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Effects of SiO_2, CaO_2, and MgO Additions on the Grain Growth of Alumina

Chan Woo Park and Duk Yong Yoon*,†

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Taejon 305–701, Korea

When pure alumina is sintered at 1620°C, normal grain growth occurs with equiaxial grains and curved grain boundaries. When 100 ppm of SiO_2 together with 50 ppm of CaO is added, abnormal grain growth (AGG) occurs with large grains elongated with straight grain-boundary segments in the direction of the basal planes. Some of the fine matrix grains also have straight grain boundaries, and ~10% of the grain boundaries of the matrix grains are faceted when observed by transmission electron microscopy (TEM). Some of these grain boundaries are expected to be singular with low-energy structures corresponding to the cusps in the polar plot of the grain-boundary energy against the inclination angle. No frozen liquid is found at the grain triple junctions and grain boundaries by TEM. When 600 ppm of MgO is added together with 100 ppm of SiO_2 and 50 ppm of CaO normal growth occurs. The grain boundaries are curved when observed via optical microscopy and TEM and show that all the grain boundaries are defaceted, indicating that they become atomically rough. When sintered at 1900°C after adding 150, 300, or 500 ppm of SiO_2, AGG occurs with straight and faceted grain boundaries, similar to the specimens sintered at 1620°C after CaO and SiO_2 are added. When MgO is added together with SiO_2 and sintered at 1900°C, normal grain growth occurs with rough grain boundaries. High-resolution TEM observation shows no frozen liquid layer at a grain boundary. The results indicate that the occurrence of AGG in alumina with SiO_2 or together with CaO is correlated with the formation of faceted and straight (on large and atomic scales) grain boundaries. It is proposed that these grain boundaries have singular ordered structures with low boundary energies and their growth by lateral step movement can cause the AGG. The addition of MgO causes grain-boundary roughening and, thus, normal grain growth. The grain boundaries in pure alumina also appear to be rough, and, hence, normal grain growth occurs.

I. Introduction

THE sintering of relatively pure alumina is an important industrial process for some products. It is well-known[1–3] that small amounts of CaO or SiO_2 can induce abnormal grain growth (AGG) during the sintering of alumina, but the addition of MgO can prevent AGG.[4–6] The effect of CaO and SiO_2 has been attributed to the production of liquid phases[1,3] or segregation at the grain boundaries.[7,8] It has also been suggested that MgO alters the grain-growth behavior through its segregation at the grain boundaries.[5,9–11] Although much experimental study has been focused on determining the segregation behavior of these species at grain boundaries, the evidence for these proposed effects on grain growth is still meager.

Both special and general grain boundaries in metals are often observed to be faceted with zig-zag shapes[12–18] and undergo defaceting transition when the temperature is increased.[14] Grain-boundary faceting in alumina has also been reported.[19,20] The incorporation of O in Ni[12] and Ag,[21] Bi in Cu,[15,16] and Te in Fe[17,18] each have been observed to induce grain-boundary faceting. At least some of the facet planes are expected to be singular boundaries with local minimum energies corresponding to the cusps in the polar plot of the boundary energy against the inclination angle (the γ-plot). If a grain boundary is defaceted with a curved shape, it should have an atomically rough structure, as predicted by Cahn.[22]

Recently, Lee *et al.*[23] observed a correlation between grain-boundary faceting and AGG in relatively pure polycrystalline nickel. At high temperatures close to the melting point in a carburizing atmosphere, the grain boundaries were defaceted with curved shapes and, hence, had an atomically rough structure. Then normal grain growth was observed. However, at low temperatures, the grain boundaries were faceted and AGG occurred.[23] Under low vacuum, the grain boundaries were faceted at all temperatures and AGG occurred. Such a correlation between the grain-boundary faceting and AGG was also found in pure silver when heat-treated at different temperatures either in an oxygen atmosphere or under vacuum.[21] It has been proposed that AGG occurs with faceted grain boundaries, because they move by a boundary step mechanism.[23,24] When grain boundaries become atomically rough (and, therefore, almost isotropic), normal grain growth is observed, as predicted by the analysis of Thompson *et al.*[25] and the simulation of Srolovitz *et al.*[26]

Previously, no attempt has been made to relate the grain-boundary structure in alumina to its grain-growth behavior.[19,20] The purpose of this work is to explore the possibility that CaO and SiO_2 induce the formation of singular grain boundaries and, thus, AGG, as well as the possibility that MgO induces grain-boundary roughening and, thus, normal growth in alumina without any liquid phase. The specimens with additives were made using normal powder processing techniques, and the grain boundaries were examined by transmission electron microscopy (TEM).

