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Routes to net shape electroceramic devices and thick films

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Abstract

The net shape fabrication of a range of electroceramic devices and thick films is described. The fabrication routes involve producing homogeneous and formable ceramic dough using a viscous polymer processing technique, with various subsequent shape-forming operations to produce devices with sizes ranging from tens of millimetres to tens of microns. The advantages of these processing routes are discussed and examples of large (>1 mm) planar and 3-D components (hemispheres, tubes and helices) and structures with small (<150 μm) feature sizes (thick films and microrod arrays) are presented.

Keywords: Films; Functional applications; Pressing; PZT; Shaping

1. Introduction

Success in applications of electroceramic materials depends not only on their performance but also on their processability and cost. Powder or colloidal powder processing is still the predominant fabrication method in industry for electroceramic devices with dimensions larger than 10 μm and these are generally regarded as low cost manufacturing routes. Other chemical and/or vapour methods are only viable in thin film (<10 μm) applications. We have previously reported the applicability of plastic forming routes to the fabrication of novel piezoelectric devices in net shape form such as tubular springs for seismic sensing and helical structures for actuator applications.[1]

Miniaturization of electroceramics has shown an increasing trend for the design of useful electromechanical devices such as microelectromechanical systems (MEMS) in the last decade. Currently, MEMS primarily use silicon technology and have typical feature sizes of the order of microns or smaller. However, in many practical applications, MEMS are too small to provide the required sensitivity as sensors or to provide the required forces as actuators owing to the small volume of active material. In addition, silicon is often not the ideal substrate material in terms of, for example, its electrical and thermal conductivity, capacitance, resistance to corrosion and hermetic sealing. There is a need to develop three-dimensional ceramic microstructures with dimensions between those of silicon-based MEMS and those of conventional macroscopic electromechanical devices in order to overcome the above problems.

This paper presents some new developments in the area of net shape forming of ceramic structures based on the viscous polymer processing (VPP).[2] The combination of micromachining technologies with standard plastic forming methods has enabled net shape ceramics with a fine 3-D structure <100 μm to be achieved. Films with a thickness range of 10–150 μm have been fabricated with smooth surfaces and good adhesion. The microstructure and properties of the films and devices are presented and discussed. The potential of the fabrication technology as a viable and cost effective manufacturing route is demonstrated.

2. Experimental

A general fabrication procedure for different net shape ceramic structures via the VPP route is shown in Fig. 1. Two types of lead zirconate titanate (PZT-5A and PZT-4D) powders from Morgan Electroceramics were used, depending on the final application, and polymer binder systems based on either polyvinyl alcohol (PVA) or

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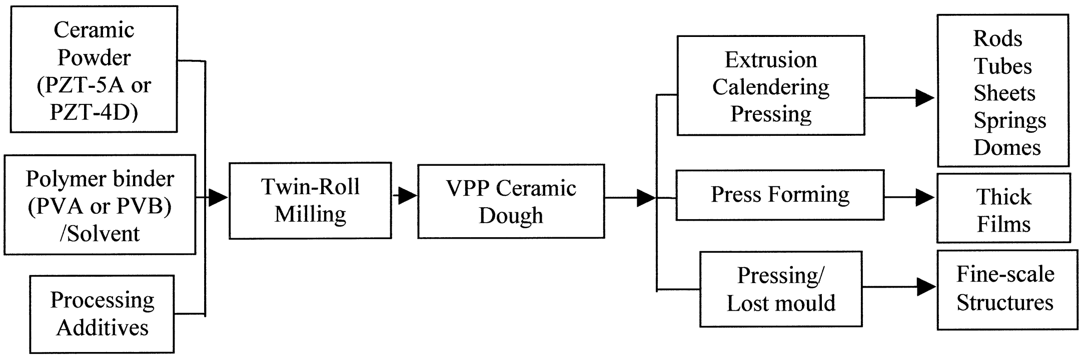

Fig. 1. A general flow chart for the fabrication of net shape electroceramic devices and structures.

polyvinyl butyral (PVB) were used depending on the actual processing route chosen. The details of the binder systems are described in reference.[3] After mixing and twin-roll milling, a VPP ceramic dough with a shear viscosity of ca. 10^5 Pas at a shear rate of 5–10 s^{-1} was obtained. Net shape ceramic components and devices such as rods, tubes, domes etc. were fabricated via extrusion, calendering or pressing of the dough. Thick films were produced by press-forming the dough onto Pt coated alumina substrates. For fine scale PZT structures the dough was press formed into a plastic mould which was subsequently removed chemically after drying and crosslinking of the green ceramic structure. Finally, the green films and structures were subjected to a binder burnt-out cycle up to 550°C and then sintered at 1200–1260°C in a controlled Pb-rich atmosphere. After silvering and poling, the dielectric and ferroelectric properties were measured.

