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Rate-controlled organic burnout of multilayer green ceramics

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Abstract

Rate-controlled thermogravimetry was used for organic burnout in multilayer PZT ceramics. A proportional-derivative control algorithm operating on specimen weight adjusted the furnace power to maintain a specified rate of weight loss. Specimens heat-treated with mass loss rates of 0.01 to 0.001 mg min^{-1} showed no microstructural defects resulting from organic removal.

Keywords: Algorithm; Burnout; Ceramic; CRTA; DTA; PID; PZT; TG

1. Introduction

Multilayer ceramics are laminated two-dimensional viscoelastic thin types (usually < 50 μm) compressed at temperatures slightly higher than room temperature. Prior to lamination, these types may be electroded and/or machined, e.g. hole perforations, etc., if required. A slurry ($\approx 65\%$) used to cast the tapes contains a liquid system (solvent), deflocculant/dispersant, binder, plasticizer, and surfactants, in addition to (≈ 35 vol%) ceramic powder. After controlled drying of the tapes (removal of solvents), ≈ 35 vol% of organic remain along with ≈ 15 vol% porosity [1]. The concentrations of binder, plasticizer, and pores are optimized for a specific

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slurry system to achieve the desired properties of the tapes, such as strength, viscoelasticity, and permeability.

Of crucial importance is control of the concentration, size, shape, and distribution of the pores in a dried tape: a high concentration of pores may result in strength degradation of both green and fired specimens; a low concentration may not permit adequate permeability of gaseous species to escape during binder burnout. For industries producing multilayer ceramics, a complete binder burnout process typically requires approximately seven days. Optimization of the burnout process would allow processing of these materials more efficiently and at the same time, minimize defect formation. Common defects produced during organic burnout in multilayer ceramics are delamination, blister, warping, swelling, and cracks. These defects are caused by the rapid escape of gaseous phases, formation of bubbles in the green body, and non-uniform binder burnout resulting in non-uniform shrinkage.

More of the reactions during organic removal are exothermic in nature and may generate enough heat for uncontrolled burnout if care is not taken. Multicomponent organic systems aid, in some respects, in the burnout process. Solvent and plasticizer elimination occurs at lower temperatures and increases the gaseous permeability of the green body.

Because removal of organics is a time-consuming (and thus expensive) process, several attempts have been made to optimize the burnout process. Methods employed to control organic removal include the use of a controlled atmosphere, and broadening the temperature interval of burnout by using combinations of selected organic constituents [2]. Perhaps the most sophisticated solution has been specimen loss rate-controlled burnout, first proposed by Johnsson et al. [3] for injection-molded green ceramics. Subsequently, a similar rate-controlled binder burnout technique was devised for multilayer green ceramics by Verweij and Bruggink [4]. These systems are developing examples of "smart processing" in which the thermal processing schedules are adjusted *in situ* in response to the rate of weight loss.

Presented herein is a rate-controlled binder burnout system using a reconfigured thermogravimetric analyzer (TG). While previous investigations have used proportional-integral control [4], this work used a proportional-derivative control algorithm with good success. A green multilayer PZT ($PbO-ZrO_2-TiO_2$) was chosen as the test material to exemplify the rate-controlled binder burnout process.

2. PID algorithm

Proportional-integral derivative (PID) control is the common algorithm for feedback control of furnace temperature as well as other processing variables such as the rate of fluid flow. The algorithm has been described in greater detail in a previous work [5]. Briefly, the control function is described by

$$P = P_0 - U_P(T - T_s) - U_I \int_0^t (T - T_s)\mathrm{d}t - U_D\left(\frac{\mathrm{d}T}{\mathrm{d}t} - \frac{\mathrm{d}T_s}{\mathrm{d}t}\right)$$

where P is the furnace power instruction, P_0 is the startup furnace power instruction, T is the furance temperature, and T_s is the setpoint (specified) furnace temperature. The constants U_P, U_I, and U_D, are associated with the proportional, integral and derivative terms, respectively. The setpoint temperature generally increases with time at a constant rate, or is isothermal for a specified time. The proportional term changes the power instruction proportionally with the deviation of the furnace temperature from the setpoint. Proportional control alone causes a non-oscillatory furnace temperature trend which runs parallel, but not coincident with the setpoint temperature schedule. Integral control sums the difference between setpoint and furnace temperature as a function of time. This area continues to accumulate, and influences the power instruction until the temperatures are coincident. Under derivative control, corrective action is taken if the setpoint and furnace temperature slopes are not identical. Thus, derivative control can act as a predictive function which, for example, will act to decrease the power instruction if the furnace temperature is below the setpoint, but is rising too rapidly. The overall control function is the sum of proportional, integral, and derivative terms, each with associated constants. By adjusting these constants, each term can be emphasized or deemphasized. Under weight loss rate control, the mass difference between actual and setpoint are substituted for temperature difference in the above function, and the signs of the proportional, integral, and derivative terms are inverted.

