Towards highly conductive silver pastes for LTCC power electronics

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Abstract

The realization of high current conductors in LTCC multilayer architectures was studied. By mixtures of spherical silver powders, maximum tap densities above 7 g/cm³ could be obtained. On pressed cylinders a good correlation between tap density and total shrinkage was found. Pastes were made of the highly packed silver powders and detailed investigations regarding paste sintering kinetics and interactions between paste ingredients among one another as well as between paste ingredients and LTCC substrates were made. The pastes did not show a pronounced correlation between tap density and total densification. With increasing solid content of the pastes, the shrinkage printed-dry, the shrinkage dry-fired and the specific sheet resistance decreases. These findings can be used to control the filling degree of channels or grooves as well as the properties of the fired conductor. Expansion effects of the pure silver powders during sintering could be correlated to gas pressure effects, whereby there are obviously different kinds of gas formation in fine and coarse powders. Avoiding of camber of freely sintered LTCC should be attained if new LTCC materials are showing different sintering behavior, e. g. strong and early crystallization building of diffusion barriers or the possession of a glass phases which will not incorporate silver oxide. Research on this target should be done. The realization of high current conductors in constrained sintered LTCC was successfully shown. A paste comparable to standard values for direct copper bond (DCB) substrates with a thickness 35 μ m of 0,48 mOhm/sq is introduced.

Keywords: silver powder, silver paste, sintering, LTCC, power electronics, resistivity

1 Introduction

In recent years the common attention has been more and more focused on green energies like wind power or green applications like electric vehicles or high efficient LED electric lightings. Appropriate technologies are emerging and there is a growing need for small, robust and highly integrative power electronic modules which can handle high current loads in a sufficient way. In this market segment, electronic packages based on ceramics possessing thermal conductivities, high e.g. Alumina (20 W/mK), Aluminum nitride (180 W/mK) as well Beryllium oxide (260 W/mK) are as well established. Besides those materials, Low Temperature Co-fired Ceramics (LTCC) materials are candidates for many future power applications. The LTCC heat conductivity is relatively low (2 W/mK), compared to the established ceramics, but in trade of that LTCC offer great advantages like great multilayer capability, low cost and high integration potential regarding passive elements as well as flexibility in architectures, e.g. micro channels for cooling. Moreover, LTCC are capable of integrating power circuits and logic circuits on the same substrate.

Silver shows excellent conductivity and low sintering temperature and is therefore the preferred

conducting material in LTCC. On the other side, issues linked to the use of silver are known. Silver has a high mobility at elevated temperatures which can be an issue during co-firing with LTCC because these materials consist of considerable amounts of glass phases. Often silver enters the LTCC glass phase during firing changing its viscosity and sintering behavior, which can have disadvantageous effects on the geometry of an assembly like cambering [1]. In addition, the sintering interval of silver differs somewhat from that of most LTCC materials. Thick conducting structures may deteriorate the multilayer sintering by the impact of the mechanical sintering tension mismatch [2].

With this in mind, the development of modern LTCC circuits for power electronics requires two main challenges. Firstly, the silver amount and density in power conductors has to be maximized to achieve low sheet resistances enabling high power load. The target value is related to standard values for direct copper bond (DCB) substrates with a thickness of 35 μ m and amounts to 0.48 mOhm/sq Secondly, the interaction of those highly silver containing structures with the LTCC surrounding must be controlled carefully.

In this paper integration possibilities of thick silver structures in LTCC multilayer architectures are

studied in the framework of a joint research project. The aim of this project is the realization of a buried thick film transformer in a LTCC multilayer LEDcontroller (Fig. 1). Therefore, dedicated silver powders were blended to increase the tap density and were characterized with respect to sinter shrinkage in comparison to commercial products. Pastes with different inorganic loadings were manufactured and characterized in test structures regarding drying and firing behavior and the resulting sheet resistivities. The pastes were also deposited in a LTCC transformer assembly to investigate the co firing behavior. Silver migration in the LTCC was measured on polished cross sections. The results of this work are presented and discussed in terms of performance of the resulting conductors, critical parameters in the paste composition and LTCC chemistry. Conclusions regarding the existing possibilities and future potential for the use of LTCC in power electronics are drawn.



