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Improvements in the structural integrity of green ceramic microcomponents by a modified soft moulding process

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Abstract

In this paper, a soft moulding method involving the use of elastomeric poly(dimethylsiloxane) (PDMS) moulds is described for micropatterning and microfabrication of ceramic components for microelectromechanical systems (MEMS) applications. The properties and microstructure of the green bodies have a direct effect on the ability to carry out some of the moulding procedures, as well as affecting the properties of the final sintered microcomponents. High packing density and mechanical strength are required for maintaining structural integrity and resisting the demoulding forces. Centrifuging force and appropriate binder systems have been introduced in the soft moulding process, and shown to be helpful in achieving uniform and dense green microcomponents with feature sizes of $\leq$100 μm and high aspect ratio structures (<10).

Keywords: Al_2O_3; Shaping; Microstructure-prefiring; Strength; Microfabrication

1. Introduction

Micropatterning and microfabrication of ceramics have gained considerable attention due to their ability to produce components with excellent mechanical properties and high temperature resistance, and can extend MEMS technologies to much broader applications, compared to silicon-based traditional MEMS materials.[1,2] In addition, the unique magnetic, piezoelectric, electro-optical and chemical inertness properties of different ceramic materials can also offer MEMS many new and novel applications.[3] Among a wide range of techniques, soft lithography is collectively a set of non-lithographic techniques based on printing, moulding and embossing for the fabrication of micro- and nanostructures and devices.[4–6] The key issue in these techniques is an elastomeric stamp or mould for the realisation of the pattern transfer, which is also the initiation of the "soft" in the soft lithography. Poly(dimethylsiloxane) (PDMS) polymer is the most used soft mould material due to its low interfacial free energy, chemical inertness and very good durability which allows moulds to be reused many times.[7,8]

The soft moulding process is an extension of soft lithography in the fabrication of ceramic components with feature structures in the micrometer size range.[9–11] Several soft moulding methods have been developed for the fabrication of alumina microcomponents. Firstly, embossing and microtransfer moulding (μTM), which are normally utilized in the patterning of nanostructures, have been demonstrated for the patterning and fabrication of ceramic microcomponents.[10] Due to the high viscosity of alumina suspensions used in these processes, centrifugal casting was introduced to improve the filling of the mould and densification of the green body within the moulds, resulting in the process of centrifugal aided soft moulding (CASM). Based on CASM, a novel processing method was developed for the fabrication of three-dimensional free-standing ceramic microcomponents.[11] All these methods compose the soft moulding process for the fabrication of ceramics in the size range from a few microns to millimetres.

A net-shape processing route is essential for components in this size range as it is difficult to process them further by, for example, grinding or polishing. It is therefore essential to guarantee the uniformity in the green ceramic body, the smoothness of the surfaces, and to achieve an even shrinkage during drying and sintering. The structure of the ceramic green body has a direct effect on the quality of sintered ceramic components. The integrity, uniformity and strength are all important criteria in assessing green ceramic bodies. To maintain the integrity of the high aspect ratio green ceramic microstructures during drying and demoulding, a high green strength is essential. In

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this study stable, well dispersed suspensions with high solids loadings have been used and the effects of appropriate binder systems and the introduction of a centrifugal casting process on the ceramic green structures are presented. Although most of the alumina components have overall sizes in the range of millimetres, the key features of the structures of the components are often in the size range of 100 μm or even less, which gives a very high aspect ratio (~10) for these structures.

2. Experimental

2.1. Mould preparation

Poly(dimethylsiloxane) (PDMS) was chosen as the elastomeric mould material. A 10:1 (weight ratio) mixture of Sylgard Silicone Elastomer 184 and Sylgard Curing Agent 184 (Dow Corning Corp.) was mixed and left for half an hour to allow deairing of the pre-polymer. Then the mixture was poured onto the master template (e.g., SU-8 photoresist structures) in a vacuum desiccator and kept in the vacuum condition until all the bubbles dispersed. The PDMS was cured at 65 °C for 4 h according to the recommended schedule of Dow Corning. After cooling to room temperature, the rigid PDMS was carefully peeled from the master template.