3. Experimental procedure

Thin cross sections of multilayer PZT actuators (Martin Marietta Laboratories, Baltimore, MD) were used, which consisted of viscoelastic laminated tapes with Pt electrodes. These samples were sliced into specimens of mass within the full scale range of the microbalance (Cahn-2000, Cahn Instruments, Cerritos, CA), i.e. ± 100 mg. The total organic content of these specimens was 9.5 wt% based on thermogravimetric analysis (Fig. 1). From this trace, all organic material is removed by 500°C; however, the onset and termination temperatures of organic burnout are a function of heating rate.

The microbalance has a manufacturer's reported resolution of 0.1 μg. It is computer interfaced (Innovative Thermal System, Atlanta, GA) for furnace power control and data aquisition. A Pt specimen basket is suspended with a platinum wire into the hot zone of a sealed mullite gas-flow tube. Kanthal (Kanthal Corporation, St. Bethel, CT) Al wires are wrapped around the heating zone of this tube without any insulation. Power to the windings is provided by a triac (SCR module) (Model 425, Eurotherm Corp., Reston, VA) which receives a 4–20 mA instruction, converted from the variable voltage of the digital-to-analog converter. A fan is directed at the exterior of the exposed furnace windings, and a constant flow of compressed air enters the gas flow tube from above the specimen, exiting from the base. Both these cooling effects compete against the heat generated from the resistance heating elements to permit moderately rapid heating or cooling of the specimen, based on the requirements of the control system. An alumina-encased

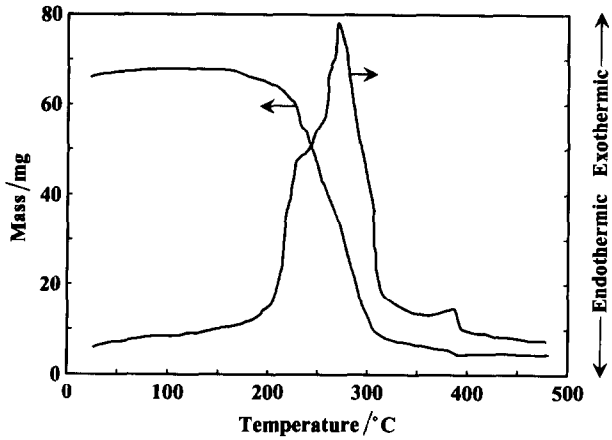

Fig. 1. Thermogravimetric analysis and differential thermal analysis (DTA) of as-received green multilayer PZT ceramics.

Pt–Pt10%Rh thermocouple is mounted from the bottom of the gas-flow tube so that the junction was close to, but not in contact with, the underside of the specimen basket. The same thermocouple is used for both specimen temperature monitoring and furnace control power. The voltage outputs from the thermocouple, the room-temperature compensation circuit, and the microbalance are amplified to exploit the full-scale range of a twelve-bit analog-to-digital converter (SP Innovations, Mabel, MN). The total number of data sets is set at 1000, and data are stored at even time intervals. The time rate of the change in temperature and mass are updated every time the computer cycles through the loop, which was generally faster than one second.

The weight loss rate in mg min^{-1} is user-specified, along with a limit temperature which is the maximum allowed temperature under weight loss rate control. A therminal weight loss is also user-specified so that the program can calculate the time after which to switch back to temperature control. After setup specifications are provided by the user, the computer begins the initial heating ramp schedule, nominally 25°C min^{-1}, followed by a slower (5°C min^{-1}) rate to a specified switchover temperature (time) at which point weight loss control takes over.

The initial power instruction (P_0) under weight loss control is set to the last power instruction under temperature control, and the starting setpoint specimen mass is set to the mass at switchover. The constants U_P, U_I, and U_D are reset to different values at switchover; this accounts for the fact that the specimen and setpoint mass loss values are of different orders of magnitude from the setpoint and specimen temperatures. To the limit of the data presented herein, integral control was not activated and the following weight loss profiles were generated under proportional-derivative control.

