Low Temperature Co-fired Ceramic (LTCC) Technology: General Processing Aspects and Fabrication of 3-D Structures for Micro-fluidic Devices

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Abstract

LTCC technology is based on sintering of multi-layered thick-film sheets (50-250µm) or so-called green tapes, which are screen-printed with thick-film pastes such as conductors, resistors, etc. The terms low temperature and co-fired originate from the relatively low sintering temperatures (<900°C) compared to conventional ceramics and simultaneous firing of tapes together with screen-printed thick-film material, respectively. These characteristics are achieved by improving the tapes' properties and adopting the physical and chemical thick-film properties to that of tape, whilst retaining their functional properties. Evidently, mastering the technology requires fundamental understanding of the compatibility issues between the tape and the pastes and the effect of processing conditions on this relation. In this perspective, this paper aims to point the origin and extent of chemical and physical interactions between co-fired materials and explain the use of carbon-black sacrificial paste to fabricate 3-D micro-fluidic devices without sagging of the channel walls.

1. Introduction

LTCC technology has recently been one of the most attractive solutions in micro-technology for versatile applications [1]. For a long time, it has been used as the ideal substrate for devices operating at high frequencies, which require faster signal speeds in reduced dimensions. This is facilitated by the low dielectric constant and loss of LTCC tapes, which can be fired at low temperatures with low-resistance conductors (Au, Ag, Cu, etc) at low temperatures. Moreover easy handling of tapes for 3-D structuration, screen-printing with thick-film electronic components, chemical inertness and hermeticity make the technology interesting for other applications such as sensors and micro-fluidics.

One of the most cited problems encountered is the incompatibility of the materials used: LTCC tape and thick-film electronic pastes [2]. The LTCC tape usually contains ceramic filler, which is bonded by glass. This glass is used as a sintering aid, which basically reduces the sintering temperature and increases the dielectric strength, and may be formulated to crystallize after sintering to improve stability. The thick-film materials, on the other hand, have different functions and vary in composition. For instance the conductors are metal-based and may contain glass (fritted conductors) and / or oxide additions to increase adhesion to the substrate and enhance sintering, whereas resistors are formed of conducting oxides surrounded by a glass matrix, which determines the resistivity. In either case, glass plays a major role in determining the extent of materials interaction, especially at high temperatures. This arises as a result of the increased mobility of the glass above the glass transition temperature, T_g, which takes place before the densification of the tape/paste. Consequently glass in each component softens over T_g and moves easily due to reduced viscosity, which can lead to chemical and physical incompatibilities in the co-fired module.

Chemical issues are best observed using microscopy imaging and measuring functional properties of the components (thermistors / piezo-resistors, conductivity, etc). Additionally chemical analysis such as EDXS (electro dispersive X-ray analsis) provides quantitative information for the chemical interactions occurring between the materials.

Physical issues are detectable rather macroscopically, without a direct need for a microscopic investigation. The differential shrinkage rate between the tape and the pastes, which is observed as warping, curling of the tape, is the major source of physical incompatibility. The deformation arises from different sintering of the pastes prior to the tape. Moreover the oxidation-reduction reactions in the pastes, which may lead to gas evolution at temperatures higher than the LTCC open-porosity elimination temperature, can cause swelling in the buried (sandwiched) LTCC structures. From fabrication standpoint, the physical problems are mostly due to sagging in cavities (membranes, channels, etc), which can be avoided by use of a support, such as a sacrificial layer [3].

Thus, the primary aim of this paper is to address the processing-related problems widely encountered in LTCC technology. These will be treated in two sections: chemical and physical issues. In each section, an alternative solution for improved processing will be proposed. Additionally, preparation and utilization of carbon-sacrificial layer will be described and corresponding structures fabricated such as membranes of different specifications will be demonstrated. The investigations will be made using SEM (scanning electron microscopy), EDXS, dilatometry analysis and the electronics for characterization.

2. Chemical Issues

As explained previously, the glass phase of the fired components plays a major role in the extent of chemical reactions. This is because of the increased diffusion rates of the elements in the softened glass following T_g.
Figure 1 shows the difference between heavily fritted (Ag/Pd) and frit-poor (Au) conductor pellets, which are prepared from the powdered-pastes (details of the process in [4]). SEM images illustrate large glass melts in the Ag/Pd conductor and much smaller vitreous regions on the Au matrix. According to the EDXS analysis, the Ag/Pd conductor contains a high glass load of Bi-Zn-Si (~20% atomic), whereas the Au has a trace Bi-Pb-Si load.

