journal

J. Am. Ceram. Soc., 87 [1] 119–24 (2004)

Dependence of Grain Growth and Grain-Boundary Structure on the Ba/Ti Ratio in $BaTiO_3$

Young Kyu Cho, Suk-Joong L. Kang,* and Duk Yong Yoon*

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

The grain-growth behavior and grain-boundary structure in titanium-excess $BaTiO_3$ depend on the amount of excess titanium at 1250° and 1300°C. With excess titanium, abnormal grain growth (AGG) occurs and the grain boundaries are mostly flat or faceted with hill-and-valley shapes. With 0.5 at.% excess titanium, the large grains have flat {111} faces forming singular grain boundaries parallel to {111} double twins. With excess-titanium content between 0.1 and 0.3 at.%, the abnormal grains appear to have polyhedral shapes with {100} faces. These flat or faceted grain boundaries are expected to have singular structures, and hence AGG can occur by the step growth mechanism. When the excess-titanium content is decreased to 0, the grain boundaries become curved, indicating a rough atomic structure, and normal grain growth occurs.

I. Introduction

During the sintering of $BaTiO_3$ at temperatures below the eutectic temperature of 1332°C, both normal and abnormal grain growth (AGG) have been observed. These grain-growth modes were found to depend on the Ba/Ti ratio. Schmelz and Meyer[1] observed that, when $BaTiO_3$ specimens with 3 at.% excess titanium were sintered at 1225°C, a few grains with double twins grew to very large sizes, whereas the other grains grew very little. These abnormally large grains were elongated in the {111} double twin directions with their {111} planes forming nearly flat grain boundaries with the fine matrix grains. Hennings *et al.*[2] observed similar abnormal grain growth (AGG) with double twins in 5.6 at.% Ti-excess $BaTiO_3$ sintered at 1222°C. Lee *et al.*[3–6] also observed AGG with double twins in $BaTiO_3$ with 0.4, 0.7, and 2.3 at.% excess titanium sintered at 1250°C, and found that the number density of the abnormal grains increased with the excess-titanium content.

On the other hand, Yamamoto *et al.*[7,8] examined the grain-growth behavior in a relatively narrow composition range between ~0.1 and −0.1 at.% excess titanium. When sintered at temperatures between 1250° and 1300°C, the specimens with excess titanium between 0 and 0.13 at.% showed abnormal grains with equiaxial polyhedron shapes, whereas those with excess barium (0.1 at.%) showed normal grain growth (NGG).

These results thus indicate that there are three grain-growth modes in solid state: AGG with double twins at excess-titanium content >0.4 at.%, AGG with equiaxial shapes with excess-titanium content up to 0.1 at.%, and NGG with excess barium. The accuracy of the excess-titanium contents in the specimens used in these experiments may not, however, have been very high, because the purities of the starting powders were usually in the range 99.8%–99.9% and the Ba/Ti ratios (typically 0.996−0.998) specified for some $BaTiO_3$ powders used might be somewhat uncertain. Furthermore, because the specimens were prepared by using slightly different processes (e.g., different sintering temperatures and times), it was not clear if the grain-growth variation arose solely from the composition difference. The first purpose of this work is to determine more precisely the Ba/Ti concentration ratios for the three grain-growth modes in $BaTiO_3$. This will be achieved by adding barium or titanium to the same $BaTiO_3$ at varying Ba/Ti ratios in a narrow range that are expected to produce the different grain-growth behaviors. The specimens of different compositions will be prepared by an identical process to eliminate any effect arising from different processing conditions.

The second purpose of this work is to seek understanding of the reasons for the dependence of the grain-growth mode on the Ba/Ti ratio in this oxide. Previously, Yamamoto *et al.*[9,10] observed that the grain boundaries in the titanium-excess specimens that showed AGG with equiaxial shapes of the large grains were faceted with hill-and-valley shapes, whereas in the barium-excess specimens that showed NGG, the grain boundaries were curved without any faceting. Lee *et al.*[3,4] also observed that most of the grain boundaries in the titanium-excess specimens that showed AGG with large grains elongated in the double twin directions were faceted. When heat-treated in hydrogen, the grain boundaries became curved (defaceted) and the grain growth became normal.

The AGG with faceted grain boundaries has been also observed in nickel,[11] copper,[12] silver,[13] 316L stainless steel,[14] a nickel-based superalloy,[15] and alumina.[16] When the grain boundaries in these polycrystals became curved and therefore atomically rough, either at high temperatures or with additives, NGG occurred. It was proposed that AGG occurred with faceted grain boundaries because their singular segments migrated by the boundary step mechanism.[11–17] With rough grain boundaries, in contrast, the atoms could jump across the boundaries relatively freely and normal growth occurred. Likewise, in this work, the variation of the grain-growth modes with the Ba/Ti ratio will be examined in terms of the changes of grain-boundary structure, migration mechanism, and twin boundary formation.

