15

Phase Boundaries, Particles, and Pores

CHAPTER PREVIEW

This chapter is both an extension of the chapters on surfaces and grain boundaries (GBs) and essential preparation for those on sintering and phase transformations. The theme of the chapter could be reworded as *interfaces between ceramics and different materials*; the material can be crystalline, amorphous (glassy), liquid, or gaseous (pore). Hence the topics include three critical areas for ceramics: phase boundaries (PBs), particles, and pores. Examples of PBs include ceramic/metal interfaces, crystal/crystal interfaces, and crystal/glass interfaces. Because we also include any interfaces that interact with pores it is a very large and important topic. By definition, PBs are the essential feature of composite materials. Solid-state reactions and reactions involving liquids and gases all occur by the movement of these interfaces, but the details of how this motion occurs are often even less well understood than the interfaces themselves.

15.1 THE IMPORTANCE

In ceramic materials, as in other materials systems, interfaces are the most important region of the material because that is where most of the action takes place. Phase boundaries are particularly important because they are the interfaces between dissimilar phases.

- Phase transformations take place by the movement of PBs.
- Growing one material on a different material generates a PB (a heterojunction).
- Bonding one material to another generates a PB.
- Most commercial and natural ceramics contain two or more phases and thus many PBs.

Forming PBs—Film Growth

Increasingly, we are growing thin films of ceramic materials on substrates, coating glass, coating metals, etc. A PB separates a ceramic film from the substrate. The behavior and properties of that PB will determine the usefulness of the thin film. This is not a new field—the electronics industry has been built on the ability to deposit layers of SiO_2 and Si_3N_4 on Si. The high-Tc superconductors in thin-film form are made this way. GaN is revolutionizing the lighting industry with thin films grown on Al_2O_3 and SiC.

Forming PBs—Processing

We usually process ceramic materials in the solid state (although small amounts of liquid may be present) either to control the grain morphology or because going to the melting temperatures would be too expensive. Particles of different phases join together to form PBs.

Moving PBs

New phases form by a solid-state reaction when ceramic powders are reacted. The new phase grows at the expense of the starting phases: the reaction occurs by PBs moving. We will examine these reactions in Chapter 25; here we will concentrate on the interfaces themselves.

Properties of PBs

Whether the PBs separate thin films from a substrate or a bulk grain of one composition from one of another composition, the properties of the interface determine the usefulness of the material. There are innumerable examples of why PBs are important to ceramics: seals on Na-vapor lamps are the most likely source of failure; loss of adhesion of thermal barrier coatings (TBCs) leads to failure when the coating separates from the metal; GaAs on Si is not as widely used as was once hoped because the films do not align perfectly at the interface and they would be unlikely to remain perfect during cooling from the growth temperature.

15.2 DIFFERENT TYPES

Clearly there are many types of PB. We have already considered the solid/vapor and liquid/vapor PBs in Chapter 14; we also touched on the solid/liquid PB. Here we will

TABLE 15.1 Examples of PBs in Multiphase Ceramics

PB	*Material*
Glass/ceramic	Crystallization of a glass to form a glass-ceramic
Fiber composite	Ceramic fiber (e.g., SiC) with metal, ceramic, or polymer matrix
Geomaterial	Granite contains quartz along with other minerals such as orthoclase and microcline; there are multiple PBs
Cement	A ceramic matrix composite; cement is the matrix and aggregate (sand and small pebbles, or historically pumice) is the reinforcement
Porous ceramic	A very large developing topic, e.g., bioceramics, where we want controlled pore size for tissue ingrowth

discuss the solid/solid PB and use earlier concepts on the solid/gas PB.

We will examine two types of particles and the PBs between these and the matrix.

- Particles are a distinct second phase. Some could dissolve in the matrix if the temperature were high enough; some may never be able to dissolve until we exceed the melting temperature. They can be equiaxed, platelets, or needles. Note that in metals, the particles are often precipitates and the two words are used interchangeably. Particles in ceramic materials are less likely to have formed by precipitation.
- Pores are essentially negative particles, but there are some big differences: (1) there is a gas/solid PB, (2) there are no solid-state reactions at the interface, and (3) kinetics of point defect motion are fastest at the surface of the pore (the PB).

The idea of the pore as a particle may seem to be stretching the point at first. We will justify including this topic by showing that pores behave like particles and are a major component of many ceramic systems, including composites. Thin interfacial phases can also lie along PBs just as they do along GBs. When the intergranular films at a GB or triple junction become thicker than ~10 nm, it is already a second phase and there are two PBs instead of one GB. We discussed intergranular films (IGFs) in Chapter 14 because the GB is essential to their existence (by definition).

Because PBs are everywhere in oxide minerals this is an enormously varied topic. We discuss this topic in more detail in Chapter 19, but for now a summary of some systems is given in Table 15.1. A point to keep in mind is that today's minerals are tomorrow's ceramics.

15.3 COMPARED TO OTHER MATERIALS

How are ceramics different from metals? Metals can be very clean. If particles are wanted they can often be precipitated by moderate heat treatments. In ceramics, particles are more likely to result from inclusion of insoluble impurities than from precipitation.

Impurities are common in all ceramics except in pure semiconductors.
Heat treatment may change the oxidation state of the constituent ions.

Alumina with 0.1 mol% impurities would be regarded as being a pure alumina; many commercial aluminas contain less than 98% alumina. In metals, we use precipitates to pin dislocations. In such materials, the aim is to optimize the number and spacing of the particles while controlling the total content. This is not usually done in ceramics—we do not need to pin the dislocations because they are not moving anyway. However, particles in ceramics have become more useful in preventing the movement of cracks—they help to toughen the ceramic. We can use ion implantation to harden ceramics (including glass). The process does produce particles, but again the defects that are impeded are cracks not dislocations. This technique is clearly restricted to the near-surface region.

Historical note. For many years, pores dominated the ceramics literature because of sintering—we wanted to remove them to make dense material. Now we may want to keep them or we may simply avoid them in the processing route. Intergranular phases are really special for ceramics and can be extremely useful, or disastrous, or both, but they are much more common than in metals. Particles are becoming more than just accidental inclusions present in impure materials as we start to use them in ways that are special for ceramics (e.g., in toughening). The mechanical strength of pores is not great(!) but pores can affect the mechanical properties in different ways. If the pore is small, it actually may be difficult to deform it.

15.4 ENERGY

In the same way that GBs have an associated energy, an interface between two different phases has a PB energy: the energy necessary to form a unit area of a new PB. (Two of these PBs were treated in Chapter 13 on surfaces.) If this interfacial energy is not less than the sum of the separate surface energies of the two phases the two phases will not join.

A low-energy geometry arises by minimizing the surface energy. In general, the interfacial energy between chemically similar phases is low compared with the sum of the surface energies. Thus, liquid metals or oxides on sapphire (or other solid oxides) generally have a small interface energy. The interface energy is also low when there is a strong chemical attraction, i.e., when the two materials are likely to react readily.

Although new approaches have been developed for creating these interfaces, it has always been difficult to control the initial interface. In this example the structure is well known but the energy is usually still a mystery.

15.5 THE STRUCTURE OF PBs

Phase boundaries can be like GBs where the adjoining two grains may not only be rotated relative to one another but will also (or instead) be structurally and/or chemically different; of course, one or both phases may be a glass, which means the interface is not structured. As with heterojunctions, the word "hetero" is implied when we say "phase boundaries." Semiconductor heterojunctions are examples of PBs; "heterojunction" usually indicates that we are talking about flat interfaces and a thin-film geometry. As is the case with GBs, almost all the detailed studies have been concerned with "special" PBs. We can summarize this idea and compare some PBs to GBs.

The "$\Sigma = 1$" PB is particularly important since it is often associated with epitactic growth.

NiO grows on MgO with both grains aligned so that corresponding planes and directions in the two crystals are nearly parallel. The difference in lattice parameter (Δa) will be accommodated by a square array of misfit dislocations.

When two phases have similar or related structures and are in close alignment, the mismatch due to differences in the lattice parameter may be accommodated by arrays of misfit dislocations. Such dislocations have been extensively studied in semiconductor systems and in some oxide systems. The image of Fe_2O_3 on Al_2O_3 in Figure 15.1 is complex because the $\Sigma = 1$ and the $\Sigma = 3$ interfaces exist side by side (the Fe_2O_3 films contain twin boundaries). In the $\Sigma = 1$ PB, Δa is accommodated by a hexagonal array of dislocations with Burgers vector $\frac{1}{3}\langle 11\bar{2}0\rangle$; these are the displacement-shift-complete lattice (DSCL) vectors for this interface. In the $\Sigma = 3$ PB, the misfit dislocations are $\frac{1}{3}\langle 10\bar{1}0\rangle$ (so they are closer together and more difficult to image).

The $\Sigma = 3$ PB often occurs in thin-film growth on {111} or (0001) substrates: it is the PB version of the twin boundary.

If the corresponding planes [e.g., in the $(001)_{NiO}/(001)_{MgO}$ interface] are rotated about an axis that lies in the plane, then the interfacial dislocations must have a component that is normal to the plane of the interface. Again, this situation has been demonstrated for both semiconductors and oxides. The presence and distribution of these different dislocations have a direct relevance to the movement of any phase boundary and hence to the mechanisms of solid-state reactions because they are associated with steps in the PB. The latter point is not usually considered when discussing heterojunctions in semiconductor systems since the location of the interface is usually fixed before the growth of the epilayer.

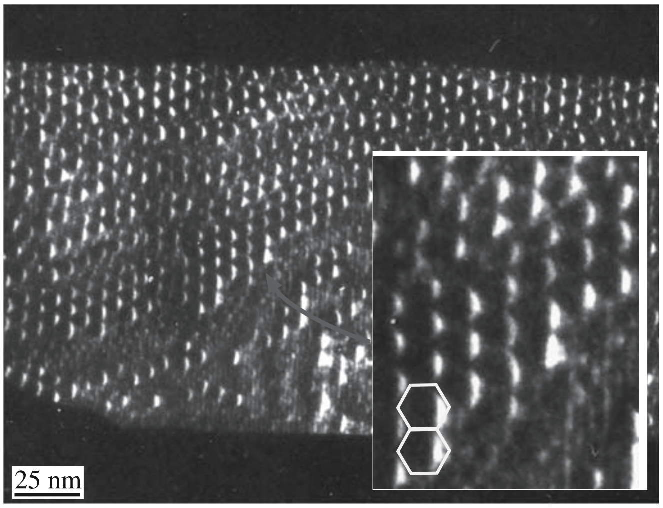


FIGURE 15.1 Image of an Fe_2O_3 film on an Al_2O_3 substrate showing both $\Sigma = 1$ and $\Sigma = 3$ PBs. The inset shows the hexagonal dislocation network.

