Precipitation from a reactive silicate on MgO

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For this paper, high-temperature interactions between a reactive silicate liquid and the (001) surface of a MgO single crystal were studied. The paper discusses the influence of the morphology of the MgO surface on both the dewetting of a silicate liquid and the mechanism of precipitation of excess MgO out of this silicate liquid. Alternative pathways were considered for MgO precipitation; it may occur by nucleation and growth of plateaus on the MgO surface or by MgO absorption at surface steps. On flat MgO(001) surfaces, precipitation of MgO from the continuous layer of silicate liquid led to the formation of plateaulike precipitates. Precipitation from disconnected silicate droplets onto stepped MgO(001) surfaces resulted in the growth of ridges at steps on the surface.

I. INTRODUCTION

Interactions between intergranular phases and crystalline grains frequently define the properties of liquid-phase sintered ceramics.[1] The complexity of multicomponent polycrystalline starting materials usually allows numerous processes to occur simultaneously at grain boundaries during sintering of a ceramic product, which considerably complicates studies of such processes. A typical approach taken in ceramics research is to identify these processes so they can be recreated separately under controlled conditions in model systems with fixed geometries and known chemical composition. Bicrystals[2] or single-crystal surfaces coated by thin films whose composition corresponds to—or is closely related to—typical intergranular phase compositions[3,4] provide such model systems.

When ceramic materials are processed in the presence of a liquid phase, the integrity of interfaces developing in the sintered product depends directly on the mechanism of interactions between the ceramic grains and the reactive liquid phases present at the grain boundaries.[5] The present work illustrates directly how the morphology of the surface of a ceramic grain can affect crystallization of material from a liquid intergranular phase. The system chosen for this study is the (001) surface of single-crystal MgO in contact with a common constituent of the intergranular phase in MgO-based ceramics,[6,7] namely, calcium magnesium silicate (monticellite, $CaMgSiO_4$).

II. BACKGROUND

At elevated temperatures, the processes dominating the transfer of material at the $CaMgSiO_4$/Mg(001) interface include melting and crystallization of the monticellite,[8] wetting and dewetting of the MgO(001) surface by a silicate liquid,[8] and dissolution and precipitation of MgO in and out of the silicate phase.[9] According to the CaO–MgO–SiO_2 phase diagram,[8,10,11] crystalline $CaMgSiO_4$ may melt incongruently at 1765 ± 6 K, resulting in the precipitation of solid MgO and the formation of a liquid silicate phase. It has been suggested that this process may be accompanied by the precipitation of merwinite ($Ca_3Mg[SiO_4]_2$),[12] and that the merwinite then melts incongruently at 1773 K to give solid MgO and liquid.[11] In the present study, for which annealing temperatures in the range of 1920 ± 50 K were used, there was no evidence for the formation of merwinite at any stage of the process. In the present study, annealing temperatures in the range 1920 ± 50 K were used, so any possible effect of formation or decomposition of merwinite on the morphology of the $CaMgSiO_4$/MgO interface would be minimized.

According to the phase diagram, the monticellite silicate liquid continues to dissolve MgO up to approximately 1955 ± 7 K,[8,10] the liquidus temperature. At this temperature, the liquid attains the nominal chemical composition of $CaMgSiO_4$.[8] If such liquid is annealed above approximately 1955 ± 7 K by itself, i.e., in the absence of additional quantities of MgO, it will behave as a one-component system as T is increased.[8,10] If, however, the $CaMgSiO_4$ liquid is maintained in contact with solid MgO, such a system will follow the liquidus on the CaO–MgO–SiO_2 phase diagram, and on heating above

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approximately 1955 ± 7 K, the process of dissolution of MgO into the silicate phase will continue;[8,10,11] this is the usual peritectic reaction.

On cooling $CaMgSiO_4$/MgO from approximately 1955 ± 7 K to approximately 1765 ± 6 K,[10,11] precipitation of MgO out of the silicate liquid occurs. At approximately 1765 ± 6 K, the reaction between the silicate phase and MgO leads to the formation of monticellite crystals.[10,11] At lower temperatures, monticellite exists in equilibrium with solid MgO. If the $CaMgSiO_4$/MgO system is rapidly quenched from a temperature above approximately 1765 ± 6 K, the crystallization of monticellite may not occur, and the silicate liquid will be oversaturated with MgO.[10] It is expected that if monticellite crystallization does not take place on cooling the $CaMgSiO_4$/MgO system, precipitation of MgO out of the supercooled liquid phase may still continue at temperatures below approximately 1765 ± 6 K. The present paper specifically discusses the mechanism of the crystallization of MgO from the overcooled silicate phase in the $CaMgSiO_4$/MgO system as it relates to the changing morphology of the MgO(001) surface.

III. EXPERIMENTAL

Films of monticellite composition were deposited onto single-crystal MgO substrates of (001) orientation by pulsed-laser deposition. The MgO surfaces were prepared by cleaving prior to deposition. Surfaces of clean MgO, before and after annealing, have been discussed elsewhere.[13–16] The films were grown in 12 mtorr oxygen. During the film growth, the substrates were maintained at 520–770 K. The average thickness of the films varied from about 50 to approximately 200 nm.

Samples 2 × 2 × 1 mm were annealed in air in Lindberg^{TM} (Lindberg, Watertown, WI) furnaces at 1870–1970 k in closed single-crystal MgO crucibles. Upon completion of the heat treatment, the specimens were either quenched or slowly cooled at room temperature. Heat-treatment times varied from 60 to 720 s. Quenching and slow cooling took about 10 and approximately 300 s, respectively.

