Indian Journal of Engineering & Materials Sciences
Vol. 21, June 2014, pp. 329-332

Precision forming of micro-sized piezoceramics with a high aspect ratio

Jae-Ho Jeon[a]*, Si-Young Choi[b], Jong Hyun Kim[c] & Suk Sang Chang[c]

[a]Nanofunctional Materials Laboratory, [b]Advanced Characterization & Analysis Laboratory, Korea Institute of Materials Science,
66-Sangnam-Dong, Changwon, Korea

[c]Pohang Accelerator Laboratory, Pohang University of Science and Technology, San 31, Hyoja-Dong, Nam-Gu, Pohang, Korea

Received 1 July 2013; accepted 11 February 2014

In order to fabricate micro-sized PMN-PT piezoceramics with an aspect ratio of 5 for 1-3 composites by injection molding process, two novel methods are developed depending on the size of samples. In the case of a sample with 700 µm in side length of the post, a cassette or monolithic mold is designed and made by machining. The injected samples in the cassette or monolithic mold are effectively separated from the mold by pushing ejecting pins. On the other hand, in the case of sample with 60 µm in side length of the post, PMMA polymer based sacrificial mold inserts are fabricated by using synchrotron radiation. After the injection of PMN-PT powder mixture into the mold inserts, instead of mechanical demolding, PMMA mold inserts are chemically dissolved into acetone. Heat-treating at 800°C in an oxygen atmosphere is more effective for removing organic binders than a conventional de-binding at 500°C in air. Finally, micrometer-scale PMN-PT piezoceramics with the aspect ratio of 5 are successfully fabricated by sintering at 1100°C for 10 h in air.

Keywords: Micro-sized piezoceramics, Injection molding, Monolithic mold, Sacrificial mold, PMN-PT

By utilizing unique properties to convert electric energy to mechanical energy or vice versa, piezoelectric materials have wide range applications such as sensors, actuators and ultrasonic transducers in electromechanical industries[1]. The most widely used piezoelectric materials at present are PZT-based solid solutions. However, it was reported in late 1990 s that PMN-PT and PZN-PT single crystals exhibit much higher piezoelectric coefficients and electromechanical coupling factors than those of polycrystalline PZT ceramics[2,3].

Several single crystal growth techniques, such as flux[4,5], Bridgman[6,7], and solid-state single crystal growth (SSCG)[8,9], have been applied to grow piezoelectric single crystals. Among them, SSCG method has an advantage to produce complex-shaped piezoelectric single crystals because this process can directly convert polycrystalline ceramic preforms to single crystals with almost the same shape and size. Therefore, SSCG method is expected to be useful to produce 1-3 type near-net shaped piezoelectric single crystals. On the other hand, other methods should use an additional machining process, such as dicing or deep-ion-etching technique[10], to fabricate 1-3 type piezoelectric single crystals from ingots. The machining process inevitably adds processing cost and additional materials cost due to the waste of valuable single crystals.

In the case of forming 1-3 type piezoelectric ceramics with mm-size in the side length of quadrangle post, conventional ceramic powder injection molding (CIM) process can be applied. However, conventional CIM process is not available to form micro-sized piezoceramic preforms due to difficulty of ejecting samples from injection molds. We developed two novel forming methods depending on the size of PMN-PT based 1-3 type polycrystalline preforms which have a high aspect ratio of 5.

In the case of preforms with the range of 500~1000 µm in side length of the post, a mechanically machined cassette mold or a monolithic mold were designed and made by machining. On the other hand, in the case of post smaller than 100 µm in side length, mechanical machining is not available to fabricate their mold and ejecting pins. Therefore, PMMA polymer based sacrificial mold inserts were fabricated by using synchrotron radiation.

Development of Injection Mold to Fabricate 1-3 Type Piezoelectric Ceramic Preforms

Cassette and monolithic mold for preforms with 700 µm in side length of posts

In general, ceramic powder injection molding is a process of manufacturing various ceramic powder

---

*Corresponding author (E-mail: jjh@kims.re.kr)

products by putting ceramic powders mixed with organic binders in an injection cylinder of an injection molding machine. The metal mold used in the injection molding is called an injection mold. The injection mold is manufactured to correspond to the size and shape of a product that is injection molded. The molded product formed in the injection mold is usually separated by pushing ejecting pins[11].

