8

Reactions and transformations

- What is dynamic equilibrium?
- What defines a martensitic transformation?
- What is the main driving force for sintering?

The direction of a chemical reaction or a phase transformation can be determined from the equilibrium thermodynamic properties of the phases involved. Note, though, that the speed of any transformation is not accessible from thermodynamics. Thermodynamics clearly states that diamond will transform into graphite at room temperature, but the rate of the reaction is insignificant. This chapter is concerned mainly with the kinetics of reactions, the speed at which they occur. Marrying this aspect with thermodynamics lies outside the scope of this chapter, but some introductory notes are given in Section S3.2.

8.1 Dynamic equilibrium

Dynamic equilibrium is an important and powerful concept in many areas of science. It is useful when discussing matters as diverse as the population of plants or animals in a region, the ozone layer in the upper atmosphere or the number of dust particles at a particular height in a column of air.

8.1.1 Reversible reactions and equilibrium

Chemical equations are usually written to represent a change in one direction only, from reactants to products:

$$\mathrm{Si} + \mathrm{O_2} \rightarrow \mathrm{SiO_2}$$

The tendency for silica, SiO_2, once formed, to disproportionate into elemental silicon and oxygen is very small indeed. However, there are a number of important chemical reactions where the reverse tendency of a reaction is similar to the forward tendency. These can be represented by an equation:

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons x\,\mathrm{X} + y\,\mathrm{Y}$$

where the double arrows signify that the reaction can take place in either direction. In such a reversible reaction, the reactants and products are not at all clearly defined, and either A and B or X and Y fulfil both roles. A feature of reversible reactions is that they often appear to be static, as if there were no change occurring. This state of affairs is illusory. Reactants are being consumed and regenerated by the forward and backward reactions continuously. If no change seems to be taking place it is because the rates of the reactions in each direction

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are balanced. In this case, the system is said to be in equilibrium.

These concepts can be illustrated by reference to a simple reversible reaction involving the dimerisation of nitrogen dioxide, NO_2. The reaction is written:

$$N_2O_4 \rightleftharpoons 2\,NO_2$$

If a quantity of N_2O_4 is introduced into an evacuated vessel at a fixed temperature, ultimately the vessel will contain a mixture of both N_2O_4 and NO_2 molecules. Similarly, if a quantity of NO_2 is introduced into an identical evacuated vessel at the same temperature, after a time the vessel will again contain a mixture of the two molecules. After a sufficient length of time, the ratio of the two species present will be the same in both cases (Figure 8.1). The system is then at equilibrium. At equilibrium, N_2O_4 and NO_2 molecules are continuously changing from one to another, and the rate of the forward reaction will be the same as the rate of the reverse reaction. The important feature is that the equilibrium is a dynamic state of affairs.

However, the ratio of the two species in the container is constant when a time average is taken. The equilibrium position will be obtained no matter where we start. That is, it does not matter whether we take a vessel that, at the outset, contains only N_2O_4 or only NO_2. In either case the same mixture will eventually form. The appearance of stasis is an illusion created by the large number of reacting molecules involved.

A change of conditions may change the apparent equilibrium because it may effect one of the reactions, say the forward reaction, more than the other, the reverse reaction. The equilibrium state that will finally prevail is found to be dependent on external conditions of temperature, pressure (for gas reactions) and the concentration of reactants.

8.1.2 *Equilibrium constants*

In any reversible reaction involving gases or solutions that can be written

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons x\,\mathrm{X} + y\,\mathrm{Y}$$

the equilibrium constant, K_c, is given by:

$$K_c = \frac{[\mathrm{X}]^x[\mathrm{Y}]^y}{[\mathrm{A}]^a[\mathrm{B}]^b} \qquad (8.1)$$

where [A] denotes the concentration of compound *A*, and so on when the reaction has come to equilibrium. The units of K_c are concentration units. The value of the equilibrium constant, K_c,

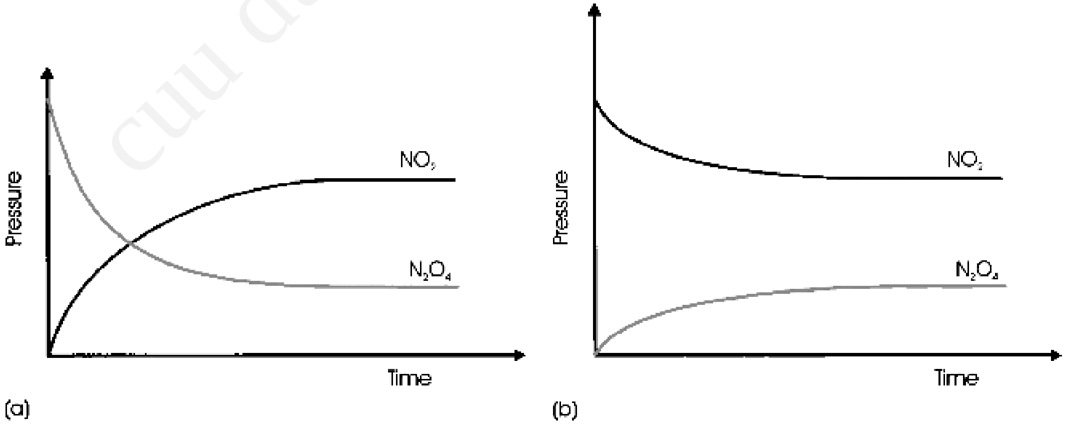

Figure 8.1 The equilibrium in a reversible reaction does not depend on initial conditions: (a) starting point 100 % N_2O_4; (b) starting point 100 % NO_2

depends only on temperature. It does not change when concentrations, volumes or pressures change. Pure liquids or pure solids that appear in the reaction equation (such as water for reactions in solution) do not figure in the equilibrium constant equation.

In reactions involving gaseous species, it is more convenient for the equilibrium constant to be expressed in terms of the partial pressures of the components:

$$K_p = \frac{p_X^x p_Y^y}{p_A^a p_B^b} \quad \text{at equilibrium,}$$

where (p_A) is the partial pressure of compound A, and so on.

For the reaction:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

$$K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}}$$

The units of K_p are pressure units.

8.1.3 Combining equilibrium constants

In the environment, or in many industrial processes, it is often necessary to work with several successive reversible reactions. The combination of equilibrium constants is straightforward. For any reversible reaction:

$$K(\text{reverse reaction}) = \frac{1}{K(\text{forward reaction})}$$

If several reactions can be added to produce an overall reaction, the equilibrium constants can be multiplied together to produce the overall equilibrium constant. For example:

$$C(s) + H_2O \rightleftharpoons CO(g) + H_2(g)$$

$$K_1 = \frac{p_{CO}p_{H_2}}{p_{H_2O}}$$

Note: Pure solids do not figure in equilibrium constants.

$$CO_2(g) + 2\,H_2(g) \rightleftharpoons 2\,H_2O(g) + C(s)$$

$$K_2 = \frac{p_{H_2O}^2}{p_{CO_2}p_{H_2}^2}$$

The overall reversible reaction is

$$CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

for which the equilibrium constant, K_3, is given by

$$K_3 = \frac{p_{H_2O}p_{CO}}{p_{CO_2}p_{H_2}} = K_1\,K_2$$

8.1.4 Equilibrium conditions

It is useful, and often vital, to know how a change in conditions will affect an equilibrium. For example, there is considerable debate at present about how a change in global temperature, global warming, will affect the (equilibrium) climate of the Earth. Le Chatelier's principle describes what will happen when a reaction at equilibrium is subjected to a change in conditions. It is found that the reaction proceeds towards a new equilibrium state that (at least partially) offsets the change in conditions.

The conditions of greatest importance are the concentrations of reactants or products, the volume or pressure and the temperature. Remember that the equilibrium constant depends only on temperature. It does not change when concentrations, volumes or pressures change. The following examples illustrate le Chatelier's principle.

8.1.4.1 Concentration

Addition of a reactant appearing in the equilibrium constant equation changes the equilibrium to remove as much as possible of the added component. For example, for

$$C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$$

if $CO_2(g)$ is added to the mixture, the equilibrium will shift from the left-hand side to the right-hand side to reduce the amount of $CO_2(g)$ present. In the new equilibrium state the amount of $CO_2(g)$ and CO will both be greater than in the original state. If CO(g) is added, the equilibrium will shift from the right-hand side to the left-hand side to decrease the amount of CO present. The addition of C(s) produces no change, as the concentration of a solid does not influence the equilibrium constant.

8.1.4.2 Volume and pressure

A decrease in volume or an increase in applied pressure shifts the reaction equilibrium towards the side with fewer moles of gas. For example, with the reaction

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

an increase in pressure or decrease in volume will cause the equilibrium to move from the right-hand side to the left-hand side, which helps to offset the change applied. If the number of molecules is constant then volume and pressure changes do not affect the equilibrium.

8.1.4.3 Temperature

An increase in temperature shifts the reaction equilibrium in the direction in which heat will be absorbed. A decrease in temperature shifts the equilibrium in the direction in which heat will be liberated.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \quad \Delta H_R^\circ = +158\,\text{kJ}$$

is an endothermic reaction in which 158 kJ are consumed for each mole of CaO produced (see Section S3.2). An increase in temperature will shift the reaction in the direction that causes more heat to be consumed. The reaction will shift from left-hand side to the right-hand side, and there will be an increase in the amount of $CO_2(g)$ present at a higher temperature.

8.1.5 Pseudochemical equilibrium

Many nonchemical reactions can be treated by using similar techniques. One such is the creation of mobile electrons and holes in an intrinsic semiconductor. In this case, thermal energy excites some electrons from a filled valence band to the energetically nearby empty conduction band, the result of which is a population of mobile holes in the valence band and a population of mobile electrons in the conduction band. At ordinary temperatures, this is a dynamic equilibrium. There is a continuous excitation of electrons, and these are continuously falling back to the valence band and recombining with holes. The appearance of stasis is illusory.

This situation can be represented by a pseudochemical equation. As the electrons and holes are generated by thermal energy, the equation can be written:

$$\text{null} \rightleftharpoons [\text{n}] + [\text{p}]$$

where [n] is the concentration of electrons in the conduction band and [p] is the concentration of holes in the valence band. The equilibrium concentration is then

$$K = [\text{n}][\text{p}]$$

K will depend on temperature, in the expected way, but not on pressure or how much semiconductor is in the sample.

In an intrinsic semiconductor, the number of holes will equal the number of electrons. However, the equilibrium equation also applies to doped semiconductors, and the equilibrium constant derived for a pure intrinsic semiconductor is valid for a doped sample of the same semiconductor. This is an extremely useful finding because it means that as the concentration of electrons in a semiconductor is increased by doping the concentration of holes decreases, and vice versa. Thus an n-type semiconductor can be changed to a p-type semiconductor simply by increasing the number of holes present, by appropriate doping, and vice versa. This possibility underlies the fabrication of semiconductor devices. This information is used in Sections 13.2.2 and 13.2.4.

The equilibrium population of point defects is another example of a pseudochemical equilibrium. For the creation of a Frenkel defect on a cation array:

$$\text{null} \rightleftharpoons [\text{cation interstitial}] + [\text{cation vacancy}]$$

with an equilibrium constant

$$K = [\text{cation interstitial}][\text{cation vacancy}]$$

where square brackets indicate the concentrations of the defects. Other intrinsic point defect equilibria can be treated in the same way.

8.2 Phase diagrams and microstructures

Many of the processes that are used to make a useful material are grounded in reactions that involve a change of chemical composition or a change in the microstructure or nanostructure of the solid. The processing of steel is aimed largely at obtaining the correct microstructure, and the preparation of semiconductors involves altering the populations of defects present. This section outlines some of the ways in which these changes are accomplished.

8.2.1 Equilibrium solidification of simple binary alloys

One of the most important phase transitions occurs when a liquid transforms into a solid. A great deal of information concerning the microstructure of the solid can be obtained from a consideration of the phase diagram of the material, even though phase diagrams refer to equilibrium conditions and solidification is rarely carried out so slowly as to be an equilibrium process. For example, consider the solidification of a simple nickel–copper alloy, from the point of view of the phase diagram, reproduced in Figure 8.2.

In the liquid state, any nickel–copper alloy is homogeneous. Solid will begin to form as soon as the temperature reaches the liquidus, at T_1 (Figure 8.2a). The initial composition of the liquid is l_1, (virtually equal to c) and that of the solid is s_1. The solid is rich in nickel compared with the original liquid composition. If the material is held at a temperature of T_1 for long enough, a dynamic equilibrium will be achieved. In this state, although the system appears to be static, the solid is continually dissolving and reforming. The atoms that are in the liquid and solid phases are continually being exchanged.

As the mixture is slowly cooled, this exchange leads to a continuous change in the composition of the solid and liquid phases. Consider the situation that will hold when the temperature drops slightly to T_2 (Figure 8.2b). In this case, the original solid of composition s_1 has been replaced by a solid of composition s_2 (much exaggerated in the figure). The new composition of the liquid in equilibrium with the solid is l_2. At all times, the atoms in the solid are dissolving in the liquid, and other atoms in the liquid are crystallising to form solid. Over a period of time the crystal present will always have the composition s_2, although the actual atoms that comprise the solid are forever changing. The same is true of the liquid. Further slow cooling, to temperature T_3, will cause the composition of the solid to change gradually to s_3, in equilibrium with liquid of composition l_3 (Figure 8.2c). This imaginary process can be continued until all of the original composition c is identical to the point on the solidus s_4, at temperature T_4 (Figure 8.2d). The final trace of liquid in composition with this solid has a composition l_4.

