25

Solid-State Phase Transformations and Reactions

CHAPTER PREVIEW

A phase transformation occurs when one material changes its composition or structure. The transformation can be caused by a change in temperature so that no other material is involved, or it may involve the reaction with another material, which may or may not be a ceramic and may be in the liquid or gaseous phase. In this chapter, we restrict the discussion to phase transformations where the ceramic is in the solid state. Whenever a phase transformation occurs, a phase boundary must move.

Phase transformations occur at interfaces and require the interface to move. A solid-state phase transformation occurs when the interface between two grains that are chemically or structurally different moves. If the grains are chemically the same but have different structures, the process is referred to as a (structural) phase transformation, and local atomic movements can induce the change; if the grains have a different chemistry, then long-range diffusion must occur and the process is most likely part of a solid-state reaction. Clearly, there are many features in common with grain growth where the grains are chemically and structurally the same. In particular, the ideas of curvature and capillarity carry over. This chapter thus builds on our discussion of all types of interfaces.

25.1 TRANSFORMATIONS AND REACTIONS: THE LINK

In Chapters 14 and 15, we discussed grain boundaries (GBs) and phase boundaries (PBs), respectively. Those two chapters described the interfaces and crystal defects. In Chapter 24, we then examined how the movement of GBs can lead to sintering, grain growth, and densification. In the present chapter, we examine how the movement of PBs leads to transformations and reactions. Some examples of reactions involving the movement of a PB are given in Table 25.1: not all of these are solid-state reactions.

How special is this topic for ceramics? These processes do occur in metal/semiconductor systems. In ceramics, solid-state reactions usually involve the movement of two species because the species are likely to be charged, and we must maintain electrical neutrality. The special feature in ceramics is therefore the movement of charge and the requirement for overall electrical neutrality. We can thus apply a voltage to the system and cause an electric or ionic current to flow. As in other systems, the slower-moving species controls the rate of the reaction.

The reason phase transformations are so important for ceramics is that ceramics are usually processed in the solid state. A major difficulty in studying these processes is that they usually occur at high temperatures.

We consider three types of phase transformation: (1) crystal → crystal, (2) glass → crystal, and (3) crystal → amorphous. Transformations (1) and (2) are closely related to solidification from the melt and dissolution into a liquid. Solidification is a major theme in Chapter 29. The two topics to address are:

Do atoms move further than atomic distances?
Is charge transferred during the process?

We can put these questions another way: is the driving force due to a gradient in the chemical potential or in the electrochemical potential? It is important to remember that phase diagrams describe the equilibrium state. Phase transformations occur because the system is not in its equilibrium state. We can change *P*, *T*, or *c* and then examine how long it takes to reach equilibrium and how we can get there. Our main tool is our understanding of point defect mobility and diffusion. In general, we consider model systems but even then the data available are often not very good.

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TABLE 25.1 Reactions by Phase Boundary Movement

System	*Examples of special features and challenges*
Calcination	Removing CO_2 and other gases during firing
Dehydration	Removing water before and during firing
Gas/solid reactions	Vapor phase at high temperature: oxidation or corrosion
Hydration reactions	Cement; changes over long time periods
NiO/Al_2O_3	Large structure change at one interface, less at the other
NiO/CoO	Need diffusion data; the Darken equation required
Precipitation	With control: glass-ceramics
	Lacking control: devitrification of glass
Transport through a fluid	Important for glass crystallization (e.g., after nucleation)
	Phase separation in glass
Vitrification	Pottery; salt glazes

25.2 TERMINOLOGY

As we described in Chapter 5, the polymorphic form of a material that has the lowest free energy is the most stable. The free energy, G, of each phase is given by the usual relation $G = E - TS$. At absolute zero, the entropy term (TS) is zero, and the phase with the lowest internal energy is most stable. However, at higher temperatures, other polymorphic forms can exist despite their higher internal energy because of the dominance of TS (see Figure 5.10).

- Polymorphic transformation: the chemistry is unchanged.

Polymorphic transformations can be classified in two general types, depending on the kind of changes occurring in the crystal. Displacive transformations, as the name suggests, involve displacements of the atoms only; there is no structural rearrangement. The displacive transformation that has been extensively studied in metals is the martensite transformation. Martensitic transformations are actually quite common in ceramics, but they are generally not as rapid as in metals even though they are transformations.

Reconstructive phase transformations are associated with high activation energies. The structural change involves breaking of bonds. The energy required is at least partly recovered when the new structure is formed. Reconstructive transformations are frequently sluggish, and consequently the high-temperature forms can often be cooled to room temperature without reverting to the thermodynamic stable form.

- Displacive transformations: atoms remain attached to the same neighbors.
- Reconstruction transformations: bonds are broken, and atoms are rearranged.

The driving force for reactions is either a chemical potential or an electrochemical potential. The electrochemical potential takes account of the fact that in ceramics we have charged defects, and these charged defects may move at different rates.

25.3 TECHNOLOGY

From a general technological viewpoint, not only are polycrystalline ceramics almost always very impure by metallurgical standards (3N, i.e., 99.9%, being typical high purity), but it is common practice to add other oxides to enhance densification during processing. If the concentration of the additives exceeds the solubility, a second phase may form. Remembering our discussion in Section 24.1, imagine sintering blue and yellow colored marbles. If the temperature stays low, the marbles remain distinct but deform and rearrange to form a dense material. It the temperature increases, the glasses may mix to give a uniform green glass, which in our analogy is the reacted material. So, whether or not a reaction takes place depends on such factors as the temperature; changes in the morphology of reactants can be affected by other considerations.

25.3.1 New Materials

Solid-state reactions are also used to produce new materials. For example, although equimolar Mg-Al spinel (i.e., $MgAl_2O_4$ or $MgO.Al_2O_3$) powder is available commercially, nonequimolar Mg-Al spinel powders may be less easy to obtain. (A similar processing method is used to produce many of the spinel-structured ferrites). These spinel powders may have useful properties because they can be used to produce polycrystalline compacts that deform more readily than the equimolar material. Such materials can be prepared by firing an intimate mixture of the equimolar spinel with high-purity alumina powder. A closely related process (structurally the opposite) occurs when γ-alumina is transformed to α-alumina, as takes place when alumina is prepared from boehmite.

Yttrium barium copper oxide (YBCO), $(Sr,Ba)TiO_3$, bismuth strontium calcium copper oxide (BSCCO), and lead zirconate titanate (PZT) are all essentially prepared by combining oxides or their precursors.

25.3.2 Multiphase Materials

There is a growing interest in the development of multiphase ceramics. Both the processing and the use of each of the materials described above may involve a solid-state reaction and the movement of a phase boundary. There are, of course, many other situations where solid-state reactions are important. In electronic packaging, chromium is first bonded to alumina; and the copper conduction lines are

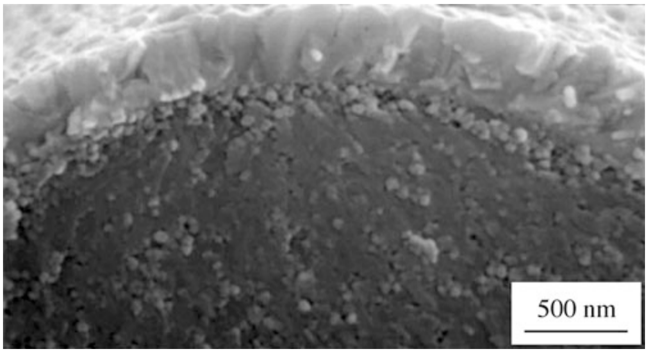

FIGURE 25.1. Technical application 1. Monazite on alumina fibers as a barrier layer in a ceramic matrix composite.

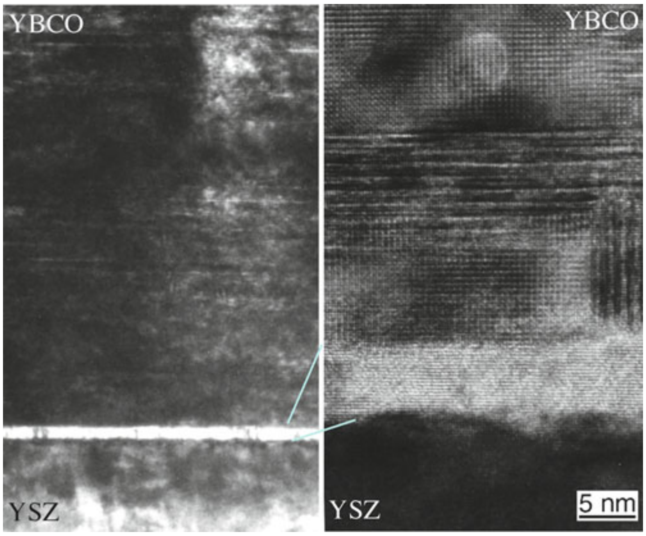

FIGURE 25.2. Technical application 2. Yttrium barium copper oxide (YBCO) on yttria-stabilized zirconia (YSZ).

then, in turn, bonded to the chromium. It is likely that thin spinel layers are formed in the process. Ore reduction is another important example, as illustrated by the reduction of hematite to Fe via magnetite and wüstite. A special case is the reaction that can take place when fibers are encapsulated in a matrix to enhance mechanical properties of the matrix, as illustrated in Figure 25.1. If the fiber reacts with the matrix, the two are no longer able to deform independently, and the mechanical properties of the composite is degraded. For this reason, barrier layers may be used to coat the fibers before enclosing them in the matrix.

25.3.3 Growth of Thin Films

The first example of the growth of thin films, shown in Figure 25.2, occurred when YBCO was grown on a substrate of ZrO_2. The intermediate layer grew by a solid-state reaction during the deposition. This can be a problem because complicated multilayer devices are needed for many new applications. The use of ferroelectric materials almost always involves manufacturing multilayers. It is essential that the layers should not react with one another.

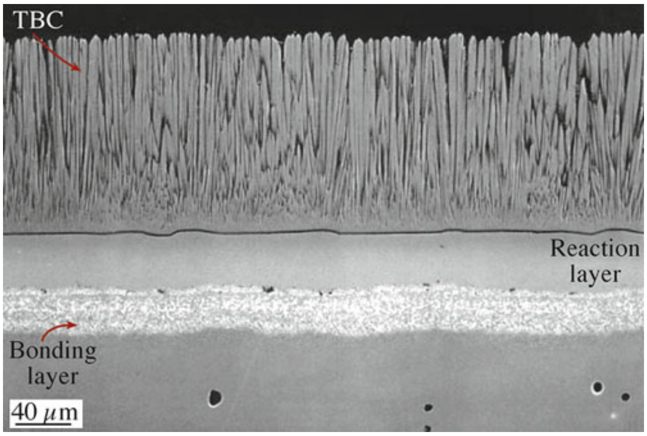

FIGURE 25.3. Technical application 3. Thermal barrier coating on a metal with a reaction layer and a bonding layer.

25.3.4 Changing Properties

We can add a second phase to modify the mechanical properties of a ceramic. An example that we discussed in Chapter 18 is the toughening of alumina using zirconia. In this application, again, the materials should not react (which is why zirconia is used).

25.3.5 Degrading Thermal Barrier Coatings

A model thermal barrier coating (TBC) is shown in Figure 25.3. The white band separates the Al-rich bond coat from the underlying Ni-rich superalloy. Capping the structure is the columnar yttria-stabilized zirconia (YSZ) TBC. The role of the bond coat, as its name implies, is to ensure that the coating continues to adhere to the metal during oxidation. Between the bond coat and the YSZ is an oxide layer that forms during oxidation (the overlayer or thermally grown oxide, or TGO). Between the bond coat and the superalloy is a thin reaction layer.

