APPLICATION OF SEM TO THE STUDY OF CERAMIC SURFACES

N. Ravishankar and C. Barry Carter

Department of Chemical Engineering and Materials Science, University of Minnesota
421 Washington Ave SE, Minneapolis, MN 55455-01432

Abstract

Scanning electron microscopy is a particularly suitable technique for studying surfaces of ceramics. For these materials, an improved understanding of processing requires a greater knowledge of the structure of surfaces at a sub-micron level. High spatial resolution, combined with analytical capability and relative ease of sample preparation, makes SEM an ideal technique for the study of surfaces. The dewetting of liquids on single-crystal substrates, the crystallization of glass on surfaces and the behavior of the liquids in grain boundaries are examples of such studies that are presented in this paper to bring out the versatility of the technique in studying different kinds of interfacial phenomena.

Keywords: scanning electron microscopy, high spatial resolution, surface, ceramics

Resumen

La microscopía electrónica de barrido es una técnica particularmente apropiada para el estudio de superficies cerámicas. Para estos materiales, un entendimiento mejorado del proceso requiere un mayor conocimiento de la estructura de la superficie a un nivel submicrométrico. La alta resolución espacial, combinada con la capacidad analítica y una relativamente fácil preparación de la muestra, hacen de la MEB una técnica ideal para el estudio de superficies. La no mojabilidad de líquidos sobre substratos de cristales simples, la cristalización de vidrio sobre superficies y el comportamiento de los líquidos en los bordes de grano son ejemplos de estos estudios que se presentan en este trabajo para mostrar la versatilidad de la técnica en el estudio de los diferentes tipos de fenómenos interfaciales.

Palabras clave: microscopia electrónica de barrido, alta resolución, superficies, cerámicas

1. Introduction

Ceramic oxides constitute one of the most important class of materials and exhibit a wide range of properties. The processing of ceramics (particularly liquid-phase sintering) frequently involves solid–liquid interactions that are not fully understood. Microstructural examination of these interactions in model systems can shed light on many of the complex processes that occur in a real material. In most cases, the surface structure and morphology dictate the behavior and hence it is important to study the surface topography at a high resolution.

Scanning electron microscopy (SEM) is used in the secondary-electron (SE) imaging mode to image surface topography. Recent advances in electron optics and lens design have enabled surface spatial resolution that approaches the resolution obtainable from a conventional TEM [1]. The resolution depends directly on the probe size; such a small probe size which still has sufficient current is achievable using a field-emission gun as the electron source. The use of lower accelerating voltages reduces the interaction volume and improves the resolution in topography. The focal length of the probe-forming lens can be significantly lowered to the order of millimeters so as to minimize spherical aberrations. In the present generation of in-the-lens SEMs, the lens field is used to collect the secondary electrons onto a detector placed just above the lens so that the collection efficiency is vastly improved. A high signal-to-noise Autrata
surfaces is well known[2,3]. In particular, the faceting of the m-plane (10\overline{1}0, the first-order prism plane) of sapphire has been studied in great detail. This plane is unstable and can reconstruct into \{10\overline{1}1\} and \{10\overline{1}2\} facets, which intersect along a <\overline{1}2\overline{1}0> direction.

When the length scale of faceting is of the order of the size of the droplets on the surface, interesting types of solid–liquid interactions take place [4-7]. The use of FESEM at low voltages (-5 kV) provides suitable resolution for studying these interactions.

Figure 1 is a secondary-electron (SE) image of a dewet droplet on the m-plane of sapphire. The sample was annealed at 1700°C for 7h. The faceting of the substrate is seen clearly. The height of the facets is of the order of tens of nanometers. The facets intersect along a <\overline{1}1\overline{2}0> direction, i.e., the straight lines that are seen are parallel to this direction. The cross-section of the liquid droplet is not circular in this case.

The faceting behavior of the alumina surface in the presence of glass has been studied earlier. The liquid preferentially wets one type of facet on the surface. There is a significant bending of the steps in the vicinity of the solid–liquid–vapor (SLV) triple-junction.

The backscattered detector gives excellent backscattered electron (BSE) resolution at low voltages. The SEM was carried out in a Hitachi S-900 field-emission SEM (FESEM). The microscope has an immersion objective lens with the SE resolution capability of 0.7nm at an accelerating voltage of 30kV (about 3nm at 3kV).

2. Experimental

In the present study, the alumina (Al₂O₃)/anorthite (CaAl₂Si₂O₈) system is chosen as a model system to examine many of the interesting aspects of solid–liquid interactions. In particular, the following aspects have been studied. The process of dewetting of liquids on solid substrates depends on the roughness of the surface. Reconstruction of high-index surfaces produces a stepped structure with the size of the steps of the order of a few tens of nanometers. When the dimensions of the liquid droplet is of the order of the length scale of faceting, additional interesting interactions can occur. The study of such surfaces using an FESEM provides insight into the wetting behavior on stepped surfaces.

