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# CHAPTER 5

## **Eutectic Alloy Systems**

IF THE TWO-PHASE FIELD in the solid region of Fig. 5.1 is expanded so that it touches the solidus at some point, as shown in Fig. 5.2(a), complete miscibility of the components is lost. Instead of a single solid phase, the diagram now shows two separate solid terminal phases, which are in three-phase equilibrium with the liquid at point P, an invariant point that occurred by coincidence. Then, if this two-phase field in the solid region is even further widened so that the solvus lines no longer touch at the invariant point, the diagram passes through a series of configurations, finally taking on the more familiar shape shown in Fig. 5.2(b). The three-phase reaction that takes place at the invariant point, E, where a liquid phase freezes into a mixture of two solid phases, is called a eutectic reaction (from the Greek word for "easily melted"). The alloy that corresponds to the eutectic composition is called a eutectic alloy. An alloy having a composition to the left of the eutectic point is called a hypoeutectic alloy (from



**Fig. 5.1** Schematic binary phase diagram with a minimum in the liquidus and a miscibility gap in the solid state. Source: Ref 5.1



**Fig. 5.2** Schematic binary phase diagrams with invariant points. (a) Hypothetical diagram with miscibility gap in the solid that touches the solidus curve at invariant point *P*; an actual diagram of this type probably does not exist. (b) and (c) Typical eutectic diagrams for (b) components having the same crystal structure and (c) components having different crystal structures; the eutectic (invariant) points are labeled *E*. The dashed lines in (b) and (c) are metastable extensions of the stable-equilibria lines. Source: Ref 5.1

the Greek word for "less than"); an alloy to the right is a hypereutectic alloy (meaning "greater than").

In the eutectic system described, the two components of the system have the same crystal structure. This, and other factors, allows complete miscibility between them. Eutectic systems, however, also can be formed by two components having different crystal structures. When this occurs, the liquidus and solidus curves (and their extensions into the two-phase field) for each of the terminal phases (Fig. 5.2c) resemble those for the situation of complete miscibility between system components.

A generic eutectic phase diagram is shown in Fig. 5.3. Eutectic systems form when alloying additions cause a lowering of the liquidus lines from both melting points of the pure elements. At a specific composition, there is a minimum melting point, where the mixed solid-liquid phase regions  $(L + \alpha \text{ and } L + \beta)$  vanish. This is the eutectic point, *e*, which defines an alloy composition that has the lowest melting point of the *A-B* system. The eutectic composition also solidifies completely at a single temperature that is referred to as an invariant point.

In a eutectic reaction, a liquid freezes to form two solid solutions:

## Liquid $L \rightarrow \text{Solid } \alpha + \text{Solid } \beta$

The maximum solid solubility of element B is defined by point a on the A-rich side of the diagram, and the maximum solid solubility of element A in the lattice of element B is defined by point b. The methods of determining the equilibrium temperature ranges for solidification, fractions of phases, and compositions of phases are all similar to those illustrated for the isomorphous systems.

Consider the eutectic phase diagram in Fig. 5.4, which contains five different alloy compositions (*A*-*E*). Alloy *C* has exactly the eutectic composition. On cooling from the liquid state, it converts from a liquid to a solid at the eutectic temperature. The resulting solid consists of  $\alpha$  and  $\beta$  phases of the eutectic structure. Next, consider alloys *A* and *E*, which do not cross the eutectic isotherm line. Thus, their final microstructures do not contain any eutectic. Instead, they form solid solutions of  $\alpha$  and  $\beta$  for alloys *A* and *B*, respectively. On cooling, alloy *B* forms  $\alpha$  crystals in liquid when it passes through the liquidus. When alloy *B* cools through the eutectic



Fig. 5.3 Phase diagram containing a eutectic reaction. Source: Ref 5.2



Fig. 5.4 Crystalline structures on cooling in a eutectic phase diagram

temperature, the remaining liquid freezes to form a eutectic mixture of  $\alpha$  and  $\beta$ . Therefore, the final microstructure of alloy *B* contains proeutectic  $\alpha$  in a matrix of eutectic ( $\alpha$  and  $\beta$ ). The situation is similar for alloy *D*, except the final microstructure has proeutectic  $\beta$  in a matrix of eutectic.

Because eutectic alloys have a single melting/solidification point, eutectic compositions include important types of commercial alloys. Traditional lead-tin solder alloys are based on their eutectic compositions. Casting alloys are often based on eutectic compositions for various reasons, including the minimization of both energy input and coring, or alloy segregation. For example, the iron-carbon system has a eutectic at composition of 4.3 wt% C, which is the basis of cast irons. Many other binary systems have phase diagrams with multiple eutectic transformation compositions.

