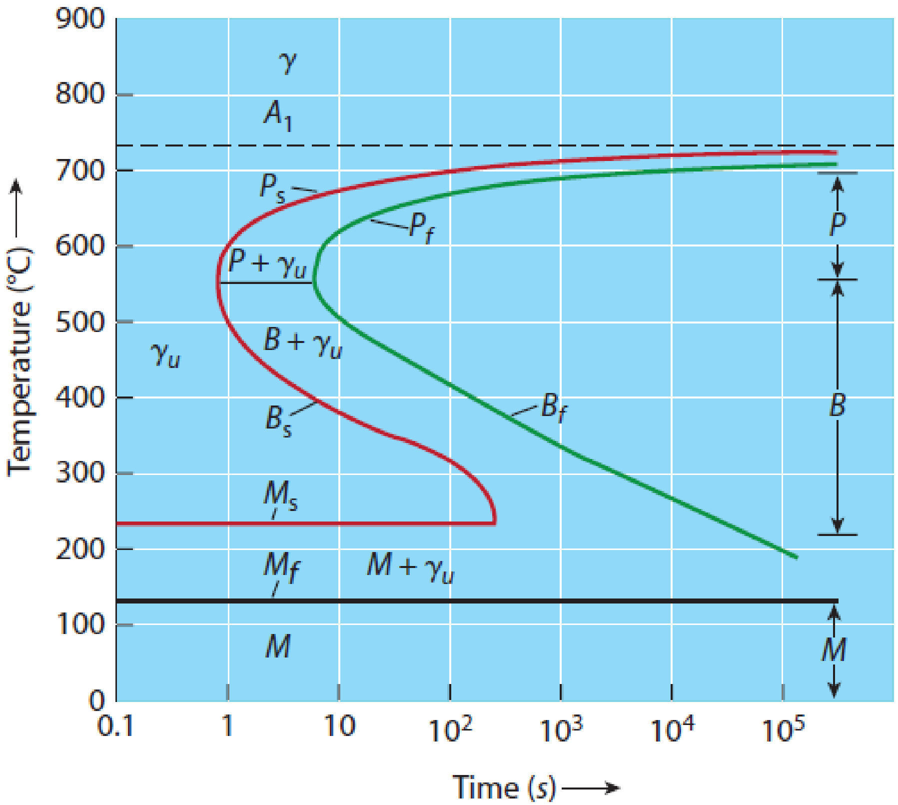
= (100 g)(0.512) = 51.2 g

Fig. 9.24, *Callister & Rethwisch 9e.*
[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.]



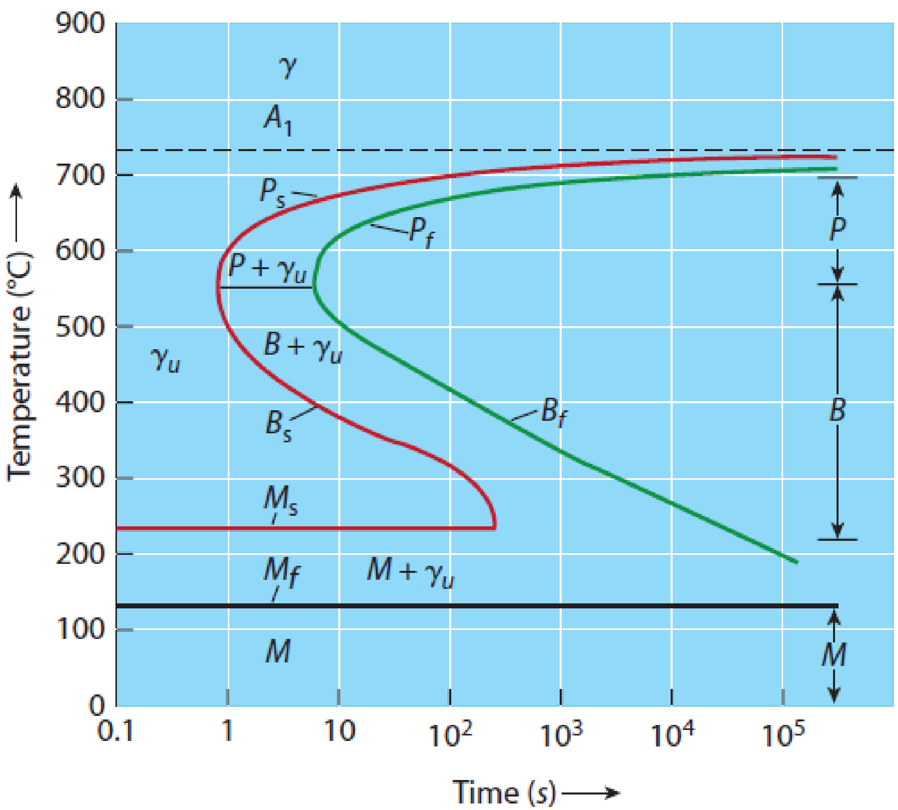
The Iron-Carbon Phase Diagram and Martensitic Phase Transformations: Time-Temperature-Transformation Diagrams for Plain-Carbon Steel