25.3.6 Impurity Phases

A well-known example of this process is the addition of MgO to alumina to permit sintering to theoretical density, as required for the production of translucent alumina tubing (see Section 24.17). If, in this example, MgO is added in excess of the solubility limit (~210 ppm is used; the actual solubility varies with temperature), spinel is formed, which may in turn react with Na during use to produce a precipitate of β'''-alumina. This reaction can cause the failure of sodium-vapor lamps. Because oxides are frequently processed at high temperatures, it is also likely that the vapor pressure can become appreciable for certain additive oxides.

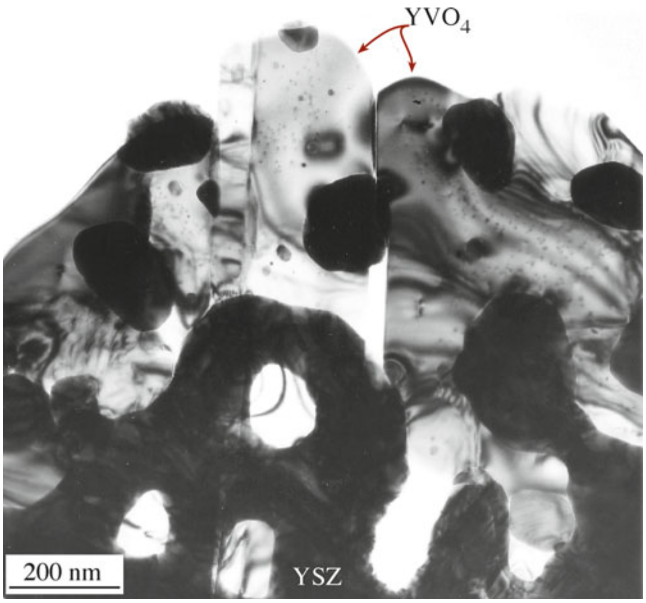

FIGURE 25.4. Corrosion of YSZ by V_2O_5 vapor.

25.3.7 Corrosion of Oxides

Even sapphire and YSZ can be corroded at relatively low temperatures. Figure 25.4 shows polycrystalline YSZ being corroded by V_2O_5 vapor to form a reaction layer of YVO_4. This process may actually be important when a burning fuel contains V and the TBC contains YSZ. The Y that is stabilizing the YSZ diffuses out to react with the V_2O_5 and form YVO_4. The result is that the Y is no longer available to stabilize the ZrO_2, which therefore undergoes a phase change and can fracture.

25.4 PHASE TRANSFORMATIONS WITHOUT CHANGING CHEMISTRY

Phase transformations are, of course, closely linked to phase diagrams; but remember that if a phase transformation is occurring, the system is not in equilibrium and the equilibrium phase diagram can be used only as a guide. Metastable phases may form during a reaction. The stability of a phase is determined by the relative value of *G*. Although the chemistry does not change, the redistribution of charge can be very significant, leading, for example, to the piezoelectric effect. Polymorphic transformations do not change the chemistry of the material. Because displacive transformations do not require a change in the first coordination of the atoms, there is no bond breaking, only bond bending. The distorted form is a derivative structure of the starting material, usually losing one or more symmetry elements. Displacive transformations to lower-temperature forms commonly result in twins. As we saw in Chapter 14, a crystal is twinned when one portion of the lattice is a mirror image of the neighboring portion, the mirror being the twinning plane. This can lead to the formation of twinned "particles," as shown in Figure 25.5A. You can get an idea of how this might occur by considering Figure 25.5B. The particle effectively contracts along its length by the $(001)_c$ planes, rotating to the $(001)_m$ planes of twin-variant 1 and back to the $(001)_m$ planes of twin-variant 2, so there is no long-range shear. Where $(001)_{m1}$ planes change to $(001)_{m2}$ planes, we form a twin boundary. Depending on the details of the crystallography (which planes match best), the twin boundaries my lie along the short (as here) or long axis.

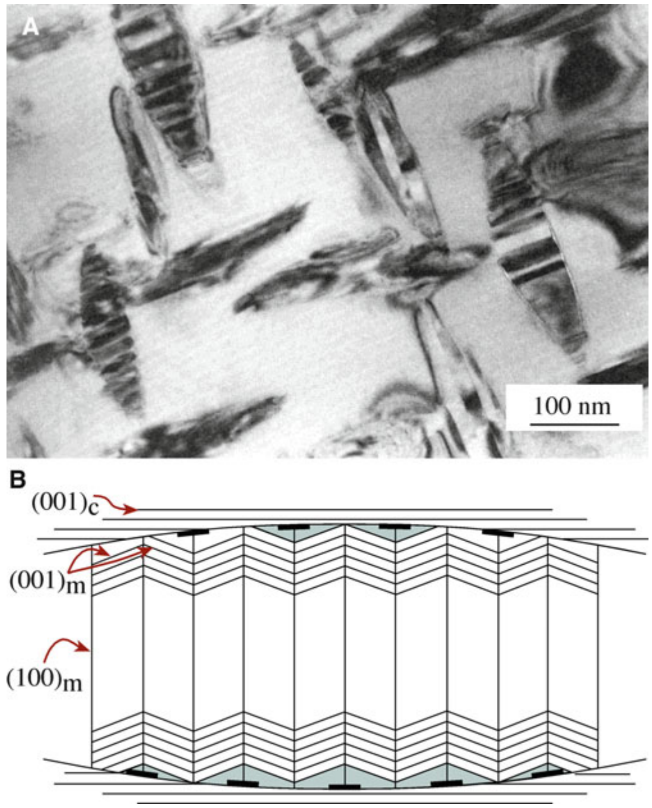

FIGURE 25.5. Twins in transformed particles. (A) Experimental observation. (B) A possible mechanism.

A displacive transformation is diffusionless and requires only a shear of the parent structure to produce the new phase; consequently, the rate of transformation at any temperature occurs nearly instantly. An important example of the displacive transformation is the change from tetragonal to monoclinic ZrO_2. In this example, there is a 5 vol% increase during cooling, which can result in internal stresses in the ceramic and lead to weakening or even fracture. However, the controlled transformation of ZrO_2 particles in a ceramic matrix (e.g., Al_2O_3) can be used as a means of strengthening of the matrix. (We discussed fracture of ceramic materials in Chapter 18). The addition of MgO, CaO, or Y_2O_3 to ZrO_2 can stabilize the cubic (fluorite) structure. When ZrO_2 transforms from the cubic to the tetragonal phase or from the tetragonal to the monoclinic phase, the volume changes. This volume change is the key to using such mechanisms in toughening ceramics because it relaxes local stresses at a crack tip.

Barium titanate is cubic with the perovskite structure. However, at room temperature (actually below the Curie temperature of 120°C), it is tetragonal with a spontaneous electric polarization in the direction of the c-axis (only the higher temperatures form is shown in Figure 7.2). In this ferroelectric condition, a crystal of $BaTiO_3$ has a domain structure.

The classic example of a reconstructive phase transformation in ceramics is the transformation between the low and high forms of SiO_2: the distorted form of quartz structure is stable at the lower temperature. Twins are, again, often formed during reconstructive phase transformations when they lead to a decrease in symmetry because the change often occurs in symmetry-related ways; the twins are then related by the "lost" symmetry element.

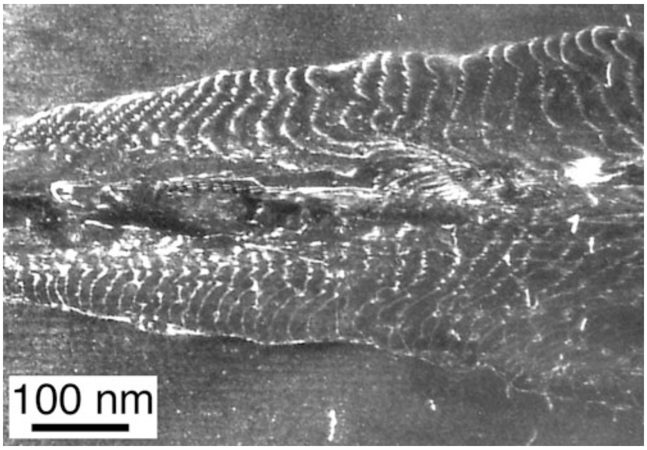

FIGURE 25.6. Movement of interfacial dislocations between hematite and $NiFe_2O_4$ spinel during oxidation, leading to thickening of the precipitate.

25.5 PHASE TRANSFORMATIONS CHANGING CHEMISTRY

For short-range or long-range chemistry changes, it is necessary for ions to move. Atoms diffuse, and charge is transferred. If charge is moved, then an electric field may develop in the material or we can influence the transformation by applying an electric field. The structure may also change, so the beginning of the process (the nucleation stage) may be controlled by the difficulty in changing the structure. At a later stage, diffusion almost invariably controls such reactions.

The reaction can be considered as involving three steps.

1. Transport to the interface
2. Reaction at the interface
3. Transport away from interface of the product and heat

As usual, the slowest step controls the rate. The rate of such reactions is controlled by gradients in the chemical potential or, if there is a local variation in charge, by the electrochemical potential.

This concept is very important because the chemical potential and the electrical potential can act in opposite directions. There are many model and technological applications of this concept.

Silver sulfides provide a model system for studying this effect, partly because the processes occur at relatively low temperatures.

In oxides such as ZrO_2, flow of oxygen ions can be measured and related to the difference in oxygen partial pressure across the ZrO_2 layer because an electrochemical potential is generated.

In the formation of $NiAl_2O_4$ by solid-state reaction, we have diffusion of Al^{3+} ions and Ni^{2+} ions. If the Al^{3+} ion moves faster than the Ni^{2+} ion, then we would build up charge, which would create an electric field that in turn would act to reverse the flow of ions, rather than allow a buildup of charge. (More details are in Section 25.9).

25.5.1 Precipitation

Precipitation usually involves a change in local chemistry. Because we are creating a new particle, we form a new PB (see Chapter 15). As the particle grows, this PB moves. The balance between kinetics (of interface motion and diffusion) and energy (of the new bulk and the new PB) may determine the shape of the particle during growth. Three factors in particular must be considered.

1. Number of particles per unit volume
2. Shape of the particles
3. Size of the particles (and hence volume fraction of the precipitate)

As for metals, we can change the temperature or the chemical potential. Particles in ceramics have not been as widely used as in metals because we don't need to pin dislocations. However, particles can still inhibit GB motion, act as sinks for impurities, or modify mechanical properties. The widespread occurrence and usefulness of precipitation in ceramics is becoming more fully recognized. Things happen slowly in ceramics. If there is good alignment between the matrix and the precipitate, the transformation can occur by the movement of dislocations, as in Figure 25.6, which shows a plate of hematite growing in an Ni-Fe spinel matrix. Notice that the interfacial dislocations bow out in the direction of movement and that the plate thickens as they move.

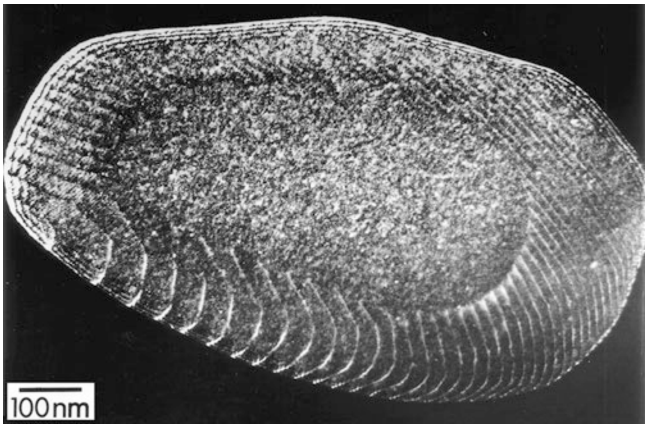

FIGURE 25.7. Growing particle of spinel in a matrix of Fe-doped Al_2O_3 during internal reduction.