Because the eutectic is the lowest melting composition in the alloy, it can often cause problems during hot working and heat-treating operations. During casting of an ingot, due to nonuniform cooling rates, there is often quite a bit of segregation of the alloying elements. The low-melting eutectic composition is normally the last portion of the metal to freeze, normally along the grain boundaries. On reheating the metal for hot working operations, if the lowest melting eutectic temperature is exceeded, melting can occur along the grain boundaries and the part is frequently ruined. It should also be noted that alloying systems with a number of different alloying elements will often form lower-melting-point eutectics than for a simple binary system. To help prevent some of these problems, as-cast ingots are often reheated to temperatures just below the melting point and soaked for long times (called homogenization) to create more uniform structures prior to hot working or heat treating.

## 5.1 Aluminum-Silicon Eutectic System

Aluminum-silicon alloys are a family of industrially important casting alloys. The phase diagram for the aluminum-silicon system is shown in Fig. 5.5, along with micrographs of representative structures. The micro-



Fig. 5.5 Aluminum-silicon phase diagram. Source: Ref 5.3 as published in Ref 5.4

structure of 99.95 wt% Al has the typical equiaxed structure of a pure metal. The microstructure of the 8 wt% Si alloy shows long dendrites of primary  $\alpha$  solid solution surrounded by the eutectic microconstituent. In contrast, when the primary solid phase is the silicon-rich  $\beta$  phase, as in the 20 and 50 wt% silicon alloys, the primary crystals have geometric shapes due to the pronounced difference between aluminum, a metal, and silicon, which has predominately nonmetallic properties.

Consider an alloy containing 50 wt% Si. When the alloy is cooled from the liquid state, it starts to solidify at approximately 1080 °C (1975 °F). Solidification begins with the nucleation and growth of primary crystals of  $\beta$  solid solution. At 870 °C (1600 °F), point *b*, the alloy compositiontemperature point lies in the two-phase *L* +  $\beta$  field. The ends of the tie line drawn across the two-phase field determine the chemical composition of the phases: The liquid phase is 34 wt% Si and the  $\beta$  solid-solution phase is 98 wt% Si. The lever rule can be used to determine the amounts of the two phases:

% 
$$\beta$$
 phase =  $\frac{ab}{ac} = \frac{50 - 34}{98 - 34} \times 100 \approx 25$  wt%

Because the remaining portion of the alloy is liquid phase, there must be 75 wt% liquid.

As the 50 wt% Si alloy continues to cool, the amount of primary  $\beta$  phase increases until the eutectic temperature is reached. At this temperature (580 °C, or 1075 °F), the liquid phase reaches the eutectic composition of 12 wt% Si. On cooling through the eutectic temperature, the liquid solidifies at a constant temperature to form the eutectic structure consisting of an intimate mixture of  $\alpha$  and  $\beta$  phases. A phase analysis at room temperature is representative of the condition of the alloy in the solid  $\alpha + \beta$  region:

% 
$$\beta$$
 phase =  $\frac{de}{df} = \frac{50-1}{99-1} \times 100 \approx 50$  wt%

This amount of  $\beta$  phase (50 wt%) is the sum of the weight fractions of primary and secondary  $\beta$ . To determine the amount of primary  $\beta$  that formed prior to the eutectic reaction (in the  $L + \beta$  region of the phase diagram), a phase analysis can be conducted at a temperature immediately above the eutectic temperature. At this temperature, solidification of the primary  $\beta$  is complete, and all the remaining liquid will solidify as part of the eutectic microconstituent.

% primary 
$$\beta$$
 phase =  $\frac{gh}{gi} = \frac{50 - 12}{98 - 11} \times 100 \approx 44$  wt%

As previously mentioned, aluminum-silicon alloys are extensively used for castings. The primary reason for their widespread use is that silicon greatly increases the fluidity, or lowers the viscosity, of aluminum during casting, allowing for better mold filling and fewer casting defects. As shown in Fig. 5.6, tensile strength increases with silicon additions, while ductility (elongation) decreases. Slowly cooled aluminum-silicon castings form a eutectic structure in which the eutectic grows as thin, flat plates that appear needlelike. The silicon plates are stress risers that reduce ductility and toughness. In commercial castings, modifiers, such as 0.2% Na or 0.01% Sr are added to the melt and modify the eutectic structure producing more rounded particles. If the alloy is rapidly cooled, such as in a die casting, modification is not necessary because rapid cooling produces a fine structure. In hypereutectic alloys that are used for engine blocks because of their high silicon contents and thus high wear resistance, the primary silicon that forms is normally very coarse, causing poor machinability, poor castability, and gravity segregation where the lighter silicon particles float to the top of the casting. In this case, the addition of 0.05% P encourages the nucleation of primary silicon, refining its size and minimizing its deleterious properties.



