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Microstructure transition from normal to abnormal grains for $BaTiO_3$

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Abstract

Quantitative characterization on the microstructure evolution during sintering of barium titanate has been conducted. The microstructure of the specimens sintered at 1320–1360 °C exhibits a typical mixture of normal and abnormal grains. The size of normal grains and abnormal grains differs by two orders of magnitude. No grain with an intermediate size is observed. A "pseudo-abnormal" region composing of many partially oriented normal grains is found instead. The formation of such pseudo-abnormal regions may help the transition from fine normal grains to coarse abnormal grains.

Keywords: Grain growth; Microstructure-final; Barium titanate; Liquid phase

1. Introduction

The abnormal grain growth behaviour of barium titanate ($BaTiO_3$) has attracted considerable attention for several decades.[1–9] It is partly due to that the ferroelectric performance of $BaTiO_3$ depends strongly on its grain size.[10–13] The formation of abnormal grain has to be suppressed in order to improve its performance.[13,14] Partly, the abnormal grain growth behaviour of $BaTiO_3$ has been treated as a model system for the understanding on microstructure control.[13,15,16]

The formation of abnormal $BaTiO_3$ grains depends strongly on its Ba/Ti ratio,[1,3,4,8,12–14,16–19] the sintering temperature,[3,5,12,14–16,20] the type and amount of impurity[7,12–16,20] and the sintering atmosphere etc.[3,4,7,8,14,17,18] An excess of TiO_2 in $BaTiO_3$ is a must for the formation of abnormal grains. As the sintering temperature is lower than the $BaTiO_3$–$Ba_6Ti_{17}O_{40}$ eutectic temperature (1332 °C), an order grain boundary phase is present between abnormal grain and normal grain.[5,8,19] A liquid phase is formed instead at a temperature higher than the eutectic temperature.[3,4,14,21,22] The presence of impurity, especially SiO_2, can lower the eutectic temperature to a temperature ~1260 °C.[20] The formation of abnormal grains can be suppressed by sintering or annealing $BaTiO_3$ specimen in an atmosphere of low oxygen partial pressure.[4,8,17,22]

The morphology of abnormal grains also shows strong dependence on the sintering temperature. As the sintering temperature is lower than the eutectic temperature, the abnormal grains with {1 1 1} twin lamellae are formed. The presence of {1 1 1} twin assists the formation of large $BaTiO_3$ platelet.[3,4,7,8,16,17,21] As the sintering temperature is higher than the eutectic temperature, the abnormal grain is equiaxed.[1,21]

In the present study, the abnormal grain growth behaviour of barium titanate above the eutectic temperature is investigated. The microstructure of sintered specimen is carefully characterized. A possible mechanism for the transition from normal grains to abnormal grains is proposed.

2. Experimental

A commercial $BaTiO_3$ powder (NEB, Ferro Co., USA) with a Ba/Ti ratio of 1.000 ± 0.002 was used as the raw material. The impurities in the raw powder as reported by the manufacturer were SrO 150 ppm, and Fe_2O_3, SiO_2, Al_2O_3 <75 ppm. The powder was ball-milled in ethyl alcohol for 4 h and the grinding media were zirconia balls. After drying and sieving, discs with the diameter of 10 mm and thickness of 1.5 mm were formed by uniaxial die-pressing at 30 MPa. The discs were pre-fired at 600 °C in air for 1 h with 1 °C/min rate for both heating and

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cooling. Then, the compacts were sintered in a covered alumina crucible at 1320–1410 °C for various times. Both the heating and cooling rates were 5 °C/min.

The phase identification was performed by using X-ray diffractometry (XRD, MXP18, MAC, USA) with Cu Kα radiation. The density was determined by using the Archimedes' method. The cross-sections of the sintered specimens were exposed by grinding with SiC sand papers. The grain boundaries were revealed by thermal etching at a temperature around 100 °C lower than the sintering temperatures for 1 h. The microstructure was observed by using scanning electron microscopy (SEM, Philips XL30, Netherlands) and field-emission scanning electron microscopy (FE-SEM, Leo 1530, LEO Instrument, Cambridge, U.K.). The grain size was determined by sketching every grain boundary on SEM micrographs. An image analysis technique was then employed to convert each grain area into one grain diameter by assuming that the grain was spherical in shape. For each sintering condition, at least 800 normal grains and/or 600 abnormal grains were counted. The grain size distribution curves could then be determined.

