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Microstructures of Impurity Precipitates in Sintered Alumina used as a Crucible to Anneal Lead Titanate

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Abstract. Impurity precipitates at grain boundaries in sintered alumina were characterized with a scanning electron microscope (SEM) and a transmission electron microscope(TEM) and by energy dispersion analysis of X-ray (EDX). Spherical and cylindrical impurity precipitates were found at grain boundaries in the alumina obtained after annealing 1700°C-sintered alumina at 1000°C. On the other hand, filmy precipitates of an amorphous phase about 2.5 nm in thickness were found at grain boundaries in the alumina quenched to room temperature from 1700°C. The EDX data indicated that the elements of impurity precipitates contained Na, Ca, Al, and Si. The formation mechanisms of the spherical and cylindrical precipitates and the reaction between the precipitates and $PbTiO_3$ were briefly discussed.

Keywords: alumina, precipitates, grain boundary, microstructure

1. Introduction

It is well known that alumina is an important ceramic material for various applications such as integrated packages, IC substrates, crucibles for high temperature, and many others. Consequently, many workers have studied the sintering behavior of alumina [1–6] In industrial fabrication processes, alumina powder usually mixed with a binder and well water are slip-cast to various shapes and sintered. During the processes, some impurities such as Na, Ca, and Si are introduced from the water, the binder, and/or a furnace into the sintered alumina. The impurity precipitates are often present as a glassy phase at the grain boundaries. The shape, size, and other properties of the precipitates affect the grain growth [7–8], the life time, and other properties of sintered alumina. Therefore, it is important to know what kinds of precipitates are present at grain boundaries. We investigate the shape and size of precipitates by observing grain boundaries in sintered alumina with SEM and TEM and by EDX, and discuss the formation mechanisms of impurity precipitation and the reaction between precipitates and $PbTiO_3$ at grain boundaries.

2. Experimental

Impurity levels of up to 400 ppm total of Na, Ca, Si, and others were detected by an ICP analysis in alumina powder used in this experiment. The powders were uniaxially pressed to compacts at 50 MPa without binders. The compacts were sintered at 1700°C for 3 h in air in a molybdenum disilicide furnace. Some sintered compacts (Sample (A)) were quenched from the sintering temperature to room temperature in air. The compacts were sufficiently small so that quenching did not cause extensive cracking. The other sample (Sample (B)) was prepared by reheating Sample (A) at 1000°C for 3 h in air. The sintered densities of both Samples (A) and (B) were measured by the Archimedes method. The density obtained was 97% of theoretical. Both samples (A) and (B), filled with $PbTiO_3$ powder, were pressed to compacts at 50 MPa. The compacts were heated at 1300°C for 2 h in air. The obtained samples were mechanically fractured. The fracture surfaces of sintered bodies in both samples were observed by SEM and TEM. The precipitates at grain boundaries in the fracture surfaces were analyzed with an SEM equipped with an EDX apparatus.

