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Rapid prototyping technique for ceramic mini-devices containing internal channels with asymmetrical contour

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Abstract

The electrophoretic deposition (EPD) is used to serve as rapid prototyping technology (RPT) to manufacture ceramic mini-devices containing internal channels or asymmetrical contour patterns to overcome the technical obstacles by conventional ceramic forming techniques. The spacing and geometry of such internal channels, either liner, curvilinear, symmetrical or asymmetrical, can be considered at the preliminary design stage to prepare the fugitive inactive inserts to be involved in EPD operations. Such inserts are limited to any undesirable chemical reaction with the EPD suspension and of easy elimination from EPD-formed ceramic green body followed by pyrolysis or solvent dissolution to remove from embedment. In this study, ferroelectric ceramic mini-devices based on barium titanate with the pattern containing internal channels was deposited via EPD route unto electrically conducting or non-conducting inserts buried in the ceramic laminates. The inserts can be removed after drying step. Effects of EPD conditions on shape integrity of internal channel in the mini-devices were examined. This novel ceramic shaping technique enables us to produce the ceramic mini-devices in terms of formation of desirable array patterns for the unique prototype of ceramic components such as dielectric resonators, waveguide or mini-actuators.

Keywords: Electrophoretic deposition (EPD); Rapid prototyping technology (RPT); Ferroelectric ceramics; Ceramic mini-devices; Ceramic shaping; Barium titanate; Colloidal stability

1. Introduction

In past two decades, electrophoretic deposition (EPD) techniques[1–5] has been applied in numerous technological and industrial aspects including thin or thick film formation and deposition using the aqueous[6] or non-aqueous[7] suspension of metal powders, oxides, carbides, fluorescent materials, cermets, polymers, paints, organic photoresists, glass powders under an applied direct current electrical field. The EPD method is practiced rather commonly in pursuing the fundamental requirements of product manufacturing in a wide range of industrial products with dimensions from the gigantic size of steel framework for the building construction, car bodies or metallic utensils to the miniature size of mechanical parts such as screws and bolts.[8]

Previously we have already used the EPD process to deal with various thicknesses of deposited films or dense layers of ceramic, metallic or polymeric materials on the electrically conductive substrates. In particular, the EPD process is an acceptable and effective manufacturing method for advanced ceramic components and electrical ceramic devices by offering several technical merits such as easy hardware setting and process simplicity, low equipment investment, viability to form ceramic bodies onto the substrates of complex geometries, better control of layer thickness, better sintering performance of ceramic bodies by using none or minimal use of organic binders or plasticizers, suitable for fabrication of oxide and non-oxide materials as well as composite, and higher deposition rate as compared to other film or layer manufacturing route such as physical vapor deposition, chemical vapor deposition and electrochemical deposition.

In addition, the functionally gradient materials (FGMs) such as ZrO_2–Al_2O_3 or $BaTiO_3$–$SrTiO_3$ multilayer devices can be produced by EPD means with outstanding properties as well as sophisticate material and structural designs.[9–11] In this study, our goal in introducing new engineering aspects and functionalities to be incorporated into EPD process is to gain greater control of EPD colloidal stability, electrophoretic mobility and electrokinetic behaviors of ceramic particles, establishment of desirable electrical field strength and distribution in order to achieve novel forming or shaping of ceramic materials by attempting

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a reliable and easy process to form miniature ceramic devices containing internal channels with symmetrical or asymmetrical contour. At present the above-mentioned ceramic mini-device would pose some technical challenges and restrictions through the conventional forming techniques such as pressing, cold isostatic pressing, extrusion, slip casting or tape casting associated with mutilayer lamination. When we want to produce the ceramic components with embedded openings or internal channels with asymmetrical or symmetrical geometry during the early design or pre-production stage, normally the rapid prototyping technology (RPT) is called upon to serve as the function or performance validation of new ceramic component design. The spacing and geometry of such internal channels, either liner, curvilinear, symmetrical or asymmetrical, can be designed via the preliminary stage of computer-aided design to prepare the fugitive inactive inserts such as graphite, polymer, wood, or non-absorbing paper, which are positioned with a desired distance in front of working electrode in the EPD operational environment. Noting that such inserts should avoid any undesirable chemical reaction with the EPD suspension and are of easy elimination from EPD-formed ceramic green body followed by pyrolysis or solvent dissolution to remove these embedded inserts.

