Fabrication of LTCC Micro-fluidic Devices Using Sacrificial Carbon Layers

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Abstract

Ease of fabrication and design flexibility are two attractive features of low temperature co-fired ceramics (LTCC) technology for fabrication of complex micro-fluidic devices. Such structures are designed and processed using different shaping methods, the extent and complexity of which depends on the final device specifications (dimensions, mechanical and functional properties). In this work, we propose a sacrificial layer method based on carbon-black paste, which burns out during the LTCC firing stage. The paper will summarize the preparation of the paste, influence of processing conditions on the final dimensions, and demonstrate the mechanically integrated structures obtained using this technique. Some of those are membranes of various diameters (7-12mm) with a thickness of 40µm and a variety of internal spacing (15-60µm), free-hanging thick-film resistors (TFR) bridges on LTCC for heating micro-volumes. The main methods of the study will be thermo gravimetric analysis (TGA), scanning electron microscopy (SEM) and dilatometry in addition to electronic instruments for device characterization.

Keywords: LTCC, 3-D structuration, sacrificial layer, microfluidics

Introduction

Although micro-fluidic devices have been an interesting domain of micro engineering for a long time, it is quite recently that the application areas have diversified significantly. Requirements for fabrication of highly functional micro-devices in addition to the industrial interests have pushed the sector to the search and development of new materials and technologies, which has actually become the driving force for this diversification. Among all these efforts, LTCC technology has been pointed as the most suitable and attractive choice for a wide range of applications[1-9].

The technology is based on low temperature firing (<900°C) of dielectric sheets, which can be screen-printed and laminated with thick-film pastes of electronic components. The most interesting properties for micro-fluidic device fabrication are the ease of utilization of LTCC tapes, their excellent thermal and chemical stability and hermeticity. Additionally mechanical, fluidic and electrical functions are combined under one system, which is very attractive for sensor applications[10-15].

In spite of these benefits, there are quite a number of studies in the literature, which summarizes the difficulties encountered during the fabrication of micro-fluidic devices using the LTCC technology[16-18]. These basically arise from the nature of the functional elements in the LTCC tape and the effects of processing conditions on these materials. For instance the glass content of the (fitted) tape is used to enhance the densification at relatively low temperatures[19] (<900°C). Its effect on the 3-D structure during firing is due to the glass softening temperature (T_g), at which viscosity reduces considerably and the glass is subjected to mechanical constraints exerted by the device features. This usually results in sagging in structures such as micro-channels, membranes, etc unless they are mechanically supported. This is especially an important issue for production, if critical dimensions are of interest (e.g. membranes with a thickness and internal spacing of 40-50µm and 20-30µm respectively).

Thus the objective of this paper is to propose a simple and effective method for realization of 3-D LTCC micro-fluidic structures by reducing the so-discussed defects. The motives for selecting the proposed sacrificial layer – carbon-black paste, its processing and application will be explained. Additionally the fabricated structures, which are prepared at different processing conditions, will be demonstrated. The resulting structures, their mechanical and functional properties will be analysed and discussed with respect to the results of SEM, TGA, dilatometry.

Selection of the sacrificial layer

Sacrificial layers are widely used to retain the shape and the integrity of the 3-D LTCC structures[16-18]. They are intended to prevent deformations such as sagging, disintegration, etc, which are usually observed after firing. However using sacrificial layers is not always necessary. The need is rather dependent on the specifications of the functions and the physical dimensions of the final product. For instance careful lamination and firing of LTCC sheets for fabrication of a cavity does not necessarily require a mechanical support (sacrificial layer) unless the sheet thickness and cavity spacing are desired below few hundred microns. However a uniform spacing thickness that can be obtained without sagging in this way does not ensure the physical integrity of the fired layers. Figure 1 demonstrates the clear difference between the close to and far away from cavity edge layers, where the former shows lack of integration. Such a result can especially be a burden for a micro-fluidic channel or membrane, where the pressure in the well-defined volumes must be defined precisely.