3. Results and Discussions

Sample (A): Fracture of the sintered alumina usually took place through both grains and grain boundaries. From a SEM micrograph (Fig. 1), it was easy to distinguish grain and boundary surfaces, since grain surfaces were sharp due to cleavage. Impurity precipitates at grain boundaries were easily distinguished by back scattered electron microscope images. They were usually not in fracture surfaces in a grain, but were present at grain boundaries (Fig. 2). In many cases, they were filmy without crystal habits as indicated by an arrow in Fig 2a, but some impurity precipitates exhibited crystal habits as shown in Fig. 2b. The EDX data of the precipitates indicated by arrows in Fig. 2a and 2b showed that they were composed of Na, Ca, Al, and Si (Fig. 3), where the Pt peak comes from the Pt coating applied to prevent the charge-up of samples. Since SiO_2, Al_2O_3, and CaO and Na_2O are glass network formers, intermediates, and modifiers, respectively, the precipitates are expected to have a high likelihood of being glassy at room temperature. In fact, as shown in an electron diffraction pattern later, the precipitates were amorphous. A lattice image observed by TEM indicates a filmy precipitate of thickness of about 2.5 nm was present at this grain boundary as shown in Fig 4, where $(12\bar{3}1)$ describes a crystal plane in alumina normal to the incident electron beams, and $\langle 10\bar{1}\bar{1} \rangle$ and $\langle 1\bar{1}01 \rangle$ indicate two directions of the crystal. Almost all grain boundaries had such filmy precipitates. However, other grain boundaries had no impurity precipitates (Fig. 5). This would indicate that impurity precipitates distributed inhomogeneously, that is, some grain boundaries, had impurity precipitates while others did not. Three grain junctions always had impurity precipitates (Fig. 6). The EDX analysis of the precipitates with white contrast also showed the presence of Na, Ca, Al, and Si. They were glasses, since the electron diffraction pattern of the precipitates was a halo as inset in the figure. On the other hand, the electron diffraction patterns of the particles with dark contrast in the three grain junctions were the same as that of alumina. The particles of alumina were apparently transported by the flow of the glassy phase composed of SiO_2, Al_2O_3, CaO, and Na_2O from other grain boundaries to the three grain junctions during grain growth at 1700°C.

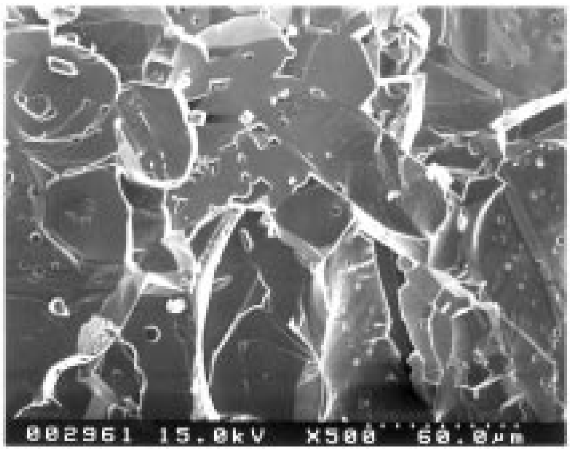

Fig. 1. SEM micrograph of a fracture surface in alumina (Sample (A)) sintered at 1700°C for 3 h in air.

Sample (B): The typical SEM micrograph of a fracture surface was fundamentally the same as that of Sample (A). Although some grain boundaries had impurity precipitates, they were not filmy but as isolated granular particles. The size of the particles was different from grain boundary to grain boundary, and some grain boundaries had spherical and cylindrical precipitates (Fig. 7). The EDX analysis of the precipitates showed that Ca, Al, and Si were the main elements but the existence of Na was not clear. It is difficult to judge whether the precipitates at grain boundaries are crystals or not, but an electron diffraction pattern of precipitates at three grain junction indicates a glassy phase. Figure 8 showed impurity precipitates at grain boundaries in sintered alumina, which reacted with $PbTiO_3$ by annealing at 1300°C for 2 h in air. As can be seen in the figure, the grain boundaries are wet by precipitates with white contrast as indicated by the arrows. EDX data clearly showed the presence of Na, Pb, Ca, Al, and Si in the precipitates. Some impurity precipitates also with white contrast are present discontinuously on fracture surfaces in the bulk.

The formation processes of spherical and cylindrical precipitates in Sample (B) may be considered in