Phase boundaries between ceramic oxides are particularly complex because the structure, the lattice misfit, and the different cations can each be influenced by external conditions, particularly the oxygen activity. The model system $AO/AB_2O_4/B_2O_3$ allows all of the above variables to be considered; A is a divalent cation and B is a trivalent cation. There is an extensive, although by no means complete, database for both the thermodynamic and kinetic aspects of such systems. The growth of spinel into alumina can take place by the movement of interfacial steps rather than dislocations as we will see in Chapter 25. Structurally different variations of the same "chemical" interface can exist as illustrated in Figure 15.2; new interfaces such as that in Figure 15.2b can be thought of as high-angle PBs. This particular PB can also be thought of as a plane-matching boundary, which has been recognized as a special form of GB (see Section 15.14).

At the interface between $NiFe_2O_4$ and NiO, which is shown in Figure 15.3, the oxygen sublattice is undisturbed by the presence of the interface. The distribution of the cations has changed in a way that is analogous to the stacking fault in spinel in that only the cations are shifted. Since there is actually a lattice-parameter difference, as this particle grows larger, dislocations must be nucleated at the interface. The resulting misfit dislocations are illustrated in Figure 15.3b.

Two notes: (1) PBs are more likely to be structured if the particles form by precipitation than if they form by inclusion during two-phase sintering. (2) Particles and

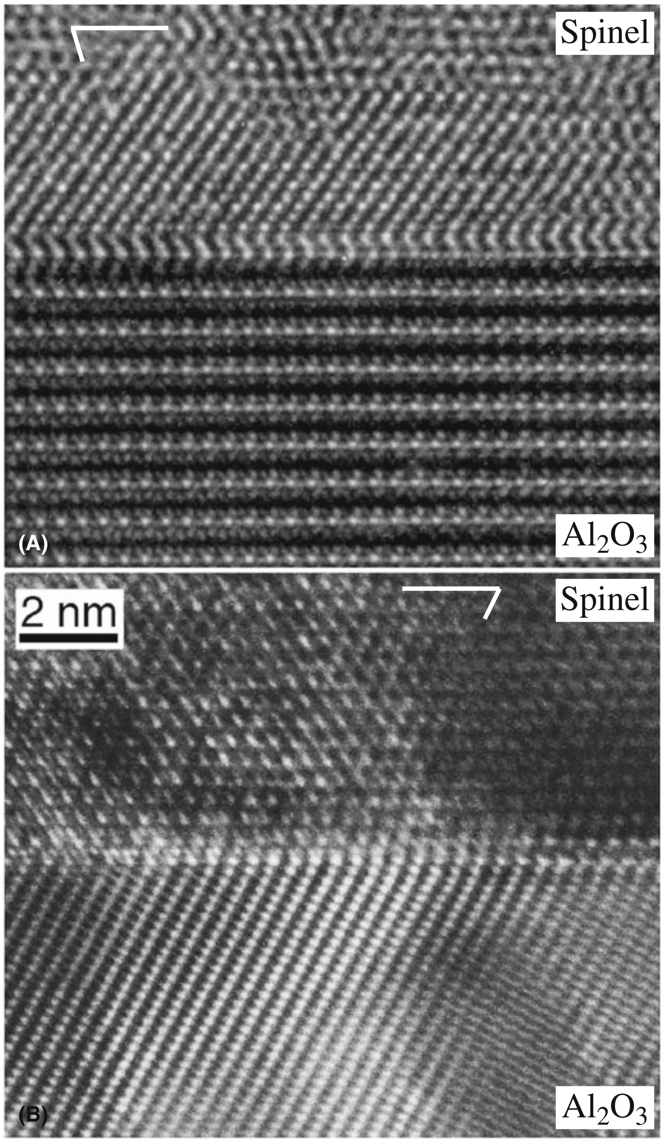


FIGURE 15.2 HRTEM images of crystallographically two different spinel/Al_2O_3 PBs (a and b). White lines show the {111} planes in the spinel.

powders have a common feature—both are contained within another phase.

15.6 PARTICLES

Two particles that are located within the matrix can always lower the total surface energy by coalescing to form a single particle with the same volume but less surface; we ask the following questions: what is the driving force, how long will it take (thermodynamics and kinetics), and what is the influence of crystallinity?

For particles, we need to consider size, shape, and orientation.

The coalescence process, which is similar to the sintering of two particles that we discussed in Chapter 24, depends on the size of the particle. The phenomenon is known as Ostwald ripening—large particles grow while small particles shrink. The difficulty is that the initial joining of the particles must involve diffusion through the lattice unless there are defects connecting the particles. Particles of NiO that have grown in Ni titanate spinel are shown in Figure 15.4. The particles have grown following nucleation, but there is a thin layer of spinel separating the particles. This is similar to observations in Ni-based superalloys.

Shape: An example of spinel particles growing in an NiO matrix is given in Figure 15.5. The particles have an interesting shape consisting of six dendrites extending along <001> directions as they grow. This shape is determined by the soft elastic directions in the matrix and not by the gradients of the diffusing Fe^{3+}: so the shape is determined by the orientation. When the same particle is

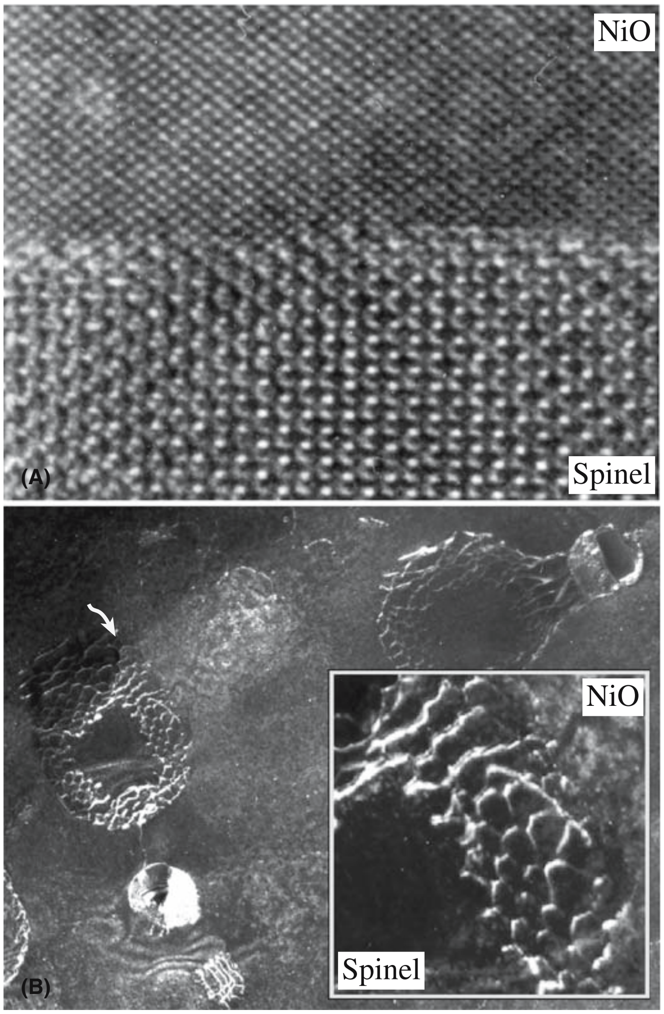


FIGURE 15.3 The spinel/NiO PB. (a) HRTEM image of lattice-matched PB; (b) dislocations are present at the interface after relaxation to accommodate lattice misfit. The inset is from the arrowed region.

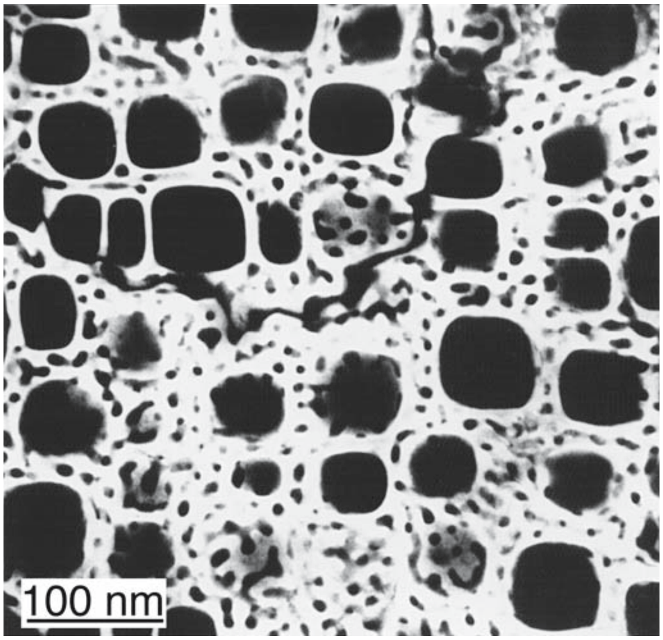


FIGURE 15.4 Lattice-matched particles of NiO in Ni–Ti spinel. Dark-field TEM image was formed by using a spinel reflection (that was not also an NiO reflection).

annealed after using all the available Fe^{3+} ions, the shape changes from kinetics controlled to energy controlled and becomes the octahedron enclosed by the low-energy {111} planes. (More details on internal oxidation and reduction of ceramics are given in Chapter 25.)

These processes are similar to those affecting isolated powders. Nanoparticles of inert materials can be extremely reactive because of the driving force for reactions and growth caused by their high surface-to-volume energy ratio.

One low-energy PB: Some examples of particles formed by precipitation are summarized in Table 15.2. The particles of $\beta''''\text{-Al}_2\text{O}_3$, which can grow in a relatively pure (99.8%) α-alumina matrix, tend to grow parallel to the basal plane of the $\beta''''\text{-Al}_2\text{O}_3$ no matter what the orientation of the surrounding grain or grains as illustrated in Figure 15.6a. Figure 15.6b shows two types of precipitates in a garnet matrix. The large particles of ilmenite are randomly oriented, but the rutile needles are aligned with the matrix. The rutile particles gives us the star garnets (like star sapphire, but rarer), which we discuss in Chapter 36. The $\beta''''\text{-Al}_2\text{O}_3$ particles have grown as platelets because