Surface imaging was performed by scanning probe microscopy in air in the contact mode using a Nanoscope III (Digital Instruments, Santa Barbara, CA) with Si_3N_4 V-shaped cantilevers (Digital Instruments), which have a nominal spring constant of 0.12 M/m.

IV. RESULTS

Figure 1 shows a film of $CaMgSiO_4$, with thickness ≤ 100 nm, deposited on the MgO(001) substrate. The appearance of the continuous film resembles a dense packing of small (approximately 50 nm diameter) particles. The cleavage steps on the substrate surface,[17] which are clearly visible under the silicate film, are oriented along the [001] direction of the MgO. Monticellite melts at approximately 1765 ± 6 K;[8,10] it is therefore expected that the small "particles" in the deposited film may correspond to both crystalline and glassy regions.

As discussed above, when the $CaMgSiO_4$/MgO(001) system is annealed at temperatures above 1771 K,[8,10] a layer of liquid phase forms on the MgO(001) surface. When rapidly quenched to room temperature, the silicate liquid does not crystallize, but, instead, dewets[18] the MgO(001) surface by forming dome-shaped droplets.[9,19] When the quenching rate is too high, the silicate liquid may not complete the dewetting before vitrification occurs. Figure 2 shows the image of the same surface area as that in Fig. 1 after the specimen was annealed at 1963 K and rapidly (in ≤10 s time) quenched to room temperature. In Fig. 2, the silicate liquid did not form dewet droplets but instead broke into the irregularly shaped pools of glass. It is proposed that the liquid pools were formed in the initial stages of dewetting when the continuous layer of the silicate phase melted and fragmented. The shape and position of the liquid areas on the MgO(001) surface do not correspond to the shape and positions of the grains in the original monticellite film (compare Figs. 1 and 2), which indicates that the silicate liquid spread across the MgO(001) surface in the course of the 60-s annealing.

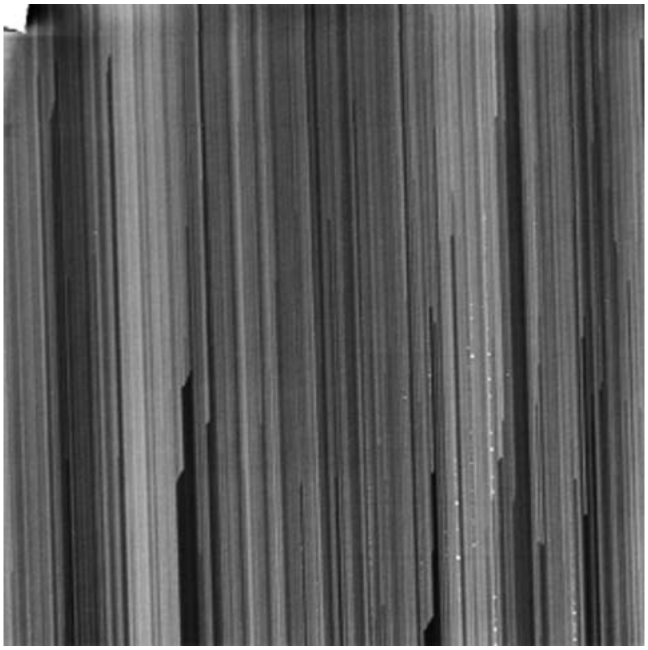

FIG. 1. SPM image, 20 × 20 μm height mode, of a thin (≤100 nm) $CaMgSiO_4$ film deposited onto a cleaved (001) MgO surface. The cleavage steps on the MgO surface, which are seen as vertical lines in the image, are aligned along the [100] direction of the crystal. The average film shows approximately 50 nm granularity. The black to white height scale is 20 nm.

Figure 3 shows the flat $CaMgSiO_4$-coated surface of MgO(001) which was quenched at a slower rate (in about 30 s time) after the 360-s annealing at 1923 K. Precipitation of MgO from the silicate phase resulted in the formation of concentric plateaus positioned underneath the dewet droplets. The circular precipitates in Fig. 3 are themselves found on large irregular plateaus. It is proposed that these plateaus were created during the earliest stages of the dewetting process. The texturing of the MgO surface between the droplets is attributed to the formation of small MgO precipitates, which formed prior to the completion of the dewetting transition.

If, instead of rapid quenching, the system is allowed to cool more slowly (300 s) to room temperature, the shape of the precipitate plateaus becomes rectangular, with sides faceted close to the [100] and [010] directions of the MgO crystal (see Fig. 4). The surface of the slowly cooled sample is smoother than that of an otherwise similarly treated quenched specimen (compare Figs. 3 and 4), which indicates that, on slow cooling, the silicate liquid tends to dewet the MgO(001) surface before extensive MgO precipitation occurs.

Crystallization of MgO from the spherically symmetric silicate droplets frequently yields irregularly shaped precipitates. Thus, in Fig. 4, many of the droplets are located adjacent to a precipitate, in contact with both the upper and lower precipitate layers. Because such droplets are dome-shaped, their positioning is unlikely to be caused by incomplete dewetting of the MgO(001) surface by the silicate phase.

MgO precipitation can also occur from silicate droplets located at steps on the MgO(001) surface. Observations show that for droplets attached to a surface step, MgO precipitation occurs predominantly onto the step, rather than onto the terrace. Thus, as demonstrated in Fig. 5, silicate droplets in contact with a large cleavage step on the MgO(001) surface do not produce large MgO plateaus.

In some instances, the precipitation of MgO may proceed both at the base and at the side of the dewet droplet. As seen in Fig. 6, precipitates formed from the silicate droplets on quenching can have a complex morphology after annealing for 60 s at 1923 K. The lower layers of the precipitated material surrounding each droplet in Fig. 6 appear as plateaus. The narrow surface ridges of MgO, which connect the silicate droplets to the steps on the MgO(001) surface, appear to lie above these plateaus. This observation indicates that the plateaus formed before the ridges. All the ridges shown in Fig. 6 point from the droplets to the neighboring upper steps.