Based on the progressive modification of prior device design as witnessed by rapid prototyping technology, one can simply begin with the intended pattern design of internal channels in ceramic mini-devices to select the particular specification of inserts such as material type (graphite, wood, plastic or metal), dimensions, shape (wire, thread, rod or mesh), position with respect to working electrode, and pitch between inserts. As the ceramic green body is completely formed after EPD process, these fugitive inserts embedded in the ceramic body will be eventually removed either by a simple mechanical separation or direct elimination of inserts from green body followed by pyrolysis during the binder burn-off stage or solvent dissolution to remove these inserts. Furthermore, it is interesting for us to examine the effect of EPD suspension stability on final microstructure and properties of deposited ceramic layers. The novel ceramic shaping technique via EPD is capable of making the ceramic mini-devices with array patterns of ceramic components such as dielectric resonators, waveguide or mini-actuators, which can be obtained by subsequent dicing the desirable array of green or sintered bodies during the prototyping stage. In this study, we selected barium titanate as experimental subject since it is widely applied for ceramic dielectric resonator design and manufacturing.

2. Experimental

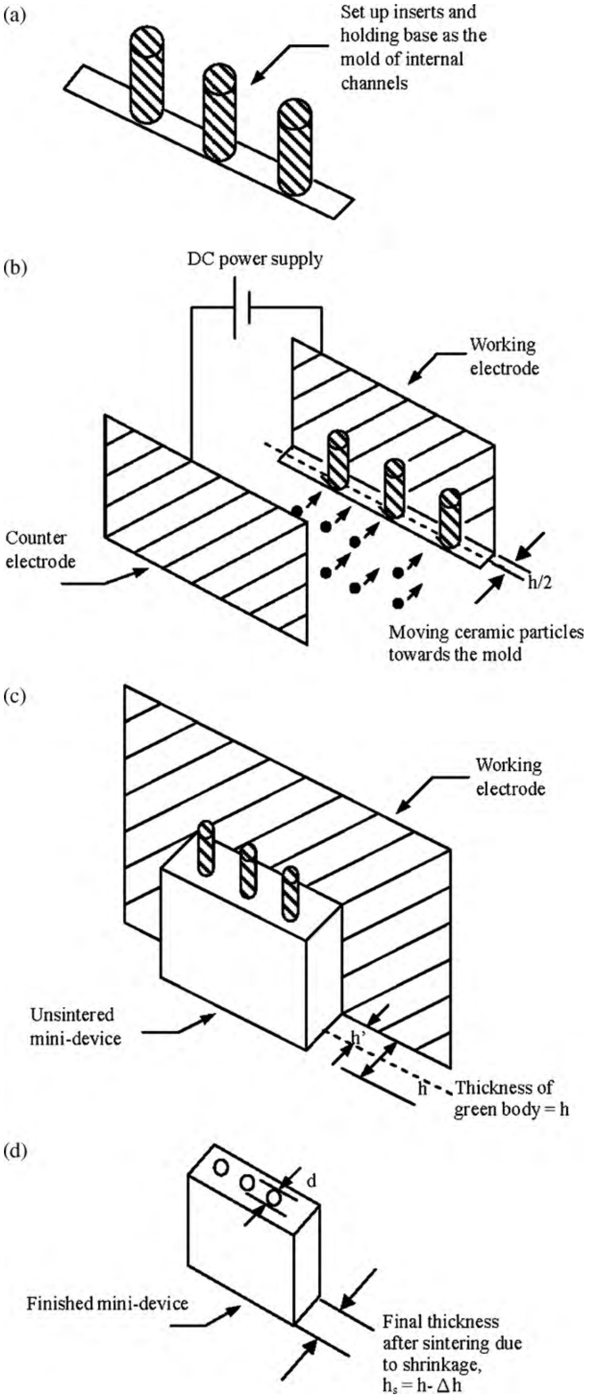

Fig. 1. Processing schematic of rapid prototyping technology (RPT) for manufacturing ceramic mini-devices containing internal channels: (a) preparation of inserts and holding base as the mold of internal channels, (b) EPD process, (c) formation of mini-device green body onto the working electrode, and (d) finished mini-device through drying, sintering and machining.

To realize a novel idea of rapid prototyping technology (RPT) for those ceramic mini-devices containing internal channels with special geometrical shapes including symmetrical or asymmetrical contours and linear or curvilinear passage layouts, thus we use the experimental procedure schematic depicted in Fig. 1 via the EPD route. A batch of micron-sized barium titanate powder (avg. size of 1.21 μm) of 3–20 g was weighed and tested for dryness before preparing the EPD suspension. Different amount of $BaTiO_3$ powder, which was completely blended in the mixture of 75 ml ethanol and 75 ml acetyl acetone with ultrasonic agitation, to obtain different barium titanate solid content of 20 g/L, 100 g/L and 133.3 g/L of EPD suspension. A number of pH controlling chemical agents such as ammonium hydroxide, acetic acid and sulfuric acid and organic dispersants such as polyvinyl alcohol (PVA) or polyvinyl butyral (PVB)[12] were applied to alter the surface charge situation of $BaTiO_3$ particles in the suspension to acquire its better colloidal stability.

