論文・Paper

Fabrication of Grain-Oriented $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Ceramics by Normal Sintering (Part 2)

Sintering Mechanisms

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The sintering mechanism of the compacts formed by tapecasting a plate-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powder was studied by densification measurement and microstructure observation. The sintering behavior is characterized as follows: the dominant mechanism responsible for densification is particle rearrangement, which leads to well-oriented regions of grains and flat and elongated pores, whose long axes are parallel to the sheet plane. The increases in the size of the well-oriented regions and in the contact area between them break up pore connection, resulting in the formation of closed pores at a low density. Grain growth occurs above 1050°C and broadens the grain size distribution.

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普通焼結による配向性 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ セラミックスの作製 (第2報)

焼結機構

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板状 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 粉末をテープ成形して作製した成形体について焼結中のち密化速度及び微細構造 (結晶粒子と気孔) の変化を調べ、板状粒子の焼結機構を考察した。ち密化を支配する機構は主に粒子の再配列で、焼結初期の早いち密化や収縮率の異方性が認められた。また、粒子の再配列の結果、粒子のよく配向した領域とその間の平板状の気孔が生成した。焼結の進行に伴いこれらの領域は大きくなり、これらの領域で挟まれた気孔を切断し、等軸粒子より低密度で閉気孔が生成した。粒成長は 1050°C 以上で顕著になり、粒径分布も広がった。

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Key-words: Sintering mechanism, Plate-like particles, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, Particle rearrangement, Closed pore

1. Introduction

Grain-oriented ceramics have been prepared by normal sintering¹⁾⁻⁴⁾. The powder particles with plate- or needle-like shape are aligned in a green sheet by tapecasting and sintered to increase the density and grain orientation. In the previous paper⁴⁾ we studied the effects of preparation and firing conditions of the cast sheet on the density and grain orientation of sintered sheets and found that densification occurred above 900°C and grain orientation increased above 1050°C by grain growth.

In ceramic science sintering is extensively studied in the spherical or equiaxed particle systems but information on the sintering behavior of particles with a large degree of shape anisotropy is rather limited⁵⁾⁻⁷⁾. An understanding of sintering behavior of particles with shape anisotropy is essential to prepare grain oriented ceramics by the tapecasting-normal sintering technique⁴⁾, because powders with shape anisotropy are used as a starting material. This paper describes the sintering behavior of a green sheet made by tapecasting of a plate-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

powder. The mechanisms of densification and microstructure development have been discussed based on the shrinkage measurement and microstructure observation. The change in pore structure has been examined by mercury penetration porosimetry and compared with that for an equiaxed powder.

2. Experimental

The plate-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powder and green compacts used in this study are the same as those used in our previous paper⁴⁾. Briefly, the plate-like powder was prepared by molten salt synthesis using sulfate salts (cf. Fig. 1 of Ref. 4) for particle morphology). Sixty grams of the powder were mixed with 30 cm^3 of an organic vehicle with the viscosity of 400 cP and tapecast at the blade opening of 0.6 mm. The sheet so obtained was cut to small pieces, stacked, pressed to make compacts of about 2 mm thick and slowly heated to 500°C to burn out the binder. The resultant compacts had the density of 4.10 g/cm^3 , 51% of theoretical, 8.04 g/cm^3 .

The equiaxed powder particles were made by heating a Bi_2O_3 and TiO_2 powder mixture at 900°C for 3 h and wet-milled in a ball-mill for 1 h. The particle size was about $1.2\text{ }\mu\text{m}$. The powder was uniaxially pressed under the pressure of 1 t/cm^2 using a 10 wt% PVA solution as a binder. The density after binder burn-out was 62% of theoretical.

The green compacts were sintered at the heating rate of 200°C/h and kept at a desired temperature for a desired time period, and then cooled to room temperature by taking them out of a furnace. Linear shrinkage and density were determined by measuring dimensions and weight. The microstructure of sintered compacts was observed by scanning electron microscopy (SEM) on polished and thermally etched sections perpendicular and parallel to the cast sheet plane. Pore structure was studied by the hysteresis observed in mercury penetration porosimetry. Isothermal sintering behavior was studied using a dilatometer; green compacts were heated to a temperature between 900° and 1100°C within 4 min and dimensional change was measured after reaching a desired temperature.

3. Results and discussion

3.1 Densification

Figure 1 shows the effects of sintering tempera-

Fig. 1. Sintered density as functions of temperature and time.

Fig. 2. Shrinkages (a) perpendicular and (b) parallel to the sheet plane as a function of temperature.

Fig. 3. Densification isotherms in the direction perpendicular to the sheet plane. The data parallel to the sheet plane are shown in broken lines.

ture and time on the density. The time dependence of the density was different below and above 1050°C ; below 1050°C the density increased continuously and above 1100°C the densi-

fication was almost completed within 10 min and further heating slightly increased the density. A special feature of the sintering behavior of these sheets was anisotropic densification as shown in Fig. 2; the linear shrinkage perpendicular to the sheet plane was almost $3/2$ times as large as that parallel to the sheet plane over the whole temperature range examined.

