Journal of the European Ceramic Society 20 (2000) 731–737

Effect of sintering temperature on the secondary abnormal grain growth of $BaTiO_3$

Ho-Yong Lee [a,*], Jae-Suk Kim [a], Nong-Moon Hwang [b,c], Doh-Yeon Kim [b]

[a] *Division of Metallurgical and Materials Engineering, Sunmoon University, Chungnam, Asan, 336-840, South Korea*
[b] *School of Materials Science and Engineering, and Creative Research Center for Microstructure Science of Materials, College of Engineering, Seoul National University, Seoul, 151-742, South Korea*
[c] *Korea Research Institute of Standards and Science, PO Box 102, Taejeon, 305-600, South Korea*

Received 27 April 1999; accepted 4 July 1999

Abstract

When $BaTiO_3$ specimens containing a small amount of excess TiO_2 were sintered for more than 15 h, some grains grew abnormally to several millimeters in size. This phenomenon may be referred to as the secondary abnormal grain growth (SAGG) because it occurred from a large and uniform grain structure (average grain size: 70 μm) after completion of primary abnormal grain growth. SAGG was observed only at a very narrow temperature range between 1360 and 1370°C, where the solid–liquid interface structure was atomically smooth. Almost all the secondary abnormal grains contained the (111) double twin, which provides the persistent twin-plane re-entrant edge (TPRE). During SAGG, the growth of matrix grains was strongly suppressed and material transfer occurred preferentially to the grains with a (111) double twin. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Abnormal grain growth; $BaTiO_3$; Grain growth; Microstructure-final; Sintering

---

1. Introduction

The abnormal grain growth (AGG; referred to as discontinuous grain growth or exaggerated grain growth) during sintering of $BaTiO_3$ ceramics has been extensively studied.[1–4] During AGG, a few grains grow much faster than the surrounding fine matrix grains so that the microstructure exhibits bimodal distribution of grain size. Abnormal grains usually grow until they impinge each other and AGG is completed by the recovery of uniformity in grain size distribution. The resultant microstructure composed of abnormally grown large grains is usually very stable and remains unchanged during further heat-treatment.

Recently, Yoo et al.[5,6] have reported that, when a small amount of SiO_2 was placed on the top of $BaTiO_3$ powder compacts, some $BaTiO_3$ grains containing a (111) double twin appeared near the top and continued to grow to several millimeters at a rate higher than about 200 μm/h. After completion of the primary AGG above the eutectic temperature between $BaTiO_3$ and $Ba_6Ti_{17}O_{40}$, the fast and extensive growth of some $BaTiO_3$ grains occurred. This again disturbed the uniformity of the microstructure in the grain size distribution. In order to distinguish this from the well-known or primary AGG, this phenomenon is called the secondary abnormal grain growth (SAGG). SAGG has been explained in terms of the enhanced growth of grains with a (111) double twin by the twin-plane re-entrant edge (TPRE) growth mechanism.[5–8] They have also demonstrated that $BaTiO_3$ single crystals of a few centimeters in size could be grown from polycrystalline specimens by adding SiO_2 in a very restricted region of a $BaTiO_3$ powder compact.[5,7]

Although the addition of SiO_2 was observed to enhance the formation of (111) double twins inside $BaTiO_3$ grains,[5] it does not seem to be essential to their formation. In our preliminary experiments, the (111) double twins were observed in grains of $BaTiO_3$ specimens without SiO_2 addition although their frequency is much lower. Thus, if the TPRE growth mechanism is responsible for the SAGG, it is expected that the SAGG may also take place among $BaTiO_3$ grains with a double twin in the specimen without SiO_2 addition.

In order to investigate this possibility, undoped commercial $BaTiO_3$ powder compacts were sintered under

---

[*] Corresponding author.

0955-2219/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0955-2219(99)00197-1

usual processing conditions for up to 50 h at various temperatures. When specimens were sintered at temperatures between 1360 and 1370°C, SAGG was observed to occur. This growth behavior was very sensitive to sintering temperature. It did not occur at temperatures $>1370°C$ or $<1360°C$. The results were discussed in terms of the TPRE growth mechanism, which depends on the atomic structure of the solid–liquid interface.

2. Experimental procedure

Commercial $BaTiO_3$ powder with a purity of 99.5% and average particle size of 1 μm was used. The Ba/Ti ratio was about 0.997 and major impurities were SrO (0.15 wt%), P_2O_5 (0.1 wt%), and SO_3 (0.1 wt%), as determined by the manufacturer. The SiO_2 concentration was less than 300 ppm. The powder was ball-milled for 12 h in a Nalgene bottle with ethanol and zirconia balls. After drying and sieving, the square powder compacts (20×20 mm) of 2 mm in height were prepared by uniaxial pressing at 5 MPa. The compacts were pressed hydrostatically at 200 MPa and then sintered at five different temperatures (1355, 1360, 1365, 1370, and 1380°C) in air for up to 50 h. The heating and cooling rate was 4°C/min.