II. Experimental Procedure

The specimens were prepared from α-alumina powder (AKP-50, >99.98% pure, Sumitomo Chemicals, Tokyo, Japan). $Si(OC_2H_5)_4$ (>99.999% pure), $Ca(NO_3)_2{\cdot}XH_2O$ (>99.99% pure), and $Mg(NO_3)_2{\cdot}6H_2O$ (>99.9%) were used as the sources of SiO_2, CaO, and MgO. The alumina powder was mixed with the dopants in ethyl alcohol and dried at 70°C. The doped powder was pressed into cylindrical compacts and then pressed isostatically at 100 MPa. The compacts were heated to 950°C for 1 h to convert the dopant chemicals to oxides and remove ethyl alcohol. Then, the

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*Member, American Ceramic Society.
†On leave at the National Creative Research Initiative Center for Microstructure Science of Materials, Seoul National University, Seoul, Korea.

compacts were sintered at either 1620° or 1900°C. The sintering at 1620°C was performed in air in a high-purity alumina tube furnace. The sintering at 1900°C was performed in a tungsten-mesh furnace under vacuum ($\sim 10^{-3}$ Pa). The compacts were placed in a high-purity alumina crucible that was packed with the same powder as the compact for the sintering at 1900°C. The polished surfaces of the sintered specimens were thermally etched at 1550°C for ~30 min for examination by optical microscopy and scanning electron microscopy (SEM) (Model 515, Philips Research Laboratories, Eindhoven, The Netherlands). The specimens for TEM analysis (Model JEM-3010, JEOL, Tokyo, Japan) were thinned by mechanical grinding and ion-beam milling.

III. Results and Discussion

Figure 1(a) shows that normal grain growth was observed in a pure alumina specimen sintered at 1620°C with equiaxed grains. At the magnification used for this micrograph, all grain boundaries appeared to be smoothly curved with uniform dihedral angles at the triple junctions, although the apparent dihedral angles in the specimen cross section usually do not correspond to the true values. Some pores were present in the sintered specimens. Previous observations[1–3] also showed that normal grain growth occurred when the compacts of high-purity alumina were sintered in well-protected atmospheres. The TEM observations of approximately one hundred grain boundaries showed that each was smoothly curved (without any faceting), as shown in Fig. 1(b). There was no second phase at either the grain triple junctions or the grain boundaries. The curved shapes of these boundaries indicate that they are rough, on atomic scales.

When 100 ppm of SiO_2 with 50 ppm of CaO was added to alumina, AGG occurred, as shown in Fig. 2(a). Some of the large abnormal grains had lath shapes elongated in the directions that were probably parallel to their basal (0001) planes, as shown in the previous studies.[20] These large elongated grains often showed straight boundary segments in contact with many fine grains in the elongated direction, as shown in Figs. 2(a) and (b). These straight boundaries are likely to coincide with the (0001) planes of the elongated grains, as shown in the previous studies.[20] These micrographs also show clusters of fine matrix grains, and some of them were also slightly elongated with straight boundaries in contact with several grains (as shown, for example, in the elliptical highlight in Fig. 2(b)). However, at the magnification used for Fig. 2(b), some of the grain boundaries between the fine grains appeared to be curved. Previously, AGG was also observed with similar grain shapes when >300 ppm of SiO_2 or >30 ppm of CaO were added to pure alumina and sintered at 1900°C for 1 h.[1] Approximately one hundred grain boundaries of the fine matrix grains were examined by TEM, and seven or eight of them were faceted with hill-and-valley shapes, as shown in Fig. 2(c), whereas the others were apparently either straight or slightly curved at the relatively high magnification used for Fig. 2(c). (In this paper, the