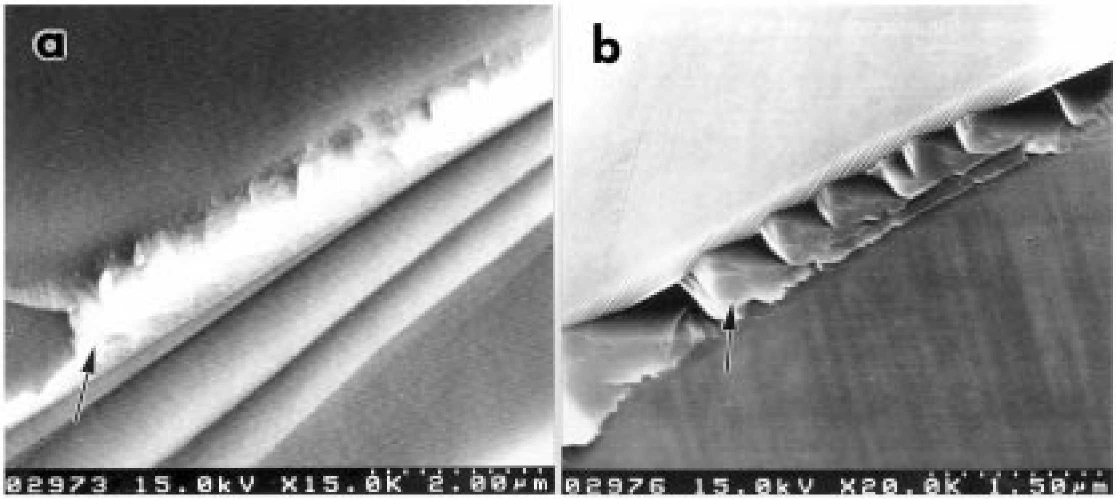

Fig. 2. SEM micrographs of a fracture surface in sintered alumina (Sample (A)). Some grain boundaries are wetted by impurity precipitates and are imaged by the white contrast indicated by arrows.

the following. At high temperature, a homogeneous liquid is the minimum free-energy state, and is thermodynamically stable [9]. As the temperature is lowered, the minimum free energy state becomes a mixture of two phases rather than a single phase, with phase separation expected. Since phase separation is generally considered to take place at lower temperature, it would proceed during the time for which samples quenched from 1700°C were reheated at 1000°C for 3 h in air. Then, the precipitates in quenched alumina, Sample (A), initially as a Na_2O-CaO-Al_2O_3-SiO_2 glass at room temperature, would separate into two phases during the reheat-treatment at 1000°C. As reported for the soda lime-

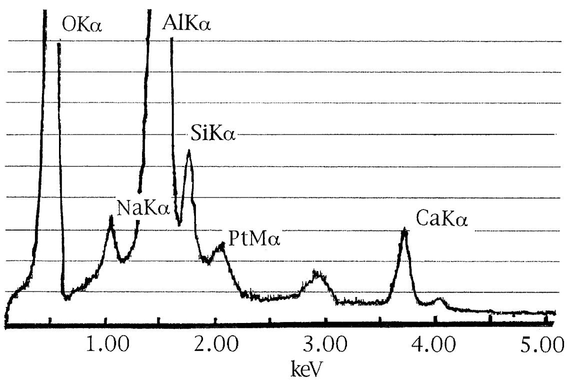

Fig. 3. The main elements in the precipitates of Fig. 2 analyzed by EDX were Na, Ca, Al, and Si. The Pt peak in the figure comes from the Pt coating applied for preventing charge-up.

silica system [10], two glasses of high and low Na contents would be formed by the phase separation at grain boundaries during reheating at 1000°C. The glass of low Na content would be embedded in a continuous matrix of the glass of high Na contents. If the former glass had low solubility and the latter glass had high solubility in alumina at lower temperature, the former glass would remain at the grain boundaries while the other would dissolve into the alumina grains forming a solid solution with alumina. Then, only the glass with low Na content would be left behind at the grain boundaries. The precipitates would tend to become spherical and cylindrical, since glass is isotropic.

A problem of technical importance is the swelling of sintered alumina, when it was used at high temperature as refractories such as bricks and crucibles, due to impurity precipitates at grain boundaries. The experimental data obtained here suggested that the swelling often took place in sintered alumina with continuously filmy precipitates, when the alumina crucibles were used to anneal $PbTiO_3$. In this case, Sample (A) often swelled faster than Sample (B) during heating at high temperature. The reasons for this may be related to different reactivity between the precipitates at grain boundaries and Pb in $PbTiO_3$. A glass formed by reaction of precipitates with Pb is expected to have low viscosity. The glass containing Pb is easily softened at low temperature, so gases could be enclosed in the pores

