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# Development of a heating schedule for rapid thermal debinding of green multilayer ceramic capacitors

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A method has been demonstrated to debind rapidly green multilayer ceramic capacitors by a thermal route. The binder consists of a blend of an acrylic polymer and a polyester adipate; the dielectric is a titanate-based material. The thermal decomposition kinetics of the binder, the gas permeability of the open-pore green body, and the failure conditions of the green body were determined from the results of both experiments and modeling. An algorithm based on variational calculus was then used to prescribe a rapid heating schedule for binder removal, without introducing defects into the green components. The cycle developed was 80% shorter than the corresponding cycle used in industry.

Key words: Binder removal, multilayer ceramic capacitors

### Introduction

In the fabrication of ceramic components, the processing step of binder removal [1-9] is often the longest unit operation, and development of the heating schedule is usually achieved by trial-and-error in order to avoid introducing defects into the green ceramic body [10-15]. Over the last decade, however, we have developed an algorithm to predict the minimum time heating cycle (MTHC) for binder removal from open-pore ceramic components [8, 9, 16]. To specify the MTHC, knowledge is required of the physical attributes of the green body, the kinetics of binder degradation [15, 16], the permeability of the green body [17, 18], and the conditions at which failure occurs [15, 19, 20]. All of these model inputs can be determined from a combination of experiments and modeling, as has been described in more detail elsewhere [20].

Although we have reported previously on the procedures to obtain the individual model inputs, it is only recently that we have demonstrated how to apply them to actual ceramic components in order to achieve rapid heating cycles while still maintaining a high yield [20]. The system chosen earlier for evaluation was based on a barium titanate dielectric for use in multilayer ceramic capacitors, although no electrodes were used in the fabrication of the green ceramic bodies. The binder system utilized for these components was based on a widely-used formulation of ~65 weight% poly(vinyl butyral) plasticized with ~35 weight% dioctyl phthalate. Components fabricated from this binder system were then subjected to linear heating rates to establish that the samples failed at temperatures of 210-240 °C. Then, using the MTHC methodology combined with a safety factor, rapid heating schedules of  $\sim$ 20 h were developed, and the ceramic components survived these heating cycles with no evidence of visual defects such as cracking or delamination. The developed cycles were estimated to be  $\sim$ 50-100 h shorter than the cycles that might be prescribed in industry for components of comparable size and physical attributes.

In recognition that the MTHC procedure is new and requires further validation, we demonstrate in this study the methodology for developing rapid heating cycles on a different binder system and dielectric. The system studied herein has several differences from the system examined earlier, namely, in that the binder blend is completely different and now consists of a high molecular weight acrylic polymer plasticized with a polyester adipate. The multilayer ceramic components fabricated from this binder blend, now including noble metal electrode layers, thus exhibited different decomposition behavior and different failure behavior. The most notable feature of the rapid heating cycle developed is that it is approximately 80% shorter than the heating schedule used in industry for these components.

### **Experimental**

Green tapes were prepared by combining 73.3 weight% of a titanate-based N2200 powder and 26.7 weight% of a binder solution containing 31.5 weight% of B72 acrylic resin (Rohm & Haas, Ontario, CA), 6.1 wt.% of G50 polyester adipate plasticizer (C. P. Hall, Bedford Park, IL) and 62.4 weight% methyl ethyl ketone. After tape casting and drying, the individual green tapes were laminated at 29 MPa at 85 °C for 10 minutes into multilayer ceramic

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capacitors (MLCs) that had 41 active layers separated by noble metal electrodes. The dimensions of the MLC after lamination were approximately  $2.1 \times 2.0 \times 1.0$  cm.