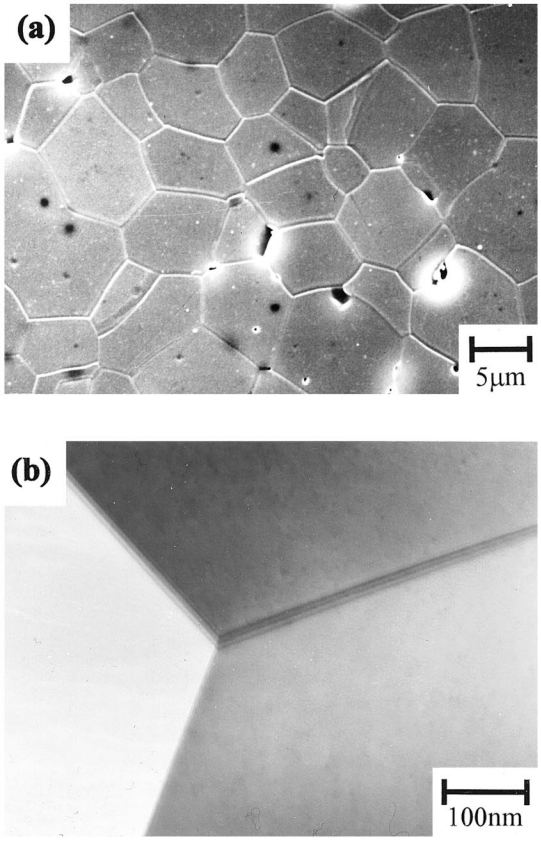

Fig. 1. (a) SEM microstructure of pure alumina sintered at 1620°C for 12 h; (b) grain boundaries at high magnification, as observed by TEM.

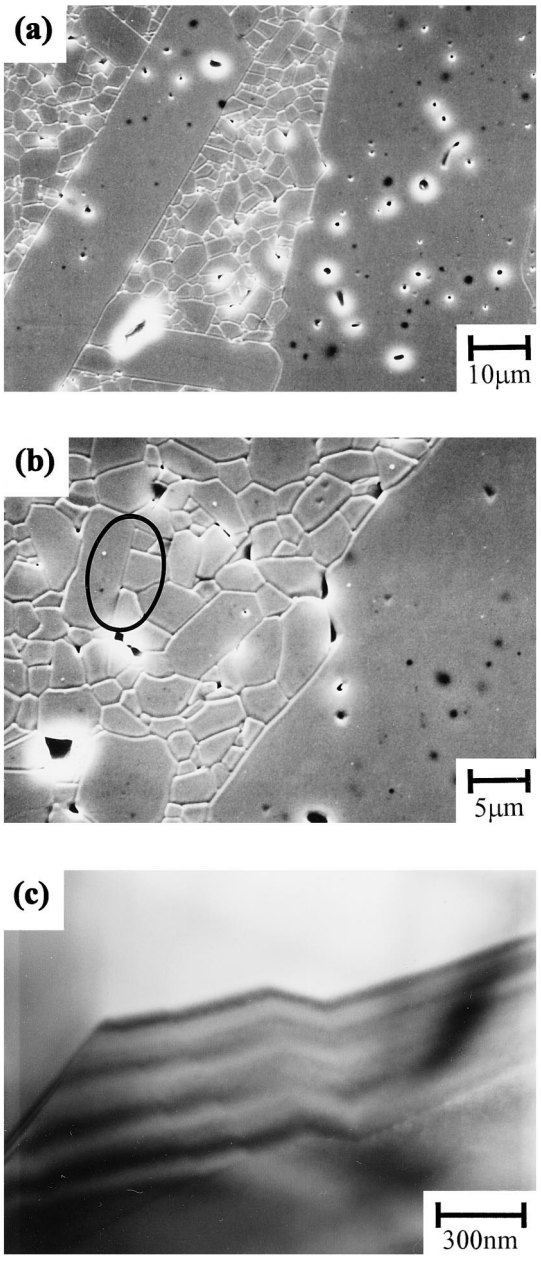

Fig. 2. Microstructures of alumina doped with 100 ppm of SiO_2 and 50 ppm of CaO and sintered at 1620°C for 12 h at (a) low magnification and (b) an intermediate magnification (each as observed by SEM). Figure 2(c) shows a grain boundary at high magnification, as observed by TEM.

faceted grain boundaries refer to those with flat boundary segments forming hill-and-valley shapes, as shown in Figs. 2(c) and 5.)

