Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 32 (2012) 1199–1204

www.elsevier.com/locate/jeurceramsoc

# Fabrication of ceramic micro-scale hollow components by micro-powder injection moulding

Usama M. Attia [a,*], Jeffrey R. Alcock [b]

[a] Building 56, Cranfield University, Wharley End, Cranfield, Bedfordshire, MK43 0AL, UK
[b] Building 61, Cranfield University, Wharley End, Cranfield, Bedfordshire, MK43 0AL, UK

Received 25 October 2011; accepted 19 November 2011
Available online 10 January 2012

**Abstract**

Rapid developments in microsystem technologies demand ceramic microcomponents of increasing geometrical complexity. State-of-the-art microfabrication routes of ceramics are either limited in geometrical complexity and/or high volume capabilities. This paper presents a process route by which ceramic microcomponents with relatively complex three-dimensional architectures could be realised by a high-volume technique. The proposed strategy, in which yttria-stabilised zirconia was implemented, combines the capabilities of insert-micromoulding, powder micro-overmoulding, catalytic debinding and sintering. The produced architectures demonstrate the capability of the technique to combine the high performance of ceramic materials with the dimensional accuracy and mass manufacturability of powder micromoulding.


*Keywords:* A. Injection moulding; D. $ZrO_2$; Microfabrication; E. Functional applications

## 1. Introduction

Ceramic microsystems are gaining increasing significance in applications, such as healthcare, where properties such as biocompatibility and chemical resistance are desirable. Several fabrication techniques have been developed for producing ceramic micro-components,[1–3] but a major limitation of such techniques is in their ability to produce truly three-dimensional component with relatively complex geometries. The ability to produce precise micro-scale cavities or enclosed channels in ceramic structures is crucial for applications such as microfluidic devices for future chemical and biochemical analysis. Within state-of-the-art technology, such hollow structures are done by lab-scale techniques and usually require post-processing.

One approach to overcoming process limitations on component geometry is to use lost core techniques. For relatively large, 'macro-scale', ceramic components, there has been increased interest in the idea of using lost cores as part of the powder injection moulding (PIM) process, in order to be able to mould internal geometries that could not be produced with slides or cores in conventional moulding.[4–6] However, these routes introduce additional process steps for the addition of the core, and for its removal, and they have not yet been tested for micro-scale components.

Micro-powder injection moulding (μPIM) is a process for producing microcomponents of metallic or ceramic structures. The advantages of the process include shape complexity, replication fidelity, net-shape or near net-shape forming, availability of commercial feedstock for metals and ceramics, and mass-manufacturability.[7] The ability to implement a lost-core approach within a μPIM process to produce micro-scale ceramic components would potentially combine the advantages of shape complexity and mass manufacturability.

μPIM is at an early development stage as a microfabrication technique of ceramics, so there appear to be no comprehensive design rules for lost-core processes based on PIM in general. However, authors have proposed several conditions for a successful lost-core process. One is the necessity of producing a core from a higher melting temperature material than the overmoulded feedstock, in order to improve shape retention. A second is the necessity of avoiding full encapsulation of the core to ensure successful core removal.[6] This paper assesses both

* Corresponding author.
*E-mail addresses:* u.attia@cranfield.ac.uk (U.M. Attia), j.r.alcock@cranfield.ac.uk (J.R. Alcock).

0955-2219/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2011.11.045

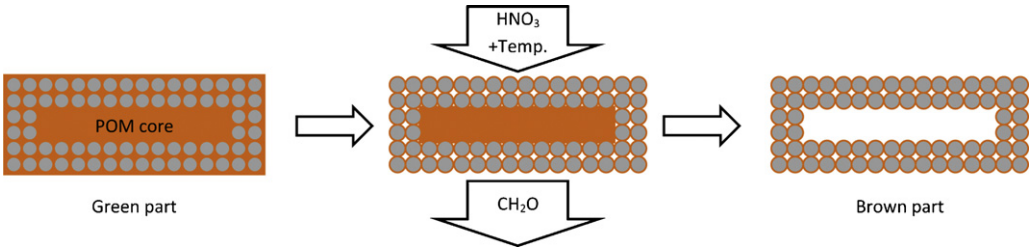


Fig. 1. A schematic illustration of catalytic debinding with a sacrificial core.

conditions through a case study of a ceramic microcomponent with a fully encapsulated polymeric lost core.