To determine the void volume,  $\varepsilon$ , of the MLCs, the water uptake at 50 °C in the pores of the sample was determined as a function of time [21] for green samples and samples laminated at 3.5-29.6 MPa. The porosity is then related to the volume fractions of the solid,  $\varepsilon_s$ , and binder,  $\varepsilon_b$ , as:

$$\varepsilon = 1 - \varepsilon_b - \varepsilon_s \tag{1}$$

To determine the permeability and pore diameter of the green and laminated tapes, a procedure described in detail elsewhere was used [17, 18]. Briefly, samples were inserted into a sample holder (Millipore, Billerica, MA) with an open area 1.56 cm in diameter and sealed with a flexible o-ring. The molar flow rate of nitrogen through the substrate was then determined for different pressure drops, DP, and the molar flux, N, was calculated. As shown elsewhere, when Knudsen flow can be neglected, a plot of the normalized flux,  $N/\Delta P$ , versus average pressure across the sample,  $P_{ave}$ , yields linear behavior given by [22]:

$$\frac{N}{\Delta P} = AP_{ave} + B \tag{2}$$

where A is the slope and B is the intercept. The ratio:

$$\frac{A}{B} = \frac{3\bar{r}}{4\pi\mu\bar{\nu}} \tag{3}$$

can then be used to determine the characteristic pore radius,  $\overline{r}$ . In Eq. 3,  $\mu$  is the viscosity of the gas and  $\overline{v}$  is the average velocity, as determined by the kinetic theory of gases. The characteristic pore size was then used to determine the specific surface, *S*, in terms of an equivalent pore diameter as:

$$S = \frac{4\varepsilon}{(1-\varepsilon)D} \tag{4}$$

If the pore size is sufficiently large, then Poiseuille flow is the dominant transport mechanism and the permeability can be calculated using Darcy's Law [17, 18]:

$$\kappa = -2RTN\mu \frac{L}{P_2^2 - P_1^2} \tag{5}$$

The permeability in Eq. 5, which is based solely on flux measurements, was then expressed in terms of microstructural attributes of the green body by the Kozeny-Carman equation as [17, 18]:

$$\kappa = \frac{\varepsilon^3}{k(1-\varepsilon)^2 S^2} \tag{6}$$

where k is a parameter to account for tortuosity and constrictions in the pore space.

Binder removal by thermal oxidation was performed

on the MLCs using a Thermolyne Ashing Furnace equipped with a PID Temperature controller. To determine the kinetics of binder degradation, weight loss experiments were conducted in flowing air at 60 cm<sup>3</sup>minute<sup>-1</sup> with a thermogravimetric analyzer (TGA) at a linear heating rate of  $\beta$ = 1 K·minute<sup>-1</sup>. The TGA data were then analyzed using the method of Lee and Beck [23] to obtain values of the preexponential factor, *A*, and the activation energy, *E*, from:

$$\ln\left[\frac{F(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta(E+2RT)}\right] - \frac{E}{RT}$$
(7)

where  $\alpha$  is the conversion. For first order kinetics,  $F(\alpha) = -ln(1 - \alpha)$ , which is related to the initial binder volume fraction,  $\varepsilon_{bo}$ , via  $\alpha = 1 - \varepsilon_b/\varepsilon_{bo}$ . The rate of binder decomposition, *r*, can then be expressed as an activated process as:

$$r = -\frac{d\varepsilon_b}{dt} = A \exp\left(-\frac{E}{RT}\right)\varepsilon_b \tag{8}$$

### Model

Because the model for the binder removal process has been derived in detail elsewhere [8, 9, 16], only the main governing equations are presented here. We first focus on the pressure buildup within the green body that arises from the decomposition of binder into gas-phase species. For a body with open porosity, the buildup of pressure is relieved in the pore space by convective flow, which can be described by Darcy's Law. For slow heating rates, the temperature can be taken as constant across the green body, and conservation of mass then leads to the pressure distribution within the green body as arising from the competing processes of binder decomposition and forced convection. Under these circumstances, the normalized maximum pressure,  $(P/P_o)_o$ , occurs in the center of the body, and is given by [8, 9, 24]:

$$\left(\frac{P}{P_o}\right)_o = \left(1 + 0.8365 \frac{1}{2\rho_o^2 \kappa R} \frac{\mu r \rho_b}{M} \frac{T}{T_o^2 L_x^2 L_y^2 + L_y^2 L_z^2} \right)^{1/2} \\
= \left(1 + G \frac{rT}{\kappa}\right)^{1/2}$$
(9)

where the component dimensions are  $L_x$ ,  $L_y$ , and  $L_z$ . All of the quantities in *G* in Eq. 9 are taken as constants, and thus *G* is itself a constant given by:

$$G = 0.8365 \frac{\mu \rho_b}{2\rho_o^2 R M T_o^2 L_x^2 L_y^2 + L_y^2 L_z^2} \frac{L_x^2 L_y^2 L_z^2}{2\rho_o^2 R M T_o^2 L_x^2 L_y^2 + L_y^2 L_z^2 + L_x^2 L_z^2}$$
(10)

where  $\rho$  is the density and subscripts *b* and *o* denote binder and initial gas conditions in the furnace, respectively.