- The transformation of γ- to $\alpha + Fe_3C$- phase can be understood using a Time-Temperature-Transformation (TTT) diagram.
- X-axis: Time and Y-axis: Temperature.
- For nucleation and growth phase transformations:
  - The TTT is obtained by keeping the material at an isothermal (constant temperature).
  - Then find the percent transformation as a function of time.

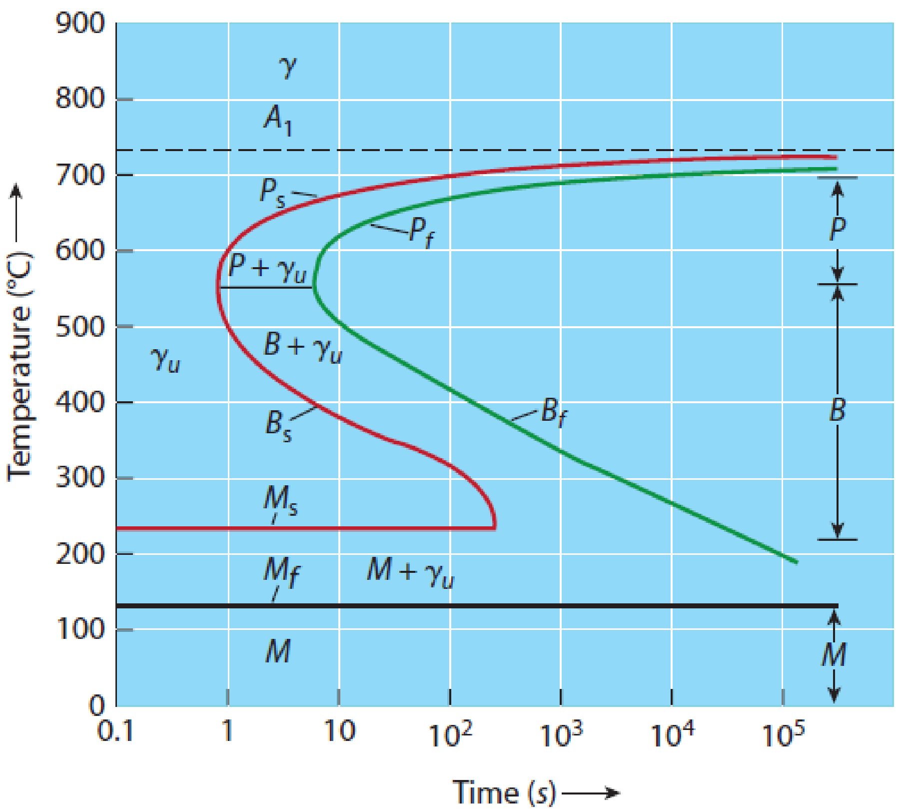


A_1- Austenite (γ FCC phase of iron). Stable above 727° C (unstable below this temp).

