4

Phase diagrams

- What is a binary phase diagram?
- What is a peritectic transformation?
- What is the difference between carbon steel and cast iron?

4.1 Phases and phase diagrams

A phase is a part of a system that is chemically uniform and has a boundary around it. Phases can be solids, liquids and gases, and, on passing from one phase to another, it is necessary to cross a phase boundary. Liquid water, water vapour and ice are the three phases found in the water system. In a mixture of water and ice it is necessary to pass a boundary on going from one phase, say ice, to the other, water.

Phase diagrams are diagrammatic representations of the phases present in a system under specified conditions, most often composition, temperature and pressure. Phase diagrams relate mostly to equilibrium conditions. If a diagram represents non-equilibrium conditions it is called an existence diagram. Phase diagrams can also give guidance on the microstructures that form on moving from one region on a phase diagram to another. This aspect is described in Chapter 8. Phase diagrams essentially display thermodynamic information, and phase diagrams can be constructed by using thermodynamic data. The conditions limiting the existence and coexistence of phases is given by the thermodynamic expression called the phase rule, originally formulated by Gibbs. Some aspects of the phase rule are described in Section S1.5.

The phases that are found on a phase diagram are made up of various combinations of components. Components are simply the chemical substances sufficient for this purpose. A component can be an element, such as carbon, or a compound, such as sodium chloride. The exact components chosen to display phase relations are the simplest that allow all phases to be described.

4.1.1 One-component (unary) systems

In a one-component, or unary, system, only one chemical component is required to describe the phase relationships, for example, iron (Fe), water (H_2O) or methane (CH_4). There are many one-component systems, including all of the pure elements and compounds. The phases that can exist in a one-component system are limited to vapour, liquid and solid. Phase diagrams for one-component systems are specified in terms of two variables, temperature, normally specified in degrees centigrade,

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Understanding solids: the science of materials. Richard J. D. Tilley

ISBNs: 0 470 85275 5 (Hbk) 0 470 85276 3 (Pbk)

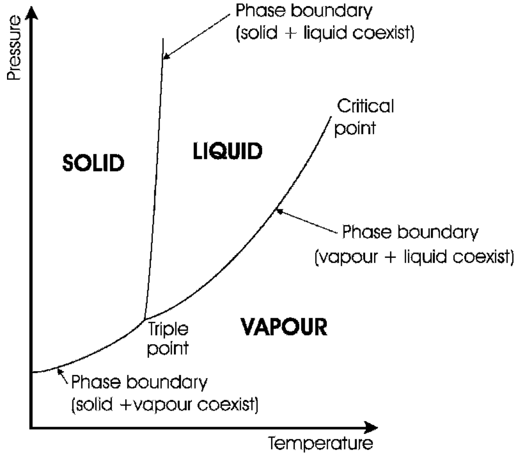

Figure 4.1 The generalised form of a one-component phase diagram

and pressure, specified in atmospheres (1 atmosphere = 1.01325×10^5 Pa).

A generalised one-component phase diagram is drawn in Figure 4.1. The ordinate (y-axis) specifies pressure and the abscissa (x-axis) the temperature. The areas on the diagram within which a single phase exists are labelled with the name of the phase present. The phase or phases occurring at a given temperature and pressure are read from the diagram. The areas over which single phases occur are bounded by lines called phase boundaries. On a phase boundary, two phases coexist. If the phase boundary between liquid and vapour in a one-component system is followed to higher temperature and pressures, ultimately it ends. At this point, called the critical point, at the critical temperature and the critical pressure, liquid and vapour cannot be distinguished. A gas can be converted to a liquid by applying pressure only if it is below the critical temperature. At one point, three phases coexist at equilibrium. This point is called the triple point. If there is any change at all in either the temperature or the pressure, three phases will no longer be present. The triple point is an example of an invariant point.

Perhaps the most important one-component system for life on Earth is that of water. A simplified phase diagram for water is drawn in Figure 4.2. The three phases found are ice (solid), water (liquid) and steam (vapour). The ranges of temperature and pressure over which these phases are found are read from the diagram. For example, at 1 atm pressure and 50 °C, water is the phase present. In a single-phase region, both the pressure and the temperature can be changed independently of one another without changing the phase present. For example, liquid water exists over a range of temperatures and pressures, and either property can be varied (within the limits given on the phase diagram) without changing the situation.

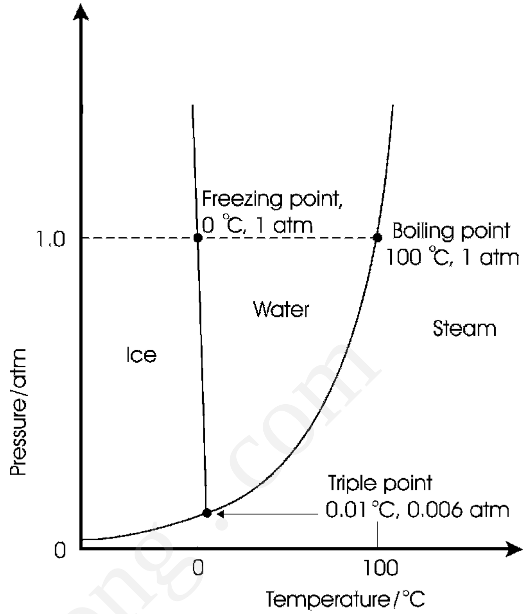

Figure 4.2 The approximate phase diagram for water; not to scale

On the phase boundaries, two phases coexist indefinitely, ice and water, water and steam, or ice and steam. If a variable is changed, the two-phase equilibrium is generally lost. In order to preserve a two-phase equilibrium, one variable, either pressure or temperature, can be changed at will, but the other must also change, by exactly the amount specified in the phase diagram, to maintain two phases in coexistence and so to return to the phase boundary.

The critical point of water, at 374 °C and 218 atm, is the point at which water and steam become identical. The triple point is found at 0.01 °C and 0.006 atm (611 Pa). At this point and only at this

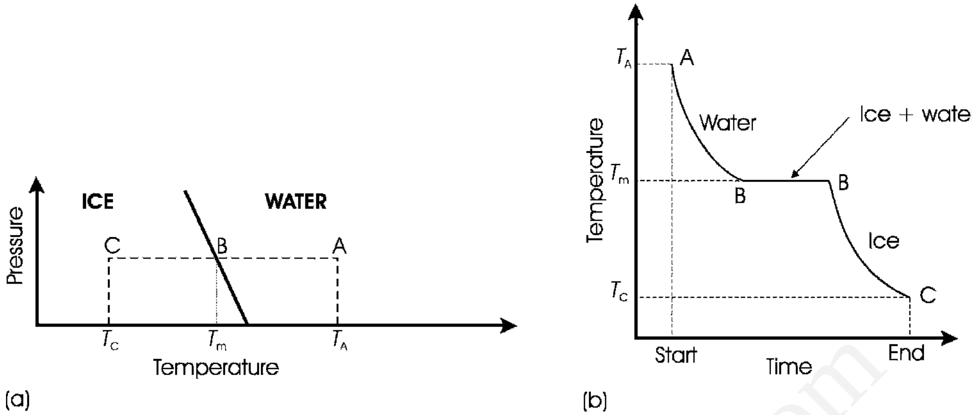

Figure 4.3 (a) A small part of the water phase diagram and (b) the cooling curve generated as a uniform sample of water cools from temperature A (liquid) to temperature C (solid; ice)

point the three phases water, ice and steam occur together. Any change in either the temperature or the pressure destroys the three-phase equilibrium.

The slopes of the phase boundaries give some information about the change of boiling and freezing points as the pressure varies. For example, the phase boundary between water and steam slopes upwards to the right. This indicates that an increase in pressure will favour liquid compared with vapour, and that the boiling point of water increases with increasing pressure. The ice–water phase boundary slopes upwards towards the left. This indicates that an increase in pressure will favour the liquid over the solid. An increase in pressure will cause the water to freeze at a lower temperature, or ice to melt. This is one reason for supposing that liquid water might be found at depths under the surface of some of the cold outer moons in the solar system.

A phase diagram can be used to explain the pattern of temperature changes observed as a substance cools (Figure 4.3). For example, a sample of water at A will cool steadily until point B, on the water–ice phase boundary, is reached. The slope of the temperature versus time plot, called a cooling curve, will change smoothly. At point B, if there is any further cooling, ice will begin to form and two phases will be present. The temperature will now remain constant, and more and more ice will form until all of the water has become ice. This follows directly from the phase rule (see Section S1.5). Thereafter, the ice will then cool steadily again to point C, and a smooth cooling curve will be found.

This form of cooling curve will be found in any one-component system as a sample is cooled slowly through a phase boundary, so that the system is always at equilibrium. Normal rates of cooling are faster, and experimental curves often have the form shown in Figure 4.4. The property at the dip in the curve is called supercooling or undercooling. Supercooling reflects the fact that energy is needed to cause a microscopic crystal nucleus to form. In a very clean system, in which dust and other nucleating agents are absent, supercooling can be appreciable.

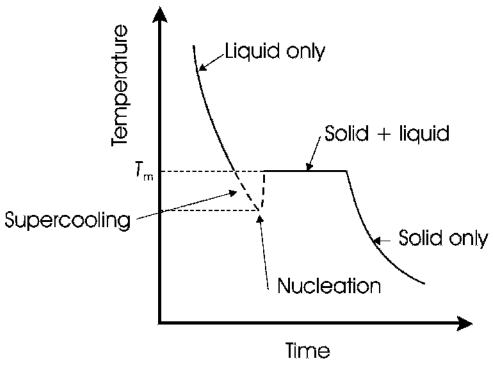

Figure 4.4 A cooling curve showing supercooling

Glasses, which form in systems in which nucleation is difficult or prevented, are called supercooled liquids, because they reach the solid state before crystallisation.

A change in slope of a cooling curve is an indication that the system is passing across a phase boundary, irrespective of the complexity of the system. Cooling curves are therefore useful in mapping out the presence of phase boundaries and in the construction of phase diagrams.