II. Experimental Procedures

The specimens were prepared from the same commercial $BaTiO_3$ (HPBT-1, Fuji Titanium, Kanagaea, Japan), TiO_2 (Aldrich Chemical Co., Milwaukee, WI), and $BaCO_3$ (Aldrich Chemical Co.) powders as in our earlier work.[3,4] The purities of $BaTiO_3$, TiO_2, and $BaCO_3$ powders were 99.8, 99.9, and 99.999 wt%, respectively. The average particle size of the $BaTiO_3$ powder was 0.66 μm and the Ba/Ti ratio was determined to be 0.997 by X-ray fluorescence analysis using the mixtures of high-purity TiO_2 and $BaCO_3$ powders as standards. Excess amounts of TiO_2 or $BaCO_3$ powder were added to obtain estimated net excess-titanium atom fractions of 0.5, 0.3, 0.1, and 0. Each specimen series will be designated by these

D. W. Johnson—contributing editor

Manuscript No. 187357. Received November 1, 2001; approved July 29, 2003.
Supported by the Korean Ministry of Science and Technology through the National Research Laboratory (NRL) Program.
*Member, American Ceramic Society.

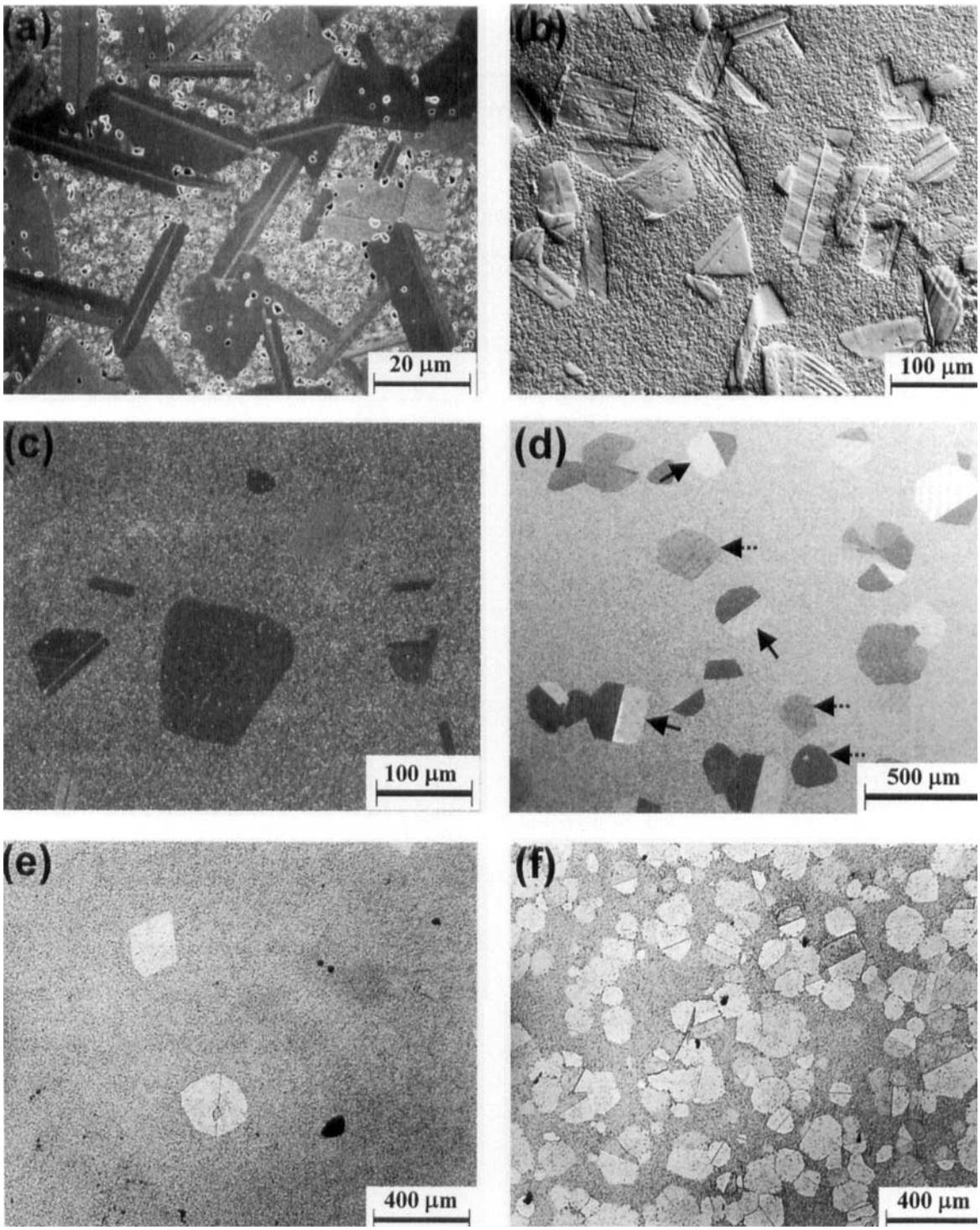

Fig. 1. The SEM or optical microstructures of (a) 0.5 Ti/1250°C/12 h, (b) 0.5 Ti/1300°C/8 h, (c) 0.3 Ti/1250°C/24 h, (d) 0.3 Ti/1300°C/8 h, (e) 0.1 Ti/1250°C/24 h, and (f) 0.1 Ti/1300°C/8 h specimens.

estimated net excess-titanium atom fractions; thus, for example, the specimen 0.3 Ti for that with estimated excess 0.3 at.% Ti. The experimental procedure was also nearly identical to our earlier work.[3,4] The powder mixture or undoped $BaTiO_3$ powder was ball-milled in ethyl alcohol for 24 h using polyprophylene bottle and zirconia balls. The impurities in the powders were analyzed before and after ball-milling by inductively coupled plasma method, and it was verified that the zirconia pickup was <4 ppm. The dried slurry was crushed in an agate bowl and sieved to 180 μm. The mixed powder was slightly pressed into disks of 9 mm in diameter and 5 mm in thickness and then isostatically pressed under 200 MPa. The compacts were sintered at 1300°, 1250°, and 1200°C in air. The heating and cooling rates were 300°C/min. The sintered specimens were cut, polished, and chemically etched in a $95H_2O{\cdot}4HCl{\cdot}1HF$ (vol%) solution.

