JOURNALOF

Ceramic Processing Research

# Effect of green body size and heating rate on failure during thermal debinding and on the debinding cycle time

Rajiv M. Sachanandani<sup>a</sup> and Stephen J. Lombardo<sup>a,b,\*</sup>

<sup>a</sup>Department of Chemical Engineering, University of Missouri, Columbia, MO 65211, USA <sup>b</sup>Department of Mechanical & Aerospace Engineering, University of Missouri, Columbia, MO 65211, USA

Multilayer ceramic green bodies, prepared with barium titanate as the dielectric and poly(vinyl butyral) and butyl benzyl phthalate as the main components of the binder, have been subjected to rapid heating cycles in order to cause failure to occur. In one approach, the heating rate was held constant and the dimensions of the green bodies were varied, while in the second method, the size of the green body was held constant and the heating rate was varied. In all cases, failure of the green body occurred between 115-140 °C. Models were then used to establish that at failure, the binder loading was high and that the internal pressure in the center of the green body was nearly constant, independent of the method used to cause the samples to fail. The internal pressure was then used as an input into a previously-developed algorithm in order to develop rapid debinding cycles without causing component failure.

Key words: Thermal Debinding, Failure, Binders, Barium Titanate.

### Introduction

In the processing of green ceramic components, binders are often used to impart mechanical strength for handling, and, furthermore, may be added to aid in subsequent processing steps such as in the lamination of green ceramic tapes. In spite of the processing advantages afforded by the binder, it must ultimately be removed from the green body, and this is most commonly performed in a furnacing operation prior to sintering. In general, the development of debinding heating schedules [1, 2] is accomplished by trial-and-error, which includes decreasing ramp rates and introducing hold temperatures and hold times in order to avoid failure of the green component.

Presumably, if the conditions at which the green body fails were known, including the failure temperature, the failure pressure, the failure stress, and the binder loading, then the development of debinding heating cycles would be less arbitrary. In general, though, the complex interrelationship between binder loading, binder decomposition, pressure buildup, and stress precludes the easy identification of when failure will occur. To be specific about some of these interrelationships, the green body will fail during debinding when a local stress [3-5] arising from the distribution of pressure [3-10] within the green body exceeds the local strength. The pressure distribution, in turn, is a complex, coupled function of the temperature distribution, the decomposition kinetics of the binder, and the gas per-

\*Corresponding author:

Fax: +573 884-4940

E-mail: LombardoS@missouri.edu

meability, all of which are changing with time. In addition, because the pressure distribution arises not as an external applied force but rather as an internal body force, the failure behavior of green ceramic components becomes difficult to probe by traditional testing methods.

To circumvent the above difficulties and yet still be able to provide some insight into the failure behavior of green bodies during thermal debinding [11-16], two procedures may be used instead. In one case, green bodies of different sizes may be fabricated and then subjected to rapid debinding cycles at a constant heating rate. Such a procedure may be relevant to scale-up, whereby a heating cycle is first developed for a small test sample, but the ultimate component size will be larger. In a second procedure, green bodies of constant size may be fabricated, which are then subjected to rapid debinding cycles at different heating rates. This approach may be relevant for complex-shaped components, where the expense of a mold or die precludes the fabrication of green bodies of different dimensions. Regardless of which procedure is used, however, it is of interest to know if the green bodies will fail at the same temperature, at the same internal pressure, or at the same volume fraction of binder. Thus, one aim of this work is to present experimental data on the failure temperature of green bodies subjected to these two types of debinding procedures. If the failure temperature is constant or nearly so, then this may help to alleviate some of the difficulty in specifying a debinding heating schedule.

In earlier work [10, 17], we have developed a methodology based on variational calculus to determine the minimum time heating cycle (MTHC) for thermal debinding from open pore compacts. The methodology consists of determining the physical attributes of the green body, the

Tel : +573 884-1644

decomposition kinetics of the binder, the permeability of the green body, and the temperature at which the green body fails. This latter quantity can be determined in different ways, two of which are mentioned above. A second aim of this work is thus to use the failure temperatures of green bodies subjected to these two debinding procedures, along with models, to assess the values of other difficult to measure parameters at failure such as the volume fraction of binder and the internal pressure. Finally, the differences in failure behavior of green bodies subjected to the two debinding procedures can then be used to assess the uniqueness of the MTHCs determined from the variational calculus algorithm. If the MTHCs are not unique or vary widely depending on the sample size or heating rate used, then the development of rapid heating cycles may be further compounded. If the MTHCs are similar, however, which is the case found herein, then the development of practical, rapid heating cycles is relatively straight forward, as is demonstrated in this work.

