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RESEARCH ARTICLE

Optimization of fluidic microchannel manufacturing processes in low temperature co-fired ceramic substrates

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Abstract

The processing of starch powder and polymer based sacrificial layer for fabrication of microfluidic structures in low temperature co-fired ceramics (LTCC) is described in the paper. Sacrificial volume material (SVM) was placed into the channel of LTCC sheets to avoid sagging by supporting embedded, three-dimensional structures such as channels, cavities during firing. Sagging of laminated structures is a common problem in the processing of the LTCC. A series of experiments were carried out for different lamination schemes which affect the quality of LTCC sheets. Samples were tested by an acoustic microscope to reveal the internal inhomogeneities and delaminations. As a consequence of burnout, the increased fraction of evolving gases from SVM requires an adequate adaptation of the firing process to provide a residue-free burnout without damaging the structure. Using thermal analysis the intensity of the evaporating gases was determined during co-firing. Based on these results, the modification of the heating profile could be done. It is proposed that the fabrication of embedded structures in a multi-layer LTCC platform could be achieved by controlling SVM burnout with a modified heating profile. Using this approach, fabrication of embedded channels in LTCC substrate is demonstrated.

Keywords

LTCC · fluidic channel · lamination · firing · scanning acoustic microscopy

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1 Introduction

For the implementation of high reliability, – frequency or – temperature multilayer circuits the LTCC technology has been used for almost 30 years [1]. Since LTCC technology has already been applied successfully for the realization of microsystems, the construction of cavities and channel networks with well defined geometry brought challenges to the researchers [2]. Nowadays, the LTCC technology has become an excellent addition of silicon-based microfabrication techniques for the production of three-dimensional structures using a multilayer approach. The fabrication process of LTCC systems is simple, fast and inexpensive [3]. Integration and miniaturization of vias, channels and cavities are being developed in LTCC circuits. The LTCC materials combine good electrical properties with the capability of creating microstructures. These features are mainly preferred in microsystem technology. The scope of the LTCC technology in microfluidics is very wide. Different heating and cooling systems can be realised in microreactors. Several mixer formation and sensor applications are feasable in LTCC substrate e.g.: snake mixer, T mixer, X mixer, pressure sensor, flow sensor, temperature sensor and radar sensor. The technology is applied to build Micro Total Analysis Systems (uTAS), particle separators and MEMS, fiber optic and electro-optic packaging as well [3]. Investigation of DuPont 951 for few applications has proven biocompatibility of the tape, although some conductor pastes have negative influence on biological processes, which can be avoided by covering the functional layers with the basis tape [4].

Resolution of the LTCC structure compared to the silicon or photosensitive polymer micromachined systems is lower because the lithography technique is finer than the laser or CNC machining but higher than molding technique in rapid polymer technology. The main advantage of LTCC based microfluidics is the integratability of the electronics, fluidics and package in one unit using arbitrary number of layers which enables highly integrated complex systems.

The materials used to create low temperature co-fired ceramics circuits (produced from raw glass-ceramic “green” tape and various pastes such as conductive, resistive, dielectric and via

filler paste) can be processed by the equipment of the conventional thick-film technology (screen printing machine, drying and burning ovens). The equipment needed to produce multilayer boards (laminator, punching machine or Nd:YAG laser) can be installed with relatively low investment. The cost of the whole LTCC line investment is also much lower than in silicon or thin film equipments [3]. A typical LTCC module consists of glass-ceramic sheets, internal and external conductive networks, connecting vias and passive elements (resistors, capacitors, inductors) [5]. This study highlights only the channel fabrication for micro-fluidic systems. Fabrication of embedded structures in a LTCC platform involves steps of structuring, (printing), prelaminating, filling the cavity with fugitive material, lamination and co-firing. There are three technological factors, the adjustment of heating profile, the lamination method and the choice of SVM, that are very important to the success of the production. One of the fabrication challenges is that the embedded structures tend to deform and sag during lamination. To minimize these defects carbon materials are widely used as SVM due to their easy burnout but the pores of the LTCC often close before the end of the SVM burnout which can lead to structure defects [2, 6]. It can be avoided by using lower temperature decomposing SVM (polymer, polysaccharide, cethyl-alcohol) which burns away cleanly leaving no contamination.

