

All of these arguments, of course, refer to thermal equilibrium conditions, as phase diagrams do in general. No matter what the final state is, it must have been reached very slowly, so that the sample had time to equilibrate fully.

8.3.3 Microstructure Development

The final question, and for materials properties the crucial question, is how the features of the phase diagram determine the microstructure of a material with a certain composition, especially in the context of solidification.

We will begin by examining a material with the eutectic composition, $X_0 = 72 \text{ wt \% Ag}$ (cooling path 1 in Fig. 8.10).

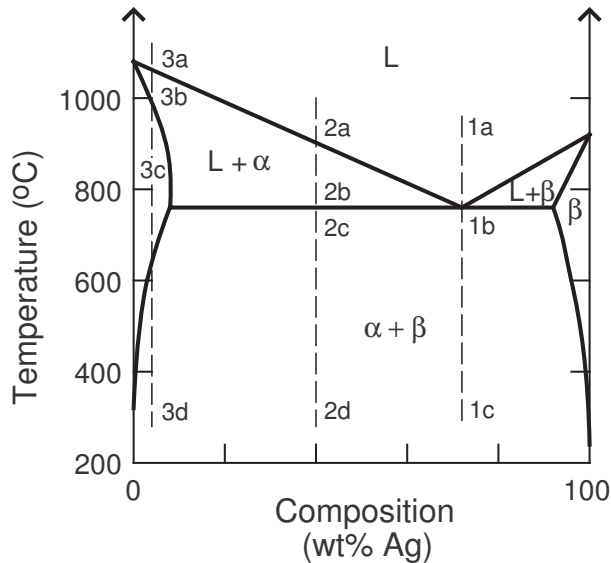


Figure 8.10: Cu-Ag phase diagram with three cooling paths at three different compositions.

We will start our thought experiment, as usual, with the material in the molten state: point 1a in Fig. 8.10. We will cool the sample very slowly, maintaining thermal equilibrium, and we are interested the microstructure that arises at point 1b just below the eutectic temperature T_E and also at point 1c at a much lower temperature. As we said above, when the temperature crosses the eutectic line, the phase diagram requires that the liquid turn into all solid at once. So how does this happen?

I will use a simple color scheme to aid in the explanation. For the sake of argument let us assume that Cu is black and Ag is white. Hence the liquid, being a uniform single phase would look medium gray. But what will the eutectic

solid look like just below T_E , where it must separate into two phases α and β while maintaining its average system composition of 72 wt % Ag?

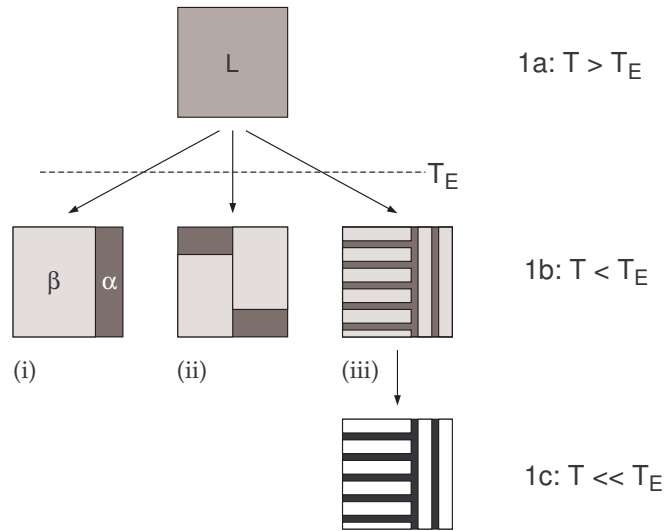


Figure 8.11: Possible microstructures of eutectic solid just below T_E .

If we want to know the compositions of α and β just below T_E , we draw a tie line. This tells us that just below T_E , $X_\alpha = 8$ wt % Ag and $X_\beta = 92$ wt % Ag (see Fig. 8.8). In our color scheme, this makes α dark grey and β light grey. Furthermore, the lever rule tells us that a fraction 0.24 of the sample must be α and 0.76 must be β .

But how are the α and β arranged in the eutectic solid? Fig. 8.11 displays some hypothetical microstructures. Panels (i) and (ii) show the phases as large chunks, with the proper compositions and about the correct fractional amounts. However, these are not correct microstructures. Experience shows that the eutectic solid looks something like Panel (iii): It consists of grains, and each grain is composed of fine alternating layers of α and β phase. (Panel (iii) shows two grains).