As for entering the RPT phase, the inserts to be embedded inside of mini-devices can be either conductive materials such as metal objects or non-conducting like wood or polymer parts and they would act as the subjects to occupy the designated volume of ceramic openings or channels inside the mini-devices, however, there are a few measures that we have to take into considerations: (a) the inserts should not cause any chemical reaction with the suspension before or during the EPD process, (b) the removal of inserts from the green body after EPD process can be easily achieved by mechanical or thermal means, and (c) the size of inserts and the distance between the center of insert and the front surface of working electrode are strictly determined by the size of ceramic mini-devices and relative positions of internal channels to assure the damage-free deposit after insert retreat and final integrity of ceramic green body. During the EPD process, the suspended ceramic particles would electrophoretically move towards onto the surface of working electrode and continuously deposit and pack densely such that the inserts are completely surrounded and covered with deposited powders until the ceramic body is eventually built up to firmly embed the inserts inside. The EPD process is terminated as the desired size of the ceramic body is eventually achieved. There was a separation between inserts and the surrounding material due to the presence of slight shrinkage (<0.2%) at the circumference of internal channels inside the ceramic body after the drying step at 75–85 °C for 3–6 h. Thus the inserts were easily removed before or during successive sintering and densification step. Fig. 2 depicts the individual step and the entire process flow based on the RPT concept for producing $BaTiO_3$ ferroelectric mini-devices with internal channel patterns.

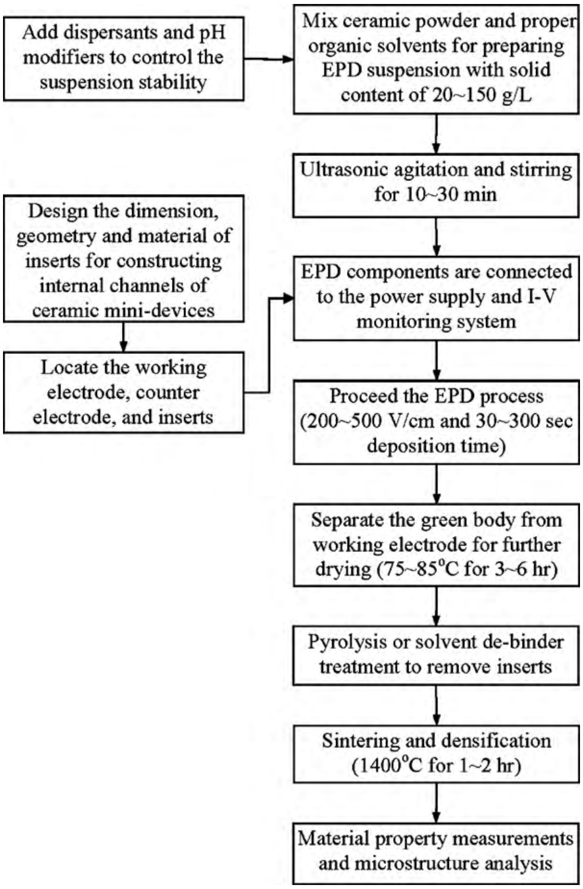

Fig. 2. Process flow based on the RPT concept for the fabrication of $BaTiO_3$, $SrTiO_3$ and $(Ba_{1-x}Sr_x)TiO_3$ ceramic mini-devices with internal channel patterns.

3. Results and discussion

Fig. 3 shows that specific deposited weight of $BaTiO_3$ per unit area depends on the applied electrical field (200–500 V/cm) under various $BaTiO_3$ suspension concentrations. As the $BaTiO_3$ concentration of EPD suspension was 33.3 g/L, the specific deposition weight per unit area was ranging from 467.3 to 617.1 mg/cm^2 under E-field of 200–500 V/cm for deposition time of 5 min. Furthermore the specific deposition weight became 2123.6 mg/cm^2 when the EPD concentration of 133.3 g/L and E-field of 500 V/cm were employed. Apparently the applicable EPD efficiency was determined by suspension concentration and electrical field strength in the EPD process; however, the case of higher specific deposition weight did not always guarantee better surface smoothness of deposited layers.