Fig. 5.6 Properties of aluminum-silicon alloys. Source: Ref 5.3 as published in Ref 5.2

## 5.2 Lead-Tin Eutectic System

Although lead-tin alloys are too weak for use as structural materials, they are widely used as solders for everything from joining copper plumbing to soldering electrical circuits. However, there is an international effort to develop lead-free solders because of the health concerns associated with lead. Nevertheless, lead-tin solders are still widely used. Consider alloy 1 in the lead-tin phase diagram (Fig. 5.7). At 183 °C (361 °F), which is the eutectic temperature, all of the liquid solidifies by the eutectic reaction and forms a eutectic mixture of solid solutions of  $\alpha$  (19.2% Sn) and  $\beta$  (97.5% Sn) according to the reaction:

Liquid (61.9% Sn)  $\rightarrow \alpha$  (19.2% Sn) +  $\beta$  (97.5% Sn)

Next, consider alloy 2 in Fig. 5.7. At point *a*, the alloy is 100% liquid. On cooling to the liquidus at point *b*, proeutectic  $\alpha$  crystals will start forming in the liquid. Within the  $\alpha + L$  region at 40% Sn and 230 °C (446 °F), which is point *c*, a phase analysis yields:



Fig. 5.7 Lead-tin phase diagram. Adapted from Ref 5.5

DI é	T · · · 1	
Phases present:	Liquid	α
Compositions of phases:	48% Sn in L	15% Sn in α
Amounts of phases:	wt% in L phase	wt% in $\alpha$ phase
	$\left(\frac{40-15}{48-15}\right)(100\%) \approx 76\%$	$\left(\frac{48-40}{48-15}\right)(100\%) \approx 24\%$

On further cooling to just above the eutectic temperature (183 °C, or 361 °F), the 40% Sn alloy at point d yields:

Phases present:	Liquid	α
Compositions of	61.9% Sn in L	19.2% Sn in α
phases:		
Amounts of phases:	wt% in L phase	wt% in $\alpha$ phase
	$\left(\frac{40-19.2}{61.9-19.2}\right)(100\%) \approx 49\%$	$\left(\frac{61.9-40}{61.9-19.2}\right) (100\%) \approx 51\%$

When the alloy cools to just below the eutectic temperature, the 40% Sn alloy at point e now yields:

Phases present:	α	β
Compositions of	19.2% Sn in α	19.2% Sn in β
phases:		
Amounts of phases:	wt% in $\alpha$ phase	wt% in $\beta$ phase
	$\left(\frac{40-19.2}{61.9-19.2}\right)(100\%) \approx 49\%$	$\left(\frac{61.9-40}{61.9-19.2}\right)(100\%) \approx 51\%$

Eutectic alloys frequently form a lamellar, or platelike, structure on freezing (Fig. 5.8). This structure permits the lead and tin atoms to diffuse short distances through the liquid to form the lamellar-type structure. It should be pointed out that although eutectics frequently form a lamellar-type structure on freezing, this not always the case.

The lead-tin phase diagram is useful for selecting the best solder for a particular application. For soldering delicate electronic components where it is desirable to minimize heat, a low-melting-point solder such as the eutectic solder in Fig. 5.9 would be selected. On the other hand, when soldering copper plumbing connections, the plumber's solder would be a logical choice because it stays molten longer and allows the worker to wipe off excess flow from the joint. Finally, for joints that will be exposed to moderately high temperatures, the high-temperature solder may be the best choice.



Fig. 5.8 Lamellar eutectic growth. Source: Ref 5.2



Fig. 5.9 Selection of lead-tin solders. Source: Ref 5.2

## 5.3 Eutectic Morphologies

Eutectic structures are characterized by the simultaneous growth of two or more phases from the liquid. Three or even four phases are sometimes observed growing simultaneously from the melt. However, because most technologically useful eutectic alloys are composed of two phases, only this type is discussed here. Eutectic alloys exhibit a wide variety of microstructures, which can be classified according to two criteria:

- Lamellar or fibrous morphology of the phases
- Regular or irregular growth

**Lamellar and Fibrous Eutectics.** When there are approximately equal volume fractions of the phases (nearly symmetrical phase diagram), eutectic alloys generally have a lamellar structure, for example,  $Al-Al_2Cu$  (Fig. 5.10). On the other hand, if one phase is present in a small volume fraction, this phase will in most cases tend to form fibers, for example, molybdenum in NiAl-Mo (Fig. 5.11).