The electron back scatter diffraction (EBSD, TSL Co., Japan) patterns were also taken during FE-SEM observation to identify the grain orientations of the polished sections. A tilt of 70° was used to obtain the EBSD patterns.

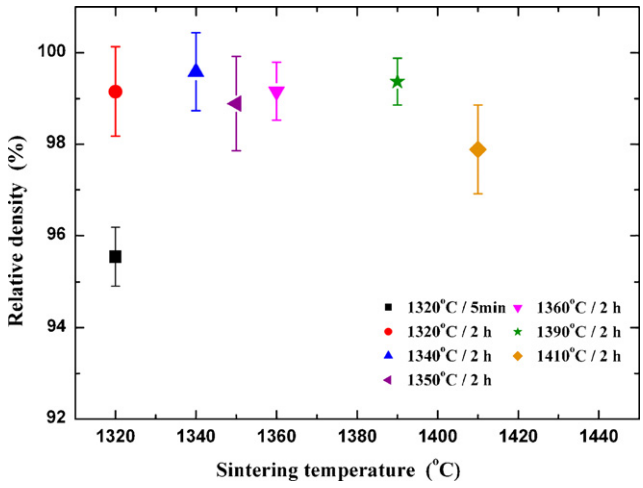

Fig. 1. Relative density of the $BaTiO_3$ specimens after sintering.

3. Results

The XRD analysis reveals the presence of only tetragonal $BaTiO_3$ phase in the sintered specimens. No other phase is found. Fig. 1 shows the relative density of the barium titanate specimens after sintering with various temperature/time profiles. The error

