SAMPLE PROBLEM 5.4

Figure 5-23 shows the microstructural development for an 80 wt % B alloy. Consider instead 1 kg of a 70 wt % B alloy.

a. Calculate the amount of β phase at T_3.
b. Calculate what weight fraction of this β phase at T_3 is proeutectic.

SOLUTION

a. Using Equation 5.10 gives us

$$m_{\beta,T_3} = \frac{x - x_\alpha}{x_\beta - x_\alpha}\,(1\text{ kg}) = \frac{70-30}{90-30}\,(1\text{ kg})$$

$$= 0.667\text{ kg} = 667\text{ g}$$

b. The proeutectic β was that present in the microstructure at T_2:

$$m_{\beta,T_2} = \frac{x - x_\mathrm{L}}{x_\beta - x_\mathrm{L}}\,(1\text{ kg}) = \frac{70-60}{90-60}\,(1\text{ kg})$$

$$= 0.333\text{ kg} = 333\text{ g}$$

This portion of the microstructure is retained upon cooling through the eutectic temperature, giving

$$\text{fraction proeutectic} = \frac{\text{proeutectic }\beta}{\text{total }\beta}$$

$$= \frac{333\text{ g}}{667\text{ g}} = 0.50$$

……

PRACTICE PROBLEM 5.4

In Sample Problem 5.4, we calculate microstructural information about the β phase for the 70 wt % B alloy in Figure 5-23. In a similar way, calculate **(a)** the amount of α phase at T_3 for 1 kg of a 50 wt % B alloy and **(b)** the weight fraction of this α phase at T_3, which is proeutectic. (See also Figure 5-24.)

SAMPLE PROBLEM 5.11

A fireclay refractory ceramic can be made by heating the raw material kaolinite, $Al_2(Si_2O_5)(OH)_4$, driving off the waters of hydration. Determine the phases present, their compositions, and their amounts for the resulting microstructure (below the eutectic temperature).

SOLUTION

A modest rearrangement of the kaolinite formula helps us to more easily appreciate the production of this ceramic product:

$$Al_2(Si_2O_5)(OH)_4 = Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$$

The firing operation yields

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \xrightarrow{\text{heat}} Al_2O_3 \cdot 2SiO_2 + 2H_2O \uparrow$$

The remaining solid has, then, an overall composition

$$\text{mol \% } Al_2O_3 = \frac{\text{mol } Al_2O_3}{\text{mol } Al_2O_3 + \text{mol } SiO_2} \times 100\%$$

$$= \frac{1}{1+2} \times 100\% = 33.3\%$$

Using Figure 5-39, we see that the overall composition falls in the SiO_2 + mullite two-phase region below the eutectic temperature. The SiO_2 composition is 0 mol % Al_2O_3 (i.e., 100% SiO_2). The composition of mullite is 60 mol % Al_2O_3.

Using Equations 5.9 and 5.10 yields

$$\text{mol \% } SiO_2 = \frac{x_{\text{mullite}} - x}{x_{\text{mullite}} - x_{SiO_2}} \times 100\% = \frac{60 - 33.3}{60 - 0} \times 100\%$$

$$= 44.5 \text{ mol \%}$$

$$\text{mol \% mullite} = \frac{x - x_{SiO_2}}{x_{\text{mullite}} - x_{SiO_2}} \times 100\% = \frac{33.3 - 0}{60 - 0} \times 100\%$$

$$= 55.5 \text{ mol \%}$$

Note. Because the Al_2O_3–SiO_2 phase diagram is presented in mole percent, we have made our calculations in a consistent system. It would be a minor task to convert results to weight percent using data from Appendix 1.