Thus, during equilibrium cooling, the composition of the solid will run down the solidus line, s_1 to s_2 to s_3, and so on, and the composition of the liquid in equilibrium with the solid runs down the liquidus from l_1 to l_2 to l_3, and so on, as the liquid cools. The composition of the solid phase when all of the liquid has solidified will be equal to that of the original liquid phase. Not only does the composition of the solid and liquid phases change continuously as the temperature falls through the two-phase region, but the number of small crystals present also increases. When temperature T_4 is reached, the microstructure of the solid consists of crystallites or grains

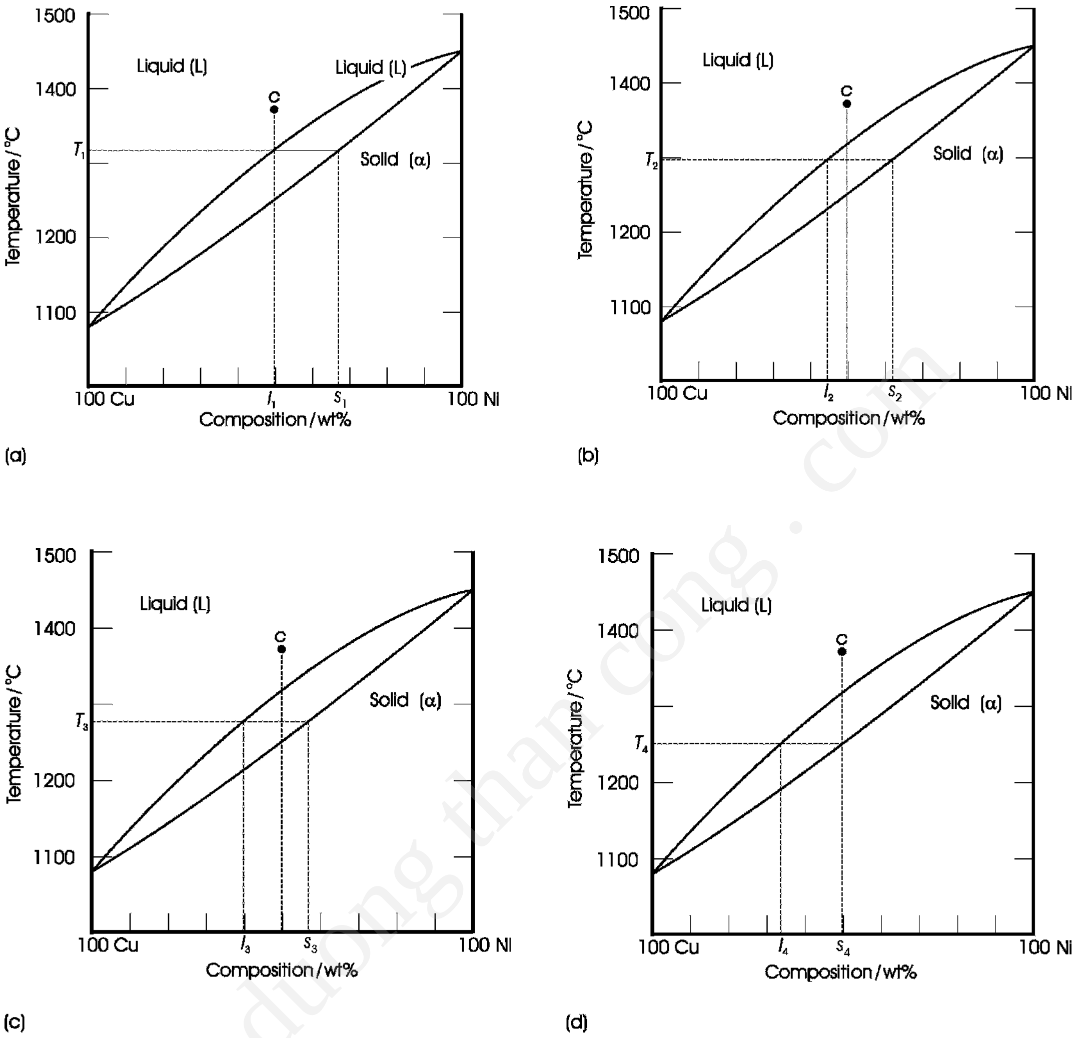

Figure 8.2 A sample of composition c in the nickel–copper system will consist of liquid, liquid plus solid, or solid, depending on the temperature T_i: (a) at T_1, the liquidus, the liquid has a composition l_1, virtually equal to c, and the infinitesimal amount of solid has a composition s_1; (b) at T_2, the liquid has a composition l_2 and the solid a composition s_2; (c) at T_3, the liquid has a composition l_3 and the solid a composition s_3; (d) at T_4, the solidus, the infinitesimal amount of liquid has a composition l_4 and the solid a composition s_4, equal to c

(Figure 8.3a). Further cooling in the solid will not initiate change of composition.

8.2.2 Nonequilibrium solidification and coring

During normal processing, cooling is usually rather fast, and solidification is rarely an equilibrium process. Solidification in these conditions is extremely complex. If cooling is not too fast, the first material to precipitate will still have a composition s_1 (Figure 8.2a). However, there will be insufficient time on further cooling for the original solid to equilibrate, and new material of composition s_2 (Figure 8.2b) will start to form on the nucleus of composition s_1. Ultimately, the solid will consist of

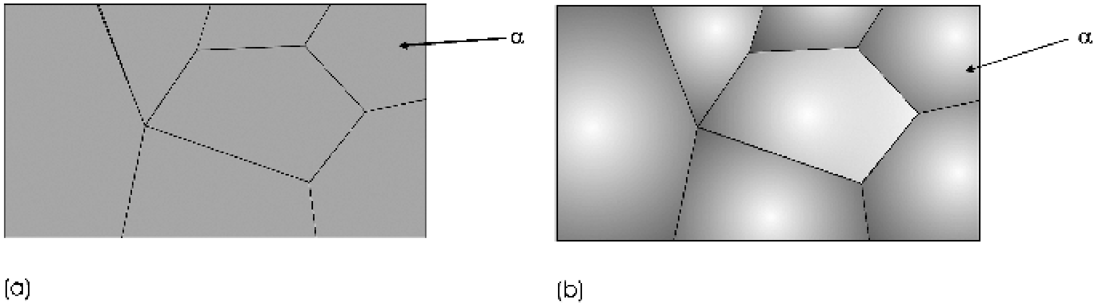

Figure 8.3 Microstructures of a solidified nickel–copper alloy: (a) after slow cooling the grains are homogeneous; (b) after rapid cooling, the grains are richer in one component (Ni) at the grain centres (paler shading) and richer in the other (Cu, darker shading) at the grain surfaces

a core that is richer in nickel than the outer regions, and there will be a gradation of composition of the alloy from the inside to the outside (Figure 8.3b). This is called coring. Coring can occur in all crystallites formed rapidly, including dendrites.

These nonequilibrium structures can be removed by heating the solid for an appropriate amount of time at a temperature below that of the solidus, a process called annealing. Annealing is effective only if the atoms can diffuse in the solid to correct the compositional differences generated during the cooling.

8.2.3 Solidification in systems containing a eutectic point

The composition and microstructure of a solid formed in a system showing a eutectic point depends critically on the composition of the liquid with respect to the eutectic composition. The situation will be explained by using the lead–tin (Pb–Sn) phase diagram described in Section 4.2.3.

In a liquid lead–tin alloy the two atom species are mixed at random. A liquid alloy with the same composition as that of the eutectic point, c_e, called the eutectic composition, is unique. It will pass directly into the solid state at a temperature 183 °C, without traversing a two-phase solid plus liquid region as it cools (Figure 8.4a). The solid that forms must contain two phases, solid α and solid β. Thus, the random arrangement of atoms in the liquid must separate into the appropriate solid compositions on solidification. It is found that each grain contains a characteristic microstructure that consists of thin alternating lamellae of the two phases, α and β, called eutectic α and eutectic β (Figure 8.4b). The actual thickness of the lamellae and their shapes will depend on the relative diffusion coefficients of the two species. Note, though, that the *average* composition of the solid will be the same as that of the eutectic point.

The idealised microstructure of a solid formed when other liquid compositions cool is derived in a similar way. Suppose that the liquid with composition c_1, richer in lead than the eutectic composition (Figure 8.5a), is slowly cooled. At temperature T_1, below the liquidus, some solid α phase will have nucleated (Figure 8.5b). The composition of the solid phase, given by the tie line, is s_1. Similarly, the composition of the liquid phase is l_1. As slow cooling continues, the composition of the solid α crystallites will move along the solidus, as described in Section 8.2.1 for the nickel–copper alloys. At the same time, the composition of the liquid phase in contact with the crystallites will move along the liquidus. For example, at temperature T_2 the solid has a composition of s_2 and the liquid a composition of l_2 (Figure 8.5a). Ultimately, the horizontal solidus line will be reached at the eutectic temperature. At this point, any further drop

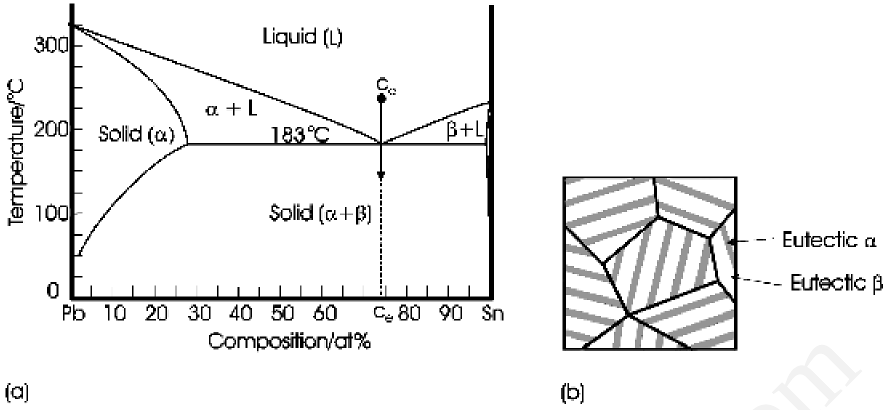

Figure 8.4 (a) The binary lead–tin phase diagram; c_e is the eutectic composition. (b) The microstructure of an alloy of composition c_e; each grain consists of alternating lamellae of eutectic α and eutectic β

in temperature will cause the remaining liquid to solidify. The microstructure of this latter material will be the same characteristic eutectic structure described above. The solid is a mixture of eutectic α and β, and crystallites of the α phase that formed in contact with the liquid, called primary α (Figure 8.5c).

A similar situation will occur for compositions on the tin-rich side of the eutectic point. In this case, the microstructure will consist of precipitates of primary β in a eutectic matrix.

In the case of a composition such as c_2 (Figure 8.6a), the first phase to form as the temperature passes the liquidus is solid α in liquid. Ultimately, the temperature will fall below the solidus and, at a temperature T_1, for example, the solid will consist of grains of α phase (Figure 8.6b). On cooling further, at temperature T_2, for example (Figure 8.6a), the temperature will fall below the solvus, and the solid will consist of precipitates of the β phase in grains of the α phase (Figure 8.6c).

The compositions and amounts of the phases present at all times can be calculated by use of tie lines and the lever rule, as explained in Section 4.2.2.

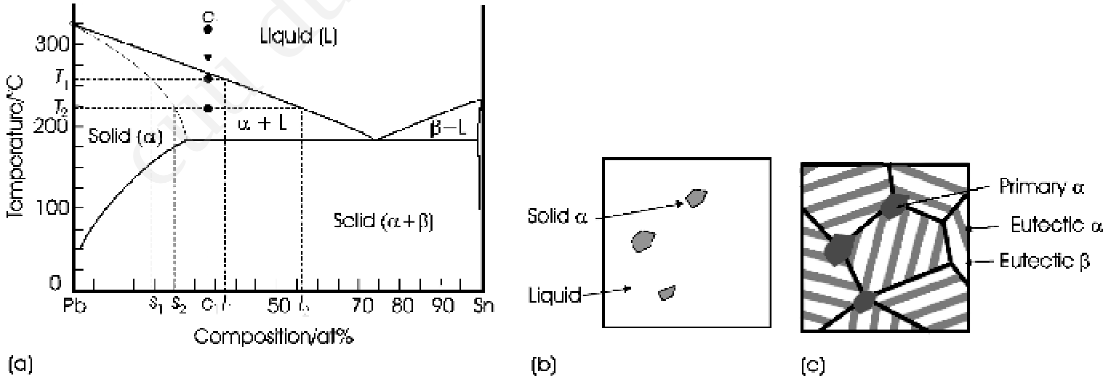

Figure 8.5 (a) The binary lead–tin (Pb–Sn) phase diagram; c_1 is a composition on the lead-rich side of the eutectic composition. (b) Cooling into the $(\alpha + \mathrm{L})$ two-phase region results in the formation of crystallites of solid α in a liquid matrix. (c) Cooling to below the solidus causes the remaining liquid to solidify into alternating lamellae of eutectic α and eutectic β. The grains of primary α are located in the grain boundaries

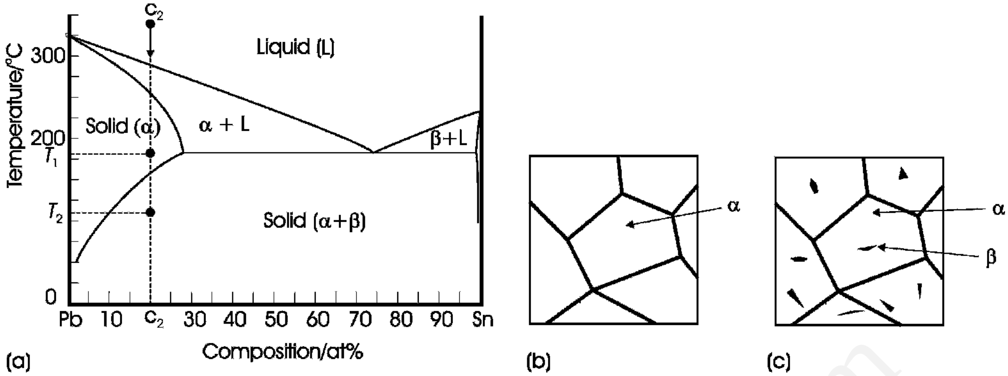

Figure 8.6 (a) The binary lead–tin (Pb–Sn) phase diagram; c_2 is a very lead-rich composition. (b) On cooling to a temperature T_1 the solid consists of homogeneous grains of composition c_2. (c) Cooling to T_2 results in the formation of small precipitates of β in each grain of α

8.2.4 *Equilibrium heat treatment of steels*

Steel is an alloy containing mainly iron, together with small amounts of carbon and other metals. Much of the usefulness of steel centres on the fact that the properties of the alloy, especially the mechanical properties, can be modified by changing the microstructures present in the finished product.