The sintered specimens were heat-treated again at 1200°C for 5 h in a reducing atmosphere of $(95)N_2$–$(5)H_2$ (vol%). (111) Double twins are known to appear clearly in the microstructure by such treatment.[9] The heat-treated specimens were ground and polished for microstructural observation. The polished surfaces were chemically etched in an aqueous 5 (vol%) HCl solution containing a small amount of HF.[10] In some cases, the surface structures were observed directly after heat-treatment of sintered specimens with prepolished planes. Microstructures were examined by optical and scanning electron microscopes (JSM-6400, JEOL Ltd., Japan). For grain size measurement, the average intercept length was determined and then multiplied by the factor of 1.775 to determine the 3-dimensional grain size.[11]

3. Results and discussion

Fig. 1(a) and (b) shows the microstructures of $BaTiO_3$ specimens sintered for 1 h at 1300 and 1355°C, respectively. From Fig. 1(a), it can be noted that the microstructure consists of small matrix grains of about 2 μm and abnormally grown large grains of about 35 μm. In this respect, AGG has occurred at 1300°C. This is below the eutectic temperature of the pseudo-binary $BaTiO_3$-$Ba_6Ti_{17}O_{40}$ system, which was reported to be 1332°C.[4] Because of impurities and excess TiO_2 in the starting powder, the liquid formation temperature was lowered and AGG was likely due to the resultant acceleration in material transfer, as observed in previous studies.[12–14] When the $BaTiO_3$ powder compact was sintered at 1355°C for 1 h [Fig. 1(b)], the fine matrix grains were completely replaced by a new set of abnormally grown coarse grains. The average size of these grains was approximately 70 μm. Therefore, AGG was complete and the microstructure was uniform in terms of grain size distribution. At this temperature, no further significant microstructural evolution occurred during sintering for up to 50 h.

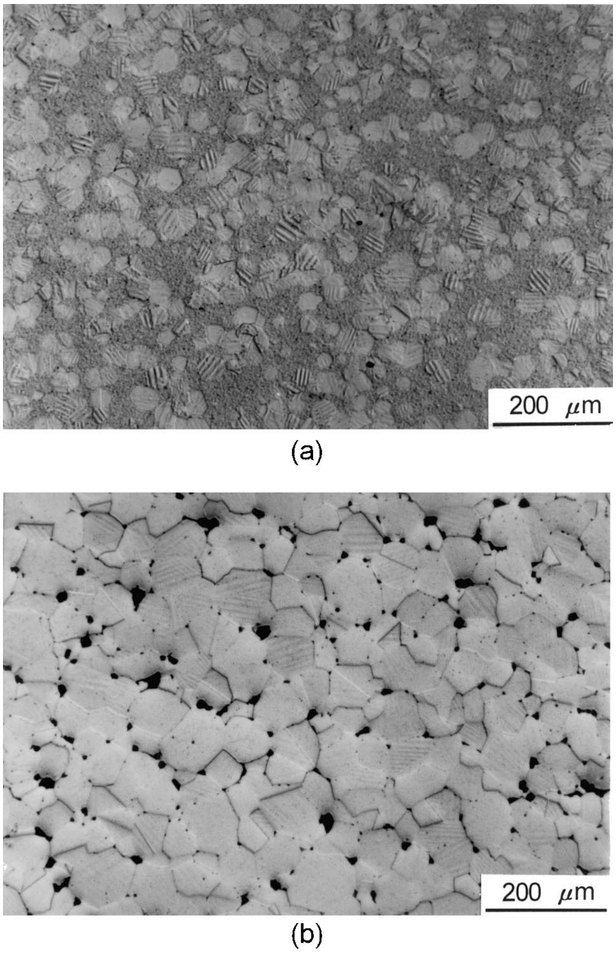


Fig. 1. Microstructures of $BaTiO_3$ specimens sintered at (a) 1300°C and (b) 1355°C in air for 1 h.

A slight increase in temperature did result in a significant change in the microstructure. When the $BaTiO_3$ powder compact was sintered at 1360°C, a few grains grew abnormally from the coarse uniform grained matrix. In the overall microstructure of the specimen sintered at 1360°C for 15 h [Fig. 2(a)], the appearance of giant grains is clearly discerned. These can be observed with the naked eye. The grains which are ten times larger than the mean grain size were counted and their number per square centimeter was defined as the number density of SAGG, NA. For the specimen sintered