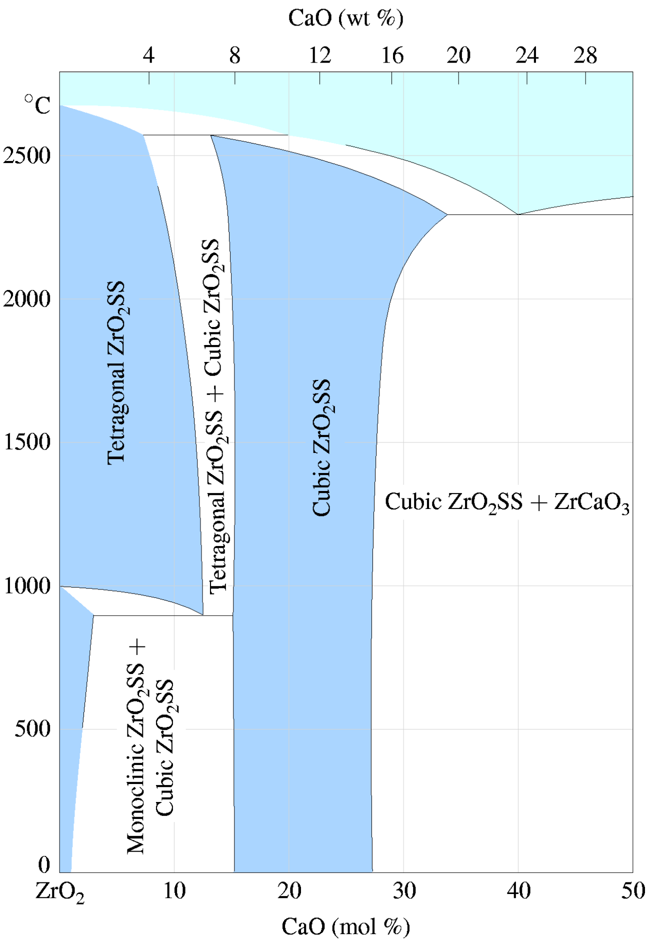


FIGURE 5-42

SAMPLE PROBLEM 5.12

A partially stabilized zirconia is composed of 4 wt % CaO. This product contains some monoclinic phase together with the cubic phase, which is the basis of fully stabilized zirconia. Estimate the mole percent of each phase present at room temperature.

SOLUTION

Noting that 4 wt % CaO = 8 mol % CaO and assuming that the solubility limits shown in Figure 5-42 do not change significantly below 500°C, we can use Equations 5.9 and 5.10:

$$\text{mol \% monoclinic} = \frac{x_{\text{cub}} - x}{x_{\text{cub}} - x_{\text{mono}}} \times 100\%$$

$$= \frac{15 - 8}{15 - 2} \times 100\% = 53.8 \text{ mol \%}$$

$$\text{mol \% cubic} = \frac{x - x_{\text{mono}}}{x_{\text{cub}} - x_{\text{mono}}} \times 100\%$$

$$= \frac{8 - 2}{15 - 2} \times 100\% = 46.2 \text{ mol \%}$$

PRACTICE PROBLEM 5.5

In Sample Problem 5.5, we found the amount of each phase in a eutectoid steel at room temperature. Repeat this calculation for the hypereutectoid steel (1.13 wt % C) illustrated in Figure 5-29.

PRACTICE PROBLEM 5.6

Calculate the amount of proeutectoid cementite at the grain boundaries in 1 kg of the 1.13 wt % C hypereutectoid steel illustrated in Figure 5-29. (See Sample Problem 5.6.)

PRACTICE PROBLEM 5.7

In Sample Problem 5.7, the amount of carbon in 1 kg of a 3 wt % C gray iron is calculated at two temperatures. Plot the amount as a function of temperature over the entire temperature range of 1135°C to room temperature.

PRACTICE PROBLEM 5.8

In Sample Problem 5.8, we monitor the microstructural development for 1 kg of a 10 wt % Si–90 wt % Al alloy. Repeat this problem for a 20 wt % Si–80 wt % Al alloy.

PRACTICE PROBLEM 5.9

In Sample Problem 5.9, we calculate the weight percent of θ phase at room temperature in a 95.5 Al–4.5 Cu alloy. Plot the weight percent of θ (as a function of temperature) that would occur upon slow cooling over a temperature range of 548°C to room temperature.

PRACTICE PROBLEM 5.10

Calculate microstructures for **(a)** a 40:60 Pb–Sn solder and **(b)** a 60:40 Pb–Sn solder at 200°C and 100°C. (See Sample Problem 5.10.)

PRACTICE PROBLEM 5.11

In the note at the end of Sample Problem 5.11, the point is made that the results can be easily converted to weight percent. Make these conversions.

PRACTICE PROBLEM 5.12

In Sample Problem 5.12, the phase distribution in a partially stabilized zirconia is calculated. Repeat this calculation for a zirconia with 5 wt % CaO.

REFERENCES

ASM Handbook, Vol. 3: *Alloy Phase Diagrams,* ASM International, Materials Park, Ohio, 1992.

Binary Alloy Phase Diagrams, 2nd ed., Vols. 1–3, T. B. Massalski, et al., eds., ASM International, Materials Park, Ohio, 1990. The result of a cooperative program between ASM International and the National Institute of Standards and Technology for the critical review of 4700 phase-diagram systems.

Phase Diagrams for Ceramists, Vols. 1–9, American Ceramic Society, Columbus, Ohio, 1964, 1969, 1975, 1981, 1983, 1987, 1989 (Vol. 7), 1989 (Vol. 8), and 1992.

PROBLEMS

SECTION 5.1 • THE PHASE RULE

5.1 Apply the Gibbs phase rule to the various points in the one-component H_2O phase diagram (Figure 5-3).

5.2 Apply the Gibbs phase rule to the various points in the one-component iron phase diagram (Figure 5-4).

5.3 Calculate the degrees of freedom for a 50:50 copper–nickel alloy at **(a)** 1400°C where it exists as a single, liquid phase, **(b)** 1300°C where it exists as a two-phase mixture of liquid and solid solutions, and **(c)** 1200°C where it exists as a single, solid-solution phase. Assume a constant pressure of 1 atm above the alloy in each case.