Khoong et.al. have studied the sag of the suspended LTCC laminate over a cavity in case of different lamination pressures, while the separation of the layers has not been investigated [6]. In the literature several different lamination and firing adjustments are used. Khoong and Malecha have applied low pressure lamination [6, 7] Wang utilized short time (2 min) lamination [8]. Jurkow has developed a cold chemical lamination technique [9], Gongora and Golonka used double step lamination, which can prevent chambers sagging [10, 11] while the others have applied the typical laminating parameters that are 200 atm at 70 ˚C for 10 minutes [2, 12–14]. Although some different lamination method have been reported (the set pressure was in the range of 2 MPa to 30 MPa, the dwell time was 3 min – 10 min, the applied temperature was 40 ˚C – 100 ˚C) without complete structure examination there is no clear conclusion of the whole structure formation. Low pressure lamination results in less sag of the cavity but the chance of the delamination is increasing [7]. On the other hand high pressure supports the sufficient integration between the ceramic layers but usually deforms the cavity [11]. Most of the experiments have investigated the cross-section of the samples but this method examines only a region of it. By applying adhesives between the layers the lamination pressure can be reduced.

It should be noticed that the co-firing profile has to be adjusted taking into consideration both the structure geometry and the degradation kinetics of the filler material. In some cases the SVM requires extra dwell time for the total burnout [14]. However these parameters have not been investigated together yet.

Birol et. al. have measured the thermogravimetrical curves of the graphite-based SVM, they have slowed down the heating profile in the whole process instead of only in the burning region of SVM [15].

In my present work a series of experiments were carried out for two different sacrificial volume materials: corn starch and a UV-polymerized material; for 12 different lamination schemes (time, pressure, temperature) which affect the quality of the channel. As a consequence of burnout, the increased fraction of evolving gases from SVM requires an adequate adaptation of the firing process considering the channel length to provide a residue-free burnout without damaging the structure. Using thermal analysis the intensity of the evaporating gases was determined during co-firing. The geometry of the resulting structures was analyzed by scanning acoustic microscopy (SAM), which has not been used as a verifying method of the lamination until now. Based on these results, with the modification of the heating profile embedded channels with dimensions of 5 mm/15 mm/45 mm × 1 mm × 0.50 mm in LTCC substrate were realized.

2 Experimental

In this section the manufacturing process of two types of test structures, the acoustic microscopic examination of the laminated structures and the thermal characterization of the SVM and LTCC are described.

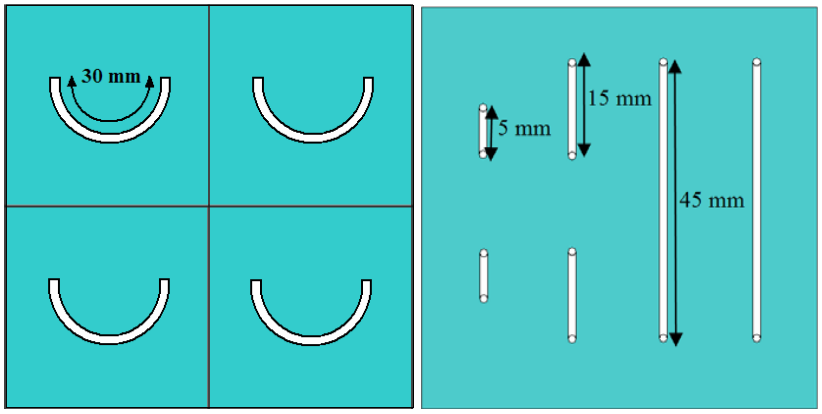
2.1 Manufacturing process

Six layers of DuPont 951 green tape (6 cm × 6 cm) were used to fabricate the test structures. The thickness of the tape was 254 μm before firing. The top two layers have the channel outlets, the inner ones contain the channels, and the bottom ones are base layers. For sufficient mechanical stability, the layers with different functionality were doubled. The channels were cut in the raw tape by UV Nd:YAG laser (Coherent AVIA 355-4500).

Two types of test structures were designed: U-shape channel for examination of lamination parameters (U pattern), straight channels with three different lengths (I pattern) for investigation of heating profile. The “U pattern” and “I pattern” designed structure have the lengths of 30mm and 5mm/15mm/45mm, the width and height of the channels are the same: 1 mm and 0.50 mm respectively.The layouts of the inner layers of the test structures are presented in Fig. 1. The structure was prepared with the following parameters:

- Pulse repetition frequency: 50 kHz
- Deflection speed of the beam: 10 mm/s
- Number of scans: 3
- Average power: 4 W

After laser cutting, the ceramic tape layers were stacked together in the proper order and initially pre-laminated using isostatic press (IL-4004 series, PTC) with a pressure of 2 MPa at



a.) b.)