## 2. Methodology

### 2.1. Manufacturing principle

The concept behind the fabrication methodology is the ability to "evacuate" a hollow core inside a miniaturised component by catalytic debinding. Fig. 1 illustrates the concept in which a ceramic powder shell is overmoulded over a sacrificial core.

The powder feedstock consists of the ceramic powder mixed with a catalytically debindable polymer, in this case polyoxymethylene (POM). The sacrificial core is made of the same polymer so that both the polymeric content of the powder feedstock and the core could be simultaneously eliminated during catalytic debinding.

During debinding, nitric acid vapour is used to hydrolyse the POM of both the core and the encapsulation material into formaldehyde, which is extracted leaving a hollow core inside the structure.

Catalytic debinding was particularly selected for this route, because it is a direct solid-gas transition process that takes place below the $T_g$ of the polymer. The process, therefore, results in higher dimensional accuracy, tighter tolerances and better surface finish relative to other debinding techniques.[8]

### 2.2. Encapsulation design and technique

For the demonstration of the fabrication principle, the structure selected was a miniaturised cube with a fully enclosed 3-D cavity. A POM core was micromoulded as a 900-μm-side cube with outer radii of 150 μm. The core was then used as an insert inside a mould to overmould one half of a ceramic powder shell. The resulting component was used as an insert in another mould for full encapsulation by the powder shell. This sequential moulding technique was implemented to ensure that the core is placed such that the powder shell thickness is equal on all sides.

To ensure accurate alignment of the POM core within the powder shell, a micro-mould system was designed to hold the core in place during micro powder overmoulding. Fig. 2 illustrates the mould designed for the different stages of the hybrid structure realisation.

## 3. Experiments

The fabrication technique comprises three stages: micro-overmoulding, catalytic debinding and sintering:

*Stage 1*: Polymer micromoulding is used to produce the green hybrid component following the procedure in Fig. 2. Mould inserts were manufactured in hardened steel (Toolox® 33) using a KERN Evo micro-milling machine. A set of cutting micro-tools was used to cut and finish the mould inserts, including a high-aspect ratio tool with a diameter of 300 μm and a cutting length of 2 mm. Finishing was performed with a 300-μm diameter tool, using a spindle rotational speed of 30,000 rpm, a feed-rate of 40 mm/min and a cutting step between 5 and 10 μm, depending on cutting direction. Cutting steps at both vertical and horizontal directions are responsible for the linear texture on the mould walls, which is replicated into the architectures.

Polymer moulding and powder overmoulding were performed using a Battenfeld Microsystem 50 micro-moulding machine. The core was moulded of POM (BASF Ultraform® W2320 003) with melt flow index of 25 to ensure better filling of micro-cavities; the powder feedstock was composed of a mixture of yttria-stabilised zirconia particles with average particle size ($d_{50}$) of 0.3 μm[9] and POM (BASF Catamold® TZP-A). The moulding conditions of both the POM and the PIM feedstock are shown in Table 1.

*Stage 2*: Catalytic debinding took place following the BASF technique[10] at a dwell temperature of 110 °C in high-concentration nitric acid (>98%) at an acid feed of approximately 30 ml/h. Debinding takes place following the shrinking core mechanism illustrated in Fig. 1, by which POM is eliminated layer-by-layer from the outside into the core. Nitrogen was used as a purging gas at a flow rate of approximately 500 l/h. The debinding cycle takes approximately 5–6 h.

After debinding, the structure was composed of a powder form within which there was a hollow cavity.

*Stage 3*: Sintering was conducted following the schedule shown in Table 2, with air as the gaseous environment. The ceramic powder densified to the final shape.

## 4. Results

Figs. 3–5 show the resulting structures of Stages 1–3 described in the previous section, respectively. Fig. 3 shows the encapsulation procedure described in Fig. 2 of Section 2.2.

