9.4 Microstructural Development During Slow Cooling

We are now in a position to follow closely the **microstructural development** in various binary systems. In all cases, we shall assume the common situation of cooling a given composition from a single-phase melt. Microstructure is developed in the process of solidification. We consider only the case of *slow* cooling; that is, equilibrium is essentially maintained at all points along the cooling path. The effect of more rapid temperature changes is the subject of Chapter 10, which deals with time-dependent microstructures developed during heat treatment.

Let us return to the simplest of binary diagrams, the case of complete solubility in both the liquid and solid phases. Figure 9.32 shows the gradual solidification of the 50% A–50% B composition treated previously (Figures 9.6, 9.8, and 9.30). The lever rule (Figure 9.31) is applied at three different temperatures in the two-phase (L + SS) region. It is important to appreciate that the appearance of the microstructures in Figure 9.32 corresponds directly with the relative position of the overall system composition along the tie line. At higher temperatures (e.g., T_1), the overall composition is near the liquid-phase boundary, and the microstructure is predominantly liquid. At lower temperatures (e.g., T_3), the overall composition so of the liquid and solid phases change continuously during cooling through the two-phase region. At any temperature, however, the relative amounts of each phase are such that the overall composition is 50% A and 50% B, which is a direct manifestation of the lever rule as defined by the mass balance of Equation 9.8.

The understanding of microstructural development in the binary eutectic is greatly aided by the lever rule. The case for the eutectic composition itself is straightforward and was illustrated previously (Figures 9.12 and 9.15). Figure 9.33 repeats those cases in slightly greater detail. An additional comment is that the composition of each solid-solution phase (α and β) and their relative amounts



FIGURE 9.32 Microstructural development during the slow cooling of a 50% A–50% B composition in a phase diagram with complete solid solution. At each temperature, the amounts of the phases in the microstructure correspond to a lever-rule calculation. The microstructure at T_2 corresponds to the calculation in Figure 9.30.



*The only differences between this structure and the T_1 microstructure are the phase compositions and the relative amounts of each phase. For example, the amount of β will be proportional to

$$\frac{x_{\text{eutectic}} - x_{\alpha}}{x_{\beta} - x_{\alpha}}$$



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FIGURE 9.34 *Microstructural development during the slow cooling of a hypereutectic composition.*

will change slightly with temperature below the eutectic temperature. The microstructural effect (corresponding to this compositional adjustment due to solidstate diffusion) is generally minor.

Microstructural development for a noneutectic composition is more complex. Figure 9.34 illustrates the microstructural development for a hypereutectic composition (composition greater than that of the eutectic). The gradual growth of β crystals above the eutectic temperature is comparable to the process found in Figure 9.32 for the complete solid-solution diagram. The one difference is that, in Figure 9.34, the crystallite growth stops at the eutectic temperature with only 67% of the microstructure solidified. Final solidification occurs when the remaining liquid (with the eutectic composition) transforms suddenly to the eutectic microstructure upon cooling through the eutectic temperature. In a sense, the 33% of the microstructure that is liquid just above the eutectic temperature undergoes the eutectic reaction illustrated in Figure 9.33. A lever-rule calculation just below the eutectic temperature (T_3 in Figure 9.34) indicates correctly that the microstructure is 17% α_3 and 83% β_3 . However, following the entire cooling path has indicated that the β phase is present in two forms. The large grains produced during the slow cooling through the two-phase $(L + \beta)$ region are termed **proeutectic** β ; that is, they appear "before the eutectic." The finer β in the lamellar eutectic is appropriately termed *eutectic* β .

Figure 9.35 shows a similar situation that develops for a **hypoeutectic composition** (composition less than that of the eutectic). This case is analogous to that for the hypereutectic composition. In Figure 9.35, we see the development of large grains of proeutectic α along with the eutectic microstructure of α and β layers. Two other types of microstructural development are illustrated in Figure 9.36. For an overall composition of 10% B, the situation

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FIGURE 9.35 *Microstructural development during the slow cooling of a hypoeutectic composition.*

is quite similar to that for the complete solid-solution binary in Figure 9.32. The solidification leads to a single-phase solid solution that remains stable upon cooling to low temperatures. The 20% B composition behaves in a similar fashion except that, upon cooling, the α phase becomes saturated with B atoms. Further cooling leads to precipitation of a small amount of β phase. In Figure 9.36(b), this precipitation is shown occurring along grain boundaries. In some systems, the second phase precipitates within grains. For a given



FIGURE 9.36 *Microstructural development for two compositions that avoid the eutectic reaction.*

system, the morphology of the second phase can be a sensitive function of the rate of cooling. In Section 10.4, we shall encounter such a case for the Al–Cu system, in which precipitation hardening is an important example of heat treatment.