4. Results and discussion

The switchover point from temperature to mass control was selected in the range of the onset of binder burnout, which was determined from a prior TG trace (Fig. 1). The choice of this temperature aided in optimum tracking of the setpoint loss in the early stages of burnout. Assigning the switchover time well after the onset of burnout results in temporary control system imbalance; the specimen temperature first drops to slow the burnout rate, then rises again, etc. If the imbalance results in steep temperature oscillations, a self-feeding, uncontrolled burnout is seen (Fig. 2), especially in cases of higher setpoint mass loss rates after switchover. Selecting the switchover temperature in the range where the instantaneous slope of the weight loss trace nearly matches the setpoint mass loss, minimizes the initial control system imbalance.

In the case of self-feeding burnout (Fig. 2), U_P is 2.0. Decreasing the value of U_P to 1.0 results in non-catastrophic binder burnout, but with oscillation of the specimen mass about the setpoint (Fig. 3). A further decrease in U_P to 0.5 (Fig. 4) nearly eliminates the oscillation but the difference between setpoint and actual weight loss, as well as their slopes, becomes greater.

The observed oscillation with larger values of U_P are analogous to temperature oscillations about the setpoint under "on-off" control. This form of control requires the furnace power to shut off if the temperature exceeds the setpoint, and go to full power if it drops below the setpoint. The furnace temperature thus oscillates about the setpoint. Proportional control, where U_P is large, behaves as an on-off control because a slight furnace temperature deviation from the setpoint, multiplied by a large U_P, will cause the power instruction to approach maximum (on) or minimum (off). This is the equivalent to having too narrow a "proportional band". With decreasing U_P, corrective action with temperature deviations are more

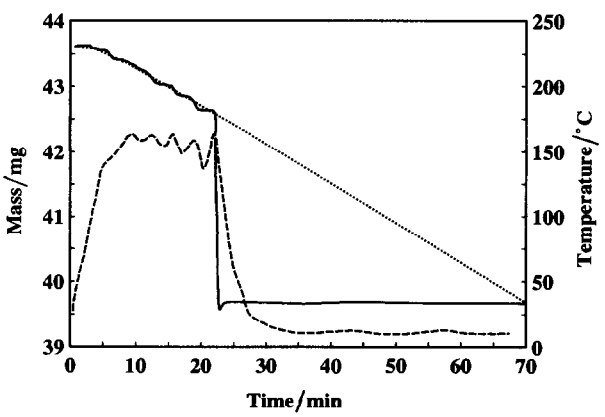

Fig. 2. Binder burnout at a setpoint mass loss rate of 0.06 mg min^{-1}, switchover temperature of 155°C and $U_P = 2.0$. In all plots of this form, the solid line is the specimen mass, the dotted line is the setpoint mass, and the dashed line is the temperature profile.

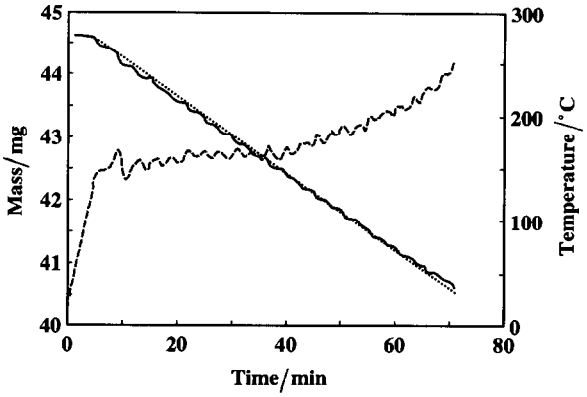

Fig. 3. Binder burnout at a setpoint mass loss rate of 0.06 mg min^{-1}, switchover temperature of 155°C and $U_P = 1.0$.

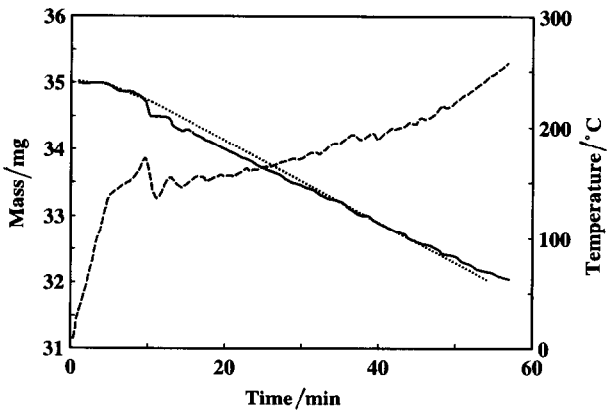

Fig. 4. Binder burnout at a setpoint mass loss rate of 0.06 mg min^{-1}, switchover temperature of 155°C and $U_P = 0.5$.

gentle, and oscillation is attenuated. This was observed herein for weight loss control. The non-coincidence of setpoint and actual mass loss could be corrected by implementation of integral control.