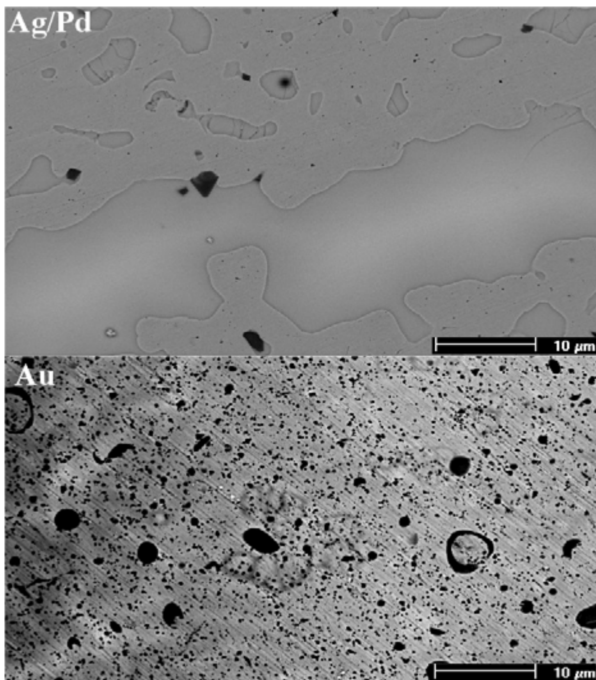


Figure 1. SEM images of Ag/Pd (DuPont 9473) and Au (DuPont 5744) conductor pellets.

The LTCC tape-conductor-resistor interface, which is analysed by SEM-imaging the cross-section of the fired structures, is demonstrated in figure 2. It is observed that the Ag/Pd conductor has an open structure forms an extensive reaction zone (RZ) with the LTCC, which is observed in light grey colour. The EDXS analysis carried out in this region shows that it contains elements such as Pb, Bi, which come from the glass phases of the LTCC tape and the conductor, respectively. Additionally needle-like structures are observed, which are found to be Al-Si-rich particles on the RZ. On the other hand, the Au conductor is dense and forms a distinct layer between the tape and the resistor without any further reaction, which is also confirmed by the EDXS analysis.
The effect of processing conditions on the extent of reaction can be seen in figure 3, which shows the evolution of the RZ on increased sintering temperature. The thickness of this region increases from 13µm to 16µm and then to 20µm upon increased firing temperature from 850°C to 875°C and then to 900°C.

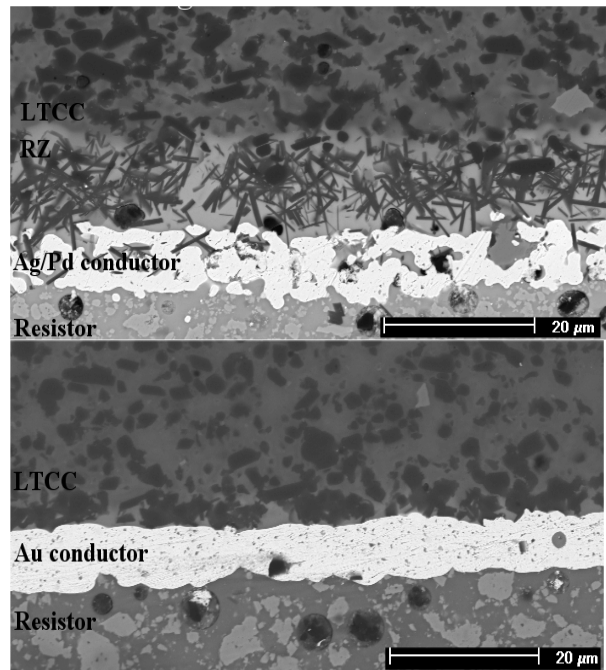


Figure 2. Microstructure of the interface. Reaction zone (between the LTCC and the conductor denoted as RZ) formation next to the fritted (above) conductor.