Fig. 1. Pictures of a thick film coil for a transformer in a LTCC multilayer. A) CAD design, b) photograph of lasered channels inside the green tape

2 Experimental

The sintering temperature of silver is dependent on the particle diameter and can drop to lower than 250 °C for nano sized particles [3]. Therefore, rather coarse silver powders showing particle radii between 4 µm and 50 µm were chosen to minimize the mechanical tension mismatch between the silver paste and the LTCC, which sinters around 850 °C. Moreover, coarse powders have a comparably low surface, a fact which could help to minimize silver migration effects during the sintering cycle. In the literature [4] a maximum tap densities of steel balls obtained at a diameter were ratio of fraction A : fraction B of 10:1 and volume amounts of coarse fraction A around 75 % per volume. Based on these findings with the aim to obtain silver powders showing high tap densities, blendings of silver powder A (monomodal, $d_{50} = 4 \ \mu m$) and silver powder B (monomodal, $d_{50} = 0.4 \mu m$) were made: ALF_1 (100% powder A), ALF 2 (67% powder A, 33% powder B), and ALF 4 (74.4% powder A, 25.6% powder B). In

comparison to these model powders, 3 commercial coarse powders were tested D.6, B.7, and B.9. In Fig. **2** REM photographs of the investigated

Fig. 2 REM photographs of the investigated powders are shown. It is obvious, that the commercial powders are coarser relative to the model blendings. Moreover, it is evident that the commercial powders can also be referred to as bimodal. From image analysis one can estimate the following particle size ratios: D.6 - 66 vol% particles 6-10 µm and 34 vol% particles <1 µm, B.7 - 66 vol% particles 1-30 µm and 34 vol% particles $\approx 10 \,\mu\text{m}$, B.9 - 75 vol% particles 6-50 µm and 25 vol% particles <1 µm. The glow losses of the powders amount to 0.12 to 0.22 % by weight. All powders are commercial ones, small amounts of additions ore trace elements inside the silver are not known.



Fig. 2. REM pictures of three bi-modal model powders a) Silver powder A, b) Silver powder B, and three commercial coarse powders c) D.6, d) B.7, e) B.9

The tap densities of the powders were measured using a stamp volumeter (STAV 2003; cylinder 25 cm^3 , 3000 cycles per measure). For the determination of the shrinkage behavior of the pure powders, cylindrical pressings with height and diameter of 2 mm were manufactured by unidirectional pressing using 64 MPa. These pressings then were characterized in their green density (geometry and mass) and subsequently their sinter shrinkage was monitored in a Hot Stage Microscope (Leica, Wetzlar). This HSM was also used to characterize the shrinkage behavior of LTCC tapes. From the silver powders then pastes were made by different additives of an organic vehicle (14, 12, 10, 8 wt% Ethylcellulose and Terpineol as solvent) which were homogenized in a speed mixer. The pastes were then deposited on alumina and LTCC substrates by stencil printing (template thickness 120 µm, Printer E5, EKRA, Bönningheim) and were sintered in a standard thick film temperature profile with 10 min at 850 °C dwell time in a laboratory furnace (PEO 601, AVT, Vaterstetten). The thickness of printed, dried, and fired structures was determined by FRT (Microprof, Bergisch Gladbach) measurements. From the mass of the deposited paste and the geometry of the structures, rough densities were estimated after printing, drying, and firing. Electrical resistances of fired conductors were measured by the 4-point probes method (multimeter Keithley 2000, Germering). On selected samples cross sections were polished and observed by use of an SEM (FESEM, Zeiss, Oberkochen).

3 Results

Powders

The measured tap densities of the six silver powders under investigation are listed in **Table 1**. It is obvious that the commercial powders used may be designed bi-modal to have high tap densities above the value 6 g/cm³. The highest value of 7.8 g/cm³ is attained by the model powder ALF_4.