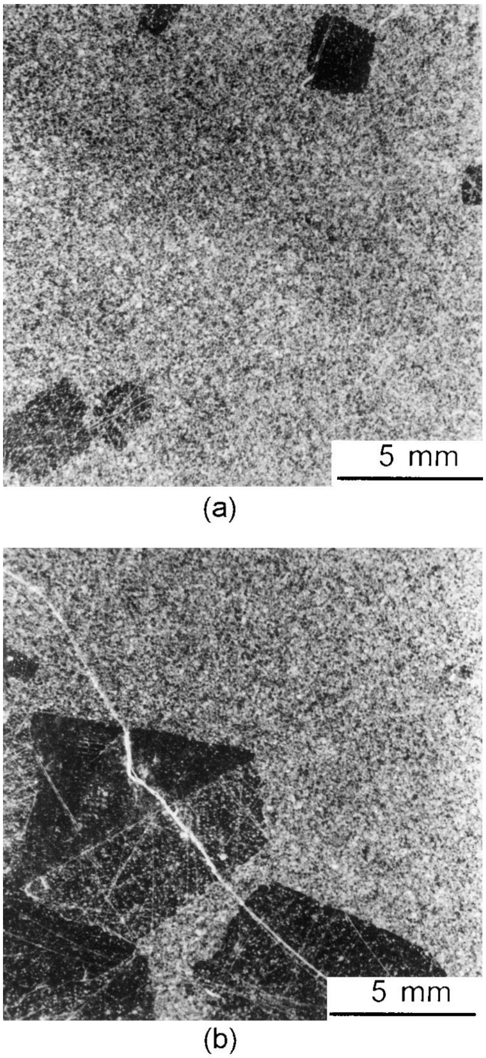


Fig. 2. Overall microstructures of $BaTiO_3$ specimens sintered at 1360°C for (a) 15 h and (b) 50 h.

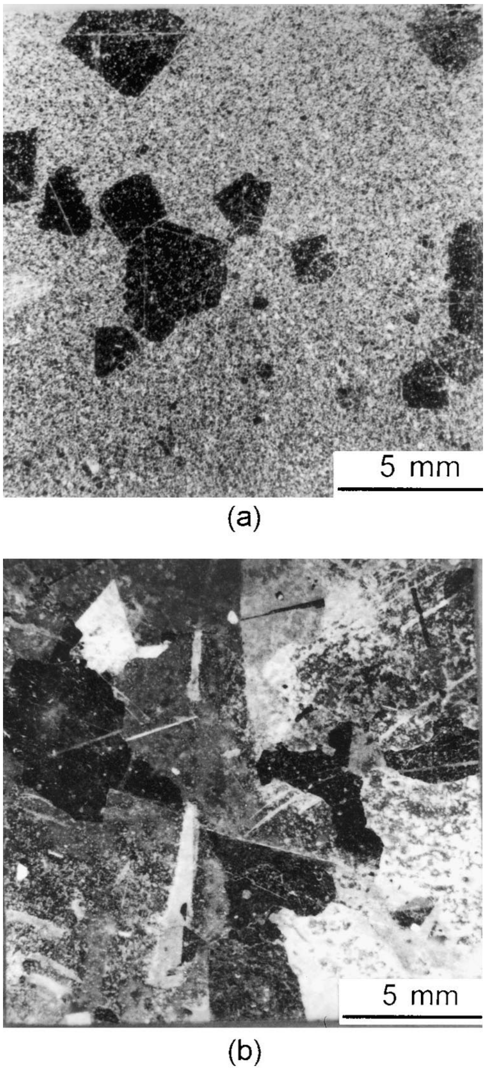


Fig. 3. Overall microstructures of $BaTiO_3$ specimens sintered at 1365°C for (a) 15 h and (b) 50 h.

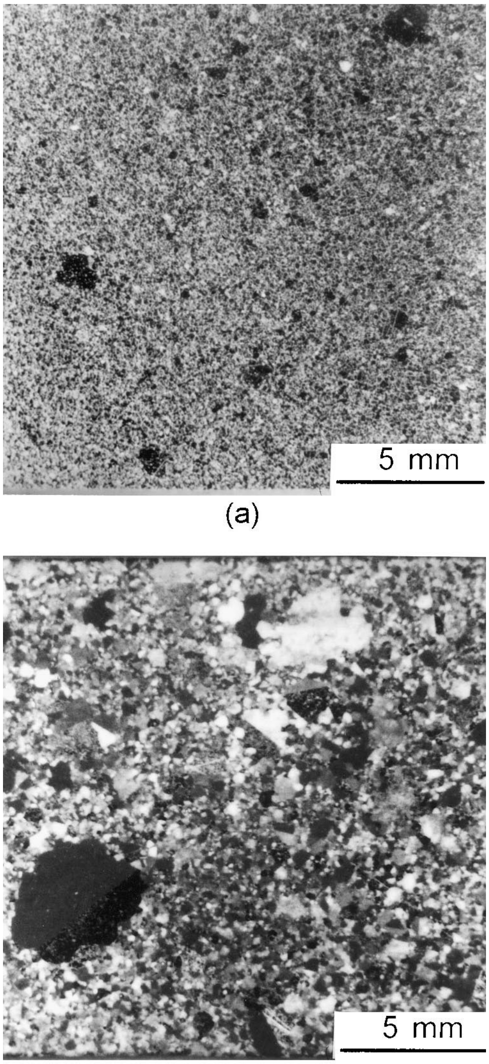
at 1360°C for 15 h [Fig. 2(a)], N_A was 2.2. During further heat-treatment for 50 h at the same temperature, they continued to grow to about 1 cm in size as shown in Fig. 2(b). In this respect, the grain growth phenomenon observed in Fig. 2 can be referred to as the secondary abnormal grain growth (SAGG) because it has been preceded by the primary AGG shown in Fig. 1.