This amounts to the fact that there is not just one steel but a vast range of steels, each suited to a particular function. The changes in properties are brought about by different heating and cooling regimes and exploit the phases present in the iron–carbon (Fe–C) system. The principle microstructures found in steels can be explained by reference to the partial Fe–C phase diagram (Figure 8.7).

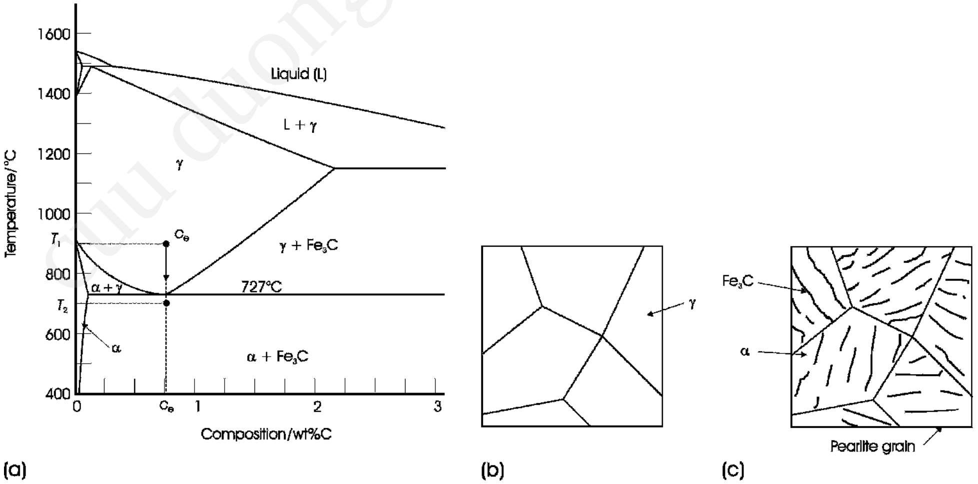

Figure 8.7 (a) The existence diagram of the iron–carbon system; note that Fe_3C is metastable, and the true equilibrium is between iron and graphite. (b) The microstructure of the solid at temperature T_1 consists of γ (astenite) with composition c_e, the eutectoid composition. (c) The microstructure of a solid of composition c_e at a temperature T_2 below the eutectoid composition consists of grains of pearlite, composed of alternating lamellae of Fe_3C and α

The most important transformation point in the Fe–C phase diagram from the point of view of steel is the eutectoid point. This point is at 0.76 wt% carbon (0.034 at% carbon or $\mathrm{FeC}_{0.036}$) and a temperature of 727 °C. Above this temperature (T_1, Figure 8.7a), an alloy with the eutectoid composition, c_e, is a single phase, composed of grains of austenite (Figure 8.7b). On cooling through a eutectoid point, a single solid phase transforms to two solid phases. In the present case, on slow cooling, the single homogeneous phase austenite, which consists of face-centred cubic (fcc) iron containing 0.76 wt% carbon as interstitial carbon atoms, transforms into a two-phase mixture of ferrite (α-ferrite) and cementite (Fe_3C) at a temperature of 727 °C (T_2, Figure 8.7a). The driving force for the transformation into ferrite and cementite is likely to be internal strain. The fcc structure of austenite is strained by the interstitial carbon atoms, and this increases substantially as the temperature falls and the fcc unit cell contracts.

The transformation is complex. The phase diagram shows that the body-centred cubic (bcc) ferrite, one of the phases existing below the eutectoid temperature, is hardly able to dissolve any carbon. The transformation requires diffusion of the carbon to create carbon-poor regions that become ferrite, and carbon-rich regions that become cementite. At the same time the iron atoms must rearrange considerably. The transformation of the fcc austenite array into the bcc ferrite array requires considerable shuffling of the iron atoms. The rearrangement of the iron atoms in austenite to that found in cementite is much more complex. The structure of cementite is made up of hexagonal close-packed (hcp) layers of iron atoms twinned on every third $(1\,1\,\bar{2}\,2)$ plane with respect to the hcp unit cell. The transformation thus involves changing the ABC packing of austenite into multiply twinned ABAB packing. This twinning is a method of minimising the internal strain in the structure while maintaining the overall shape and volume of the solid (further information is found Section 8.3.3 in the discussion of shape-memory alloys). The carbon atoms lie in the twin planes of the cementite structure, where most room occurs.

The newly formed cementite nucleates at many sites simultaneously. The resulting solid, which is a mixture of ferrite and cementite, is called pearlite because it has a lustrous appearance in an optical microscope. Pearlite is not a compound or single phase but is a microstructure, made up of thin lamellae of cementite and α-ferrite side by side (Figure 8.7c). In this context, these phases are called eutectoid ferrite and eutectoid cementite.

The microstructures formed at compositions away from the eutectoid point mirror those previously described for eutectic transformations. Compositions to the iron-rich side of the eutectoid are called hypoeutectoid alloys. For example, a hypoeutectic composition c_1, at temperature T_1 (Figure 8.8a), consists of homogeneous grains of austenite (Figure 8.8b). As these cool slowly, the austenite region is exchanged for a two-phase region (temperature T_2, Figure 8.8a). This material is transformed to ferrite plus austenite. The ferrite often forms at grain boundaries, as the reaction is kinetically favoured in the disordered regions at grain boundaries (Figure 8.8c). The ferrite has an almost constant composition and holds only a very small amount of dissolved carbon in its bcc structure. The remaining austenite thus becomes carbon-rich. As cooling continues, the compositions of the two phases, determined by using tie lines, run down the phase boundaries. Ultimately, the temperature reaches the eutectoid temperature, 727 °C. Further cooling causes the remaining austenite to transform to pearlite (temperature T_3, Figure 8.8a). The microstructure now consists of pearlite (eutectoid ferrite and eutectoid cementite), together with the precipitates of the ferrite formed earlier, called proeutectoid ferrite (Figure 8.8d).

Compositions on the carbon-rich side of the eutectoid are called hypereutectoid alloys. Once again, as such an alloy is cooled slowly it will pass from single-phase austenite into a two-phase region. Consider a hypereutectic composition c_2 at temperature T_1 (Figure 8.9a). The microstructure will consist of grains of austenite (Figure 8.9b). On cooling to temperature T_2 (Figure 8.9a), cementite separates from the austenite, forming preferentially at the grain boundaries (Figure 8.9c). One reason

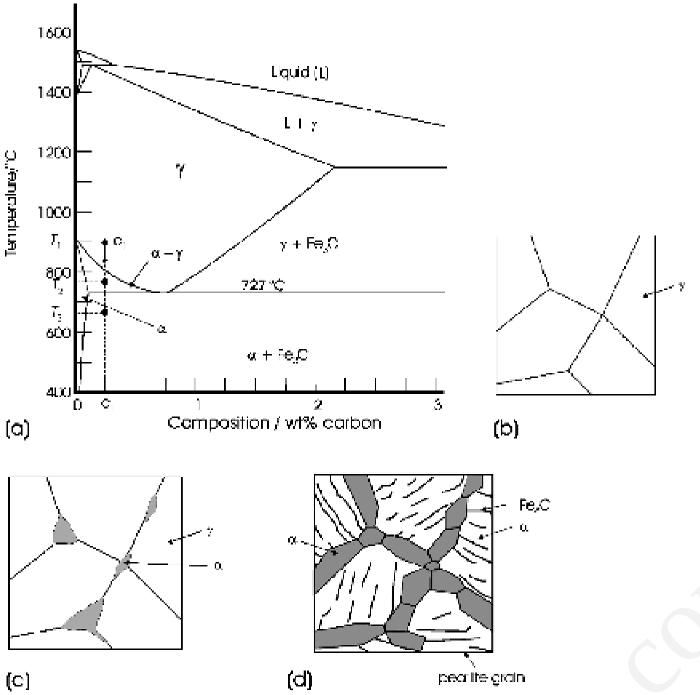

Figure 8.8 (a) The existence diagram of the iron–carbon system. (b) The microstructure of the solid with composition c_1, a hypoeutectoid composition, at a temperature T_1. (c) On cooling to a temperature T_2 the microstructure consists of grains of γ with precipitates of proeutectoid α at the grain boundaries. (d) At a temperature T_3 the microstructure consists of grains of pearlite with proeutectoid α at the grain boundaries

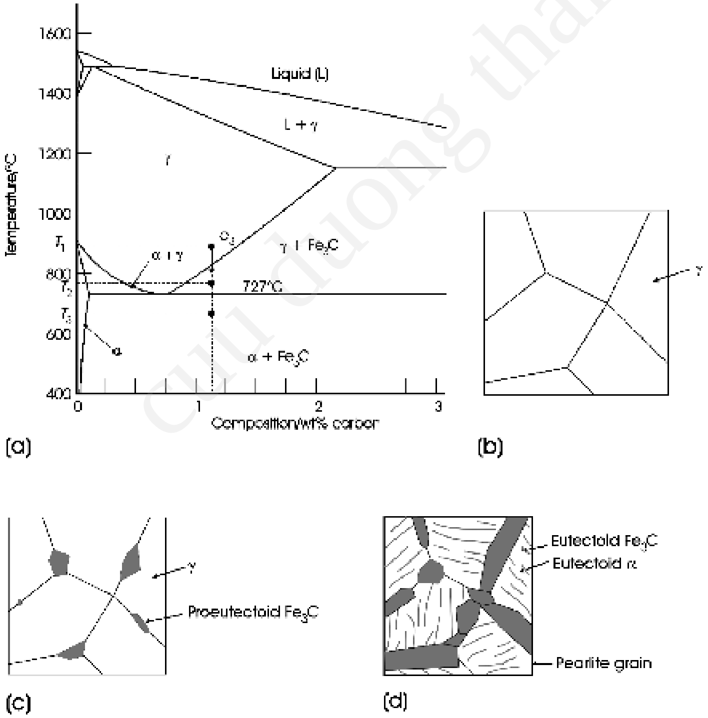

Figure 8.9 (a) The existence diagram of the iron–carbon system. (b) The microstructure of the solid with composition c_2, a hypereutectoid composition, at a temperature T_1. (c) At a temperature T_2 the microstructure consists of grains of γ with precipitates of proeutectoid Fe$_3$C at the grain boundaries. (d) At a temperature T_3 the microstructure consists of grains of pearlite with regions of proeutectoid Fe$_3$C at the grain boundaries

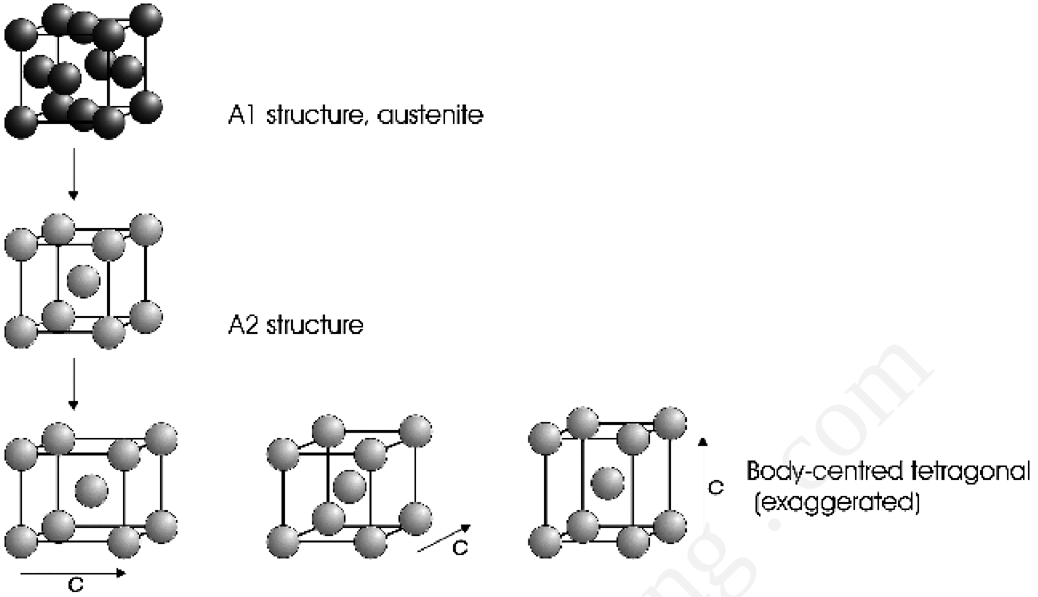

Figure 8.10 Transformations occuring during the formation of martensite

for this is that the strain generated in the complex transformations taking place is more easily relieved at grain boundaries. This material is called proeutectoid cementite. As cooling continues, more proeutectoid cementite will form in the grain boundaries, and the composition of the remaining austenite will run down the phase boundary to the eutectoid point. Further cooling, below the eutectoid temperature, will cause any remaining austenite to transform into pearlite (temperature T_3, Figure 8.9a). The microstructure of the final solid will consist of proeutectoid cementite and pearlite, which itself consists of eutectoid cementite and eutectoid ferrite (Figure 8.9d).

