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Kinetic study of the polymeric binder burnout in green low temperature co-fired ceramic tapes

**Sigrid Lüftl · Bruno Balluch ·
Walter Smetana · Sabine Seidler**

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Abstract The binder decomposition and burnout process of a commercial low temperature co-fired ceramic (LTCC) tape and an alumina tape which is used as a sacrificial tape for the constrained sintering process of the LTCC-tape was investigated by thermogravimetry (TG) and derivative thermogravimetry (DTG) up to 550 °C at different heating rates (from 1.5 to 10 K min^{-1}) in air. TG revealed a multistage degradation behaviour of the binder system for both tapes, but the temperature range of the different degradation stages varied. The activation energy of decomposition was determined by the Flynn–Wall isoconversional method and the Coats–Redfern method.

Keywords Al_2O_3 · Kinetic analysis · LTCC · Thermogravimetry

Introduction

Low temperature co-fired ceramic (LTCC) technology has been proved to be a valuable development of thick film technology which establishes new application areas. The LTCC process has long been used for the fabrication of electronic circuit components, especially for radio frequency (RF) applications [1]. Originally LTCC technology was developed to manufacture multilayer circuits with high reliability. However, LTCC technology launches new application areas since it becomes evident that complex three-dimensional structures can be easily realized. It covers areas like microfluidic, integrated device packaging where optical fibres may be integrated, bioreactors, sensors and transducers. Fields of application are similar to that of microelectromechanical systems (MEMS) but only realized in a mesostructure performance [2–4].

LTCC technology provides high flexibility with regard to the availability of tapes of appropriate physical performance (e.g. permittivity, permeability, elasticity, etc.) and thickness [5]. The process technique for making a 3D-architecture with LTCCs is rather simple and standardized. It starts with structuring of single layers of unfired ceramic tapes which are stacked to a module. Different methods, like laser micromachining, embossing, stamping, etc. may be applied to form the tapes in the desired shape. The stack of tapes is laminated in an isostatic or uniaxial press, respectively. Afterwards the compacted module is exposed to a firing cycle. That is a critical process where heating rate, holding time at burnout temperature, and total firing cycle time have to be accommodated to the thickness of the ceramic stack. In order to avoid a lateral shrinkage the LTCC-tape may be co-laminated with an alumina tape. On the one hand, the alumina tape prevents the lateral shrinkage of the LTCC-tape but induces on the other hand an increased shrinkage in tape thickness [6].

Typical material combinations of LTCC are composites of glass and ceramic, crystallized glass, composites of crystallized glass and ceramic, and liquid phase sintered ceramics. These considered compositions provide a rather low sintering temperature of <900 °C [7]. The so-called green state LTCC is typically a composite consisting of alumina particles (Al_2O_3, about 20–30% by mass of fired

S. Lüftl (✉) · S. Seidler
Institute of Materials Science and Technology, Vienna University of Technology, Favoritenstrasse 9-11, 1040 Vienna, Austria
e-mail: lueftl@mail.zserv.tuwien.ac.at

B. Balluch · W. Smetana
Institute of Sensor and Actuator Systems, Vienna University of Technology, Gusshausstrasse 25-29, 1040 Vienna, Austria

product) and glass frit particles (SiO_2, CaO, B_2O_3, MgO, SrO, TiO_2 and PbO) held together by an organic binder [8]. To prepare the green state tapes usually a slurry consisting of dispersant, solvent, plasticizer, binder and glass–ceramic composites is mixed, cast on a moving carrier substrate (usually a film of cellulose acetate or polyester) and dried [9]. A firing process has to be applied in order to convert the LTCC-tape into a solid dense material. The sintering occurring in LTCC is of the viscous flow type. A temperature profile for LTCC-tape sintering has to be adjusted which provides that all organic vehicle constituents are removed from the tape composition before sintering starts. Manufacturer's instructions concerning the temperature profile and heating rate are only standard values which have to be adapted to the actual requirements. This processing procedure becomes critical if the stack of laminated tapes comprises a considerable larger number of layers than usually applied for conventional applications [10].

