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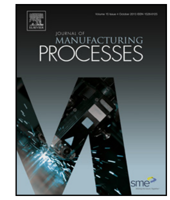

Technical Paper

Powder injection molding of PNN-PMN-PZN doped low temperature sintering PZT ceramics

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ABSTRACT

A complete process of powder injection molding was developed and optimized for the low temperature sintering PZT ceramics. A commercialized PNN-PMN-PZN doped PZT ceramics was used for the process development. The torque rheometer experiment was conducted to determine the optimal solids loading to injection molding rectangular type specimen. Appropriate debinding conditions were developed by thermogravimetry. Holding temperatures were determined based on the decomposition behavior of binder system and the volatilization temperature of Pb. Due to the fine particle size and low solids loading, a slow thermal debinding rate was required to prevent the crack defect. The densification behavior during sintering was analyzed by dilatometry. Low temperature sintering PZT ceramics shows a strain rate peak point at 1015 °C which is relatively lower than the peak point of conventional PZT ceramics. Even though a relatively long (3 h) holding time was required to achieve 98% of relative density, the powder injection molded low temperature sintering PZT ceramics showed 7.66 (10^3 kg/m^3) of density and 635 (pC/N) of piezoelectric charge constant which are 98 and 99% of reference value of powder.

1. Introduction

Piezoelectric material is one of the important functional materials, which have the unique electrical properties of energy transduction. The ferroelectric and piezoelectric nature has led to develop numerous transducer applications in diverse electronic devices [1–3]. Recently, these applications have come to require miniaturization, higher reliability, and low voltage driving issues. Especially for low voltage driving, the multilayered piezoelectric devices which consist of numbers of piezoelectric stacks have been developed [4,5]. The conventional manufacturing process for these types of stack transducer was conducted by the tape-casting [6]. PZT slurry is casted as thin layers and the silver or palladium is generally used as inner electrodes for stacking. After align the each layer, the multilayered PZT ceramic is laminated and co-fired for the densified piezoelectric transducer.

For the co-firing of PZT ceramic with the electrode material, sintering temperature is required to be less than the melting point of electrodes. The general PZT ceramics have sintering temperatures of 1200–1300 °C [7] but at such high temperature, inner electrodes cannot be used. To lower the sintering temperature of piezoelectric ceramics, many different techniques have been developed, e.g. fine powder technique [8–10], additives of low-melting-temperature materials [11,12], and doping of perovskite-structured materials [4]. Using the developed low temperature sintering material, multilayered stack actuator has been developed through tape casting method.

In the aspect of manufacturing process for piezoelectric materials, near net shape manufacturing approaches has been interest because of its shape complexity. Injection molding [13,14], casting [15,16], embossing [17], and fused deposition method [18] have been developed to fabricate the piezoelectric ceramic without conducting post-processing. Among various near net shaping process, powder injection molding (PIM) is one of the most promising candidates because of its high production rate [19]. The PIM with PZT ceramic enables to fabricate the complex shaped, micro-sized transducer without applying any damage to sintered ceramic. Due to the advantages of PZT-PIM, many researchers have been investigated on the fabrication of complex micro-scale transducer by using PIM [20,21].

However for the low temperature sintering PZT ceramics, there was almost none of research regarding with the PIM technology. The process steps of PIM especially the sintering process were not optimized and developed. Up to now, almost every reported research was focused on the fabrication of piezoelectric transducer

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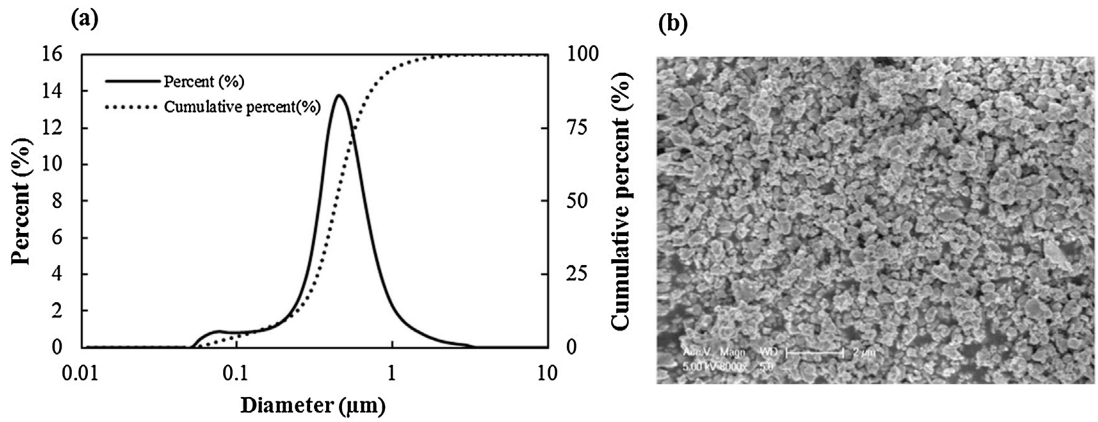

Fig. 1. Characteristics of low sintering temperature PZT powder: (a) Particle size distribution; (b) Shape morphology.

