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Effect of SiO_2 and TiO_2 Addition on the Exaggerated Grain Growth of $BaTiO_3$

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Abstract

The exaggerated grain growth (sometimes referred to as secondary recrystallization) during sintering of $BaTiO_3$ was studied with two different liquid-forming additive oxides, TiO_2 and SiO_2. The liquid phase was distributed inhomogeneously by placing a small amount of TiO_2 and SiO_2, respectively, on top of the $BaTiO_3$ powder compact. The exaggerated grain growth was observed to occur more rapidly in the SiO_2-containing specimen than in the TiO_2-containing specimen. Once the initial fine-grained structure was completely replaced by the exaggeratedly grown grains, the TiO_2-containing specimen exhibited practically no more microstructural evolution. For the SiO_2-containing specimen, on the other hand, a few grains continued to grow without limit. The observed unusual growth has been explained in terms of twin-assisted growth mechanism. © 1997 Elsevier Science Limited. All rights reserved.

1 Introduction

A significant amount of work has been performed on the microstructure of $BaTiO_3$,[1–4] and it was shown that the inhomogeneous presence of small amounts of liquids gives rise to the exaggerated grain growth during sintering.[5,6] The grains grown to a much larger size than the average by the enhanced material transfer through the non-uniformly distributed liquids are believed to be the 'nuclei' for exaggerated grain growth.[7,8] On the other hand, Schmelz *et al.*[9,10] reported that (111) twin lamellas are found in nearly all the exceptionally grown $BaTiO_3$ grains, and derived a model of twin-assisted grain growth. In their model, the twinned grains with the re-entrant facet angles are suggested to act as the 'nuclei' for exaggerated grain growth. In this respect, either the locally enhanced material transfer by liquid phase and/or the formation of the (111) twins is likely to be crucial for the exaggerated grain growth during sintering of $BaTiO_3$.

The aim of this investigation was to identify and distinguish the nature of these 'nuclei'. For this purpose, the liquid phase which can be present during the sintering of $BaTiO_3$ was non-uniformly distributed by placing a small amount of TiO_2 and SiO_2 powders, respectively, on top of the $BaTiO_3$ powder compact. Note that TiO_2 which forms a eutectic at 1320°C is an additive most widely used to promote the densification of $BaTiO_3$.[11] The addition of SiO_2 is also known[12] to result in the formation of liquid at 1260°C. It is also noteworthy that SiO_2 is an impurity ubiquitously present in normal ceramic processing. Although they both form liquid phase during the sintering of $BaTiO_3$ and promote material transfer, their effect on the formation of (111) twins is not expected to be identical. In fact, an enhanced formation of (111) twins was observed in the SiO_2-containing specimen in the preliminary experiments.

The microstructural evolution of the SiO_2- and TiO_2-containing specimens was indeed quite different. Once the initial fine-grained structure was replaced completely by the abnormally grown grains, the TiO_2-containing specimen exhibited practically no further microstructural evolution and maintained a uniform microstructure. On the other hand, a few grains grew further to an enormous size up to a few millimetres in the SiO_2-containing specimen. The results are discussed in terms of the difference in the nature of the 'nuclei'.

2 Experimental Procedure

The physical and chemical characteristics of the $BaTiO_3$ powder (TAM Ceramics, Niagara Falls NY) used in this experiment were reported previously.[4]

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Its average particle size and Ba/Ti ratio determined by the manufacturer are 1·5 μm and 0·999, respectively. The SiO_2 impurity content of the powder used is 0·01 wt%. The powder was slightly compacted into cylindrical specimens 10 mm in diameter and then pressed hydrostatically at 250 MPa. On the other hand, the slurries of TiO_2 (99·9%, Aldrich Chemical Co., Milwaukee) and SiO_2 (99·5%, Junsei Chemical Co., Tokyo) powders, respectively, were prepared using ethyl alcohol. By using a pipette, the slurries were dropped on top of the green $BaTiO_3$ compact, and the mass of slurry was controlled so that the specimens contain 1 mol% of SiO_2 and TiO_2, respectively. After drying, the compacts were sintered at 1350°C for periods ranging from 0 to 20 h. The sintering for 0 h means that the specimens were cooled immediately after the sintering temperature was reached. The heating and cooling rates were 60°C/min.

