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Micropatterning of ceramics by slip pressing

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Abstract

Slip pressing is a modified pressure assisted slip casting method for the fabrication of ceramic microcomponents. By this method a ceramic slip is consolidated in a special compaction tool containing a nonporous mould. A porous piston which at the same time serves as a filter, enables the liquid to be pressed out and the remaining powder to be compacted simultanously. Thus the liquid transport is not performed through the mould and a nonporous mould can be used, as suited porous moulds for microcomponents are not available. Al_2O_3 slips and PMMA moulds were used in this process for the micropatterning of column and nozzles structures with a size of some ten microns and aspect ratios of more than 20.

1. Introduction

At present microsystem technology uses primarily silicon, polymers or metals which can be deposited by either thin film techniques, plastic forming or by galvanoforming. If special properties such as mechanical, thermal or chemical resistance or piezoelectric effects are required, ceramic materials can offer new fields of applications.

Considering a microshaped component with internal dimensions in the range of micrometers, it is obvious that precision and homogenity must fulfil enhanced requirements. Therefore submicron or nanosized powders should be used for the ceramic shaping process. The properties of such powders are dominated mainly by the formation of agglomerates. Best shaping results are achieved by wet processing technologies [1] where the interparticle forces are controlled in a liquid dispersion. Slip casting is the most established example for wet processing, provided a porous mould is available. The moulds which are available for microcomponents are generally nonporous metal or polymer tools and hence slip casting in its tradtional form is impossible.

The following paper describes a modification of pressure slip casting that enables the manufacturing of ceramic microcomponents using nonporous moulds. In this method a slip is consolidated in a modified powder pressing die. The separation of the liquid is performed via a permeable piston which simultanously densifies the remanent powder particles into an inserted dense mould. During consolidation a densification front starts at the piston and moves in the direction of the mould whereas the liquid is removed in the opposite direction. This mechanism is opposite to slip casting and is comparable to a pressing process. Therefore it is more appropiate to describe the process by means of a pressing method and subsequently this shape forming method is named *slip pressing*.

2. Description of the method

Usually a ceramic powder, which is prepared for dry compaction, contains a certain amount of humidity. Humidity is advantageous for lubrication, but it also favours agglomeration of the particles, leading to insufficient flowability of the powder and preventing the complete filling of complex shaped moulds. For this reason and because of friction forces acting internally in the powder as well as between the powder and the large surface of the mould, dry pressing is not a favourable method for the shaping of microcomponents with high aspect ratios. Using a dispersion, it is possible to destroy weak agglomerates and to eliminate strong agglomerates [1]. If dispersions are dried, the agglomerates will rearrange. For that reason the consolidation should be accomplished directly from the slip. In addition, slips

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exhibit good flow characteristics and usually fill the cavities without the application of pressure. Producing a shaped body from a slip is possible by concentrating the solid by removal of the liquid. In slip casting a permeable mould having a particular shape, is used for that reason. Driving forces are the capillary suction of the mould or an external pressure applied to the slip. Moulds for microcomponents are commonly made from plastics or metals, shaped by injection moulding, galvanoforming or micromachining [2]. They have no permeability and the separation of the liquid must be performed in another way. In slip pressing, a filtering device which is permeable only for the liquid, is inserted between the slip and a piston with a central duct (Fig. 1) [3,4]. Pressing the piston, the liquid is forced through the filter and the duct and simultanously the remanent powder is being compacted. Shaping is performed by a mould which is inserted into the pressing die. As with this method a transport of the liquid through the mould is not necessary, the mould can be made from a non-porous material.

The compact must withstand the drying shrinkage, ejection and further handling without fracture. As the green strength of the compact is strongly reduced by the liquid, a sufficient drying is necessary before the body can be ejected. With pressure, a removal of the liquid is only possible until the particles contact each other. Additional drying is performed by warming the die and by removing the evaporating gas through the duct using a pump.

3. Slip preparation

In order to replicate components with structural dimensions in the micron range, it is necessary to use a ceramic powder, whose particle size should be at least about one order of magnitude smaller than the minimum internal dimensions of the components. For the production of alumina parts, a submicron powder with a particle size of 0.35 μm has been used (A16SG Alcoa Industrial Chemicals, Pittsburgh, PA, USA, BET-surface area = 8–11 m2/g, purity = 99.8 %). As the polymer moulds are sensitve against organic solvents, only aqueous slips could be taken into account. The dispersant used was polyacrylic acid (PAA) with a molecular weight of 2000 (Aldrich-Chemie GmbH & Co. KG, Steinheim, DE) [5]. The slips were dispersed with an Ultra Turrax and subsequently homogenized with a laboratory mixer. A binder was added for increasing the green strength and therefore reducing the probability of crack formation. Polyvinylpyrrolidone (PVP, Fluka Chemie AG, Buchs, CH) is a binder which effects a neglectable change of viscosity, compared to standard polyvinylacohol (PVA) or cellulose based binders (Fig. 2). Using PVP, highly concentrated slips can be prepared without loosing flowability, even when a high molecular type PVP is added, which has the best binder properties.

