Investigation of inhomogeneous shrinkage of partially crystallizing Low Temperature Co-fired Ceramics (LTCC)"

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ABSTRACT

The aim of our study is an improved level of geometrical design fidelity of LTCC microsystems by consideration of location-dependent shrinkage under free sintering conditions. To achieve this, the commercial low temperature co-fired ceramic (LTCC) systems: DuPont GT 951, DuPont 9k7 and Heraeus CT 702 have been investigated experimentally with special regard to the local lateral shrinkage over a 4 inch x 4 inch substrate typically used for the fabrication in multiple panels. Partially crystallizing LTCC materials reveal a significant local dependence of the lateral shrinkage. This dependence is introduced as a shrinkage field. Furthermore, we present an approach for shrinkage field approximation and forecasting. Applied to shrinkage allowance, it allows for minimizing the geometrical deviations after sintering from designed dimensions. Alternatively to a design adapted to the forecasted shrinkage field, local shrinkage deviations can be minimized by sintering for homogeneous shrinkage. Detailed analyses of the DuPont GT 951 system indicate a strong influence of the temperature profile during the free sintering on the shrinkage field. By utilizing this influence, a homogenous shrinkage field can be achieved for optimized heating rate and dwell time at the peak temperature 850 °C.

Keywords: LTCC; Glass-ceramic composites; Shrinkage field; Production yield; Free sintering; Partial crystallization

I. INTRODUCTION

For several years, the LTCC technology is in the focus of interest for the development of highly functional circuit boards, stable sensor packages or fluidic and sensory microsystems for harsh environmental conditions [1-3]. Its three-dimensional structuring, the multitude of potential functionalization as well as available materials and the cost-effective production of large piece numbers in multiple panels distinguish this technology in particular. However, current trends demand for a continuous miniaturization of feasible structures with a constant high manufacturing yield. This requires a precise knowledge of the manufacturing technology, the material properties and their interactions. Specifically, the precise control of the lateral shrinkage (shrinkage allowance) plays an important role. It substantially determines the component properties (e. g. for MEMS, packages and interposers) and the yield of the post-processes in the technology sequence.

A recent study determined unacceptable functional variances of MEMS components fabricated in multiple panels on a LTCC substrate [4]. One source of these deviations is the inhomogeneous lateral shrinkage of the multiple-component substrate and the resulting different dimensions of the components after sintering and separation [4] which influences strongly the functionality. It is well known that shrinkage variation in lateral direction of LTCC materials is up to ± 0.5%. However there is no general rule to handle this. One approach to suppress shrinkage variation under ± 0.05% is constrained sintering of LTCC laminates. Relevant techniques are presented in [5]. This approach is certainly not feasible for all applications and requires advanced equipment as well as advanced material composites. Especially the fabrication of MEMS components limits the utilization due to the fact that freestanding structures will be destroyed during pressure assisted sintering or self-constrained laminates provides inhomogeneous material properties. The first purpose of this work is to determine the inhomogeneous local shrinkage and to find feasible approximation for a shrinkage control with a geometry variation of the fired structures under ± 0.05%.

The second purpose includes the determination of the dependencies and causes for the local shrinkage which are mostly expected in the sinter process. Kemethmüller et al. [6]; Mohanram et al. [7] and Eberstein et al. [8] investigated the sintering of commercial or model glass-ceramic composites. The results indicate a strong influence of the sinter profile and the composition on the shrinkage behavior, the densification and crystallization of the glass phase. Thus possible dependencies for the local shrinkage are expected here too. Additionally Makarovic et al. [9] studied the influence of the temperature profile

on the phase composition, the micro structure and material properties. Due to that this work extend the knowledge about LTCC glass-ceramic composites regarding the shrinkage and improves the design process for LTCC-based components.

(1) Local shrinkage

To investigate the shrinkage of the green tapes in the multiple panel process we used 4 inch x 4 inch laminates with integrated measurement structures. The samples consist of at least two layers which were cut at the specified geometry. 5 Stacking holes and 100 via holes (Ø0.2 mm) were punched in each layer in the green state. Afterwards the single layers were stacked (twisted at 90°) and laminated with 200 bar at 70 °C for 10 min. Finally the laminates were fired in a ATV PEO 6330 box furnace (ATV GmbH, Germany) with the sinter profiles shown in Table 1.

