Structuration of Micro-fluidic Devices Based on Low Temperature Co-fired Ceramic (LTCC) Technology

H. Birol, T. Maeder, C. Jacq, G. Corradini, Y. Fournier, I. Saglini, S. Straessler and P. Ryser

Ecole Polytechnique Fédérale de Lausanne (EPFL), Laboratoire de Production Microtechnique (LPM), CH-1015 Lausanne, Switzerland

Tel: + 41 21 693 77 58, Fax: + 41 21 693 38 91, E-mail: hansu.birol@epfl.ch

Abstract

Smart packaging concept has been the driving force for the search of advanced technologies to produce multi-functional micro-scale devices for long years. In this sense, LTCC technology has been recently addressed as the suitable choice for a wide range of applications. In addition to its attractive characteristics for high-frequency applications those have been profited for a long time, it receives a growing attention for sensor applications in the recent years as well. This is due to the easy maschinability of the LTCC tapes, which permits realization of complex structures such as membranes, channels, making it a suitable environment for micro-fluidic devices. These devices require utilization of supporting layers in order to prevent defects, often observed in forms of sagging, warpage or curling. The methods for elimination of these defects vary from passive precautions taken during lamination and firing to more elaborate methods such as use of sacrificial layers. The basic idea in the latter method is the preparation of a support, which can then be removed, leaving behind the desired structure. Among a number of alternatives, this paper focuses on and proposes the carbon-black sacrificial paste as an effective and simple method to fabricate membranes. Additionally determination of the open porosity elimination temperature in LTCC and effect of processing parameters on the fabricated structures, will be discussed. The methods of analysis will be TGA (thermo gravimetric analysis), dilatometer and SEM (scanning electron microscopy) analysis.

Key words: LTCC, sacrificial layer, 3-D structuration, porosity elimination.

Introduction

Since the early stages of its introduction to the market, LTCC has been extensively used for high frequency applications[1-4] due to its interesting dielectric characteristics such as high dielectric strength and low dissipation factor at high frequencies. This makes it an attractive solution as these properties play an important role in high-speed propagation of the signals in the circuit. Moreover design flexibility, which is introduced by multi-layering, and compatibility with low-resistance thick-film conductors (Au, Ag, Cu), contribute to these advantages.

Other than these benefits related to dielectric characteristics, the easy machining of tapes plays an important role as well in its multi-purpose application in micro-technology, which permits realization of complex features such as membranes and channels, making it a suitable environment for micro-fluidic devices[5]. This comes with other advantages such as excellent thermal and chemical stability, hermeticity and possibility of integration with other technologies. Thus mechanical and electrical functions unite under one system, which justifies its suitability for sensor applications[6-7].

In spite of these advantages, production of complex and fine structures is strongly dependent on the desired feature dimensions, which requires utilization of sacrificial layers[8-9]. Thus the scope of this study is to propose an effective method, which is the utilization of carbon-black paste as sacrificial layer, to make membranes and channels for micro-fluidic devices.

Selection of the materials for the paste, the effect of processing conditions on the final structures is studied and the resulting structures are demonstrated in terms of processing variables. Membranes with 40µm of thickness, at various diameters (7-15 mm) with different spacing (15-400µm) are obtained opening horizons for new applications. The methods of the study are TGA (thermo gravimetric analysis), dilatometer, SEM (scanning electron microscopy) analysis and electronic instrumentation for testing the produced structures.

Preparation of the Sacrificial Layer and Fabricated Structures

As explained previously, use of sacrificial layer depends strongly on the desired quality and the application field of the fabricated structure. Although the literature cites precautions[8-9] such as improving the lamination conditions, firing profile, etc to avoid sagging in cavities, it usually results in a sacrifice in mechanical and structural properties (figure 1). Utilization of a sacrificial layer is a necessity to improve integration and retain the shape of the desired structure. This is particularly important for membranes with well-defined dimensions.

Among the proposed methods for production of sacrificial layer, we used the graphite powder-based paste, which we will be referring to as carbon-black paste from here on. Table 1 summarizes the materials used for the preparation of this material.

We used powders with two different particle sizes: finer (1-2µm) and coarser. The latter size was used to fabricate larger cavities (membrane structures mainly) with increased spacing. In either case, the graphite powder was blended with an organic vehicle to reach a desired rheology for screen-printing. The ratio of graphite to organics by weight was 24 to 76.

The suspension was homogenized using a 3-cylinder, and was then screen-printed on the LTCC sheets according to the layout shown in figure 2. The sheets were dried and laminated with a second layer of LTCC tape (Du Pont 951-C2), to complete the membrane structure. Lamination was carried out at 25MPa of uni-axial pressure at 70°C. This was followed by firing in air in an LTCC oven (ATV-PEO 601) according to the profile illustrated in figure 3.