The microstructures were observed by optical microscopy, scanning electron microscopy (SEM; Model SEM515, Phillips, Eindhoven, Netherlands), and transmission electron microscopy (TEM; JEM-3010, JEOL, Tokyo, Japan) operated at 300 kV. For TEM observation, the specimens were ultrasonically cut into 3-mm disks, mechanically grounded to a thickness of 100 μm, dimpled to a thickness of <10 μm, and finally ion-milled. The equivalent sphere diameters of the grains were measured by

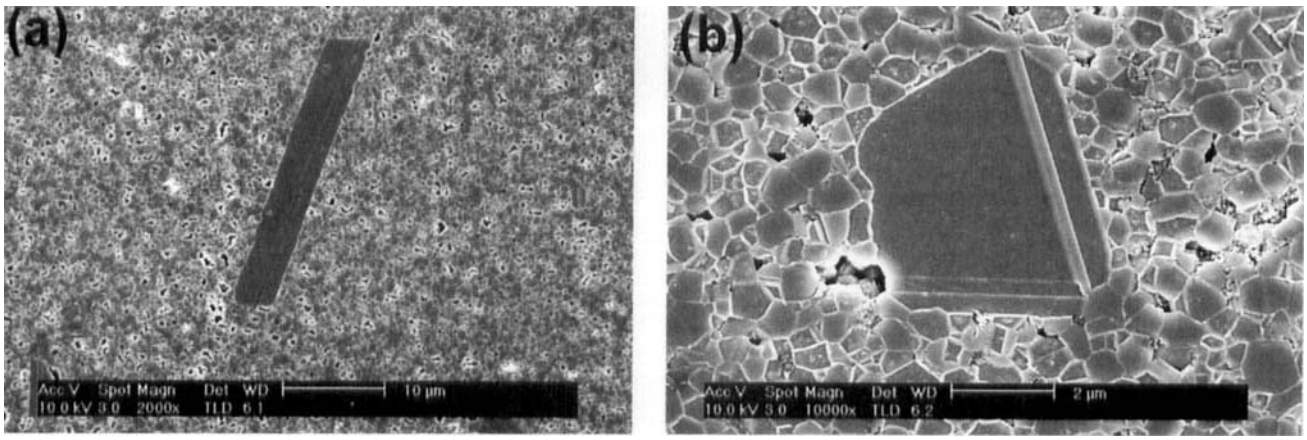

Fig. 2. The SEM microstructures of abnormal grains with (a) a double twin and (b) two double twins in the 0.5 Ti/1250°C/10 h specimen.

tracing along the grain boundaries on SEM micrographs using a digitizer connected to a personal computer.

III. Results and Discussion

After sintering for 1 h at either 1250° or 1300°C, the specimens were almost fully densified. Because the sintering treatment was not performed separately, we will use the term heat treatment. Each specimen will be specified by the excess-titanium content/heat-treatment temperature/heat-treatment time. After heat-treating at 1250°C for 1 h, the 0.5 Ti specimen showed grains of a narrow-size distribution with an average diameter of 0.49 μm. After 12 h, the specimen showed large grains elongated along the double twins, which were always found to be located near their centers, as shown in Figs. 1(a) and 2(a) at different magnifications. When a large grain had two double twins at different {111} planes, it grew in both directions with a nearly equiaxial shape, as shown in Fig. 2(b). The large elongated grains formed mostly flat grain boundaries with the fine matrix grains along their {111} planes, as shown earlier[18] by TEM. When the 0.5 Ti specimen was heat-treated at 1300°C (below the eutectic point of 1332°C), AGG with double twins was again observed, as shown in Fig. 1(b). The aspect ratio of the large elongated grains was smaller than those in the 0.5 Ti/1250°C/12 h specimen shown in Fig. 1(a).

Although the large abnormal grains appeared after heat-treating for 12 h as shown in Fig. 1(a), the small matrix grains hardly grew—to an average size of ~0.51 μm after 24 h. The fraction of the matrix grains with double twins was ~1% in the 0.5 Ti specimens heat-treated at both 1250° and 1300°C and did not change with the heat-treatment time longer than 1 h. (The fraction of the grains with single twins was ~10% in both specimens.) These observations show that, among the initial grains with a narrow size distribution, only those grains with double twins grew to very large sizes. Therefore, in this specimen series, both double-twin and large initial size appear to be the necessary condition for abnormal growth of a grain.