In order to establish the temperature profile for a LTCC stack comprising a high number of layers a study has been started to investigate the removal of organics from a LTCC-tape and an alumina tape (applied for a constrained sintering process) as a function of the heating rate, and to determine the evolution of the shrinkage in dependence of the temperature.

Experimental

The two types of tape which have been analysed were the Ceramtape GC (GC-tape) and Ceramtape A (A-tape). Both products are supplied by Ceram Tec AG (Plochingen, Germany). The tapes are applied on a polyethyleneterephthalate (PET) backing of about 50-µm thickness to ensure sufficient stability for the handling during the processing. Ceramtape GC is a glass–ceramic composite, which consists of Al_2O_3 and anorthite glass (volume fraction of 55–70%), where the Al_2O_3 particle size ranges between 1.0 and 1.5 µm. The density of the GC-tape in the green state is 1.78 and 2.92 g cm^{-3} after firing according to the manufacturer's specifications. Ceramtape A is an alumina tape which is co-laminated with the Ceramtape GC in order to prevent lateral shrinkage during sintering. It is a sacrificial tape which becomes brittle and can be easily removed from the Ceramtape GC after the sintering process. The green density is 2.34 g cm^{-3}. No additional information concerning binder, plasticizers, and solvent is available from the material data sheet. Both tapes are of white colour.

Samples used for thermogravimetric analysis (TG) were cut in a disc shape with a diode-pumped NdYAG-laser from the delivered sheets to attain samples with a diameter of approximate 7.6 mm. The backing foil was removed prior to laser processing. The average mass of GC-tape discs was about 23 mg, while that of the A-tape discs was about 32 mg.

The unfired tape samples were placed individually in a platinum crucible and heated up with a rate of 1.5, 2.5, 5, 7.5 and 10 K min^{-1} from room temperature to 550 °C (1,000 °C for shrinkage studies) in a TGA 2050 (TA-Instruments, USA). The purge gas of the sample compartment was dry air with a flow rate of 90 mL min^{-1}.

The thermal and thermooxidative degradation of polymeric materials is a complex process involving successive and/or parallel steps. Nevertheless the kinetic analysis of non-isothermal thermogravimetric data is commonly performed by the use of a single step kinetic equation (1) [11]:

$$\beta\frac{d\alpha}{dT} = Af(\alpha)\exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

where α representing the fractional conversion, T is the temperature, β is the heating rate, $f(\alpha)$ is the differential conversion function, A is the pre-exponential factor, E_a is the activation energy and R is the gas constant. The activation parameters (A, E_a and $f(\alpha)$) are often referred in the literature as "kinetic triplet."

Equation (1) can be transformed to the following expression:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E_a}{RT}\right)dT = g(\alpha) \qquad (2)$$

Using the isoconversional Flynn and Wall method [12, 13] Eq. 1 can be rearranged to calculate the activation energy from the slope of a plot of log β versus $1/T$ by the following Eq. 3:

$$E_a = \frac{-R}{b}\left(\frac{d\log\beta}{d(1/T)}\right) \qquad (3)$$

with $b = 0.457/K$.

To calculate the activation energy by means of the Coats–Redfern approach [14] a plot of ln $(g(\alpha)/T^2)$ versus $1/T$ should be drawn. Choosing an appropriate $g(\alpha)$ a straight line through the points should result. The slope of this line equals $-E_a/R$ [15]. The algebraic expressions of the functions [$f(\alpha)$ and $g(\alpha)$] in differential and integral form often used for thermal degradation during reactions are reported in, e.g. [16, 17].

Results and discussion

According to Geffroy et al. [18] green tapes made by tape casting process show a multistage degradation behaviour for the organic vehicle. In the first step of firing, the lower molar mass organic additives like dispersant and plasticizer are burned out. In a second step occurs the extraction of the higher molar mass organic binder [19, 20].