In this specimen, therefore, there seems to be three different types of grain boundaries: (i) grain boundaries that are curved on both large and fine (atomic) scales, as those in the pure alumina specimen (these must have an atomically rough structure); (ii) grain boundaries that are straight on both large and atomic scales, coinciding with the (0001) and possibly other low-index planes of the grains (if these represent the equilibrium grain-boundary structures, they will be the singular boundaries corresponding to the cusps in the polar plot of the grain-boundary energy (the γ-plot) against the inclination angle or the boundary normal); and finally (iii) grain boundaries that may appear to be either curved or almost straight on the macroscopic scales used for Figs. 2(a) and (b) but actually have faceted zig-zag shapes on the fine scales shown in Fig. 2(c). (The faceted grain boundaries in the specimens doped with SiO_2 and sintered at 1900°C are also shown in Fig. 5.) All or some of these facet planes are likely to be also singular, corresponding to the cusps in the γ-plot.

The faceted grain boundaries were observed previously in various alumina specimens.[19,20] Morrissey and Carter[19] found that several high-angle grain boundaries in a commercial alumina were faceted when observed via TEM and that the facet planes of the special low-Σ boundaries followed the directions of either the high-coincidence site lattice (CSL) or the O-site lattice points. Gülgün *et al.*[20] also found straight or faceted high-angle grain boundaries in alumina doped with 1000 ppm of Y_2O_3; they also found that the grain-boundary facets coincided with the (0001) and $\{0\bar{1}12\}$ planes of one of the grains. These are likely to be the singular planes corresponding to the cusps in the γ-plot.

Normally, if even a small amount of liquid phase is present, frozen liquid pools can be detected via TEM at the triple junctions. However, in these specimens, no liquid layer was observed at the triple junctions and the grain boundaries, even at a magnification of 300 000×.

When 600 ppm of MgO was added together with 100 ppm of SiO_2 and 50 ppm of CaO, the grains seemed to grow normally, as shown in Fig. 3. The grain size of this specimen was slightly smaller than that of pure alumina sintered for the same period shown in Fig. 1, probably because of a retarding effect of the additives segregating at the grain boundaries. It also is possible that the average grain-boundary energy was reduced by the segregating solute atoms. At low magnifications, most of the grain boundaries were smoothly curved (as shown in Figs. 3(a), (b), and (c)) and, at high magnification, almost straight (as shown in Fig. 3(d)). None of the approximately one hundred grain boundaries examined showed faceted shapes when examined via TEM at high magnifications. These results show that the addition of MgO caused the grain boundaries to become defaceted with curved shapes on both large and fine scales and, therefore, atomically rough as those in the pure alumina specimen shown in Fig. 1.

The specimens with only SiO_2 or together with MgO sintered at 1900°C showed essentially the same results. The pure alumina specimen sintered at 1900°C for 3 h had an average grain size slightly larger than the pure alumina sintered at 1620°C for 12 h (shown in Fig. 1) and a typical normal growth structure with equiaxial grains. Almost all the grain boundaries seemed to be curved at low magnifications and almost straight without any faceting at the high magnifications used for TEM analysis. Thus, these boundaries must have been rough on the atomic scale. The microstructures of the specimens with 150, 300, and 500 ppm of SiO_2 sintered at 1900°C showed typical AGG structures with the large grains elongated along the basal planes, as exhibited in Fig. 4. Some boundaries of the matrix grains also seemed to be straight. Approximately 10% of the grain boundaries of the matrix grains had faceted shapes when observed via TEM, as shown in Fig. 5. High-resolution TEM observation of the specimen with 300 ppm of SiO_2 showed no indication of a frozen liquid layer at a grain boundary. The specimen with 300 ppm of SiO_2 together with 2000 ppm of MgO showed normal growth with equiaxial grains and smoothly curved grain boundaries. TEM analysis showed that all