2.2. Preparation of A-16 SG powder suspensions

A-16 SG alumina powder (Alcoa Manufacturing (GB) Ltd., Worcester, UK) was added to distilled water (17 MΩ cm) with 0.14 wt.% (based on dry weight of alumina) dispersant, ammonium polyacrylate (NH_4^+PAA) (Dispex A40, Allied Colloids, Bradford, UK) under constant stirring to achieve a solids loading of 80.0 wt.%. All samples were weighed to ±0.001 g and typical batch size was 50 g. The suspensions were ball milled with zirconia balls for 15 h. In some suspensions 0.5–1.5 wt.% PVA binder (KH17, Nippon Synthetic Chemical Industry Co. Ltd., Japan) was added, followed by further slow milling. Two drops of 1-octanol were added to reduce the surface tension of the suspension. Finally, the suspensions were left for 24 h to de-air.

2.3. Preparation of CT-3000 SG powder suspensions

A second alumina powder, CT-3000 SG (Alcoa Industrial Chemicals Europe, Frankfurt, Germany), was also used in this study. Following the same preparation procedures described above for A-16 SG alumina powder, a solids loading of 84.0 wt.% was obtained for CT-3000 SG alumina suspension, however, by using different dispersant and binders, 0.20 wt.% (based on dry weight of alumina) NH_4^+PAA (D-3021, Duramax, Chesham Chemicals Ltd., UK) and additional 3.0 wt.% B-1000 and 2.0 wt.% B-1007 (acrylic polymer emulsion, Duramax) binders, respectively.

2.4. Moulding technique

The soft moulding process for fabricating ceramic microcomponents has been detailed previously,[10] including embossing and microtransfer moulding (μTM). In brief, for μTM, the suspensions were carefully dropped onto the patterned surface of a PDMS mould. After removing the excess suspension, the PDMS mould was placed face down in contact with a freshly cleaned alumina substrate. The green structures were dried in the moulds at room temperature for 24–48 h depending on the size of the patterned areas and the thickness of the ceramic body, and then further dried at an oven at 40 °C for 12–24 h in still air. The PDMS moulds were then carefully peeled off the substrate, starting normally at a corner or one side, to leave the patterned structures on the substrate.

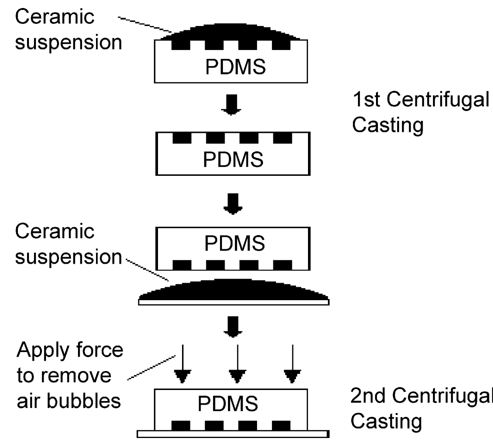

Fig. 1. Schematic procedures of centrifugally aided soft moulding (CASM).

Centrifugally aided soft moulding (CASM) is a combination of embossing and microtransfer moulding with the aid of centrifugal casting, as shown in Fig. 1. Similar to μTM, drops of the suspensions were introduced onto the patterned structures of a PDMS mould using a pipette. Then the PDMS mould was put inside the centrifuge and cast at the speed of 3000 rpm for 1–2 min. After centrifugal casting, some more ceramic suspension was carefully dropped onto a freshly cleaned alumina substrate and then, the PDMS mould was placed face down to the suspension. After gently pushing away any visible air bubbles, the PDMS mould with the substrate was centrifugally cast once more at the speed of 3000 rpm for 5–10 min, followed by drying and demoulding as described for μTM.

After demoulding, the PDMS moulds used for suspensions with PVA binder were cleaned in an ultrasonic bath with distilled water and ethanol, respectively, and the moulds used for suspensions with the Duramax binder system were cleaned in the ultrasonic bath with acetone and ethanol, respectively, and then ready to reuse.

