Silver processing in thick film technology for power electronics

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Abstract

Processing of Ag-equipped thick film modules is still challenging due to well-known issues of warpage of Ag-containing LTCC substrates or undesired coloring of Ag-surrounding ceramics. To increase the workability of Ag based thick film modules, enhanced control over these effects is necessary. From the experimental background as well as the chemical and thermodynamic nature of the element Ag, conclusions regarding essential properties during Ag-high temperature processing, like initial oxidation, transport via the vapor and glassy phase, and reduction are discussed. Taking into consideration a possible occurrences of this phenomenas as activated/deactivaed dependent on sintering conditions, explanation of unwanted maufacturing results like LTCC staining, warpage, glass thinning and setter memory effects are possible. From a technical standpoint, there are roughly two temperature ranges of relevance for processing silver metalized thick film structures. Between approximately 300 °C and 700 °C fast transport mechanisms of silver through the gaseous phase take place. Control can be achieved via governing the silver manufacturing, oxygen partial pressure, organic composition, powder conditioning and temperature-time schedule. Above approximately 600 °C, slower transport mechanisms of silver through the glassy phase and possible reduction of Ag(I) become evident. These effects originate corresponding impacts on the sintering kinetics. Here, control can be achieved via governing the glass composition, redox potential and, again, temperature-time schedule.

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

1 Introduction

Due to its outstanding properties, Ag is a preferred material for conductors in wide areas of thick film technology and also in the Low Temperature Co-fired Ceramics (LTCC) technology. Silver has a high specific conductivity at relative low cost and can be fired in air. However, processing of Ag-equipped thick film modules can be challenging due to the well-known issues of warpage of Ag-containing LTCC substrates, undesired coloring of Ag-surrounding ceramics or the so called ‘setter memory effect’. Those issues are commonly explained by high mobility of Ag during the firing process as well as strong interactions between Ag and glassy phases in thick film substrates. It is state of the art that there are some means which allow to minimize the silver diffusion in a given sinter profile, for example by firing in nitrogen atmosphere or by changing the temperature-time schedule. However, only a rare number of publications are focused on detailed thermodynamic and chemical mechanisms forcing Ag to move under thick film firing conditions, yet. Also, the mechanisms of LTCC warpage due to silver contamination are still under discussion.

In current developments for power electronic circuits, there are increasing trends towards thicker Ag-conductors as well as improved control of substrate geometry. For example, **Fig. 1** depicts a design, taken from a curent research project, for a thick film coil for LTCC power electronics consisting of buried conductors having a width of 0.85 mm and a thickness of 50 µm in the fired state. Successful realization of complex substrate architectures, including high volume silver conductors and precise geometry, requires improved knowledge about silver sintering and interactions with surrounding thick film materials. This paper will summarize data published regarding Ag movement due to temperature and atmosphere and on the other hand will present current results of Ag action in ceramic processing for power electronics. From these facts essential effects during Ag-high temperature processing, like initial oxidation, transport in the gaseous and glassy phase, and reduction will be discussed. Suggestions for more reliable processing of Ag thick film structures will be acquired.

2 Experimental

The determination of the shrinkage behavior of the pure silver powders was performed on cylindric compacts with a diameter and length of 2 mm. The compacts were manufactured by unidirectional pressing using 64 MPa. After the measurement of the green density (geometry and mass) their sinter shrinkage was monitored in a Hot Stage Microscope (Leica, Wetzlar). From the silver powder a paste was made by adding an organic vehicle (10 wt% ethyl cellulose and terpineol as solvent) which were homogenized in a speed mixer. The paste was then deposited on alumina and LTCC substrates by stencil printing (template thickness 120 µm, Printer E5, EKRA,

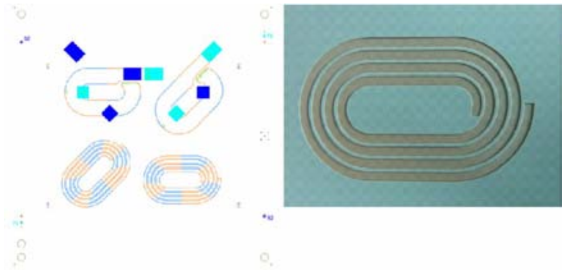

Fig. 1. Pictures of a thick film structure for a coil as transformer part in a LTCC multilayer, left: CAD design, right: Photograph of lasered channels inside the green tape.