4.2 Binary phase diagrams

4.2.1 Two-component (binary) systems

Binary systems contain two components, for example, Fe + C, $NaNbO_3 + LiNbO_3$, Pb + Sn. The added component means that three variables are needed to display a phase diagram. The variables are usually chosen as temperature, pressure and composition. A binary phase diagram thus needs to be plotted as a three-axis figure (Figure 4.5a). A single phase will be represented by a volume in the diagram. Phase boundaries form two-dimensional surfaces in the representation, and three phases will coexist along a line in the phase diagram.

However, as most experiments are carried out at atmospheric pressure, a planar diagram, using temperature and composition as variables, is usually sufficient (Figure 4.5b). These sections at a fixed pressure are called isobaric phase diagrams, although often this is not stated explicitly. In metallurgical phase diagrams, compositions are usually expressed as weight percentages (wt%). That is, the total weight is expressed as 100 g (or in kilograms and so on), and the amount of each component is given as x g and $(100 - x)$ g. In chemical work, atom percentages (at%) or mole percentages (mol%) are used. In these cases, the amounts of each component are given by x atoms (or moles) and $(100 - x)$ atoms (or moles). In these constant-pressure diagrams, the temperature is specified in degrees centigrade. A single phase occurs over an area in the figure, and phase boundaries are drawn as lines. A point in such a binary phase diagram defines the temperature and composition of the system.

In all of the binary phase diagrams discussed here, it is assumed that pressure is fixed at 1 atm. The sources of the experimental phase diagrams that have been adapted for this chapter are given in the Further Reading section.

4.2.2 Simple binary diagrams: nickel–copper

The simplest form of two-component phase diagram is exhibited by components that are very similar in chemical and physical properties. The nickel–copper

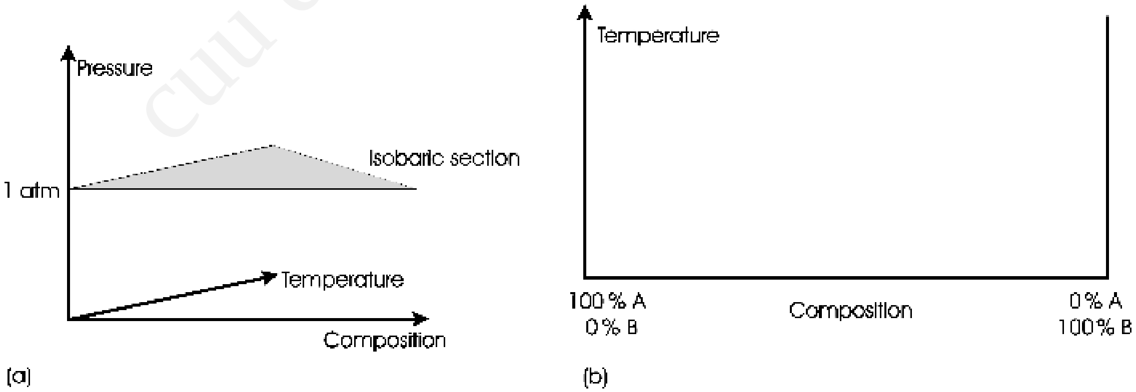

Figure 4.5 (a) A three-axis pressure–temperature–composition frame, required to display the phase relations in a binary system, and (b) isobaric sections, in which the pressure is fixed and only temperature and composition are used

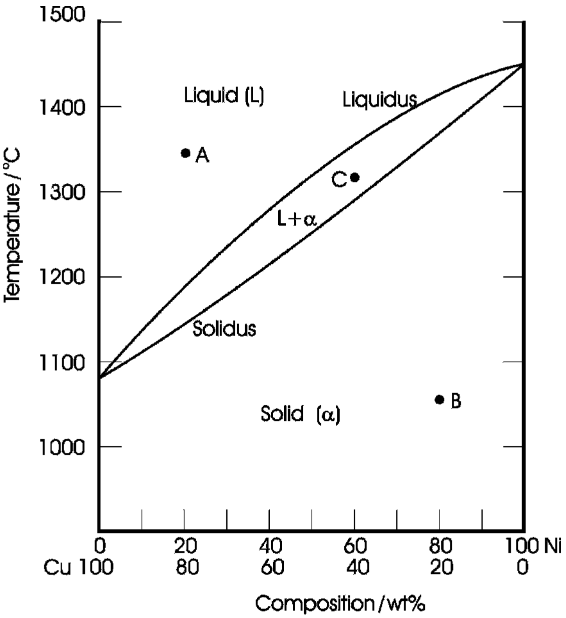

Figure 4.6 The nickel–copper (Ni–Cu) phase diagram at atmospheric pressure

(Ni–Cu) system provides a good example (Figure 4.6). At the top of the diagram, corresponding to the highest temperatures, one homogeneous phase, a liquid phase, occurs. In this liquid, the copper and nickel atoms are mixed together at random. In the copper-rich part of the diagram (left-hand side), the liquid can be considered as a solution of nickel in molten copper, and in the nickel-rich region (right-hand side), the liquid can be considered as a solution of copper in liquid nickel.

At the bottom of the diagram, corresponding to the lowest temperatures, another homogeneous phase, a solid, called the α phase, is found. Just as in the liquid phase, the copper and nickel atoms are distributed at random and, by analogy, such a material is called a solid solution. Because the solid solution exists from pure copper to pure nickel it is called a *complete* solid solution. (The physical and chemical factors underlying solid solution formation are described in Section 6.1.3.)

Between the liquid and solid phases, phase boundaries delineate a lens-shaped region. Within this area solid (α) and liquid (L) coexist. The lower phase boundary, between the solid and the liquid + solid region is called the solidus. The upper phase boundary, between the liquid + solid region and the liquid only region is called the liquidus.

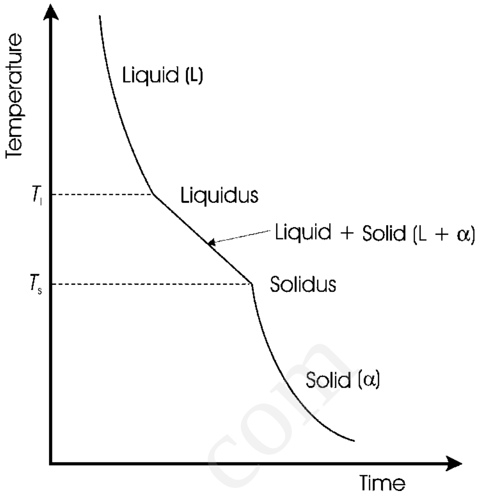

Figure 4.7 A cooling curve for a sample passing through a two-phase liquid + solid region

The cooling curve of the liquid through the two-phase region shows an arrest, just as in a one-component system. However, in this case the change of slope of the cooling curve is not so pronounced. Moreover, breaks in the smooth curve occur as the sample passes both the liquidus and the solidus (Figure 4.7). Carefully interpreted cooling curves for samples spanning the whole composition range can be used to map out the positions of the solidus and liquidus.

The most obvious information found in the diagram is the phase or phases present at any temperature. Thus, suppose that a mixture of 50 g copper and 50 g nickel is heated. At 1400 °C, one phase will be present, a homogeneous liquid. At 1100 °C, one phase will also be present, a homogeneous solid, the α phase. At 1250 °C two phases are present, liquid (L) and solid (α).

The composition of any point in the diagram is simply read from the composition axis. Thus, point A in Figure 4.6 has a composition of 80 wt% copper (and thus 20 wt% nickel). Point B has a composition of 20 wt% copper (and thus 80 wt% nickel). Point C

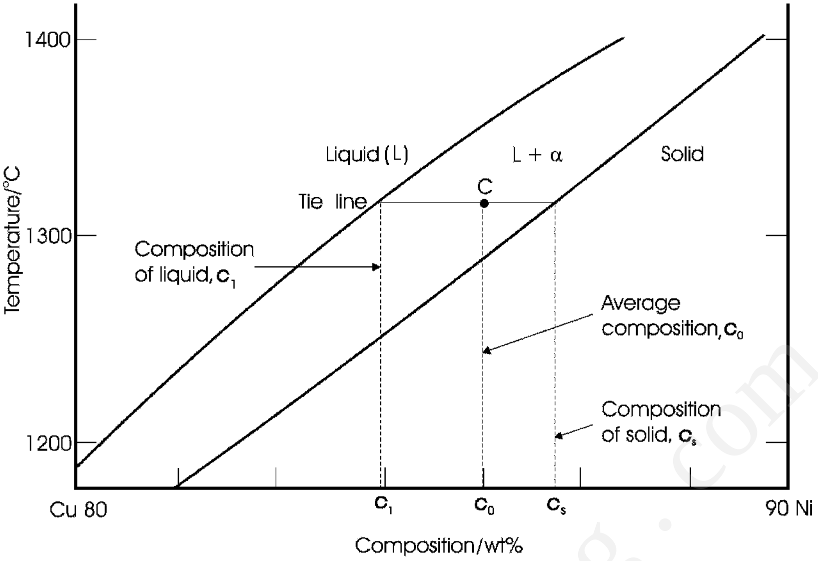

Figure 4.8 Part of the nickel–copper (Ni–Cu) phase diagram; not to scale

has an *average* composition of 40 wt% copper (and thus 60 wt% nickel). The average is quoted for point C because there are two phases present, solid and liquid. To determine the composition of each of these phases it is simply necessary to draw a line parallel to the composition axis, called a tie line. The composition of the solid phase is read from the diagram as the composition where the tie line intersects the solidus. The composition of the liquid is read from the diagram as the composition where the tie line intersects the liquidus (Figure 4.8). The composition of the liquid phase, c_l, is approximately 51 wt% copper, and that of the solid, c_s, is approximately 33 wt% copper.

