Constrained Sintering of dielectric and ferrite LTCC tape composites

Marcel Hagymási[1], Andreas Roosen[1], Roman Karmazin[2], Oliver Dernovsek[2], Werner Haas[3]

[1]: University of Erlangen-Nuremberg, Department of Materials Science, 91058 Erlangen, Germany, [2]: Siemens AG, CTMM2, 81739 Munich, Germany,[3]: Kerafol GmbH, 92676 Eschenbach, Germany

Abstract

The miniaturisation potential of LTCC devices would be drastically improved, if inductances could be directly integrated into the multilayer structure. Co-firing of ferrite green tapes in combination with dielectric green tapes, which offers this possibility, is the focus of the paper. Commercial dielectric LTCC tape and a new developed ferrite green tape on the basis of $BaFe_{12}O_{19}$ were characterised. To manufacture composite structures of these two types of green tape via LTCC technology, the ferrite tape must densify at temperatures around 900°C. The characterisation of the tapes included the green tape structure and shrinkage behaviour by means of density measurements, thermogravimetry, thermomechanical analysis, optical dilatometery and microstructure investigations. The shrinkage and warpage behaviour of both single tapes and composites was characterised. By combination of the different tapes a constrained sintering behaviour could be generated. Stress effects during sintering and cooling cycles could be related to occurring defects.

Keywords: LTCC, Ferrites, Composites, Defects, Co-firing stresses

Introduction

The integration of magnetic properties into existing dielectric LTCC structures would have a dramatic impact on the miniaturization and application potential of LTCC devices for applications in communication and automotive technologies. Transducer, antennas and circulators are only some of many possible passive devices that could be realised if a ferrite tape is available. In general, spinel ferrites and hexaferrites are materials of interests. A hexaferrite, the M-type $BaFe_{12}O_{19}$, was used in this study, which has the advantage of a constant permeability in a wide frequency range. The permeability values of spinel ferrites are higher, but decrease rapidly in the MHz frequency range.

For the integration, the ferrite tape must be co-fired with the dielectric tape. To achieve a defect-free LTCC composite, the shrinkage of both tapes must be controlled. In this connection, zero-shrinkage and constrained sintering concepts become important[1,2]. One concept is based on constrained sacrificial layers that are laminated on both sides of the multiplayer structure. The friction force between the LTCC layer and the non-sintering sacrificial layer suppress the in-plane shrinkage. In the present study the in-plane shrinkage of the ferrite tape was reduced by using a dielectric tape, which densifies in a different temperature region than the ferrite tape[3]. The dielectric tape should densify at low temperatures, where it is constrained by the non-sintering green ferrite tape. At higher temperatures, the ferrite tape densifies, but the shrinkage is inhibited by the already dense dielectric tape. Thereby, a self-constrained sintering is accomplished, because each tape acts beside its functional performance as a constraining layer.

Cracks, debonding and other defects observed in multiplayer composites are caused by mismatch stresses at different sintering stages[4,5]. They can be caused by different densification rates of the individual layers during the sintering process, or by non-adapted coefficients of thermal expansion during cooling. Thereby, the layer with the higher coefficient is under tensile stress and is most susceptible to crack forming.

Experimental Procedure

A commercial dielectric green tape (DuPont 951 AT, Bristol, UK, abbreviation: DT) and a new developed ferrite tape (abbreviation: FT) on basis of $BaFe_{12}O_{19}$ with a low glass content of < 10 vol.-% was used. A higher glass content proved disadvantageous for the required permeability of the glass-ceramic composite. Both cast tapes are characterized concerning their behaviour during thermal treatment.

Thermomechanical (942 Thermomechanical Analyzer, DuPont Instruments, USA) and thermogravimetric analysis (951 Thermogravimetric Analyzer, DuPont Instruments, USA) were carried out on both tapes (5 K/min up to 780°C). The organic content was acquired by mass loss determination after thermal treatment up to 600°C. The green tape density and laminated density was determined geometrically.