Bönningheim) and was sintered in a standard thick film temperature profile at 850 °C with 10 min dwell time in a laboratory furnace (PEO 601, AVT, Vaterstetten). Air and nitrogen were used as furnace atmosphere, respectively. Polished cross sections were analysed by SEM (FESEM, Zeiss, Oberkochen).

Temperature dependent vapor analysis of the Ag thick film pastes were performed in a *Knudsen-effusion* setput. The headspace analysis was performed by mass spectroscopy (Varian MAT 212) with an ionisation energy of 70 eV.

The investigation of staining effects on different processed LTCC powders were performed on cylindric powder compacts of 20 mm diameter and 5 mm thickness. Silver paste was brushed on the half surface. After firing coloration was characterized by measuring the UV/Vis reflectance with a double-beam spectrophotometer UV-3101PC (Shimadzu) equipped with an integrating sphere assembly ISR-260 (Shimadzu) and using $BaSO_4$ as reference.

3 Results and discussion

(i) Manufacturing of silver powders

Various ways are used in the manufacturing of commercial silver powders: For example electrolytic manufactured silver powder (microcrystalline powder), chemical precipitation (agglomerate powders) or spaying of the molten bath (spheric powders) [1]. Processes based on flame synthesis, thermic molten bath spaying or furnace process result in nanoscal aerosol particles [2]. More modern process such as spray pyrolitic technique is used to produce nanoscale silver-, glas- and silver-glas-composit powders. These powders show a reduced agglomerate tendency and speric particles geometry [3,4]. Also the production of glass coated silver particles can be achieved [5].

(ii) Thermodynamic properties of silver and silver oxide

Metallic silver is in a stable state at room temperature. However, in air environment small amounts of oxygen are dissolved in thermodynamic equilibrium in the silver bulk, even below the Ag_2O stoichometry. The oxygen solubility is shown in the two phase diagram (**Fig. 2**) measured by Assal [6]. Above 531 °C, an Ag-O liquid phase is formed, where the oxygen solubility is decreasing with increasing temperature until zero is reached at the silver melting point of 962 °C. This nature of the metal can be considered for the significant influence of the oxygen partial pressure on the sinter behavior of pure silver powder. Also the interaction with oxide ceramics and glasses are likely to be influenced by oxygen solubility in silver. Further, one has to consider that oxygen will not be present in each silver powder one can buy. Panzer and co-workers [7] found an oxygen solubility related catalytic activity of an electrolytic manufactured silver powder at 330 °C, which was initiated after a first heating over 450 °C. The authors conclude, that oxygen can diffuse into the silver bulk in order to manage the thermodynamic equilibrium not before a temperature of 450 °C is attained. So, silver manufactured electrolytic or by chemical precipitation at low temperature might have significant lower oxygen content than silver manufactured pyrolytic far above 450 °C. Consequently, upon heating a suchlike powder in air an uptake of oxygen from the environment will occure when passing the temperature of 450 °C.

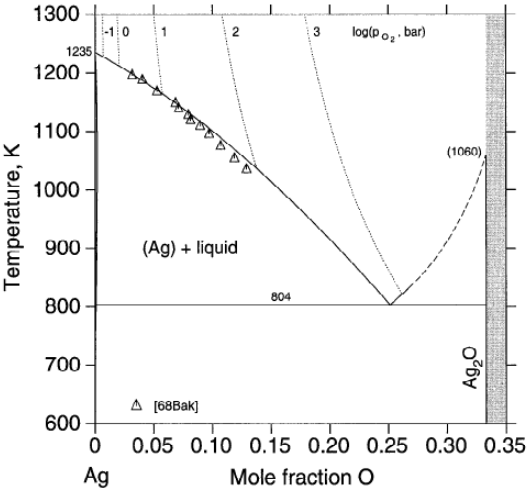

Fig. 2. Calculated Silver-Ag_2O phase diagram with experimental data (△) [6].