#### Experimental

Green ceramic tapes were prepared from barium titanate powder (Tamtron X7R 422H, Ferro Electronic Materials, Niagara Falls, NY), which had a mean particle diameter of 1.1  $\mu$ m and specific surface area of 3.0 m<sup>2</sup>/g. A slurry was prepared at 65 weight% powder with 35 weight% binder solution consisting of 14.5 weight% poly(vinyl butyral) binder (Butvar B98, Richard E. Mistler, Inc., Yardley PA), 10.9% butyl benzyl phthalate plasticizer (Santicizer 160, Richard E. Mistler, Inc.) and 3.8% blown Menhaden fish oil (Z-3, Richard E. Mistler, Inc.) in a mixture of 35.4% each of xylene and ethanol. After ball milling, the slurry was de-aired and then filtered through a 53 µm nylon mesh. The slurry was then tape cast with a single stationary doctor blade on a Mylar carrier film. After drying, the thickness of the tapes was approximately 150-160 µm. The total organic content of the substrates was 10.8% by weight, as determined by thermal gravimetry in air. The dried tapes were stacked and laminated in a press at 7 MPa and 85 °C for 10 minutes and then cut into parallelepipeds of different dimensions.

To obtain the temperature,  $T_{f_5}$  at which failure of the green body occurs, the front door of the box furnace was replaced with a thermally resistant window. The green components were then placed in the furnace in air and subjected to rapid linear heating rates. In addition to visual observation of the samples, a 6 megapixel digital camera (Canon EOS 10D, Lake Success, New York) was used to take images of the samples at 1 degree C intervals with a remote timer (Canon TC-80N3).

#### Model

Because the model and governing equations have been derived and presented in detail elsewhere, we will only succinctly summarize the relevant equations here along with references to the earlier work. The rate of binder decomposition, r, can be represented as:

$$r = -\frac{d\varepsilon_b}{dt} = A \exp\left[-\frac{E}{RT}\right]\varepsilon_b \tag{1}$$

where *t* is the time, *A* is the pre-exponential factor, *E* is the activation energy, *T* is the temperature, *R* is the gas constant, and  $\varepsilon_b$  is the volume fraction of binder. The solution to Eq. 1, for a linear heating rate,  $\beta$ , is [18]:

$$\frac{\varepsilon_{b}}{\varepsilon_{bo}} = exp\left[-\frac{A}{\beta}\left\{\frac{\left(\frac{RT^{2}}{E}\right)exp\left(-\frac{E}{RT}\right)}{1+\frac{2RT}{E}} - \frac{\left(\frac{RT_{o}^{2}}{E}\right)exp\left(-\frac{E}{RT_{o}}\right)}{1+\frac{2RT_{o}}{E}}\right\}\right]$$
(2)

where  $\varepsilon_{bo}$  is the initial volume fraction of binder and  $T_o$  is the initial temperature.

During the thermal debinding heating cycle, the normalized pressure in the center of the green body,  $(P/P_o)_o$ , is given by [19]:

$$\left(\frac{P}{P_o}\right)_o \approx \left(1 + 0.8365 \frac{L_x^2}{2\rho_o^2 \kappa_x R} \frac{\mu^r \rho_b}{M} \frac{T}{T_o^2} \frac{W^2 H^2}{W^2 H^2 + W^2 + H^2}\right)^{1/2} (3a)$$

$$= \left(1 + G \frac{rT}{\kappa_y}\right)^{1/2} (3b)$$

The stretched dimensionless lengths, W and H, of the green body are in terms of the dimensions  $L_x$ ,  $L_y$ , and  $L_z$ , of the component as given by:

$$W = \sqrt{\frac{\kappa_x}{\kappa_y} \frac{L_y}{L_x}}; \qquad H = \sqrt{\frac{\kappa_x}{\kappa_z} \frac{L_z}{L_x}}$$
(4)