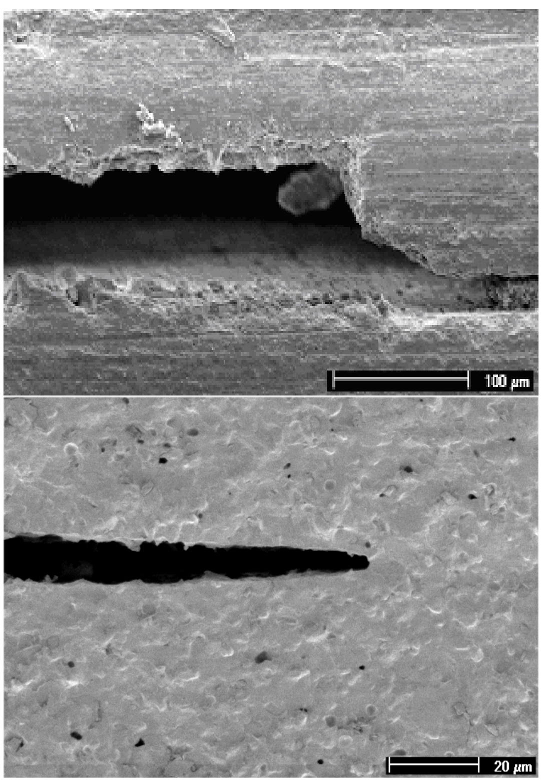

Figure 1: Poor integration (above) and improved integration using sacrificial layer.

Table 1. Materials used for the sacrificial paste

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

** : particle size*

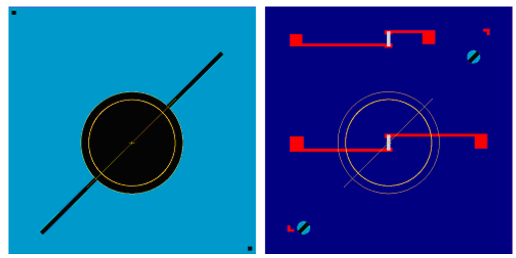

Figure 2: Layout for the membrane (left) and the conductor and resistors.

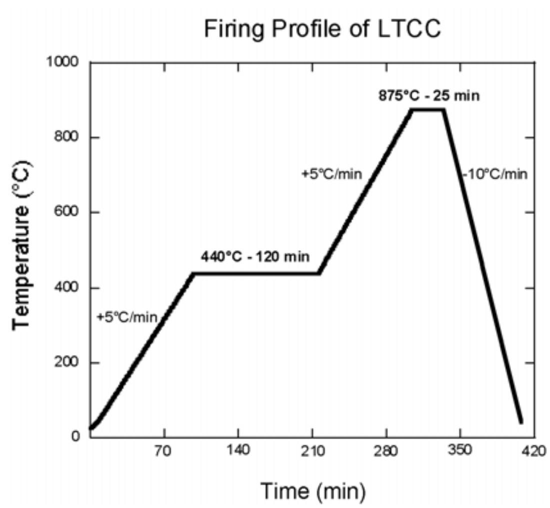

Figure 3: LTCC firing profile.

The properties of the fabricated membranes are overviewed in table 2. The surface profiles and the SEM images of these structures are presented in figure 4. The former data is obtained by a profilometer that scans the membrane using laser, whereas the latter information is gathered by SEM imaging the cross-sectional areas of the membranes. The results demonstrate that the paste with coarser graphite was effective in increasing the cavity spacing and resulted in swollen membranes. This was especially observed in larger membranes, which ended up with increased cavity spacing: 200-400µm. The final module was completed by integration of the inlet and outlet ports (figure 5).

Table 2. An overlook of fabricated membranes+

Graphite	Diameter	Profile	Spacing°
d_{50} : 1-2µm	7mm 10mm	Flat Flat	~13µm ~13µm
d_{50}: 15. 3µm	7mm 10mm 14mm	Flat Swollen Swollen	~60µm ~110µm ~260µm

+: membranes fired at 5°C/min of heating rate
o: by SEM

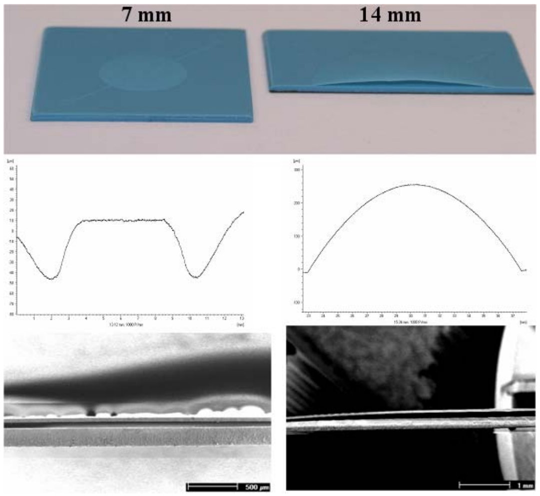

Figure 4: Comparison of flat (left column) and swollen membranes (surface profile -second row- and cross-section by SEM -third row).