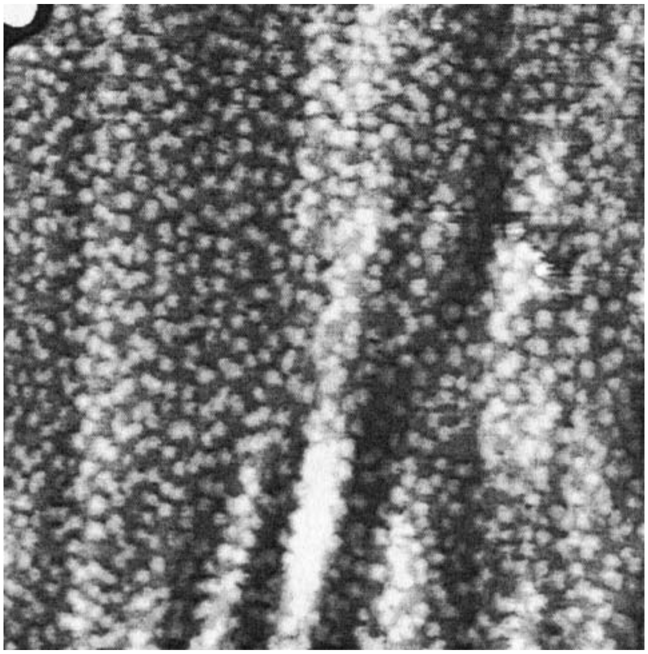

FIG. 2. SPM image, 20 × 20 μm height mode, after annealing the $CaMgSiO_4$-coated (001) MgO surface at 1963 K for 60 s and then quenching in ≤10 s to room temperature. The image shows the same surface area as that in Fig. 1. The silicate film, which melted on heating, partially dewet the MgO(001) surface on cooling, forming irregularly shaped fragments. The average size of the fragments is approximately 500 nm. Large cleavage steps on MgO(001) surface are seen under the silicate film; the smaller cleavage steps are not now visible. The black to white height scale is 10 nm.

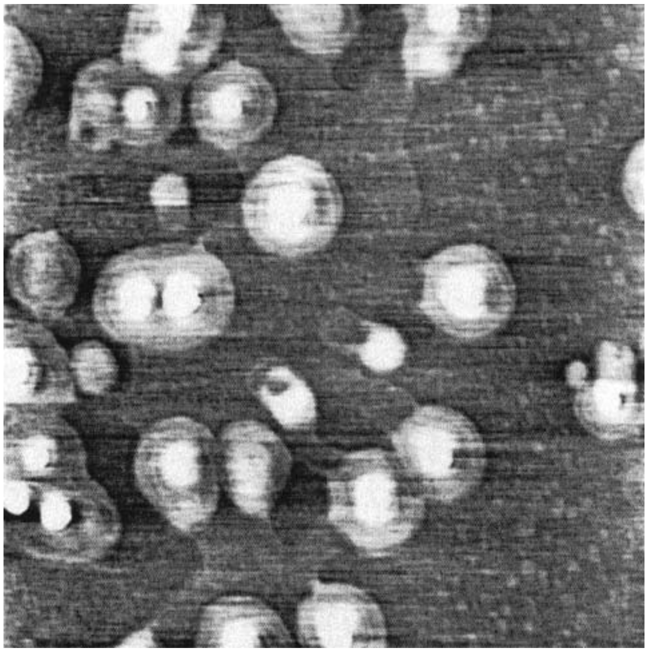

FIG. 3. SPM image, 5 × 5 μm height mode, after annealing the $CaMgSiO_4$-coated (001) MgO surface at 1923 K for 360 s and quenched in approximately 30 s to room temperature. The silicate liquid dewet the MgO(001) surface on quenching and formed hemispherical droplets. The droplets sit atop concentric layers of MgO precipitates. Low broad precipitate plateaus of irregular shape underlie some of the droplets. The surface of the MgO substrate between the droplets is decorated with small MgO precipitates. The black to white height scale is 15 nm.

The formation of whiskers was also observed when the $CaMgSiO_4$/MgO(001) system was repeatedly annealed. Figure 7 shows the same area of surface as in Fig. 2; the image was recorded after the specimen was subjected to an additional 60 s annealing/quenching cycle at 1963 K. The silicate phase dewetted the MgO surface by forming droplets connected to the steps on the MgO(001) surface by narrow ridges. These ridges, which are on average approximately 500–1000 nm long and approximately 0.8–2.5 nm high, have flat tops and faceted sides. The average thickness of the ridges is the same as that of steps on the MgO(001) surface (approximately 0.2–0.4 nm). Those in Fig. 7 connect silicate droplets to the upper surface steps. However, the droplets in Fig. 7 do not appear to have formed MgO plateaus.

As demonstrated in Fig. 8, the ridges may be as long as about 1.5 μm when the $CaMgSiO_4$/MgO(001) system is maintained under the oscillatory heat-treatment conditions (1920 ± 50 K with the oscillation period of approximately 60 s) for an extended period of time (12 min). Like those shown in Figs. 6 and 7, these ridges also connect the droplets of the dewet silicate phase to the upward steps on the MgO(001) surface. However, unlike those in Figs. 6 and 7, many of the ridges seen in Fig. 8 curve.