25.5.2 Internal Oxidation and Reduction

A thought experiment: imagine a 1-mm cube of Fe-doped Al_2O_3 where all the Fe is in the 3+ state. Now heat the cube in a reducing atmosphere at ~1,500°C. The matrix is unchanged (it's Al_2O_3), but the Fe^{3+} is reduced to Fe^{2+}. Initially, this phase change can happen only at the surface, where the oxygen activity has been lowered; but then the "reduction" front moves into the cube like a PB (but there is no change in phase). The Fe^{2+} is no longer soluble in the matrix and precipitates out as $FeAl_2O_4$ spinel. The result is that we can see where the front has passed through by where the precipitates, such as that in Figure 25.7, have formed. (Notice the curvature of the dislocations, implying their direction of movement). The converse process (i.e., internal oxidation) can be demonstrated using a similar cube of Fe(II)-doped NiO.

25.6 METHODS FOR STUDYING KINETICS

We need to understand what controls the rate of a phase transformation. We can monitor both chemical and structural changes to address the sometimes subtle question: which change (chemistry or structure) occurs first? The answer depends on why the phase change itself occurs. The experimental techniques we use are those given in Chapter 10, so we just give some specific illustrations here. The classical approach used to study the kinetics of solid-state reactions between two ceramic oxides is to react a bulk diffusion couple in much the same way as, for example, when studying the Kirkendall effect in metals.

25.6.1 Using Weight Change

We can weigh the sample and plot the fraction that has reacted as a function of time, as illustrated in Figure 25.8. Today's microbalances allow us to make this technique very sensitive. A modern microbalance can weigh samples up to 3.5 g with an accuracy of 0.1 μg. A quartz-crystal microbalance (QCM) can actually measure mass changes in the nanogram range. Therefore, we use a piezoelectric ceramic, a thin plate of quartz, to make the device that then allows us to study reactions in ceramics (and other materials).

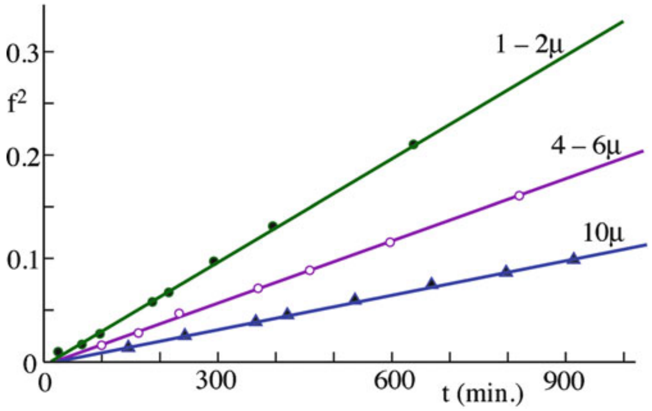

FIGURE 25.8. Reaction by weight, where f^2 is the square of the fraction reacted.

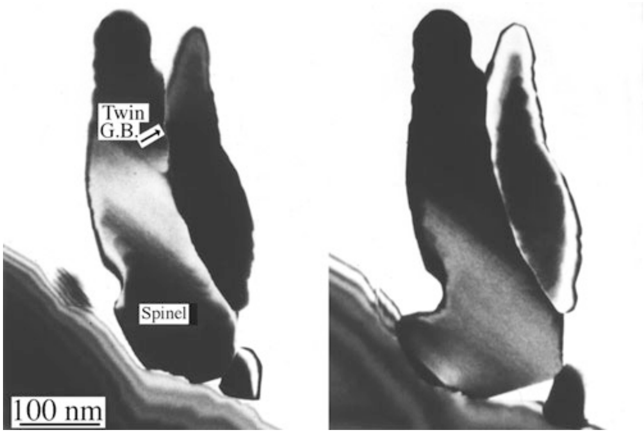

FIGURE 25.9. Particle of Ni-Al spinel growing on an Al_2O_3 thin film.

25.6.2 Using VLM, the Microprobe, and SEM

The reacted microstructure is often best analyzed using low-voltage scanning electron microscopy (LVSEM) in the backscattered-electron (BSE) imaging mode. The low voltage means that we need only a thin conductive coating (if any) to prevent an insulator from charging. The BSE mode allows the phases present to be readily recognized because the backscatter coefficients are likely to be different for the reactants and the reaction product.

25.6.3 Using TEM

The movement of a particular PB is illustrated in Figure 25.9. A spinel particle has been grown on the edge

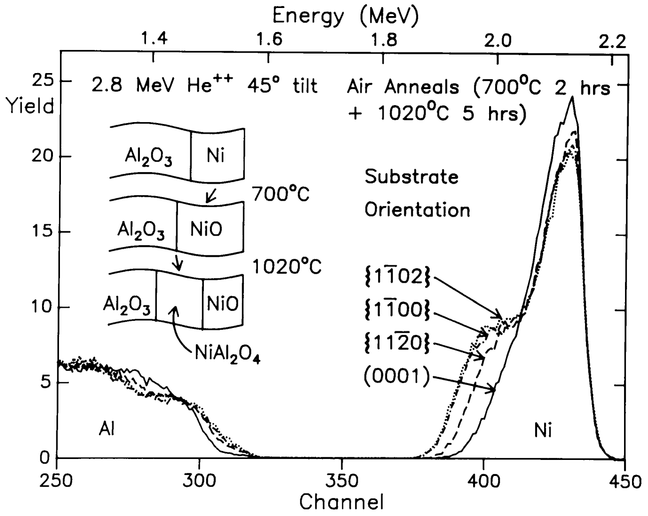

FIGURE 25.10. Rutherford backscattering spectrometry (RBS) of a reaction between NiO and Al_2O_3 substrates for different surface orientations.

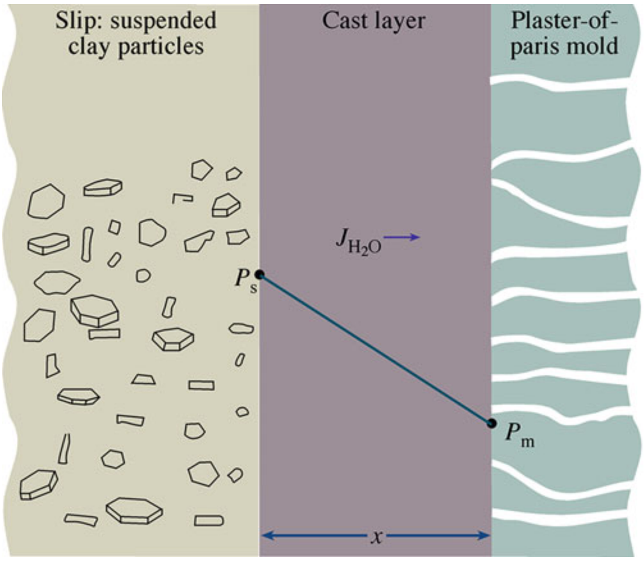

FIGURE 25.11. Slip drying to form a slip-cast layer.

of a thin film of Al_2O_3 by reacting the film with NiO vapor, looked at by transmission electron microscopy (TEM), replaced in the reaction chamber, and looked at again. You can see that the spinel has grown into Al_2O_3. In this case, the PB moves in the solid state, but the NiO is provided from the vapor phase. The spinel particle changes only when it grows into the sapphire.

25.6.4 Using RBS

Rutherford backscattering spectrometry (RBS) is very direct and measures the thickness of a reaction layer. The lateral resolution is the width of the ion beam (~0.1 μm). An example from a thin layer of NiO reacting with differently oriented surfaces of Al_2O_3 is illustrated in Figure 25.10. The thickness of the spinel is obtained by fitting the data to a simulated profile (using RUMP). It shows in this example that the rate of growth of the spinel layer does indeed depend on the orientation of the surface.

25.7 DIFFUSION THROUGH A LAYER: SLIP CASTING

We consider the kinetics of slip coating or slip casting for two reasons: (1) as a model for the transport of a reactant through a planar boundary layer, and (2) because it is a very important aspect of ceramic processing. The model actually applies to reduction, oxidation, and MgO/Al_2O_3 reactions. In slip casting, a mold is made from gypsum (plaster of Paris: $CaSO_4{\cdot}2H_2O$). Gypsum contains fine capillaries that remove water from a slip at a predictable rate. The clay particles in the slip are platelets, as shown in Figure 25.11, so a more compact layer forms as the water is removed. In the compacted cast layer, there are fewer capillaries, so it becomes more difficult to remove more water. Hence, as the thickness increases, the rate of material transported decreases.

We can write an expression for the flow (current) of atoms (the transport equation) as:

$$J = \frac{KdP}{dx} \tag{25.1}$$

where dP/dx is the water pressure gradient, and K is the permutation coefficient, which depends on the particle size, viscosity, and temperature. The pressure at the surface of the slip, P_{slip}, is 1 atm. The pressure at the slip/mold interface (B), P_{mold}, is determined by the surface tension in the capillaries (which are assumed to have a fixed radius r_c).

$$\Delta P = P_s - P_m = \frac{2\gamma}{r_c} \tag{25.2}$$

The flux can also be expressed as a volume (proportional to ρ^{-1}) multiplied by the velocity of the slip/layer interface.

$$J = \frac{1}{(\kappa\rho)}\frac{dx}{dt} \tag{25.3}$$

HOW THIS PARABOLIC RELATIONSHIP ARISES

- J is proportional to $\frac{dx}{dt}$: J depends on velocity.
- J is also proportional to $\frac{1}{x}$: ΔP is the driving force.

So, $\frac{dx}{dt}$ is proportional to $\frac{1}{x}$: hence it is parabolic

When x is very small, $\frac{dx}{dt}$ is very large.

When x is very large $\frac{dx}{dt}$ is very small.

Combining equations 25.1–25.3 gives:

$$J = 1/(\kappa\rho)\frac{dx}{dt} = K\frac{dP}{dx} = -K\frac{\Delta P}{x} = -K\frac{2\gamma}{r_c x} \qquad (25.4)$$

Then, by rearranging we get an expression for the interface velocity.

$$\frac{dx}{dt} = -K\kappa\rho\frac{2\gamma}{r_c x} \qquad (25.5)$$

If we integrate, we find that x^2 is proportional to t, so the kinetics are parabolic.

A pot can be slip cast to a thickness of several millimeters in a few hours. The potter would then pour off the remaining slip, let the pot dry and shrink, and remove it from the mold, which can then be re-used.

25.8 DIFFUSION THROUGH A LAYER: SOLID-STATE REACTIONS

In solid-state reactions, the reactants are initially in contact and combine chemically to form the reaction product. The kinetics of the initial stage of such a reaction depends on the parameters of the interface (e.g., the crystallography of the contacting surfaces). The fundamental point is that we start with one interface and immediately create two new interfaces. We consider the example of NiO/Al_2O_3. Similar systems include MgO/Al_2O_3 and FeO/Fe_2O_3.

The mechanism for such reactions was proposed by Wagner to be the counter-diffusion of cations. It has been found that this mechanism does occur for purely ionic materials. Counter-diffusion of cations in ionic systems is dictated by charge-balance considerations rather than cation mobilities. Thus, significant deviations from the predicted balance may occur when electronic carriers (i.e., electrons and holes) are present.

The initial position of the interface between the reactant oxides can be labeled by “inert” Pt markers or recognized by the presence of voids. Some early measurements were not in agreement with this model but may have suffered from the fact that inert markers can move even though they remain inert.

