Structuration of zero-shrinkage LTCC using mineral sacrificial materials

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Abstract

Recently, LTCC (low-temperature co-fired ceramic) technology has increasingly found applications beyond pure electronics, in fields such as microfluidics, sensors and actuators, due to the ease of shaping the tapes in the green (unfired) state. Accurate control of hollow structures such as channels, membranes, cavities and gaps below cantilevers has remained difficult, however, although carbon-based sacrificial materials and adhesive/solvent-assisted low-pressure lamination techniques are adequate for several uses.

Mineral sacrificial pastes (MSP), introduced by several groups including our laboratory, allow in principle much better control of open structures such as bridges and cantilevers, as they are removed only after the firing step. In practice, accurate dimensional control has been limited by deformation of the LTCC during sintering, due to shrinkage mismatch with the MSP. Attempts to eliminate this problem have met with limited success, as it is very difficult to perfectly match the shrinkage curve of the MSP (which must retain open porosity) to that of the LTCC substrate. Therefore, in this work, we endeavour to investigate MSP materials on self-constraining "zero-shrinkage" LTCC tape, which is therefore compatible with a low degree of sintering of the MSP. We present results of optimising the MSP formulation accordingly, to achieve reasonable consolidation, low deformation of LTCC and easy removal in weak acid solutions. Important topics such organic vehicle formulation and complete release processes (etching, rinsing and drying) of thin structures are also addressed.

Key words: sensors, thick-film, LTCC, 3D structuration, mineral sacrificial layers / MSP, processing.

Introduction

Thick-film technology is a versatile tool for the manufacture of sturdy and reliable devices, at relatively low cost, and has thus made important inroads into sensor applications [1], albeit with relatively simple products, a limitation due to the difficulty and cost of shaping the substrates. The relatively recent development of LTCC has heralded new possibilities in 3D structuration [2], with devices such as chemical microreactors & mixers [3], hot-plate gas sensors [4] and structured force sensors [5].

The 3D shaping of LTCC devices raises several issues regarding the lamination step, which, due to the common presence of closed cavities, channels, etc., is much less straightforward than that of "standard" electronic modules. In the simple "cut-and-laminate" method, lamination parameters are a compromise between ensuring sufficient quality and avoiding excessive deformation. To address this issue, several techniques have been successfully applied, such as solvent- or adhesive-assisted lamination to ensure a good bond between LTCC layers even at low lamination pressures and temperatures, and carbon-based sacrificial layers that allow lamination, then burn away during firing [6].

Nevertheless, these techniques do not fully address the problem of slender structures, which tend to warp due to sagging and/or to stresses imposed by thick-film materials having different sintering curves. Therefore, there has been a continuing effort [7-13] to develop, for both thick-film and LTCC technology, mineral-based sacrificial layers (MSP, mineral sacrificial paste) that would survive during firing, supporting the structures, and then could be removed by a post-etching step in a relatively benign substance such as a weak acid.

Very recently [13], success has been obtained for thick-film technology with MgO sacrificial layers using H_3BO_3 (or a limited amount of borax) as a "glue" between the MgO grains. MgO is a well-known sacrificial material in surface micromachining [14]. In order to allow easy later etching, it is important that the material remain porous [11], which makes for a relatively low shrinkage. While this is fine for traditional thick-film technology, the low shrinkage is less suited for integration with standard LTCC materials using the

free-sintering process. Previous tests resulted in important deformations [6], which could be somewhat lowered by incorporating some carbon powder to provide some shrinkage due to partial burnout.

Therefore, it is a logical idea to turn to constrained sintering, with essentially zero shrinkage in the plane. This may be accomplished by constraining the LTCC with setter tape or, much more easily, by using self-constrained tapes such as the Heraeus Heralock 2000 (HL2000) and 800 (HL800) compositions [15]. This work therefore endeavours to explore the compatibility of these tapes with the mineral sacrificial layer process. Also, a standard (shrinking) LTCC composition known to have sufficient chemical resistance to the acid etching used to remove the MSP after firing [12], DuPont (DP) 951 was used for comparison purposes.