Fig. 3a and b shows the mould and the replicated POM core respectively. Partial encapsulation of the POM core is shown in

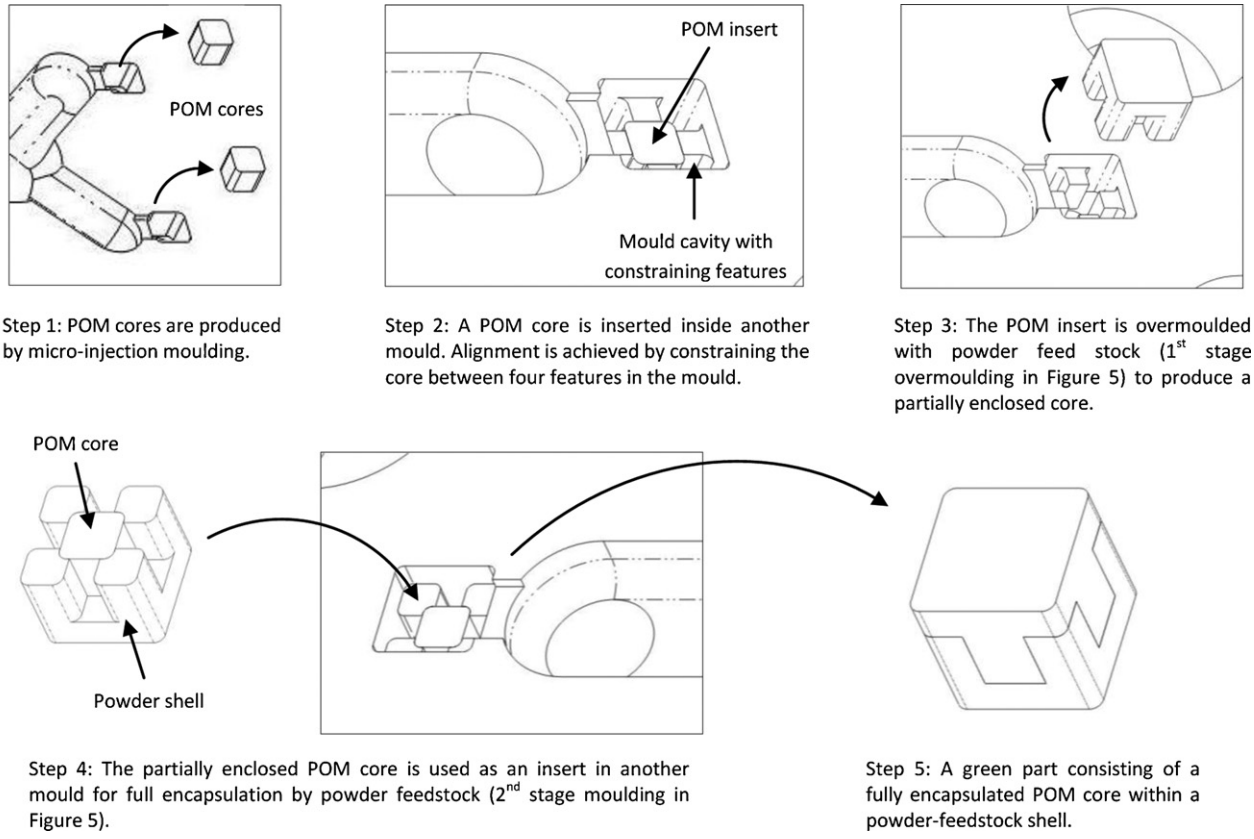


Fig. 2. A schematic diagram of the moulding process of a hybrid structure.

Table 1
Moulding conditions for POM and powder/POM.

| Material | Melt temperature (°C) | Mould temperature (°C) | Holding pressure (bar) | Injection velocity (mm/s) | Cooling time (s) |
|---|---|---|---|---|---|
| POM | 190 | 100 | 300 | 250 | 10 |
| Powder/POM | 190 | 140 | 300 | 250 | 10 |

Fig. 3c and d, where the former shows the encapsulation mould, and latter shows the partially encapsulated core in a ceramic powder shell. Fig. 3c shows how the mould was designed with four constraining features to secure the central positioning of the POM core inside the powder shell. Full encapsulation is shown in Fig. 3e and f, where the former shows the third, and final, mould cavity, and the latter shows the fully encapsulated green zirconia "cube". Fig. 3g shows a cross section in the hybrid green cube.

Table 2
Typical sintering schedule for zirconia debound structures.

| Stage | Schedule |
|---|---|
| 1 | From room temperature to 270 °C at the rate of 3 °C/min |
| 2 | Hold at 270 °C for 1 h |
| 3 | From 270 °C to 1500 °C at the rate of 3 °C/min |
| 4 | Hold at 1500 °C for 1 h |
| 5 | From 1500 °C to 600 °C at the rate of 5 °C/min |
| 6 | Furnace cooling |

Fig. 4 shows the "brown" components after catalytic debinding. Fig. 4a shows an image of the full and sectioned parts. Fig. 4b shows an ESEM image of a debound sectioned component, where no traces of the polymeric core are left.