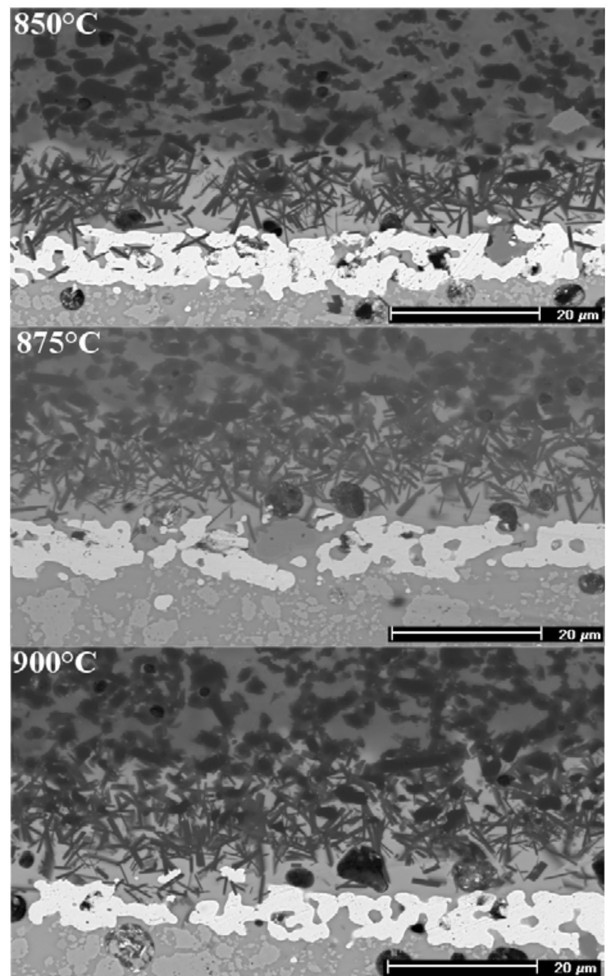


Figure 3. Evolution of reaction zone (RZ) upon increased firing temperature for the fritted Ag/Pd conductor.

3. Physical Issues

Physical issues are observed as defects such as warpage, curling, sagging, swelling, etc. From this paper's point of view, our focus will be on warpage (this section) and sagging.

Warpage is the most frequently encountered type of defect in co-fired LTCC structures. LTCC tapes, which are screen-printed and co-fired with thick-film pastes, are deformed due to the usually faster shrinkage of the pastes at earlier stages of sintering. Therefore, the shrinkage of the different components has to be matched to that of the LTCC. In this study, this possibility is investigated by blending the previously studied Ag/Pd conductor paste with 10 and 20% by weight of SiO_2 (Sihelco, Sikron B-600, quartz) and LTCC tape (DuPont 951-AX) powders and homogenizing on a three-cylinder mill. The former additive is used due to its network-promoting character in glass (increases Tg), whereas the latter is used to end up with shrinkage behaviour similar to that of LTCC tape. The shrinkage behaviour of the pellets of LTCC tape, the unmodified and blended (with SiO_2 and LTCC powders) conductor pastes are shown in figure 4 (details of pellet preparation explained in [4]). We have not used any additives to match the shrinkage rate of the resistors with the tape, as their electrical properties would presumably seriously be affected. From figure 4, it is seen that the pure conductor starts densification at around 516°C, reaching a shrinkage value of 23% at the onset of tape shrinkage temperature, 670°C. This is modified to 644°C by addition of 20% SiO_2, which corresponds to 2.3% of shrinkage at the onset of tape shrinkage. LTCC addition, on the other hand, leads to expansion after 700°C, the exact nature of which is currently being studied.

Figure 5 compares the extent of warpage of tapes which are co-fired with pure and 20%-SiO_2-added conductor pastes. It is clearly seen that 20% SiO_2 addition shifts the densification temperature of the paste close to that of the tape and thereby decreases the amount of warpage on the fired structure.

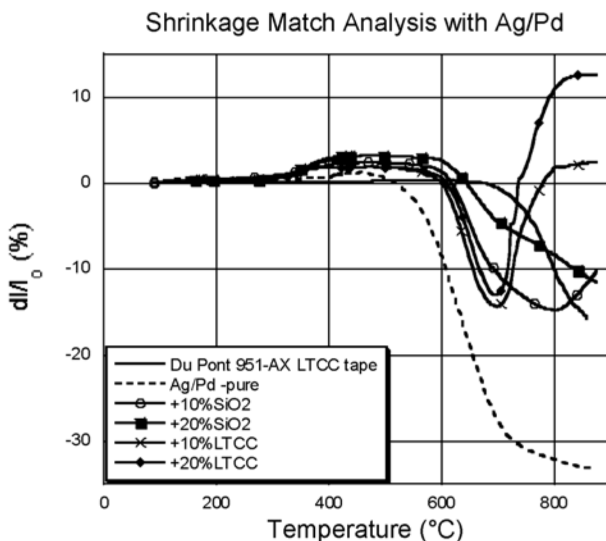


Figure 4. Shrinkage behaviour of the LTCC tape, pure and blended conductors.

