14

Interfaces in Polycrystals

CHAPTER PREVIEW

This chapter is part two of the three-part series on interfaces. Crystalline solids usually consist of a large number of randomly oriented grains separated by grain boundaries (GBs). Each grain is a single crystal and contains many of the defects already described.

A GB is defined as the surface between any two grains that have the same crystal structure and composition.
Many GBs, but not all, can be modeled as arrays of dislocations.

The dislocation model can be misleading. The GBs that may be most important in a ceramic may be the ones that do not appear to contain dislocations. Thus, the warning is: we may sometimes concentrate on a particular type of GB just because we can understand that type of GB. Unless we fully understand GBs in ceramics, we can never have a full understanding of what happens during ceramic processing or why ceramics have certain mechanical properties, conductivity (thermal or electrical), etc. GBs become even more important as fine-grained nanostructured ceramics become more available. We also need to understand the junctions formed when three or four grains join: these are known as triple junctions (TJs) and quadruple junctions (QJs), which we might regard as new line and point defects, respectively. We conclude with a discussion of properties, not because they are unimportant (nor because of the bias of the authors). We want to understand GBs so as to explain some properties and to predict others.

14.1 WHAT ARE GRAIN BOUNDARIES?

Grain boundaries are internal interfaces and behave much like external surfaces; but now we have to be concerned with two crystal orientations, not one. Just as for surfaces, we have a pressure difference associated with the GB curvature and a driving force that tends to lead to an overall increase in grain size whenever possible. Grain morphology and GB topology are two aspects of the same topic. It is instructive to think of the model of soap foams: a soap film is flat when in equilibrium, and it has a finite thickness. Three soap films meet along a line—a triple junction. If you blow on a soap film (apply a pressure) it bows out until the "surface tension" balances the applied pressure.

Whenever we join two grains of the same composition and structure, we form a GB. The grains are related to one another by a rotation axis and meet on a plane, which may be curved. The rotation axis is fixed only for a given boundary and is not unique even for that boundary; there are different ways to form the same GB. We start by considering two identical grains. Fix one grain and rotate the other about any axis. Cut each crystal parallel to a particular flat plane (to keep it simple) in space and join the grains at this plane. This plane is the GB. Then allow the atoms to relax to a low-energy configuration (which may not be the minimum energy).

The conventional approach is to consider four types of GB based on the symmetry operation used to create them: twist, tilt, mixed, twin.

The first two (and hence the third) designations are really helpful only when the misorientation angle is small (low-angle GBs). This description is based on the location of the rotation axis.

- Tilt boundary: rotation axis (**n**) in the boundary plane
- Twist boundary: rotation axis normal to the boundary plane

TWIST, TILT, TWIN, LOW, HIGH & 'GENERAL'

Twist	**n** normal to plane
Tilt	**n** parallel to plane
Twin boundary	Mirror across GB plane
Low-angle GB	$\theta < 10^\circ$ (Low is small!)
High-angle GB	Structured, $\theta > 10^\circ$
General GB	Not a special GB!

C.B. Carter and M.G. Norton, *Ceramic Materials: Science and Engineering*,
DOI 10.1007/978-1-4614-3523-5_14,

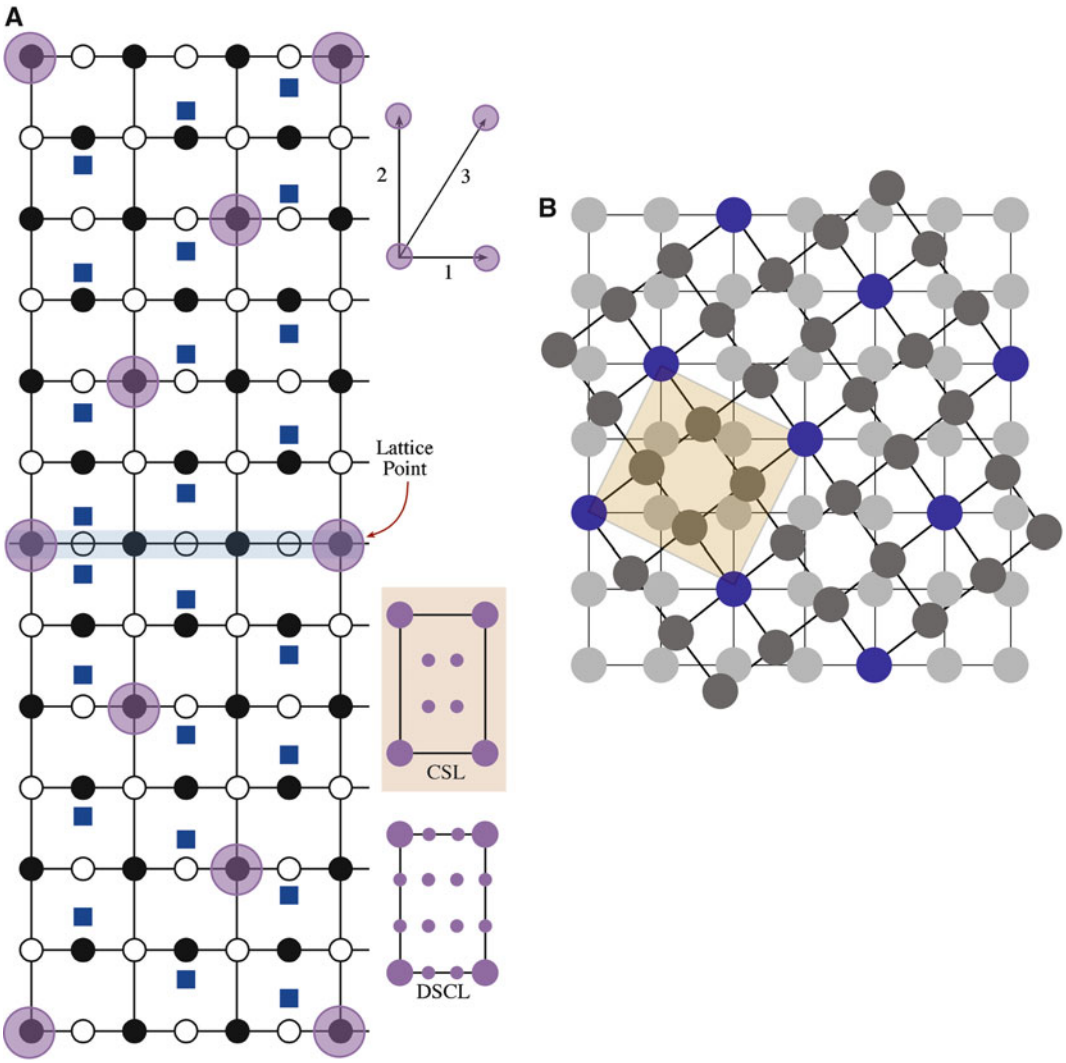

FIGURE 14.1. Two low-$\sum$ grain boundaries (GBs). (A) $\sum = 3$. (B) $\sum = 5$.

A symmetric twin boundary can also be described as a twist boundary or a tilt boundary. The difference depends on which aspect of the symmetry we think is most important. Not all twin boundaries are parallel to a mirror plane.

There are two well-known models of GBs that were developed primarily from studies of metals by considering the relative misorientation of the adjoining grains. These are the coincidence-site lattice (CSL) theory and the displacement-shift-complete lattice (DSCL). We first define two special quantities, $\sum$ and Γ. Imagine two infinite arrays of lattice points (one array for each crystal): they both run throughout space and have a common origin. For certain orientations, a fraction of the points in each lattice is common to both lattices.

We call this fraction $\sum^{-1}$. (Then $\sum$ is always an integer). The lattice made up by these points is called the CSL.

The CSL is a lattice of common lattice sites, not common atoms.

If you translate one grain relative to the other, $\sum$ is not changed.

14.1.1 The Idea of $\sum$

It's easiest to understand these concepts by looking at simple illustrations, as shown in Figure 14.1 for both $\sum = 3$ (for Al_2O_3) and $\sum = 5$ (for MgO). (Look back to Chapter 6 for the crystal structures.) The $\sum = 3$ diagram shows two twin-related unit cells with the lattice sites identified. Overlapping these two cells produces the pattern in the shaded box, and you can see that one in three lattice sites are common to the two grains (the ones at the corners of the box). The CSL for $\sum = 5$ (just the lattice sites are shown) is also identified in the shaded box. Note that we must take both ions into account when considering the actual structure (see later). Sometimes it appears that the most valuable feature of the CSL model is that it gives a shorthand notation for talking about GBs. Low-angle

boundaries are all $\sum = 1$ GBs. Especially in ceramics, not all twin boundaries have $\sum = 3$. [$\sum = 3$ occurs in face-centered cubic (fcc) crystals because the stacking of close-packed planes is ABCABC so one in three planes are coincident across the twin boundary.] For a particular GB, if we choose any plane, then a certain fraction of points lie on this plane in both lattices. We call this fraction Γ^{-1}. Again, it is easiest to appreciate the meaning of these definitions by studying the examples in the following sections. Γ is not widely used but might be the most important factor; and it reminds you that the different planes may be very different. Γ can equal 1 for the $\sum = 3$ GB but could be 3, 9, or greater.

Throughout our discussion of GBs, you should keep in mind that there are many similarities to surfaces.

- There is a *pressure difference* across a curved GB just as there is across a surface.
- Charge affects the structure and chemistry of GBs.
- The structure of a GB determines its properties and behavior.
- GBs can be wetted and dewetted by GB films just as surfaces are by surface films.

Computer modeling of GBs can give considerable insights, but be careful when using older results in the literature. The complexity of ceramics structures and the Madelung problem cause difficulties, and some older simulations may not be reliable—in part because they used too little material in the calculation because of the capabilities of the computers.

We discuss the properties of GBs later, but you should keep in mind some features as we work through the chapter.

- The density of atoms in GBs is less than in the bulk crystal.
- The chemistry of a GB is not the same as the bulk (because the bonding must be different).
- Properties of GBs must differ from those of the bulk.

All GBs have a thickness (just like the soap films), and the GB is not uniform across that thickness. Therefore, GBs are actually volume defects.

14.2 FOR CERAMICS

Ceramics are usually used in a polycrystalline form. GBs in ionic and covalent materials must be better understood to improve the science of processing of many modern ceramic materials; the properties of polycrystalline ceramics depend directly on the geometry and composition of GBs. The types of GBs commonly found in ceramic materials range from situations where the distance between the grains is $\geq$0.1 μm—such grains are separated by a second phase (glass)—to the basal twin boundary in Al_2O_3, which is atomically abrupt and potentially very clean.

We need to understand how the presence of glass affects GBs in crystalline materials. This glass can be present on the surface of grains or within GBs as an intergranular film (IGF) in single-phase materials or in materials with an intentionally high (or unavoidable) glass content.

The type of GB present in a sintered (or hot-pressed) compact may be significantly influenced by the surface characteristics of individual particles before and during sintering. Obviously, if there is glass on the particle, there is likely to be glass in the GB. We need to understand the behavior of the surface at high temperatures under conditions appropriate to sintering (see Chapter 24). As GBs can be structured or can contain a thin noncrystalline layer, the chemistry of the region close to the GB is important.

Therefore, we start with asking what is special about GBs in ceramics. This is the question we asked about surfaces and dislocations, and the answer is basically the same.

- Ceramics have localized charge or covalent bonds. Dangling bonds exist at GBs.
- There may be large local changes in density at the interface because the bonding is ionic, covalent, or mixed ionic/covalent. Ceramic GBs have a space charge.
- Because the unit cells of all but the simplest binary compounds are large, it is likely (rather than possibly) that a GB with a fixed misorientation angle and interface plane exists in more than one (meta)stable configuration. There would still be only one minimum energy.
- Energy is dependent on the GB plane, just as it is for surfaces. Accordingly, steps and facets (large steps) on these GBs are also important. They are actually necessary for the GB to move.
- Many ceramics are processed in the presence of a second or third phase far away from conditions of thermodynamic equilibrium, and a remnant of this phase may remain at the GB even if it is not the lowest-energy configuration. Impurities segregate to GBs, as illustrated by the X-ray energy dispersive spectroscopy (XEDS) and EELS plots in Figure 14.2.
- There is the problem of specimen preparation for analysis of interfaces in ceramics. In general, we can't prepare a sample without altering the GB in some way.

The extra difficulty is that we may never see a clean GB; and unlike surfaces, we have no way to clean one: ultra-high vacuum (UHV) doesn't help us once the GB is there. What is different in comparison to metals? Metals try to make the density of atoms uniform due to the nature of the electron gas. GBs in ceramics may be much more open. The density of atoms in the GB can be very different from that in the bulk grains.

Is the CSL theory important for ceramics? The CSL theory is relevant only when the adjoining grains are in

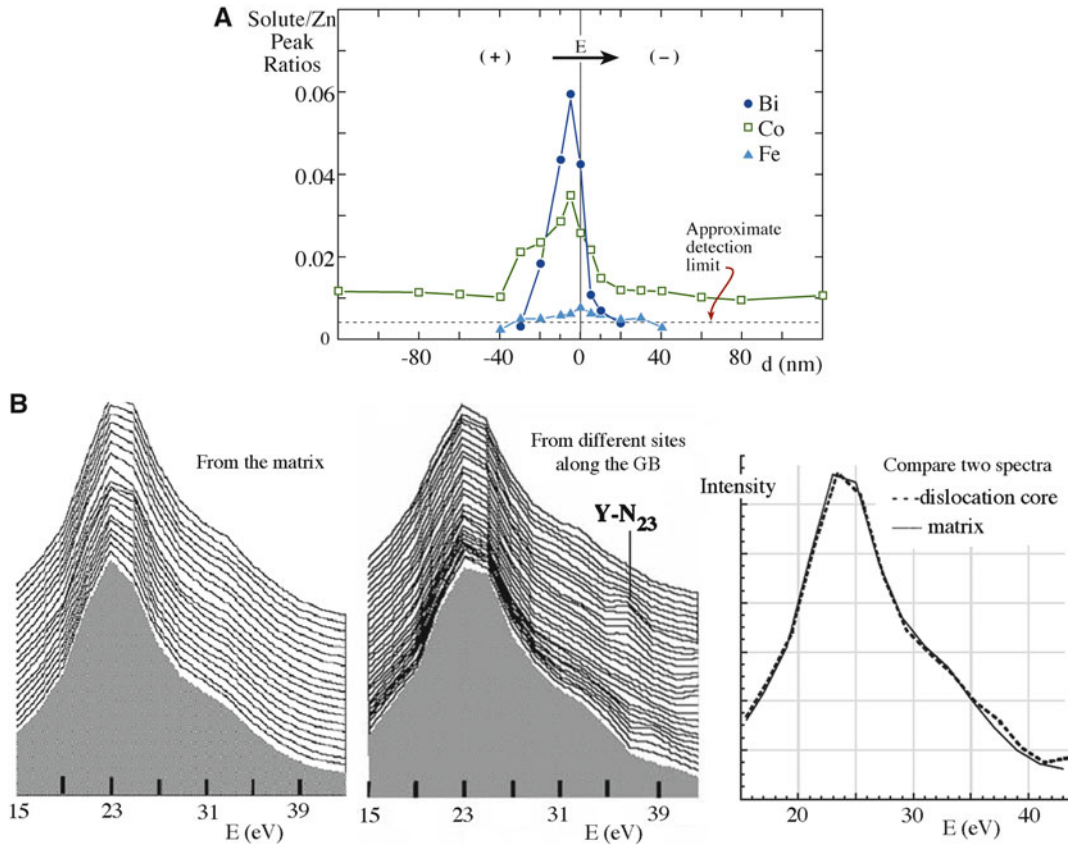

FIGURE 14.2. Solute distribution at GBs. (A) Profiles using X-ray energy dispersive spectroscopy (XEDS). The integrated X-ray solute/Zn peak ratios are plotted against the distance, d, from the GB. (B) Electron energy loss spectroscopy (EELS) spectra used to analyze a GB in sapphire.

direct contact. In ionic materials, we know that surfaces are almost never clean. Adsorption phenomena occur at internal interfaces as they do at surfaces. The driving force for segregation to GBs can be large. In fact, most GBs that have been studied have been "dirty." Pure polycrystalline ceramic materials do not exist. The layer of glass that may be present at the GB is invariably associated with impurities. Such films are unusual in semiconductors (although they can exist) and would be exceptional in metals.

