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Structuring of LTCC Substrates by a Combination of Pressure-Assisted Sintering and Hot Embossing

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Abstract

A novel technology for structuring low-temperature co-fired ceramic (LTCC) surfaces is introduced. The commercial LTCC Ceramtape GC was shaped in a zero-shrinkage process by embossing a glass-like carbon mold into the softened LTCC during pressure-assisted sintering. Diverse raised and lowered structures including rings, grids, and characters were fabricated. It was found that de-airing of mold cavities is crucial for the molding of embossments. De-airing is possible through pore channels in the LTCC if embossing is performed at intermediate temperatures. The influence of LTCC viscosity on the mold filling behavior during the formation of raised structures is discussed. For accurate molding and proper densification of the LTCC, hot embossing with 0.41 MPa at 775 °C and subsequent heating under load to 850 °C is proposed. Embossing of precise, 40-µm-deep circular cavities and 50-µm-high raised bars and characters is demonstrated. Thereby, the high potential of the hot-embossing process for micro-patterning of LTCC is illustrated.

Keywords: Low-temperature co-fired ceramics, pressure-assisted sintering, glassy carbon, hot embossing, structuring

I. Introduction

A well-known strength of LTCC (low-temperature co-fired ceramics) multilayer technology is the possibility to fabricate structured components for microsystems and sensor applications. Two general strategies can be distinguished: structuring of the green part and structuring of the sintered part. The latter is typically a milling process. Although versatile geometries with small tolerances can be fabricated by milling, it is also often a critical manufacturing step. Sintered LTCC are prone to brittle fracture. Considering components with small wall thickness, for example sensor substrates, clamping of the sintered part can already be a challenge. That is why structuring of the green part is much more common. Diverse processes have been described to structure green tapes and laminates [1–4]. The typical approach is punching or laser-cutting of green tapes that are then stacked to build up a structured laminate. Likewise, machining of laminates by milling or laser ablation [5] is possible. Patterning of green tapes by hot embossing [6] or micro roller embossing [7] has also been described. With selection of the suitable technology, precise structuring of the green part is possible. However, the quality of the structures often deteriorates during sintering. Deformation, differential shrinkage, as well as delamination of the multilayer can occur.

In this paper, a technology is introduced to structure LTCC by hot embossing during pressure-assisted sintering. Thereby, the negative effect of shrinkage on the dimensional accuracy of the structures should be avoided. Glass-like carbon is used as mold material. It is a pure carbon material with a fullerene-like microstructure [8]. The successful use of glass-like carbon as non-sticking substrate for ultrathin free-standing ceramic layers [9] and as a mold for nano-imprinting of glass [10–12] has been reported. In earlier work, we demonstrated the fabrication of thin-film suitable LTCC substrates by pressure-assisted sintering with smooth glass-like carbon setters [13, 14]. Here we describe the further development of this technology for the generation of raised and lowered surface structures on LTCC during pressure-assisted sintering.

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II. Experimental Procedure

(1) Sample preparation

Test substrates of different sizes were prepared from commercially available lead-free LTCC tape Ceramtape GC (CeramTec, Germany, green thickness 300 µm). The material is a glass-ceramic composite. It consists of a calcium aluminosilicate glass with 30 – 45 vol% of alumina filler [15]. Four single sheets without metallization were stacked on one layer of alumina release tape (Ceramtape A, CeramTec, Germany) and laminated isostatically (70 °C, 25 MPa, ILS 6, KEKO, Slovenia). The edges of the laminate were cut straight using a hot-knife (CM 14 M, KEKO, Slovenia).

Glass-like carbon plates with an initial thickness of 3 mm (Sigradur G, HTW Hochtemperatur-Werkstoffe, Germany) were used as mold material. Raised and lowered surface structures like rings, circles, grids, channels, and characters were fabricated by milling. Fig. 1a shows

a milled mold with circular test structures. An optical surface scan of the mold is shown in Fig. 1b. The structure heights are given in the figure. The widths of the ring structures from left to right are 1 mm, 1.5 mm, and 2 mm, respectively. Different tools and milling parameters were tested for the preparation of the molds. In the framework of a milling parameter screening, it was observed that the surface of a glass-like carbon plate exhibits areas of different hardness. Thus, machining of a plate with constant parameters results in areas of varying surface properties. Values of average surface roughness R_a between 0.02 µm and 1.03 µm were measured on different positions and different molds. Lowered structures that were milled into the glass-like carbon plate generally exhibit increased surface roughness. Edge disruptions of milled structures were observed. As these results were obtained in a very early stage of the development of the process, significant improvements of mold surface quality are expected with further optimization of tool selection and machining parameters.