In **Table 1** the vapour pressure of silver is compared to that of the well known high mobile element bismuth. Although the silver vapour pressure is some orders of magnitude lower, values of about 2×10^{-3} Torr at moderate temperatures of 900 °C point at the presence of silver in the gasours phase [8]. The obtained vapour perssure corresponds to a concentration of about 2 ppm in the near environment of a silver sample at this temperature. Even so, Cui and co-workers observe a signifianct silver diffusion at 840 °C in the precence of connective pores, but in the absence of melt glass-ceramic matrix [9].

Further evidence for the presence of a sufficient silver transport via the vapor phase gives the

Table 1 Comparison of the vapour pressure in Torr of bismuth and silver at selected temperatures [8],[10]

T in °C	vapour pressures [Torr]	
	Bi	Ag
500	10^{-4}	10^{-8}
900	2	$2*10^{-3}$

occurrence of the well-known setter memory effect. Thereby, silver is transported form a metalized substrate to the setter, presumable through the poures, unfired material. In a subsequent firing process of an other, silver free, substrat a slight silver deposition is observed on the back side.

From a chemical point of view, silver is known as a noble metal and has a reduced tendency to react with oxygen compared to the homologous copper. However, a huge varity of stable silver compounds with inorganic as well as organic derivatives is known. The dominant oxidation state of silver in compounds is +1, which represents an electron configuration of d^{10}. The halide salts show a low solubility as well as Ag_2S. The latter is formed on air even in the presence of trancers of H_2S and results in the black coating of silver powders. Versitail is the complex-chemistry of silver(I). The d^{10} configuartion shows no perfered coordination geometry and no prefered set of donor atoms. Thus, a huge variety of inorganic and organic compounds is known. Therefore, the predictions of interactions and the resulting physical properties between silver and the thick film paste composites and/or decomposition intermedieds of the organic binder at various temperatures during the firing process is difficult. An enhance silver(I) mobility or formation of silver oxid aided by such Ag(I)-complex species is most likely. Preliminary experiments of Ag based thick film pastes on a commercial LTCC material in a *Knudsen* setup show the presence of substantial quantities of Ag(I) in the vapor phase above temperatures of 130 °C.

Pure silver oxide is thermodynamic stable up to about 180 °C. Above this temperature Ag_2O will be decomposed according to

$$2\ Ag_2O_{isolated} \rightarrow 4\ Ag + O_2\uparrow \qquad (T > 180\ °C) \qquad (1)$$

and has to be regarded to act like metallic silver. However, in case of direct contact to an oxide material or glass, it has been shown that silver oxide can easily dissolve in this material. Even metallic silver was found by [11] and [12] to dissolve as silver oxide in oxide materials according to

$$4\ Ag_{contact\ to\ oxide} + O_2 \rightarrow 2\ Ag_2O \quad (T > 180\ °C) \qquad (2)$$

The oxygen necessary for this dissolution reaction can be delivered by

- O_2 dissoluted in the silver bulk,
- O^{2-} from polyvalent ions inside a glass melt.

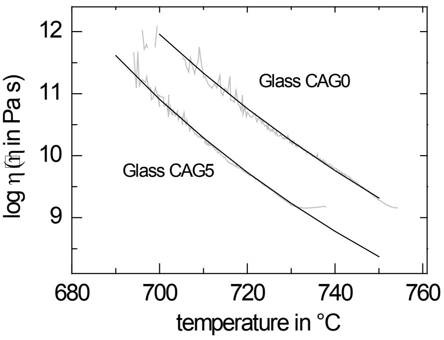

Fig. 3 Viscosity dependence on the temperature of a Al_2O_3-CaO-B_2O_3-SiO_2-glass (CAG0) and the same glass when 5 mol% Ag_2O is added (CAG5) in the composition [14]. Thin lines: measured data, black lines: fitted using the Vogel-Fulcher-Tammann-equation.