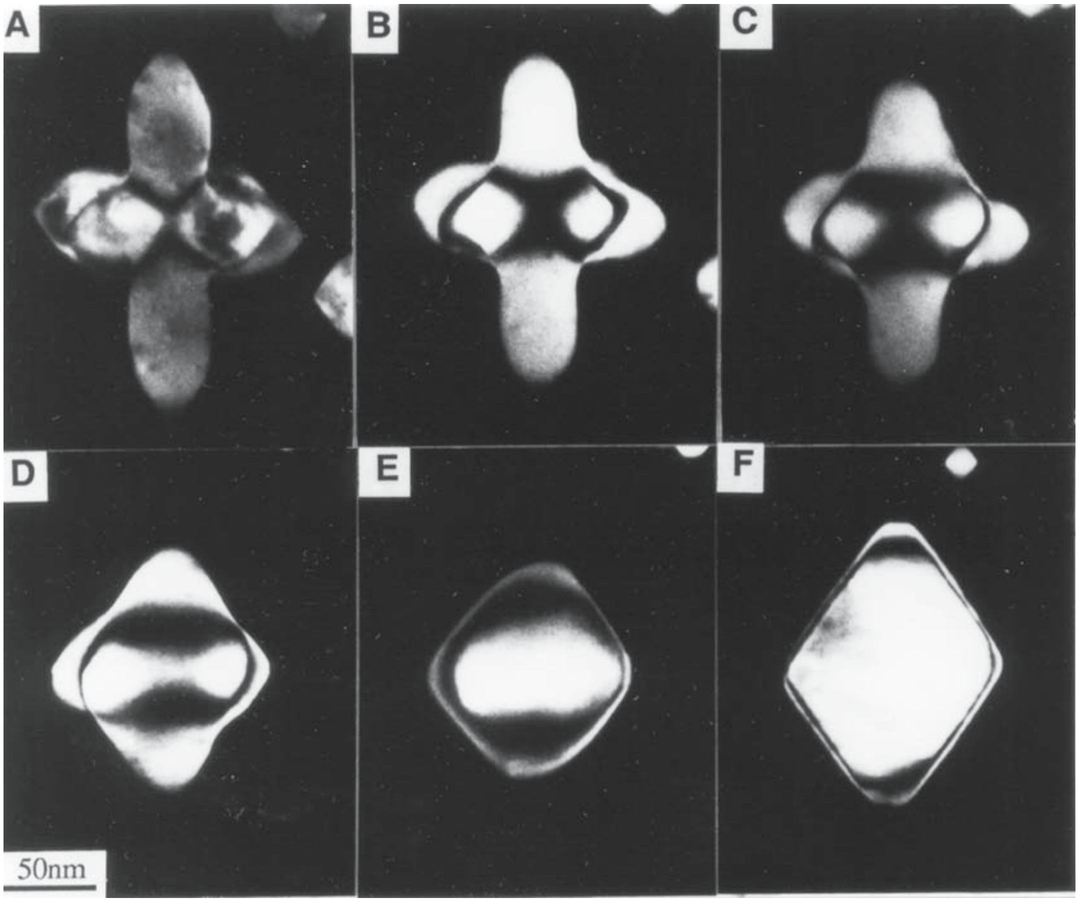


FIGURE 15.5 Spinel particles changing shape in NiO due to heat treatment. (The image is formed as for Figure 15.4.) (A) Looking along [011]: 30-minute heat treatment between images: (B) 800°C, (C) 825°C, (D) 850°C, (E) 875°C, (F) 900°C. The shape change is summarized in the schematics (G–I). The 3D figures shows the original shape.

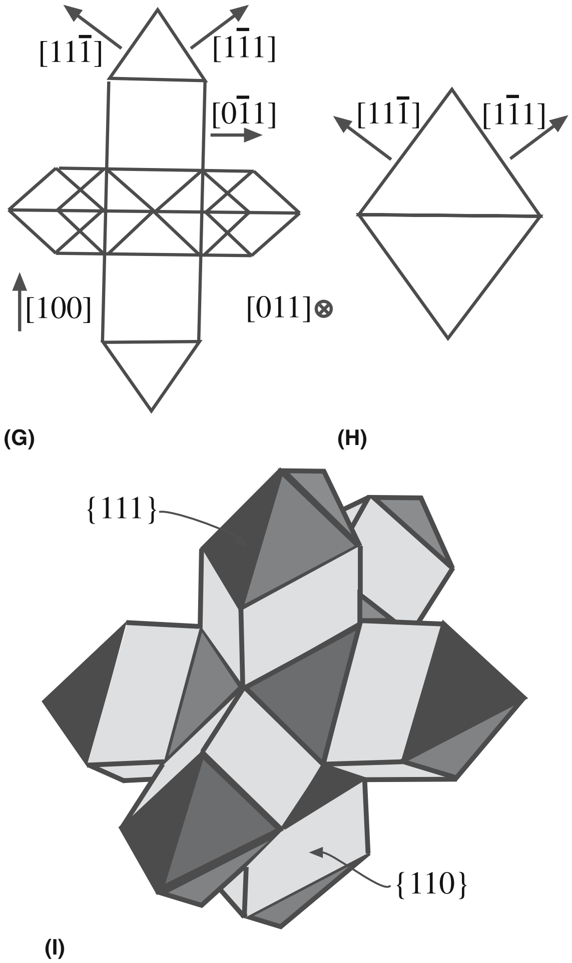


FIGURE 15.5 *Continued*

TABLE 15.2 Examples of Particles in Ceramics

Material	*Situation*
Spinel in NiO	Nucleation and growth
ZrO_2 in Al_2O_3	Toughening (ZTA)
TiO_2 in Al_2O_3	The gem stone, star sapphire
Y_2O_3 in AlN	Sink for oxygen, forms garnet (YAG) at the triple junctions
Xe in MgO	Ion implantation; Xe is immiscible with MgO

there is a good lattice match along one plane; the rutile particles are needles because the match is really good only along one direction.

Particles need not be crystalline as is illustrated in Figure 15.7 where a particle of glass has been grown in a thin-film matrix of α-Al_2O_3. The particle has a shape that is determined by the crystallography of the matrix.

Figure 15.8 shows two examples of precipitate-free zones (PFZ). Figure 15.8a is the classical PFZ at a GB. During cooling from the processing temperature, the Fe^{3+} ions in the doped NiO have segregated to the dislocations in the low-angle GB. Figure 15.8b is a little complex. Here the Fe^{3+} ions have precipitated out onto large $NiFe_2O_4$ spinel particles that were present at high temperature. As the sample was cooled, the misfit dislocations around these large particles could not move because such movement requires defects on the oxygen sublattice. Hence the spinel particles grow out between the dislocations—the spinel grows into the NiO.

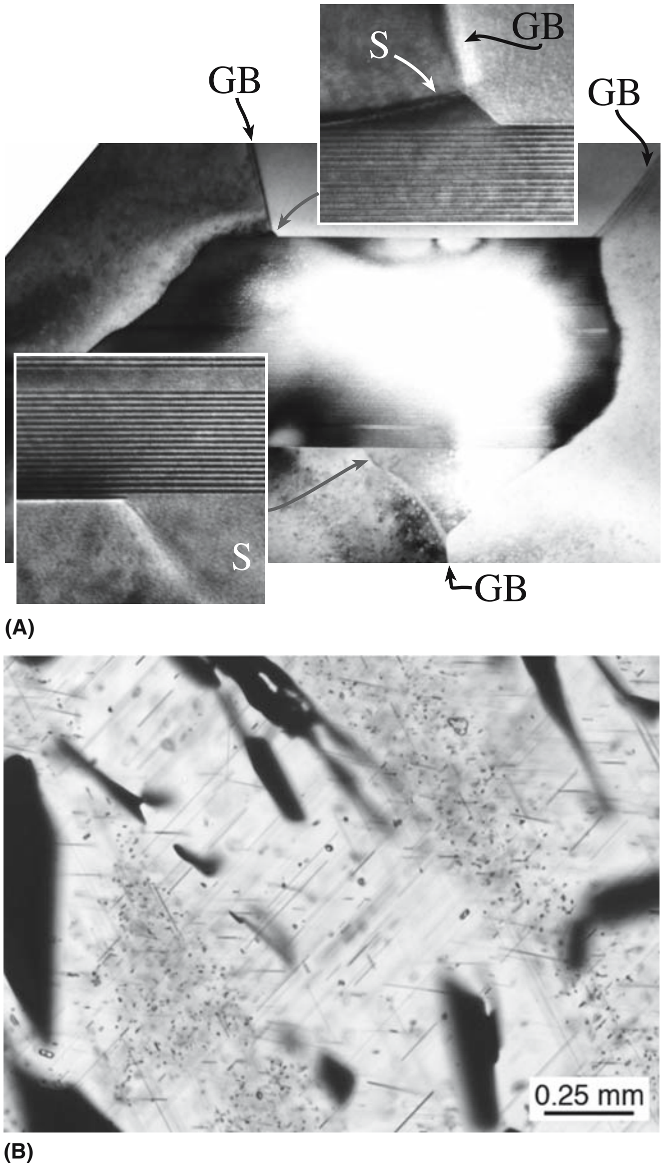


FIGURE 15.6 Particle in a matrix. (a) TEM image of a second-phase β-Al_2O_3 growing along a GB in α-Al_2O_3. The insets show spinel (S) growing up the GBs. (b) VLM of rutile needles growing in a garnet grain.

Finally, you can recognize several triple junctions (TJs) in the images shown in this chapter. For example, the spinel is forming at one TJ in Al_2O_3 in Figure 15.6 and