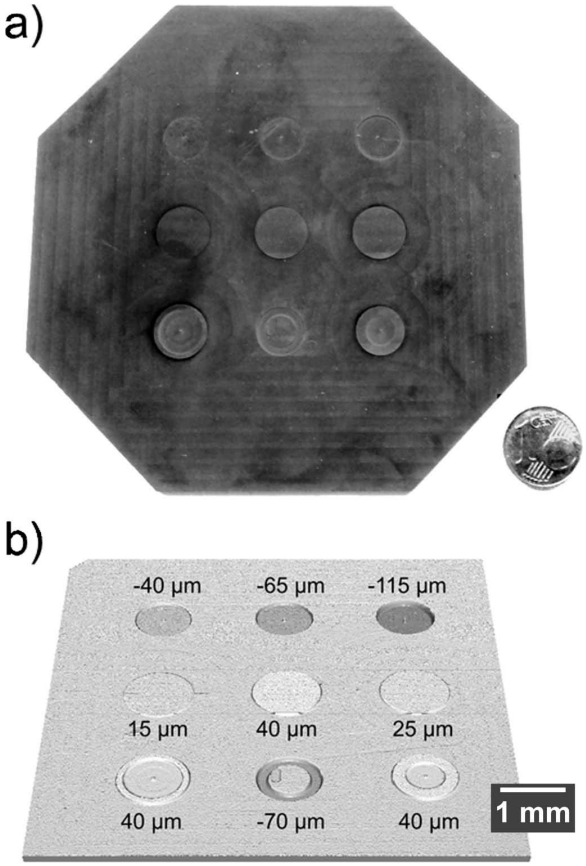

Fig. 1: a) Glass-like carbon mold with raised and lowered circular test structures, b) optical surface scan of the mold with heights and depths of the test structures.

(2) Pressure-assisted sintering and hot embossing

The combined sintering and hot process was performed using a LTCC sintering press (PHP603, ATV Technology, Germany). This is a programmable batch furnace with a fused silica muffle suitable for 8" substrates and temperatures up to 1000 °C that is extended by a feedthrough for alumina pressure stamps. The stamps are driven by a 50 kN hydraulic press. A stack of setters as shown in Fig. 2 was used for the experiments. Besides the LTCC multilayer in the center, the stack consists of dense SiC-plates that assure homogeneous distribution of the load, a porous SiC plate that enables thermal debinding of the LTCC multilayer, and the dense glass-like carbon mold. The LTCC is in close contact with the glass-like carbon mold during the entire process. A constant load of approximately 10 N is applied by the dead weight of the mold and the SiC pressure plate. That equals a pressure of 2 kPa on a 70 × 70 mm² substrate, or 1 kPa on a 100 × 100 mm² substrate, respectively. Glass-like carbon as mold material requires nitrogen flushing of the furnace at temperatures above 500 °C. To ensure thermal debinding of the LTCC, air flushing was performed up to that temperature. Additionally, a dwell time of 60 min at 500 °C was maintained. During the subsequent heating step, shrinking of the LTCC occurs only in thickness direction. The release tape laminated to the bottom and the small constant load are sufficient to fully constrain the sintering multilayer.

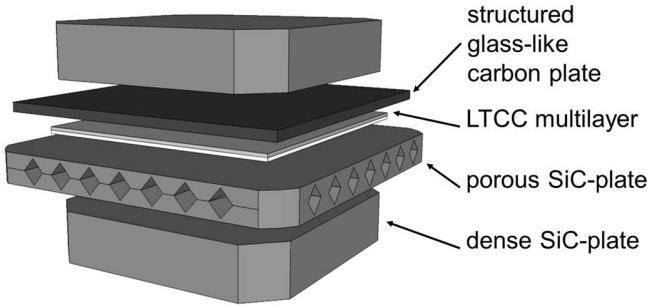

Fig. 2: Setter stack for sintering and embossing experiments.