(iii) Ag_2O as a glass compound

In the context of this paper it is of interest how sintering properties of thick film substrates can be changed if in contact to silver. In this respect, the most dramatic changes are commonly observed on glass containing substrates, such as 96% Al_2O_3 or LTCC. Silver oxide acts in a glass as network modifier. The chemical bonds built by network formers like SiO_2 or B_2O_3 are cracked by Ag_2O due to the substitution of bridging oxygens by non-bridging oxygens in the glass structure. Subsequently a high mobility of the relevant metal is observed. The diffusion coefficient D of silver(I) at 850 °C was measured to be $D_{\mathrm{Ag(I)850°C}} \approx 10^{-8}\ \mathrm{cm^2/s}$, which is comparable to the remarkable high diffusion coefficient of the common known network modifier sodium(I) [13]. An estimation based on Fick's law

$$x = \sqrt{4Dt} \qquad (3)$$

leads to a diffusion velocity of silver in a substrate glass phase of up to 15 µm/min at 850 °C. Nonetheless, if crystallization takes place in the diffusion volume, the precipitated crystals will act as barriers and hinder the diffusion movement of the silver ions.

The incorporation of Ag_2O (5 mol%) in a glass melt leads to a drastic decrease in the viscosity, which is illustrated in **Fig. 3**. In the case of fine dispersed LTCC the glass melt viscosity can be lowered throughout the whole glass phase volume which accelerates viscous flow and sintering. When working in constrained sintering technology using sacrificial layers, the LTCC tape can glue to the sacrificial tape in an undesired way by this glass flow. Additonally, due to lower viscosity and structural weakening by bond cracking, the crystallization tendency of a substrate glass melt can increase significantly and/or shift towards

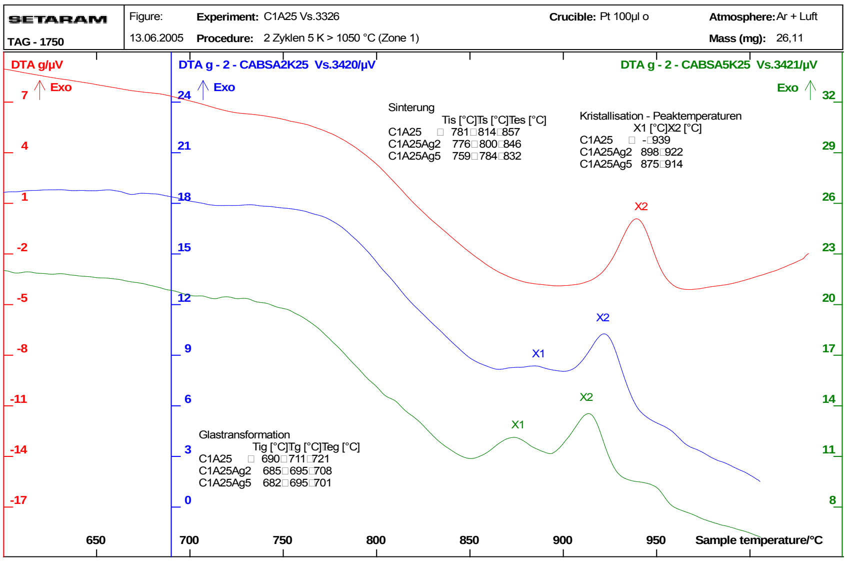

Fig. 4. DSC plots showing transformation range, sintering ramp and crystallization peaks of a Al_2O_3-CaO-B_2O_3-SiO_2-glass (CAG0) and the same glass containing additions of 2 and 5 mol% of Ag_2O (CAG2 and CAG5) in the composition.

lower process temperatures [14-16]. In **Fig. 4** this shift is illustrated using DTA investigations on model LTCC composites made of CaO-Al_2O_3-B_2O_3-SiO_2-glasses with increasing Ag_2O content and 25 vol% Al_2O_3.