5.4 In Figure 5-7, the Gibbs phase rule was applied to a hypothetical phase diagram. In a similar way, apply the phase rule to a sketch of the Pb–Sn phase diagram (Figure 5-38).

5.5 Apply the Gibbs phase rule to a sketch of the MgO–Al_2O_3 phase diagram (Figure 5-40).

5.6 Apply the Gibbs phase rule to the various points in the Al_2O_3–SiO_2 phase diagram (Figure 5-39).

SECTION 5.2 • THE PHASE DIAGRAM

5.7 Describe qualitatively the microstructural development that will occur upon slow cooling of a melt of equal parts (by weight) of copper and nickel (see Figure 5-36).

5.8 Describe qualitatively the microstructural development that will occur upon slow cooling of a melt composed of 50 wt % Al and 50 wt % Si (see Figure 5-33).

5.9 Describe qualitatively the microstructural development that will occur upon slow cooling of a melt composed of 87.4 wt % Al and 12.6 wt % Si.

5.10 Describe qualitatively the microstructural development that will occur upon slow cooling of an alloy with equal parts (by weight) of aluminum and θ phase (Al_2Cu) (see Figure 5-34).

5.11 Describe qualitatively the microstructural development that will occur upon slow cooling of a melt composed of **(a)** 20 wt % Mg, 80 wt % Al and **(b)** 80 wt % Mg, 20 wt % Al (see Figure 5-35).

5.12 Describe qualitatively the microstructural development during the slow cooling of a 30:70 brass (Cu with 30 wt % Zn). See Figure 5-37 for the Cu–Zn phase diagram.

5.13 Repeat Problem 5.12 for a 35:65 brass.

5.14 Describe qualitatively the microstructural development during the slow cooling of a melt composed of **(a)** 30 wt % Pb–70 wt % Sn, **(b)** 40 wt % Pb–60 wt % Sn, and **(c)** 50 wt % Pb–50 wt % Sn (see Figure 5-38).

5.15 Repeat Problem 5.14 for a melt composed of 38.1 wt % Pb–61.9 wt % Sn.

5.16 Describe qualitatively the microstructural development during the slow cooling of **(a)** a 50 mol % Al_2O_3–50 mol % SiO_2 ceramic and **(b)** a 70 mol % Al_2O_3–30 mol % SiO_2 ceramic (see Figure 5-39).

SECTION 5.3 • THE LEVER RULE

5.17 Calculate the amount of each phase present in 1 kg of a 50 wt % Ni–50 wt % Cu alloy at **(a)** 1400°C, **(b)** 1300°C, and **(c)** 1200°C (see Figure 5-36).

5.18 Calculate the amount of each phase present in 1 kg of a 50 wt % Pb–50 wt % Sn solder alloy at **(a)** 300°C, **(b)** 200°C, **(c)** 100°C, and **(d)** 0°C (see Figure 5-38).

5.19 Repeat Problem 5.18 for a 60 wt % Pb–40 wt % Sn solder alloy.

5.20 Repeat Problem 5.18 for an 80 wt % Pb–20 wt % Sn solder alloy.

5.21 Calculate the amount of each phase present in 50 kg of a brass with composition 35 wt % Zn–65 wt % Cu at **(a)** 1000°C, **(b)** 900°C, **(c)** 800°C, **(d)** 700°C, **(e)** 100°C, and **(f)** 0°C (see Figure 5-37).

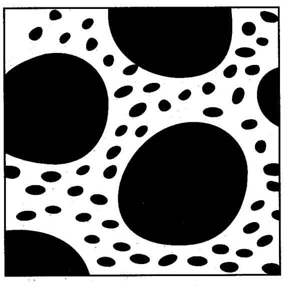
5.22 Calculate the amount of each phase present in a 1-kg alumina refractory with composition 70 mol % Al_2O_3–30 mol % SiO_2 at **(a)** 2000°C, **(b)** 1900°C, and **(c)** 1800°C (see Figure 5-39).

5.23 Some aluminum from a "metallization" layer on a solid-state electronic device has diffused into the silicon substrate. Near the surface, the silicon has an overall concentration of 1.0 wt % Al. In this region, what percentage of the microstructure would be composed of α-phase precipitates, assuming equilibrium? (See Figure 5-33 and assume the phase boundaries at 300°C will be essentially unchanged to room temperature.)