2.5. Characterisation

The rheological behaviour of the suspensions was tested using a CSL Rheometer (Carri-med 115/A) with the cone and plane system (Truncation: 55 μm; Core: 4 cm, 20°) at 20 °C. The scanning electron microscopy (SEM) photos were taken using JSM-5410 (Jeol, Tokyo, Japan) and Philips XL30 (Philips, Oxford, UK) microscopes.

3. Results and discussion

3.1. Defects in green bodies

Some ceramic microcomponents in the green state made from a 80.0 wt.% A-16 SG alumina suspension via the microtransfer moulding process are shown in Fig. 2. The results indicate typical examples of the defects due to the air bubbles. The uneven surfaces of the four block structures next to the cross in Fig. 2(a), as well as the poor resolution of tips of the cross, show the effects of air bubbles during the soft moulding process. The big void in the gear body also clearly identifies the existence of an air bubble, as shown in Fig. 2(b). In the application of embossing or microtransfer moulding techniques, air bubbles were easily incorporated into the moulded ceramic bodies. The air bubbles originate mainly from two sources. While bubbles can be present in the suspension itself, more commonly, most air bubbles are introduced by adding and mixing the binder improperly. In addition, air can be easily trapped inside the PDMS mould during casting. Some air bubbles can be easily recognized since the PDMS mould is transparent. Although the air bubbles are visible, it is very difficult to remove them. Consequently, the air bubbles result in defects or voids in the green bodies after drying and demoulding. This problem becomes more prominent for low solids loading suspensions due to increased shrinkage.

The strength of the green body is vital in determining whether the green structure can survive the demoulding process, especially for green bodies with high aspect ratio features. The broken parts in the gear teeth and handle, as shown in Fig. 2(c), are a result of the weak resistance to the peeling force in the demoulding of the soft PDMS mould. Furthermore, the teeth structures show a blurred resolution. The break-down of the edges of a hole are shown in Fig. 2(d).

3.2. Modification to suspensions

The variation of viscosity with the percentage of PVA additive to the 80.0 wt.% A-16 SG alumina suspensions and the effects of ball mill time are shown in Fig. 3. The 80.0 wt.% alumina suspensions without binder had a viscosity of 0.09 Pa s measured at a shear rate of 100 s^{-1}. PVA concentrations of 0.5 and 1.0 wt.% resulted in increased viscosities, but the resulting suspensions

