Structuration of the low temperature co-fired ceramics (LTCC) using novel sacrificial graphite paste with PVA-propylene glycol-glycerol-water vehicle

Name and address of the person to whom proofs are to be sent:

Karol Malecha, PhD

Faculty of Microsystem Electronics and Photonics

Wrocław University of Technology

Wybrzeże Wyspiańskiego 27

50-370 Wrocław, Poland

e-mail: karol.malecha@pwr.wroc.pl

phone: +48 71 355 4822 fax: +48 71 328 3504

Structuration of the low temperature co-fired ceramics (LTCC) using novel sacrificial graphite paste with PVA-propylene glycol-glycerol-water vehicle.

Karol Malecha

Wrocław University of Technology, Faculty of Microsystem Electronics and Photonics, Wybrzeże S. Wyspiańskiego 27, 50-370 Wrocław, Poland

Thomas Maeder, Caroline Jacq, Peter Ryser

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

ABSTRACT

A novel formulation for thick-film graphite sacrificial pastes is studied in this paper. It is composed of coarse graphite powder (grain size: 25 μm), dispersed in a vehicle consisting of polyvinyl alcohol (PVA) dissolved in a propylene glycol (PG) – glycerol (G) – water mix, which is not aggressive to thin LTCC sheets. The presented sacrificial paste has been successfully applied for fabrication of thin (< 50 μm) membranes and microchannels in LTCC (Low Temperature Co-fired Ceramics) substrate. The properties of the graphite-based paste have been examined using thermo-gravimetric analysis (TGA), differential thermo-gravimetric (DTA) and differential thermal analysis (DTA). The obtained membranes and microchannels have been investigated using scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX) and optical profile measurements gauge.

Key words: sacrificial volume material (SVM), polyvinyl alcohol-propylene glycol-glycerol-water vehicle, LTCC, membrane, channel

Introduction

Low Temperature Co-fired Ceramics (LTCC) technology has been used to produce hybrid circuits and multichip ceramic modules (MCM-C) since the 1980s [1,2]. The LTCC material is characterized by chemical inertness and resistance, high temperature stability, matching of thermal expansion coefficient with silicon and ease of micromachining. Thanks to these features LTCC is well established in both for low volume, high performance (military, space) and high volume, low cost (car industry, wireless communication) applications. Recently, the low temperature co-fired ceramics has found new practical application in the fabrication of sensor, actuator and microfluidic devices and microsystems [3-5]. A common LTCC structure is composed of several dielectric tapes mechanically and electrically connected. Electrical connections are provided by surface and buried conductive lines (Au, Ag, PdAg) and passives (resistors, capacitors, inductors). The conductors and passives may be deposited by screen-printing or ink-jet printing techniques. After printing, all ,,green" ceramic tapes are stacked together in proper order, laminated and co-fired at a peak temperature of ca. 850^{o}C. Additional passive and active components can be placed on the top or bottom surface of the fired LTCC module using standard SMT (Surface Mounting Technique), wire bonding and flip-chip techniques. The most critical technological steps in the fabrication process are lamination and co-firing; these two stages determine the quality of the final LTCC multilayer device. The typical method used for bonding ,,green" ceramic tapes is thermo-compression. In this technique LTCC layers are joined together at high pressure (10-30 MPa) and elevated temperature (40-90^{o}C) for 1-20 minutes. Although this method provides very strong final bonding between ceramic layers, high pressure and temperature affect the geometry of the spatial structures and precludes realization of complex features (e.g. membranes, channels, cavities) inside ceramic modules. Deformation of the three-dimensional (3-D) structures can

be reduced by supporting them with special sacrificial volume materials (SVM). A considerable number of papers reporting of successful application of different types of substances as an SVM: wax [6], carbon/graphite-based layers [3,7-11], polymers [12,13] and mineral materials [14-16]. Application of various sacrificial volume materials for LTCC 3-D microstructuration has been the object of several reviews [11,17,18]. Formulating sacrificial inks for screen-printing onto LTCC can be problematic, given the large amount of printed material, as common solvents such as terpineol and dibutyl carbitol also dissolve / excessively soften the LTCC binder of most commercial compositions [19].

Based on this work, a graphite sacrificial paste with a new polyvinyl alcohol (PVA) dissolved in a propylene glycol (PG) – glycerol (G) – water vehicle was formulated, with water being the principal solvent for PVA, and PG / G acting in the wet state as co-solvents and humectants, i.e. hindering water evaporation. Given its high boiling point, G essentially does not evaporate during paste drying, and remains in PVA as a plasticizer. This new SVM paste is less aggressive with ceramic tapes in „green" state in comparison with typical terpineol-based ones; the PG-G-water solvent mix essentially eliminates the problem of dissolution of unfired LTCC layers, which is especially crucial for the relatively thin (~50 μm) ceramic tapes used for sensitive structures, while being environmentally friendly and essentially non-toxic.