It is interesting to realize that mixed solvent systems used for EPD suspension such as isopropyl alcohol/ethanol, acetyl acid/ethanol, isopropyl alcohol/toluene, isopropyl alcohol/acetone, which are prepared with optimized volume ratio varying from 50/50 to 60/40, would give rise to a better deposition efficiency as compared to using strictly one single kind of organic solvent system. Among the various concentration conditions of EPD suspension (33.3–133.3 g/L), an increased thickness of deposited layer was obviously conjunction with increasing applied electrical field, as shown in Fig. 4. A relatively ceramic layer thickness approximately 4–5 mm could be obtained by EPD process under electrical field of 500 V/cm and deposition time within 5 min and EPD suspension concentration of 133.3 g/L. Our results clearly suggest that EPD method offers an effective route to manufacture ceramic thick films or stand-alone ceramic slabs and multilayer devices. For the con-

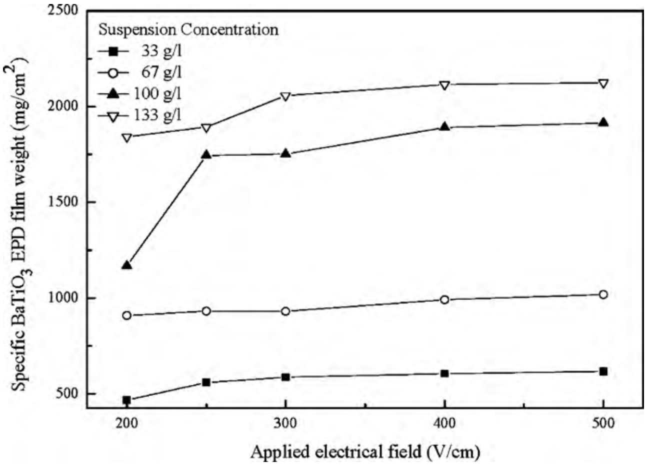

Fig. 3. Specific deposited weight per unit area varies with the applied electrical field strength (200–500 V/cm) using various $BaTiO_3$ suspension concentrations.

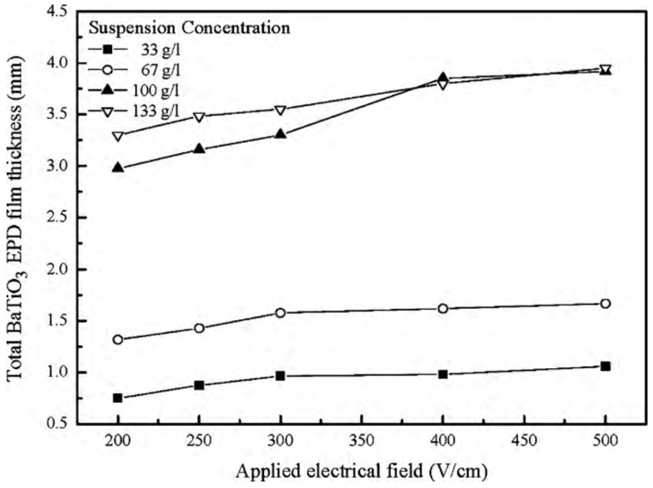

Fig. 4. Thickness of $BaTiO_3$ green bodies varies with applied electrical field strength and concentrations of EPD suspension.

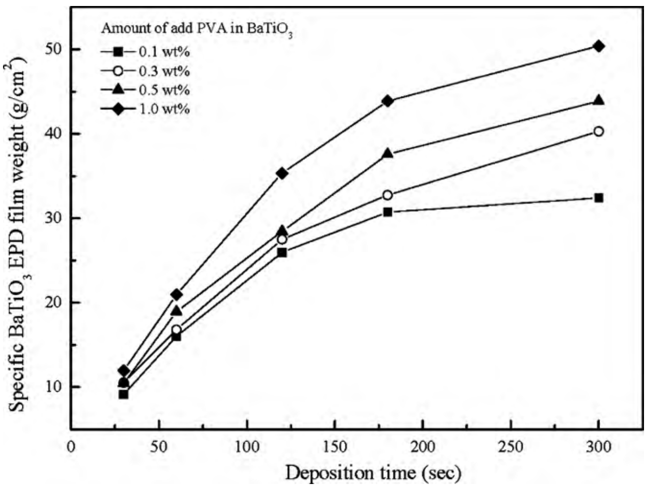

Fig. 6. Specific deposited weight per unit area varies with the deposition time (30–300 s) at the applied electrical field strength of 120 V/cm by using different PVA binder amount of 0.1–1.0 wt% in solvent mixture of isopropyl alcohol/toluene (60/40).