All laminates were manufactured by uniaxial thermo-compression (80°C, 25 MPa, 10 min). For shrinkage investigations these laminates were cut into samples of 26 x 26 mm² in size. Two kinds of laminates were produced. 1) Monolithic laminates: composed of 4 layers of DT or 4 layers of FT. The tape´s top side was laminated on the bottom side of the following tape. 2) Dielectric - ferrite composite laminates: composed of 4 FT layers that are covered on each side with 2 DT green tapes.

For firing, the samples were heated up to 450°C (1.5 h) with heating rates between 0.5 – 2 K/min. After binder burnout the temperature was increased to 900°C (5 h dwell time). Cooling rates were between 1 and 3 K/min. Sintering was performed in air in an oven of high temperature accuracy.

For accurate in-plane shrinkage determination hardness indentations were introduced at the edge of the laminated sample by a Vickers diamond pyramid. The distance between these indentations were measured before and after sintering with a resolution of 1 µm by means of a scanning laser microscope (UBM Messtechnik GmbH, Germany). The z-shrinkage was determined by using a micrometer screw. The thermal expansion coefficient of the sintered ferrite was measured (cylinders of 25 mm length, 3 K/min) in a conventional dilatometer (Netzsch GmbH, Selb, Germany).

The laminates were sintered in an optical dilatometer for *in situ* observation of the free shrinkage and warpage behaviour by means of horizontal and vertical CCD-cameras. This equipment permits the shrinkage analysis in all 3 directions without any holding forces[6]. The porosity in the sintered samples was analysed by image analysis (IMTRONIC GmbH, Germany).

Results and Discussion

Tab. 1 summarizes the green tapes characterisation. Compared with DT, both the relative green tape density and relative laminate density of FT are much lower. Because the shrinkage values are related to the green density, considerable higher shrinkage of the low packed FT can be expected. One reason of the low ferrite density can be found in the high organic content of 18.0 wt.-%. Nevertheless, the binder burnout was already finished at 350°C for FT, compared to 400°C for DT. The TMA results indicate a shrinkage onset temperature of 650°C for DT, and of 740°C for FT. The shrinkage results of the optical dilatometer (Fig. 1) shows, that the DT densification begins at a temperature of 700°C and is finished at 840°C. Because the tape casting process lead to direction depending packing densities, the shrinkage is anisotropic: 12.7 % in casting direction, 13.9 % in cross direction and 12.8 % in height.

The FT tape needs higher temperatures for densification. Sintering starts at a temperature of ~760°C and is characterised by a slow densification rate; the tape requires more time and higher temperatures for densification than DT. Thus, during the dwell time of 5 h at 900°C, where DT exhibits no shrinkage, FT shrinks for additional 9 %. In agreement with the low green density, FT shows very high shrinkage values: 23.2 % in x-y direction, and 21.7 % in thickness. To reduce the dwell time, temperatures higher than 900°C are necessary which are not admissible for co-firing with the metal pastes. Using a sintering temperature of 950°C for 3 h instead of 900°C for 5 h, the measured porosity decreases form 6.0 to 1.7 vol.-%.

During heating-up of the FT laminate, convex warpage to the tape top side could be observed in the range of binder burnout from 200°C to 350°C (Fig. 2) independent of the tape position in the furnace. That means a local thermal gradient can be excluded. This camber, that shows a maximum at 300°C, remains during the further sintering and cooling process. The reduction of the heating rate from 2 to 0.5 K/min during binder burnout avoids this warpage and leads to a flat sintered sample. From these results it is assumed that the high binder concentration is not distributed homogenously over the tape height and leads to camber during binder burnout.

Since the sintering intervals of the dielectric and ferrite tapes overlap between 760°C – 840°C, an absolute zero-shrink behaviour of the composite cannot be expected. Nevertheless, a clear constrained sintering was achieved (Fig. 3). The limited resolution of the optical dilatometer of 80 µm/pixel (which is equal to +/- 0.3 % according to the sample size) and the low shrinkage values lead to an increase of data scattering in Fig. 3. In the range of 700°C to 760°C the densification of DT is inhibited by the non-sintering ferrite tape. Different densification rates could be the reason for the low shrinkage value of only 1.5 % between 760°C and 840°C, although both single tapes densify within this temperature range. At temperatures above 840°C the ferrite shrinkage is constrained by the non-sintering DT. During 5 h dwell time at 900°C mainly thickness shrinkage was observed. The total in-plane shrinkage was 3.25 % for the casting direction, 2.97 % for the cross direction, and 33.1 % in z-direction, due to the inhibited in-plane shrinkage.

