3D structuration of LTCC and related technologies for thermal management and microfluidic structures

Thomas Maeder, Conor Slater, Bo Jiang, Fabrizio Vecchio, Caroline Jacq and Peter Ryser

Abstract: Ceramic technologies such as LTCC (Low Temperature Co-fired Ceramic) and thick-film are used widely in electronic circuits exposed to harsh environments, for applications in fields such as aerospace, automotive and energy exploration, where, owing to their thermal and chemical stability, they have an extensive and successful track record. Recently, the extensive structuration possibilities afforded by LTCC have led to its use in sensors, microfluidics and thermal management (hotplates). In the first part of this work, we present both new and classical techniques for structuring ceramic devices for thermal management, microfluidics or both. Critical aspects for achieving successful structuration and reliable device operation are discussed, such as lamination and sealing techniques, materials formulation and selection, as well as thermomechanical design. These considerations are illustrated in the second part of this work with several examples: micro-hotplates for various applications, microfluidic coolers, chemical reactors and solid-oxide fuel cell (SOFC) components.

Key words: Thick-film technology, LTCC, 3D structuration, microfluidics, thermal management.

1. Introduction

Originally introduced as a chip / multichip module packaging and high-reliability circuit technology [1-4], LTCC has found important additional applications in the field of advanced packaging, sensors and microfluidics. This requires more advanced 3D structuration techniques, required to form features such as thin bridges, cavities, membranes, channels and hotplates [5-16].

In the green state, LTCC tape is easily shapeable, and may be cut and further processed by a wide variety of methods (Table 1), which in principle easily allows features such as channels, bridges and membranes (Figure 1). An overview of the resulting LTCC applications is given in Table 2 (see also other paper at this conference [17] for mechanical sensors). The very wide range of devices and applications attest for the excellent 3D structurability of LTCC.
However, problems that appear at the different stages of processing (handling, lamination and firing, Table 1) in practice severely hamper many applications. Moreover, the properties and limitations of LTCC as a material must also be taken into account, such as mechanical strength (short- and long-term), chemical durability and thermal stability. Also, physical properties such as the coefficient of thermal expansion (CTE) and elastic modulus are important for device performance.

The purpose of the present work is therefore to give an overview of the applications of LTCC structuration, centred on microfluidics and thermal management, with the associated themes:
- Processing issues and how they are resolved
- Properties and limitations of LTCC as a material
- Implications on device design

**Figure 1:** Example LTCC structures (see table 2) (1-3) Meander channel (1) and heater module (2) for gas viscosity sensor (3, with membrane) [18-20]; 4) chemical microreactor with complex fluidic circuit [16, 20]; 5) thermal bubble inclinometer (with membrane) [9]; 6) cantilever sensor for low forces [9, 16, 21, 22].

**Table 1:** Methods and operations used in 3D structuration of LTCC.† SVM = sacrificial volume material. # MSM = mineral / fugitive sacrificial (volume) material.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Methods</th>
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| Cutting / drilling / shaping | - Mechanical microdrilling / end milling [7, 23]  
- Punching / stamping [24]  
- Laser cutting of LTCC [24-26]; of conductors [27, 28]  
- Embossing [24, 29, 30]  
- Controlled laser ablation [31]  
- Solvent vapour jet cutting [32]  
- None (lamination directly around SVM†) [7, 33, 34] |

| Lamination methods and conditions (LP/HP = low-/high-pressure) | No sacrificial material  
- Uniaxial, HP, cold [13, 35]  
- Uniaxial, minimal-pressure, cold [36] or warm [37]  
- Adhesive tape, LP [38, 39]  
- Solvent / adhesive paste / adhesive solution, LP [12, 40-44]  
- Hot-melt adhesive layer, LP [45]  
With sacrificial material  
- Warm, HP, uniaxial or isostatic (standard methods) |

| Lamination order | All at once (standard procedure)  
- Sequence of partial laminations, often with different methods/parameters [13, 44, 46, 47] |

| Firing | No sacrificial material or MSM#  
- Standard, in air (usually)  
With FSM#  
- Air (match sintering and burnout kinetics) [10, 48-51]  
- Air-N2-air (sinter in N2, then oxidise FSM) [17, 52] |

| Post-firing operations (depending on device) | MSM† removal by chemical dissolution [52-57] or mechanical blowing [8]  
- Screen-printing of materials incompatible with co-firing  
- Cutting of temporary supports [58 2012]  
- Singulation by dicing or breaking |

**Table 2:** Applications of LTCC structuration techniques beyond purely electrical ones. † M(O)EMS: micro (opto) electromechanical system. # µ-SOFC: micro solid-oxide fuel cells.