Figure 3 shows the densification isotherms perpendicular and parallel to the sheet plane. Zero time and initial size were taken at the moment when the compacts reached a desired temperature. Because of densification during heating-up, the linear shrinkage shown in Fig. 3 were smaller than the total shrinkage shown in Fig. 2. The isotherm at 1100°C indicates again that the densification almost ceases after about 10 min. The initial slopes of isotherms perpendicular to the sheet plane were characterized to be unity over the entire temperature range studied, whereas those parallel to the sheet plane were less than unity, which increased with increasing the temperature.

The microstructure developed during the early stage (at 950°C for 60 min) is shown in Fig. 4. The grain shape was plate-like, whose major plane aligned nearly parallel to the sheet plane. In the cross section perpendicular to the sheet plane, the microstructure consisted of well-oriented regions and pores between the well-oriented regions. In the well-oriented regions plate-like grains aligned face-to-face with no pore. In the cross section parallel to the sheet, on the other hand, the plate faces of the plate-like grains can be observed. Necks in an ordinary sense of sintering were formed between them.

The rapid initial densification (Fig. 1) with the

slope of unity (Fig. 3), anisotropic shrinkage (Fig. 2) and the formation of well-oriented regions (Fig. 4 (a)) indicate that particle rearrangement plays a dominant role in densification at an early stage⁶⁾. In general, particle rearrangement occurs by unsymmetric neck formation and induced stresses in the compacts made of equiaxed particles⁸⁾, but in this case the rotational motion of particles so as to form face-to-face contact between particles is the origin of the particle rearrangement, which results in the anisotropic densification and the formation of well-oriented regions. Densification along the perpendicular direction to the sheet plane would have proceeded mainly by the particle rearrangement during first 10 min. Above 1100°C densification by this mechanism is almost finished and below 1050°C the continuing increase in density after 10 min occurred by the combined mechanisms of the particle rearrangement and some other material transport. Densification along the parallel direction to the sheet plane would have been caused by the combination of the particle rearrangement and material transport responsible for the neck formation. The former would dominate with an increase in the sintering temperature.

3.2 Microstructure development

The microstructures developed above 1000°C are shown in Fig. 5. The grain size of 1000°C sintered compact was almost the same as that of 950°C compact (Fig. 4). The increase in pore size was obvious especially in the cross section parallel to the sheet plane (Fig. 5 (b)). The size of the well-sintered regions and the contact area between them increased, resulting in pore growth by coalescence⁹⁾. The cross sections of the pore were either rectangular or wedge-like, and their

Fig. 4. The microstructures of the cross sections of the sintered compact at 950°C for 60 min (a) perpendicular and (b) parallel to the sheet plane.

Fig. 5. The microstructures of the compacts sintered at (a) (b) 1000°C, (c) (d) 1050°C (e) (f) 1100°C for 60 min. The left and right hand side pictures are for the cross sections perpendicular and parallel to the sheet plane, respectively.

long axis aligned nearly parallel to the sheet plane. Pore volume decreased and grain growth occurred above 1050°C. A considerable amount of pore between well-oriented regions was eliminated. The pore remained attached to the grain boundaries and no intragrain pores were formed. The parallel alignment of small grains, which is observed in the cross section parallel to the sheet plane (Fig. 5 (d)), would be revealed by sectioning the well-oriented regions of plate-like grains slightly misoriented with respect to the sectioning plane, i. e., the sheet plane. At 1100°C grain growth was obvious and pore size increased. Grain growth with the small increase in density

(81% at 1050°C and 87% at 1100°C) caused pore coalescence, resulting in pore growth⁹⁾. The intragrain pores with spherical or cylindrical shape are observed in Fig. 5 (f). The pores on the grain boundaries retained the rectangular or wedge-like cross section (Fig. 5 (e)) and were surrounded by the plate-like grains, whose major planes consist of (001). Although the pore with the rectangular or wedge-like cross section has larger surface area than a cylindrical pore, it is stable because of the smallest surface energy of (001) in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Once the pore is entrapped in a grain, its shape changes to spherical or cylindrical to lower the total surface energy.

Grain growth during the sintering of the plate-like particles is different from that of equiaxed particles; the former results in broad grain size distribution as shown in Fig. 5 (e) and (f). Grain growth in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is anisotropic and equiaxed particles change to plate-like grains during grain growth^{7),10)}. The orientation of equiaxed particles in the green compact is random and there is no special grain which grows faster than others, resulting in a narrow grain size distribution as shown by microstructures in Refs. 7) and 10). In contrast to the formation of plate-like grains by grain growth for the equiaxed particles, the plate-like grains formed below 1000°C in this study were originated from the original particle shape, because grain growth did not occur below 1000°C up to 360 min. Above 1050°C grains grew to large plate-like grains. In the tapecast sheet of the plate-like particles, preferred particle orientation exists⁴⁾. If a grain has the same orientation with neighboring grains with respect to not only *c*-axis but also *a*-axes ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is tetragonal above 675°C¹¹⁾ and *c*-axis is perpendicular to the major plane of plate-like particles¹²⁾), they can grow to large grains faster than others. Once large grains are formed, they grow at the expense of small grains, resulting in a broad grain size distribution. Fast grain growth results in the formation of intragrain pores.

