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Coarsening Advantage of Twinned $BaTiO_3$ Seed Particle

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ABSTRACT

The coarsening process of two different $BaTiO_3$ single crystal seeds, one with a (111) double twin and the other without it, was investigated. Due to the presence of Twin Plane Reentrant Edge (TPRE), the coarsening rate of the twinned seed crystal was significantly higher than that without a twin. For the coarsening by the 2-dimensional nucleation and lateral growth, the energy barrier for nucleation at the TPRE was analyzed to be about a half compared with that at the terrace planes.

Key words*: *Grain growth mechanism, $BaTiO_3$, Twin plane reentrant edge

1. Introduction

During heat-treatment of $BaTiO_3$ powder compacts, two types of abnormal grain growth were observed to occur. First, a few gains grow rapidly to the size of 40~70 μm at the expense of the fine matrix grains of 2~3 μm. Once they impinge each other, usually, no further microstructural change occurs, because the coarse matrix grains have only a small capillary driving force. However, when the specimens were further heat-treated at somewhat higher temperatures, it was observed that a few grains again started to grow by consuming coarse matrix grains and their sizes reached up to few millimeters. These have been referred to as primary and secondary abnormal gain growth (PAGG and SAGG), respectively. Furthermore, most of the grains grown by the SAGG were observed to contain (111) double twins.[1-5]

In order to clarify the role of (111) double twin on SAGG, Kang *et al.*[2] prepared two kinds of seed particles (~30 μm in size) with and without a (111) double twin, and monitored their coarsening process. They showed that the SAGG occurs only in the specimen containing seeds with a (111) double twin. From these, the Twin Plane Reentrant Edge (TPRE) growth mechanism proposed earlier by Schmelz *et al.*[6] has been suggested to be the cause of SAGG.

The aim of this investigation was to determine more precisely the effect of TPRE on the coarsening process of $BaTiO_3$. For this, two different kinds of large $BaTiO_3$ single crystals of the same orientation and size, one with a (111) double twin and the other without it, were prepared. They were embedded into powder compacts and we compared their coarsening behavior during heat-treatment. Based on the results, the growth advantage provided by the TPRE could be quantitatively estimated.

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2. Experimental Procedure

Commercial $BaTiO_3$ powder (99.5%, Ferro Corp., NY, U.S.A.) with the average particle size of ~1 μm was used. Its Ba/Ti ratio determined by the manufacturer was 0.997, and other detailed characteristics of the powder can be found in the previous reports.[1-5] Using the technique reported earlier,[4,7] a large $BaTiO_3$ crystal with a double twin was fabricated. For this, the powder compact of 10 mm in diameter and 4 mm in height was prepared by cold isostatic pressing of 150 MPa, and then sintered at 1360°C for 50 h in air.

Fig. 1(a) shows a resultant large $BaTiO_3$ single crystal of ~7 mm in size obtained. Electron Back-Scattered Diffraction (EBSD) (Oxford/link Opal, Bucks, U.K.) analysis showed that the surface normal is close to <111> direction. Along the diagonal of the crystal, the presence of a (111) double twin is clearly discerned. Using this, we prepared three seed

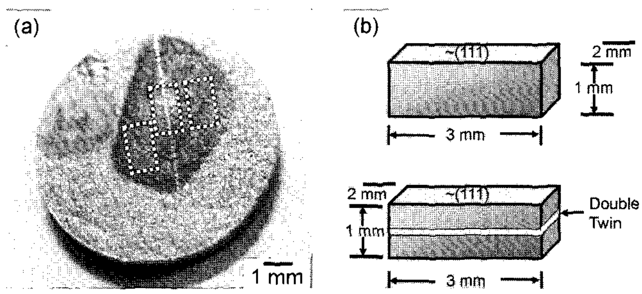

Fig. 1. (a) $BaTiO_3$ specimen containing an abnormally-grown large crystal with a double twin, and (b) schematic illustration of seed crystals with and without a double twin.

single crystals with the dimension of 1 × 2 × 3 mm by cutting along the dotted line in the figure; one containing a double twin and two others without it. Fig. 1(b) schematically illustrates the shape of two different seed single crystals prepared. The top and bottom surfaces of seed crystals were carefully polished to be parallel to each other.

The seed crystals were embedded separately into $BaTiO_3$ powder compacts in a rectangular mold (15 × 15mm). During the compaction, the (111) surface of each seed was placed parallel to the compact surface to avoid any complexity arising from the orientation effect. After cold isostatic pressing under 150 MPa, two specimens containing twinned and twin-free seed were heated at the rate of 0.5°C/min, and maintained at 1355°C for 55 h in air. The heat-treatment was also carried out at 1320°C for the third specimen containing twin-free seed crystal. The specimens obtained were mirror-polished, and chemically etched in a dilute HCl with a small amount of HF. The microstructures were observed either by optical or scanning electron microscope (JSM-5600, JEOL Ltd., Japan). The average size of the matrix grains was determined by multiplying 1.775 to the mean intercept length.[8)]