With the variety of cases encountered in this section, we are now in a position to treat any composition in any of the binary systems presented in this chapter, including the general diagrams represented by Figure 9.25(b).

The cooling path for a **white cast iron** (see also Chapter 11) is shown in Figure 9.37. The schematic microstructure can be compared with a micrograph in Figure 11.1(a). The eutectoid reaction to produce pearlite is shown in Figure 9.38. This composition (0.77 wt % C) is close to that for a 1080 plain-carbon steel (see Table 11.1). Many phase diagrams for the Fe–Fe₃C system give the eutectoid composition rounded off to 0.8 wt % C. As a practical matter, any composition near 0.77 wt % C will give a microstructure



FIGURE 9.37 *Microstructural development for white cast iron (of composition 3.0 wt % C)* shown with the aid of the $Fe-Fe_3C$ phase diagram. The resulting (low-temperature) sketch can be compared with a micrograph in Figure 11.1(a).

EXAMPLE 9.6

Figure 9.34 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 9.10 gives us

$$m_{\beta,T_3} = \frac{x - x_{\alpha}}{x_{\beta} - x_{\alpha}} (1 \text{ kg}) = \frac{70 - 30}{90 - 30} (1 \text{ kg})$$
$$= 0.667 \text{ kg} = 667 \text{ g}.$$

that is predominantly eutectoid. The actual pearlite microstructure is shown in the micrograph of Figure 9.2. A **hypereutectoid composition** (composition greater than the eutectoid composition of 0.77 wt % C) is treated in Figure 9.39. This case is similar in many ways to the hypereutectic path shown



FIGURE 9.38 *Microstructural development for eutectoid steel (of composition 0.77 wt % C). The resulting (low-temperature) sketch can be compared with the micrograph in Figure 9.2.*

FIGURE 9.39 *Microstructural development for a slowly cooled hypereutectoid steel (of composition* 1.13 *wt* % C).

in Figure 9.34. A fundamental difference is that the **proeutectoid** cementite (Fe₃C) is the matrix in the final microstructure, whereas the proeutectic phase in Figure 9.34 was the isolated phase. The formation of the proeutectoid matrix occurs because the precipitation of proeutectoid cementite is a

(b) The proeutectic β was that which was present in the microstructure at T_2 :

$$m_{\beta,T_2} = \frac{x - x_{\rm L}}{x_{\beta} - x_{\rm L}} (1 \text{ kg}) = \frac{70 - 60}{90 - 60} (1 \text{ kg})$$
$$= 0.333 \text{ kg} = 333 \text{ g}.$$

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

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

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

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FIGURE 9.40 Microstructural development for a slowly cooled hypoeutectoid steel (of composition 0.50 wt % C).

solid-state transformation and is favored at grain boundaries. Figure 9.40 illustrates the development of microstructure for a **hypoeutectoid composition** (less than 0.77 wt % C).

The Fe–C system (Figure 9.20) provides an illustration of the development of the microstructure of **gray cast iron** (Figure 9.41). This sketch can be compared with the micrograph in Figure 11.1(b).

EXAMPLE 9.7

For 1 kg of 0.5 wt % C steel, calculate the amount of proeutectoid α at the grain boundaries.

SOLUTION

Using Figure 9.40 for illustration and Figure 9.19 for calculation, we essentially need to calculate the equilibrium amount of α at 728°C (i.e., 1 degree above the eutectoid temperature). Using Equation 9.9, we have

$$m_{\alpha} = \frac{x_{\gamma} - x}{x_{\gamma} - x_{\alpha}} (1 \text{ kg}) = \frac{0.77 - 0.50}{0.77 - 0.02} (1 \text{ kg})$$
$$= 0.360 \text{ kg} = 360 \text{ g}.$$

Note. You might have noticed that this calculation near the eutectoid composition used a value of x_{α} representative of the maximum solubility of carbon in α -Fe (0.02 wt %). At room temperature (see Example 9.4), this solubility goes to nearly zero.