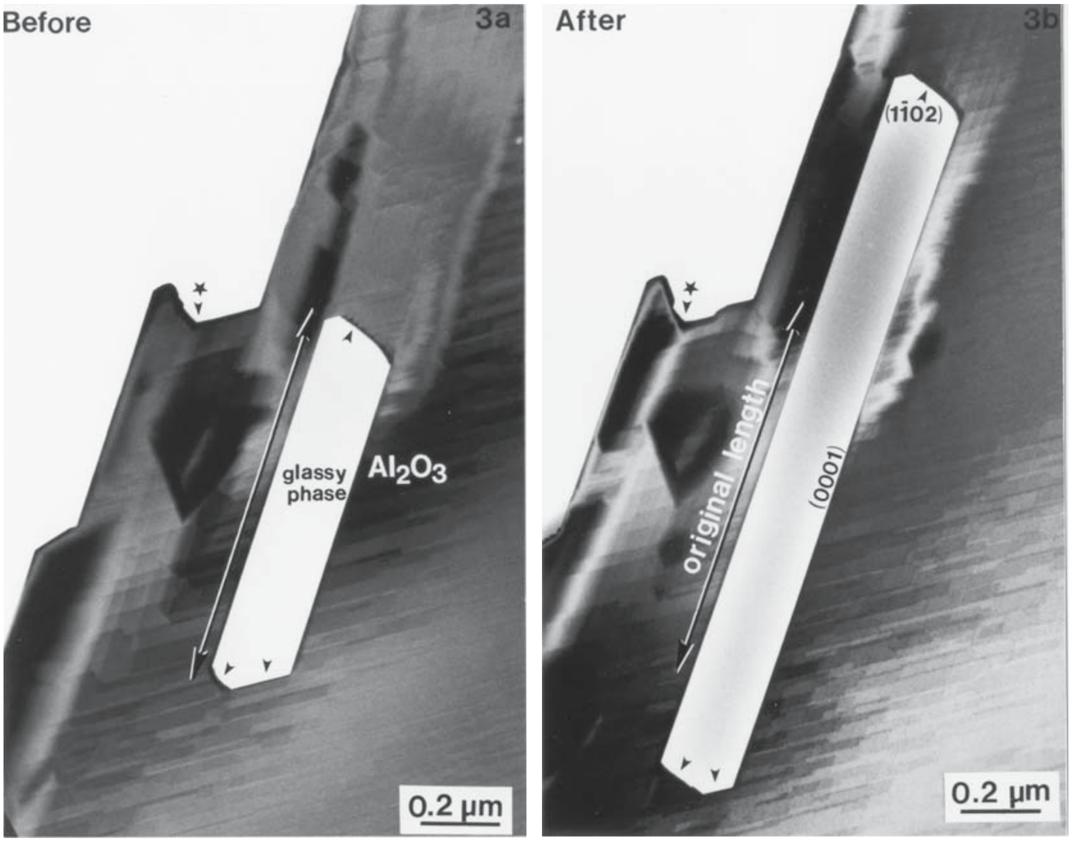
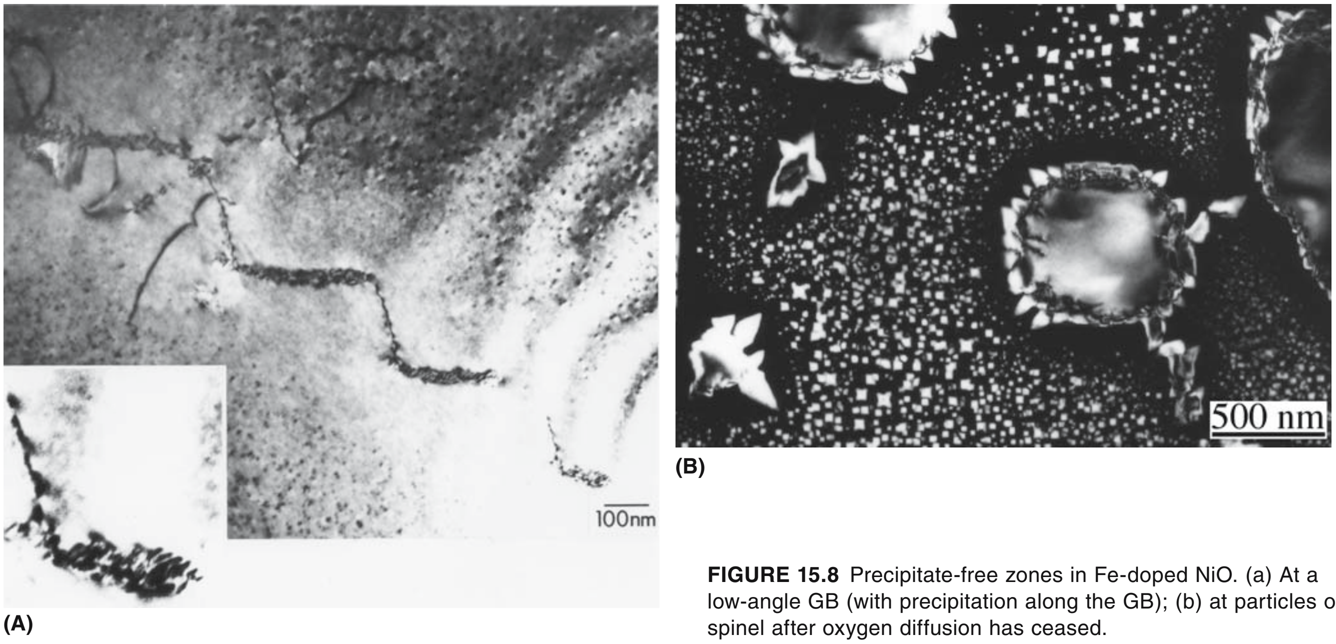


FIGURE 15.7 Glass "particles" in a thin film of α-Al_2O_3 before and after additional heat treatment.



(A)

(B)

FIGURE 15.8 Precipitate-free zones in Fe-doped NiO. (a) At a low-angle GB (with precipitation along the GB); (b) at particles of spinel after oxygen diffusion has ceased.

β''''-Al_2O_3 is forming at the other two. Clearly the new phase is not wetting the Al_2O_3 GB.

15.7 USE OF PARTICLES

What are the properties of particles in ceramics and can we make use of them? Examples of the uses of ceramic particles in a matrix (rather than as a powder) include the use of glass beads for hardening rubber for tires and adding kaolin to paper to make it smoother and easier to print on. The properties depend not only on the particle but also on the PB that encloses it. Particles are used to seed crystallization and other phase transformations. Hematite particles can be used to seed the growth of α-Al_2O_3 at temperatures lower than the usual phase transformation so that the grain size can be kept small. This is now the basis of the widely used technique of crystal templating as illustrated in Figure 15.9. The principle involved is the use of particles for nucleating phase transformations so as to control the grain size during subsequent processing. In Chapter 26 we will use nanoparticles to seed crystallization in glass ceramics and in other specialty glasses such as Vycor.

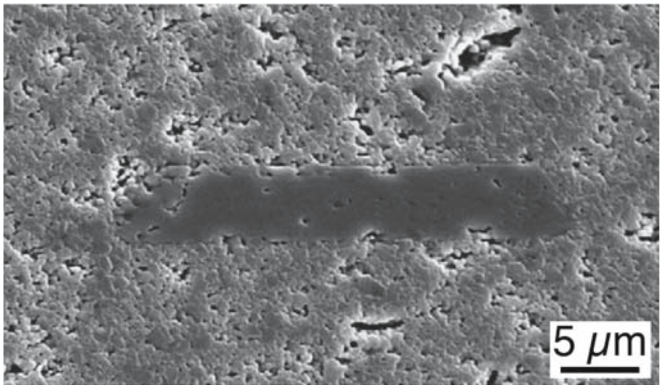


FIGURE 15.9 Templating grain growth. The seed is the elongated grain in the center.

If a polycrystalline sample of α-Al_2O_3 containing particles of ZrO_2 is heating during consolidation to a temperature at which the ZrO_2 is in the tetragonal phase, the matrix can stabilize the high-temperature phase as the sample is cooled. This is the concept used to toughen α-Al_2O_3 in Chapter 18.

PARTICLES IN RELATED FIELDS

You will find many of these processing techniques applied to particles in pharmaceuticals, cosmetics, pigments, paints, etc.

NUCLEATION OF A SPHERE

The free energy for a spherical particle depends on the surface area and the volume:

$$\Delta G_r = 4\pi r^2 \gamma_{sl} + \frac{4}{3}\pi r^3 \Delta G_V \qquad \text{Box 15.1}$$

The two energy terms balance when

$$\frac{\partial(\Delta G_r)}{\partial r} = 0 \qquad \text{Box 15.2}$$

The critical particle radius is

$$r^* = -2\frac{\gamma_{sl}}{\Delta G_V} \qquad \text{Box 15.3}$$

The critical value of ΔG^* is then

$$\Delta G^* = \frac{4}{3}\pi r^{*2}\,\gamma_{sl} = \frac{16}{3}\pi\frac{\gamma_{sl}^3}{\Delta G_V^2} \qquad \text{Box 15.4}$$

15.8 NUCLEATION AND GROWTH OF PARTICLES

In metals we often form particles by precipitation from a solid solution as a result of heat treatment. The particles can adopt different shapes and set up different strain fields in the matrix during cooling. We can follow the same process in ceramics or we can add particles to the matrix during processing. We actually have an extra variable—we can change the oxygen activity and thus change the oxidation state of an ion. This process is illustrated in Figure 15.5.

Nucleation

The formation of nuclei requires the formation of an interface between the two phases (e.g., between a liquid and a solid). Thus, the formation of very small par-ticles generally increases the total free energy of the system.

Growth

Once such particles reach a sufficiently large size, the interface energy increase is small compared with the volume energy decrease so that the total free energy begins to decrease as the particle size increases.

The classic example of precipitate nucleation in metals is the formation of GP zones in Al–Cu alloys. In ceramics, analogous examples include spinel in NiO, rutile in sapphire, or platelets of nitrogen in diamond. When particles are very small, the surface energy dominates. The calculation in Eqs. Box 15.1–Box 15.4 is instructive. Remember that the calculation is for a spherical nucleus and it ignores kinetics; kinetics are actually important as we saw in Figure 15.5.

Assuming a spherical nucleus, the total energy required for the formation of a nucleus of radius r is ΔG_r, which is a combination of two terms. The first term relates to the energy required to create the solid/liquid interface; γ_{sl} is

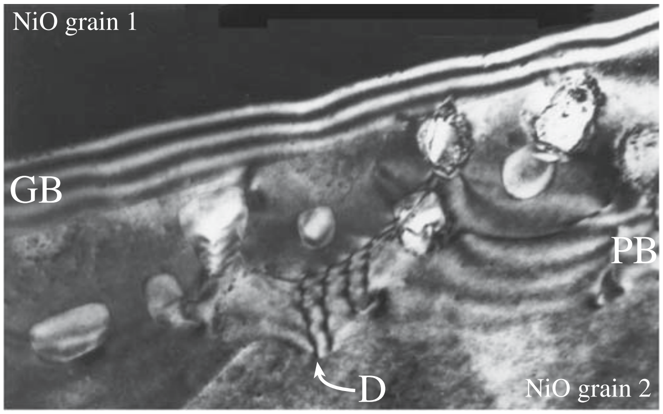


FIGURE 15.10 Growth of a particle along a GB. The particle is topotactically aligned with one NiO grain (along PB at grain 2) but not the other (grain 1). D shows a dislocation at the coherent interface.

the solid/liquid interfacial energy. This term dominates for small particles. The second term relates to the energy liberation associated with the volume change; ΔG_v is the free-energy change per unit volume for the new phase. The second term dominates when the particle size increases, so that once the particles reach some critical size further growth leads to an increasingly lower free energy and hence a more stable system.

We can deduce the size of the particle that has the maximum free energy, and that on further growth leads to a continuous decrease in free energy, by differentiating ΔG_r in Eq. Box 15.2. The critical value of r is given by Eq. Box 15.3 and implies there is a critical value of ΔG^*. When the particles have $r < r^*$ we call them clusters or embryos; nuclei are the stable particles with $r > r^*$.

Heterogeneous Nucleation

If particles nucleate at GBs or at surfaces they generally require less energy since an interface is already present. This is illustrated in Figures 15.8a and 15.10. The plate of spinel growing along the NiO GB has a topotactic alignment with one grain but not with the other since it is a high-angle GB. The presence of such particles in grain boundaries can change the properties of the material. For example, since β''''-Al_2O_3 is a fast ion conductor, such particles in polycrystalline Al_2O_3 provide short-circuit paths for rapid diffusion of Na, which can accelerate the degradation of Na-vapor lighting products.

15.9 PORES

Pores are very important in ceramics, in part because powder processing automatically creates them. The properties of pores are related to the surfaces that define them, but because the surfaces are usually curved they are not well understood. In ceramics, pores are everywhere and always contain some gas, although for simplicity we often think of them as surfaces enclosing a vacuum. Pores are not so important in metals because they tend to collapse to form dislocation loops unless they contain a gas that cannot dissolve in the metal.

Pores or voids? We generally use the term *pore* since the term *void* suggests that the pore is empty. Most pores in ceramics are created during processing and most processing does not occur in a vacuum. Hence, in ceramics most pores contain at least some amount of gas.

These volume defects can have very important effects on the properties of crystalline solids and clearly relate closely to Chapter 13. Examples of these defects follow.