As with other materials, it is difficult to discuss so-called general GBs rather than special ones. Even special GBs in ceramics are not well understood. Both general and special boundaries are likely to be far less clean than models of such interfaces might lead us to assume. Methods for analyzing interfaces containing IGFs have been compared. It has been concluded that the results can be ambiguous even when a combination of techniques is used. Unambiguous characterization is achieved only when the structure, chemistry, and bonding are assessed simultaneously.

What *facts* are actually known about GBs in ceramics? We can make the following statements.

- *Structured GBs do exist in ceramic materials*. This conclusion applies to both high- and low-angle GBs.
- *GBs in ceramic materials do exist that are not "structured"* but are, instead, wet over their entire area by an amorphous phase (an IGF).
- *The structure of GBs in ceramic materials tends to be relatively more open* (less dense) than is found for interfaces in metals that are otherwise crystallographically similar.
- *The effects of several ions* being present in the unit cell can be recognized. They can produce special interfaces where only one sublattice is affected or can cause a modification of the interface structure itself.
- *A particular interface may not have a unique structure* because of the presence of two ions or because two or more structures are possible that do not have significantly different energies. It is also likely that the presence of impurities at the interface modifies the structure by favoring different polyhedral sites.

14.3 GB ENERGY

The energy of a GB is a very important quantity, but it is even less well known than for surfaces. It is usually determined in relation to surface energies. There are two key questions.

- How do we define the energy of a grain boundary?
- What factor causes a GB to have low interfacial energy?

The GB energy, γ, depends on the misorientation of the two grains and on the orientation of the plane. We can again use the Wulff plot (γ versus θ, where θ now means the misorientation) and the inverse Wulff plot (γ^{-1} versus θ). The challenge of γ versus θ plots is to define the orientation of the GB plane; that is, having fixed θ, you must still fix **n**, the GB normal for both grains. Keep in mind that we expect γ to decrease as the temperature increases, as is found for surfaces (Eötvos rule); this dependence on T is important for sintering. One approach to the problem is to plot out the individual Wulff plots for the two separate grains and then to consider what happens when the two grains are joined along a particular plane.

14.3.1 MgO Smoke

One method used to examine the possibility of low-energy GBs is the classic MgO smoke experiment. Mg metal is burned in air, and the resulting MgO smoke particles are caught on a grid. The relative orientations between cube particles can be determined using transmission electron microscopy (TEM). The angles between different {001} planes are measured much as Haüy originally did for single crystals; now we do this more accurately using diffraction patterns or high-resolution TEM (HRTEM) images. This experiment is special for ceramics because we are joining nanoparticles at high temperatures although we don't actually know when they joined so we don't know the sintering temperature. Figure 14.3 shows an example of such particles together with the frequency of occurrence, $f(\theta)$, of the misorientation angle. The oxide bicrystal particles form with a strong preference for certain orientations in which the two crystals have a fraction of their lattice sites in common: the coincidence boundaries. This experiment has long been one of the bases for believing that $\sum$ is an important parameter in determining energy of GBs. It doesn't measure γ but does suggest that γ is related to $\sum$. Unfortunately, results from computer modeling suggest that this is not necessarily the case, but it is such an attractive intuitive concept that it persists.

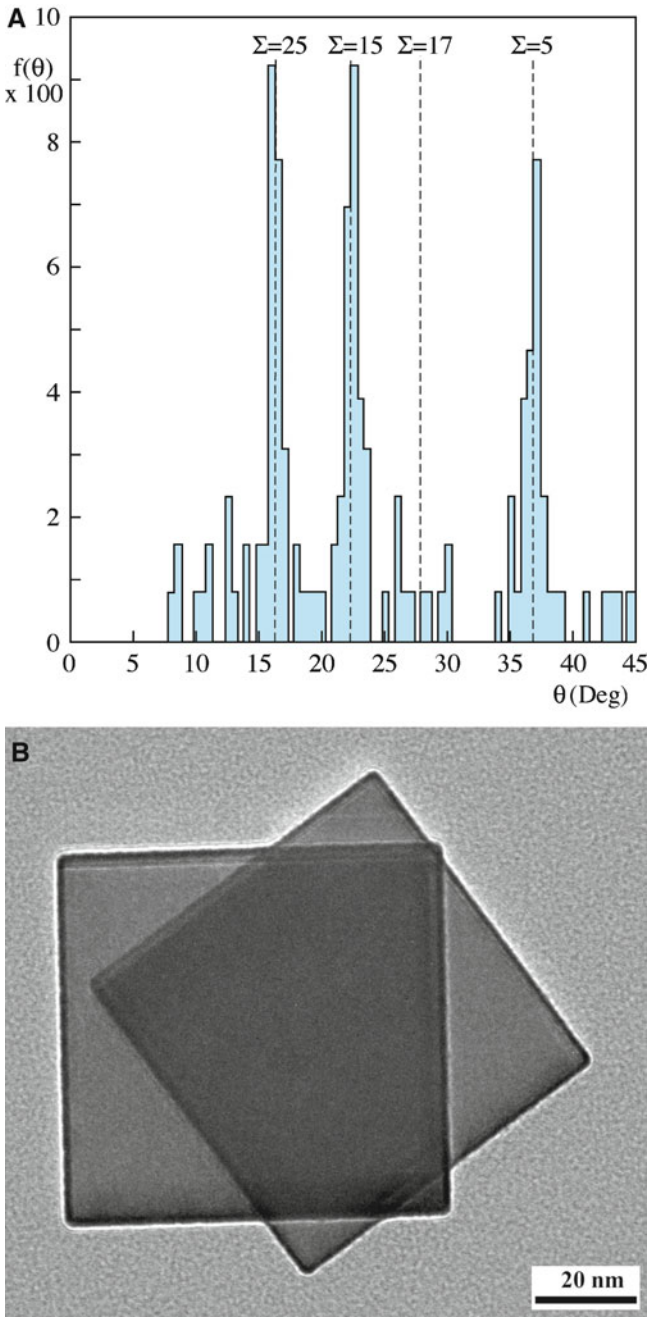

FIGURE 14.3. Rotated MgO nanoparticles and their relation to $\sum$. The frequency of measuring a rotation θ is f(θ).

14.3.2 Energy of Low-Angle GBs

When θ is small, the energy of a low-angle GB is approximated as the total self-energy of the dislocations within a unit area of the boundary. However, as θ increases, the stress fields of the dislocations progressively cancel out, so the energy increases at a decreasing rate and may peak before decreasing to a low value at a special orientation, as shown in Figure 14.4. When the dislocation spacing is small, the dislocation cores overlap, so when θ exceeds 10° (somewhere in the range of, say, 10–16°) it is not possible to identify the individual dislocations.

The Read-Shockley formula for the energy, E, of a low-angle GB considers the stress field and the core energy of the dislocations.

$$E = E_0\theta(A - \ln\theta) \qquad (14.1)$$

where E_0 is a constant that is a function of the elastic properties of the material (and hence of the stress field), and A is a constant that depends on core energy (remember our discussion of r_0, the dislocation core radius).

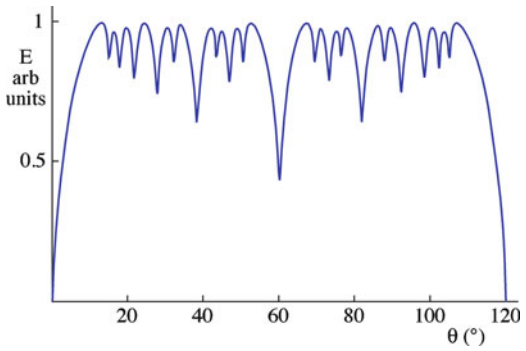

FIGURE 14.4. Cusp in a plot of GB energy versus the misorientation angle, θ.

We can also define the Gibbs adsorption isotherm for grain boundaries. We extend the analysis from surfaces to the internal interface.

$$\frac{\partial \gamma}{\partial \mu_i} = -\Gamma_i \tag{14.2}$$

where Γ_i is the excess moles of i per unit area of the GB. All the other variables (e.g., P and T) are held constant.

14.4 LOW-ANGLE GBs

Low-angle GBs contain arrays of dislocations. In its simplest form, the structure of the twist boundary consists of two sets of orthogonal screw dislocations, as shown in Figure 14.5A, B; the schematics show the structure before and after relaxation to form the screw dislocations. Figure 14.5C shows how dislocations in a twist boundary might be seen emerging at the surface; you can see that one part of the grain is physically twisted relative to the other because of the screw dislocations. The simplest tilt GBs consist of one set of edge dislocations, as shown in Figure 14.6. Note that the statements both include the word "simplest." Most tilt boundaries have two different sets of edge dislocations, and twist boundaries in noncubic materials may be accommodated by only one set of dislocations! Figure 14.6B shows that we must use two sets of edge dislocations if the GB is not symmetric. (We sometimes have to, even if it is symmetric).

Figure 14.7 is a TEM image of a twist boundary in Si; a tilt boundary in NiO is shown in Figure 14.8. The image of this tilt boundary is particularly interesting because it shows that the density is different at the GB.

The spacing of the dislocations, D, is related to the boundary misorientation angle, θ, and the Burgers vector of the dislocations, b.

$$D = \frac{\frac{b}{2}}{\sin\frac{\theta}{2}} \approx \frac{b}{\theta} \tag{14.3}$$

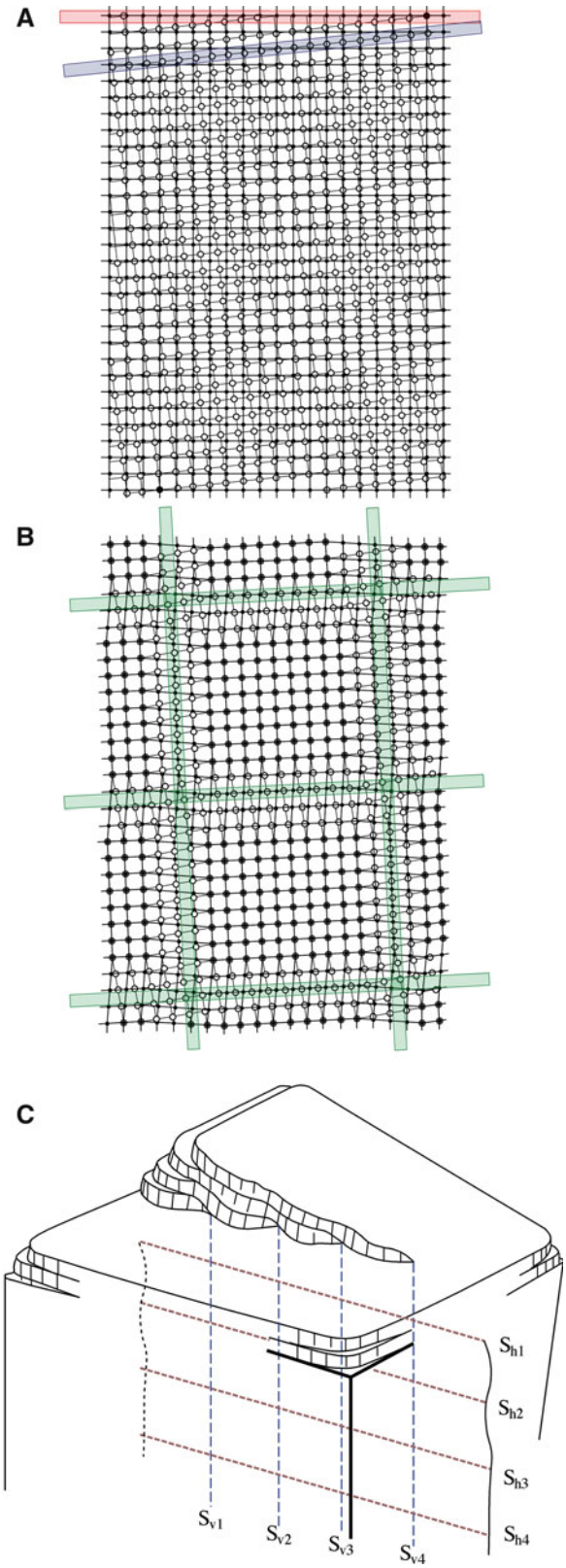

FIGURE 14.5. Low-angle twist GB. (A) Before and (B) after local atomic relaxations. (C) The twist when the GB emerges at the surface.

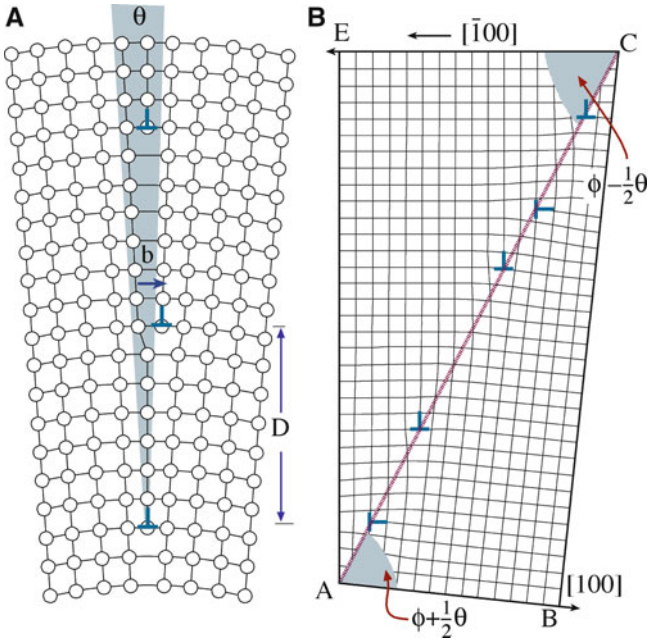

FIGURE 14.6. Low-angle tilt GBs. (A) Symmetric. (B) Asymmetric.