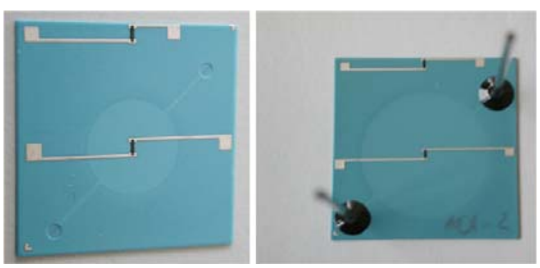

Figure 5: Completed device with inlet and outlet ports (left).

Experimental Analysis and Discussions

Before elucidating with the effects of processing conditions on the final structures, the selection of the carbon-black paste as the sacrificial layer is to be attributed to the followings

-the oxidation of the graphite powder at relatively low temperatures compared to LTCC sintering temperature according to

$$C(s) + O_2(g) \rightarrow CO_2(g) \ldots (1)$$

- screen-printing of the paste in desired form
- non-reactivity of the graphite with LTCC

Among all, the first statement is the most important one, as it is related both to the properties of the graphite powder and the LTCC (Du Pont 951-AX) tape. This suggests that the burnout products, which are formed as a result of oxidation of the organics, must leave the LTCC before the closure of the open porosity. This process is based on the kinetic competition between these parameters, the consequences of which effect the final structures.

Thus we made TGA of graphite powders (from table 1) in order to determine the graphite burnout temperature. Powders were heated in air at a rate of 10°C/min. The results are demonstrated in figure 6.

On the other hand we made dilatometric analysis of the pelletized LTCC tape to find out the shrinkage behavior of the LTCC (figure 7). Pellets were prepared by a treatment, based on separation of the LTCC powder form the organics in acetone, in an ultrasonic bath. This was followed by heating the acetone-rich mixture up to 250°C gradually and then grinding the residue in an agate mortar to reduce the particle size. The powder was pressed uni-axially at 25MPa to prepare the pellets, which were than placed into the dilatometer (Setaram). The identical firing profile to the previously described one (figure 3) was used. The result of dilatometer analysis is shown in figure 7.

According to these results, fine and coarse-size graphite powders are burnt out approximately at 780°C and 865°C, respectively (figure 6). On the other hand the LTCC tape densifies at around 875°C, which is slightly higher than it is shown in figure 3. Although the temperature, at which the density of LTCC reaches 85%, can be considered as the temperature of closure of the open porosity, we developed a closed chamber (figure 8) in order to determine this point precisely. The essence of this system is to demonstrate the air leakage through the LTCC substrates, in terms of pressure relaxation time. In light of dilatometer analysis, we focused on the substrates fired in the 750-800°C range. We observed rapid air leak between 750°C and 770°C, whereas the substrates fired at 775°C demonstrated a gradual pressure drop (figure 9). Finally it was found that the porosity closure in LTCC occurs in the 780-785°C range.

In conjunction to the TGA data, this result is useful in explaining the properties of the fabricated structures. According to TGA results, coarser graphite powders are not completely burnt out at the onset temperature of the porosity closure on LTCC. Approximately 35% of the powder remains in the closed structure at 785°C, which is partially oxidized due to the insufficient oxygen transport to the membrane area that can occur only via the inlet and outlet channels. Under these circumstances, the imprisoned gas is believed to be the result of the partial oxidation of the graphite powder according to the reaction

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

For the fine-size graphite powders, on the other hand, oxidation is completed (reaction 1) approximately at the same temperature of porosity closure. As a result of this, swelling is not observed and the cavity spacing remains at a constant value, almost independent of membrane diameter. Figure 10 demonstrates the cross-sectional details of both types of membranes.

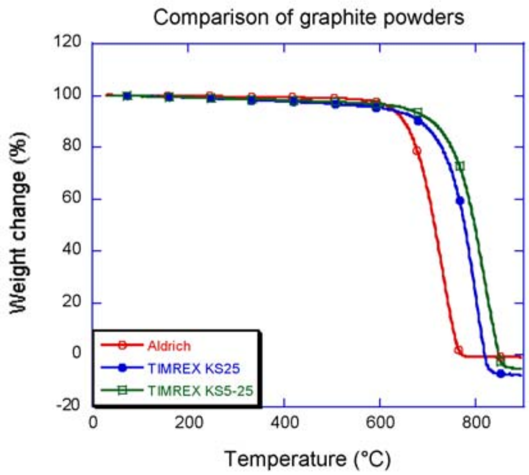

Figure 6: TGA of commercial graphite powders.