At high solid concentrations even small additions of binder lead to a large increase in the viscosity and the handling e.g. the de-gasing of these slips, will become complicated. On the other hand, the solid concentration should be as high as possible because this will result in a higher green density (Fig. 3). In comparision with that, the influence of the compaction pressure on the green density is neglectable. Al_2O_3-slips with sufficient flowability have been prepared with solid concentrations up to 50 vol%. The viscosity of these slips was less than 100 mPas, even after the addition of the PVP binder.

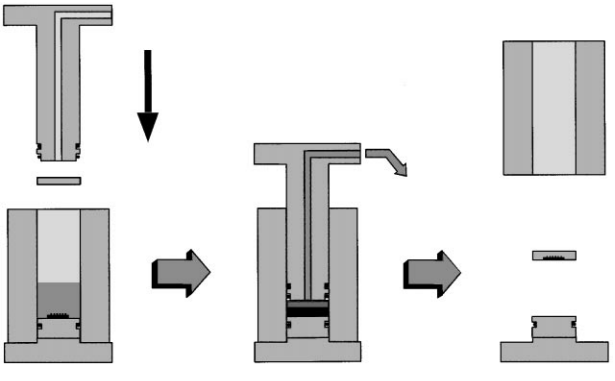

Fig. 1. Schematic description of slip pressing.

4. Shaping

Consolidation was performed in a cylindrical die with an inner diameter of 32 mm. Due to the buoyancy of plastic materials in the slip, the mould must be slightly fixed at the bottom of the die. The piston closing the die has a central duct, which is leading to the outer side. Between the piston and the slip a filtering device is inserted, which is composed of a partially sintered steel disk, backed with a solid steel disk containing larger holes and a 0.2 μm nuclepore foil. An O-ring seals the

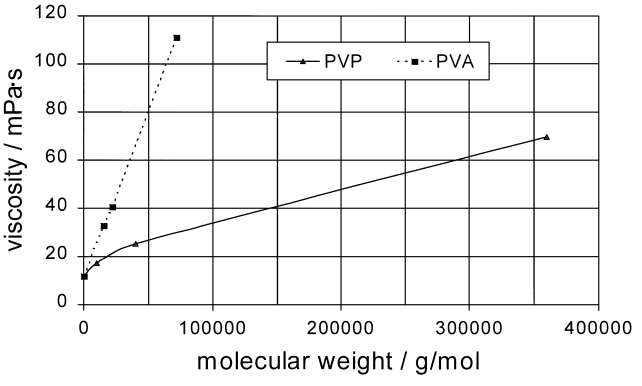

Fig. 2. Viscosity of Al_2O_3 slips vs molecular weight of the binder, 75 wt % Al_2O_3, 1M % binder (dry weight base of Al_2O_3).

filter from the outer cylinder. This equipment reliably holds back fine particles even at a pressure of more than 30 MPa. As a filter cake quickly forms in the initiate state of pressing, the device could be used even for higher pressures and for particles which are smaller than the pore sizes of the installed filter. Nethertheless a limitation of the appliable pressure is given by the strength of the plastic mould. A patterned PMMA mould will be damaged at pressures less than 20 MPa. In a well dispersed slip, however, the particles pack to their optimum density at relatively low pressures and consolidation is nearly independent of the applied pressure. With optimized slips sufficient densification can be obtained even at pressures below 10 MPa. A reduction of pressure is also favourable as less elastic energy is stored in the compact. When the load is removed the strain relaxation produces an increase in the dimensions, called springback. Different Youngs moduli of die, compact and plastic mould can cause cracks in the powder compact if the load was too high. The tendency for defects can be decreased also by a reduction of the load removing rate. As optimum load reducing rates were found to range from 0.001 to 0.05 MPa/s, load reduction dominates the processing time when a high compacting pressure is necessary.

At the intitial state the kinetics of slip pressing is determined by the mutual permeability of the filter and the consolidation layer which is formed next to the filter. It is assumed that a sharp demarcation exists between the layer, where the particles are fixed in a loose network and the dispersed slip where they are still free-flowing. When the demarcation has reached the mould, further consolidation takes place by rearrangement of the deposited particles.