FIGURE 9.41 Microstructural development for gray cast iron (of composition 3.0 wt % C) shown on the Fe-C phase diagram. The resulting low-temperature sketch can be compared with the micrograph in Figure 11.1(b). A dramatic difference is that, in the actual microstructure, a substantial amount of metastable pearlite was formed at the eutectoid temperature. It is also interesting to compare this sketch with that for white cast iron in Figure 9.37. The small amount of silicon added to promote graphite precipitation is not shown in this two-component diagram.

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EXAMPLE 9.8

For 1 kg of 3 wt % C gray iron, calculate the amount of graphite flakes present in the microstructure (a) at $1,153^{\circ}$ C and (b) at room temperature.

SOLUTION

(a) Using Figures 9.20 and 9.41, we note that 1,153°C is just below the eutectic temperature. Using Equation 9.10 gives us

$$m_{\rm C} = \frac{x - x_{\gamma}}{x_{\rm C} - x_{\gamma}} (1 \text{ kg}) = \frac{3.00 - 2.08}{100 - 2.08} (1 \text{ kg})$$
$$= 0.00940 \text{ kg} = 9.40 \text{ g}.$$

(b) At room temperature, we obtain

$$m_{\rm C} = \frac{x - x_{\alpha}}{x_{\rm C} - x_{\alpha}} (1 \text{ kg}) = \frac{3.00 - 0}{100 - 0} (1 \text{ kg})$$
$$= 0.030 \text{ kg} = 30.0 \text{ g}.$$

Note. This calculation follows the ideal system of Figure 9.41 and ignores the possibility of any metastable pearlite being formed.

EXAMPLE 9.9

Consider 1 kg of an aluminum casting alloy with 10 wt % silicon.

- (a) Upon cooling, at what temperature would the first solid appear?
- (b) What is the first solid phase, and what is its composition?
- (c) At what temperature will the alloy completely solidify?
- (d) How much proeutectic phase will be found in the microstructure?
- (e) How is the silicon distributed in the microstructure at 576°C?

SOLUTION

We follow this microstructural development with the aid of Figure 9.13.

- (a) For this composition, the liquidus is at \sim 595°C.
- (b) It is solid solution α with a composition of ~1 wt % Si.
- (c) At the eutectic temperature, 577° C.
- (d) Practically all of the proeutectic α will have developed by 578°C. Using Equation 9.9, we obtain

$$m_{\alpha} = \frac{x_{\rm L} - x}{x_{\rm L} - x_{\alpha}} (1 \text{ kg}) = \frac{12.6 - 10}{12.6 - 1.6} (1 \text{ kg})$$
$$= 0.236 \text{ kg} = 236 \text{ g}.$$

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(e) At 576°C, the overall microstructure is $\alpha + \beta$. The amounts of each are

$$m_{\alpha} = \frac{x_{\beta} - x}{x_{\beta} - x_{\alpha}} (1 \text{ kg}) = \frac{100 - 10}{100 - 1.6} (1 \text{ kg})$$
$$= 0.915 \text{ kg} = 915 \text{ g}$$

and

$$m_{\beta} = \frac{x - x_{\alpha}}{x_{\beta} - x_{\alpha}} (1 \text{ kg}) = \frac{10 - 1.6}{100 - 1.6} (1 \text{ kg})$$
$$= 0.085 \text{ kg} = 85 \text{ g}.$$

However, we found in (d) that 236 g of the α is in the form of relatively large grains of proeutectic phase, giving

$$\alpha_{\text{eutectic}} = \alpha_{\text{total}} - \alpha_{\text{proeutectic}}$$
$$= 915 \text{ g} - 236 \text{ g} = 679 \text{ g}$$

The silicon distribution is then given by multiplying its weight fraction in each microstructural region by the amount of that region:

Si in proeutectic
$$\alpha = (0.016)(236 \text{ g}) = 3.8 \text{ g}$$
,
Si in eutectic $\alpha = (0.016)(679 \text{ g}) = 10.9 \text{ g}$,

and

Si in eutectic $\beta = (1.000)(85 \text{ g}) = 85.0 \text{ g}.$

Finally, note that the total mass of silicon in the three regions sums to 99.7 g rather than 100.0 g (= 10 wt % of the total alloy) due to round-off errors.