The minimum time,  $t^*$ , to remove the binder from the green body can then be obtained from variational calculus as [8, 9, 16]:

$$t^* = \frac{GT_s k S^2}{P_t^2 - 1} \left\{ \ln \frac{1 - \varepsilon_s}{1 - \varepsilon_s - \varepsilon_{bo}} - 2 \left[ \frac{1}{1 - \varepsilon_s - \varepsilon_{bo}} - \frac{1}{1 - \varepsilon_s} \right] \right\}$$

$$+\frac{1}{2}\left[\frac{1}{\left(1-\varepsilon_{s}-\varepsilon_{bo}\right)^{2}}-\frac{1}{\left(1-\varepsilon_{s}\right)^{2}}\right]\right\}$$
(11)

The quantity  $T_s$  is the starting temperature for the debinding cycle, and  $P_t$ , the threshold pressure, is the value of  $(P/P_o)_o$  in Eq. 9 corresponding to the temperature when failure in the green body occurs. Equation 11 is thus the approximate minimum time for binder removal in terms of all the dimensional and transport parameters appearing in the problem.

The minimum time in Eq. 11 does not explicitly depend on the kinetic parameters of binder degradation such as the pre-exponential factor, A, and the activation energy, E. The starting temperature of the binder removal cycle does, however, depend on the specifics of the kinetic expression as given by:

$$T(\varepsilon_b) = \frac{-E}{R} \left[ \ln \frac{\kappa (P_i^2 - 1)}{\varepsilon_b \ GT_s A} \right]^{-1}$$
(12)

Equations 1, 6, 8, and 9-12, in conjunction with the procedure described in more detail in Ref. [20], thus constitute the model that will be used for predicting the minimum cycle time for binder removal.

#### **Results and Discussion**

# Determination of porosity, pore diameter, and permeability

The porosity of the green tapes, laminated tapes, and the MLCs were measured by submerging samples in water at 50 °C until the curves of water uptake versus time reached a plateau; the water uptake was then converted to porosity. Fig. 1 shows that after ~40 h, plateaus in the porosity versus time for all the samples have been reached. Fig. 1 also



Fig. 1. Porosity versus time as determined from water uptake at 50 °C on one unlaminated green tape, and on five tapes and MLCs laminated at the indicated pressures at 85 °C for 10 minutes.

shows that as compared to the green tapes, increasing the lamination pressure leads to a strong reduction in the porosity. For the green tapes, the porosity was 34%, which decreased to 10% in the laminated MLCs. We note that the porosity of five laminated tapes is not the same as for the MLC; although the origin of this is unclear, it may be related to the fact that the process of lamination depends on the number of tapes laminated together, as discussed in more detail elsewhere [18].

Pore diameters were determined by plotting the normalized flux,  $N/\Delta P$ , versus  $P_{ave}$  [17, 18, 22] for five tapes laminated at different pressures, as seen in Fig. 2. The linear behavior was then used to obtain the slopes and intercepts to determine the pore size from Eq. 3. As seen in Table 1, with increasing lamination pressure, the pore diameter in the tapes decreases and ultimately reaches a value of  $\sim 0.41 \,\mu\text{m}$ . For this pore size, Poiseuille flow is the dominant contributor to the flux, and thus the permeability was estimated from Eq. 5. Table 1 also shows that, as expected, the permeability decreases with increasing lamination pressure. The permeability values in Table 1 were then parameterized according to Eq. 6, and Table 1 lists the values of S and k corresponding to the different lamination pressures. For the highest lamination pressure, the permeability is  $7.6 \times 10^{-19} \text{ m}^2$ , which corresponds to values of  $S = 1.24 \times 10^6 \text{ m}^{-1}$  and k = 11,500 for describing the



Fig. 2. Normalized flux versus average pressure for five tapes laminated at different pressures at 85 °C for 10 minutes.