When the sintering temperature was raised to 1365°C, SAGG became more pronounced. After sintering at 1365°C for 15 h [Fig. 3(a)], the number and sizes of giant grains increased i.e. more secondary abnormal grains have been formed and their growth rate increased. In this case, NA value was determined to be 8.5. Heat-treatment for 50 h at this temperature resulted in a uniform structure composed only of these secondary abnormal grains. They grew until they impinged each other and all the original matrix grains disappeared completely [Fig. 3(b)]. The average size of secondary abnormal grains of the specimen shown in Fig. 3(b) was determined to be 5.2 mm. Note that this size is smaller than that of Fig. 2(b), because the secondary abnormal grains could not continue to grow due to impingement with each other. We have also observed that there was an induction period for SAGG in $BaTiO_3$. For example, the sintering at 1365°C for 5 h did not exhibit any SAGG behavior. The overall microstructure of the specimen maintained uniformity during sintering for up to 5 h and thus was similar to Fig. 1(b).

Further increases in sintering temperature appeared to suppress SAGG. After sintering at 1370°C for 15 h [Fig. 4(a)], SAGG was still observed to occur, but its number density was greatly reduced: NA was about 4. The microstructure obtained after sintering at 1370°C for 50 h is shown in Fig. 4(b). Compared to those in Figs. 2(b) and 3(b), the size of secondary abnormal grains in Fig. 4(b) is smaller, but that of matrix grains has notably increased. At 1380°C, no SAGG was observed to occur. N_A was zero and the uniform grain structure was maintained for up to 50 h as shown in Fig. 5. However, an appreciable and uniform increase in matrix grain size was observed to occur at this temperature. The above results indicate that SAGG of $BaTiO_3$ specimens occurs only at a narrow temperature range between 1360 and 1370°C.

Fig. 6 shows the increase in average size of matrix grains during heat-treatment. At 1355°C, SAGG did not occur and the matrix grains have shown a uniform and slight growth. Although SAGG at the expense of matrix grains is a major phenomenon at 1360 and 1365°C, the slight growth of matrix grains was also noted during the heat-treatments. Note that the matrix grain size of the specimen sintered at 1365°C for 50 h is not available, as they were all consumed by SAGG. These results showed that the growth of matrix grains was strongly suppressed at the temperatures of 1365°C and below. At temperatures of 1370°C and above, notable growth of matrix grains was detected and the specimen was observed to exhibit a normal grain growth behavior.

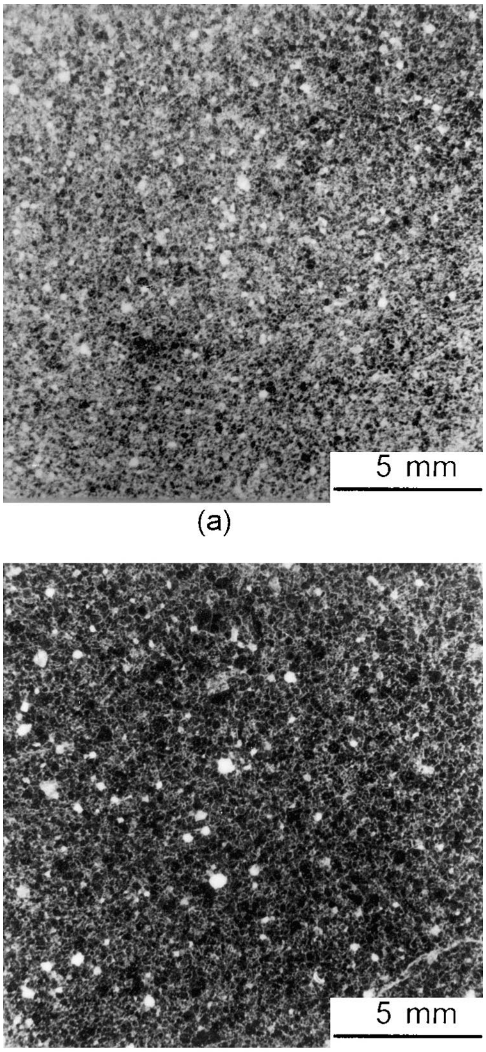
Recently, Kang et al.[8] have investigated the growth behavior of large $BaTiO_3$ seed grains in $BaTiO_3$ powder compacts. They showed that seeds containing a (111) double twin continued to grow extensively and resulted in SAGG. On the other hand, the growth of normal seeds without a (111) double twin was observed to be limited. Once the uniform microstructure is obtained by primary AGG, practically no more microstructural evolution occurred in the specimen containing the normal seeds. Furthermore, it has been shown that when SiO_2 is present locally in a $BaTiO_3$ specimen, the (111) double twins are generated in grains of the very restricted region and the extensive grain growth is triggered.[5–7] From the results, the re-entrant angle created by the (111) double twin has been suggested to play a major



(a)

(b)

Fig. 4. Overall microstructures of $BaTiO_3$ specimens sintered at 1370°C for (a) 15 h and (b) 50 h.