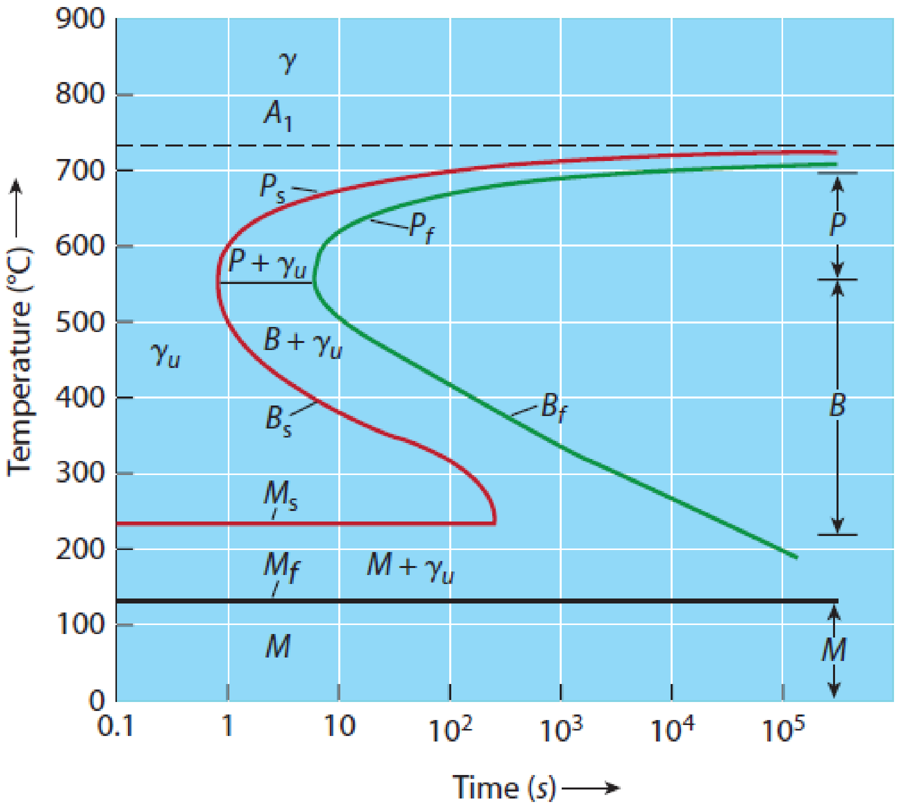
- TTT diagram of an eutectoid composition of iron+0.77%C cooled from 800° -600° C and kept at this temperature.
- No phase transformation is seen for 1 second before the Pearlite start line (P_s) is intersected.
  - Pearlite Start Line- Time required for nucleus of pearlite to form to a significant size (as a function of temperature).
- At 600° C, the transformation is complete when the Pearlite finish line is intersected (6.3 seconds).
  - Pearlite Finish Line- Time for unstable γ to be completely transformed to Pearlite.



- If this alloy is cooled to room temperature, the structure of Pearlite remains.
  - Because it is comprised of the equilibrium phases of γ-iron and Fe_3C.
- Below 550° C (isothermal), Bainite (B) is formed than Pearlite.
  - Bainite has an α-matrix with thin narrow ribbons (laths) of Fe_3C.
  - The laths are smaller and closer spaced than in pearlite: At lower temperatures, diffusion of C-atoms is much slower.