With regard to (ii) and (iii), from a rough practice point of view the overall diffusion range of silver throughout a LTCC firing cycle is the sum of two diffusion mechanisms:

- temperature interval 300 – 700 °C (presence of open porosity in LTCC bulk):
  - High velocity diffusion from silver bulk into the gaseous phase as silver by vapour pressure and/or silver (I) by gaseous compound formation, may reach up to some millimeters and may be terminated by condensation or chemisorption at LTCC-particles,
- temperature interval 600 – 900 °C (presence of softened glass matrix in LTCC bulk):
  - Low velocity diffusion of silver in oxidized state through the liquid phase.

The impact of silver related acceleration of LTCC sintering is restricted to the silver contaminated volume and can be locally selective, e.g. only some microns below a silver conductor. This narrow range densifies earlier than the substrate bulk, crystallizes and forms a hardened shell underneath the silver conductor. Later the substrate bulk shrinks, the hardened shell cannot follow appropriate and is bend upwards. **Fig. 5** depicts this so called warpage mechanism, which was first described by Totokawa [17]. In some cases in conventional LTCC sintering, suchlike warpage can be surpressed by firing under nitrogen atmosphere. The oxygen concentration is minimized and only minor amounts of silver can be transferred into the oxide state and enter the LTCC glass by consuming the O_2 dissolved in the silver bulk. However, when firing very thick silver layers for power electronics as described above, the oxygen reservoir provided by the silver powder itself is large enough to provide a sufficient amount of Ag_2O for warpage, as shown on the LTCC substrates in **Fig. 6**, which were fired in air, nitrogen or constrained in air.

(iv) Reduction of Ag_2O

Depending on the present oxygen partial pressure and the redox potential of a distinct substrate surface or glass melt volume the silver oxid can be reduced. The reduction can occur either in a gaseous atmosphere or in a glass volume after a transport according to high or low velocity diffusion mechanisms.

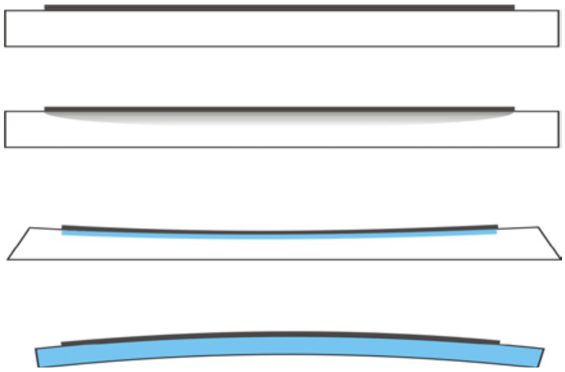

Fig. 5. Four stages warpage mechanism after [17]. Heating of the silver metalized LTCC substrate leads to Ag diffusion into the porous LTCC bulk over the gaseous phase and/or into the glass phase of the softening LTCC glass (grey). The Ag contaminated area sinters, crystallizes and hardens faster than the substrate bulk. Shrinking of the LTCC bulk, finally, leads to warpage of the early hardened shell.

Fig. 6. Pictures of 50 µm silver coil structures in Fig. 1 in LTCC after firing unconstrained in air (left) and unconstrained under N_2-atmosphere (center). For comparison result of a firing using constrained layer on top and bottom (right). Unconstrained sintering leads to strong warpage according to the mechanism shown in Fig. 5. In contrast to experiences with conventional Ag conductors of 10 µm thickness, firing in N_2 could not prevent the effect, presumable due to a larger amount of oxygen dissolved in the silver powder used.

In glass melts, the reduction is initiated by the presence of polyvalent ions less noble than silver. For example, in a heated silver metalized float glass, silver first entered the glass bulk on the tin(IV) rich tin bath side [18]. After the diffusion of approximately 2 microns into the bulk and entering the tin(IV) poor but tin(II) rich volume, silver was found to behave after the following redox equation:

$$2\ Ag^{+}_{glass} + Sn^{2+} \rightarrow 2\ Ag + Sn^{4+} \qquad (4)$$

PbO- or Bi_2O_3-rich glasses also show this redox interaction when Ag_2O is incorporated. By adding increasing amounts of 2 vol% and 20 vol% of silver powder to those glass powders, a precipitation of Pb- or Bi-colloids could be surpressed in trade of a Ag-colloid precipitation [19] when printed and fired on Si wafers.