The properties of the presented sacrificial paste were investigated using combined thermo-gravimetric analysis (TGA), differential thermal analysis (DTA) and differential thermo-gravimetry (DTG). The PVA-PG-G-water based SVM was applied to fabrication of surface/buried channels and thin membranes. The resulting structures were examined using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and optical profile measurement gauge.

Experimental

The presented graphite paste was made by the same procedure as for commercial thick-film compositions. The processing steps required first preparation of the polyol/water vehicle consisting (weight ratios) of 10 PVA binder (9 Mowiol® 4-88 + 1 Mowiol® 40-88), in 80 PG – 5 G – 15 deionized H_2O solvent mix, with G also acting as plasticizer (PVA, PG & G used as procured from Aldrich). Both PVA grades are in fact random copolymers of polyvinyl (alcohol 88% + acetate 12%), "88% hydrolysis", with the ratio of short-chain (4-88) to long-chain (40-88) PVA and the overall binder concentration being tunable to obtain the right viscosity and rheology for screen-printing. Then, the functional element, synthetic graphite powder (TIMREX KS25, TIMCAL, Switzerland, grain size ≤25 μm) was added to the vehicle, with a 37:63 graphite to vehicle ratio by weight. Finally, this mixture was homogenized using a three-roll mill [7-9]. This ready-to-use sacrificial paste was applied to fabricate surface/buried channels and thin membranes in LTCC substrate. A flow chart of the test structures manufacturing process is presented in Figure 1. Membranes and buried channels were made using the ,,collate and laminate" technique (Figure 1a). First the graphite paste is screen-printed on the surface of DuPont (DP) 951 LTCC tape. After deposition, the SVM layer was dried for 10 minutes in air at 120^{o}C. Then, the tape with printed SVM is collated with another ceramic layer by isostatic lamination. Alternatively, LTCC test structures with open channels were fabricated using the ,,define and fill" method (Figure 1b). First, channels were cut in ,,green" ceramic tapes by Nd-YAG laser (Aurel NAVS 30). The cutting process was followed by an initial lamination at a relatively low pressure of 1 MPa, at room temperature for 5 minutes. Next, channels were filled in by screen-printing of the graphite paste through a mask made of polymer (Mylar®, DuPont). After printing and drying the test structure with open channels was laminated a second time at a standard pressure of

20 MPa at a temperature of 70^{o}C for 10 minutes. Finally, all test structures were co-fired in a box furnace (Nabertherm L3/S) with a standard two-step thermal profile. In the first step, the LTCC module was heated up to 450^{o}C with heating rate 7^{o}C/min, in order to burn out the organics. In the second stage, at temperature of 850^{o}C with peak dwell time of 15 minutes, sintering process took place (heating rate 6^{o}C/min). The graphite paste was removed during the burnout process, leaving empty volume in the LTCC substrates.

Results and discussion

TGA/DTA/DTG analyses of the graphite paste

The thermal properties of the applied PVA-PG-G-water-based sacrificial layer were characterized using combined TGA/DTA/DTG analyses. The graphite paste was heated in air at a rate of 3^{o}C/min, and the results are presented in Figure 2. The solid green line – the DTA curve – indicates the measured heat flow. Changes in sample weight during the firing process are shown as a solid blue line (TG curve). The green dotted line – the DTG curve – illustrates the rate of the sample weight loss in the specific temperature. According to the thermo-gravimetric analysis the graphite sample weight loss takes place in three stages. In a first phase (up to ca. 250°C), the solvents and plasticizer evaporate rapidly (H_2O → PG → G), without well-separated peaks (minimum at the DTG curve, 139^{o}C), yielding a total weight loss of ca. 63%. The endothermal nature of the evaporation process is confirmed by a minimum at the DTA curve. In a second phase, thermal decomposition of the non-volatile part of the vehicle, essentially the PVA binder, occurs up to ca. 500°C, in agreement with previous work [20], and is linked with a smaller decrease of the SVM weight (~8%). According to TGA and DTG curves, graphite oxidation process starts at a temperature of circa 500-550^{o}C and lasts to the end of the firing process.