In accordance with the above-mentioned studies both tapes show a multistage degradation of the binder system that progressed in a similar way up to about 175 °C (Fig. 1). Beyond this temperature the degradation process of the two tapes differs: while the GC-tape proceeds to loose mass, the mass loss of the A-tape slows down up to ca. 200 °C. In the temperature range of 200 °C to ca. 300 °C occurs a second degradation phase, which exhibits the highest mass loss among all stages. Between 300 and 450 °C a third degradation stage can be observed for the A-tape. At the end of the TG as the sample has been exposed to a temperature of 550 °C the residue of the A-tape disc was about 91% of the initial sample mass.

The mass reduction of the GC-tape corresponds nearly the twofold mass loss of the A-tape as can be seen in Fig. 1. At 550 °C the residual mass of the GC-tape is 84% of the initial sample mass. Considering the resulting derivative TG (DTG) curves, with the respective shape and temperature range of the degradation peaks, it became clear that the binder system of the two tapes was different regarding the chemical composition.

For the following kinetic analysis solely the binder decomposition conversion is considered, so the 9% respective 16% binder content are equivalent to 100% conversion.

The α-temperature curves in Figs. 2 and 3 show a dependence of the binder burnout process on the heating rate even the temperature range is narrow. At lower heating rate the different degradation stages become more pronounced and the binder burnout is completed at lower temperature as well.

Critical are residues of carbon black which may prevent the tape densification at the later stage of the sintering process [21, 22]. However, in disc samples heated up to 500 °C not any traces of carbon black could be detected which means that the organic compounds of the binder system can be removed without any residual critical carbon formation. Thus, no problem which may be related to carbon residues is to be expected during the later sintering process.