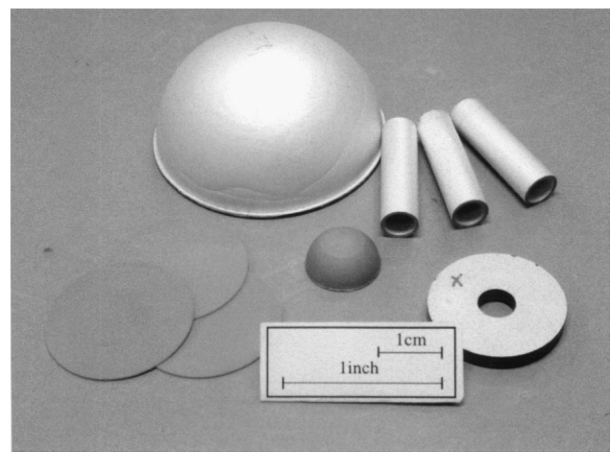

Fig. 2. PZT transducer components fabricated to net shape using VPP techniques.

3. Results and discussion

3.1. Net shape PZT devices

Recent work has been involved with the fabrication of a range of standard transducer shapes in hard and soft PZT materials. Examples of hemispheres, discs, tubes and rings are shown in Fig. 2. For the soft PZT-5A material, the improved microstructure resulting from the high shear mixing technique has been shown to result in improved mechanical properties (e.g. average bend strengths of 130 MPa compared to 80 MPa for powder pressed samples produced from the same powder) and improved functional properties.[4] We are also investigating some novel actuator devices based on helically wound bimorph tapes for use in digital loudspeaker and other applications as shown in Fig. 3.

3.2. Fine scale PZT structures

1–3 Piezocomposites composed of high aspect ratio PZT microrod arrays embedded in a polymer matrix are used for applications such as ultrasonic medical imaging. However, for operation at the high frequencies required for improved imaging resolution, the size of the individual PZT microrods is so small, e.g. 25 μm for a 7.5 MHz phased-array probe,[5] that the conventional dice-and-fill fabrication technique cannot meet this requirement. Therefore, the cost effective processing of fine scale PZT structures is a constant technological challenge. Among various alternative techniques, the lost mould method is the most promising. Wang et al.[6] reported a lost silicon mould method to fabricate a PZT microrod array with a feature size of ca. 50 μm. The problem is the formation of the pyrochlore phase and free lead due to the interaction between the PZT and the silicon mould during hot isostatic pressing. A polymer mould can avoid this problem. Hirata et al.[7] reported a lost polymer mould method to fabricate a structure with an even finer feature size — arrays of PZT microrods with diameters of 25 μm and aspect ratios of 3–9. Synchrotron radiation lithography was employed to make a polymer mould and the PZT slurry was cast into the cavities. The problem with this method is that the polymer mould had to be removed by a slow plasma etching process because the cast PZT rod was too weak to survive the thermal stresses during a conventional polymer