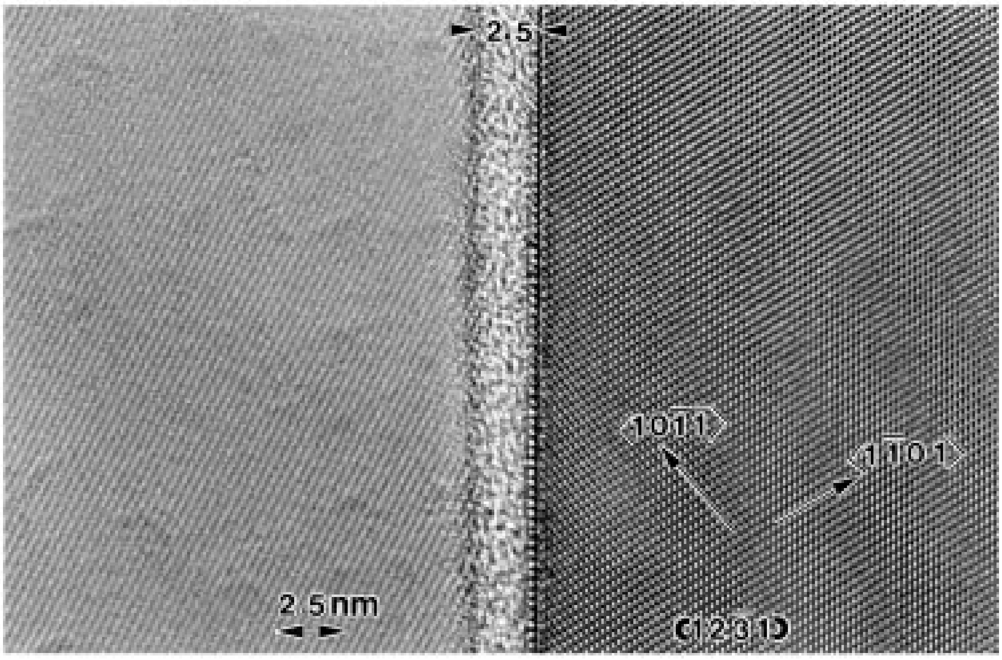

Fig. 4. Lattice image of a grain boundary in Sample (A). It is clear from the image that an amorphous phase of about 2.5 nm thickness is present.

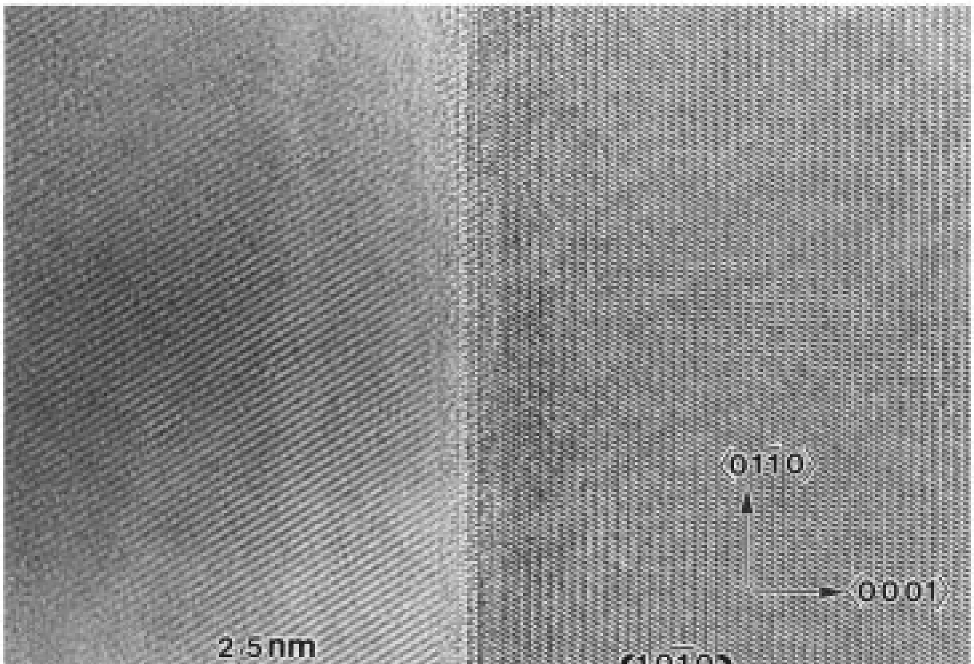

Fig. 5. Some grain boundaries in Sample (A) had no impurity precipitates as indicated in the figure.