The double twins were observed to enhance the growth of fcc crystals with {111} faces in melts[19] and solutions.[20] This effect was attributed to the nucleation of crystal layers at the re-entrant edges formed at the intersections between the double twins and the singular surfaces.[21–23] It was previously shown[18] that the flat grain boundaries between the {111} faces of the abnormal grains and the fine matrix grains in the titanium-excess $BaTiO_3$ were singular corresponding to the cusps in the polar plots of the grain-boundary energy $\gamma(n)$ against the normal direction n. If there are the same singular grain boundaries at the thin end faces of the disk-shaped large grains, the double twins can form re-entrant edges and enhance the grain growth in their directions in analogy to the crystal growth. The large {111} faces of the abnormal grains without any intersecting double twins cannot grow as rapidly. It was thus suggested that AGG with elongated grain shapes induced by double twins was a definitive evidence for the step growth mechanism of AGG.[17] As is quite often observed in metals and ceramics,[11–16] AGG occurs even without double twins. But in $BaTiO_3$ with excess titanium over ~0.4 at.%, the step free energy of the {111} grain boundaries is apparently so high that AGG cannot begin by two-dimensional nucleation without the double twins. There were thus no abnormal grains without any double twins in these specimens.

With decreasing excess-titanium content, the abnormal grains became equiaxial, as shown in Figs. 1(c)–(f). In the 0.3 Ti/1300°C/8 h specimen, some grains showed double or single twins, as shown in Figs. 1(d) and 3 at different magnifications. Neither the double nor the single twins appeared to influence AGG, because the abnormal grains grew in all directions independently of the twins (Fig. 3). Some abnormal grains (indicated by dotted arrows in Fig. 1(d)) did not show any twins.

Some abnormal grains showed flat grain boundaries (indicated by single arrows in Fig. 1(d)) that were parallel to their twins and, hence, {111} plane. But there were also other flat grain boundaries of the abnormal grains that were not parallel to their twins (Fig. 4). These flat grain boundaries appeared to lie parallel to the {100} planes of the abnormal grains from the various shapes observed at the cross sections. The flat faces of the abnormal grains thus lay on their {111} and probably {100} planes. Some faces of the abnormal grains also appeared to be curved at the low magnification used for Fig. 1(d), but they were observed to consist of flat and hill-and-valley segments at higher magnifications.

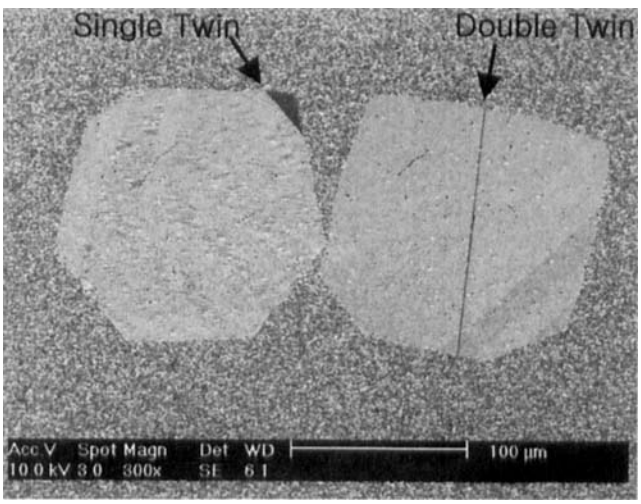

Fig. 3. The SEM microstructure of abnormal grains with a single twin and a double twin in the 0.3 Ti/1300°C/8 h specimen (shown also in Fig. 1(d)).