(a)

(b)

Fig. 5. Overall microstructures of $BaTiO_3$ specimens sintered at

role in SAGG of $BaTiO_3$. Note that the re-entrant angles provide sites for easier growth, as reported in previous studies on $BaTiO_3$[15–17] and other systems.[18,19] This mechanism is known as the twin-plane re-entrant edge (TPRE) growth mechanism that results in a high rate of crystal growth.[20,21]

In this respect, SAGG observed in this experiment is also expected to be due to TPRE of the (111) double twin. For the specimen sintered at 1360°C for 15 h, we examined all the secondary abnormal grains and the fraction of secondary abnormal grains having the (111) double twin was determined to be about 80%. It was about 53% in the specimen sintered at 1360°C for 50 h. In the specimens sintered at 1365°C for 15 h, about 42% of secondary abnormal grains were observed to contain a (111) double twin. Assuming that the grains are spherical and the (111) double twin is located at the center of grains, the probability that the (111) double twin is observed in two-dimensional section is about 50%. Although this probability will vary with grain shape and location of a (111) double twin in a grain, this analysis strongly indicates that almost all the secondary abnormal grains have the (111) double twin.

Fig. 7 shows a (111) double twin in a matrix grain (or a primary abnormal grain) observed from the surface of specimen heat-treated at 1355°C for 15 h. For this observation, the specimen sintered at 1355°C for 1 h was polished and then heat-treated again at 1355°C for 14 h. Such treatment clearly revealed the surface structure of the specimen without any etching. Note that the microstructure of this specimen consists of uniform and coarse grains of about 80 m after completion of the primary AGG. The thickness or spacing between two (111) twin planes was determined to be about 2 m, which is similar to the values reported in previous studies.[22–26] Fig. 8 displays a (111) double twin in a secondary abnormal grain observed from the specimen heat-treated at 1360°C for 15 h. In this case, the thickness of the (111) double twin was usually very thick up to 60 m, but its thickness was frequently observed to vary inside a secondary abnormal grain. From these observations, it is predicted that SAGG is triggered by the thin (111) double twins in some matrix grains of the microstructure evolved after the primary AGG, and that the (111) double twins also get thicker during the SAGG process. At present, the thickening mechanism of a (111) double twin during heat-treatment as well as its effect on SAGG is not clearly understood, although several proposals[22–26] for the origin of (111) double twins in matrix grains have been made.

TPRE growth implies that the material transfer during grain growth occurs by a process similar to the 2-dimensional (2-D) nucleation. For the grains with

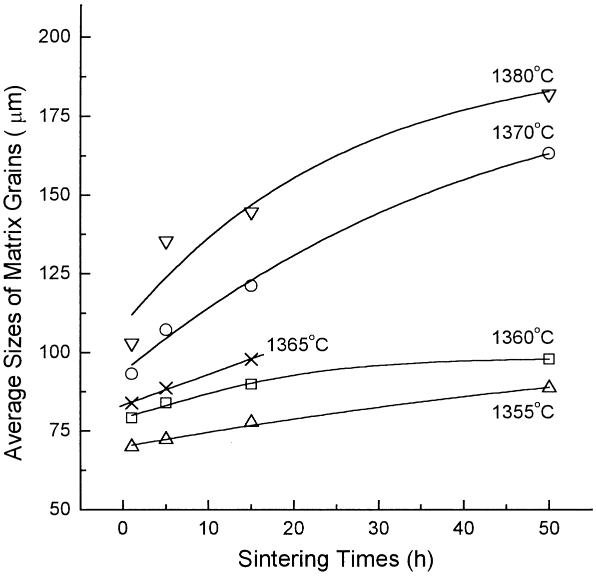


Fig. 6. Average sizes (S_M) of matrix $BaTiO_3$ grains with sintering time.

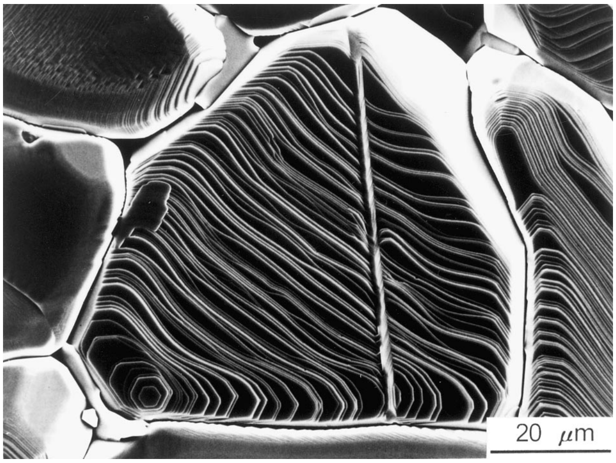


Fig. 7. Surface microstructure displaying a (111) double twin in a matrix grain of the specimen sintered at 1355°C for 15 h.