Fig. 1. Layout of the inner layers in the 3D LTCC module. a. U-shape channel for examination of lamination parameters, b. channels with three different lengths for investigation of heating profile

70 ˚C temperature for 10 minutes. To avoid the deformation of the bottom layers a 2 mm thick aluminum plate was put under the stack during lamination. In order to minimize channel sagging an initial lamination was made without upper cover plating, only the two base layers and the inner layers were laminated together. Then all channels were filled up by the appropriate sacrificial material. In case of starch SVM the channels were filled up using a squeegee through protecting Mylar film which was not removed from the green tape.

The process of channel filling with polymer (FullCure 720) consisted of two steps. First, the structure of the SVM was designed, then a 3D Printing System (Objet Eden 250) finalized the desired structure using UV light, which polymerized the raw SVM. The x and y (lateral) dimension accuracy of the production of this solid state SVM is 42 μm and 16 μm in z (thickness) direction which is in the range of the LTCC cutting accuracy, because the diameter of the laser beam is 20 μm. Second, the polymerized material was put into the channel. After the filling process the covering layers were applied onto the structure and laminated for second time. Table 1 shows the applied pressure, temperature and lamination time. Starch was the SVM for the examination of laminating parameters.

The last step of the technology was the co-firing of the substrate. In the first experiment, the heating rate was 6 ˚C/min up to 450 ˚C for the first period. In the second experiment a slower rate of only 2 ˚C/min was applied. During this process organic compounds evaporate from the substrate, the glass-matrix melts and converges, then the substrate shrinks, its structure solidifies and the SVM burns out.

2.2 Acoustic microscopic examination of laminated structures

Acoustic microscopy is suitable to determine the delaminated areas in the stack. From the boundary surface of different layers the acoustic waves are reflected, thus from a delaminated area more reflected waves can be detected.

By decreasing the lamination pressure the probability of delamination is increasing. Since the effect is not always visible the use of SAM is recommended. Examination of samples was carried out using an acoustic microscope (Sonix HS1000) with the transducer frequency of 15 MHz and speed of 164 mm/s. The measurement was evaluated from the images taken from more than one internal layer.

The lamination of tapes incorporating channels and cavities for the fabrication of microfluidic devices is a critical processing step. Differences in laminating pressure along the sample geometry may result in inhomogeneous densification effects inside of LTCC-stacks with embedded channels and cavities. The advantage of high pressure impact is that the layers permanently bond together, however it causes undesirable deformation, distortion, sagging or even crack formation during unconstrained firing. On the other hand, low pressure is not able to laminate the layers together, which finally leads to delaminations. Furthermore, related tearing effects could be detected around the channel outlets (Fig. 2) for high lamination pressures if no appropriate support, e.g. sacrificial volume material (SVM) filling, has been applied.

Few pits can be observed and some samples seem flawless. However large internal delaminations and internal inhomogeneities were noticed with acoustic microscope afterwards. Pictures show strong shade difference caused by large acoustic impedance changes. SAM analysis method could be also integrated into a mass production line as inline characterization if it is combined with an image processing tool.

2.3 Thermal characterization of the SVM and LTCC

A 20-layer LTCC-laminate sample (size of 13mm×9mm×5mm) was specifically designed for the measurement, because the sample has to reach a minimum thickness. To characterize the densification behavior and dimensional changes of LTCC-laminate thermo–mechanical analyses (TMA) was carried out. The twenty layers of green sheet were laminated together, after that the samples were cut and polished in order to adjust the size and the shape of the

Tab. 1. Different lamination methods were applied to determine the optimal lamination parameters (temperature, pressure, dwell time) in case of starch SVM.