Table 1: *General temperature profiles for the debindering and sintering of DuPont GT 951, DuPont 9k7 and Heraeus CT 702.*

Segment	debindering	sintering		
GT 951	As recommend in [10]	600°C to 850 °C 2 K/min	Hold 60 min	850 °C to 50 °C; -20,4 K/min
9k7	As recommend in [10]			
CT 702	As recommend in [11]			

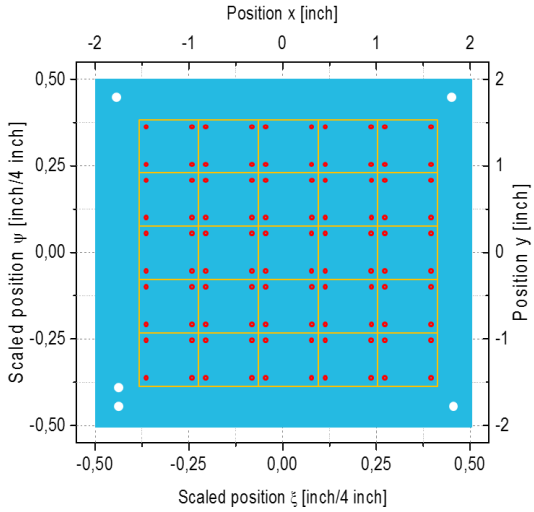

Figure 1: *Sample layout for the characterization of the local shrinkage $S_{L\_x/y}$.*

The 100 via holes on the fired substrate (Figure 1) were used to determine the shrinkage during the fabrication process with a Nikon measurement microscope (x; y-accuracy = 1 µm). To investigate the local shrinkage over the substrate, the punched measurement structure is separated into 25 structure units each with 4 measurement points. Each vertical and horizontal segment was determined and the shrinkage of these segments was calculated relating to the CAD-layout in the green state (punching layout). The mean value of the 4 segments of each structure unit provides the local shrinkage $S_{L\_x/y}$ on its position. For the discussion of different substrate sizes (green state) it is suitable to manifest dimensions which are scaled to this substrate size: ξ for the x-dimension and ψ for the y-dimension.
The local shrinkages of the 25 structure units can be qualitative analyzed in a 2D-contour diagram as shown in Figure 2. This manifests the local shrinkage as a function of the scaled position (ξ; ψ) on the panel, which is established as shrinkage field. Furthermore, the character of this specific field can be thought of equipotential lines around the center of the substrate. Due to that, it is reasonable to describe the locale shrinkage as a function of the radial displacement from the substrate center. The radial displacement ρ is also scaled to substrate size in the green state due to the reasons described above. As shown in Figure 3, the local shrinkage over the substrate can be approximated with the quadratic equation:

$$S_{L\_x/y}(\rho) = C_0 + C_1\rho^2 \qquad \text{(E.1)}$$

With the vertex C_0 as the base shrinkage and C_1 as a dimension of the inhomogeneity of the local shrinkage $S_{L\_x/y}(\rho)$ on the substrate.

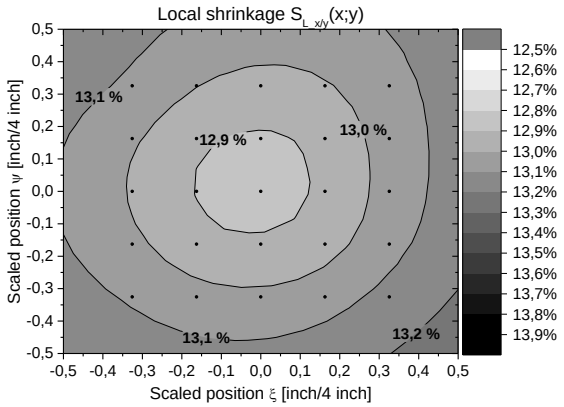

Figure 2: *2D-contour diagram of the local shrinkage $S_{L\_x/y}$ at 25 positions on a GT 951 substrate consisting of 2 layers (PX) and laminated at 200 bar and 70 °C*

To compare the shrinkage inhomogeneity of different LTCC materials and different processed substrates, it is suitable to discuss the local shrinkage differential $\Delta S_{L\_x/y}$ with:

$$\Delta S_{L\_x/y}(\rho) = S_{L\_x/y}(\rho) - C_0. \qquad \text{(E.2)}$$

The determined resolution of the local shrinkage differentials for these investigations is ± 0.05 %. Differentials inside of this restriction are supposed to be homogeneous. This area is defined as homogeneous band in this study.

