A soft lithography process for manufacture of alumina micro-components

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Abstract

This paper presents a soft lithography technique to fabricate alumina microcomponents. The process uses elastomer polydimethylsiloxane (PDMS) and makes the green patterns in tact after demoulding. The five steps of the soft lithography process are: (I) fabricating thick SU-8 moulds using UV photolithography; (II) producing PDMS soft mold from the SU-8 masters; (III) making aqueous high solids loading alumina suspension; (IV) filling patterned PDMS moulds with the aqueous alumina suspension; (V) demoulding and sintering. The rheological properties (Zeta potential and viscosity) of aqueous alumina suspensions was characterized in relation with varying pH values and concentration of dispersant (D-3005). The optimal parameters of the alumina suspension for the mould filling have been achieved as pH value = 11; concentration of dispersant (D-3005) = 0.05 g/ml; amount of binder (B-1000+B-1007) = 0.75%, the highest solid loading = 70 wt.%. After pressurised mould filling, the complete, dense and free-standing microcomponents have been achieved by using 70wt.% alumina suspension and optimum fabrication technique, while the overall shrinkage is found as ca. 22%.

Keywords: SU-8 moulding, microceramics, soft lithography, UTSP, alumina microcomponents

1. Introduction

Microceramic components have outstanding thermal-mechanical property against temperature of up to 1500°C makes them suitable for high power laser [1] and microcombustors [2] applications. The biocompatible property makes them suitable for implant applications[3]. The highly chemical stable property makes them suitable for micronozzles and microchannels applications of strong acids. The high temperature resisted alumina ceramic microcomponents remains a significant challenge to current MEMS technology [3].

Soft lithography is a set of techniques that offers simple routes to microstructures formed from low costs polymers and this process has been thoroughly described in many literatures [4]. A soft lithography based micromoulding process has three main advantages over traditional photolithography in microceramic fabrication. The first is that it is less sensitive to surface topography than photolithography. The second is that it works for a wide range of materials, as opposed to photosensitive only materials of a photolithographic process. And the third one is that some chemically and physically sensitive materials such as dyes and biomolecules can be patterned using this technique [5].

Due to the vast potential of soft lithography technique, many researches have used the techniques to produce patterned structures. Schönholzer et al firstly provided the idea to fabricate ceramic structure with surface patterns in the range of several micrometers using soft lithography. They studied the influence of different particle sizes on the pattern resolution of ceramic component, but their research was limited to cavities only [6]. Heule et al demonstrated the application of micromoulding in capillaries (MIMIC) for a simple thick-film gas-sensing device based on tin oxide by combining photolithography and MIMIC with ceramic suspensions, PDMS served as mould that were spontaneously filled owing to capillary forces with suspensions of 0.1 - 40 vol% solid loading SnO2 [7]. This technique was limited to patterns with dimensions around 10 µm or less and aspect ratios of no more than 2-3. Kim et al used Al and Cu micro/nano powder to successfully fabricate three-dimensional micro Al-based alloy components. With some modifications, they can utilize this technology to produce another metallic microcomponent [8].

The paper presents a study of producing high temperature resisted alumina ceramic microcomponents using soft lithography technology and investigating the rheological behaviours and optimized conditions of high solids loading Al2O3 suspension. After the introduction, the paper provides the experimental details starting from producing hard moulds and soft moulds. The composition of the ceramic suspension is then described in details before the sintering conditions are introduced. The measurements and results on both the rheological behaviours and the property of the alumina microcomponents are presented. The microceramic components and their measurements show that the proposed soft lithography process is successful in producing microceramic components while retaining their fine features in micron scale.

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2. Experimental

The proposed fabrication of microceramic components involves producing hard moulds using photolithography techniques, producing the mirror PDMS soft moulds from the hard moulds, filling ceramic suspension in the cured soft moulds with pressure, demoulding and sintering. Fig. 1 shows the schematic diagram of ceramic pattern formation using soft lithography technique. The particulars of each step are described in the following sections.

2.1. Fabrication of master moulds and negative moulds

The fabrication process starts from producing hard master moulds. High precision master moulds can be either produced using deep reactive ion etching (DRIE) for a depth up to 500 µm or ultra thick SU-8 process (UTSP) for a depth up to over 1000 µm. The UTSP also has the advantage of low cost in comparison to the DRIE process and thus is extensively used in the study. SU-8 is a well known negative, epoxy-type photoresist based on EPON resin. The most attractive characteristics of SU-8 photoresist are its low light absorption in the near-UV range and its extraordinarily viscosity. Recently, Jin et al have used UV-light lithography to produce ultra-thick SU-8 micromoulds and the aspect ratio of a 1000 µm thick SU-8 microdevice can be as high as 40:1[11]. The optimized process for producing a 1000 µm thick SU-8 layer consists of the following steps. (a) SU-8-50 (Microchem Corp., U.S.) is poured onto a well-level wafer by direct casting and deposited SU-8 on the wafer is then left for 20 min to get flat; (b) the wafer is prebaked at 65 °C for 2 h, and then at 95 °C for 20 h; (c) after it cooled down to room temperature, the coated wafer is exposed under UV light with energy density 2.5 J/cm²; (d) the post exposure bake is carried out first at 65 °C for 15 min and then at 95 °C for 25 min. (e) The exposed wafer is immersed in EC solvent (Chestech, UK) for 1.5 h for development. More details could be found in the literature [12-13]. An SU-8 microgear fabricated using the UV-light lithography is shown in Fig. 2. The height and diameter of the microgear are 1 mm and 2.5 mm and two through holes are set inside the gear.

