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Ceramic microstructures and potential applications

R. Knitter, E. Günther, C. Odemer, U. Maciejewski

Abstract The developed process of tape casting with subsequent stamping is a promising way to make three-dimensional ceramic microstructures. Examples of different ceramic materials illustrate, that a good quality of the moulding with high form fit can be attained after optimisation of the slurry and the stamping process. The sintered microstructures are characterised by lateral dimensions in the micron range and high aspect ratios. The unique properties of ceramic materials in combination with this new process can be used to produce microstructured ultrasonic transducers or micro heat exchangers/reactors.

1 Introduction

In contrast to microelectronics the structures of microsystems often require a high ratio of structure height to lateral dimension (aspect ratio). Very high aspect ratios can be realised by the LIGA-process (x-ray lithography, electroplating and moulding) (Bley and Menz, 1991), but it is only possible to produce structures out of metal or plastics. The use of metallic or plastic microstructures within microsystems is limited, when high chemical or thermal resistance or special properties, (e.g. piezoelectricity), are required. In these cases ceramic microstructures can open new fields of applications. The preparation of a cross-flow micro heat exchanger and of a microstructured ultrasonic transducer with a design of a 1–3 composite will be used in this paper to demonstrate such applications.

2 Experimental

For the fabrication of ceramic microstructures the demands upon powder preparation and preprocessing are particularly high. Considering the lateral dimensions of microstructures in the micron range, it becomes evident, that the starting powder must be chemically homogeneous and have a particle size, small enough to achieve a good moulding (Knitter et al., 1994). The presented process is based on the Doctor-Blade-Process (Williams, 1976), which is widely used in electronics for the preparation of thin substrates. In this process the ceramic powder is suspended in a solvent, mixed with suitable organic additives and then cast to thin, flexible tapes. After stamping these tapes with microstructured metallic dies the organics are burnt out during dewaxing and densification is achieved by sintering. Figure 1 gives a schematical running of the whole process.

2.1 Powder preprocessing

Yttria stabilised zirconia with an addition of 20 wt % alumina (Y–ZrO_2/Al_2O_3, TZ–3Y20A, TOSOH), and lead zirconate titanate (PZT) ($Pb(Zr_{0.54}Ti_{0.46})O_3$) were used as starting materials for the micro heat exchanger and the micro ultrasonic transducer respectively. The zirconia/alumina powder was milled in ethanol for 24 h to destroy the granules. The mean particle size was thereby reduced from 50 to 1 μm but due to the porosity of the spray dried granules the specific surface area of about 15 m^2/g remained unchanged. According to the supplier the grain size was only about 30 nm.

The piezoceramic powder was prepared from Pb-acetate ($Pb(CH_3CO_2)_4$), Zr-propylate ($Zr(C_3H_7O)_4$) and Ti-ethylate ($Ti(C_2H_5O)_4$) by a thermal two-stage process and subsequently calcined at 650 °C/5 h (Günther and Maciejewski, 1994). The particle size of the given granules was reduced to about 0.8 μm by milling for 24 h.

2.2 Slurry preparation

Various amounts of the ceramic powders were mixed with organic additives to form stable suspensions. In all samples ethanol was used as a solvent, polyvinyl butyral (PVB, WACKER CHEMIE) as a binder, dibutyl phthalate (DBP, BIESTERFELD) as a plasticizer and a dispersant (KV 9021, KV 9027, ZSCHIMMER & SCHWARZ) was added. At first the ceramic powder, the solvent and the dispersant were ballmilled and subsequently the plasticizer and binder were dispersed. These slurries were cast on glass plates, levelled to a thickness of about 500 μm and allowed to dry for at least 12 h under ambient conditions. After evaporation of the solvent the amount of ceramic powder in the tape was between 78 and 86 wt % for Y–ZrO_2/Al_2O_3 and between 84 and 90 wt % for the piezoceramics. After drying the tapes were removed from the plates and cut into smaller pieces. For the moulding of dies with particularly large structure heights, up to 4 individual tapes were stacked upon each other and pressed with 80 N/mm^2.