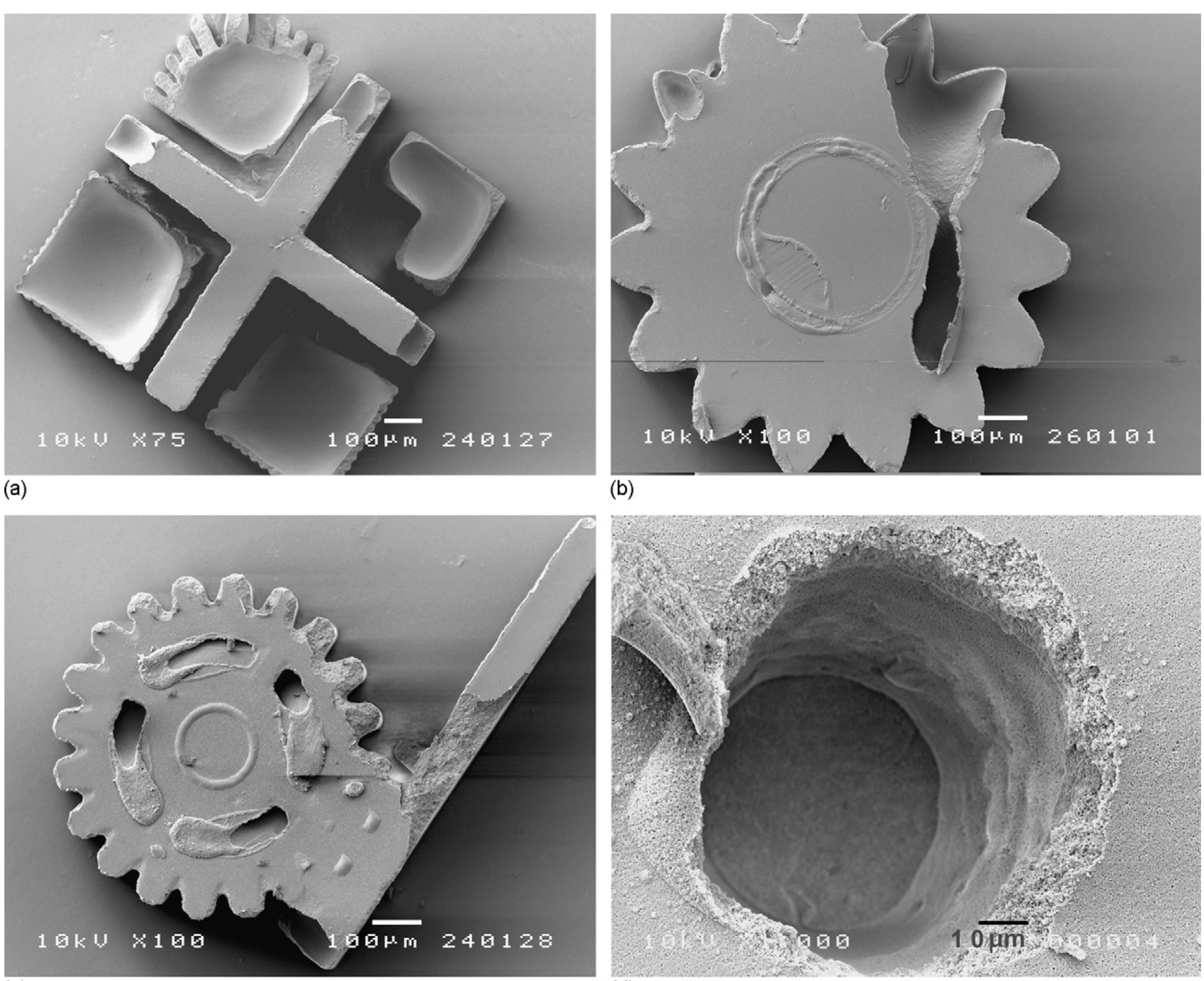

Fig. 2. Some typical defects in the green structures made from 80.0 wt.% suspension of A-16 SG alumina powder with NH_4^+PAA dispersant via microtransfer moulding process.

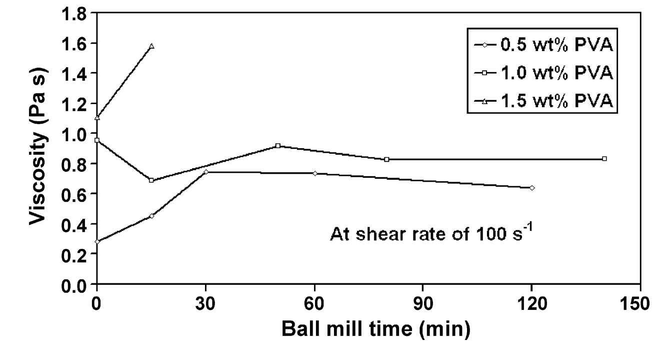

Fig. 3. Effects on the viscosity of different ball mill time with different PVA concentration at shear rate of $100\,s^{-1}$ of 80.0 wt.% suspension with 0.14 wt.% NH_4^+PAA. The viscosity of such suspensions before adding the PVA at $100\,s^{-1}$ was 0.0925 Pa s.

were stable and still suitable for casting. However, a 1.5 wt.% PVA addition resulted in severe flocculation and a large increase in viscosity. The suspension became too viscous for rheological measurement after milling for 15 min. Therefore, 1.0 wt.% PVA was chosen for 80.0 wt.% A-16 SG alumina suspensions in subsequent experiments.