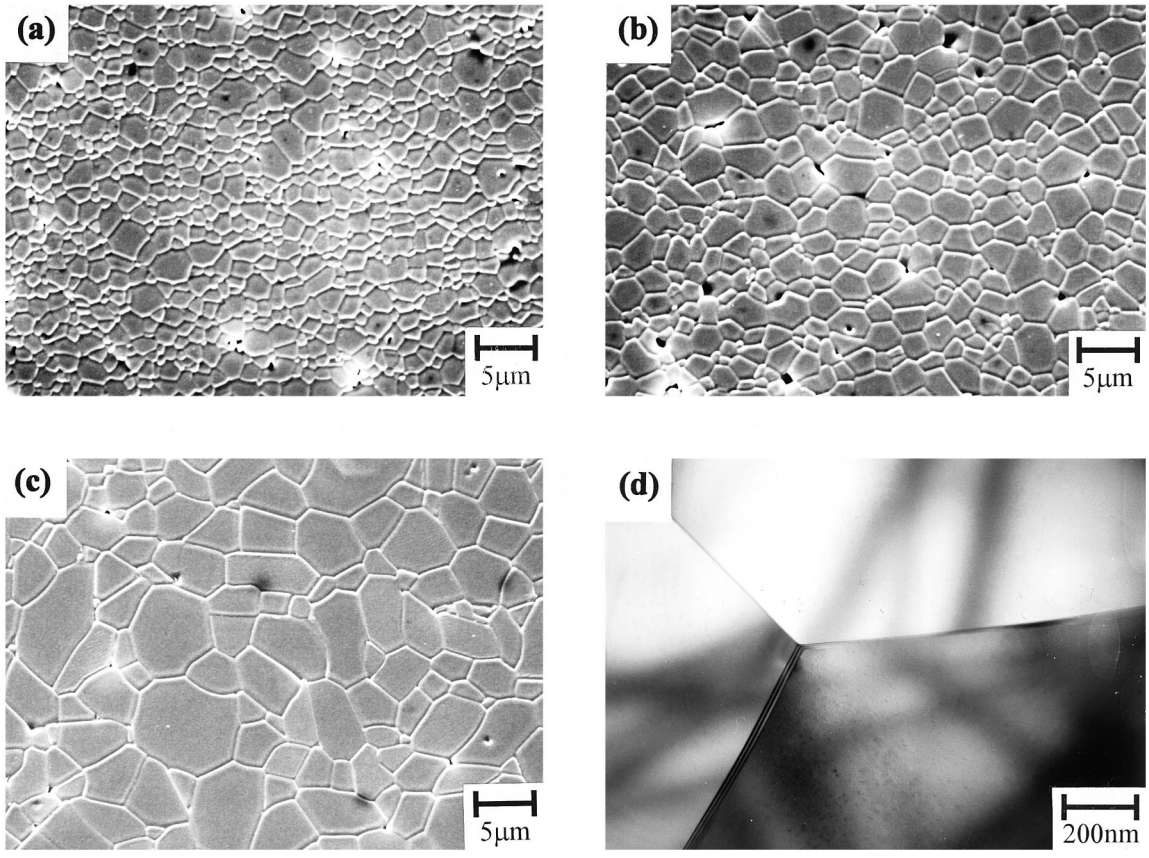

Fig. 3. SEM microstructures of alumina doped with 100 ppm SiO_2 + 50 ppm CaO + 600 ppm MgO and sintered at 1620°C for (a) 10 min, (b) 1 h, and (c) 12 h; Fig. 3(d) shows the grain boundaries at high magnification (as observed by TEM).