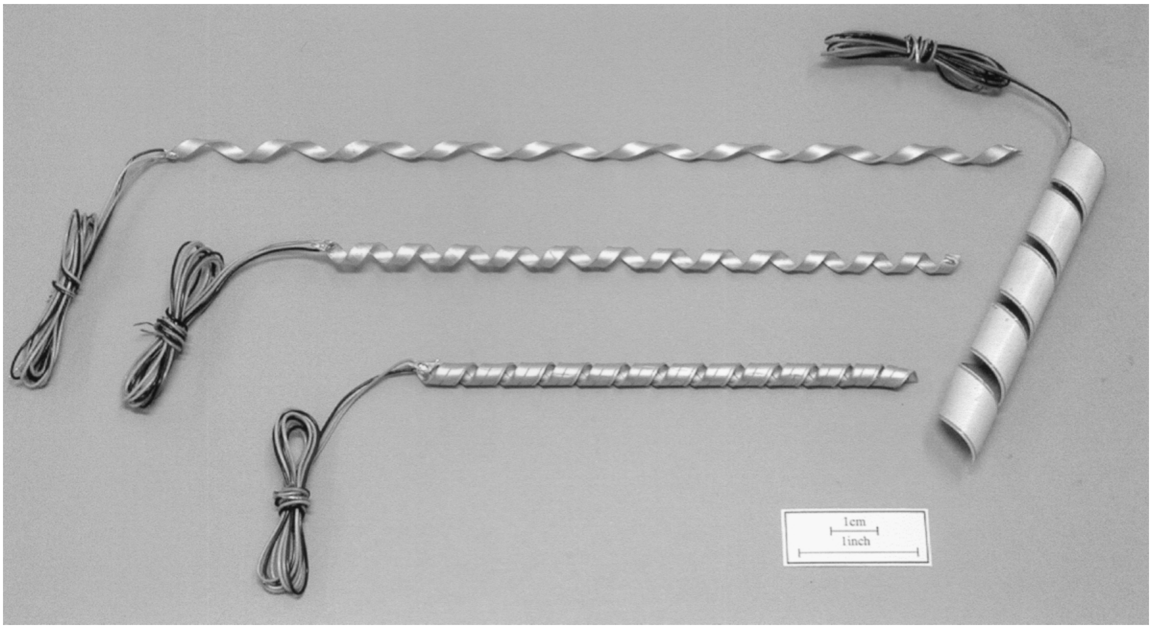

Fig. 3. Helical bimorph structures for application in digital loudspeaker applications.

burnt-out cycle. We have made two improvements to the lost polymer mould method described above. Firstly, the PZT microrod was press formed from a VPP tape. The advantages of using the VPP technique include the high formability of the dough and the high density and strength of the green bodies. Secondly, a room temperature chemical method was used to remove the polymer mould and thus avoid any thermal stresses. Fig. 4 shows the micrographs of a PZT microrod array from a micromachined polymer mould. The feature size is ~150 μm and aspect ratio ~10. The individual microrods exhibit much smoother surfaces and denser structures compared to those reported from a slip casting technique. More importantly, the PZT array has a pure perovskite structure. Further work is underway to reduce the feature size of the PZT microrod.

3.3. Thick PZT films

A cost effective technology for producing films with thickness, e.g. >10 μm is of interest because of the improved dielectric, piezoelectric, pyroelectric and electro-optic effects of ferroelectric ceramics with thickness larger than that attainable by thin film routes.[8] Screen printing is presently the most practical method for the fabrication of films with thickness exceeding 10 μm.[9] We propose here a method based on press-forming a pre-prepared VPP tape on to a substrate to make ferroelectric films with resulting thickness ranging from 10 to 150 μm. The processability of PZT films using this technique is shown in Fig. 5. It was observed that crack-free, adherent thick PZT films could be fabricated on alumina substrates. The film thickness is controlled by

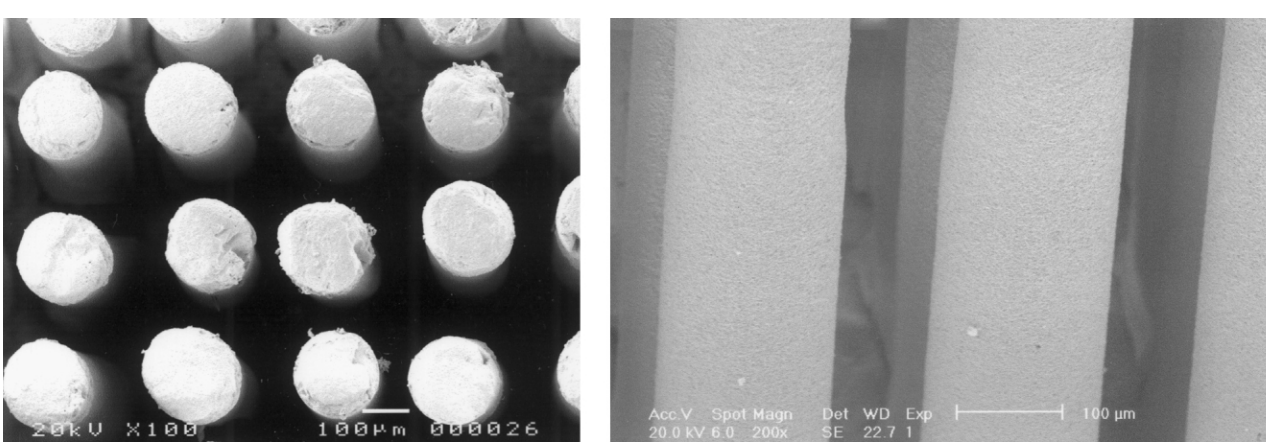

Fig. 4. SEM micrographs of the PZT microrod arrays produced via a lost mould method.