Reduction of silver oxide in glass melts leads to formation of nano colloidal silver particles some tenths in diameter [20]. These silver colloids show a special kind of light absorption (plasmon resonance) which leads to coloring of the host glass. The center of the silver colloid light absorption band is located between 390 and 410 nm. Low concentrations of colloidal silver color a white glass intensively yellow; the so called silver rubin glasses are well-known since the middle age. Higher concentrations of colloidal silver lead to strong brown or black glass colors.

The yellow coloring is frequently encountered in thick film processing of silver metalized 96 % Al_2O_3 substrates and especially LTCC substrates. The effect is observed up to some millimeters around the silver conductors and is commonly called “yellowing” or “staining”. In order to clarify the origin of the yellowing, a co-firing LTCC sample looking white to the naked eye and two samples showing significant yellowing were compared in their light absorption properties in the UV/Vis range. In **Fig. 7** the light reflexion in dependence on the wavelength of the three samples are are shown. Whereas the white sample does show negligible relexion in the visible range, the light yellow sample shows a maximun reflexion at about 350 nm and the stronger yellow sample shows relexion maximum at about 410 nm. This points at growing nano colloidal silver particles as the major reason for the LTCC yellowing [21]. Interestingly, the graded color intensity could be achieved by varying the powder preparation. In other words, the activation of the respective powder surfaces for adsorption of silver present in the atmosphere during the firing cycle could be controlled.

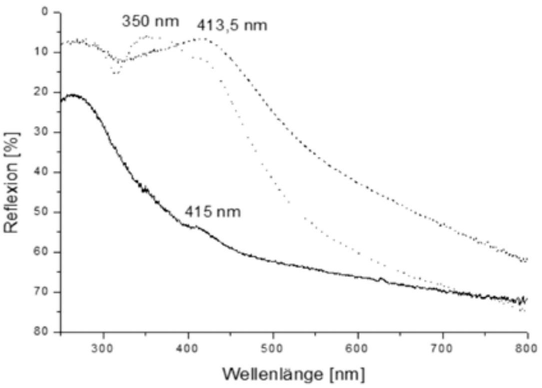

Fig. 7. Light reflexion in dependence on the incident wavelength of three LTCC samples after co-firing with silver paste. Solid line: white appearance to the naked eye, dotted line with main band 350nm: light yellow, dotted line with main band 413nm: strong yellow.

4 Conclusions

Silver is an element possessing outstanding properties due to its special electron configuration, like the high electrical and thermal conductivity and the thermodynamic stability in air. However, challenges in manufacturing occure due to other silver properties, namely the oxygen uptake and the exist in different stable solid states. The latter are highly sensitive to temperature and in dependence of the close by and contacted materials. Moreover, silver has a significant vapour pressure and can be present in different aggregate states. In this paper some aspects of silver properties important to thick film technology are described.

Silver Bulk

Heating silver powder will lead to first sintering shrinkage above 300 °C. Passing 450 °C will lead to an uptake of oxygen from the environment in case of silver powders obtained by electrolytic or by chemical precipitation at low temperature. This could lead to a transient reducing microatmosphere, which can influenc the burn out of the organic composits in thick film pastes. Passing the temperature of 531 °C will initiate an Ag-O liquid phase coexistent to the silver phase. The oxygen solubility decreases continuously up to silver melting at 962 °C. This will accelerate silver