In general, the microstructure obtained will usually be fibrous when the volume fraction of the minor phase is lower than 0.25; otherwise, it will be lamellar. This is because of the small separation of the eutectic phases (typically several microns) and the resulting large interfacial area (of the order of  $1 \text{ m}^2/\text{cm}^3$ ) that exists between the two solid phases. The system will therefore tend to minimize its interfacial energy by choosing the morphology that leads to the lowest total interface area. For a given spacing (imposed by growth conditions), the interface area is smaller for fibers than for lamellae at volume fractions below 0.25. However, when the minor phase is faceted, a lamellar structure may be formed even at a very low



**Fig. 5.10** Example of a lamellar eutectic microstructure (Al-Al<sub>2</sub>Cu) with approximately equal volume fractions of the phases. Transverse section of a directionally-solidified (DS) sample. As-polished. Source: Ref 5.6



**Fig. 5.11** Example of a fibrous eutectic microstructure with a small volume fraction of one phase (molybdenum fibers in NiAl matrix). Transverse section of a directionally-solidified (DS) sample. As-polished. Courtesy of E. Blank. Source: Ref 5.6

volume fraction, because the interfacial energy is then considerably lower along specific planes, along which the lamellae can be aligned. Growth of faceted phases occurs on well-defined atomic planes, thus creating planar, angular surfaces (facets). Typical examples of faceted phases are graphite, silicon, and intermetallic compounds. In the case of gray cast iron (Fig. 5.12), the volume fraction of the graphite lamellae is 7.4%.

Many eutectic microstructures can be classified as lamellar or fibrous, but there is an important exception, namely, spheroidal graphite cast iron (Fig. 5.13). In this case, there is no cooperative eutectic-like growth of both phases; instead, there is separate growth of spheroidal graphite particles as a primary phase (at least during the initial stages), together with austenite dendrites, known as divorced growth. Cast iron often exhibits intermediate microstructural forms, such as vermicular or chunky graphite.

**Regular and Irregular Eutectics.** If both phases are nonfaceted (usually when both are metallic), the eutectic will exhibit a regular morphology. The microstructure is then made up of lamellae or fibers having a high



**Fig. 5.12** Microstructure of a gray cast iron showing flake graphite. Transverse section etched with nital. Source: Ref 5.6



**Fig. 5.13** Graphite in spheroidal cast iron, which results from the divorced growth of the phases. Etched with nital. Original magnification: 130×. Source: Ref 5.6

degree of regularity and periodicity, particularly in unidirectionally-solidified specimens (Fig. 5.10).

On the other hand, if one phase is faceted, the eutectic morphology often becomes irregular (Fig. 5.12 and 5.14). This is because the faceted phase grows preferentially in a direction determined by specific atomic planes. Because the various faceted lamellae have no common crystal orientation, their growth directions are not parallel, and the formation of a regular microstructure becomes impossible. The two eutectic alloys of greatest practical importance, iron-carbon (cast iron) and aluminum-silicon, belong to this category.

Although the examination of metallographic sections of irregular eutectics seems to reveal many dispersed lamellae of the minor phase, these lamellae are generally interconnected in a complex three-dimensional arrangement. In the foundry literature, such eutectic grains are often referred to as eutectic cells. In the solidification literature, the term *cell* defines a certain interface morphology; therefore, the term *eutectic grain* is used throughout this section.

The regularity of some eutectic microstructures can be used to make in situ composites. By using a controlled heat flux to achieve slow directional solidification, it is possible to obtain an aligned microstructure throughout the entire casting. When one of the phases is particularly strong, as in the case of TaC fibers in the Ni-TaC eutectic, the mechanical properties of the alloy can be enhanced in the growth direction. In contrast, an equiaxed microstructure can be formed by inoculation, and there is no long-range orientation.

Interpretation of Eutectic Microstructures. Eutectic microstructures, as seen in metallographic section, are two-dimensional images of a threedimensional arrangement of two (or more) phases. One must therefore be



**Fig. 5.14** Irregular "Chinese script" eutectic consisting of faceted Mg<sub>2</sub>Sn phase (dark) in a magnesium matrix. Etched with glycol. Original magnification: 250×. Source: Ref 5.6

very careful in interpreting these metallographic sections. For example, Fig. 5.15 shows a longitudinal section of a directionally-solidified (DS) lamellar eutectic (white cast iron) covering two different grains. Despite their different appearances, the two grains have the same lamellar spacing. However, the sectioning plane is perpendicular to the lamellae of one grain, but is at a small angle with respect to the lamellae of the other grain. Therefore, in DS samples, the lamellar spacing of eutectic microstructures must always be measured perpendicular to the growth direction. In a casting containing equiaxed grains, only a mean spacing can be measured. Eutectic grains are often difficult to identify, as can be seen in Fig. 5.10.