centration of EPD suspension of 20 g/L, the specific deposition weight per unit area changes under different solvent mixture ratios of isopropyl alcohol/toluene along with deposition time of 30–300 s is shown in Fig. 5, which depicts the ceramic deposit with a maximum EPD efficiency was obtained at isopropyl alcohol to toluene volume ratio of 50/50 at deposition time of 300 s. Nevertheless, such a green body prepared under a faster deposition rate turned out to have less uniform surfaces and minor cracking at surface after drying step. Our result implies that the optimized isopropyl alcohol and toluene solvent ratio was 60/40 to assure the evenly distributed green density along the direction from the working electrode side, location around the holes created by inserts, to the suspension side.

When adding different polyvinyl alcohol (PVA) binder amount of 0.1–1.0 wt% in solvent mixture of isopropyl alcohol/toluene with optimized volume ratio of 60/40, Fig. 6 shows specific deposited weight per unit area varying with the deposition time up to 300 s at the applied electrical field strength of 120 V/cm indicates that PVA binder additive did facilitate the $BaTiO_3$ powder packing in the deposited layer via EPD, thereby, the case with higher concentration of PVA additive in EPD suspension give rise to a better deposition efficiency. The microstructural analysis of sintered body involving with PVA binder suggests that the effect of PVA binder would aid particle contact intimacy in the green body, which leads to enhanced necking during densification and higher sintered density of 5.50 g/cm^3, as compared to 4.13 g/cm^3 for those $BaTiO_3$ samples without using PVA binder. In contrast, use of polyvinyl butyral (PVB) binder of 0.1–1.0 wt% in the same solvent mixture of isopropyl alcohol/toluene (60/40), the specific deposited $BaTiO_3$ weight per unit area varying with the deposition time went in almost opposite trend as compared to the PVA case, as shown in Fig. 7. The very small amount of PVB binder (0.1 wt%)

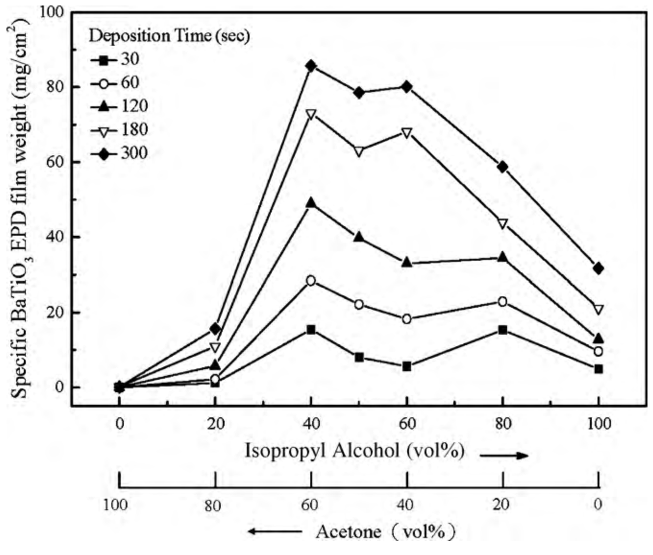

Fig. 5. Change of specific deposited weight per unit area against various solvent mixture ratios of isopropyl alcohol/toluene at different deposition time (30–300 s).

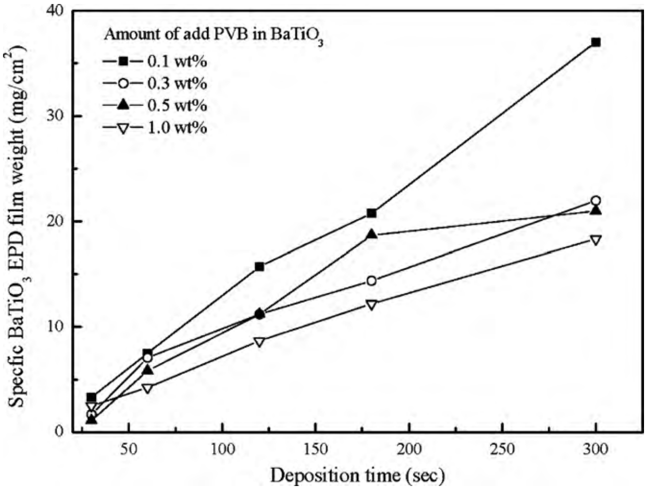

Fig. 7. Specific deposited weight per unit area varies with the deposition time (30–300 s) at the applied electrical field strength of 120 V/cm by using different PVB binder amount of 0.1–1.0 wt% in solvent mixture of isopropyl alcohol/toluene (60/40).