The sintered specimens were then heat-treated at 1000°C for 1 h using the graphite element-heated vacuum furnace. After such a heat treatment which results in the lowering of tetragonality, (111) twins are known[13] to clearly appear in the microstructure. The vertical cross-section of the specimen was polished with 0·05 μm alumina powder for microscopic examinations. Photographs were obtained after etching with a solution of 10% HCl containing a little HF.[14] An average intercept length was obtained and then multiplied by 1·776 to obtain the average grain size.[15,16]

3 Results and Discussion

The specimens in this investigation were very similar to those prepared by infiltration: the eutectic liquids of SiO_2 and TiO_2 formed at the top surface of the specimen during sintering were completely absorbed into the $BaTiO_3$ skeleton. The specimens which were prepared with SiO_2 and TiO_2 are hereafter referred to as 'S' and 'T' specimens, respectively.

Figure 1 shows the microstructure of the S specimen after sintering for 0 h at 1350°C. Although the infiltrant SiO_2 has already been completely absorbed into the $BaTiO_3$ specimen, the presence of liquid was rather confined to the specimen surface (about 900 μm in depth). Note from Fig. 1(a) that the top surface region exhibits a uniform microstructure with larger grains compared to that of the interior. The liquid penetration did not continue into the whole specimen probably because it was consumed by dissolution into $BaTiO_3$. The dihedral angle which is greater than zero and consequent entrapment of liquid at the triple boundary junctions may also be the reason.

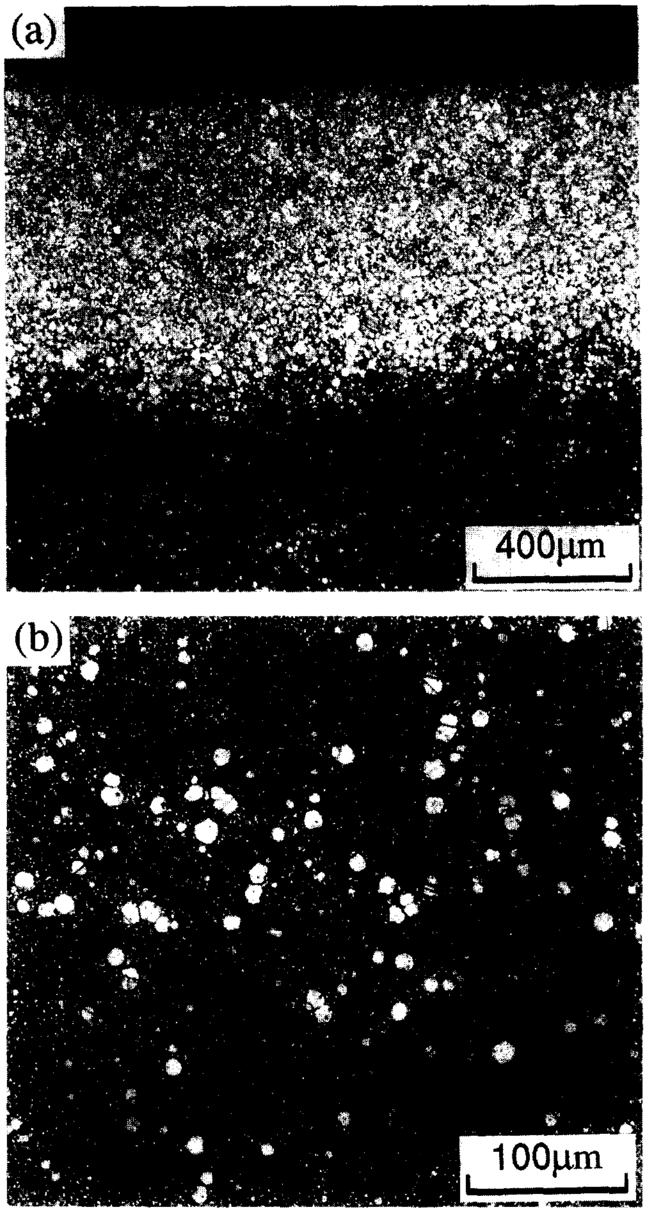

Fig. 1. Microstructures of the S specimen sintered at 1350°C for 0 h: (a) near top surface region and (b) interior.