## 5.4 Solidification and Scale of Eutectic Structures

A schematic eutectic phase diagram is shown in Fig. 5.16. When a liquid, L, of eutectic composition  $C_{\rm E}$  is frozen, the  $\alpha$  and  $\beta$  solid phases solidify simultaneously when the temperature of the melt is below the eutectic temperature,  $T_{\rm E}$ . A variety of geometrical arrangements can be produced. For simplicity, the case of a lamellar microstructure is considered in this discussion; the solidification of fibers can be described in terms of similar mechanisms. Because eutectic growth is essentially solute diffusion controlled, there is no fundamental difference between equiaxed



**Fig. 5.15** Longitudinal section of directionally-solidified (DS) white cast iron. The two grains in the micrograph have the same lamellar spacing but are oriented differently with regard to the plane of polish. Etched with nital. Source: Ref 5.6



Fig. 5.16 Schematic eutectic phase diagram. See text for explanation. Source: Ref 5.6

and directional solidification. Therefore, the mechanisms described are valid for both cases.

**Regular Eutectic Growth.** During eutectic solidification, the growing  $\alpha$  phase rejects *B* atoms into the liquid because of their lower solubility with respect to the liquid concentration. Conversely, the  $\beta$  phase rejects *A* atoms. If the  $\alpha$  and  $\beta$  phases grow separately, solute rejection would occur only in the growth direction. This involves long-range diffusion. Therefore, a very large boundary layer would be created in the liquid ahead of the solid-liquid interface, as shown in Fig. 5.17(a).

However, during eutectic solidification, the  $\alpha$  and  $\beta$  phases grow side by side in a cooperative manner; the *B* atoms rejected by the  $\alpha$  phase are needed for the growth of the  $\beta$  phase, and vice versa. The solute then needs only to diffuse along the solid-liquid interface from one phase to the other (Fig. 5.17b). The solute buildup in the liquid ahead of the growing solid-liquid interface is considerably lowered by this sidewise diffusion (diffusion coupling), thus being thermodynamically favorable. This is the fundamental reason for the occurrence of eutectic growth. As can be seen in Fig. 5.17(b), the smaller the lamellar spacing,  $\lambda$ , the smaller the solute buildup, if the driving force for diffusion provided by the concentration gradient remains constant.

On the other hand, at the three-phase junction  $\alpha$ - $\beta$ -L, the surface tensions must be balanced to ensure mechanical equilibrium (Fig. 5.18). This imposes fixed contact angles, leading to a curvature of the solid-liquid interface. This curvature is thermodynamically disadvantageous. Because



**Fig. 5.17** Diffusion fields ahead of the growing  $\alpha$  and  $\beta$  phases in (a) isolated and (b) coupled eutectic growth. The dark arrow represents the flux of *B* atoms. Source: Ref 5.7 as published in Ref 5.6



**Fig. 5.18** Surface tension balance at the three-phase ( $\alpha$ - $\beta$ -L) junction and the resulting curvature of the solid-liquid interface. Source: Ref 5.6

the contact angles are material constants, this curvature is higher when the lamellar spacing is small.

The scale of the eutectic structure is therefore determined by a compromise between two opposing factors:

- Solute diffusion, which tends to reduce the spacing
- Surface energy (interface curvature), which tends to increase the spacing

The lamellar spacing,  $\lambda$ , and the growth undercooling,  $\Delta T$  (defined as the difference between the eutectic temperature,  $T_{\rm E}$ , and the actual interface temperature during growth), are given by:

$$\lambda = \frac{\varphi k_1}{\sqrt{R}} \tag{Eq 5.1}$$

$$\Delta T = \frac{(\varphi + 1/\varphi)}{2} k_2 \sqrt{R}$$
 (Eq 5.2)

where *R* is the solidification rate (velocity at which the solid/liquid interface advances),  $k_1$  and  $k_2$  are constants related to the material properties, and  $\phi$  is a regularity constant whose value is close to unity for regular eutectics. Figure 5.19 shows typical values for the  $\lambda(R)$  relationship (Eq 5.1). It can be seen that regular eutectics have spacings between the coarse ones of irregular eutectics and the fine ones of eutectoids. In the latter, the effect of diffusion on spacing is more marked because it occurs in a solid phase.

The scale of the eutectic microstructure depends on the solidification rate, not directly on the cooling rate. The reason is that the thermal gra-



Fig. 5.19 Typical spacings of eutectics and eutectoids as a function of growth rate. Source: Ref 5.7 as published in Ref 5.6

dient has a negligible effect on the size of the eutectic microstructure. Because the cooling rate is the product of the solidification rate and the thermal gradient, two growth conditions characterized by the same cooling rate but with different thermal gradients lead to different solidification rates and therefore to different spacings. An important characteristic of regular eutectic growth is that the lamellae (or fibers) are parallel to the heat flow direction during solidification and perpendicular to the solidliquid interface.