The reason why the microstructure of Panel (iii) is favored over Panels (i) and (ii) is that below the eutectic line, Cu and Ag atoms have to separate, and they can only do this by diffusion. If they were to form chunks of largely Cu or Ag atoms, the atoms would have to diffuse over very large distances. By contrast, they can form thin layers by diffusing only over a much smaller distance, in opposite directions, perpendicular to the layers. A layered structure like the one in Panel (iii) is known as a **eutectic microstructure**. It is characteristic of how a liquid of eutectic composition solidifies.

As the eutectic sample cools further, to a final temperature of 200°C or lower, further changes occur but these are fairly subtle. As I mentioned earlier, at that

low a temperature α is essentially Cu, with very few Ag impurities, and β is essentially Ag, with very few Cu impurities. So the compositions of α and β continue to change during further cooling: α continues to lose Ag and β continues to lose Cu. You can also convince yourself that at temperatures of 200°C and below, the fractional amounts of α and β phase will be 0.22 and 0.78, respectively, which is very close to what they were just below T_E . The final microstructure is displayed schematically in the bottom panel 1c in Fig. 8.11.

Scanning electron micrographs of two real experimental eutectic Cu-Ag microstructures are shown in Fig. 8.12:

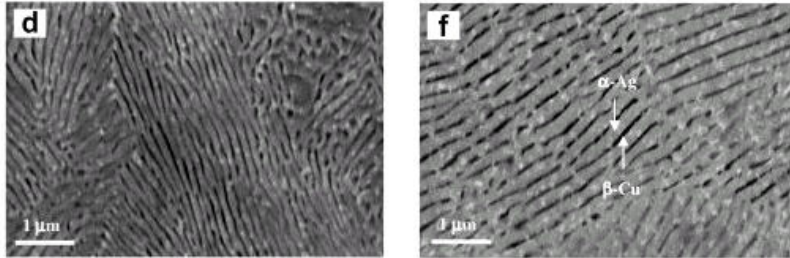


Figure 8.12: Scanning electron micrographs of Cu-Ag eutectic microstructures.

The difference between panel d) and panel f) is that the material for f) was cooled more slowly than for d). In both panels, the α - β layered structure is evident. In addition, you can discern individual grains, i.e. regions where the α and β layers are parallel but oriented differently than in other grains nearby. Note that the notation is reversed in Fig. 8.12: The α phase is Ag-rich, and the β phase is Cu-rich. However, in terms of composition, the dark and light phases have the same meaning in Fig. 8.11 and Fig. 8.12. Also, given the 1 μm scale bar in the lower left corner, note how thin these layers are.

With a good grasp of the eutectic microstructure, we are in a position to deduce the microstructures along the other cooling paths of Fig. 8.10. These are summarized graphically on Fig. 8.13 below.

Focusing now on path 2 you realize that it starts out as in path 1. However, when the system on path 2 approaches the eutectic line, there is a substantial amount of solid α phase present already! This kind of α is sometimes called **proeutectic** (for: prior to eutectic). It is displayed as the two grains in panel 2b of Fig. 8.13. In fact, a glance at the lever rule indicates that, just above T_E , about half the system is solid α and half still liquid. As the temperature now moves just below T_E , the remaining liquid transforms into eutectic solid, i.e. the layered α - β structure (panel 2c). As the temperature is lowered further, the α phase becomes more enriched in Cu, and the β phase more enriched in Ag (panel 2d), as before with path 1.