- Pores in the matrix: Isolated pores and surfaces
- Pores at grain boundaries and other grain junctions

We often start with very porous material so the "concentration of pores" may be large. We will extend this discussion in Chapter 24 (sintering). We may want a porous material (e.g., MCM-41). Pores interact with grain boundaries, phase boundaries, etc.

Does the pore have an equilibrium shape? The shape of the pores is determined by the surface energies. Faceted pores are shown in Figure 15.11. A technique has been developed to study systematically the annealing of pores

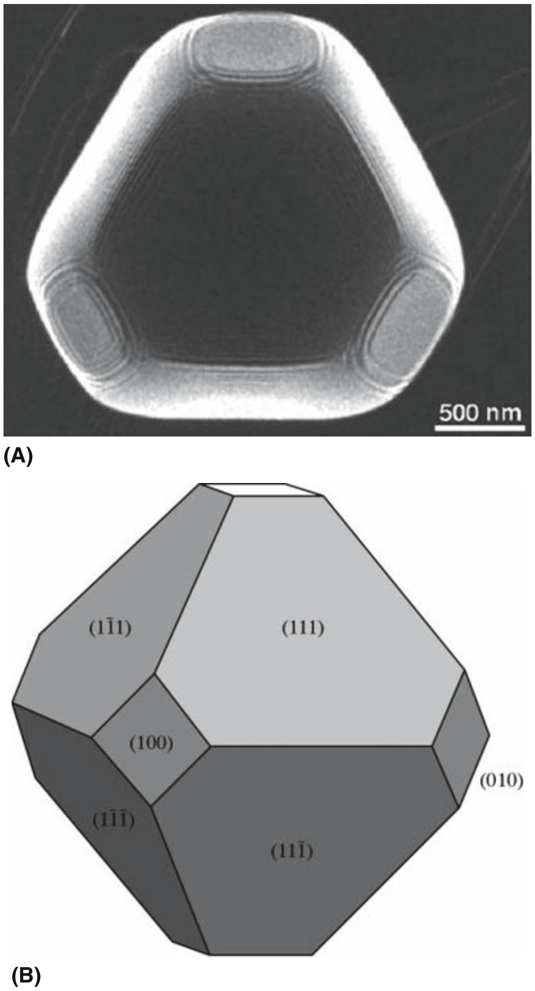


FIGURE 15.11 A faceted pore in UO_2.

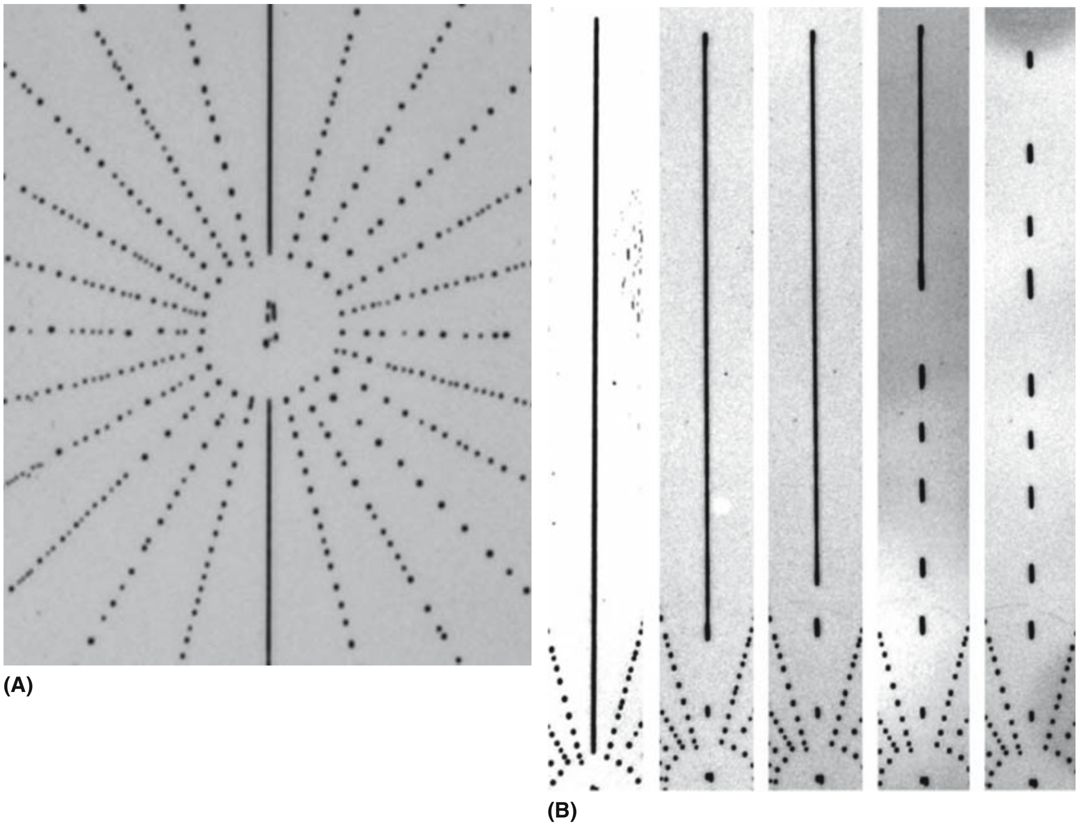


FIGURE 15.12 A method for systematically studying voids. (a) Grooves lying along different crystallographic directions break up to form pores at different rates. (b) The break up of one channel pore can be followed over time.

and the effect of dopants on this process. Channels or pores can be created in a $\Sigma = 1$ or high-angle GB by joining together two flat plates after patterning the surface of one grain using lithography as illustrated in Figure 15.12. The formation of such pores will occur when two nearly flat plates are joined, but will not be controlled. The technique has been extensively used to study pore annealing and the effect of dopants on this process in Al_2O_3, but could easily be extended to other materials including glass. (See also the discussion of Figure 14.33.)

Pores can coalesce just as particles can. (Think of them as inverse particles.) The driving force is the same, namely, reduction of the total energy by reducing the area of the interface. The difference is that in order to shrink, the pore must nucleate a vacancy first. This vacancy must diffuse away through the lattice, along a dislocation or along an interface.

What is the effect of gas in pores? You can not remove the gas easily once the pore has separated from an interface because you then have to move a neutral atom through the lattice. Pores can move through the matrix as we will discuss in Section 24.15, but this process is likely to be slow and involves surface diffusion from one side of the pore to the other; as for a bubble rising in a liquid, we need a driving force.

Pores are also the principal defect in cement and concrete (see Section 2.7), which makes controlling porosity one of the main tasks of the cement industry. Here, one way of minimizing porosity is to minimize the amount of water used in the cement. With suitable use of plasticizers and so-called microsilica, compressive strengths of >100 N/mm^2 and tensile strengths of ~15 N/mm^2 can be achieved. The plasticizers used for this are water soluble and mainly improve the packing density, thus decreasing pore content. Incidentally, cement can also be reinforced with up to 5% glass fiber and concrete may be reinforced with polypropylene fiber and of course steel "fibers."

15.10 MEASURING POROSITY

We are interested in three quantities: (1) the size of the pores, (2) the distribution of the porosity, and (3) the total amount of porosity in the sample. Usually the actual shape of the pores is less important, although there may be situations in which the shape would be a critical factor. We can see pores in transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). If they are large enough, we will also see them in visible light microscopy (VLM). None of these observations will give a statistical measurement of the amount of porosity.

The total amount of porosity can be estimated quite accurately if you know the phases present in the sample. You estimate

PORE PARAMETERS

Some closely related topics include pore size, particle size, total surface area, active surface area, and total material density.

FIGURE 15.13 A commercial porosimeter.

the theoretical density, deduce the actual density, and thus estimate the porosity. The other two quantities are much more difficult to determine. We can infiltrate a liquid and apply mercury-intrusion porosimetry. The principle is that the capillary pressure depends on the radius of the pore. If we vary the pressure on the Hg, it will fill pores down to a different size. If we then increase the pressure, more pores will be filled. The drawback to this approach is that we only measure the pores that are connected to the exterior. Commercially available equipment for measuring porosimetry is illustrated in Figure 15.13.

A related technique uses nuclear magnetic resonance (NMR) to measure the time taken by a liquid to fill the pores. It measures the relaxation times of the liquid filling the pores and relates this relaxation time to the thickness of the liquid and hence determines a surface-to-volume ratio for the pores. It is also possible to obtain information on the porosity using electron paramagnetic resonance (EPR), but neither EPR nor NMR is widely used for this purpose.

There are many other uses of porosity measurements; the oil exploration industry is a major example. There is clearly a strong link to powders: in some applications surface area may be more important than pore/particle size, but the two are not independent.

15.11 POROUS CERAMICS

We discussed the structure of zeolites in Chapter 7. The special feature of the crystal structure is the large void that is surrounded by a silicate cage but linked to other voids. A related void is that found in C_{60} and the other buckyballs. This type of void is not what we mean by the term pore since these voids are an essential component of those crystalline structures. They may become filled with gas or liquid, but this is more closely analogous to an impurity occupying an interstice in other crystal structures as He can, for example, in the fluorite-structured UO_2.

The new mesoporous materials have extremely high surface-to-volume ratios. An example of these materials is MCM41, which was invented by DuPont. A simple structure that can be manufactured in the laboratory is illustrated in Figure 15.14. The structure initially contained a periodic array of polymer spheres. When close packed, these spheres leave 26% of the volume empty. We can then infiltrate a liquid into these pores, burn out the spheres, and convert the liquid to a polycrystalline ceramic. Another synthesized porous ceramic is the cordierite honeycomb structure used to support the Pt catalyst in automobile catalytic converters. In this case the cylindrical pores are introduced mechanically in the extrusion process.

Pumice is a natural porous ceramic. It is produced by volcano eruptions and the gas is trapped inside the solid as it rapidly cools. The matrix is mainly glass, but it can contain small crystals. Synthetic ceramic foam is illustrated in Figure 15.15. Uses for ceramic foam are summarized in Table 15.3. One of the best-known applications for a porous ceramic is the space shuttle tile. An SEM image of such a tile is shown in Figure 15.16. Notice that in this case, the ceramic consists mainly of fiber (pressed not woven), so the principle is the same as for ceramic (glass) fiber for house insulation.

The structures shown in Figure 15.17 illustrate the result of computer modeling of foams. A thin membrane connects the structural ribs, as in a soap bubble in a wire frame. Since this film is amorphous, its surface energy is uniform and the film will be flat. The structure, of course,

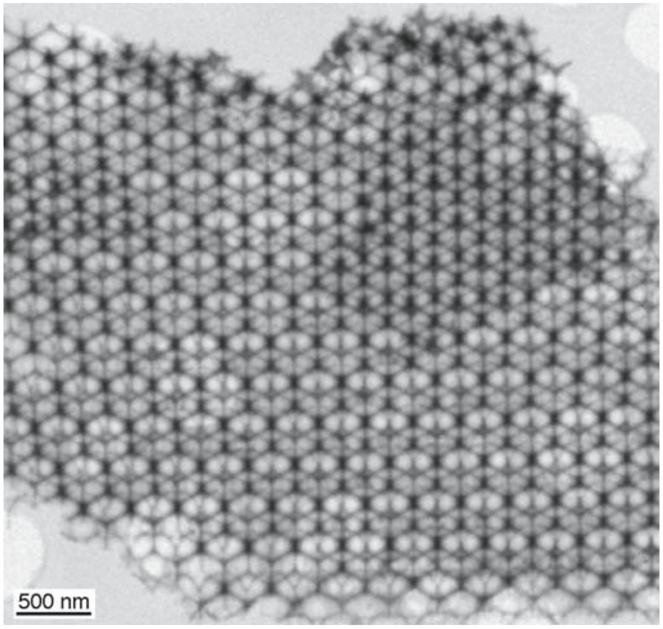


FIGURE 15.14 An ordered mesoporous material.