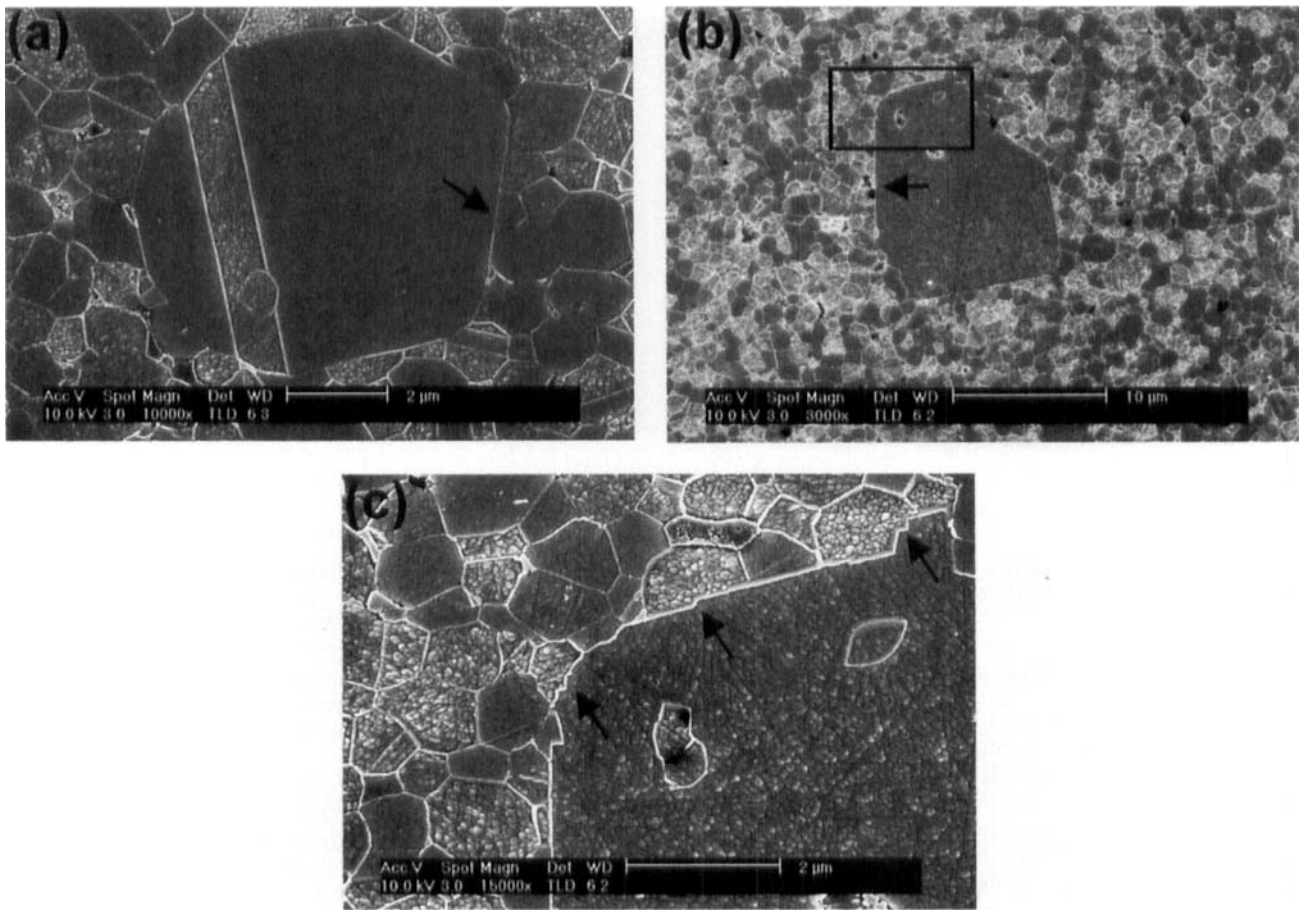

Fig. 4. The SEM microstructures of (a) an abnormal grain with a double twin and flat grain boundaries, (b) an abnormal grain without apparently any double twin, and (c) the rectangular corner area of the abnormal grain shown in (b) at a higher magnification in the 0.1 Ti/1300°C/8 h specimen (also shown in Fig. 1(f)).

As pointed out earlier in this report and proposed previously,[3,4,18] the flat {111} and {100} grain boundaries between the abnormal grains and the matrix grains are singular. This proposal was partly based on the frequent observations of grain boundaries in metals,[24–29] NiO,[29–31] spinel,[32] alumina,[33] and titanium-excess $BaTiO_3$[9,10,18] lying on low-index planes of one grain and high-index planes of the other. Ichinose and Ishida[24,25] called these the low-index crystal plane grain boundaries, but for brevity we prefer to call them the low-index grain boundaries. As shown earlier,[18] in a schematic analysis using the capillarity vectors,[34,35] the flat shapes of the low-index grain boundaries of the abnormal grains at the triple junctions with the grain boundaries between the matrix grains were also consistent with their singular characteristics. When these grain boundaries became atomically rough by heat-treating in hydrogen, they became curved with the dihedral angles at the triple junctions that were characteristic for isotropic boundaries.[3,4]

It thus appears that there was a change of the stable {111} grain boundaries in the 0.5 Ti specimens to a mixture of stable {111} and {100} grain boundaries in the 0.3 Ti specimen. Although the double twins produced the re-entrant edge effect on the growth of the abnormal grains with only {111} boundaries in the 0.5 Ti specimens, they do not seem to produce the same effect when the {100} singular boundaries appear at 1300°C in the 0.3 Ti specimen, as shown in Figs. 1(d) and 3. There are two possible reasons for the absence of the re-entrant edge effect in the latter case: The first is a geometrical one that, when a {111} double twin intersects {100} boundaries, re-entrant edges are formed in all directions. Second, the step energies of the low-index boundaries decreased so much with decreasing titanium content and increasing temperature that the two-dimensional step nucleation could readily occur without the re-entrant edges.

The AGG behavior also varied with temperature. The 0.3 Ti/1250°C/24 h specimen shown in Fig. 1(c) exhibited both elongated abnormal grains with double twins resembling those in the 0.5 Ti specimens and equiaxial grains without double twins resembling those in the 0.3 Ti/1300°C /8 h specimen (Fig. 1(d)).

The shapes of the abnormal grains changed further when the excess-titanium content was decreased to 0.1 at.%, as shown in Figs. 1(e), 1(f), and 4 at different magnifications. In these specimens, there were very few abnormal grains with boundaries parallel to the twin boundaries. From their shapes, most of the abnormal grains appeared to have {100} grain boundaries, which were again flat across many matrix grains, as indicated by arrows in Figs. 4(a) and (b). Some boundary segments at the corners of the abnormal grains were faceted (shown by arrows in Fig. 4(c)). A small fraction of the abnormal grains had double twins (Fig. 4(a)), but their growth did not appear to be affected by the double twins. A large fraction of the abnormal grains had single twins, which probably formed during their growth. These results indicated that as the excess-titanium content decreased, the {100} grain-boundary energy decreased relative to the {111} grain-boundary energy, causing the shape change of the abnormal grains. When heat-treated at 1250°C (Fig. 1(e)), the number of abnormal grains was much smaller than that observed at 1300°C (Fig. 1(f)).