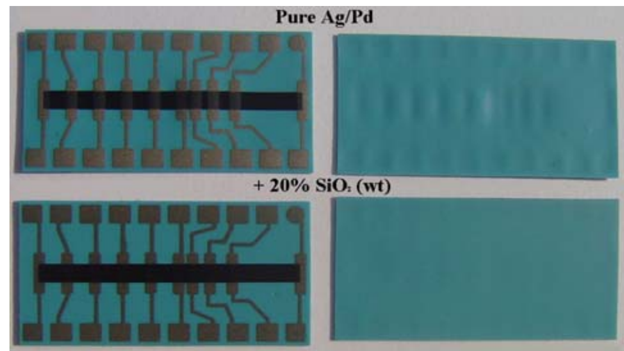


Figure 5. Reduced warpage in the 20%-SiO_2-added Ag/Pd conductor (below).

Figure 6 shows the microstructure of the previously studied (figure 1, first image) fritted Ag/Pd conductor. The black particles, which are dispersed in the matrix, are SiO_2. According to this microstructure, silicate particles seem to hinder the mobility of the glass phase in the conductor, which reduces the warpage.

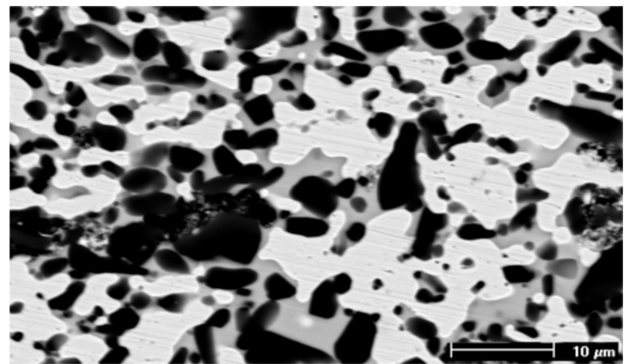


Figure 6. Microstructure of the 20% SiO_2 –added Ag/Pd conductor. Black particles are SiO_2 and whites regions are Ag/Pd at 3:1 atomic ratio.

4. Fabrication of 3-D Structures

Ease of tapes' handling provides fabrication of various structures such as sensors and micro-fluidic devices for different applications. In this section, we will focus on membranes and the necessity of using a sacrificial layer to avoid defects. Among these defects, sagging is the most frequently observed one, which occurs as a result of tape deformation upon lamination and firing (figure 7). In order to support the membrane and retain the form of the cavity, our choice of sacrificial layer is the carbon-paste. It is prepared by blending the graphite powders with the organic vehicle, which contains binder, solvent and dispersant. Homogenization is made on a three-cylinder mill, which is followed by screen-printing on the LTCC sheets for membrane preparation. The dried sheet is then laminated with a second LTCC tape uni-axially at 70°C and 25MPa and fired at 875°C.

Before demonstrating the fabricated structures, we would like to make a remark on the effect of preparation and processing conditions. The crucial parameters are the ratio of graphite to organics, graphite particle size, heating rate during firing, diameter of the membranes (amount of paste deposited). The kinetics of graphite burn-out and the temperature of open-porosity elimination in LTCC are directly influenced by the

processing conditions. Consequently the correlation of these parameters determines the final device properties.
Figure 8 shows 40µm-thick membranes with diameters of 7 and 18mm respectively. A well-defined spacing, without sagging, is observed in both membranes. The final micro-fluidic device with post-fired conductor and resistors in addition to integrated inlet and outlet ports is illustrated in figure 9. The ports are connected to the membrane area via channels.
Such devices can be used for several purposes depending on the selection of the resistors: flow meters, pressure sensors, etc. The resistor on the edge is used as a reference.