Figure 1(b) is the microstructure of the interior region far enough from the influence of SiO_2. In fact, it shows a typical characteristic of abnormal or exaggerated grain growth of $BaTiO_3$ observed by others,[5,6] i.e. a duplex microstructure with a small number of grains of much larger size (up to around 20 μm) than the matrix particles (less than 3 μm, in general). Those large grains grow very rapidly until they impinge upon each other and then the growth rate slows down. When all the matrix grains of small size disappear, the uniform microstructure is recovered and finally the occurrence of exaggerated grain growth is unnoticed. The grains in the top surface region shown in Fig. 1(a) are apparently such a new set of

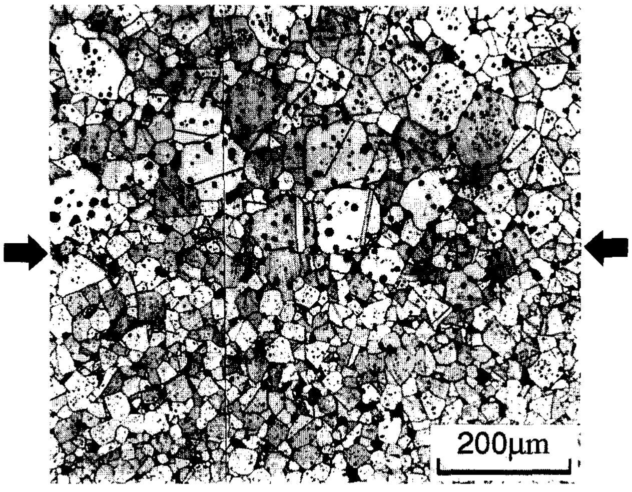

Fig. 2. Microstructure of the S specimen sintered at 1350°C for 0·5 h. The border-line between the top surface region and the interior of the specimen is indicated by arrows.

abnormally grown grains which have completely replaced the initial fine-grained structure. Examinations of the surface and the interior region indicate that the addition of SiO_2 accelerates the material transfer and results in a fast microstructural evolution. As a consequence, the exaggerated growth has been completed earlier at the top surface than in the interior.

Figure 2 is the microstructure of the S specimen obtained after the sintering for 0·5 h. In this specimen, the initial fine-grained structure has completely disappeared even in the interior of the specimen. However, near the top surface region which had been affected by SiO_2 exhibited an average grain size larger than that of the interior. The average grain sizes of the surface region and the interior were determined to be 59 and 31·3 μm, respectively. The borderline between the two regions is indicated by arrows in Fig. 2. Note that (111) twin lamellas are present in many of the large grains in the top surface region. For the grains in the interior, on the other hand, the presence of single-twins is occasionally noted but the double-twins (twin lamellas) are not observed to present.

When the same S specimen was further heat-treated, a few grains were observed to grow to a very large size. As shown in Fig. 3(a), the sintering of the S specimen for 8 h resulted in a very unusual microstructure. In comparison with Fig. 2, the grains which were located at the borderline grew up to a few millimetres in size by consuming the grains in the interior. In those giant grains, the presence of (111) twin lamellas is noted without exception. The depth of the top surface region of this 8-h sintered specimen was practically the same as that of the 0-h sintered specimen shown in Fig. 1(a). The results indicate that the grains at the top surface region initially affected by SiO_2 were stable and only the grains in the interior were consumed. Figures 3(b) and (c) are the detailed microstructures of the upper and lower regions (marked in Fig. 3(a)), respectively. From these, it can be confirmed that only the grains in the upper part contain (111) twin lamellas.

In case of the T specimen, the microstructural evolution was different from that of the S specimen, and Fig. 4 is the microstructure obtained after sintering for 0 h. Contrary to the S specimen (Fig. 1(a)), the growth rate of the grains in the top surface region is observed to be slower than that in the interior. Note that the microstructure of the interior shown in Fig. 4 is almost identical to that of the S specimen sintered for 0 h (Fig. 1(b)). In both specimens, the interior is expected to have an identical initial powder composition with a slight excess of TiO_2. In this respect, the increase of TiO_2-rich liquid has rather inhibited the exaggerated grain growth. The change from abnormal to normal growth has been already reported with the increase of TiO_2-rich liquid.[17,18] Although the exaggerated grain growth was initiated in the interior in this T specimen, it occurred also at the surface without much delay. As a consequence, the specimen sintered for more than 5 min exhibited a uniform microstructure without a notable difference between surface and interior.