The mold shown in Fig. 1 was used to emboss circular test structures into a 70 × 70 mm² substrate. After debinding, the substrate was heated to 850 °C with 8 K/min without additional pressure. A 12-min dwell at peak temperature of 850 °C was maintained to ensure termination of shrinkage. Then, axial load was applied in two steps with a 10-min dwell at 1 kN (0.2 MPa) to slowly push the mold into the softened LTCC. The maximum load of 3 kN (0.61 MPa) was maintained for 15 min. Subsequently, the sample was cooled down without axial load. A cooling rate of -10 K/min was applied.

Further experiments were performed using a polished mold with milled bars and grids. The substrate size in this series of experiments was 95 × 95 mm². One embossing experiment at 850 °C was performed as described for the circular test structures. The load steps of 1 kN and 3 kN correspond to 0.11 MPa and 0.33 MPa, respectively. As a supplement, peak temperatures of 775 °C and 830 °C were investigated. In these cases a maximum load of 4.15 kN (0.46 MPa) was applied in one step at the respective temperature without preceding dwell time. The load was maintained at peak temperature for 10 min. Subsequently, the substrates were cooled without additional load at a cooling rate of -25 K/min. Another embossing experiment was performed with loading (0.46 MPa) at 775 °C and further heating to peak temperature of 850 °C under constant load. The heating rate for heating under load was 3 K/min. A 20-min dwell at peak temperature and load was maintained, followed by unloading and cooling at -25 K/min.

(3) Characterization

The molds and the embossed LTCC surfaces were characterized using an optical profilometer (µScan, Nanofocus, Germany) equipped with a chromatic white light sensor (CLA 2.5, Nanofocus, Germany). A height resolution of 75 nm is specified by the manufacturer. Additionally, SEM investigations (scanning electron microscopy, Gemini Supra 40, Carl Zeiss, Germany) of sample surfaces and polished sections were performed. Conductivity of the samples was ensured by carbon coating. The porosity of different sections of sintered substrates was measured by evaluating the pore area ratio in different SEM images using the image processing software ImageJ (ImageJ 1.47v, public domain, Wayne Rasband, National Institute of Health, USA). Five different, adjacent images of a particular section were evaluated. Thereby, a continuous area of 0.05 mm^2 of each particular section was considered. The Archimedes method was applied to determine the sintered densities of the substrates. All densities are given in relative density in relation to 2.92 $g \cdot cm^{-3}$, which is the experimentally determined full density of Ceramtape GC after conventional pressure-assisted sintering at 850 °C.

III. Results and Discussion

Generally, the structuring of LTCC with the described process is possible without sticking or cracking of the substrate. No problems regarding incomplete debinding have been observed. The densification of LTCC can mainly be attributed to viscous flow of the glassy phase [16]. Depending on green density, heating profile and axial pressure during sintering, densification of Ceramtape GC takes place in the temperature regime between 760 °C and 920 °C. The glassy phase of Ceramtape GC is prone to solution of alumina and crystallization of anorthite. However, during constant heating with 3 K/min the onset of crystallization is not expected at temperatures below 860 °C [17]. Still, after a dwell time at peak temperature anorthite formation has to be considered. An anorthite content in the sintered LTCC of up to 45 wt% is possible [17]. Thus, given the sintering profiles applied in this study, it can be assumed that molding of the LTCC is driven by viscous flow of the glassy phase.

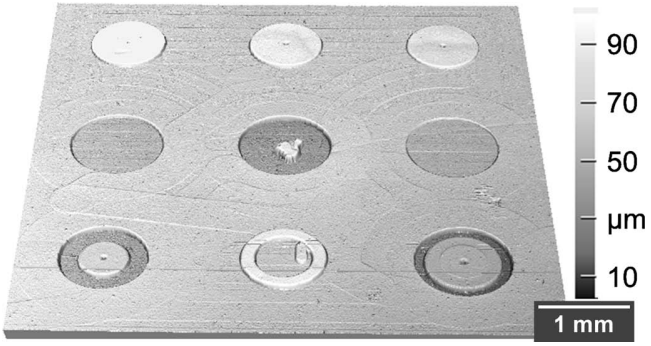

Fig. 3: Optical surface scan of Ceramtape GC substrate hot-embossed at 850 °C with 0.61 MPa.