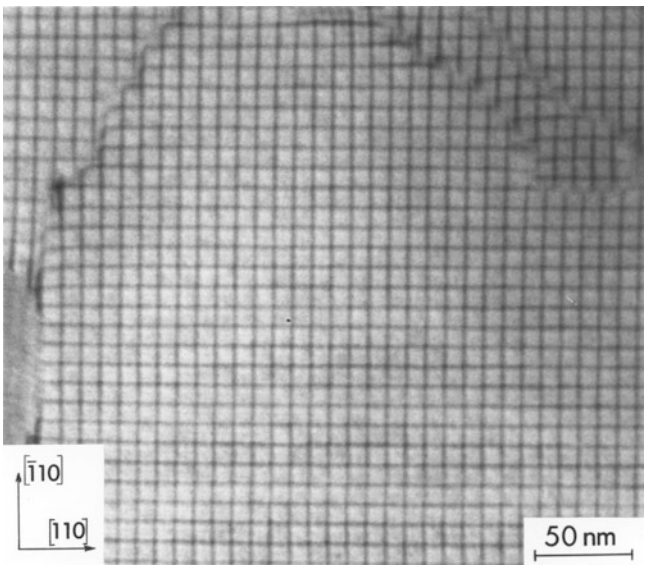

FIGURE 14.7. Two sets of orthogonal screw dislocations in a low-angle (001) twist GB in Si.

The latter relation holds only if θ is very small. In this case, we can reveal the individual dislocations either by decorating them or by etching the surface, as shown in Figure 14.9. Equation 14.3 has been well tested for face-centered cubic (fcc) metals and some simple ceramics.

The structure of dislocations and interfaces in ionic and covalent materials has been the subject of much theoretical and experimental research, motivated in part by the realization that the extensive body of information and concepts that have been accumulated for metallic systems cannot necessarily be directly transferred to these nonmetallic systems.

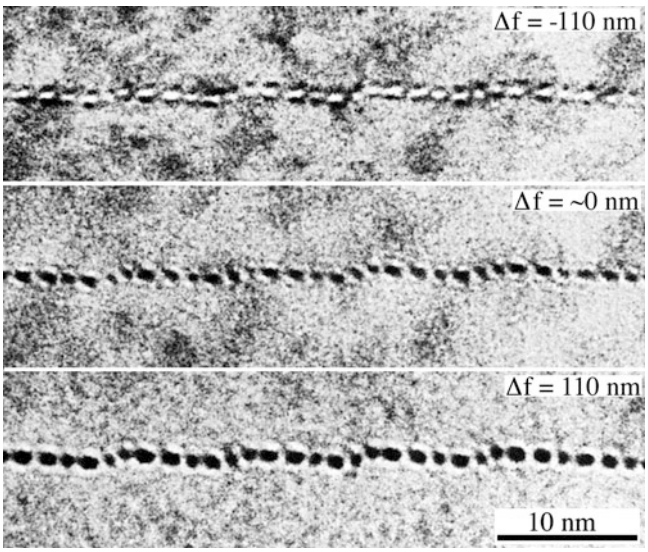

FIGURE 14.8. Dislocations in a low-angle tilt GB in NiO. The defocus (Δf) images show a change in density at the dislocation cores.

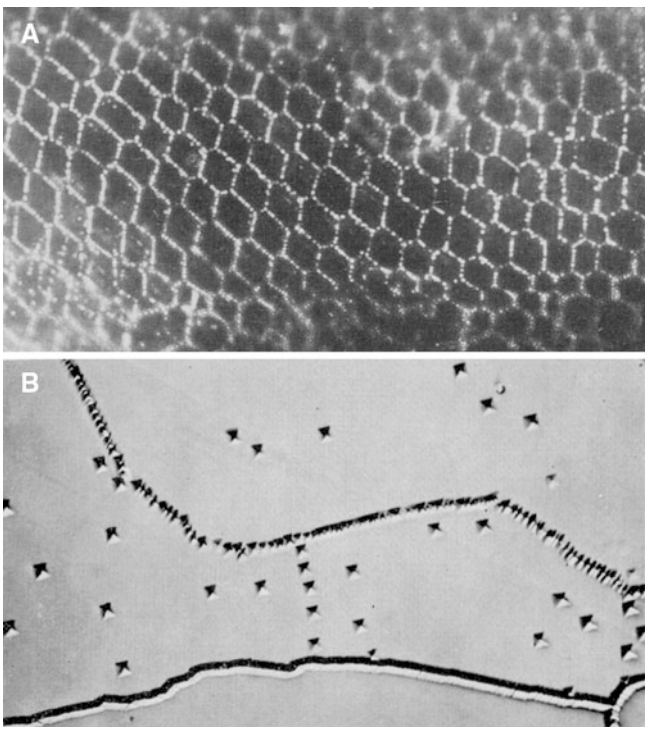

FIGURE 14.9. Seeing low-angle GBs by (A) decoration (silver particles on a GB in KCl) and (B) etch pits (LiF).

The structures of all defects in ceramic materials can be more complex than those of similar defects in the more thoroughly studied pure metals because of the presence of two or more ionic species on two sublattices. The implication of the presence of two types of ions is well known in ceramics as it results in the phenomenon of dissociation by climb of dislocations in the lattice or in the GB. The phenomenon has been recorded for such materials as spinel, Al_2O_3, and garnet. Actually, this phenomenon can also

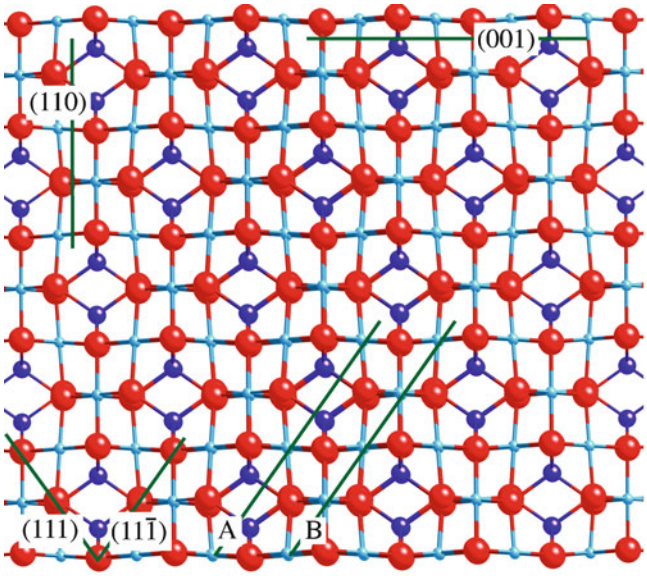

FIGURE 14.10. Spinel structure projected along <1$\bar{1}$0>, summarizing the important crystallographic planes. A and B are parallel but structurally different (111) planes.

occur in more complex metallic, ordered alloys for precisely the same reason. In Al_2O_3 and $MgAl_2O_4$, the partial dislocations created by the dissociation process are "perfect" dislocations of the oxygen sublattice; the stacking fault thus formed is therefore only a fault on the cation sublattice.

The effect of the large unit cell is well illustrated by the low-angle 111 twist boundary in $MgAl_2O_4$. The (111) interface plane can be chosen as A or B in the schematic of the crystal structure shown in Figure 14.10. In the spinel (111) twist boundary, an $^a/_2[1\bar{1}0]$ screw dislocation can dissociate on the (111) plane into two parallel $^a/_4[1\bar{1}0]$ screw partial dislocations (because a is large, and this dissociation produces dislocations that would have been perfect if we considered only the O ions). Because the self-energy of a dislocation is proportional to b^2, this dissociation halves the total dislocation self-energy. The partial dislocations are separated by a stacking fault (SF) but the energy of this fault depends on whether the glide plane of the plane of the stacking fault is A or B. Thus, there are two different stacking faults on a {111} plane and two different stacking fault energies (SFEs). The consequence of this multiplicity in the value of the SFE is illustrated in Figure 14.11, where the width of the SF takes on two distinct values for both GBs.

MULTIPLICITY

Low-angle and high-angle GBs, twin boundaries that appear to be macroscopically the same can exist with more than one different structures.

Figure 14.12 shows the climb dissociation of edge dislocations in a spinel tilt boundary. (This is just an extension of Figure 12.15.) In Figure 14.13, we can see a so-called extrinsic dislocation (along [100]) interacting

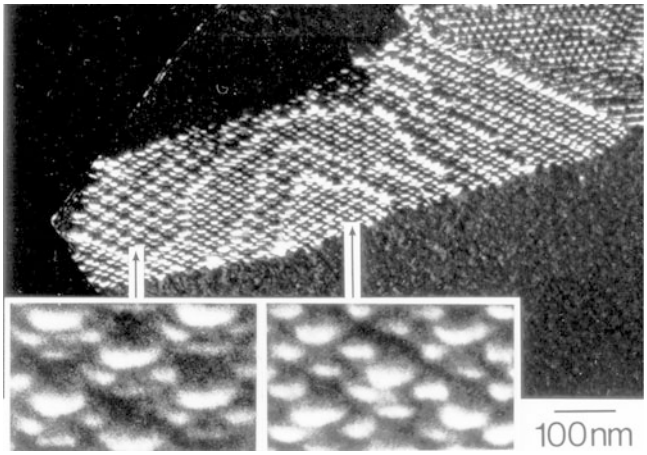

FIGURE 14.11. Low-angle {111} and {001} twist GBs in spinel, showing two structures in each case.

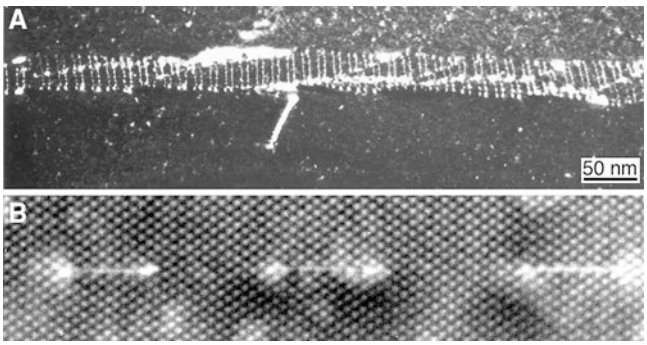

FIGURE 14.12. Low-angle tilt GB in spinel showing an array of climb-dissociated edge dislocations. (A) GB viewed at an angle. (B) Dislocations viewed end-on at higher magnification.

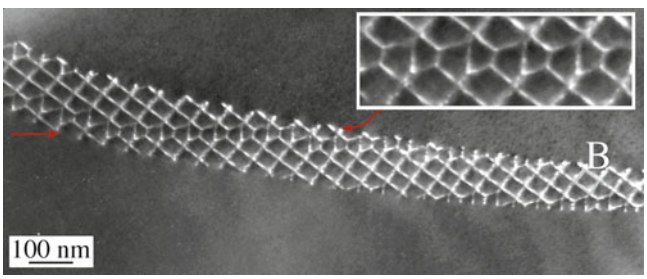

FIGURE 14.13. Extrinsic dislocation interacting with a low-angle {001} twist GB in spinel. Inset: note how all the dislocations are changed by the interaction.

with the screw dislocations that are already present in the interface (to accommodate the twist) in the (001) twist GB.

14.5 HIGH-ANGLE GBs

When θ is >10°, the interface is referred to as a high-angle GB. Figures 14.14 and 14.15 show schematics of the $\sum = 5$ GB in NiO in the tilt and twist configurations,

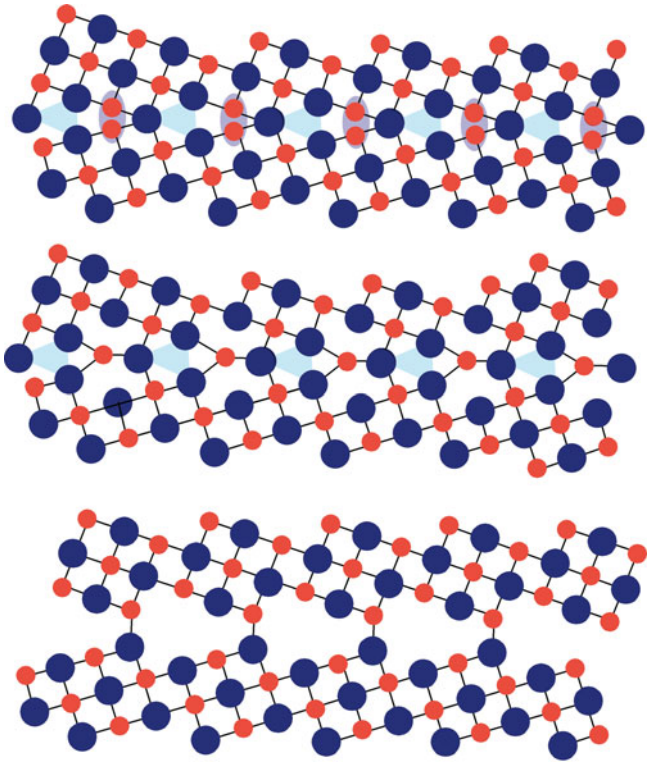

FIGURE 14.14. The [001] $\sum = 5$ tilt GB in NiO. Only the lower one is actually possible.

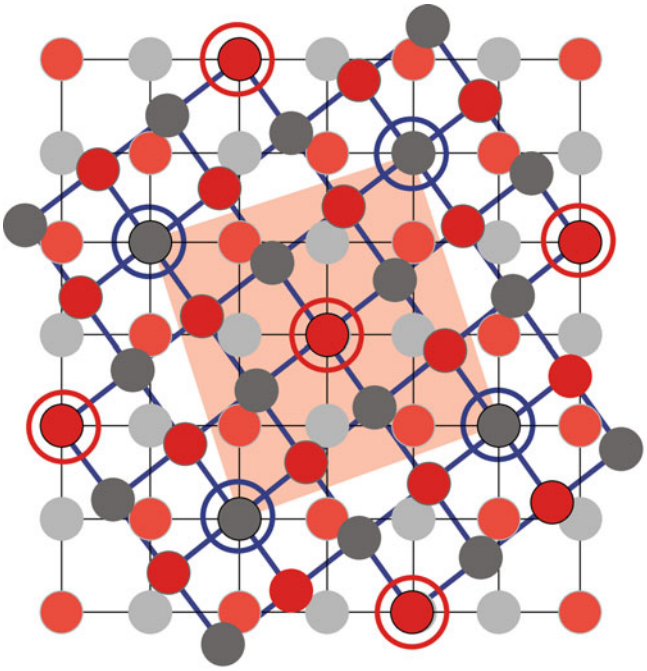

FIGURE 14.15. The (001) $\sum = 5$ twist GB in NiO showing anions and cations. This structure cannot occur unless some ions are removed.

