

MASTER CURVE MODEL FOR CHARACTERIZATION OF DECOMPOSITION AND DENSIFICATION BEHAVIOR OF PbAlNbO₃-PbZrTiO₃ CERAMICS

In this study, decomposition and densification behavior of PbAlNbO₃-PbZrTiO₃ (PAN-PZT) ceramics were characterized for powder injection molding process. Thermal gravity analysis and *in-situ* dilatometer experiment were carried out to construct master curve. Based on master curve model approach, one-combined master debinding curve (MDC) and master sintering curve (MSC) were constructed for piezoelectric PAN-PZT ceramics. Derived curves matched well with the experimental data. Process optimization and material development will be conducted based on characterization of master curve parameters.

Keywords: Master debinding curve, Master sintering curve, PAN-PZT, Powder Injection Molding, Dilatometer

1. Introduction

Pb(Al_{0.5}Nb_{0.5})O₃-Pb(Zr_{0.52}Ti_{0.48})O₃ ceramics is one of the promising piezoelectric ceramics for ultrasound, sensor, and multilayer actuator applications. It is widely used in various industrial applications because of its strong performances [1]. To maximize piezoelectric performance, many of manufacturing researches have been conducted to fabricate near-net-shaped high-aspect-ratio piezoelectric ceramic structure [2-5]. Among various manufacturing process, powder injection molding (PIM) is one of the promising candidates because of its high productivity and shape flexibility [6]. Using PIM process, complex shaped metal and ceramic structure can be efficiently manufactured without conducting additional shape machining process.

Optimization of processing conditions is very important issue in manufacturing process development. Experimental condition-based optimization process is usually considered as an intuitive technique to achieve best processing condition but, it usually requires lots of processing time and cost. For an example, to optimize sintering temperature of certain powder, experimental condition-based method requires preparation of individual samples which sintered at different target temperatures and times. If powder composition is changed, it requires repeatable sample preparation for each condition to compare characteristics of powder. In order to characterize material and process effectively, model-based optimization process is needed

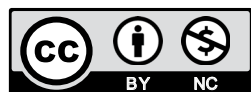
to be developed. As modeling the material behavior, we can numerically compare and expect change of input conditions without conducting time-consuming sample preparation.

Especially, for thermal debinding and sintering process in PIM, thermal gravity analysis (TGA) [7] and *in-situ* dilatometer [8] are one of the widely used to characterization method for material behavior. Based on master curve approach proposed by Johnson and Su [9-10], decomposition and densification behavior of material can be characterized as one combined curve. These master curve analyses can adequately predict process results as independent to the heating history. Developed constitutive function and parameter can be used to optimize processing cycle as well as development of material composition. Several research works have been conducted using MDC and MSC to analyze the decomposition behavior [11-12] and densification behavior [13-14], in respectively. However, for PZT ceramics, there has not many reported researches because of its special sintering characteristics. Unlike conventional metal and ceramics, there has crystal structure change and chemical composition change [15] which make difficult of characterization of sintering shrinkage of material. In advance of our previous research with piezoelectric ceramics [16-17], we analyzed debinding and sintering behavior of piezoelectric ceramics. Thermal decomposition behavior of pre-mixed PAN-PZT feedstock was analyzed by TGA experiment and densification behavior of PAN-PZT ceramics was analyzed by *in-situ* dilatometer experiment.

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2. Experimental

Figure 1 shows scanning electron microscope (SEM) image of powder morphology. Mean particle size was around 2.13 μm and pycnometer density was around 7.98 (10^3 kg/m^3). For debinding characterization PAN-PZT ceramics powder were mixed with Paraffin wax (PW), Polypropylene (PP), Polyethylene (PE), and Steric acid (SA).