Fig. 3 shows the surface scan of a LTCC substrate embossed with the mold shown in Fig. 1. All test structures are visibly molded to the substrate. Even the traces of the traverse path of the milling tool in between the test structures have been transferred from the glass-like carbon mold to the LTCC. The circular indentation in the center of the test structure array exhibits an irregular shaped bump. That is an impression of a defect in the mold that was created in previous experiments. The sample features lowered and raised test structures. Thereby it is shown that not only indentation of the LTCC is possible. It also demonstrates that cavities in the mold can be filled by viscous flow of the LTCC to achieve raised structures.

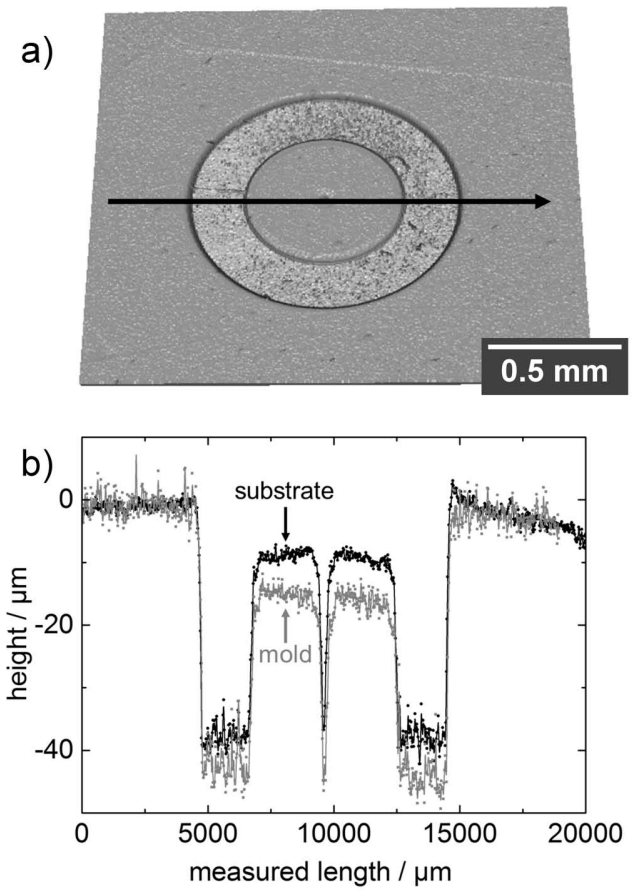

Fig. 4: a) Optical surface scan of hot-embossed ring structure (850 °C, 0.61 MPa), b) height profiles of glass-like carbon mold (grey) and embossed LTCC (black). The path of the profile is indicated by the black arrow in the surface scan.

Fig. 4a shows the circular cavity at the bottom left of Fig. 3. It is a 40-µm-deep ring with an outer diameter of 10 mm and a width of 1 mm. The inner surface of the ring is 10 µm below the surface level of the multilayer. A 25-µm-long tapered pin with a decreasing diameter of 460 µm to 60 µm from base to tip indicates the center of the structure. The lateral dimensions of this structure have been molded precisely, as shown in Fig. 4b. Even the tapered pin was molded in repeated experiments without fracture. The height of the structure exhibits a tolerance of roughly 5 µm. The entire mold covers a 70 × 70 mm^2 substrate and exhibits a concave camber of up to 50 µm from side to side. It is assumed that the deviation in height of the molded structure is due to an incomplete indentation of this particular test structure into the substrate. Such effects can be avoided by further optimization of mold fabrication. However, this test structure demonstrates that

precise molding of lowered structures with lateral dimension from the micrometer range (tapered pin) to the millimeter range and depth of several 10 µm is possible using 0.61 MPa at 850 °C.