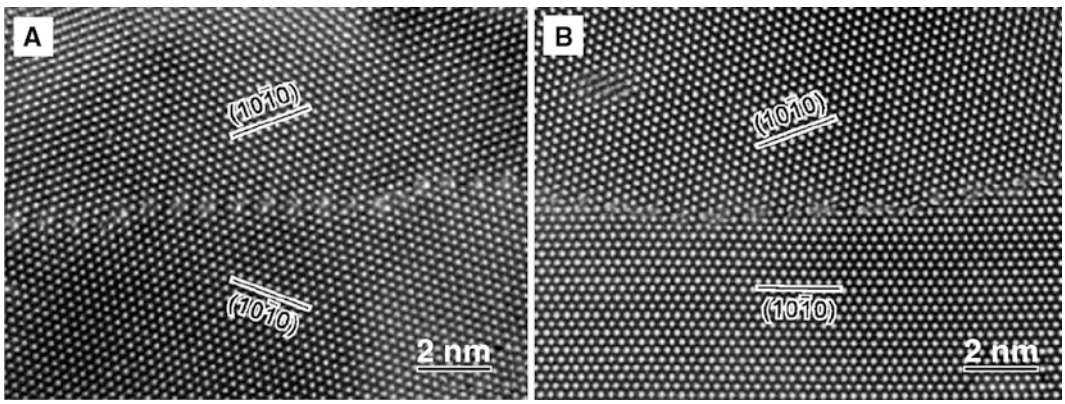

FIGURE 14.16. High-resolution transmission electron microscopy (HRTEM) images of two high-angle GBs in ZnO. (A) Near-symmetric. (B) Asymmetric.

respectively, and taking into account the presence of two ions. The situation is clearly complex: only the lower structure in Figure 14.14 could exist (the others have similarly charged ions too close together). The same considerations hold for the twist GB shown in Figure 14.15: when two ions of like charge are adjacent, one must be removed. As in the low-angle case, high-angle GBs can exist with more than one structure. Figure 14.16 shows images of two special GBs in ZnO; the difference between a symmetric high-angle GB and the lower-angle asymmetric counterpart is striking; this type of asymmetric faceting often involves low-index planes, as shown here. You can imagine why asymmetric units might be favored after examining Figure 14.17, which shows a schematic of a GB in Al_2O_3. Polyhedra that were not present in the perfect crystal in Chapters 6 and 7 can be present at a high-angle GB, and they can accommodate larger impurity ions than can the bulk.

More complex high-angle GBs have been the subject of far fewer studies, in part because of the experimental difficulties in characterizing them. This lack of information is unfortunate as these interfaces are ubiquitous in sintered materials. High-angle GBs formed by hot-pressing together two single crystals of MgO appear to behave as would have been anticipated from studies on the corresponding interfaces in fcc metals and semiconductors. They support the earlier interpretation of experiments on MgO "smoke." However, such interfaces have been the

subject of extensive computer-modeling studies that often give a contradictory view.

As these observations show, the plane adopted by a high-angle GB is a very important factor. Such GBs in ceramic materials show a particularly strong tendency to facet, so the plane must be important. These facet planes are almost invariably parallel to low-index planes in one or both grains. The basic argument is that low-index planes are the most widely separated planes and thus involve less energy when a "stacking error" is present in the crystal.

A particularly striking illustration that makes us question the importance of $\sum$ as a measure of the energy of a GB is provided by observations of the $\Sigma = 99$ and $\Sigma = 41$ boundaries in spinel where, by chance, the interface can facet parallel to several pairs of (different) low-index planes in both grains simultaneously. A similar situation exists for phase boundaries. It could be that the faceting onto low-index planes lowers the energy to below that of similar GBs having a lower $\sum$. There are no atomistic calculations for such GBs.

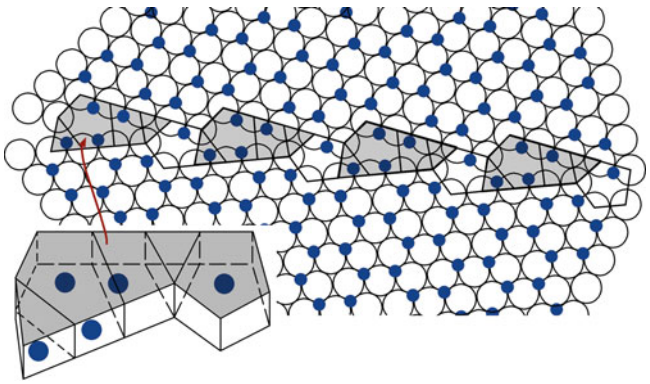

FIGURE 14.17. GB in Al_2O_3 shows the creation of new polyhedra in the GB. Inset: tilted view of the repeating group of polyhedra.

14.6 TWIN BOUNDARIES

As in metals, twin boundaries are common in many ceramic materials, including MgO, spinel, Al_2O_3, Fe_2O_3, the rare earth oxides quartz, and Si, and of course the new high-T_c superconductors. Indeed, it seems certain that such interfaces occur in all crystalline ceramic materials. Some special twin relationships observed in minerals are illustrated in Figure 14.18. The observation of so many twin boundaries is interesting because they are found to facet parallel to low-index planes in at least one grain. We noted that such interfaces can accommodate impurity ions, and this can lead to the phenomenon of chemical twinning, wherein apparently different crystal structures can be related to one another by the periodic repetition of a pair of twin interfaces. This concept can be used to understand the actual mechanism of a phase transformation in a ceramic system.

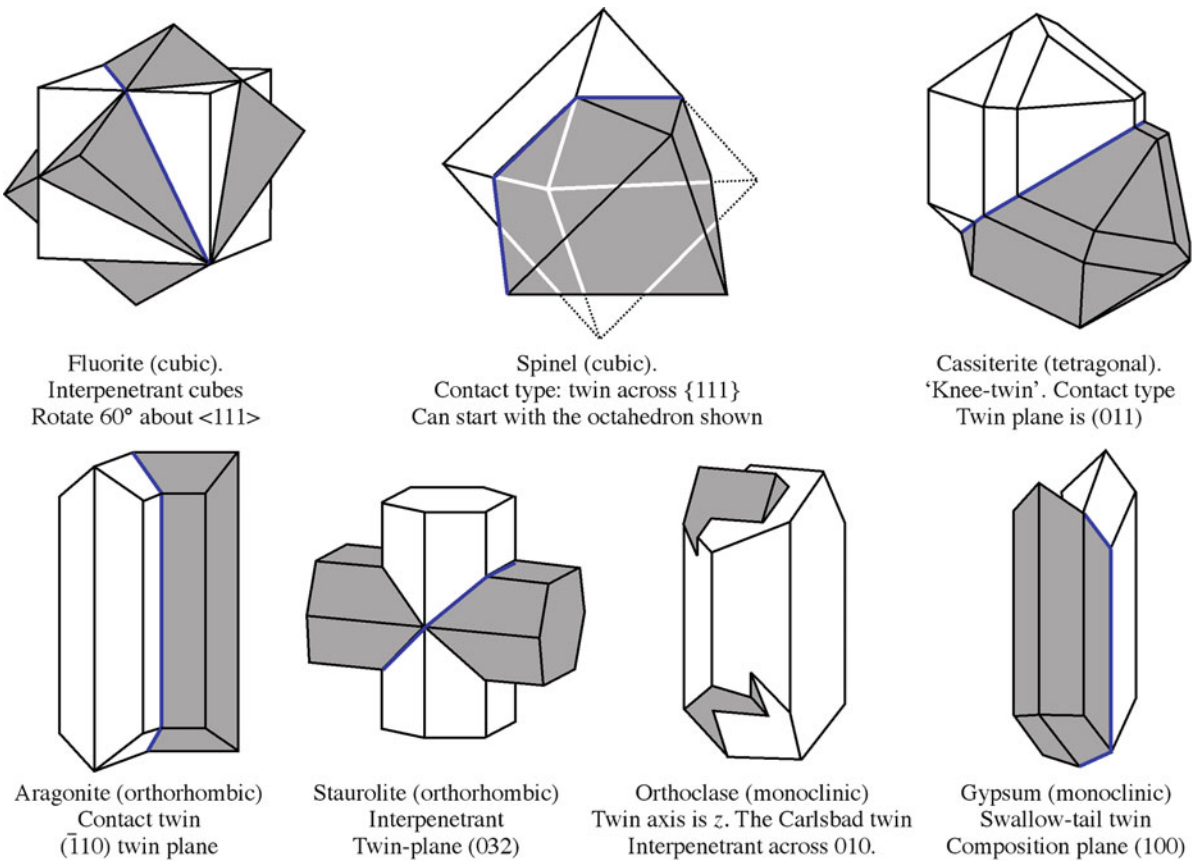

FIGURE 14.18. Examples of twinned grains found in different minerals. The twin plane is outlined in *blue*.

14.6.1 Al_2O_3

Several different types of twin boundaries have been seen in Al_2O_3; the basal twin boundary is the $\sum = 3$ GB that was discussed in Figure 14.1A. We can form a variety of twin boundaries in Al_2O_3 by mirroring the structure across low-index planes that are not mirror planes in the perfect crystal; hence, the $(\bar{1}102)$ plane, the $(1\bar{1}04)$ plane (illustrated in Figure 14.19), and the $(11\bar{2}3)$ plane all give twin boundaries [as does the (0001) plane, of course]. A rhombohedral twin boundary [the $(10\bar{1}2)$ twin boundary] is shown in Figure 14.20; notice that it is faceted.

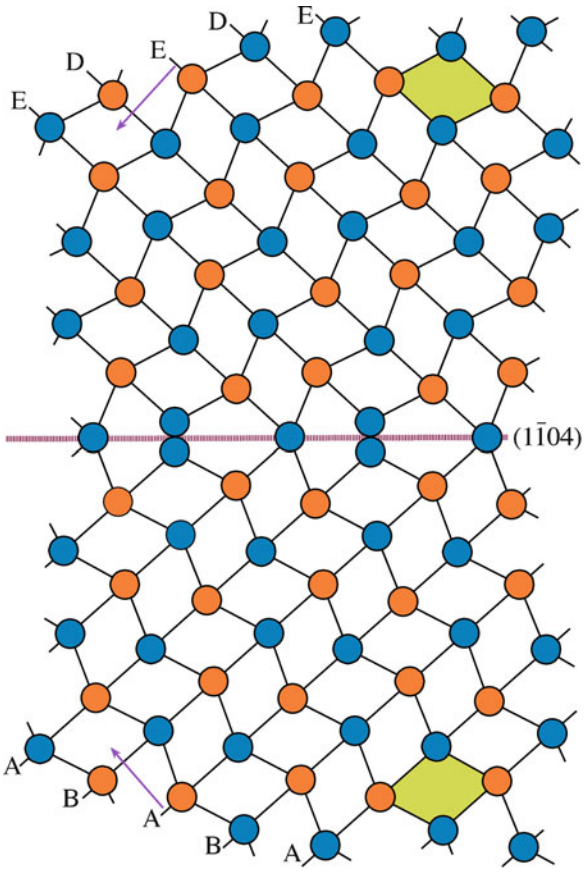

FIGURE 14.19. A $(1\bar{1}04)$ twin boundary in Al_2O_3. The *arrows* show the <0001> directions; the letters show the hexagonal close-packed (hcp) stacking of the anions. The cations are omitted but sit in the octahedral, shown by the *shaded rhombi*.

THE TWINS
A twin is a grain; a twin boundary is a GB.

14.6.2 Spinel

All interfaces in spinel, even the $\sum = 3$, (111) twin boundary, can exist with at least two different structures. In a formal treatment of such interfaces, the different structures considered here can, in principle, be described by choosing different rigid-body translation vectors. However, such translations are not the small relaxations familiar in, for example, the {112} lateral twin boundary in Al but are more closely related to stacking faults in fcc metals. The image in Figure 14.21 shows two parallel {111} twin boundaries (separated by a microtwin). The translations at the two twin boundaries are different, as you can see in the insets. This translation, which is parallel to the {111} plane, is seen because of the location of the cations. As far as the oxygen sublattice is concerned, the twin interface is actually a mirror plane: it's just like the {111} twin boundary in fcc Cu.

The lateral $\Sigma = 3$ twin boundary in spinel is also special. The structure of this interface can be entirely described in terms of {111} segments (which may have different structures, as noted above) and triangular-prism channels, which lie along <110> directions and are observed as white spots in high-resolution TEM images. The faceting consists entirely of ordered (aligned) arrays of these prism columns; the interface shown here is actually dislocation-free, although the prisms can be modeled as an

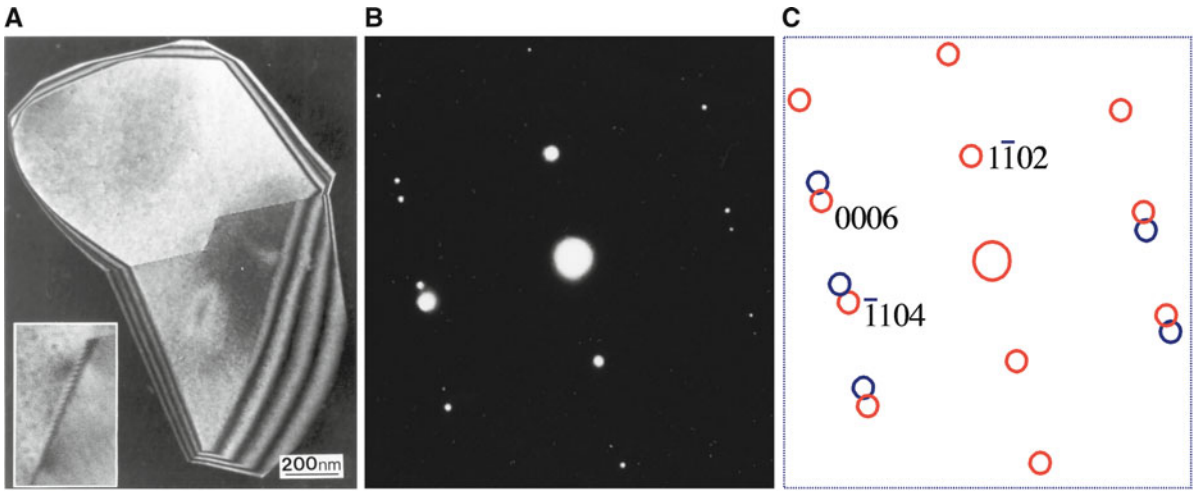

FIGURE 14.20. Rhombohedral twin boundary in Al_2O_3 and its diffraction pattern.