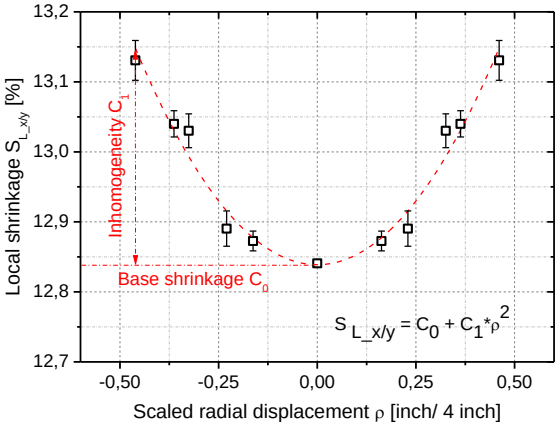

***Figure 3**: The local shrinkage $S_{L\_x/y}$ of a GT 951 substrate as a function of the scaled radial displacement ρ from the substrate center and determination of a quadratic approximation.*

(2) Effect of the sinter profile on the Shrinkage

With varying the heating rates *HR* (2 K/min; 5 K/min; 10 K/min and 15 K/min) after the binder burnout and the dwell times t_d (0 min and 60 min) at the peak temperature 850 °C, the effect of the sinter profile on the local shrinkage of the LTCC tape GT 951 was investigated. The samples were processed with two 4 inch x 4 inch layers twisted at 90° and laminated at 20 bar and 70 °C for 10 min. The determination and evaluation of the shrinkage was carried out as specified in section II (1).

(3) Qualitative Phase Analysis

The X-ray diffraction was used to determine the types and the mass ratio of the crystalline phases (ID 3003TT). For all investigations, the angular range 2Θ was 5° to 90° with a step width of 0.03° and a measurement time of 3 s. The analysis were carried out at GT 951 substrates fired with several sinter profiles. The qualitative determination of the phases were performed. For the mass ratio between the crystalline phases, the Rietveld refinement was used.

(4) Quantitative Phase Analysis

To determine the ratio between the glass phase, the corundum phase and the anorthite phase at selected positions on a fired GT 951 substrate we used Scanning Electron Microscope (SEM) pictures of polished sections performed with in combination with a quantitative image evaluation (QWIN analySiS five). The analysis of the different gray scales allows the determination of the area ratios representing the different phases and the evaluation of any local differences. 10 pictures were used at each position on the substrate to get representative data.

III. RESULTS

(1) Local shrinkage

In Figure 4 the local shrinkage differential of the green tape DuPont GT 951 is compared with the behavior of two other commercial available LTCC-tapes: DuPont 9k7 and Heraeus CT 702 which were processed respectively. While the samples GT 951 and CT 702 shows a relevant inhomogeneity, the sample 9k7 provides an almost homogeneous shrinkage over the whole substrate. Interesting is the fact that the GT 951 and the CT 702 are partially crystallized LTCC whereas the 9k7 crystallizes completely. The sample "GT 951 - 20 bar" which was laminated with a deviant pressure (20 bar) than the other samples shows only little deviations compared to the lamination pressure of 200 bar (GT 951 - 200 bar).