Lamination method No.	1	2	3	4	5	6	7	8	9	10	11	12
Temperature; ˚C	40	40	40	40	55	55	55	55	70	70	70	70
Pressure; MPa	10	10	20	20	10	10	20	20	10	10	20	20
Time; min	5	10	5	10	5	10	5	10	5	10	5	10

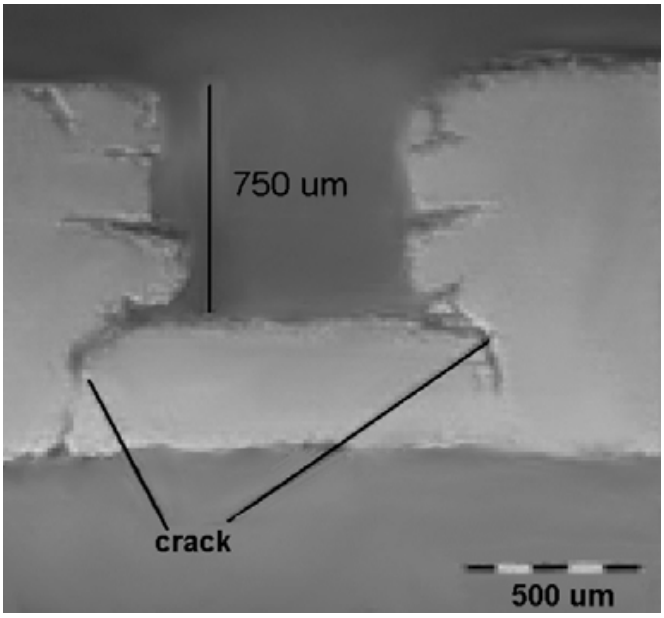


Fig. 2. Few cracks can be observed in the LTCC stack due to the inhomogeneous forces around the channel outlet.

specimens precisely for the TMA machine, afterwards they were heated by the recommended heating profile of DuPont. Dimensional change in z direction which corresponds to thickness variation of the laminates, was recorded at a heating rate of 5 ˚C/min, by using TMA dilatometer (Dilatonic Tokyo Industry, Japan). The sample of 13 mm×9 mm×5 mm was used for the TMA measurement. It is important to know the change of the thickness in the region of the decomposition area of the SVM, because it can lead to further deformation.

The two SVMs (starch, polymer) were characterized using thermo-analytical measurements (TGA Q500, TA Instruments). Open platinum crucible, a heating rate of 3, 5, 10 ˚C/min, sample weight of about 10 mg and flowing N_2 and air (50 mL/min) were used for purging the thermo-analytical furnace during the evolved gas analytical measurements. By the thermal analyses the temperature region where SVM burnout takes place was determined.

3 Results and discussion

Empirical investigations have been carried out to obtain the optimal fabrication process of LTCC with integrated channel elements. Channels were produced by different lamination processes and have been examined by scanning acoustic microscopy. This non-destruction test provides a complete scan of the 3D structure showing the embedded defects.

Experiments show that with higher pressure, more deformed are the shapes of the channels, and the sag is also higher in the case of compressible SVM. Lower pressure, however, is not sufficient to laminate the layers together, which leads to delamination.

The polymer SVM has the benefit of no compressibility, ensures the desired shape dimensions of the 3D structure even in case of wide channels. The CAD designed SVM is a breakthrough in this field, it is the most precise method of realizing sag-free cavities due to the fact that it does not deform and move during the lamination and provides accurate filling up. Furthermore the solid SVM going through more layers inhibits a typical delamination effect namely the slipping of the layers.

In Fig. 3a. the sample has been prepared with the 6th lamination method (55 ˚C, 10 MPa, 10 minutes). On the surface and at the upper layers of almost every sample minor unevenness problems can be observed. Between the inner layers of the stack large delamination was detected. The next sample (Fig. 3b) was produced at 55 ˚C and with the pressure of 20 MPa for 10 minutes. The sample has no significant delamination.