Experimental

LTCC tapes

The nominal supplier data for the three LTCC compositions are given in table 1. We used several thicknesses of DP 951, but only a single one for HL2000 and HL800 (HL2000 is available in several thicknesses, in contrast to HL800, a newer material for which a better chemical resistance is claimed [15]).

MSP formulations – organic phase

As sacrificial layers are often printed in large amounts, there is an issue of the solvent in the printing vehicle attacking the tape, especially if the latter it thin. However, the nonaggressive formulation developed before [16] for sacrificial carbon pastes on LTCC was not suitable, as it contains some water, with which MgO (slowly) reacts. Therefore, a new vehicle was formulated (table 2), with an effort to minimise aggressivity towards LTCC.

MSP formulations – mineral phase

The mineral content of the sacrificial pastes was composed of various mixtures of MgO (magnesium oxide) and CaB_2O_4•$2H_2O$ (Vimsite, hydrated calcium borate), both from Sigma-Aldrich, in order to adjust the degree of sintering and shrinkage. MgO, being very refractory, essentially does not sinter, which, from a dimensional standpoint, is appropriate for HL2000 and HL800, while the moderate melting point of CaB_2O_4 [17] leads us to expect significant sintering of this compound, with additional shrinkage coming from dehydration (loss of the 2 H_2O molecules). Five different mixes (table 3), progressively going from pure MgO (P00) to pure CaB_2O_4•$2H_2O$ (P40) were prepared and first tested on the three tapes. From the aforementioned considerations, one would expect the MgO-rich mixes to have good compatibility with HL2000 and HL800, whereas MSPs rich in CaB_2O_4•$2H_2O$ would fare better with DP 951.

Manufacturing of test device structures

Two kind of test structures were designed for this study: 1) bridges and cantilevers for capacitive sensors, having only conductors (DP 6146, co-firing Ag:Pd) on the thin elements, and 2) anemometric flow sensors, where the thin structures are bridges carrying a thick-film thermistor element (DP 5092D, PTC 100 Ω). Please see companion paper in the same conference [18] for more details.

Table 1. LTCC tapes
(nominal supplier data)

Tape	XY shrinkage [%]	Green thickness [μm]	Fired thickness [μm]
HL2000	0.2	133	91
HL800	0.2	130	88
DP 951	12.7	254 165 114 50	216 140 97 43

Table 2. Formulation of screen-printing vehicle for MSP (chemicals: Sigma-Aldrich, reagent grade; filled with ca. 40% vol. mineral phase).

Role	Compound	Parts (by mass)
Solvent	1-Hexanol	10
	Butylene glycol	20
Binder	Ethylcellulose 46 cps 48% ethoxyl	3

Table 3. MSP mineral formulations
(as paste with vehicle from table 2).

Code	Composition (by mass)
P04	MgO only
P13	CaB_2O_4·$2H_2O$: MgO 1 : 3
P22	CaB_2O_4·$2H_2O$: MgO 1 : 1
P31	CaB_2O_4·$2H_2O$: MgO 3 : 1
P40	CaB_2O_4·$2H_2O$ only

Lamination of the structures processed with MSPs was carried out using a pseudo-isostatic

process, whereby the stacks were pressed uniaxially between two flat metal plates, but with a thick rubber disk inserted between the LTCC device and the top metal plate [19]. This process combines a reasonable approximation of true isostatic lamination with the simplicity of uniaxial pressing. All the structures (the three kinds of tapes) were always fired together, with a firing profile adapted to the requirements of the HL tapes, with a sintering ramp at 3 K/min and 30 min peak dwell at 880°C.

After firing, chemical etching was carried out, at ca. 50°C or room temperature, with 10% acetic or phosphoric acid solutions.