Fig. 5 shows a cross section in the final 'brown' component after sintering. The image shows the hollow core at the centre of the cube.

## 5. Discussion

The results illustrated in Fig. 3 show that the micro-overmoulding based fabrication route is a viable process for introducing sacrificial cores in ceramic powder moulding. One of the precautions suggested in the literature on lost-core techniques in using the same polymer (POM) for both the powder matrix and the core is the likeliness of deformation at the interface due to the similar thermal properties.[6] However, this was not observed during processing, and the cross section in Fig. 3g shows a hybrid green component with good shape retention, especially at the round corners, and clear boundaries between the powder shell and the polymer core.

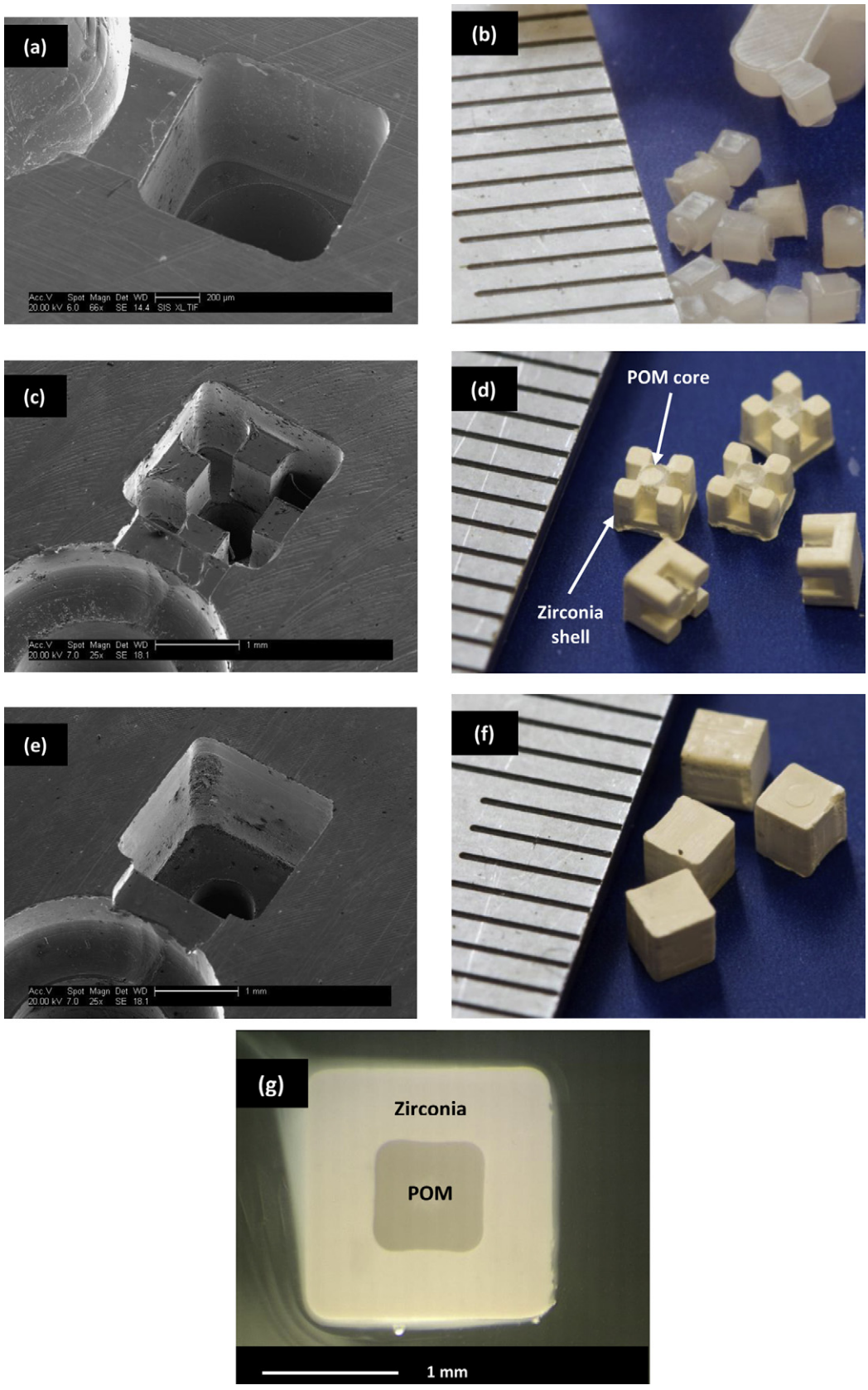