Table 1
Chemical composition of commercialized low sintering temperature PZT powder.

Contents	Percent (%)
Pb (Ti, Zr) O_3	75–85
Pb (Ni, Nb) O_3	2–4
Pb (Mg, Nb) O_3	4–6
Pb (Zn, Nb) O_3	2–4
$SrTiO_3$	2–4
La_2O_3	0.5–1
Co_2Or	0.25–1

with the high dielectric PZT ceramics even though the PIM technology with low temperature sintering PZT ceramics has plenty of potential to be used for the development of innovative piezoelectric transducer application such as an injection-molded multilayered-stack actuator.

In this research, as a first study to use the low temperature sintering PZT ceramics with the PIM technology, entire manufacturing processing steps were developed and optimized. Mixing process was optimized based on torque rheometer experiment and the bulk specimen was injection molded. Debinding conditions were optimized based on the thermal gravity analyzer and the sintering conditions were determined based on the dilatometer approach. Especially, the densification behavior of low temperature sintering PZT ceramics was investigated while compare to the densification behavior of conventional PZT feedstock. With the optimized process, the density and piezoelectric performance of PIMed specimens were measured to evaluate the validity of developed manufacturing process.

2. Experimental procedures

2.1. Materials

The commercialized low temperature sintering PZT powder doped with PNN, PMN, and PZN was used in this study. Table 1 summarizes the provided chemical composition of commercialized low sintering temperature PZT powder [22]. Important characteristics of the powder for process development are summarized in Table 2. The particle size distribution was measured by the particle size distribution analyzer (Horiba LA-950V2) as shown in Fig. 1(a). The pycnometer density, used as a reference value for the theoretical density was measured by the automatic helium pycnometer (Micrometrics AccuPyc 1330). The piezoelectric charge constant used as a reference value for the evaluation of piezoelectric performance was provided by the powder vendor. Fig. 1(b) shows the shape morphology of the PZT powder observed by the scanning electron microscopy (SEM Philips XL30S FEG). It is observed that the fine powders are irregular in shape and agglomerated.

The wax-polymer binder system, mixture of paraffin wax (PW), polypropylene (PP), polyethylene (PE) and stearic acid (SA) was used as a binder system. PP and PE were used as a primary binder to strengthen primal products. PW was used as a secondary binder to enhance the rheological property of feedstock. SA was used as a surfactant to enhance the wetting of ceramic powder. The characteristics of binder system are summarized in Table 3.

2.2. Development of powder injection molding process

Process of PIM including mixing, injection molding, debinding and sintering were developed and optimized based on experimental approaches. Fig. 2 shows schematic process of PIM. It include four main steps; mixing, injection molding, debinding and sintering. Mixing process which formulate powder binder mixture was conducted with the twin extrude mixer at 160 °C with 47 vol.% powder loading conditions. The appropriate loading contents were determined by the torque rheometer (HAAKE Rheomix, PolyLab QC Lab Mixer) experiment. While adding the PZT powder to closed batch, mixing torque was measured and analyzed to determine the appropriate mixing ratio. Injection molding process which fabricated desired green body structure was conducted with the conditions of 80 MPa injection pressure, 160 °C injection temperature, and 45 °C mold temperature using molding machine (TR 30EH, Sodick Plustech). After injection molding, green body was debound by two step debinding process. Solvent debinding was carried out in a bath of N-hexane at 45 °C for 10 h and thermal debinding was conducted in argon (Ar) atmosphere according to the developed thermal schedule by the thermal gravity analyzer (TGA/DSC 1, Mettler Toledo). Sintering process which densifies debound structure was conducted in a closed crucible with 1100 °C of sintering temperature with 3 h holding time. In order to identify the sintering behavior of low sintering temperature PZT ceramics, the in-situ linear shrinkage was measured using a dilatometer (Netzsch DIL 402C). The densification behavior of low sintering temperature PZT ceramics was compared to the densification behavior of conventional PMN-PZT ceramics. Optimized sintering condition was acquired as observing the temperature effects on the density, microstructure and piezoelectric charge constant. Archimedes method was used for density evaluation and microstructure was observed by SEM. For the piezoelectric performance evaluation, silver was deposited as electrodes on the sintered surface and the poling process was conducted in an oil bath under at 100 °C, at a voltage of 2.0 kV/mm and a holding time of 15 min. The poling conditions were provided by the powder vendor. The piezoelectric