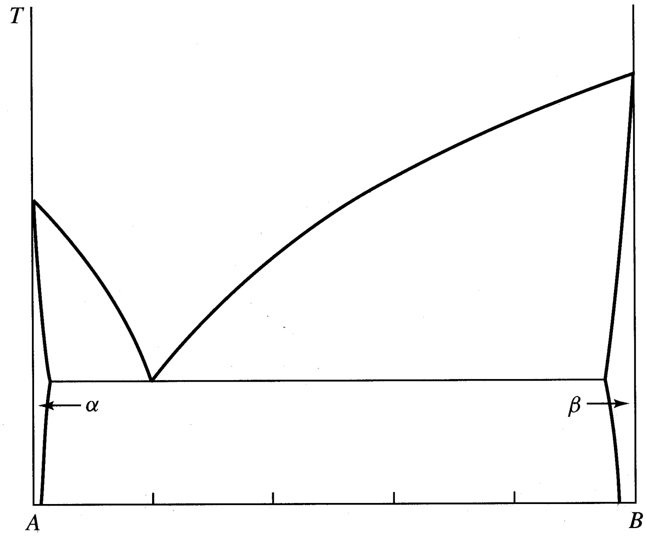
5.24 In a test laboratory, quantitative x-ray diffraction determines that a refractory brick has 25 wt % alumina phase and 75 wt % mullite solid solution. What is the overall SiO_2 content (in wt %) of this material? (See Figure 5-39.)

5.25 An important structural ceramic is partially stabilized zirconia (PSZ), which has a composition lying in the two-phase ZrO_2-cubic ZrO_2(ss) region. Use Figure 5-42 to calculate the amount of each phase present in a 10 mol % CaO PSZ at 500°C.

• **5.26** In a materials laboratory experiment, a student sketches a microstructure observed under an optical microscope. The sketch appears as



The phase diagram for this alloy system is



Determine **(a)** whether the black regions in the sketch represent α or β phase and **(b)** the approximate alloy composition.

SECTION 5.4 • MICROSTRUCTURAL DEVELOPMENT DURING SLOW COOLING

5.27 Calculate **(a)** the weight fraction of the α phase that is proeutectic in a 10 wt % Si–90 wt % Al alloy at 576°C and **(b)** the weight fraction of the β phase that is proeutectic in a 20 wt % Si–80 wt % Al alloy at 576°C (see Figure 5-33).

5.28 Plot the weight percent of phases present as a function of temperature for a 10 wt % Si–90 wt % Al alloy slowly cooled from 700 to 300°C (see Figure 5-33).

5.29 Plot the weight percent of phases present as a function of temperature for a 20 wt % Si–80 wt % Al alloy slowly cooled from 800 to 300°C (see Figure 5-33).

5.30 Calculate the *weight* fraction of mullite that is proeutectic in a slowly cooled 20 mol % Al_2O_3–80 mol % SiO_2 refractory cooled to room temperature (see Figure 5-39).

5.31 Microstructural analysis of a slowly cooled Al–Si alloy indicates there is a 5 *volume* % silicon-rich proeutectic phase. Calculate the overall alloy composition (in weight percent) (see Figure 5-33).

5.32 Repeat Problem 5.31 for a 10 volume % silicon-rich proeutectic phase.

SECTION 5.5 • SOME IMPORTANT BINARY DIAGRAMS

5.33 Calculate the amount of proeutectic γ that has formed at 1149°C in the slow cooling of the 3.0 wt % C white cast iron illustrated in Figure 5-27. Assume a total of 100 kg of cast iron.

5.34 Plot the weight percent of phases present as a function of temperature for the 3.0 wt % C white cast iron illustrated in Figure 5-27 slowly cooled from 1400 to 0°C.

5.35 Plot the weight percent of phases present as a function of temperature from 1000 to 0°C for the 0.77 wt % C eutectoid steel illustrated in Figure 5-28.

5.36 Plot the weight percent of phases present as a function of temperature from 1000 to 0°C for the 1.13 wt % C hypereutectoid steel illustrated in Figure 5-29.

5.37 Calculate the amount of proeutectoid α present at the grain boundaries in 1 kg of a common 1020 structural steel (0.20 wt % C).

5.38 Repeat Problem 5.37 for a 1040 structural steel (0.40 wt % C).

5.39 Plot the weight percent of phases present as a function of temperature from 1000 to 0°C for a common 1020 structural steel (0.20 wt % C).

5.40 Repeat Problem 5.39 for a 1040 structural steel (0.40 wt % C).

5.41 Plot the weight percent of phases present as a function of temperature from 1000 to 0°C for the 0.50 wt % C hypoeutectoid steel illustrated in Figure 5-30.

5.42 Plot the weight percent of phases present as a function of temperature from 1400 to 0°C for a white cast iron with an overall composition of 2.5 wt % C.

5.43 Plot the weight percent of all phases present as a function of temperature from 1400 to 0°C for a gray cast iron with an overall composition of 3.0 wt % C.

5.44 Repeat Problem 5.43 for a gray cast iron with an overall composition of 2.5 wt % C.

5.45 In comparing the equilibrium schematic microstructure in Figure 5-32 with the actual, room temperature microstructure shown in Figure 7-1b, it is apparent that metastable pearlite can form at the eutectoid temperature (due to insufficient time for the more stable, but slower, graphite formation). Assuming that Figures 5-31 and 5-32 are accurate for 100 kg of a gray cast iron (3.0 wt % C) down to 738°C but that pearlite forms upon cooling through the eutectoid temperature, calculate the amount of pearlite to be expected in the room temperature microstructure.