The amounts of each of the phases in a two-phase region can be calculated using the lever rule (Figure 4.8). The fraction of solid phase x_s, is given by:

$$x_s = \frac{c_0 - c_l}{c_s - c_l} \tag{4.1}$$

The fraction of liquid phase, x_l, is given by:

$$x_l = \frac{c_s - c_0}{c_s - c_l} \tag{4.2}$$

In these equations, c_0 is the average composition of the sample, c_s the composition of the solid phase present in the two-phase mixture, and c_l the composition of the liquid phase present in the two-phase mixture. These compositions are read from the composition axis as described above. Note that if the composition scale is uniform, these amounts can simply be measured as a distance.

4.2.3 Binary systems containing a eutectic point: lead–tin

The vast majority of binary phase diagrams are more complex than the example described above. Typical of many is the diagram of the lead–tin (Pb–Sn) system (Figure 4.9).

At high temperatures, the liquid phase is a homogeneous mixture of the two atom types, lead and tin. However, the mismatch in the sizes of the lead and tin atoms prevents the formation of a complete homogeneous solid solution in the crystalline state. Instead, partial solid solutions occur at each end of the phase range, close in composition to the parent phases. The solid solutions, also referred to a terminal solid solutions, are normally called α, which is found on the lead-rich side of the diagram, and β, found on the tin-rich side. These solid solutions adopt the crystal structure of the parent phases. Thus, the α phase has the same crystal

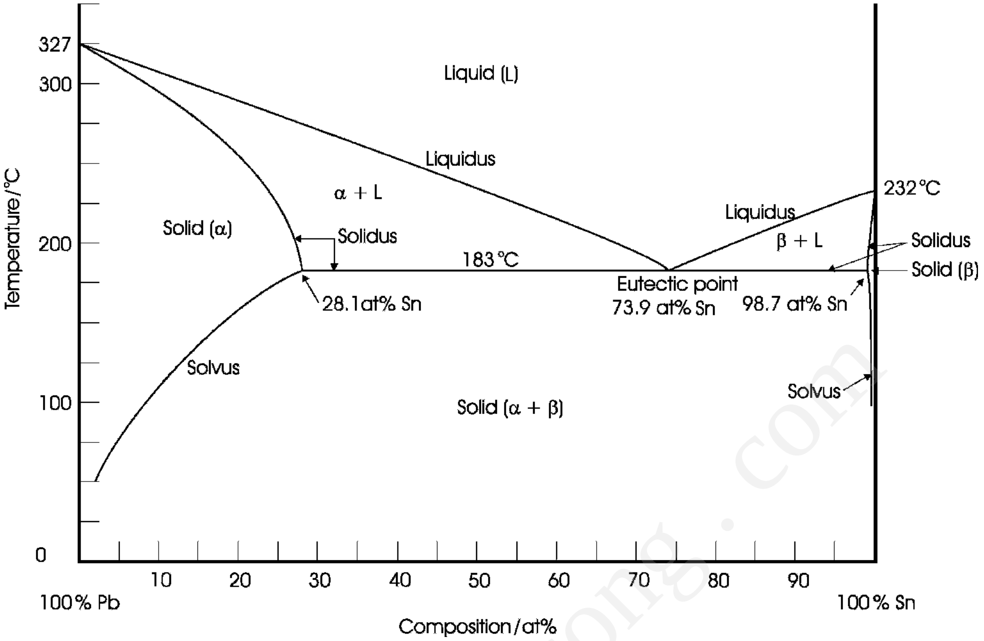

Figure 4.9 The lead–tin (Pb–Sn) phase diagram at atmospheric pressure

structure as lead, and the tin atoms are distributed at random within the crystal as defects. The β phase has the same crystal structure as that of pure tin, and the lead atoms are distributed at random within the crystal as defects. The extent of solid solution in the α phase is much greater than that in the β phase, as the smaller tin atoms are more readily accommodated in the structure of the large lead atoms than are lead atoms in the tin structure. The extent of the solid solution increases with temperature for both phases. This is because increasing temperature leads to greater atomic vibration, which allows more flexibility in the accommodation of the foreign atoms.

The overall composition of a crystal in the solid solution region is simply read from the composition axis, as in the nickel–copper system. The amount of the phase present is always 100 %. Thus point A in Figure 4.10 corresponds to a homogeneous α-phase solid of composition 15 at% tin, 85 at% lead, $Pb_{0.85}Sn_{0.15}$, at a temperature of 200 °C.

Between the partial solid solutions, in the solid, a two-phase region exists. This is a mixture of the two solid solutions, α and β, in proportions depending

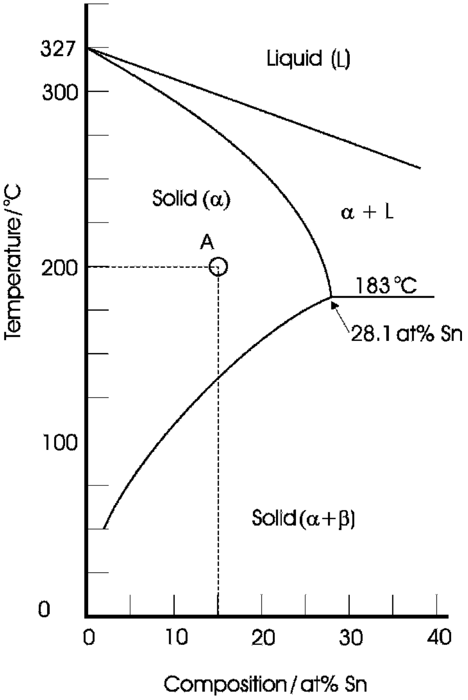

Figure 4.10 The lead-rich region of the lead–tin phase diagram

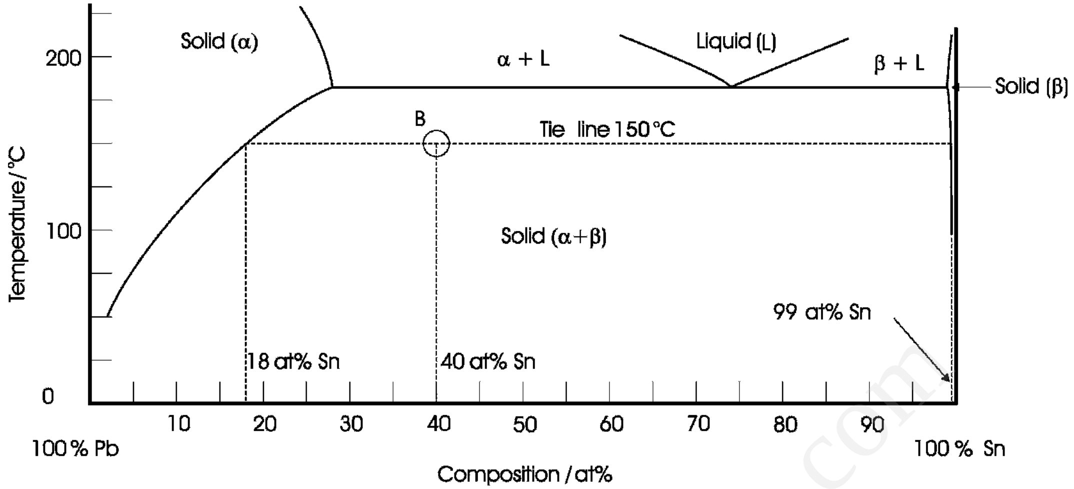

Figure 4.11 The central region of the lead–tin phase diagram

on the overall composition of the system. The phase boundaries between the solid solutions and the two-phase region are called the solvus lines. The overall composition of any sample is read from the composition axis. The compositions of the two phases present are given by the compositions at which the tie line intersects the appropriate solvus, drawn at the appropriate temperature. Thus, in Figure 4.11, the overall composition of point B is 40 at% tin, 60 at% lead. The composition of the α phase is 18 at% tin, 72 at% lead, and the composition of the β phase is 99 at% tin and 1 at% lead, at 150 °C. The amounts of the two phases are found by application of the lever rule, using the compositions just quoted. Thus:

$$\text{Amount of } \alpha \text{ phase} = \frac{99 - 40}{99 - 18} = 72.8\,\%;$$

$$\text{Amount of } \beta \text{ phase} = \frac{40 - 18}{99 - 18} = 27.2\,\%.$$

The liquidus has a characteristic shape, meeting the solidus at the eutectic point. The eutectic composition, which is the overall composition at which the eutectic point is found, solidifies at the lowest temperature in the system, the eutectic temperature. At this point (and only at this point, as explained below) a liquid transforms directly into a solid, consisting of a mixture of α and β phases. The eutectic point in the lead–tin system is at 73.9 at% tin and a temperature of 183 °C.

A eutectic point, in any system, is characterised by the coexistence of three phases, one liquid and two solids. At a eutectic transformation, a liquid transforms directly into two solids on cooling:

$$\mathrm{L(l)} \rightarrow \alpha(\mathrm{s}) + \beta(\mathrm{s}).$$

The eutectic point is therefore analogous to a triple point in a one-component system and, like a triple point, it is also an invariant point. The three phases can be in equilibrium only at one temperature and composition, at a fixed pressure (see Section S1.5). The reaction that occurs on cooling or heating through a eutectic point is called an invariant reaction. A cooling curve shows a horizontal break on passing through a eutectic.