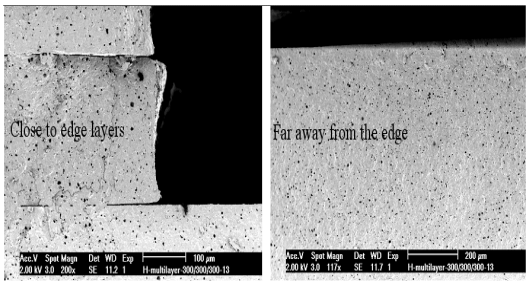

Figure 1. Lack of integration on the regions close to the edge layers of the cavity (on the left image).

Our preliminary trials yielding similar results shown in figure 1 forwarded us to the utilization of sacrificial layers. Although different methods are cited in the literature such as use of glass or polymeric layers as the fugitive phase17, we decided on the carbon black paste, which we obtained by mixing the synthetic graphite powder with suitable organics. Its handling simplicity both as a powder during firing and as a paste during screen-printing, burnout at relatively low temperatures compared to LTCC densification temperature, its non-reactivity with the tape made it an attractive choice for our application.

Among these features, the most critical one is the burnout characteristics of the used graphite powder. The burnout reaction in the air atmosphere is typically

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

which later necessitates the total removal of the gas product from the environment. It is clear that in case of a membrane structure, which we will be focusing our attention to from here on, the burnt paste must leave the surroundings before the porosity in the tape is totally closed. This process is simultaneously dependent on the kinetics of the graphite burnout in the paste and the densification of the LTCC, which is referred in figures 2 and 3 respectively.

The former figure shows the TGA (Mettler Toledo system) of the powder (1-2μ). The vertical axis is the change of weight in terms of the temperature (x-axis). The analysis was carried out in air atmosphere at a heating rate of 10°C/min continuously up to the peak temperature. It is evident that this relation has a correlation to the powder size and the heating rate (e.g. finer particle sizes and slower heating rates result in a full burnout at lower temperatures)

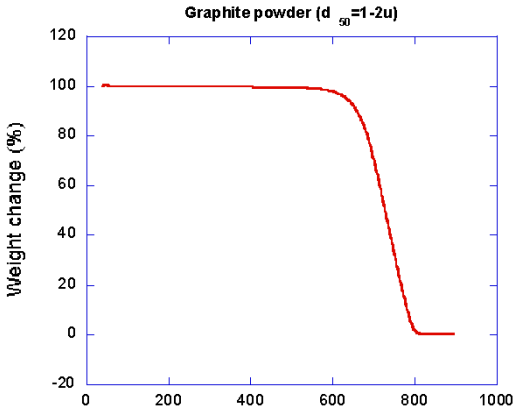

Figure 2. TGA of the graphite powder (1-2μm).

On the other hand figure 3 shows the characteristics of the tape densification (Dupont 951-AX). Dilatometry analysis (Setaram) was carried out according to a two-step firing profile that is commonly applied to LTCC. This is to say a dwell time of 120 minutes at 440°C was followed by a peak firing temperature at 875°C at a heating rate of 5°C/min and a dwell peak time of 25 minutes. Test was performed on the LTCC pellets, which were prepared by removing the organic content of the tape using acetone in ultrasonic bath and then heating it slowly up to 250°C. This was followed by grinding the residue in the mortar and uni-axially pressing the powders.

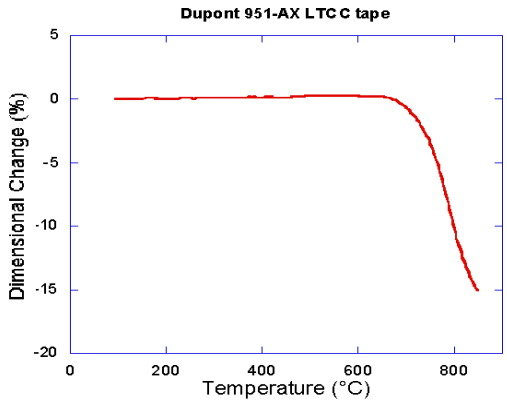

Figure 3. Densification behavior of the LTCC pellet.