It is important to be sure that the precipitated materials are MgO and not monticellite. Both the plateaus and the ridges in question exhibit a terrace-and-ledge morphology. The height of the ledges decorating the plateaus and the ridges is equal to the height of the ledges observed on the surface of MgO(001) substrate (usually of about 1 Å, or integer multiples of 1 Å, which is close to ¼ of the lattice parameter of MgO structure, for which b = 4.2 Å). Similarly, the terraces on the plateaus and the ridges have orientation identical to that of the (001) plane of the MgO(001) substrate. It is unlikely that monticellite crystals [space group P*pnm*, a = 4.82 Å, b = 11.11 Å, c = 6.38 Å)] could form the plateaus and ridges, which have ledges and terraces with height and orientation identical to those of terraces and ledges on the MgO(001) surface.

The ridges (such as those seen in Figs. 5–8) appear to have grown directly out of the bunched ledges on the surface of the substrate, with no boundaries or trenches separating them from one another. If the ridges were monticellite, well-defined grain boundaries would separate them from the substrate. No such boundaries were seen in the images. The explanation for this is that the ridges formed from MgO grown out of the droplets onto

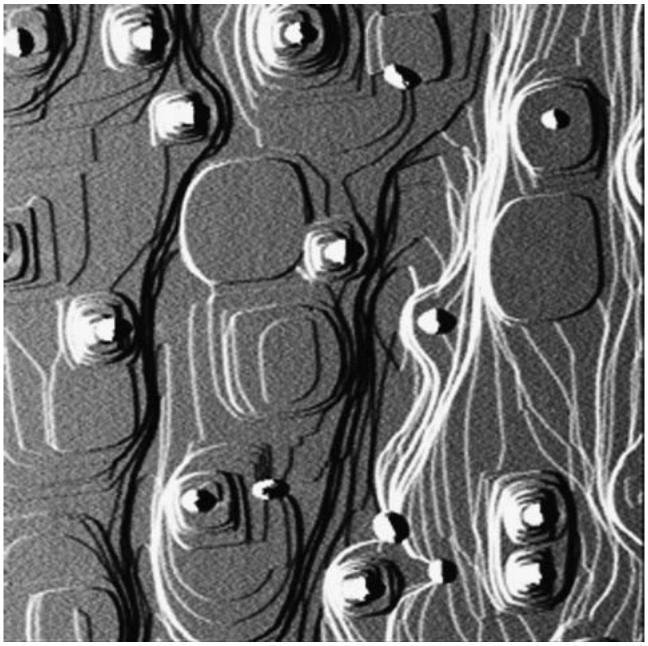

FIG. 4. SPM image, 10 × 10 μm deflection mode, after annealing the $CaMgSiO_4$-coated (001) MgO surface at 1923 K for 360 s and cooling in approximately 300 s to room temperature. The direction of scanning was from left to right. In the image, the dark and bright lines indicate the down and up surface steps, respectively. The flat surface areas appear gray. The dewet droplets sit atop the flat tiered layers of MgO precipitates. The precipitate sides are oriented close to the [100] and the [010] directions of the MgO substrate. The remnants of two large cleavage steps on the MgO surface extend from the top to the bottom of the image. The black to white height scale is 50 nm.

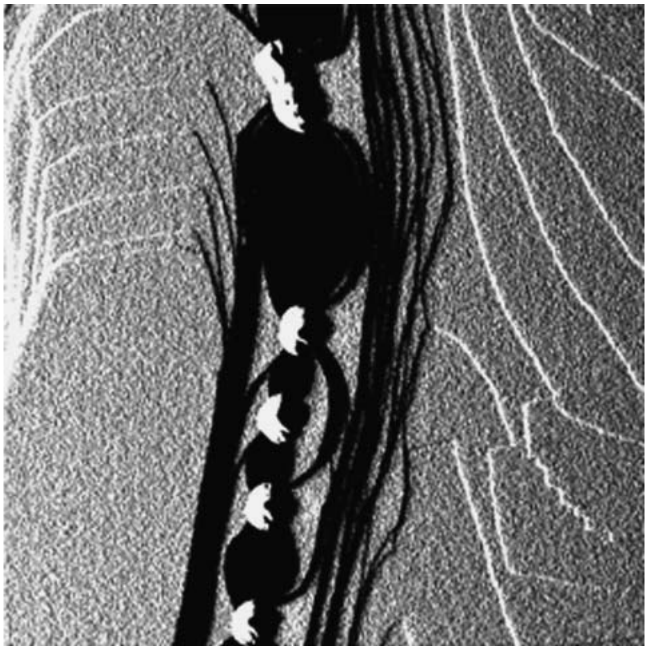

FIG. 5. SPM image, 5 × 5 μm deflection mode, after annealing the $CaMgSiO_4$-coated (001) MgO surface at 1923 K for 360 s and cooling in 300 s to room temperature. The direction of scanning was from left to right. Dark and white lines correspond to down and up surface steps, respectively. Flat surface areas appear gray. A large cleavage step on the surface of the MgO substrate, which decomposed into a train of smaller surface ledges on annealing, is seen as group of dark lines extending from the top to the bottom of the image. The steps bow out between the droplets. The bowing of the lower ledges may be due to etching by the silicate liquid during heating. The black to white height scale is 50 nm.

the ledges on the MgO(001) surface. Furthermore, x-ray diffraction analysis performed on several crushed specimens did not reveal the presence of crystalline phases other than MgO.

V. DISCUSSION

Based on these observations of the morphology of the MgO precipitates, two major routes can be identified for the crystallization of MgO out of the silicate liquid in the $CaMgSiO_4$/Mg(001) system. A MgO plateau can form at the silicate/MgO(001) interface under the glass droplet. The plateau morphology is shown in Figs. 3 and 4. Alternatively, ridges can develop where the droplet touches a step on the MgO(001) surface (Figs. 5 and 7). The mechanism of the MgO precipitation may change during a single annealing/quenching cycle from plateau growth to ridge growth (Fig. 6).