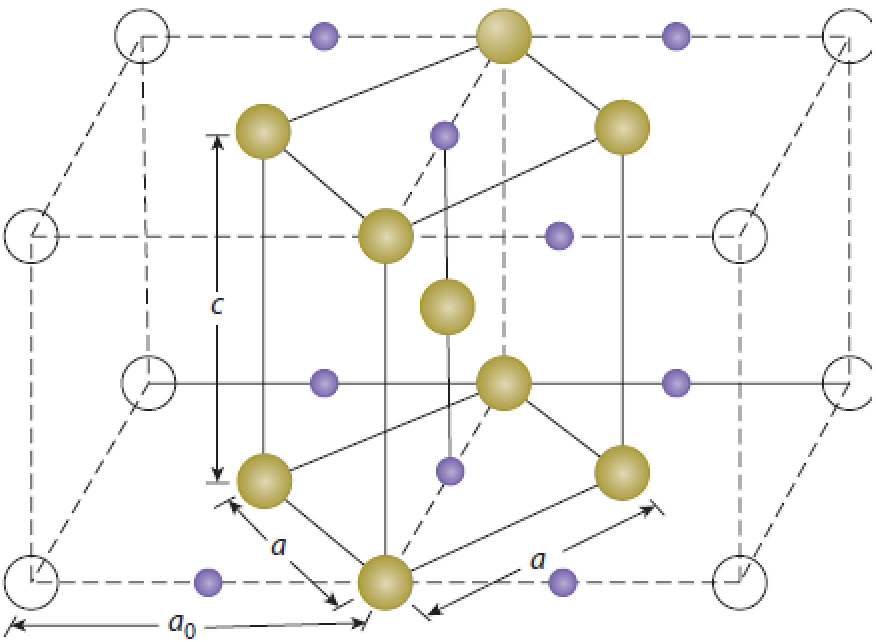
- At low temperatures:
  - Driving force for eutectoid reaction is large.
  - BUT, mobility of atoms is lowered.
  - Smaller diffusion distance favored hence finer Bainite than coarser Pearlite is formed.
- If the eutectoid alloy is quenched to 500° C and kept constant.
  - Bainite is first observed after 1-second.
  - After 10-seconds, unstable austenite phase is completely transformed to Bainite at B_f.
- When cooled to room temperature, the Bainite structure remains (equilibrium phases of α-iron and Fe_3C).



M_s- Start of a Martensite transformation.

- If the temperature of Fe-0.77%C alloy is quenched from the eutectoid temperature to a low temperature (without crossing the P_s or B_s lines):
  - Not enough time for Pearlite or Bainite to form.
- In a Martensite transformation, the FCC γ-phase iron transforms to a Body-Centered Tetragonal Unit Cell.

Unit Cells of an FCC Cubic Iron

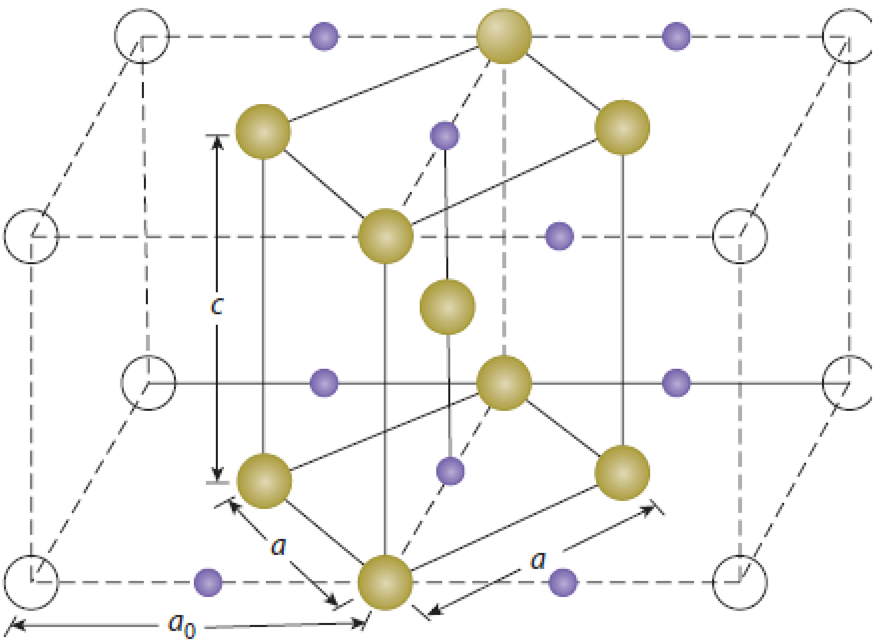


Iron atoms are depicted by large circles.

Carbon atoms are the small solid circles.

- Lattice Parameters of a Tetragonal Unit Cell.
  - a=b with c≠b and c≠a.
  - All unit cell corner angles are 90° .
- The FCC unit cell can be indexed as a Body-Centered Tetragonal (BCT) unit cell.
  - However, when a=c, the BCT lattice is now BCC.
- Below 727° C, the equilibrium structure of iron-carbon alloys is BCC.
- If the alloy is rapidly cooled: No time for diffusion (nucleation/growth) to occur for FCC to transform to BCC.