In light of figures 2 and 3, it is possible to make an approach to the burnout versus degassing relation between the paste and the LTCC substrate, which is a critical issue for the applicability of the proposed method. According to the dilatometry result, the tape shrinkage starts at 670°C and goes up to 875°C (slightly higher than the value in the figure 3) resulting in 15% of shrinkage. In this range, the total burnout temperature of the graphite powder takes place at 800°C (figure 2), which corresponds to 10% shrinkage of the tape. So we focused our attention on this temperature range at which the porosity in the LTCC is eliminated. For this purpose we developed a closed-chamber system, which is shown in figure 4. The essence of this system is to detect the leakage through the fired LTCC substrate, which is placed between the two O-rings, by exerting air pressure on the surface by the piston. The air leak, which is quantified by the pressure relaxation time, is actually a qualitative assessment of the open porosity. The measuring system is composed of a power supply, a multimeter, which reads the current coming from the pressure sensor and the PC system.

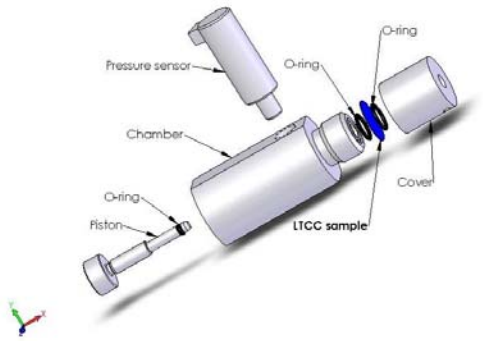

Figure 4. Closed-chamber system built to measure the temperature at which the open porosity on the LTCC tape closes.

The results, which are obtained using this technique, are illustrated in figure 5 and 6. Figure 5 shows the obvious leakage through the substrate that is fired at 750°C. The two peaks indicate the pressure application, which is then released through the porous LTCC. On the other hand, figure 6 shows a different behavior of pressure change. It is clearly seen that the 4 sets of lines, which are accumulated in the upper part of the figure, indicate the substrates free of open porosity. The decrease in their values is attributed to the minor leakage, which is not detected by us and probably existing in the system. Moreover the absolute values they are referring to are dependent on the degree of their connection to the chamber via O-rings. Thus differences between these samples are not meaningful.

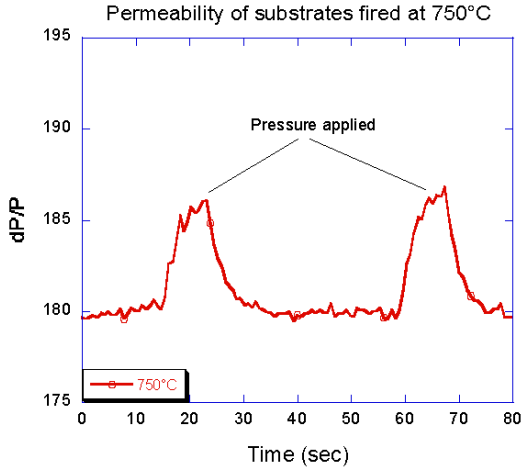

Figure 5. Leakage due to porous substrate fired at 750°C.

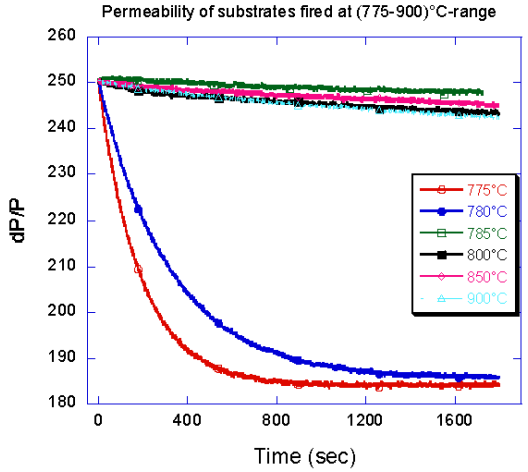

Figure 6. Qualitative detection of the porosity elimination temperature.

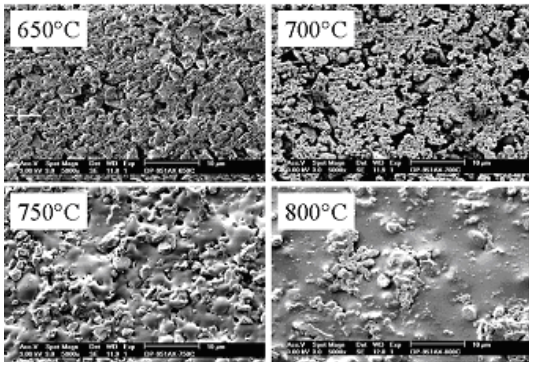

Figure 7. Macroscopic porosity (closed at 800°C).