**Irregular Eutectic Growth.** Irregular eutectics grown under given growth conditions exhibit an entire range of spacings because the growth direction of the faceted phase (for example, graphite in cast iron or silicon in aluminum-silicon) is determined by specific atomic orientations and is not necessarily parallel to the heat flux. In this case, growth involves the following mechanism: When two lamellae converge, the growth of one simply ceases when  $\lambda$  becomes smaller than a critical spacing,  $\lambda_{min}$ , because the local interface energy becomes too large. Thus, the spacing is increased. This mechanism is illustrated in Fig. 5.20. Conversely, diverging lamellae can grow until another critical spacing,  $\lambda_{br}$ , is reached. When this occurs, one of the lamellae branches into two diverging lamellae, thus reducing the spacing. Growth of an irregular eutectic thus occurs within the range of interlamellar spacings between  $\lambda_{min}$  and  $\lambda_{br}$ .



**Fig. 5.20** Growth of irregular eutectics. (a) Schematic of branching of the faceted phase at  $\lambda_{brr}$  termination at  $\lambda_{minr}$  and the corresponding shape of the solid/liquid interface. (b) Iron-carbon eutectic alloy directionally solidified at  $R = 0.017 \mu m/s$ . Branching was induced by a rapid tenfold increase in *R*. Longitudinal section. As-polished. Source: Ref 5.8 as published in Ref 5.6

It can be shown that the growth temperature of the region of small  $\lambda$  is higher than that in the large  $\lambda$  zones. The solid-liquid interface is therefore nonisothermal; that is, its shape is irregular (Fig. 5.20a) and is the opposite of the isothermal planar solid-liquid interface that characterizes regular eutectic growth (Fig. 5.18 and 5.21).

A mean spacing,  $\langle \lambda \rangle$ , and a mean undercooling,  $\langle \Delta T \rangle$ , can be defined and are still given by Eq 5.1 and 5.2. In this case,  $\phi$  (the ratio of the mean spacing,  $\langle \lambda \rangle$ , to the minimum undercooling spacing, which is close to  $\lambda_{min}$ ) is greater than unity. Therefore, the spacings and undercoolings obtained are higher than those observed in regular eutectics (Fig. 5.19).

## 5.5 Competitive Growth of Dendrites and Eutectics

The solidification of a binary alloy of exactly eutectic composition was examined earlier in this chapter. In this case, provided the growth is regular, the solid-liquid interface is planar. However, when alloy composition departs from eutectic, or when a third alloying element is present, the interface can become unstable for the same reason as in the case of a simple solid-liquid interface. As shown in Fig. 5.22, two types of morphological instability can develop: single-phase and two-phase.

A single-phase instability (Fig. 5.22a) leads to the solidification of one of the phases in the form of primary dendrites plus interdendritic eutectic. This situation is primarily observed in off-eutectic alloys because one phase becomes much more constitutionally undercooled than the other. For example, during the solidification of a hypoeutectic alloy, the  $\alpha$  phase is heavily undercooled because the liquidus temperature at that composition



**Fig. 5.21** Nearly planar solid-liquid interface of a regular cadmium-tin eutectic as revealed by quenching. Etched with ferric chloride. Original magnification: 210×. Source: Ref 5.6



**Fig. 5.22** Types of instability of a planar solid-liquid eutectic interface. (a) Single-phase instability leading to the appearance of dendrites of one phase. (b) Two-phase instability leading to the appearance of eutectic cells or colonies in the presence of a third alloying element. Source: Ref 5.6

is much higher than  $T_{\rm E}$  (Fig. 5.16). The  $\alpha$  phase can therefore grow faster (or at higher temperature) than the eutectic.

A two-phase instability (Fig. 5.22b) is characterized by cellular-like growth and leads to the appearance of eutectic colonies. This situation is observed when a third alloying element that partitions similarly at both the  $\alpha$ -L and  $\beta$ -L interfaces produces a long-range diffusion boundary layer ahead of the solid-liquid interface, thus making the growing eutectic interface constitutionally undercooled with respect to this element.

**Coupled Zone of Eutectics.** The eutectic-type phase diagram appears to indicate that microstructures consisting entirely of eutectic can be obtained only at the exact eutectic composition. In fact, experimental observations show that purely eutectic microstructures can be obtained from off-eutectic alloys over a range of growth conditions. On the other hand, dendrites can sometimes be found in alloys with the exact eutectic composition if the growth rate is high. This is of considerable practical importance because the properties of a casting can be significantly changed when single-phase dendrites appear.