In the case of injection molding 1-3 type piezoceramic preforms with 700 μm in side length of the post, the ejecting pins for separating molded products should have a thin and long shape. Therefore, such ejecting pins may be deformed or broken due to the load that is vertically applied during ejecting of molded products. Therefore a cassette mold was designed and fabricated. Figure 1(a) shows a perspective view of the cassette mold which consists of an inner block and outer blocks. Figure 1 (b) and (c) shows a perspective view and a cross-sectional view along a dotted line A-B of the inner block, respectively. Compared with ejecting pins in a conventional injection mold, the cassette mold contains much shorter ejecting pins (a red object in Fig. 1 (c)) which can safely push the injected sample (a green object in Fig. 1 (c)) out. An ejecting jig is additionally needed to separate injected samples from the cassette mold, as shown in Fig. 2.

In order achieve process automation by overcoming the inconvenience from using the ejecting jig, a monolithic injection mold was designed as shown in Fig. 3. Figure 3(a) is a perspective view of the monolithic injection mold and Fig. 3 (b) is cross-

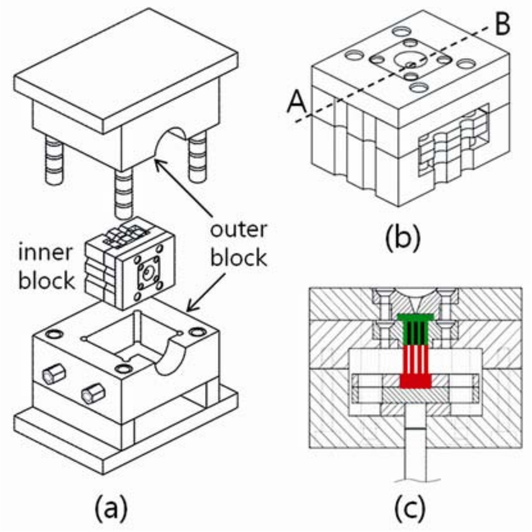

Fig. 1–(a) A perspective view of the cassette mold, (b) a perspective view of the inner block, and (c) a cross-sectional view along the dotted line A-B

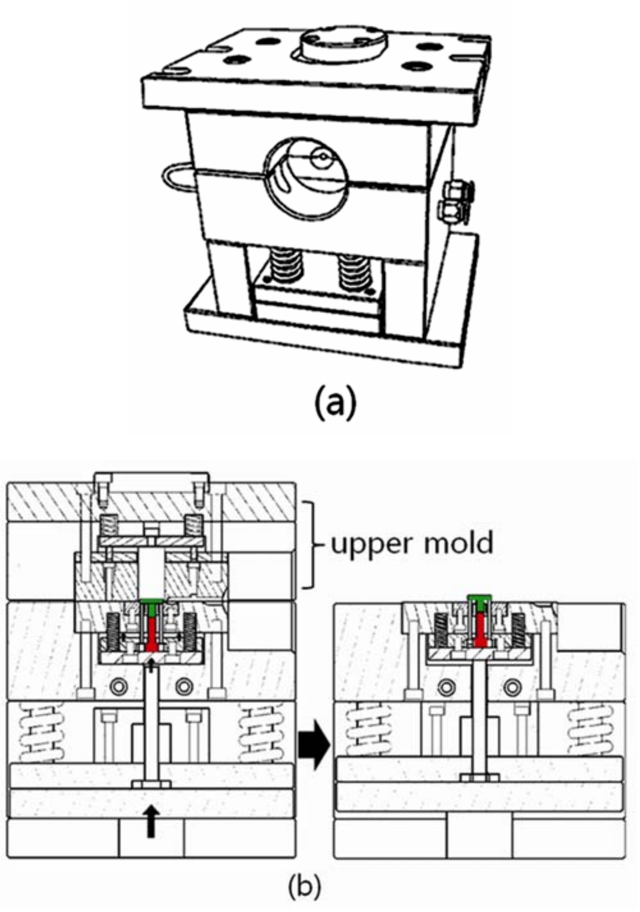

Fig. 3–(a) A perspective view of the monolithic mold and (b) cross-sectional view illustrating how to separate samples from mold