As a result, figure 6 clearly points the open porosity elimination temperature for the LTCC, which is in the 780-785°C range. This result agrees with the SEM images of the surfaces, which are shown in figure 7.

We believe that the applicability of the proposed method is better understood and evaluated by data compilation from figures 2, 3, 5 and 6.

Although it will be investigated in details in the following section, it is crucial to make a remark at this point; depending on the heating rate, the burnout of the carbon can be incomplete at the point where the LTCC porosity closes.

Preparation and screen-printing of the sacrificial layer

The sacrificial layer was prepared in a fashion similar to that of commercial thick-film pastes. Namely, the functional phase, which is the graphite powder, was mixed with an organic vehicle to gain appropriate rheology for screen-printing.

Constituents were blended at 26/74 ratio by weight of powder to organics. Initially, the binder and the solvent were mixed at 87°C until the complete dissolution of the binder. This was followed by gradual introduction of the graphite powder on the mixture simultaneously with the dispersant. The preparation was finalized by rolling the suspension on 3-cylinder system (figure 8), which is widely used to homogenize the thick-film pastes. The functions and the properties of the materials used are given in table 1 (selection of 3 different types of graphite powder is explained in the subsequent chapters).

The prepared sacrificial layer was screen-printed according to the layout shown in figure 9 (left), which is used for fabrication of a membrane that is connected to the inlet and outlet by channels. The layout on the right is for the post-fired conductor and resistor pastes to complete the micro-fluidic device. Screen-printing on the 254µm-thick LTCC tape was followed by drying the paste at 120°C in the oven (Heraeus) for 20 minutes. For increased sensitivity of the device, a thin LTCC layer of 50µm (Du Pont 951-C2) was laminated on this layer at 70°C. Lamination was performed using a uni-axial press at 25MPa and under rubber to retain the desired membrane profile. The laminated structure was then fired in a special LTCC furnace (ATV-PEO 601) under continuous air flow according to the profile described in the previous section.

Fabricated structures - membranes

As explained in the previous sections, the properties of the graphite powder used have a direct influence on the final structure. This is a consequence of the kinetics-dependent competition between paste burnout process and pore-elimination. In this sense, this section aims to explain the important parameters such as powder size, heating rate, powder burnout temperature and the dimensions of the desired structure.

Table 1. Materials used for the sacrificial layer

Product	Function	Specification	Supplier
Graphite	Sacrificial	d_{50} : 1-2µm (used lot)	Aldrich, 28,286-3
		d_{50} : 11µm	TIMCAL, Timrex-KS25
		d_{50} : 15. 3µm	TIMCAL, Timrex-KS5-25
Ethyl cellulose	Binder	control of rheology	Aldrich, 43,383-7
Terpineol	Solvent	slurry viscosity	Fluka, 86480
Acetyl acetone	Dispersant	dispersing additive	Sigma-Aldrich, P775-4

Figure 8. Three-cylinder for homogenization of the sacrificial paste.

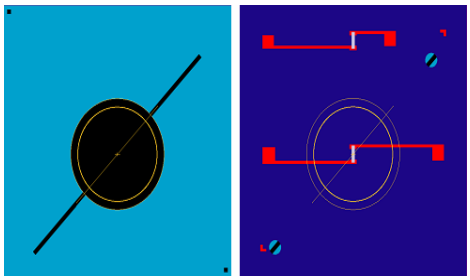

Figure 9. Basic layout for screen-printing of the sacrificial layer (on the left) and the thick-film passive components for membranes.

The early stages of the membrane fabrication were carried out by using fine-size graphite powder (d_{50}~1-2µm). The processing parameters are identical to those explained previously (heating rate of 5°C/min). Figure 10 shows the cross-section details of the structures obtained using this powder. As can be seen from the SEM pictures, membrane is continuous and free of sagging with a spacing of 13µm. Moreover it is flat with a thickness of 41µm, which allows post-firing of thick-films.