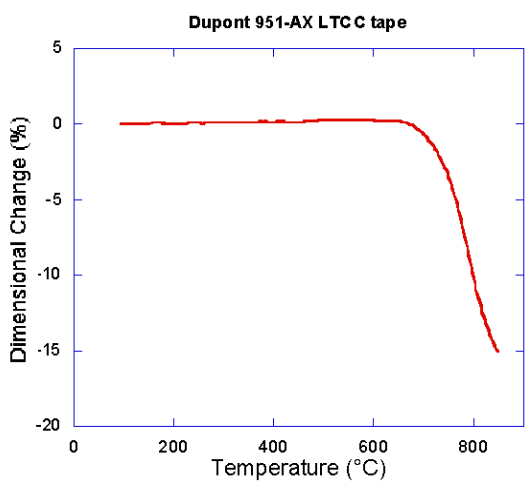

Figure 7: Shrinkage behavior of LTCC tape.

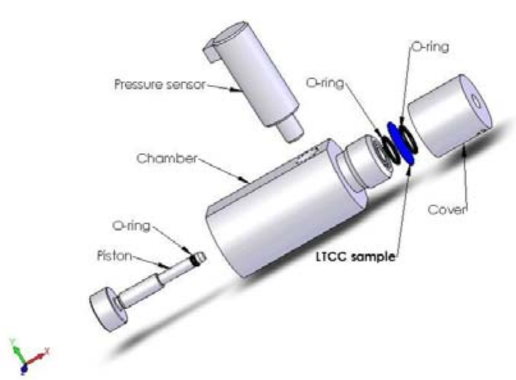

Figure 8: Closed chamber for determination of LTCC open-porosity elimination temperature.

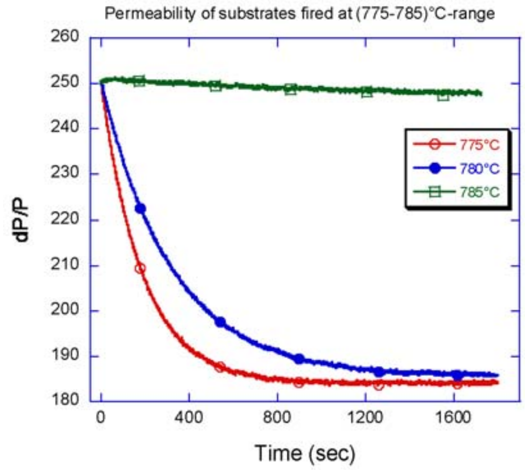

Figure 9: Pressure-change in time. Decreasing pressure at 785°C attributed to the experimental set-up.

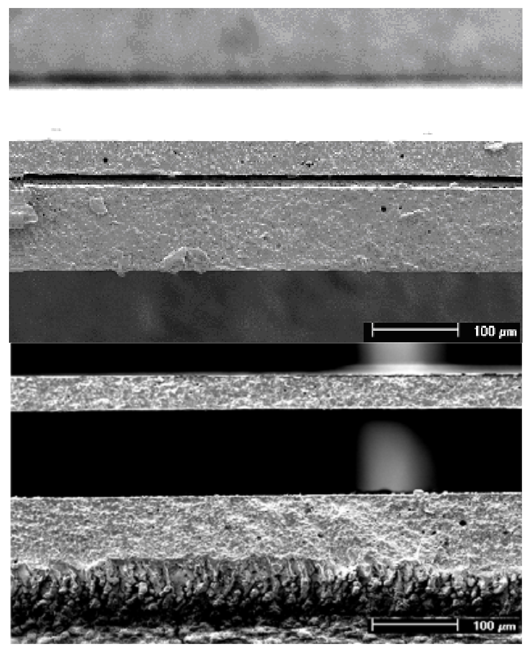

Figure 10: Smaller (above) and larger cavity spacing by use of fine and coarse graphite powders respectively (identical magnification).

Conclusions

Preparation and application of carbon-black sacrificial paste to fabricate LTCC-based membranes is explained. The material properties and the effects of processing conditions are outlined in details.

It is shown that the proposed method is applied successfully to produce membranes of different dimensions. The structural properties of the produced membranes are ascribed to the competition between the burnout kinetics of the graphite powder used for the paste and the open porosity elimination temperature of LTCC. According to this, it is seen that pastes with coarser particle size are burnt at temperatures higher than the open-pore closure temperature of LTCC, resulting in swelling.

Additionally a closed chamber system, which qualitatively determines the open-pore elimination temperature of LTCC, is introduced.

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