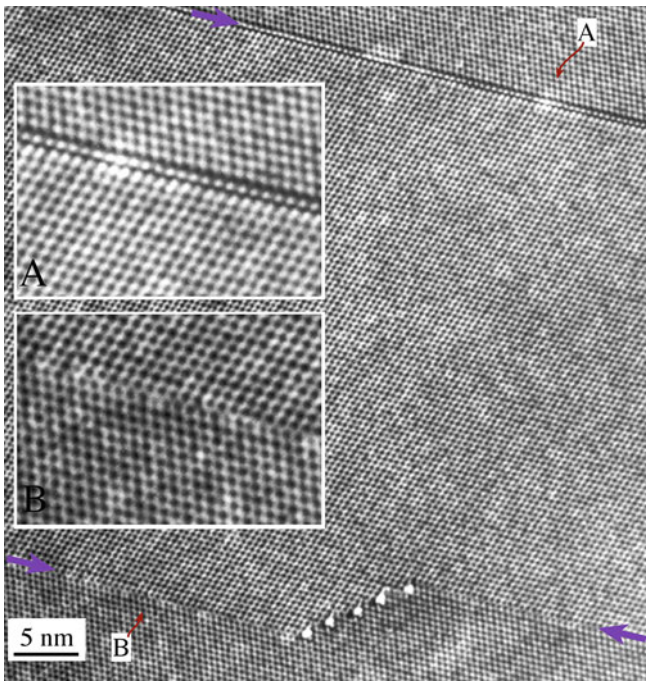

FIGURE 14.21. Two parallel {111} $\sum = 3$ twin boundaries in spinel having different structures (identified by arrows). Insets: Regions A and B at higher magnification.

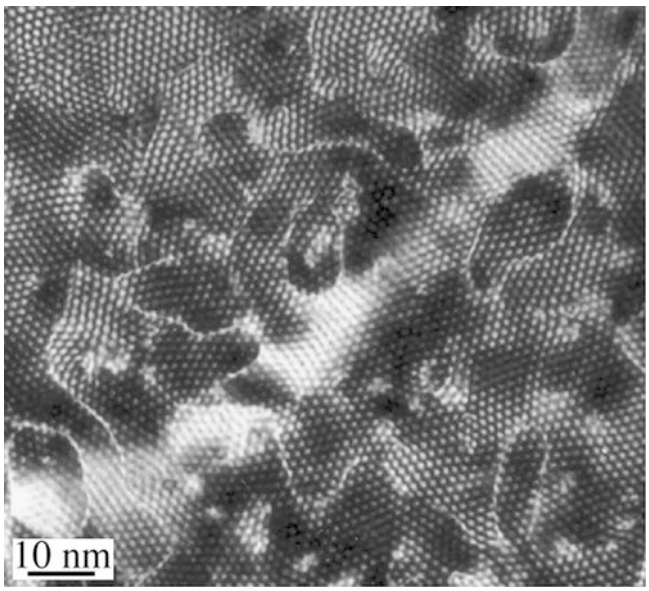

FIGURE 14.22. Curved twin boundaries in a thin film of NiO on an Al_2O_3 substrate. (The hexagonal pattern is a moiré interference effect).

array of dislocation dipoles. There was no local strain contrast in the TEM image.

14.6.3 NiO

The images shown in Figure 14.22 are from a thin film of NiO and remind us that GBs that correspond to a special twin orientation are not necessarily flat. In that case, they are probably more similar to other high-angle boundaries. The twin boundaries in the NiO film occur because NiO

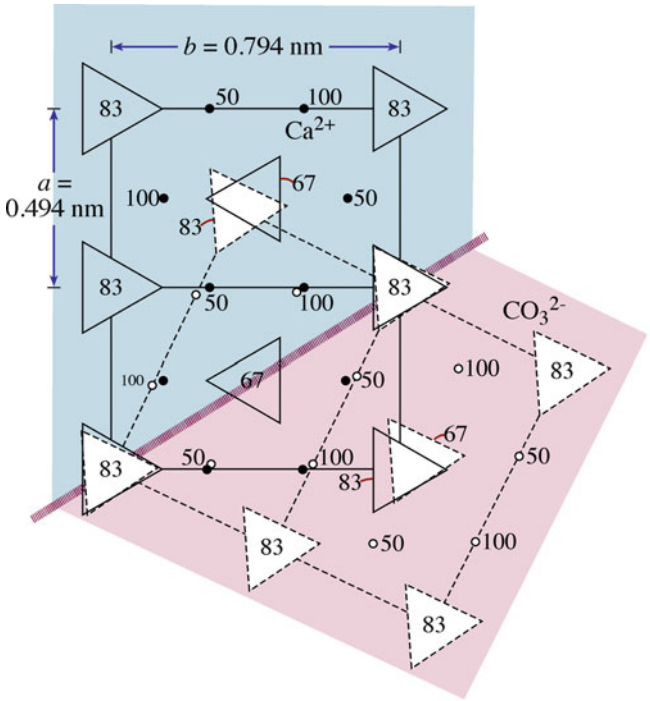

FIGURE 14.23. Mimetic twinning in aragonite. This gives rise to trilling twins when the operation is repeated.

can grow on a basal-alumina substrate in two twin-related orientations. We see the twin boundaries because the density is lower at the GB.

14.6.4 Aragonite

An example of how twins can form in a more complex system twins is shown in Figure 14.23 for aragonite. This figure shows the CO^{2-} anions as triangles (as we saw in calcite), and the closed circles represent Ca^{2+} ions. (The numbers give the heights of ions in the cells and serve to emphasize the twin symmetry).

14.6.5 Chemical Twins

A special group of closely related oxides is illustrated in Figure 14.24. These oxides consist of blocks of MO_6 octahedra (seen as squares along the cube direction), which can be shifted parallel to certain crystallographic planes (known as shear planes) to produce new structures. The circles are tetrahedral cations. Essentially, the shearing acts to change the chemistry along that plane. *Crystallographic shear planes* are thus like regular stacking faults but the chemistry also changes—they are called *chemical stacking faults*. An example of WO_{3-x} encapsulated in WS_2 is shown in Figure 14.25.

Twin boundaries, like other GBs, can accommodate new ions so that the chemistry changes along the twin plan. A periodic repetition of alternating twin planes, each of which accommodates ordered impurities, can then give rise to a new structure. This process is known as *chemical twinning*. The result for β-alumina is illustrated in

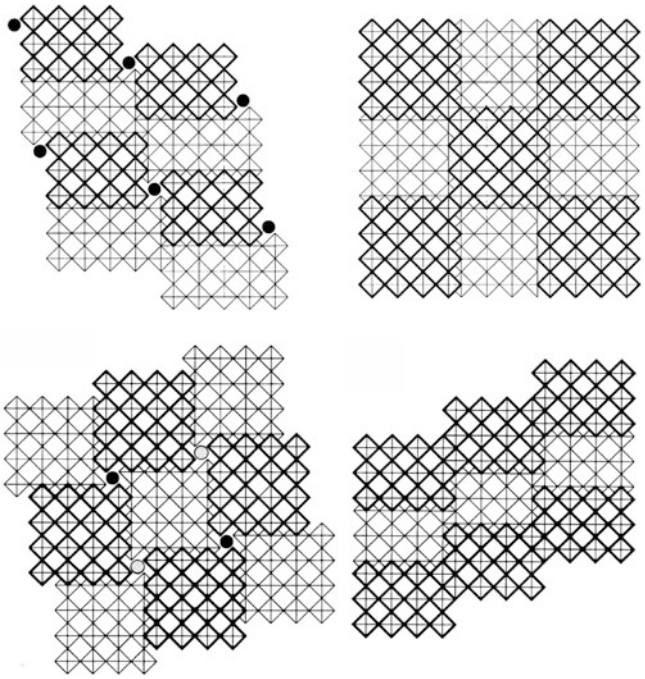

FIGURE 14.24. Shear planes in WO_3. *Dark* and *light* lines are at heights 0 and 0.5.

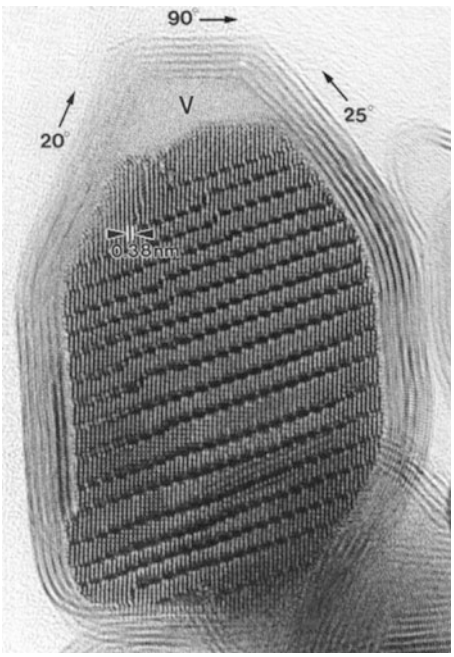

FIGURE 14.25. Defect W oxide encapsulated in a fullerene.

Figure 14.26. Planar defects can readily be incorporated into this structure. This particle of β‴-alumina contains a sheet of spinel; the spinel is like a sheet of a second phase. As we saw in Section 7.12, we can also think of the structure of the β‴-Al_2O_3 as being blocks of spinel that twin on every six {111} oxygen planes. The attractive part of this description is that we can then understand the fault in the structure where the twin occurs after only four {111} oxygen planes. Remember that the twin planes are not

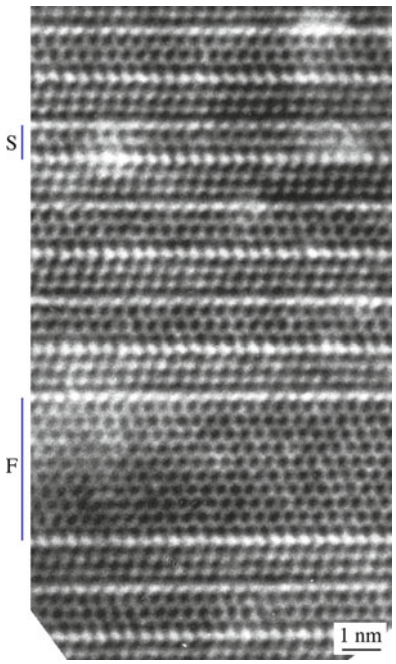

FIGURE 14.26. Structure of β-alumina as a repetition of chemical twin boundaries. S and F are a block of spinel and a stacking fault, respectively.

actually spinel twin planes because the chemistry is different on the twin plane.

14.7 GENERAL BOUNDARIES

General boundaries may be curved with no specific value of $\sum$. Can we know if the GB is clean, or what its structure is? We can know if it is not clean and put an upper limit on the impurity content but we still won't know its structure.

The relationship between the physical parameters of any individual interface and the mechanical strength or properties of that interface has not been directly determined for any ceramic material. As with many properties of ceramic materials, measurements on GBs are likely to be controlled by dopants or impurity phases; the latter may be present at the 10% level. Computer modeling is usually carried out for pure materials. Finite element modeling (e.g., used for fracture studies, crack initiation and propagation), generally makes assumptions regarding the elastic parameters that may be very different at an impure interface in comparison to bulk material; the bonding at the interface is different, so the elastic properties must be different too.

14.8 GB FILMS

In Chapter 13, we discussed how a liquid behaves on a solid surface if the solid is not inert. We noted that the situation could change due to evaporation at high temperatures and that the wetting phase need not be a liquid to wet or dewet.

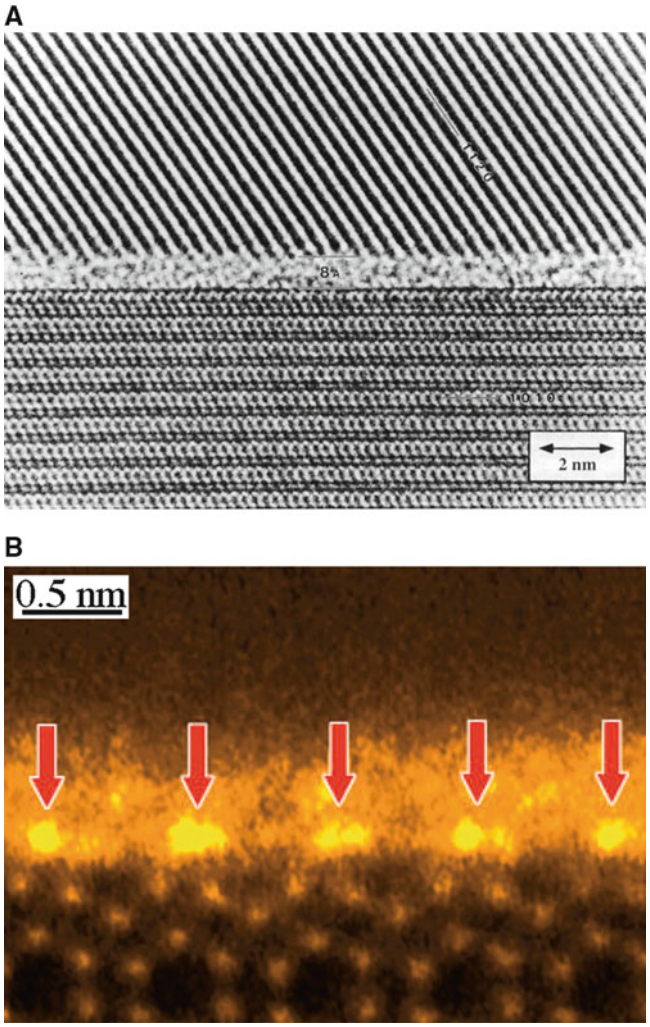

FIGURE 14.27. HRTEM images of intergranular films (IGFs) in Si_3N_4. (A) Phase contrast image. (B) Z-contrast image showing ordering of rare-earth dopant at the glass/crystal interface.

- GB films are directly analogous to films on surfaces or substrates.
- How thick must a film be before it's a new phase?
- Is a GB containing a film one interface or two?

The simple view of whether a glass film is energetically favorable is that if $2\gamma_{sl} < \gamma_{GB}$ the film is preferred. This statement is too simplistic, in part because GB films are unlikely to be uniform across their thickness. If γ_{sl} is $\sim\gamma_{GB}$, we would expect the GB to be stable; but even in this case the glass must go somewhere.

Any of the four types of GB could contain a GB film. How stable the film would be clearly depends on the energy of the GB with the film versus without it and the availability of a mechanism for removing the film if it would lower the energy.

We know that liquid phases can be very important in polycrystalline ceramic materials. We know that most interfaces in some ceramics (e.g., Si_3N_4) contain a very thin (~1–5 nm) intergranular film (IGF), as illustrated in Figure 14.27A. Thin amorphous layers have been reported to be present in a wide range of ceramic materials (see Table 14.1). It is sometimes incorrectly assumed that all GBs (other than special twin boundaries) in Al_2O_3 contain such a thin amorphous film. In some materials, the same interface may or may not contain an amorphous film, depending on how it was processed.

- Glass is very often present in ceramic materials, whether intentionally included or not. In many oxides, it is present because of impurities in the initial materials used to process the compact. In others, it is intentionally added to lower the processing temperature via the process of liquid-phase sintering.
- The width of glassy GB films can vary from ~1 nm to >1 μm.
- The TEM techniques used to identify these films do not always give unambiguous results.
- At high temperatures, the mechanical properties of a ceramic may be drastically lowered if a glass is present. For example, the viscosity of the glass decreases significantly at a relatively low temperature, leading to enhanced creep and related phenomena; remember that the viscosity of soda-lime-silica glass varies from 10^{15} dPa s at 400°C to 10^2 dPa s at 1,300°C. At the higher temperature, glass cannot support a shear stress and allows rapid deformation of the material. In other circumstances, the presence of the glass may be beneficial because it may assist in the branching and blunting of cracks by generally weakening grain boundaries.
- It is much easier to process ceramics in the presence of a liquid phase, in part for the same reason—the glass allows deformation at lower temperatures; diffusion is also faster through a glass. The glass thus allows the sample to be shaped and/or densified at lower temperatures.
- The composition of the IGF may vary across its width. In Figure 14.27B, the rare-earth dopant has formed an La-rich monolayer at the glass/crystal interface.