5.46 For the assumptions in Problem 5.45, calculate the amount of flake graphite in the room temperature microstructure.

5.47 Plot the weight percent of phases present as a function of temperature from 800 to 300°C for a 95 Al–5 Cu alloy.

5.48 Consider 1 kg of a brass with composition 35 wt % Zn–65 wt % Cu (see Figure 5-37). **(a)** Upon cooling, at what temperature would the first solid appear? **(b)** What is the first solid phase to appear, and what is its composition? **(c)** At what temperature will the alloy completely solidify? **(d)** Over what temperature range will the microstructure be completely in the α-phase?

5.49 Repeat Problem 5.48 for 1 kg of a brass with composition 30 wt % Zn–70 wt % Cu.

5.50 Plot the weight percent of phases present as a function of temperature from 1000 to 0°C for a 35 wt % Zn–65 wt % Cu brass.

5.51 Repeat Problem 5.50 for a 30 wt % Zn–70 wt % Cu brass.

5.52 Repeat Problem 5.50 for 1 kg of brass with a composition of 15 wt % Zn–85 wt % Cu.

5.53 For a 15 wt % Zn–85 wt % Cu brass, plot the weight percent of phases present as a function of temperature from 1100°C to 0°C.

5.54 Calculate the amount of β phase that would precipitate from 1 kg of 95 wt % Al–5 wt % Mg alloy slowly cooled to 100°C.

5.55 Identify the composition ranges in the Al–Mg system (Figure 5-35) for which precipitation of the type illustrated in Sample Problem 5.9 can occur (i.e., a second phase can precipitate from a single-phase microstructure upon cooling).

5.56 Plot the weight percent of phases present as a function of temperature from 700 to 100°C for a 90 Al–10 Mg alloy.

5.57 The ideal stoichiometry of the γ phase in the Al–Mg system is $Al_{12}Mg_{17}$. **(a)** What is the atomic percentage of excess Al in the most aluminum-rich γ composition at 450°C? **(b)** What is the atomic percentage of excess Mg in the most magnesium-rich γ composition at 437°C?

5.58 A solder batch is made by melting together 64 g of a 40:60 Pb–Sn alloy with 53 g of a 60:40 Pb–Sn alloy. Calculate the amounts of α and β phase that would be present in the overall alloy, assuming it is slowly cooled to room temperature, 25°C.

5.59 Plot the weight percent of phases present as a function of temperature from 400 to 0°C for a slowly cooled 50:50 Pb–Sn solder.

• **5.60** Suppose that you have a crucible containing 1 kg of an alloy of composition 90 wt % Sn–10 wt % Pb at a temperature of 184°C. How much Sn would you have to add to the crucible to completely solidify the alloy *without* changing the system temperature?

5.61 Determine the phases present, their compositions, and their amounts (below the eutectic temperature) for a refractory made from equal molar fractions of kaolinite and mullite ($3Al_2O_3 \cdot 2SiO_2$).

5.62 Repeat Problem 5.61 for a refractory made from equal molar fractions of kaolinite and silica (SiO_2).

• **5.63** Given that you have supplies of kaolinite, silica, and mullite as raw materials, calculate a batch of composition (in weight percent) using kaolinite plus *either* silica *or* mullite necessary to produce a final microstructure that is equimolar in silica and mullite.

5.64 Calculate the phases present, their compositions, and their amounts (in weight percent) for the microstructure at 1000°C for **(a)** a spinel ($MgO \cdot Al_2O_3$) refractory with 1 wt % excess MgO (i.e., 1 g MgO per 99 g $MgO \cdot Al_2O_3$), and **(b)** a spinel refractory with 1 wt % excess Al_2O_3.

5.65 Plot the phases present (in mole percent) as a function of temperature for the heating of a refractory with the composition 60 mol % Al_2O_3–40 mol % MgO from 1000 to 2500°C.

5.66 Plot the phases present (in mole percent) as a function of temperature for the heating of a partially stabilized zirconia with 10 mol % CaO from room temperature to 2800°C.

5.67 A partially stabilized zirconia (for a novel structural application) is desired to have an equimolar microstructure of tetragonal and cubic zirconia at an operating temperature of 1250°C. Calculate the proper CaO content (in weight percent) for this structural ceramic.