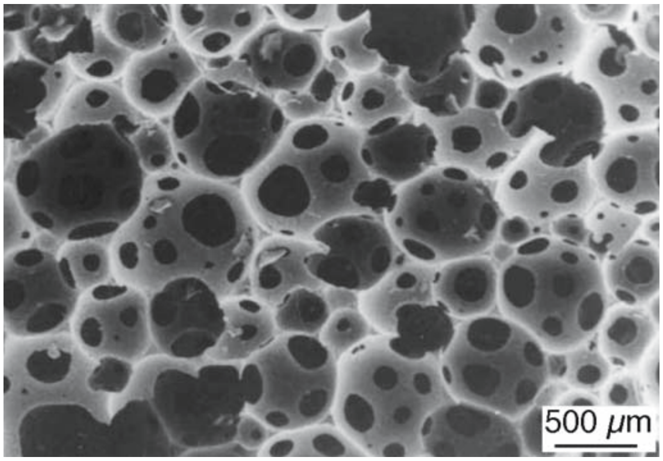


FIGURE 15.15 Sintered alumina foam made using a soap-nut slurry with a 40 volume % ceramic.

looks very similar to the glass films between grain boundaries, at triple junctions and at 4-fold junctions as discussed in Chapter 14, but all the "grain boundaries" are now flat (because the *grains* are pores).

15.12 GLASS/CRYSTAL PHASE BOUNDARIES

Crystals have been grown in glass matrices for hundreds of years. The luster glaze used on some medieval pottery owes its sparkle to nanoparticles of copper in the glass.

TABLE 15.3 Uses for Ceramic Foam

Foam material	*Application*
Sieves	Molten metal filters
Sieves, microporous	Gas filters
Catalyst supports	Catalytic converter
Thermal insulators	Space shuttle tiles
Artificial opal	Optical

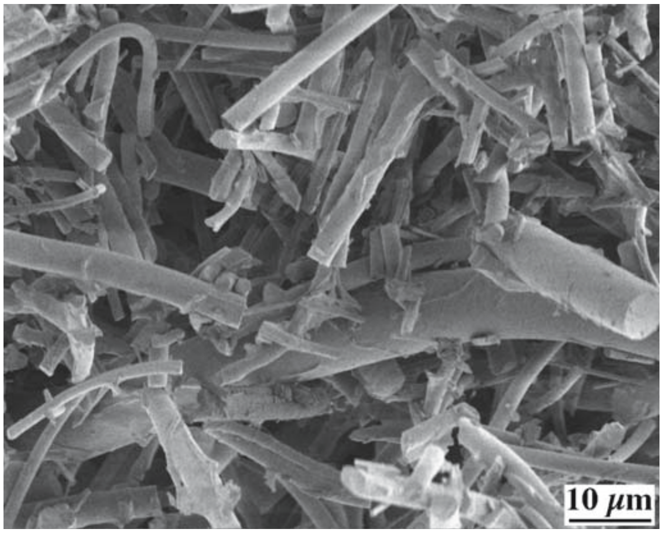


FIGURE 15.16 The porous material used to make insulating tiles for the space shuttle. The silica fibers are 2–4 μm in diameter.

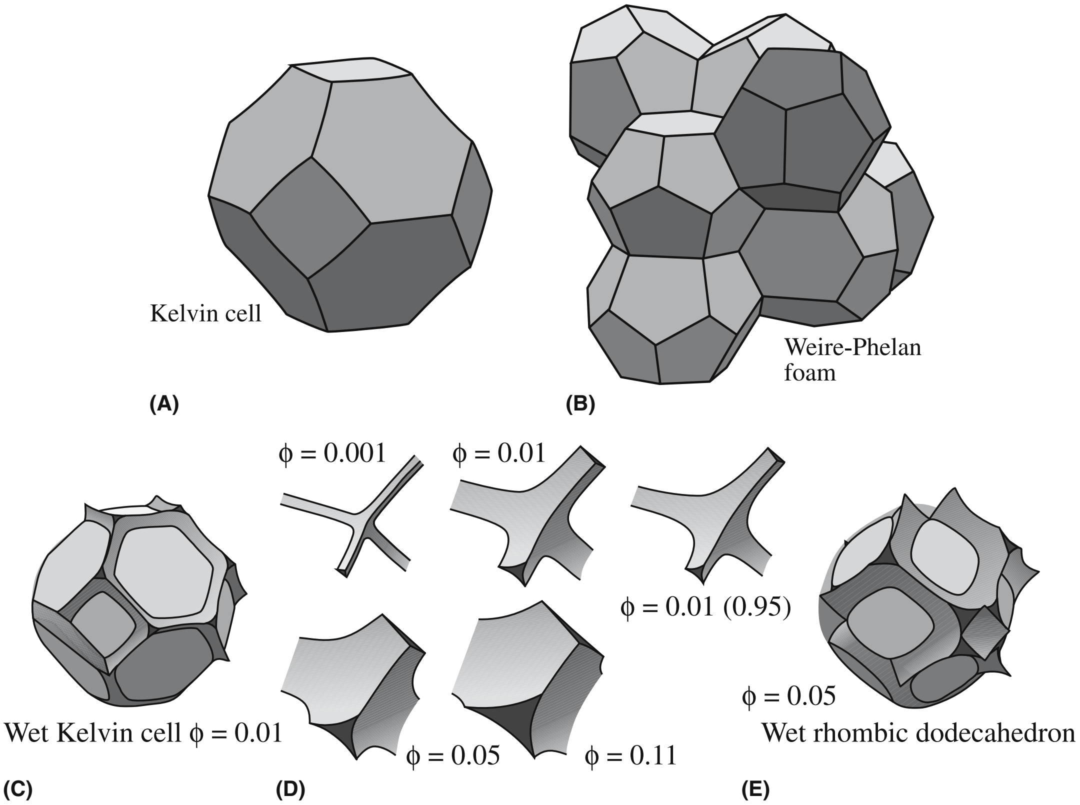


FIGURE 15.17 IGFs without grains. (a and b) Models of the Kelvin cell and a Weaire–Phelan foam used to describe soap bubbles; (c–e) how these relate to the structure of TJs and QJs.

TABLE 15.4 Observed Microstructures in Some Ceramic Eutectic Systems

System	T_{eut} *(°C)*	*Growth Rate (cm/hour)*	*Comments*
PbO–$Pb_2Fe_2O_4$ (12.8 wt% Fe_2O_3)	730	0.5–2	Broken lamellar, two-phase matrix
PbO–$Pb_3Nb_2O_8$ (6.85 wt% Nb_2O_5)	835	2	Lamellar
V_2O_5–$Pb_2V_2O_7$ (5.7 wt% V_2O_5)	760	Cast	Lamellar
Pb_4GeO_6–$Pb_3Ge_2O_7$ (15.0 wt% GeO_2)	707	1.45	Circular rod
WO_3–$BaWO_4$ (18.5 wt% BaO)	935	Cast	Water soluble
V_2O_5–BaV_2O_6 (32.2 wt% BaO)	550	Cast	Glassy
$Bi_4Ge_3O_{12}$–$Bi_{14}GeO_{24}$ (10.3 wt% GeO_2)	880	Cast	Unbranched dendrites
V_2O_5–ZnV_2O_6 (14.2 wt% ZnO)	640	Cast	Coarse unbranched dendrites
V_2O_5–NiV_2O_6 (9.2 wt% NiO)	650	Cast	Coarse unbranched dendrites
V_2O_5–MnV_2O_6 (9.10 wt% $MnCO_3$)	660	2	Coarse unbranched dendrites
PbO–Pb_2WO_5 (17.6 wt% WO_3)	725	Cast	No fine two-phase areas seen
Bi_2O_3–$Bi_{26}Zn_2O_{38}$ (1.24 wt% ZnO)	750	2	Circular rod, spheroidized
$BiFeO_3$–$Bi_{40}Fe_2O_{63}$ (1.14 wt% Fe_2O_3	790	0.5–2.5	Ciruclar rod, matrix may be faceted
Li_2WO_4–WO_3 (19.1 wt% WO_3)	695	Cast	Porous, very soluble in water
V_2O_5–CuV_2O_6 (12.7 wt% CuO)	620	Cast	No fine two-phase areas seen
V_2O_5–CaV_2O_6 (2.74 wt% CaO)	618	Cast	No fine two-phase areas seen
Bi_2O_3–$Bi_2Mn_2O_9$ (12.2 wt% Mn_2O_3)	790	Cast	Lamellar
Bi_2O_3–Bi_8TiO_4 (0.53 wt% TiO_2)	835	Cast	Lamellar
WO_3–$CaWO_4$ (7.46 wt% CaO)	1135	Cast	Triangular rods
WO_3–$SrWO_4$ (17.1 wt% $SrCO_3$)	1075	Cast	Triangular rods
WO_3–$MgWO_4$ (12.6 wt% $MgCO_3$)	1120	2	Lamellar "Chinese script"
La_2O_3–$LaFeO_3$ (28.5 wt% La_2O_3)	1430	~2	Triangular rods
Fe_2O_3–$YFeO_3$ (15.9 wt% Y_2O_3)	1455	Coil	Lamellar/rod, matrix forms three-pronged webs
Gd_2O_3–$GdFeO_3$ (15.0 wt% Gd_2O_3)	1500	Cast	Lamellar/rod, matrix forms three-pronged webs
$BaTiO_3$–$BaTiSiO_5$ (9.9 wt% SiO_2, 90.1 wt% $BaTiO_2$)	1260	2	Rodlike
$BaTiO_3$–$BaTiO_4$ (41.9 wt% TiO_2)	1563	2	Lamellar and rod
Zn_2TiO_4–TiO_2 (43.0 wt% ZnO)	1418	2	Lamellar
Al_2O_3–$ZrO_2(Y_2O_3)$ (55 wt% Al_2O_3, 38.3 wt% ZnO_2)	1890	0.5–10	Circular rod, matrix may be faceted

Household window glass will eventually form crystals of devitrite, an orthorhombic crystal with a formula like $Na_2Ca_3Si_5O_{16}$; these crystals usually form at the surface first. Crystalline glazes, which can make a pot look so spectacular, actually rely on spherulites consisting of many willemite (Zn_2SiO_4) crystals, with each acicular crystal growing in the [001] direction, to achieve the effect. (More on this topic in is presented in Section 21.11.)