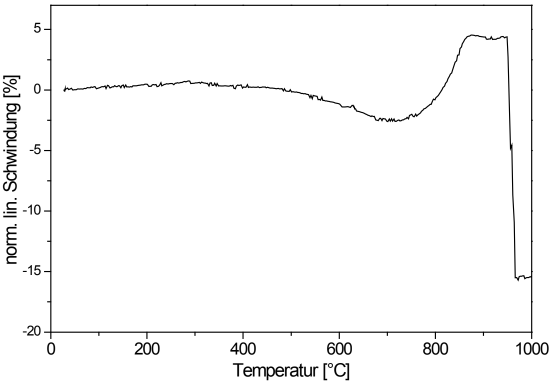

Fig. 8. Linear shrinkage of a silver powder compact in dependence on temperature. Shrinkage starts at around 300 °C and continues up to 700 °C. After that, a no further shrinkage is observe due to an overlap with expansion effects.

sintering but can also lead to bubbling effects dependend on the powder morphology and powder size distribution. **Fig. 8** shows a typical shrinkage of a silver powder mixture (74.4 % monomodal, d_{50} = 4 µm and 25.6% monomodal, d_{50} = 0.4 µm). The green density of the powder compact is up to 55 % of the theoretical density, therefore an overall shrinkage of at least 15 % is expected for full densification. Powder shrinkage starts around 300 °C and continues up to 650 °C. After that, no further shrinkage was observed due to an overlap with expansion effects. The microstructure of a powder compact which was submitted to an interupted firing at the maximum expansion at 900 °C is shown in **Fig. 9**. Bubbles equally distributed in a homogen silver matrix indicate an outgassing after bulk densification. This outgassing can be easily correlated to the temperature range above 531 °C, in which decreasing oxygen solubility is evident. Therefore, the high temperature expansion effect of a number of silver powders might be the consequence of oxygen outgassing.

Silver in gaseous phase

Thermodynamic considerations leads to the main result, that silver can be present in an sinter atmosphere due to its own vapour pressure or the formation of volatile silver(I)-complex species. The diffusion kinetics can be regarded as very fast compared to diffusion through a liquid or bulk. Condensation of the silver from the gaseous phase is dependent on temperature and on the surface chemistry of the powder that is co-fired. The silver condensation is e.g. the major course of the well known setter memory effect.

From a technical standpoint, for processing of silver metalized thick film structures there are roughly two temperature ranges of relevance. Approximately between 300 °C and 700 °C fast transport mechanisms of silver through the gaseous phase can take place by the aid of organic silver complexes and silver vapor. Control can be achieved via governing the silver manufacturing, oxygen partial pressure, organics composition, powder conditioning and temperature-time schedule. Above approximately 600 °C, slower transport mechanisms of silver through the glassy phase and possible reduction become evident. These effects originate corresponding impacts on the sintering kinetics. Here, control can be achieved via governing the glass composition, redox potential and, again, temperature-time schedule.

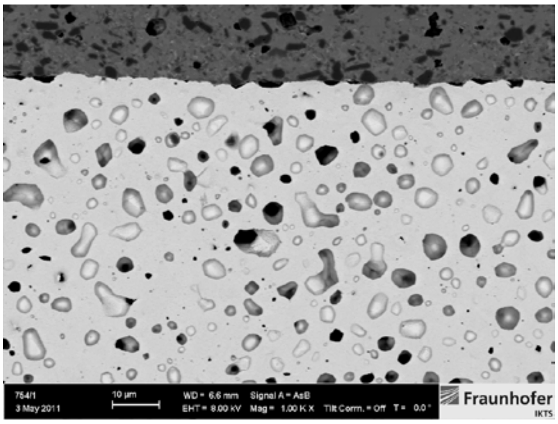

Fig. 9. The microstructure of a powder compact according to Fig. 8 which was submitted to an interupted firing at 900 °C. Bubbles equally distributed in a homogen silver matrix indicate an outgassing after bulk densification.

Starting from this background, targeted selection of raw materials, paste recipe, LTCC composition and firing conditions can be used to optimize the firing performance and open ways to silver metalized high precise and high performance LTCC power electronics.

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Literature

[1] Doduco, A. (2007). Retrieved http://www.amidoduco.com/d_version/pdf/Ag-Pulver.pdf.

[2] Ku, B. K. and Maynard, A. D., (2006). "Generation and investigation of airborne silver nanoparticles with specific size and morphology by homogeneous nucleation, coagulation and sintering" J. Aerosol Sci. **37**(4): 452-470.