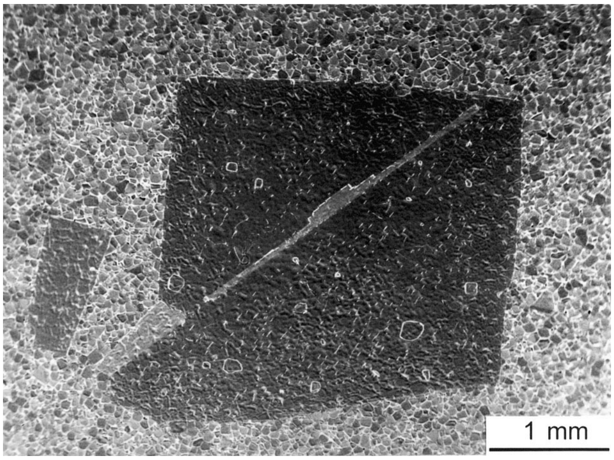


Fig. 8. Surface microstructure displaying a (111) double twin in a secondary abnormal grain of the specimen sintered at 1360°C for 15 h.

faceted and flat crystal planes such as a secondary abnormal grain in Fig. 8, the interface structure is atomically smooth so that the coarsening of grains proceeds by the lateral growth in comparison with the continuous growth which is operative for the rough interface. Since the rate of 2-D nucleation has the exponential dependence on the driving force, the rate tends to be negligible below a certain critical value of the driving force, but increases abruptly above it. Therefore, for grains with faceted interfaces to achieve an appreciable growth rate, the driving force for coarsening should be high enough to overcome the barrier for 2-D nucleation. Since the driving force arising from capillarity is inversely proportional to the average grain size, it will be small in the coarse grain structure after primary AGG. The very slight growth of matrix grains observed during heat-treatment at temperatures $<1365°C$ is due to the small driving force. However, the 2-D nucleation rate can be high on the TPRE because the activation energy of 2-D nucleation at TPRE is much lower than that on the flat surfaces of grains. This means that 2-D nucleation on TPRE may be the main contributor to the growth of grains with a double twin. Therefore, a few grains with a double twin can grow abnormally at a high rate by 2-D nucleation on TPRE resulting in the SAGG while the other matrix grains grow at a relatively low rate.

When the interface structure is atomically rough, however, the facet planes are not developed and the solid grains exhibit a spherical shape. In this case, the atomic attachment at the rough interface has no energy barrier, so grains can grow continuously. TPRE does not play a role as a favorable growth site, therefore SAGG will not take place. In this respect, the absence of SAGG at temperatures above 1370°C is believed to result from the roughening transition of the solid/liquid interface.

Fig. 9(a) and (b) shows the surface microstructures of $BaTiO_3$ specimens heat-treated at 1365 and 1380°C for 15 h in air, respectively. The same technique was used for the observation of surface microstructures. The specimen, sintered at 1355°C for 1 h, was polished and then heat-treated again for 15 h at each temperature. As shown in Fig. 9, the grain shape is quite angular in the specimen heat-treated at 1365°C [Fig. 9(a)], while it is rounded in the specimen treated at 1380°C [Fig. 9(b)]. The important point in Fig. 9 is that the grain shape has clearly changed with temperature. Compared to that inside the heat-treated specimen, the liquid content in the surface microstructure was observed to be high. Even though its reason is unclear, the high amount of liquid at the surface enables us to observe the shape of grains well dispersed in a sufficient liquid. The increase of temperature has induced disordering of interface atomic structure and consequently a disappearance of anisotropic character in interfacial energies. This results in the rounding of grains.[27,28] At 1365°C where the interface structure is atomically smooth, the growth is controlled by a 2-D nucleation mechanism. In this case, TPRE formed by a (111) double twin lowers the activation energy for 2-D nucleation. This accelerates the growth kinetics of the grains with TPRE compared to the usual 2-D nucleation on the flat surface and thus brings about the SAGG. At temperatures of 1370°C and above, however, the interface structure becomes rough, therefore, no preferential growth can occur on the TPRE. Normal grain growth occurred at 1380°C (Fig. 5) as a consequence of diffusion controlled growth mechanism. The interface structure transition shown in Fig. 9(a) and (b) supports our explanation as to why SAGG did not occur above 1370°C.