EXAMPLE 9.10

The solubility of copper in aluminum drops to nearly zero at 100°C. What is the maximum amount of θ phase that will precipitate out in a 4.5 wt % copper alloy quenched and aged at 100°C? Express your answer in weight percent.

SOLUTION

As indicated in Figure 9.27, the solubility limit of the θ phase is essentially unchanging with temperature below ~400°C and is near a

Shackelford, James. Introduction to Materials Science for Engineers, Global Edition, Pearson Education Limited, 2015. ProQuest Ebook Central, http://ebookcentral.proquest.com/lib/ethz/detail.action?docID=5173617. Created from ethz on 2020-02-12 03:20:31. composition of 53 wt % copper. Using Equation 9.10 gives us

wt %
$$\theta = \frac{x - x_{\kappa}}{x_{\theta} - x_{\kappa}} \times 100\% = \frac{4.5 - 0}{53 - 0} \times 100\%$$

= 8.49%.

EXAMPLE 9.11

In Example 9.1, we considered a 50:50 Pb–Sn solder.

- (a) For a temperature of 200°C, determine (i) the phases present, (ii) their compositions, and (iii) their relative amounts (expressed in weight percent).
- (b) Repeat part (a) for 100° C.

SOLUTION

- (a) Using Figure 9.16, we find the following results at 200°C:
 - i. The phases are α and liquid.
 - ii. The composition of α is ~18 wt % Sn and of L is ~54 wt % Sn.
 - iii. Using Equations 9.9 and 9.10, we have

wt %
$$\alpha = \frac{x_{\rm L} - x}{x_{\rm L} - x_{\alpha}} \times 100\% = \frac{54 - 50}{54 - 18} \times 100\%$$

= 11.1%

and

wt % L =
$$\frac{x - x_{\alpha}}{x_{\rm L} - x_{\alpha}} \times 100\% = \frac{50 - 18}{54 - 18} \times 100\%$$

= 88.9%.

- (b) Similarly, at 100°C, we obtain
 - i. α and β .
 - ii. α is ~5 wt % Sn and β is ~99 wt % Sn.
 - iii. wt % $\alpha = \frac{x_{\beta} x}{x_{\beta} x_{\alpha}} \times 100\% = \frac{99 50}{99 5} \times 100\% = 52.1\%$ and

wt %
$$\beta = \frac{x - x_{\alpha}}{x_{\beta} - x_{\alpha}} \times 100\% = \frac{50 - 5}{99 - 5} \times 100\% = 47.9\%.$$

EXAMPLE 9.12

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

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SOLUTION

A modest rearrangement of the kaolinite formula helps to clarify the production of this ceramic product:

$$\operatorname{Al}_2(\operatorname{Si}_2\operatorname{O}_5)(\operatorname{OH})_4 = \operatorname{Al}_2\operatorname{O}_3 \cdot 2\operatorname{SiO}_2 \cdot 2\operatorname{H}_2\operatorname{O}.$$

The firing operation yields

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

The remaining solid, then, has an overall composition of

mol % Al₂O₃ =
$$\frac{\text{mol Al}_2O_3}{\text{mol Al}_2O_3 + \text{mol SiO}_2} \times 100\%$$

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

Using Figure 9.23, we see that the overall composition falls in the SiO_2 + mullite two-phase region below the eutectic temperature. The SiO₂ composition is 0 mol % Al_2O_3 (i.e., 100% SiO₂). The composition of mullite is 60 mol % Al₂O₃.

Using Equations 9.9 and 9.10 yields

mol % SiO₂ =
$$\frac{x_{\text{mullite}} - x}{x_{\text{mullite}} - x_{\text{SiO}_2}} \times 100\% = \frac{60 - 33.3}{60 - 0} \times 100\%$$

= 44.5 mol %

and

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

= 55.5 mol %.

Note. Because the Al_2O_3 -SiO₂ 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.

PRACTICE PROBLEM 9.6

In Example 9.6, we calculate microstructural information about the β phase for the 70 wt % B alloy in Figure 9.34. In a similar way, calculate (a) the amount of α phase at T₃ 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 9.35.)

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