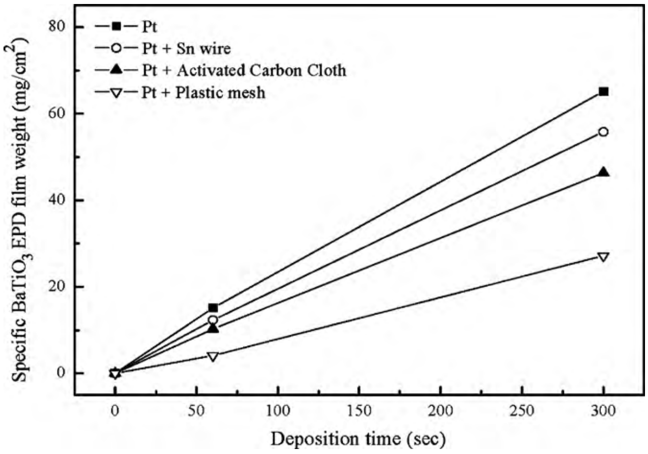

Fig. 8. Specific deposited weight per unit area varies with the deposition time (60–300 s) at the applied electrical field strength of 120 V/cm by using conductive and insulating insert materials.

provides a good stability and a lower viscosity of EPD suspension. However, the higher amount of PVB additive (>0.3 wt%) would offer a satisfactory dispersion due to the steric hindrance effect in conjunction with the formation of hydrogen bonding by hydroxyl groups of PVB molecules to be adsorbed onto the surfaces of barium titanate particles. The sintered density of EPD deposit sample with PVB binder is relatively lower (5.07 g/cm^3) than the previous sample.

To take technical advantage of an outstanding controllability of deposition thickness and deposition rate where ceramic thick films or multilayer devices made by EPD process, we would further apply the same technique to fabricate ceramic containing special hollow pattern or structure internally based on the demands of rapid prototyping technology. Fig. 8 illustrates that specific deposition weight of BaTiO$_3$ mini-devices using different inserts changes with deposition time (30–300 s) at the electrical field of 120 V/cm. In this case, the inserts such as electrically conductive steel-needles or activated carbon fiber/textile and non-conducting linen thread or plastic mesh were positioned in front of platinum working electrode. For deposition time of 60 s, barium titanate particles were not transported fast enough in the EPD suspension under a relatively weak electrical field and a low electrophoretic mobility were involved. It implies that the RPT function was hindered by shorter deposition time, where the deposited ceramic powder had substantial difficulty to completely surround the inserts inside the ceramic body as the EPD process underwent. The average thickness of ceramic deposited body would increase as the deposition time was increased to be 300 s. In a special account of using non-conductive inserts, the deposited ceramic particles could not be packed densely to embed the inserts entirely, when shorter deposition time or lower electrical field was selected. In contrast to the instance above, the results of EPD efficiency and deposition rate were substantially improved as the electrically conductive inserts such as metal wires or carbon fiber or textile were employed due to the establishment of electrostatic force associated with the inserts would attract the moving particles in the EPD tank. Unfortunately it was found that the conductive inserts will induce the density gradient along the direction normal to the surface of working electrode and have less uniform density distribution between the circumference of the hole defined by inserts and slightly faraway neighborhood. This result has a propensity to encounter the densification defects attributed to pronounced stresses in the ceramic body throughout firing shrinkage.

Under the situation that the positions of counter-electrode and working electrode were placed horizontally, the deposited ceramic body resulted in smooth and flat surfaces and the deposited ceramic particles were densely packed and surrounded the whole body of inserts with a longer deposition time of 1 h. Nevertheless, the ceramic part experienced cracking at its surface immediately after the moment when the ceramic was retrieved from the EPD tank. The potential causes for defects induced in the ceramic body may result from the uneven internal stress distribution in the vertical direction along the interface between insert and ceramic green body for longer deposition duration and the presence of unbalanced capillary forces among deposited particles during the drying step; therefore, cracking was thus generated through the stress relaxation. When both counter-electrode and working electrode were placed vertically in EPD tank, we observed that the electrical field lines can distribute evenly across the spacing between these electrodes and gives rise to a complete embedment of inserts by deposited ceramic powders. Fig. 9 illustrates ceramic green body by EPD process using non-conductive linen thread as insert by deposition of 20 min where even deposit surface was viewed at working electrode side and the wavy surface with some mild ripples was observed at the suspension side. The various sizes of conducting and non-conducting inserts (diameter of 0.1–2.0 mm) were tested. For the cases using non-conducting inserts such as