Nearly all the grain boundaries between the fine matrix grains in these titanium-excess specimens were faceted when observed under TEM, as shown in Fig. 5 and in our earlier report.[3,4] Because the faceted grain boundaries are likely to have singular segments, they will move by atom attachment to the grain-boundary steps and extrinsic dislocations or to the steps produced by two-dimensional nucleation at high driving forces as proposed by

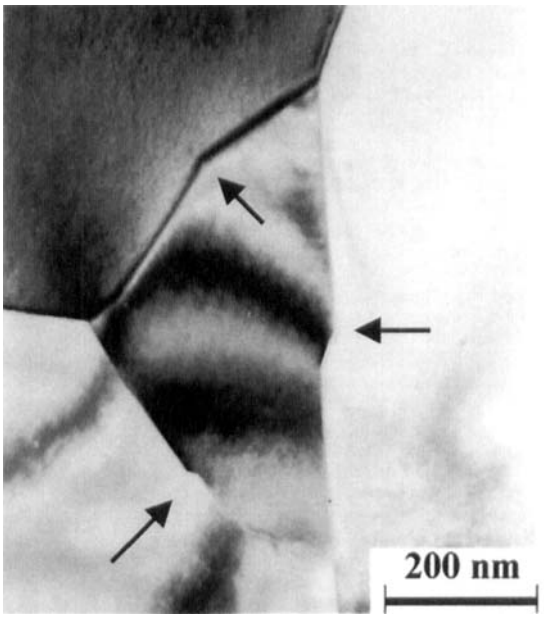

Fig. 5. The TEM microstructure of faceted grain boundaries in the 0.3 Ti/1250°C/48 h specimen.

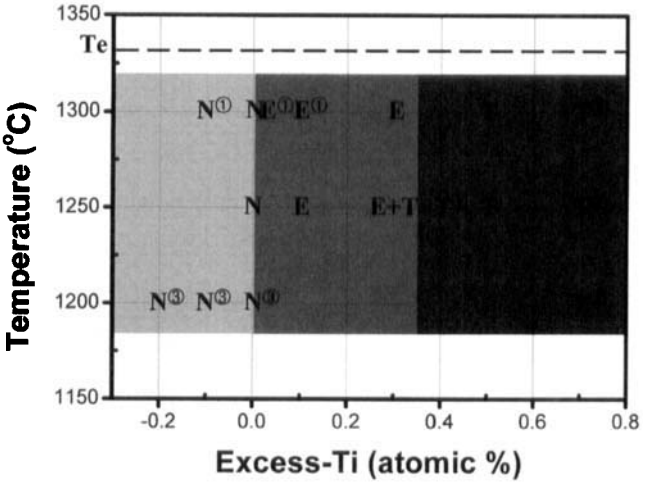

Fig. 7. The observed variation of the grain-growth behavior with excess-titanium content at the temperature range between 1200° and 1300°C. (The normal growth, AGG with equiaxial shapes, and double twin assisted AGG are indicated as N, E, and T respectively. Points 1, 2, and 3 are from Refs. 7–10, 3–6, and 40, respectively.)

others.[36–39] When the faceted grain boundaries move by such a step mechanism, AGG occurs as observed in this and previous works.[11–16]

The grain-growth behavior changed drastically when the excess-titanium content was decreased to 0 at.%. Figure 6 demonstrates the fracture surface of the 0 Ti/1250°C/24 h specimen showed equiaxial grains of fairly narrow size distributions without any indication of AGG. The grains appeared to grow normally from the initial average size of ~0.5 μm to ~9.8 μm for the 0 Ti/1250°C/24 h specimen and to ~12.5 μm for the 0 Ti/1300°C/24 h specimen. The variation of the grain-growth behavior with the Ba/Ti ratio observed in this work agrees well with that observed by Yamamoto *et al.*[7,8] and Hu *et al.*,[40] as shown in Fig. 7. For 0 excess titanium at 1300°C, Yamamoto *et al.*[4,5] showed AGG, whereas the present results showed NGG; however, this discrepancy probably arose from small uncertainties in the amount of excess titanium.

The intergranular fracture surface of the 0 Ti/1250°C/24 h specimen displayed in Fig. 6 showed smoothly curved shapes, even when observed at higher magnifications in SEM. The curved shapes indicate that the grain boundaries are rough at atomic scale, and such a correlation between the rough grain boundaries and normal grain growth was also observed previously in a number of metals[11,13–15] and alumina.[16] In $BaTiO_3$ with 0.4 at.% excess titanium, Lee *et al.*[3,4] showed that, when heat-treated in hydrogen at 1250°C, the grain boundaries became defaceted (curved) and normal grain growth occurred.

With rough grain boundaries, NGG occurred in the 0 Ti specimens while maintaining a narrow grain size distribution (Fig. 6). In contrast, the matrix grains in the specimens with excess-titanium contents grew very little, whereas only a small fraction of the grains grew to very large sizes. These results are consistent with the continuous grain-boundary movement with its rate linear to the driving force for rough boundaries and step growth of the faceted singular grain boundaries with a nonlinear variation of the migration rate to the driving force. The step growth mechanism is also consistent with the observed increase of the number density of the abnormal grains with temperature, as shown in Fig. 1 and in other materials.[11–16] Because the growth of abnormal grains is a thermally activated process with high-activation energies, the number of abnormal grains can increase with temperature as previously suggested.[12] Furthermore, the boundary step free energy can decrease with temperature, thereby lowering the barrier for grain growth and hence increasing the number density of the abnormal grains.