<table>
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<tr>
<th>Field</th>
<th>Applications</th>
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| Advanced & high-reliability hermetic packaging | MOEMS† package [59]  
- Packages + quality control [60, 61]  
- MEMS pressure sensor package for medical applications [62]  
- Active getter module [63] |
| Pressure sensing | Piezoresistive (membrane) [64, 65]  
- Piezoresistive high-pressure cell (direct compression) [20, 66]  
- Piezoelectric (resonance) [67]  
- Capacitive (membrane) [68, 69]  
- Complete piezoresistive pressure sensor (+electronics) [15, 17, 70, 71] |
| Force & accel. sensing | Low forces [9, 16, 21, 22]; applied to low pressures (indirect) [72]  
- Acceleration [17] |
| Optical sensors | pH [73]  
- Absorbance [74] & fluorescence [75] |
| Flow & liquid sensing | Fuel injection (thermal) [76]  
- Flow sensor, thermal [17, 71, 77, 78] or mechanical [79]  
- Thermal bubble inclinometer [9] |
| Flow control | Valve [80]  
- Substrate for electrovalves [13] |
2. Processing techniques

The present section reviews the different techniques and issues at each stage of processing. Processing issues are usually exacerbated when using fine structures, such as required for sensitive device.

2.1. Basic processing routes

The most straightforward processing route is the “cut-and-laminate” one, whereby each LTCC laser is simply cut (usually by laser), with the resulting stack being uniaxially laminated and fired (Figure 2). This simple route is feasible for applications involving relatively robust structures, where crushing and sagging of layers are not a big issue, such as the chemical microreactor shown on Figures 5 & 6.

If slender membranes or bridges are used, sacrificial volume materials (SVMs) may be used to avoid crushing / sagging (Figure 3), using uniaxial or (pseudo-)isostatic lamination.

![Rigid lamination plate (top)](image1)

![Rigid lamination plate (bottom)](image2)

![Compliant elastomer block](image3)

![Rigid lamination plate (top)](image4)

![Rigid lamination plate (bottom)](image5)

If slender membranes or bridges are used, sacrificial volume materials (SVMs) may be used to avoid crushing / sagging (Figure 3), using uniaxial or (pseudo-)isostatic lamination.

Finally, cavities may be directly created by printing SVM onto LTCC, without removing the corresponding volume from the tape (Figure 4), which requires (pseudo-)isostatic lamination.

![Pseudo-isostatic (similar to isostatic)](image6)

2.2. Handling during screen-printing

Structural features such as intricate channels and thin bridges exacerbate the usual difficulties of handling fine LTCC tapes. Especially, simply cutting out complex channel networks (Figure 6) in one layer is difficult or even impossible, as this would structurally separate the tape, or weaken it excessively. To get around this issue, two techniques are commonly used:

- “Stitching” the fluidic circuit across several layers allows fabrication of complex and strongly meandering structures, as often seen in fluidic process devices such as microreactors (Table 2, corresponding section; Figure 6), using the classical “cut-and-laminate” route. This requires an additional layer (or two, if crossovers are desired),
and creates some additional dead volumes due to alignment tolerances.

- **Sacrificial volume materials (SVMs)** allow “printing” of channels without requiring the tape to be cut out: the channel is then formed during or after firing by removal of the SVM (Figure 4). However, this technique does have restrictions: it requires “standard”, high-pressure isostatic or pseudo-isostatic lamination to deform the LTCC tapes around the printed SVM, and results in significant deformation of the tapes and of the surface of the device [8, 11, 13, 59], which may not be the most convenient method for shaping other structures such as large cavities. Also, there are practical limits to the achievable aspect ratios, stemming from the screen printing process and restricted deformability of the LTCC tapes [14]. Finally, printing large amounts of sacrificial material can destroy the tape through attack from the SVM paste solvent. However, recent developments in screen-printing vehicle formulation show progress in formulating SVM inks that have low aggressivity towards LTCC tapes, and even allow removal of misprints by rinsing in water [33, 34, 108].