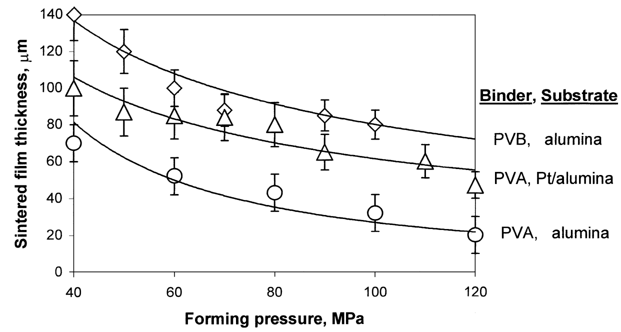

Fig. 5. Sintered film thickness versus forming pressure for PZT films from different polymer binder systems and on different substrates.

the forming pressure, the formulation of the VPP tape and the surface roughness of the substrates. VPP formulations incorporating aqueous PVA binder systems could produce thinner PZT films than non-aqueous PVB systems at the same pressure. This is attributed to the fact that the PVB systems exhibit 2–3 times higher extensional stress than PVA systems under film squeeze flow.[3] The film thickness is also dependent on the roughness of the substrate. It can be seen in Fig. 5 that, for the same forming pressure, a larger film thickness was obtained on Pt coated alumina substrates compared to standard alumina substrates. This is thought to be due to the increased roughness of the Pt-coated substrates caused by the Pt coating being discontinuous, therefore needing a higher pressure to facilitate the film flow.

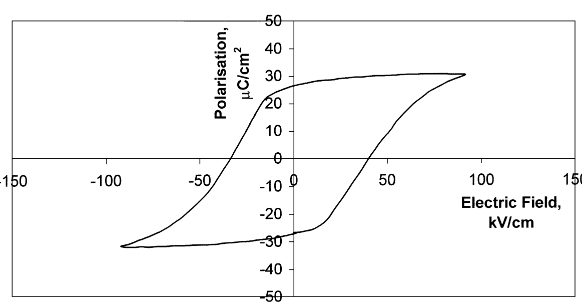

Fig. 6. P–E hysteresis trace for a 70 μm thick PZT-5A film press formed on a 99% alumina substrate and sintered at 1200°C for 1 h.

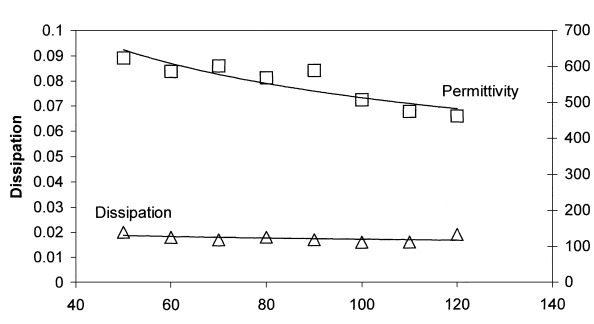

Fig. 7. Dielectric properties (at 1 kHz) versus forming pressure for PZT films.

The P–E hysteresis loop of a PZT thick film press formed onto a 99% alumina substrate is shown in Fig. 6. A square P–E loop was obtained. The remanent polarisation (Pr) and coercive field strength (Ec) were 26.7 μC/cm^2 and 40 kV/cm, respectively, which are comparable to sol–gel derived films.[10] The dielectric properties of the PZT thick films are shown in Fig. 7. The dielectric permittivity of the films decreases slightly with the increase of forming pressure, while the dissipation factor remains almost constant (~0.02). The lower values of dielectric permittivity (~500–700) compared to those of the sol-gel derived PZT films (~1300–1400)[10] may be attributed to the interactions between the PZT films and alumina substrate at the current sintering temperature (1200°C).

4. Conclusions

Processing routes based on VPP have been demonstrated as potentially cost effective and viable techniques not only for net shape fabrication of electroceramic devices but also for structures with small feature sizes such as thick PZT films and fine scale 1–3 PZT arrays. The devices and structures obtained using various plastic forming techniques can exhibit advantages of better performance and simpler processing methods and, therefore, provided a potential alternative route for mass production of net shape electroceramics and devices.

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