To explain these observations, one must consider the growth mechanisms of the competing phases. Because of the differing growth characteristics of eutectics and dendrites, the solidification of eutectic (high-efficiency diffusion coupling) can be faster than the isolated growth of one phase (primary dendrites), even for off-eutectic alloys. In this case, the dendrites are overgrown, and a purely eutectic microstructure is obtained over a range of off-eutectic compositions (the volume fraction of both phases in this case is determined by alloy composition and is therefore different from that obtained in the eutectic alloy). Conversely, if one of the phases (for example,  $\beta$ ) is faceted, the growth of this phase (and consequently of the eutectic) is slower at a given undercooling. Dendrites of  $\alpha$  phase may then grow more rapidly than the eutectic at the eutectic composition; purely eutectic microstructures are obtained only in hypereutectic alloys.

The temperature of a growing eutectic solid-liquid interface is a function of the growth rate. This relationship is used, together with the dendrite tip temperatures of  $\alpha$  and  $\beta$  primary crystals, to establish the coupled zone. In the diagrams shown in Fig. 5.23, each point below the eutectic temperature is associated with a solidification rate through Eq 5.2 (that is, the lower the temperature, the higher the solidification rate). The coupled zone (a shaded region) then represents the solidification rate dependent composition region in which the eutectic grows more rapidly (or at a lower undercooling) than  $\alpha$ - or  $\beta$ -phase dendrites. This zone corresponds to an entirely eutectic microstructure. Outside the coupled zone, the microstructure consists of primary dendrites and interdendritic eutectic.

The coupled zone of a regular eutectic system is shown in Fig. 5.23(a). In this case, a purely eutectic microstructure is obtained at the eutectic composition for all growth conditions. However, in the case of the skewed coupled zone of an irregular eutectic (Fig. 5.23b, where  $\beta$  is the faceted phase), the alloy composition must be carefully chosen as a function of the growth rate imposed by the casting process if a completely eutectic microstructure is required. For example, the composition of cast iron or aluminum-silicon alloys must often be hypereutectic if one wants to eliminate metal dendrites, especially when using high-solidification-rate casting techniques.

## 5.6 Terminal Solid Solutions

The terminal solid-solution Al-4% Cu alloy shown in Fig. 5.24 is completely a solid solution of  $\alpha$  above 480 °C (895 °F). If the alloy is brought to equilibrium by subjecting it to a long heat treatment at a temperature of approximately 510 °C (950 °F), it will be composed of the single  $\alpha$  phase. During this homogenization heat treatment, equilibrium is approached in two ways simultaneously: (1) coring segregation is eliminated by a redistri-



**Fig. 5.23** Coupled zones (shaded regions) on eutectic phase diagrams. The coupled zones represent the interface temperature (solidification rate) dependent composition region in which a completely eutectic structure is obtained. (a) Nearly symmetrical coupled zone in regular eutectic. (b) Skewed coupled zone in an irregular eutectic. In both cases, the widening of the coupled zone near the eutectic temperature is observed only in directional solidification (positive thermal gradient). Source: Ref 5.6



**Fig. 5.24** Aluminum-copper phase diagram and the microstructures that may develop during cooling of an Al-4% Cu alloy. Adapted from Ref 5.9

bution of the components, and (2) the  $\theta$  phase is dissolved in the  $\alpha$  phase. When the alloy is slowly cooled from 510 °C (950 °F), it starts rejecting or precipitating  $\theta$  when it reaches the solvus temperature at 480 °C (895 °F).

However, if the alloy is quenched to room temperature, there is not enough time for the  $\theta$  phase to precipitate, and the alloy will contain a supersaturated solid solution containing only the  $\alpha$  phase. On aging at room temperature or moderately elevated temperatures, such as 150 °C (300 °F), a series of transition phases form that strains the matrix and forms the basis for precipitation hardening, as discussed in Chapter 16, "Nonequilibrium Reactions—Precipitation Hardening," in this book.

The remainder of this section covers precipitation structures formed during slower cooling rates from temperatures in the single-phase region.