When two crystalline oxides are joined together to form a GB or PB, they are often thought of as being ionic materials even though the bonding may have a relatively large covalent component. Glass is usually viewed in the opposite way. Clearly we should take the nature of the bonding and the possibility of an interface space charge into account when we examine the glass/crystal interface. This point is particularly relevant to an understanding of glass-ceramic materials.

15.13 EUTECTICS

Is there anything special about ceramic eutectics? Not really (although they are very interesting), but it is sometimes a bit of a surprise that they can be formed just as they can in metal systems. Eutectic structures are well known in metals, but have not been exploited in ceramics. One reason for this is that eutectics are associated with solidification of a liquid phase and we do not usually process ceramics using a liquid phase; this also means that processing temperatures are generally higher. In the examples listed in Table 15.4, one column gives the morphology of the respective phases. The minority phase can be sheets, rods, or particles; which of these actually occurs is determined in part by the energy of the PBs and the way in which the sample is cooled from the eutectic temperature. Directional solidification is generally required to optimize rods and platelets.

In the CoO/ZrO_2 eutectic solid, the two ceramics are both cubic, but they have very different structures. They grow in the cube-on-cube orientation, which means that all directions and planes in one material are parallel to the same directions and planes in the other material. As a possible application of such a material, oxygen diffuses rapidly in ZrO_2. It can then react with the CoO to produce a layer of Co_3O_4 at the interface between the two materials, resulting in the structure illustrated in Figure 15.18. Notice how uniform this spinel layer is: the growth is controlled by the reaction, not diffusion of O through the ZrO_2.

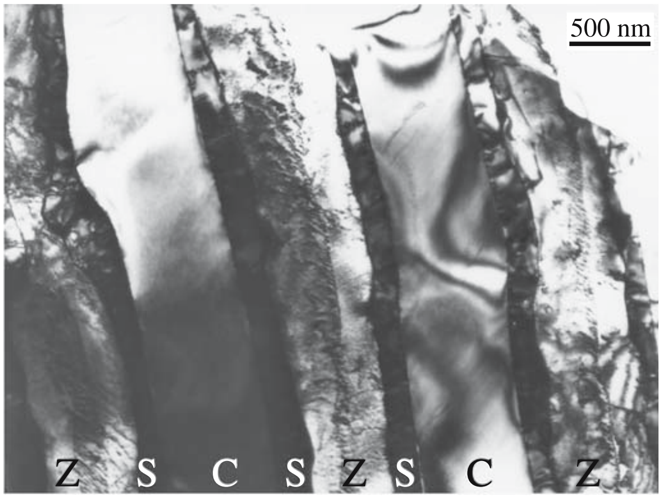


FIGURE 15.18 A CoO/ZrO$_2$ eutectic after solidification and subsequent oxidation. Z, ZrO$_2$; C, CoO; S, Co$_3$O$_4$ (spinel).

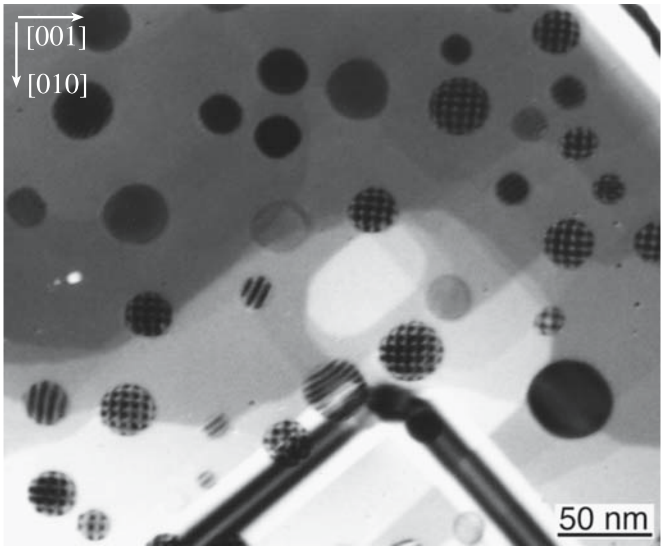


FIGURE 15.19 Particles of W on SiC. When crossed fringes are present (because of the lattice misfit), the alignment is excellent, otherwise; the islands are tilted relative to the substrate.

15.14 METAL/CERAMIC PBs

Metal/ceramic PBs are not only the most important feature in ceramic-reinforced metal-matrix composites, but they also occur when metals are oxidized or when oxides are reduced to the metal or when a metal film is grown on a ceramic substrate (or vice versa). In Figure 15.19 particles of W have grown on a single-crystal thin film of SiC. The alignment and lattice mismatch of the two phases can be appreciated from the moiré fringes in the image.

High-resolution TEM (HRTEM) has now shown more details on such interfaces. The position of the misfit dislocation actually depends on the elasticity parameters of the two materials. The schematic diagram in Figure 15.20

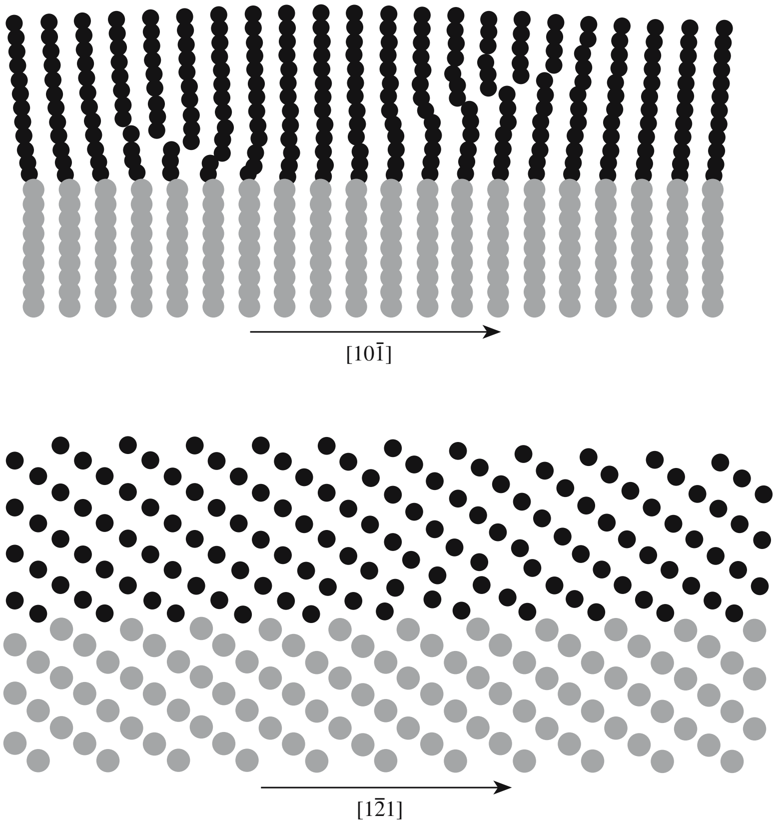


FIGURE 15.20 Schematic of stand-off dislocations accommodating lattice misfit between Nb and Al$_2$O$_3$.

TABLE 15.5 PBs in Applications

Bond	*Material*
Brazing	Join a ceramic to a metal
Metal–matrix composites	Make a two-phase material
Electronic interconnects	Bonding metal to a semiconductor
Oxidation of metal	Form an oxide from metal
Catalysis	Support catalyst particles

illustrates the dislocation stand-off, which is seen at the Nb/Al_2O_3 interface. The dislocations preferentially sit in the metal so as to lower the energy of the dislocation (remember, E depends on the elastic constants not just **b**) while still accommodating the misfit between the materials.

BRAZING AlN

Using an active metal such as Zr, we can get an idea about the possible reactions by using the Ellingham free-energy diagrams. Figure 15.21 is a plot of the free energy of formation of selected nitrides as a function of temperature. The lines represent the reaction

$$2\ Zr(s) + N_2(g) = 2\ ZrN(s)$$

Thus, when AlN is combined with Zr at high temperatures the reaction

$$Zr + AlN \rightarrow ZrN + Al$$

is favored. At 1123 K the free energy for this reaction is −83.3 kJ/mol.

15.15 FORMING PBs BY JOINING

We form PBs whenever we join dissimilar materials. Table 15.5 summarizes some applications of joining processes and the type of PB that is formed. Note that when bonding two materials together, we do not always want to produce strong bonds; some applications may prefer that the bond be weak (for example, in fiber composites). The formation of the bond has some requirements.

- Intimate contact between the two materials—the obvious requirement for a strong bond.
- Formation of a chemical bond—covalent bonding would be strong and van der Waals bonding would be weak.

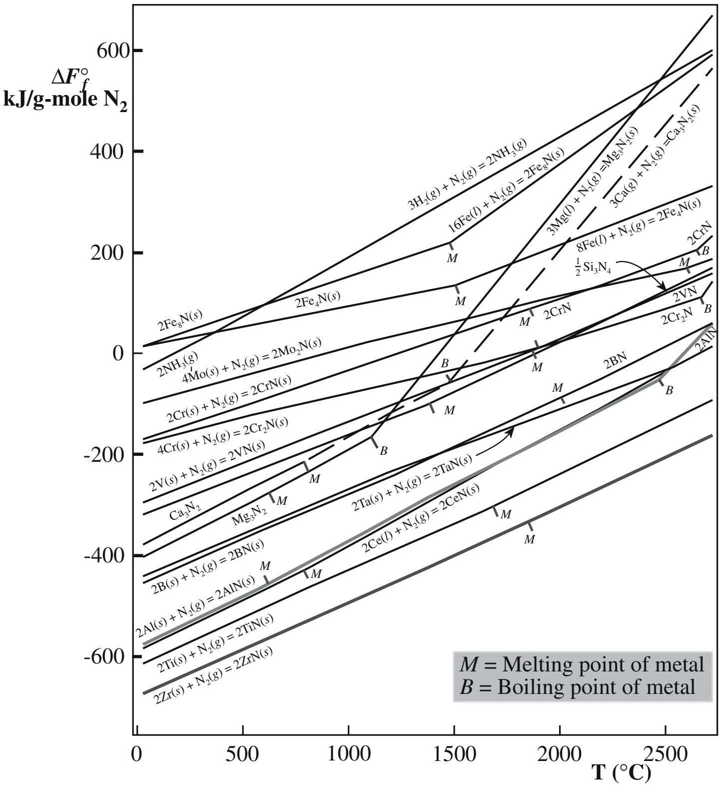


FIGURE 15.21 The Ellingham diagram. The lower line is used when brazing Zr.

- For a lasting bond, there must be a way to accommodate interfacial stresses.

The interfacial stresses may arise due to thermal expansion mismatch generated during cooling, or after fabrication, or because of temperature changes in operational conditions.

Brazing is joining a metal to a ceramic. The technique is well illustrated by considering metallization processes for AlN. There are several possible routes for forming the interfaces.