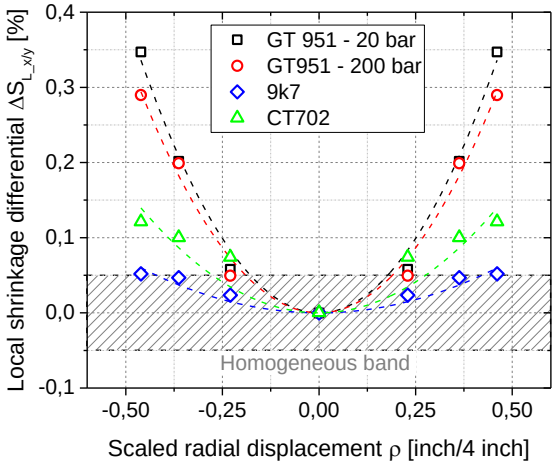

***Figure 4**: Local shrinkage differentials $\Delta S_{L\_x/y}$ as a function of the scaled radial displacement ρ for different LTCC materials: GT 951; 9k7; CT 702 and a GT 951 sample laminated at the deviate pressure 20 bar.*

The investigated shrinkages in this work are related to the CAD layout of the measurement structure. To determine the influence of the other fabrication steps on the inhomogeneity, one sample was characterized after the punching and the lamination process additionally. The results in Figure 5 indicate no significant effect on the local shrinkage due to these two steps. Therefor the cause of the shrinkage fields can be isolated on the sinter process of the LTCC tapes.

***Table 2**: Results of the quadratic approximation for the local shrinkage with $S_{L\_x/y} = C_0 + C_1\rho^2$.*

Sample	Base shrinkage C_0 [%]	Inhomogeneity C_1 [%]
GT 951 - 20 bar	13.9	1.6
GT 951 - 200 bar	12.8	1.4
9k7	8.2	0.3
CT 702	14.0	0.7

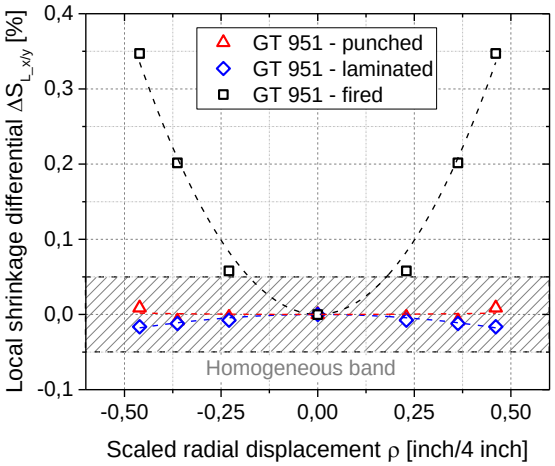

***Figure 5**: Local shrinkage differentials $\Delta S_{L\_x/y}$ as a function of the scaled radial displacement ρ measured after different fabrication steps of the sample "GT 951 - 20 bar": after punching; after laminating; after sintering.*

(2) Effect of the sinter profile on the Shrinkage

The inhomogeneity of the local shrinkage can be strongly affected by the temperature profile during the sinter process. Figure 6 illustrates the influence of the heating rate *HR* and the dwell time t_d for the LTCC material GT 951. The inhomogeneity which is indicated by the parameter C_1, decreases with rising heating rates up to the level of *HR* = 10 K/min and increases with a raising dwell time. The most homogeneous shrinkage behavior occurs at the sample with *HR* = 10 K/min and t_d = 0 min. The shrinkage field of the sample with *HR* = 15 K/min and t_d = 0 min is an exception with a negative inhomogeneity C_1.

The illustration of the inhomogeneity C_1 in Figure 7 determines the feasible parameters for the temperature profile to achieve a homogeneous local shrinkage. Thus the heating rate *HR* has to be higher than 8.75 K/min to avoid the appearance of the introduced shrinkage fields. However the dwell time t_d has to be adapted for each heating rate.

To improve the knowledge of the inhomogeneity as a function of the dwell time, further investigations will be carried out in the future to identify a valid approximation between these parameters.

(3) Qualitative Phase Analysis

To determine the causes of the shrinkage fields, X-ray patterns were measured at selected samples (Section III (2)) to analyze the crystalline phases. The comparison of different LTCC materials regarding the local shrinkage in Section III (1) point to an effect of the crystallization behavior. It is well established from [7], [9] and [12], that the crystallization depends among other things on the heating rate *HR* and the dwell time t_d. Thus these investigations are to confirm this thesis.

