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Micropatterning of fine scale ceramic structures

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We report a method which combines colloidal processing with polymer mould for the net shape fabrication of fine scale ceramic structures with feature sizes in the micrometer range and aspect ratios up to 10. Both soft and solid polymer moulds have been used, which can be made using lithography, laser micromachining or CNC machining. Fine scale ceramic structures are formed via embossing, moulding and casting. Polymer moulds are removed using either chemical or mechanical methods depending on the aspect ratio and feature size of the fine scale ceramic structures. Some fine scale ceramic structures have been demonstrated in examples such as PZT microrod arrays and alumina microgears.

1. Introduction

Fine scale ceramic structures with feature sizes <500 μm have found various applications in the field of micro-sensors and micro-actuators, as well as micro-electro-mechanical systems (MEMS) in high temperatures and harsh chemical environments. However, conventional powder processing and machining cannot be used to make such fine scale ceramic structures. Advanced technologies such as those using lasers have been available for micromachining of ceramics but are not viable for large-scale production. It is difficult and time-consuming to pattern fine scale ceramic structures using subtractive methods such as etching and ablation because of the nature of ceramics. Therefore, net shape fabrication methods for fine scale ceramic structures are needed.

Several techniques have been under development to fabricate fine scale ceramic structures. For example, chemical vapour deposition (CVD) using masks has been used to make patterned SiC or diamond [1]. The drawback is the difficulty in obtaining high aspect ratio structures due to the planar nature of the CVD process. Screen printing is another technique to pattern thicker fine scale ceramic structures. However, lateral resolutions are generally limited in the range of 100 μm for this technique. Other rapid prototyping/direct fabrication methods such as Robocasting [2], ink jet printing [3] or fused deposition [4] suffer from similar problems. For ceramics with feature sizes in the range of micrometers, techniques which could combine both the pattern resolution of lithographically generated patterns and colloidal processing are needed. There have been some recent reports concerning the microfabrication of ceramics using lithography defined moulds or patterns from polymer precursors [5–7], sol-gel [8, 9] and ceramic slurries [10, 11]. Both patterned ceramics on substrates and free-standing ceramic parts have been demonstrated. Most of the reports have been of low aspect ratio fine scale ceramic structures. In this work, we report two potentially cost-effective fabrication techniques for fine scale ceramic structures with different feature sizes and aspect ratios from a polymer mould/colloidal processing method. The polymer moulds could be made using existing lithography, laser micromachining or CNC machining depending on the feature size required. The techniques are exemplified by the fabrication of high aspect ratio piezoelectric structures suitable for medical imaging transducers and a freestanding alumina gear wheel.

2. Experimental

The two processing routes used in the fabrication of fine scale ceramic structures are illustrated in Fig. 1, depending on the sizes and aspect ratios to be produced. In general, for the low aspect ratio (<3) structures, a soft mould/casting method was used. For the high aspect ratio (>3) structures, a solid mould/embossing method was used instead. The soft mould was made by the replication of a UV lithography SU-8 master mould from polydimethylsiloxane (PDMS). The solid mould was made by the CNC or laser micromachining from polymethyl methacrylate (PMMA). An aqueous alumina powder (A16-SG, Alcoa, d_{50} 0.5 μm) slurry was prepared by ball-milling using polymethylacrylic acid (A40) as a dispersant with a solid loading of 50–55 vol% and cast into the soft mould using centrifugal casting (Clandan T52 centrifuge) at a speed of 3000 rpm. Lead zirconate titanate (PZT-5A, Morgan, d_{50} 0.5 μm) dough was prepared by viscous polymer processing (VPP) [12] using an aqueous PVA binder system and pressed in the solid mould using embossing at room temperature. The VPP PZT tape was first laminated with the PMMA mould and embossing was performed between two polished zirconia plate using an INSTRON mechanical testing machine at a speed