The effects of mismatch stress at different stages of sintering were investigated by SEM. The different densification rates generate sintering mismatch stresses; the in-plane tensile stress reduces the driving force of densification and is one defect origin. Typical observed defects are shown in Fig. 4. The cavitation in the DT layer (~ 2 vol.-%) must have formed during constrained sintering due to tensile stresses which occur, when the shrinkage of the DT layer is inhibited by the ferrite layer; probably in the temperature range of 700°C-840°C. The tensile stress also decreases the densification rate of the ferrites and cause a significant higher porosity in the ferrite layer than in DT. The porosity of the ferrite layer increases from 6.0 vol.-% for free-sintering to 8.5 vol.-% for constrained sintering. Channel cracks, perpendicular to the interface, appear only in the ferrite layer. As a result of the higher thermal expansion coefficient, the ferrite layer is under tensile stress and is during cooling most susceptible to such residual stresses, which are not reduced by viscous flow. Furthermore, the high porosity decreases the strength of FT. Thus FT presents the weakest region of the composite. Between DT and the porous ferrite layer, debonding cracks are formed in the cooling stage. Using a higher cooling rate of 3 K/min, the increase of debonding and channel cracks cause a total layer separation between DT and FT. By decreasing the cooling rate to 1 K/min the number of cracks decreases and layer separation was prevented, but the composite strength was still very low. This indicates that the layers are able to relax residual stress, especially during the initial period of cooling at high temperatures when the glass phase behaves still visco-elastic. To achieve zero-shrinkage and crack-free LTCC composites, further research is necessary.

A circulator is one interesting passive component that can be manufactured as an LTCC device on the basis of dielectric and ferrite tapes. The circulator is a three terminal device that will allow RF waves to flow between any two adjacent ports, which is restricted to only one direction. It contains three transmission lines that are located between two layers of ferrite material. On the other side of the ferrite is a non ferrous ground plane and then a magnet followed by a ferrous pole piece that shields the unit from external magnetic fields. Such circulators could find applications in UMTS-mobile phones.

Summary

The shrinkage behaviour of new LTCC ferrite green tapes in combination with a dielectric tape was investigated. Sintering of the ferrite tape starts at 760°C and requires 5 h dwell time at 900°C for densification. The low green density causes high in-plane shrinkage of 23.2 %. By manufacturing composites of ferrite and commercial dielectric tape, which densifies in the range of 700°C – 840°C, the sintering behaviour is inhibited. The in-plane shrinkage was decreased to 3.25 %, while the main shrinkage of 33.1 % occurs in the height. As a result of the significant different thermal expansion coefficients of both materials, mismatch stress occurs, which lead to channel cracks in the ferrite layer and to debonding between dielectric and ferrite layer during cooling.

Table 1. Determined green tape data

	DuPont 951 AT	Ferrite Tape
Thickness [µm]	120	130
Green tape density [g/cm³]	2.17	2.5
Laminate density [g/cm³]	2.25	2.88
Relative Laminate density [%]	72*	53*
End of binder burnout [°C]	400	350
TMA [°C]	650	740
Organic content [wt.-%]	11.4	18.0
TEC [ppm/k (25°C-300°C)]	5.8	12.2

*: theoretical density of $BaFe_{12}O_{19}$: 5.38 g/cm³

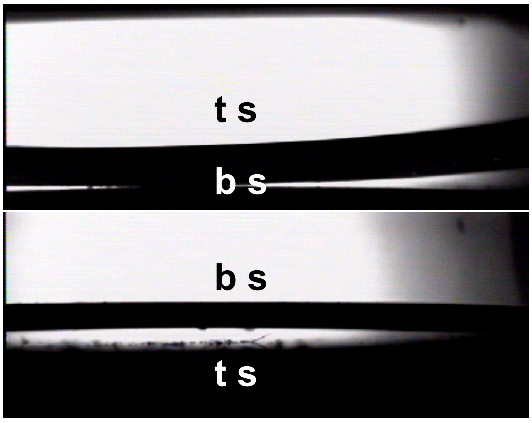

Fig. 2 Side view from ferrite laminate in the optical dilatometer at 300°C (ts=top side; bs=bottom side).