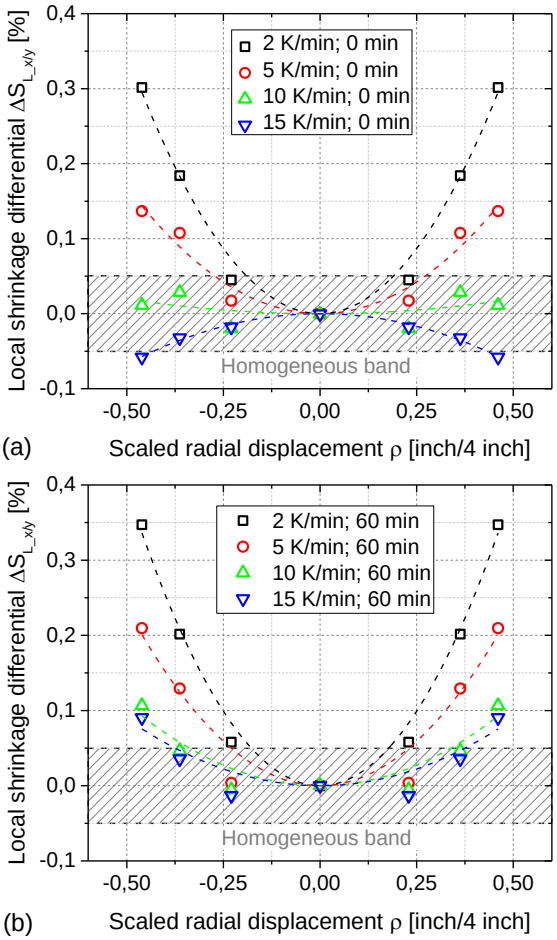

***Figure 6**: Local shrinkage differentials $\Delta S_{L\_x/y}$ as a function of the scaled radial displacement ρ for the material GT 951, fired at varied heating rates HR (2; 5; 10; 15) K/min with a dwell time at the peak temperature 850 °C of: 0 min (a); 60 min (b).*

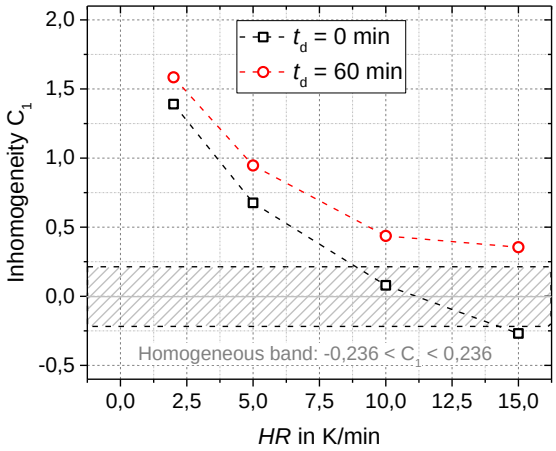

***Figure 7**: Inhomogeneity C_1 of the local shrinkage as a function of the heating rate HR with the dwell times (0; 60) min at the peak temperature 850 °C for the material GT 951.*

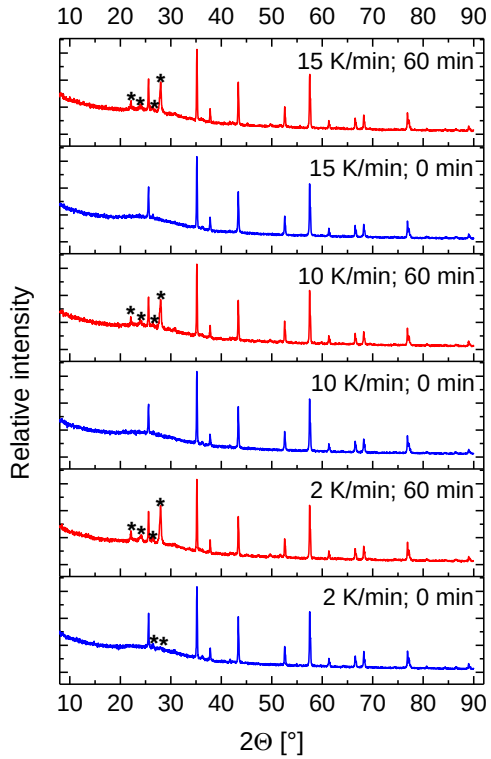

***Figure 8**: Diffraction patterns of the material GT 951 fired at varied heating rates (2; 10; 15) K/min with varied dwell times at 850 °C (0; 60) min. Peaks of anorthite are denoted by *.*