Solidification over the rest of the phase diagram involves the passage through a two-phase solid + liquid region. For example, a composition on the lead-rich side of the eutectic, on passing through the liquidus, will consist of solid α phase plus liquid. A composition on the tin-rich side of the eutectic, on passing through the liquidus, will consist of solid β phase together with liquid. The composition of the two phases is obtained by

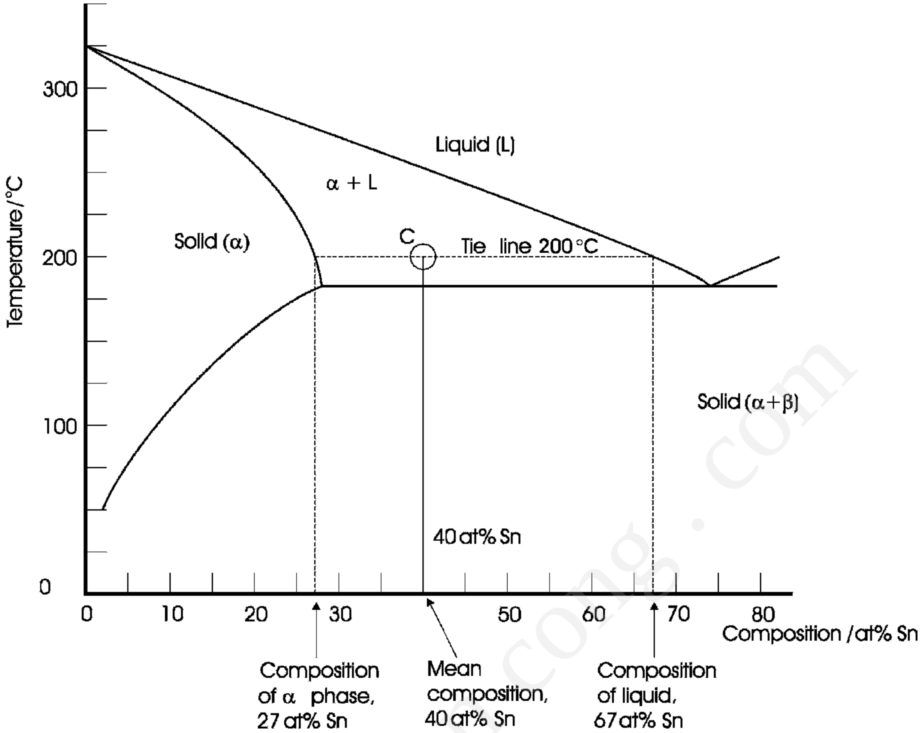

Figure 4.12 The lead-rich region of the lead–tin phase diagram

drawing a tie line at the appropriate temperature and reading from the composition axis. The amounts of the solid and liquid phases are obtained by noting the average composition and using the lever rule. For example, point C in Figure 4.12 corresponds to an overall of composition 40 at% tin. On slow cooling to 200 °C the sample will consist of liquid of composition 67 at% tin and solid α phase with a composition of 27 at% tin. The amounts of these two phases can be obtained via the lever rule, as above.

On slowly cooling a sample from a homogeneous liquid through such a two-phase region, it is seen that, as the temperature falls, the composition of the solid follows the left-hand solidus and the composition of the liquid follows the liquidus. When the eutectic temperature is reached, the remaining liquid will transform to solid with a composition equal to the eutectic composition. At this stage, the solid will contain only solid α phase and solid β phase. Further slow cooling will not change this, but the compositions of the solid α phase and solid β phase will evolve, as the compositions at a given temperature always correspond to the compositions at the ends of the tie lines.

The microstructure of the solid will reflect this history, as discussed in Chapter 8 on reactions and transformations.

4.2.4 Solid solution formation

Not all systems have parent structures that show solid solution formation. Solid solution formation is generally absent if the crystal structures and compositions of the parent phases are quite different from each other. In general, the phase diagrams of metallic systems, drawn schematically in Figure 4.13(a), are similar in form to the lead–tin diagram.

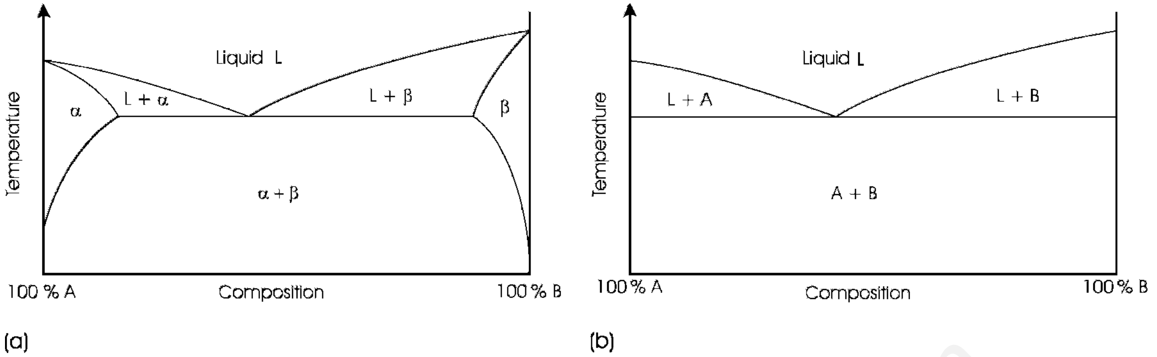

Figure 4.13 (a) A typical binary metallurgical phase diagram; (b) a typical ceramic (nonmetallic) phase diagram

The likelihood of forming a substitutional solid solution between two metals will depend on a variety of chemical and physical properties, which are discussed in Chapter 6 (see the Hume-Rothery solubility rules in Section 6.1.4). Broadly speaking, substitutional solid solution in metallic systems is more likely when:

- the crystal structures of the parent phases are the same;
- the atomic sizes of the atoms present are similar;
- the electronegativities of the metals are similar.

When oxide phase diagrams are considered, the valence is also important, as charge neutrality must be maintained in the solid solution. Thus, the similar oxides Al_2O_3, Cr_2O_3 and Fe_2O_3, all with similar sized cations and the same crystal structures and formulae (i.e. cation valence) would be expected to form extensive solid solutions, similar to that found in the nickel–copper system. Compounds containing cations with widely differing sizes, that adopt quite different crystal structures, such as B_2O_3 and Y_2O_3, would be expected to have almost no mutual solubility, even though the valence of the cations is the same. In such cases, the phase diagrams have a form similar to that in Figure 4.13(b). Compounds with different formulae often form intermediate phases, as discussed in the next section.

4.2.5 *Binary systems containing intermediate compounds*

Many binary mixtures react to produce a variety of compounds. In the context of phase diagrams, the reactants are known as the parent phases and the reaction products are called intermediate phases. For example, Figure 4.14 shows the phase diagram for the binary system comprising the parent ceramic phases calcium silicate ($CaSiO_3$), also called wollastonite, and calcium aluminate ($CaAl_2O_4$). Calcium aluminate and calcium silicate react to form a compound called gehlenite, $Ca_2Al_2SiO_7$, at high temperatures:

$$CaSiO_3 + CaAl_2O_4 \rightarrow Ca_2SiAl_2O_7$$

Gehlenite is the single intermediate phase in this system. None of the phases has any composition range, unlike the alloys described above, and such compounds are often called line phases.

The diagram is exactly like two of the phase diagrams in Figure 4.13(b) joined side by side. Thus, exactly the same methods as described above can be used to obtain quantitative information. In each two-phase region, the composition of the two phases present is obtained by drawing tie lines, and the relative amounts of the two phases are determined by use of the lever rule.

The phase diagram shows that gehlenite melts without any changes occurring. This feature is

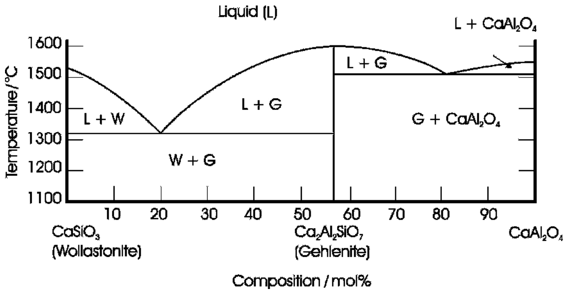

Figure 4.14 The wollastonite–calcium aluminate ($CaSiO_3$–$CaAl_2O_4$) phase diagram showing the intermediate phase gehlenite, $Ca_2Al_2SiO_7$

called congruent melting. It also reveals that every composition, except that of the parent phases and the intermediate phase, corresponds to a two-phase mixture. There are no extensive single-phase regions.

Not all intermediate compounds show congruent melting. Many intermediate compounds transform into a liquid at a peritectic point. On heating through a peritectic point, a solid transforms to a liquid plus another solid of a different composition:

$$\alpha(\mathrm{s}) \rightarrow \beta(\mathrm{s}) + \mathrm{L}(\mathrm{l}).$$

The solid is said to melt incongruently. As an example, Figure 4.15(a) shows a hypothetical ceramic system with an intermediate phase of composition AB_2, which melts incongruently at a peritectic point into liquid + solid B. At a peritectic point, three phases coexist. The point is thus an invariant point, and the reaction is an invariant reaction. The diagram also shows a eutectic point between pure A and the compound AB_2.

As described above, metallic systems invariably contain alloys with significant composition ranges (Figure 4.15b). Here the parent phases form terminal solid solutions α near to parent A, and β near to parent B. The intermediate alloy, labelled γ, has a composition close to AB_2. (The first intermediate phase is usually labelled γ in metallurgical phase diagrams.) The phase range of this material can be thought of as made up of 'terminal solid solutions' of A in AB_2, and B in AB_2. The γ phase melts incongruently at the peritectic point, and a eutectic point is found between the α and γ phases.