Care has to be taken when adding binder to the suspensions due to the very high solids loadings. Improper addition of binder to the suspension will result in a processing failure. For the CT-3000 SG alumina suspensions, Duramax B-1000 and B-1007 were employed as binders. B-1000 is an aqueous emulsion of an acrylic-based polymer with high molecular weight. As the general functionality of the binder, the emulsion polymer particles are absorbed on the powder surface and act as bridges between the alumina particles, providing interparticle flocculation and a binding action. B-1000 has low glass transition temperature of −25 °C which benefits the green body with improved flexibility. The high molecular weight of the acrylic polymer enables effective adsorption of the residual stress to prevent the possible cracking and inhomogeneous shrinkage of the green body during drying. Particularly, Duramax B-1000 has proven many advantages in the soft moulding processes. Because of its emulsion state and aqueous nature, B-1000 is very convenient to be added in the suspension and does not need to be dissolved in the water first, in contrast to the PVA binder. The emulsion has a high solids loading of acrylic polymer of 55 wt.%, but still a rather low viscosity of 0.11 Pa s at 25 °C, which are important properties for the moulding application. High solids loading of the polymer in the emulsion increases the binding effects in the green body with higher flexural strength and better flexibility. Its low viscosity has little effect on the viscosity of the alumina suspension in contrast to the PVA binder system. In fact, no obvious change of the viscosity was noticed during the soft moulding process after adding 3.0 wt.% B-1000 and 2.0 wt.% B-1007 into the 84.0 wt.% CT-3000 SG alumina suspensions. Thus the utilization of the Duramax emulsion binder system provides great convenience and benefit to the soft moulding process. According to the data sheet of B-1000,[12] other benefits include its insensitivity to moisture variation, clean burnout with very low residue (0.40 wt.% in air) after sintering and similar pH level to the alumina suspension, 9.5 at room temperature, which allows a good stability of the Zeta potential and therefore, the viscosity. In this study, a higher T_g binder, B-1007, was used in the combination of B-1000, as suggested by the supplier, to achieve the optimized green strength and flexibility by adjusting the ratio of the two binders.

3.3. Improvement in green structures

A microgear in the green state produced using a suspension of 80.0 wt.% A-16 SG alumina with 1.0 wt.% PVA via the CASM process is shown in Fig. 4. It can be seen (Fig. 4(a)), that the integrity of the green body was maintained very well after demoulding. Compared to the teeth structures in Fig. 2(b) and (d), much smoother surfaces and sharper edges were obtained after utilizing the centrifuging and the binder system. Fig. 4(b) shows an enlarged view of the teeth structure with clear evidence of the improvement of the green density and edge definition of the microgear, resulting from the higher strength of the green body.

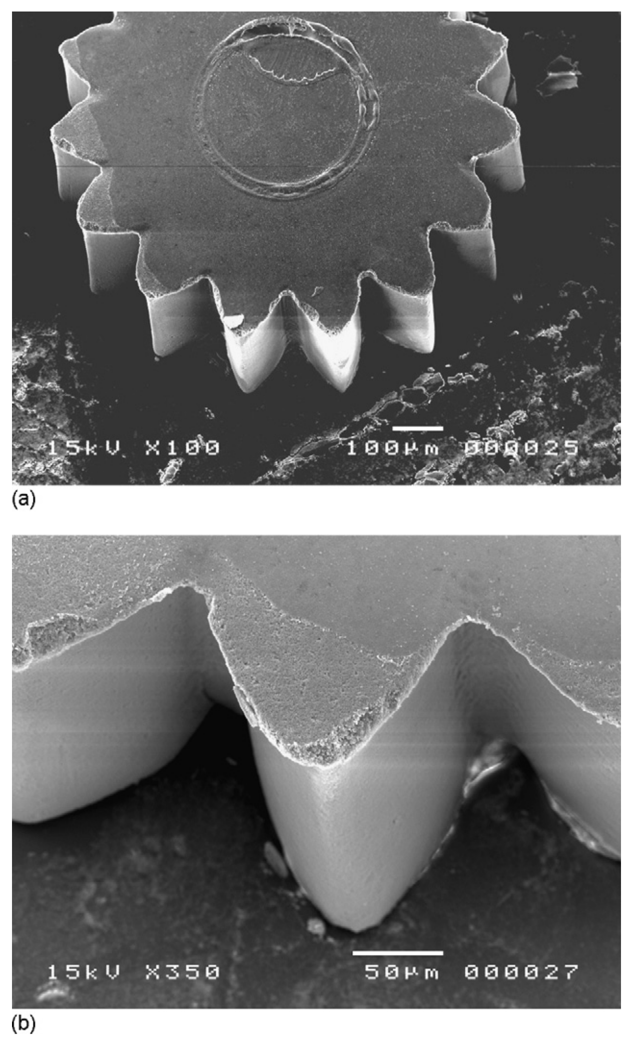

Fig. 4. SEM microscopy of (a) the green body of a microgear structure made from 80.0 wt.% A-16 SG alumina suspension with 0.14 wt.% NH_4^+PAA and 1.0 wt.% PVA via CASM process. (b) Enlarged teeth structures of the microgear green body.