8.2.5 *Rapid cooling of steels*

Rapid cooling will produce different microstructures from those obtained by slow cooling, only a few examples of which are described here. Rapidly cooling the homogeneous alloy austenite, with the fcc structure, to room temperature (a process called quenching), leads to a metastable phase called martensite. The fcc structure of the iron atoms in austenite transforms to a bcc structure of iron atoms in the process (Figure 8.10). The carbon atoms present, normally up to about 1.5 wt%, are trapped in the new structure, which causes a deformation such that one of the cubic cell edges is elongated. The phase is now body-centred tetragonal $(a = b \neq c, \alpha = \beta = \gamma = 90^\circ)$, with the c axis longer than the a and b axes. The cubic phase has a lattice parameter of about 0.286 nm. The lattice parameters of the tetragonal phase vary with carbon content, a_0 taking a value of approximately 0.285 nm, and c_0 taking values between 0.292 nm and 0.300 nm. The ratio of c_0 to a_0 increases linearly with carbon content to a maximum of 1.08 in the highest carbon steels.

The formation of martensite is extremely rapid and only a slight displacement of atoms takes place. In particular, the carbon atoms have no time to diffuse any great distance, and the iron atoms do not have time to shear to form cementite. Once a nucleus of a martensite crystal forms, it will grow to its final size in a time of the order of 10^{-7} s. This is as fast as the speed of sound in iron. The rate of formation seems to be constant down to liquid helium temperatures. The change is called a martensitic transformation. Martensitic transformations are a general class of reactions that are diffusionless.

The temperature at which the transformation to martensite takes place is found to be composition-dependent. Martensite starts to form when the temperature reaches about 700 °C for the lowest-carbon-content steels but not until a temperature of about 200 °C for austenite with a carbon content of 1.2 wt%. The temperature at which the martensite starts to form is usually labelled M_s, the martensite start temperature, and the temperature at which the transformation is complete is labelled M_f. the martensite finish temperature.

The actual microstructure of the martensite that forms is also composition-dependent. Below about 0.6 wt% carbon the martensite forms in long blades and is called lath martensite. At compositions above about 1.0 wt% carbon the form is more lens-shaped in form, and is called plate martensite. At compositions between 0.6 wt% and 1.0 wt% carbon, a mixture of the two forms is found. In addition, most rapidly-quenched steels contain some austenite that has not transformed, intergrown with the laths or plates of martensite.

During the transformation, any one of the original bcc axes might elongate. In practice, all three possibilities occur at random. The martensite grows rapidly to form a grain of body-centred tetragonal structure within the surrounding cubic matrix. The elongation of the unit cell causes a stress around the crystal. Ultimately, the solid is made up of a set of interlocking martensite grains with the *c* axes aligned at random along the original cubic axes, in a matrix of untransformed austenite (Figure 8.11). This creates a strong internal stress field. The result is that martensite is both the hardest and the most brittle constituent of quenched steels. This effect is easily demonstrated. Heat an initially flexible steel piano wire to redness and then rapidly cool it by plunging it into cold water. The cold wire will be brittle and can be snapped by hand. The broken ends will scratch glass.

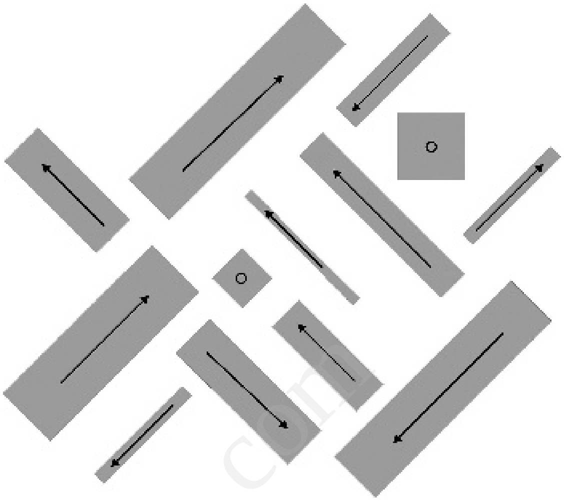

Figure 8.11 The microstructure of martensite regions in austenite. The arrows represent the direction of the elongated *c* axis; the *c* axis is normal to the figure in the domains marked ∘

Martensite reverts to ferrite and cementite when the steel is heated above a temperature at which carbon diffusion becomes possible. This process is called tempering. During tempering, the components present revert to those described in Section 8.2.4. However, the microstructure of the steel will be different from that achieved by slower cooling. The properties of steels are controlled by choosing a cycle of slow cooling, quenching and tempering to optimise the microstructure formed with respect to the end use.

8.3 Martensitic transformations

8.3.1 Displacive transitions

Phase transitions of solids that do not involve a change in chemical composition are often divided into two types, reconstructive and displacive. In a reconstructive transition the parent crystal structure is broken apart and a new structure is formed from the constituents. There is no relationship between the unit cell of the parent form and that of the product. Single crystals undergoing a reconstructive transition usually fragment, and the reactions are usually rather slow. Displacive transitions, however, involve only small, coordinated movements of atoms and are usually rapid. They are often triggered by temperature and are reversible, with the crystal structure of the reactant phase closely related to that of the product.

There are a number of displacive transitions mentioned in this book. The order–disorder transformation of hydrogen atoms in hydrogen bonds in ferroelectric ceramics (Section 11.3.5) is one example. Displacive transitions that involve a change from an ordered arrangement of atoms to a random arrangement are commonly found in alloys. A subgroup of such order–disorder transitions, martensitic transitions, which can be used to produce shape-memory alloys, are considered in Sections 8.3.2 and 8.3.3.

8.3.2 Martensitic transitions in alloys

Martensitic transformations in alloys are essentially order–disorder displacive transitions that take place very rapidly, because atomic diffusion does not occur. The discussion of the formation of martensite in the Fe–C system, in Section 8.2.5, is an example. This transition is the transformation of a cubic phase containing excess carbon in interstitial sites into a tetragonal phase. As any one of three cubic axes can be elongated, three orientations of the martensite *c* axis can occur. This is a general feature of martensitic transformations and the different orientations that can arise are called variants or domains of the martensitic phase. These variants are simply twins (see Section 3.4.10).

An important martensitic transformation occurs in the titanium–nickel (Ti–Ni) system, as it is used in shape-memory alloys, described in Section 8.3.3. The phase in question is TiNi (Figure 8.12), called Nitinol. At temperatures above 1090 °C, TiNi has a bcc structure in which the atoms are distributed at random over the available sites in the crystal. Below 1090 °C, this structure orders to form the B2 (CsCl) structure (Figure 8.13). If this latter phase is quenched (cooled rapidly) to room temperature the structure transforms via a martensitic transformation into a monoclinic B19′ type. On cooling, the transformation starts at a temperature designated M_s, the martensite start temperature, and is complete by a temperature M_f, the martensite finish temperature. For the alloy NiTi, M_s is 60 °C and M_f is 52 °C.

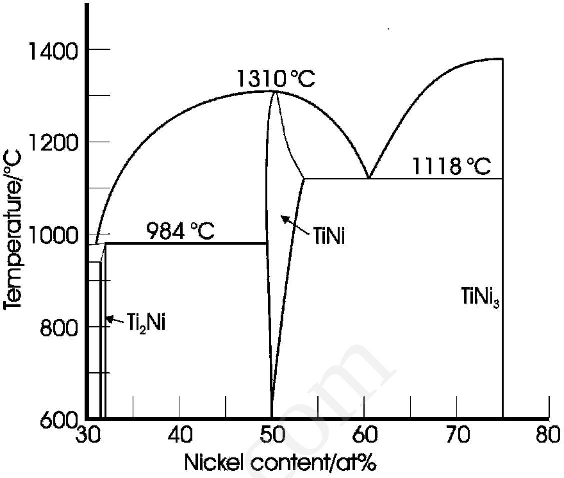

Figure 8.12 Part of the phase diagram of the titanium–nickel system

The displacement of the atoms is a shear in the {1 0 1} planes of the cubic structure (Figure 8.14). The shearing process nucleates at a number of points within the crystal as it cools, and each

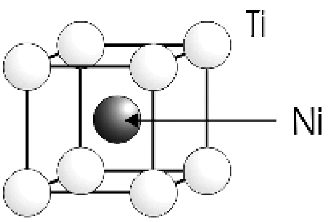

Figure 8.13 The B2 (CsCl) structure of the high-temperature form of TiNi

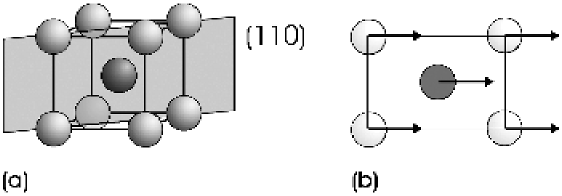

Figure 8.14 (a) The (1 1 0) plane in TiNi; (b) the atoms in the (1 1 0) plane; the shear displacement that occurs on transformation to martensite is indicted by arrows

grows to form a domain or variant. The shear operations across each side of a twin boundary are opposed to each other in direction and help to minimise the strain in the crystal (Figure 8.15). When the transformation is completed the material is highly twinned but maintains the same bulk shape as the original material (Figure 8.15c).

The formation of a heavily twinned material on cooling can be reversed by an increase in temperature, which causes the material to transform to the untwinned pre-martensite state. The transformation starts at a temperature, usually called A_s, the austenite start temperature, and is complete at a temperature A_f, the austenite finish temperature (Figure 8.16). (These terms are related to the fact that the best-known martensitic transformation is that of austenite to martensite, in steels.) For the alloy NiTi, A_s is 71 °C, and A_f is 77 °C. It is seen that M_s and M_f differ from A_s and A_f. This is a hysteresis phenomenon, commonly found in solid-state transformations.

The transformation can be greatly modified by the addition of other alloying elements or by variation of the heat treatment to which the alloy is subjected. For example, TiNi has an extension in composition from $Ni_{1.0}Ti_{1.0}$ to about $Ni_{0.86}Ti_{1.14}$ at 1118 °C (Figure 8.12). This phase range narrows at lower temperatures, so that cooling an alloy with a composition slightly richer in nickel than NiTi results in the formation of precipitates of $TiNi_3$ in the TiNi matrix. These considerably modify the mechanical properties of the martensitic phase. Moreover, this modification is dependent on precipitate morphology and size, and therefore on the rate of cooling. The formation of precipitates also influences M_s, and it has been found that a change in composition of as little as 1 at% can move M_s by more than 100 K.

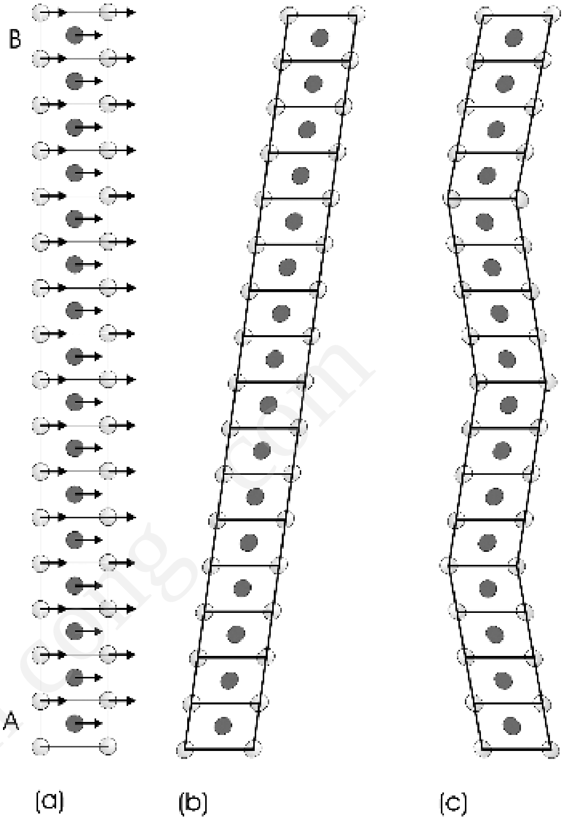

Figure 8.15 (a) A stack of unit cells of NiTi in the (1 1 0) projection; shear displacement represented by arrows is applied to each cell in sequence, starting at A and ending at B, to produce a martensitic structure. (b) The deformed structure resulting from shear. (c) The overall shape of the original stack is more nearly maintained by repeated twinning

The martensitic transformation is thus easily open to modification by heat treatment and alloying, which gives these microstructures great flexibility from the point of view of engineering design.

8.3.3 Shape-memory alloys

Shape-memory alloys are a group of metallic materials that can regain their original shape after

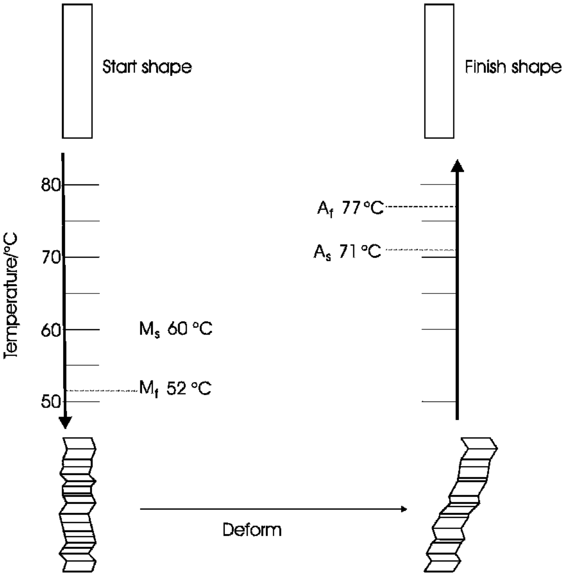

Figure 8.16 The sequence of events taking place during the deformation and recovery of a shape using a shape-memory alloy. Cooling the high-temperature shape below M_f transforms it into a multiply twinned form with the same overall shape. Deformation alters the distribution of the twin boundaries. Reheating the sample above A_f causes the material to revert to the high-temperature form. This removes the twins and allows the original shape to be recovered. The temperatures are appropriate to TiNi

deformation. This is rather remarkable and has been used in a wide variety of devices. These range from antennae on spacecraft, that can be crumpled into a small volume for launch and then unravel into a dish form on deployment, to spectacle frames that can be returned to their original shape after being sat on!