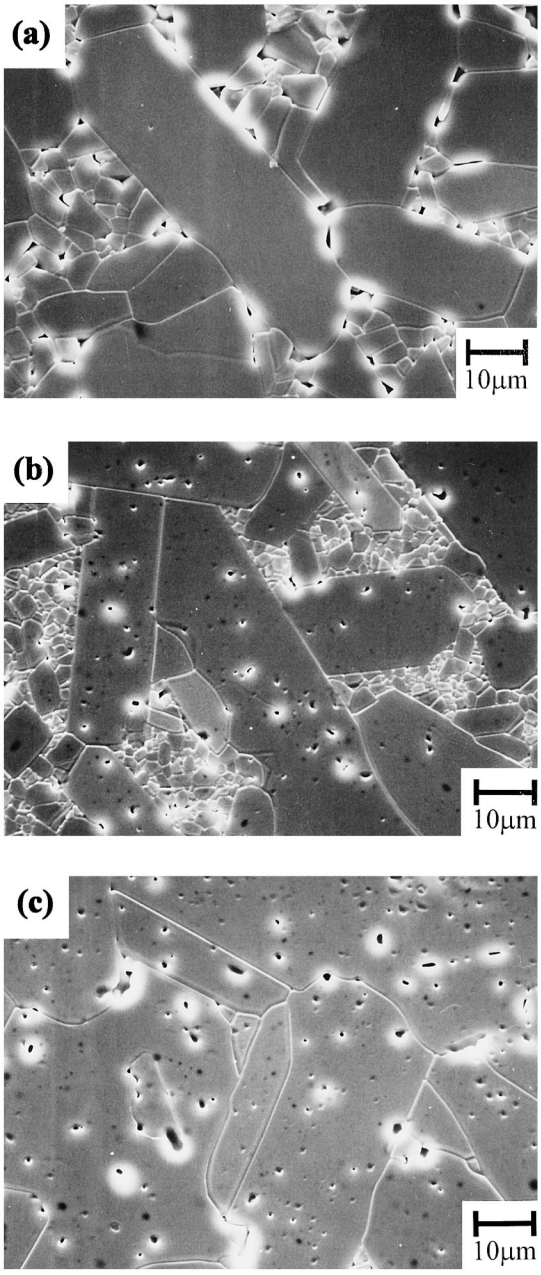

Fig. 4. SEM microstructures of alumina sintered at 1900°C for 3 h doped with (a) 150, (b) 300, and (c) 500 ppm of SiO_2.