The stability of liquid films in grain boundaries (GB) is dictated in part by the relative values of the energies of the grain boundary and the free surface. Under conditions where the liquid wets the surface and does not wet the GB, the liquid can migrate out of the GB. SEM investigation on the migration of liquid from grain boundaries can clarify many of the important aspects of the mechanisms of the liquid–phase sintering process. The crystallization of silicate glass on crystalline substrates is also dictated by the orientation and surface structure. The crystallized phase usually forms by heterogeneous nucleation on the substrate. The faceting of the underlying substrate also plays an important role in determining the morphology of the crystallized phase.

3. Results and Discussion

3.1 Dewetting of Anorthite on Sapphire Surfaces

The surface energy of a liquid is isotropic (independent of orientation) and hence a liquid droplet assumes a spherical shape to minimize the total surface energy of the system. For a liquid droplet on a flat, isotropic substrate, the shape corresponding to the minimum in energy can be described as spherical cap (a circular cross-section). The presence of a surface structure (ledges, for instance) can alter the shape of the liquid droplet.

The equilibrium shape of a solid is geometrically similar to the shape obtained by the Wulff construction on the polar plot of the surface energy (the γ-plot). Surfaces that appear in the Wulff shape are those with the lowest energy. Herring's theorem states that any surface which is not a part of the Wulff shape (high-index, higher energy planes) will reconstruct into a hill-and-valley structure comprising the low-energy facets. Edge effects are neglected. The reconstruction of high-index sapphire surfaces is well known[2,3]. In particular, the faceting of the m-plane (10\overline{1}0, the first-order prism plane) of sapphire has been studied in great detail. This plane is unstable and can reconstruct into \{10\overline{1}1\} and \{10\overline{1}2\} facets, which intersect along a <\overline{1}2\overline{1}0> direction.

When the length scale of faceting is of the order of the size of the droplets on the surface, interesting types of solid–liquid interactions take place [4-7]. The use of FESEM at low voltages (~5 kV) provides suitable resolution for studying these interactions.

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The faceting behavior of the alumina surface in the presence of glass has been studied earlier. The liquid preferentially wets one type of facet on the surface. There is a significant bending of the steps in the vicinity of the solid–liquid–vapor (SLV) triple-junction.

Figure 2 is an SE image showing the details of the SLV triple junction. The facets bend and break down into microfacets; they themselves facet. The glass pocket is flattened on one side indicating that the liquid preferentially wets one type of facet in the stepped structure [4,6]. Figure 3 is an SE image of a dewet droplet on a high-index plane of sapphire. The tendency of the
liquid to spread along one type of facet is seen in this case. Microfaceting of the facet can also be observed.

![Image](https://example.com/image1.png)

Fig. 2. SE image showing the details of the SLV triple junction. The facets bend in the vicinity of the triple junction. Microfaceting of the steps is seen in the image.

![Image](https://example.com/image2.png)

Fig. 3. SE image of a dewet anorthite droplet on a high-index plane of sapphire. The liquid preferentially spreads along one of the facet on the reconstructed surface.

3.2 Crystallization of Silicate Glass on $\text{Al}_2\text{O}_3$

Intergranular glassy phases are often observed in polycrystalline ceramics. The presence of the glassy phase leads to low creep resistance at high temperatures [8,9]. The creep resistance can be improved by crystallizing the intergranular phase. Complete crystallization of the glassy phase can be obtained by controlling the glass composition and by promoting epitactic crystallization [10]. Epitaxy relies on the matching of lattice parameters between the two phases. Epitaxy between dissimilar materials (different crystal structures) is more difficult to obtain. However, it can occur between structurally different materials that share certain structural features. Slight distortions of the structure can take place to promote epitaxy.

Crystallization proceeds via nucleation of the crystal from the glass and its subsequent growth. The interfacial energy term dominates during the early stage of crystallization and so the phase that nucleates is usually the one with the lowest interfacial energy (closest in structure to the parent/substrate phase) although it may not be thermodynamically the most stable phase. In the case of anorthite, the triclinic phase is the stable phase at room temperature and pressure. However, epitactic crystallization of anorthite on $\text{Al}_2\text{O}_3$ results in the formation of a pseudo-orthorhombic phase (o-anorthite) because of its nucleation advantage. In the case of celsian ($\text{BaAl}_2\text{Si}_2\text{O}_6$), the hexacelsian phase nucleates instead of the stable monoclinic phase.

3.2.1 Crystallization of Celsian

A BSE image of celsian crystallizing on the basal plane of sapphire is shown in Figure 4. The sample was annealed at 1400°C for 1h. The monoclinic phase of celsian is the stable form at room temperature. However, the hexagonal form is the one that nucleates due to the lower interfacial energy with the substrate. Most of the crystallites exhibit hexagonal faceting (Figure 5).

![Image](https://example.com/image3.png)

Fig. 4. BSE image of crystallites of hexacelsian on basal sapphire. The celsian phase appears bright because of its higher average atomic number.
Fig. 5. An SE image of a sample of celsian on basal sapphire that has been heat treated at 1200°C for 20h. The hexagonal faceting of the precipitates is much more pronounced in this case.