**Table 1.** Porosity, pore size, permeability, and values of S and k for five tapes laminated at different pressure at 85 °C for 10 minutes

Lamination Pressure (MPa)	8 (-)	$D = 2\overline{r}$ (µm)	$\binom{\kappa}{(m^2)}$	$S (m^{-1})$	k (-)
3.4	0.29	0.65	$1.7\times10^{-17}$	$1.26\times 10^6$	1860
6.9	0.26	0.58	$1.5 \times 10^{-17}$	$1.20 \times 10^6$	1420
10.3	0.24	0.44	$6.9  imes 10^{-18}$	$1.43  imes 10^6$	1660
29.6	0.21	0.41	$7.6 \times 10^{-19}$	$1.28  imes 10^6$	11,800

408

K (m<sup>2</sup>)





flux data using Darcy's law for five tapes laminated at 29.6 MPa at 85 °C for 10 minutes. The predicted permeability (line) by the Kozeny-Carman equation is also shown.

permeability of the green MLCs at the full binder loading. The evolution of the permeability with binder loading for the MLC was then calculated from the data obtained on the five laminated tapes by using Eq. 6 and allowing the porosity to vary, as seen in Fig. 3.

# Determination of binder decomposition kinetics and failure conditions

The weight loss of binder from an MLC as a function of temperature is displayed in Fig. 4 for a heating rate of 1 K·minute<sup>-1</sup>, and the total weight loss was 11.9%. The TGA data were next analyzed using Eq. 7 to establish a region of linear behavior as seen in Fig. 5, and this region of  $\alpha = 0.05$ -0.45 was used to obtain values of  $A = 6893 \text{ s}^{-1}$ 



**Fig. 4.** Thermogravimetric weight loss data (solid line) versus temperature for a sample of an MLC heated at 1 K minute<sup>-1</sup> in air. The predicted kinetics (symbols) for a first-order decomposition mechanism with  $A = 6893 \text{ s}^{-1}$  and E = 78.4 kJ/mol are also shown.



**Fig. 5.** Analysis of TGA data (symbols) using the method of Lee and Beck [23] (solid line) to obtain the activation energy and pre-exponential factor.

and E = 78.4 kJ/mol. As seen in Fig. 4, these values provide a good representation of the weight loss data over a wide range of conversion of  $\alpha = 0.05$ -0.9.

To determine the failure temperature,  $T_{f_5}$  at which defects occur, samples were visually monitored in the furnace through a glass window. For a heating rate of 1 K·minute<sup>-1</sup>, failure was observed at  $T_{f} \approx 175$  °C. The normalized pressure in the center of the green body,  $(P/P_o)_o$ , and  $\varepsilon_b$ were then simulated for this heating rate using Eqs. 1 and 6-10 and the model parameters in Table 2. Fig. 6 shows that as the temperature increases,  $(P/P_o)_o$  first increases, then goes through a maximum as binder continues to be decomposed, and finally decreases as  $e_b$  decreases. Fig. 6 also shows that for the observed failure temperature of 175 °C, the corresponding failure pressure is  $P_t = 12.3$ . This value is much larger than has been determined for other green bodies [20], and this may be related to the

Table 2. Values of the parameters used in the model

Symbol	Value	Units	
Po	100,000	Ра	
To	300	Κ	
М	0.044	kg/mol	
R	8.314	J/(mol K)	
μ	$2.5 \times 10^{-5}$	Pa s	
S	$1.24 \times 10^{6}$	1/m	
k	11,500	-	
$ ho_b$	1000	kg/m <sup>3</sup>	
es	0.535	-	
$\epsilon_{bo}$	0.365	-	
З	0.1	-	
L <sub>x</sub>	0.021	m	
Ly	0.020	m	
Lz	0.010	m	
А	6893	1/s	
Е	78,400	J/mol	



**Fig. 6.** Profile of the normalized pressure,  $(P/P_o)_o$ , in the body center versus temperature predicted by the model at a heating rate of 1 K·minute<sup>-1</sup> using the parameters in Table 2. The dashed lines indicate how a failure pressure of  $P_t = 12.3$  is obtained for a failure temperature of  $T_f = 175$  °C.