**General or continuous precipitation** refers to the uniform appearance of second-phase particles throughout the grains of the matrix. General precipitation does not imply homogeneous nucleation, rather, the nonlocalized precipitation of the second phase. Discontinuous precipitation can occur at regions such as grain boundaries, or cellular precipitation where precipitation begins at grain-boundary allotriomorphs but does not continue through the entire grain. General precipitation in aluminum alloys is shown in Fig. 5.25. The difference between discontinuous and continuous precipitation in AZ91 (a Mg-Al-Zn alloy) is shown in Fig. 5.26. **Widmanstätten Structures.** The continuous precipitation of plate or lathlike structures is referred to as Widmanstätten morphology. This distinctive plate or lathlike morphology is characterized by the presence of both high- and low-angle boundaries. Widmanstätten morphologies form in many alloy systems, as illustrated in Fig. 5.27 for a Ti-6Al-4V alloy. As evident by the microstructure, there are specific orientation relations between the precipitate habit plane and matrix. The long broad faces of



10 µm

**Fig. 5.25** Scanning electron micrograph of continuous precipitation in 6061 aluminum alloy, where the smaller precipitates are Mg2Si, and the larger particles are AlFeSi intermetallics at the grain boundary. Note the precipitate-free zone near the AlFeSi intermetallics. Source: Ref 5.10 as published in Ref 5.11



. 500 nm

**Fig. 5.26** Transmission electron micrograph showing a region of discontinuous (left) and continuous (right) precipitation in a specimen of AZ91 aged at 200 °C (390 °F) for 4 h. Source: Ref 5.12 as published in Ref 5.11



Fig. 5.27 Widmanstätten structure in Ti-6Al-4V alloy cooled at 3.40 °C/s (6.12 °F/s ). Source: Ref 5.13 as published in Ref 5.11

the precipitates are the coherent, low-energy interfaces. During growth, small ledges form on these faces, allowing for diffusional thickening while maintaining coherency. Typically, this morphology forms during slow cooling rates, but the Widmanstätten morphology can occur if a sufficient driving force for growth is provided by either a fast cooling rate or large undercooling.

The development of the side-plate morphology normally starts from a grain-boundary allotriomorph (as in the case of steels) and growth occurs into the grain. As cooling rates increase, the diffusion of atoms to the high-angle boundaries (where no special orientation exists between austenite and ferrite) is slow, but if diffusion distances are minimized by phase morphology and growth occurs in preferred crystallographic directions, growth rates can be increased.

**Cellular or Discontinuous Precipitation.** Grain-boundary precipitation may result in cellular or discontinuous precipitation (DP). Figures 5.28 and 5.29 are examples of the alternating lamellar structure that is common to many cellular precipitation transformations. During discontinuous precipitation, the second phase nucleates at the grain boundary, which then moves with the advancing precipitation reaction. It typically starts at a high-angle incoherent boundary, which is the most likely point to support the process of heterogeneous nucleation and boundary migration. Misfit or atomic mismatch strain are factors, although neither misfit nor atomic mismatch strain appear to be necessary conditions in several instances (e.g., Al-Li, Ni-Al, Ni-Ti, Al-Ag, and Cu-Co). The general conditions and criteria of discontinuous precipitation are not completely understood due to the complex interrelationships among boundary structure, energy, mobility, and diffusivity.

Following nucleation, the grain boundary moves with the advancing precipitation reaction. This is illustrated in Fig. 5.29b, where the grain



. 20 μm

Fig. 5.28 Discontinuous precipitation of  $\beta$  phase (Mg17Al12) in cast AZ80 zirconium-free magnesium casting alloy. Source: Ref 5.14 as published in Ref 5.11



**Fig. 5.29** Discontinuous precipitation (DP). (a) Scanning electron micrograph of lamellar structure within a DP cell in Mg-10Al (wt%) annealed at 500 K for 40 min. RF, reaction front.  $\alpha_0$ , supersaturated solid solution. (b) Light optical micrograph of early stage of the DP reaction in Mg-10Al (wt%) annealed at 500 K for 20 min. The bowing out of the grain boundary between two allotriomorphs is clearly seen. Source: Ref 5.15 as published in Ref 5.11

boundary is seen bowing out at the beginning of the reaction. Morphologically, it resembles eutectoid decomposition. Discontinuous precipitation results in reaction products that are often lamellar, fibrous, or rodlike, but rarely globular. Discontinuous precipitation is also often referred to as a cellular, grain-boundary, recrystallization, or autocatalytic reaction.

Lamellar spacing of the precipitates is dependent on aging temperature, with wider spacing occurring at higher temperatures. Free energy is limited for creating of interfaces due to the lower driving force (at higher temperature). It is termed discontinuous because the matrix composition changes discontinuously as the cell advances. Cellular precipitation is



**Fig. 5.30** Cellular colonies growing out from grain boundaries in Au-30Ni alloy aged 50 min at 425 °C (795 °F). Etchant: 50 mL 5% ammonium persulfate and 50 mL 5% potassium cyanide. Original magnification: 100×. Source: Ref 5.16 as published in Ref 5.11

observed in Fig. 5.30, clearly showing the relationship between the cells and the grain boundaries.

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