Table 1. Measured tap densities of silver powders under investigation (compare to Fig. 2)

Powder	Tap density [g/cm ³]			
ALF_1	4,88±0,06			
ALF_2	5,13±0,00			
ALF_3	4,48±0,08			
ALF_4	7,80±0,00			
D.6	6,49±0,17			
B.7	6,67±0,00			
B.9	6,23±0,06			



Fig. 3. Tap densities of bi-modal mixtures of metal spheres as a function of the fraction ratio. Black lines: data measured on steel balls [4]. Red lines: Data measured on bi modal model powders ALF_1, ALF_2, and ALF_4. Star symbols: Data estimated and measured on commercial powders D.6, B.7, B.9

Fig. 3 depicts the dependence of the tap density of the bi-modal powders under investigation on the mixing ratio (red line, star symbols). Also shown are values that were measured on steel balls [4] (black lines). The measurements on steel balls gave a maximum density at a volume ratio coarse/fine of

75/25. The commercial powders show only small variation over the mixing range, possibly due to the rough estimation of the particle sizes and volume fractions or to agglomeration effects. The highest tap density obtained with the model powder ALF_4 shows a good agreement with the maximum densities found in literature.

The shrinkage behavior of the studied silver pastes is shown in **Fig. 4** and **Fig. 5**. The shrinkage data were normalized to a green density of 55 vol% for the purpose of better comparison of the total shrinkage. The ALF model powders start shrinkage around 300 °C and densify continuously until 700 °C (**Fig. 4**).



Fig. 4. Linear shrinkage of powder compacts from the silver powders ALF_1, ALF_2, and ALF_4 as a function of the temperature

After passing this temperature, a final expansion takes place before the melting point (961 °C) is reached, assumingly to a chemical or physical transformation like e.g. oxidation or solubility of oxygen. The shrinkage curves run very close among each other. However, at the maximum densification point at 700 °C the powder ALF_4 which is possessing the highest tap density shows the lowest total shrinkage as expected.



Fig. 5. Linear shrinkage of powder compacts from the silver powders D.6, B.7, and B.9 as a function of the temperature

The sintering of the coarser commercial powders

also starts around 300 °C, but differs from that of the model powders at higher temperatures (**Fig. 5**). The coarsest powders B.7 and B.9 show a volume expansion with maximum around 500 °C to 600 °C. After this initial expansion, shrinkage occurs. The powder D.6 shrinks continuously and is the only powder which shows no initial or final expansion effect. The total shrinkage of roughly 4 % in the target range of 850 °C is similar for D.6 and B.7, the total shrinkage of the powder B.9 can be regarded as the summary of expansion and shrinkage, which compensates the expansion to yield nearly 0 % at 850 °C.

Pastes

From the silver powders pastes with 90 % by weight inorganic content were manufactured. The pastes were deposited by stencil printing in a test pattern presented in

Fig. **6** to yield printed thicknesses of about 120 μ m. Afterwards the assembly was fired at 850 °C. Resulting microstructures of the fired pastes of the powders B.9, D.6, and ALF_4 are shown in

Fig. 7. The microstructure of the film B.9 is characterized by many clusters of sintered and densified silver. However there are large pores of some tenths microns length in between these clusters, separating them from each another, obviously forming a kind of barrier for further densification. The microstructure of the film from D.6 shows a high densification grade and only low amount of residual porosity. The microstructure of the film from ALF_4 also shows a high densification grade but higher amount of porosity, which may be regarded not as residual but as temperature activated porosity because of the smooth round borders which are typical for gas forming (bubbling).



Fig. 6. Test pattern SEM for paste characterization after template printing and firing at $850 \degree$ C (paste ALF_2 on alumina substrate which was covered by a fired thick film glass paste)



Fig. 7. SEM pictures showing the microstructure of pastes made from the powders a) B.9, b) D.6, and c) ALF_4 after printing and firing at 850 °C (polished cross sections)

In Table 2 densification data and electrical resistances measured on films from the powders D.6, B.9, and ALF_4 are summarized. A good correlation between densification and electrical resistance is evident. The highest densities of 10.4 g/cm^3 are attained with the pastes from powders ALF_4 (fired at 750 °C) and D.6 (fired at 850 °C). Because of highest technological relevance for further investigations the powder D.6 was chosen. With this paste comparable to standard values for direct copper bond (DCB) substrates with resistivities of 0,48 mOhm/sq are attained.