Optical and scanning electron microscope investigation of membranes and channels

The developed sacrificial paste was applied to fabricate thin (~50 μm) membranes with various diameters (6-17 mm), surface and buried channels with different widths (100 μm - 1 mm) in LTCC. All test structures laminated and co-fired with the SVM indicated very good integration between ceramic tape layers and retained desired geometry. Moreover, the sacrificial graphite paste avoided sagging and deformations of the membranes and channels during lamination and burnout processes. The properties of the fabricated three-dimensional structures were investigated using optical and SEM microscopy. The cross-section details of the exemplary membrane obtained using graphite sacrificial paste with PVA-PG-G-H_2O vehicle are presented in Figure 3. As can be seen from the microscope image, the membrane is continuous and free of deformations with spacing of circa 120 μm and thickness of circa 40 μm. However, all fabricated membranes were somewhat swollen, which is ascribed to the use of a relatively coarse graphite powder, the absence of escape channels and the use of a relatively fast heating ramp during sintering [9,18]. For finer (~1-2 μm) graphite particles, membranes should be more flat [7,8]. The SEM images of the buried and surface channels made in the LTCC substrate are presented in Figures 4 and 5, respectively. The ceramic test structures that were fabricated according to procedures illustrated in Figures 1 and 2 exhibit complete fusion between all LTCC tape layers, i.e. the boundary between the original tapes cannot be discerned. The cross sections of the surface and buried channel structure show different features: a rather lentoid outline for the buried channels and rectangular cross-section for open channels. The difference in surface and buried channels geometry is a consequence of the applied technological procedure. The Lentoid outline of the buried channels is conditioned by shape of printed SVM paste. Skewing of the open channel walls is caused by the laser cutting process. One of the drawbacks of laser patterning is that the laser cut vias and channels normally have a tapered shape [12,21].

EDX analysis

For open channels, the presented sacrificial paste burnt away cleanly, leaving no residue. However, contamination was noticed at the bottom of membranes and buried channels. An example of contaminated surface of the test structure is presented in Figure 6. We have noticed that LTCC surface was tarnished. Moreover, agglomerates of carbonaceous contamination were noticed. The graphite paste residue was examined using the EDX method, with the results presented in Figure 7. According to the EDX analysis, the contamination agglomerates consists mainly of carbon (~80%) and oxygen (~15%) while the tarnished surface of the LTCC is composed of smaller amount of carbon (~20%), indicating incomplete burnout of the graphite powder. Carbon may have been sequestered in oxidised form by oxides such as SrO or BaO, that might be present in LTCC and are known to form very stable carbonates. Probably, the coarse graphite particles burn out at temperature higher than the open-pore closure temperature of LTCC [7-9], resulting in contamination.

Surface roughness measurements

The influence of the applied sacrificial paste on the LTCC surface morphology was analyzed using an optical profilometer (Veeco-Dektak 150 Surface Profiler). Measurements were made on both the bottom surface of the open-channel test structures presented in Figure 5 and for a reference LTCC substrate made with the standard technological process. The surfaces were scanned over 5 mm to measure the overall roughness. Surface profile plots of the investigated samples are shown in Figure 8. The average roughness (R_a) values were very similar for both tested structures. R_a for the bottom surface of the open channel made with use of the SVM paste and for the reference sample was equal to 0.31 μm and 0.34 μm, respectively, confirming that the graphite paste formulated with the novel vehicle does not damage the surface of the LTCC ceramics. As a final note, further advantages of the presented polyol-water vehicle must be mentioned: in case of a misprint, the paste can be removed from the

green LTCC with water without damaging the tape, and the vehicle is environmentally benign and essentially non-toxic.

Conclusions

The presented sacrificial carbon paste with PVA-PG-G-H_2O vehicle can be successfully used as a mechanical support during lamination and co-firing process. It has considerably decreased sagging and avoids deformations of the membranes and channels.

It has been shown that the proposed SVM-based technological procedures are suitable for fabrication of thin (~50 μm) membranes with various diameters (6-17 mm) and surface/buried channels of different dimensions (100 μm – 1 mm).

Contamination was noticed at the bottoms of buried test structures that were made with use of the presented graphite paste. This carbonaceous contamination was associated with the burnout process. Carbon residue can be eliminated by changing the thermal profile of the co-firing process (slower ramp rate up to 850^{o}C), by using a finer graphite powder in the sacrificial paste formulation, or by introducing channels of controlled dimensions to the outside.

Measurements made with an optical profile measurement gauge have shown that this novel sacrificial paste formulation does not interact with LTCC ceramics.

Acknowledgments

The authors wish to thank Wrocław University of Technology (grant no 343 660) for financial support, and TIMCAL for kindly providing the graphite powder.

The Foundation for Polish Science (FNP) is also acknowledged for financial support for Karol Malecha.

References

[1] Tummala RR, Ceramics in microelectronic packaging, *American Ceramic Society Bulletin* 1988;**67**:752-758.

[2] Nishigaki S, Fukuta J, Low-temperature, cofireable, multilayered ceramics bearing pure-Ag conductors and their sintering behavior, *Ceramic Substrates and Packages for Electronic Applications (Advances in Ceramics)* 1989;**26**:199-215.

[3] Gongora-Rubio MR, Espinoza-Vallejos P, Sola-Laguna L, Santiago-Aviles JJ, Overview of low temperature co-fired ceramics tape technology for meso-systems technology (MsST), *Sensors and Actuators A* 2001;**89**:222-41.