### 2.3. Lamination and firing

Optimal lamination is often a compromise: applying excessive pressure and temperature can result in deformation and crushing of cavities, while the reverse yields poor bonding (Figure 7). Several techniques, described in section 3, have therefore been developed to alleviate this issue in difficult cases: SVMs to protect cavities, and “glues” to facilitate lamination.

![Figure 5: Chemical microreactor: device (top), LTCC module with superposed fluidic layout (middle) and complete electrical & fluidic layout (bottom). 1) Inlet & warm-up; 2) flow sensors; 3) outlet; 4) flow sensors; 5) bottom alumina heat spreader, below LTCC; 6) alumina heat shield for reaction zone. A) Thermistor for body temperature; B) thermistor for reaction zone temperature; C) resistor for heat output calibration.](image)

![Figure 6: Chemical microreactor: LTCC layers, in unfired state, showing cut-outs for fluidic channels and thermal decoupling of calorimetric reaction zone. 1) Bottom wall; 2) bottom fluidic layer; 3) fluidic separation layer; 4) top fluidic layer; 5) top lid.](image)

![Figure 7: Lamination problems in fluidic structures: A) crushing of cavities; B) deformations combined with poor interlayer lamination below cavity due to absence of pressure; C) poor lamination, at arrow; B) good lamination with low deformation, with correct parameters [13].](image)

Firing of slender structures also may lead to deformations, stemming from shrinkage mismatch between LTCC, functional materials and SVM, or simply from sag-
ging of structures under their own weight. This may again be counteracted by SVMs, which however must be correctly formulated to avoid imparting deformations themselves during LTCC sintering [10, 13, 46, 52, 57].

3. SVM & Adhesive formulations

In addition to the LTCC tape itself and the assorted functional materials (conductors, resistors, etc.), 3D structuration may use two types of “auxiliary” materials, which are eventually removed during processing: 1) SVMs and 2) adhesives for low-pressure lamination.

3.1. Sacrificial volume materials (SVMs)

SVMs support the 3D LTCC structure during lamination, avoiding crushing, or may even be used to create cavities by themselves (see 2.1 / Figure 4). If just used to fill existing cavities, they tend to add complexity to the manufacturing process, but careful design, e.g. limiting SVM deposition to just one layer, or special processes such as filling with liquid wax [43], reduce this inconvenient.

A wide variety of SVMs have been investigated (Table 3), with carbon-based pastes or tape inserts being by far the most common.

Carbon / wax / polymer-based compositions are labelled fugitive sacrificial materials (FSMs), as they escape during firing, by evaporation, pyrolysis or oxidation to CO/CO₂, which may lead to sagging during sintering through loss of support. To avoid this issue, carbon-based (mostly graphite) materials may be used; graphite is “semi-fugitive”, as it is stable to very high temperatures in inert atmospheres, and only begins to oxidise rapidly above 600-650°C in oxygen-containing ones. This allows two strategies (see Table 1, firing):

1  **Firing in air**, carefully matching sintering of LTCC with graphite oxidation kinetics by varying temperature rise rate and graphite particle size [8, 10, 48-51]

2  **Sintering in inert atmosphere**: burnout in air, up to ca. 600°C, followed by sintering in nitrogen (which preserves the graphite), and final oxidation of the graphite by switching back to air [17, 52].

Firing in air may be carried out also without restrictions, using mineral sacrificial materials (MSMs), which however requires an additional post-firing chemical or mechanical removal step (Table 1). This restricts in practice MSMs to open structures such as cantilevers or bridges on the surface of substrates [53-57, 109]. Further issues lie shrinkage mismatch, chemical interactions and limited chemical stability of some fired LTCC materials [57].