Results and discussions

Firing of single bare tapes

Figure 1 shows the result of cutting and firing a single layer of tape (unlaminated). In line with our previous studies, DP 951 is very forgiving – in fact, good flatness is even achievable when firing a single 50 μm thick tape – and has a low process sensitivity. Given its moderate thickness, HL2000 showed little deformation as well, which means that multilayer structures should fire without problems. HL800, on the other hand, was very deformed, which hints at a larger minimal module thickness to achieve flatness.

Compatibility with the MSP vehicle

The printing vehicle selected for the MSPs did show some reactivity with the LTCC, which was principally due to the very large deposited amount of MSP (dried thicknesses ≥ 100 μm) and only a problem when printing on single thin (ca. 100 μm) HL2000 or HL800 tapes. In practice, this required pre-laminating two such layers.

Qualification of the MSPs on the LTCC tapes

The result of the rapid qualification of MSPs on the LTCC tapes is shown in figure 2. For DP 951, a very clear decrease of deformation is seen going from pure MgO to pure $CaB2O_4$•$2H_2O$. The last sample shows very little deformation, even on a single LTCC layer. On HL2000, the apparently best composition is P13; P00 has too little cohesion and turns to powder upon firing, due to the lack of sintering of MgO, and the compositions richer in $CaB2O_4$•$2H_2O$ obviously have too large shrinkage. As HL2000 is quite resistant to pull from the MSP, the latter tends to fragment instead (P31 and P40). No clear-cut trend is seen with HL800, which is expected as strong deformation was already seen on the bare tape.

The test of P40 on DP951 was repeated, this time with a cover strip (figure 3), which confirmed the low observed deformation. The MSP formulation, however, is still not ideal, as the MSP is seen to crack when fired in a thick layer.

Structure build-up and firing

Structures [18] (figures 4-6) were fabricated starting with one (DP 951) or two (HL2000 / HL800) "base" layers, followed by a cut out "channel" layer that was pre-laminated at low pressure on the base, then filled by MSP by one or several screen printing operations (up to complete filling). Then, the "structure" layer was overlaid and the stack laminated using the pseudo-isostatic process, and, finally, the LTCC was fired.

All the LTCC structures had good firing characteristics, as shown in figures 4-6. However, even with several layers, HL800 still showed some residual deformation (intrinsic, not due to the presence of MPS), indicating that the process conditions still need to be optimised for this tape.

Chemical etching

The chemical etching phase, however, turned out to be problematic, regardless of the used acid or temperature, for different reasons.

DP 951 fared the best. It is *per se* quite resistant to attack by acid, and no alteration was visible. However, as shown in figure 6, alteration of this chemical resistance was observed when fired in contact with P40. This was not observed in previous studies with $CaCO_3$ [8], and it is therefore thought that B_2O_3 evolution from CaB_2O_4 is a probable cause of the chemical alteration of the surface. Therefore, an MSP composition between P31 and P40 would probably give better results: a lower B_2O_3 volatility and less crackling. Nevertheless, free structures could be obtained, as evidenced in figure 6.

The HL2000 and HL800 LTCC compositions, in contrast to DP 951, were directly attacked by the acids; HL2000, especially, completely lost consistency, i.e. its glass matrix was entirely degraded. HL800 suffered extensive surface attack, but did show qualitatively much better chemical resistance than HL2000.