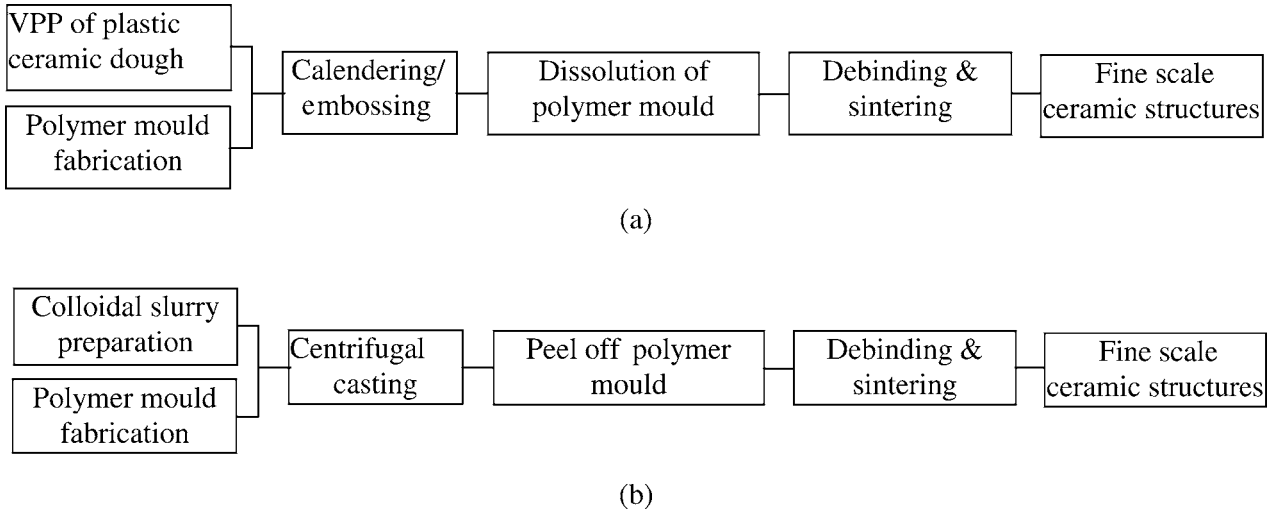


Figure 1 Two processing routes used to fabricate fine scale ceramic structures. (a) The solid mould/embossing route; (b) The soft mould/casting route.

of 0.5 mm/min and pressure <50 MPa. The embossed samples were then dried at 40°C for 24 h and 80°C for 12 h. Demoulding was carried out using either mechanical peel-off for soft mould and or chemical dissolution for solid mould using a solvent such as acetone or chloroform. The green bodies were subsequently burnout at a heating rate of 2°C/min and sintered at 1550°C/2h for alumina and 1200°C/2h for PZT respectively.

3. Results and discussion

3.1. Fine scale ceramic structures from solid polymer moulds

1–3 piezocomposites have found applications in high-resolution ultrasound medical imaging [13]. 1–3 piezocomposites are composed of high aspect ratio PZT microrod arrays embedded in a polymer matrix. As the requirement for higher frequency operation to produce higher resolution images, both the pillar size and spacing are required to be reduced to tens of micrometer size range. The conventional dice-and-fill fabrication technique becomes more difficult. For example, for a 1–3 piezocomposite working at a frequency of 30 MHz, the widths of the PZT post and the polymer kerf need to be less than 30 and 10 μm respectively. It is virtually impossible to fabricate such a composite using conventional dice and fill method because the minimum thickness of dicing saw blades at present is approximately 15 μm. In addition, the shape of the PZT post is also limited. Therefore, more robust and cost-effective processing methods for the fine scale PZT structures are technological challenges. Among various alternative techniques, the lost mould method is the most promising. Wang *et al.* [14] reported a lost silicon mould method to fabricate a PZT microrod array with a feature size of ca. 50 μm. The problem with this method is the formation of the pyrochlore phase and free lead caused by the interaction between the PZT and the silicon mould during hot isostatic pressing. The use of polymer moulds can avoid this problem. Hirata *et al.* [15] reported a lost polymer mould method to fabricate a structure with even finer feature size arrays of PZT microrods with diameters of 25 μm and aspect ratios of 3 to 9. Synchrotron radiation lithography was employed to make a polymer mould and the PZT slurry was cast into the cavities. The drawback of this method is that the polymer moulds 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 burnout cycle. In this work, we have made two improvements to the above lost mould method. Firstly, the PZT microrod was embossed from a plastic VPP tape. The advantages using the VPP technique include the high formability of the ceramic 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 excessive thermal stresses. The key is to select a polymer binder system which could survive the chemical removal process of the polymer mould. It is well known that the PVA binder used in this work is prone to forming three-dimensional crosslinking structures after drying because of the strong inter- and intramolecular hydrogen bonding. The 'good' solvent for PMMA mould such as acetone or chloroform would not generate significant stresses within the green body [16]. The additional advantage of the current method is that individual PZT microrods exhibit much smoother surfaces and denser structures compared to those reported from a slip casting technique or conventional dicing method. More importantly, the PZT array has a pure perovskite structure as confirmed by the XRD. Micrographs of a PZT microrod array produced using a CNC machined polymer mould is shown in Fig. 2. The feature size is $\sim$150 μm with spacing of 60 μm and aspect ratio $\sim$10. Finer PZT pillar arrays and smaller spacing could be achieved with the X-ray lithography processed polymer mould [16].

3.2. Fine scale ceramic structures from soft polymer moulds

The soft mould method used in this work is similar to the soft lithography proposed by Whitesides *et al.* [17] In the soft mould method, a silicone rubber mould was replicated from a pre-patterned master mould using PDMS. The master mould could be fabricated from any patterning techniques on any material, including silicon