The most striking difference compared to the S specimen is that the unusual extensive grain growth did not occur in the T specimen even after an extended period of sintering. The microstructures of the T specimen sintered for 20 h are shown in Fig. 5 at two different magnifications. These show that the microstructure is composed of uniformly distributed grains which do not contain (111) twin lamellas. From the microstructural evolution of the early stage observed in Fig. 4, it is believed that the microstructures in Fig. 5 are those which have already completed the process of secondary recrystallization. The average grain size of the T specimen shown in Fig. 5(b) was determined to be 35·8 μm.

Generally, the grain growth in the presence of liquid phase is described by Ostwald ripening[19–21] and the presence of small numbers of large grains is considered[7,8] to be a prerequisite for secondary recrystallization. As the liquid appears during sintering, the difference between the solubility of small size matrix particles of size r, $C(r)$, and that of certain number of large grains, $C(R) \simeq C_\infty$, provides the driving force for secondary recrystallization, ΔG. This can be expressed by[6]

$$\Delta G = RT \ln\left(\frac{C(r)}{C_\infty}\right) = 2V_m \frac{\gamma_{sl}}{r} \qquad (1)$$

where RT has the usual meaning, V_m and γ_{sl} are the molar volume and the solid–liquid interface energy, respectively.

However, the exaggerated growth of grains dispersed in liquid has been observed to depend on the shape of grains, which is either nearly spherical with curved surface or faceted with flat planes. In fact, no exaggerated grain growth has been reported for spherical grains such as in the case of W in Ni. In W–Ni liquid-phase sintering, for instance, the addition of a few W particles of substantially larger than average grain size did not result in exaggerated grain growth.[22] Instead, the fine matrix W grains grow faster to result in a typical homogeneous size distribution of the diffusion-controlled Ostwald ripening.[19–21] On the other hand, the faceted grains in some systems such as WC–Co[23,24] or Y–Ba–Cu–O superconductors[25] often grow exaggeratedly and exhibit apparently perfectly straight boundaries.

Park *et al.*[24] suggested recently from the atomically smooth interface structure of faceted straight crystal planes that the exaggerated grain growth