[4] Golonka LJ, Technology and applications of low temperature cofired ceramic (LTCC) based sensors and microsystems, *Bulletin of the Polish Academy of Science* 2006;**54/2**:221-31.

[5] Ibáñez-Garcia N, Martinez-Cisneros CS, Valdés F, Alonso J, Green tape ceramics. New technological approach for integrating electronics and fluidics in microsystems, *Trends in Analytical Chemistry* 2008;**27/1**:24-33.

[6] Kinzy Jones W, Liu Y, Gao M, Micro heat pipes in low temperature cofire ceramic (LTCC) substrates, *IEEE Transactions on components and packaging technologies* 2003;**26/1**:110-5.

[7] Birol H, Maeder T, Jacq C, Straessler S, Ryser P, Fabrication of low-temperature co-fired ceramics micro-fluidic devices using sacrificial carbon layers, *International Journal of Applied Ceramic Technology* 2005;**2/5**:364-73.

[8] Birol H, Maeder T, Ryser P, Processing of graphite-based sacrificial layer for microfabrication of low temperature co-fired ceramics (LTCC), *Sensors and Actuators A* 2006;**130-131**:560-7.

[9] Birol H, Maeder T, Ryser P, Application of graphite-based sacrificial layers for fabrication of LTCC (low temperature co-fired ceramic) membranes and micro-channels, *Journal of Micromechanics and Microengineering* 2007;**17**:50-60.

[10] Malecha K, Jurków D, Golonka LJ, Comparison of solvent and sacrificial volume-material-based lamination processes of low-temperature co-fired ceramics tapes, *Journal of Micromechanics and Microengineering* 2009;**19**:065022.1-10.

[11] Peterson KA, Patel KD, Ho CK, Rohde SB, Nordquist CD, Walker CA, Wroblewski BD, Okandan M, Novel microsystem applications with new techniques in low-temperature co-fired ceramics, *International Journal of Applied Ceramic Technology* 2005;**2/5**:345-63.

[12] Smetana W, Balluch B, Stangl G, Luftl S, Seidler S, Processing procedures for the realization of fine structured channels arrays and bridging elements by LTCC-technology, *Microelectronics Reliability* 2009;**49**:592-9.

[13] Kinzy Jones W, Kappagantula S, Wang J, Micro channel fabrication in LTCC substrate, *Proc. IMAPS/ACerS 1st International Conference and Exhibition on Ceramic Interconnect and Ceramic Microsystems Technologies (CICMT)* 2005; April 10-13, Baltimore (USA):29-31.

[14] Lucat C, Ginet P, Castille C, Debeda H, Menil F, Microsystem elements based on free-standing thick-films made with a new sacrificial layer process, *Microelectronics Reliability* 2008;**48**:872-5.

[15] Lucat C, Ginet P, Ménil F, New sacrificial layer based screen-printing process for free-standing thick-films applied to MEMS, *Journal of Microelectronics and Electronic Packaging* 2007;**4/3**:86-92.

[16] Maeder T Jacq C, Fournier Y, Hraiz W, Ryser P, Structuration of thin bridge and cantilever structures in thick-film technology using mineral sacrificial materials, *Proc. IMAPS/ACerS 5th International Conference and Exhibition on Ceramic Interconnect and Ceramic Microsystems Technologies (CICMT)* 2009; April 21-23, Denver (USA):175-82.

[17] Maeder T, Fournier Y, Wiedmer S, Birol H, Jacq C, Ryser-P, 3D structuration of LTCC / thick-film sensors and fluidic devices", *Proc. IMAPS/ACerS 3rd International Conference and Exhibition on Ceramic Interconnect and Ceramic Microsystems Technologies (CICMT)* 2007, April 23-26, Denver (USA):THA13.

[18] Khoong LE, Tan YM, Lam YC, Overview on fabrication of three-dimensional structures in multi-layer ceramic substrate, *Journal of the European Ceramic Society* 2010;**30**:1973-87.

[19] Maeder T, Jacq C, Fournier Y, Ryser P, Formulation and processing of screen-printing vehicles for sacrificial layers on thick-film and LTCC substrates, *Proc., XXXII International Conference of IMAPS Poland Chapter* 2008; September 21-24, Pułtusk (Poland):B16.

[20] Gurak NR, Josty-PL, Thompson-RJ, Properties and uses of synthetic emulsion polymers as binders in advanced ceramics processing, *American Ceramic Society Bulletin* 1987;**66**:1495-1497.

[21] Wang G, Folk EC, Barlow F, Elshabini A, Fabrication of microvias for multilayer LTCC substrate, *IEEE Transactions of Electronics Packaging Manufacturing* 2006;**29/1**:32-41.

Figure captions

Figure 1. Flow-chart of the (a) ,,collate and laminate" and (b) ,,define and fill" procedures.

