

H3

Teach yourself phase diagrams

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H3.1 Introduction

This programmed learning text aims to provide a working knowledge of what a phase diagram (or equilibrium diagram) is, and how to use it. It is fundamental to materials science and engineering that the properties of materials reflect their microstructure. For example, the mechanical and electrical properties of metallic alloys depend on how dislocations or charge carriers interact with solid solutions, precipitates, and so on. Microstructures are controlled by the chemistry of the material and how it is processed. Manufacturing is not only a matter of shaping and assembling engineering products and devices, but must simultaneously provide the material properties required. Most material processing operations involve a thermal history (e.g. cooling from a high temperature shaping or deposition process, or producing a controlled diffusional change in the solid). It is therefore vital to understand how processing history (particularly temperature) controls microstructure, and thus properties.

So where do phase diagrams fit into this picture? These diagrams give some fundamental knowledge of what the equilibrium structure of a metallic or ceramic alloy is, as a function of temperature and composition. The real structure may not be the equilibrium one, but equilibrium gives a starting point from which other (non-equilibrium) structures can often be inferred.

H3.2 Some essential Definitions

Definition *A metallic alloy is a mixture of a metal with other metals or non-metals. Ceramics, too, can be mixed to form ceramic alloys.*

Examples

Brass: a mixture of copper (Cu) and zinc (Zn).

Carbon steel: based on iron (Fe) and carbon (C).

Spinel: a ceramic alloy made of equal proportions of magnesia (MgO) and alumina (Al₂O₃).

Definition *The components are the chemical elements which make up alloys.*

Components are given in capital letters: A, B, C or the element symbols Cu, Zn, C. In *brass* the components are Cu and Zn. In *carbon steel* the components are Fe and C.

Definition *A binary alloy contains two components. A ternary alloy contains three; a quaternary, four, etc.*

H3.2.1 Concentration

An alloy is described by stating the components and their concentrations.

Definition *The weight % of component A:*

$$W_A = \frac{\text{weight of component A}}{\sum \text{weight of all components}} \times 100$$

The atom (or mol) % of component A:

$$X_A = \frac{\text{number of atoms (or mols) of component A}}{\sum \text{number of atoms (or mols) of all components}} \times 100$$

(Weight in grams)/(atomic or molecular wt in grams/mol) = number of mols.

(Number of mols) \times (atomic or molecular wt in grams/mol) = weight in grams (g).

H3.2.2 Phases

Processing of alloys leads to microstructures in which the components are distributed in a number of ways. For example, in a binary alloy (in the solid state) the microstructure can take one of four forms:

- (a) a single solid solution;
- (b) two separated, essentially pure components;
- (c) two separated solid solutions; or
- (d) a chemical compound, together with a solid solution.

The appearance of microstructures in binary alloys will be examined later. For the time being, it is worth reminding yourself what we mean by a solid solution. This is a solid in which an element is 'dissolved' in another so that it is homogeneously dispersed, at an atomic scale.

A region of a material which has homogeneous properties and composition is called a phase. A phase can be identified as a cluster of as few as 10 or so atoms, but it is usually much more. In the four types of microstructures listed earlier, each solid solution, or pure component, or chemical compound would be an identifiable phase.

Definition *All parts of an alloy microstructure with the same physical properties, and the same composition are a single phase.*

Questions[†]

H3.2.1 A 1.5 kg sample of α -brass contains 0.45 kg of Zn, and the rest is Cu.

The atomic weight of copper is 63.5 and zinc 65.4.

The concentration of copper in α -brass, in wt%: $W_{\text{Cu}} = \text{-----}$

The concentration of copper in the α -brass, in at.%: $X_{\text{Cu}} = \text{-----}$

The concentration of zinc in the α -brass, in at.%: $X_{\text{Zn}} = \text{-----}$

[†]Answers are given at the end of each section.

- H3.2.2 A special brazing alloy contains 63 wt% gold (Au) and 37 wt% of nickel (Ni) (which is written Au-37 wt% Ni).
The atomic weight of Au (197.0) is more than three times that of Ni (58.7). At a glance, which of the two compositions, in at.%, is likely to be the right one?
- (a) $X_{\text{Au}} = 0.34$, $X_{\text{Ni}} = 0.66$
(b) $X_{\text{Au}} = 0.66$, $X_{\text{Ni}} = 0.34$
- H3.2.3 An alloy consists of X_A at.% of A with an atomic weight of a_A , and X_B at.% of B with an atomic weight of a_B . Derive an equation for the concentration of A in wt%. By symmetry, write down the equation for the concentration of B in wt%.
- H3.2.4 Heat pure copper. At 1083°C it starts to melt. While it is melting, solid and liquid copper co-exist. Using the definition of a phase, are one or two phases present? _____
Why? _____
- H3.2.5 Three components A, B and C of an alloy dissolve completely when liquid but have no mutual solubility when solid. They do not form any chemical compounds. How many phases and of what compositions, do you think would appear in the solid state?
- Number of phases _____
Compositions _____

H3.2.3 Thermodynamics and the equilibrium constitution

First we define the constitution of an alloy.

Definition *The constitution of an alloy is described by:*

- (a) *the phases present;*
- (b) *the weight fraction of each phase; and*
- (c) *the composition of each phase*

At equilibrium, the constitution is stable: there is no further tendency for it to change. It is important to note that when we talk of equilibrium, we are referring to thermodynamic equilibrium. Hence, the equilibrium constitution is defined at constant temperature and pressure, for a given alloy composition. Temperature, pressure and composition are the independent ‘state variables’.

Definition *A sample of given composition has its equilibrium constitution when, at constant temperature T and pressure P , there is no further tendency for its constitution to change with time.*

Thermodynamics, therefore, controls the forms in which mixtures of elements can exist. Any state of a system (liquid, mixtures of solid solutions, compounds, etc) can be characterized by the Gibbs free energy, G , defined by:

$$G = H - TS$$

where H is the enthalpy, T the absolute temperature, and S the entropy of the system. Recall that enthalpy $H = U + PV$, where U is the internal energy of the system, P is the pressure and V the volume. The internal energy is due to the atom vibration and bond energies between them. For the condensed

states (liquid and solid) which are relevant to most materials processing, U dominates the enthalpy and PV is small, so $H \approx U$. Entropy is a measure of the disorder in the system—for example, when an alloy solidifies, there is a decrease in entropy as the solid has a regular lattice whereas the liquid does not. Once solid, the changes in entropy of a crystalline solid are relatively small, due to the regular atomic packing. Entropy is much more important in polymers, since the molecules have much more freedom to adopt different configurations.

The equilibrium constitution is the state of lowest Gibbs free energy, for a given composition, temperature and pressure. If the material is not at equilibrium, the difference in free energy ΔG is what drives the change of state towards equilibrium—this difference is called (rather ambiguously) the ‘driving force’.

Alloys do frequently exist and are used in non-equilibrium states, which do not change with time—such a state is termed ‘metastable’. A driving force for change is available, but nothing happens because (as we shall see) phase transformations also require a mechanism. We might say that having free energy available is a necessary, but not a sufficient, condition for change towards equilibrium. However, it is always useful to know the equilibrium constitution. It gives a base-line state for the alloy, and non-equilibrium constitutions can often be deduced from it.

H3.2.4 Equilibrium constitution (or phase) diagrams

As noted earlier, processing of engineering materials always involves materials in the liquid or solid state. In these states pressure only has a small influence on the equilibrium constitution and can be neglected for the pressures encountered in manufacturing processes. Some special processes such as chemical vapour deposition (CVD) involve the gaseous state, when pressure needs to be taken into account. From now on, however, we will only be concerned with material states which are controlled by the remaining two state variables: temperature and composition. In the next section, we show how the equilibrium constitution can be described by diagrams with these state variables as axes.

H3.2.5 Answers to questions: section H3.2

H3.2.1 $W_{\text{Cu}} = 70\%$, $X_{\text{Cu}} = 71\%$, $X_{\text{Zn}} = 29\%$

H3.2.2 (a) is the correct composition.

H3.2.3 $W_A = \frac{a_A X_A}{a_A X_A + a_B X_B}$; $W_B = \frac{a_B X_B}{a_A X_A + a_B X_B}$

H3.2.4 Two phases: liquid and solid. Although they have the same chemical composition, they differ in physical properties.

H3.2.5 Three phases: pure A, pure B and pure C.

H3.3 Simple binary phase diagrams

The equilibrium constitution of an alloy of the components A and B is determined (at a standard pressure of 1 atm) by the temperature T and the composition, X_B (or W_B). For a given composition, the equilibrium constitution as a function of temperature can be determined experimentally by metallography or thermal analysis (described later), or increasingly by thermodynamic computation.

Definition *An equilibrium diagram (or phase diagram) is a diagram with T and X_B (or W_B) as axes, showing the equilibrium constitution.*

The equilibrium diagram of an alloy made of components A and B, for all combinations of T and X_B , defines the 'A-B system'. Binary systems have two components, ternary systems three, and so on.

H3.3.1 Building up a binary phase diagram

A simple introduction

We begin with a familiar example to establish some fundamental behavior. Consider the two-component system: water and salt. Each is a compound with a definite chemical composition, so we treat their mixtures as consisting of two components, rather than as four elements.

If we take water at room temperature and add salt a little at a time, stirring thoroughly each time, we first obtain a 'solution'—the salt disperses on a molecular scale throughout the water. From the earlier definition, we have a single phase. The same amount of salt as a solid lump might take much longer to dissolve, but the end result will be the same, and at present we are only concerned with equilibrium (thermodynamics). The rate at which dissolution takes place (or any other 'phase transformation') depends not only on the driving force, but also on the kinetics (i.e. the diffusion mechanism). This is not considered further here.

After adding a certain amount of salt, we find that no more will dissolve—the solution is 'saturated'. If we add more salt, it will not dissolve, but it does not stay hard and white either. A soggy mess settles in the container—the salt has in fact dissolved some water, and become a saturated solution of water in salt. Eventually, we would have added just enough salt to absorb all the water into a saturated solution of water in salt. We could have also got to this point by starting with salt and adding water a bit at a time.

At constant temperature we have therefore defined two single-phase regions and one two-phase region, which we can plot on a graph with one axis for composition (figure H3.1).

At the left-hand end we have single-phase solutions of salt in water, over a range of compositions, while at the right-hand end we have solutions of water in salt. In between, we have two phases—both saturated solutions, one rich in water, the other rich in salt.

If we repeat this procedure at other temperatures above room temperature, we can find and plot the saturation limits for the single-phase regions by adding a temperature axis (figure H3.2).

A few points to note:

- As the temperature increases, the 'solubility' of salt in water increases—as the single-phase region extends to higher concentrations before saturating.
- The same is true for solutions of water in salt at the other end of the diagram.

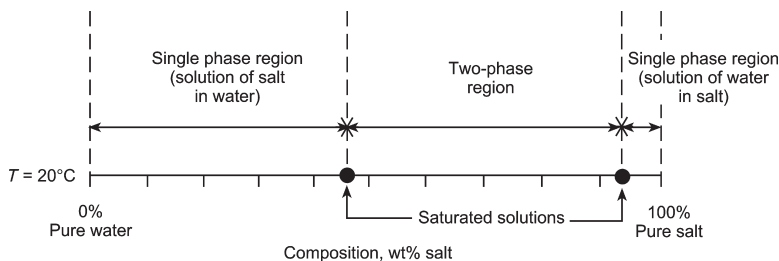


Figure H3.1. The water–salt system at room temperature.

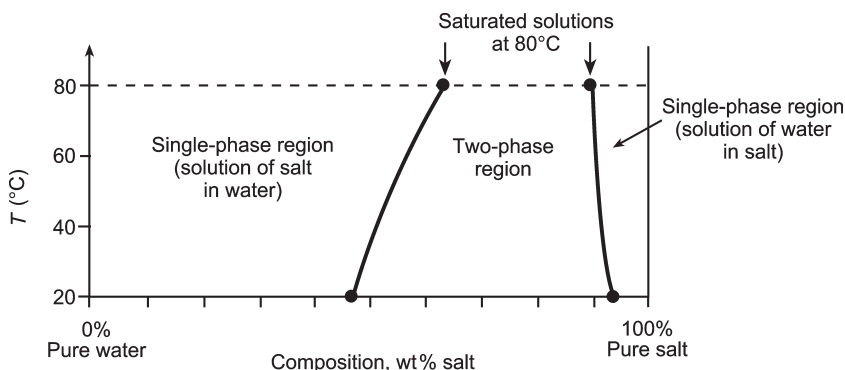


Figure H3.2. The water–salt system for a range of temperatures.

- (c) In a single-phase region, the composition of the phase is simply the composition of the overall mixture (e.g. wt% salt).
- (d) In a two-phase region, the compositions of the phases at a given temperature are fixed: they are found at either end of a horizontal line across the two-phase region which ends at the boundary with the single-phase regions to either side. Another way of saying this is that both phases are as ‘impure’ as possible, i.e. both phases are saturated solutions. Changes in overall alloy composition in this region, at constant T , are accommodated by changes in the proportions of the phases, not in the phase compositions. Evaluating the proportions of the two phases will be dealt with later.

Note: The equilibrium state of a water–salt mixture at given temperature and composition is governed by thermodynamics: i.e. whether one or two phases form, the saturation limits for the solutions, and the way these limits vary with temperature.

Metallic alloys in the solid state

The picture built up earlier is replicated exactly for many two component metallic alloys, when the whole system is solid. Clearly we would not in practice mix the two elements in the solid state, but the thermodynamics of mixing for two metallic elements reproduces the same behaviour at equilibrium. For example, figure H3.3 shows the phase diagram for Pb–Sn alloys at lower temperatures.

As noted earlier, the solubility of Pb in Sn (and of Sn in Pb) increases with temperature. Each region of the diagram in which the number of phases is constant (one or two) is called a field. The single-phase fields are labelled with the names of the elements in brackets, e.g. (Pb)—this indicates a Pb-rich phase (not pure Pb). In the two-phase field the names of the phases bounding the field to left and right are given, e.g. (Sn) + (Pb). Note that the solubilities of these elements in one another is quite low, especially Pb in Sn on the left of the diagram.

Metallic alloys at higher temperatures: liquid and solid

The solid solution behaviour outlined earlier clearly does not go on and on as the temperature increases—alloys begin to melt and become 100% liquid if the temperature is high enough. How does the phase diagram look? To answer this, we will take a new approach—take a given composition in

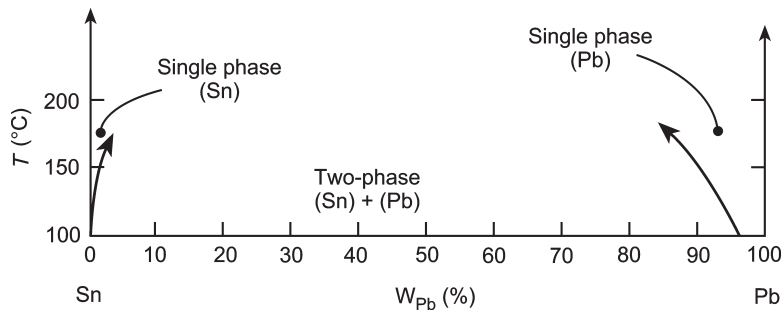


Figure H3.3. The Pb–Sn system at lower temperatures.

the 100% liquid state and slowly cool it down until it is 100% solid. Figure H3.4 shows the Sn-rich end of the phase diagram for the Pb–Sn system, at higher temperatures.

First look at pure tin. Pure materials have a unique melting point, hence on the left hand axis, this point separates two single phase regions: pure (solid) Sn, and pure (liquid) Sn. As pure molten Sn is cooled slowly, it ‘transforms’ to pure solid Sn at this temperature.

Now we add a little lead to the molten tin. Two things differ on cooling:

- The temperature at which 100% liquid is stable is reduced relative to pure Sn (almost always, alloying lowers the melting point).
- The alloy solidifies over a temperature range, so that the upper limit of 100% solid is below the lower limit for 100% liquid.

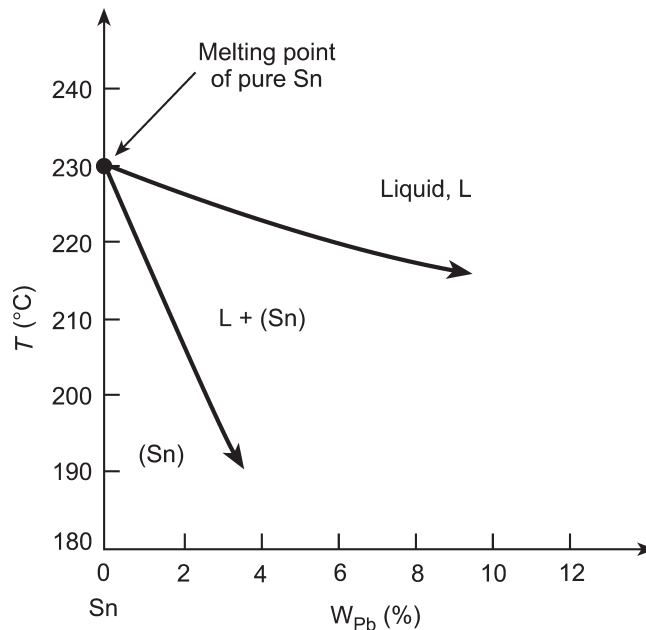


Figure H3.4. The Sn-rich end of the Pb–Sn system below the melting point of Sn.

Definition *The phase boundary which limits the bottom of the liquid field is called the liquidus line; the line giving the upper limit of the single phase solid field is called the solidus line.*

The separation of these lines as an element is made impure by alloying is known as partition.

Between the liquidus and solidus, we have a two-phase region: liquid, L + Sn-rich solid, (Sn). As noted earlier, in this field the compositions of the phases are fixed at a given temperature and variations in overall composition cause changes in the proportions of solid and liquid. The phase compositions are again those on the boundaries of the two-phase region to either side.