In soft lithography, micropatterns are transferred by casting PDMS slurry onto SU-8 master structures. The PDMS slurry was prepared by mixing Sylgard Silicone Elastomer 184 and Sylgard Curing Agent 184 (dow Corning Corp.) in a weight ratio of 10:1, and leaving it for 30 min to allow the gas bubbles escaping from the solution. The mixture was then poured on the SU-8 master mould template and placed in a vacuum condition until all residual bubbles were removed. Afterwards, it was cured at 65°C for 4h according to the recommendation by Dow Corning Corp. After cooled to room temperature, the cured PDMS moulds were peeled off from the SU-8 master mould template. The soft moulds are usually used once and the SU-8 moulds can be used 2-3 times.

2.2. Aqueous alumina suspension

High purity Al₂O₃ powder with an average particle size of 1.5 µm (Dynamic Ceramic Corp. U.K.) was used in the experiments. Duramax D-3005(Rohm and Haas, Philadelphia, USA) was used as the dispersant, Duramax B-1000 and B-1007 (Rohm and Haas, Philadelphia, USA) was used as the binder, NaOH and HCl were used to adjust the pH value of slurries in all processing, and distilled water was used as the solvent in all experiments.

All samples were weighed to ± 0.001g and typical batch size was 27g. The mixing process consists the following steps: (a) 0-1.0 g/ml Duramax D-3005 was added to the distilled water under constant magnetic stirring for 30 min. Afterward, alumina powder was slowly poured into the solution and then stirred for 3h; (b) 0.75wt% (B-1000-B-1007) was added as binder, with pH value adjusted and then stirred for 2h; (c) The slurry was then poured into a plastic bottle, covered and sealed with a sticky tape. The bottle was then put on a shaking machine and shaken for 7h, and then left overnight to make the slurry more uniform; (d) Before being used, the slurry was placed in a vacuum condition until all residual bubbles were removed.

2.3. Moulding, demoulding and sintering

The cavity of the patterned PDMS moulds were filled up with the aqueous alumina suspension and two mould filling methods were experimented. (1) Pressure free mould filling: Pouring the aqueous alumina suspension on to the moulds under gravity; (2) Pressurized mould filling: Turning the moulds with the
aqueous alumina suspension facing downwards and quickly placing them on a 99.9% alumina substrate. A slight pressure was applied on the PDMS mould to push the air bubble out and to fill the suspension in every corner of mould. The results will be discussed in Section 3.2. Meanwhile, a PDMS bar was used to clear the residual slurry. It is important to avoid cracks in the green structures by controlling the residual stress during the drying. Therefore, the drying rate should be low. Once the slurry was dry, the green component was achieved by carefully peeling off the soft PDMS moulds. The PDMS moulds were cleaned by ultrasonic bath with acetone and distilled water and ready for the next use.

The green components were placed on a 99.9% Alumina substrate, and put in a high-temperature furnace. The binder and dispersant in the component should be decomposed under 600°C. Therefore, the heating rate of the furnace to 600°C was firstly set at a low ramping rate of 75 °C/h and then set at 1600°C at a high ramping rate of 200 °C/h. The temperature remained at 1600 °C for 2h before the furnace was cooled down to room temperature.

2.4. Measurement of Zeta potential values

Zeta potential values were measured with Zeta Potential Analyzer (Zetamaster, Malvern instruments, U.K.). The suspension was diluted to 3 wt% by distilled water and the pH value was adjusted with 1M NaOH and HCl. Viscosity measurements were performed using a coaxial-cylinders viscometer (Rheomat 30, Contraves, Zurich) with the following specifications for the cylinders: internal radius: 22.9 mm; external radius: 24.2 mm; height: 56.5 mm. Microstructures were analyzed with a scanning electron microscope (SEM, Philips XI-30, UK).

3. Results and discussion

3.1. The rheological properties of alumina suspension

In the development of high performance aqueous ceramic suspension, pH value adjustment and dispersant selection are of great importance. According to the DLVO theory, the Van Der Waals forces can make the powders aggregate to form clusters, resulting in a relatively high suspension viscosity and difficulty in processing. The zeta potential has a direct relationship with the pH value. The adjustment of the pH value can produce a high surface-charged density on the particle surface which makes strong double-layer repulsion and leads to well-dispersed ceramic suspension.