While a network formed by attractive interparticle forces is more difficult to rearrange, particles with repulsive forces can slide around each other, even after they are in contact. Rearrangement is also supported by the liquid in the pores and by the organic additives, which act as a lubricant. Therefore in slip pressed bodies green densities of more than 65 % th.d. are obtained, which is much higher than in a dry pressed compact from the same powder (55-60 % th.d.). In addition, pressure gradients in the powder compact are reduced by consolidation from a slip. The densification of the network starts at the highest patterns of the mould. Without the capability of rearrangement, only insufficient densification will take place within deeper cavities. Slip pressing allows the densification of microshaped patterns to a depth of more than 1 mm, even at low pressures and nearly independent of the aspect ratio of the mould.

After consolidation the compact still contains a certain amount of liquid which cannot be removed by mechanical means only. This humidity significantly decreases the strength of the green compact [6]. In order to increase the crack resistance of the green body, its water content should be further reduced before demoulding. Further drying is performed by warming the die with an external heating device and by evacuating it through the piston. For careful drying, the temperature should be slightly below the the boiling point of water, e.g. 55°C at 200 hPa. The drying time is proportional to the thickness of the compact. For thin shaped parts it can be part of a necessary reloading time, but thicker parts require an additional drying step, which normally exceeds 1 h for parts with a thickness of 1 mm. Another reason for long drying times are the organic additives which are clogging the filter. If the binder content in the slip is too high, the filter will be blocked nearly completly and drying is getting impossible within tolerable times.

5. De-moulding

In contrast to conventional products, green microcomponents often adhere firmly to the mould. Thus, the pressed body has to be ejected from the die together with the mould. Separation of the mould can be performed by mechanical means and if plastic moulds are used, by thermal or chemical means (Fig. 4). Other

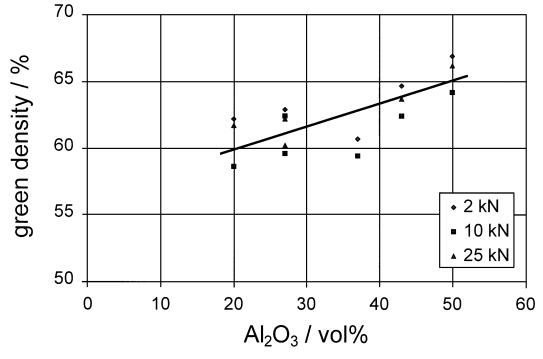

Fig. 3. Green density of suppressed bodies vs solid concentration of the alurnina slips at different loads.

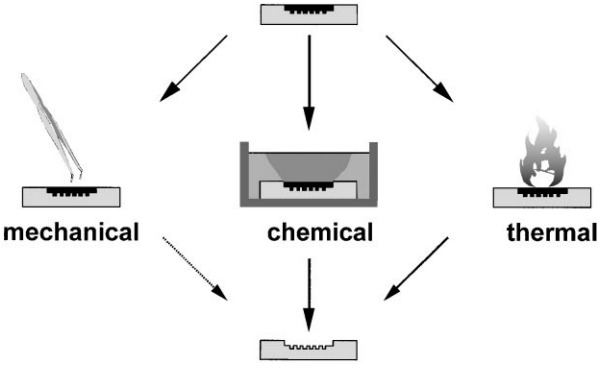

Fig. 4. De-moulding procedures for micropatterns.

methods, like O_2 plasma etching [7], have prototype character or are too time-consuming and expensive for a standard process. Mechanical pulling out should be favoured because it allows the reutilization of the mould, whereas thermical and chemical de-moulding are lost mould techniques. Unfortunately in most cases it is not possible to pull out the mould mechanically without damaging the unfired patterns. Thus using lost moulds is unavoidable. The production of lost moulds in a sufficient quantity can be done by injection moulding. By that the material of the mould will be determined by its suitability for injection moulding and not by its demoulding properties.

PMMA is the material mainly used for microshaped polymer parts. By using thermal de-moulding, the PMMA is copyrolyzed with the organic slip additives. In this temperature range it forms a melt, which is turbulently moving because of the evaporation of monomer. Since simultaneously the binder strength is decreasing, sensitive structures will be damaged in most cases. Thermal de-moulding is therefore limited to rather insensitive patterns.

Chemical de-moulding is practicable if a solvent is used that solves only the mould, but doesn't remove the binder. That condition is fulfilled by a lot of organic solvents, if a watersoluble binder is used for the slip. Unfortunately plastics tend to swell when they are dissolved. Therefore a low molecular solvent with reduced swelling tendency should be used to prevent the damage of patterns. In the case of PMMA moulds, it was found that the most appropriate method for the demoulding is a chemical de-moulding by solving the PMMA in acetone.