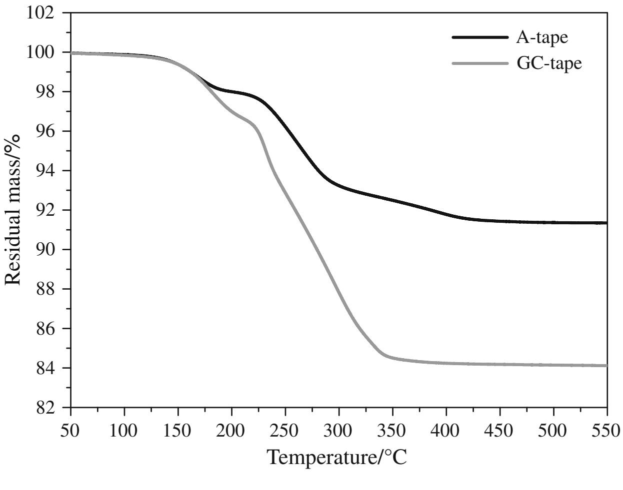

Fig. 1 TG for GC- and A-tape at a heating rate of 1.5 K min^{-1}

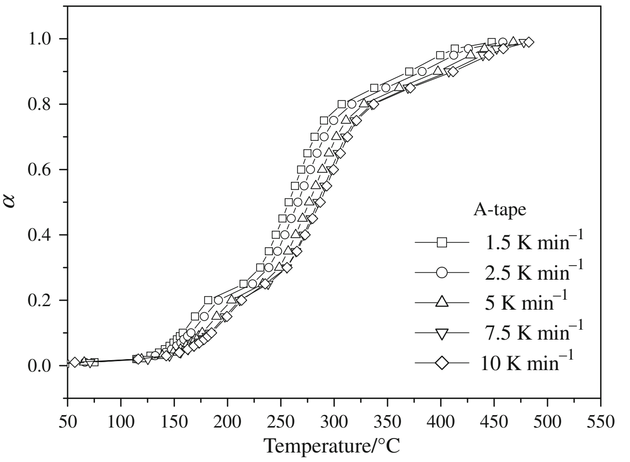

Fig. 2 Fractional conversion α versus heating rate, A-tape under air

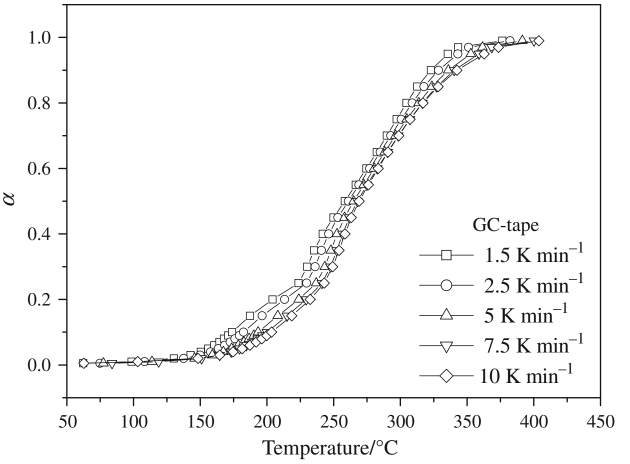

Fig. 3 Fractional conversion α versus heating rate, GC-tape under air

Figure 4 shows the activation energy in dependence of the conversion degree determined by means of the Flynn–Wall isoconversional method. For the GC-tape even a good linear approximation could be determined the condition $20 \leq E_a/RT \leq 60$ [12] was not fulfilled for $0.4 \leq \alpha \leq 0.9$ thus, the values in this range are not plotted. With the Flynn–Wall method both the A-tape and the GC-tape an activation energy in the magnitude of 100 kJ mol^{-1} was determined for $\alpha \leq 0.2$. For $\alpha \geq 0.3$ the activation energy augmented to ca. 150 kJ mol^{-1} for the A-tape. The activation energy of the GC-tape increased for $0.2 \leq \alpha \leq 0.7$ up to ca. 510 kJ mol^{-1} but this value should not be considered due to the reason mentioned above.

Selecting the three dimensional diffusion model with $g(\alpha) = (1-(1-\alpha)^{1/3})^2$ for the Coats–Redfern method straight lines could be obtained when determining the

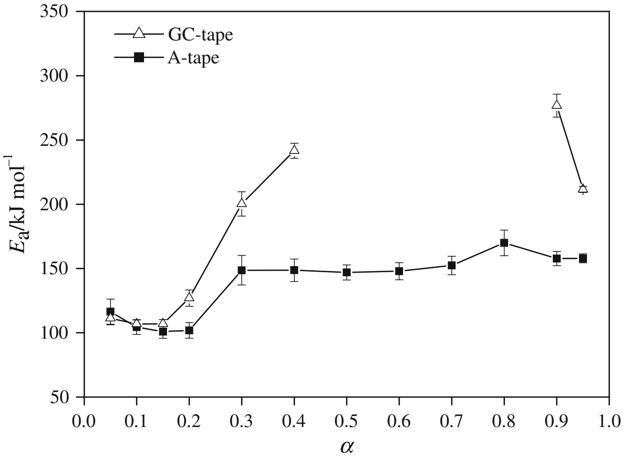

Fig. 4 Activation energy E_a versus degree of conversion α determined by the Flynn–Wall method

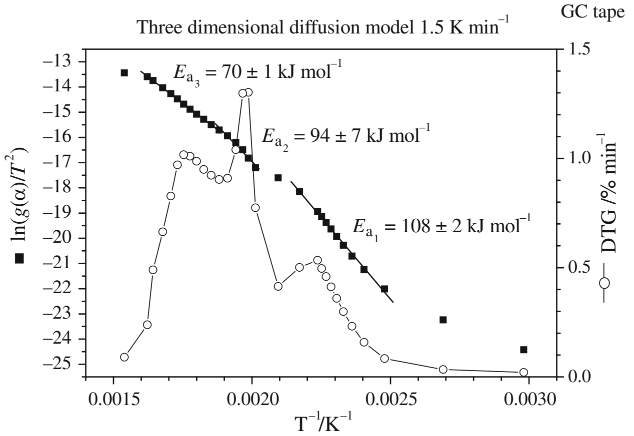

Fig. 5 Activation energy according to the Coats–Redfern method and DTG for the GC-tape