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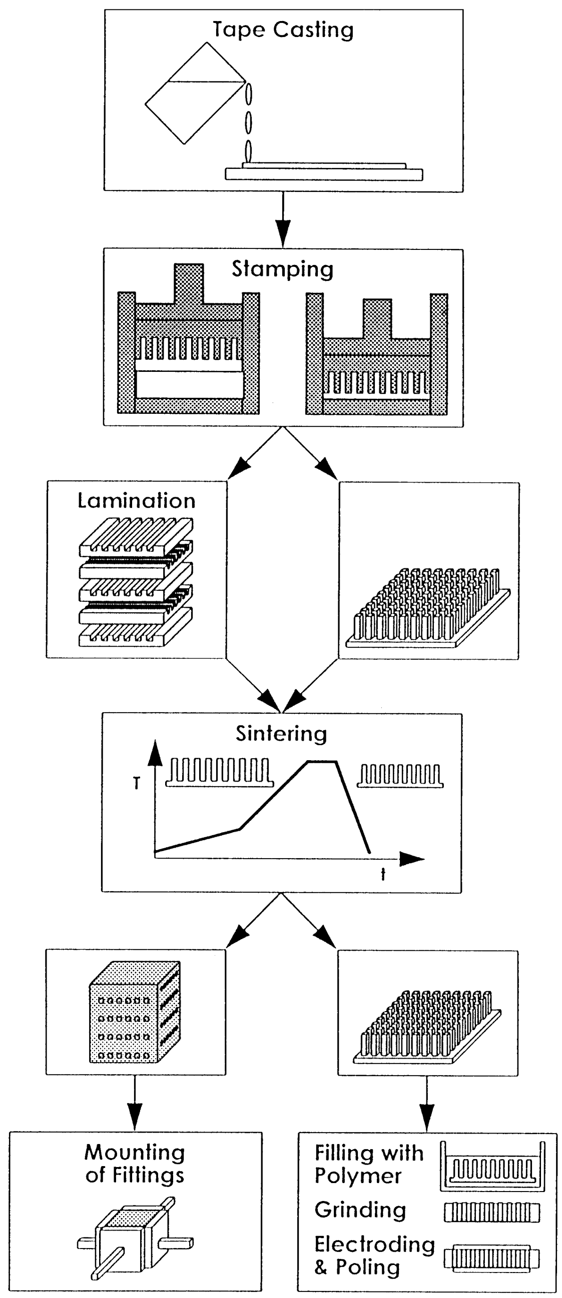

Fig. 1. Schematic representation of the preparation of micro heat exchangers and micro ultrasonic transducers

2.3
Structuring by stamping

For the stamping of tapes used for the micro heat exchanger microstructured metallic plates produced by mechanical microfabrication (Bier et al., 1991) were used as dies. These dies have groove dimensions between 50 and 200 μm and heights of up to 300 μm. To obtain an array of PZT square columns by stamping, a metallic mould was prepared, in the shape of the desired ceramic part. This metallic mould was used to make nickel negative structures via microelectromoulding. These Ni-moulds exhibit a structure height of 550 μm and square indentations with a side length of about 120 μm. The macroscopic dimensions of the structured area were in both cases about $20 \times 20\,mm^2$.

The dies were wetted with water or stearic acid as the mould release agent. Stamping was performed with pressures between 40 and 200 N/mm^2. For the preparation of the heat exchanger, the individual tapes were wetted with ethanol on the non-structured side and crosswise laminated and slightly pressed.

2.4
Thermal treatment

In order to determine the temperature for dewaxing, the decomposition of the organic additives was studied by thermogravimetry. The dispersant is burnt out in three steps in the range from 150 to 530 °C. After the loss of the plasticizer at 280 °C, the binder decomposes in at least two steps up to 550 °C. At this temperature constant weight is achieved hence a rate of only 6 °C/h was chosen for dewaxing up to 600 °C and then the samples were heated up to sintering temperature with a rate of 60 °C/h. Sintering was performed in air up to 1450 °C and 1200 °C for 1 h for zirconia/alumina and PZT, respectively.

3
Results

The moulding results were significantly influenced by the variation of the ceramic fraction and the stamping pressure (Knitter et al., 1994). The ceramic fraction has to be as high as possible to minimise the linear shrinkage and to obtain a good form fit after sintering. A high stamping pressure is necessary to yield a good filling of the mould but the separation from the die becomes more difficult. After sintering the density of the samples were measured by Hg-porosimetry. Values of 97% and 94% of the theoretical density (th.d.) were determined for $Y\text{–}ZrO_2/Al_2O_3$ and PZT samples, respectively. A linear shrinkage of 20–26% was observed for the samples, depending on the ceramic fraction of the tapes. Despite of the large surfaces no Pb-loss was determined for the PZT samples.