3. Results and Discussion

Fig. 2 shows the polished surfaces of the specimens obtained after the heat-treatment at 1355°C for 55 h. During the heat-treatment, both seed crystals (the initial size is indicated by dotted lines) have grown but their growth extents were quite different. As shown in Fig. 2(a), the $BaTiO_3$ crystal grown from the twinned seed was about 16 mm in size. On the other hand, the twin-free seed crystal shown in Fig. 2(b) grew only about 3.5 mm in size. In Fig. 2(a), the herringbone patterns, which are parallel to {101} planes,[9)] are discerned. From this, the seed crystals are determined to have grown most rapidly along the <1$\bar{1}$0> direction. Since the growth of crystals requires supersaturation provided either by undercooling or by solute accumulation at the interface, little growth could be expected during the heating-up process. Notice that the heating-up process always causes the system undersaturated. It follows that the growth distance of the seed crystals in this analysis was

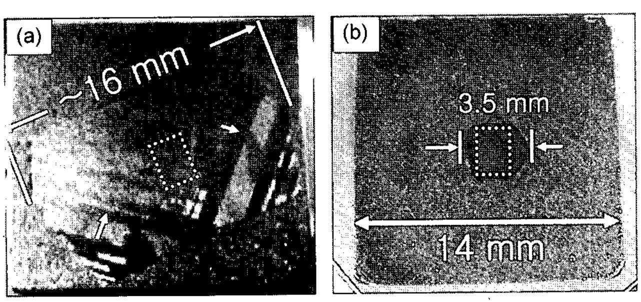

Fig. 2. $BaTiO_3$ specimen embedded with a seed crystal (a) with and (b) without a double twin. Arrows in (a) indicate the Herringbone patterns.

determined directly from the surface of the initial seed crystals. Their rates were ~130 and ~17 μm/h for twinned and twin-free seed crystal, respectively. We also noted that the shape of growing crystal remains practically the same during the heat-treatment, once it assumes the quasi-equilibrium shape under a low supersaturation.[10)]

The average size of the matrix grains after the heat-treatment was determined to be ~90 μm so that the driving force for material transfer to the seed crystal should be very small. Even though, the twinned seed could continue to grow rapidly. Since the growth of a faceted crystal with atomically smooth interface as in $BaTiO_3$ is known to proceed by the two-dimensional nucleation and lateral growth mechanism, the growth rate of a certain plane can be expressed as follows.[10,11)]

$$V_{2D} \propto hI = hK_n \exp\left(-\frac{\Delta G^*_{2D}}{kT}\right) \tag{1}$$

where h, I, and ΔG^*_{2D} are the height of the growth unit, nucleation rate and the energy barrier for two-dimensional nucleation, respectively. On the other hand, K_n is a constant determined by the atomic jumping frequency and found that it does not differ greatly from system to system.[10-12)] kT has the usual meaning.

From the grown crystal shown in Fig. 2(b), the average growth rate of {100} plane was measured to be 3.34×10^{-3} μm/s at 1355°C. On the other hand, from another twin-free seed specimen, its growth rate at 1320°C was determined to be 2.94×10^{-3} μm/s. By introducing the growth rates measured at two different temperatures into Eq. (1), we obtain hK_n; $10^{-0.54}$ /μm · sec and ΔG^*_{2D} ; 10^{-19} J/atom. Assuming that the step height, h, is the lattice constant 4.0701 Å[13], the constant K_n can be estimated to be about 10^3/μm^2 · sec. This value is far smaller than the theoretically estimated one (K_n; $10^{13\pm2}$/μm^2 · sec),[12)] which is probably due to the depletion of driving force and consequent stagnant grain growth. Note that the high preexponential factor K_n in the literature was estimated on a rapid solution growth.[12)] On the other hand, the calculated ΔG^*_{2D} in this study is in good agreement with the reported value obtained in Ga (ΔG^*_{2D}; 0.65 × 10^{-20} J/atom).[11)] In fact, it is known that ΔG^*_{2D} is rather tolerable to experimental errors due to its logarithmic dependence on the growth rate.

Based on the results, the growth advantage of the TPRE can be estimated by the following relationship,

$$\frac{\Delta G^*_{TPRE}}{\Delta G^*_{2D}} = 1 - \frac{kT}{\Delta G^*_{2D}} \ln \frac{V_{TPRE}}{V_{2D}} \tag{2}$$

where ΔG^*_{TPRE} and V_{TPRE} are the energy barrier for nucleation and the grow rate at reentrant-edges, respectively. From the growth rate of {100} plane determined from the twinned seed ($V_{TPRE} = 2.55 \times 10^{-2}$ μm/s), the ratio of the energy barrier at the TPRE to that at the terrace plane in Eq. (2) is deduced to be about a half. This is also in good agreement with the prediction reported earlier.[14)] Therefore, it can be concluded that the TPRE provides the advantage for the two-dimensional nucleation process during grain coarsening and crystal growth of $BaTiO_3$.

4. Conclusion

The effect of the TPRE on the grain coarsening of $BaTiO_3$ was investigated by using two types of seed crystals, one with a (111) double twin and the other without it. From the growth rates determined at 1320°C and 1355°C, it can be concluded that about 50% of the activation energy is needed for nucleation at a TPRE compared to that of the nucleation on a flat terrace plane. From these analyses, it is clear that a TPRE provides a favorable growth site when the coarsening or crystal growth is controlled by 2-D nucleation.

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