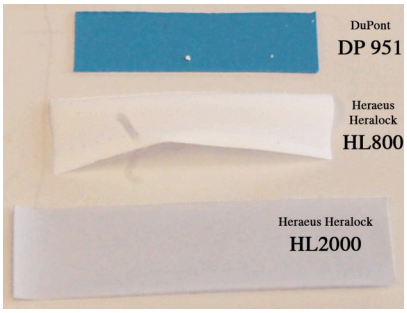


Figure 1. Single fired layers of the three LTCC compositions

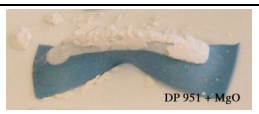
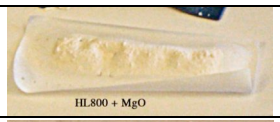
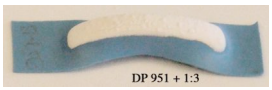
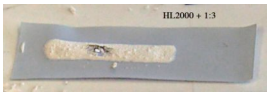
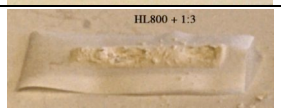
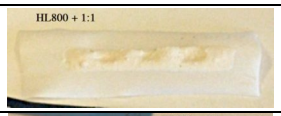
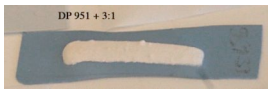
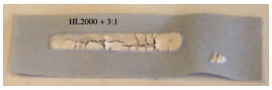
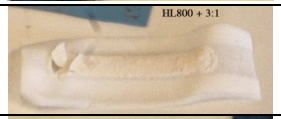
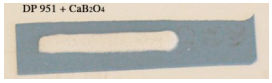
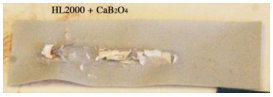
MSP	DP 951	HL2000	HL800
P04			
P13			
P22			
P31			
P40			

Figure 2. Qualification tests of the MSPs on LTCC (strips ca. 3 mm wide)

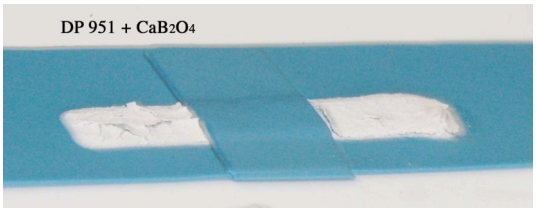


Figure 3. Cracking of P40 on DP 951.

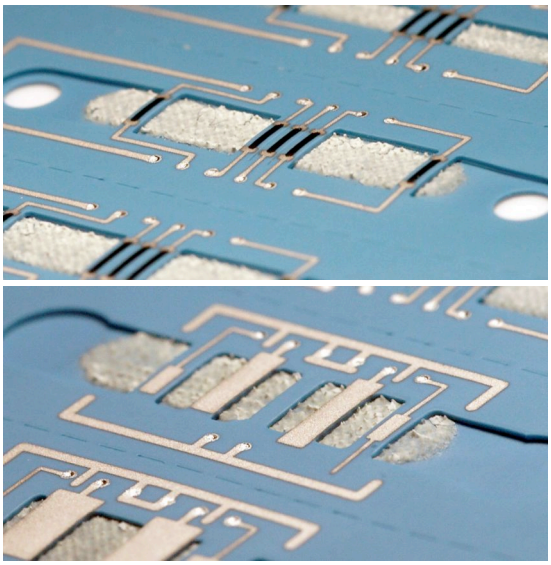


Figure 4. Flowmeter (top) and mechanical (bottom) structures – DP 951 + MSP40
(channel width : ca 4. mm).

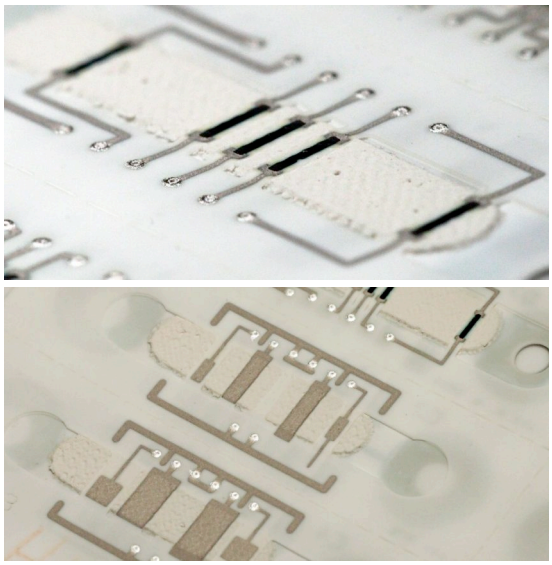


Figure 5. Flowmeter (top) and mechanical (bottom) structures – HL800 + MSP13
(channel width : ca 4. mm).