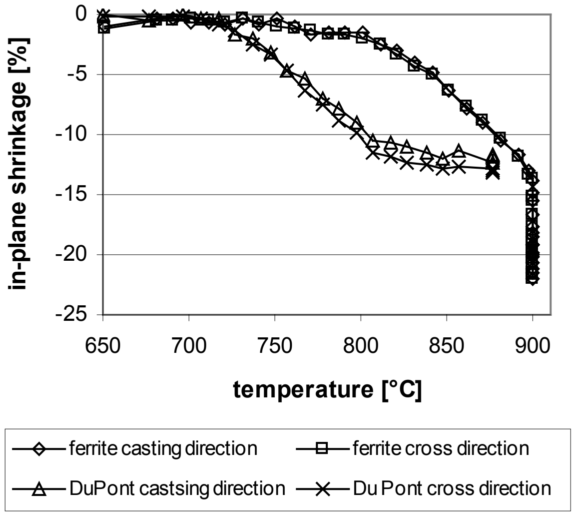

Fig. 1. Free in-plane shrinkage of dielectric and ferrite laminates

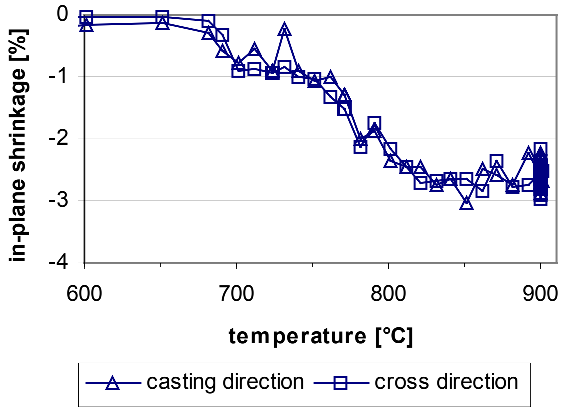

Fig. 3 Constrained in-plane shrinkage of a symmetric dielectric and ferrite composite.

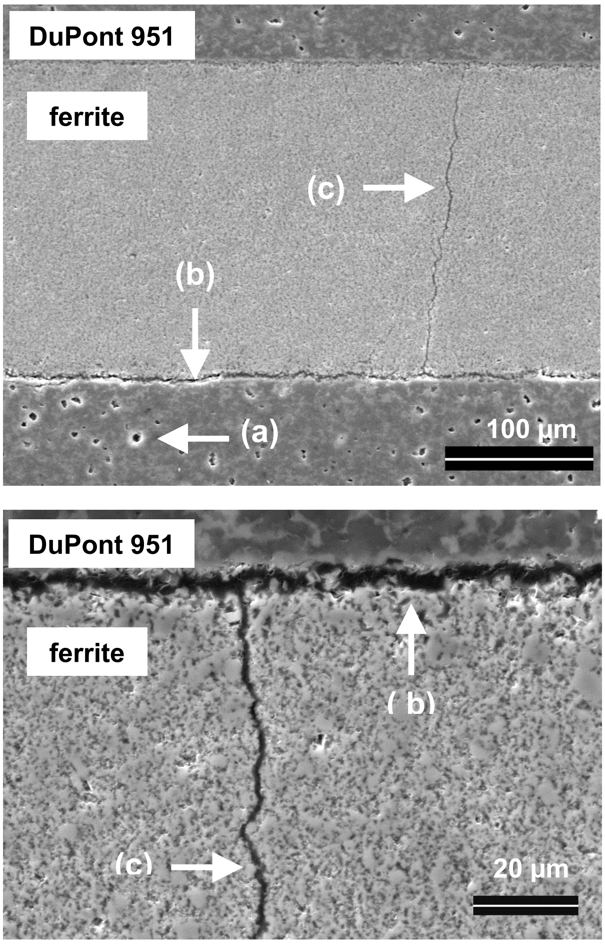

Fig. 4 Defects in sintered composite: (a) Cavitation in DuPont layer, (b) debonding crack and (c) channel crack in ferrite layer.

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