Discharged microstructure in flash sintered BaTiO$_3$

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When green compacts of ceramics are heated under application of constant electric fields, electric current in green compacts abruptly increases at a certain temperature. At the abrupt increase of electric current, the rapid shrinkage of the green compacts occurs and sintering process finishes immediately. The sintering technique is called “flash sintering”, reported by Raj et al.. [1] Sintering temperatures and times are largely decreased by the technique of flash sintering. Because of the merits, flash sintering, which are expected as a new sintering technique, is recently applied to various ceramics. [2] However, the detail mechanism of flash sintering has not been clarified yet. In this study, we applied flash sintering to BaTiO$_3$ which is widely used as electroceramics, and investigated the microstructure of flash sintered BaTiO$_3$.

We used commercially available BaTiO$_3$ powders (SAKAI chemical industry Co. Ltd., purity >99.9%, Lot. No.1308607). The grain size of the powders is 0.1μm and Ba/Ti ratio is 1.000. The powders were cold isostatically pressed under a pressure of 100MPa into a size of 2x10x30mm$^3$. The green compacts were suspended by Pt wires with Pt paste in a box type electric furnace. The Pt-wires were connected to a stabilized power supply. A constant voltages from 25~300V/cm were applied to the green compacts. After then, suspended green compacts were heated in air from room temperature up to 1300°C at 300°C/h with monitoring the current in specimens. When the currents reached at the limited value, the temperatures and currents were hold. After sintering, the microstructures were investigated by TEM and STEM.

Flash event appeared over 75V/cm. The sintering rates were confirmed to be accelerated by electric fields over 75V/cm. For example, in case of 100V/cm, the specimen shows about 90% of relative density of BaTiO$_3$ only at 1020°C. However, flash sintered specimens have discharged structures due to the large input electric powers in case of no limits of specimen current.

Figure 1(a) shows typical microstructure observed near the discharged area of the flash sintered BaTiO$_3$ at 100V/cm. A secondary phase due to discharging can be seen along grain boundaries of BaTiO$_3$ grains. The boundary between the secondary phase and BaTiO$_3$ grain seems to be sharp, suggesting that the concentration changes discretely at the interface. In case of EDS, characteristic X-ray peaks of Ba and Ti are mostly overlapping so that we performed quantification analysis using EELS for secondary phases. As a result, the Ba/Ti ratio of the secondary phases is about 0.34, which is largely different from that of BaTiO$_3$. This fact means that some of component, i.e., a part of Ba evaporated during melting due to discharging. In BaO and TiO$_2$ systems, there are some barium titanate compounds with different Ba/Ti ratio from that of BaTiO$_3$ in TiO$_2$-excess region. However, the obtained Ba/Ti ratio in the secondary phases is not coincident to that of other reported barium titanate compounds. In addition, it was found that all secondary phases observed in this study have the same Ba/Ti ratio of 0.34. These facts suggest that the secondary phase is a kind of non-equilibrium phase.
resulted from a eutectic relation between BaTiO$_3$ and the secondary phase, which occurs during a rapid quenching after discharge.

On the other hand, the observation for secondary phases performed for various kinds of grain boundaries has revealed that the secondary phases are not always formed at all grain boundaries. An example is shown in Fig. 1(b). Fig. 1(b) shows HRTEM image of grain boundary without any secondary phase. The grain boundary is a highly coherent boundary of a type of $\Sigma3$. To investigate the relation between the formation of secondary phases and the grain orientation relationship, we performed EBSD mapping for flash sintered BaTiO$_3$. The obtained EBSD map suggests that the formation behaviors of the secondary phases depend on grain boundary coherencies. Namely, high coherent grain boundary like $\Sigma3$ has no secondary phases, while most of low coherent grain boundaries have secondary phases. About the issue, we consider the contribution of oxygen vacancies at grain boundaries. The densities of oxygen vacancies in low coherent grain boundaries are larger than in high coherent grain ones. In case of BaTiO$_3$, the inclusion of oxygen vacancies in lattices increases electrical conductivity, leading that the electrical conductivity varies at grain boundaries. Thus, the electric currents flow at lower coherent grain boundaries in priority during flash event and a part of grain boundaries melt by the large electric current.

References

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