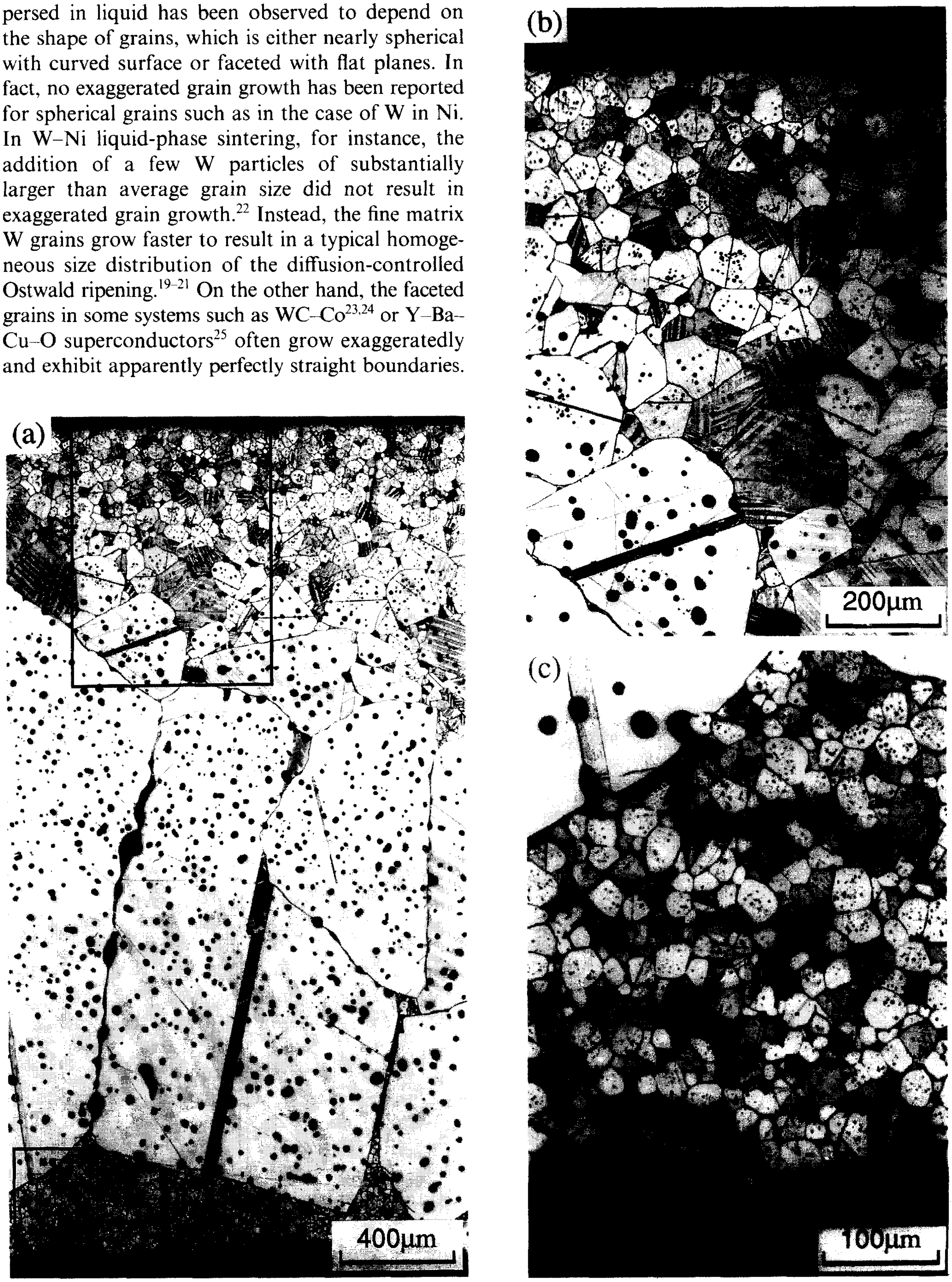

Fig. 3. Microstructures of the S specimen sintered at 1350°C for 8 h. (a) Global view of the cross-section; (b) and (c) micrographs taken at high magnification from the marked upper and lower regions, respectively.

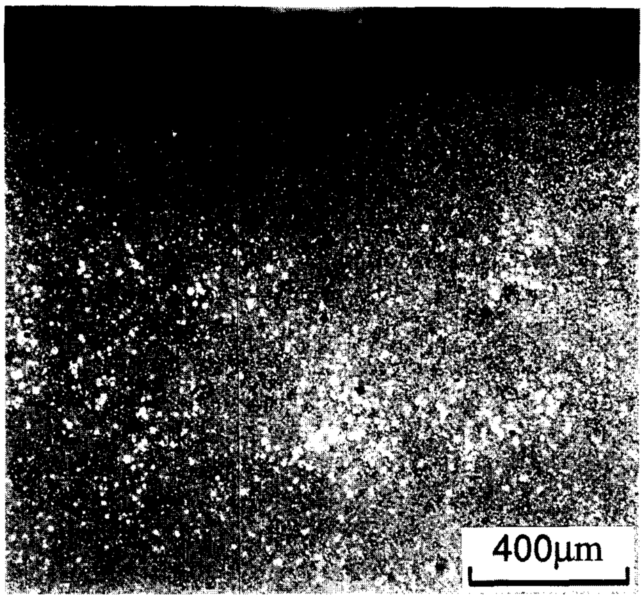

Fig. 4. Microstructure of the T specimen sintered at 1350°C for 0 h (near top surface region).

will proceed by a process similar to the two-dimensional (2-D) nucleation and growth, for which the growth rate is essentially of the form[26]

$$R = A_1 \exp(-A_2/\Delta G) \quad (2)$$

where A_1 and A_2 are constants. As a consequence, the growth rate will remain nearly at zero and increase sharply when ΔG exceeds a certain value. This means that the exaggerated grain growth will occur only when the size of matrix particles, r in eqn (1), is smaller than a certain critical value. During the sintering of Sr-Hexaferrite,[27] exaggerated grain growth has been observed to depend critically on the heating rate because the size of matrix particles is increased when the specimen is heated slowly. Furthermore, the use of starting powders with a small particle size was observed to result in the exaggerated grain growth in liquid-phase sintered alumina[28] and in WC–Co alloys.[24] From these experimental results, the model of 2-D nucleation is believed to be appropriate for explanation of the exaggerated growth of grains dispersed in a liquid.