25.9 SPINEL-FORMING REACTION

The phase transformation at the Al_2O_3/spinel PB involves both a change in the distribution of cations and a change in the structure of the oxygen sublattice. At the spinel/NiO interface, the oxygen sublattice remains cubic, although misfit dislocations may be introduced. It is not possible to observe directly the movement of particular interfaces using bulk samples. Techniques are used that allow the actual movement of individual interfaces to be studied and the kinetics of the earliest stages of the reactions to be determined.

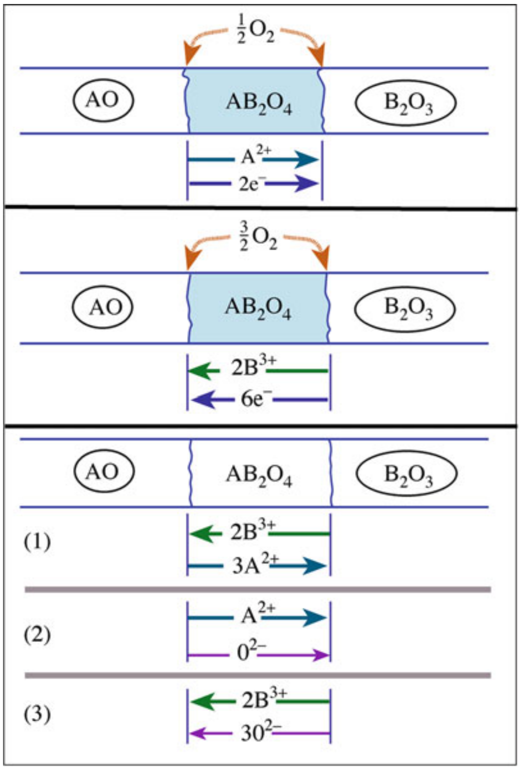

FIGURE 25.12. Mechanisms for the reaction between AO and B_2O_3.

When alumina and NiO react to form a layer, the equation is:

$$NiO + Al_2O_3 \Rightarrow NiAl_2O_4 \qquad (25.6)$$

There are many possible reaction paths. The chosen path may depend on whether or not the reaction occurs in air. In all three cases, electrical neutrality is maintained.

The three main possibilities are:

1. $2B^{3+}$ ions move in one direction; electrons or O^{2-} ions move in the opposite direction.
2. $3A^{2+}$ ions move in one direction; electrons or O^{2-} ions move in the opposite direction.
3. $2B^{3+}$ move in one direction, and $3A^{2+}$ move in the opposite direction.

These processes are summarized in Figure 25.12. Mechanisms 1 and 2 require that O^{2-} diffuse, which may not be likely, or that electrons can move, which may be the case in semiconducting oxides unless it is prevented. The third mechanism is the counter-diffusion of cations, which avoids the buildup of electric charge but does not require O^{2-} ions or electrons to move: it is a purely ionic process. When thickness is plotted against time for the bulk reaction (Figure 25.13), the gradient of the straight line depends on the temperature, and we can directly determine a value for the diffusion coefficients.

We know that if there is a charge buildup we have an electrochemical potential, η_i, rather than the simple chemical potential, μ_i. These two potentials are related by taking account of ϕ, the electrical potential acting on this charge.

$$\eta_i = \mu_i + Z_i F \varphi \tag{25.7}$$

where the subscript i refers to the ith species, which has an effective charge of Z_i; and F is the Faraday constant. The current is the product of charge and velocity.

$$j_i = c_i \mathrm{v}_i \tag{25.8}$$

Remember that velocity is mobility times force.

$$\mathrm{v}_i = -\mathrm{B_i} \cdot \mathrm{Force} = -\mathrm{B_i} \frac{1}{\mathrm{N}} \frac{\mathrm{d}\eta_\mathrm{i}}{\mathrm{dx}} \tag{25.9}$$

and

$$j_i = -\frac{c_i B_i}{N} \frac{\partial \eta_i}{\partial x} \tag{25.8}$$

We can then define a diffusion coefficient, D_i.

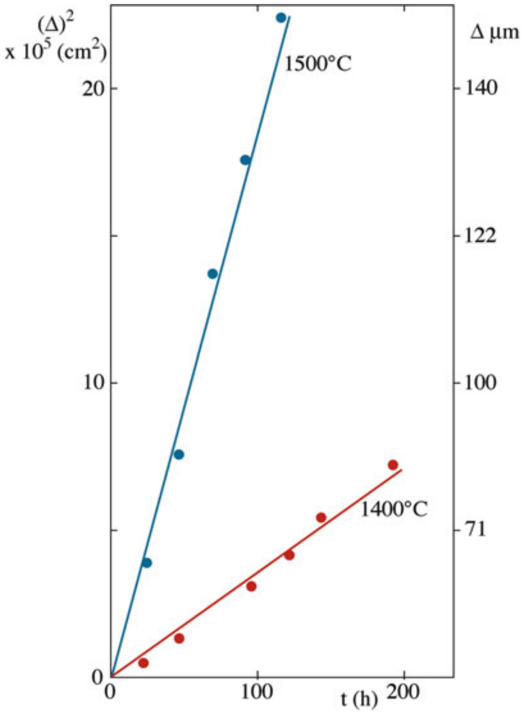

FIGURE 25.13. Kinetics of reaction between bulk NiO and bulk Al_2O_3 to form spinel.

$$D_i = -\frac{RTB_i}{N} \tag{25.10}$$

The parabolic rate law holds when the reaction layer is thick. When trying to be quantitative, there is the obvious question how do you "mark" the location of the original interface. An additional complication arises if AO and AB_2O_4 are both cubic but not lattice-matched; then misfit dislocations must be present at the interface, and they can move only if point defects on the O sublattice move.

25.10 INERT MARKERS AND REACTION BARRIERS

We saw examples of structures where reactions would destroy the device in Section 25.1 – this is where we need barriers. When we study the kinetics of reactions, we want to mark the initial location of the interface(s). This is where we need markers. In both cases, the requirement is that the barrier/marker be inert; that is, it should not participate in any reaction. This topic can be illustrated by two examples.

- Behavior of rows of Pt particles forming a marker layer
- Failure of a coating on a fiber during formation of a fiber-reinforced composite

We consider the example of diffusion couples prepared by depositing an In_2O_3 thin film on a cleaved bulk single-crystal substrate of MgO and identify the location of the initial interface by an array of Pt particles, as illustrated in Figure 25.14. The Pt particles are prepared by first sputter-coating the MgO substrate with a 2 nm thick continuous film of Pt. The Pt film/MgO substrate couple is then heated to 1,175°C for 5 min. This heat treatment causes the Pt film to dewet the MgO surface and thus form small islands. This array of small Pt particles then serves as the marker layer. After dewetting, thin films of $MgIn_2O_4$ and In_2O_3 can be deposited onto the decorated substrate using pulsed-laser deposition (PLD). This intermediate $MgIn_2O_4$ layer acts as the nucleation layer for the reaction product, so that the markers do not affect the initial nucleation of the spinel. (It can also be grown on the MgO before depositing the Pt).

Markers of various compositions and sizes have been used in numerous studies to track the movement of interfaces

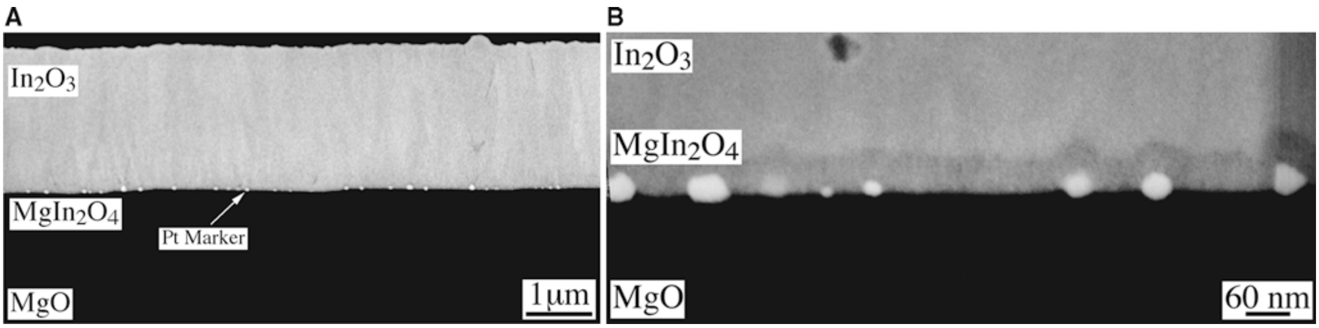

FIGURE 25.14. Scanning electron microscopy (SEM) backscattered electron images of an as-deposited In_2O_3 film on MgO with Pt markers.

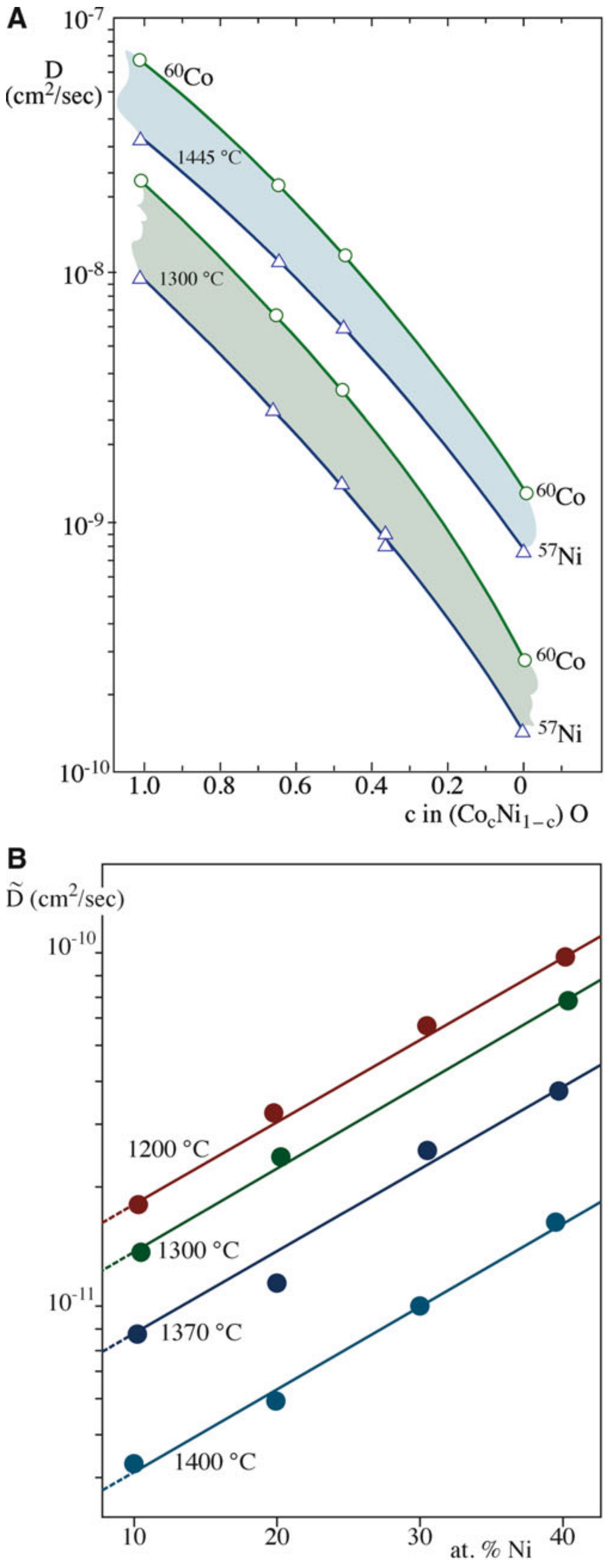

FIGURE 25.15. D as the composition varies. (A) Using tracer diffusion at two values of T in CoO–NiO mixed oxide. (B) Diffusivities for MgO–NiO mixed oxides.

in a wide variety of material systems. In many of these studies, the markers were intended to serve as a fixed reference point and were typically used to aid in determining which species were diffusing during a reaction process. In most cases when a material is used as a marker, it is assumed to be inert—the marker should neither affect nor be affected by the reaction process. Direct analysis of these thin-film diffusion couples can show directly whether or not the markers are inert and how they behave during such reactions. The markers may affect the reaction process, or the reaction process may cause the markers to move. The interface between the marker and the surrounding matrix plays a critical role in determining the inertness of the marker. This is especially significant when diffusion couples are reacted in an applied electric field.