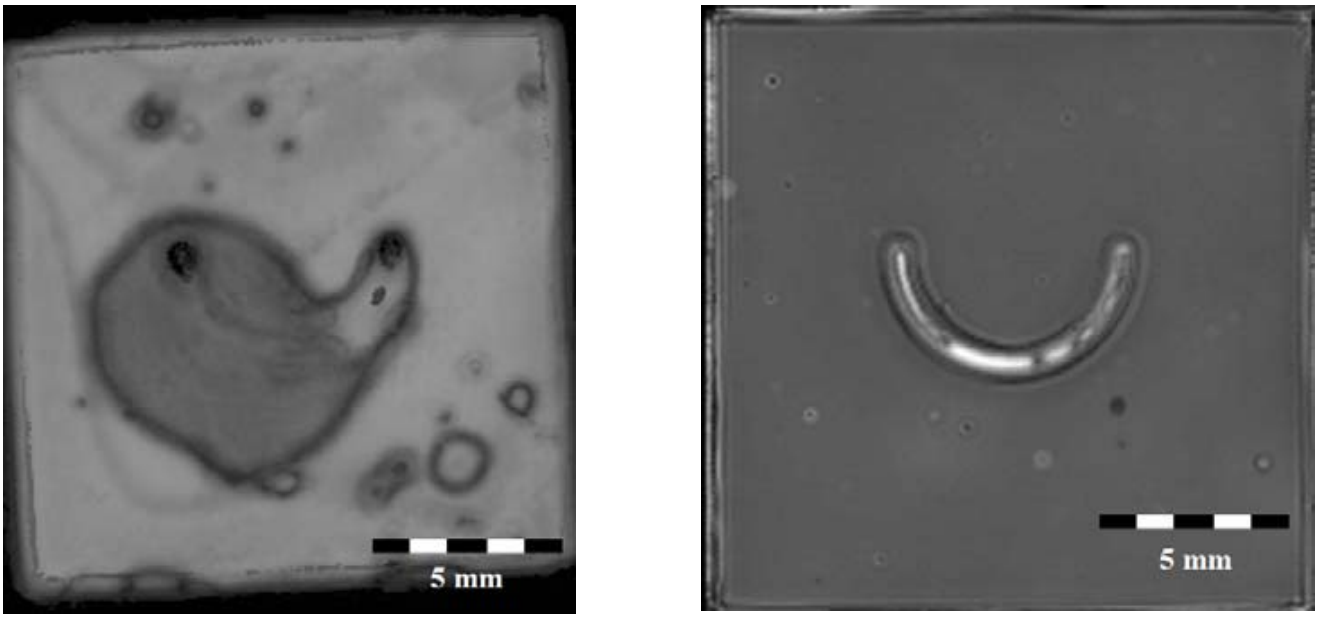
The sample in Fig. 4a. has been prepared using the 9th lamination set (70 ˚C, 10 MPa and 5 minutes, see Table 1. Although there was not any damage on the surface, in deeper layers of the substrate delamination could be observed by SAM around the channel because of the lack of integration between the LTCC layers. The right sample on Fig. 4. was made with duplicated 20 MPa pressure (11th lamination method). The sample did not have any distortion in the deeper layers.

In comparison with samples made by different parameters it is concluded that the best samples of lamination were made by the application of the maximum 20 MPa because at lower pressure there is not enough binding force between the layers to keep them together. By increasing the lamination time there was no significant improvement observed.

Regarding the TMA measurement the length of the LTCC sample did not change until 660 ˚C so the TCE is about zero. Between 660 ˚C and 760 ˚C the substrate shrinks strongly thus for this region the TCE could not be determined.

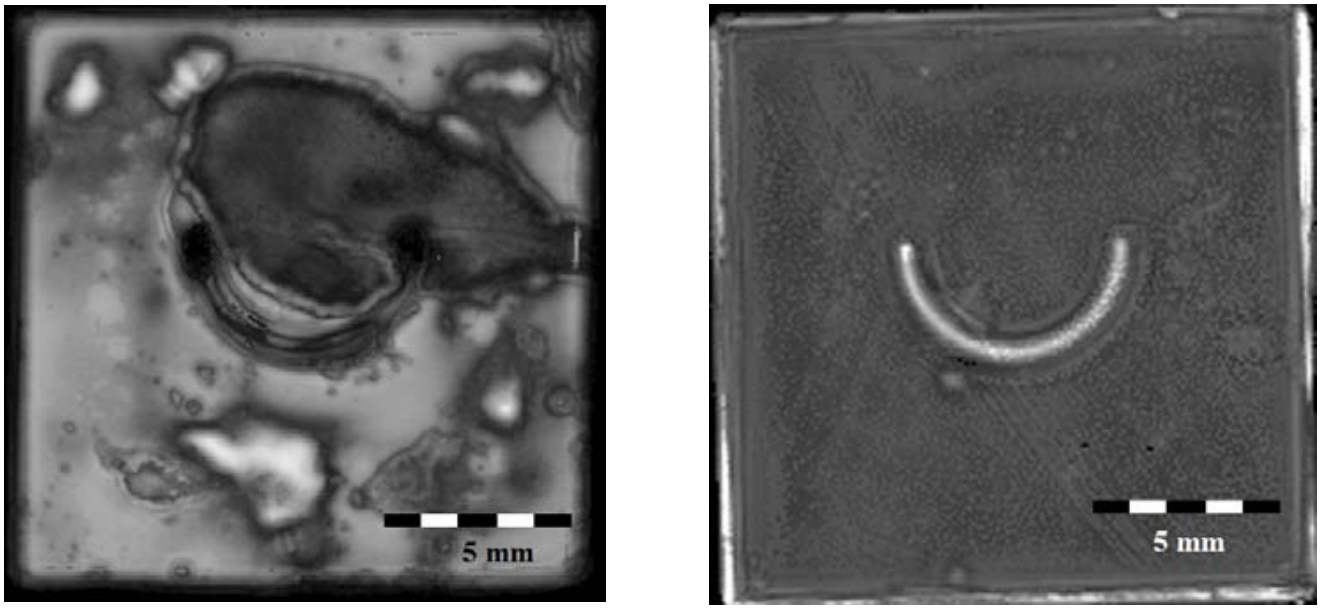
In case of starch SVM thermal expansion cannot be interpreted because of the significant change of porosity and weight. Polymer SVM is softening due to heat, thus it can not strain the substrate. The damage in LTCC is due to increased pressure from evaporating gases.