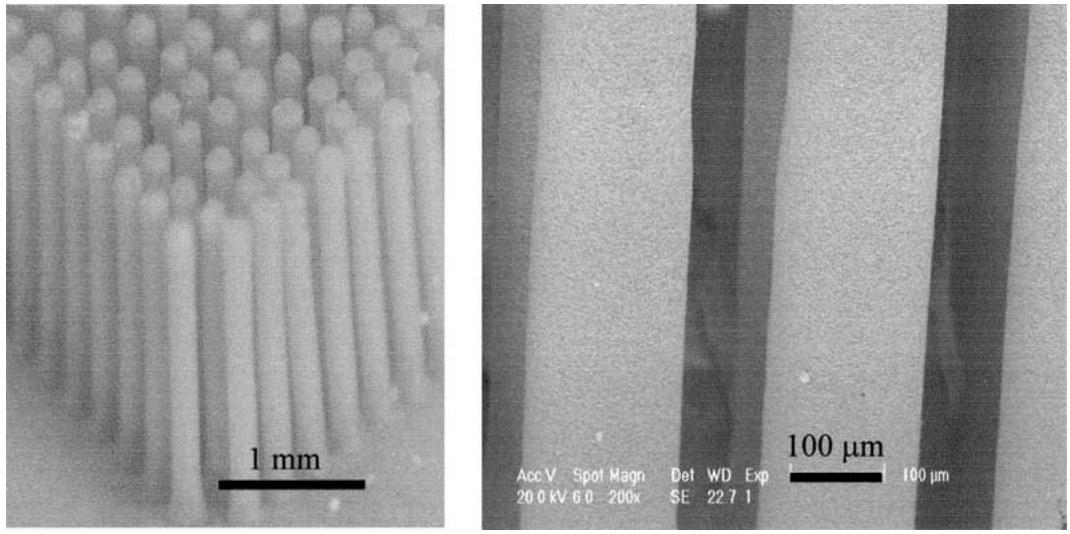
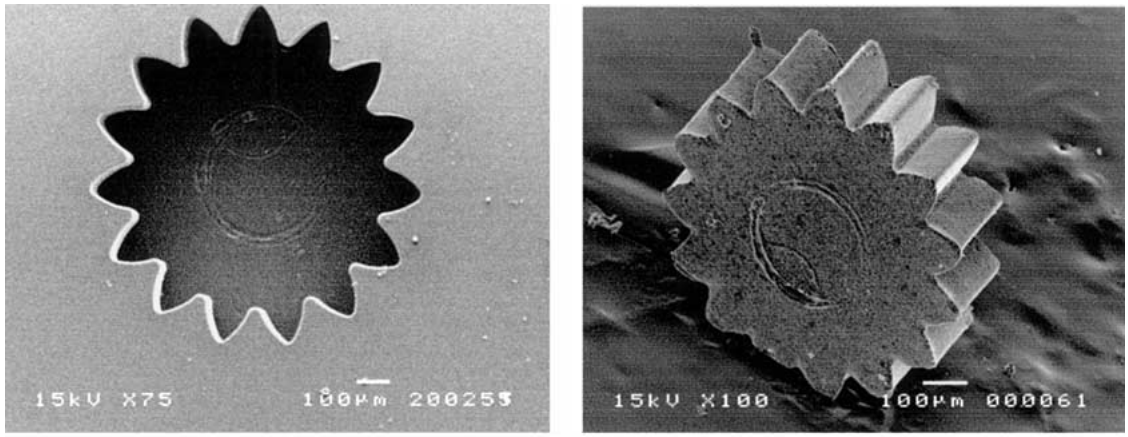


Figure 2 PZT microrod arrays fabricated from embossing/PMMA mould.



(a) (b)

Figure 3 SEM micrographs of silicone rubber mould (a) and a freestanding ceramic microgear (b). (a) PDMS soft mould replicated from a UV lithography SU-8 master mould; (b) Freestanding alumina microgear from (a) using centrifugal casting.

etching, LIGA, UV lithography or laser micromachining, depending on the feature size required. Fine scale ceramic structures could be fabricated using various processing techniques such as micro-transfer moulding and micro-moulding in capillaries utilising sol-gel solutions or preceramic precursors [5, 8]. The large shrinkages during the ceramic transformation are the major concern. For larger feature size ceramic structures, ceramic slurries instead of chemical precursors have to be used. The SEM micrographs of a PDMS soft mould and a sintered freestanding alumina microgear are shown in Fig. 3. Microgears have potential applications in high temperature micro-engines [18]. Comparing with the solid (lost) polymer mould method, the soft mould is reusable and cost-effective. It is particularly suitable for large area and relatively low aspect ratio fine scale ceramic structures. Both ceramic patterns on substrates and freestanding fine scale ceramic structures could be fabricated. As can been seen from Fig. 3, the 0.75 mm freestanding microgear is crack-free with sharp edge teeth. The typical shrinkage is ca. 25%. For smaller dimensions, nano-ceramic powders have to be used. Also dopants should be used to prevent excessive grain growth.

4. Conclusions

Fine scale ceramic structures with feature sizes <500 μm and aspect ratios <10 have been fabricated using colloidal processing/polymer mould methods. Solid and soft polymer moulds have been used to fabricate high aspect ratio (>3) and low aspect ratio (<3) fine scale ceramic structures respectively, which can subsequently be removed by chemical or mechanical means. Embossing and centrifugal casting have been employed for the net shape fabrication of the fine scale ceramic structures. Both methods are potentially cost-effective and viable for large scale fabrication comparing to current microfabrication techniques for ceramics. Two fine scale ceramic structures have been exemplified in this work.

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