If we look at the other end of the Pb–Sn diagram, the situation is exactly the same: adding Sn to pure Pb lowers the melting point and causes partition of the solidus and liquidus boundaries. The two-phase region now contains liquid, L + Pb-rich solid, (Pb). The high temperature end of the whole Pb–Sn system therefore has the form shown in figure H3.5.

Completing the picture: eutectics

Finally, we must establish how the high and low temperature parts of the diagram fit together. Consider the solubility limits of the Sn-rich single phase at the left-hand end of the diagram. As we increase the temperature from room temperature, the solubility limit for Pb in solid Sn increases. Similarly, as the temperature falls from the melting point of pure Sn, the solidus line moves to higher concentrations of Pb. Figure H3.6 shows the intersection of these two lines, and thereby closing of the single-phase field: Sn-rich solid solution, (Sn). There is thus a critical temperature at which the solubility of Pb in Sn reaches a maximum.

Now, if we had constructed the same solubility limits at the Pb-rich end of the diagram, we would find another intersection and critical temperature. For good thermodynamic reasons, the critical temperatures are one and the same: i.e. the temperature at which Sn can dissolve most Pb is also the temperature at which Pb can dissolve most Sn. It is essentially a corollary of the fact that in a two-phase region, both phases are as impure as possible.

Above this critical temperature, between the two points of maximum solubility for (Sn) and (Pb), we know that one of the phases present is liquid. Hence, a horizontal line across the diagram forms the phase boundary which closes the two-phase field Sn-rich solid, (Sn), + Pb-rich solid, (Pb) (figure H3.7).

The last question is: how does the single-phase 100% liquid field close? In figure H3.7, the two liquidus lines are descending from the two melting points of the pure elements, Sn and Pb. It will

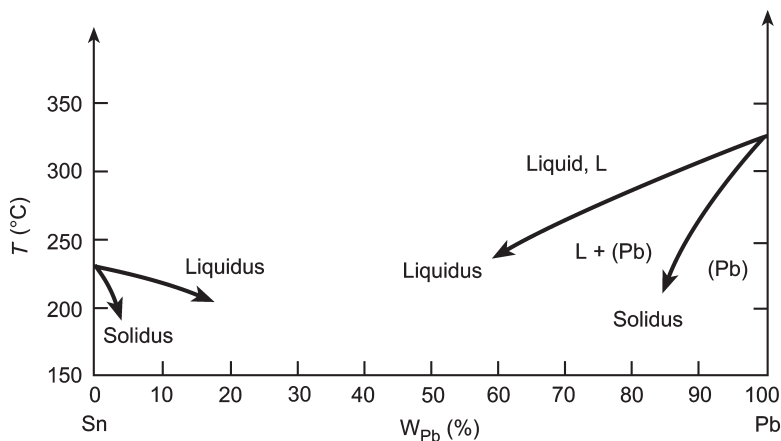


Figure H3.5. The Pb–Sn system at higher temperatures.

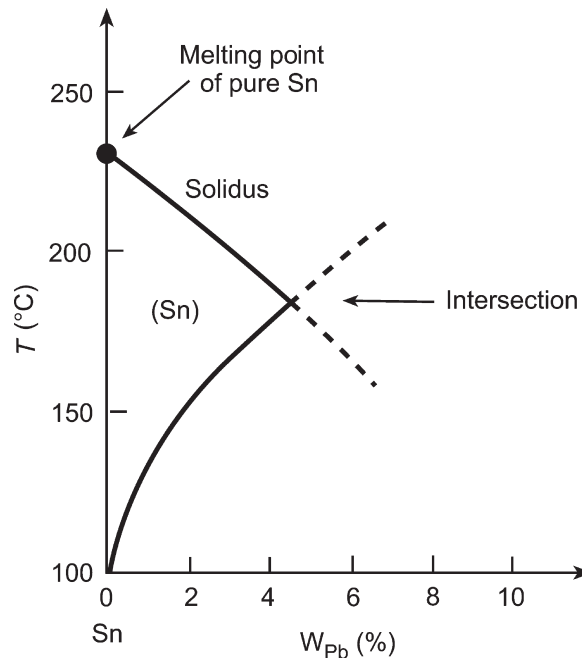


Figure H3.6. The Sn-rich end of the Pb–Sn system, showing the complete single phase region (Sn).

probably be no surprise to find that thermodynamics dictates that these two lines intersect at the same critical temperature—again, to maintain the phases in the liquid–solid regions at maximum impurity. The liquid field, therefore, closes in a shallow ‘V’: this point on the diagram is very important and is known as a eutectic point.

Definition *The lower limit of the single-phase liquid field formed by the intersection of two liquidus lines is called the eutectic point.*

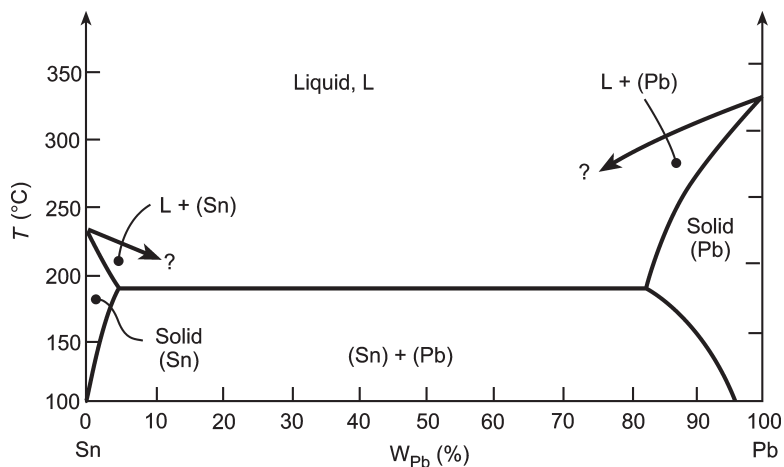


Figure H3.7. The Pb–Sn system, with incomplete liquidus lines.

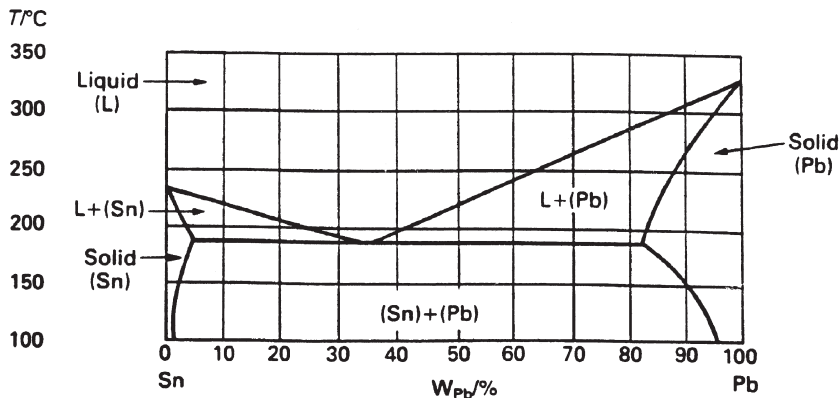


Figure H3.8. The completed Pb–Sn phase diagram.

Figure H3.8 shows the completed Pb–Sn phase diagram. For the Pb–Sn system the eutectic point is at the composition $W_{\text{Pb}} = 36 \text{ wt\%}$ and temperature $T = 183^\circ\text{C}$.

Eutectics will be discussed again later in relation to the microstructures which form when a eutectic composition solidifies. For the time being we simply note that the eutectic composition gives the lowest temperature for which 100% liquid is stable. For this reason, brazing and soldering alloys are often eutectic or near eutectic in composition.

H3.3.2 Reading a phase diagram: the constitution point

The state variables, temperature and composition, define a point on the phase diagram: the ‘constitution point’. We now wish to read off the constitution at any point. First, we look at the phases present and then how to find the fraction and composition of each phase.

Question

H3.3.1 Use the Pb–Sn diagram in figure H3.9 to answer the following questions.

- (a) What are the values of the two state variables at point 1?

Composition: _____

Temperature: _____

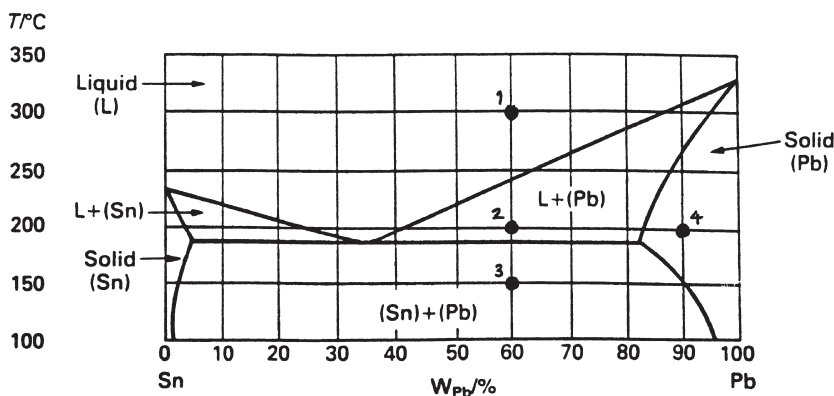


Figure H3.9. Pb–Sn phase diagram.

- (b) Mark the constitution points for Pb–70 wt% Sn and Pb–20 wt% Sn alloys at 250°C. What does the alloy consist of in each case?

Pb–70 wt% Sn: _____

Pb–20 wt% Sn: _____

- (c) The alloy corresponding initially to the constitution point 1 is cooled very slowly to room temperature.

At which temperatures do changes in the number or type of phases occur?

What phases are present at point 2? _____

What phases are present at point 3? _____

- (d) Similarly, the alloy corresponding to the constitution point 4 is cooled to room temperature. Identify the following:

Initial composition and temperature: _____

Initial phase(s): _____

Temperature at which change of phase occurs: _____

Final phase(s): _____

H3.3.3 Composition of the phases

It was noted earlier that in a single-phase region, the composition of the phase is simply the composition of the alloy itself. In this case defining the constitution is trivial.

Definition *In a single-phase region, the phase composition and alloy composition coincide.*

In two-phase regions, at a given temperature, the phase compositions are given by the values on the phase boundaries to either side of the constitution point. Recall that these were the saturation limits of the single-phase fields on the other sides of the boundaries. Consider a Sn–30 wt% Pb alloy at 150°C on the Pb–Sn phase diagram, figure H3.10. This point is in the two-phase region, with the phase compositions marked ‘X’ at either end of a horizontal line through the constitution point.

Definition *In a two-phase field the compositions of the phases are found at the ends of the isothermal line spanning the field through the constitution point. This line is called the tie-line.*

As noted before, any alloy which lies on the tie-line breaks up into the same two phases at its ends. The proportions of each phase depend on the alloy composition in such a way as to conserve the overall fractions of the two elements (see below).

Question

H3.3.2 Use the Pb–Sn diagram in figure H3.11 to answer the following questions.

- (a) The constitution point for a Sn–70 wt% Pb alloy at 250°C lies in a two-phase field. Construct a tie-line on the figure and read off the two phases and their compositions:

Phases: _____

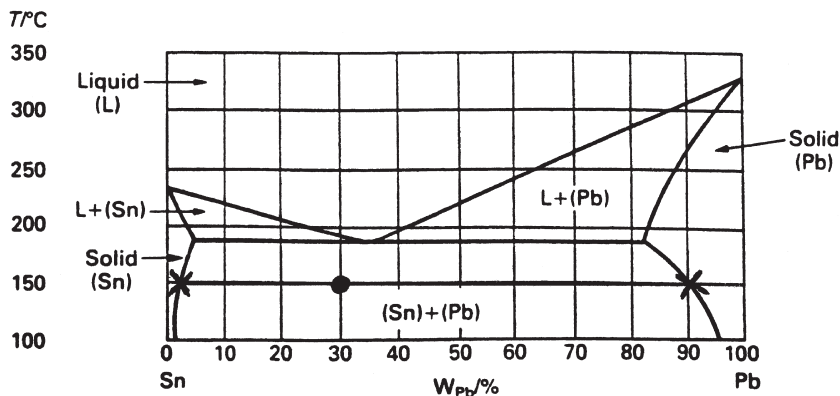


Figure H3.10. Pb–Sn phase diagram, showing a tie-line.

Composition of phase 1: _____

Composition of phase 2: _____

- (b) The alloy is slowly cooled to 200°C . At this temperature, identify the:

Phases: _____

Composition of phase 1: _____

Composition of phase 2: _____

- (c) The alloy is cooled further to 150°C . At this temperature, identify the:

Phases: _____

Composition of phase 1: _____

Composition of phase 2: _____

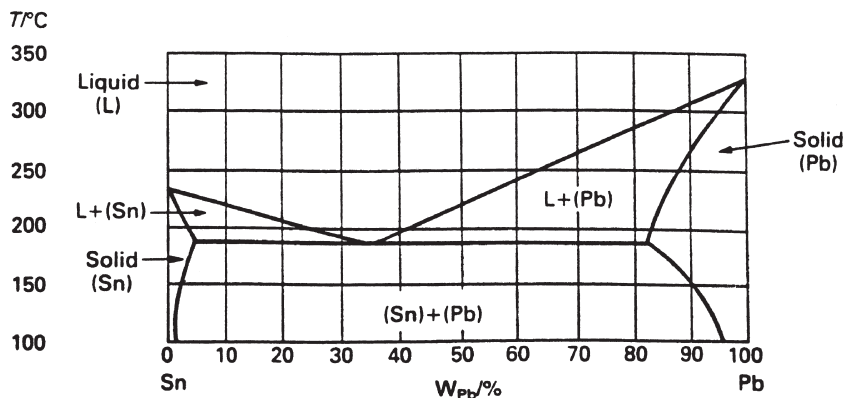


Figure H3.11. Pb–Sn phase diagram.

(d) Indicate with arrows on the figure the lines along which:

- (1) The composition of phase 1 moves
- (2) The composition of phase 2 moves

The overall composition of the alloy stays the same, of course. How do you think the compositions of the phases change? -----

H3.3.4 Proportions of phases in two-phase alloys

The relative amounts of each phase in a two-phase region can be found from the phase diagram. Consider a field containing the two phases α and β (single phases are often designated by Greek symbols, rather than by element names in brackets). If the weight fraction of phase α is W_α , then it is obvious that in a binary alloy the weight fraction of β , W_β , must be $(1 - W_\alpha)$. Note that there is not an equivalent result for the atomic (or mol) fraction of a phase. This is because a phase does not have an atomic weight (unlike a pure element, or a chemical compound of specific composition).

Consider Sn–80 wt% Pb at 250°C (figure H3.12). This constitution point falls in a two-phase region: liquid plus Pb-rich solid.

To find the proportions of each phase, we start by constructing a tie-line through the constitution point and read off the compositions of the phases:

Liquid with $W_{\text{Pb}}^{\text{LIQ}} = 64\%$; Solid with $W_{\text{Pb}}^{\text{SOL}} = 87\%$

The tie-line is of length l , while the segments of the line to either side of the constitution point are a and b , respectively (figure H3.12). The weight fractions of each phase, W_{LIQ} and W_{SOL} , are fixed by the requirement that matter is conserved. Then the weight fraction of solid in the alloy is given by the ‘lever rule’:

$$W_{\text{SOL}} = \frac{a}{l} \text{ and the weight fraction of liquid is } W_{\text{LIQ}} = \frac{b}{l}$$

Note that $W_{\text{LIQ}} + W_{\text{SOL}} = 1$

The easiest way to interpret this rule is to notice that, if the constitution point coincides with the left-hand X (the left end of the tie-line) the alloy is all liquid; and when it coincides with the right-hand X it is all solid; then provided the phase diagram has a linear weight scale, the weight fraction of each phase is

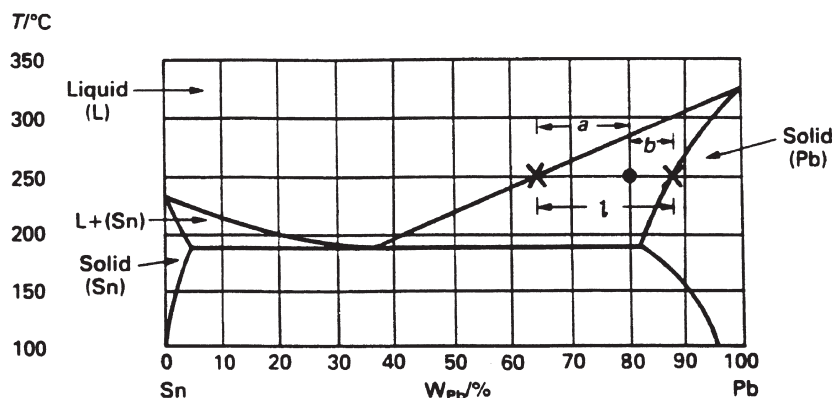


Figure H3.12. Pb–Sn phase diagram, illustrating the lower rule.

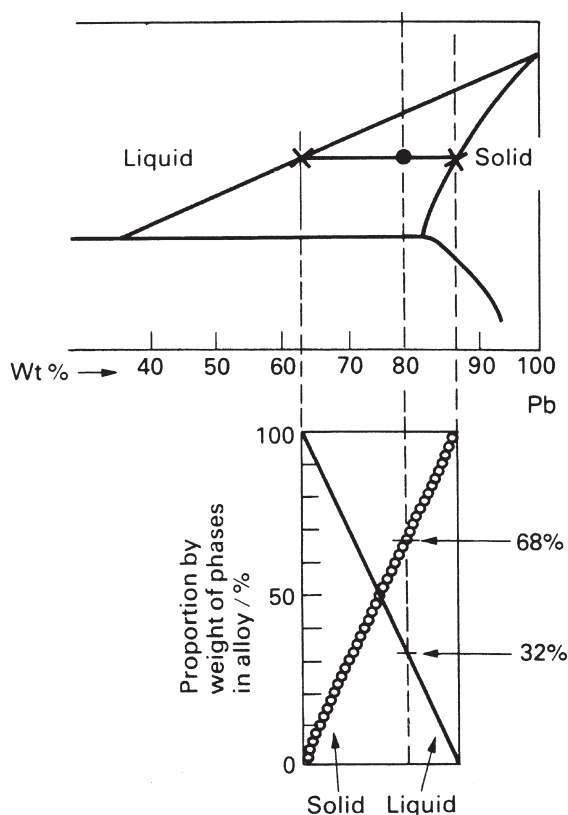


Figure H3.13. The lever rule for finding the phase proportions in a two-phase field.

proportional to the distance measured along the tie-line, as a fraction of the total length of the tie-line. Figure H3.13 shows how this relates to our example of an 80 wt% Pb alloy. The weight percentages of other alloys along the tie-line can be found in exactly the same way. The results can be calculated by reading off the three compositions (for the alloy, and the two ends of the tie-line) and applying the rule. Alternatively and more approximately, the lengths can be measured directly from the phase diagram.