[3] Koo, H. Y., Kim, J. H., et al. (2010). "Preparation of silver-glass composite powder and conducting film" J. Ceram. Soc. Jpn. **118**(1377): 353-356.

[4] Jung, D. S., Koo, H. Y., et al. (2010). "Electrical and morphological properties of conducting layers formed from the silver-glass composite conducting powders

prepared by spray pyrolysis" J. Colloid Interface Sci. **343**(1): 1-6.

[5] Koo, H. Y., Yi, J. H., et al. (2010). "Nano-sized silver powders coated with Pb-based glass material with high glass transition temperature" Colloids Surf A: Physicochem. Eng. Aspects **361**(1-3): 45-50.

[6] Assal, J., Hallstedt, B., et al. (1997). "Thermodynamic Assessment of the Silver–Oxygen System" J. Am. Ceram. Soc. **80**(12): 3054-3060.

[7] Panzer, E., Qian, M., et al. (2000) "Kinetische Untersuchungen zur Katalysatordesaktivierung bei der partiellen Oxidation von Methanol zu Formaldehyd nach dem Silberkontaktverfahren", FORKAT Teilprojekt C6; Statusbericht März 2000, 204-209.

[8] Paule, R. C. and Mandel, J. (1972) "Analysis of interlaboratory measurements on the vapor pressure of cadmium and silver" IUPAC publication, 395-431

[9] Cui, X., Li, B., et al. (2008) “The co-fired behaviors between Ag and glass–ceramics materials in LTCC” J. Electroceram. **21**: 541-544.

[10] Honig, R.E., RCA-Review (Juni 1953) S.195/204 – Skull and Sinke, Thermodynamic Properties of the Elements, Am. Chem. Soc., Washington D.C. (1956)

[11] Schulze, G. (1913). "Experiments on the diffusion of silver in glass" Ann. Phys. **40**(2): 335-367.

[12] Westermann, I. (1932). "The absorption of silver oxide by means of oxide and oxide compounds in higher temperatures" Z. Anorg. Allg. Chem. **206**(1): 97-112.

[13] Dahlmann, U. (1997). "Verhalten von Silber in Flachglasschmelzen bei der Wiederverwertung von Spiegelscherben - kinetische Aspekte (Diploma)", Aachen, RWTH Aachen.

[14] Eberstein, M., Rabe, T., et al. (2006). "Influences of the Glass Phase on Densification, Microstructure, and Properties of Low-Temperature Co-Fired Ceramics" Int. J. Appl. Ceram. Technol. **3**: 428-436.

[15] Jean, J. H., C. R. Chang, et al. (2004). "Sintering of a crystallizable CaO-B2O3-SiO2 glass with silver" J. Am. Ceram. Soc. **87**(7): 1244-1249.

[16] Tramosljika, D., Schaefer, J., et al. (2005). "Sintering behavior of a LTCC material and influence of silver on the sintering behavior" IMAPS/ACerS Ceramic Interconnected and Ceramic Microsystems Technologies, Baltimore.

[17] M. Totokawa et al., "Study of the Strain Mechanism of Multilayer Ceramic Substrate", IMC 1994 Proceedings, Omiya, April 20-April22 (1994)

[18] Takeda, S., Yamamoto, K., et al. (2000). "Coloration due to colloidal Ag particles formed in float glass" J. Non-Cryst. Solids **265**(1-2): 133-142.

[19] M. Peschel, Schilm, J., et al., "Synthesis and characterisation of new lead-free glasses for the front metallisation of solar cells" 26th European Photovoltaic Solar Energy Conference and Exhibition (26th EU PVSEC), Sep, 2011, Hamburg, Germany.

[20] Scholze, H. (1988). "Glas - Natur, Struktur und Eigenschaften” 3. Auflage, Springer Berlin Heidelberg.

[21] Zielinska, A., Skwarek, E., et al. (2009). "Preparation of silver nanoparticles with controlled particle size” Procedia Chemistry **1**: 1560-1566.