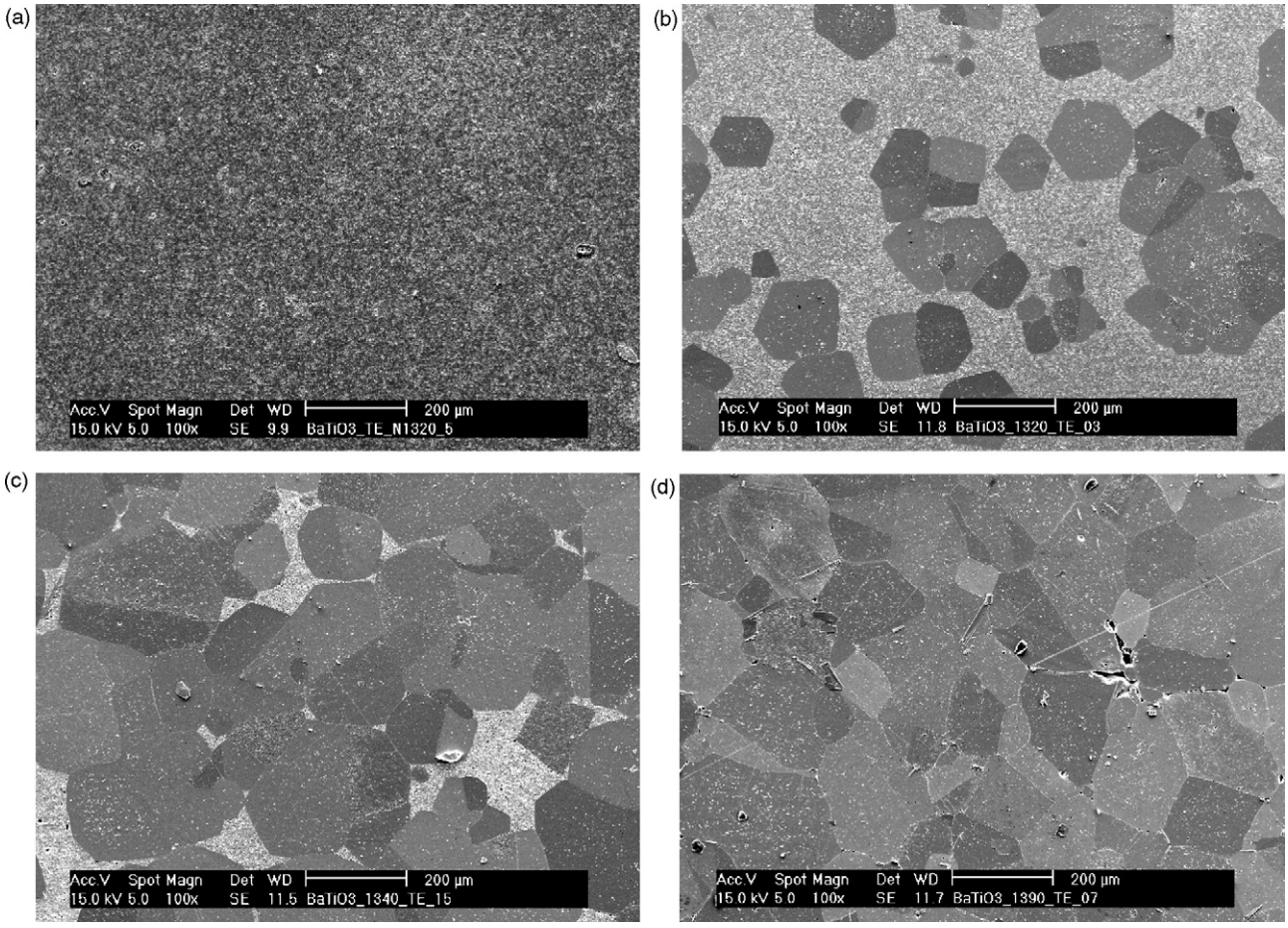

Fig. 2. Typical micrographs of the specimens sintered at: (a) 1320 °C/5 m, (b) 1320 °C/2 h, (c) 1340 °C/2 h and (d) 1390 °C/2 h.

Table 1
Microstructure characteristics of the $BaTiO_3$ specimens after sintering.

Sintering conditions	Area fraction of abnormal grains (%)	Size of abnormal grains (μm)	Size of normal grains (μm)
1320 °C/5min	0	–	2.0 ± 0.8
1320 °C/2 h	38 ± 7	122 ± 63	1.9 ± 0.8
1340 °C/2 h	86 ± 3	179 ± 82	2.2 ± 0.9
1360 °C/2 h	80 ± 8	211 ± 115	2.2 ± 0.9
1390 °C/2 h	100	159 ± 78	–
1410 °C/2 h	100	183 ± 90	–

bars show ±one standard deviation for each average value. The density of the specimens sintered at 1320 °C/5 min is slightly lower than 96%. The density of the other specimens is close to each other. Fig. 2 shows the typical micrographs of the sintered specimens. No abnormal grain is found in the specimen sintered at 1320 °C/5 min, Fig. 2(a). By prolonging the dwell time at 1320 °C to 2 h, the abnormal grains occupy 38% of the total area, Fig. 2(b). The area fraction of abnormal grains generally increases with the increase of sintering temperature, Table 1. As the sintering temperature is above 1390 °C, no fine grains are observed, Fig. 2(d). Since only coarse grains are present in the specimens sintered above 1390 °C, the coarse grains are no longer "abnormal".