activation energy of the different degradation steps. The activation energies obtained by means of this method are reported in Table 1. For the sacrificial A-tape an increase in the heating rate leads to a decrease in the activation energy of the first and second degradation step, while the activation energy of the third step remains unchanged. In contrast considering the GC-tape one can notice a decrease in the activation energy of the third degradation step with increasing heating rate. The activation energy of the second degradation step augments, and those of the first step decreases slightly with an increase in the heating rate.

Figures 5 and 6 illustrate that even both tapes show a three stage degradation behaviour the ranges of the different steps as well as their respective activation energies are not similar when comparing the DTG and the corresponding activation energy determined according to the Coats–Redfern method using a three-dimensional diffusion model. The exemplary heating rate of 1.5 K min^{-1} in the Figs. 5 and 6 locates within the recommended heating range of 1–4 K min^{-1} of the tape's manufacturer. Thus, regarding the results obtained with the heating rate of 1.5 and 2.5 K min^{-1} the highest activation energy of about 120 kJ mol^{-1} will be necessary for the second degradation step in the GC-tape.

Disc samples of both tapes which have been heated up to 1,000 °C for processing related shrinkage studies are already sintered and could be easily handled. In contrast discs just heated up to 500 °C (GC-tape) or 550 °C (A-tape) are still brittle and come apart when they are touched since sintering has not started but the binder, which is responsible for the flexibility and cohesion of the tapes,

Table 1 Activation energy determined by means of the Coats–Redfern method using a three-dimensional diffusion model

Heating rate/K min^{-1}	A-tape			GC-tape		
	Conversion range	R^2	E_a/kJ mol^{-1}	Conversion range	R^2	E_a/kJ mol^{-1}
1.5	$0.80 \leq \alpha \leq 0.98$	0.993	102 ± 3	$0.85 \leq \alpha \leq 0.98$	0.996	108 ± 2
	$0.25 \leq \alpha \leq 0.70$	0.996	88 ± 2	$0.50 \leq \alpha \leq 0.80$	0.976	94 ± 7
	$0.01 \leq \alpha \leq 0.20$	0.975	22 ± 2	$0.03 \leq \alpha \leq 0.45$	0.999	70 ± 1
2.5	$0.80 \leq \alpha \leq 0.98$	0.985	92 ± 4	$0.85 \leq \alpha \leq 0.98$	0.992	102 ± 3
	$0.25 \leq \alpha \leq 0.70$	0.981	79 ± 3	$0.50 \leq \alpha \leq 0.75$	0.997	109 ± 8
	$0.01 \leq \alpha \leq 0.20$	0.969	22 ± 2	$0.03 \leq \alpha \leq 0.45$	0.999	65 ± 1
5	$0.80 \leq \alpha \leq 0.98$	0.981	85 ± 4	$0.85 \leq \alpha \leq 0.98$	0.997	107 ± 2
	$0.25 \leq \alpha \leq 0.75$	0.992	85 ± 3	$0.80 \leq \alpha \leq 0.50$	0.981	113 ± 7
	$0.01 \leq \alpha \leq 0.20$	0.955	23 ± 3	$0.03 \leq \alpha \leq 0.45$	0.998	60 ± 1
7.5	$0.80 \leq \alpha \leq 0.98$	0.980	86 ± 4	$0.85 \leq \alpha \leq 0.98$	0.997	106 ± 2
	$0.25 \leq \alpha \leq 0.75$	0.988	83 ± 3	$0.50 \leq \alpha \leq 0.80$	0.987	118 ± 6
	$0.01 \leq \alpha \leq 0.20$	0.947	22 ± 3	$0.03 \leq \alpha \leq 0.45$	0.996	58 ± 1
10	$0.80 \leq \alpha \leq 0.98$	0.995	89 ± 2	$0.85 \leq \alpha \leq 0.98$	0.992	96 ± 3
	$0.25 \leq \alpha \leq 0.75$	0.980	79 ± 4	$0.45 \leq \alpha \leq 0.80$	0.990	124 ± 5
	$0.01 \leq \alpha \leq 0.20$	0.941	22 ± 3	$0.03 \leq \alpha \leq 0.40$	0.991	53 ± 2