5.68 Repeat Problem 5.67 for a microstructure with equal weight fractions of tetragonal and cubic zirconia.

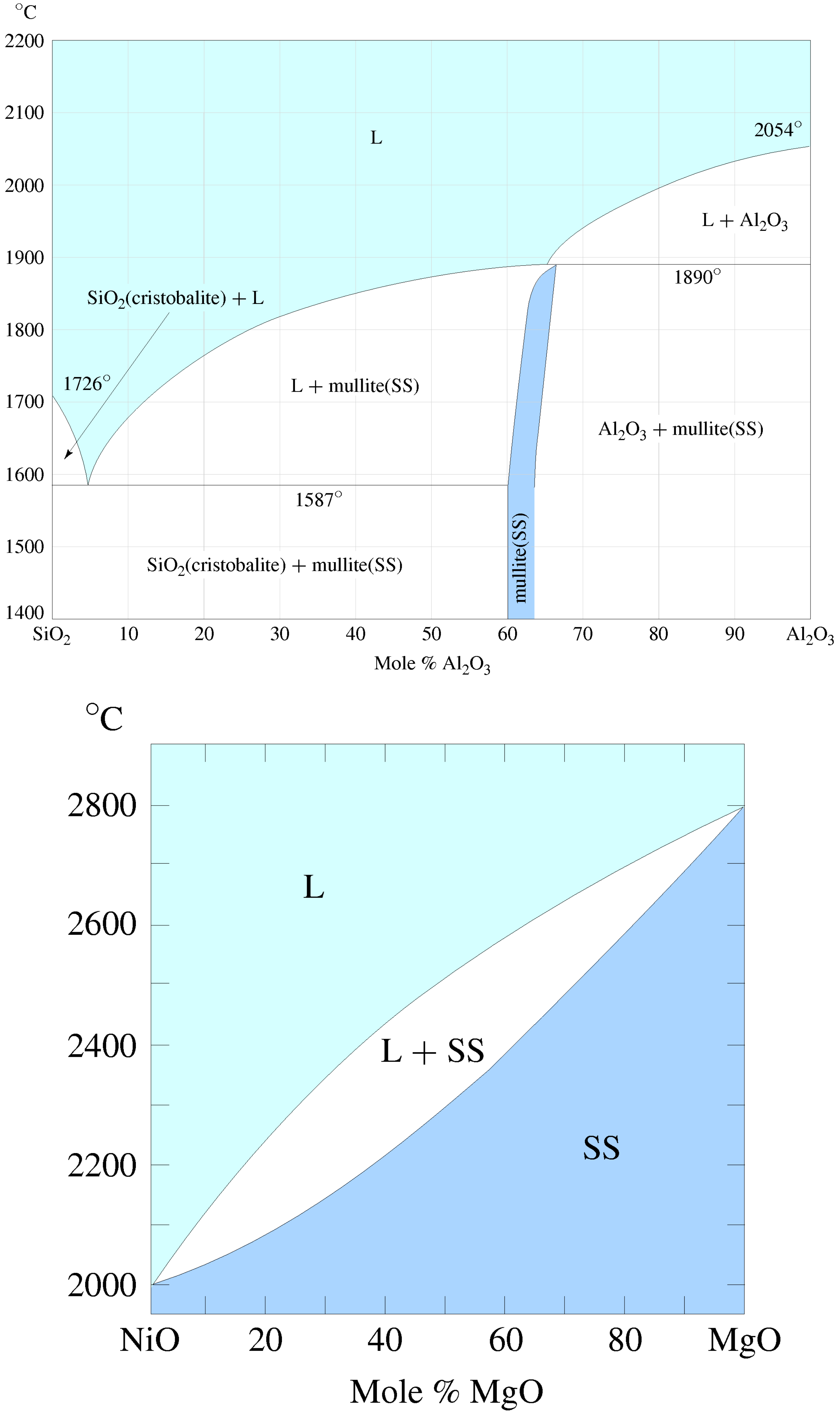

°C
2200
2100
2000
1900
1800
1700
1600
1500
1400
L
2054°
L + Al_2O_3
1890°
SiO_2(cristobalite) + L
1726°
L + mullite(SS)
Al_2O_3 + mullite(SS)
1587°
SiO_2(cristobalite) + mullite(SS)
mullite(SS)
SiO_2
10
20
30
40
50
60
70
80
90
Al_2O_3
Mole % Al_2O_3
°C
2800
2600
2400
2200
2000
L
L + SS
SS
NiO
20
40
60
80
MgO
Mole % MgO