Shape-memory alloys show a thermoelastic martensitic transformation. This is a martensitic transformation, as described above, but which, in addition, must have only a small temperature hysteresis, some 10s of degrees at most, and mobile twin boundaries, that is, ones that move easily. Additionally, the transition must be crystallographically reversible. The importance of these characteristics will be clear when the mechanism of the shape-memory effect is described.

Initially, a shape-memory alloy is formed into the desired geometry at temperatures above M_s (Figure 8.16). On cooling, this original form is maintained, but the material transforms to a heavily twinned state. If this shape is now deformed, the twin boundaries move to accommodate the stress (Figure 8.16). It is for this reason that the twin boundaries must be mobile. In effect, the size of the individual twins increases, and the number of twins decreases. Above A_f the structure returns to the high-temperature form, which is untwined and no longer deformed (Figure 8.17), which is why the crystallographic transition must be reversible. The material has 'remembered' its original shape.

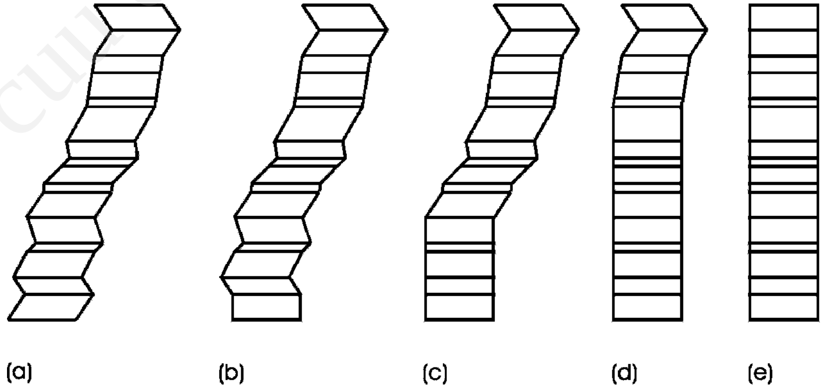

Figure 8.17 Parts (a)–(e) show the progressive recovery of the original shape of a deformed rod by reversion to the original crystal structure, which also removes twins

The process by which the stress is relieved by twin boundary migration leads to another important property, superelasticity, described in Section 10.1.3.

In the shape-memory transformation described, only the shape of the parent phase is ‘remembered’. It is called the one-way shape-memory effect. It is also possible to produce alloys that display two-way shape-memory effects. In these materials, both the shape of the parent phase and the martensitic phase is ‘remembered’. This reversible effect is caused by the fact that the nucleation of the martensite is very sensitive to the stress field. Introduction of lattice defects such as precipitates can restrict the number of variants that form and the positions where they nucleate. Such materials generate the martensitic shape on cooling below the temperature M_f. Cycling between higher and lower temperatures causes the alloy to switch alternately between the two shapes. There is considerable research interest in developing and exploiting two-way shape-memory effect alloys at present.

8.4 Sintering

8.4.1 Sintering and reaction

Sintering is the process by which a compacted powder is converted into a solid body by heating below the melting point of the main constituents, so that the object essentially remains a solid throughout the process. The first stage that occurs during sintering is an initial reduction in the surface roughness of the individual particles. This is followed by a period in which the particles start to join together. Finally, the solid becomes denser by the elimination of internal pores and voids (Figure 8.18).

Sintering is widely used in the ceramics and powder metallurgy industries. In general, the procedure involves the careful preparation of powders, pressing these powders into the desired shape and then heating to sinter the powder particles together into a strong solid. Ideally, there should be little change of overall shape during sintering, and the resulting object should be strong and pore-free. Although the initial powder is frequently a single phase, small amounts of additives are often included to achieve strength and to eliminate porosity. This desirable result is sometimes obtained by an additive that melts below the sintering temperature to form a small amount of liquid between the grains of the major component a process called liquid-phase sintering. Another variation is the technique of reaction sintering. This is exemplified by the production of silicon nitride objects. The desired shape is pressed from silicon powder, and this is heated in an atmosphere of nitrogen gas. The silicon sinters and reacts simultaneously to form a compact silicon nitride part.

Sintering can be brought about by a variety of reactions. Of these, material transport by viscous flow is important in glasses but less so in metals or ceramics. Evaporation and condensation is important in rather volatile compounds such halides and some oxides. Diffusion – bulk, grain boundary and surface diffusion – is important for refractory materials and, for these materials, the presence of traces

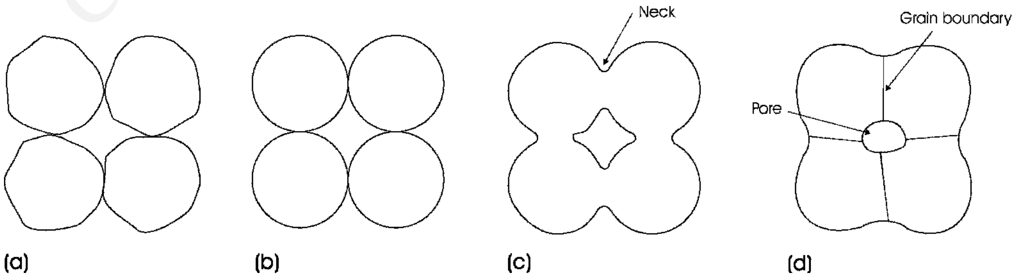

Figure 8.18 Stages in sintering. An initial compact of slightly uneven particles (part a), is gradually transformed into a solid (parts b–d). Usually, this involves shrinkage, change of shape and the formation of pores

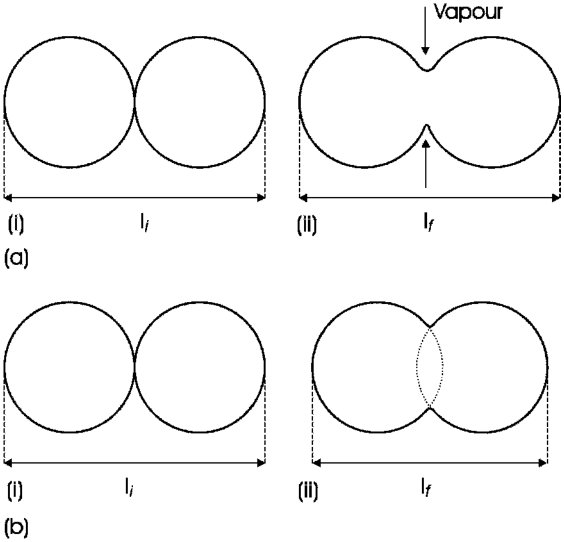

Figure 8.19 (a) Sintering via vapour transport: (i) initial configuration and (ii) final configuration. (no shrinkage). (b) Sintering via solid-state diffusion: (i) initial configuration and (ii) final configuration (shrinkage). Note: l_i and l_f, initial and final lengths, respectively

of liquid phase are also greatly beneficial in speeding up the reaction. In practice, the mechanism that operates has an influence on the final shape of the sintered object. Sintering that takes place by vapour phase transport of material gives a solid with little shrinkage, whereas sintering by way of solid-state diffusion decreases the separation between the constituent particles, often leading to significant shrinkage (Figure 8.19).

8.4.2 *The driving force for sintering*

As sintering does not usually involve chemical reactions, the driving force is not a reduction in Gibbs energy of reaction but a reduction in the surface area and the associated reduction in surface energy. This driving force can be illustrated for a flat surface that contains a spherical protuberance and a similar spherical depression, both of radius r (Figure 8.20a).

The vapour pressure over a curved surface, p, is related to the vapour pressure over a flat surface, p_0, by the Kelvin equation:

$$RT\ \ln\left(\frac{p}{p_0}\right) = \frac{2V\gamma}{r} = \Delta G$$

where V is the molar volume of the substance, γ is the surface energy of the solid–vapour interface, and ΔG is the difference in Gibbs energy between a flat surface and the curved surface. Thus the vapour pressure over a protuberance will be greater than the vapour pressure over the flat surface and will increase as the radius of the curved surface decreases. In the case of a depression, the radius r is now negative and it is necessary to write:

$$RT\ \ln\left(\frac{p}{p_0}\right) = \frac{2V\gamma}{-r} = \Delta G$$

Thus, the vapour pressure over the depression will be less than the vapour pressure over a flat surface. There will be a transfer of matter via the vapour

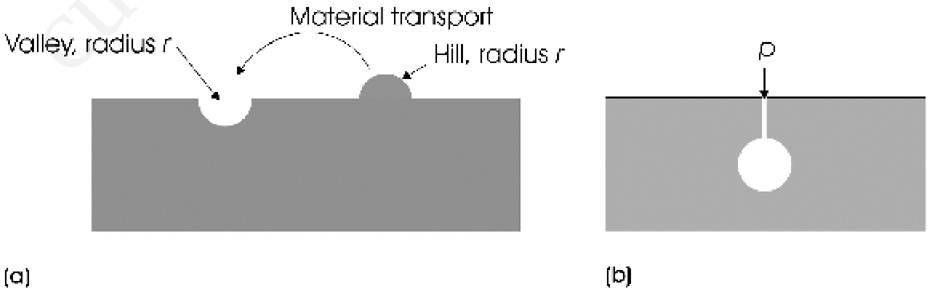

Figure 8.20 (a) Material transports from hills to valleys during vapour-phase sintering, because the vapour pressure over a hill is higher than that over a valley; the surface tends to become flat. (b) The excess pressure p inside a void balances the surface energy of the void

phase from a protuberance to a depression and the surface will tend to become flat.

It is important that articles fabricated by sintering do not contain large pores, because these lead to weakness and dimensional changes. The way in which powder granules link up during sintering will inevitably lead to pores forming unless the powders are carefully prepared. The size of the pores is dependent on the surface energy of the material in a similar way to that described above. In the case of a spherical pore (Figure 8.20b), the excess pressure in the pore, p, needed to balance the surface energy is given by:

$$p = \frac{2\gamma}{r}$$

where r is the radius of the sphere and γ is the surface energy. If the pressure is greater than that given, the pore will expand, whereas if it is smaller the pore will shrink, until equilibrium is reached. The ratio of the initial radius, r_i, to the final radius, r_f, of the pore is given by:

$$\frac{r_i}{r_f} = \left(\frac{2\gamma}{p_i r_i}\right)^{1/2}$$

where p_i is the initial pressure in the pore, and γ is the surface energy of the material. This equation indicates that small pores will tend to shrink and large pores will grow, with no change taking place when $r_i = r_f$, that is, when

$$p_i r_i = 2\gamma$$

Material transport also occurs (for a similar reason) when two spheres touch to form a neck (Figure 8.21). The spheres will have a positive and relatively large radius of curvature and the neck region a smaller negative radius of curvature. Matter will thus tend to be transported via the vapour phase from the larger spheres into the neck region, causing the particles to join. The transport of material to achieve this is not restricted to transport via the vapour phase. Bulk or surface diffusion can also be called into play to achieve the same result.

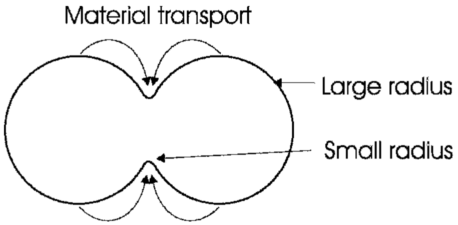

Figure 8.21 The transport of material from a surface of large radius, to a region of small radius (a neck) by vapour transport during sintering

8.4.3 The kinetics of neck growth

The rate of flow of material into the neck region between two spheres will depend on the mechanism of atomic transport. Four different mechanisms were investigated by Kuczynski, some 50 years ago. These were viscous flow, surface diffusion, bulk diffusion and vapour transport by evaporation and condensation. The rate of neck growth was found to be quite different from one mechanism to another. They are usually expressed in terms of the ratio of the neck radius x to the sphere radius r (defined in Figure 8.22):

For viscous flow,

$$\frac{x^2}{r} = k_1 t$$

For surface diffusion,

$$\frac{x^5}{r^2} = k_2 t$$

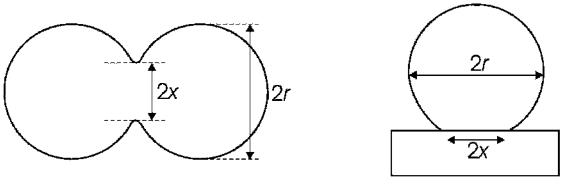

Figure 8.22 Definition of neck radius, x, and sphere radius, r, used in the kinetics of sintering

For bulk diffusion,

$$\frac{x^3}{r} = k_3 t$$

For vapour transport,

$$\frac{x^7}{r^3} = k_4 t$$

In these equations, k_1, k_2, k_3 and k_4 are constants which vary with temperature, and t is the time of reaction.

Experiments have shown that sodium chloride (NaCl) and other volatile materials sinter by a predominantly vapour transport mechanism whereas refractory oxides and metals sinter mainly by way of bulk diffusion.

8.5 High-temperature oxidation of metals

Corrosion of metals takes place by way of a variety of important chemical reactions. At ordinary temperatures, this process is often called tarnishing, and at high temperatures, scale formation. In this section, the reaction of metals with dry gases at relatively high temperatures is considered. This is referred to as direct corrosion, to distinguish it from many common forms of corrosion, including rust formation on iron, which need the presence of water. These latter reactions are considered in Section 9.4.