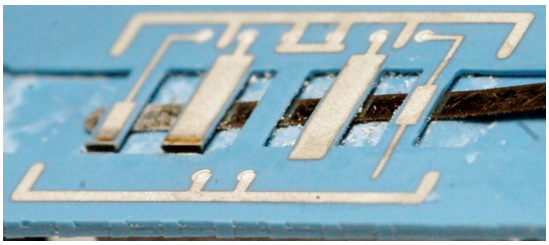


Figure 6. Mechanical structure after etching in 10% acetic acid, with insert to demonstrate opening of structures.

This poor performance, in line with other studies [20], is not necessarily intrinsic, as we did not optimise the firing conditions, which we intend to do in later studies. Moreover, the MSP compositions, which used relatively unreactive coarse MgO powder and CaB_2O_4, still need to be optimised to etch away in more benign conditions.

Conclusions

In this work, we examined new mineral sacrificial paste (MSP) processes to achieve slender suspended structures in LTCC technology. To this end, materials based on MgO (refractory alkaline earth oxide, negligible sintering) and CaB_2O_4 (lower melting temperature, sintering) were formulated and applied to both classical (shrinking in XY direction) and "zero-shrinkage" LTCC materials: DP 951, Heraeus HL2000 and HL800.

Compared to the devices laminated between two flat metal plates, the MSP method allows a much wider process window to obtain undeformed structures; (pseudo-)isostatic lamination is possible, ensuring good interlayer bonding on the whole surface of the device.

Formulation of the MSPs to have some cohesion (rather than turning into loose powder) is advantageous for later handling and in order to avoid curling up of cantilevers [13].

The MSPs exhibited reasonably good printing and firing compatibility with the LTCC tapes. Nevertheless, a lower reactivity of the vehicle solvent system with LTCC would still be desirable, and some more fine-tuning is still needed on DP 951 to more exactly match the MSP and LTCC shrinkage. This is of course not an issue on HL2000 and HL800, which is a considerable advantage of these two tapes.

The acid etching characteristics of the structures, however, did not match our expectations. DP 951 was in general unaffected by the 10% acetic or phosphoric acid etchants, but the surface in contact with CaB_2O_4 exhibited some damage, in contrast to our earlier studies with $CaCO_3$ [8], most likely due to B_2O_3 sublimation and reaction with the LTCC surface, locally affecting its chemical resistance. Nevertheless, the structures could be etched away successfully, albeit with some residue.

Future work will therefore first concentrate on optimising the LTCC firing conditions to achieve maximal chemical resistance for the zero-shrinkage LTCC compositions (not necessarily optimal for other considerations) and characterisation of the materials in a wider range of etchants. Furthermore, the formulation of the MSPs for HL2000 and HL800 will be refined to allow more benign etching conditions. One possible path is to switch to finer, more reactive MgO powder, without any "binder" such as CaB_2O_4 or with a more soluble one, in order to increase its etching rate. On DP 951 efforts will focus on decreasing the boron of the MSP loss while keeping the desirable sintering and shrinkage characteristics of CaB_2O_4.

Finally, the formulation of the screen-printing vehicle will be further refined to minimise solvent interactions with the LTCC tape during drying.

Acknowledgments

The Authors gratefully acknowledge Mrs. A. Kipka of Heraeus for providing the HL800 tape, and the help of Mr. M. Garcin in fabricating the samples.

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