However it is assumed that this factor does not play a role in the deformation of the channel because the maximal mechanical



a.) b.)

Fig. 3. a. On the SAM picture of the 6th lamination method large delamination can be observed, b. the 8th lamination method resulted in defect-free channel structure.



(a) (b)

Fig. 4. a. On the SAM picture of the 9th lamination method the delaminations are caused by the inadequate pressure, b. the 11th lamination method laminated the layers permanently together.

stress appears at the edges of the channel but according to the experiments the cracks are in the middle of it.

Furthermore, there are two other technological parameters (heating profile, SVM), the exact selection is very important to the success of the production. These two factors should be consistent with each other and with the desired structure as well. If the glass-ceramic substrate contains a channel system, the dimensions should be considered at the fabrication.

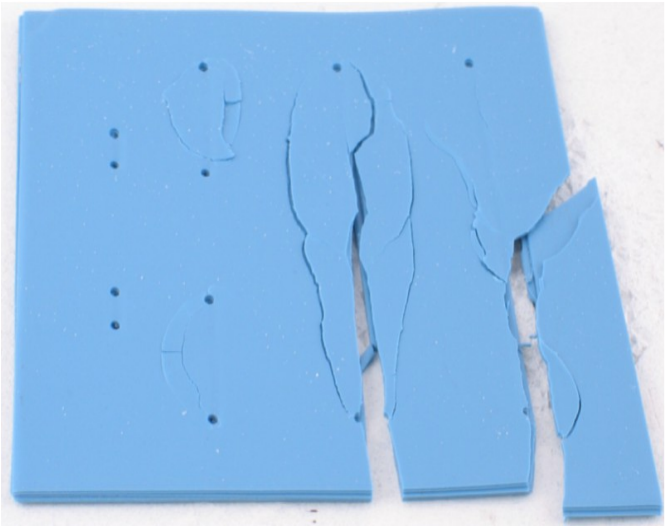


Fig. 5. Cracked LTCC substrate as a result of an inadequate firing-profile with the heating rate of 6 ˚C/min.

In the first experiment, where the heating rate was 6 ˚C/min up to 450 ˚C the longest channels were broken, medium length channels split and the shortest ones were intact, as is shown in Fig. 5. This experiment demonstrates that the firing profile requires adjustment for samples with different length.

Thermo gravimetry (TG) and differential thermal analysis (DTA) results showed the temperature interval where gases evolve from starch so in this range the heating rate has to be slowed down. Derivative thermogravimetry (DTG) is a method of expressing the results of TG by giving the first derivative curve as a function of temperature. By DTA the state change of the sample can be detected. The method is based on the temperature difference between the sample and reference substance during the period of heating. The sample is heated together with a reference standard in the same oven under identical thermal conditions If the sample changes state (melts, boils etc.) the latent heat of phase transition will be absorbed and the temperature of the sample will lag behind that of the reference material. In DTA the difference in temperature (ΔT) between the sample and the reference is plotted against temperature.