8.5.1 The driving force for oxidation

Direct corrosion can occur when a gas in the environment reacts directly with a metal. The discussion that follows applies to all gases, but reaction with oxygen will be used to illustrate this phenomenon. For example, both aluminium and calcium react rapidly with oxygen to form the appropriate oxide:

$$4\,\mathrm{Al} + 3\,\mathrm{O_2} \rightarrow 2\,\mathrm{Al_2O_3},$$
$$2\,\mathrm{Ca} + \mathrm{O_2} \rightarrow 2\,\mathrm{CaO}.$$

The driving force for these reactions is the Gibbs energy of formation of the oxide (see Section S3.2). In favourable cases, such as that of aluminium, the product of corrosion may provide a protective coating, preventing further reaction from taking place. In less favourable circumstances, such as the corrosion of iron, the product may be loose or flake off, continually exposing new surfaces for corrosion.

The oxidation reaction will be influenced by the equilibrium oxygen pressure in the surroundings (Sections S1.5 and S3.2). Calculation of the equilibrium partial pressures over metal oxides shows that values lie between approximately 10^{-7} atmospheres to 10^{-40} atmospheres. As the oxygen partial pressure in air is about a fifth of an atmosphere it is clear that metals will have a tendency to oxidise. From the point of view of thermodynamics, there is always a considerable driving force for reaction.

8.5.2 The rate of oxidation

The rates of formation of oxide films vary widely. For thin layers, nominally less than approximately 100 nm in thickness, four rate laws have been established experimentally:

The cubic law,

$$x = (k_c\, t)^{1/3}$$

The logarithmic law,

$$x = k_1 - k_2 \ln t$$

The reciprocal logarithmic law,

$$\frac{1}{x} = k_1' - k_2' \ln t$$

The parabolic law,

$$x = (k_p\, t)^{1/2}$$

In each equation, x is the thickness of the film, t is the time of reaction, and k_c, k_p, etc., are experimentally determined constants.

In the case of thick layers, nominally over 100 nm, two laws have been observed:

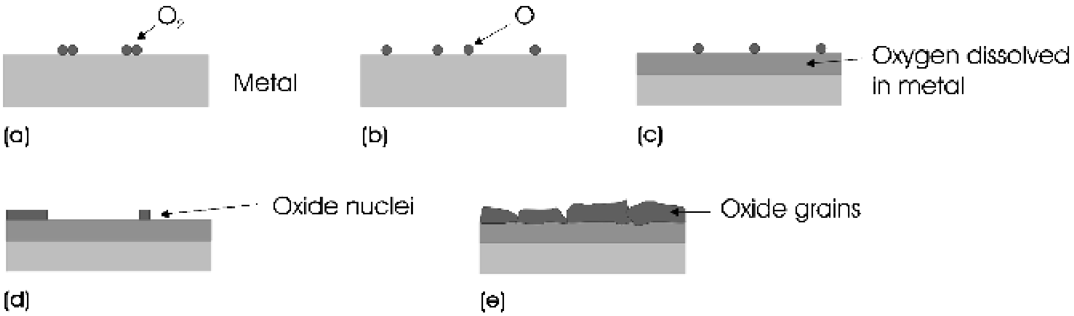

Figure 8.23 Oxide formation on a metal surface: (a) physical adsorption of oxygen (O_2) molecules from the air; (b) chemical adsorption of separated oxygen atoms (O) strongly bound to the surface; (c) penetration of some oxygen atoms into the metal to form a subsurface layer, as more oxygen arrives at the surface; (d) saturation of the surface and subsurface with oxygen, leading to formation of oxide nuclei on the surface; (e) surface layer of oxide grains

The linear law,

$$x = k\,t$$

The parabolic law,

$$x = (k_p\,t)^{1/2}$$

In both of these equations, x is the film thickness, t is the time of the oxidation, and k and k_p are experimentally determined constants. The constant k_p is called the parabolic rate constant. A linear rate is usually found when the film is porous or cracked. The parabolic equation is found when the film forms a coherent, impenetrable layer. As the rate of film growth, dx/dt, diminishes with time for the parabolic rate law, this equation is associated with protective kinetics. The parabolic rate law arises when the reaction is controlled by diffusion. The species with the lowest diffusion coefficient plays the most important role in this case.

8.5.3 Mechanisms of oxidation

The initial step of an oxidation reaction is usually the adsorption of oxygen onto the metal surface. Initially, the adsorbate will consist of oxygen molecules that are weakly bound to the surface (Figure 8.23a). This is called physical adsorption or physisorption. On most metals, the oxygen molecules rapidly dissociate into oxygen atoms, and the resulting layer of atoms is more strongly bound to the metal surface (Figure 8.23b). This stage is called chemical adsorption or chemisorption.

The oxidation begins by the diffusion of oxygen atoms into surface layers of the metal (Figure 8.23c). These do not form recognised oxides but a dilute solid solution that exists only in the surface regions. Nucleation of chemically recognisable oxides then occurs. At high temperatures and low partial pressures of oxygen, this takes place at random (Figure 8.23d). The oxide formed might be the normal oxide (e.g. MgO, on magnesium) or, if a number of oxides form, it might be a 'lower' oxide (e.g. FeO on iron). Sometimes, metastable oxides are also found that do not occur normally in the bulk. Continued growth proceeds so that the nuclei enlarge to form islands of oxide. Under some conditions, growth perpendicular to the surface might be much greater than lateral growth, in which case whiskers can form. Lateral growth is most frequent in dry conditions and, as such growth proceeds, the islands grow together to give a surface layer consisting of randomly oriented grains of oxide (Figure 8.23e).

This is an idealised picture and individual metals vary in their response to oxygen attack. Moreover, the overall reaction path is sometimes dependent on the temperature. Many other factors are important when the stability and further growth of this film is considered, including the electronic conductivity of the film and its thermal expansion coefficient compared with that of the parent metal.

One factor that is readily assessed is the volume of oxide produced by oxidation of a given volume of metal. This is called the Pilling–Bedworth ratio, X_{PB}, and is most readily expressed in terms of molar volumes:

$$X_{\mathrm{PB}} = \frac{\text{molar volume of oxide}}{\text{molar volume of metal}}$$

For the reaction

$$m\,\mathrm{M} + \frac{n}{2}\,\mathrm{O}_2 \rightarrow \mathrm{M}_m\,\mathrm{O}_n$$

it is necessary to compute the Pilling–Bedworth ratio for the same amount of metal consumed as appears in the oxide. The result is:

$$\begin{aligned} X_{\mathrm{PB}} &= \frac{(\text{molar mass of oxide } \mathrm{M}_m\,\mathrm{O}_n) \times (\text{density of the metal})}{m \times (\text{molar mass of the metal}) \times (\text{density of the oxide } \mathrm{M}_m\,\mathrm{O}_n)} \\ &= \frac{M_{\mathrm{o}} d_{\mathrm{m}}}{m M_{\mathrm{M}}\, d_{\mathrm{o}}} \end{aligned}$$

where M_{o} is the molar mass of the oxide, d_{m} the density of the metal, M_{m} the molar mass of the metal, and d_{o} the density of the oxide.

If the Pilling–Bedworth ratio is less than 1 the oxide cannot cover the metal completely and the oxide film has an open or porous structure. Oxidation takes place continuously, and the oxidation kinetics tend to be linear. This type of behaviour is found for the alkali and alkaline earth metals. In the rare cases where the Pilling–Bedworth ratio is equal to 1, a closed layer can form which is stress-free. When the Pilling–Bedworth ratio is greater than 1, a closed layer forms with a certain amount of internal compressive stress present.

The location of this stress depends on the mechanism of the reaction, as discussed below. In cases where further formation of oxide is on the outer side of the layer, the stresses are easily relieved and the layer remains coherent. This results in protective oxidation, with parabolic reaction kinetics. The oxide film is called protective scale. If the new oxide film forms between the metal and an outer oxide layer, the stresses cannot be easily relieved, the oxide layer can crack, and spalling (fragmentation) can occur. Spalling is also possible when the value of X_{PB} is significantly greater than 1, because the additional volume that has to be accommodated generates stresses that lead to cracking. In general, cracks lead to faster oxidation, called accelerating or breakaway oxidation. The kinetics typical of breakaway oxidation initially follows a parabolic rate law, but this changes to a linear rate law when the film begins to crack.

In cases where a continuous and coherent layer of oxide film is present, further reaction can proceed only by diffusion of some of the reactants across the film. There are several possible mechanisms for this transport of material. In many solids, the passage of neutral atoms is less likely than the transport of charged particles, ions and electrons. In such cases, called ambipolar diffusion, the concentration gradient is not the only constraint on the system. In addition, and at all times, overall charge neutrality needs to be maintained.

Perhaps the most obvious mechanism for oxide formation (Figure 8.24a) is the diffusion of M^{n+} cations outward from the metal towards the gas atmosphere. If this occurs, a large negative charge would remain at the metal–metal oxide interface. This negative charge would act to slow the diffusing positively charged cations, and this would bring the reaction to a halt. To maintain electrical neutrality in the system, and to allow the reaction to continue, cation diffusion must be accompanied by a parallel diffusion of an appropriate number of electrons. When the electrons arrive at the surface, they react with oxygen molecules arriving on the oxide surface, to form O^{2-} ions. These are incorporated into the oxide film and, together with the arriving M^{n+} cations, allow the film to grow at the outer surface of the film. Note that film growth cannot continue if the oxide is an electrical insulator.

A similar mechanism envisages that oxygen ions diffuse across the film from the outer surface towards the metal (Figure 8.24b). The oxygen ions cannot be generated spontaneously and, once again, it is necessary for electrons to move through the

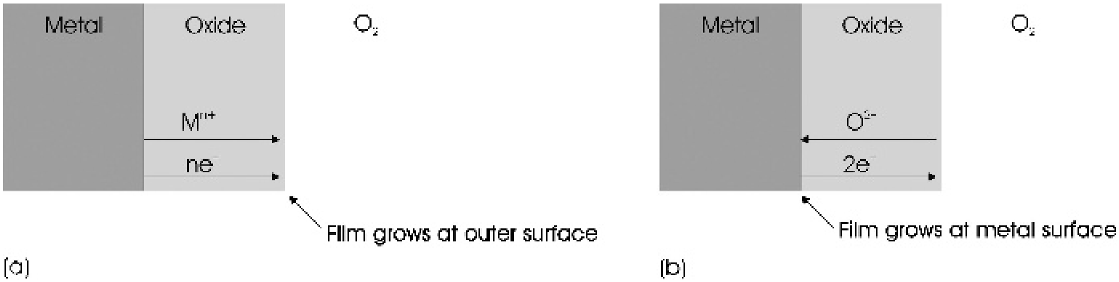

Figure 8.24 Growth of an oxide film on a metal surface: (a) diffusion of metal ions and electrons leads to growth at the outer (oxide/gas) side of the oxide film; (b) counter diffusion of electrons and oxide ions leads to growth at the inner (metal/oxide) side of the oxide film

oxide layer from the metal to make the ionisation possible. This leaves M^{n+} cations behind at the metal–metal oxide boundary. These cations are able to combine with the arriving O^{2-} anions to extend the oxide film at the metal–metal oxide inner boundary. Film growth will be curtailed if the film is an electrical insulator.

A third possibility, in which counter-diffusion of M^{n+} cations and O^{2-} anions occurs, is rare in oxide film formation and will be discussed in detail in Section 8.6.1.

The oxidation of copper metal in a low partial pressure of oxygen produces cuprous oxide, Cu_2O, by a mechanism involving diffusion of Cu^+ cations and electrons. The reaction is described by the chemical equation:

$$2\,Cu + \frac{1}{2}\,O_2 \rightarrow Cu_2O$$

The initial reaction results in the formation of a continuous film of oxide that is firmly attached to the metal surface. The rate of growth of the film is controlled by the slow diffusion of the Cu^+ ions. However, no corrosion could occur without the transport of electrons, as the mechanism depends on electron transport. The electronic conductivity of the film is therefore of major importance. The reason why both aluminium and chromium appear to be corrosion-resistant lies in the fact that, although oxide films form very rapidly in air, the films are insulators and prevent reaction from continuing. As the thin films are also transparent, the metals do not lose their shiny appearance.

8.6 Solid-state reactions

Reactions between two solids are analogous to the oxidation of a metal, because the product of the reaction separates the two reactants. Further reaction is dependent on the transport of material across this barrier. As with oxidation, cracking, porosity and volume mismatch can all help in this. In this section, the case when a coherent layer forms between the two reactants will be considered. The mechanism of the reaction may depend on whether electron transport is possible in the intermediate phase, and the rate of reaction will be controlled by the rate of diffusion of the slowest species. To illustrate the problems encountered a typical solid-state reaction, the formation of oxide *spinels*, is described.

8.6.1 Spinel formation

Spinel is a mineral with a composition $MgAl_2O_4$ (see Section 5.3.10). A large number of other oxides crystallise with the same structure, and these are collectively referred to as *spinels*. The formula of *spinels* is AB_2O_4, where A is most often a divalent cation, and B a trivalent cation, as in $MgAl_2O_4$ itself.