3.2. Lamination adhesives

In many cases, deformations mainly stem from the high pressures required to achieve good lamination. Moreover, simple uniaxial lamination of multilayer structures intrinsically faces the issues of low stresses above cavities (Figure 7B). Therefore, many techniques have been investigated to achieve satisfactory lamination quality at moderate pressures and temperatures (see Table 1, lamination), the most common being 1) application of adhesive tapes, and 2) printing of liquid / paste adhesives or solvents. There are however some drawbacks to these methods, as they require careful application of the adhesive, and handling of the resulting sticky LTCC tape can be quite cumbersome. Therefore, in order to facilitate handling, we recently proposed an alternative method using hot-melt adhesive layers [45], which are first generically deposited onto the LTCC tape. The adhesive is formulated to be tack-free or low-tack in ambient conditions, facilitating handling and minimising dust pickup, and then melt at moderate (≤60°C) temperatures, allowing low-pressure lamination at moderate temperatures.

During lamination, adhesives interact with the tape, and assist binding at low temperatures. The additional amount of organic material must be accounted for by somewhat lengthening the debinding step.

4. Materials limitations of LTCC

Fired LTCC material properties are typical of glass-ceramic materials (brittleness, relatively good thermal stability), and may be compared to thick-film multilayer dielectrics, from which they are derived.

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**Table 3: Parameters and their values. † Applied to classical thick-film technology on Al₂O₃.**

<table>
<thead>
<tr>
<th>Type</th>
<th>Sacrificial volume material (SVM)</th>
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<tbody>
<tr>
<td>FSM (fugitive)</td>
<td>Carbon paste (printed) [10, 33, 34, 49-52, 108] or tape insert [8, 43]</td>
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<tr>
<td></td>
<td>Wax, screen-printed [7] or filled as liquid [43]</td>
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<tr>
<td></td>
<td>Kapton foil, laser-ablated [7]</td>
</tr>
<tr>
<td>MSM (mineral)</td>
<td>Al₂O₃ setter tape [8]</td>
</tr>
<tr>
<td></td>
<td>PbO-2SiO₂ glass [52]</td>
</tr>
<tr>
<td></td>
<td>CaO-B₂O₃ [109]; CaO-borax [53]</td>
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<tr>
<td></td>
<td>Au [110]</td>
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<tr>
<td></td>
<td>CaCO₃ + C [55]</td>
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<tr>
<td></td>
<td>MgO-CaB₂O₄ [57]</td>
</tr>
<tr>
<td></td>
<td>SrCO₃† [54]</td>
</tr>
<tr>
<td></td>
<td>MgO-B₂O₃† [56]</td>
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4.1. Mechanical strength

LTCC has somewhat lower short-term strength than alumina, of the order of 300 MPa, depending on the grade [111-114]. In sensitive mechanical structures such as low-range force and pressure sensors, this is offset by a much lower elastic modulus [113, 115], of the order of 100 GPa, yielding a comparable strain, i.e. resulting signal.

However, ceramics may be susceptible to stress corrosion in the presence of humidity, which must be accounted for in device design. This ageing behaviour is more severe in glassy ceramics such as LTCC than in standard 96% thick-film grade alumina, with glass-free materials such as yttria-stabilised zirconia (YSZ) and zirconia-toughened alumina (ZTA) essentially unaffected at ambient temperatures. To complicate matters, short- and especially long-term strength is affected by overlying thick-film materials, an effect that has yet to be studied on LTCC [112, 116, 117].

4.2. Chemical durability

Whereas fired LTCC may be expected to be resistant to organic solvents, chemical durability in aqueous environments shows very strong variations: on the one hand, some materials (such as Du Pont 951) allow short-term operation (=1 day) of microreactors with aggressive chemicals such as HCl and NaOH at concentrations >1 M. On the other hand, 3D structuration of LTCC using MSM was found to be hindered by degradation of LTCC in the relatively weak acetic acid used to dissolve the MSM [57]. Other studies also yielded very contrasting results, depending on the LTCC material [118-120].

4.3. Thermal stability & expansion

Essentially all common LTCC grades exhibit reasonable thermal stability up to ca. 500°C. Above this temperature, performance depends on the phase assemblage and chemical composition, with the more crystalline, essentially alkali-free materials exhibiting good mechanical stability and high resistivity at temperatures in excess of 600°C [115, 121]. This, together with the moderate thermal conductivity and CTE [113-115], allows creation of a wide range of hotplate structures (Table 2).

5. Conclusions

Due to its advantageous properties and relative ease of 3D structuration, LTCC has recently found wide application in fluidic and/or heater structures. This trend is expected to intensify, due by advances in process technology and materials characterisation.

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