TABLE 14.1 Examples of Intergranular Phases

System	*Property affected*	*Notes*
Glass in Si_3N_4	Mechanical	Glass forms from components added as sintering aids and oxide on particle surfaces
Glass films in Al_2O_3	Mechanical	Impurities in the glass can affect its properties
Bismuth oxide in ZnO	Electrical	IGF is key to the operation of varistors
YAG in AlN	Thermal	Y_2O_3 added as sintering aid to allow lower cost production of substrates
Surface contamination	Chemical	Oxidation of SiC can passivate the surface
Clean GB in YBCO	Electrical	GB may not be superconducting; if very thin, they can act as weak links

It is well known that the presence of glass in GBs greatly enhances sintering, in part, because transport of matter along and across the intergranular regions is then even faster than when no glass is present. It is important to realize that the glass does not act simply as a catalyst but also changes the character of the interfacial regions. The glass can dissolve the crystalline grain and reprecipitate it elsewhere. In particular, it tends to encourage faceting of the grains; the scale of this faceting may vary from nanometers to micrometers. After processing, the glass may remain as a thin layer in the interface during preparation of the polycrystalline compact, as was initially demonstrated for Si_3N_4. The glass may also crystallize to form an intergranular crystalline layer, or it may withdraw from the planar interfaces into three-grain and four-grain junctions (the dewetting process). Even though great care may be taken to ensure that no glass is present during processing, the glass may subsequently enter the interfacial region during processing or service of the component. In either case, the properties of the ceramic may be greatly influenced by the presence of any glass in the grain boundary; a dramatic example is the effect on mechanical properties (e.g., for Si_3N_4 or Al_2O_3), which also aids sintering, although other properties (e.g., the thermal conductivity for AlN) may be just as strongly affected.

IGFs

A note on very thin films: if a film is ~1 nm thick and the system is in equilibrium, then the film may be better described as an absorbate layer. Experimentally, the challenge is knowing that the system is in equilibrium.

Figure 14.28 illustrates another feature associated with glass in crystalline ceramics. The pairs of grains joining at these two boundaries are similarly oriented. Both of the interfaces contain dislocations; that is, they were glass-free after processing. The topology of the two interfaces is, however, clearly different. In Figure 14.28A the interface is wavy, whereas in Figure 14.28B it is flat. The difference can be explained by the processing history; the bicrystal in Figure 14.28B initially contained a layer of glass whereas that in Figure 14.28A was kept as clean as possible during processing. Hence, the difference in the topography is ascribed to the effect of the glass while it was present in the interface. Clearly this effect can potentially be very important in understanding such GBs, but it presents a major difficulty as the key component required to explain the structure of the GB had already disappeared before the processed compact could be examined.

Water in silicate GBs can significantly change the mechanical properties of the GB. The GBs really are wet in the everyday sense! The crystal structure of the grains causes ordering in the water and thus changes the viscosity of the water.

The behavior and effects of water in GBs is an important topic in geology. There has been much discussion on the thickness of intergranular glass films. There may be an equilibrium thickness for such films, as has been reported for Si_3N_4; but a more common situation is shown in Figure 14.29. This sample was a dense, small-grain, glass-free polycrystal that was intentionally infiltrated with monticellite glass. Here the width of the glass layer clearly varies from boundary to boundary and even along a particular boundary. Nearby boundaries show a layer that is nearly uniformly 2 μm wide or that is apparently glass-free at this magnification. This image illustrates an important factor that is often overlooked: most of the glass is contained in triple junctions (TJs) and quadruple junctions (QJs). These junctions serve as "pipes" for transporting the glass. Very little is known of the characteristics of TJs (they are not TEM-friendly) or their role in determining mechanical properties.

Figure 14.30 shows a $\Sigma = 13$ GB in alumina that was processed with an initial layer of anorthite glass that had a uniform thickness of ~100 nm. The glass is still present in the interface after processing, but it varies in thickness along its length. Here, the explanation for the thickness

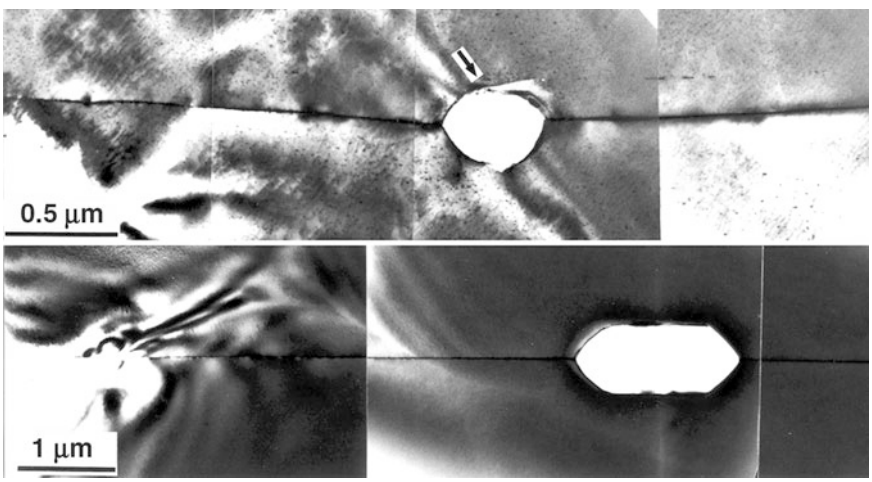

FIGURE 14.28. The same GB in Al_2O_3 processed (A) without glass and (B) with glass.

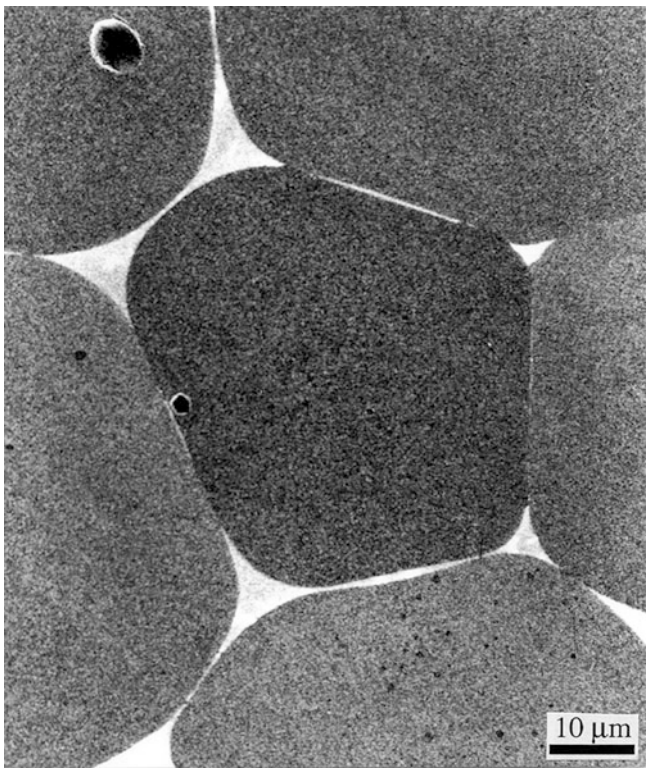

FIGURE 14.29. Scanning electron microscopy (SEM) image of glass-infiltrated MgO shows glass located at the GB and at triple junctions (TJs), but even in a GB it need not be a uniform layer.

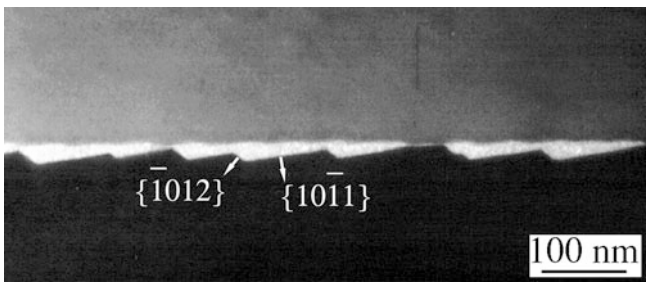

FIGURE 14.30. Intergranular film in Al_2O_3 that was initially uniformly thick but varied in thickness after heat treatment.

variations is clear: the two glass/crystal interfaces facet independently except in the regions (arrowed) where they appear to touch. The controlled preparation of such interfaces is not, in principle, limited to special boundaries because any two such surfaces can be so joined and both the composition and the initial amount of glass can be predetermined and controlled.

Dewetting of GBs has been observed in Si where the glass was the native oxide SiO_x (x~2). Figure 14.31 shows TEM images of a $\Sigma = 1$ (low angle) <110> tilt boundary and a $\Sigma = 5$ (001) twist boundary. In both cases, abrupt changes in contrast can be seen where the glass has dewet the interface to accumulate in pockets. The pockets actually facet parallel to {001} and {111} places due to the crystallography of the Si. Thus, even the $\Sigma = 5$ GB can achieve its low-energy structure, including the secondary dislocations, in the presence of a dewetting glass film.

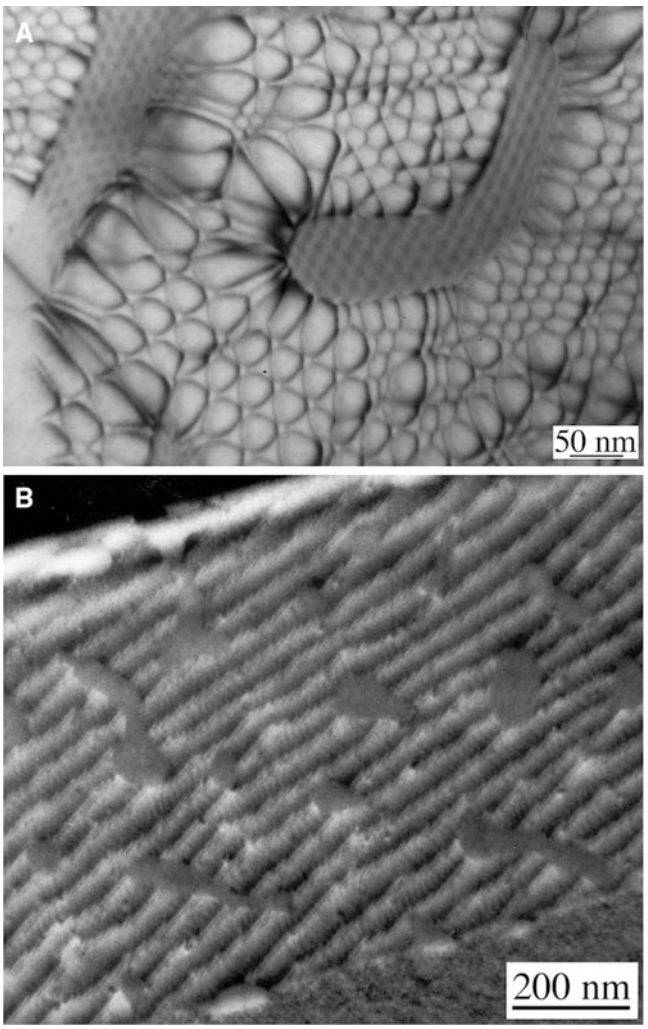

FIGURE 14.31. Dewetting of IGFs in Si GBs. (A) $\sum = 1$ {111}. (B) $\sum = 5$ {001}.

The possibility of crystallizing intergranular glass layers after processing has been used to modify the mechanical properties of the resulting compact. The yttria-rich glass in polycrystalline Si_3N_4 and monticellite glass in MgO can be crystallized after liquid-phase sintering to change the properties of the polycrystal.

An important remaining question concerns how the presence of the second glass–crystal interface (in a GB) might affect the crystallization process. If topotactic crystallization nucleates at one glass/crystal interface, it is unlikely that the crystallizing glass will form a complex (high-energy) interface when it reaches the adjacent grain. Similarly, if crystallization nucleates at both glass/crystal interfaces, a complex grain boundary, possibly with residual glass, forms when the crystallized glass layers grow together.

14.9 TRIPLE JUNCTIONS AND GB GROOVES

We don't spend much time on TJs because not much is known about them. We can identify three different types of TJ.

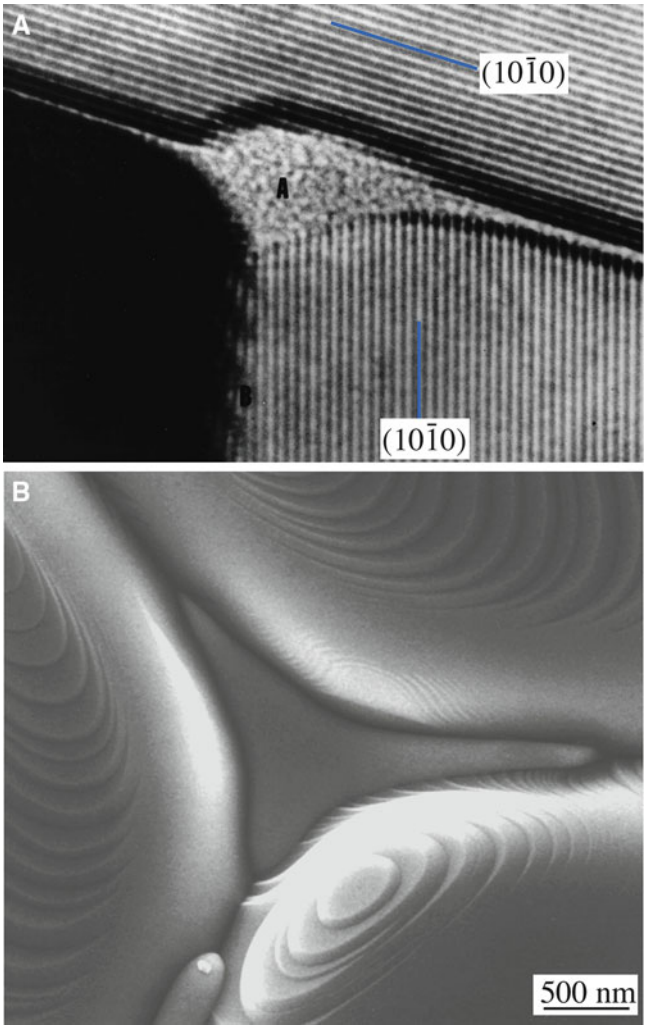

FIGURE 14.32. Examples of TJs: (A) Si_3N_4 using TEM. (B) MgO using SEM.

1. One composition: three-grain junctions
2. Two compositions: two phase boundaries plus a GB
3. Three compositions: three phase boundaries

Thus, for example, the groove formed when a GB emerges at a free surface is an example of a two-composition triple junction. Three TJs meet at a QJ. The pockets of second phase at TJs in Figure 14.32 could each be considered as sets of three two-composition TJs. Incidentally, looking at the surface does not give us an unambiguous picture of the dimensions.