The TG, DTG and DTA curves of the reduction of starch and polymer SVM (10 ˚C/min heating rate, N_2 atmosphere) are presented in figure 6-7. The main decomposition area is marked in the figure. The curves in N_2 and in air do not show significant difference in the critical interval. Experiments were carried out with different heating rate (1,3,5 and 10 ˚C/min). The non-isothermal experimental curves of thermal analysis shift to higher temperatures with increasing heating rate, but their shape does not change significantly during this shift. By decreasing the heating rate the peak value of the DTG curve is getting lower.

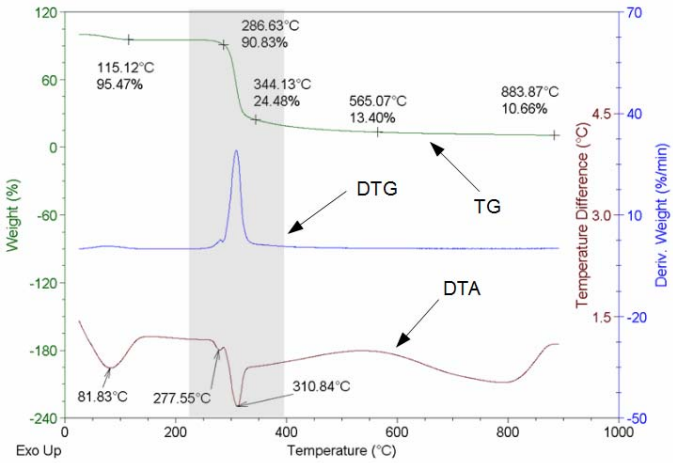


Fig. 6. Thermogravimetric curves of starch degradation in N_2 at 10 ˚Cmin^{-1} grey-marked in the main decomposition period.

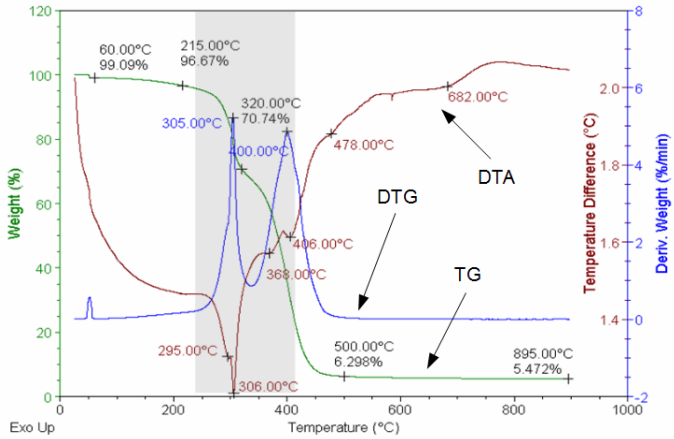


Fig. 7. Thermogravimetric curves of polymer degradation in N_2 environment at 10 ˚Cmin^{-1} grey-marked in the main decomposition period.

Consequently the shift of these thermoanalytical curves can be derived mathematically from the Arrhenius type kinetic equation. The study of starch and polymer degradation kinetics shows that degradation could be controlled by changing the heating rate. In the experiment where a slower rate of only 2 ˚C/min was applied instead of 6 ˚C/min slope the channels are intact as Fig. 8. shown. In contrast a rapid decomposition of the organic filler induces a sudden intensive production of gaseous burnout products which cannot escape adequately via the channels and this results in damage of the substrate as demonstrated for the channel.

The damage of micro-fluidic system was in consequence of the SVM decomposition which was accompanied by the evolving gases. A longer channel contains more sacrificial material, thus more gas evolves in this case. The volume of the smallest channel was 2.5 mm^3, the middle one was 7.5 mm^3 and the largest was 13.5 mm^3. The sacrificial material is proportional to the volume of the channel. Therefore in case of longer channels