4.2.6 *The iron–carbon phase diagram*

The systematic understanding of the iron–carbon (Fe–C) phase diagram at the end of the 19th century and the early years of the 20th century, was at the heart of the technological advances that characterise these years. This is because steel is an alloy of carbon and iron, and knowledge of the iron–carbon phase diagram allowed metallurgists to fabricate on demand steels of known mechanical properties. Apart from this historical importance, the phase

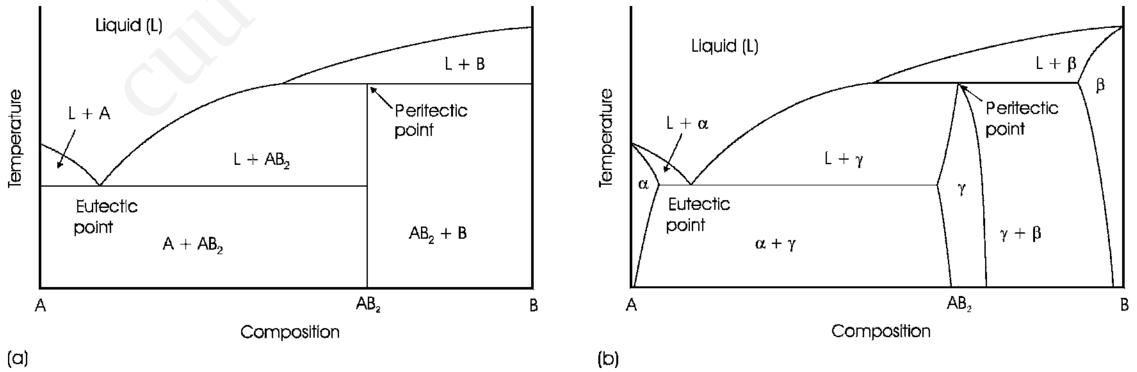

Figure 4.15 (a) A hypothetical ceramic (nonmetallic) phase diagram containing a peritectic point and (b) a hypothetical metallurgical phase diagram containing a peritectic point

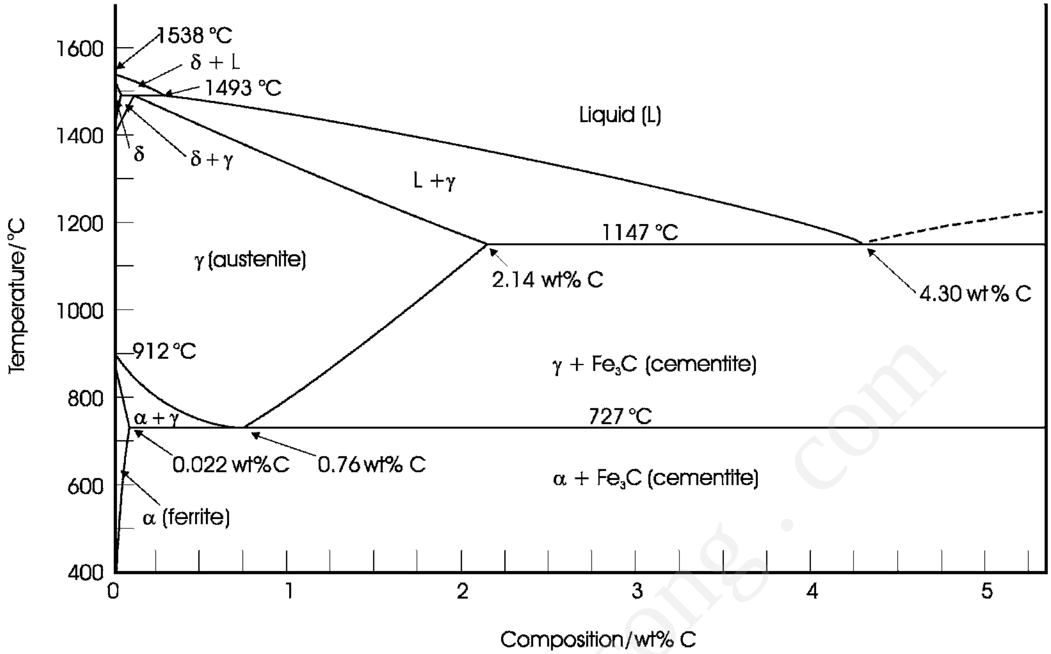

Figure 4.16 The iron-rich region of the iron–carbon existence diagram. The phase cementite (Fe_3C; not shown) occurs at 6.70 wt% carbon. This phase is a nonequilibrium phase and does not occur on the equilibrium phase diagram, which is between iron and graphite. The diagram is not to scale, and the α-ferrite and δ-ferrite phase fields have been expanded for clarity

diagram shows a number of interesting features in its own right.

The low-carbon region of the phase diagram is the region relevant to steel production. The version most used is that in which the composition axis is specified in wt% carbon (Figure 4.16). In fact, this is not the equilibrium phase diagram of the system. The intermediate compound cementite, Fe_3C, is metastable and slowly decomposes. The true equilibrium is between iron and graphite. However, cementite is an important constituent of steel, and the rate of decomposition is slow under normal circumstances, so that the figure drawn is of most use for practical steelmaking. Cementite occurs at 6.70 wt% carbon and has no appreciable composition range.

On the left-hand side of the diagram, the forms of pure iron are indicated. Pure iron has a melting point of 1538 °C. Below the melting point, pure iron adopts one of three different crystal structures (called allotropes) at atmospheric pressure. Below a temperature of 912 °C, α-iron, which has an A2 (body-centred cubic) structure (see Section 5.3.4), is stable. This material can be made magnetic below a temperature of 768 °C. The old name for the non-magnetic form of iron, which exists between temperatures of 768 °C and 912 °C, was β-iron, but this terminology is no longer in use. Between the temperatures of 912 °C and 1394 °C the allotrope γ-iron is stable. This phase adopts the A1 (face-centred cubic) structure (see Section 5.3.3). At the highest temperatures, between 1394 °C and the melting point, 1538 °C, the stable phase is called δ-iron. The structure of δ-iron is the same as that of α-iron. It is rare that low-temperature and high-temperature polymorphs share the same crystal structure.

Between the pure iron allotropes and the intermediate phase cementite, a number of solid solution regions occur. The extent of these depends on the

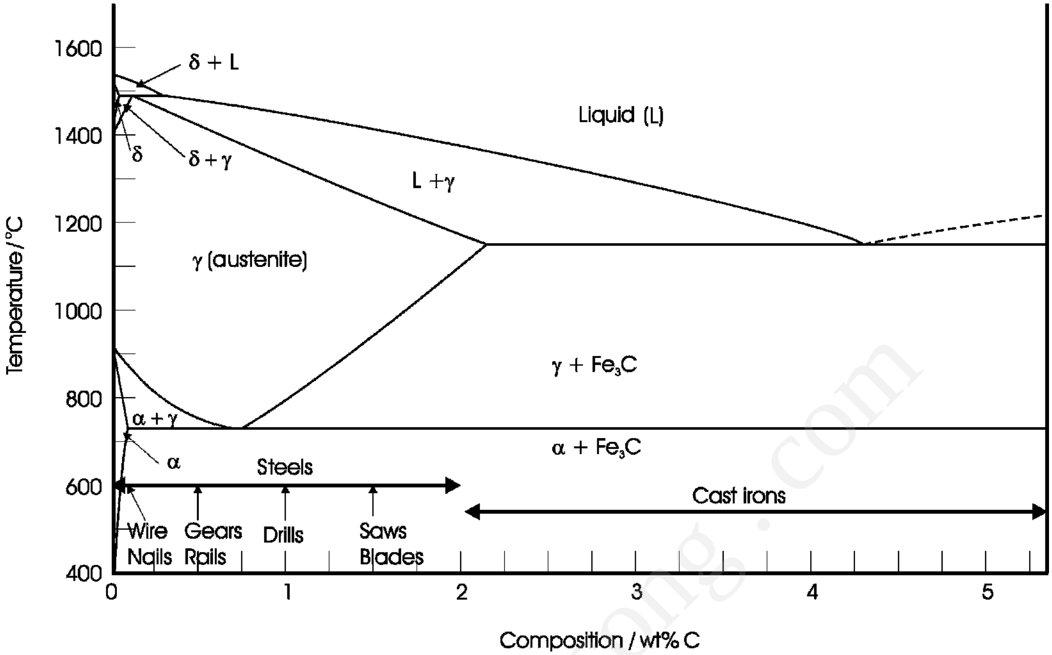

Figure 4.17 The iron–carbon existence diagram showing the approximate composition ranges for various plain carbon steels and cast irons

crystal structure of the iron. Only a small amount of carbon can enter the body-centred cubic structure of α-iron as interstitial defects between the matrix of iron atoms. At 727 °C, this amounts to 0.022 wt% carbon. This solid solution is called ferrite, or sometimes α-ferrite if it needs to be differentiated from the high-temperature solid solution. Much more interstitial carbon can be taken into solid solution in face-centred cubic γ-iron, to a maximum of 2.14 wt% carbon at 1147 °C. This material is called austenite. The amount of interstitial carbon that can enter the body-centred cubic structure of δ-iron is larger than that in α-iron, amounting to 0.09 wt% carbon at 1493 °C. This material is also called ferrite, but is generally called δ-ferrite to distinguish it from α-ferrite.

4.2.7 Steels and cast irons

The phase diagram allows us to understand the difference between plain carbon steels, that is, alloys of carbon and iron only, and cast irons. Plain carbon steels contain less than about 2 wt% carbon (Figure 4.17), although commercial steels rarely contain much more than 1.4 wt% carbon. They can be heated to give a homogeneous austenite solid solution. In this condition, they can be worked or formed as a homogeneous material. Low-carbon steel, with less than 0.15 wt% carbon, is ductile, not very hard and is used for wires. Mild carbon steel, containing 0.15–0.25 wt% carbon, is harder and less ductile. It is used for cables, chains, nails and similar objects. Medium-carbon steel, containing 0.20–0.60 wt% carbon, is used for nails, girders, rails and structural steels. High-carbon steels, containing 0.61–1.5 wt% carbon, still well inside the austenite phase region, are used in applications requiring greater hardness, such as knives, razors, cutting tools and drill bits. Recently, ultrahigh-carbon steels, containing between 1 wt% and 2 wt% carbon, have been studied and found to accept extreme deformation before fracture. This is called superelasticity (see Section 10.1.3).

When the carbon content is greater than about 2 wt% and less than about 5 wt% carbon, the material cannot be heated to give a homogeneous solid solution. At all temperatures below the eutectic temperature of 1148 °C the solid is a mixture of austenite and cementite or ferrite and cementite (Fe_3C). The effect of this is that the materials are hard, brittle and resist deformation. The material can be cast into the desired shape, and is referred to as cast iron. Commercial cast irons rarely contain much more than about 4.5 wt% carbon.

Some elements, especially silicon, which occurs naturally as an impurity in iron ores, promote the transformation of cementite into graphite. White cast iron has less than 1.3 wt% silicon, and all of the carbon is present as Fe_3C. It is very brittle and too hard to be machined. It has to be ground to shape. Gray cast iron has between 2 wt% and 5 wt% silicon. The carbon is mainly in the form of graphite flakes embedded in the metal. It is easy to cast and machine but cracks tend to form at the graphite flakes. Black cast iron is made from white cast iron by prolonged heating at about 900 °C. During the heating, the cementite is transformed to rosette-shaped graphite nodules rather than flakes. This material offers a good compromise between machinability and strength.