3.3 Pore structure

Mercury penetration porosimetry is one of the powerful means to study initial and intermediate stages of sintering¹³⁾, where pores remain open. Figure 6 shows the hysteresis curves of Hg poros-

Fig. 6. The hysteresis curves of Hg porosimetry for (a) and (b) the equiaxed particles sintered at 900° and 1000°C for 10 min, respectively and (c) and (d) the plate-like particles sintered at 900° and 950°C for 60 min, respectively.

imetry for the sintered compacts made of the equiaxed and plate-like particles. In the compact of the equiaxed particles almost all intruded Hg was not extruded during the depressurizing process. In the compact of plate-like particles, on the other hand, some part of Hg was extruded and the ratio of extruded to intruded Hg in the compact sintered at 950°C was larger than that in the compact sintered at 900°C.

Hysteresis in Hg porosimetry is explained by two factors¹⁴⁾: entrapment of Hg in pores with a "ink-bottle" shape after a penetration and the different contact angle of Hg on the pore-wall between intrusion and extrusion. The former is the case in this study because the same material is measured. The pore shape in the intermediate stage of sintering of equiaxed particles is a complex series of cylinders with various radii¹⁵⁾. The intruded Hg was not extruded because of the small entrance openings, resulting in the large volume of Hg entrapped in the pores when the pressure was reduced to zero. In the case of the sintered compacts of the plate-like particles, the fact that the large volume of Hg extruded during depressurizing process indicates that the size of entrances is not quite different from that of the interior. This result and the microstructure observation (Fig. 4 (a)) confirm that the pores are flat with the rectangular or wedge-like cross section and elongated parallel to the sheet plane.

The total-pore volume can be calculated from the measured density and the open pore volume was measured by Hg porosimetry. Figure 7 shows the open-pore ratio as a function of density,

Fig. 7. The open-pore ratio as a function of density for (a) the tapecast plate-like particles, (b) the uniaxially pressed equiaxed particles, (c) the uniaxially pressed (1 t/cm²) plate-like particles and (d) the uniaxially pressed (0.25 t/cm²) plate-like particles.

which is defined here as the volume ratio of the open pore to the total pore. When the equiaxed particles were sintered, more than 80% of the pore remained open until the density reached to about 85% of theoretical. In the tapecast plate-like particles, on the other hand, the pores started closing on densification. The open-pore ratio continued to decrease as the density increased, and all pores became closed at the density of about 90% of theoretical.

Pore closure during the early stage of sintering is attributed to particle orientation in the green compact but not to particle shape. This view was confirmed by the following experiment. The plate-like particles were uniaxially pressed under the pressure of 0.25 and 1 t/cm² and sintered. The uniaxial pressing of plate-like particles causes particle orientation, the degree of which depends on the forming pressure⁷⁾. The relation between the open-pore ratio and the sintered density of the compacts pressed under the pressure of 1 t/cm² fell between those of the equiaxed particles and the tapecast plate-like particles, whereas that of the compacts of 0.25 t/cm² was almost the same as that of the equiaxed particles (Fig. 7). These results indicate that particle orientation in the green compact is the origin of the pore closure during the early stage of sintering.

In the equiaxed particles, sintering during initial and intermediate stages results in the three-dimensionally continuous pores along grain edges, and the cross section of pores is equiaxed. They remain open until the final stage of sintering. The possible explanation of the formation of closed pores at low densities in the sintered compacts made by tapecasting plate-like particles is as follows. In the green compact the pore is continuous in three dimensions. The particle rearrangement during the early stage forms the well-oriented regions of grains, which break a part of pore connection perpendicular to the sheet plane, resulting in the formation of the flat and elongated pores. The pore connection parallel to the sheet plane would vanish when the well-oriented regions, which sandwich the pore, contact each other. The increases in the size of the well-oriented regions and in the contact area between them favor the breaking up of the pore

connection parallel and perpendicular to the sheet plane, resulting in the formation of the closed pore at low densities.

4. Conclusions

Typical features in the sintering behavior of compact made by tapecasting the plate-like particles are summarized as follows. The early stage of sintering involves particle rearrangement, leading to the formations of the well-oriented regions of grains and pores with flat cross sections, which are elongated parallel to the sheet plane. The pore connection vanishes with increasing size of the well-oriented regions and also with increasing contact area between them, which result in the closed pores at low densities. Grain growth occurs above 1050°C, which forms the broad grain size distribution.

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