The spinel formation reaction can be represented by the chemical equation

$$MgO + Al_2O_3 \rightarrow MgAl_2O_4$$

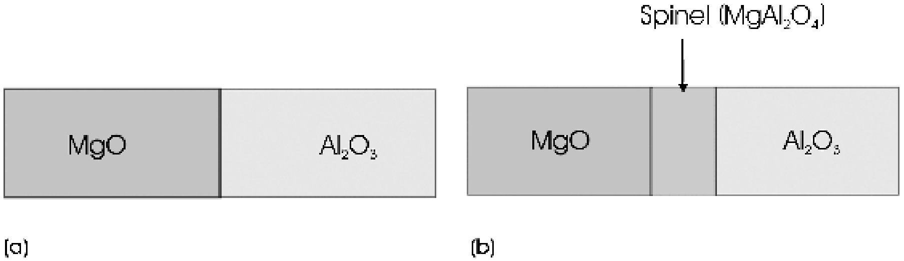

Figure 8.25 Growth of a layer of spinel ($MgAl_2O_4$) between crystals of magnesium oxide (MgO) and alumina (Al_2O_3): (a) MgO and Al_2O_3 crystals in contact; (b) separation of the reacting oxides by a layer of spinel

Suppose that a crystal of aluminium oxide, Al_2O_3, is placed in close contact with a crystal of magnesium oxide, MgO (Figure 8.25a). This arrangement, which resembles a diffusion couple (Section 7.1), is called a reaction couple. Initial reaction will result in the separation of the two reacting oxides MgO and Al_2O_3 by a layer of spinel, $MgAl_2O_4$ (Figure 8.25b). Continued reaction will depend on transport of reactants across the spinel layer. As in the case of metal oxidation, a number of mechanisms can be suggested but, because $MgAl_2O_4$ is an insulator, electron transport is not possible and so only mechanisms involving ions are permitted.

One such mechanism requires counter-diffusion of equal numbers O^{2-} anions and Mg^{2+} cations (Figure 8.26b). The electrical charges on the ions are equal and opposite, so no charge-balance problems arise. New spinel growth will take place at the Al_2O_3 interface. The diffusion of O^{2-} anions accompanied by an antiparallel diffusion of Al^{3+} cations (Figure 8.26c) is equally possible. Because of the difference in the ionic charges, the diffusion of two Al^{3+} cations needs to be balanced by the transport of three O^{2-} anions to maintain charge neutrality. Spinel growth will now take place at the MgO boundary. The counter-diffusion of Mg^{2+} and Al^{3+} is also possible (Figure 8.26d). To maintain charge neutrality, the diffusion of three Mg^{2+} cations must be balanced by the diffusion of two Al^{3+} cations. In this case, the spinel layer forms on either side of the initial boundary.

It has been found that the reaction between MgO and Al_2O_3 follows this latter mechanism. The

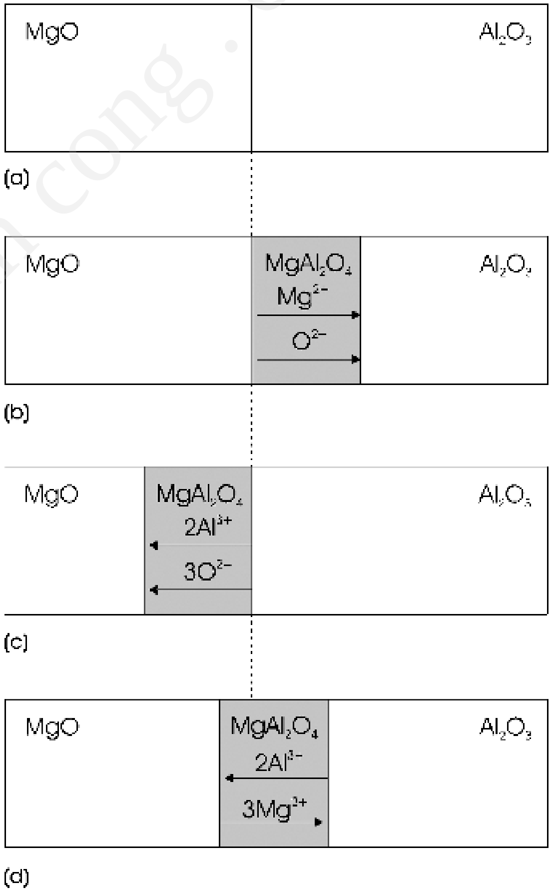

Figure 8.26 Mechanisms of spinel formation; (a) initial state; (b) diffusion of equal numbers of Mg^{2+} and O^{2-} ions; (c) diffusion of $2n$ Al^{3+} ions and $3n$ O^{2-} ions; (d) counter diffusion of $2n$ Al^{3+} ions and $3n$ Mg^{2+} ions

reactions at the boundary between Al_2O_3 and spinel are:

$$Al_2O_3 \rightarrow 2\,Al^{3+} + 3\,O^{2-}$$

and

$$3\,Mg^{2+} + 3\,O^{2-} + 3\,Al_2O_3 \rightarrow 3\,MgAl_2O_4$$

The reactions at the boundary between MgO and spinel are:

$$3\,MgO \rightarrow 3\,Mg^{2+} + 3\,O^{2-}$$

and

$$3\,O^{2-} + 2\,Al^{3+} + MgO \rightarrow MgAl_2O_4$$

These equations indicate that the spinel layer grows in an asymmetrical fashion. For every three Mg^{2+} ions that arrive at the Al_2O_3 boundary three $MgAl_2O_4$ molecules form, and for every two Al^{3+} ions which arrive at the MgO boundary only one $MgAl_2O_4$ molecule forms. Thus, the spinel layer will form in a ratio of 1:3 on either side of the initial boundary, with the thicker part on the Al_2O_3 side (Figure 8.27).

8.6.2 *The kinetics of spinel formation*

The rate at which the total thickness of the spinel layer grows is controlled by the speed of diffusion of the slowest cation. In reactions of this sort, if the spinel layer increases by an amount Δx in a period of time Δt, the rate of film growth, $d(\Delta x)/d(\Delta t)$, is given by:

$$\frac{d(\Delta x)}{d(\Delta t)} = \frac{k}{x}$$

where k is a constant and x is the film thickness at time t. Integration and rearrangement of this equation leads to the following equation:

$$x^2 = 2kt$$

where x is the thickness of the spinel layer, k is called the practical reaction rate constant, and t is the reaction time. This will be recognised as the parabolic rate law described in Section 8.5.2 for metal oxidation, and k is also called the parabolic rate constant, k_p.

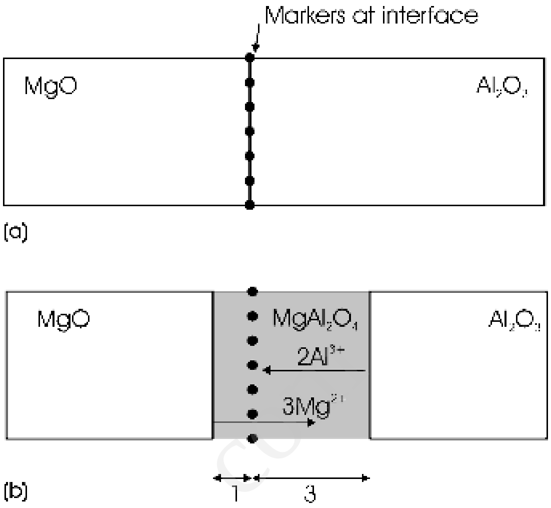

Figure 8.27 Markers used to determine the mechanism of spinel formation from magnsium oxide and alumina (a) inert markers at the interface between MgO and Al_2O_3 crystals; (b) after reaction the marker will appear to be within the $MgAl_2O_4$ layer when a cation counter-diffusion is in operation. The ratio of the layer thickness on each side of the boundary will depend on the charges on the ions

Many solid-state reactions give a parabolic rate law for the growth of an internal phase, and such a parabolic rate law is taken as evidence that the reaction is diffusion-controlled. The units of k are the same as the units of the diffusion coefficient, $m^2\,s^{-1}$. Generally, one can write:

$$k \propto D_A$$

where D_A is the diffusion coefficient of the ionic species that diffuses at the slowest speed.

Answers to introductory questions

What is dynamic equilibrium?

Dynamic equilibrium is an important and powerful concept in many areas of science. Dynamic equilibrium generally involves a reversible reaction, such as that represented by a chemical equation:

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons x\,\mathrm{X} + y\,\mathrm{Y}$$

or a physical equation:

$$\mathrm{null} \rightleftharpoons [\mathrm{n}] + [\mathrm{p}]$$

where [n] is the concentration of electrons in the conduction band and [p] is the concentration of holes in the valence band of a semiconductor. The double arrows signify that the reaction can take place in either direction.

A feature of reversible reactions is that they often appear to be static, as if there were no change occurring. This state of affairs is illusory. Reactants are continuously being consumed and regenerated by the forward and backward reactions. If no change seems to be taking place, it is because the rates of the reactions in each direction are balanced. In this case, the system is said to be in equilibrium. At equilibrium, reactant and product are continuously being formed and consumed, and the rate of the forward reaction is the same as the rate of the reverse reaction. This feature is the key to the importance of dynamic equilibrium.

What defines a martensitic transformation?

Rapidly cooling the homogeneous alloy austenite, with the face-centred cubic structure, to room temperature leads to the formation of a metastable phase called martensite. The face-centred cubic structure of the iron atoms in austenite transforms to a body-centred cubic structure of iron atoms in the process. The carbon atoms present are trapped in the new structure, which causes a deformation such that one of the cubic cell edges is elongated. The formation of martensite is extremely rapid, and only a slight displacement of atoms takes place. In particular, neither the carbon nor the iron atoms have time to diffuse any great distance. Once a nucleus of a martensite crystal forms, it will grow to its final size in a time of the order of 10^{-7} s. The change is called the martensitic transformation.

Martensitic transformations are a general class of reactions that are similar to that found in steel. The main characteristic of this class of reactions is that they are very rapid, because no atom diffusion occurs. Martensitic transformations are defined by being diffusionless reactions.

What is the main driving force for sintering?

Sintering does not usually involve chemical reactions, and the driving force is a reduction in the surface area and the associated reduction in surface energy. This driving force can be illustrated for a flat surface that contains a spherical protuberance and a similar spherical depression. The vapour pressure over a curved surface is related to the vapour pressure over a flat surface by the Kelvin equation. This shows that the vapour pressure over a protuberance will be greater than the vapour pressure over the flat surface and will increase as the radius of the curved surface decreases. Similarly, the vapour pressure over a depression will be less than the vapour pressure over a flat surface. When a solid is heated, vapour transfer of matter will take place from a protuberance to a depression, and the surface will tend to become flat.

A body to be sintered consists of many small approximately spherical grains. Material transport occurs, for a similar reason, when two spheres touch to form a neck. The spheres will have a positive and relatively large radius of curvature, and the neck region a smaller negative radius of curvature. Matter will thus tend to be transported via the vapour phase from the larger spheres into the neck region, causing the particles to join.

The transport of material to achieve reduction in surface area is not restricted to transport via the vapour phase. Bulk or surface diffusion can also be called into play to achieve the same result.

Further reading

On dynamic equilibrium, see:

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J.C. Anderson, K.D. Leaver, R.D. Rawlings, J.M. Alexander, 1998, *Materials Science*, 4th edn, Stanley Thornes, Cheltenham, Glosc.

W.D. Callister, 2000, *Materials Science and Engineering: An Introduction*, 5th edn, John Wiley & Sons, New York.

W.F. Smith, 1993, *Foundations of Materials Science and Engineering*, 2nd edn, McGraw-Hill, New York.

On shape-memory alloys, see:

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On sintering, see:

G. Bickley Remmey, 1994, *Firing Ceramics*, World Scientific, Singapore.

On high-temperature oxidation, see:

J.H.W. de Witt, 1981, 'High Temperature Oxidation of Metals', *Journal of Materials Education (JEMMSE)* **3** 343.

On solid-state reactions, see:

R.J.D. Tilley, 1998, *Principles and Applications of Chemical Defects*, Stanley Thornes, Cheltenham, Glos.

Problems and exercises

Quick quiz

1 Dynamic equilibrium is attained when:
  (a) The forward and reverse reactions come to a standstill
  (b) The forward reaction slows to zero
  (c) The forward and reverse reactions proceed at the same speed

2 The equilibrium constant depends on which one of the following:
  (a) Pressure?
  (b) Temperature?
  (c) Concentration?

3 The equilibrium constant for a reaction equation derived by adding simpler reactions is given by:
  (a) The sum of the equilibrium constants of the individual reactions
  (b) The product of the equilibrium constants of the separate reactions
  (c) The sum of the reciprocals of the equilibrium constants of the individual reactions

4 If the equilibrium constant for the forward reaction is K, that for the reverse reaction is:
  (a) $1/K$
  (b) $-K$
  (c) $K/2$

5 If the concentration of a reactant is changed in an equilibrium situation:
  (a) The equilibrium constantly changes to offset the change
  (b) The reaction proceeds to minimise the change
  (c) The reaction reverses

6 If the volume of the vessel containing gaseous reactants at equilibrium is decreased:
  (a) The equilibrium constant changes to offset the change
  (b) The reaction proceeds to change the amount of reactants present
  (c) The reaction proceeds to minimise the number of molecules present

7 If the number of electrons in a semiconductor is increased at a constant temperature, the number of holes:
  (a) Decreases
  (b) Increases
  (c) Stays the same

8 During slow cooling of a Ni-Cu alloy, the composition of the crystallites:
  (a) Is constant
  (b) Varies continuously
  (c) Has the composition of the liquid

9 When a Ni-Cu alloy is cooled fairly rapidly, the core of the crystallites will have a composition:
(a) Richer in the lower-melting-point parent phase
(b) Richer in the higher-melting-point parent phase
(c) Identical to that of the liquid phase

10 When a liquid alloy of lead and tin is cooled through a eutectic point, the microstructure of the solid produced contains
(a) Eutectic α and eutectic β
(b) Primary α and eutectic β
(c) Eutectic α and primary β

11 When a liquid alloy of lead and tin, with a composition between the eutectic point and the α phase is cooled, the microstructure of the solid produced contains
(a) Primary α and eutectic β
(b) Primary α, eutectic α and primary β
(c) Primary α, eutectic α and eutectic β

12 When austenite is cooled slowly through the eutectoid point, the material that forms is called:
(a) Cementite
(b) Ferrite
(c) Pearlite

13 The microstructure of pearlite is composed of:
(a) Eutectoid ferrite plus austenite
(b) Eutectoid ferrite plus eutectoid cementite
(c) Eutectoid cementite plus austenite