The results of the experiments performed for the burnout with setpoint mass loss rates of 0.01 and 0.001 mg min^{-1} are shown in Figs. 5 and 6. Slower burnout rates demonstrated better tracking between setpoint and actual mass losses, and this behavior was found for a broader range of U_P and U_D choices. Non-catastrophic, non-oscillatory burnout was obtained for a setpoint mass loss 0.1 mg min^{-1} only after optimum selections of switchover temperature, U_P, and U_D. Limited increase in U_D aided in dampening the oscillation. The average slope of specimen weight loss deviated more from that of the setpoint when compared to the 0.06 mg min^{-1} case.

In general, in order to maintain a constant weight loss rate, the control system developed a temperature profile of continuously increasing slope. In the extreme

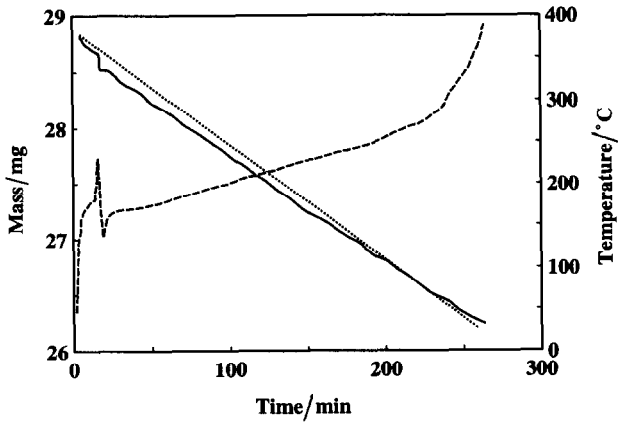

Fig. 5. Binder burnout at a setpoint mass loss of 0.01 mg min^{-1}, switchgear temperature of 185°C and $U_P = 2.0$.

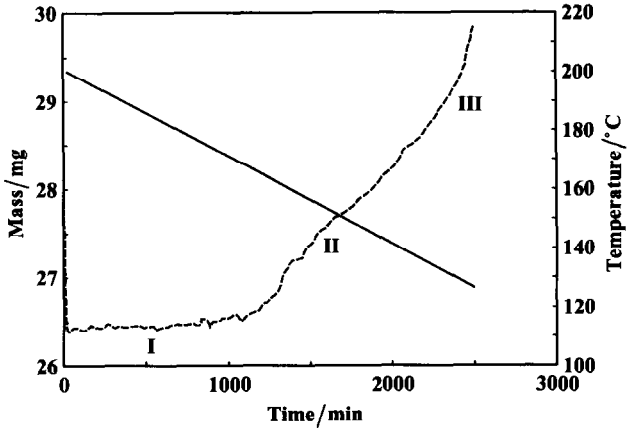

Fig. 6. Binder burnout at a setpoint mass loss rate of 0.001 mg min^{-1}, switchover temperature of 185°C and $U_P = 2.0$.

case of 0.001 mg min^{-1}, three distinct temperature regions (labeled in Fig. 6) are apparent. These are interpreted as corresponding to the combustion of individual organic additives in different temperature ranges. This separation is implied in Fig. 1, but the convolution of the DTA peaks is such that there may be more than three partially superimposed burnout events. Temperature profiles such as those in Figs. 5 and 6 should prove quite useful in designing temperature profiles and track speeds for binder burnout tunnel kilns.

After the various binder burnouts, the specimens were fired by heating at 0.2°C min^{-1} to 500°C and then at 5°C min^{-1} to 1300°C, followed by furnace cooling at 5°C min^{-1} back to room temperature. Optical microscopy of the sintered specimens

showed a wide variety in quality, depending on the binder burnout process. The specimens which were not heat-treated under mass loss control showed severe delamination due to an uncontrolled rate of organic removal. The same was observed when burnout became uncontrollably self-feeding under attempted mass loss control. Specimens for which binder burnout was controlled showed improvement in structural integrity with decreasing weight loss rates. The specimens exposed to mass loss rate of 0.01 and 0.001 mg min^{-1} showed no visible defects.

5. Conclusions

A proportional-derivative control algorithm based on microbalance measurements was successful at maintaining specified mass loss rates of PZT multilayer green ceramics. A controlled weight loss was more easily maintained with slower mass loss rates. Broader proportional bands generally eliminated on-off oscillation of sample mass about the setpoint. Specimens in which exothermic binder burnout was allowed to be self-feeding had delaminations between layers. Specimens heat-treated under slow mass loss rate control were defect-free.

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