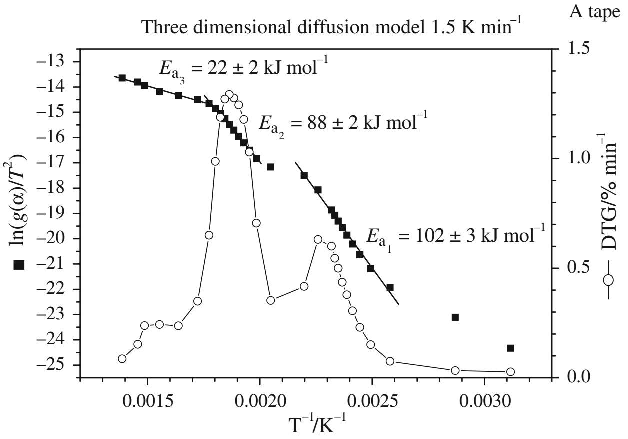

Fig. 6 Activation energy according to the Coats–Redfern method and DTG for the A-tape

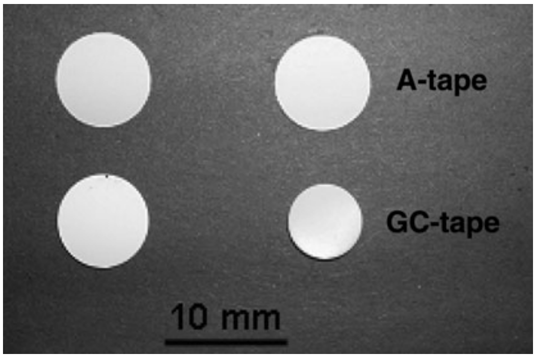

Fig. 7 Ceramic tape discs before (*left*) and after (*right*) sintering (heating rate: 10 K min^{-1}, peak temperature: 1,000 °C)

has been already removed. The sacrificial A-tape discs show as expected no significant change in diameter, while the GC-tape discs heated up to 1,000 °C exhibit a shrinkage in diameter of nearly 19% with regard to the initial dimension (Fig. 7). It can be assumed that the shrinkage primarily takes place during the sintering phase of tapes. Measurements of larger disc fragments attained from samples broken apart which have been heated up to 600 °C reveal not any significant dimensional changes for the two tapes.

Conclusions

The thermooxidative binder burnout of two types of green LTCC-tape was studied at several heating rates in order to obtain some information about its heating rate dependent degradation behaviour. The results yielded a different degradation behaviour for both tapes. The two tapes did not only differ in the amount of binder, but also in the composition of the binder system and the activation energy determined by means of the Coats–Redfern method using a three-dimensional diffusion model. It was also found that the use of the isoconversional Flynn–Wall method was restricted to the first degradation step for Ceramtape GC. Further the results showed that Ceramtape A has a lower binder content and shrinkage than Ceramtape GC. For both tapes the burnout of the binder did not lead to the formation of residual carbon black traces with detrimental effect on sintering. The binder burnout was completed at lower temperature when a low heating rate was applied.

The results of this study yield a useful approach to establish the firing profile of the considered LTCC with regard to heating rate and intermediate holding time for the preheat phase of firing process. Based on the results of TG it becomes evident that for the burnout stage of the GC-tape firing process an appropriate dwell time depending on the mass of LTCC-module has to be provided. Further, the shrinkage studies showed that shrinkage of the Ceramtape GC is associated with the sintering process at temperatures above 600 °C.

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