The idea of a barrier layer is to prevent two materials that would react from coming into contact. Applications include protecting reinforcing fibers and separating layers in multilayer thin films. Such barrier layers could also be used to exclude water from hydrophobic layers.

25.11 SIMPLIFIED DARKEN EQUATION

The diffusion coefficient actually depends on the composition. Consider NiO/CoO, which is a nearly ideal solid solution. The activity coefficient is ~1.

$$\mu_i = \mu_i{}^0 + RT \ln c_i \qquad (25.11)$$

We can write an "average" diffusion coefficient as:

$$\tilde{D} = D^T_{\mathrm{Co}} x_{\mathrm{Co}} + D^T_{\mathrm{Ni}}(1 - x_{\mathrm{Co}}) \qquad (25.12)$$

In this equation, which is known as the Darken equation, x indicates the mole fraction of Co or of Ni. The equation assumes local equilibrium everywhere; and $\tilde{D}$ is a chemical or interdiffusion coefficient in a chemical potential gradient. The matrix is $\mathrm{Co}_x\mathrm{Ni}_{1-x}\mathrm{O}$. D is plotted as a function of concentration for both Ni and Co diffusing in the mixed oxide at 1,300°C and 1,445°C in Figure 25.15A. The mean value from equation 25.12 is plotted in Figure 25.15B. It can also be plotted as a function of temperature, as shown for many more oxide systems in Figure 25.16.

This analysis is useful—but be cautious. The oppositely charged point defects Ni^{3+} and V'' form an associated defect, which diffuses at a different rate. You can measure D, but modeling $\tilde{D}$ is difficult. Essentially, predictions are tricky.

25.12 INCUBATION PERIOD

The initial stage of a solid-state reaction was historically referred to as the "incubation period." Early studies of such reactions in oxides lacked the required spatial resolution, so measurements were not made until the reaction layer was

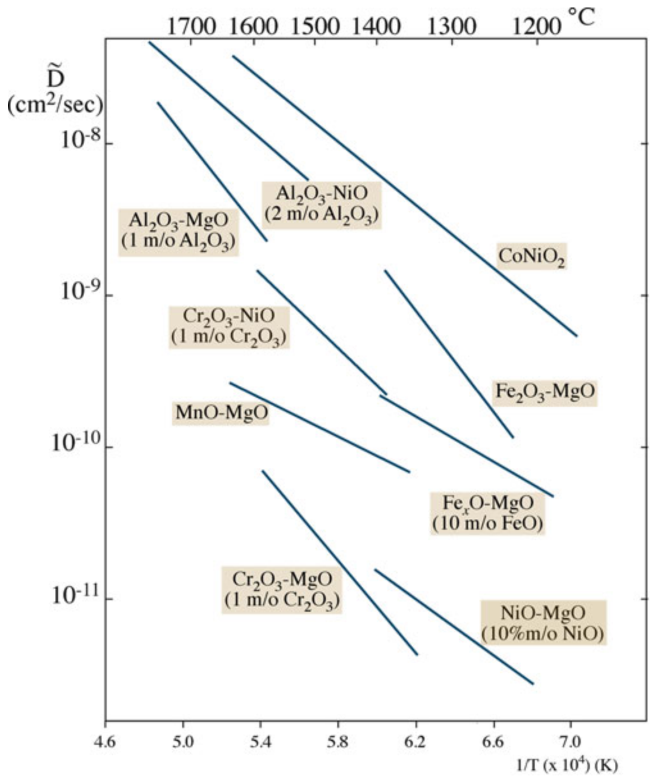

FIGURE 25.16. Dependence of diffusion coefficients on T for different oxides.

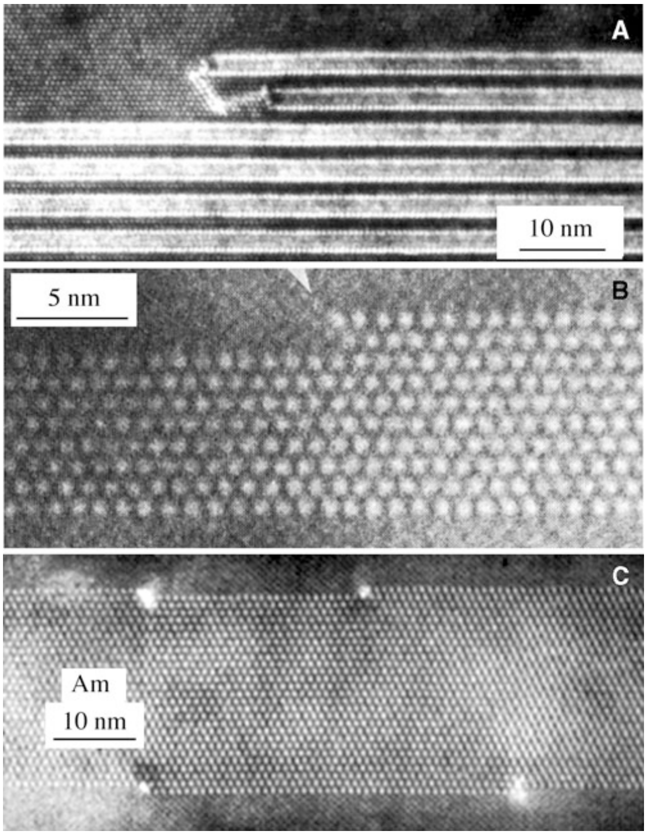

FIGURE 25.17. Chemical reactions by movement of steps on an interface. (A) β-Al_2O_3 growing in spinel. (B, C) Amphibote growing in orthodyroxene.

~1 μm thick (the resolution limit for chemical analysis in a microprobe operating at ~30 kV). Often, the reactants were not initially in ideal contact. The nucleation of spinel or other reaction products can now be detected at a very early stage using TEM. The kinetics of such early stages of reactions are often controlled by the difficulty of nucleating the reaction product, which may indicate a crystallographic factor. Thus, for example, the basal plane in Al_2O_3 tends to dissolve less readily than, say, a prismatic plane; so reactions at basal planes tend to nucleate more slowly than on prismatic planes (more in Section 25.14).

25.13 PARTICLE GROWTH AND THE EFFECT OF MISFIT

The lattice misfit at moving PBs is accommodated by misfit dislocations, lattice rotations, etc. An important consideration is the role of size in determining these effects—neither misfit dislocations nor lattice rotations may be necessary when the new phase is very small. The chemical abruptness of the interface is particularly interesting when the oxygen sublattice is almost common to the two materials, as we saw in Section 15.6 for the NiO/$NiFe_2O_4$ interface. This interface can then move by only the cations moving. However, if misfit dislocations are present, as in Figure 15.8, the anions must also move.

The growth of β-alumina into spinel, shown in Figure 25.17A, is an example of a special situation where the misfit between the precipitates and the matrix is very small along one plane, thus creating a low-energy interface. This situation is not unique, as shown in Figure 25.17B. The result of such a reaction is the formation of particles that appear to be very large in one direction: the particle may also be large in two directions—hence a platelet. Isolated steps move across the larger surface. Incidentally, always remember that most observations of such phenomena are made at room temperature.

MISFIT AND SPINEL FORMATION

When NiO and Al_2O_3 react, the lattice misfit at the initial NiO/Al_2O_3 interface (when perfectly aligned) is shared almost equally between the NiO/$NiAl_2O_4$ and the $NiAl_2O_4$/Al_2O_3 interfaces. However, when NiO and Fe_2O_3 react, the misfit at the NiO/$NiFe_2O_4$ interface is close to zero so that nearly all the misfit is accommodated at the $NiFe_2O_4$/Fe_2O_3 interface.

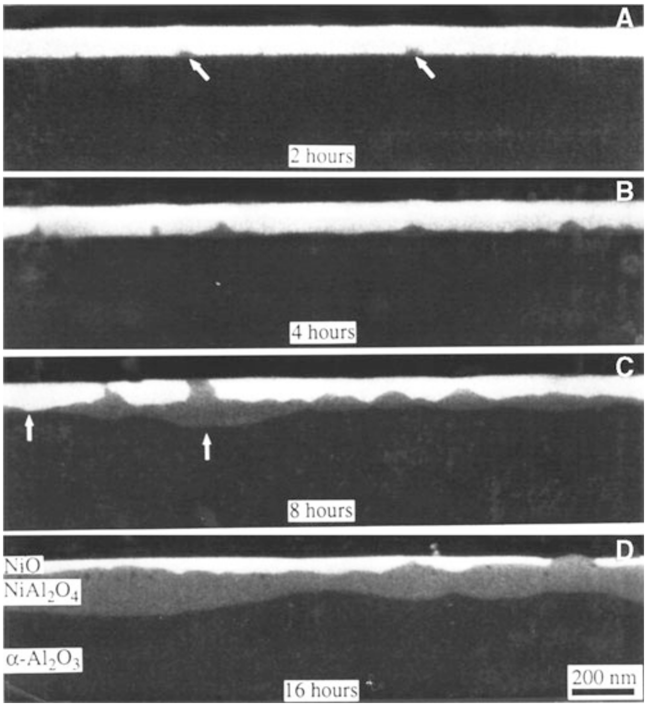

FIGURE 25.18. SEM images of reactions at grain boundaries (GBs) in thin films of NiO deposited on (0001) Al_2O_3.

25.14 THIN-FILM REACTIONS

Understanding how phase boundaries in oxides move is essential for a comprehensive understanding of solid-state reactions between ceramic oxides. The factors that determine the mobility of a PB may involve the usual aspects of structure, bonding, and chemistry. Because thin-film reactions can be carried out at low temperatures, the morphology of the interface can easily be "frozen in." GBs and other defects can affect the rate of a reaction in several ways. They can act as short-circuit paths to allow more rapid diffusion of reactants or simply act as nucleation sites for the growth of a new structure. Evidence for both of these mechanisms was found in the study of the reduction of Fe-doped Al_2O_3. It has also been shown that GBs are a necessary product of the growth of spinel into alumina.

By combining TEM and field emission gun (FEG)-SEM, we find that the formation of spinel occurs more quickly along GBs in thin-film reaction couples, as illustrated in Figure 25.18. At the earliest stages of these reactions, the kinetics are controlled by the interface mobility, rather than by diffusion through the reactant.

Thin-film reaction couples can be prepared by growing thin films on a specially prepared substrate. PLD works well for the deposition, but molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) could be equally well used. This geometry offers many advantages over bulk samples.

- The reaction temperatures can be much lower than with bulk reaction couples.
- The cooling rate can be very rapid.
- We control the microstructure, crystallography, and morphology of the substrate.
- We can study the same interface before and after the reaction.
- We can thus directly study the role played by steps on the surface of the substrates and GBs in the thin films.
- We can use a combination of materials or a graded reactant.
- We can grow material M_1 on a single crystal of material M_2, or vice versa, and thus predetermine the location of GBs.
- We can control the oxidation state of the reactants.