Due to the low aspect ratio of the microstructure needed for the heat exchange, a good moulding quality and high form fit of these $Y\text{–}ZrO_2/Al_2O_3$ tapes were soon attained after optimisation of the stamping pressure. Figure 2 shows an individual sintered tape with grooves of about 160 μm. The very good moulding results and surface quality of this material has been demonstrated earlier by much more complex microstructures (Knitter and Odemer, 1994). A difficult step of the preparation is the sintering of the laminated tapes. For the later use, it is absolutely necessary that no connections exist from one passage to the other. The stack of tapes has to be pressed before sintering without destroying the fine microstructures. During sintering it is also favourable to apply an external compressive force to ensure the sintering of the individual tapes. The experiments showed that it is possible to control the sintering so that the two passages are separated entirely. Nevertheless individual grooves were not always closed by sintering. If the sintering is successful it is not possible to distinguish the structured from the non-structured side of the tape (Fig. 3).

First experiments for the ultrasonic transducer showed that a pressure of about 45 N/mm^2 chosen at the beginning was not sufficient to fill up the mould entirely and a structure height of only about 160 μm was achieved after sintering (Fig. 4a). By increasing the stamping pressure up to 100 N/mm^2 the mould

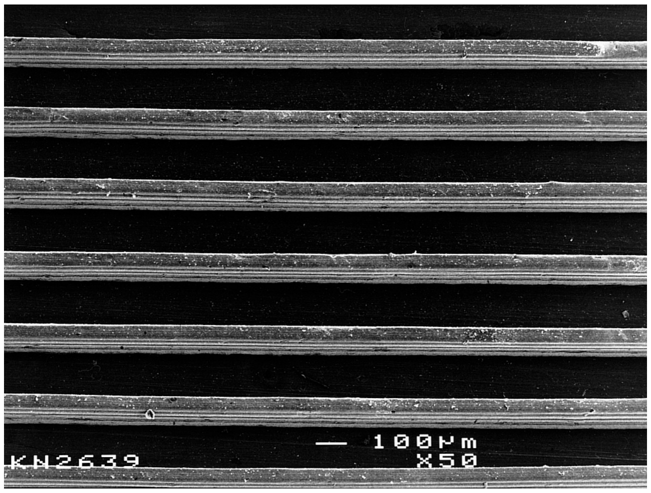

Fig. 2. Sintered Y–ZrO_2/Al_2O_3 microstructured tape, used for the micro heat exchanger

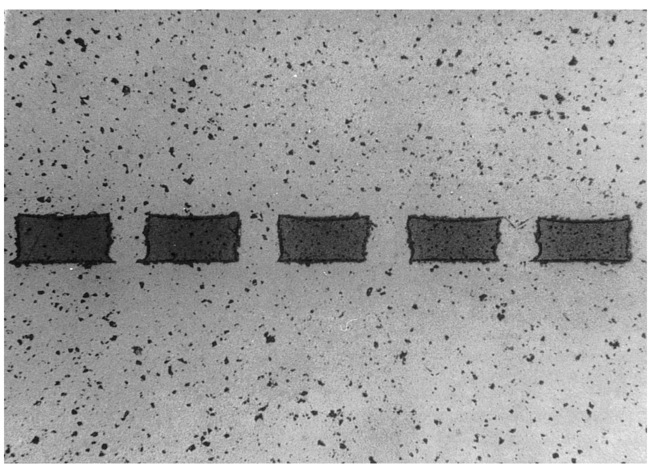

Fig. 3. Cross-section of the laminated tapes after sintering with channel dimensions of about $160 \times 80\ \mu m^2$