It is proposed that the formation of plateaus (Figs. 3 and 4) starts with the nucleation of a MgO island at the silicate/MgO(001) interface under the droplet. Once nucleated, the MgO island grows laterally [parallel to the (001) surface of the MgO substrate]. The well-defined tiered morphology of the precipitates in Figs. 3 and 4 suggests that only one island grows under each droplet. The island of MgO grows primarily by precipitation from the silicate liquid. Growth of this island stops when its edges are no longer in contact with the silicate phase. This may happen either when the growing precipitate edge reaches the air/silicate/MgO triple junction or when the moving triple junction reaches the precipitate edge; the droplet becomes smaller by a combination of MgO precipitation and silicate vaporization. In Figs. 3 and 4, the lower precipitate plateaus are larger than the upper ones, which indicates that the upper plateaus result from subsequent nucleation events (Fig. 9). Some of the plateaus in Figs. 3 and 4 are not associated with silicate droplets. Such plateaus could have formed under the continuous layer of silicate liquid, or the silicate could have already completely evaporated.

When the droplet sits on a flat MgO(001) terrace, the silicate/MgO interface is flat. When the droplet is in contact with a surface step (Fig. 10) precipitation of MgO can occur on both the terrace and the step. However, as demonstrated in Figs. 5 and 7, precipitation of MgO from such droplets occurs preferentially at the step by the growth of ridges parallel to the (001) plane of the MgO substrate.

Each ridge in Fig. 5 is connected to a droplet; the contracting droplets at steps accommodate the volume reduction predominantly through the continuous dewet-

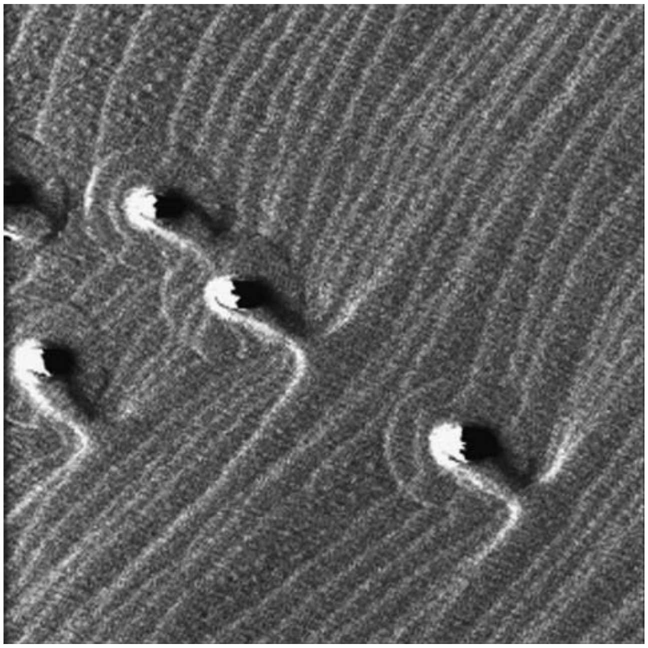

FIG. 6. SPM image, 5 × 5 μm deflection mode, after annealing the $CaMgSiO_4$-coated (001) MgO surface at 1923 K for 60 s and quenching. The direction of scanning was from left to right. Dark and white lines correspond to down and up surface steps, respectively. Flat surface areas appear gray. The droplets sit atop flat circular plateaus of MgO precipitates. The droplets are connected to the steps on the surface of MgO substrate by ridges, which lie above the round precipitate plateaus and connect the droplets to particular higher steps. The black to white height scale is 10 nm.

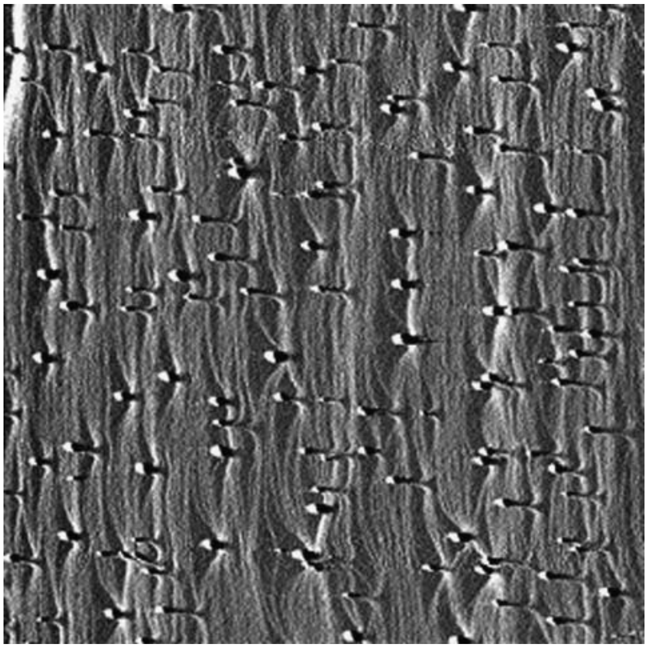

FIG. 7. SPM image, 20 × 20 μm deflection mode, after annealing the $CaMgSiO_4$-coated MgO surface at 1963 K for two separate 60 s periods. The direction of scanning was from left to right. Dark and white lines correspond to down and up surface steps, respectively. Flat surface areas appear gray. This figure shows the same surface area as Figs. 1 and 2. The droplets are connected to the steps on the surface of MgO substrate by ridges. The ridges are oriented along the steepest descent direction on the stepped MgO(001) surface. The black to white height scale is 20 nm.

ting of the lower terraces. Consider a narrow flat (010) step facet descending to a (001) flat terrace. If the effect of gravitation on the droplet shape is neglected,[20,21] the droplet will make approximately a 12° contact angle[9] with the (010) and the (001) planes simultaneously. As shown in Fig. 10, such a droplet will have a larger surface area than the droplet that wets the step and the lower surface terrace. Therefore, the droplets tend to remain attached to steps.