Zeta potential can determine the stability of aqueous ceramic slurry. The bigger the zeta potential, the higher the repulsive energy and the more stable the slurries. Fig. 3 shows the relationship between the pH value and the zeta potential. The isoelectric Point (IEP) at which the zeta potential is zero was about 6.7. The curve shows the particles are highly negatively charged when the pH value is low and positively charged when the pH value is high. At a high pH value (pH=11), the absolutely Zeta potential value is ca. 40 mV, which shows the repulsion forces between the particles are larger than Van Der Waals forces (normally ca. 30 mV), and this value is able to acquire the stable slurry.

The relationship between the viscosity of suspension and concentration of dispersant (D-3005) at shear rate of 150 s⁻¹ is shown in Fig. 4. The viscosity of Al₂O₃ suspension with 70 wt% solid content decreased firstly due to the increase of the concentration of dispersant and reached the minimum value as the dispersant content was 0.05 g/ml.

With the concentration of dispersant further increased, the viscosity of suspension increased slightly. This phenomenon can be understood as that too much dispersant could leave some unabsorbed which in turn function as an electrolyte to reduce the range and extent of the electrostatic repulsion force. Zhang et al obtained similar results using NH₄PAA as dispersant [14]. The results indicated that the D-3005 has a great effect in dispersing Alumina suspension and the optimum concentration of the dispersant for 70 wt% alumina suspension was 0.05 g/ml.

Although the viscosity of aqueous slurry was mainly determined by zeta potential, the pH value and ion strength can strongly influence the electronic properties of the particle surface and also the zeta potential [9]. Fig. 5 shows the relation between the viscosity of the suspension and the pH value at the shear rate of 150 S⁻¹ with different alumina solid contents. As polyelectrolyte was used as dispersant in the suspension, D-3005 provided the so-called steric stabilization energy to particles. The contribution of steric stabilization energy to the suspension is not strongly affected by pH value because the D-3005 is a kind of long link molecule, which could be absorbed on the surface of particles to prevent particles from contacting each other. But the change of pH value will affect the ionization of D-3005 and the structure of Double-layer, which are linked to electrostatic repulsion stabilization energy. Therefore, electrostatic repulsion energy and Zeta potential will change with the adjustment of pH value, which will contribute to the stability of slurry. Fig. 5 shows the viscosity of alumina suspension decrease quickly with the increase of pH value, which indicates electrostatic repulsion energy strongly affects the viscosity of alumina suspension. When the pH value reached ca.10, it seemed that...
electrostatic repulsion energy had less effect on the change of viscosity with further increasing pH value, just resulting in a little decrease of the viscosity. Different Al₂O₃ solid loading suspensions have the similar trend in Fig. 5 and the optimal pH value for the mould filling is ca. 11.

After adjustments of pH value, the concentration of dispersant and organic binder, the optimal parameters of the alumina suspension for the mould filling were listed as below: pH value = 11; concentration of dispersant (D-3005) = 0.05 g/ml; amount of binder (B-1000+ B-1007) = 0.75%, the highest solid loading = 70 wt.%.

3.2 The properties of alumina microcomponents

The pressure free and pressurized mould filling methods were described in Section 2.4 and their results are discussed here. Fig. 6 shows SEM micrographs of sintered microcomponents using the two different mould filling methods. The average grain size (1.5-2.0 μm) of the ceramics produced from the pressure free and pressurized mould filling methods are the same, but pressurized mould filling method results in denser structure (Fig. 6(b)), while the pressure free filling method results in some holes in the structure (Fig. 6(a)). Obviously, the pressure forced air bubbles out of the ceramic suspension more effectively.

Fig. 7 SEM micrographs of sintered free-standing alumina gear.

Fig. 7 shows an SEM image of a sintered free-standing alumina gear. It can be seen that complete, dense and free-standing ceramic microgears can be achieved by using high solid loading (70wt.%) alumina suspension and optimum fabrication technique, and the overall shrinkage is ca. 22%. This soft lithography technology to fabricate alumina microcomponents could be extended to another ceramic materials with some modification, such as ZrO₂ or SiC ceramic, and the authors are currently studying on the fabrication ZrO₂ microcomponents.

4. Conclusions

A low cost soft lithography technique to fabricate microcomponent is introduced in this paper. Traditional solid moulds have been replaced by elastomer PDMS to make demoulding easier and to reduce the damage of green patterns. The whole soft lithography, described in details in the paper, involves the following steps: (I) fabricating rigid SU-8 moulds using UV light lithography; (II) producing PDMS soft moulds from the SU-8 masters; (III) making aqueous high solids loading alumina suspension; (IV) filling patterned PDMS moulds with the aqueous alumina suspension; (V) demoulding and sintering. The rheological properties (Zeta potential and viscosity) of aqueous alumina suspensions have been characterized with varying pH value and concentration of dispersant (D-3005). The optimal parameters of the alumina suspension for the mould filling were listed as below: pH value = 11; concentration of dispersant (D-3005) = 0.05 g/ml; amount of binder (B-1000+ B-1007) = 0.75%, the highest solid loading = 70 wt.% After pressurised mould filling, complete, dense and free-standing microgears have been achieved by using 70wt.% alumina suspension and optimum fabrication technique, and the overall shrinkage is ca. 22%.

Acknowledgements

The authors should greatly acknowledge the financial supports of Royal Society Incoming Fellowship Program.

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