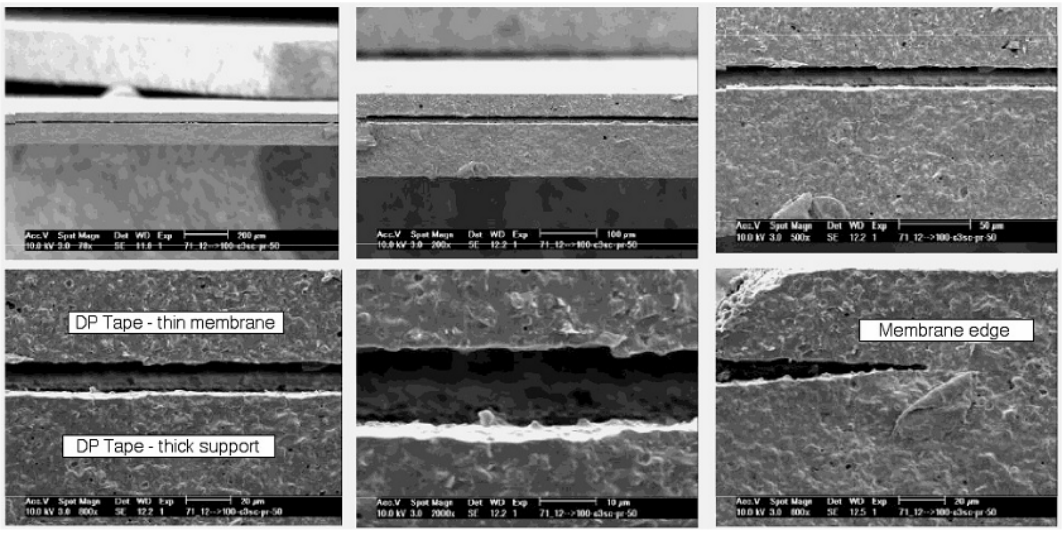

Figure 10. 7 mm-diameter membrane with 41µm thickness and 13µm spacing (white-grey solid reflections from the spacing is due to charging).

Some applications (large membranes, micro-fluidics) require larger spacing. This was impossible to achieve reliably with fine graphite powder: excessive sagging was observed. We believe that this was due to premature burn-out of the graphite, giving less support for the membrane. As a result of this, we used graphite powders with coarser particle size (Table 1): 11 and 15.3 instead of 1-2µm, expecting a shift of the burnout to higher temperatures. We prepared corresponding pastes in the same way as the previous one and used approximately the same powder to organics ratio.

Figure 11 shows the comparison by TGA of the graphite powders used. The complete burnout temperature for the coarser powders is around 860°C at 10°C/min of heating rate, well above 780°C which is the porosity closure temperature of LTCC. At this heating rate, approximately 40% of the graphite cannot leave the membrane prior to open pore elimination.

Therefore, we made new membranes, using the coarser graphite powder and varying two parameters: the heating rates for a 10mm-diamater membrane and the diameter of the membrane at 5°C/min heating rate and checked the corresponding deformation (figure 12 and 13 respectively).

The primary value of interest is t_{UBM}, which corresponds to the height of the swollen membrane surface in the middle of the membrane (maximum value) and it is shown on the y-axis. It is measured by a sensitive profilometer (UBM) that plots the surface topography of the membrane, using laser, and correlates with the membrane spacing.

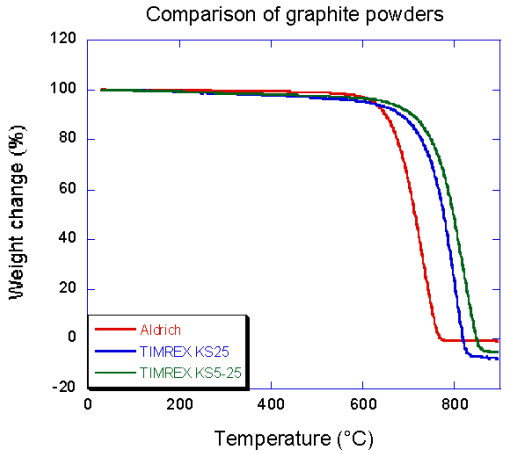

Figure 11. Comparison of burnout temperatures for the graphite powders used (heating rate: 10°C/min).