**Fig. 7.** Minimum time heating cycle (MTHC, solid line) determined for  $P_t = 12.3$  with the parameters in Table 2. Heating cycles (solid lines) with a safety factors of 2 and 3 applied to the time are also shown. The dashed lines with the filled circles are the heating schedules programmed into the temperature controller.

differences in porosity and permeability between five laminated tapes and the MLCs. In spite of this uncertainty, with the model formulation used here, the permeability of the green body does not influence the minimum time heating cycle, as described in more detail elsewhere [19].

At this point, all of the model parameters necessary to calculate the minimum time heating cycle have been established and are listed in Table 2. The MTHC corresponding to these parameters is shown in Fig. 7, where it is seen that the cycle starts at  $T_s \approx 174$  °C. The temperature profile with time is non-linear in nature, and the cycle duration is approximately 6 h. Based on earlier work and in recognition of the uncertainly in model parameters as well as in the assumptions and approximations in the model [20], an empirical safety factor is then applied to the MTHC to establish a more conservative heating cycle. Fig. 7 also shows the heating cycles obtained when safety



**Fig. 8.** Images of green multilayer ceramic capacitors  $(2.1 \times 2.0 \times 1.0 \text{ cm})$  subjected to rapid heating cycles. a) Sample that failed when subjected to the 2× heating schedule. b) Sample that exhibited no defects when subjected to the 3× heating schedule



**Fig. 9.** Comparison of the  $3 \times$  heating cycle used in this study (solid line), the cycle programmed into the temperature controller (dotted line with circles) and the cycle used in industry (dashed line with squares).

factors of two  $(2^{\times})$  and three  $(3^{\times})$  are applied to the time, and the temperature range is left unchanged from the original MTHC.

Green MLCs were then subjected to the more conservative  $2^{\times}$  and  $3^{\times}$  heating cycles, and these cycles were implemented in the furnace temperature controller as a sequence of linear ramps and constant-temperature holds, as indicated in Fig. 7. For both cycles, an initial ramp rate of 1 K·minute<sup>-1</sup> was used to the start temperature of the cycle, a 1 h hold was placed at 410 °C, and a cooling rate of ~1 K minute<sup>-1</sup> was also used. Images of MLC samples after these two heating cycles are shown in Fig. 8. For a safety factor of 2, Fig. 8a shows that a defect occurred during the heating cycle in the form of a large delamination at the center of the body. For a safety factor of 3, Fig. 8b shows that the MLC does not suffer any visible damage. Three additional samples were next subjected to this  $3 \times$  cycle, and none of the samples exhibited any types of defects.

Fig. 9 presents a comparison of the thermal cycle used in the industrial setting for these MLCs and the heating cycle developed here with the safety factor of 3. The industrial cycle lasts ~162 hours, and contains a series of ramps and holds, whereas the experimental cycle with a safety factor of 3 requires  $\sim 27$  hours. This corresponds to a reduction of  $\sim 83\%$  in processing time with concomitant decreases in energy, labor costs, and furnace capital costs.

In summary, the strategy of combining experiments and modeling to develop the MTHC, and then modifying the MTHC with a safety factor, leads to a rapid heating cycle for the thermal debinding of MLCs. Although not all of the model parameters can be determined to high accuracy, the use of safety factors accommodates both uncertainty in model parameters as well as in approximations and assumptions in the model. The methodology has now been applied to two different binder systems and to components with different failure behaviors, and in both instances it was possible to develop rapid heating cycles.

### Conclusions

A rapid heating schedule for binder removal from an open-pore green multilayer ceramic capacitor has been developed. The heating schedule was determined by establishing values for the physical attributes of the green body, the decomposition kinetics of the binder, the permeability of the green body, and the conditions at which the green body fails. These values were then incorporated into an algorithm based on variational calculus in order to prescribe a minimum time heating cycle. The MTHC was then modified by a safety factor in order to account for uncertainty in model parameters and for assumptions and approximations in the model. The heating cycle determined in this manner was approximately 80% shorter than the corresponding cycle used in industry.

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