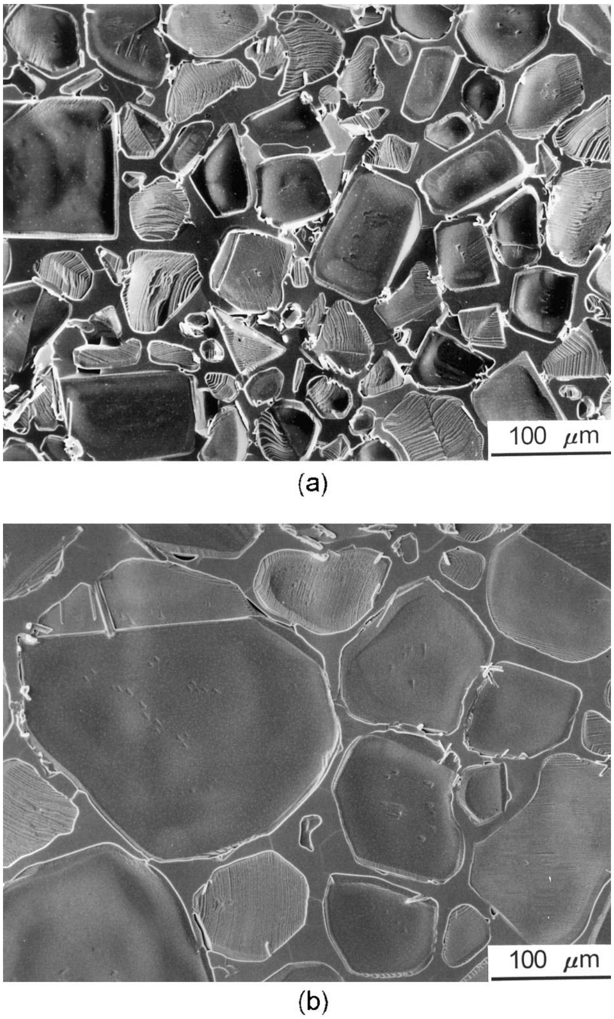


Fig. 9. $BaTiO_3$ grain morphologies in the specimens sintered in air for 15 h at (a) 1365°C and (b) 1380°C.

The absence of SAGG during sintering at temperatures below 1360°C could also be explained by focusing on the role of TPRE. Note at this condition that the interface structure is atomically smooth. In this case, (111) double twins are present, but they do not induce the SAGG. This means that appreciable 2-D nucleation on TPRE did not seem to occur in this temperature range. The temperature decrease can have two effects on the suppression of 2-D nucleation on TPRE. One is related to the fact that the 2-D nucleation rate is an exponential function of temperature. The other is related to the temperature dependence of the edge energy, which is a critical factor for 2-D nucleation.[29] The temperature decrease is known to increase the edge energy,[30] which will increase the barrier of 2-D nucleation. Although we can not decide which factor should be more dominant, it is likely that the appreciable rate of 2-D nucleation on TPRE was not achieved by these effects at temperatures below 1360°C.

4. Conclusions

During sintering of $BaTiO_3$ powder compacts at temperatures higher than the eutectic one, the secondary abnormal grain growth (SAGG) was observed to occur. At a very narrow temperature range between 1360 and 1370°C, a few grains grew abnormally at the expense of coarse and uniform matrix grains. As long as they did not impinge each other, the secondary abnormal grains continued to grow so that their size reached to approximately 1 cm. Furthermore, almost all the secondary abnormal grains were observed to contain the (111) double twin.

At the temperature range where the SAGG occurred, the structure of solid–liquid interface was atomically smooth so that the grain coarsening controlled by 2-D nucleation could be suggested. In this condition, the twin-plane re-entrant edge (TPRE) is a favorable growth site and thus the grains containing a (111) double twin can continue to grow without limit. At temperatures $\geqslant 1370°C$, the interface structure was observed to be atomically rough. Therefore, diffusion processes control grain coarsening and thus no SAGG occurs. When the temperature was $\leqslant 1355°C$, SAGG did not occur either. This is likely to be due to a negligible 2-D nucleation rate at this temperature and/or to the variation of edge energy. The thickening process of (111) double twins during the SAGG is a subject of future investigation.