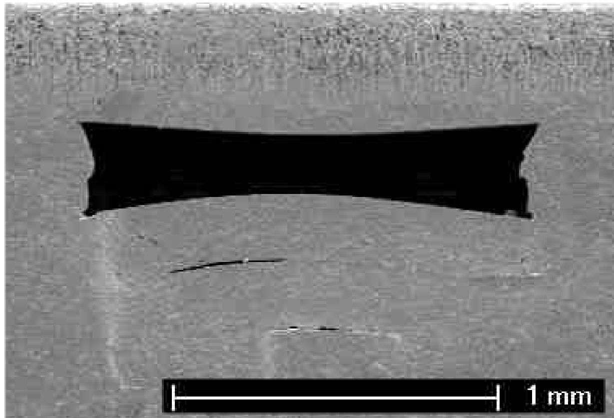
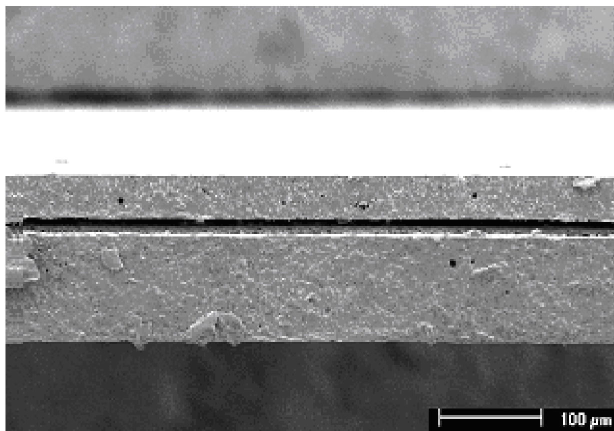


Figure 7. Sagging and de-lamination (below the cavity). No sacrificial layer is used.



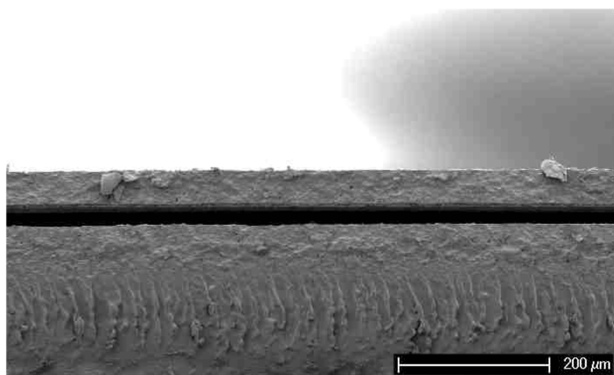


Figure 8. 7 (above) and 18mm-diameter membranes free of sagging, fabricated using carbon-sacrificial paste. Constant spacing of 13 and 28µm, respectively.

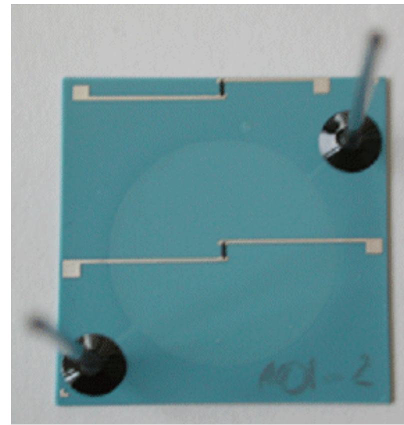


Figure 9. 14mm-diameter membrane with post-fired conductors and resistors (black) and integrated inlet and outlet ports.

5. Conclusions

The paper addresses several common chemical and physical issues encountered in LTCC processing. The glass phase, which is used in LTCC tapes and most of the thick-film components to reduce the sintering temperature, is identified as the responsible constituent for initiating the materials interactions during processing and influencing the chemistry of the components. Warpage, a major defect in the co-fired structures, is attributed to the shrinkage mismatch between the pastes and the LTCC tape. An effective method is proposed to limit its extent by matching the shrinkage behaviour of conductor paste with that of the LTCC tape, which is achieved by modifying the paste with selected additives.
The paper, additionally, gives a brief insight to the preparation and application of carbon-sacrificial paste for fabrication of micro-fluidic devices. Membranes, which are free of sagging, are demonstrated with varying diameter and spacing.
It is estimated that better understanding and improvement of materials used, will lead to increased demands for use of LTCC in a wider range of applications.

6. References

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