H3.3.5 Phase diagrams with at.% scales

Phase diagrams may also be plotted showing the composition as a linear at.% scale. In these diagrams it is common to add the corresponding (non-linear) wt% scale along the top. Figure H3.14 shows the Pb–Sn phase diagram re-plotted in this way.

Note that as the wt% scale is not linear then the values of l , a and b cannot be measured directly from the diagram, but must first be evaluated from the three compositions by reading from the non-linear wt% scale:

$$l = W_{\text{Pb}}^{\text{SOL}} - W_{\text{Pb}}^{\text{LIQ}}$$

$$a = W_{\text{Pb}} - W_{\text{Pb}}^{\text{LIQ}}$$

$$b = W_{\text{Pb}}^{\text{SOL}} - W_{\text{Pb}}$$

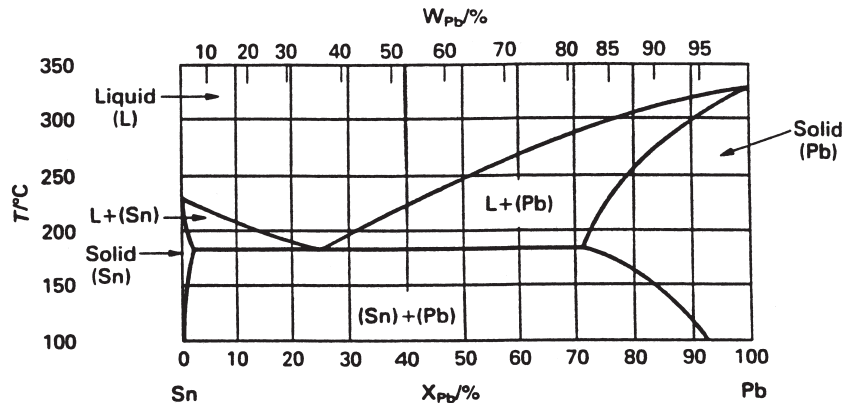


Figure H3.14. The Pb–Sn phase diagram with a linear at. % scale.

where $W_{\text{Pb}}^{\text{SOL}}$ is the percentage of lead in the solid and $W_{\text{Pb}}^{\text{LIQ}}$ in the liquid. The weight fractions may then be calculated from the lever rule.

Questions

Use the Pb–Sn phase diagram in figure H3.15 to answer the following questions.

H3.3.3 Pb–Sn alloy with composition $W_{\text{Pb}} = 80\%$ is held at a temperature T .

- At $T = 280^\circ\text{C}$ which is the dominant phase? _____
- At $T = 200^\circ\text{C}$ which is the dominant phase? _____
Indicate by arrows on the figure the changes in the compositions of the liquid phase and the solid phase as the alloy is cooled from 280° to 200°C .

H3.3.4 The alloy is cooled to 150°C .

- How many phases are present? _____
- Give the approximate composition of the phase(s) _____

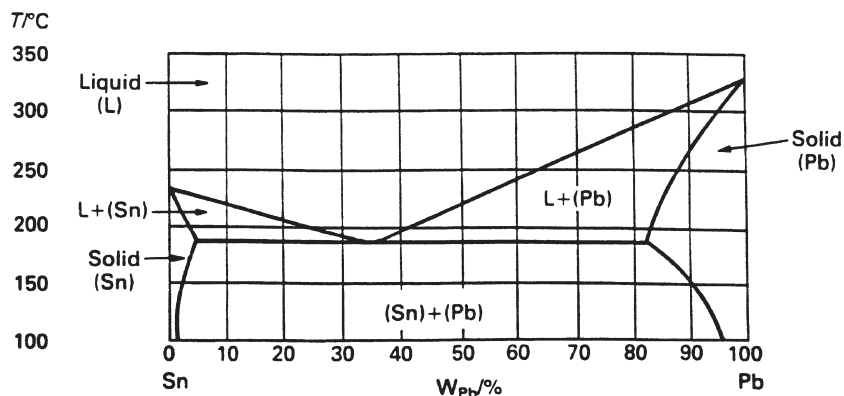


Figure H3.15. Pb–Sn phase diagram.

- (c) Which is the dominant phase? _____
- (d) What (roughly) are the proportions by weight of each phase? _____

H3.3.6 Other forms of binary phase diagram

The form of phase diagram examined so far, that of the Pb–Sn system, is found in many alloy systems, but many are more complicated. In the remainder of section H3.3 we look at some other important forms and features of binary phase diagrams. All the rules for describing the constitution of the alloy continue to apply however.

H3.3.7 Intermediate phases

Many systems show intermediate phases: compounds which form between components. Examples are CuAl_2 , Al_3Ni and Fe_3C . If the components are both metallic, they are called intermetallic compounds. Note that the at.% of the components in an intermediate compound can be stated by inspection, e.g. Fe_3C contains 25 at.% C. These specific compositions have unique melting points and as the composition moves away from the correct proportions the melting point usually falls. They, therefore, behave like pure elements, and eutectics can form between the compound and a solid solution: CuAl_2 and (Al) for example. The eutectic point is always the apex of the more or less shallow V formed by the liquidus lines.

Figure H3.16. shows the rather unusual silver—strontium phase diagram.

This system has four intermetallic compounds. Note that it is just five simple phase diagrams (like the Pb–Sn diagram) stuck together: the Ag– SrAg_5 diagram, the SrAg_5 – Sr_3Ag_5 diagram and so on. Each has a eutectic. Diagrams including intermediate phases can usually be dissected in this way. Note also that as the composition is varied at a given temperature, all the two-phase fields are still separated by a single-phase field, but in this case the field has collapsed to a unique composition. In some systems, the intermediate phases do have some limited solubility for a little more or less of one component. The single-phase field then appears as a tall thin region aligned above the exact stoichiometric composition for the compound.

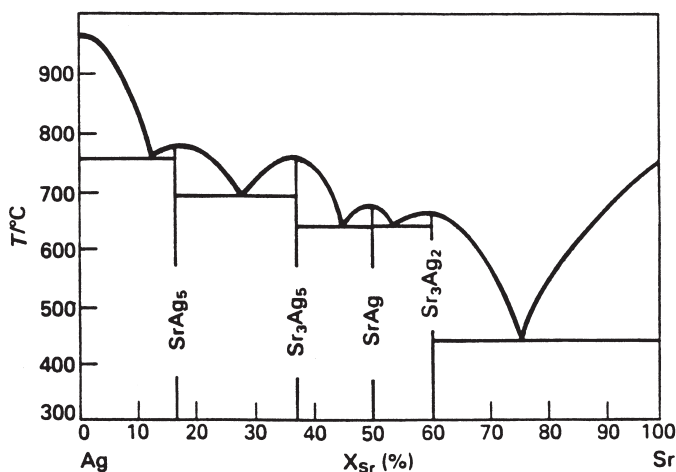


Figure H3.16. The Ag–Sn phase diagram.

Question

H3.3.5 The three phase diagrams (or parts of diagrams) in figure H3.17 have a eutectic point.

- (a) Mark the eutectic point on each figure and list the eutectic temperature and composition in at.% in each case.

Cu–Al: _____

Al–Si: _____

Cr–Ni: _____

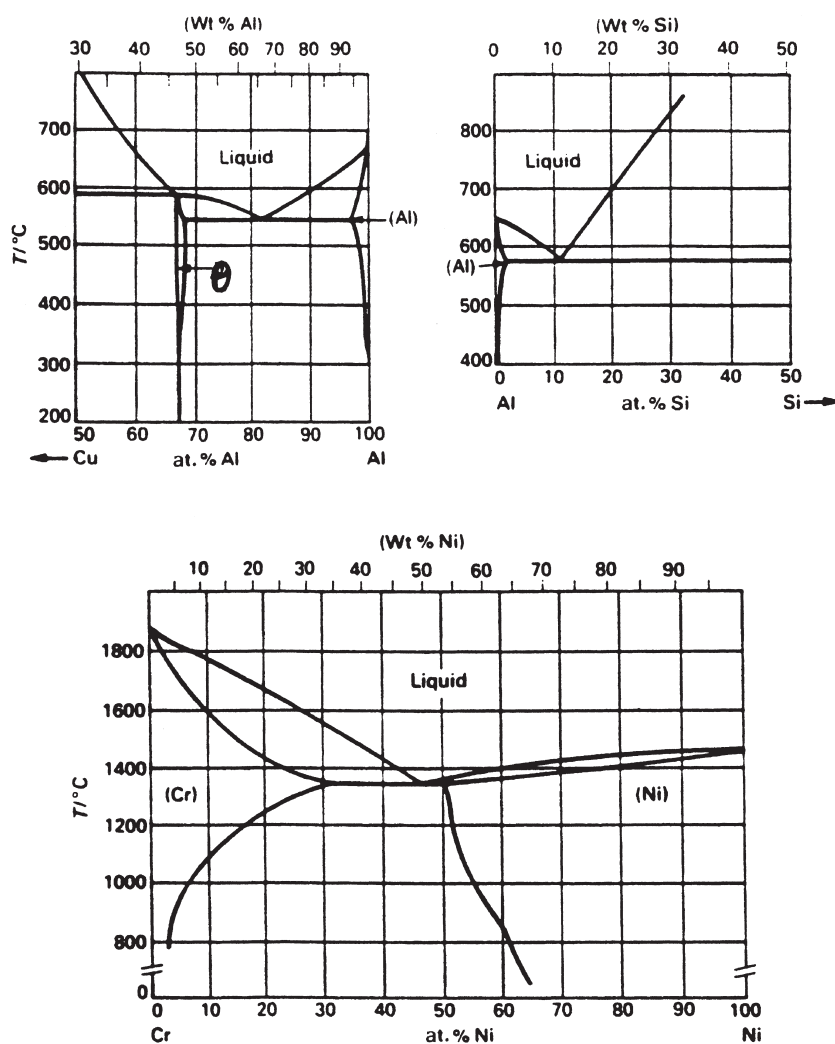


Figure H3.17. Phase diagrams (or partial diagrams) for the Cu–Al, Al–Si and Cr–Ni systems.

- (b) In the Cu–Al system, identify a single-phase field corresponding to an intermetallic compound. What is the compound? -----

H3.3.8 The iron–carbon system and eutectoids

The iron–carbon phase diagram is important in engineering as it provides the basis for understanding all carbon steels and their heat treatment. Here, we introduce the diagram itself and use it to illustrate another feature found on many phase diagrams—a eutectoid point. Figure H3.18 shows the important part of the Fe–C system, covering all carbon steels and cast irons, up to 6.7 wt% carbon (corresponding to Fe_3C with 25 at.% C, as C is a much lighter element than Fe). The phases are:

Ferrite: α -iron (bcc) with up to 0.035 wt% C dissolved in solid solution.

Austenite: γ -iron (fcc) with up to 1.7 wt% C dissolved in solid solution.

δ -iron: (bcc) with up to 0.08 wt% C dissolved in solid solution.

Cementite: Fe_3C , a compound, at the right-hand edge of the diagram.

Ferrite (or α) is the low temperature form of iron. On heating pure iron changes to austenite (or γ) at 914°C and switches from a bcc lattice to a fcc lattice. This change in crystal structure again takes place for thermodynamic reasons. Pure austenite is stable up to 1391°C, when it changes back to another bcc structure, δ -iron, before melting at 1530°C.

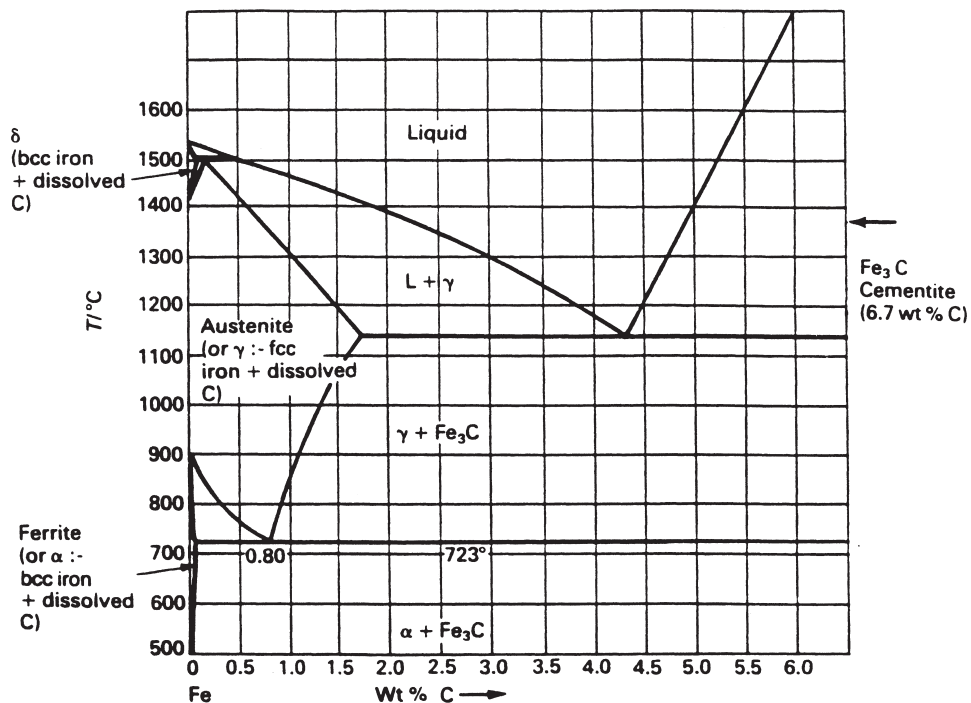


Figure H3.18. The Fe-rich end of the Fe–C phase diagram.

The phase diagram shows that the addition of C changes the temperatures of these transitions, stabilizing γ over a wider temperature interval. Note also that the solubility of C in the fcc lattice of austenite is very much greater than in either of the bcc lattices (α or δ). This reflects the fact that C dissolves interstitially in iron (being a much smaller atom) and the interstitial spaces are larger in fcc lattices than bcc (which in turn means a lower energy penalty in dissolving C in fcc Fe). The great difference in solubility of C in Fe between high and low temperatures is the basis of the excellent response of carbon steels to heat treatment to improve the yield properties. Carbon is first dissolved in austenite at high temperature, then trapped in a super-saturated solid solution by quenching. This is followed by tempering which causes the hard iron carbide phase to form in a fine dispersion. The final microstructure contains the equilibrium phases, but finely dispersed to provide much more effective strengthening than would result from slow cooling. In passing this makes an important point—knowing the proportions of two phases tells us nothing about the properties, which also depends critically on how the phases are dispersed microscopically.

The iron–carbon system has a eutectic: find it and mark it on the diagram. If we now look at the bottom of the austenite field, we see that this too closes in a shallow V with a single-phase field (austenite) bordered by two-phase fields. This feature of the diagram, therefore, resembles a eutectic, but with the single liquid phase replaced with a single solid phase (austenite, or γ). Such a feature on a phase diagram is called a eutectoid point. Figure H3.19 shows schematics of eutectics and eutectoids, for comparison.

H3.3.9 Peritectics and peritectoids

Eutectics and eutectoids look like a shallow V enclosing a single-phase field resting on a horizontal line above a two-phase field (as in figure H3.19). Many phase diagrams show features which look exactly the same, but inverted: an upside-down V enclosing a single solid phase, touching a horizontal line. Figure H3.20 shows two schematics of such features on phase diagrams.

In the left-hand diagram, the two-phase field above the inverted V contains one liquid phase and one solid phase: the tip of the V is then called a peritectic point; in the right-hand diagram, the two-phase field above the inverted V contains two solid phases: in this case the point is called a peritectoid point.

Compared to eutectics and eutectoids, peritectics and peritectoids are of less engineering significance. They are included partly for completeness, and also to avoid being confused with other features of the phase diagram.

Questions: section H3.3

H3.3.6 Examine the phase diagram for the Fe–C system (figure H3.18). Is the point at the top of the austenite field a peritectic or a peritectoid? _____

Why? _____

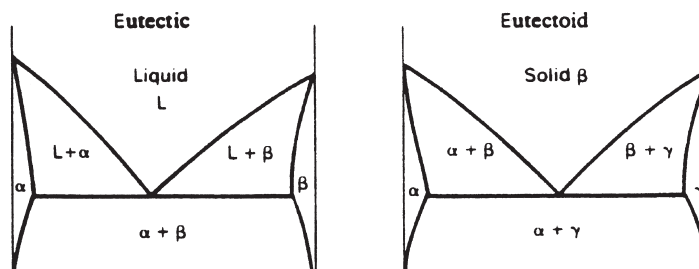


Figure H3.19. Eutectic and eutectoid points.

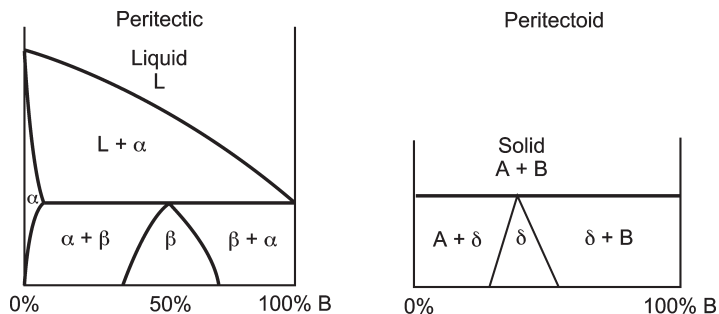


Figure H3.20. Peritectic and peritectoid points.