The permeability,  $\kappa$ , of the body is taken as anisotropic and is given in the *i*th direction by:

$$\kappa_i = \frac{\varepsilon^3}{k(1-\varepsilon)^2 S^2}$$
(5)

where  $\varepsilon$  is the porosity, *S* is the specific surface, and *k* is a constant. The volume fractions of binder, porosity, and ceramic,  $\varepsilon_c$ , are related by:

$$\varepsilon_{\rm b} + \varepsilon + \varepsilon_{\rm c} = 1 \tag{6}$$

The quantity G in Eq. 3b is a constant given by:

$$G = 0.8365 \frac{\mu \rho_b L_x^2}{2\rho_o^2 R M T_o^2} \frac{W^2 H^2}{W^2 H^2 + W^2 + H^2}$$
(7)

where M is the molecular weight of the gas decomposition species and  $\rho$  is the density, and the subscripts b and odenote binder and initial gas conditions in the furnace, respectively.

When Eq. 3 is used to determine the threshold pressure,  $P_t = (P/P_o)_o$ , at which the green body fails, then the following holds:

$$P_t = \left(1 + G \frac{r_f T_f}{\kappa_{xf}}\right)^{1/2} \tag{8}$$

where subscript f denotes the value of a quantity at the failure temperature,  $T_{f}$ . In light of this,  $P_t$  is thus also a value, which will ultimately be used to determine the MTHC. The minimum debinding cycle time,  $t^*$ , is obtained by variational calculus, as described elsewhere [9, 10], by rearranging and integrating Eq. 1 to yield:

$$t^* = \int_o^{\varepsilon_{bo}} \frac{d\varepsilon_b}{r} \tag{9}$$

which when combined with Eq. 3b yields:

$$t^{*} = \int_{0}^{\varepsilon_{bo}} \frac{GT}{\kappa_{x} \left[ \left( \frac{P}{P_{o}} \right)^{2} - 1 \right]} d\varepsilon_{b}$$
(10)

When the value in brackets is set to the constraint that the pressure inside the green body may not exceed  $P_t$  as given by Eq. 8, then the minimum time becomes:

$$t^{*} = \int_{o}^{\varepsilon_{bo}} \frac{T}{\kappa_{x} \left[\frac{r_{f}T_{f}}{\kappa_{xf}}\right]} d\varepsilon_{b} = \frac{T_{s}}{\left[\frac{r_{f}T_{f}}{\kappa_{xf}}\right]} \int_{o}^{\varepsilon_{bo}} \frac{1}{\kappa_{x}} d\varepsilon_{b}$$
(11)

where on the right-hand side we have further used the approximation that  $T = T_s$ , the start temperature of the heating cycle [9, 10]. In this form, Eq. 11 indicates that the minimum time depends directly on the values associated with when the green body fails and on how the permeability evolves during the heating cycle. Although Eq. 11 has no direct dependence on the size of the green body or on the kinetics of binder degradation, these quantities presumably will influence the minimum time heating cycle by the manner in which they influence the values of  $T_s$ ,  $r_f$ ,  $T_f$  and  $\kappa_{xf}$ . Finally, the evolution of temperature during the MTHC is related to the volume fraction of binder by [9, 10]:

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

### **Results and Discussion**

For the first type of experiment, a multilayer sample was placed in the furnace and heated at a fixed rate of 7.5 K minute<sup>-1</sup>; the temperature at which the green body failed was then determined by recording images of the green body within the furnace during the heating cycle. In some instances, it was also possible to observe through the window in real time the occurrence of failure. This procedure was then repeated for other sized samples spanning a range of 12 in volume. Table 1 shows that for each body size, the failure temperatures of two replicates are within 3-4 degrees C. With increasing body size, the

**Table 1.** Failure temperature, binder content at failure, threshold pressure, cycle starting temperature, and minimum cycle time for multilayer samples of different size subjected to a heating rate of  $7.5 \text{ K minute}^{-1}$ 

$L_x \times L_y \times L_z$	Sample ID	$T_{\rm f}$	$\epsilon_{bf}$	$\mathbf{P}_{t}$	Ts	ť
(cm)	(-)	(°C)	(-)	(-)	(°C)	(h)
$0.37 \times 1 \times 1$	$A_1$	136	0.298	1.006	135.2	1.52
	$A_2$	139	0.298	1.008	138.1	1.32
$0.42 \times 2 \times 2$	$B_1$	124	0.299	1.013	123.6	2.73
	$B_2$	127	0.299	1.015	126.5	2.35
$0.49 \times 3 \times 3$	$C_1$	114	0.300	1.016	113.8	4.60
	$C_2$	118	0.299	1.020	117.7	3.72