***Table 3**: The relative mass fractions of the phases alumina and anorthite of the material GT 951 fired at varied heating rates (2; 10; 15) K/min with varied dwell times at 850 °C (0; 60) min.*

Sample	Relative mass fraction alumina [wt.%]	Relative mass fraction anorthite [wt.%]
2 K/min; 0 min	97,6	2,4
2 K/min; 60 min	72,5	27,5
10 K/min; 0 min	100	0
10 K/min; 60 min	75,7	24,3
15 K/min; 0 min	100	0
15 K/min; 60 min	75,2	24,8

Figure 7 illustrates the diffraction patterns of GT 951 samples fired at different heating rates *HR* (2 K/min; 10 K/min and 15 K/min) with a varied dwell time t_d (0 min and 60 min) at the peak temperature 850 °C. All patterns show the intensity peaks for the alumina phase besides the typical noise caused by the glass phase. In some samples new peaks appeared which correspond to the crystalline phase anorthite (*****). This fact regards all samples with the low heating rate (2 K/min) and the samples with a dwell time of 60 min. In addition they are also characterized by a comparable high inhomogeneity of the local shrinkage. However the homogeneous sample (10 K/min; 0 min) indicates no anorthite phases. Besides the exception with the negative inhomogeneity (15 K/min; 0 min) exhibit no further crystalline phase too. Due to that a general dependence is not feasible.
Table 3 lists the mass ratio between the alumina and the anorthite for the selected samples.

(4) Quantitative Phase Analysis

Three cross section of structural units from a sample (2 K/min; 60 min) of section III (2) were prepared for a quantitative phase analysis. The selected structural units represent three different positions on the 4 inch x 4 inch substrate (corresponding to Figure 1):

i. **Left-down**; ρ = 0.46 inch/4 inch,
ii. **Center**; ρ = 0 inch/4 inch,
iii. And **right-top**; ρ = 0.46 inch/4 inch.

10 SEM pictures (Figure 9) of each cross section were recorded and analyzed with a quantitative image evaluation regarding the area fraction of the different phases (alumina, anorthite and glass) to review if any difference can explain the appearance of the shrinkage fields.
The results illustrated in Figure 10 indicates no significant differences of the area ratios between the three sections. As expected the crystallization is homogeneous on the whole substrate and provides no local effect on the shrinkage.

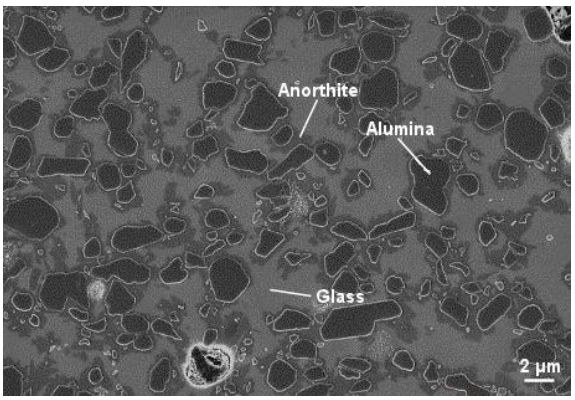

***Figure 9**: Microstructure of the GT 951 fired at 850 °C with a heating rate = 2 K/min and a dwell time = 60 min. Visualization of the different phases.*

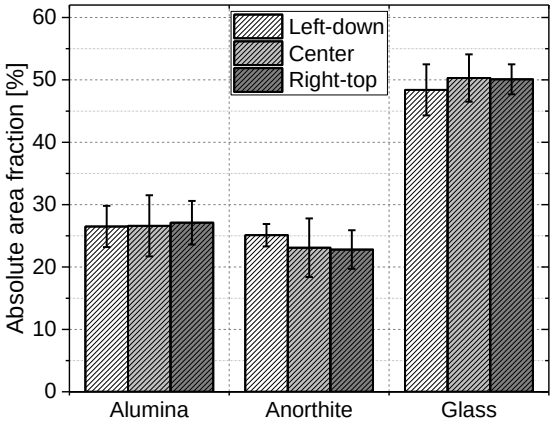

***Figure 10**: Absolute area fraction of the phase alumina, anorthite and glass at three different positions on GT 951 – 4 inch substrate.*

IV. DISCUSSION

The appearance of inhomogeneous shrinkage fields in partially crystallized LTCC substrates after free sintering requires new approaches for design and fabrication of LTCC-based, miniaturized components in multiple panels. The measured deviations of the local shrinkage up to 0.35 % influence the accuracy of all postfiring processes and therefore the geometrical dimensions and functional characteristics of MEMS-components. This, in general, limits yield and miniaturization potential as well.