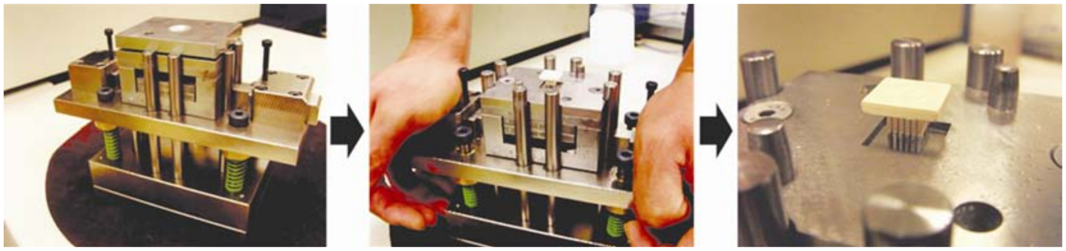

Fig. 2–Schematic diagram of the procedure of sample separation from the inner block by using an ejecting jig

sectional views illustrating how to operate this mold. After injection of ceramic powder into the mold, the upper mold was firstly moved upward and then the ejecting pins (a red object in Fig. 3 (b)) can push injected samples (a green object in Fig. 3 (b)) out.

Sacrificial polymer mold inserts for preforms with 60 µm in side length of posts

Figure 4 illustrates the overall process for fabricating poly methyl methacrylate (PMMA) sacrificial mold inserts. An X-ray mask with 60 µm in lateral dimensions of patterns was fabricated in advance using a typical photolithography process. Through the X-ray mask, synchrotron X-rays were selectively exposed to PMMA with 0.3 mm in thickness. The utilized X-ray energy range was from 4 to 8 or 10 keV. After the first X-ray exposure, subsequent development was carried out using a GG developer for several hours. In order to separate the injected samples from the PMMA sacrificial mold inserts, PMMA mold inserts were exposed again to a white beam X-ray with the dose rate of 1.2 kJ/cm^2. This 2nd X-ray exposure is necessary to dissolve PMMA mold insert into acetone by cutting off the molecular chain of PMMA.

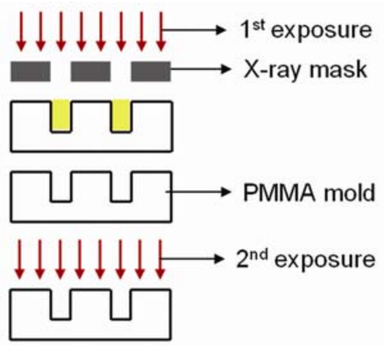

Fig. 4–Schematic diagram of the fabrication procedure of PMMA sacrificial mold insert

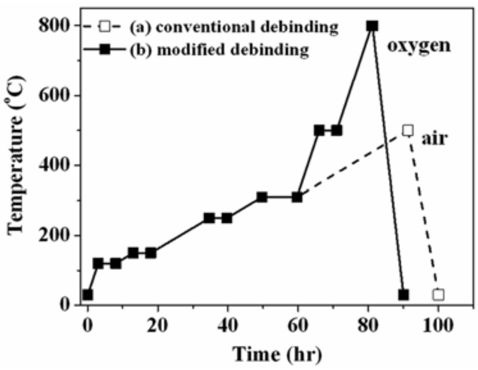

Fig. 5–Heating profiles for removing organic binders by (a) a conventional debinding and (b) a modified debinding

Results and Discussion

Injection molding of piezoelectric ceramic powders

A feedstock consisting of 55% PMN-PT powder, 5% stearic acid, 36% paraffin wax, and 4% carnauba wax was injected into the cassette mold, monolithic mold, or PMMA sacrificial mold inserts. During the injection molding process, the temperature of the nozzle and the mold were set at 80 and 60°C. After the feedstock was injected, samples were separated by pushing ejecting pins in the cassette mold and the monolithic mold. On the other hand, the PMMA sacrificial mold inserts were removed by a chemical dissolution in acetone at 35°C for 90-110 min.