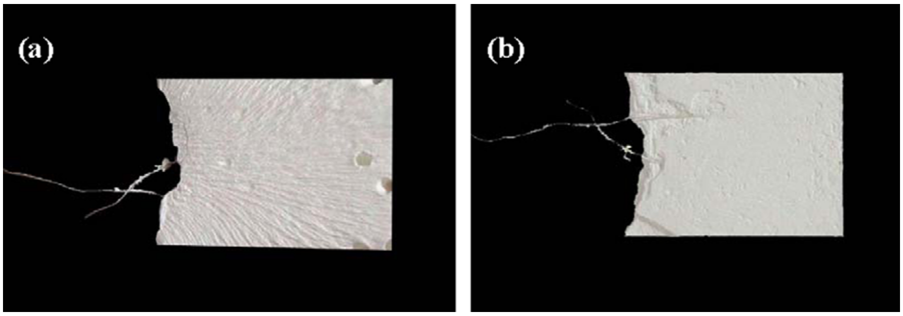

Fig. 9. Ceramic green body by EPD process using non-conductive linen thread as insert by deposition of 20 min viewed at (a) suspension side and (b) working electrode side.

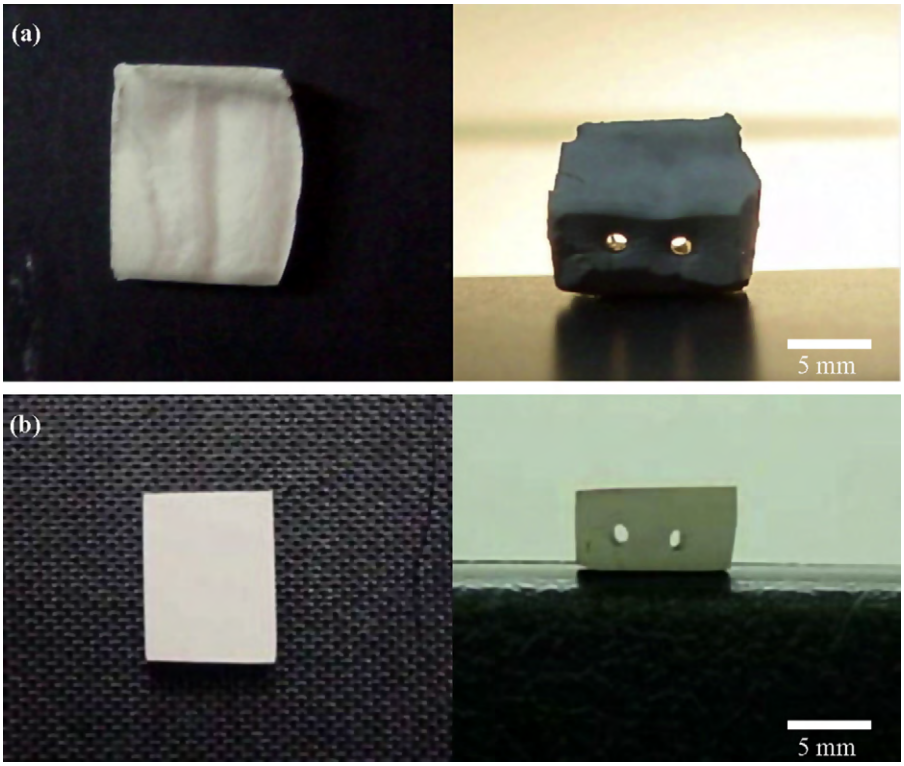

Fig. 10. (a) Top view and side view of sintered body by EPD process with a suspension concentration of 100 g/L and use of conductive steel needle inserts for deposition time of 8 min and (b) top view and side view of ceramic body after surface machining.

Teflon® thread, plastic mesh, cotton thread or linen thread, we found the result of powder packing around the insert was better for the thin inserts because of the minor shielding effect regarding to the electrical field lines; therefore, the average surface roughness (R_{a}) of ceramic deposit and its green density were improved. As for the cases involved with conducting inserts such as carbon fiber, sliver wire, tin wire or graphite rod, the greater size of inserts renders poor powder packing uniformity at the circumferential region of the insert due to interference of electrical field line distribution, which led to a few instances of cracking defects associated with EPD deposits. It is worth noting that the geometrical arrangement of inserts ultimately affect the microstructure of deposits, namely the plastic mesh insert had a difficulty to completely avoid the substantial density gradient in the green body and resultant cracking defect after sintering step because the height of knots, horizontal lines, and vertical lines in the mesh are not on the identical level. On the other hand, the inserts such as threads, wires or rods being positioned in parallel can be immune of green density gradient issues.