The results above reveal two principal approaches to control the inhomogeneity of the local shrinkage after free sintering for the LTCC material GT 951:

i. Local shrinkage considering design
ii. Sintering for homogeneous shrinkage

The first approach requires knowledge about the shrinkage field and shrinkage field forecast (See section II (1)). Based on such a local shrinkage model the shrinkage allowance can be locally adapted for minimizing the shrinkage error F_S of the fired components. This approach improves the conventional procedure of applying a mean shrinkage value for a whole substrate. Figure 11 compares the expected shrinkage error for a quadratic shrinkage field approximation and the conventional procedure of a constant shrinkage rate. The second approach could be called sintering for homogeneous shrinkage. Its aim is to minimize the shrinkage field inhomogeneity by using optimized sintering parameters. Compared to the first approach, a deeper understanding of the LTCC material and its sintering is required. The results in section III (2) demonstrate a feasible control of the shrinkage field by adaption of the heating rate and the dwell time at the recommended peak temperature. The analysis of the most homogeneous sample (10 K/min; 0 min) suggests best shrinkage behavior of the GT 951 if no crystallization occurs during the sinter process. However, the exception sample (15 K/min; 0 min) indicates a point where the shrinkage inhomogeneity C_1 becomes a negative value. For this reason, additional still unknown influences on the shrinkage must exist. It is well known, that the densification is strongly affected by the heating rate and the dwell time [7].

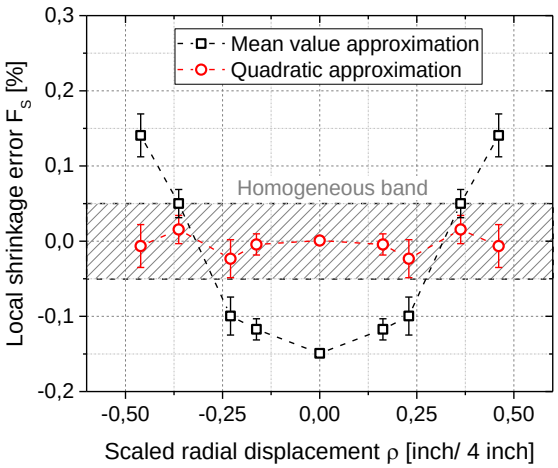

***Figure 11**: Local shrinkage error F_S as a function of the scaled radial displacement ρ. Comparison of two approaches for the shrinkage control: mean value approximation and quadratic approximation.*

V. CONCLUSIONS

Free sintering of the commercial LTCC base tapes was investigated experimentally with special regard to the local lateral shrinkage over a 4 inch x 4 inch substrate.

It was measured that the partially crystallizing tapes DuPont GT 951 and Heraeus CT 702 point inhomogeneous local shrinkages whereas the completely cristallizable tape DuPont 9k7 exhibit an almost homogeneous local shrinkage. Further investigations on the LTCC material GT 951 indicate that the shrinkage fields depends on the temperature profile (heating rate and dwell time) during the sinter process. It was shown that an adopted sinter profile significantly decreases the inhomogeneity. Based on the experimental results, two approaches were presented to control shrinkage over a substrate for the multiple panel process of LTCC-based components, (i) model based local shrinkage allowance and (ii) sintering for homogeneous shrinkage. Both contribute to a higher accuracy of MEMS fabrication and in the post-firing process which imply a higher feasible miniaturization rate and geometry fealty. However, further investigations are necessary to expand the knowledge about the discussed phenomenon. That includes the continuing investigations regarding the sinter profile (dwell time and peak temperature), the densification of the material and the porosity. Another purpose of our future work is the extension of the investigation on other commercial LTCC materials.

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