It is noteworthy that the columnar grain growth observed in the S specimen (Fig. 3(a)) has taken place after the completion of exaggerated grain growth. Although the process itself, the growth of a small fraction of the grains by consuming the uniform-grain-size matrix, is similar to the process of general exaggerated grain growth, the nature of the nucleation and the driving force for the observed columnar grain growth are expected to be different. Note that this process occurs in a matrix of large grains that were already grown up to around 30 μm in size and consequently ΔG in eqn (1) will be very small and R in eqn (2) in turn will be negligible. The material transfer based on size difference of grains is expected to lead only to the quasi-stable and uniform microstructure as observed in the T specimen.

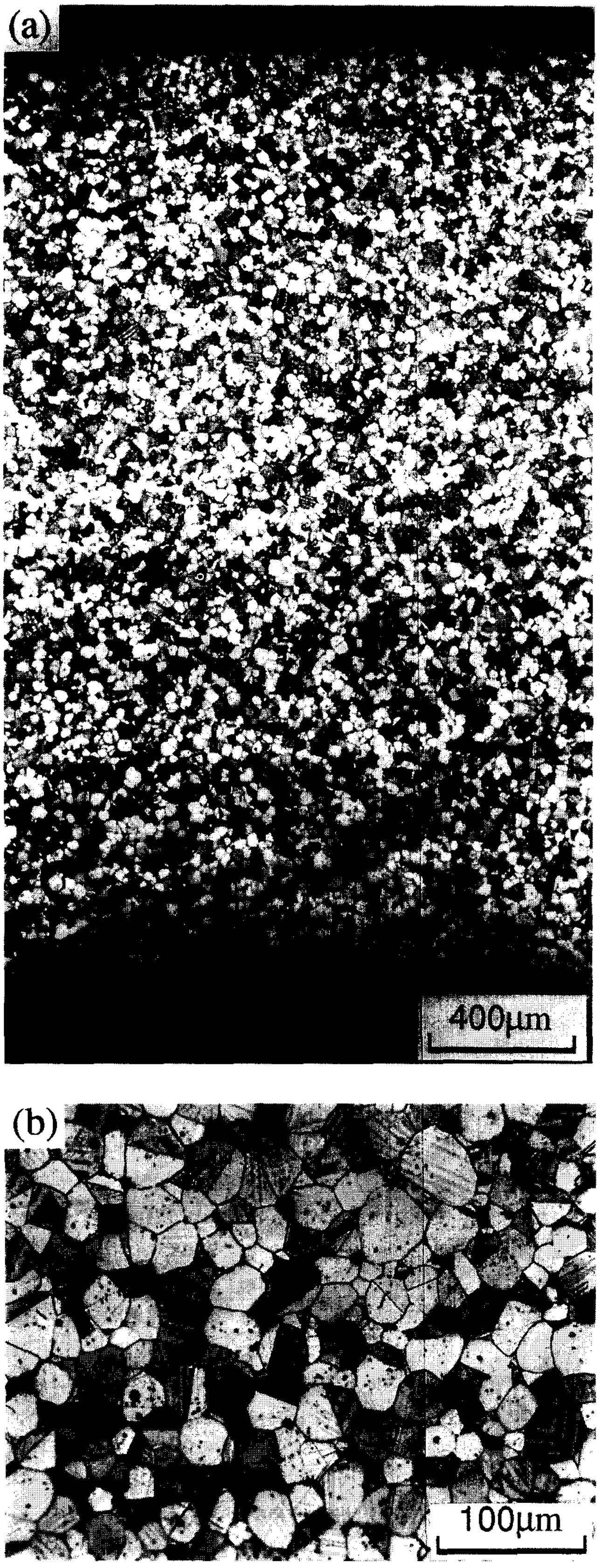

Fig. 5. Microstructures of the T specimen sintered at 1350°C for 20 h. (a) Global view of the cross-section and (b) micrograph taken at high magnification.