This approach overcomes the difficulty encountered using classical bulk diffusion: we know that there is intimate contact between the substrate and the thin film. If the materials are not in direct contact, the earliest stages of the reaction likely involve a vapor phase component.

The key feature is always that PBs move during solid-state reactions. Defects and GBs influence both the mechanisms and the rates of solid-state reactions; but with bulk reactants you don't know what is there to start with. The volume probably changes during the reaction.

When the epilayer contains GBs, the thin-film approach allows us to examine how the nucleation rate depends on the type of GB (e.g., misorientation, GB) intersecting the PB. The growth of the product depends on the nucleation site.

If, as is often drawn schematically, a continuous reaction layer forms, the volume change may be accommodated by an expansion normal to this layer (analogous to the tetragonal distortion in semiconductor multilayers). If the reaction occurs initially along the triple junction where a GB meets the substrate, the constraints are very different. The thin film can become extensively deformed in accommodating this volume change. There is, for example, an ~7% volume expansion when NiO reacts with Al_2O_3 to form the spinel.

Two types of reaction sample are illustrated in Figures 25.18 and 25.19. In the first, the reactant material is grown directly on the substrate so as to examine the *nucleation* of the reaction product and to quantify the role of GBs in the polycrystalline material. We can easily reverse the layer/substrate geometry to examine the role of GBs in the two materials separately.

In the second type of sample, a *buffer layer* of the reaction product or a *reaction-barrier layer* is grown before growing the reactant layer. This geometry allows us to quantify the *kinetics of the reaction* separately from the nucleation. We can then examine the morphological development of the two moving interfaces and the effect of lattice misfit on this morphology. The expansion that occurs when the spinel forms can be readily accommodated if a buffer layer is present and forming a uniform layer, as you can see in Figure 25.19. In this case, the kinetics can be deduced directly, as shown in Figure 25.20. Notice that T and $\Delta\xi$ are much smaller than in Figure 25.13 and that the kinetics are linear. At the early stages of the reaction, the rate is determined by the interface.

This reaction geometry can be extended to the situation where there are several reaction products, as illustrated for the Al_2O_3/Y_2O_3 system in Figure 25.21. Finally, we should note that reactions often take place more easily at surfaces because there is no volume constraint.

A special thin-film reaction (though it becomes more general as it proceeds) is the corrosion of a ceramic by a

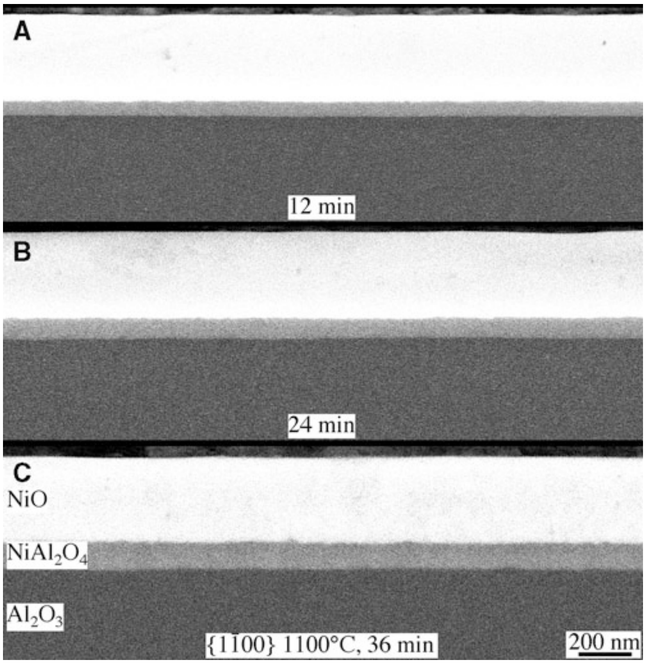

FIGURE 25.19. SEM images of the growth of spinel between thin films of NiO and (0001) Al_2O_3 when an initial buffer layer of spinel is present.

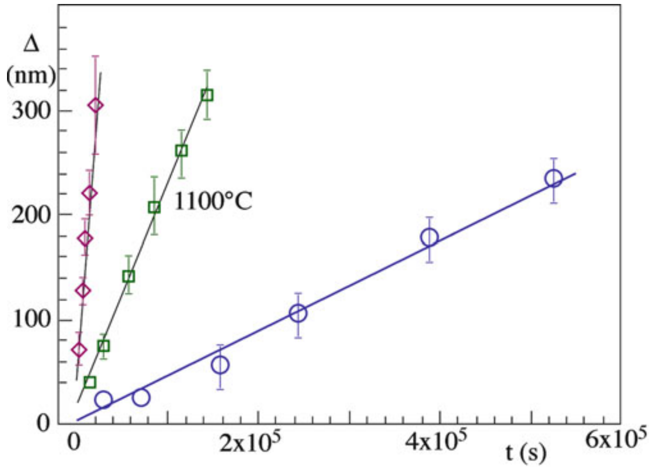

FIGURE 25.20. Kinetics of reactions between thin films of NiO deposited on (0001) Al_2O_3 when an initial buffer layer of spinel is present.

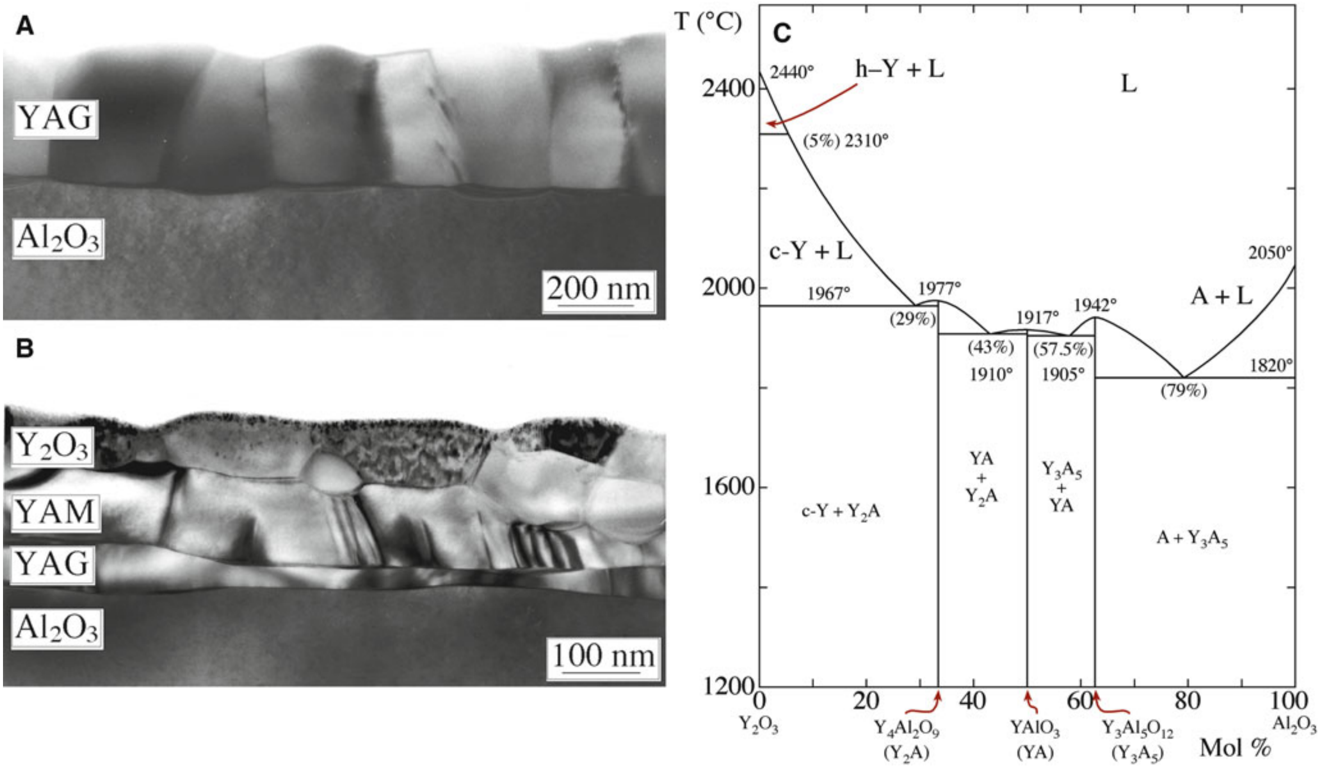

FIGURE 25.21. Forming yttrium aluminum garget (YAG) by a thin-film reaction. (A) Intermediate state. (B) Final state for the same film. (C) Equilibrium phase diagram.

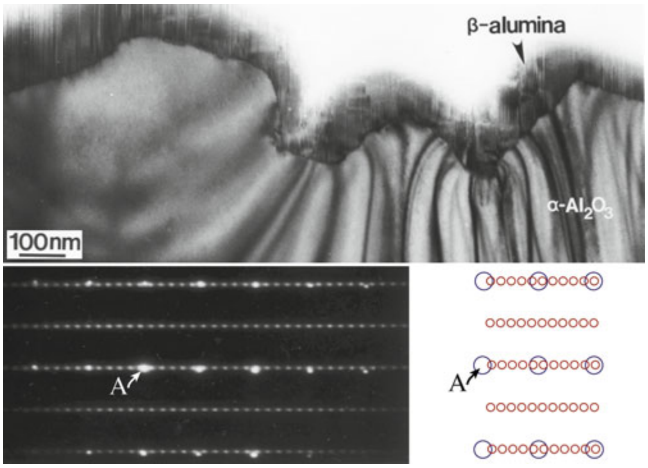

FIGURE 25.22. Corrosion of Al_2O_3 by reaction with K_2O vapor showing a transmission electron microscopy image, the DP, and a schematic of the DP.

metal or another ceramic. PBs form during the corrosion process just as they do when a metal oxidizes or when an oxide is reduced; the only special feature is that the action takes place close to the surface so there are fewer constraints. Figure 25.22 illustrates the PB formed when K_2O vapor corrodes (reacts with) alumina. The diffraction pattern (DP) shows that the two phases are topotactically aligned.

25.15 REACTIONS IN AN ELECTRIC FIELD

Diffusion in ionic materials occurs primarily by the movement of charged species. Therefore, the application of an electric field can provide a very powerful driving force for mass transport. There have been numerous studies on the effects that electric fields have on transport phenomena. Several studies have been performed on the evaporation of alkali halides in the presence of an external field. These investigations showed that the application of an electric field caused enhancement of the evaporation of the crystal species. Similar studies have been performed on oxide ionic conductors, including ZrO_2 and β-aluminas. However, there have only been a few experiments performed on classical insulating oxides such as α-Al_2O_3 and MgO (perhaps because they are insulators).

Polycrystalline diffusion couples can be studied in a similar way. Results show increased transport and consequently an increase in the growth of the reaction product. However, the polycrystalline nature of the compacts makes it difficult to separate the influence of GB diffusion and bulk diffusion.

This thin-film geometry can also help us understand how an electric field affects heterogeneous solid-state reactions and transport phenomena. The spinel-forming reaction between MgO and Fe_2O_3 deposited on thin single-crystal films of iron oxide on {001} MgO using PLD is shown in Figure 25.23A. The diffusion couples are then reacted at elevated temperatures under an applied electric field. The electric field can increase mass transport in the bulk and can change the resulting microstructure and the interface topology, as shown in Figure 25.23B, C. The controlled nature of the experiment and the simple reaction geometry allow the transport phenomena and reactions to be examined directly. We can study the reaction with NiO, instead of MgO, with the electronic contribution to the process removed by including layers of ZrO_2 next to the Pt electrode.