14 A hypoeutectoid steel has a composition that lies to the:
(a) Iron-rich side of the eutectoid
(b) Carbon-rich side of the eutectoid
(c) Carbon-rich side of austenite

15 Slow cooling of a hypereutectoid steel composition produces a microstructure composed of:
(a) Proeutectoid ferrite plus eutectoid cementite plus eutectoid ferrite
(b) Proeutectoid cementite plus proeutectoid ferrite plus pearlite
(c) Proeutectoid cementite plus eutectoid cementite plus eutectoid ferrite

16 Martensite is produced from austenite by:
(a) Quenching the austenite
(b) Annealing the austenite
(c) Tempering the austenite

17 A martensitic transformation is described as:
(a) A reconstructive transformation
(b) A diffusionless transformation
(c) An equilibrium transformation

18 Shape-memory alloys utilise:
(a) Martensitic transformations
(b) Eutectoid transformations
(c) Reconstructive transformations

19 The shape-memory effect in shape-memory alloys requires that the solid contain:
(a) Fixed twin boundaries
(b) Mobile twin boundaries
(c) No twin boundaries

20 The shape-memory alloy Nitinol has an approximate formula:
(a) $NiTi_3$
(b) NiTi
(c) Ni_3Ti

21 The transformation of a compacted powder into a solid by heating is called:
(a) Annealing
(b) Tempering
(c) Sintering

22 Liquid-phase sintering involves using:
(a) Only liquids for the reaction
(b) Solids mixed with liquids for the reaction
(c) An additive which melts during the reaction

23 The driving force for sintering is:
(a) Reduction in surface area
(b) Reduction in total volume
(c) Reduction in Gibbs energy of reaction

24 Direct corrosion of a metal requires the presence of:
  (a) A gas plus water
  (b) A dry gas
  (c) Air

25 The parabolic rate law for oxidation arises when:
  (a) The oxide film is cracked
  (b) The oxide film is thin
  (c) Diffusion controls the reaction

26 The Pilling–Bedworth ratio is used to predict the:
  (a) Likelihood of corrosion of a metal
  (b) Reactivity of a metal with a gas
  (c) Rate of corrosion of a metal

27 The counter-diffusion of ions is sometimes called:
  (a) Reaction diffusion
  (b) Ambipolar diffusion
  (c) Solid-state diffusion

28 The formation of spinel, $MgAl_2O_4$, involves the diffusion of:
  (a) Mg^{2+} and O^{2-} ions
  (b) Al^{3+} and O^{2-} ions
  (c) Mg^{2+} and Al^{3+} ions

29 A parabolic rate constant is characteristic of a reaction between two solids which is controlled by:
  (a) Sintering
  (b) Ionic diffusion
  (c) Vapour transport.

Calculations and questions

8.1 Write down the expression for the equilibrium constants K_c and K_p of the following reactions:
  (a) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$.
  (b) $C\ (s) + 2H_2\ (g) \rightleftharpoons CH_4\ (g)$.
  (c) $2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$.
  (d) $Zn(s) + CO_2\ (g) \rightleftharpoons ZnO(s) + CO(g)$.

8.2 $CaCO_3$ (limestone, chalk) is heated in a sealed container, initially in a vacuum, at 1000 K.
  (a) What will happen to the pressure in the vessel?
  (b) The equilibrium constant for the reaction (see Question 8.1) is $K_p = 0.039$ atm. What will be the pressure in the vessel at 1000 K?
  (c) The size of the vessel is doubled and equilibrium reestablished. What will be the new pressure?
  (d) A quantity of $CO_2(g)$ prepared from radioactive carbon-14 is admitted to the vessel at equilibrium. What will occur initially?
  (e) What will the final distribution of radioactive carbon-14 be in the vessel?
  (f) During cement production $CaCO_3$ is heated in a kiln. Why does all of the limestone transform to CaO?

8.3 Deduce the relationship between K_c and K_p for the reaction:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

8.4 Copper sulphate, $CuSO_4$, exists as hydrates $CuSO_4 \cdot 5\,H_2O$, $CuSO_4 \cdot 3\,H_2O$ and $CuSO_4 \cdot H_2O$.
  (a) Write equations for the equilibria between these forms.
  (b) Sketch the variation of water vapour pressure over a sample of copper sulphate as the average water content varies between $5\,H_2O$ and zero. [Note: answer is not shown at the end of this book.]
  (c) The equilibrium water vapour pressure at 25 °C (i) over a mixture of 50:50 $CuSO_4 \cdot 5\,H_2O{:}CuSO_4 \cdot 3\,H_2O$ is 6.266×10^3 Pa, (ii) over a 50:50 mixture of $CuSO_4.3\,H_2O{:}CuSO_4 \cdot H_2O$ is 4×10^3

Pa, and (iii) over a 50:50 mixture of $CuSO_4 \cdot H_2O$ and $CuSO_4$ (anhydrous) is 600 Pa. Calculate the equilibrium constants of the reactions involved in the dehydration of $CuSO_4$.

8.5 The number of intrinsic electrons in pure germanium at 300 K is 2.4×10^{19} m^{-3}. The material is doped with a concentration of phosphorus donors of 10^{22} phosphorus atoms per metre cubed. What is the equilibrium concentration of electrons and holes?

8.6 The intrinsic hole concentration in gallium arsenide at 200 °C is 4.1×10^{17} m^{-3}. The material is doped with a concentration of zinc acceptors of 10^{19} zinc atoms per metre cubed. What is the equilibrium concentration of electrons and holes?

8.7 The intrinsic electron concentration in a silicon sample at 500 °C is 6.5×10^{20} m^{-3}. (a) What quantity of aluminium dopant needs to be added to reduce the electron concentration to 6.6×10^{-19} m^{-3}? (b) The unit cell of silicon is cubic with a cell edge of 0.5431 nm and contains eight atoms of silicon. What percentage of silicon atoms will be replaced by aluminium atoms?

8.8 The gold–silver system forms a complete solid solution. The melting point of gold is 1064.43 °C and that of silver is 961.93 °C.

(a) During rapid cooling of a 50 at% gold:50 at% silver mixture, which phase will be richest in the core of a grain?

(b) Sketch the microstructure of the solid at a temperature of 800 °C if the melt is cooled very slowly. [Note: answer is not shown at the end of this book.]

(c) Sketch the microstructure of the solid at a temperature of 800 °C if the melt is cooled quickly. [Note: answer is not shown at the end of this book.]

8.9 The ruthenium–rhenium (Ru–Re) system forms a complete solid solution (for the phase diagram, see Figure 4.24, page 111). The melting point of ruthenium is 2334 °C and that of rhenium is 3186 °C.

(a) During rapid cooling of a 45 at% Re: 55 at% Ru mixture, which phase will be richest in the core of a grain?

(b) Sketch the microstructure of the solid at a temperature of 2000 °C if the melt is cooled very slowly. [Note: answer is not shown at the end of this book.]

(c) Sketch the microstructure of the solid at a temperature of 2000 °C if the melt is cooled quickly. [Note: answer is not shown at the end of this book.]

8.10 The corundum–chromia (Al_2O_3–Cr_2O_3) system forms a complete solid solution (for the phase diagram, see Figure 4.23, page 110). The melting point of corundum is 2035 °C and that of chromia is 2330 °C.

(a) During rapid cooling of a 33 mol% Al_2O_3: 67 mol% Cr_2O_3 melt, which phase will be richest in the core of a grain?

(b) Sketch the microstructure of the solid at a temperature of 2000 °C if the melt is cooled very slowly. [Note: answer is not shown at the end of this book.]

(c) Sketch the microstructure of the solid at a temperature of 2000 °C if the melt is cooled quickly. [Note: answer is not shown at the end of this book.]

8.11 With respect to the phase diagram of the copper–silver system (Figure 8.28):

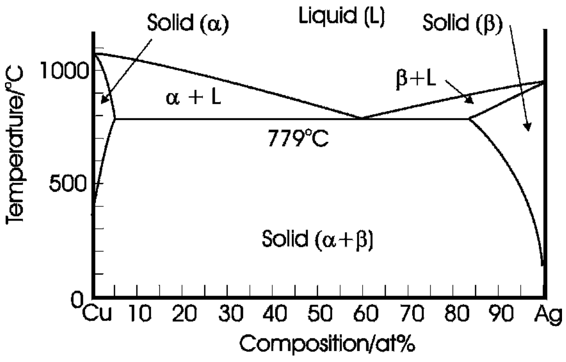

Figure 8.28 Phase diagram of the copper–silver system, for Question 8.11

(a) Sketch and label the microstructure of a solid containing 2.5 at% silver (about halfway across the α phase field at 800 °C) when the melt is slowly cooled to 800 °C and then to 400 °C. [Note: answer is not shown at the end of this book.]

(b) Sketch and label the microstructure of a solid containing 30 at% silver when the melt is slowly cooled to 700 °C. [Note: answer is not shown at the end of this book.]

(c) Sketch and label the microstructure of a solid formed by slowly cooling the eutectic composition, containing 60 at% Ag, to 700 °C. [Note: answer is not shown at the end of this book.]

8.12 With respect to the iron–carbon phase diagram (Figure 4.16; page 102):

(a) Sketch and label the microstructure of a solid containing 3.44 wt% carbon when the melt is slowly cooled to 800 °C, and then to 600 °C. [Note: answer is not shown at the end of this book.]

(b) Sketch and label the microstructure of a solid containing 62 wt% carbon when the melt is slowly cooled to 800 °C. How much of each phase is present? [Note: answer is not shown at the end of this book.]

(c) The alloy in part (b) is further cooled to 600 °C. What phases will now be present? [Note: answer is not shown at the end of this book.]

8.13 With respect to the iron–carbon phase diagram (Figure 4.16, page 102):

(a) Sketch and label the microstructure of a solid containing 1.0 wt% carbon when the melt is slowly cooled to 1000 °C, and then to 750 °C and, finally, to 700 °C. [Note: answer is not shown at the end of this book.]

(b) Sketch and label the microstructure of a solid containing 0.3 wt% carbon when the melt is slowly cooled to 1000 °C, and then to 750 °C and, finally, to 700 °C. [Note: answer is not shown at the end of this book.]

(c) Sketch and label the microstructure of a solid containing 0.76 wt% carbon when the melt is slowly cooled to 1000 °C, and then to 750 °C and, finally, to 700 °C. [Note: answer is not shown at the end of this book.]

8.14 The surface energy of solid corundum, Al_2O_3, at 1850 °C is 0.905 J m^{-2}. Calculate the relative pressure, p/p_0, over a hemispherical 'hill' of diameter 1×10^{-7} m on the surface of a flat plate of corundum at this temperature.

8.15 The surface energy of solid magnesia, MgO, at 1500 °C is 1.2 J m^{-2}. Estimate the pressure differential between a spherical pit of diameter of 5×10^{-7} m and that over the surface of a flat plate of magnesia at this temperature.

8.16 Assuming that the ideal gas law $(pV = nRT)$ holds, deduce the formula

$$\frac{r_i}{r_f} = \left(\frac{2\gamma}{p_i\, r_i}\right)^{1/2}$$

where r_i and r_f are the initial and final radii of the pore in the material, respectively, p_i is the initial gas pressure in the pore, and γ is the surface energy of the material. [Note: answer is not provided at the end of this book.]

8.17 A spherical pore in a soda-lime glass at 1200 K contains trapped gas. Assuming the gas trapped in the pore is at atmospheric pressure, and the surface energy of the glass at 1200 K is 0.350 J m^{-2}, calculate the equilibrium pore size when the initial pore is of diameter:

(a) 0.4 μm.

(b) 4 μm.

(c) 40 μm.

8.18 Using the data in Question 8.17, what is the equilibrium size of a pore that will neither shrink nor expand?

8.19 Solid titanium nitride, TiN, has a surface energy of 1.19 J m^{-2} at 1200 °C. If the voids in this material contain nitrogen gas at the same partial pressure as found in the atmosphere, approximately 8×10^4 Pa, estimate the maximum void size to ensure that voids in a sintered ceramic will shrink.

Table 8.1 Data for Question 8.20

Metal/metal oxide	Density/kg m^{-3} Metal	Oxide
Cu/CuO	8933	6315
Fe/Fe_2O_3	7873	5240
K/K_2O	862	2320
Ti/TiO_2	4508	4260
Al/Al_2O_3	2698	3970
Na/Na_2O	966	2270

8.20 Which of the metals listed in Table 8.1 are likely to be protected from corrosion by the formation of a protective oxide film?

Table 8.2 Data for Question 8.21

Time of heating/h	Film thickness/ nm
1	4.74×10^{-7}
2	0.67×10^{-6}
3	0.82×10^{-6}
4	0.95×10^{-6}
5	1.06×10^{-6}
6	1.16×10^{-6}

8.21 A nickel foil is oxidised at 1000 °C. The film thickness as a function of time is given in Table 8.2. Confirm that the rate is parabolic and calculate the parabolic rate constant.

8.22 When copper is oxidised under low partial pressures of oxygen gas, it forms Cu_2O via a parabolic rate law. The rate constant is 5.38×10^{-10} m^2 s^{-1} at 0.05 atm pressure and 900 °C.

(a) What will the film thickness be after oxidation of copper foil for 10 h at this temperature?

(b) What will the weight of the copper oxide film be?

(c) Experimentally, it is easier to measure the weight gain as a function of time rather than film thickness. What will the weight gain of the film be?

8.23 The thickness of the layer of the *spinel* $NiAl_2O_4$ formed between NiO and Al_2O_3 when reacted at 1350 °C is given in Table 8.3. Check that the reaction is diffusion controlled and calculate the rate constant. The reaction equation is:

$$NiO + Al_2O_3 \rightarrow NiAl_2O_4$$

Table 8.3 Data for Question 8.23

Layer thickness/μm	time/h
1.0	20
1.4	40
1.8	60
2.0	80
2.3	100