Figure 2. Results of TGA/DTA/DTG analyses for a propylene glycol-glycerol-water-based sacrificial paste.

Figure 3. Cross-section details of the 17 mm-diameter membrane with 40 μm thickness.

Figure 4. SEM images of the buried channels made in LTCC substrate using glycol-glycerol-water-based sacrificial paste.

Figure 5. SEM images of the open channels made in LTCC substrate using glycol-glycerol-water-based sacrificial paste.

Figure 6. Contamination at the bottom of the channel.

Figure 7. Atomic composition of the sacrificial paste debris (EDX analysis).

Figure 8. Measured roughness plot for (a) reference LTCC structure and (b) bottom of the microchannel made with the sacrificial paste.

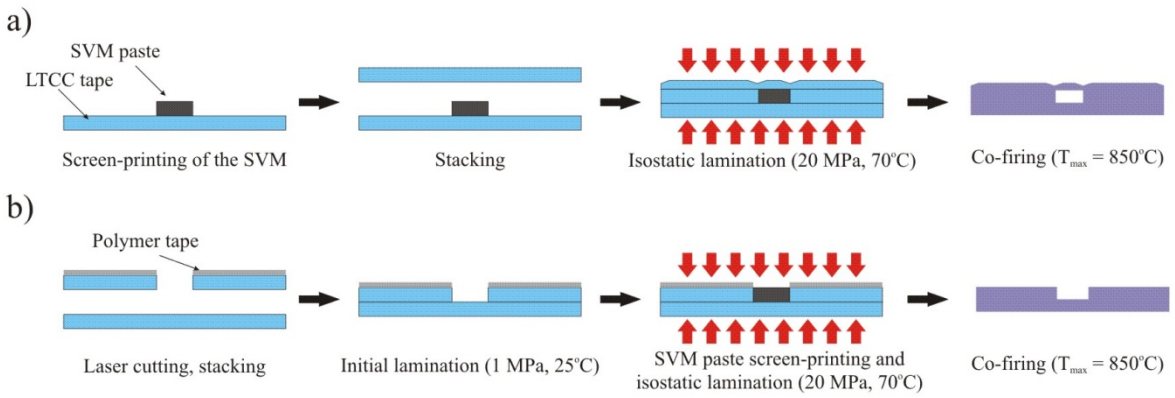

Figure 1. Flow-chart of the (a) ,,collate and laminate" and (b) ,,define and fill" procedures.

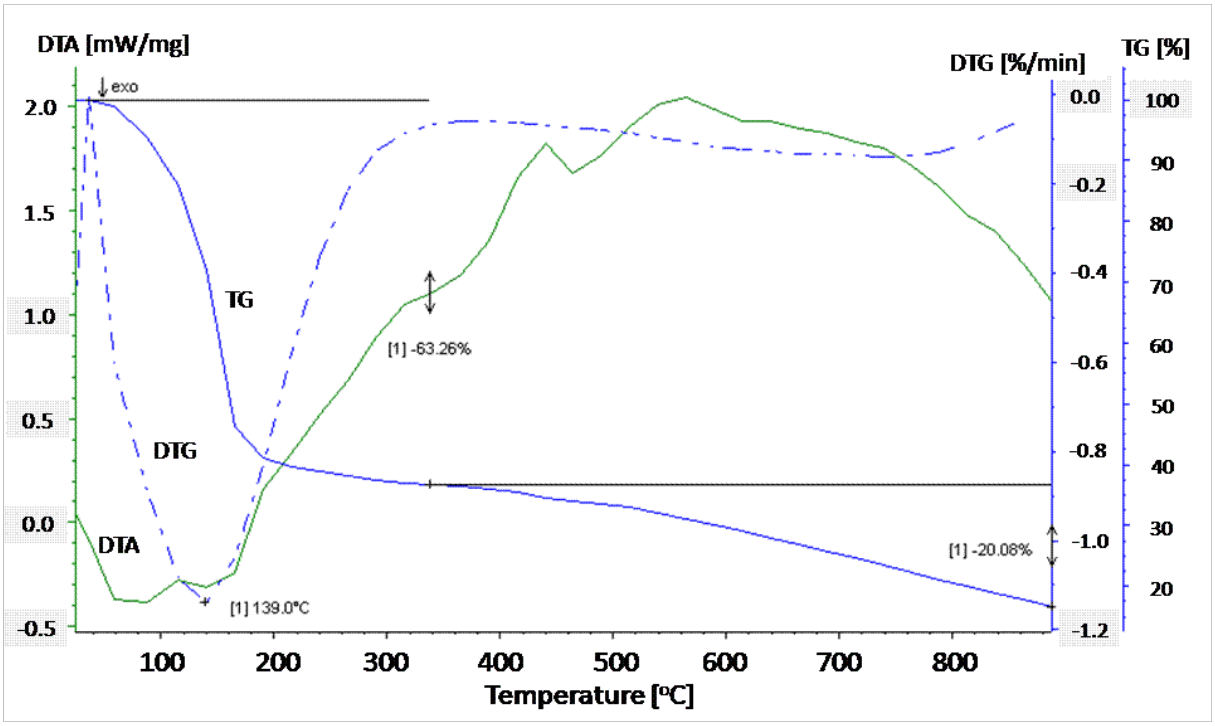

Figure 2. Results of TGA/DTA/DTG analyses for a propylene glycol-glycerol-water-based sacrificial paste.