DIFFUSION COUPLES

The diffusion couple (approximately 1-mm thick) is placed between two Pt electrodes with the thin film in contact with the cathode and the bulk MgO substrate in contact with the anode as illustrated in Figure 25.23A. The reaction takes place in air with a voltage of ~210 V applied across the sample. T depends on the material, ~1,350°C for In_2O_3/MgO but as low as 700°C for Fe_2O_3/MgO. A second diffusion couple, without the applied field, is placed with the thin film down on a piece of Pt foil to ensure similar reaction conditions. The two samples are kept close together to ensure they are reacted at the same temperature.

We can grow thin films of AlN on sapphire by applying an electric field to a sample heated in a nitrogen-rich atmosphere with extremely low oxygen partial pressure. By applying an electric field with an appropriate electrode material at elevated temperatures across Al_2O_3, a flux of Al^{3+} cations toward the cathode is induced. The cations arriving at the surface of the Al_2O_3 then react with a nitrogen gas atmosphere to form a thin epitactic film of AlN on the Al_2O_3. The hydrogen portion of the mixture serves to help reduce the oxygen activity in the gas atmosphere so that Al_2O_3 does not reform.

GROWING AlN IN AN ELECTRIC FIELD

Place a single-crystal of α-Al_2O_3 between two Pt electrodes in an N_2-rich environment. The Pt electrodes act as chemically inert conductors with a high melting temperature. We have to scratch the Pt electrodes with an abrasive to roughen the surface and thus allow the nitrogen to reach the entire surface of the Al_2O_3. If N_2 transport across the surface is inadequate, the Al^{3+} cations arriving at this surface would either evaporate or form an alloy with the Pt electrodes. After the furnace is evacuated to 10^{-6} Torr and heated to remove excess water, backfill with a 5%H_2/95%N_2 gas mixture and react.

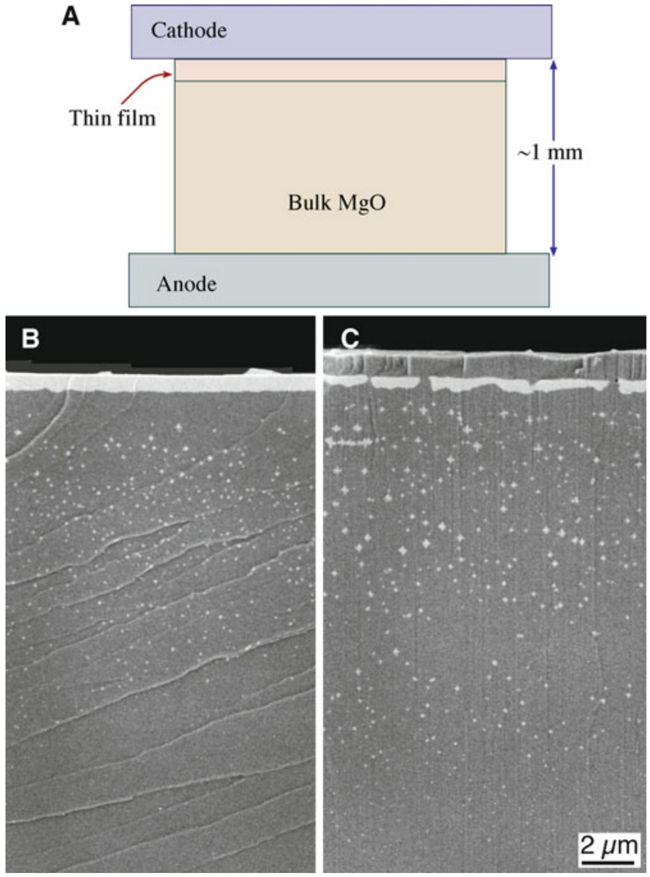

FIGURE 25.23. Reaction between a thin film of Fe_2O_3 and a layer of MgO in an electric field at 1,150°C for 2 h. (A) The setup. (B) Field with nothing applied. (C) Field with 2 kV/cm applied. The MgO has grown on *top* of the spinel. The reaction is fastest at GBs in the thin film.

Under the reaction conditions used for the formation of these films, it is estimated that the partial pressure of oxygen in the chamber is between 10^{-21} and 10^{-26}! For a more accurate determination, we would need to know the amount of water vapor in the chamber. The gas mixture used for this study is critical: for example, using 99.999% N_2 gas results in the formation of only Al_2O_3 (the oxygen activity is too high). The Al_2O_3 is reacted at, for example, 1,250°C for 2 h. The properties of AlN make it an interesting material for applications in the microelectronics industry: it has a large band gap, good thermal conductivity, high-temperature stability, and chemical inertness. Thin AlN films on basal Al_2O_3 substrates are used as buffer layers for the growth of GaN on alumina.

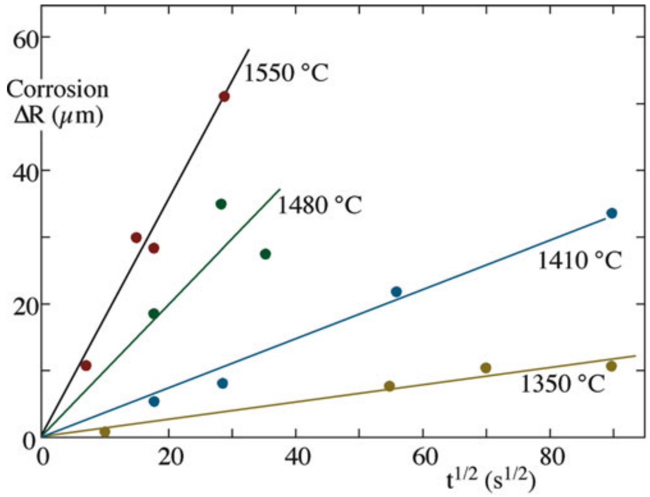

FIGURE 25.24. Dissolution of sapphire in a $CaO–Al_2O_3–SiO_2$ silicate melt.

25.16 PHASE TRANSFORMATIONS INVOLVING GLASS

The crystallization of glass is so well established it is responsible for the development of a whole class of materials known as glass-ceramics. There is therefore a large body of literature on this subject. When glass is present in a GB, there is an additional constraint on the crystallization because a second "nucleating" interface is present. For example, it is possible that a glass that crystallizes on a free surface may not do so in a GB due to the competition between the two "seed" grains. There are a growing number of studies of the crystallization of glass in different systems, but few relationships between the new crystals and the crystalline grains have been reported. Much of the work on this topic has been carried out on commercially available material, where other elements may be present in the glass.

NUCLEATING AGENTS

Different types are used to promote the process of crystallization.

The Pt group and noble metals: concentration ~0.05%

Fluorides (e.g., Na_2AlF_6 or Na_2SiF_6): concentration 2–4%

TiO_2: concentration 2–21 wt%

Glass can dissolve crystal. The kinetics of dissolving crystalline sapphire in a $CaO–Al_2O_3–SiO_2$ melt are shown in Figure 25.24. We see parabolic kinetics—it's a diffusion-controlled reaction.

Glass can penetrate polycrystalline compacts and dissolve or redistribute the crystalline phase. In the case of polycrystalline MgO, further heat treatment caused the glass to crystallize as monticellite. A particularly interesting observation in this study was that the impurities that were present in the sintered MgO (primarily ZrO_2: a grain-growth inhibitor) were swept into the residual glass regions between the crystalline monticellite grains (known as the snow-plowing process).

Glass can crystallize. Glass-ceramic materials are produced by the controlled crystallization of appropriate glasses. The glass-ceramic consists of typically 95–98 vol% of very small crystals, generally <1 μm in size, with the residual glass phase making up the rest of the pore-free material. When these materials are fabricated, the required shape is produced using conventional glass-forming techniques. To obtain small crystals of uniform size in the glassy matrix, a uniform density of nuclei of the order of 10^{12}–10^{15} cm^{-3} is required. Selected nucleating agents are added to the batch during the melting operation and while performing a controlled heat treatment.

The role of the different nucleating agents and the mechanism that leads to subsequent volume crystallization is not yet entirely clear. For the metals, the solubility decreases as the temperature in the glass melt decreases and small metallic particles precipitate out. In the case of oxide nucleating agents, the crystallization process appears to take place by an induced phase separation (demixing) followed by crystallization. (We considered phase separation of glasses in Section 21.11). For TiO_2-nucleated Li_2O–Al_2O_3–SiO_2 glass-ceramic, the nucleation involves a phase separation on a scale of ~5 nm followed by the formation of a crystalline TiO_2-rich nucleating phase.

As a result of carefully controlled thermal treatment, the initial glass is converted to a polycrystalline material in which the final properties depend on the nature of the precipitated phases, the final degree of crystallinity, the size of the crystallites, etc. The material is generally opaque, although translucent and even transparent glass-ceramics have been produced. The small size of the grains and the absence of porosity are characteristics of glass-ceramics, which results in excellent mechanical properties. This is explained in part by the action of the microcrystallites, which limit the propagation of flaws. (See also the discussion in Section 21.11, including the mention of devitrite).

25.17 POTTERY

The phase transformations that take place in pottery and glazes on pottery have not been studied to the same detail as the model NiO/Al_2O_3 reaction in part because the processes are complex and perhaps because they are not the basis of high-tech applications. The glazes are usually silica-based with high concentrations of dopants to lower T_g or produce other special properties. The best example of a phase transformation in a glaze is the crystallization glaze discussed in Section 21.12. So, what happens when we heat clay depends on the clay which depends on where you are since most clay firing is local. The topic is enormous and varied. When we glaze the pot, the formation and behavior of the different glazes depend not only on the composition of the glaze but also on the firing temperature and environment.

25.18 CEMENT

Cement is not only an extremely important ceramic but is also a very complex one. One factor in this complexity results from the importance of hydration reactions. Cements are, by definition, powder ceramics that react with a liquid (usually, though not necessarily water) to undergo a chemical reaction to form a solid structure. A cement paste is the suspension of this powder in a liquid phase. Some cement pastes require the presence of air or CO_2, to harden, while others can harden under water. Pozzolanic cements are Si- or Al-based powders that can react with water providing $Ca(OH)_2$ is also present. The situation can be further confused by the presence of non-reactive constituents that are added to change the rheology of the mixture. The rheological properties change as the fresh cement hardens. This setting process is thus quite like the solidification of glass but takes place at ambient temperature and involves a change in structure. (So, it's completely different). The two fundamental (don't say basic, since the basicity of CaO is an important factor here) reactions with CO_2 and H_2O are illustrated by these simple equations.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (25.13)$$

$$CaO{\cdot}Al_2O_3 + 10H_2O \rightarrow CaO{\cdot}Al_2O_3{\cdot}10H_2O \qquad (25.14)$$

The water content can vary producing different hydrate phases. If sulfur is present (in gypsum), the reaction becomes more complex and leads to the formation of the mineral ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$, during the hydration of Portland cement.

In an alkali silica cement, we see a new setting/hardening reaction, with quartz becoming a factor.

$$2(Na_2O{\cdot}nSiO_2) + Na_2SiF_6 \rightarrow (2n+1)SiO_2 + 6NaF \qquad (25.15)$$

We mentioned cement terminology in Chapter 2: C is CaO, S is SiO_2, and A is Al_2O_3. CA is the main constituent in calcium aluminate cement (referred to as CAC). In high-alumina cement (HAC), the Al_2O_3 content ranges from 40%

PORTLAND CEMENT

Hydraulic cement produced by pulverizing Portland-cement clinker and usually containing $CaSO_4$ ($<5\%$).
Portland clinker is produced by heating a mixture of CaO, SiO_2, Al_2O_3 and Fe_2O_3 until partly molten.
C_3S is the essential constituent of Portland clinker; C_2S, C_3A and $C_2(A,F)$ will also be present.

to 80%; it contains some C_2S but no C_3S. Its value is that it sets much more quickly than Portland cement.