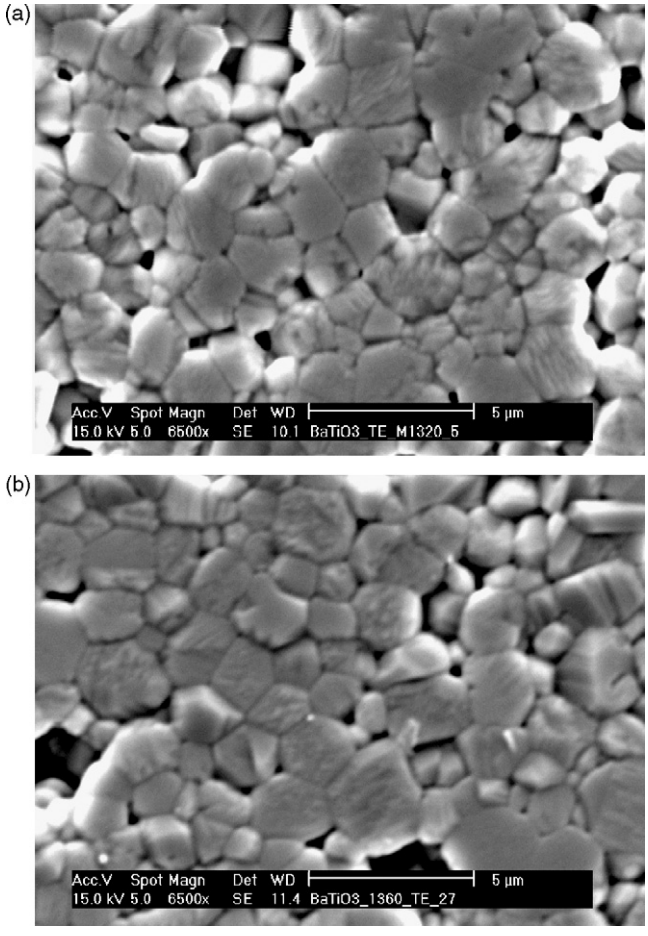

Fig. 3. Typical normal grains in the specimens sintered at (a) 1320 °C/2 h and (b) 1360 °C/2 h.

Fig. 3 shows the typical micrographs of the area composing of only fine normal grains in the specimens sintered at 1320 °C/2 h and 1360 °C/2 h. Though the area fraction of the fine grains decreases from 62% to 20% as the sintering temperature increases from 1320 °C to 1360 °C, the size of the normal grains changes little, Table 1.

Fig. 4 shows the grain size distribution of the barium titanate specimens after sintering. The size variation of normal grains (the left-hand side of the figure) exhibits a typical log-normal distribution. Most of the normal grains vary from 1 μm to 4 μm (average size from 1.9 μm to 2.2 μm). Though the increase of sintering temperature reduces significantly the area fraction of normal grains, the peaks of the distribution curve moves little toward its right-hand side. The size of abnormal grains also demonstrates a log-normal size distribution (the right-hand side of Fig. 4). Most of the coarse grains vary from 100 μm to 400 μm (average size from 122 μm to 211 μm as the sintering temperature increases from 1320 °C to 1360 °C). The increase of sintering temperature shifts slightly the distribution curves to their right-hand side. The size of the coarse abnormal grains is two orders of magnitude larger than that of the fine matrix grains. It is surprising to note that no grain with an intermediate size is found. A discontinuous grain growth behaviour, in terms of size variation, is displayed for the sintered barium titanate specimens. The average size of either only normal grains or only abnormal grains as a function of sintering temperatures is shown in Fig. 5. The dwell time is 2 h. For comparison reason, the data for the specimens sintered at 1320 °C for 5 min

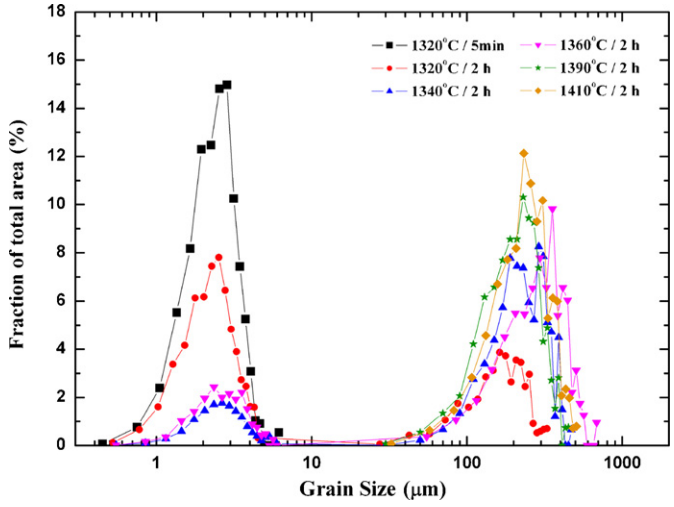

Fig. 4. Size distribution curves for the $BaTiO_3$ specimens after sintering.