Figure 3. Cross-section details of the 17 mm-diameter membrane with 40 μm thickness.

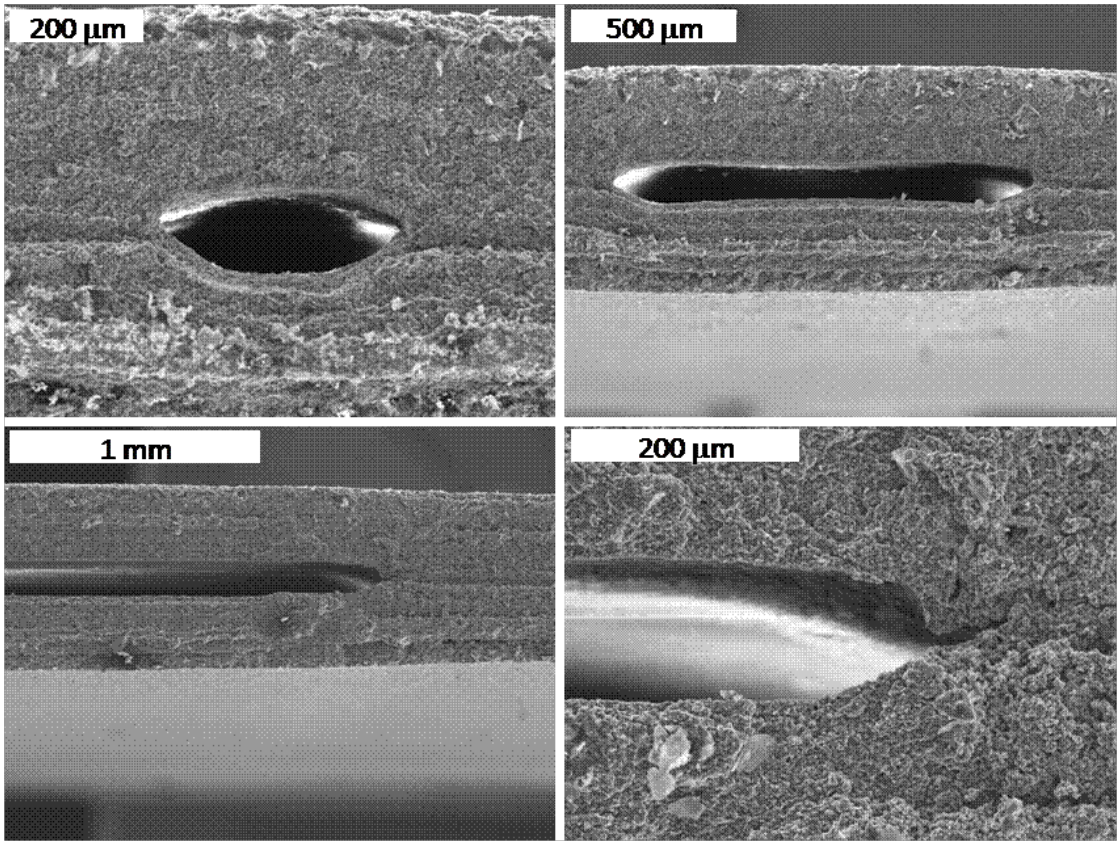

Figure 4. SEM images of the buried channels made in LTCC substrate using glycol-glycerol-water-based sacrificial paste.