Table 2. Densification data (p-printed, d-dried, f-fired) and resistivities measured on pastes from the powders D.6, B.9, and ALF_4

	D.6	B.9	ALF4_850°	ALF4_750 °C
$D \left[\frac{\sigma}{cm^{3}} \right]$	47	19	16	16
P _P [g/CIII]	4,7	4,0	4,0	4,0
P _D [g/cm ³]	6,7	6,1	6,6	6,4
P _F [g/cm ³]	9,4	6,7	8,2	8,5
R [Ohmm]	1,2*10 ⁻⁸	4,0*10 ⁻⁸	2,5*10 ⁻⁸	2,4*10 ⁻⁸

Setting of a matched shrinkage behavior between LTCC and paste requires aspects of the shrinkage printed-dried PD (filling of a channel of e.g. $60 \mu m$ depth) as well as the shrinkage dried-fired (DF) (co-firing LTCC and paste). In

Fig. **8** these shrinkage values are compared as a function of the particle content of the paste.



Fig. 8. Printed, dried and fired densities as well as resistivities (triangles) of pastes made from powder D.6 and different amounts of organic vehicle: 8, 10, 14, 18 % by weight

The densification states PD and DF of the deposited paste layer are dependent on the inorganic content of the paste. With increasing solids content there are decreasing shrinkage values for PD as well as DF. In the same direction the resistivity of the fired layers is decreasing. The resistivity of the paste with the highest solids content amounts to $1.8 \ 10^{-8}$ Ohm m.

A point of special interest in using pastes with high silver contents is the interaction of the paste with the LTCC during firing. Warpage or cambers have been reported. Warpage can happen due to silver diffusion in the glassy phase of the tape, inducing located early sintering and hardening underneath the silver layer, and final cambering of the hardened layer when the LTCC bulk shrinks [1]. Besides that, warpage due to mechanical tensions between shrinking silver and LTCC because of different sintering temperatures was observed [2]. In Fig. 9 element mappings recorded by microprobe analysis on polished cross sections of co-fired assemblies of pastes from powder D.6 and LTCC A (crystallizing) as well as LTCC B (non crystallizing at LTCC firing conditions) are presented. Both the tapes show silver incorporation into the LTCC up to a distance of 50 µm around the silver conductor. In case of the crystallizing tape LTCC A the total amount of incorporated silver seems to be somewhat lower than in the non-crystallizing LTCC B, which has a considerable higher volume amount of glass phase. Assemblies of the tapes with thick silver structures for high current loads showed camber after firing, obviously due to locally promoted sintering [1]. However, cambering of an assembly as shown in Fig. 1 can be completely avoided by constrained sintering using sacrificial layers inhibiting shrinkage in x-y-direction.



Fig. 9. Element mappings recorded by microprobe analysis on polished cross sections of co-fired assemblies of pastes from powder D.6 and a) LTCC A (crystallizing) as well as b) LTCC B (non crystallizing at LTCC firing conditions)

4 Discussion

Tap density and shrinkage

Powders having high tap densities are expected to have also high sinter densification and, therefore, are the right choice for LTCC metallization for high current loads. On pressings a good correlation between tap density and total shrinkage was found. However, the pastes did not a pronounced correlation between tap density and total densification. Obviously, the paster rheology during deposition superimposes the tap density effects.

Bubbling

In **Fig. 4** all the finer model powders pass maximum densification at around 700 °C and expand afterwards to approximately the initial geometry. With reference to the smooth boarders and the round shape of the pores in

Fig. 7 the reason for the microstructure observed is seen in a temperature activated gas formation. This finding implies the question after the origin of the initial expansion of the coarse powders (see Fig. 5). To get an image of the microstructure in the expansion temperature interval from 400 °C to 650 °C, the pastes from the powders D.6 and B.9 were heated up to 550 °C at a rate of 10 K/min and then removed from the furnace immediately. The still fragile silver layers then were cut by focused ion beam (FIB) and imaged by SEM as shown in Fig. 10.