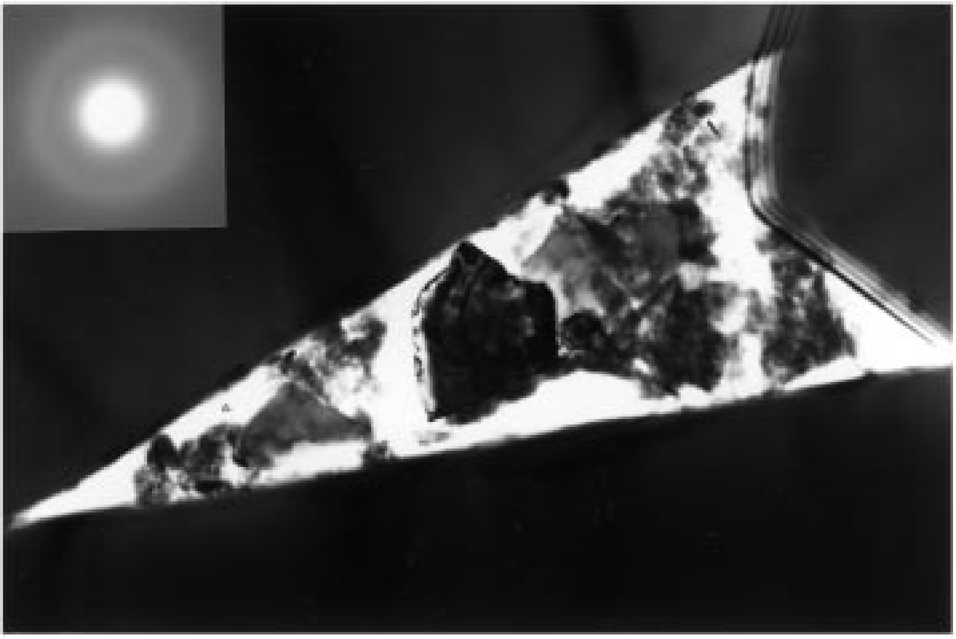

Fig. 6. Impurity precipitates at three grain junctions in sample(A). The diffraction pattern inset from a part with white contrast in the three grain junctions is a halo indicating it to be amorphous. EDX data indicated that the particles with dark contrast in three grain junctions are alumina particles.

surrounded by the glass. Then, as the temperature is further raised, the expansion of the enclosed gases could spread the softened glass phase. This would explain why the sintered alumina swelled when it was used as a crucible to anneal $PbTiO_3$. We found that Sample (A) swelled within 5 cycles of heating from room temperature to 1300°C. On the contrary, Sample (B) with spherical and cylindrical impurity precipitates at grain boundaries did not swell in more than 5 heating cycles. This would indicate that the reactivity