**Fig. 1.** Images of multilayer green ceramic components in the furnace that were subjected to a linear heating rate of 7.5 K minute<sup>-1</sup>. a) Sample A<sub>1</sub> (0.37 × 1 × 1 cm) that failed at  $T_f$ = 136 °C b) Sample B<sub>1</sub> (0.42 × 2 × 2 cm) that failed at  $T_f$ = 124 °C c) Sample C<sub>1</sub> (0.49 × 3 × 3 cm) that failed at  $T_f$ = 114 °C. The locations of delamination are indicated by arrows.

**Table 2.** Failure temperature, binder content at failure, threshold pressure, cycle starting temperature, and minimum cycle time for multilayer samples of  $0.42 \times 2 \times 2$  cm subjected to different heating rates

β	Sample ID	$T_{\rm f}$	$\epsilon_{bf}$	Pt	Ts	t*
(K minute <sup>-1</sup> )	(-)	(°C)	(-)	(-)	(°C)	(h)
5	D1	128	0.298	1.016	127.3	2.26
	$D_2$	131	0.298	1.019	130.1	1.96
7.5	$B_1$	124	0.299	1.013	123.6	2.73
	$B_2$	127	0.299	1.015	126.5	2.35
10	$F_1$	117	0.300	1.009	116.8	3.91
	$F_2$	122	0.299	1.012	121.7	3.01



(a)



(b)



**Fig. 2.** Images of multilayer green ceramic components of dimensions  $0.42 \times 2 \times 2$  cm in the furnace that were subjected to rapid linear heating rates. a) Sample D<sub>1</sub> heated at 5 K minute<sup>-1</sup> that failed at  $T_f = 128$  °C. b) Sample B<sub>2</sub> heated at 7.5 K minute<sup>-1</sup> that failed at  $T_f = 127$  °C. c) Sample F<sub>1</sub> heated at 10 K minute<sup>-1</sup> that failed at  $T_f = 117$  °C. The locations of delamination are indicated by arrows.

failure temperature also decreases over a span of approximately 20 degrees C. Fig. 1 shows images of failed samples of each size. In all cases, the mode of failure is delamination near the mid-plane region of the sample. This location of failure is consistent with the results from earlier modeling work [4, 5], which predicts for open pore compacts that both the maximum pressure and maximum normal stress occur in the center of the sample.

For the second type of experiment, samples of a fixed size were subjected to heating rates of 5, 7.5, and 10 K minute<sup>-1</sup>, and the temperature at which failure occurred was again recorded. Table 2 shows that for each replicate, the samples fail within 3-5 degrees C, and that as the heating rate increases, the failure temperature decreases slightly over approximately 10-15 degrees C. The images in Fig. 2 show that the mode of failure in all cases again corresponds to delamination near the mid-plane region.

To provide some insight into the values of other quantities at the failure temperature, we next use the equations presented earlier to determine the evolution of pressure within the center of the body,  $(P/P_o)_o$ , as a function of the heating cycle. The values of the parameters used in the model are listed in Table 3, and all are based upon measured data, as described in more detail elsewhere [17]. Fig. 3 shows that for components of different size subjected to a fixed heating rate,  $(P/P_{o})_{o}$  first increases during the heating cycle as binder is decomposed and then goes through a maximum before decreasing as binder is consumed and more porosity is created within the green body. Fig. 3 also shows the evolution of binder volume fraction with temperature during the heating cycle. For all three body sizes, the curves of  $\varepsilon_{\rm b}$  are identical, which arises from the form of Eq. 2. The increasing branch of the  $(P/P_o)_o$  profile corresponds to a relatively high binder loading, and the maximum