Fig. 10. SEM pictures showing the microstructure of pastes made from the powders a) B.9, b) D.6, after printing and firing at 850 °C (cross sections by focused ion beam)

The microstructure from paste D.6 shows a typical intermediate state of continuous sintering characterized by formation of sintering necks, a distinct densification grade and residual porosity. The microstructure of the paste from B.9 shows in addition a second kind of pores with round shape and smooth boarders. It is visible that these bubbles appear inside densified silver clusters preferably at grain boundaries, which can be distinguished by contrast changes inside the silver granules. It is therefore concluded that also the initial expansion effect of the coarse powders under investigation can be explained with a gas formation and a bubbling effect. Possibly, the gas species responsible for high temperature expansion in the finer powders and for low temperature expansion in the coarser powders are different. In the fine powders first a bulk is formed by sintering, and then the bubbles are formed equally distributed over the whole volume. This leads to the fact that the gas pressure rises in the sintered bulk volume after densification and the bubbles are formed by nucleation. So, the gas origin could be a decreased solubility of oxygen or a chemical reaction inside the bulk. By contrast, in the coarse powders the bubbles appear highly selective at former grain boundaries. In this case it is rather probable that organic relicts from the manufacturing, i.e. agglomeration process to attain coarse particles, remained inside the agglomerated particles and are not removed by usual burn out processes. These relicts trigger the effect of a delayed burn out effect resulting in bubbling and the expansion observed.

Shrinkage and sheet resistance

Whereas it is to expect that the shrinkage PD decreases with increasing solids content because of the decreasing volumes of solvent in this case, the decreasing shrinkage DF was expected to be negligible dependent on the solids content of the paste. For a given kind of particles the manner of deposition during evaporation of the solvent should be similar. However, the results demonstrate that there is a higher densification of particles from pastes which have higher inorganics content. Further investigations on the real geometries of a targeted assembly design will show what the preferences on a high current load paste in a real environment are, the right shrinkage behavior and a matched sheet resistance or vice versa.

Camber

Cambering of freely sintered LTCC in the presence of silver has been an issue for years. An in-situ profilometer (home-made at BAM, Berlin) showed that cambering evolves above from a temperature of about 800 °C on. Mechanical tensions between silver layer and tape will be present already at temperatures below. This and the silver migration found (**Fig. 9**) point to the fact, that rather silver diffusion into the glass phase of the LTCC might force the cambering than a sinter mismatch. Avoiding of LTCC camber is to expect if new LTCC materials showing (i) strong and early crystallization building a diffusion barrier or (ii) glass phases which will not incorporate silver oxide are available.

5 Conclusion

The realization of high current load conductors in LTCC multilayer architectures was studied. The results of this work are presented and discussed in terms of performance of the resulting conductors, critical parameters in the paste composition and LTCC chemistry.

By mixtures of spherical silver powders, maximum tap densities above 7 g/cm^3 could be realized. Powders having high tap densities were shown to

have also high sinter densification and, therefore, are the right choice for LTCC metallization for high current loads. On pressings a good correlation between tap density and total shrinkage was found. Expansion effects of the pure silver powders could be correlated to gas pressure effects, whereby in fine and coarse powders obviously there are different kinds of gas formation.

Pastes were made of respectively high packed silver powders and detailed investigations regarding paste sintering kinetics were carried out. However, the pastes did not a pronounced correlation between tap density and total densification. Obviously, the paste rheology during deposition superimposes the tap density effects.

With increasing inorganics content of the pastes, the shrinkage printed-dry, the shrinkage dry-fired and the specific sheet resistance decrease. This behavior can be used to find an optimum between the filling degree of grooves and the properties of the fired conductor. A paste comparable to standard values for direct copper bond (DCB) substrates with a thickness of 35 μ m, resistivities of 0,48 mOhm/sq is introduced.

Avoiding of camber of freely sintered LTCC should be attained if new LTCC materials are showing varied sintering behavior, e. g. strong and early crystallization building a diffusion barrier or possessing glass phases which will not incorporate silver oxide. Research on this target should be done.

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