4.2.8 Invariant points

There are three invariant points in the iron–carbon diagram (Figures 4.16 and 4.17). A eutectic point is found at 4.30 wt% carbon and 1148 °C. At a eutectic point, a liquid transforms to two solids on cooling:

$$\mathrm{L(l)} \rightarrow \alpha(\mathrm{s}) + \beta(\mathrm{s})$$

A similar feature, but involving only solid phases, occurs at the lowest temperature of the austenite phase field, 727 °C, and at 0.76 wt% carbon. This is also an invariant point, called a eutectoid point. At a eutectoid point, a solid transforms to two solids on cooling:

$$\gamma(\mathrm{s}) \rightarrow \alpha(\mathrm{s}) + \beta(\mathrm{s})$$

The eutectoid transformation, which takes place as austenite is cooled below the eutectoid temperature, is of great importance in steelmaking. (See Section 8.2.4.)

The phase diagram also contains a peritectic point, at the highest temperature of the austenite phase region, 1493 °C. At this peritectic point, austenite transforms into liquid and δ-ferrite on heating:

$$\alpha(\mathrm{s}) \rightarrow \gamma(\mathrm{s}) + \mathrm{L(l)}$$

Similar transformations, in which only solid phases occur, are called peritectoid transformations. On heating through a peritectoid point, we find:

$$\gamma(\mathrm{solid}) \rightarrow \alpha(\mathrm{solid}) + \beta(\mathrm{solid})$$

4.3 Ternary systems

4.3.1 Ternary phase diagrams

Ternary systems have three components. These require five-axis coordinate systems to display the phase relations – three for the compositions, one for pressure and one for temperature. In practice, the three components are arranged at the vertices of an equilateral triangle, and the composition of each component is indicated along the sides of the triangle. The temperature axis is drawn normal to the composition plane, to form a triangular prism (Figure 4.18a). It is necessary to draw a different prism for each pressure. Working phase diagrams are normally sections through the prism at a chosen value of temperature and a pressure of 1 atm (Figure 4.18b). The diagrams are called isothermal sections. The composition of the components, in wt%, at% or mol%, are measured along the three sides of the equilateral triangle. Each of the three faces of the prism is the binary phase diagram A–B, A–C or B–C. In Figure 4.18(a), these are simple eutectic diagrams rather like Figure 4.13(b).

The compositions in isothermal sections are most easily plotted with use of triangular graph paper (Figure 4.19). The composition of a point on one of the edges is read directly from the diagram. For

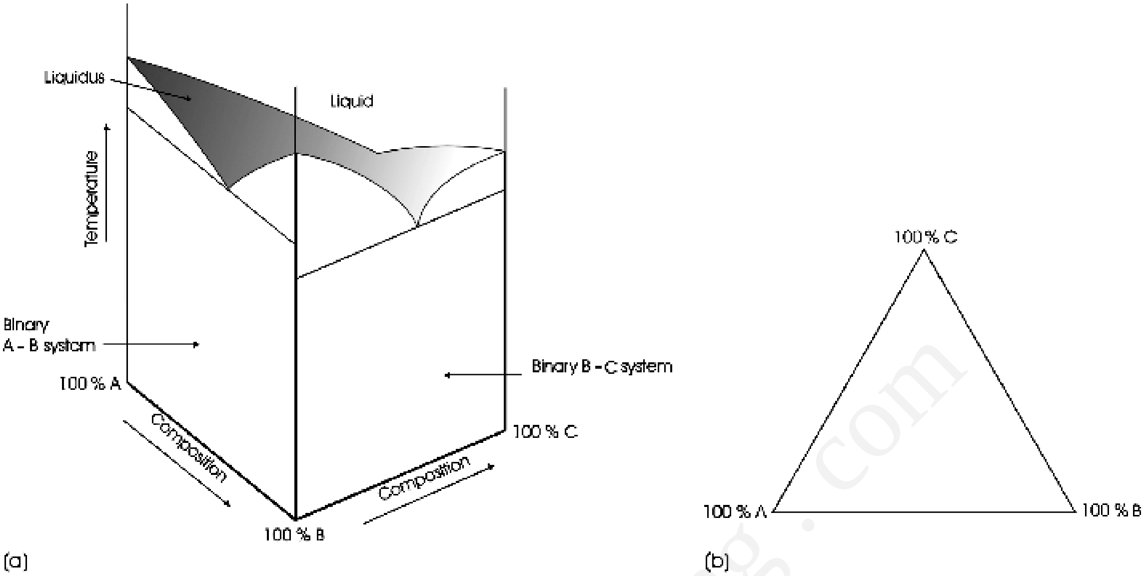

Figure 4.18 (a) The general form of an isobaric ternary phase diagram and (b) an isothermal section through part (a)

example, point D in Figure 4.19 represents a composition of 60 % A and 40 % C. The material consists of solid A + solid C. The amounts of the two phases can be determined via the lever rule, as explained below.

The composition of an internal point such as E is also found from the composition axes. The point lies on the line s–t. This line is the locus of all points with a composition of 20 % C, and so E corresponds to 20 % C. Similarly it lies on line u–v, corresponding to the locus of all points containing 50 % A, and on line w–x, corresponding to the locus of all points containing 30 % B. The composition at E is therefore 50 % A, 30 % B and 20 % C.

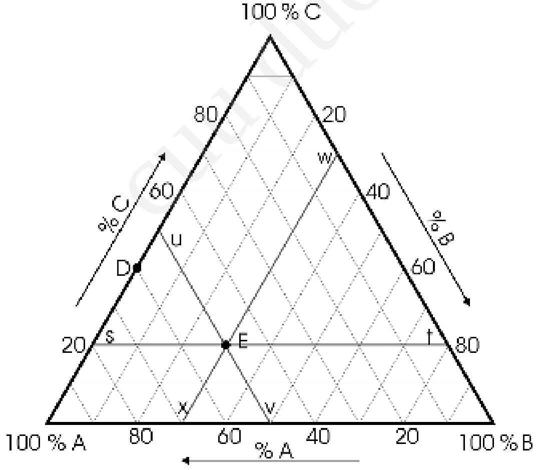

Figure 4.19 Representations of compositions on an isothermal three-component phase diagram

Phases, with or without composition ranges, are plotted in an analogous way to those on binary phase diagrams. A simple ternary phase diagram is drawn in Figure 4.20. It represents the system WO_3–WO_2–ZrO_2 at approximately 1400 °C, which is part of the ternary W–Zr–O system. There are no phases lying within the body of the phase diagram, and all of the phases represented are to be found in the appropriate binary phase diagrams. It is seen that the area of the diagram is divided up into triangles. This is because a point in such a diagram must represent three solid phases if it lies within a triangle, two if it lies on a triangle edge, or one if it lies at a triangle vertex. Thus, point G represents a composition containing WO_2, WO_3 and ZrO_2 at 1400 °C. A composition represented by point H would consist of the phases ZrW_2O_8 and $W_{18}O_{49}$.

The amount of a phase present at a vertex of a triangle is 100 %. The amounts of the phases

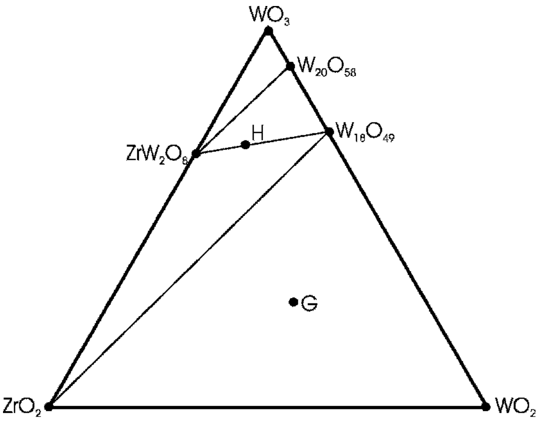

Figure 4.20 The simplified WO_3–WO_2–ZrO_2 phase diagram

present for points lying on the side of a triangle can be determined by the lever rule. For example, the amounts of the two phases present at point I in Figure 4.21 are given by:

$$\text{Amount of } W_{18}O_{49} = \frac{a}{a+b}$$

$$\text{Amount of } ZrO_2 = \frac{b}{a+b}$$

The amounts of the three phases present at point J can be determined by an extension of the lever rule. The phase triangle made up of $W_{18}O_{49}$–WO_2–WO_3 is called a tie triangle, by analogy with the tie line of binary systems. Lines are drawn connecting the point J to the vertices of the tie triangle, as shown in Figure 4.21. The amounts of the phases are then given by the lengths of these lines. For example, at point J:

$$\text{Amount of } W_{18}O_{49} = \frac{c}{c+d}$$

$$\text{Amount of } ZrO_2 = \frac{e}{e+f}$$

$$\text{Amount of } WO_2 \text{ present} = \frac{g}{g+h}$$

This method is called the triangle rule. Note that, just as in the lever rule, we assume that the composition scales are linear. If they are not, actual compositions must be used, not distances. However, this is rarely the case in ternary diagrams, which always use a linear scale for the composition axes.