H3.3.7 The phase diagram for the copper–zinc system (which includes brasses) is shown in figure H3.21. Use the diagram to answer the following questions.

- (a) The copper–zinc system has one eutectoid point, and five peritectic points.

Write down the composition and temperature of all six points.

Eutectoid: _____

Peritectics: (1) _____ (2) _____ (3) _____
(4) _____ (5) _____

- (b) The two common commercial brasses are:

70/30 brass : $W_{\text{Cu}} = 70\%$

60/40 brass : $W_{\text{Cu}} = 60\%$

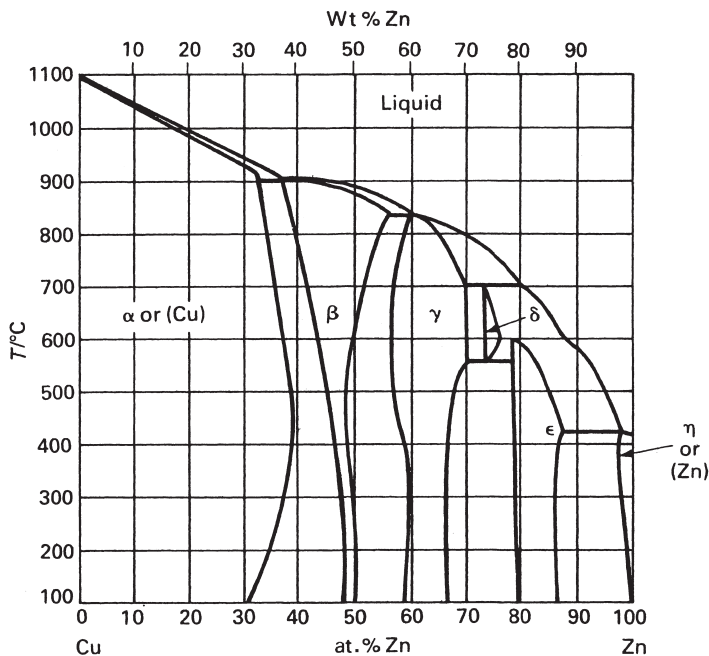


Figure H3.21. Cu–Zn phase diagram.

Locate their constitution points on the diagram at 200°C

What distinguishes the two alloys? _____

What roughly is the melting point of 70/30 brass? _____

What are the phase(s) in 60/40 brass at 200°C? _____

Give the approximate phase composition(s): _____

Estimate approximately the proportions of each phase: _____

H3.3.8 The copper–tin system (which includes bronzes) is shown in figure H3.22.

Write down the composition and temperature of the four eutectoids in this system.

Eutectoids: (1) _____ (2) _____
(3) _____ (4) _____

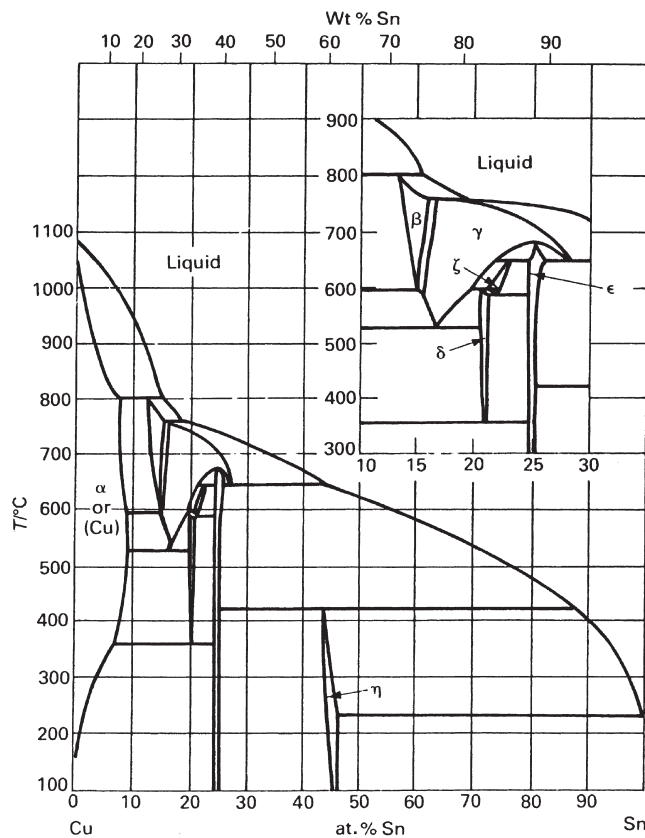


Figure H3.22. Cu–Sn phase diagram.

Answers to questions: section H3.3

H3.3.1 (a) 60 wt% Pb, 40 wt% Sn, 300°C.

(b) See figure H3.23.

A: Pb–70 wt% Sn: Liquid

B: Pb–20 wt% Sn: Liquid, plus Pb-rich solid (Pb)

(c) 240°C, 183°C.

At point 2: liquid, plus Pb-rich solid, (Pb).

At point 3: two solids, Sn-rich (Sn) and Pb-rich (Pb).

(d) $W_{\text{Pb}} = 90\%$, $T = 200^\circ\text{C}$.

Pb-rich solid (Pb).

150°C.

Pb-rich solid (Pb) and Sn-rich solid (Sn).

H3.3.2 (a) Liquid plus Pb-rich solid (Pb) at 250°C

$W_{\text{Pb}} = 63\%$ in the liquid

$W_{\text{Pb}} = 88\%$ in the solid

(b) Liquid plus Pb-rich solid (Pb) at 200°C

$W_{\text{Pb}} = 42\%$ in the liquid

$W_{\text{Pb}} = 82\%$ in the solid

(c) Sn-rich solid (Sn) plus Pb-rich solid (Pb) at 150°C

$W_{\text{Pb}} = 2\%$ in the Sn-rich solid

$W_{\text{Pb}} = 91\%$ in the Pb-rich solid

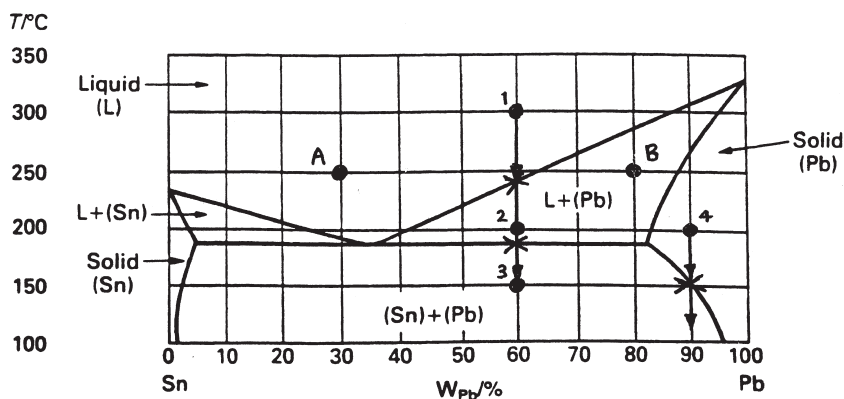


Figure H3.23. Pb–Sn phase diagram.

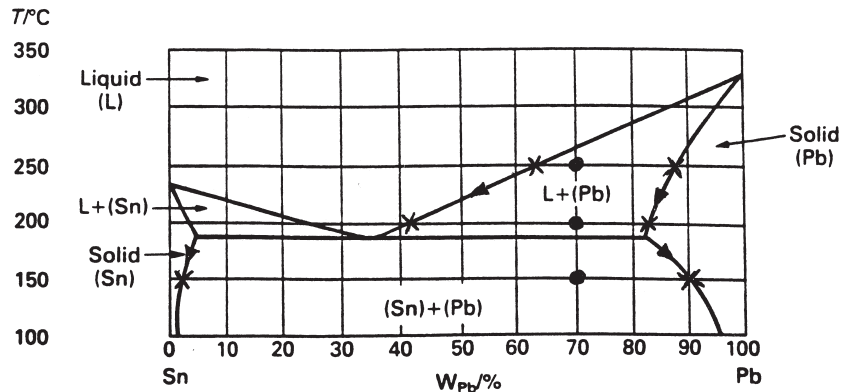


Figure H3.24. Pb–Sn phase diagram.

- (d) See figure H3.24. To maintain the same overall alloy composition, changes in the compositions of the phases are accompanied by changes in their relative proportions. The adjustments in the proportions of the phases and of their compositions, take place by diffusion.

H3.3.3 (a) Liquid; (b) Solid (Pb-rich); See figure H3.25.

H3.3.4 (a) 2.

(b) $W_{\text{Pb}} = 2\%$, $W_{\text{Pb}} = 90\%$.

(c) The Pb-rich solid.

(d) Sn-rich solid 11% of total weight.

Pb-rich solid 89% of total weight (see figure H3.25).

H3.3.5 (a) See figure H3.26.

Eutectics are:

Cu–Al: 550°C, 82 at.% Al

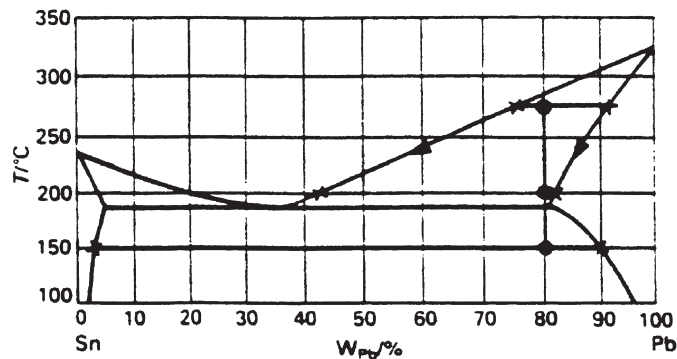


Figure H3.25. Pb–Sn phase diagram.

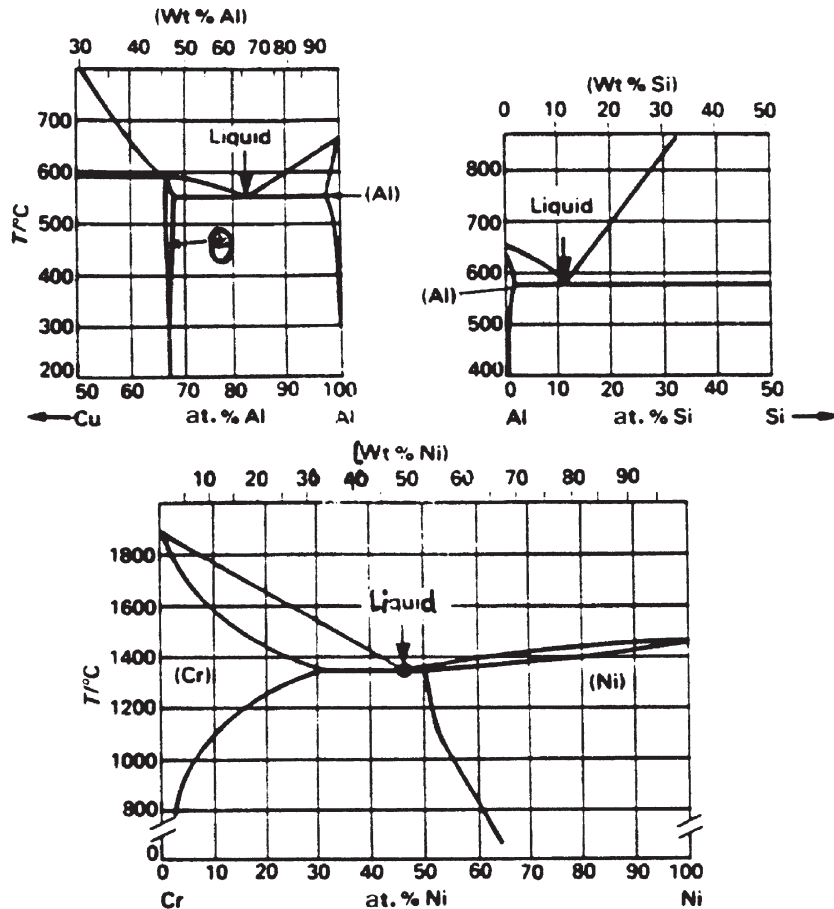


Figure H3.26. Phase diagrams (or partial diagrams) for the Cu–Al, Al–Si and Cr–Ni systems.

Al–Si: 580°C, 11 at.% Si

Cr–Ni: 1350°C, 47 at.% Ni

- (b) Intermetallic compound is CuAl_2 (66 at.% Al). This is an example of a compound which can dissolve some excess Al, as the right-hand phase boundary of the θ -field moves off-vertical towards higher % Al in the phase as the temperature increases. The left-hand boundary remains essentially vertical so excess Cu cannot be accommodated.

H3.3.6 Peritectic—the two phase field above includes a liquid phase.

H3.3.7 (a) See figure H3.27.

Eutectoid at: $X_{\text{Zn}} = 73\%$, $T = 555^\circ\text{C}$

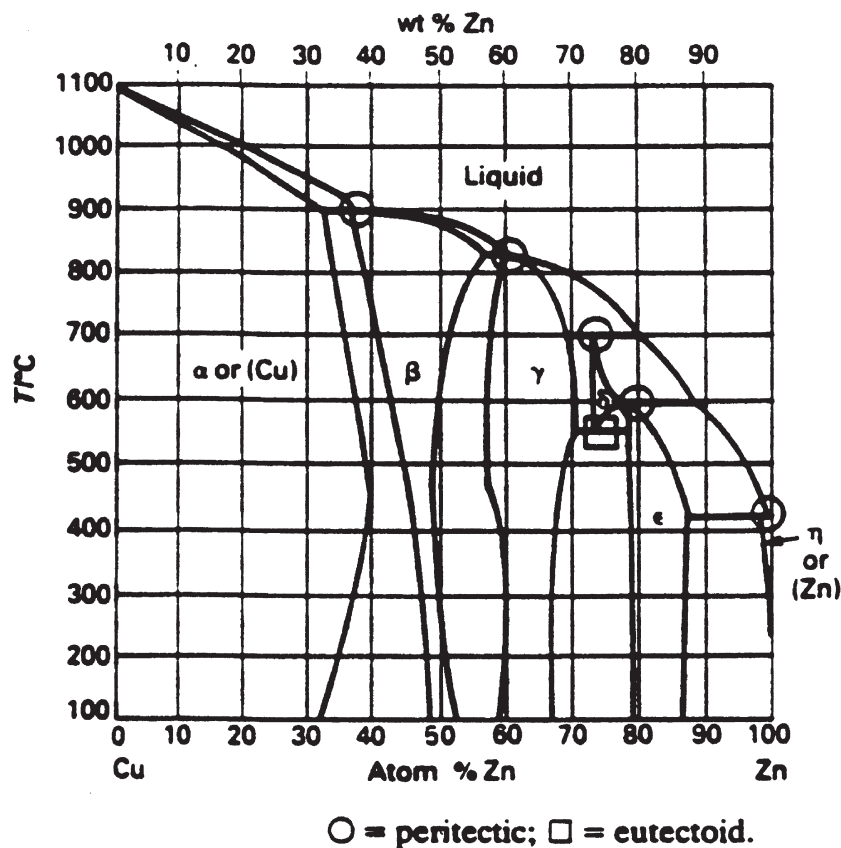


Figure H3.27. Cu–Zn phase diagram.

Peritectics at: (1) $X_{\text{Zn}} = 37\%$, $T = 900^\circ\text{C}$; (2) $X_{\text{Zn}} = 60\%$, $T = 825^\circ\text{C}$; (3) $X_{\text{Zn}} = 73\%$, $T = 700^\circ\text{C}$; (4) $X_{\text{Zn}} = 79\%$, $T = 600^\circ\text{C}$; (5) $X_{\text{Zn}} = 99\%$, $T = 420^\circ\text{C}$.

(b) 70/30 brass is single-phase, but 60/40 brass is two-phase.

70/30 brass starts to melt at 920°C and is completely liquid at 950°C .

At 200°C : α (copper-rich solid) and β (roughly CuZn).

$W_{\text{Zn}} \approx 33\%$, $W_{\text{Zn}} \approx 48\%$

Very roughly, 50–50; more precisely: $\frac{\text{wt\% of } \alpha}{\text{wt\% of } \beta} = \frac{48 - 40}{40 - 33} = \frac{8}{7}$

H3.3.8 See figure H3.28

Eutectoids at: (1) $X_{\text{Sn}} = 15\%$, $T = 590^\circ\text{C}$; (2) $X_{\text{Sn}} = 17\%$, $T = 515^\circ\text{C}$;
(3) $X_{\text{Sn}} = 20\%$, $T = 340^\circ\text{C}$; (4) $X_{\text{Sn}} = 22\%$, $T = 580^\circ\text{C}$.