FIGURE 5-41

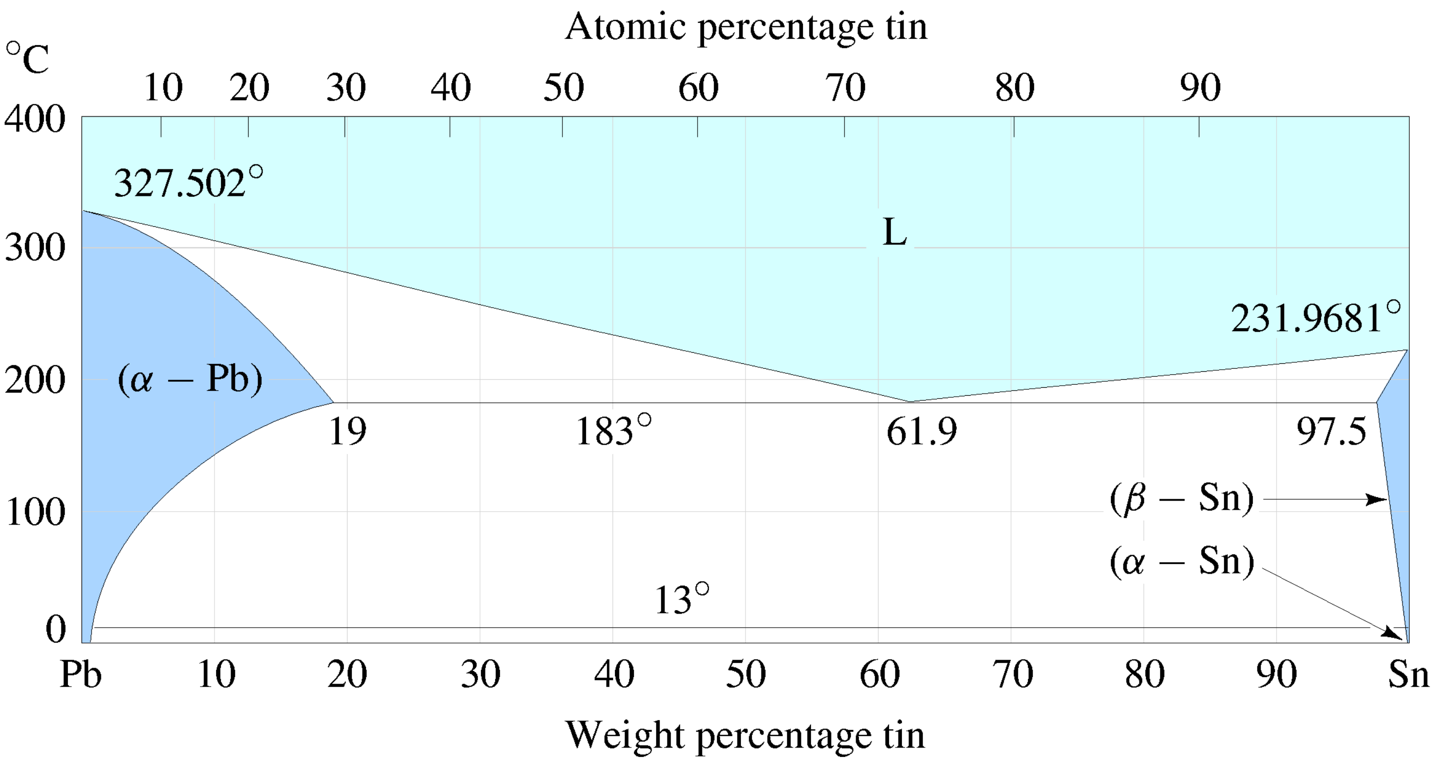


FIGURE 5-38

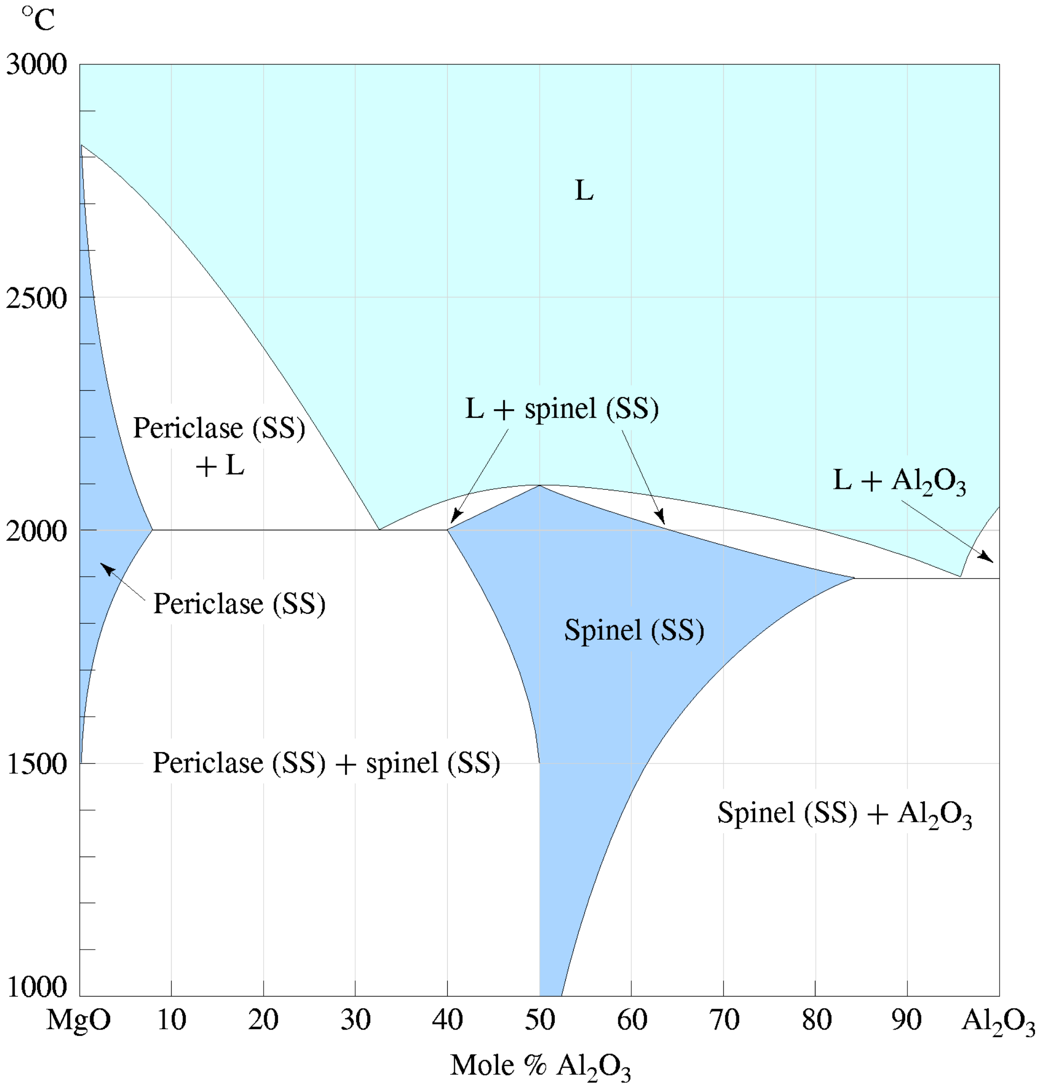
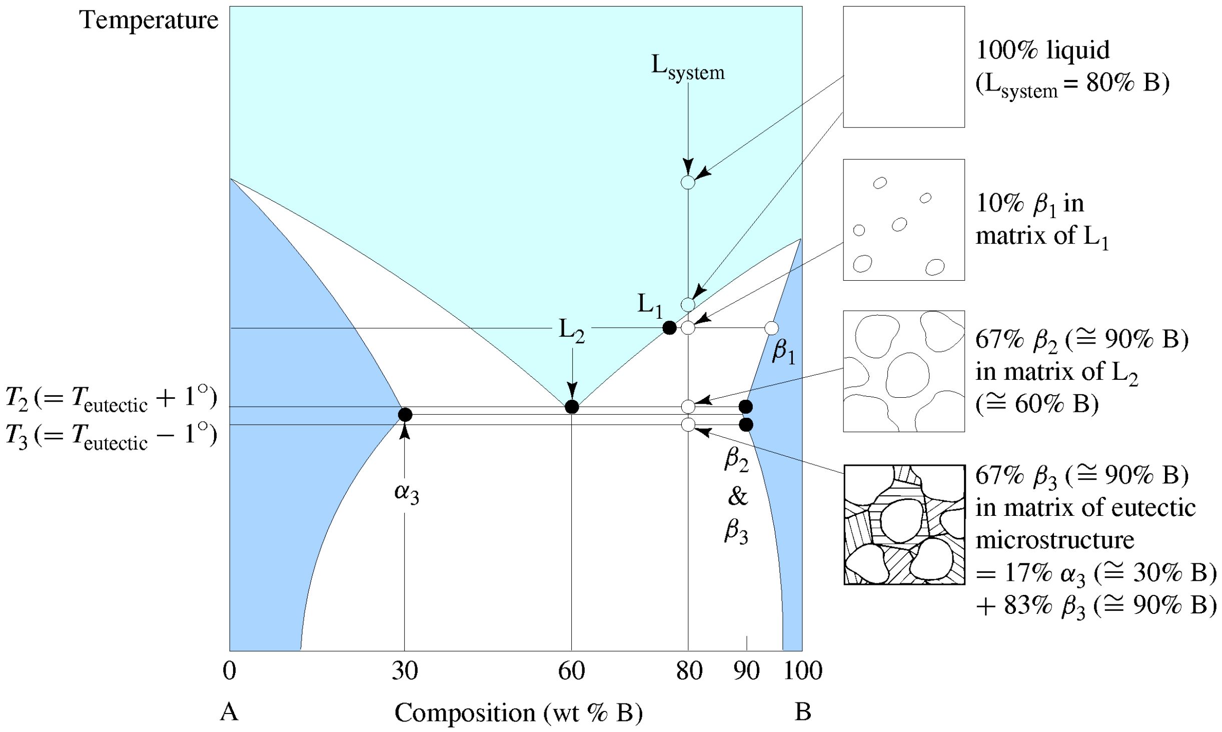


FIGURE 5-40



Temperature
L_{system}
L_1
L_2
β_1
T_2 (= $T_{eutectic}$ + 1°)
T_3 (= $T_{eutectic}$ − 1°)
α_3
β_2
&
β_3
0
30
60
80
90
100
A
Composition (wt % B)
B
100% liquid
(L_{system} = 80% B)
10% β_1 in
matrix of L_1
67% β_2 (≅ 90% B)
in matrix of L_2
(≅ 60% B)
67% β_3 (≅ 90% B)
in matrix of eutectic
microstructure
= 17% α_3 (≅ 30% B)
+ 83% β_3 (≅ 90% B)

FIGURE 5-23