A diagram showing how GBs, TJs, and QJs change with changes in wetting behavior is shown in Figure 14.33. Wetting is clearly important when we process ceramics using a liquid phase. For the liquid phase to be effective in densification, we want it to wet the grains: hence $\phi = 0$. However, for optimum properties of the final ceramic, we may not want the grains covered with a second phase. A good example is in AlN ceramics for electronic packaging. The second phase, which almost always has much lower thermal conductivity, should form isolated pockets at the TJs, leaving a "clean" GB, enabling maximum phonon transport.

A TJ can act like a capillary. The TJ in Figure 14.34 was covered with liquid glass at the processing temperature. When the sample was cooled, the liquid withdrew into the TJ like water escaping a bath (but the physics is different).

14.10 CHARACTERIZING GBs

When studying a GB, we want to know the structure, chemistry, and bonding. How do we characterize a GB? What are the parameters we need? Just to understand the structure, we have to know all the crystallographic parameters, then the chemistry, and then the bonding. No single technique gives us all this information. No ceramic GB has been fully characterized, although we are getting close with a few.

Plane of boundary—Is the GB flat?
Axis of misorientation—The GB is an internal interface, so we need the orientations of both grains.
Atomic structure of boundary—The GB must be flat for HRTEM.

Internal interfaces are fundamentally different from surfaces because of their inaccessibility. The key tool for studying GBs is TEM. This should be obvious from the number of TEM images in this chapter! Although the material must usually be thinned prior to examination by TEM, the area of the GB we do examine is unchanged.

TEM can be used to observe a periodic array of edge dislocations. We use a Burgers circuit to characterize the dislocations.
We can probe a GB by scanning tunneling microscopy (STM) only where the GB intersects the surface. Atomic force microscopy (AFM), on the other hand, is a key tool for characterizing GB grooves.

The specimen-preparation problem for TEM: GBs in ceramics must be considered in terms of both their structure and chemistry (even in so-called pure materials). Because the wetting behavior of a surface may be altered by the doping of the surface layer, it is important to identify and characterize the segregation of impurities and additives to GBs in these materials. The problem here is twofold: the features of the GB (its misorientation and plane) must be identified, and the distribution of "foreign" elements must then be accurately measured. The last part of this process is actually even more difficult than you might expect. The added complexity arises from the methods that are, at present, routinely used to prepare samples of ceramic materials for examination by TEM.

The TEM specimen is usually thinned by ion-milling; crushing fractures the sample along the GBs. This thinning process has been shown to result in cross-contamination of

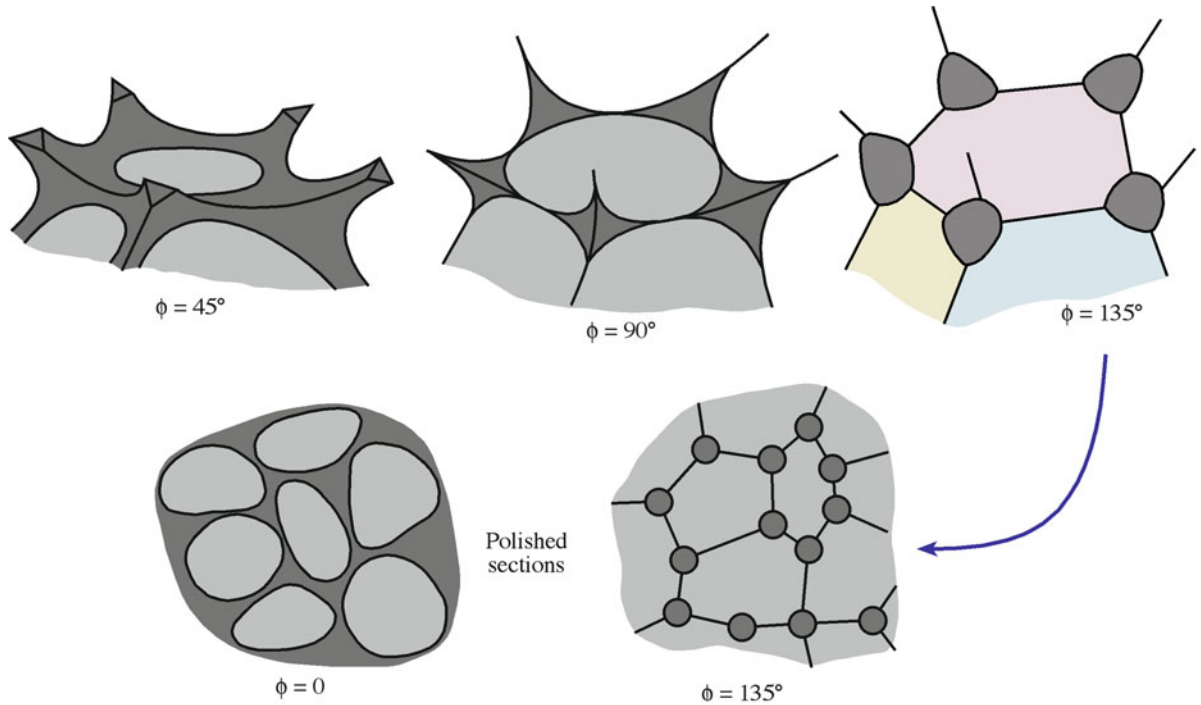

FIGURE 14.33. Three-dimensional relationships between IGFs, TJs, and QJs as the wetting angle is changed. Lower: a reminder that we usually see sections of these structures.

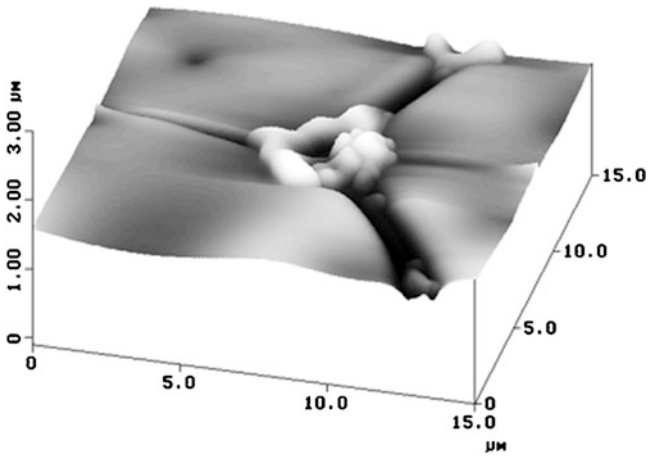

FIGURE 14.34. Direct evidence for the capillary effect at a TJ. The glass recedes into the TJ on cooling.

the specimen and in the formation of a groove at the interface. The degree of contamination depends on a large number of factors.

The type of oil used in the diffusion pump of the ion-miller. (Old ion-millers may use a silicone-based diffusion pump oil because it is less expensive and more resistant to cracking than are Si-free oils).

The cleanliness of the system used to carbon-coat the thinned TEM specimen is a factor.

The ion-thinning process also preferentially removes the lighter atoms and may deposit what it removes somewhere else on the sample.

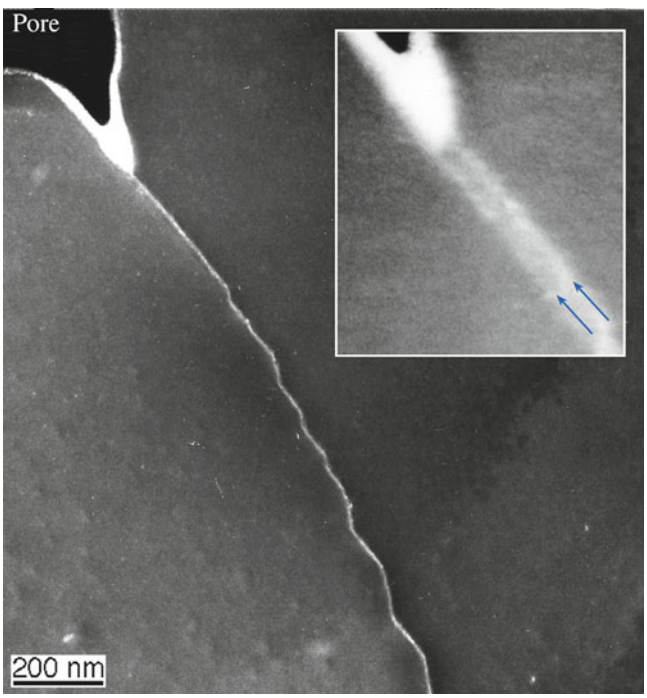

FIGURE 14.35. A cautionary tale. The "glass" in the faceted GB is actually material deposited in surface grooves during sample preparation.

Ion thinning can implant Ar into loose, or open, structures (e.g., GBs).

Ion thinning may thus both preferentially thin the GB (forming a groove) and then deposit material in that groove. (Figure 14.35 shows the problem).

It is always best to use bicrystals for model experiments to relate the chemical profile of an interface to its structure because we can then know the initial composition of the GB—but these are not "real" materials.

The principal techniques are:

- Fresnel-fringe technique
- Diffuse-scattering technique
- Direct lattice-fringe imaging where the geometry of the interface is suitable

The diffuse-scattering technique suggests amorphous-film thicknesses, which are 50–100% larger than are found by high-resolution electron microscopy (HREM); that is, at least part of the image obtained from diffusely scattered electrons must be due to factors other than the presence of a thin amorphous film. It is important to use a combination of techniques to characterize, as fully as possible, any given interface. For example, diffuse scattering is very dependent on the specimen preparation techniques. The reasons for using these techniques can be appreciated by noting that the amorphous layer, which may be present at the interface, may be only 1 nm wide. The complexity of image interpretation when examining thin (1 to >5 nm wide) GB films makes computer analysis and simulation necessary. We can use image simulation programs to simulate the formation of Fresnel fringes, taking into account the possibility of GBs grooving at both surfaces.

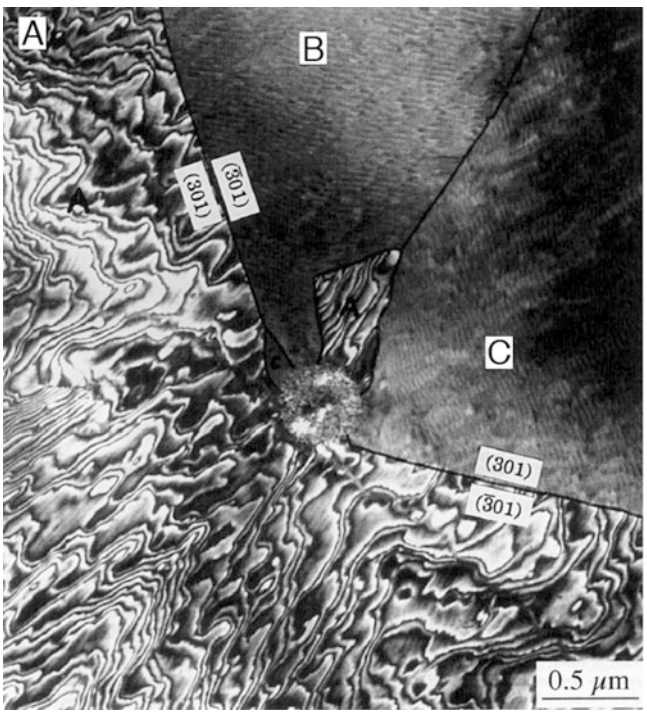

FIGURE 14.36. Example of GBs in thin films of anorthite on Al_2O_3. The three grains correspond to three epitactic orientations, but only one shows the misfit dislocations in this TEM image.

14.11 GBs IN THIN FILMS

Why are we interested in GBs in thin films? Ceramic thin films are becoming increasingly important in the electronics industry for their novel magnetic and electrical properties. Often these films are neither amorphous nor single crystal, so GBs are relevant. There are TJs in the film and at the substrate/film interface (even if the substrate is amorphous). The TJ can form a pit (a three-dimensional groove) at the surface, but it generally doesn't groove at the substrate.

Figure 14.36 is a dark-field TEM image from recrystallized anorthite glass on sapphire. The substrate appears dark, and the anorthite grains have faceted edges. The facets often meet at 60° or 120° angles. The three orientation variants are shown. Two TJs between all three variants can be seen in the image. Variant A contains irregular contrast associated with the interfacial dislocation network; variants B and C show moiré fringes.

14.12 SPACE CHARGE AND CHARGED BOUNDARIES

We introduce this topic now because it shows the fundamental relationship between point defects and interfaces. The concept of a space charge is special for ceramics. Simply put, it is possible for an excess charge of one sign to be present at the interface. This excess charge must be balanced by a space charge farther away from the boundary. There are not many experimental data, but the concept is widely accepted.

Consider NaCl: ions on either sublattice can, in principle, move to a new site on the GB, leaving a vacancy in the lattice.

$$Na_{Na} \rightarrow V'_{Na} + Na^{\bullet}_{GB} \tag{14.4}$$

$$Cl_{Cl} \rightarrow Cl'_{GB} + V^{\bullet}_{Cl} \tag{14.5}$$

In general, the energy required to form these point defects at the GB is not the same as it is in the bulk and differs for the two ions. Therefore, we get more of one than the other at the grain boundary. Overall, the crystal is neutral; hence, there must be a space charge in the bulk. Now add $CaCl_2$ to the NaCl crystal. The impurities (or dopants) give charged point defects.

$$CaCl_2 \rightarrow Ca^{\bullet}_{Na} + V'_{Na} + Cl_{Cl} \tag{14.6}$$

We are adding the positively charge Ca^{2+} ion and thus increasing the concentration of vacancies on the Na sites. We know that

$$\text{null} \leftrightarrow V'_{Na} + V^{\bullet}_{Cl} \tag{14.7}$$

so adding $CaCl_2$ to the bulk decreases $\left[V^{\bullet}_{Cl}\right]$ in the bulk (because it increases $\left[V'_{Na}\right]$). Because we have increased $\left[V'_{Na}\right]$ in the bulk, $\left[Na^{\bullet}_{GB}\right]$ must decreases in the GB, which implies that $\left[Cl'_{GB}\right]$ increases in the GB. Hence, the GB potential is negative. There is a complication: what about $Ca^{\bullet}_{Na}$? What if it all goes to the GB? The radii of the Ca^{2+} and Na^{+} ions are about the same (~0.1 nm). We don't know the radius of the Ca ion on the Na site. We have also not considered the possibility of forming a defect complex such as $\left(Ca^{\bullet}_{Na}, V'_{Na}\right)$; the binding energy is quite large, ~0.4 eV. Therefore, the idea of the GB space charge is important but far from simple, and experimental data are sparse.

14.13 MODELING

The extensive analysis of the structure of GBs in ceramic oxides using computer modeling does not appear yet to explain the experimental observations. One limitation of the modeling approach is that the GB plane is fixed in the calculation. Furthermore, computer modeling of asymmetric interfaces is not routine—constructing the unit cell for asymmetric GBs is difficult. Most of this computer modeling has been directed at understanding the structure of GBs in materials with the rock salt structure. In these materials (primarily NiO and MgO), the oxygen-ion sublattice is in an fcc arrangement, and the cations are located at the octahedral sites. The situation is more complex for most other oxides when different interstices are occupied. As you know, in spinel two-thirds of the cations occupy octahedral interstices, and one-third occupy tetrahedral interstices.