Fig. 3. Steps for producing fully encapsulated hybrid green ceramic component. (a) An SEM image of the core insert. (b) A selection of replicated POM cores, some attached to their sprue. (c) An SEM image of a mould insert with constraining features to position the core. (d) A partially encapsulated POM core in a zirconia powder shell. (e) A mould insert for final encapsulation stage. (f) An image of a zirconia parts with fully encapsulated POM core. (g) A cross section in a hybrid green component.

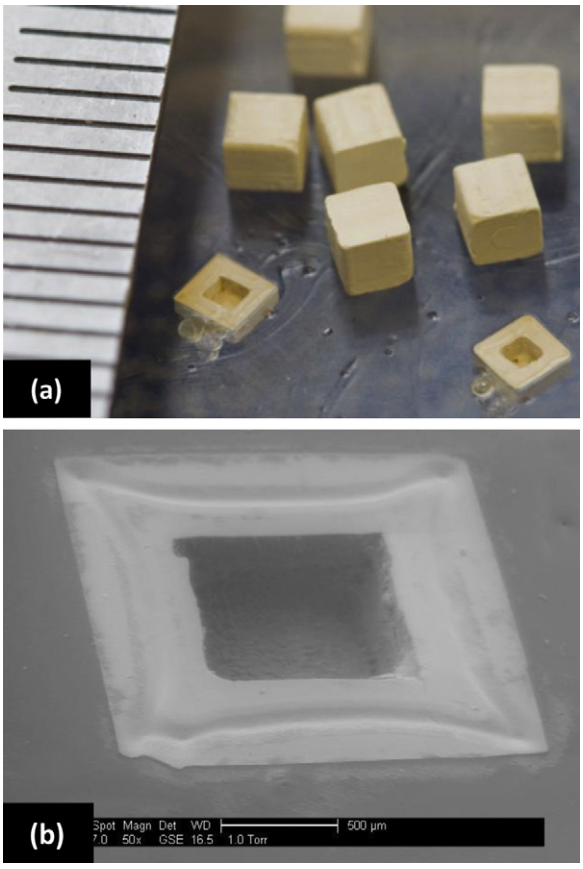


Fig. 4. (a) An image of debinded components before sectioning and after sectioning whilst immersed in resin. (b) An ESEM image of a sectioned brown component showing the hollow core.

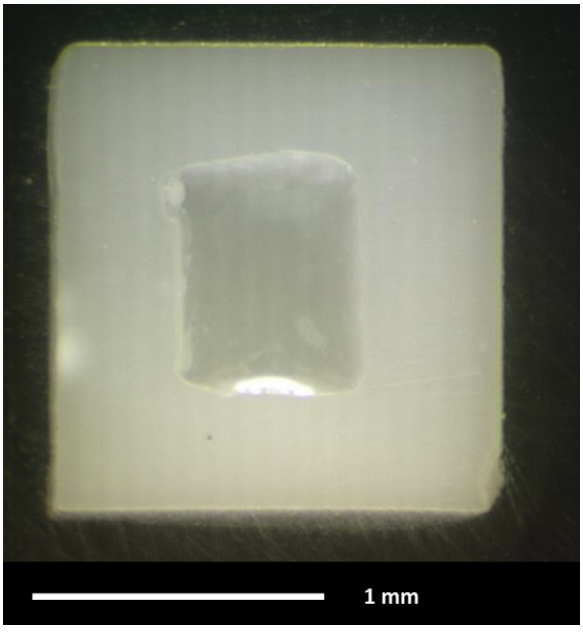


Fig. 5. Core removal by catalytic debinding and sintering: an optical micrograph of a cross section of a sintered metallic architecture.