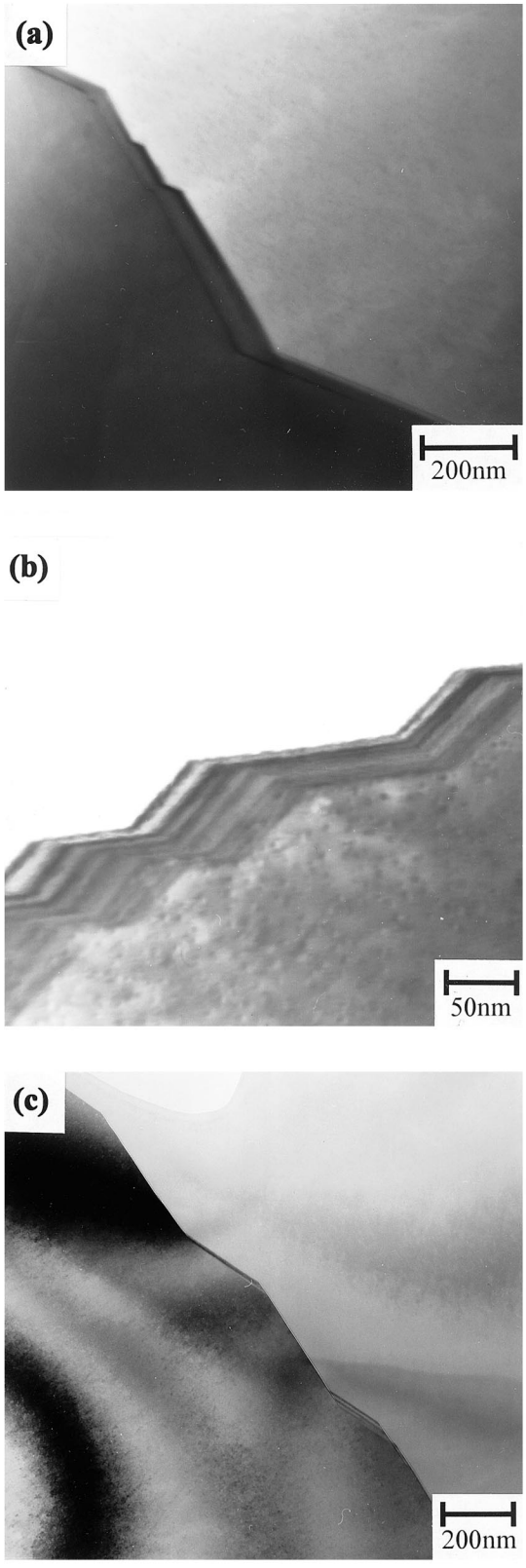

Fig. 5. Faceted grain boundaries in alumina sintered at 1900°C for 3 h doped with (a) 150, (b) 300, and (c) 500 ppm of SiO_2.

the grain boundaries were defaceted, indicating an atomically rough structure.

The roughening effect of MgO seems to apply generally to all types of interfaces in alumina. We observed that the faceted alumina surfaces in air or in contact with anorthite liquid became rough when MgO is added.[27] Previously, Handwerker *et al.*[28] observed that the distribution of the dihedral angles at the grain-boundary/surface junctions of alumina became narrower when MgO was added. Their observation is consistent with the roughening of both grain boundaries and surfaces induced by MgO.

Summarizing our observations, in the pure and MgO- (together with SiO_2 and CaO) doped specimens, normal grain growth occurs with rough grain boundaries, and in specimens doped with SiO_2 and CaO, AGG occurs, with faceted and straight grain boundaries. This correlation between the grain-boundary structure and the growth behavior is similar to those found in Ni[23] and Ag.[21] In Ni, it was also observed that AGG occurred even when only a fraction of the grain boundaries were faceted at relatively high temperatures.[23] The normal grain growth with defaceted and, hence, atomically rough grain boundaries seems to be possible because the grains grow by a continuous process where the growth rate of a grain is linear with driving force. This correlation also is consistent with the analysis of Thompson *et al.*[25] and the simulation of Srolovitz *et al.*,[26] which predict normal growth if the grain boundaries are isotropic and the growth rate is linear with the driving force. If the grain boundaries are singular with either

straight or faceted shapes, they may migrate by either two-dimensional nucleation of the surface steps or on the surface steps produced by dislocations, as proposed by Gleiter,[29–31] in analogy with the growth of atomically flat crystal surfaces. Then, the migration rate will vary nonlinearly with the driving force. Because the growth rate of the grains of intermediate size will be very small while the growth rate of the large grains will be relatively high, AGG can occur, as suggested previously.[23,24]

The roughening effect of the MgO addition is equivalent to causing the decrease of the boundary-step free energy. Both the two-dimensional nucleation theory[32] and the spiral growth on screw dislocation theory[33] indicate that the number of the abnormally growing large grains will increase as the step free energy decreases, as proposed earlier by Yoon *et al.*[24] Therefore, as the step free energy decreases with increasing MgO content, the number of the abnormally growing grains will increase with an apparent enhancement of the AGG behavior. However, when the MgO concentration is sufficiently high to cause the step free energy to become zero, all the grains can grow continuously and, hence, normal growth occurs. Therefore, the transition from AGG to normal growth with increasing MgO concentration will be continuous as the number of the rapidly growing grains increases. A similar transition from AGG to normal growth is expected with increasing temperature, as proposed earlier.[24]

IV. Conclusions

The results of this work indicate the possible correlation between the faceted and straight grain boundaries and abnormal grain growth (AGG) in alumina when SiO_2, CaO, and MgO are added. With SiO_2 alone or together with CaO, ~10% of the grain boundaries were faceted. The remainder might be straight along the low-index planes of one of the grains, or either thermodynamically or kinetically rough. The effect of these additives on the grain-boundary faceting in alumina needs further study in, perhaps, bicrystals with stationary grain boundaries to distinguish between the thermodynamic and kinetic roughening. It is possible that, even when singular and rough grain boundaries coexist, the singular grain boundaries control the growth behavior, hence resulting in AGG.

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