For the columnar grain growth of $BaTiO_3$ observed in Fig. 3, the re-entrant angles created by the formation of a (111) twin boundary intersecting two faceted surfaces are expected to play a major role because they provide sites for easier growth compared to the two-dimensional nucleation. This mechanism has been known in crystal growth as twin-plane re-entrant edge (TPRE) growth,[29] and reported to result in a fast rate of crystal growth. During solid-state sintering of $BaTiO_3$, Schmelz *et al.*[9,10] observed an exaggerated grain growth initiated by the twinning process. They considered the growth of single and double-twinned crystals, and only the latter was proposed to grow without limitation. The presence of double twins (twin lamellas) without exception in the large grains shown in Fig. 3(a) thus supports the TPRE growth mechanism. The important feature of the experimental result is that the formation of (111) twin lamellas is greatly enhanced by the presence of the SiO_2 liquid.

Taking into account the above TPRE growth mechanism, it is easy to understand the different microstructural evolutions observed in the S and T specimens. In the S specimen, the exaggerated growth occurs mainly by the TPRE growth mechanism, while in the T specimen it is governed by the material transfer due to grain size difference. With the penetration of the SiO_2-rich liquid during sintering of the S specimen, a small number of grains are expected to grow very rapidly at the surface because the twinning occurs due to SiO_2. Without much delay, the exaggerated grain growth also occurs in the interior from the grains of considerably larger size than the average. Note, however, that the (111) twin lamellas are not formed in the interior (Fig. 3(c)) because SiO_2 is not present. Grains having a twin lamella at the borderline (Fig. 2) can thus grow very rapidly by consuming mainly the grains of interior. Since most of the grains at the surface region have a (111) twin lamella as observed in Fig. 3(b), the material transfer by TPRE growth is not operative between them.

In the T specimen, on the other hand, the grains that are considerably larger than other matrix grains are believed to be the nuclei for secondary recrystallization. The retardation of exaggerated grain growth at the surface is due to the increased amount of the TiO_2-rich liquid. The rate of material transfer will be slowed because of the increasing thickness of the liquid layer.[6] Once the initial fine grains are replaced by a new set of large grains of around 30 μm, further driving force for grain growth is decreased and the growth kinetics becomes negligible. Therefore, the quasi-stable microstructure as observed in Fig. 5 is obtained.

The (111) twins or twin lamellas in $BaTiO_3$ are known to form when the grains grow rapidly either by coalescence or by the appearance of liquid during sintering.[30] From the experimental results of this investigation, however, it is evident that the formation of (111) twins in $BaTiO_3$ is not only related to such rapid grain growth but also closely related to the presence of SiO_2. Note from Fig. 5 that the exaggerated grain growth observed in the T specimen with the appearance of liquid did not result in the formation of (111) twin lamellas. At present, the enhanced formation of twin lamellas by SiO_2 is not clearly understood. A plausible mechanism which can be suggested is the stabilization of face-shared TiO_6 octahedra (Ti_2O_9 groups) by the substitution of Ti^{4+} at the (111) twin boundary of $BaTiO_3$ by Si^{4+}.

From the results, it can be deduced that the local presence of SiO_2 in $BaTiO_3$ should be avoided because it is very harmful for the production of uniform-microstructure material. The presence of SiO_2-rich liquid results in the formation of double-twinned crystals which trigger the extensive grain growth. When the SiO_2 is homogeneously present throughout the specimen, however, the effect of SiO_2 may not be so pronounced because all the matrix grains would have the twinned structure, i.e. a (111) twin lamella. In that case, the uniform microstructure will be maintained after the completion of secondary recrystallization.

4 Conclusions

The exaggerated grain growth (secondary recrystallization) during sintering of $BaTiO_3$ with a small amount of liquid-forming additive has been investigated. When TiO_2 is added in excess, the uniform microstructure is maintained after the completion of secondary recrystallization. This is due to the two-dimensional nucleation characteristics of secondary recrystallization; the growth rate of abnormally large grains becomes negligible with the increase of matrix grain size. When SiO_2 is added, on the other hand, the exaggerated grain growth is observed to occur mainly by the twin-plane re-entrant edge (TPRE) growth mechanism. The re-entrant angles created by double-twinned crystals provide sites for easier growth compared to the two-dimensional nucleation. When SiO_2 is present locally in the $BaTiO_3$ specimen and the (111) twin lamellas are present in the grains of a very restricted region, those grains may grow without limitation by the TPRE growth mechanism.

Acknowledgements

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