The upper row of test structures in Fig. 3 is a series of circular embossments with approximate heights of 35 µm, 30 µm and 25 µm from left to right, respectively. The tapered pins in the center of the embossments have also been molded. Compared to the mold, the lateral dimensions of the structures are accurate, but the height is significantly reduced. The corresponding cavities in the mold are 115 µm, 65 µm, and 40 µm deep. These cavities were not filled completely at 850 °C and 0.61 MPa. Presumably, mold filling is hindered by air in the cavity. In this experiment, embossing was performed after closure of pores in the LTCC. Thus, the air in the cavity is entrapped and compressed by the LTCC that flows into the mold. At a given volume of LTCC in the cavity, the resulting pressure is higher in the 40-µm-deep cavity than in the 115-µm-deep cavity. If one assumes a threshold pressure in the cavity that suppresses further filling of the mold, a deeper cavity can take up more LTCC than a flat cavity until this pressure is established. Consequently, the embossments formed by deeper cavities are higher than embossment formed by flat cavities. From this it follows that a mold design with de-airing holes is necessary for complete mold filling with LTCC after closure of the pores. Alternatively, embossing should be performed at lower temperatures before the pores in the LTCC close to enable de-airing of the mold cavity through pore channels.

To investigate the influence of embossing temperature on mold filling, experiments with another mold layout were performed. That particular mold only features cavities for the molding of different embossments on the LTCC. A significant influence of temperature on moldability was expected, as the viscosity of the LTCC is strongly temperature-dependent. In contrast to glasses, LTCC viscosity does not simply decrease with rising temperature. The effective viscosity of the material depends on temperature, density and crystallinity in a complex way. For isothermal processes, an increase of viscosity with density has been consistently reported, whereas at same densities, the viscosity is lower at higher temperatures [15,18,19]. In constant-heating-rate measurements on different LTCC compositions, an almost constant low viscosity of approximately 1 GPa·s was observed in the intermediate stage of sintering. The final state of sintering, when pores are already closed, is characterized by a steep increase in viscosity up to 100 GPa·s [18]. For Ceramtape GC, a steep increase in viscosity was also observed for intermediate densities during isothermal sintering at 775 °C [19]. Consequently, an increase of embossing dwell time is not expected to have a beneficial effect on mold filling. Furthermore, viscosity increases with progressing crystallization, which again is temperature- and heating-rate-dependent. Ceramtape GC shows crystallization of anorthite above 860 °C [17]. Based on these considerations, hot embossing at 850 °C and below was further investigated.

To illustrate the mold layout for the series of embossing experiments, Fig. 5 shows a photograph of a 95 × 95 × 0.66 mm^3 substrate (four layers of Ceramtape GC) with raised grids and characters that has been hot-embossed at 775 °C. The top left, top right and bottom right structures on the substrate are raised grids with a line width of 600 µm and a depth in the mold of 50 µm. The line spacing of the top right and bottom right grids is 600 µm. The top left grid features a reduced line spacing of 300 µm. This particular structure was evaluated to determine the influence of embossing temperature and density on moldability. Further structures shown are characters (bottom center) with a line width of 600 µm and an array of raised rings (bottom left) with an outer diameter of 600 µm and a line width of 200 µm. The substrate is free of cracks. No deformation of the substrate edges can be observed. All structures have been distinctly and visibly molded. The following discussion focuses on the top left structure.

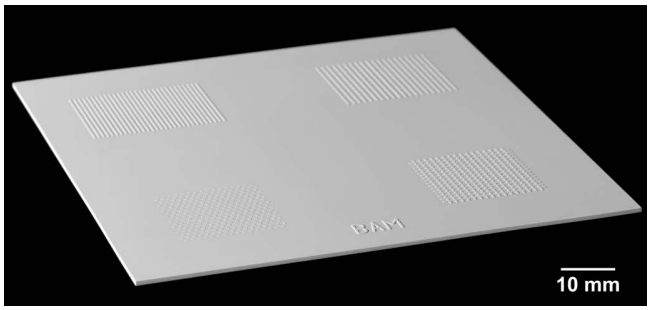

Fig. 5: Photograph of a sintered and embossed (775 °C, 0.41 MPa) Ceramtape GC substrate with 95-mm edge lengths and raised grids and characters.