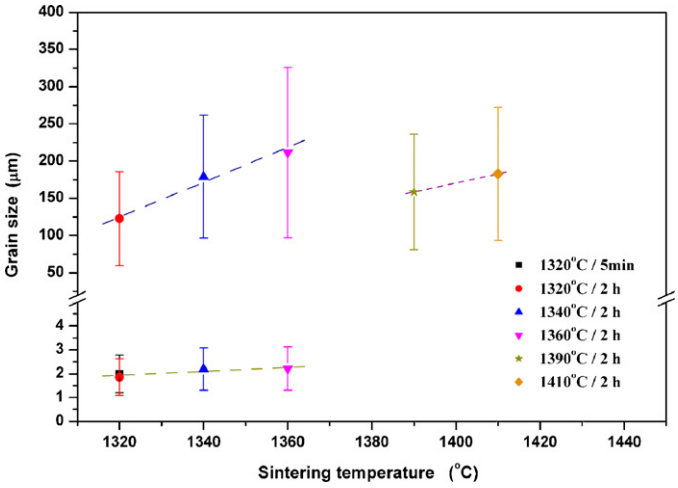

Fig. 5. Average size of normal grains and abnormal grains in the $BaTiO_3$ specimens after sintering at the indicated temperatures.

are also included in the figure. For the specimens sintered at 1320 °C/5 min, 1390 °C/2 h and 1410 °C/2 h, the microstructures exhibit a single mode size distribution. For the specimens sintered at 1320 °C/2 h, 1340 °C/2 h and 1360 °C/2 h, a bimodal size distribution is observed.

4. Discussion

The abnormal grain growth (or exaggerated grain growth) has taken place in the present barium titanate system during sintering. The abnormal grains grow much faster than the surrounding matrix grains, a bimodal size distribution is therefore observed for the specimens sintered at 1320–1360 °C, Fig. 2(b) and (c). These abnormal grains grow until they impinge each other. The morphology of the abnormal grains is equiaxed, indicating that a small amount of eutectic liquid is present.[4] Though the Ba/Ti ratio of the starting powder is close to unity, some Ba may dissolve into the milling liquid,[23] or some BaO near the surface may vaporize during firing at elevated temperature,[5] the Ba/Ti ratio of the $BaTiO_3$ specimens during sintering may thus be smaller than unity. A small amount of the liquid phase may still be present despite the amount of $Ba_6Ti_{17}O_{40}$ (B6) phase is below the detection limit of the XRD technique employed. For the specimens sintered at 1320 °C/2 h, many equiaxed abnormal grains are observed. It may be related to the presence of a small amount of SiO_2, which lowers the liquid formation temperature to below 1320 °C.

Quantitative microstructure analysis is also conducted in the present study. For the specimens sintered in the temperature range from 1320 °C to 1360 °C, the area fraction of abnormal grains increases rapidly with the increase of temperature/time, see Table 1. Meanwhile, the size of abnormal grains increases little. For the $BaTiO_3$ system investigated in the present study, the size of the abnormal grains is much larger than that of normal grains. It is also worth noting that no grain with the intermediate size is present. As both fine normal grains and coarse abnormal grains are present within one specimen, the driving force, $\Delta G_{transition}$, for the growth of abnormal grains into normal grains can be estimated as[6]

$$\Delta G_{transition} = 2\gamma V_M\left(\frac{1}{r_{normal}} - \frac{1}{r_{abnormal}}\right) \quad (1)$$