The approximate phase diagram of a more complex system, MgO–Al_2O_3–SiO_2, is drawn in Figure 4.22. Ceramic bodies are rarely pure phases, and cordierite ceramics, for example, have compositions over a region around the composition of cordierite itself, as shown by the right-hand shaded area. In addition, the composition of some of these phases is

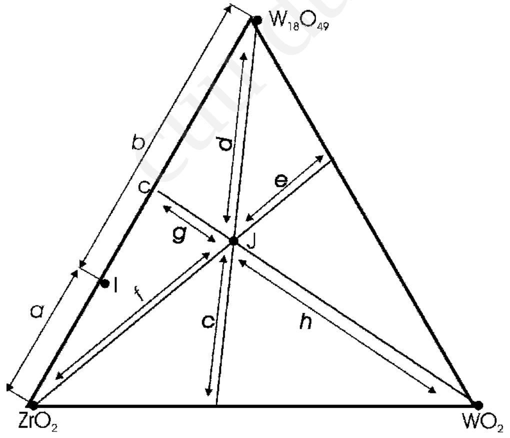

Figure 4.21 The method of determination of compositions on an isothermal phase diagram

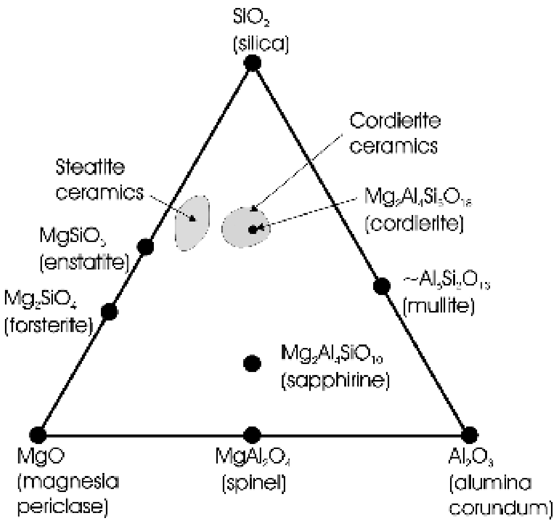

Figure 4.22 Schematic phase diagram for the MgO–Al_2O_3–SiO_2 system, which contains several important ceramic materials

open to confusion. Sapphirine, for example, is sometimes written as $Mg_2Al_2SiO_{10}$, and sometimes as $Mg_4Al_{10}Si_2O_{23}$, a fact that indicates the variable composition of many minerals. Additionally, mullite is a nonstoichiometric compound with a variable composition, and the point drawn for this compound on Figure 4.22 is simply representative of this phase. Steatite ceramics, also noted, have a composition range but are associated with the mineral talc, which does not occur in the phase diagram, as it contains hydroxyl, which is not one of the components.

Answers to introductory questions

What is a binary phase diagram?

Binary systems contain two components, for example, Fe + C. A binary phase diagram displays the phase relations found in a binary system. The diagram is plotted with three variables, temperature (°C), pressure (atm) and composition. In metallurgical phase diagrams, compositions are usually expressed as weight percentages (wt%). In chemical work, atom percentages (at%) or mole percentages (mol%) are used. A single phase in a binary phase diagram will be represented by a volume in the diagram. Phase boundaries form two-dimensional surfaces in the representation, and three phases will coexist along a line in the phase diagram.

As most experiments are carried out at atmospheric pressure, a planar diagram, using temperature and composition as variables, is sufficient for many purposes. These sections at a fixed pressure are called isobaric phase diagrams. In these constant-pressure diagrams a single phase occurs over an area in the figure, and phase boundaries are drawn as lines. A point in such a binary phase diagram defines the temperature and composition of the system.

What is a peritectic transformation?

On heating through a peritectic point, a solid transforms to a liquid plus another solid of a different composition:

$$\text{solid A} \rightarrow \text{solid B} + \text{liquid}.$$

The solid is said to melt incongruently. Many intermediate compounds transform into a liquid at a peritectic point. At a peritectic point, three phases coexist. The point is thus an invariant point, and the reaction is an invariant reaction.

What is the difference between carbon steel and cast iron?

The difference between plain carbon steels (i.e alloys of carbon and iron only) and cast irons can be understood from the iron–carbon phase diagram (Figure 4.17). Plain carbon steels contain less than about 2 wt% carbon, although commercial steels rarely contain much more than 1.4 wt% carbon. The significance of this is that it corresponds to the austenite phase range. This means that steels can be heated to give a homogeneous austenite solid solution. In this condition, they can be worked or formed as a homogeneous material.

When the carbon content is greater than about 2 wt% and less than about 5 wt% carbon, the material cannot be heated to give a homogeneous solid solution. At all temperatures below the eutectic temperature of 1148 °C the solid is a mixture of austenite and cementite, or ferrite and cementite. The effect of this is that the materials are hard, brittle and resist deformation. The material can be cast into the desired shape, and is referred to as cast iron. Commercial cast irons rarely contain much more than about 4.5 wt% carbon.

Further reading

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Problems and exercises

Quick quiz

1 A phase is:
(a) A compound in a system
(b) An element in a system
(c) A homogeneous part of a system enclosed in a boundary

2 A component is:
(a) A compound in a phase diagram
(b) An element in a phase diagram
(c) An essential substance used to construct a phase diagram

3 The phase diagram of a one-component system is described in terms of:
(a) One variable
(b) Two variables
(c) Three variables

4 How many phases coexist at a triple point in the iron phase diagram:
(a) One?
(b) Two?
(c) Three?

5 On a phase boundary in the sulphur system:
(a) One phase exists
(b) Two phases exist
(c) Three phases exist

6 At a critical point in a unary system:
(a) Vapour and liquid cannot be distinguished
(b) Solid and liquid cannot be separated
(c) Freezing cannot occur

7 A cooling curve changes slope when:
(a) An invariant point is passed
(b) A phase boundary is crossed
(c) Crystals form

8 A binary system is one in which:
(a) There are two components present
(b) There are two variables needed
(c) A solid and a liquid are present

9 The number of variables needed to specify phase relations in a binary system are:
(a) Two
(b) Three
(c) Four

10 The liquidus is a boundary that separates:
(a) Two different liquids
(b) The liquid from the solid phase
(c) The liquid from the solid + liquid region

11 The solidus is a boundary that separates:
(a) A solid from a liquid
(b) A solid from a solid + liquid region
(c) Two different solid phases

12 A tie line is drawn:
(a) Parallel to the pressure axis
(b) Parallel to the temperature axis
(c) Parallel to the composition axis

13 A binary phase diagram in which the pressure is always constant is:
(a) An isobaric section
(b) An isostatic section
(c) An isothermal section

14 The solvus line on a phase diagram separates:
(a) A solid from a solid + liquid region
(b) A solid solution from a two-solid region
(c) A solid from a solid solution region

15 A eutectic point on a binary phase diagram is:
(a) An invariant point

(b) A triple point

(c) A critical point

16 On cooling a homogeneous liquid sample through a eutectic point:

(a) A liquid plus a solid forms

(b) Two solid phases form

(c) A homogeneous solid forms

17 A line phase on a phase diagram is a phase that:

(a) Exists along a phase boundary

(b) Has a composition range along a tie line

(c) Has no apparent composition range

18 Solid phases that melt congruently melt to form:

(a) A liquid of the same composition and a solid of a different composition

(b) A solid of the same composition and a liquid of a different composition

(c) A liquid of the same composition

19 Heating a solid through a peritectic point produces:

(a) A solid with a different composition, and a liquid

(b) A solid with the same composition, and a liquid

(c) A liquid with a different composition

20 Pure iron has:

(a) Two allotropes

(b) Three allotropes

(c) Four allotropes

21 Steel is an alloy of iron and carbon in which the carbon occupies:

(a) Substitutional sites

(b) Interstitial sites

(c) Vacancies

22 Ferrite is:

(a) An allotrope of iron

(b) An intermediate phase

(c) An iron–carbon alloy

23 Austenite has:

(a) No appreciable composition range

(b) A narrow composition range compared with ferrite

(c) A wide composition range compared with ferrite

24 Austenite has the same crystal structure as:

(a) α-iron

(b) β-iron

(c) γ-iron

25 Steel is an alloy of iron that has a composition less than:

(a) The maximum austenite composition

(b) The maximum ferrite composition

(c) The maximum cementite composition

26 Cast irons generally have compositions of iron and:

(a) Exactly 2 wt% carbon

(b) More than 2 wt% carbon

(c) Less that 2 wt% carbon

27 On cooling a homogeneous solid phase through a eutectoid point it forms:

(a) Two solid phases

(b) A solid and a liquid phase

(c) A homogeneous single solid phase

28 On heating a homogeneous solid through a peritectoid point it forms:

(a) A solid and a liquid phase

(b) A homogeneous single solid phase

(c) Two solid phases

29 A ternary system is one in which there are:

(a) Three components

(b) Three variables

(c) Three phases

30 To represent all possible phase relations, a ternary system needs:

(a) Five axes

(b) Four axes

(c) Three axes

31 A triangular representation of the phase relations in a ternary system is:
  (a) An isothermal section
  (b) An isobaric section
  (c) An isobaric and isothermal section

32 Within a tie triangle on a ternary phase diagram, a point will correspond to:
  (a) Two solid phases
  (b) Three solid phases
  (c) Four solid phases

Calculations and questions

4.1 A copper–nickel alloy is made up with 28 g copper in 100 g alloy. What is the atom percentage of nickel in the alloy?

4.2 A solid solution of aluminium oxide (Al_2O_3) and chromium oxide (Cr_2O_3) has a composition $Al_{0.70}Cr_{1.30}O_3$. What mass of Cr_2O_3 needs to be weighed out to prepare 100 g of sample?

4.3 A copper–zinc alloy is made up with 35 g copper in 100 g alloy (35 wt%). What is the atom percentage of zinc in the alloy?

4.4 A solder contains 50 wt% tin (Sn) and 50 wt% lead (Pb). What are the atom percentages of tin and lead in the solder?

4.5 An intermetallic compound in the titanium–aluminium (Ti–Al) system is found at 78 wt% Ti and 22 wt% Al. What is the approximate formula of the compound?

4.6 An equilibrium sample of a copper–nickel (Cu–Ni) alloy with a composition of 65 wt% nickel is prepared. With reference to the Cu–Ni phase diagram shown in Figures 4.6 and 4.8:
  (a) What is the atom percentage of copper present in the alloy?
  (b) On heating the alloy from room temperature, at what temperature does liquid first appear?
  (c) What is the composition of the liquid?
  (d) At what temperature does the solid disappear?
  (e) What is the composition of the final solid?

4.7 For the sample in the previous question, the alloy is held at a temperature of 1340 °C:
  (a) What phase(s) are present?
  (b) How much solid is present, if any?
  (c) How much liquid is present, if any?