De-binding and sintering

In order to remove organic binders, injection molded 1-3 type PMN-PT samples were heat-treated by a conventional de-binding process and a modified de-binding process, as shown in Fig. 5. The conventional de-binding is usually carried out below 600°C in air. However, in the case of the modified de-binding process, the maximum temperature was increased to 800°C and the atmosphere was changed to oxygen. The residual carbon content of 0.045wt% and 0.006wt% was detected from PMN-PT samples which were de-binded by the heating profile (a) and (b), respectively. Figure 6 shows SEM micrograph of samples sintered at 1100°C for 10 h after debinding by profile (a) and (b). A severe exaggerated grain growth observed in Fig. 6(a) was thought to be due to an incomplete removal of organic binders[12], and which will be harmful for conversion of the polycrystalline preforms to single crystals by SSCG method[9]. On the other hand, the exaggerated grain growth was effectively suppressed by the modified de-binding schedule as shown in Fig. 6(b). Further study will be necessary to understand the mechanism how residual carbon influences the grain growth behaviour of PMN-PT material during sintering. Figure 7 shows optical and SEM micrograph of sintered samples fabricated by injection molding using (a) the cassette/monolithic mold and (b) PMMA sacrificial mold inserts, respectively. Since they were de-binded by the modified de-binding schedule 2, they were expected to be converted to single-crystals with almost same shape and size by SSCG method.

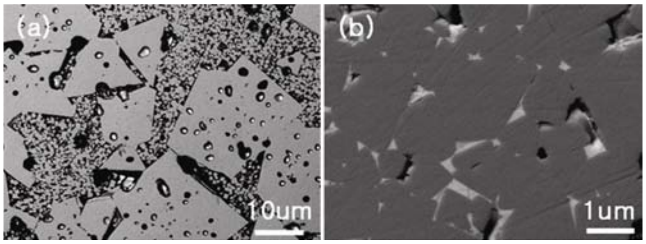

Fig. 6–Microstructure of sintered samples experienced (a) conventional debinding and (b) modified debinding

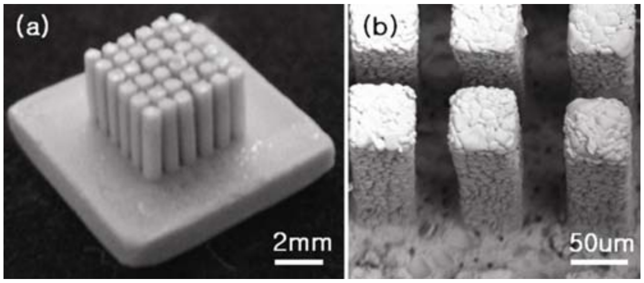

Fig. 7–Optical and SEM micrograph of sintered samples fabricated by injection molding using (a) cassette/monolithic mold insert and (b) PMMA sacrificial mold insert, respectively

Conclusions

Two novel methods were developed to fabricate micro-sized polycrystalline piezoceramics with an aspect ratio of 5. Since a cassette and monolithic mold was designed to have short ejecting pins, it was possible to separate 1-3 type PMN-PT samples with 700 µm in side length of the post. PMMA based sacrificial mold inserts made by using synchrotron radiation were effective to fabricate 1-3 type PMN-PT samples with 60 µm in side length of the post. The proposed two methods can be applied in replication processes for other structures that are difficult to demold due to their high aspect ratio.

Acknowledgements

This research was supported by a grant from the Center for Advanced Materials Processing (CAMP) of the twenty-first Century Frontier R&D Program funded by the Ministry of Knowledge Economy (MEK), Republic of Korea.

References

1 Gallego-Juarez, *J Phys E: Sci Instrum,* 22 (1989) 804-816
2 Park S E & Shrout T R, *J Appl Phys,* 82 (1997) 1804-1811
3 Fu H & Cohen R E, *Nature,* 403 (2000) 281-283
4 Kuwata J, Uchino K & Nomura S, *Ferroelectrics,* 37 (1981) 579-582
5 Kuwata J, Uchino K & Nomura S, *Jpn J Appl Phys,* 21 (1982) 1298-1302
6 Xu J Y, Tong J, Shi M, Wu A & Fan S J, *J Cryst Growth,* 253 (2003) 274-279
7 Benayad A, Kobor D, Lebrun L, Guiffard B & Guymar D, *J Cryst Growth,* 270 (2004) 137-144
8 Lee H Y, Chan H M & Harmer M P*, J Korean Ceram Soc,* 35 (1998) 905-910
9 Lee H Y, Kim J S & Kim D Y, *J Eur Ceram. Soc, 20* (2000) 1595-1597
10 Rehrig P W, Jing X, Hackenberger W S, Yuan J R & Romly R, *US Pat.*, 7,622,853 (to the Port Matilda), 2009
11 Song J Y & Je D K, *KR Pat,.* 10-0344901 (to the Korea Institute of Machinery and Materials), 2002
12 Yun J Y, Jeon J H, & Kang S J L, *J Korean Powder Met Inst,* 4 (2005) 261-265