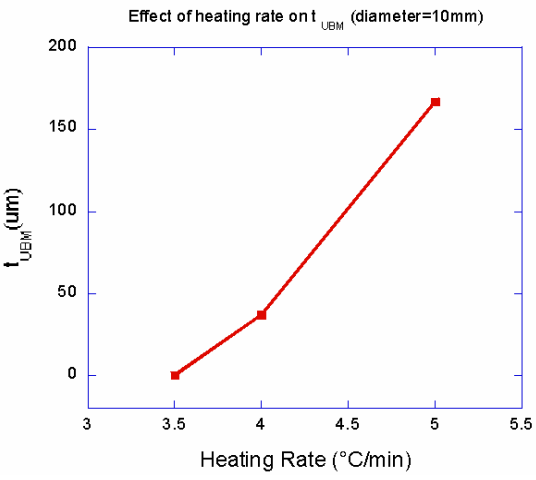

Figure 12. Effect of heating rate on the surface profile of the 10mm-diameter membrane (coarse powder/ TIMREX KS5-25).

According to figure 12, the extent of membrane swelling can be directly controlled by the heating rate. Slower rates provide long burning times, which facilitate easy burnout and degassing before porosity closure resulting in less swelling.

The extent of swelling upon increased membrane diameter at constant rate is shown in figure 13. This is a result of the amount of organics printed on the surface, which requires more time for complete burnout.

The membrane surface profiles and structures fabricated in light of the obtained results are shown in figure 14. The larger membrane, which has a diameter and spacing of 14mm and 260µm respectively, is demonstrated for comparison.

It can be seen from figure 14 that the processing parameters have direct influence on the fabricated structures, the extent of which can reach to undesired shapes. The smaller membrane is flat (by surface profiler) with a spacing of 63µm by cross-sectional SEM images (figure 15). These pastes therefore allow to increase the spacing to values higher than 13µm (figure 15). However, strong dependence of the membrane flatness on the heating rate and the diameter is observed, which we ascribe to competition between the kinetics of the graphite burnout and sintering. After the LTCC porosity closes, transport of oxygen and CO/CO2 essentially occurs through the narrow inlet/outlet channels. In this case, the membrane cavity is likely to be depleted in oxygen during sintering, and the volume increase could be due to the progressive shift under these conditions of the CO/CO2 equilibrium in favor of CO as the temperature rises.

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$

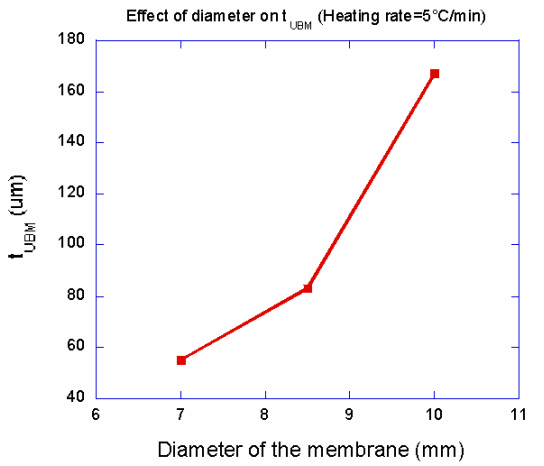

Figure 13. Effect of membrane diameter on the surface profile at 5°C/min heating rate (coarse powder/ TIMREX KS5-25).

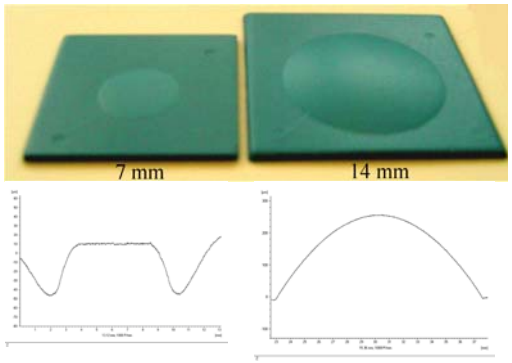

Figure 14. Membranes with diameters of 7 and 14 mm, both fired at 5°C/min heating rate. The corresponding surface profiles are shown below the image.