H3.4 Phase transformations and microstructures

You should now be able to read most of the important features of phase diagrams, and state the proportions of phases found at equilibrium at a given temperature and composition. The purpose of this

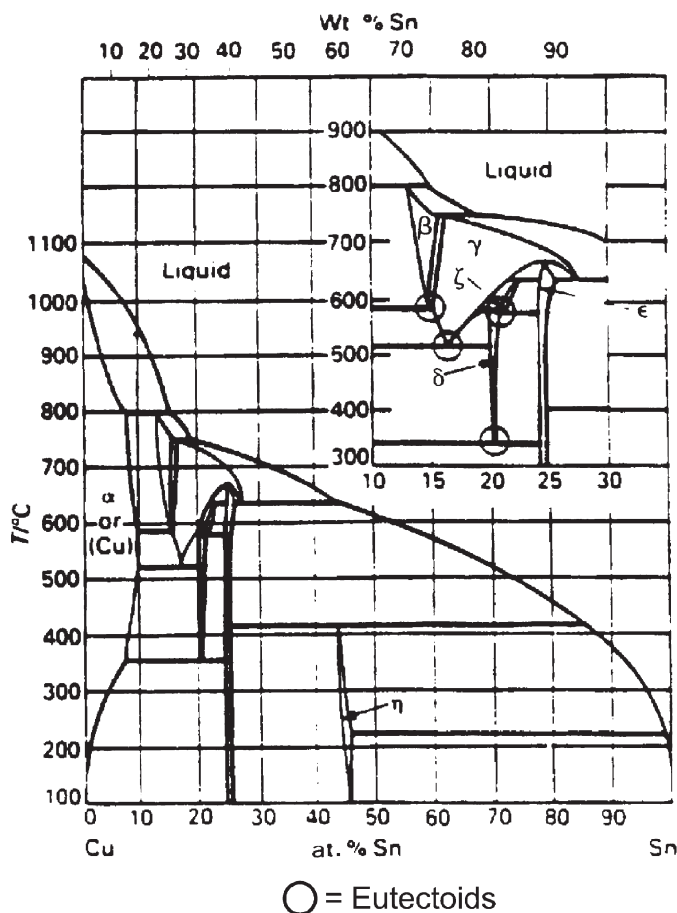


Figure H3.28. Cu–Sn phase diagram.

section is to begin to connect this fundamental understanding of phase diagrams to real industrial processes.

Almost all manufacturing processes involve some combination of heating and cooling. For example, casting is filling a mould with molten metal, which solidifies and cools; rolling reduces the thickness of metal sheets in many steps, with the temperature steadily falling; welding causes a thermal cycle of heating followed by cooling; and often the last stage of manufacture is a separate heat treatment, of the whole component or just its surface. When the temperature varies in a process, then the equilibrium condition of the material keeps changing (e.g. as boundaries on the phase diagram are crossed)—hence phase transformations take place. These transformations determine which phases are present after processing, and how they are distributed amongst one another—that is, the final microstructure. This in turn controls the material properties.

Phase diagrams give some (but certainly not all) of the information needed to predict the phase transformations and final microstructure which result from a given thermal history. As phase diagrams are equilibrium diagrams, we start by looking at very slow cooling when it is reasonable to assume that the structure can always evolve to maintain equilibrium.

H3.4.1 Solidification of pure metals

Observing phase transformations

Figure H3.29 shows the phases found in pure iron along a temperature axis. At 1 atm iron melts at 1536°C and boils at 2860°C. If we start with iron vapour and cool slowly, then the temperature as a function of time shows two shelves in the cooling curve, called arrest points, at the boiling and melting points. At each of these temperatures there is a phase change: vapour to liquid at the boiling point, and liquid to solid at the melting point. When a phase transformation takes place, the latent heat of the transformation is released (on cooling), or absorbed (on heating). As a result, the temperature remains effectively constant during the transformation until the phase change is complete.

Alloys frequently solidify over a range of temperature (between the liquidus and solidus lines). In this case, the latent heat is released progressively as the temperature falls across the solid plus liquid region of the phase diagram. The cooling curve does not therefore show a shelf at constant temperature, but a fall in the cooling rate for the time that latent heat is being released.

As noted in the iron–carbon phase diagram in section H3.3, iron solidifies initially to bcc δ -iron and on further cooling transforms to fcc γ -iron at 1391°C and back again to bcc α -iron at 914°C. Note that these solid–solid phase transformations also release latent heat, but the amount is much smaller. It can be detected with sensitive equipment for recording temperature. Indirect observation of phase changes by this technique is an important part of the experimental determination of phase diagrams. It is worth noting that as it is impossible to observe microstructures directly at high temperature with conventional microscopes, other methods are required to infer what is going on. Greater accuracy is possible with differential thermal analysis (DTA): a sample with the same thermal mass as the test sample, but showing no phase transformations, is cooled (or heated) with the test sample. The difference ΔT between the temperature–time curves is amplified and plotted to reveal the phase change temperatures. Other ‘remote sensing’ techniques for monitoring phase transformations include precision density measurement or dilatometry and *in situ* X-ray crystallography.

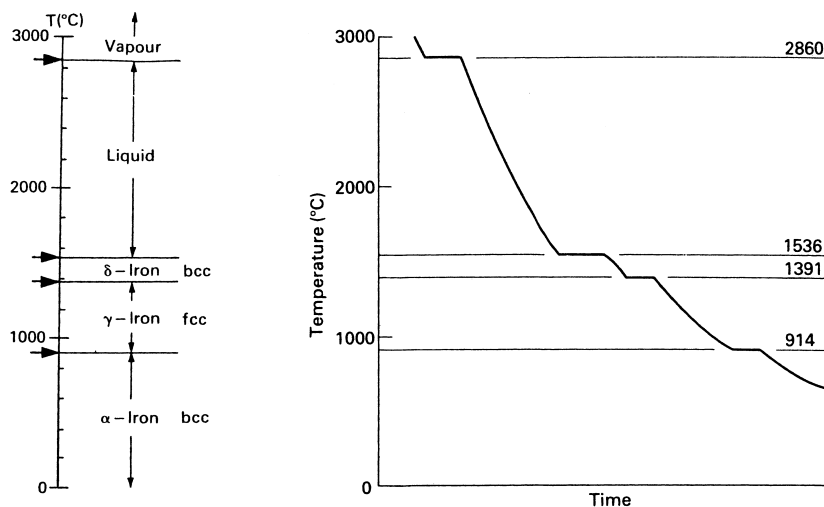


Figure H3.29. The phases in pure iron, and a schematic cooling curve for pure iron.

Microstructures on cooling of pure metals

When liquids solidify, the process is triggered by the formation of a *nucleus*: a small region of solid which forms, either spontaneously, or more commonly on the surface of the solid containing the melt (the mould wall). Atoms then transfer across the solid–liquid interface and the solid nucleus grows, consuming the liquid. Many such nuclei will form when the melting point is reached and each will grow with its own crystal orientation. When two growing colonies impinge, a grain boundary is formed, and eventually all the liquid has transformed to solid. The shape of the grains depends on all sorts of details of where the nuclei occur and the direction of the heat flow which removes the latent heat from the system, but this need not concern us here. If nuclei form randomly throughout the melt, then the final structure is roughly equiaxed—and a polished section has the appearance shown in figure H3.30.

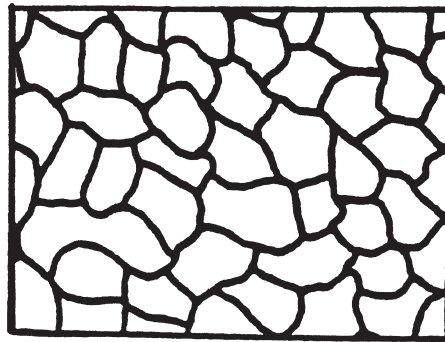


Figure H3.30. Schematic view of grain structure in a polished section.

Pure iron also shows a solid–solid phase change. This too occurs by a process of nucleation and growth. The nuclei of the new phase form on the grain boundaries of the one being replaced. Atoms transfer across the phase boundary by diffusion, adopting the structure of the growing phase as they do so. Figure H3.31 shows the solid–solid transformation underway in pure iron at 914°C, with about 20% of the γ -iron transformed to α -iron. The arrows show the direction of migration of the interfaces, which actually move by millions of sequential atomic jumps in the opposite direction. When the growing α colonies impinge, the new α – α grain boundaries are formed.

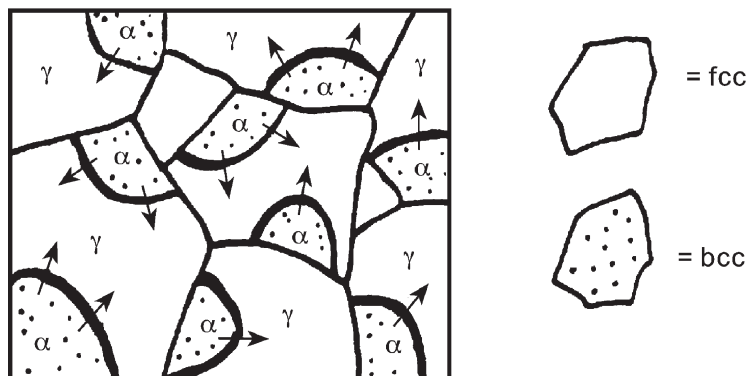


Figure H3.31. Schematic view of the γ – α transformation underway in pure Fe.

This solid–solid transformation also takes place in steel and is used commercially for grain refinement. Each old grain nucleates more than one new grain, so the grain size reduces. This is an important heat treatment as it is the only one which can simultaneously increase both yield strength and toughness.

The mechanisms of transformation described so far should give you a hint of how important cooling rate can be in controlling phase transformations. Since the mechanisms involve *diffusion*, the time which the sample spends at a given temperature is critical in determining how closely the phase change can ‘keep up’ with equilibrium. In real processes, therefore, we need to consider not only equilibrium phase changes, but also the *rate of transformation*—which is determined not only by the thermodynamic driving force but also by the kinetics of diffusion.

H3.4.2 Solidification of dilute alloys

When an alloy is cooled the constitution point for the alloy drops vertically on the phase diagram. In a single phase field, the composition of the phase is, of course, that of the alloy. In a two-phase region the compositions of the two phases are given by the ends of the tie-line through the constitution point section H3.3. In general, as the constitution point falls vertically, the ends of the tie-line do not—instead they run along the phase boundaries. The compositions of the two phases then change with temperature.

Definition When the compositions of the phases change with temperature, we say that a phase reaction takes place.

Cooling without a phase reaction therefore occurs:

- (a) in a single-phase field;
- (b) in a two-phase field, when both phase boundaries on either side of the constitution point are vertical.

Cooling with a phase reaction occurs when the constitution point lies in a two-phase region, and at least one of the phase boundaries is not vertical. Figure H3.32 shows the cooling of a lead–tin alloy with $X_{\text{Pb}} = 80$ at. %.

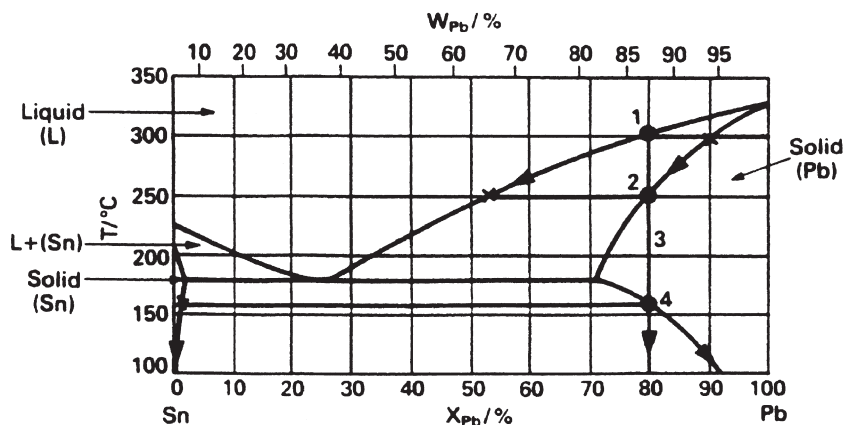


Figure H3.32. Pb–Sn phase diagram.

On cooling from 350°C the following regimes appear:

- (a) From 350 to 305°C. Single-phase liquid; no phase reaction.
- (b) From 305 to 255°C. The liquidus line is reached at 305°C; the reaction liquid \rightarrow solid (Pb-rich solid solution) starts. The solid contains less tin than the liquid (see first tie-line), so the liquid becomes richer in tin and the composition of the liquid moves down the liquidus line as shown by the arrow. The composition of the solid in equilibrium with this liquid also changes, becoming richer in tin also, as shown by the arrow on the solidus line: a phase reaction is taking place. The proportion of liquid changes from 100% (first tie-line) to 0% (second tie-line).
- (c) From 255 to 160°C. Single-phase solid, with composition identical to that of the alloy; no phase reaction.
- (d) From 160°C to room temperature. The lead-rich phase becomes unstable when the phase boundary at 160°C is crossed. It breaks down into two solid phases, with compositions given by the ends of the tie-line through point 4. On further cooling, the composition of the two solid phases changes as shown by the arrows: each dissolves less of the other. A phase reaction takes place. The proportion of each phase is given by the lever rule. The compositions of each are read directly from the diagram (the ends of the tie lines).

How does the microstructure evolve throughout this sequence? And what is the mechanism by which the solid Pb-rich phase breaks down into two solid phases? Figure H3.33 shows schematics of the structure which emerges as the temperature falls. Between points 1 and 2, isolated colonies of Pb-rich solid are shown surrounded by liquid; between points 2 and 4 single-phase Pb-rich solid exists, so only a grain structure is indicated; below point 4, a small proportion of Sn-rich solid has separated out from a surrounding matrix of Pb-rich solid, in the form of many small particles, known as a precipitate.

The mechanism of formation of this precipitate is again one of nucleation and growth, but on a much finer scale than the grain structure. Small clusters of Sn-rich solid nucleate spontaneously within the Pb-rich matrix. The fraction of this phase increases as the nuclei grow, by depleting the surrounding matrix of some of its Sn. The compositions of the phases (particles and matrix) continually adjust by inter-diffusion of Pb and Sn atoms.

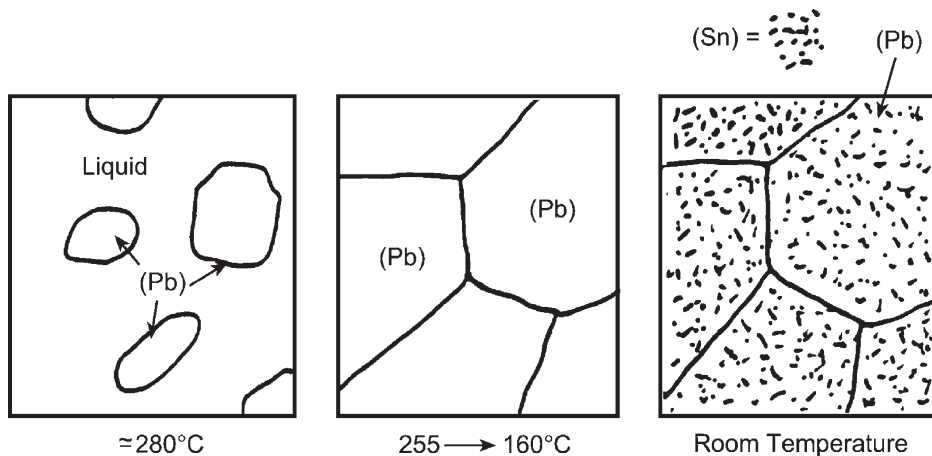
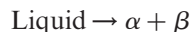


Figure H3.33. Schematic diagrams of the microstructures formed on cooling of a Pb–Sn alloy ($X_{\text{Pb}} = 80$ at. %).

H3.4.3 Eutectic solidification

Consider now the cooling of an alloy with 50 at.% lead. Starting from 300°C, the regions are shown in figure H3.34.

- From 300 to 245°C. Single-phase liquid; no phase reactions.
- From 245 to 183°C. The liquidus is reached at 245°C, and solid (a lead-rich solid solution) first appears. The composition of the liquid moves along the liquidus line, that of the solid along the solidus line. This regime ends when the temperature reaches 183°C. Note that the alloy composition in weight % (64) is roughly half way between that of the solid (81 wt%) and liquid (38 wt%); so the alloy is about half liquid, half solid, by weight.
- At 183°C. The liquid composition has reached the eutectic point (the bottom of the V). This is the lowest temperature at which liquid is stable. At this temperature all the remaining liquid transforms to two solid phases: a tin-rich α phase, composition $X_{Pb} = 1.5\%$ and a lead-rich β phase, composition $X_{Pb} = 71\%$. This reaction:



at constant temperature is called a *eutectic reaction*.

Definition A eutectic reaction is a three-phase reaction by which, on cooling, a liquid transforms into two solid phases at the same time. It is a phase reaction, of course, but a special one. If the bottom of a liquid-phase field closes with a V, the bottom of the V is a eutectic point.

At the eutectic point the three phases are in equilibrium. The compositions of the two new phases are given by the ends of the line through the eutectic point.

- From 183°C to room temperature. In this two-phase region the compositions and proportions of the two solid phases are given by constructing the tie line and applying the lever rule, as illustrated. The compositions of the two phases change as the temperature decreases, following the phase boundaries, that is, a further phase reaction takes place. Note that the occurrence of a phase reaction does not always imply that a phase boundary is being crossed.

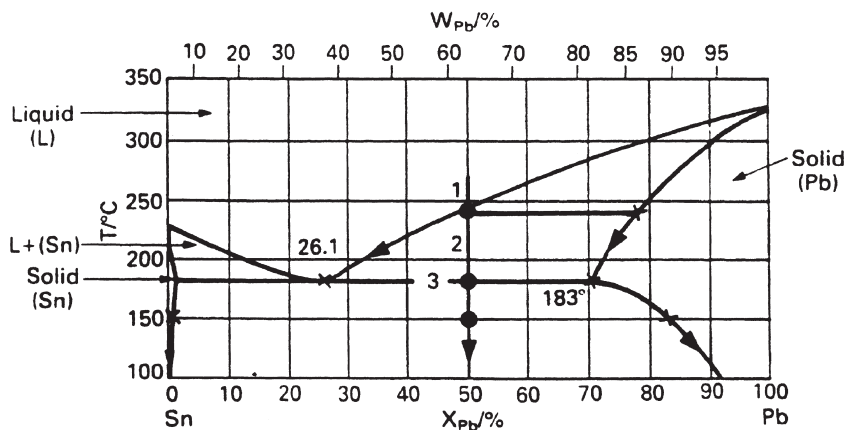


Figure H3.34. Pb–Sn phase diagram.

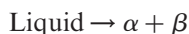
Eutectic compositions

What would happen if we took an alloy of eutectic composition? Look at the Pb–Sn phase diagram for $X_{\text{Pb}} = 26.1\%$. If we cool from the liquid, the first phase reaction to occur is at the eutectic point, at which time the whole volume transforms to two solids, (Pb) and (Sn). This behaviour is attractive for solders: on the one hand this composition has the lowest melting point of all Pb–Sn alloys (minimizing the heat input, and thereby limiting the damage to the components being soldered); in addition, the joint becomes fully solid very rapidly, giving it strength for handling.