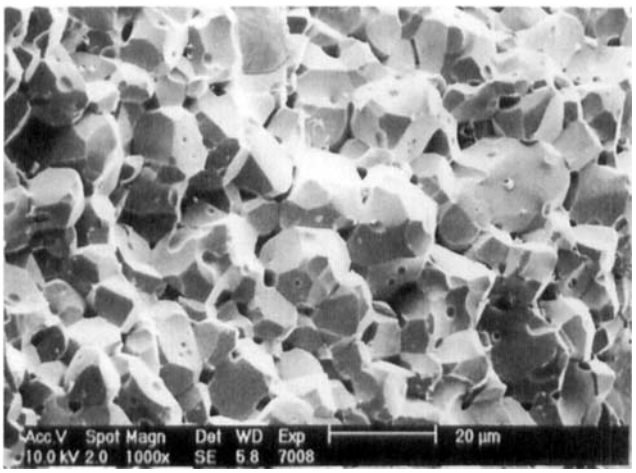

Fig. 6. The SEM microstructure of the fracture surface of the 0 Ti/1250°C/24 h specimen.

IV. Conclusions

This work shows that there are three grain-growth modes in $BaTiO_3$ at 1250° and 1300°C, depending on the excess-titanium content. Normal grain growth (NGG) occurs with excess barium, abnormal grain growth (AGG) with equiaxial grains occurs with excess titanium between 0 and 0.3 at.% Ti, and double twin-assisted AGG occurs with excess titanium >0.3 at.%. The NGG occurs when the grain boundaries are apparently rough with curved shapes. The AGG occurs when the grain boundaries are singular with faceted hill-and-valley or flat shapes. The {111} double twins facilitate AGG when the singular {111} grain boundaries exist at high excess-titanium contents. This re-entrant edge effect may arise from the special geometrical relationship between the {111} double twins and {111} grain boundaries with high step energy. With the excess-titanium content in the 0 to 0.3 at.% range, the {100} grain boundaries appear to be the dominant singular boundaries and the {111} double twin boundaries do not produce the re-entrant edge effect. The effect of double twins on AGG provides strong evidence for the step growth mechanism of AGG. The orientations and structures of many faceted grain

boundaries in these specimens need to be determined by high-resolution TEM and other methods to verify their singular characteristics.

References

[1]H. Schmelz and A. Meyer, "The Evidence for Anomalous Grain Growth below the Eutectic Temperature in $BaTiO_3$ Ceramics," *Ber. Dtsch. Keram. Ges.*, **59** [8/9] 436–40 (1982).

[2]D. F. K. Hennings, R. Janssen, and P. J. L. Reynen, "Control of Liquid-Phase-Enhanced Discontinuous Grain Growth in Barium Titanate," *J. Am. Ceram. Soc.*, **70** [1] 23–27 (1987).

[3]B.-K. Lee, S.-Y. Chung, and S.-J. L. Kang, "Grain Boundary Faceting and Abnormal Grain Growth in $BaTiO_3$," *Acta Mater.*, **48** [7] 1575–80 (2000).

[4]B.-K. Lee, "Formation of {111} Twins and Abnormal Grain Growth in $BaTiO_3$"; Ph.D Thesis, Korea Advanced Institute of Science and Technology, Taejon, Korea, 2000.

[5]B.-K. Lee, S.-Y. Chung, and S.-J. L. Kang, "Necessary Conditions for the Formation of {111} Twins in $BaTiO_3$," *J. Am. Ceram. Soc.*, **83** [11] 2858–60 (2000).

[6]B.-K. Lee and S.-J. L. Kang, "Second-Phase Assisted Formation of {111} Twins in Barium Titanate," *Acta Mater.*, **49** [8] 1373–81 (2001).

[7]T. Yamamoto, "Influence of Small Ba/Ti Non-Stoichiometry on Grain Growth Behavior in Barium Titanate," *Br. Ceram. Trans.*, **94** [5] 196–200 (1995).

[8]T. Yamamoto and T. Sakuma, "Abnormal Grain Growth of $BaTiO_3$ with Small Cation Nonstoichiometry," *Mater. Sci. Forum*, **204–206**, 491–96 (1996).

[9]T. Yamamoto, Y. Ikuhara, K. Hayashi, and T. Sakuma, "Grain Boundary Structures in TiO_2-Excess Barium Titanate," *J. Mater. Res.*, **13** [12] 3449–52 (1998).

[10]T. Yamamoto, Y. Ikuhara, K. Hayashi, and T. Sakuma, "Grain Boundary Structures in $BaTiO_3$ with a Small Excess of Ti-Site Dopant," *Mater. Sci. Forum*, **294–296**, 247–50 (1999).

[11]S. B. Lee, N. M. Hwang, D. Y. Yoon, and M. F. Henry, "Grain Boundary Faceting and Abnormal Grain Growth in Nickel," *Metall. Mater. Trans. A.*, **31** [3] 985–94 (2000).

[12]J. B. Koo and D. Y. Yoon, "Abnormal Grain Growth in Bulk Cu: The Dependence on Initial Grain Size and Annealing Temperature," *Metall. Mater. Trans. A*, **32** [8] 1911–26.

[13]J. B. Koo and D. Y. Yoon, "The Dependence of Normal and Abnormal Grain Growth in Ag on Annealing Temperature and Atmosphere," *Metall. Mater. Trans. A.*, **32** [3] 469–75 (2001).

[14]J. S. Choi and D. Y. Yoon, "The Temperature Dependence of Abnormal Grain Growth and Grain Boundary Faceting in 316L Stainless Steel," *ISIJ Int.*, **41** [5] 478–83 (2001).