Table 3. Parameters used in the simulations in Figs. 3-7

Symbol (units)	Value			
P <sub>o</sub> (MPa)	0.1			
$T_{o}(K)$	300			
M (kg/mol)	0.044			
R (m <sup>3</sup> Pa/mol K)	8.314			
μ (Pa s)	$2.5 \times 10^{-5}$			
S (m <sup>-1</sup> )	$6 \times 10^5$			
k (-)	430			
$\rho_b (kg/m^3)$	1000			
ε <sub>c</sub> (-)	0.55			
ε <sub>bo</sub> (-)	0.3			
ε <sub>0</sub> (-)	0.15			
$\kappa_{y}, \kappa_{z} (m^{2})$	$100  imes \kappa_{\mathrm{x}}$			
$\rho_o (mol/m^3)$	40.09			
$A(s^{-1})$	$1.7  imes 10^4$			
E (J/mol)	68000			



**Fig. 3.** Normalized pressure in the body center,  $(P/P_o)_o$ , and binder volume fraction,  $\varepsilon_b$ , versus temperature as predicted by the model at a fixed heating rate of 7.5 K minute<sup>-1</sup> for samples of different size (A :  $0.37 \times 1 \times 1$  cm; B :  $0.42 \times 2 \times 2$  cm; C :  $0.49 \times 3 \times 3$  cm). The symbols indicate the average temperature in the heating cycle when failure occurred.



**Fig. 4.** Normalized pressure in the body center,  $(P/P_o)_o$ , and binder volume fraction,  $\varepsilon_b$ , versus temperature predicted by the model at different heating rates for samples of a fixed size of  $0.42 \times 2 \times 2$  cm. The symbols indicate the average temperature in the heating cycle when failure occurred.

in  $(P/P_o)_o$  corresponds to ~17% degradation of the total binder content.

Fig. 4 illustrates how  $(P/P_o)_o$  varies with temperature when green bodies of a fixed size are subjected to different heating rates. Now, in contrast to Fig. 3, the profiles of  $(P/P_o)_o$ shift to higher temperature with increasing heating rate, and the overlap in the increasing pressure branch persists to closer to the maxima. The curves of  $\varepsilon_b$  are now distinct and also shifted to parallel the trends in  $(P/P_o)_o$  with heating rate; in all cases, however, the maxima in  $(P/P_o)_o$  occur at ~17% of the binder being decomposed.

The observed failure temperatures in Tables 1 and 2 can now be used with Figs. 3 and 4, along with the model equations used to generate the  $(P/P_o)_o$  profiles, to determine values of other quantities at the failure temperature. For

example, for green bodies of different dimensions subjected to a constant heating rate, Table 1 and Fig. 3 show that the binder volume fractions at failure are very high and nearly constant, as is  $P_t$ . The value of  $P_t$ , however, exhibits a ~2% increase with increasing size of the green body. For green bodies of a fixed size subjected to different heating rates, Table 2 and Fig. 4 show that at failure, the binder volume fraction is once again high and nearly constant, and  $P_t$  is nearly constant as well. The similarity in the high binder loadings in Tables 1 and 2 indicates that in all instances, failure occurs at a low value of the gas permeability of the green body.

The results of the two types of failure experiments suggest that for the samples and heating schedules examined here, failure occurs over a narrow range of 25 degrees C in temperature. Thus, the temperature of failure does not appear to be a constant "property," but instead depends on the size of the sample and on the rate at which the sample is heated. In earlier work [16], the effect of increasing body size at a fixed heating rate was also seen to lead to a decrease in the failure temperature, and thus this type of behavior may have general validity. Conversely, no strong trend was indicated for the effect of heating rate on the failure temperature of bodies of constant size in earlier work [17], although the majority of the samples again failed at high binder loading.

In light of the values for  $T_f$  and  $P_t$  obtained here, we can now address their influence on the minimum time heating cycles. Fig. 5 shows that for bodies of different size which failed at a fixed heating rate, the MTHC profiles have similar start temperatures that are slightly below the failure temperatures, as discussed in more detail elsewhere [16]. Fig. 5 also shows that the MTHC shape and duration are similar for the sample replicates. The largest sample has the longest cycle by about a factor of 3 as compared to the smallest sample. This behavior is consistent with the



**Fig. 5.** Minimum time heating cycles predicted by the model for samples of different size (A :  $0.37 \times 1 \times 1$  cm; B :  $0.42 \times 2 \times 2$  cm; C :  $0.49 \times 3 \times 3$  cm) which failed at a fixed heating rate of 7.5 K minute<sup>-1</sup>.