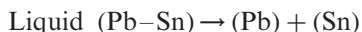
Questions

H3.4.1 Not all alloys in the Pb–Sn system show a eutectic, for example, pure lead, does not. Examine the Pb–Sn phase diagram and list the composition range for which you would expect a eutectic reaction to be possible.

H3.4.2 A eutectic reaction is a three-phase reaction by which, on cooling, a liquid transforms into two solids. In general, on cooling:



or, for the Pb–Sn system:



- (a) What happens on heating? _____
- (b) Over what temperature range do eutectics freeze or melt? _____

H3.4.4 Eutectic microstructure

The aluminium casting alloys are mostly based on the Al–Si system (figure H3.35). It is a classic eutectic system, with a eutectic point at about 11 at.% Si and 577°C.

Consider the cooling of an Al–6% Si casting alloy—illustrated by schematics in figure H3.36. The liquidus is reached at about 635°C, when solid (Al) starts to separate out (figure H3.36(a)). As the temperature falls further the liquid composition moves along the liquidus line and the amount of solid (Al) increases. When the eutectic temperature (577°C) is reached, about half the liquid has solidified (figure H3.36(b)). The solid that appears in this way is called primary solid, primary (Al) in this case.

At 577°C the eutectic reaction takes place: the liquid decomposes into solid (Al) mixed with solid Si, on a fine scale (figure H3.36(c)). This intimate mixture of secondary (Al) with secondary Si is the eutectic structure. In this system the Si has no solubility for Al, so the secondary Si is pure Si. Note that the primary (Al), which forms large grains, and the secondary (Al), which forms the matrix of the fine scale eutectic, are the same phase. So two-phase solids do not just consist of grains of the two phases, but in general the phases are distributed between grains of different microstructures.

On further cooling to room temperature the composition of the (Al) changes—it dissolves less silicon at the lower temperature. So silicon diffuses out of the (Al), and the amount of Si in the eutectic structure increases a little. The final structure still looks like figure H3.36(c).

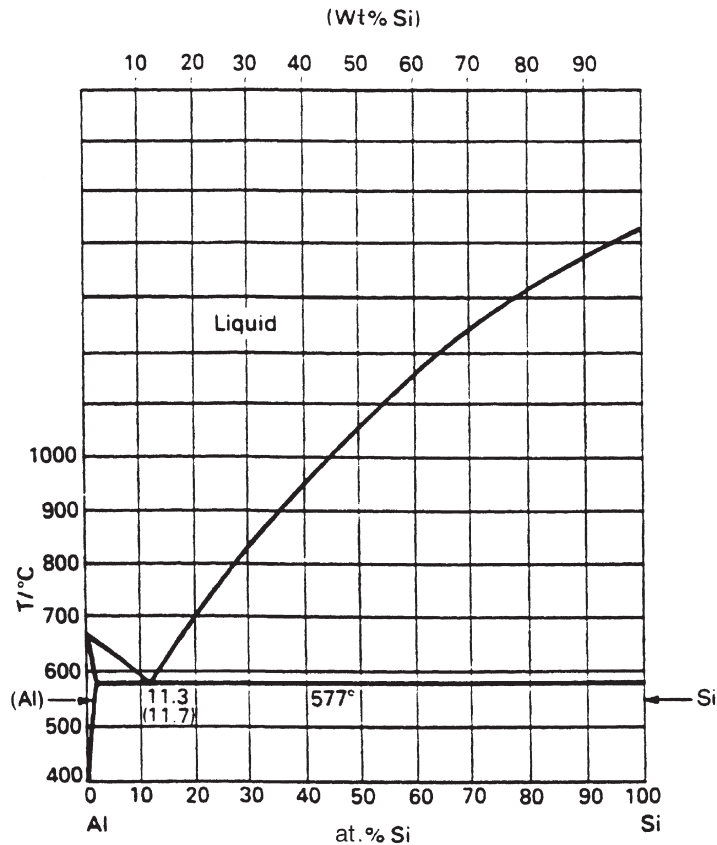


Figure H3.35. Al-Si phase diagram.

Surface energy and phase shape

Why is the eutectic structure a fine mix of the two phases? Thermodynamics dictates that these phases form, but there is an additional small driving force to minimize the surface area of interface between the two phases. This is because these interfaces have a surface energy, exactly analogous to the surface tension of a drop of liquid in contact with the air.

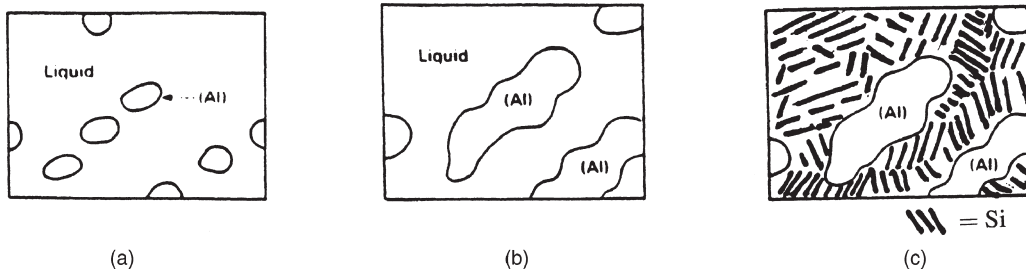


Figure H3.36. Schematic diagrams of the solidification of Al-6 % Si casting alloy.

Energetically, therefore, the optimum microstructure for two phases would appear to be very large spheres of one phase surrounded by the other. The reason that eutectics are not like this is that there has to be a mechanism for the eutectic reaction to take place. The mechanism involves diffusion (albeit relatively fast in a liquid), which limits the length scale on which atoms can move to separate out into two phases.

Hence the eutectic structure is efficient in dividing up the structure into two distinct compositions, but this occurs at a small energy penalty in terms of surface energy (i.e. it is not quite at true equilibrium). This energy can still be sufficient to cause further microstructural change if the temperature is high enough. The needles of Si in the (Al) matrix can coarsen, that is, the small ones re-dissolve bit by bit and the Si deposits onto the larger ones. This reduces the number of needles at constant volume fraction, and reduces the area of Si–(Al) interface per unit volume.

A further detail is that the surface energy depends on the crystallographic orientation between the phases: good crystal matching has a lower energy. Hence second phase particles tend to form plates or needles, rather than spheres, as this maximizes the surface area of low energy interface.

All this fine detail may seem unimportant, but many commercial heat treatments are specifically aimed at tuning the size, shape and spacing of the second phase particles in the microstructure. This is because the nature and spacing of the particles determines how difficult it is to push dislocations through the gaps between the particles. The yield strength, and the toughness, thus depend critically on the microstructure at this scale. It is also worth being aware that the structure and properties of a finished component are not necessarily static, but may continue to evolve (slowly) during the service life of the component. Frequently, this plays a role in component failure.

Question

- H3.4.3 Describe the solidification of an Al–20% Si alloy, and sketch the final microstructure. How would the microstructure of an Al–Si alloy of eutectic composition differ?

H3.4.5 Segregation

When solidification starts, either on the walls of a mould or spontaneously as nuclei throughout the melt, the first solid to form is purer in composition than the alloy itself (due to partition of the liquidus and solidus lines). Consider solidification of Pb–Sn containing $X_{\text{Pb}} = 80\%$. The first solid appears at 305°C and is primary (Pb) with a composition of about 90% Pb (see figure H3.37). This means that tin is *rejected* at the surface of the growing crystals and the liquid grows richer in tin: that is why the liquid

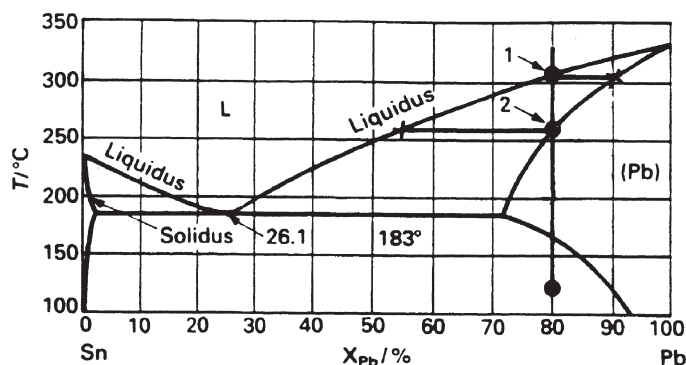


Figure H3.37. Pb–Sn phase diagram.

composition moves along the liquidus line. From 305 to 255°C the amount of primary (Pb) increases, and its composition, which (at equilibrium) follows the solidus line, changes: it becomes richer in tin. This means that lead must diffuse out of the solid (Pb), and tin must diffuse in.

This diffusion takes time. If cooling is slow, time is available and equilibrium is maintained. However, practical cooling rates are not usually slow enough to allow sufficient time for equilibrium diffusion, so there is a composition gradient in each (Pb) grain, from the middle to the outside. This gradient is called segregation and is found in almost all alloys (figure H3.38).

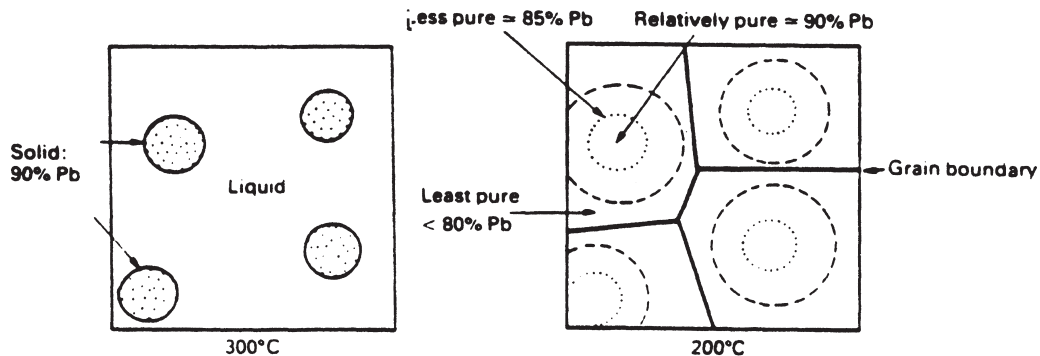


Figure H3.38. Schematic diagram of segregation.

Note that in some cases sufficient excess solute is rejected into the liquid for the liquid composition to reach the eutectic point. The eutectic microstructure is likely to be on the grain boundaries, as these are the last part to solidify. Hence in practice, eutectics can appear even if the phase diagram indicates that the given composition should not form a eutectic (i.e. the constitution point on cooling does not intersect the tie-line through the eutectic point).

Segregation gradients can to some extent be 'smoothed out' after casting by *homogenization*: holding a casting at a temperature to allow some redistribution of solute by diffusion. They can never be eliminated completely.

Segregation is particularly important in respect of impurities. No alloy is truly binary, ternary, or whatever, but will contain traces of other elements (mostly from the ore used as the source of the metal, or from the extraction process). These impurities also dissolve more readily in the melt than in the solid, often very markedly. Hence when alloys are solidified, the impurities concentrate in the last bit to solidify.

Even if the alloy contains a fraction of 1% of a given impurity overall, locally the concentration can be very much higher. This is particularly detrimental when the impurity is brittle, or forms brittle phases with the alloy, and the impurity ends up on the grain boundaries—this can be disastrous from the point of view of toughness. An example is sulphur in steel, which forms brittle iron sulphide. Alloy manufacturers go to considerable lengths to control impurities—usually by further alloying to form harmless compounds at higher temperatures, before the segregation takes place. For example, plain carbon steels all contain manganese, which forms MnS during solidification and, therefore, removes the sulphur before it does any harm.

Another example of the importance of impurity segregation is in fusion welding. We may think of fusion welding as a casting process on a small scale. The melt pool between the parts being welded solidifies in from either side. Segregation leads to a concentration of impurities on the weld centre-line,

and the stresses produced by contraction of the joint can sometimes crack the weld along these weakened grain boundaries: this is known as *solidification cracking*.

H3.4.6 The eutectoid reaction

In section H3.3 we looked at the most important eutectoid point in the Fe–C system at $W_C \approx 0.8\%$. We now consider what happens as austenite containing this amount of carbon is cooled through the eutectoid temperature.

Definition A eutectoid reaction is a three-phase reaction by which, on cooling, a solid transforms into two other solid phases at the same time. If the bottom of a single-phase solid field closes (provided the adjacent two-phase fields are also solid), it does so with a eutectoid point.

The compositions of the two new phases are given by the ends of the tie-line through the eutectoid point. The general eutectoid reaction is therefore:



Figure H3.39 shows part of the Fe–C phase diagram. The eutectoid reaction at 723°C , 0.8% C is:

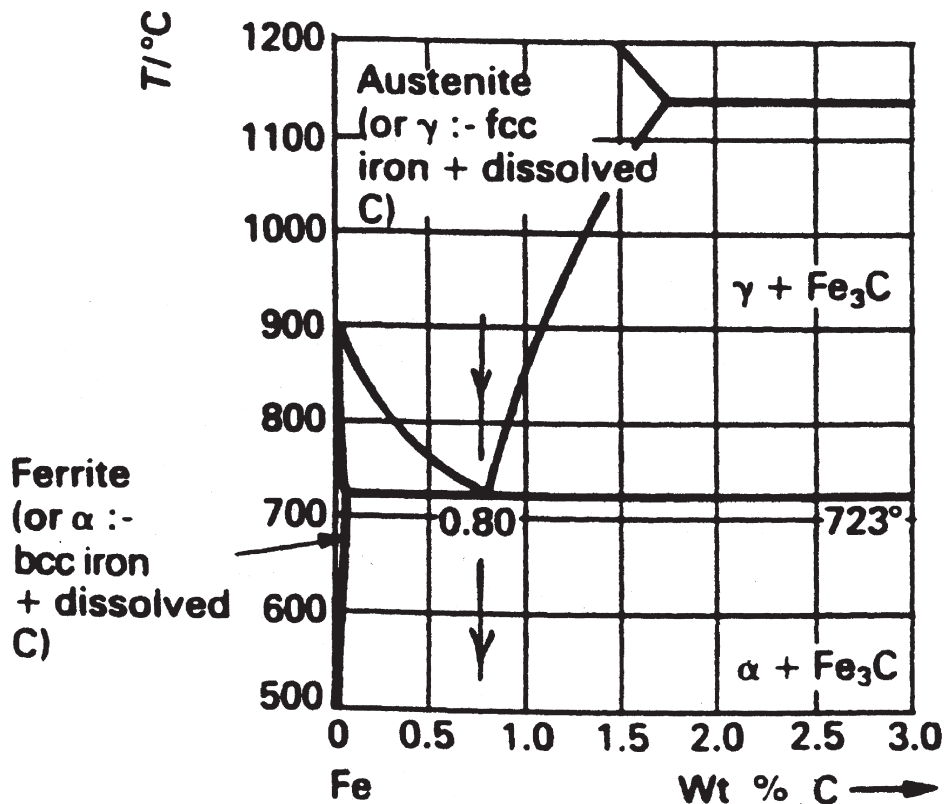
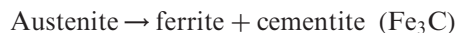


Figure H3.39. The Fe-rich end of the Fe–C phase diagram at lower temperatures.

H3.4.7 Eutectoid microstructures

The mechanism of eutectoid transformation must transform a single solid phase into two others, both with compositions which differ from the original. Taking the eutectoid decomposition of iron as an example, austenite containing 0.8% C changes into ferrite (iron containing almost no carbon) and cementite (Fe_3C , containing 25 at.% carbon). Hence carbon atoms must diffuse together to form Fe_3C , leaving ferrite. Nuclei of small plates of ferrite and cementite form at the grain boundaries of the austenite, and carbon diffusion takes place on a very local scale just ahead of the interface (figure H3.40). Thus the plates grow, consuming the austenite as they go.

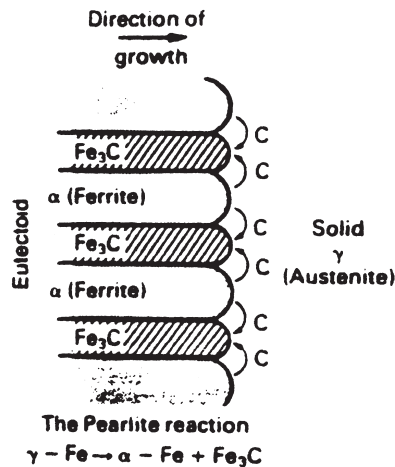


Figure H3.40. Schematic of the pearlite reaction in carbon steel.

Note that this structure has a very large area of phase boundary between ferrite and cementite, so there is a surface energy penalty in forming this plate-like structure. However this is a very efficient mechanism of transformation, as C atoms on average diffuse only one plate spacing, while the interface between the new phases and the austenite traverses whole grains.

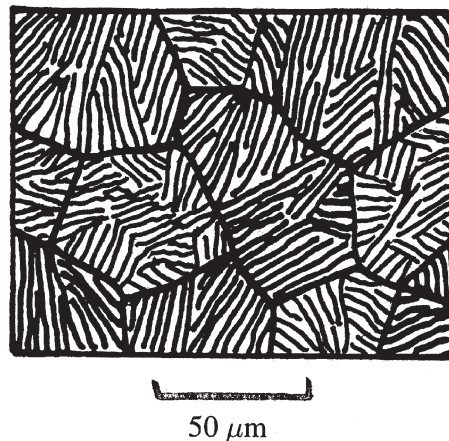


Figure H3.41. Schematic diagram of grains of pearlite in eutectoid steel.

The eutectoid structure in iron has a special name: it is called pearlite (because it has a pearly look). Figure H3.41 shows a schematic view of pearlite grains. It is important to note that pearlite is *not* a phase, but a mixture of two phases: ferrite and cementite.