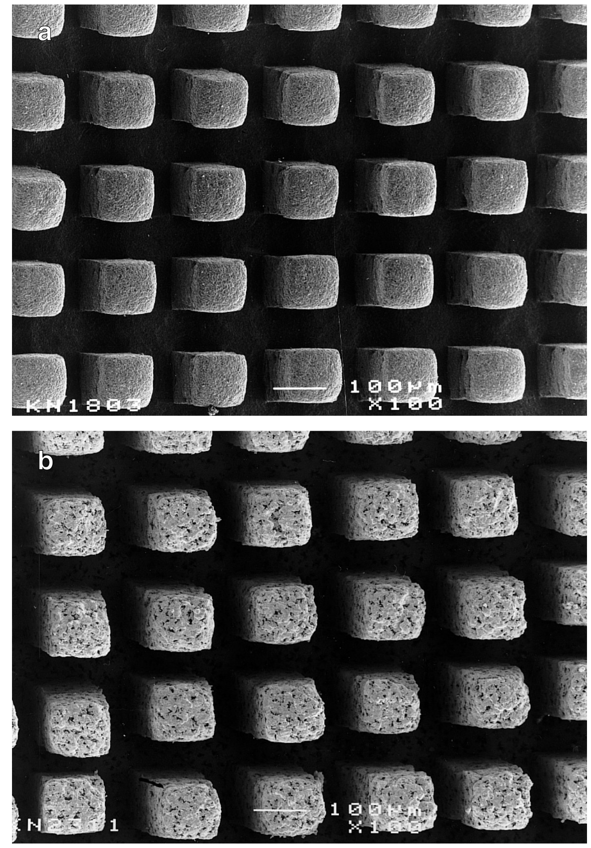

Fig. 4a, b. Sintered PZT rod arrays, moulded with different stamping pressures

was filled entirely and a structure height of more than 400 µm, equivalent to an aspect ration of more than 4, was obtained but only 90% of the about 5000 columns could be separated from the die and the final density was decreased (Fig. 4b). A further increase of the pressure led to an increase of the density up to 94% of the theoretical density and to a decrease in missing PZT rods. Recent experiments show, that further improvement will be reached by optimisation of the stamping die design. After sintering these structures, with an active area of 25%, were filled with polymer, ground until the rod surfaces appear on both sides and subsequently electroded for poling (Fig. 5).

4 Discussion

The fabrication of metallic micro heat exchangers with excellent properties has been reported earlier by Bier et al. (1993), but the use of these microsystems are limited to much lower temperatures than that of ceramic ones. Especially when these microstructures are used as microreactors the corrosion behaviour is an important property because of the large surface to volume ratio of the structures. The results presented here are a promising step to solve these problems. Besides the optimisation of lamination and sintering the objective of further work has to be the mounting of the fittings.

The process of tape casting and stamping with metallic dies has a lot of advantages compared with lost mould techniques used for the preparation of 1–3 composites. The use of PMMA moulds, which are filled with slurry led to restrictions for the choice of the additives. Furthermore the drying of the slurry in the plastic mould is much more difficult to control than the drying of tapes (cp. Bast et al. (1991)). The separation of the tape from the die before dewaxing avoids many difficulties, which occur during the decomposition of the PMMA as lost mould. Hirata et al. (1995) removed the resist mould by plasma etching to overcome these problems. Finally the costs of the mechanical microfabrication of the metallic dies with subsequent electromoulding are much lower than for the fabrication of moulds using the LIGA-technique and a redesign of the mould is much easier and less expensive. However, the design of the moulds is less flexible by mechanical microfabrication than by the LIGA-technique (cp. Lubitz et al. (1993)).

The process of tape casting with subsequent stamping presented here is a promising new route to produce ceramic microstructures. It was illustrated that, with this process, three-dimensional structures with lateral dimensions in the micron range and with high aspect ratios can be obtained which

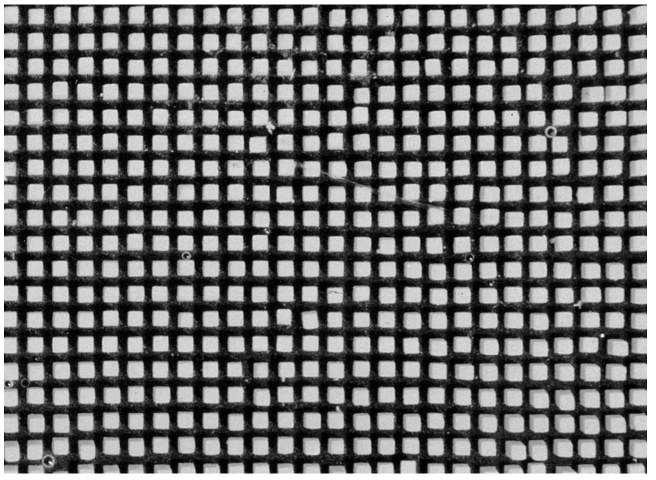

Fig. 5. PZT rod array filled with polymer

exhibit good moulding results and high form fit. The two examples given demonstrate, that it is possible to combine the desirable properties of ceramic materials with microstructuring techniques for new promising applications. The process is applicable to a great variety of materials and as a time and cost effective method for the structuring of ceramics, it represents an economical alternative to the existing methods like slip casting, mechanical or laser treatment especially for a large number of pieces.

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