Effect of Residual Binder on Grain Growth during Sintering of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$

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Abstract

Organic binders are usually pre-mixed with ceramic powders to enhance the formability during the shape forming process. These binders, however, must be eliminated before sintering in order to avoid pore formation and unusual grain growth during sintering. The present work was performed to investigate the effects of residual binder on grain growth behavior during sintering of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ piezoelectric ceramics. The microstructures of sintered samples were examined for various thermal processes and atmosphere at debinding. Addition of binder seems to promote abnormal grain growth especially in incompletely debinded regions and to make the grain shape change from corner-rounded to faceted.

Keywords : PMN-PT, abnormal grain growth, binder, debinding

1. Introduction

Complex-shaped polycrystalline ceramics have been widely used for structural, electronic, porous, and architectural components. Various forming technologies, including uniaxial pressing, extrusion, and injection molding, have been developed. For shaping, organic binders (e.g. PVB, PVA, PW, PP, EVA, etc.) are usually mixed with raw powders to enhance the shape formability. Selection of binder materials and control of debinding are considered critical for obtaining samples with a uniform sintered microstructure and preventing the formation of defects such as huge pores, cracks and blistering.

$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) ceramic has been attracted by a number of investigations due to its excellent dielectric and piezoelectric properties. Material design and characterization of dielectric and piezoelectric properties have been intensively studied. However, few investigations have been made into the effects of organic binders on microstructure and properties. Understanding of the binder effect is required to produce complex-shaped PMN-PT. In the present work, the effect of binder on grain growth behavior during sintering of 92(70PMN-30PT)-8PbO (mol%) piezoelectric ceramics has been studied.

2. Experimental and Results

The general formula of the materials studied is 92(70PMN-30PT)-8PbO(mol%). The powders were prepared by the columbite method. Proportioned powders of $4MgCO_3 . Mg(OH)_2 . 4H_2O$ and Nb_2O_5 were ball-milled using zirconia balls and then calcined at 1100℃ for 4 h in air to form $MgNb_2O_6$ (columbite). $MgNb_2O_6$ was mixed with PbO and TiO_2 by ball-milling and then calcined at 800 ℃ for 6 h in air to form 70PMN-30PT powder. 92(70PMN-30PT)-8PbO powder mixture was ball-milled and then dried.

For ceramic injection molding, feedstocks having 55 (vol%) solid loading were mixed with kneader and subseguently pelletizied. Total binder content was 45 (vol%) and composed of 33 (vol%) ethylene vinyle acetate (EVA), 34 (vol%) paraffine wax (PW), 18 (vol%) stearic acid (SA) and 15 (vol%) dibutyl phthalate (DBP). The tube shape ceramics having 29mm height, 23mm outer diameter and 19mm inner diameter, were injected by injection molding machine.

Injected tube specimens were debinded in air and oxygen-rich atmosphere, respectively. The debinded specimens were sintered using double enclosed crucible method. The debinding schedule was determined based on a thermogravimetric analysis (TGA; SDT2960, TA Instruments, USA). Microstructures of the sintered samples were examined by optical microscopy (EPIPHOT 200, NIKON, JPN) and scanning electron microscopy (JSM-5800, JEOL, Japan). The content of the residual carbon of the debinded samples was analyzed using a Carbon Determinator (CS600C, LECO Co., USA).

The debinding schedule was established with TGA results. Figure 1 shows the thermograms of binders and mixture. The thermograms show that initial binder evolution temperature and the maximum binder evolution rate temperature were different with each of them.

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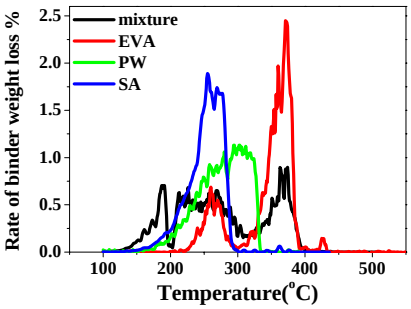


Fig. 1. Thermograms for binders and mixture.

To investigate the effects of debinding schedule and debinding atmosphere on binder removal, five different debinding schedules were adopted based on TGA results and injected tube specimens were debinded in air and O_2-rich atmosphere.

Figure 2 shows the residual carbon contents for differently debinded specimens. The residual carbon contents showed that the debinded specimen in air was 0.045 (wt%) and the debinded specimen in with O_2-rich atmosphere was 0.006 (wt%). Consequently, perfect debinding would be attained when debinding was performed in O_2-rich atmosphere.

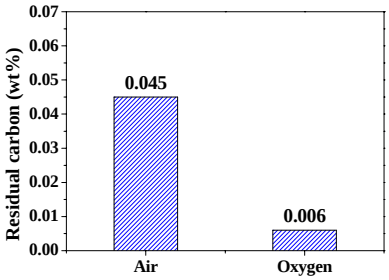
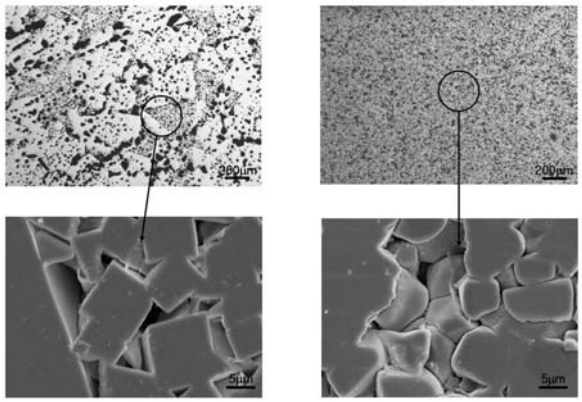


Fig. 2. Variations of the residual carbon contents.

Figure 3 shows the micrographs of the sintered specimens after differently debinded. A number of large pores are observed when binder removal was conducted in air. However, in O_2-rich atmosphere, the large pores are not showed. The formation of large pores was obviously induced by abrupt remained binder removal from the specimens. When the debinding was incomplete (Fig. 3(a)), the grains are well faceted and numerous abnormal grains are showed. However, when the debinding was performed in O_2-rich debinding atmosphere (Fig. 3(b)), the grain shape is corner-rounded and abnormal grain is not showed. It appears therefore that residual binder (e.g, residual carbon) in incomplete debinded specimen make the grain shape change to well-faceted and enhances abnormal grain growth.



(a) (b)

Fig. 3. Micrographs of sintered specimens after binder removal following different debinding schedules and atmospheres. (a) debinded in air, (b) debinded in O_2-rich atmosphrere.

3. Summary

In order to investigate the binder effect on grain growth in complex-shaped PMN-PT ceramics, PMN-PT powders were mixed with organic binders and injection molded to form tube shapes. The debinding schedule was established with TGA results. Sintered microstructures of injected specimen after different debinding schedule and atmosphere have been investigated. Incomplete debinding due to an improper debinding schedule and atmosphere resulted in a high content of residual carbon and the formation of numerous large pores in the sintered specimen. Moreover, abnormal grains with faceted shapes were observed in incompletely debinded specimen. Residual binder appears to be responsible for the change in grain shape from corner-rounded to well-faceted and for subsequent abnormal grain growth.

4. References

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