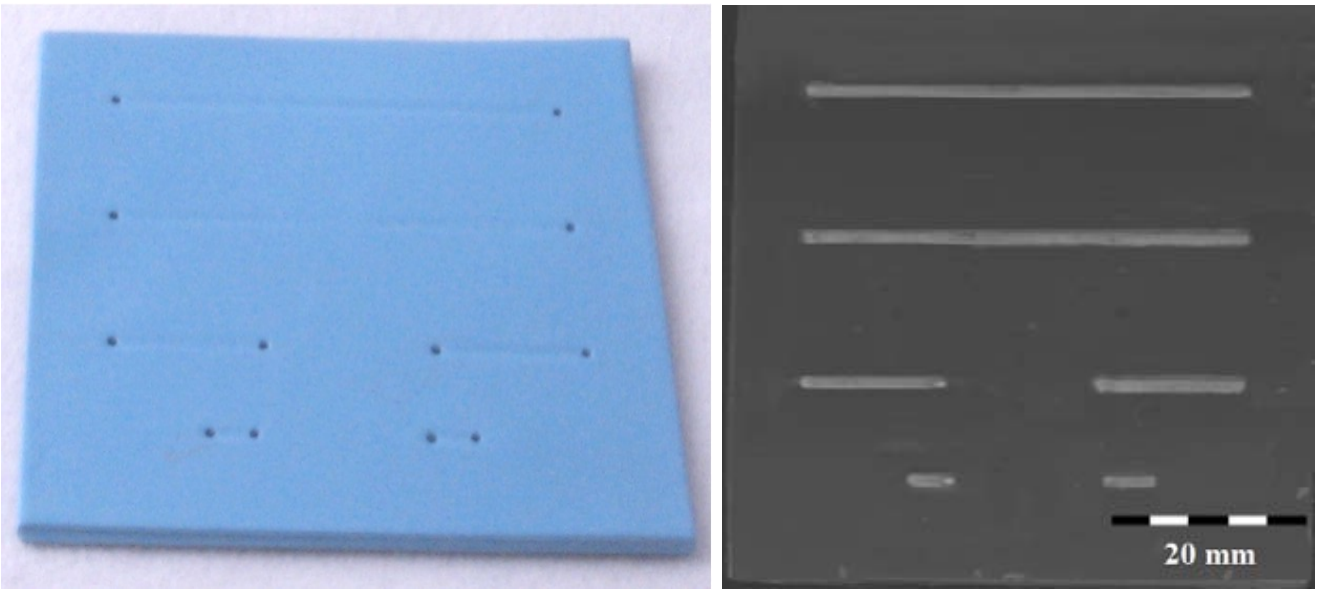


Fig. 8. a. The intact LTCC substrate was realized by the optimized heating profile, b. SAM picture proves the delamination-free structure.

the volume of the generated gas was also significantly increased. However, the outlets have the same size so the generated pressure inside the channels is growing proportionally to the length of the channel. The pressure can reach a critical level which can crack the glass-ceramic substrate.

One possible solution is, as experiments show to slow down the heating profile thus the amount of evolving gas per unit time is decreasing. This way the pressure is reduced inside the channels. Another possible solution is the use of sacrificial material, which has slower burning in the function of the temperature so the decomposition is slower. This way less gas evolves and less pressure is imposed on the channels.

Considering the temperature region where SVM burnout takes place the firing profile is altered to provide enough time for the burnout of SVM. Thermo-gravimetric analyses have been conducted to optimize the firing profile in order to avoid crack formation or delamination.

Based on the results of TGA it becomes evident that the heating rate has to be decreased for the period of the burnout stage of the tape firing process. A still slow pyrolization has to be started which enables the exhaust of the gaseous decomposition products via the channels.

Thus the three technological factors can not be universally defined, but design and the circumstances will provide the optimum combination.

4 Conclusions

Improved methods for realizing and verifying fluidic microchannel in LTCC substrate were presented.

- The optimal parameters for the isostatic lamination for LTCC substrate containing embedded channel were determined.
- The predesigned and formed solid state SVM is an absolute novel and innovative solution in the field of the multilayer LTCC formation technology and provides accurate channel geometry in case of wider channel as well.
- A verifying method of channel quality (delamination rate) determination using scanning acoustic microscopy was developed. The samples made by different parameters were examined by this method. It is concluded that the best samples of lamination was made, when the maximum 20 MPa pressure was applied. By increasing the lamination time there was no significant improvement observed.
- The heating profile and SVM should be consistent with each other and with the desired structure. The dimensions of the channel should be considered at the firing process.
- The study of SVMs degradation kinetics shows that its degradation could be controlled by changing the heating rate.

In conclusion, the degradation is caused by the SVM gassing and it could be controlled by the accurate heating profile. Based on these results, embedded structures in a multi-layer LTCC platform were realized with this modified heating profile.

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