The formation of plateau precipitates occurs on the flat areas of the MgO(001) surface. To avoid the nucleation of these plateaus, the droplets must stay in contact with the steps on MgO(001) surface (see Figs. 5 and 7). This is unlikely for droplets located on the large flat platforms of MgO precipitates, shown in Figs. 3 and 4. However, if the amount of silicate liquid formed on heating is not sufficient to produce a continuous layer, on cooling, the droplets may contact the surface steps and grow ridges.

The development of the two precipitate morphologies during one annealing treatment, such as that shown in Fig. 6, requires that, upon creating plateaulike MgO precipitates, the silicate droplets remain in contact with surface steps at the perimeter of the plateaus. Precipitation of MgO from the continuous liquid layer may remove steps and thus smooth the MgO(001) surface. It is suggested that in the case of mixed plateau/ridge MgO precipitation, the melting of the monticellite film produced disconnected fragments rather than a continuous layer of silicate liquid on the MgO(001) surface. On initial quenching, the liquid precipitates plateau under these fragments. On further cooling, when the liquid dewets the substrate surface, the droplets attach to surface steps, which are numerous on the MgO(001) surface (Fig. 6). These droplets contact the upper steps located at the edges of the plateau. Any further MgO precipitation from

FIG. 8. SPM image, 10 × 10 μm deflection mode, after annealing the $CaMgSiO_4$-coated MgO(001) surface for 720 s, cycling from 1870 to 1970 K with a period of approximately 30 s. Dark and white lines correspond to down and up surface steps, respectively. Flat surface areas appear gray. The droplets are connected to the curved ledges on the MgO(001) surface by ridges. Some of the ridges are curved and follow local changes in the direction of the steepest descent on the stepped MgO(001) surface. The hillocks and wells on the MgO(001) surface are expected to have formed during the precipitation and dissolution of MgO while the surface was covered with the silicate liquid in the initial stages of annealing. The black to white height scale is 20 nm.

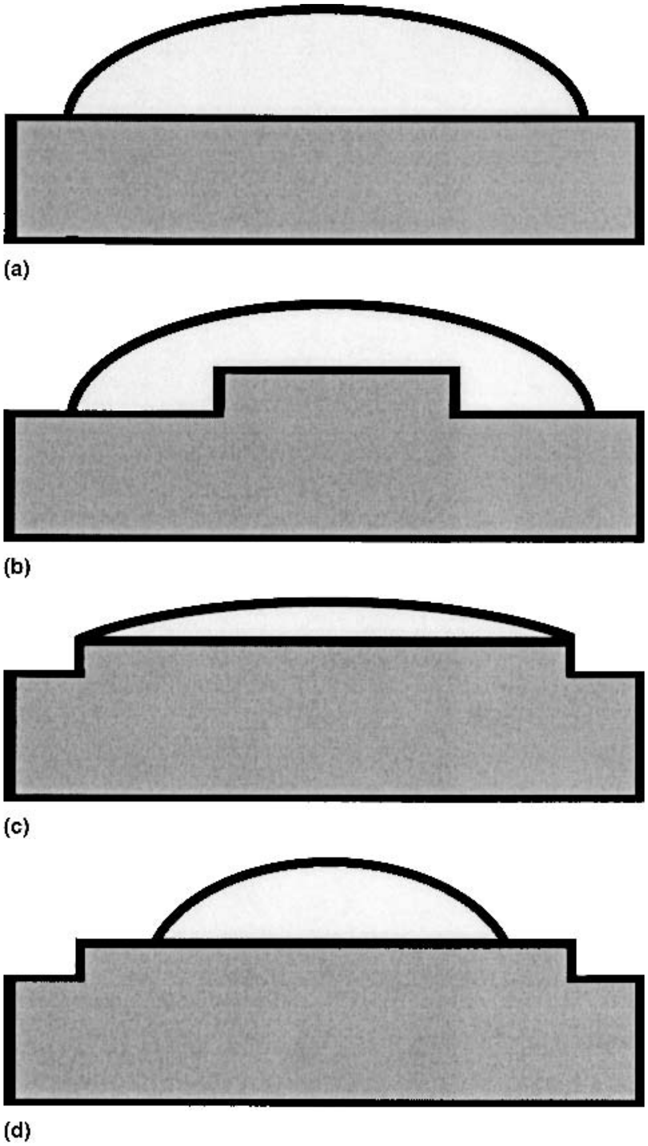

FIG. 9. Schematic of the formation of a MgO plateau under a droplet of silicate liquid on a flat MgO(001) surface. (a) The domed droplet is formed. (b) The MgO precipitate nucleates at the silicate/MgO interface at the droplet base. (c) The MgO precipitate reaches the triple air/silicate/MgO boundary at the droplet circumference. (d) The contracting droplet dewets the newly formed precipitate.

the droplets in contact with steps proceeds by ridge growth. The presence of some reverse bowing of the surface steps in Fig. 6 may indicate that the silicate liquid in the fragments etched the surface of MgO substrate during annealing.