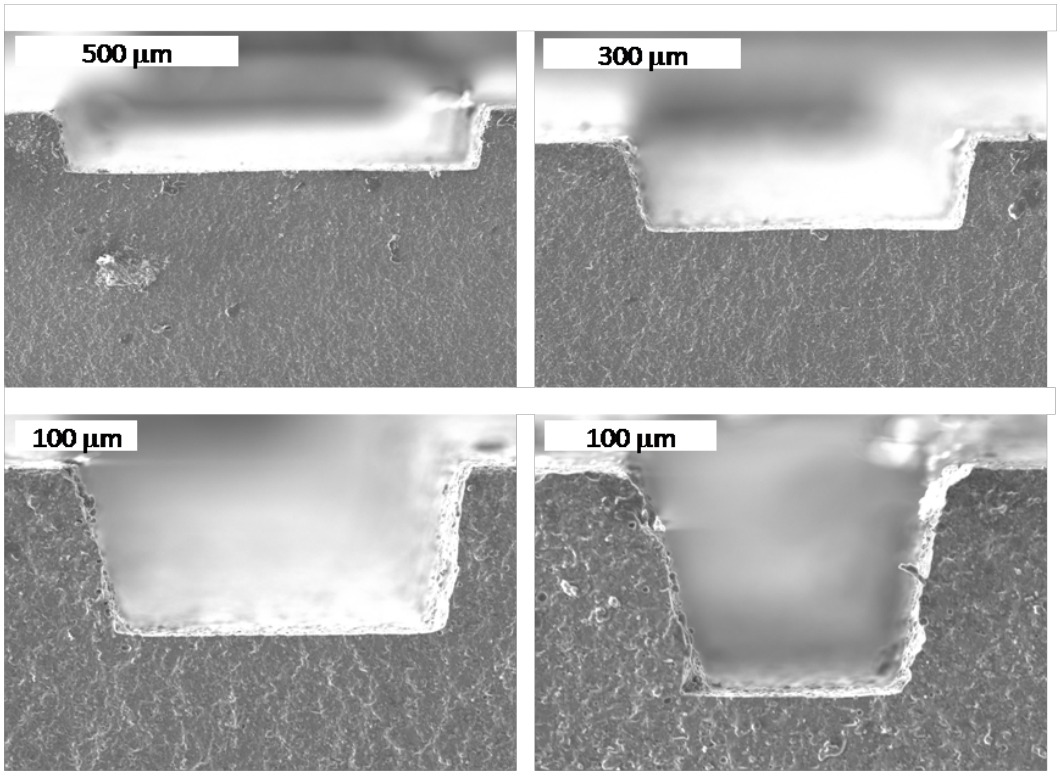

Figure 5. SEM images of the open channels made in LTCC substrate using glycol-glycerol-water-based sacrificial paste.

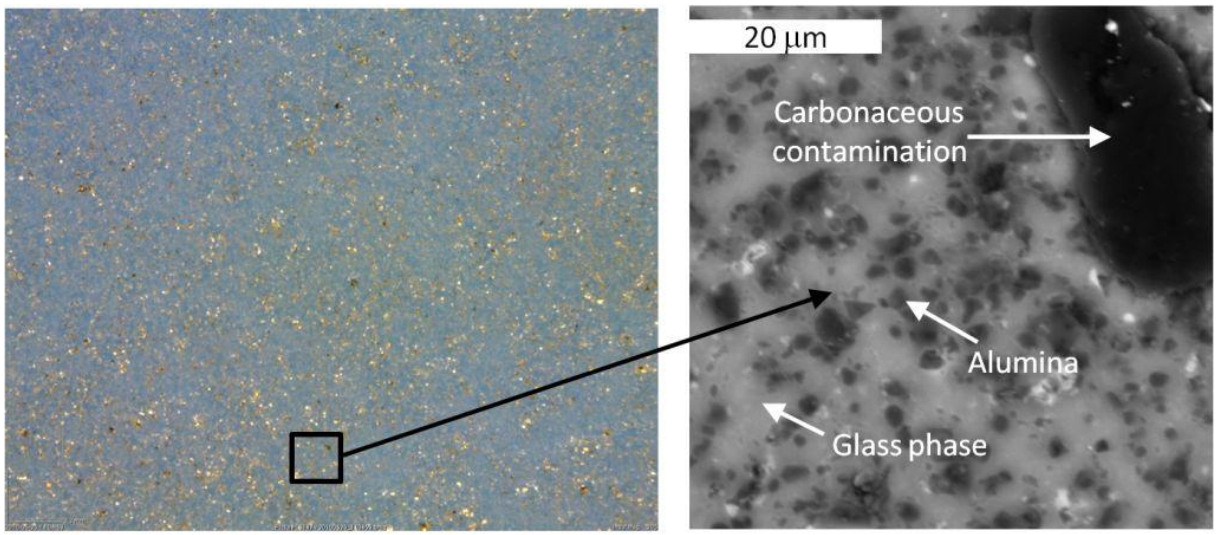

Figure 6. Contamination at the bottom of the channel.