To overcome the defects in the green microcomponents, centrifugal casting was introduced in the soft moulding in order to improve compaction and densify the green body inside the PDMS mould. For processes utilising centrifugal casting followed by an embossing process, the solvent and air separated from the powders tends to congregate inside the PDMS mould, while alumina powders condense towards the substrate, resulting in a concave surface of the final component after drying and sintering. Therefore, in this work, centrifugal casting was combined with microtransfer moulding to obtain microcomponents with even surfaces. As described in centrifugally aided soft moulding (CASM), embossing can be utilized to help the transferring of patterned microstructures to a flat substrate, together with a second round centrifugal casting.

A micropiston in the green state made from 84.0 wt.% CT-3000 SG alumina suspension with 0.20 wt.% D-3021 dispersant and additional 3.0 wt.% B-1000 and 2.0 wt.% B-1007 binders, via centrifugally aided soft moulding (CASM), is shown in Fig. 5. The micropiston exhibits very good integrity with smooth surfaces and good definition, although some small defects are still visible on the surface of the micropiston, as shown in Fig. 5(a) and (b). Some marks on the micropiston wall, as shown in Fig. 5(a), were caused by using the TEM tweezer to clip and hold it.

For the fabrication of a microengine component,[13] the important criteria include surface flatness and smoothness, shrinkage controllability and the assembly compatibility, and these issues become even more critical for the moving parts, like the