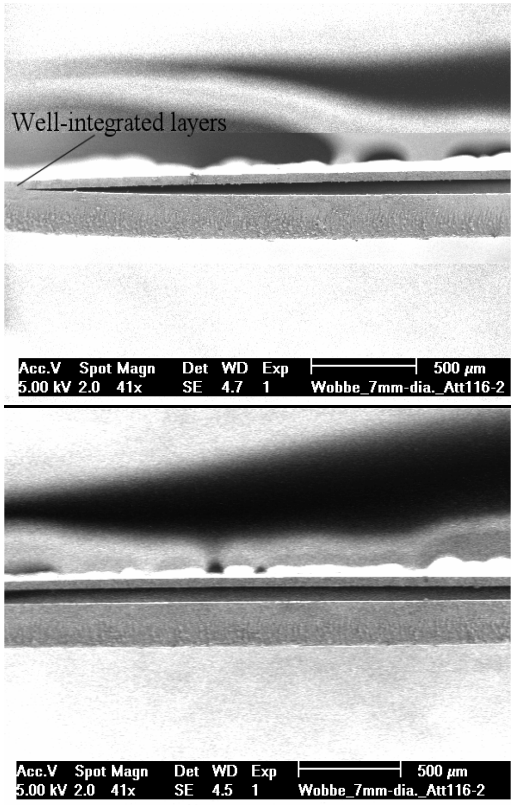

Figure 15. SEM images of the 7mm-diameter membrane. Well-integrated layers on the edges (above) and approximately 60µm of well-defined spacing shown.

Firing of the membrane is followed by screen-printing and post-firing of the conductor and resistor pastes, which complete the micro-fluidic device (figure 16). In this case firing is performed in belt furnace (Sierratherm) according to a 45 minute-cycle at 850°C of peak temperature.

The tests have demonstrated expected flow and mechanical properties. Functional characterization of these devices will be the object of a future paper.

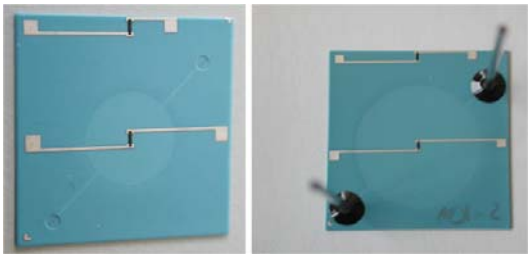

Figure 16. Screen-printed membrane (left). Post-firing followed by completion of inlet and outlet ports.

Another structure produced by using the described technique is shown in figure 17. It is a free-hanging PTC resistor bridge, which is fabricated on LTCC.

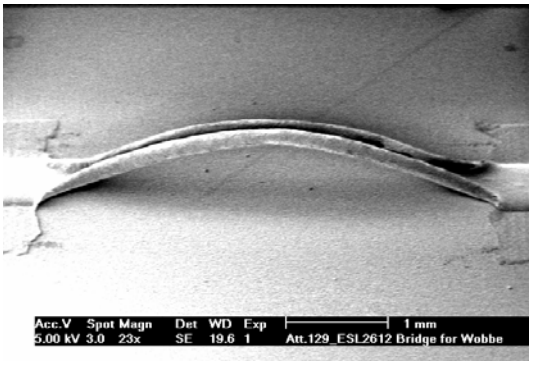

Figure 17. PTC resistor bridge fabricated on LTCC substrate (height from the surface ~ 600μm).

It is fabricated with the purpose of heating and measuring the amount of this heat in micro-modules, although the electrical characterization is still being studied.

Conclusions

This paper summarizes the processing and application of a sacrificial layer, carbon-black paste. Moreover fabricated structures are demonstrated in light of the test results obtained. According to our results, the most critical parameters with this method can be listed as;

- properties of the graphite powder (size, burnout temperature, etc),
- properties of the LTCC tape (densification behavior, thickness, open-pore elimination temperature, etc)
- heating rate,
- the size of the membrane.

With respect to these parameters, swollen membranes occur due to the organics burnout in the paste, which occurs after the porosity elimination. Although this can be compensated by manipulation of heating rate, it arises from the intrinsic material properties of the graphite powder (burnout) and the LTCC tape (porosity elimination).

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