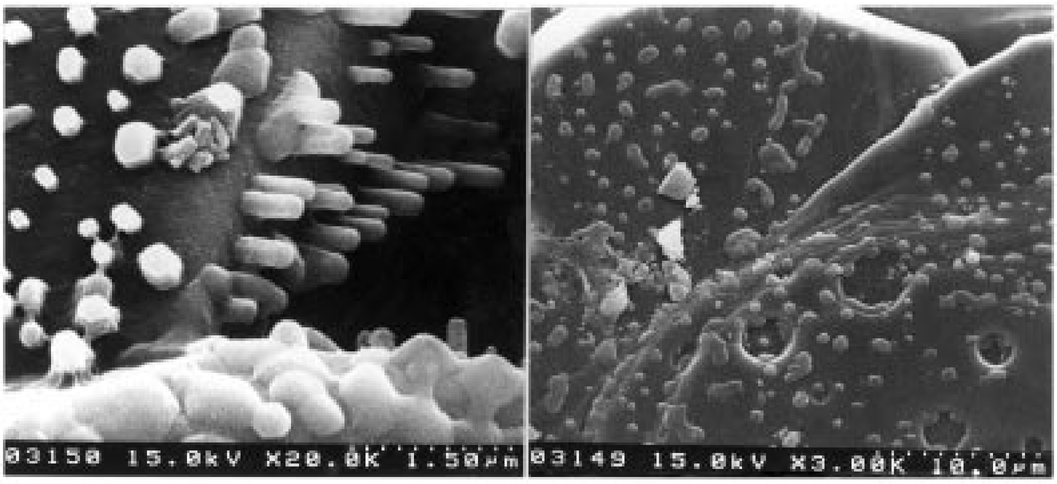

Fig. 7. Spherical and cylindrical precipitates at grain boundaries. The main elements of the precipitates analyzed by EDX were Ca, Al, and Si.

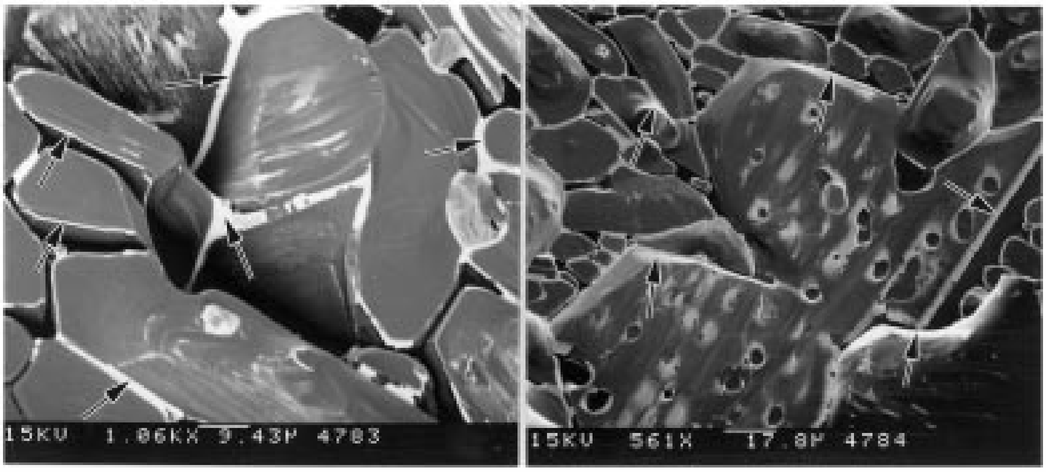

Fig. 8. Impurity precipitates at grain boundaries in Sample (B). EDX data indicate that the main elements of the precipitates with white contrast as shown by arrows are Pb, Ca, Al, and Si.

between precipitates at grain boundaries and Pb in $PbTiO_3$ was different in filmy precipitates and isolated granular precipitates, and that the nature of the preciptates at the grain boundaries was very important for the life of alumina crucible.

4. Conclusions

Impurity precipitates at grain boundaries in sintered alumina quenched from 1700°C to room temperature and reheated at 1000°C for 3 h were characterized by SEM, TEM and by EDX. Spherical impurity precipitates were found at grain boundaries in the alumina reheated at 1000°C. On the other hand, filmy precipitates of an amorphous phase about 2.5 nm in thickness were found at grain boundaries in alumina quenched to room temperature from 1700°C. The EDX data indicated that the impurities were Na, Ca, Al, and Si. Quenched alumina with continuously filmy precipitates swelled after a few heating cycles at high temperature, when used as a crucible to anneal $PbTiO_3$. On the contrary, reheated alumina with spherical and cylindrical impurity precipitates showed longer cycles before swelling than quenched alumina with filmy precipitates. The reasons for this were speculated from the viewpoint of formation of glass with low viscosity.

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