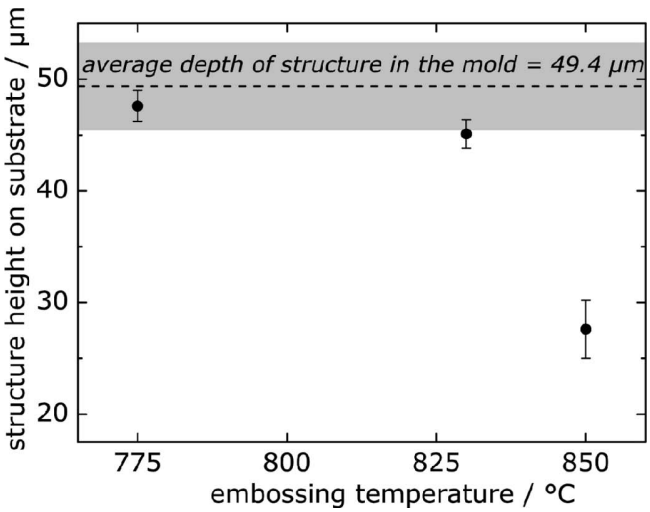

Fig. 6: Height of the narrow-spaced raised grid in relation to the embossing temperature. The dashed line represents the depths of the mold. The grey bar represents the standard deviation of the mold depth. Please note that embossing load was 0.41 MPa for 775 °C and 830 °C, but 0.61 MPa for 850 °C.

Fig. 6 shows the height of the narrow-spaced raised grid structure in respect of the embossing temperature. A significantly better mold filling is observed at lower temperature. The height of the structure that was hot-embossed at 850 °C amounts to 27 µm, which corresponds to only half of the mold depth (Fig. 7). After hot embossing at 850 °C, a relative density of 92.2 % was obtained. The edges of the single bars of the raised grid are visibly rounded, as shown in Fig. 7. By contrast, hot embossing at 775 °C leads to

nearly complete filling of the mold and therefore a structure height of almost 50 µm with sharp edges of the bars. At this sintering temperature a relative density of only 74.5 % and an open-porous microstructure is achieved. At 830 °C, the sintered density is increased to 81.5 % and the profile height is slightly reduced. From this, it can be deduced that open porosity in the LTCC substrate improves mold filling during hot embossing. This observation substantiates the assumption that de-airing of the mold cavity through pore cannels in the LTCC microstructure is possible.

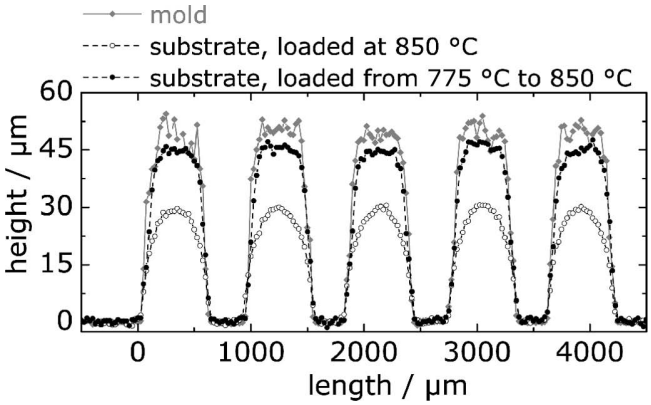

Fig. 7: Comparison of contours of grids that were embossed with different loading profiles in respect of the contour of the corresponding mold.

To summarize, a low viscosity and pore channels in the microstructure of the substrate yield better mold filling and thus higher structures. A combination of good mold filling and proper densification can be obtained by hot embossing at 775 °C and further heating under load up to 850 °C. Raised structures with 45 µm height could be formed on a substrate with a relative sintered density of 98.8 %. The geometry of the mold is precisely transferred to the substrate, as demonstrated for the narrow-spaced bars in Fig. 7. All structures of the mold, including the characters and the crossed grid have been accurately molded.