For reasons that are obvious, pores are an important component in concrete and are the main flaw in the material. This is unfortunate in a material primarily needed for its strength.

Not all cement is based on CS_x or CA_x. A group of cements known as glass ionomer cements (GICs) are used as cements in dentistry. The reaction involves an ion-leachable alumina-silicate glass and an aqueous solution of polyalkenoic acid. The resulting cement consists of glass particles in a polysalt matrix. This is a specialty topic but with far-reaching applications.

25.19 REACTIONS INVOLVING A GAS PHASE

The gas phase becomes important when a vapor is intentionally used in a reaction or a vapor is created during a reaction, as is the case of decomposition of a product. The problem is illustrated by the carbonate reaction shown in Figure 25.25. Many ceramics are processed from their salts rather than from the oxides themselves. As the $CaCO_3$ decomposes to form the oxide, emitting CO_2, heat moves into the core of the particle, and CO_2 moves outward. The result is another reaction layer forming, which slows down further decomposition. Of course, in this case we can expect the CaO to be porous, so that the CO_2 can evolve quite easily.

When SiO_2 dissociates, the situation is not as simple. This reaction is important not just because SiO_2 itself is important but also because SiO_2 is present in glass, furnace bricks, and alumina furnace tubes.

$$2SiO_2(s) \Rightarrow 2SiO(g) + O_2(g) \qquad (25.16)$$

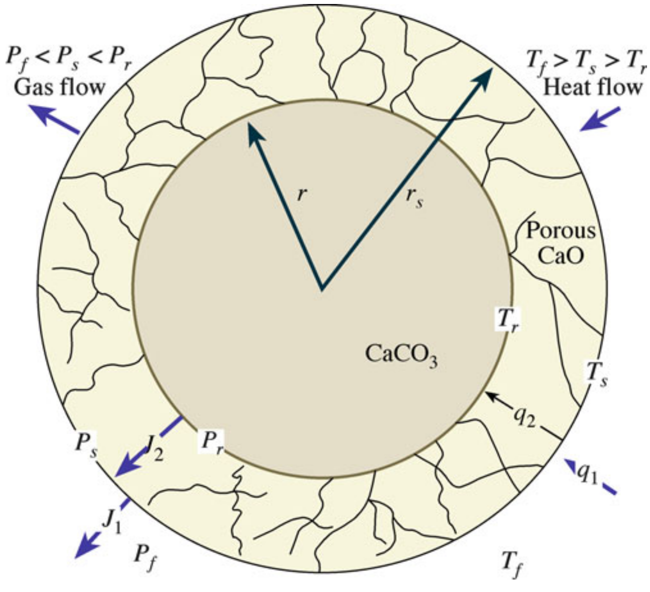

FIGURE 25.25. Processes involved in decomposing a carbonate.

At 1,320°C, we can write the reaction coefficient in terms of the partial pressures.

$$K_{\text{eq}} = \frac{(P_{\text{SiO}})^2 pO_2}{(a_{\text{SiO}_2})^2} = 10^{-25} \qquad (25.17)$$

Assuming the concentration of SiO_2 to be unity (it is the principal component), we can express P_{SiO} in terms of the oxygen partial pressure. [We are using pO_2 (as conventional) to represent the partial pressure of O_2 but P_x for the partial pressure of X—to keep the notation clear!]

$$P_{\text{SiO}} = \frac{K_{\text{eq}}^{1/2}}{pO_2{}^{1/2}} \qquad (25.18)$$

This equation tells us that the oxygen partial pressure controls the vaporization of the silica. For example, if the pO_2 is 10^{-18} atm (a reasonable value in a reducing atmosphere of H_2 or CO), then the P_{SiO} is ~3×10^{-4}, which is quite high so the SiO_2 evaporates. Hence, SiO_2 would not be a good refractory in a dry reducing atmosphere. You can minimize the effect by adding a small amount of H_2O if H_2 is present.

A similar situation arises when reacting an oxide in a chloride gas. This reaction is actually used in growth of thin films by vapor transport.

$$FeO(s) + 2HCl(g) \Rightarrow FeCl_2(g) + H_2O \text{ at high } T \qquad (25.19)$$

$$FeO(s) + 2HCl(g) \Leftarrow FeCl_2(g) + H_2O \text{ at low } T \qquad (25.20)$$

The reaction of the active gas with the ceramic increases the vapor transport. What we are actually doing is controlling the chemical potential (concentration) of the reaction gases and hence controlling the rate of deposition. We can apply Fick's law.

$$\frac{dn}{dt} = -AD\frac{\partial c}{\partial x} = -AD\frac{\Delta c}{L} = -AD\frac{c_{\text{h}} - c_{\text{c}}}{L} \qquad (25.21)$$

With some manipulation, we can express the concentration difference as a pressure difference. We see that the diffusion from hot (h) to cold (c) is driven by the concentration gradient, and the direction of the reaction is just due to the enthalpy of the reaction. At equilibrium, we can write an expression for ΔG.

$$\Delta G_{\text{h}} = -RT \ln\left(\frac{P_{\text{FeCl}_2} P_{\text{H}_2\text{O}}}{P_{\text{HCl}}{}^2}\right) \qquad (25.22)$$

In a closed system, the initial amount of HCl is B atm. Then two molecules of HCl gives one molecule of $FeCl_2$ and one molecule of H_2O.

$$P_{\text{HCl}} = B - 2P_{\text{FeCl}_2} + P_{\text{H}_2\text{O}} = P_{\text{FeCl}_2} \qquad (25.23)$$

and

$$\Delta G_{h,c}{}^{0} = -RT \ln\left(\frac{P_{FeCl_2}{}^{2}}{(B - 2P_{FeCl_2})^{2}}\right) \qquad (25.24)$$

25.20 CURVED INTERFACES

The equation give by Thompson and Freundich (the Thompson-Freundich equation) relates the concentration in equilibrium with a curved surface to that in equilibrium with an infinite flat surface.

$$RF \ln\left(\frac{c_a}{c_{pi}}\right) = \frac{2E}{a}\frac{M}{\rho} \qquad (25.25)$$

where c_a is the concentration at the curved interface, c_{pi} is the concentration at planar interface, M is the molecular weight, E is the interfacial energy, and ρ is the density. Thus, the concentration in equilibrium with a curved surface differs from that for a flat surface. This result is not just due to the reduction of surface area. This phenomenon is known as the Gibbs-Thompson effect.

CHAPTER SUMMARY

The key idea for solid-state reactions and phase transformations is that they occur by the movement of interfaces no matter what phase is involved. A phase transformation can occur by one interface moving; but even if a reaction starts at one interface, we have two interfaces as soon as a reaction product forms. When either a solid-state reaction or a phase transformation occurs, the system is not in equilibrium, and the equilibrium phase diagrams can serve only as a guide to what the final product will be. Diffusion of point defects is an essential feature in solid-state reactions, but understanding the kinetics of these processes is not necessarily straightforward because the diffusion coefficients change as the composition of the phase changes (the Darken equation). The situation can be even more complex if the structure of the reaction product is also new and if misfit dislocations form at the phase boundary. The use of slip casting to explain the physical basis of parabolic reaction kinetics is extremely instructive and builds on a real ceramic process. Like slip casting, many phase transformations in ceramics involve the transfer of water or a gas phase. The setting of cement and the corrosion of TBCs are two such examples.

PEOPLE AND HISTORY

Schmalzried, Hermann (1932–). An exception to the rule. Formerly a postdoctoral student with Carl Wagner, Hermann has been a mentor and inspiration to many of the current generation of researchers in the field of solid-state reactions in ceramic systems and is profusely thanked by the authors.

Wagner, Carl (1901–1977). He was born in Leipzig and died in Göttingen. He wrote the seminal text with Schottky and laid the foundations for understanding corrosion and reactions between oxides.

EXERCISES

25.1 Two cubes (400 μm long on each side) of NiO and Al_2O_3 are reacted at 1,600°C. Assuming that the reaction takes place without significant movement of electrons or oxygen and that a reaction layer is produced that is 100 μm thick, what are the respective thicknesses of the remaining NiO and Al_2O_3?

25.2 Given the densities of some of the polymorphs of SiO_2, should it be possible to convert β-cristobalite to some of the other forms by applying pressure? Briefly explain the reasoning behind your answer and indicate to which of the four forms, if any, the transformation might occur.

25.3 Calcium carbonate ($CaCO_3$) exists in two polymorphic forms: calcite and aragonite. The standard state enthalpy of calcite is −1,207.37 kJ/mol, and that of aragonite is −1,207.74 kJ/mol. The entropies of aragonite and calcite under the same conditions are 88 $J\ mol^{-1}\ K^{-1}$ and 91.7 $J\ mol^{-1}\ K^{-1}$, respectively. What is the stable polymorph at 25°C and 1 atm? Is there a temperature above which the other polymorph would be the equilibrium phase? If so, what is that temperature? If not, why not?

25.4 You want to prepare a sample of mullite by reacting alumina and silica powders. If the activation energy is 210 kJ/mol and the reaction is 10% complete at 1,400°C, how long would it take to convert 50% to mullite at 1,400°C and at 1,500°C? How do you determine that 50% has indeed been converted?

25.5 You place two perfect crystals of alumina and magnesia in contact with flat (0001) and (111) surfaces in contact. What orientation do you choose to produce the fast reaction when you heat these to 1,400°C for 1 h? You make the assumption that oxygen does not move during this heat treatment, but this cannot be strictly true. Explain.

25.6 You react two samples of alumina and magnesia at 1,400°C for 1 h. This time the MgO is a perfect single crystal, but the alumina is 100-nm grain size polycrystalline material. Does the reaction proceed more quickly or more slowly on average?

25.7 Explain the geometry of the precipitates in Figure 25.5 and the defects they contain.

25.8 Consider Figure 25.13. What can you determine about the activation energies involved and the diffusion processes?

25.9 Consider Figure 25.21. How do you explain the experimental observations in the images in view of the phase diagram and other factors you know about these materials?

25.10 Consider Figure 25.24. What can you determine about the energies involved in this reaction?

25.11 Imagine the particle in Figure 25.7 growing as the sample is internally reduced. Discuss the diffusion of point defects that must occur.

25.12 Draw a schematic to show six atomic planes of Fe_2O_3 and six of $NiFe_2O_4$ aligned with (0001) and parallel to (111). Label them as if they were hexagonal close-packed (hcp) and face-centered cubic (fcc) crystals and suggest how the hematite might grow in the spinel by exsolution.

25.13 Draw a nucleus of the particle of the type shown in Figure 25.5, and then draw it again as it begins to grow. Thereby, suggest when and how the twins might form.

25.14 Consider Figure 25.10. Which surface of the sapphire is reacting the fastest, and why do you think this is so?

25.15 Determine equation 25.5 for yourself and suggest reasonable values for each of the variables and "constants" for the case of water penetrating through a layer of slip.

25.16 A layer of MgO reacts with a layer of Al_2O_3 such that only the cations move. By considering Figure 25.12, show that the spinel grows into the sapphire faster than into the periclase.

25.17 Consider equation 25.12 and Figure 25.15. What can you deduce about the average diffusion coefficient?

25.18 Consider Figure 25.18B. Explain quantitatively why the spinel nucleates where the grain boundary (GB) meets the substrate surface.

25.19 Consider Figure 25.20. Are the three straight lines consistent with one another? (Is T the only factor that is different in the three experiments?)

25.20 Consider Figure 25.24. What can you deduce about the dissolution of sapphire in silicate glass?

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