Both platinum foil as working electrode and titanium-plated hollow platinum cylinder as counter-electrode were placed inside of the EPD tank made of polytetrafluoroethylene (PTFE) mold. The EPD procedure was preceded for 6 min under an electrical field of 500 V/cm before placing inserts in front of working electrode to prevent influence or disturbance of electrical lines of force. Subsequently the EPD procedure was conducted for additional 2 min by introducing two pieces of steel needles as electrically conductive inserts to be associated with working electrode, where the inserts were successfully covered by deposited ceramic particles by means of the EPD process. Furthermore, the counter-electrode with different geometry such as titanium-plated hollow platinum box or rectangular metal mesh cage could also ensure a uniform distribution of electrical lines of force to improve the better dense packing of ceramic particles in the green body. Fig. 10a shows that holes of 1 mm size with pitch of 3.5 mm appeared in the sintered body of 10 mm × 8 mm × 5 mm was formed by using conductive steel needle inserts with deposition time of 8 min and electrical field of 500 V/cm. Furthermore, Fig. 10b illustrates the ceramic body with smoother surfaces after it was polished and finished with #1500 mesh silicon carbide sand paper and fine abrasive slurry. Regarding the ratio of insert diameter ($d = 0.1$–2.0 mm) to the thickness of ceramic prototype ($h = 0.75$–5.0 mm), it is found that the workable ratio of d/h through our EPD process for forming ceramic min-device should be constrained not more than 0.4. When the height from insert center to level of working electrode (h') can be adjusted with respect to the total thickness of deposit (h), the accessible h'/h value of 0.2–0.5 is recommended with our rapid prototyping technique. Our experimental results would support the idea that use of EPD technique associated with appropriate inserts would offer a feasible route to obtain the ceramic objects based on the concept of rapid prototyping technology or manufacturing.

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References

1. P.S. Nicholson PS. Electrophoretic deposition (EPD): mechanisms, kinetics, and application to ceramics. *Journal of the American Ceramic Society* 1996;**79**:1987–2002.
2. Van der Biest OO, Vandeperre LJ. Electrophoretic deposition of materials. *Annual Review of Materials Science* 1999;**29**:327–52.
3. Boccaccini AR, Zhitomirsky I. Application of electrophoretic and electrolytic deposition techniques in ceramics processing. *Current Opinion in Solid State and Materials Science* 2002;**6**:251–60.
4. Besra L, Liu M. A review on fundamentals and applications of electrophoretic deposition (EPD). *Progress in Materials Science* 2007;**52**: 1–61.
5. Uchikoshi T, Furumi WS, Shirahata N, Suzuki TS, Sakka Y. Conductive polymer coating on nonconductive ceramic substrates for use in the electrophoretic deposition process. *Journal of the American Ceramic Society* 2008;**91**:1674–7.
6. Tabellion J, Clasen R. Electrophoretic deposition from aqueous suspensions for near-shape manufacturing of advanced ceramics and glasses-applications. *Journal of Materials Science* 2004;**39**:803–11.
7. Besra L, Samantaray P, Bhattacharjee S, Singh BP. Electrophoretic deposition of alumina on stainless steel from non-aqueous suspension. *Journal of Materials Science* 2007;**42**:5714–21.
8. Fukada Y, Nagarajan N, Mekky W, Bao Y, Kim HS, Nicholson PS. Electrophoretic deposition-mechanisms, myths and materials. *Journal of Materials Science* 2004;**39**:787–801.
9. Put S, Vleugels J, Van Der O, Biest. Gradient profile prediction in functionally graded materials processed by electrophoretic deposition. *Acta Materialia* 2003;**51**:6303–17.
10. Ilschner B. Processing-microstructure–property relationships in graded materials. *Journal of the Mechanics and Physics of Solids* 1996;**44**:647–56.
11. Koizumi M. FGM activities in Japan. *Composites: Part B, Engineering* 1997;**28**:1–4.
12. Doungdaw S, Uchikoshi T, Noguchi Y, Eamchotchawalit C, Sakka Y. Electrophoretic deposition of lead zirconate titanate (PZT) powder from ethanol suspension prepared with phosphate ester. *Science and Technology of Advanced Materials* 2005;**6**:927–32.