**Fig. 6.** Minimum time heating cycles predicted by the model for samples of fixed size  $(0.42 \times 2 \times 2 \text{ cm})$  which failed at different heating rates (D : 5 K minute<sup>-1</sup>; B : 7.5 K minute<sup>-1</sup>; F : 10 K minute<sup>-1</sup>).

idea that larger green bodies require longer heating cycles [16]. In all instances, however, the heating cycles are very short. Fig. 6 shows the MTHCs determined for samples of fixed size that failed at different heating rates. Once again, the MTHCs for each replicate are fairly similar, whereas the duration of the heating cycles determined for the failure conditions at each heating rate differ by a factor of  $\sim 2$ .

The failure temperatures reported in Tables 1 and 2 and Figs. 3 and 4, although based on observation, have a degree of uncertainty due to the inherent difficulties associated with their method of determination and, furthermore, likely have statistical fluctuation due to sample-tosample variability. The values of  $\varepsilon_b$  and  $P_i$ , however, are purely calculated quantities and although the underlying parameters in the model have been determined by experiments, measurement errors and approximations in the model equations, combined with the coupling of thermal, kinetic, and transport models, contribute to further uncertainty in their values.

In consideration of all of the coupled uncertainties and approximations mentioned above and in light of the short duration of the heating cycles in Figs. 5 and 6, safety factors, as discussed in more detail elsewhere [20], can next be applied to determine a more conservative debinding cycle. For the MTHC determined for a sample of dimensions  $0.42 \times 2 \times 2$  cm, multiplicative safety factors of  $\sim 2$  and ~3.5 were applied to the time, whereas safety factors of 20-25 degrees C were subtracted from the temperature. These more conservative heating cycles were then programmed (see Fig. 7 for an example) into the temperature controller as a series of ramps and holds that closely mimics the underlying more conservative heating cycle. For samples subjected to the heating cycles with a safety factor of 2 in time and 20 degrees C in temperature, the green body failed, but the degree of damage to the sample



Fig. 7. The MTHC for sample  $B_1$  and the more conservative heating cycle with a safety factor of 3.5 applied to the time and a safety factor of 25 degrees C applied to the temperature. The cycle programmed into the temperature controller is also shown.

was less than is seen in Figs. 1 and 2. For a safety factor of 3.5 in time and 25 degrees C in temperature, two samples survived this heating schedule with no observed damage (see Fig. 8). The MTHC, the more conservative heating cycle, and the heating cycle programmed into the controller are all shown in Fig. 7. For comparison, green multilayer samples of comparable size, composition, and physical properties would require heating cycles of 50-150 h, as compared to the cycle duration of 16 h obtained here.

Based on the results in this study, the green bodies examined here failed over a narrow range of temperature of 25 degrees C, regardless of the component size or the heating rate. Over the same temperature range, the quantities of binder loading and the pressure in the center of the body appear to be nearly constant, although these are computed values and are dependent on all of the coupled assumptions, approximations, and uncertainty in values determined by experiment. Nevertheless, the narrow range over which the green samples fail may suggest that the failure conditions of the green body can be taken as at least approximately



Fig. 8. Image of a green multilayer ceramic component that survived the programmed heating schedule shown in Fig. 7.

constant, and thus a smaller subset of experiments leading to failure of the green body may suffice to establish the MTHC. We note, though, that samples prepared by other forming methods and with other binder systems may exhibit different failure behavior than is observed here.

Once the MTHC is established by the methods utilized herein, safety factors can then be used to account for all of the uncertainties, approximations, and variability mentioned above. This procedure is analogous to the use of safety or design factors in component design, whereby a component is only stressed to a fraction of its design strength, and, in fact, this reasoning underlies the rationale of the MTHC methodology.