In the above equation, γ is the surface energy, V_M the molar volume, r_{normal} the radius of normal grains and $r_{abnormal}$ the radius of abnormal grains. By taking $\gamma = 0.3\ J/m^2$,[6] $V_M = 3.85 \times 10^{-5}\ m^3/mol$,[6] $r_{normal} = 2\ \mu m$, $r_{abnormal} = 200\ \mu m$, the driving force for the growth of abnormal grain into normal grains is as large as 11 J/mol. The size variation of either only normal grains (1–4 μm) or only coarse grains (100–400 μm) is relatively narrower, the driving force for the growth of normal grains to normal grains and for the growth of abnormal grains to abnormal grains is therefore relatively smaller. Due to the large driving force for the growth of abnormal grains into a matrix of fine normal grains, the normal grains are consumed fast. Meanwhile, the growth of matrix normal grains is very limited, see Fig. 5.

A thorough microstructure characterization is conducted in the present study. Through careful observation, some peculiar regions are found in all the specimens with bimodal size distribution. These peculiar regions are composing of a cluster of fine grains. Fig. 6 shows two typical clusters found in the specimens sintered at 1340 °C for 2 h. One cluster of fine grains is found near an abnormal grain, Fig. 6(a). The cross-section was thermal etched at 1240 °C for 1 h. A grain boundary is

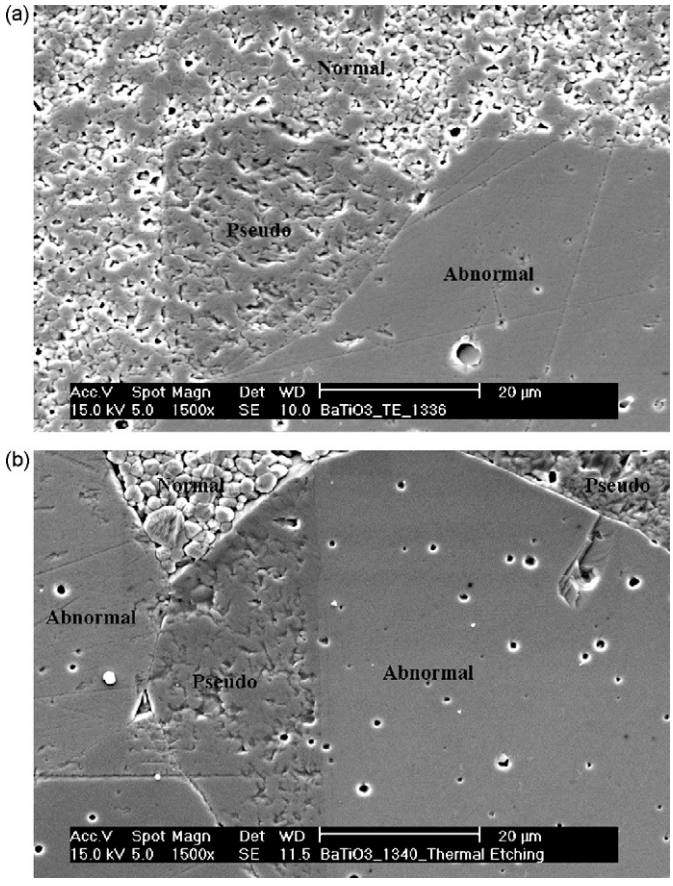

Fig. 6. Two typical "pseudo-abnormal" grains observed in the specimen sintered at 1340 °C for 2 h.

located between the abnormal grain and the cluster. Many grain boundaries also exist between the fine grains outside the cluster. However, the grain boundaries are hardly observed within the cluster. It implies that the crystallographic orientations of the fine grains within the cluster might be very close to each other. For the cluster near an abnormal grain, such cluster is ready to merge into the abnormal grains, as demonstrated in Fig. 6(b). Some isolated clusters are also found.