Although the densification of the bulk substrate is satisfactory, a reduced density of 90.1 ± 1.3 % was found in the microstructure of the raised bars by means of SEM image processing. For comparison, a bulk density of 97.3 ± 0.6 % was determined with the same method. Fig. 8 shows SEM images of representative microstructures of the bulk (a) and the embossed raised grid (b). The difference in bulk density determined with image processing and the Archimedes method is due to the different measuring methods and the sample selection. Image processing of the bulk microstructure was performed at a section in the vicinity of the embossed structure, while the Archimedes method was performed at a sample that was cut out of a substrate region without any embossed structure. Further investigations are necessary to fully clarify the cause for this reduced densification. Presumably, the intensified viscous flow during mold filling causes pore agglomeration. The enlarged closed pores, or an increased number of large pores in the molded microstructure, respectively, results in a reduced sintered density in these regions. Moreover, the increased porosity in the molded microstructure could be a consequence of de-airing of the mold cavity through the pore channels of the LTCC. Still, the results prove the applicability of the introduced hot embossing process for the fabrication of precise surface structures in and on LTCC substrates during pressure-assisted sintering.

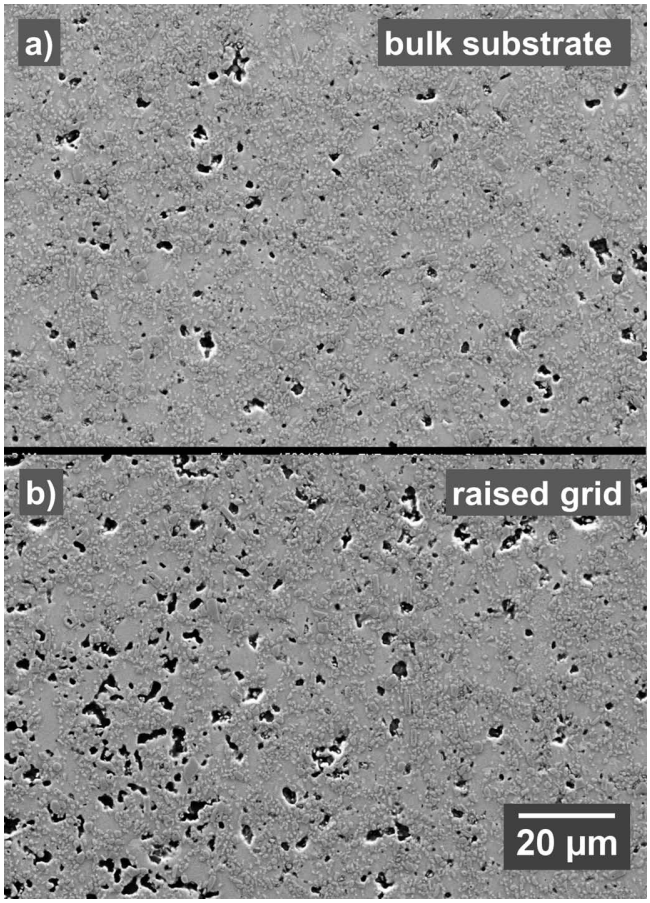

Fig. 8: Microstructures of hot-embossed Ceramtape GC (loading from 775 °C to 850 °C), a) section of the bulk substrate in the vicinity of the surface, b) section of raised bar on the surface.

IV. Conclusions

Hot embossing of glassy carbon molds into softened LTCC is a promising technique for the patterning or structuring of LTCC substrates or components. Ceramtape GC appears to be well suited for the process conditions investigated in this study. In principle, the molding of small structures, like a 25-µm-long tapered pin with a 60-µm tip, is possible with high dimensional accuracy. Structures with lateral dimension up to the ten millimeter range and heights and depths up to 50 µm can also be generated. In individual cases, mold design and process parameters have to be adjusted. Mold fabrication is critical with regard to the molded surface quality. For the formation of embossments on the LTCC, de-airing of the mold cavity must be enabled either by vent holes in the mold or pore channels in the substrate. Accurate structures and high substrate density are achieved by hot embossing at intermediate temperatures (775 °C) and further heating under load to 850 °C for full densification.

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