We cannot assume that all the ions have found their "ideal" sites in sintered material (e.g., some Al^{3+} ions in $MgAl_2O_4$ may be on tetrahedral sites). The structure predicted by computer modeling for the {112} lateral twin interface in NiO contains a rigid-body translation. Such a translation is not observed experimentally for the same type of interface in spinel, which has the same oxygen sublattice. It may be that the reason for this difference is that the translation-free configuration is that which is present on a migrating GB, and it becomes "frozen in" when the sample is cooled. The structure predicted by minimum energy calculations is a stationary structure.

The disagreement between experiment and modeling may be due also to the difficulty in preparing ideal clean interfaces in ceramic materials. For example, the $\Sigma = 5$ GB in NiO can be stabilized by adding Schottky defects to the interface (i.e., by decreasing the density at the GB while keeping it "pure.") Experimental observations do show that the density at interfaces is generally lower than that of the bulk material.

Most programs use a cell that repeats the structure of the GB, and hence most calculations have been carried out for low-$\sum$ GBs.

14.14 SOME PROPERTIES

Grain boundaries are everywhere in ceramics. The *formation* of GBs is discussed in Chapter 24 because the GB is the initial product of the sintering process. The *movement* of GBs is a necessary process, allowing grain growth to occur, and is also discussed there. GBs influence the behavior of polycrystalline ceramics—both bulk materials and thin films. We discuss their properties extensively in later chapters. Here, we just list a few examples, so you can see their importance.

Example 1: GBs are probably the most important defect in ceramic superconductors. They can dramatically reduce critical currents (J_c). The idea is that the GB acts as if it's a second phase. This sheet is not a superconductor—it may act like a sheet of insulator inside the superconductor. If the GB is very thin, it is possible to use its weak-link nature to fabricate a Josephson junction. Figure 14.37 is a high-resolution TEM image of a near $\Sigma = 29$ GB in an yttrium barium

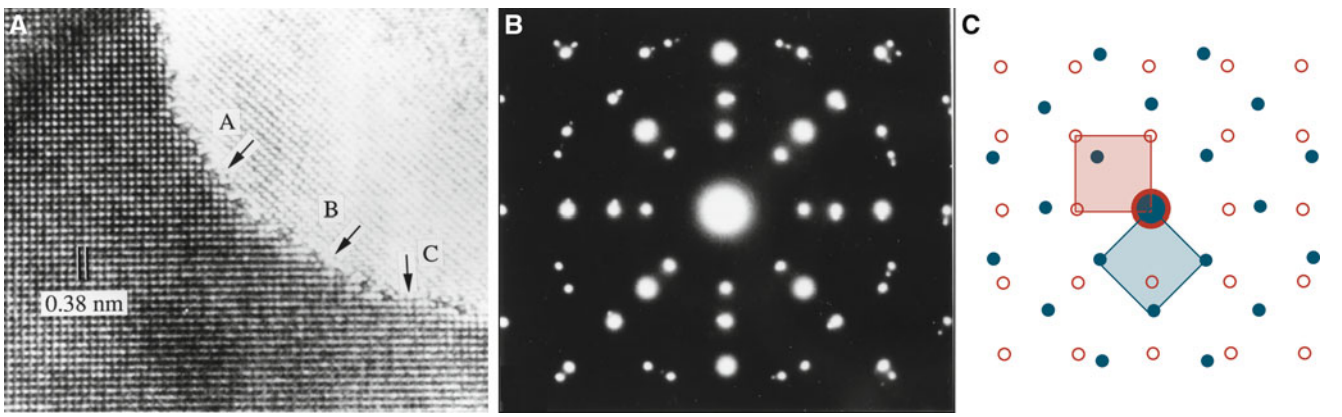

FIGURE 14.37. HRTEM image of the 45° GB in yttrium barium copper oxide (YBCO) and the diffraction pattern.

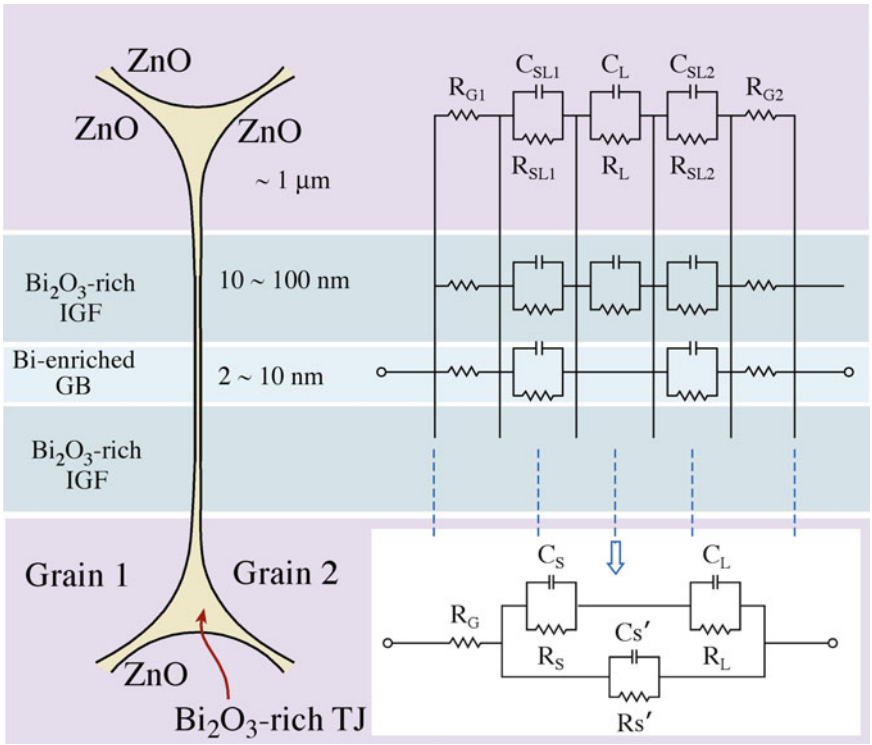

FIGURE 14.38. Modeling IGFs in ZnO varistor materials.

copper oxide (YBCO) thin film. The GB is narrow, abrupt, and faceted. We revisit this topic in Chapter 30.

Example 2: GBs in AlN can reduce the thermal conductivity if they are not clean. Because AlN is difficult to sinter to high density without the use of a liquid phase (the bonding is mainly covalent), the GBs often contain a second phase, which always has lower thermal conductivity (see Chapter 34). Yttria may be added to react with oxide in the GBs to form YAG at the triple junctions—a GB-dewetting process.

Example 3: GBs in ZnO are processed intentionally to include a glass film. This film allows the ceramic to be used as a varistor (voltage-dependent resistor), a device that protects circuits from high-voltage spikes (see Chapter 30). Figure 14.38 illustrates an IGF of varying thickness in ZnO and how this films controls the resistance.

Example 4: GBs in Si_3N_4 invariably contain glass films, as shown earlier. At high temperatures, they can lose their mechanical strength when the films soften (see Chapter 18).

Example 5: GBs in magnetic ferrites affect the initial permeability, μ. The permeability of Mn-Zn ferrite increases from about 0.8×10^{-3} up to 3.5×10^{-3} when the grain size is increased from 5 to 15 μm (see Chapter 33). Although porosity has a role, it has been determined that grain size is more important.

Example 6: GBs affect the scattering of light in transparent materials. Light scattering is greatest when the grain size is close to the wavelength. In addition, IGFs produce a change in refractive index as light passes through a material (see Chapter 32).

In metals, GBs control mechanical properties when the grain size is small, as seen from the Hall–Petch equation.

$$\sigma_y = \sigma_0 + \frac{B}{d^{\frac{1}{2}}} \tag{14.9}$$

The yield strength (σ_y) is expressed in terms of the yield stress, σ_0 (σ_0 is related to the intrinsic stress, σ_i, resisting dislocation motion), and the grain size, d. When this relationship was deduced, it applied to a situation where the grains deformed by plastic deformation and the GBs acted as barriers to dislocation motion. This model is unlikely to be valid in general for ceramics because deformation by dislocation glide is not common. However, the relationship between d and σ_y does hold, as we saw for polycrystalline MgO in Figure 1.2.

CHAPTER SUMMARY

Grain boundaries in ceramic materials are important in almost all applications of these materials because ceramics are usually polycrystalline. GBs have a thickness—we can think of them as thin films even if they are structured. This means that a polycrystalline material is really a composite one. An added difficulty is that essentially every GB "film" is different, but we can think of an *average* GB, which is especially good if there actually is an amorphous film (IGF) at the interface. The most important point to remember is the relationship between GB energy and GB (interface) tension, which includes the idea that there is a pressure difference across a curved GB just as there is across a curved surface. You should be able to define the words twist, tilt, mixed, and twin and understand the concept of $\sum$ (and Γ), how it relates to structure, and why it can be related to GB energy. TJs and the space charge at GBs are very important, but we know little about them. There are two special features for ceramics: the space charge and IGFs. IGFs are special for ceramics because glass is easily formed and maintained, especially when the ceramic contains at least small concentrations of Si.

PEOPLE AND HISTORY

Bollmann, Walter was the pioneer in explaining and popularizing the O-lattice concept. He was an early pioneer of TEM. He died in 2009 at age 88.

Friedel, George was an early contributor to the development of the coincidence-site lattice. Jacques Friedel (Ph.D. from Bristol) is his grandson. The Friedel-Crafts reaction honors George's father.

Matthews, John. He was best known for his work on misfit, epilayer growth and MgO smoke. His son Dave achieved greater fame.

Mullins, William W. explained and predicted observations on grain boundary grooving. He died in 2002.

EXERCISES

14.1 Using the idea of capillarity and relating it to a triple junction, what happens as the temperature increases (so that viscosity decreases)?

14.2 Consider a 1-cm cube of a 100% dense ceramic that contains 5% glass that can wet the crystal grains. If the grain size changes from 100 to 10 mm due to heat treatment, how does the distribution of the glass change? Be careful to summarize your assumptions and list as many variables as you can.

14.3 Consider two small-angle (2°) tilt grain boundaries in MgO, both having a [001] tilt axis. For one the boundary plane is nearly (100), and for the other it is (110). Discuss the structure of these two grain boundaries.

14.4 The structure of the spinel, $MgAl_2O_4$, projected onto the (110) plane in shown in Figure 7.1B. Spinel twins on {111} planes. Draw all the different allowed structures for the coherent (IT) plane and discuss which of them is most likely to occur, giving clear reasons. Consider how your analysis might change if the spinel was not equimolar.

14.5 If the surface energy for (001) MgO is 1 J/m^2, what is that in electron volts per oxygen ion on the surface? How does this number compare to the formation energy of the Schottky defect? How would this number be different if the material were NaCl instead of MgO?

14.6 Dislocations in a tilt boundary on the (011) plane in silicon lie 200 nm apart. What is the misorientation of the two grains? Would the etch-pit method be a good way to examine this boundary? Explain your answer.

14.7 (1) For the TJ shown in Figure 14.34, derive a relationship between GB, SL, and the dihedral angle, , which is the angle subtended by the liquid. (2) Assuming that SL is 700 mJ/m^2, determine GB.

14.8 Construct a model for a $= 7$ twin boundary in sapphire that is also a tilt boundary with a [0001] rotation axis.

14.9 Consider what might happen to the grain boundary charge when MgO is added to Al_2O_3.

14.10 A tilt boundary in olivine lies on the (100) plane with a [001] rotation axis. The dislocations are all the same Burgers vector and are 100 nm apart. What is the rotation angle?

14.11 By looking at Figure 14.5B, estimate the maximum twist that could be described by an array of screw dislocations.

14.12 By considering Figure 14.6B, show how the dislocation spacing changes when a [001] tilt GB changes from the mean (100) plane to the mean (110) plane.

14.13 By referring to the original source of Figure 14.9A, why are we seeing the dislocations? Explain what type of GB we are observing. Justify the assumptions that you make.

14.14 Describe the GB plane and the dislocation spacing and character of the GBs in Figure 14.9B. Explain the assumptions that you make.

14.15 Propose a model for the dislocation arrangements seen in Figure 14.10.

14.16 What are the Burgers vectors of the dislocations shown in Figure 14.12? What are the misorientation angle and the GB plane?

14.17 Assuming that the GB in Figure 14.13 is mainly a (100) twist boundary, suggest an explanation for the disruption from a square array of dislocations.

14.18 What is the $\sum$ for the GB shown in Figure 14.16? Explain your argument.

14.19 Confirm that the GB plane shown in Figure 14.19 is the $(1\bar{1}04)$ plane.

14.20 If the brighter white dots in Figure 14.26 indicate interfaces, what plane do they lie on in the spinel? Why are they not interfaces in the β-alumina (it's β'').

REFERENCES

GBs have been extensively reviewed in several recent books. These texts cover all crystalline materials but you will still need to go to the original papers to learn more about GBs in ceramics.

GENERAL REFERENCES

Bollman W (1970) Crystal defects and crystalline interfaces. Springer, New York, The original book giving the analysis of $\sum$, O lattice, etc

Howe JM (1997) Interfaces in materials: atomic structure, thermodynamics and kinetics of solid/vapor, solid/liquid and solid/solid interfaces. Wiley, New York, A very readable book with a practical emphasis

Hull D, Bacon DJ (2011) Introduction to dislocations, 5th edn. Butterworth-Heinemann, Amsterdam, A review of the basics

Kelly A, Groves GW, Kidd P (2000) Crystallography and crystal defects. Wiley, New York, Not broad or up-to-date but an excellent basic text

Read WT, Shockley W (1950) Dislocation models of crystal grain boundaries. Phys Rev 78(3):275–289, A classic readable paper with great diagrams

Smith DA, Pond RC (1976) Inter Met Rev 205:61, Very readable discussion of the background to the GBs

Stokes RJ, Evans DF (1997) Fundamentals of interfacial engineering. Wiley, New York, Bob Stokes retired from Honeywell and joined the U of MN part time

Sutton A, Balluffi R (1996) Interfaces in crystalline materials. Oxford University Press, Oxford, UK

Wolf D, Yip S (eds) (1992) Materials interfaces: atomic-level structure and properties. Chapman and Hall, London

SPECIFIC REFERENCES

Amelinckx S (1958) Dislocation patterns in potassium chloride. Acta Met 6:34, Seeing GBs in KCl by decoration

Chaudhari P, Matthews JW (1971) Coincidence twist boundaries between crystalline smoke particles. J Appl Phys 42:3063–3066, Original description of the MgO smoke experiment for GBs

Zhu Y, Granick S (2001) Viscosity of interfacial water. Phys Rev Lett 87(9):096104, The idea is that the viscosity of a liquid (water) can be very different if it is constrained to be a film in a silicate grain boundary

MIDAS