Unit Cells of an FCC Cubic Iron

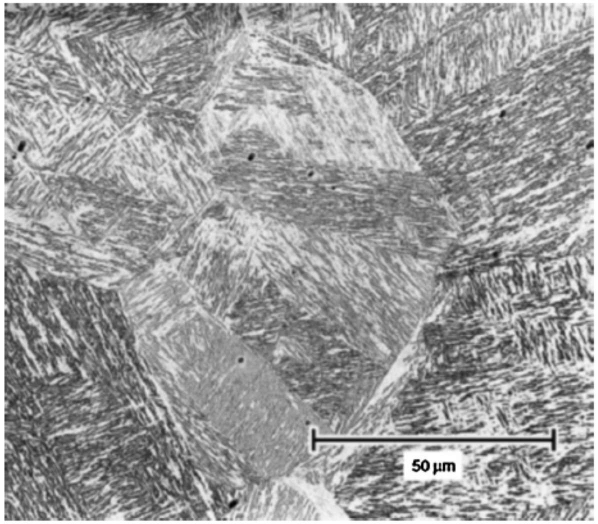


Iron atoms are depicted by large circles.

Carbon atoms are the small solid circles.

- The FCC structure instead transforms to BCT:
  - By diffusionless martensitic transformation.
- In a martensitic transformation, the lattice distorts into a new lattice with no long-range diffusion.
- If carbon atoms go preferentially into the position shown:
  - The a parameter expands, and the c parameter contracts: Lattice distorts.
  - Bain's Distortion where a=b=0285nm and c=0.295nm.
  - Body-Centered Tetragonal Unit Cell (close to BCC unit cell).

The Iron-Carbon Phase Diagram and Martensitic Phase Transformations: Time-Temperature-Transformation Diagrams for Plain-Carbon Steel



The microstructure of Martensite in low-carbon steel is acicular (needle-like as seen to the right).

The motion of the carbon atoms in Martensite transformation is more rapid than the long-range diffusion (required to form Pearlite or Bainite).

The Martensite transformation in plain carbon steel is athermal.

- ***Athermal means the amount of transformation depends on the temperature but not time.***

The Iron-Carbon Phase Diagram and Martensitic Phase Transformations: Time-Temperature-Transformation Diagrams for Plain-Carbon Steel

- Iron-carbon Martensite is hard and brittle.
  - Hence rarely used in engineering applications after quenching.

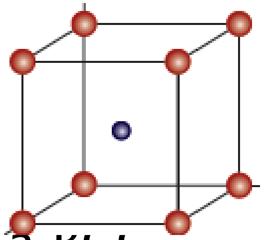
- Tempering:
  - Heating to an elevated temperature 600° C.
  - Martensite transforms to BCC α-phase iron and Fe_3C.
  - Quenching and tempering leads to the Fe3C precipitate being nucleated throughout the alloy.
  - Tempering leads to iron-carbon alloys of high strength and good ductility.
    - E.g. Cutting tools, Crank shafts, Springs and Pistons.

Reversible Martensitic Phase Transformations

- Martensite phase transformation in iron-carbon alloys is irreversible.
  - Due to dislocation formation during Bain's Distortion.
  - Dislocations allow material to be continuous during Bain distortion in martensitic transformations..
- Formation of dislocations in a material is irreversible.

- A <u>reversible</u> martensitic transformation occurs in materials without dislocations during transformation.
  - Dislocation is accommodated by the reversible stretching and bending of atomic bonds.
  - Change in Gibbs Free energy is zero.
  - Negative change in GFE from change in structure= Positive change in GFE from bond stretching and bending.