Three microstructure features are observed for these clusters, see Fig. 6. Firstly, the amount of porosity in the cluster is higher than that in an abnormal grain. The amount of porosity is more close to that in the fine grains matrix. Secondly, the shape of pores within the abnormal grains is spherical. It can be related to the absence of grain boundaries within the abnormal grains. However, the shape of the pores in the cluster, similar to the pores in the fine grain matrix, is irregular. Thirdly, the grain boundaries are hardly observed within the cluster. Based on these three microstructural features, the cluster is termed as a "pseudo-abnormal" grain. However, the cluster may also be a part of an abnormal grain, as demonstrated in Fig. 6(b). The cluster is ready to grow into the nearby abnormal grain. The EBSD analysis has been conducted to identify the crystallographic orientations of the fine grains within a pseudo-abnormal region. Since the density of the pseudo-abnormal region is relatively low, the presence of many pores renders the preparation of a flat surface a difficult job. For some pseudo-abnormal regions, the orientations of the fine grains are not the same. For some pseudo-abnormal regions, only one to two orientations for the fine grains are observed. Therefore, no conclusive remarks can be given by saying that the crystallographic orientations of the fine grains within a pseudo-abnormal grain are the same. Further detailed microstructure analysis (such as TEM) is still needed to prove the presence of such pseudo-abnormal grains.

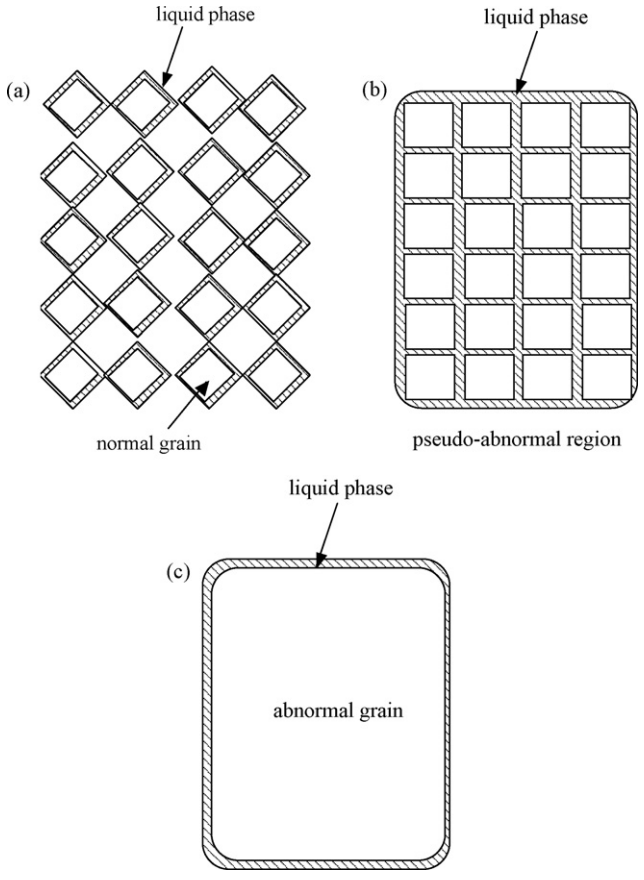

Fig. 7. Typical EBSD analysis results for the specimen sintered at 1340 °C then thermal etched at 1240 °C. The specimens were tilted by 70° to facilitate the EBSD analysis, the SEM micrograph is slightly distorted.

The present study proposes a possible transition stage for the transformation of ~2-μm normal grains to ~200-μm abnormal grain. The sequence for the formation of a "pseudo-abnormal" grain is demonstrated in Fig. 7. Several normal grains with random orientations are re-oriented to form a "pseudo-abnormal" region. The pseudo-abnormal region then transforms into an abnormal grain. However, the mechanism for such re-orientation needs further investigation.

5. Conclusions

In the present study, the size variation of normal and abnormal grains in sintered $BaTiO_3$ specimens is carefully characterized. For the specimens composing of both normal and abnormal grains, the area fraction of abnormal grain increases rapidly during abnormal grain growth. However, the size of abnormal grains increases slightly in the same time. The size of abnormal grains is two orders of magnitude larger than that of normal grains. One possible mechanism for the transition from 2-μm normal grains to 200-μm abnormal grain is proposed. Several nearby normal grains are partially re-orientated to form a cluster (or pseudo-abnormal grain). The pseudo-abnormal grain is then transformed into an abnormal grain.

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