References

1. Hennings, D. F. K., Recrystallization of barium titanate ceramics. *Sci. Ceram.*, 1984, **2**, 405–409.
2. Hennings, D. F. K., Janssen, R. and Reynen, P. J. L., Control of liquid-phase-enhanced discontinuous grain growth in barium titanate. *J. Am. Ceram. Soc.*, 1987, **70**, 23–27.
3. Kolar, D., Discontinuous grain growth in multiphase ceramics. In *Sintering of Advanced Ceramics (Ceramic Transactions, Vol. 7)*, ed. C. A. Handwerker, J. E. Blendell and W. A. Kaysser. American Ceramic Society, Westerville, OH, 1990, pp. 529–545.
4. Kirby, K. W. and Wechsler, B. A., Phase relations in the barium titanate–titanium oxide system. *J. Am. Ceram. Soc.*, 1991, **74**, 1841–1847.
5. Yoo, Y.-S., Study on the formation of (111) twins and exaggerated grain growth of $BaTiO_3$ ceramics. Ph.D. thesis, Seoul National University, Seoul, Korea, 1995.
6. Yoo, Y.-S., Kim, H. and Kim, D.-Y., Effect of SiO_2 and TiO_2 addition on the exaggerated grain growth of $BaTiO_3$. *J. Eur. Ceram. Soc.*, 1997, **17**, 805–811.
7. Yoo, Y.-S., Kang, M.-K., Han, J.-H., Kim, H. and Kim, D.-Y., Fabrication of $BaTiO_3$ single crystals by using the exaggerated grain growth method. *J. Eur. Ceram. Soc.*, 1997, **17**, 1725–1727.
8. Kang, M.-K., Yoo, Y.-S., Kim, D.-Y. and Hwang, N.-M., Growth of $BaTiO_3$ seed grains by the twin plane re-entrant edge mechanism. *J. Am. Ceram. Soc.*, Submitted for publication.
9. DeVries, R. C., Lowering of Curie temperature of $BaTiO_3$ by chemical reduction. *J. Am. Ceram. Soc.*, 1960, **43**, 226.
10. Kulcsar, F., A microstructure study of barium titanate ceramics. *J. Am. Ceram. Soc.*, 1956, **39**, 13–17.
11. Han, J.-H. and Kim, D.-Y., Analysis of the proportionality constant correlating the mean intercept length to the average grain size. *Acta Metall. Mater.*, 1995, **43**, 3183–3188.
12. Eastman, C., Elyard, C. A. and Warren, D., The effect of silica additions on the semi-conducting properties of doped barium titanates. *Proc. British Ceram. Soc.*, 1970, **18**, 77–85.
13. Matsuo, Y. and Sasaki, H., Exaggerated grain growth in liquid-phase sintering of $BaTiO_3$. *J. Am. Ceram. Soc.*, 1971, **54**, 471.
14. Xue, L. A. and Brook, R. J., Promotion of densification by grain growth. *J. Am. Ceram. Soc.*, 1989, **72**, 341–344.
15. DeVries, R. C., Observation on growth of the $BaTiO_3$ crystals from KF solutions. *J. Am. Ceram. Soc.*, 1959, **42**, 547–558.
16. Schmelz, H., Twining in $BaTiO_3$ ceramics. *Ceram. Forum Int., Ber. Dtsch. Keram. Ges.*, 1984, **61**, 199–204.
17. Oppolzer, H. and Schmelz, H., Investigation of twin lamellae in $BaTiO_3$ ceramics. *J. Am. Ceram. Soc.*, 1983, **66**, 444–447.
18. Hamilton, D. R. and Seidensticker, R. G., Propagation mechanism of germanium dendrite. *J. Appl. Phy.*, 1960, **31**, 1165–1168.
19. Faust, J. W. Jr. and John, H. F., The growth of semiconductor crystals from solution using the twin-plane reentrant-edge mechanism. *J. Phys. Chem. Solids*, 1964, **25**, 1407–1415.
20. Elwell, D. and Scheel, H. J., *Crystal Growth from High-Temperature Solutions*, Academic Press, London, 1975, pp. 190.
21. Brice, J. C., *The Growth of Crystals from Liquids*, North-Holland Publishing Co., Amsterdam, 1973
22. Eibl, O., Pongratz, P. and Skalicky, P., Formation of (111) twins in $BaTiO_3$ ceramics. *J. Am. Ceram. Soc.*, 1987, **70**, C-195–C-197.
23. Krasevec, V., Drofenik, M. and Kolar, D., Genesis of the (111) twin in barium titanate. *J. Am. Ceram. Soc.*, 1990, **73**, 856–860.
24. Recnik, A., Bruley, J., Maser, W., Kolar, D. and Ruhle, M., Structural and spectroscopic investigation of (111) twins in barium titanate. *Phil. Mag. B*, 1994, **70**, 1021–1034.
25. Kastner, G., Wagner, R., Lacayo, G. and Hilarius, V., Twins and grain growth during liquid-phase sintering of $BaTiO_3$ ceramics. *J. Mater. Sci. Lett.*, 1989, **8**, 802–804.
26. Kastner, G., Wagner, R. and Hilarius, V., Nucleation of twins by grain coalescence during the sintering of $BaTiO_3$ ceramics. *Phil. Mag. A*, 1993, **69**, 1051–1071.
27. Burton, W. K. and Carbrera, N., Crystal growth and surface structure. *Disc. Faraday Soc.*, 1949, **5**, 33–48.
28. Jackson, K. A., Interface structure. In *Growth and Perfection of Crystals*, ed. R. H. Doremus et al. John Wiley, New York, 1958, pp. 319–324.
29. Bennema, P., Growth and morphology of crystals: integration of theories of roughening and Hartman-Perdok theory. In *Handbook of Crystal Growth*, ed. D. T. J. Hurle. North-Holland, Amsterdam, 1993, pp. 481–581.
30. Williams, E. D. and Bartelt, N. C., Thermodynamics and statistical mechanics of surfaces.. In *Physical Structure*, ed. W. N. Unertl. North-Holland, Amsterdam, 1996, pp. 51–99.