- Apply the metal in a liquid form
- Deposit either material from the vapor phase
- Use a solid-state reaction involving oxidation or reduction

Liquid metals have much higher surface energies than most ceramic oxides, and the PB energy is also high. The result is that liquid metals do not readily wet a ceramic and spread, unless special precautions are taken. Two approaches have been used for the development of metal brazes for oxides. In one method, active metals such as Ti or Zr are added to the metal; these effectively reduce the interfacial energy because the additives have a strong chemical attraction to the oxide and hence they enhance wetting behavior. The active metal is essentially acting as a surfactant! A braze must react with both the metal and ceramic components that you are joining and reach chemical equilibrium at the interfaces. Metal systems are generally compatible, resulting in wetting; the braze can then bond (by solution or diffusion) to the metal component.

Braze alloys for Al_2O_3-based ceramics might be Ag–Cu, Au–Ni, or Ag–Cu–Zn, but these alloys generally do not wet ceramics. The oxidation potentials of Cu and Ag are less than that of Al, so they do not react with the ceramic. If a small percentage of an active metal, e.g., Ti, is added, then the high oxidation potential of the Ti causes it to undergo a redox reaction with the ceramic (Al_2O_3). The result is the spreading of the braze because an oxide that is compatible with both phases forms at the interface; a chemical bond forms at the interface. Similar approaches have been used to braze nonoxide ceramics. Zr may be a suitable candidate for an active metal for brazing of AlN ceramics.

In making electronic interconnects it is often necessary to metallize the surface of Al_2O_3 (in ceramic packaging for integrated circuit applications). We describe how metallization is accomplished using thick-film processing in Chapter 27. The development of an interlocking glass/ceramic and glass/metal structure is required for good adhesion because it provides mechanical interlocking in addition to chemical bonding between phases. To achieve the required microstructure at the conductor–substrate interface it is necessary for the glass to have the appropriate surface tension and viscosity during the firing process, and for it to wet the substrate.

In thin-film metallization by evaporation or sputtering of thin metal films onto a ceramic surface (Chapter 28), it has been demonstrated that a sequence of layers of different metals is required for optimum film properties. The first layer is usually a refractory metal such as Ti, Cr, or NiCr; this layer provides adhesion to the ceramic. These elements are reactive and bond through redox reactions with the substrate. The second layer acts as a diffusion barrier. The barrier material will usually be a noble metal, preferably Pt or Pd. The top layer will be the metal of choice for the particular application, for example, Au for wire-bonding applications and Ni or Ag–Pd for solderability.

A schematic for the process of anodic bonding is shown in Figure 15.22. The concept is that two materials are joined together by heating them while applying a voltage across the assembly (hence it is also known as field-assisted bonding). The temperature is typically between 300°C and 450°C while the applied voltage is ~80 V. Glass can be bonded to glass or to Si with this process. In principle, the limiting factor is being able to polish the abutting surfaces to a roughness of <100 nm. Glass works particularly well because the cations are quite mobile.

Some final examples of PBs are given. In catalysis, it is usually not possible to examine the interface between the support and the catalyst particle. An example of catalyst particles on a silica nanowire is shown in Figure 15.23. We will discuss composite materials in more detail later, but we note that the filler material (fiber or particle) and the matrix can be glass, crystalline ceramic, or another (see Chapter 20).

METALLIZING ALUMINA

A commercial process for metallizing debased alumina uses Mo or W; the alumina grains in the debased alumina are held together by a glassy phase binder. The Mo is applied to the surface as a powder, often mixed with manganese oxide, and fired in a reducing atmosphere with a controlled dew point so that the Mn is present as MnO and Mo as the metal. The MnO reacts with both the alumina grains and the liquid glassy phase. The glassy phase from the Al_2O_3 migrates into the metal powder under the influence of capillary forces and bonds the metal particles to each other and to the Al_2O_3 surface, producing a wettable surface layer. In the case of pure Al_2O_3 and oxides without binder phases, it is necessary to add glasses to the metallizing mixtures. The Mo coating is generally electroplated with Ni to provide a clean and continuous surface as well as one on which an applied braze would easily spread. A similar process is applied for W metallization.

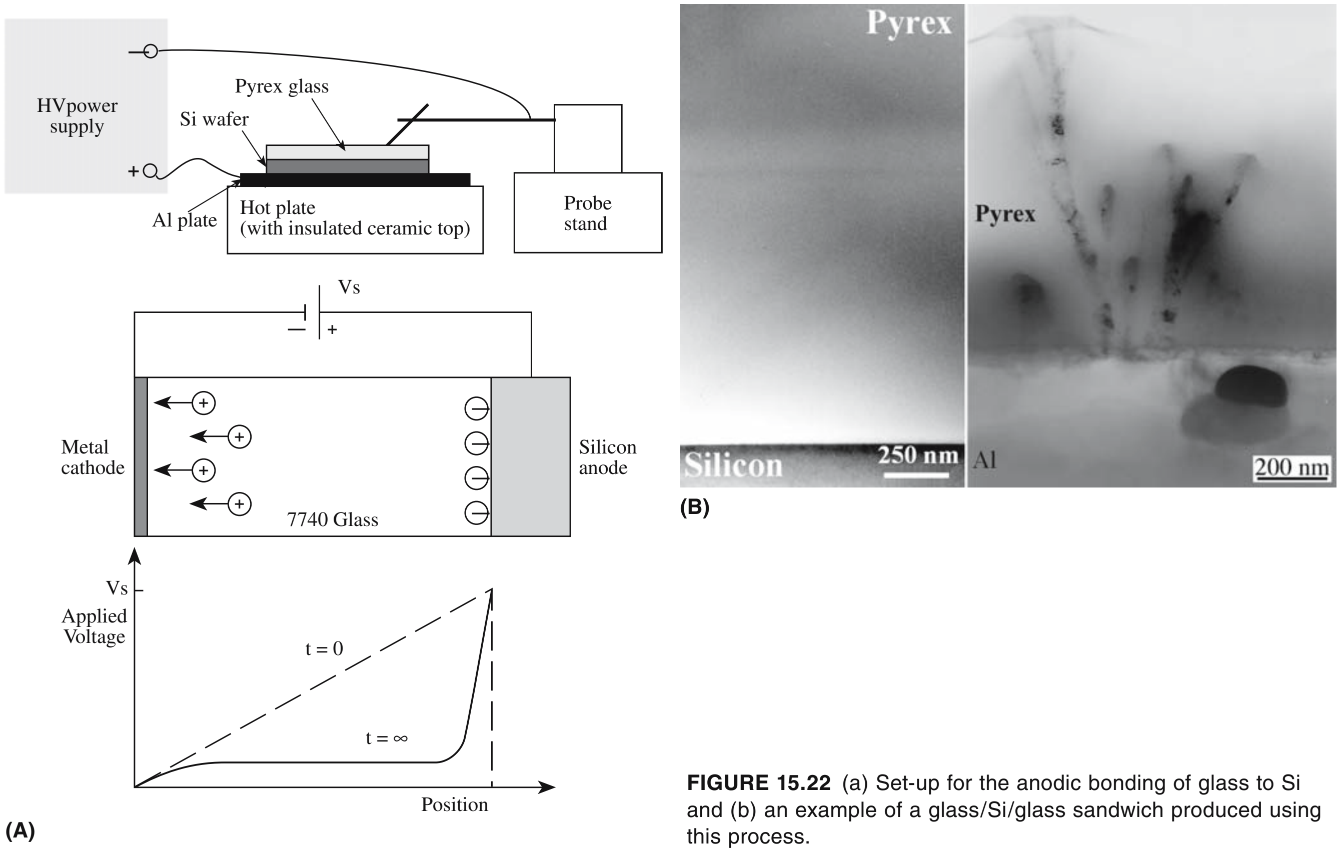


FIGURE 15.22 (a) Set-up for the anodic bonding of glass to Si and (b) an example of a glass/Si/glass sandwich produced using this process.

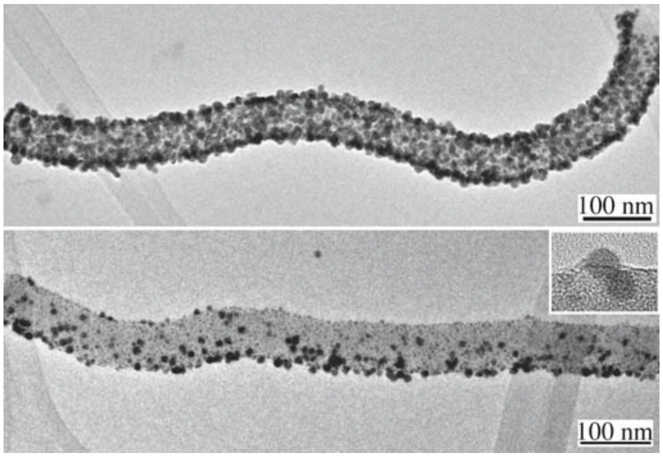


FIGURE 15.23 Au catalyst particles on a ceramic nanowire.

CHAPTER SUMMARY

There are several key ideas in this chapter. PBs are present wherever we have a second phase, particle, or precipitate in a matrix; we treat pores as a special particle. (The surface is actually a special PB.) Like GBs, PBs are everywhere in ceramics; we could develop a notation similar to the Σ for GBs but rarely use it. When a phase transformation occurs, the mechanism is the movement of a PB. Particles can be different in structure and/or composition in a ceramic matrix; precipitates are particles that have developed by a specific process. Pores are present in most ceramics and play important roles in determining properties. We have developed special methods for characterizing porosity and ceramics in which the pores are actually the major phase—porous ceramics. We just touch on some special PBs, namely glass/crystal interfaces and metal/ceramic interfaces; we will see much more of the former in later chapters.

GENERAL REFERENCES

The details of nucleation and growth theory are given in many standard textbooks on kinetics and phase transformations: see the books on interfaces in Chapter 15 and on phase transformations in Chapter 25.

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EXERCISES

15.1 Given the information in the text, determine the orientation of the samples.

15.2 What is the crystallographic relationship between the two grains shown in Figure 15.2a? How does it differ from that of the interface shown in Figure 15.2b?

15.3 Using reasonable values of the solid/liquid interface energies and ΔG_v, estimate r^* for spinel in MgO versus Cu in Si.

15.4 Do you expect the conduction of Na^+ ions in an ionic conductor to depend on crystallography? If so, why, and what are the implications?

15.5 How would you propose characterizing nanoparticles in the glaze on a priceless pot? Breaking the pot, even a little bit, is not allowed.

15.6 In Section 15.14 we note that dislocations can be present at metal/ceramic interfaces. When is this most likely; when is it least likely? How will the interfacial energies and strengths differ?

15.7 What is the relationship between the methods used to form the images in Figures 15.4 and 15.8? Explain why this technique works.

15.8 Assuming the interfaces labeled in Figure 15.7 are all viewed edge on, what is the viewing direction (the direction defined with respect to the sapphire crystal)?

15.9 Suggest reasons for the shape of the particle shown in Figure 15.5. How does this explanation compare with that for the shape of the particle in Figure 15.11?

15.10 List the possible applications for zeolites and mesoporous ceramics.