As illustrated in Fig. 11, the developing ridge distorts the domed shape of the droplet.[18] As in the formation of a precipitate plateau, the development of the ridge also decreases the volume of the silicate phase. To restore the wetting contact angle and to reduce the surface area, the droplet at the ridge dewets the step but remains attached to the tip of the ridge (Fig. 11). This suggestion is supported by the observed widening of the ridges near the steps and away from the droplets; this widening indicates that the droplets connected to these segments were originally larger in size. As long as the ridges continue to develop, the droplets are expected to continuously dewet them by moving closer to the growing ridge tips (Fig. 10).

The driving force for the droplet rearrangement, which leads to the formation of the ridges, is the reduction of the surface area of the droplet and the restoration of the force balance at the air/silicate/MgO triple junction. The dewetting droplets adopt shapes and positions that will optimize the balance of forces along their circumferences.[20,21] The droplets attached to the ridges in Figs. 6–8, which are only approximately 100–500 nm in

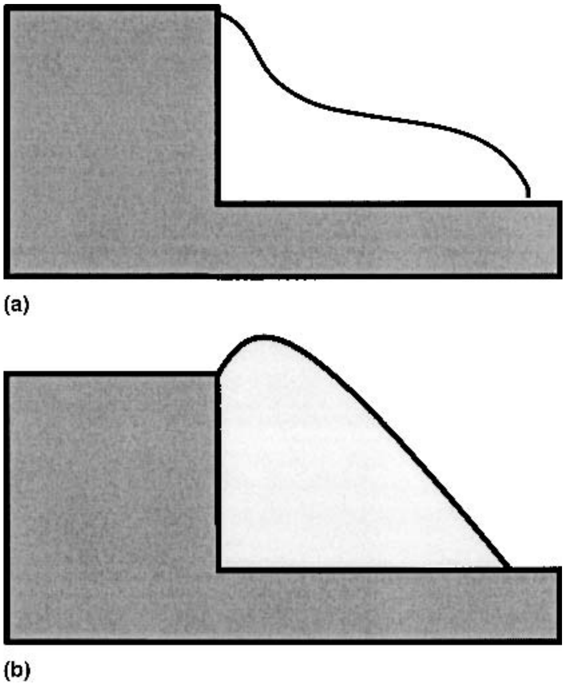

FIG. 10. Schematic of the dewetting at a surface step. (a) The droplet dewets both the step and the lower terrace and makes the same contact angle with both surfaces; the surface area of the droplet is large. (b) The droplet dewets only the lower terrace minimizing the surface area for the same volume of liquid.

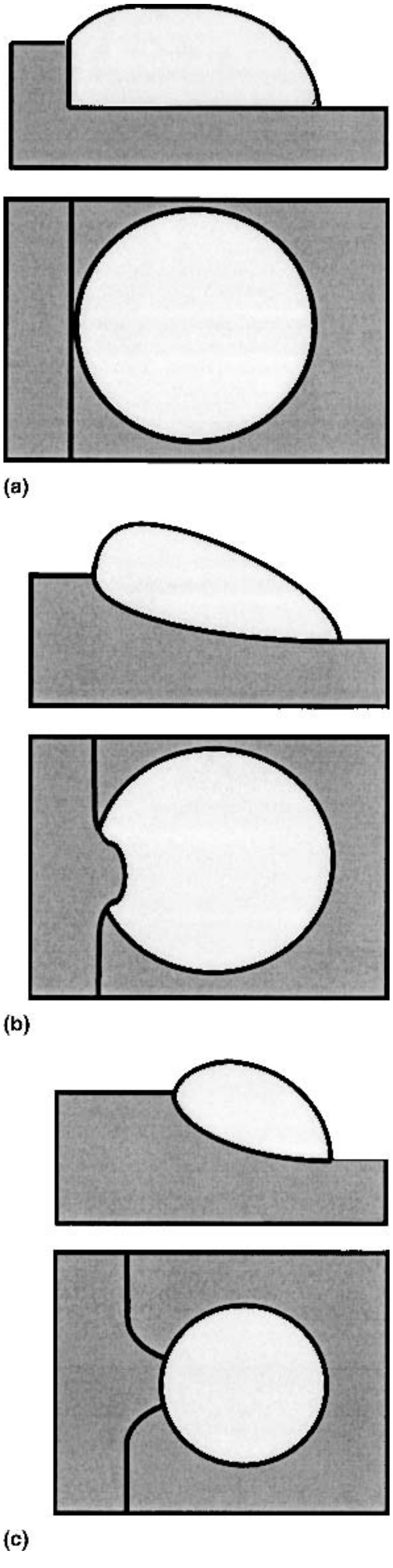

FIG. 11. Schematic of the formation of a ridge on a stepped MgO(001) surface. In each figure, the upper schematic represents the cross section, while the lower schematic shows the plan view. (a) A domed droplet just touches the step. (b) MgO precipitates out of the silicate liquid onto the step. The growing ridge distorts the surface of the droplet. (c) The ridge grows and forces the droplet to move.

diameter, are smaller in size and have a higher surface-to-volume ratio than the ridge-less droplets observed in the $CaMgSiO_4$/MgO(001) system.[9,19] The smaller droplets will be more susceptible to changes in the force balance at the triple junctions. In particular, changes induced by the growing ridges exert a force on the attached droplets. For a small droplet, the direction of this force coincides with that of the surface tension at the site of contact with the ridge and may exceed the surface tension elsewhere at the droplet circumference. The growing ridge may either cut the stationary droplet into two parts, which is unfavorable as two new silicate/MgO interfaces are created, or force the droplet to move to a new position to reduce the force imbalance.

Droplet motion occurs at elevated temperatures when the silicate liquid is sufficiently viscous. For small droplets, the rate of ridge growth depends primarily on the rate of absorption of MgO from the silicate phase and should be less dependent on the rate at which the MgO in the liquid is supplied to the moving interface. Therefore, small droplets at steps are expected to create long ridges, while large, less-mobile silicate droplets may not do so.