6. Sintering

After chemical de-moulding no thermal step for the mould burnout is neccessary. The green bodies were heated to 600°C in air at 1 K/min in order to remove the binder and other organics and subsequently sintered at 1500°C with a ramp of 2 K/min and 1 h soaking time. Sintered density of the alumina was about 99% of theoretical, measured by the Archimedes principle in water. The sintering shrinkage depends on the solid concentration of the used slip, usually the linear shrinkage ranged from 12 to 18%.

7. Results

Originally designed for a piezoelectric composite transducer, an array of columns can also be used as a testing device for the development of micropatterning methods. The unsupported columns react very sensitive upon detrimental loads, especially in the unfired state. Using slip pressing, arrays of more than thousand columns have been prepared with smooth sidewalls and sharp edges. In Fig. 5 a section of an array of microdimensional columns is shown. One broken column is lying on the tops of intact columns. It shows that the sintered columns are 455 μm high and 115 μm wide.

An application for slip pressing is the fabrication of microdimensional ceramic profile nozzles (Fig. 6). The described method has the ability to prepare complex profiles which cannot be realized by mechanical machining. An example are spinnerets for the manufacturing of man-made fibers. With high wear and chemical resistance, the use of ceramic nozzles is a measure effective in delaying nozzle corrosion. Compared to recently used stainless steels and noble metals a longer lifetime will result with these materials. After pressing and sintering, the bottom of the blind hole structure has to be removed by grinding. This step improves the quality of the nozzle, because smooth surfaces and

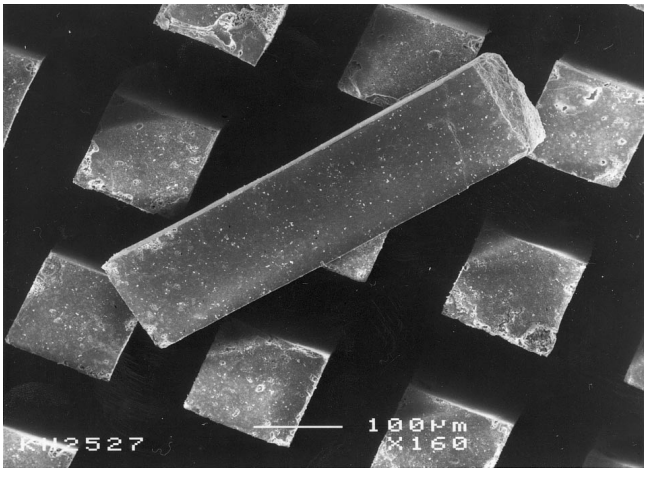

Fig. 5. SEM micrograph of an Al_2O_3 column array.

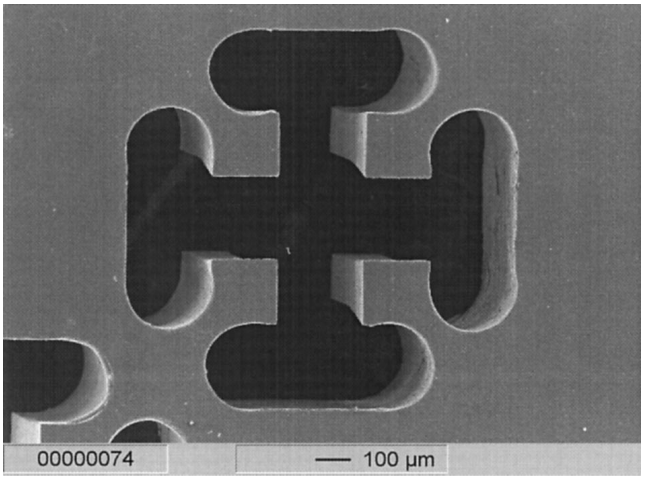

Fig. 6. SEM micrograph of an Al_2O_3 profile nozzle.

edges without burrs are obtained. Nozzles were prepared with structural heights of more than 1 mm and smallest wall thicknesses of about 20 μm.

8. Conclusion

Slip pressing was developed as a shaping method for the production of ceramic microcomponents. It allows the manufacturing of three-dimensional structures with high aspect ratios. With alumina samples, structures with a size of some ten microns and aspect ratios of more than 20 have already been realized. Due to the low compaction pressures, upscaling should be possible to a size of about 100 cm^2 . However, the pressing of parts whose wall thickness exceeds a few millimeters becomes rather time consuming. Slip pressing is therefore best suited for the patterning of disk-like substrates.

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