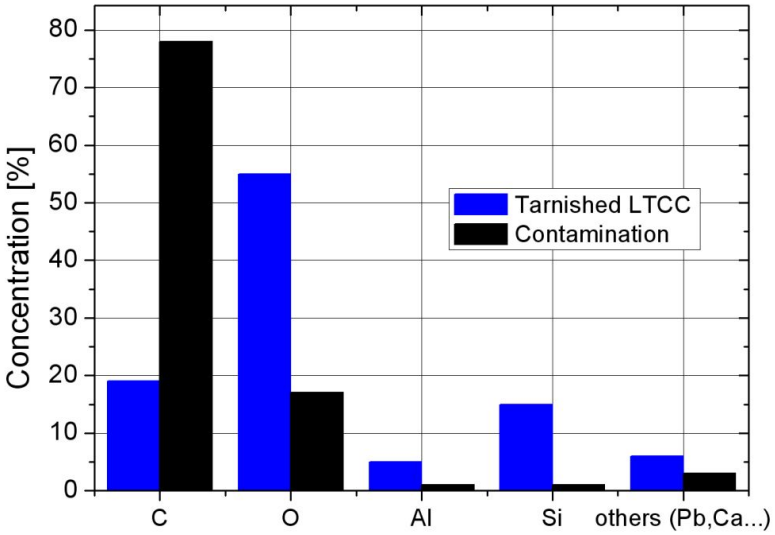

Figure 7. Atomic composition of the sacrificial paste debris (EDX analysis).

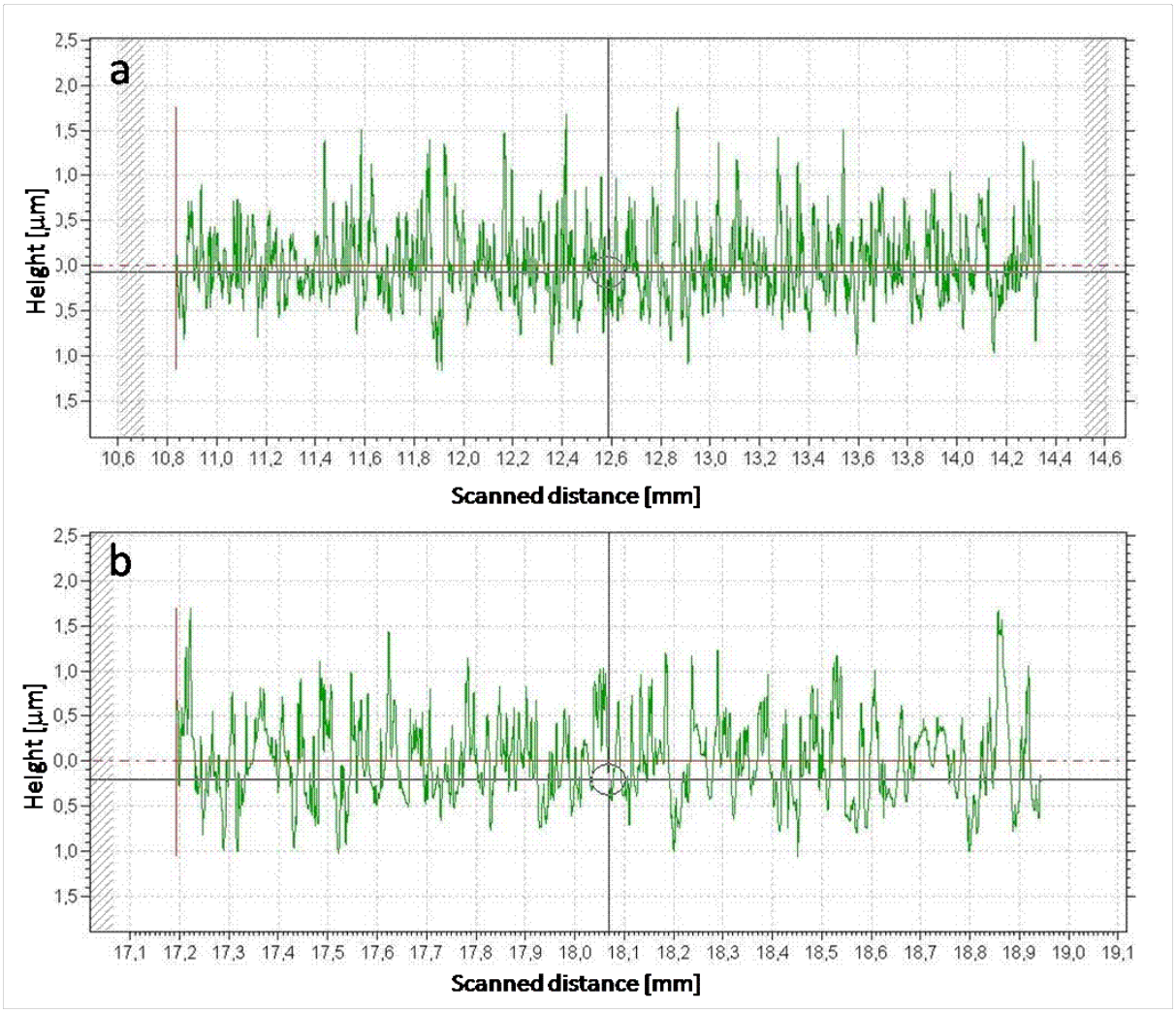

Figure 8. Measured roughness plot for (a) reference LTCC structure and (b) bottom of the microchannel made with the sacrificial paste