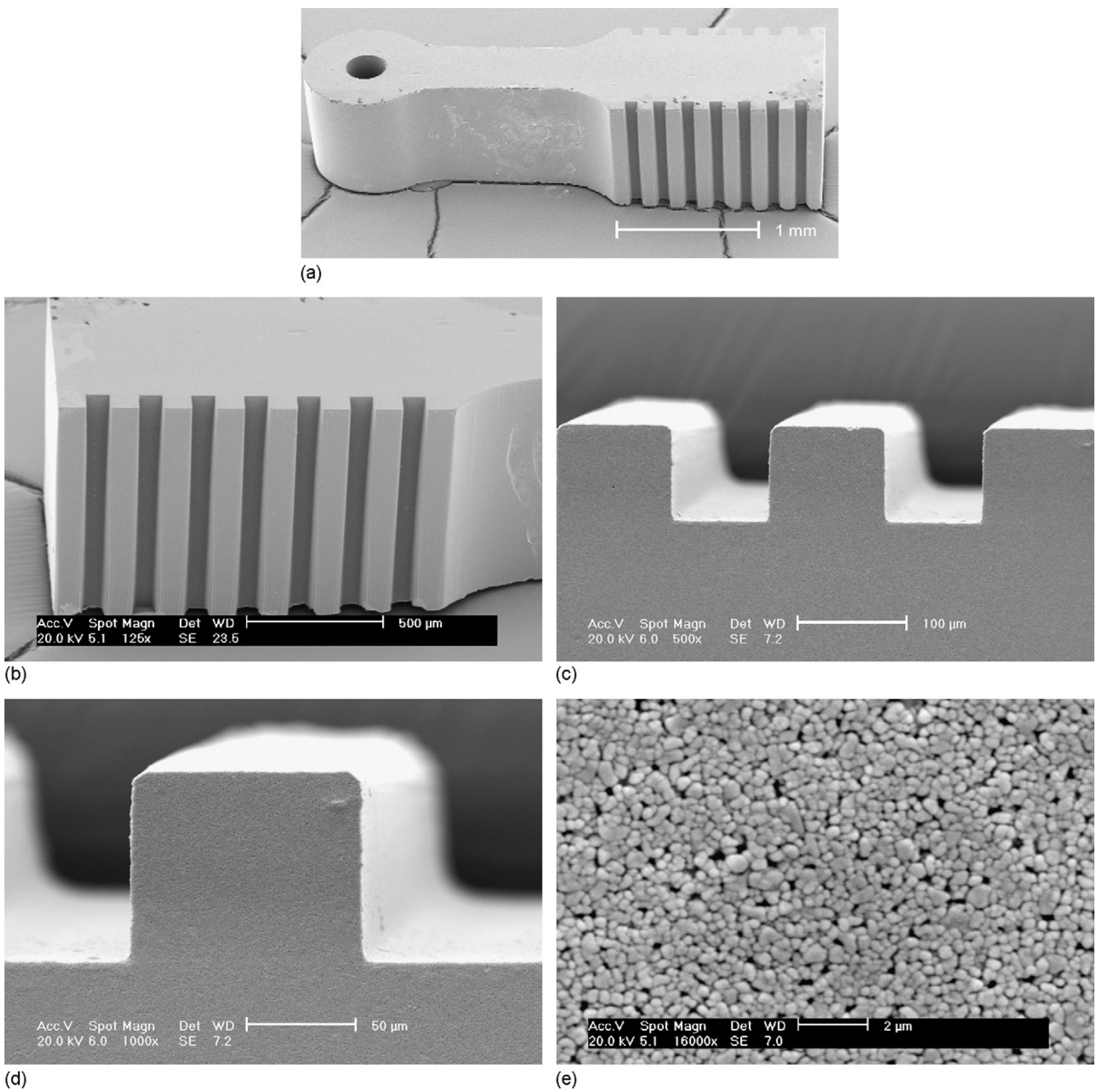

Fig. 5. SEM microscopy of the green body of a micropiston made from 84.0 wt.% CT-3000 SG alumina suspension with 3.0 wt.% B-1000 and 2.0 wt.% B-1007 binders. (a) A complete free standing micropiston; (b) Sealing teeth structures of the micropiston; (c) and (d) Enlarged teeth structures; (e) Surface morphology of the micropiston at a high magnification of 16,000×.

micropiston. As shown in Fig. 5(b), the teeth array used for sealing the combustion chamber shows very well-formed structures with a very high aspect ratio. A little swelling apparent in the middle part of the teeth is due to the distortion of the SEM image as the green ceramics are always apt to the charging problems during the microscopic observation. Two detailed images of the green teeth exhibit very sharp and straight edges, as shown in Fig. 5(c) and (d), identifying that the mechanical strength was high enough to resist the demoulding forces, which was also confirmed by the complete connecting hole of the micropiston in Fig. 5(a). Moreover, for the whole micropiston, no cracking was observed after drying and demoulding, especially at the joints of the teeth and the main body of the micropiston. All the four SEM photos of Fig. 5(a)–(d) show very smooth, even and low-defect surfaces. The high magnification SEM photo of the micropiston surface in Fig. 5(e) shows a highly compacted green body. The homogenous distribution of the alumina powder with an average particle size around 0.7 μm indicated the powder was dispersed very well in the suspension. Therefore, all the results of the green micropiston identified the significant contribution of using the binders and the centrifugal casting in the soft moulding process to the high green strength and good integrity. Worthy of mention again is the high solids loading and well dispersed suspension, which also play equally important roles.

4. Conclusion

A soft moulding process has been described for the fabrication of alumina microcomponents using elastomeric PDMS moulds. Preliminary results of green bodies of microcomponents exhibited low density and strength, and defects related to the entrapment of air bubbles, although high solids loading suspensions were used. An improved centrifugally aided soft moulding (CASM) process was developed by introducing a centrifugal force in the moulding process which, especially with the combination of microtransfer moulding, was found useful in densifying the green body inside the PDMS mould. Binder was also identified as useful for increasing the green strength of the ceramic. Duramax B-1000, together with B-1007, was found very suitable for the soft moulding process. Dense, uniform and complete green microcomponents were obtained. Fine structures in the green body with feature sizes around 100 μm or below, and aspect ratio as high as 10, were obtained.

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