As for the debinding stage, Fig. 4 shows that the manufacturing principle detailed in Section 2.1 is viable for producing enclosed cavities. The images show that the core was totally consumed whilst the overall component retains its geometry. Other than a few defects inherited from the moulding process, such as the broken-gate remains or ejection-pin marks, the debinding process did not distort the geometrical integrity of the hollow component.

The sintered component illustrated in Fig. 5 shows the cavity maintained in the structure. No visible signs of slumpage or deterioration have been detected, and shape retention appears of high quality. Again no signs of particular problems related to full cavity encapsulation were observed.

Fig. 5 indicates the feasibility of the presented process chain in producing ceramic components with internal micro-scale cavities. This approach should enable the development of micro-components that are not viable using state-of-the-art technology. The approach could be used for producing ceramic microfluidic devices with controlled channel dimensions without the need for attaching a lid in post processing as is typically done with current manufacturing techniques.

It should be noted, however, that the fabrication strategy has a number of limitations. Firstly, knowing that the hollow core was originally a moulded polymer, the geometry of the core is limited by moulding design rules, such as demouldability and maximum aspect ratio.[11] Secondly, considering the powder shell, the shell size is limited by the particle size, as it's recommended that the minimum feature size should be at least 10–20 times the particle size.[12,13] In addition, in case the presented technique is used to produce long, tube like cavities, e.g. microfluidics, there will be relatively long unsupported areas that are likely to sag during debinding and/or sintering. This needs to be considered in part design.

## 6. Conclusion

This paper aimed at presenting a manufacturing route for producing ceramic microcomponents with hollow structures. The fabrication technique combines the advantages of micro-powder over-moulding and catalytic debinding. A fully encapsulated micro-component was used as a demonstrator for the methodology. Three-dimensional micro-scale cavities were successfully fabricated in zirconia. The technology presented in this paper establishes a fabrication route for ceramic microsystem components with complex cavities for use as micro-engines or high-performance microfluidics.

## Acknowledgments

The authors would like to thank the EPSRC and the Cranfield IMRC for their support of this work. They would also like to acknowledge Dynamic-Ceramic Ltd. for their assistance with the sintering of the debound forms.

## References


1. Khoong LE, Tan YM, Lam YC. Overview on fabrication of three-dimensional structures in multi-layer ceramic substrate. *J Eur Ceram Soc* 2010;**30**:1973–87.
2. Zhu Z, Hassanin H, Jiang K. A soft moulding process for manufacture of net-shape ceramic microcomponents. *Int J Adv Manuf Technol* 2010;**47**: 147–52.
3. Liu F-H, Liao Y-S. Fabrication of inner complex ceramic parts by selective laser gelling. *J Eur Ceram Soc* 2010;**30**:3283–9.
4. Chartier T, Delhomme E, Baumard JF, Veltl G, Ducloux F. Injection moulding of hollow silicon nitride parts using fusible alloy cores. *Ceram Int* 2001;**27**:821–7.
5. Anonymous. PM2010: case studies highlight global successes of metal and ceramic injection moulding. *PIM Int* 2010;**4**:48–54.
6. Zhang SX, Ong ZY, Li T, Li QF, Ng FL. Feasibility study on producing components with embedded channel by powder injection moulding. *Key Eng Mater* 2010;**447–448**:401–5.
7. Attia UM, Alcock JR. A review of micro-powder injection moulding as a microfabrication technique. *J Micromech Microeng* 2011:21 [art. no.: 043001].
8. German RM. A rationalization of the powder injection molding process for stainless steels based on component feature. In: *International conference and exhibition on powder metallurgy and particulate materials*. 1999.
9. Krug S, Evans JRG, ter Maat JHH. Differential sintering in ceramic injection moulding: particle orientation effects. *J Eur Ceram Soc* 2002;**22**:173–81.
10. Bloemacher M, Weinand D. Catamold – a new direction for powder injection molding. *J Mater Process Technol* 1997;**63**:918–22.
11. Attia UM, Marson S, Alcock JR. Micro-injection moulding of polymer microfluidic devices. *Microfluid Nanofluid* 2009;**7**:1–28.
12. Piotter V, Finnah G, Oerlygsson G, Ruprecht R, Haußelt J. Special variants and simulation of micro injection moulding. In: *Injection moulding 2005: collected papers of the 5th international conference*. 2005.
13. German RM. Medical and dental applications for microminiature powder injection moulding (microPIM) – a roadmap for growth. *PIM Int* 2009;**3**:21–9.