[15]S. B. Lee, D. Y. Yoon, and M. F. Henry, "Abnormal Grain Growth and Grain Boundary Faceting in Model Ni-Base Superalloy," *Acta Mater.*, **48** [12] 3071–80 (2000).

[16]C. W. Park and D. Y. Yoon, "Effects of SiO_2, CaO, and MgO Additions on the Grain Growth of Alumina," *J. Am. Ceram. Soc.*, **83** [10] 2605–609 (2000).

[17]D. Y. Yoon, C. W. Park, and J. B. Koo, "The Step Growth Hypothesis for Abnormal Grain Growth"; in *Properties and Applications IV*, Proceedings of the International Workshop on Ceramic Interfaces (Taejon, Korea, September 1998). Edited by S.-J. L. Kang and H. I. Yoo. The Institute of Materials, London, U. K., 2001.

[18]S. B. Lee, S.-Y. Choi, S. J.-L. Kang, and D. Y. Yoon, "TEM Observations of Singular Grain Boundaries and Their Roughening Transition in TiO_2-Excess $BaTiO_3$," *Z. Metallkd.*, **94** [3] 193–99 (2003).

[19]R. S. Wagner, "On the Growth of Germanium Dendrites," *Acta Metall.*, **8**, 57–60 (1960).

[20]J. F. Hamilton and L. E. Brady, "Twinning and Growth of Silver Bromide Microcrystals," *J. Appl. Phys.*, **35** [2] 414–21 (1964).

[21]D. R. Hamilton and R. G. Seidensticker, "Propagation Mechanism of Germanium Dendrites," *J. Appl. Phys.*, **31** [7] 1165–68 (1960).

[22]R. Jagannathan, R. V. Metha, J. A. Timmons, and D. L. Black, "Anisotropic Growth of Twinned Cubic Crystals," *Phys. Rev. B.*, **48** [18] 13261–65 (1993).

[23]N. Ming and I. Sunagawa, "Twin Lamellae as Possible Self-Perpetuating Step Sources," *J. Cryst. Growth*, **87**, 13–17 (1988).

[24]H. Ichinose and Y. Ishida, "Observation of [110] Tilt Boundary Structures in Gold by High Resolution HVEM," *Philos. Mag. A.*, **43** [5] 1253–1264 (1981).

[25]H. Ichinose and Y. Ishida, "High Resolution Electron Microscopy of Grain Boundaries in fcc and bcc Metals," *J. Phys.*, **43 C-4** suppl. [12] 39–49 (1985).

[26]J.-M. Penisson, "Atomic Structure of Tilt Boundaries in Mo Bicrystals," *J. Phys.*, **49 C-5** suppl. [10] 87–97 (1988).

[27]K. L. Merkle and D. Wolf, "Low-Energy Configurations of Symmetric and Asymmetric Tilt Grain Boundaries," *Philos. Mag. A.*, **65** [12] 513–30 (1992).

[28]K. L. Merkle, "High-Resolution Electron Microscopy of Grain Boundaries in fcc Materials," *Colloq. Phys.*, **51 C-1** suppl. [1] 251–56 (1990).

[29]K. L. Merkle, "Atomic Structure of Grain Boundaries," *J. Phys. Chem. Solids*, **55** [10] 991–1005 (1994).

[30]K. L. Merkle, "Atomic Resolution Electron Microscopy of NiO Grain Boundaries," *Ultramicroscopy*, **22**, 57–70 (1987).

[31]K. L. Merkle, "Atomic Structure of Symmetric Tilt Grain Boundaries in NiO," *Phys. Rev. Lett.*, **59** [25] 2887–90 (1987).

[32]C. B. Carter, "Σ=99 and Σ=41 Grain Boundaries," *Acta Metall.*, **36** [10] 2753–60 (1988).

[33]C. W. Park, D. Y. Yoon, J. E. Blendell, and C. A. Handwerker, "Singular Grain Boundaries in Alumina and Their Roughening Transition," *J. Am. Ceram. Soc.*, **86** [4] 603–11 (2003).

[34]D. W. Hoffman and J. W. Cahn, "A Vector Thermodynamics for Anisotropic Surfaces: I, Fundamentals and Application to Plane Surface Junctions," *Surf. Sci.*, **31**, 368–88 (1972).

[35]J. W. Cahn and D. W. Hoffman, "A Vector Thermodynamics for Anisotropic Surfaces: II, Curved and Faceted Surfaces," *Acta Metall.*, **22**, 1205–14 (1974).

[36]H. Gleiter, "The Mechanism of Grain Boundary Migration," *Acta Metall.*, **17**, 565–73 (1969).

[37]H. Gleiter, "Theory of Grain Boundary Migration Rate," *Acta Metall.*, **17**, 853–62 (1969).

[38]R. W. Balluffi, Y. Komem, and T. Schober, "Electron Microscope Studies of Grain Boundary Dislocation Behavior," *Surf. Sci.*, **31**, 68–103 (1972).

[39]C. M. F. Rae and D. A. Smith, "On the Mechanisms of Grain Boundary Migration," *Philos. Mag. A.*, **41** [4] 477–92 (1980).

[40]Y. H. Hu, M. P. Harmer, and D. M. Smyth, "Solubility of BaO in $BaTiO_3$," *J. Am. Ceram. Soc.*, **68** [7] 372–76 (1985). □