Question

H3.4.4 In general will the length scale of the phases be larger in a eutectic or a eutectoid microstructure. Why?

H3.4.8 Microstructure in steels

Some commercial steels have a eutectoid composition—steel for railway track is an example of a ‘pearlitic steel’. Most steels are ‘hypo-eutectoid’, containing less than 0.8 wt%. Mild steels contain 0.1–0.2 wt% C, medium carbon steels around 0.4%. Here we will look at how the equilibrium structures relate to the phase diagram (figure H3.42).

Consider slow cooling of a steel containing 0.3% C. Starting with austenite at 900°C, we have a solid solution of C atoms in the interstitial spaces of the fcc lattice. At 800°C, we enter the two phase region: ferrite plus austenite. Ferrite does not appear as particles in an austenite matrix, since it must lose its excess carbon, rather than cluster it together into a new structure; it must also transform from fcc to bcc in the process. The mechanism is exactly the same as in pure iron—nuclei of ferrite form on the austenite grain boundaries. The ferrite rejects carbon into the remaining austenite, the composition of

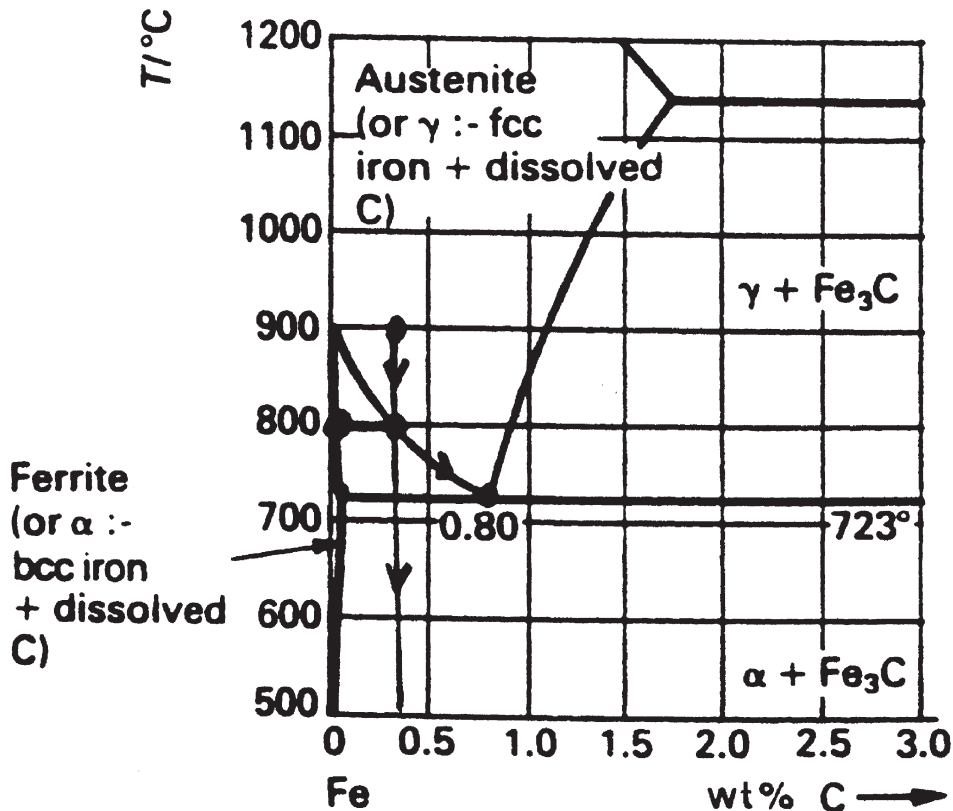


Figure H3.42. The Fe-rich end of the Fe–C phase diagram, for lower temperatures.

which increases accordingly. The ferrite colonies grow until at 723°C , the remaining austenite has reached $0.8\% \text{ C}$ and is at the eutectoid point. The austenite then decomposes into pearlite, the two-phase mixture of ferrite and cementite.

Figure H3.43 shows the reaction underway just above and just below the eutectoid temperature. Note that as before the final structure is still only two-phase, but different grains have very different structures. The ferrite within the pearlite structure is the same stuff as the ferrite forming whole grains—it is all one phase.

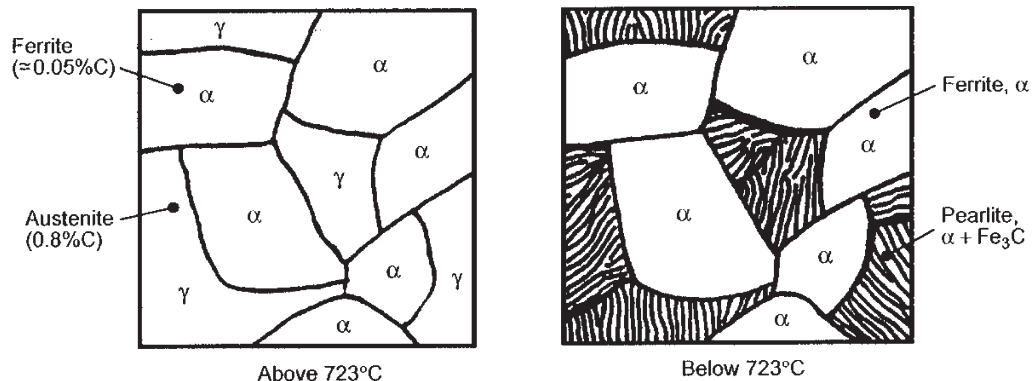


Figure H3.43.

Question

H3.4.5 (a) Pure iron cooled slowly contains 100% ferrite; the eutectoid composition contains 100% pearlite. Estimate the carbon content of the steel sketched in figure H3.44, and sketch the structure of a 0.2% carbon steel after slow cooling to room temperature.

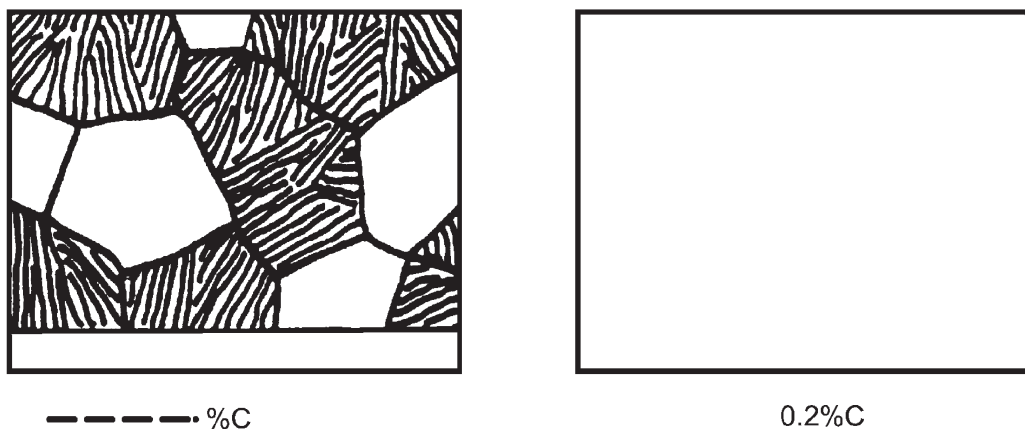


Figure H3.44. Schematic ferrite-pearlite grain structures in hypo-eutectoid steels.

(b) 'Hyper-eutectoid' steels contain $> 0.8 \text{ wt\% C}$. A hyper-eutectoid steel containing 1.0 wt\% C is cooled slowly from the austenite field.

Referring to the Fe–C phase diagram in figure H3.18, answer the following:

At what temperature does a phase transformation begin? _____

What new phase appears then? _____

What are the compositions of the phases just above 723°C? _____

What phase transformation takes place at 723°C? _____

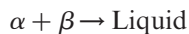
What are the final phases at room temperature and their compositions? _____

Evaluate the proportions of the two phases at room temperature? _____

Answers to questions: section H3.4

H3.4.1 From $X_{\text{Pb}} = 1.5$ to 71 at. %

H3.4.2 (a) Remember that this is an equilibrium diagram, so on heating the reaction simply goes in reverse. The two solids ‘react’ to give a single liquid. In general, on heating:



or, for the Pb–Sn system:



(b) 0°C.

H3.4.3 See figure H3.45.

(a) Liquid is stable until 700°C

(b) At 700°C regions of pure solid Si begin to form, and grow as the temperature falls to 577°C; the Si content of the liquid decreases (following the liquidus line);

(c) At 577°C, the structure is about 10% primary Si, and 90% liquid of eutectic composition, 11.3 at. %.

(d) The eutectic reaction takes place, converting the liquid into a two-phase mixture of solid Si needles in a matrix of Al-rich solid. The final microstructure is shown schematically in figure H3.46.

A solidified alloy of eutectic composition would be 100% eutectic, with no primary Si.

H3.4.4 In general, eutectic reactions form coarser microstructures than eutectoids, since the spacing of regions of the same phase in the two-phase mixture is characteristic of the diffusion distance at the temperature concerned. Eutectic reactions take place at a melting point, giving greater scope for diffusion than in a solid well below melting.

H3.4.5 (a) Carbon content ≈ 0.6 wt%: the structure is about 75% pearlite, so the carbon content is about 75% of 0.8 wt%.

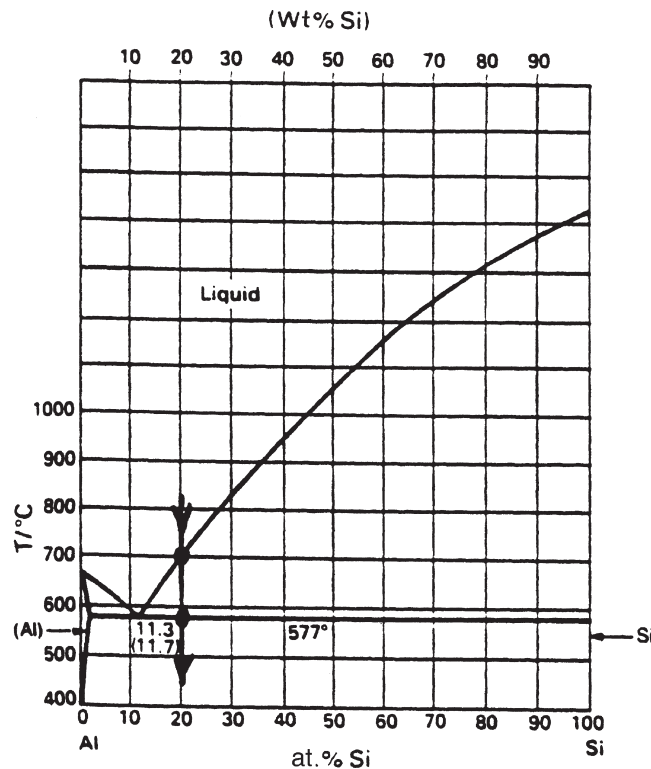


Figure H3.45. Al-Si phase diagram.

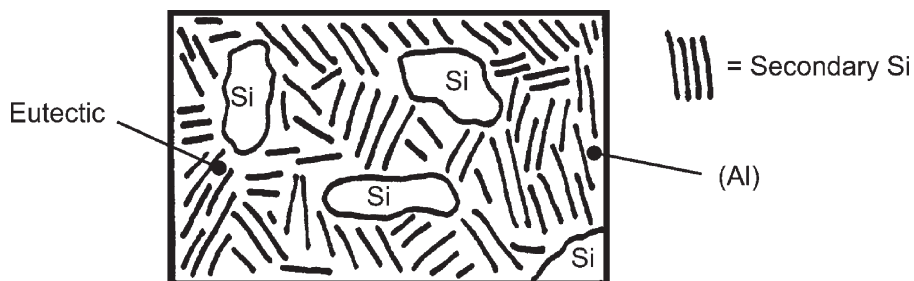


Figure H3.46. Schematic final microstructure of Al-20% Si after solidification.

(In effect we have applied a sort of 'lever rule' between the two microstructures at 0 and 0.8 % C—not to be confused with the true definition of the lever rule, for evaluating the proportions of two phases at the ends of a tie-line).

Similarly, 0.2 wt% C would give about $0.2/0.8 = 25\%$ pearlite at equilibrium, as shown schematically in figure H3.47.

(b) See figure H3.48. Transformation begins at 865°C ; new phase to appear (again on the austenite grain boundaries) is cementite, or iron carbide, Fe_3C .

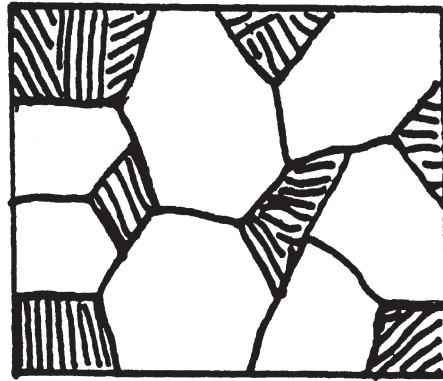


Figure H3.47. Schematic ferrite–pearlite grain structure in Fe–0.2 % C steel.

Austenite: 0.8 wt% C; Fe_3C : 6.7 wt% C.

At 723°C, the eutectoid reaction takes place—the austenite transforms to pearlite (a two-phase mixture of ferrite and more cementite).

Final phases at room temperature: ferrite, ≈ 0 wt% C; cementite, 6.7 wt% C.

Proportion of ferrite: $5.7/6.7 = 85$ wt%; cementite: $1.0/6.7 = 15\%$

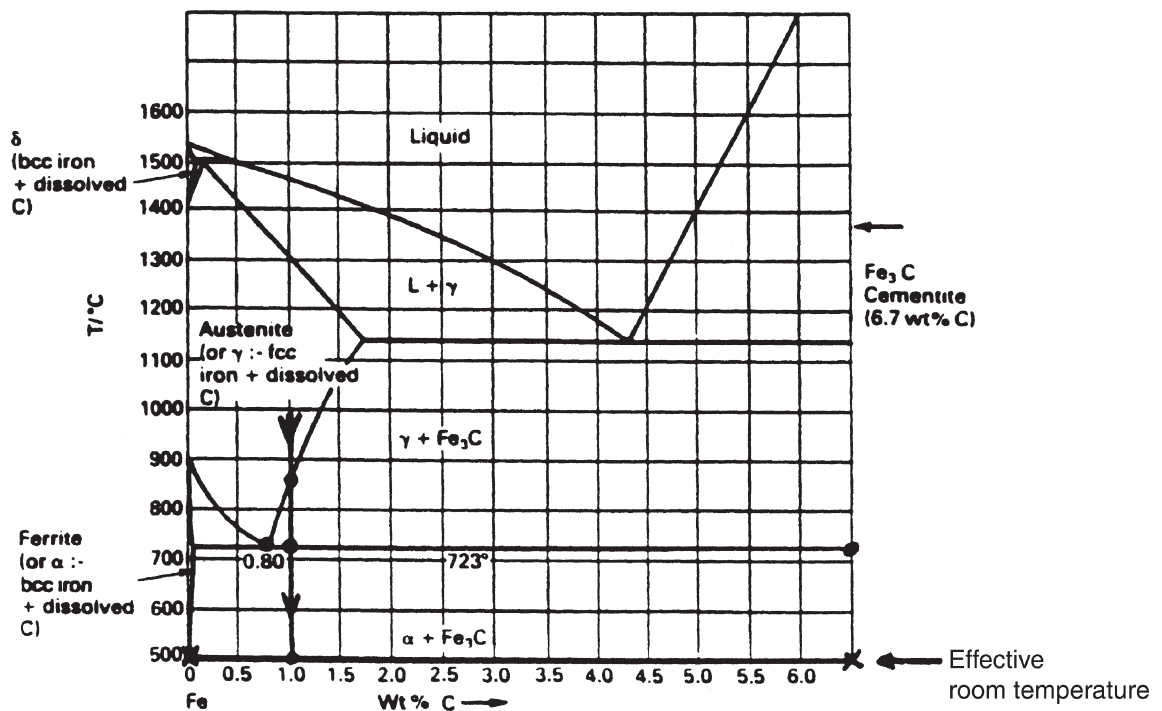


Figure H3.48. Fe-rich end of the Fe–C phase diagram.

H3.5 Final problems

H3.5.1 The $\text{SiO}_2\text{--Al}_2\text{O}_3$ phase diagram is shown in figure H3.49.

Use the diagram to answer the following:

- the compound mullite could be considered as having the formula $\text{SiO}_2(\text{Al}_2\text{O}_3)_X$. Find the approximate value of X . (Atomic weights of Si, Al and O are 28.1, 26.9 and 16.0, respectively).
- use the lever rule to find the equilibrium constitution of a 50 wt% Al_2O_3 alloy at 1700°C . Is it valid to measure directly from the diagram in this case? Why?

H3.5.2 (a) By analogy with the definitions for eutectic and eutectoid reactions, and consideration of the phase diagrams in section H3.3 define:

- a peritectic reaction.
 - a peritectoid reaction.
- (b) Figure H3.50 shows the Ti–Al phase diagram (important for the standard commercial alloy Ti–6% Al–4% V).
- Ring the two peritectic points.
 - Give the approximate chemical formulae for the two intermetallic compounds.
 - Shade all two-phase fields.
 - At what temperature does a Ti–6 wt% Al alloy start to melt?
 - Over what temperature range does it change from the α (hcp) to the β (bcc) structure?