In addition to the specifics of the experimental results presented here on failure behavior, this study also serves to demonstrate a methodology for developing rapid thermal debinding cycles. This procedure, although still having an element of trial-and-error in regards to the determination of the safety factors, leads in relatively few iterations to rapid debinding cycles without introducing defects into the green body. Based on previous work in our laboratory and in this study, 2-3 iterations with safety factors on time (typically factors of 3-4) and temperature (typically 0-25 °C) lead to the desired debinding cycles. This quick convergence on a successful and rapid heating cycle likely arises because the temperature region of green body failure is first identified, and the MTHC methodology then optimizes the heating cycle using information obtained at the failure temperature. This optimization does not, however, involve the possibly arbitrary specification of ramp rates, hold temperatures, and hold periods, which taken together may unnecessarily prolong the heating cycle. This tailoring of the heating cycle around the temperature region where failure occurs is likely to be difficult to achieve on an ad hoc basis, and this difficulty may arise because of the strong exponential effect that temperature has on the kinetics of binder decomposition, which in turn leads to pressure within the green body. In contrast, the variational calculus algorithm [9, 10] underlying the MTHC predicts the optimal balance between temperature increase, the increase in the decomposition rate constant, and the increase in the permeability of the green body as binder is decomposed. Although the MTHC is ultimately not the heating cycle which is used, an approximate balance between the competing processes of pressure buildup and forced convection is likely preserved in the more conservative heating cycle, albeit at a lower level of threshold pressure. Or, in other words, the use of safety factors applied to the time and temperature retains the qualitative shape of the MTHC without unnecessarily prolonging it.

## Conclusions

The failure behavior of multilayer green ceramic components has been determined for samples subjected to rapid thermal debinding cycles. In one case, the heating rate was held fixed for components of different size, whereas in the second case, the body size was held constant and the heating rate was varied. Under both circumstances, it was observed that the failure temperature of all the samples fell in a narrow range, and that both the binder loading and maximum pressure in the center of the green body were nearly constant, independent of the size of the green body and the heating rate. The near constancy of these parameters leads to fairly consistent, relatively short, minimum time heating cycles. Safety factors can then be applied to develop more conservative debinding cycles, which, however, are also still fairly rapid and do not lead to component failure.

#### Acknowledgements

This work was supported in part by the NSF/IUCRC Center for Dielectric Studies.

#### References

- 1. R.M. German, Int. J. Powder Metall. 23 (1987) 237-245.
- 2. J.A. Lewis, Annual Rev. Mater. Sci. 27 (1997) 147-173.
- G.Y. Stangle and I.A. Aksay, Chem. Eng. Sci. 45 (1990) 1719-1731.
- 4. D-S. Tsai, AIChE J. 37 (1991) 547-554.
- Z.C. Feng, B. He and S.J. Lombardo, J. Appl. Mech. 69 (2002) 497-501.
- S.A. Matar, M.J. Edirisinghe, J.R.G Evans and E.H. Twizell, J. Mater. Res. 8 (1993) 617-625.
- J.H. Song, M.J. Edirisinghe, J.R.G Evans and E.H. Twizell, J. Mater. Res. 11 (1996) 830-840.
- Y. Shengjie, Y.C. Lam, S.C.M. Yu and K.C. Tam, Metall. & Mat. Trans. B-Process Metall. & Mat. Process. Sci. 33 (2002) 477-488.
- S.J. Lombardo and Z.C. Feng, J. Am. Ceram. Soc. 6[12] (2003) 2087-2092.
- 10. S.J. Lombardo and Z.C. Feng, J. Mat. Res. 18 (2003) 2717-2723.
- G. Bandyopadhyay and K.W. French, J. Europ. Ceram. Soc. 11 (1993) 23-34.
- 12. J.G. Zhang, M.J. Edirisinghe and J.R.G. Evans, Ind. Ceram. 9 (1989) 72-82.
- J. Woodthorpe, M.J. Edirisinghe and J.R.G. Evans, J. Mat. Sci. 24 (1989) 1038-1048.
- J.R.G. Evans and M.J. Edirisinghe, J. Mat. Sci. 26 (1991) 2081-2088.
- 15. S.A. Matar, M.J. Edirisinghe, J.R.G. Evans, E.H. Twizell and H. Song, J. Mat. Sci. 30 (1995) 3805-3810.
- J.W. Yun, D.S. Krueger, P. Scheuer and S.J. Lombardo, J. Am. Ceram. Soc. 89[1] (2006) 176-183.
- J.W. Yun and S.J. Lombardo, Adv. Appl. Ceram. 109 (2009) 92-101.
- 18. T.V. Lee and S.R. Beck, AIChE J. 30 (1984) 517-519.
- 19. S.J. Lombardo and Z.C. Feng, J. Mat. Res. 17 (2002) 1434-1440.
- J.W. Yun and S.J. Lombardo, J. Ceram. Process. Res. 8 (2007) 402-410.