Reversible Martensitic Phase Transformations

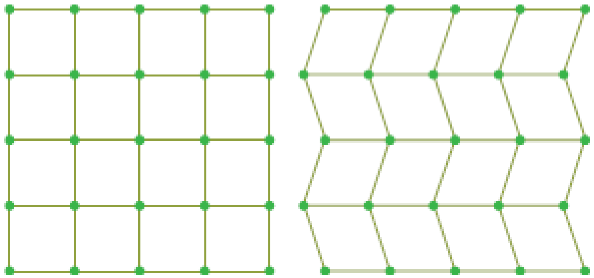


- Mostly seen in metal alloys especially TiNi.
- TiNi is a random mixture of Titanium and Nickel atoms in a BCC structure.

- The Martensite start temperature (M_s) for TiNi is around 70° C, and can be described as a shear distortion.
- The Martensite finish temperature (M_f) is one where TiNi is 100% Martensite, and is around 30° -40° C below the start temperature.

- The reversible martensitic transformation in TiNi doesn’t cause the overall shape of the specimen to change, even though the crystal lattice changes shape.

Reversible Martensitic Phase Transformations

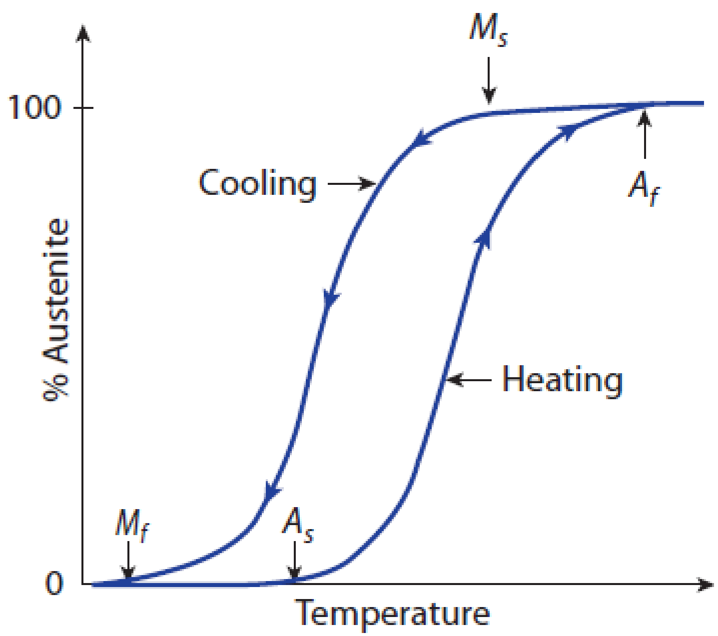


Left: 2D diagram of cubic austenite phase.
Right: Distorted Martensite lattice (reversible).

- The amount of Martensite in this transformation depends only on temperature (and not time).

- If the Martensite lattice (on the right) is heated, it will transform back into cubic austenite by reversing bond stretching and bending.

Reversible Martensitic Phase Transformations



- The Martensite to Austenite begins at the Austenite start temperature (A_s) and completes at the Austenite finish temperature (A_f).
- Where 100% of the Martensite has transformed to Austenite.

- In TiNi: Can go through cycles of cooling Austenite to form Martensite and heating Martensite to form Austenite.

Reversible Martensitic Phase Transformations: The Shape-Memory Effect and Training in Metal Alloys

- Shape-Memory effect is due to reversible Martensitic transformation in TiNi.
- Bend the wire into a desired shape, causes variations in distortion (that allow it to bend).
- When the wire is heated above A_f it returns to cubic structure and initial straight shape.
- If the wire is heated above A_f and bent to a different shape, it returns to that shape above A_f.

- The characteristic temperatures can be varied by changing the TiNi alloy composition.

Reversible Martensitic Phase Transformations: The Shape-Memory Effect and Training in Metal Alloys

- E.g. Coronary stents use shape-memory effect.
  - But need to reduce the temperature of martensitic transformation so that human body temperature is above A_f.

Summary

- Phase diagrams are useful tools to determine:

  -- the number and types of phases present,
  -- the composition of each phase,
  -- and the weight fraction of each phase

  given the temperature and composition of the system.

- The microstructure of an alloy depends on

  -- its composition, and
  -- whether or not cooling rate allows for maintenance of equilibrium.

- Important phase diagram phase transformations include eutectic, eutectoid, and peritectic.