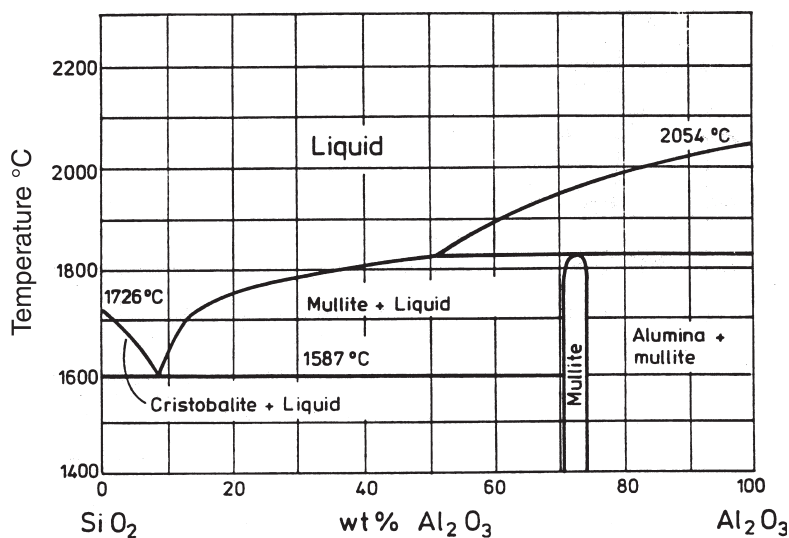


Figure H3.49. $\text{SiO}_2\text{--Al}_2\text{O}_3$ phase diagram.

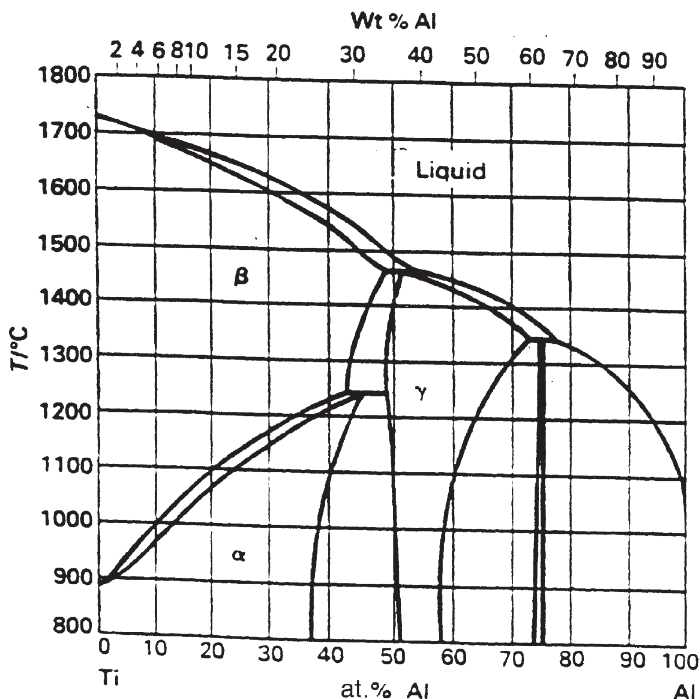


Figure H3.50. Ti–Al phase diagram.

H3.5.3 Typical heat-treatable aluminium alloys are ternary alloys of Al, Mg and Si. They are hardened by forming a fine dispersion of Mg_2Si in the Al-rich grains. An alloy of this type contains 0.9 wt% Mg, and just enough Si to form the compound Mg_2Si .

- (a) Calculate the Si content of the alloy and thus the wt% of Mg_2Si . (The atomic weights of Mg and Si are 24.3 and 28.1, respectively.)

The phase diagram in figure H3.51 is a ‘pseudo-binary’ diagram for Al– Mg_2Si . This simply means that in the single-phase regions we have a solution of Mg and Si (in the atomic ratio 2:1) in Al, while in the two-phase low temperature region we have Al-rich solid solution and Mg_2Si (which has zero solubility for aluminium). In all other respects we can treat it exactly as a binary phase diagram.

- (b) Our sample Al–Mg–Si alloy is cooled slowly from the melt. Describe and sketch the evolution of microstructure, identifying the phases present. (Hint: Mg_2Si will precipitate out of the (Al) solid solution in a manner similar to the formation of (Sn) from (Pb), described in section H3.4.)

H3.5.4 A hypothetical equilibrium diagram between two elements A and B shows the following features:

A has three solid forms, with change temperatures of 800 and 1150°C, and melts at 1980°C. These form solid solutions of B in A, called α , β and γ , in order of increasing temperature.

An intermediate compound A_2B_3 melts at 1230°C. It has some solubility for A forming solid solution ϵ but has no solubility for B.

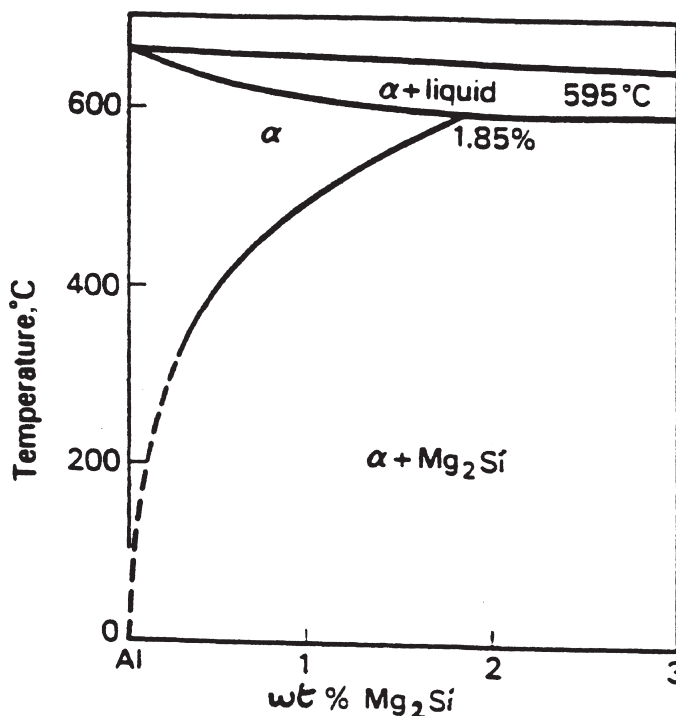


Figure H3.51. Pseudo-binary Al–Mg₂ Si phase diagram.

B melts at 800°C and has negligible solubility for A at all temperatures. At 0°C the solubilities of B in A and A in A₂B₃ are negligible.

Eutectic reactions:

at 1000°C, liquid (55% B) → β (25% B) + ε (60% B)

at 650°C, liquid (90% B) → A₂B₃ + B

Peritectic reaction at 1300°C:

γ (8% B) + liquid (35% B) → β (15% B)

Eutectoid reaction at 600°C:

β (12% B) → α (5% B) + ε (65% B)

All percentages given are by weight. The atomic weight of B is twice that of A.

Draw the equilibrium diagram assuming that all phase boundaries are straight lines.

For an alloy containing 30% B, describe the changes that occur as it is cooled from 1600 to 0°C. Give the proportions of phases present immediately above and immediately below each temperature at which a reaction occurs.

Answers to problems: section H3.5

H3.5.1 (a) Mullite contains approximately 73 wt% Al₂O₃ (27% SiO₂).

The molecular weight of SiO₂ is 28.1 + (16 × 2) = 60.1

The molecular weight of Al_2O_3 is $(26.9 \times 2) + (16 \times 3) = 101.8$

Molecular weight of mullite = 1 mol of SiO_2 + X mols of $\text{Al}_2\text{O}_3 = 60.1 + 101.8X$

Alumina fraction by weight $\approx 0.73 \approx 101.8X / (60.1 + 101.8X)$

Hence $X \approx 1.6$.

- (b) At 1700°C and 50 wt% Al_2O_3 , the phases are liquid containing 13 wt% Al_2O_3 and mullite containing 71 wt% Al_2O_3 .

Weight fraction of liquid = $(71 - 50) / (71 - 13) = 36\%$

Weight fraction of mullite = $(50 - 13) / (71 - 13) = 64\%$

It would be valid to measure the lengths of the tie-line directly in this case because the phase diagram has a linear weight % scale.

- H3.5.2 (a) (1) A peritectic reaction is a three-phase reaction by which, on cooling, two phases (one of them liquid) react to give a single new solid phase:



- (2) A peritectoid reaction is a three-phase reaction by which, on cooling, two solid phases react to give a single new solid phase:



- (b) (1) see figure H3.52.

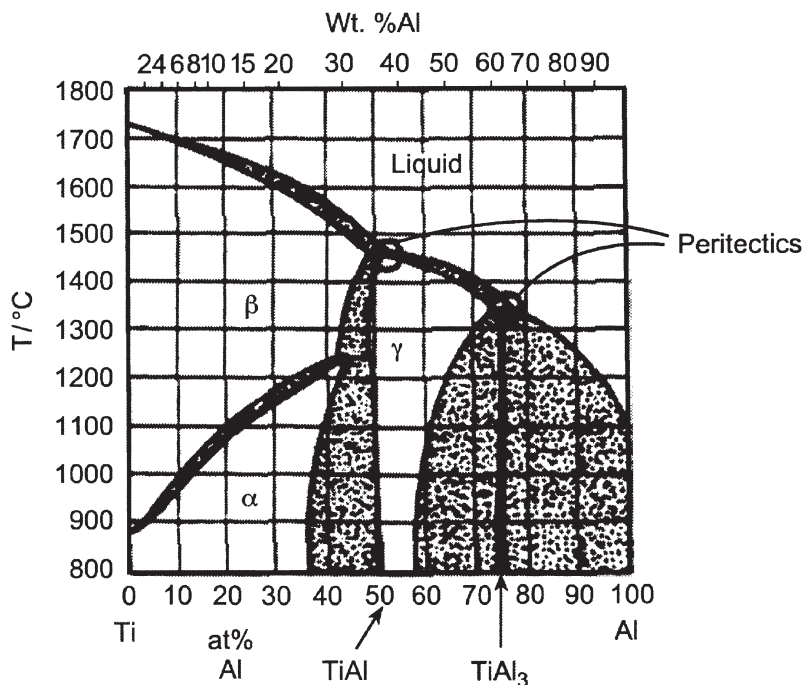


Figure H3.52. Ti–Al phase diagram.

- (2) TiAl, TiAl₃
- (3) see figure H3.52
- (4) 1680°C
- (5) 980°C–1010°C

H3.5.3 (a) To form Mg₂Si using all the available Mg, the amount of Si is calculated as follows:

The atomic weight of Mg is 24.3 and of Si is 28.1.

1 g of Mg contains $1/24.3 \text{ mol} = 0.0412 \text{ mol}$

For every 2 mol of Mg atoms we need 1 mol of Si atoms, therefore the no. of mols of Si is $0.5 \times 0.0412 = 0.0206$

Hence, the mass of Si which forms Mg₂Si with 1 g of Mg is $0.0206 \times 28.1 = 0.578 \text{ g}$.

The wt% of Mg in the alloy is 0.9, so the wt% of Si in the alloy is $0.9 \times 0.578 = 0.52 \text{ wt\%}$.

Hence, the wt% of Mg₂Si is $0.9 + 0.52 = 1.42 \text{ wt\%}$.

- (b) The constitution point moves down the vertical line on the phase diagram as shown in figure H3.53:

If we assume that equilibrium is maintained throughout, the phases change as follows (illustrated schematically in figure H3.54):

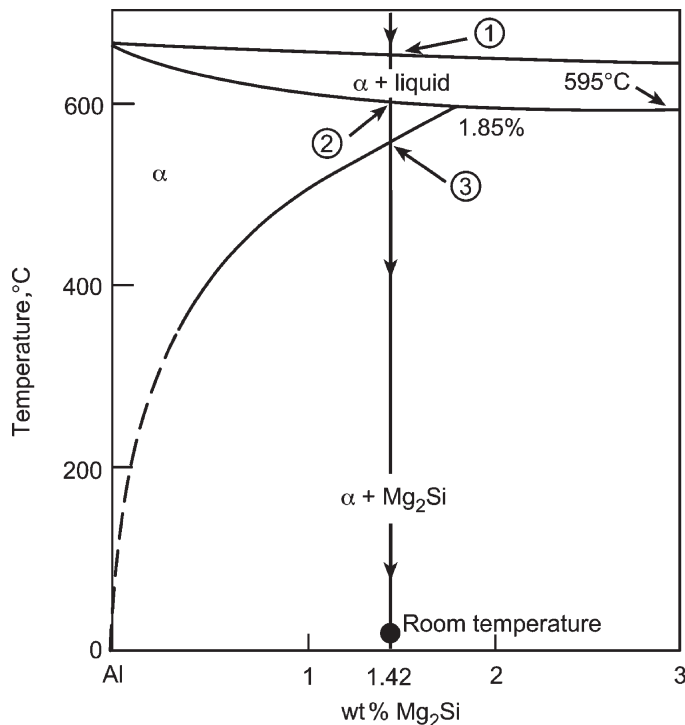


Figure H3.53. Pseudo-binary Al–Mg₂Si phase diagram.

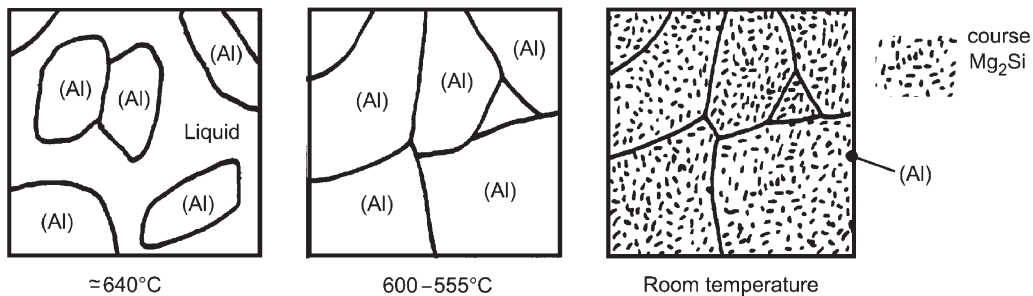


Figure H3.54. Schematic diagrams of microstructure on solidification and cooling of Al–Mg–Si alloy (wt. % $\text{Mg}_2\text{Si} = 1.42$).

- (1) At point 1, $T = 655^\circ\text{C}$, solid α (Al-rich solid) nucleates from the liquid, at a composition well below 1.42%.
- (2) From $T = 655$ to 600°C (point 2) the fraction solid increases from 0 to 100%; the composition of α increases steadily by diffusion of Mg and Si into the solid, until at 600°C we have 100% solid solution containing 1.42 wt% total of Mg and Si.
- (3) From $T = 600$ to 555°C (point 3), solid solution of α , no reaction.
- (4) At $T = 555^\circ\text{C}$, precipitates of Mg_2Si form, depleting the surrounding α of Mg and Si. As the temperature falls, the precipitates grow and the composition of the α steadily falls (theoretically to $\approx 0\%$ at room temperature).

H3.5.4 A_2B_3 contains $\frac{3 \times 2}{2 \times 1 + 3 \times 2} = 75\%$ B by weight. Start by plotting a vertical line to the melting point of A_2B_3 , and mark the melting points of pure A and B, and the change in temperatures of pure A. Locate the two eutectics, the eutectoid and the peritectic. The ends of the tie-lines through these four points are given by the compositions in the four reactions, given in the question—construct the tie-lines next. Complete the diagram using straight lines for the phase boundaries between the salient points plotted previously (see figure H3.55).

On cooling 30% B mixture from 1600°C :

- (a) at 1397°C , solidification commences by separation of γ crystals from the melt.
- (b) From 1397 to 1300°C , more γ separates until at 1300°C , all γ + some liquid form β in peritectic reaction.
 Just above 1300°C : $\frac{22}{27}$ (= 82%) liquid (35% B) + $\frac{5}{27}$ (= 18%) γ (8% B).
 Just below 1300°C : $\frac{15}{20}$ (= 75%) liquid (35% B) + $\frac{5}{20}$ (= 25%) β (15% B).
- (c) From 1300 to 1000°C , more β separates, until at 1000°C , all liquid forms β and ε in eutectic reaction.
 Just above 1000°C : $\frac{5}{30}$ (= 17%) liquid (55% B) + $\frac{25}{30}$ (= 83%) β (25% B).
 Just below 1000°C : $\frac{5}{35}$ (= 14%) ε (60% B) + $\frac{30}{35}$ (= 86%) β (25% B).
- (d) From 1000 to 600°C , β precipitates ε and ε precipitates β , until at 600°C all β forms α and ε in eutectoid reaction.

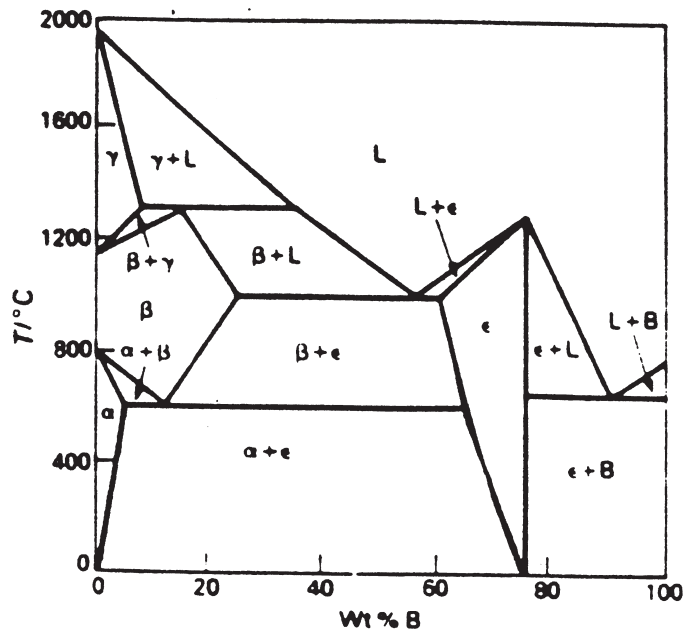


Figure H3.55. Idealized A–B phase diagram (question H3.5.4).

Just above 600°C: $\frac{18}{53}$ (= 34%) ϵ (65% B) + $\frac{35}{53}$ (= 66%) β (12% B).

Just below 600°C: $\frac{25}{60}$ (= 42%) ϵ (65% B) + $\frac{35}{60}$ (= 58%) α (5% B).

(e) From 600 to 0°C, α and ϵ approach pure A and A_2B_3 , respectively.

At 0°C: $\frac{45}{75}$ (= 60%) ϵ (75% B) + $\frac{30}{75}$ (= 40%) α (0% B).