The ridges, which predominantly grow in the (001) surface plane, force the droplets to move along the surface in the downward direction; i.e., the droplets descend the surface steps, since climbing steps requires the droplets to perform work against gravity. Therefore, the direction of alignment of ridges may not necessarily be directly related to the crystallography of the MgO(001) surface. In Figs. 6–8, surface steps descend in the same direction, so all ridges appear to be crystallographically aligned.

For the ridgelike precipitates to grow, two conditions must be met. The surface of the MgO(001) substrate should be stepped, and precipitation should occur predominantly from isolated droplets, rather than a continuous liquid layer. The second condition is met when there is insufficient liquid to form a continuous film on the MgO(001) surface. Alternatively, to fragment a continuous liquid layer without causing a considerable MgO precipitation, the $CaMgSiO_4$/MgO(001) system must be rapidly quenched, as shown in Fig. 2. However, at low temperatures, both the dewetting and MgO precipitation are slow. To promote the growth of ridges, it is necessary to subject the system to an additional heat treatment. The repetitive annealing/quenching of the stepped $CaMgSiO_4$-coated MgO(001) surface thus appears to be a requirement to produce the growth of ridge-like step nodes on MgO(001) surface.

As demonstrated in Fig. 2, the first annealing/quenching of the system results in the formation of the disconnected regions of the silicate liquid on the MgO(001) surface. The comparison between the image of the MgO(001) surface under the as-deposited $CaMgSiO_4$ film (Fig. 1) and the image of the same surface area after two consecutive annealing/quenching cycles (Fig. 7) show that no large precipitate plateaus were formed during the two annealing cycles, which indicates that the quenching prevented MgO precipitation from the continuous layer of silicate liquid, while, as Fig. 2 shows, still causing it to fragment. The layer of silicate phase formed on melting is thin because the deposited layer was thin (Fig. 1). As a result, on completion of the second annealing/quenching cycle, the fragments of silicate layer dewet the MgO(001) surface and form small droplets, which are nearly all about 100–500 nm in diameter (Fig. 7). The inter-step distance in this area of the MgO(001) surface (approximately 100–500 nm) is smaller than the average size of the liquid regions formed on the first quenching of the system (approximately 500–1000 nm; Fig. 2). The majority of the dewet droplets created on the second quenching thus contact surface steps. The formation of ridges seen in Fig. 7 occurred in a manner similar to that of ridge growth from droplets in Fig. 6. However, due to the rapid first quench, the droplets in Fig. 7 did not form the plateaus first.

In Fig. 7, some of the larger droplets attached to surface steps did not create ridges. Steps could bow around such droplets during the second heating cycle when regions of the silicate liquid, which formed on the first quench, wet the terraces on MgO(001) surface. The spreading silicate liquid could then etch the MgO, starting at step edges, and cause the surface steps to bow. On the second quench, when the silicate liquid dewet the MgO(001) surface, the large droplets in Fig. 7 would not create ridges but instead remained over-saturated with MgO (as suggested by their larger than average size). This is in contrast to the droplets attached to the ridges, which also etched the MgO(001) surface on the second annealing, but which, on quenching, were driven away from the etched sites by the growing ridges. Thus, in Fig. 7, the ridges frequently connect the droplets to large clean surface areas bound by the bunched bowing steps; such sites probably indicate the original droplet locations.

The mechanism of the formation of ridges in Fig. 8 and Fig. 7 differ mainly in that those in Fig. 8 were grown in the system, which was not brought to room temperature during the annealing cycles. The longer heat treatment of the sample shown in Fig. 8 resulted in the formation of the longest ridges. The longer ridges in Fig. 8 follow the trajectory of motion of the silicate droplets across the more topographically complex area of the MgO(001) surface and produced curved ridges.

The precipitation of MgO in this study is similar to the process of liquid-phase epitaxy since the newly grown MgO has the same orientation as the substrate. Since it precipitates from a liquid of a different composition, the process is also similar to flux growth of single crystals. The ridges are themselves similar to single-crystal whiskers, which grow from a liquid in the vapor–liquid–solid process.[22] Here, the ridges have a lower total surface energy since one side of the "whisker" is not required. This is very similar to the process proposed for the growth of indium tin oxide whiskers along the surface of a substrate.[23] Finally, in this material system the dewetting process does not occur because of the change in composition of the glass due to heating above the melting point;[24] rather, it occurs because of the dependence of surface energy on temperature.

VI. CONCLUSIONS

At elevated temperatures, the interface between the MgO crystal and the silicate phase in the $CaMgSiO_4$/MgO(001) system is shaped by several processes which, depending on the heat treatment, may occur simultaneously. The wetting of the MgO(001) surface by a silicate liquid formed on incongruent melting of crystalline $CaMgSiO_4$ is accompanied by the dissolution of MgO into the liquid on heating; MgO precipitates out of the liquid on cooling. The dewetting of MgO(001) by a silicate liquid on cooling is accompanied by MgO precipitation.

The MgO precipitation may occur either through the nucleation and growth of plateaus from droplets on MgO(001) surfaces or by deposition of MgO from droplets in contact with steps on the MgO(001) surface. The former process occurs on flat MgO(001) surfaces when a continuous layer of silicate liquid is formed. The second mechanism leads to the development of ridges on the surface. Ridge growth occurs on stepped MgO(001) surfaces during precipitation from the disconnected regions of the silicate liquid. The intermediate plateau/ridge morphology is expected when MgO precipitation occurs out of the disconnected liquid regions onto the stepped MgO(001) surface.

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