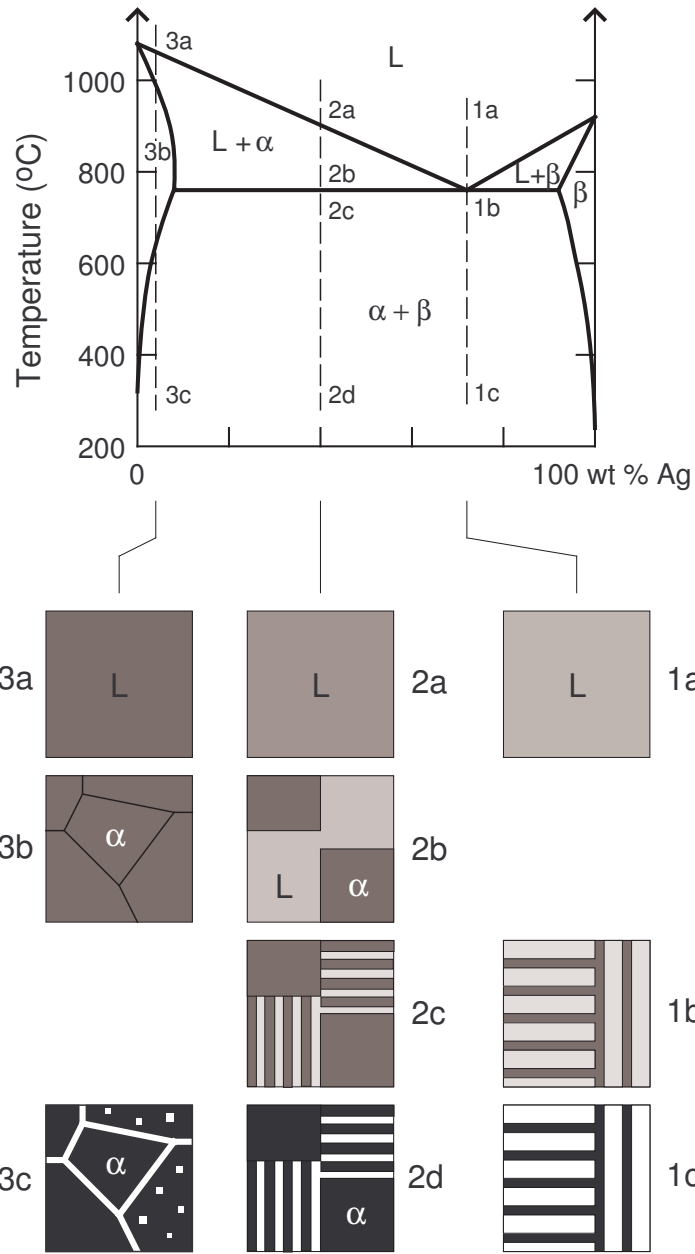


Figure 8.13: Schematic graphical summary of microstructure development in the eutectic Cu-Ag system. Note that, of course, the real grains in conditions 2b, 2c, etc., are not square.

Let us work out again the phase amounts for path 2, using the lever rule at points 2b and 2c. Just *above the eutectic line* we have for the *proeutectic* α :

$$\frac{m_{\alpha}}{m_t} = \frac{72 - 40}{72 - 8} = 0.50 \quad (8.20)$$

Make sure you know why the compositions are what they are. On the other hand, just *below the eutectic line* we have for the *total* α :

$$\frac{m_{\alpha}}{m_t} = \frac{92 - 40}{92 - 8} = 0.62 \quad (8.21)$$

The total α is made up of proeutectic and eutectic parts. Therefore, the fractional amounts are 0.50 for the proeutectic α , 0.12 for the eutectic α (hence a total amount of α of 0.62), and 0.38 for the eutectic β .

Path 3 is, at the beginning, very similar to the case of complete solubility. From panel 3a to 3b, the liquid forms a single α phase without any change in concentration. However, this all changes as the temperature goes below the solvus line. At that point, the complete solubility is lost, and the system begins to separate into two phases, α and β . In this case, the new β phase nucleates and grows in the α solid, at a rather low temperature. This process is initiated at defects, either along the grain boundaries of the α solid, or inside the grains. Both alternatives are indicated schematically in panel 3c. In practical systems, the growth of β usually occurs in one or the other type of location.

Whereas we have concentrated so far on cooling paths for concentrations of $X_0 \leq X_E$, similar results are obtained for concentrations $X_0 > X_E$. For example, you can easily convince yourself that for $X_0 \approx 0.85$ the outcome would be very similar to path 2 in Fig. 8.10, but with the roles of α and β reversed.

8.4 Other Binary Systems

In this section, we will examine briefly the phase diagrams of a few other binary systems of interest. This is to give you an idea of the complexities that are possible. For the most part, solubilities are limited in these binary systems. We will not go into any details of analysis, but the methods outlined above will apply to these systems as well.

8.4.1 The Pb-Sn System

The phase diagram of the Pb-Sn system is shown below. You will recognize it as another eutectic system. In its overall shape, it looks much like the phase diagram for Cu-Ag, but the critical parameters are different. For Pb-Sn the eutectic point is at $T_E = 183^\circ\text{C}$ and $X_E = 62 \text{ wt } \% \text{ Sn}$. The ends of the eutectic line are at $X_{\alpha E} = 18 \text{ wt } \% \text{ Sn}$ and $X_{\beta E} = 18 \text{ wt } \% \text{ Sn}$.