The evaporation from the surface of sapphire at higher temperatures is affected by the presence of the silicate phase. It is observed that the evaporation can be considerably slower in the region that contains the celsian phase. Figure 6 is an SE image of a sample which had celsian on basal sapphire. This sample has been heat treated at 1850°C for 2h. At this temperature, there is considerable evaporation from the surface. The exposed surface of sapphire (with no silicate phase) evaporates by the removal of atoms from the step sites causing the movement of the steps. When the steps encounter a particle (where the rate of evaporation is possibly lower), they curve around it. Figure 6 shows a series of steps bending around a region that had been covered by a celsian crystallite. The hexagonal shape of the particle is maintained in this case (the inclined steps are all faceted).

3.2.2 Crystallization of Anorthite

Anorthite crystallizes in the pseudo-orthorhombic form on the sapphire substrate [11,12]. The crystallites are usually present in the form of elongated islands. In the case of anorthite on basal sapphire, three variants of crystallites form well-defined groups which radiate from a central position in a star-like fashion. Electron diffraction experiments reveal that there is an epiplectic relationship between the crystallites and the substrate.

The crystallization of anorthite on the m-plane of sapphire is similar to that on the basal surface. The anorthite glass crystallizes in the form of long rods on the surface as shown in the SE image of crystallized anorthite on the m-plane of sapphire (Fig. 7). The crystallized rods on the surface presumably correspond to the o-anorthite phase and align along the steps (<1120> direction) on the surface. Longer rods break up into smaller segments due to beading instability. The instability is evident from the necked regions in the long rods. Many small segments can be seen on the surface.

Fig. 6. SE image showing evaporation from a region containing a silicate phase on a basal sapphire surface. Evaporation is slowest from the region beneath the droplet. The steps on the surface curve around the droplet and form a series of plateaus.

Fig. 7. Secondary electron image of anorthite crystallized on the m-plane of sapphire. The m-plane of sapphire is unstable and reconstructs into a hill-and-valley structure on annealing at high temperature. The crystallized rods align along the steps on the surface. Longer rods break up into smaller segments due to beading instability.
3.3 Behavior of Liquids in Grain Boundaries

The use of a liquid phase during sintering accelerates the densification process considerably and is a common processing route for ceramics. The process, referred to as liquid-phase sintering involves liquid/solid interactions that depend on the crystallography of the solid surface or the grain boundaries. The use of bicrystals with controlled crystallography is very useful to study the influence of crystallography on specific types of interactions [13].

The SE image in Figure 8 shows a bicrystal assembly that has been heat treated at 1650°C for 2h. The bounding planes of the bicrystals are of basal orientation. The surface of the bicrystal was polished to 0.5μm finish before the annealing treatment. At the annealing temperature, the glass that is contained within the boundary forms a liquid. The liquid migrates out of the grain boundary and spreads to the free surface. On cooling the sample, the liquid dewets on the surface. Dewet droplets can be seen on the surface on either side of the boundary. The morphology of the droplets is different on either side of the boundary. It is now well established that the morphology of dewet droplets is dependent on the surface structure and surface energy [4-7].

![Fig. 8 SE image from a bicrystal that has been annealed at 1650°C for 2h. The liquid that was contained in the boundary migrates to the free surface at high temperatures. The liquid dewets on cooling the sample.](image1)

This provides a driving force for the migration of the liquid out of the boundary. On cooling the sample, the liquid that has spread to the surface dewets and forms discrete droplets. The surface undergoes reconstruction during annealing (enhanced by the glass) and the morphology of the dewet droplets depends on the reconstructed surface structure.

![Fig. 9 SE image from a bicrystal bound by different planes (c-plane and m-plane). The boundary that was straight initially migrates during the annealing treatment. The initial position of the boundary is seen to the right.](image2)

The SE image shown in Figure 9 is from a bicrystal in which the bounding planes are different (one of the bounding planes is of basal orientation and the other plane is of m-orientation). The free surfaces are crystallographically different in this case. One surface is unstable at the annealing temperature and reconstructs into a hill-and-valley structure. While the initial boundary was straight, the boundary after annealing has moved from its initial position. The migration is driven by the difference in surface energies between the two bounding planes in the boundary. Investigation of many different boundaries shows that there is no migration in the samples in which the bounding planes are the same.

At higher magnification (Figure 10), ledges are seen along the boundary that has undergone migration. The migration of the grain boundary presumably occurs by the motion of these ledges.

![Fig. 10 SE image showing ledge migration along the boundary.](image3)
Fig. 10. Higher magnification SE image from a migrated grain boundary. The presence of ledges is seen. The boundary migration is due to the motion of these ledges at the boundary.

4. Conclusions

It is seen that the field-emission SEM is an extremely useful and powerful tool to study various problems related to surfaces of ceramic materials. The relative ease of sample preparation and the high resolution of modern machines makes them ideal for studying a variety of surface-related phenomena.

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6. References