4.8 An equilibrium sample of a copper–nickel (Cu–Ni) alloy with a composition of 37 wt% nickel is held at a temperature of 1250°C:
  (a) What are the amounts of solid and liquid present?
  (b) If the density of the solid is $8.96 \times 10^{-3}\,kg\,m^{-3}$, and the density of the liquid is 90 % of that of the solid, calculate the volume percentage of the solid and liquid present

4.9 The phase diagram of the aluminium oxide (Al_2O_3) and chromium oxide (Cr_2O_3) system is given in Figure 4.23. An equilibrium

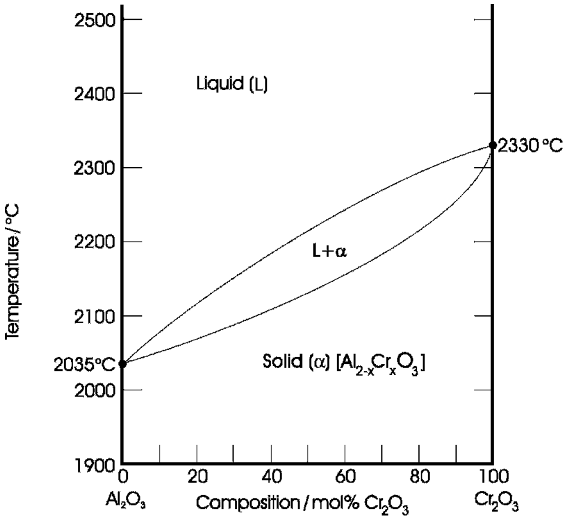

Figure 4.23 Phase diagram of the aluminium oxide (Al_2O_3) and chromium oxide (Cr_2O_3) system, for Questions 4.9–4.12

sample of composition 50 mol% Cr_2O_3 is prepared.

(a) What is the weight percentage of Al_2O_3 present?

(b) The sample is held at 2200 °C. What is the composition of the solid phase present?

(c) How much liquid phase is present?

(d) At what temperature will the last of the solid disappear?

(e) What will the composition of this solid be?

4.10 With reference to the phase diagram of the aluminium oxide (Al_2O_3) and chromium oxide (Cr_2O_3) system given in Figure 4.23, a sample of composition 30 mol% Cr_2O_3 is held at 2300 °C and then slowly cooled.

(a) At what temperature does solid first appear?

(b) What is the composition of the solid

(c) At what temperature does the liquid finally disappear?

(d) What is the composition of the last drop of liquid?

4.11 With reference to the phase diagram of the aluminium oxide (Al_2O_3) and chromium oxide (Cr_2O_3) system given in Figure 4.23, a sample of composition 30 mol% Cr_2O_3 is held at 2180 °C.

(a) What is the composition of any solid phase present?

(b) What is the composition of any liquid phase present?

(c) How much of each phase is present?

4.12 With reference to the phase diagram of the aluminium oxide (Al_2O_3) and chromium oxide (Cr_2O_3) system given in Figure 4.23, a sample of composition 30 mol% Cr_2O_3 is held at 2100 °C.

(a) What is the composition of any solid phase present?

(b) What is the composition of any liquid phase present?

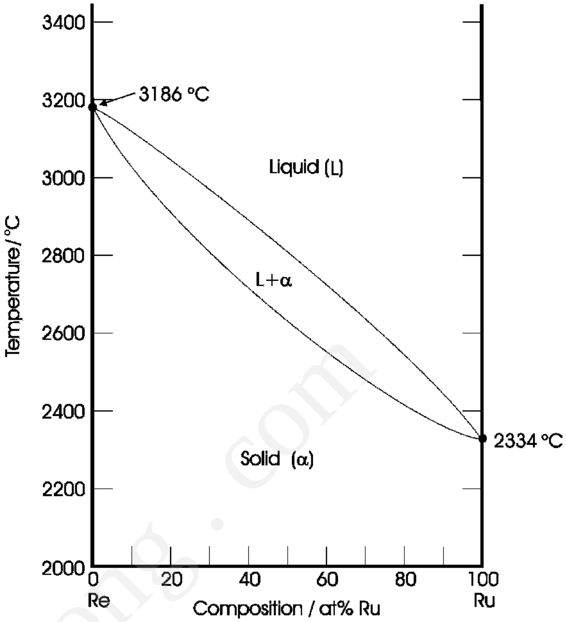

Figure 4.24 Phase diagram of the ruthenium–rhenium (Ru–Re) system, for Questions 4.13 and 4.14

(c) How much of each phase is present?

4.13 The phase diagram of the ruthenium–rhenium (Ru–Re) system is given in Figure 4.24.

(a) What are the melting points of pure Re and pure Ru?

(b) A sample of composition 70 at% Ru is made up. What weights have to be added to prepare 100 g of sample?

(c) This alloy is held at a temperature of 2200 °C. What phases are present and what are their compositions?

(d) The alloy is held at 3000 °C. What phases are present and what are their compositions?

4.14 The phase diagram of the ruthenium–rhenium (Ru–Re) system is given in Figure 4.24. A sample of composition 60 at% Ru is made up and held at 2700 °C.

(a) What is the composition of any solid phase present?

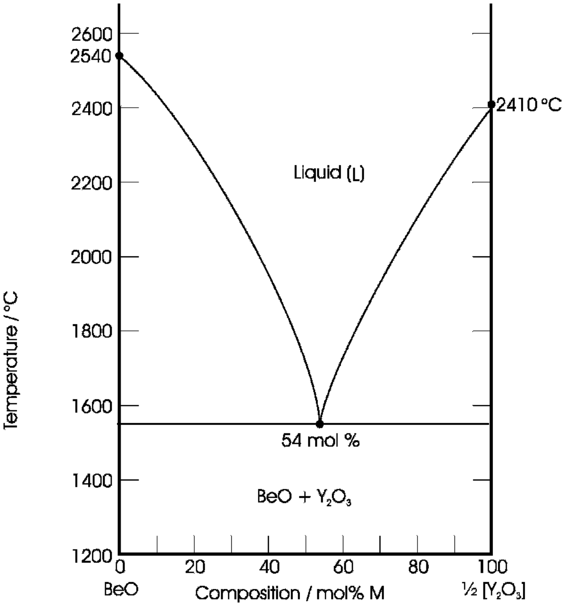

Figure 4.25 Phase diagram of the BeO–Y_2O_3 system, for Questions 4.15–4.17

(b) What is the composition of any liquid phase present?

(c) How much of each phase is present?

4.15 The phase diagram of the BeO–Y_2O_3 system is shown in Figure 4.25. Explain why this figure differs from that of the lead–tin system, Figure 4.9, and comment on the composition axis chosen. [Note: answer is not provided at the end of this book.]

4.16 With respect to the phase diagram for BeO–Y_2O_3, shown in Figure 4.25, a composition is made up with 80 mol% BeO and held at 2000 °C.

(a) What weights of the components are needed to make 100 g of sample?

(b) How much solid is present?

(c) What is the composition of the solid?

(d) How much liquid is present?

(e) What is the composition of the liquid?

4.17 With respect to the sample in Question 4.16, the material is cooled to 1400 °C.

(a) What phases are present?

(b) What are the compositions of the phases?

(c) What are the proportions of each phase present?

4.18 With respect to the lead–tin (Pb–Sn) phase diagram shown in Figures 4.9–4.12, a sample is made up with 40 at% tin.

(a) What weights of lead and tin are needed to make 100 g solid?

(b) What phase(s) is (are) present when the sample is held at 300 °C?

(c) What is (are) the composition(s) of the phase(s)?

(d) How much of each phase is present at 300 °C?

4.19 With respect to the lead–tin (Pb–Sn) phase diagram shown in Figures 4.9–4.12, the sample made up with 40 at% tin is cooled slowly to 250 °C.

(a) What phases are present at 250 °C

(b) What is the composition of each phase?

(c) How much of each phase is present?

4.20 With respect to the lead–tin (Pb–Sn) phase diagram shown in Figures 4.9–4.12, the sample made up with 40 at% tin is cooled further to 100 °C.

(a) What phases are present at 100 °C?

(b) What is the composition of each phase?

(c) How much of each phase is present?

4.21 With respect to the iron–carbon (Fe–C) diagram shown in Figures 4.16 and 4.17, an alloy with a composition of 1.5 wt% carbon is homogenised by heating for a long period at 1000 °C.

(a) What phase(s) is (are) present?

(b) How much of each phase is present?

(c) What is (are) the composition(s) of the phase(s)?

4.22 With respect to the iron–carbon (Fe–C) diagram shown in Figures 4.16 and 4.17, the alloy with a composition of 1.5 wt% carbon is homogenised by heating for a long period at

1000 °C and is subsequently cooled slowly to 800 °C.

(a) What phase(s) is (are) present?

(b) How much of each phase is present?

(c) What is (are) the composition(s) of the phase(s)?

4.23 With respect to the iron–carbon (Fe–C) diagram shown in Figures 4.16 and 4.17, an alloy with a composition of 5 at% carbon is homogenised by heating for a long period at 1350 °C.

(a) What is the composition of the liquid phase present?

(b) How much of the liquid phase is present?

(c) What is the composition of the solid phase present?

(d) How much solid phase is present?

4.24 With respect to the phase diagram of the WO_3–WO_2–ZrO_2 system shown in Figure 4.20, a sample is made up of an equimolar mixture of WO_3, WO_2 and ZrO_2, (1:1:1) and heated at 1100 °C to equilibrium.

(a) What phases are present?

(b) How much of each phase is present?

4.25 With respect to the phase diagram of the WO_3–WO_2–ZrO_2 system shown in Figure 4.20, a sample is made up of a mixture of 80 mol% WO_3, 10 mol% WO_2 and 10 mol% ZrO_2 (8:1:1) and heated at 1100 °C to equilibrium.

(a) What phases are present?

(b) How much of each phase is present?

4.26 According to Figure 4.22, what phases are present in steatite ceramics and cordierite ceramics? [Note: answer is not provided at the end of this book.]