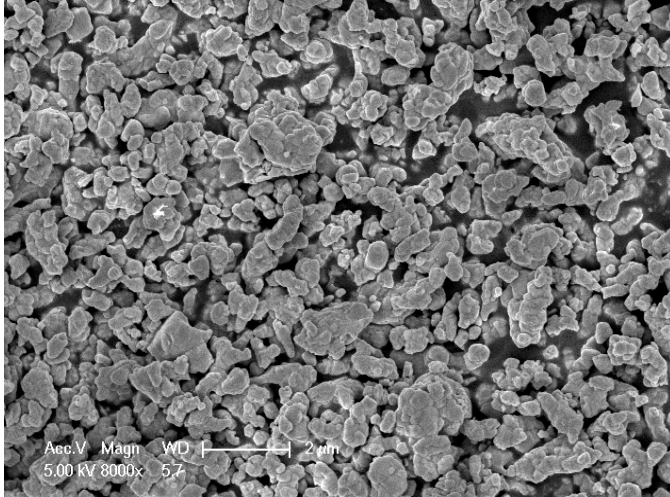


Fig. 1. Powder shape of PAN-PZT ceramics

Thermal debinding process in powder injection molding was modeled by MDC theory. Mass change of pre-mixed feedstock was characterized and analyzed with three different heating rates. Based on master curve theory, one-combined decomposition curve was constructed. For sintering analysis, PAN-PZT powder was compacted using hydraulic press machine with 100 MPa. Densification behavior of PAN-PZT ceramics was characterized by *in-situ* dilatometer with three different heating rates. Similar to MDC theory, densification behavior of PAN-PZT ceramics was modeled by MSC theory. Based on master curve approach, one-combined densification curve was constructed.

3. Results and discussion

3.1. Master debinding curve

Based on master curve analysis, experimental term and weight fraction term can be separated and the representative decomposition curve can be plotted regardless of heating cycles. Detailed expressions are described as follows [17]. The thermal degradation of polymeric binders can be described by first-order reaction kinetics as shown in Equation 1:

$$\frac{d\alpha}{dt} = -K\alpha \quad (1)$$

where α is the remaining weight fraction of binder, t is the time, and K is the constant for thermal degradation of binder, which

can be also expressed using the Arrhenius equation in Equation 2:

$$K = k_0 \exp\left(-\frac{Q}{RT}\right) \quad (2)$$

here, k_0 is the specific rate constant, Q is the apparent activation energy for thermal degradation of binder, R is the gas constant and T is the absolute temperature.

As combining Equation (1) and Equation (2), Equation (3) can be achieved:

$$-\int_1^\alpha \frac{d\alpha}{\alpha} = -\ln \alpha = \int_0^t k_0 \exp\left(-\frac{Q}{RT}\right) dt = k_0 \Theta \quad (3)$$

where Θ is defined as work of decomposition which related to the temperature and activation energy for a specific feedstock system. The formula of it can be described in form of Equation (4).

$$\Theta(t, T; Q) \equiv \int_0^t \exp\left(-\frac{Q}{RT}\right) dt \quad (4)$$

and from Equation (3), the remaining weight fraction of binder can be expressed using the work of decomposition Θ as shown in Equation (5).

$$\alpha(\Theta, k_0) = \exp(-k_0 \Theta) \quad (5)$$

To calculate work of decomposition, apparent activation energy needs to be determined. In this work, Kissinger [18] method was used to calculate apparent activation energy. The Kissinger method uses the temperature T_{\max} where the maximum rate of weight loss occurs as seen in Equation (6) and under the condition of a constant heating rate r , Equation (6) can be expressed as Equation (7). Thus, from Equation (7), we can derive the activation energy as plotting the relations between $\ln[r/(T_{\max})^2]$ and $-1/RT_{\max}$.

$$\frac{d}{dt} \left(-\frac{d\alpha}{dt} \right) = 0 \quad \text{and} \quad T = T_{\max} \quad (6)$$

$$\frac{rQ}{RT_{\max}^2} = k_0 \exp\left(-\frac{Q}{RT_{\max}}\right) \quad \text{at} \quad T = T_{\max} \quad (7)$$

By using derived apparent activation energy, experimental results can be plotted using Equation (4) and weight fraction results can be plotted using Equation (5). Using MDC which means of Equation (5), experimental results can be merged into one representative curve.

Figure 2 shows TGA results of pre-mixed feedstock. Figure 2(a) shows tendency of weight loss change and Figure 2(b) shows tendency of weight loss rate with three different heating rates. Based on MDC theory, activation energy of decomposition was calculated as shown in Figure 3(a) and two-stage sigmoid type decomposition curve was constructed as shown in Figure 3(b). Activation energy of first sigmoid which derived by PW, SA was 96 kJ/mol, and second sigmoid which derived by PP, PE was 242 kJ/mol, respectively. Constructed curve matched well with experimental data. As expected, high molecule PP and PE

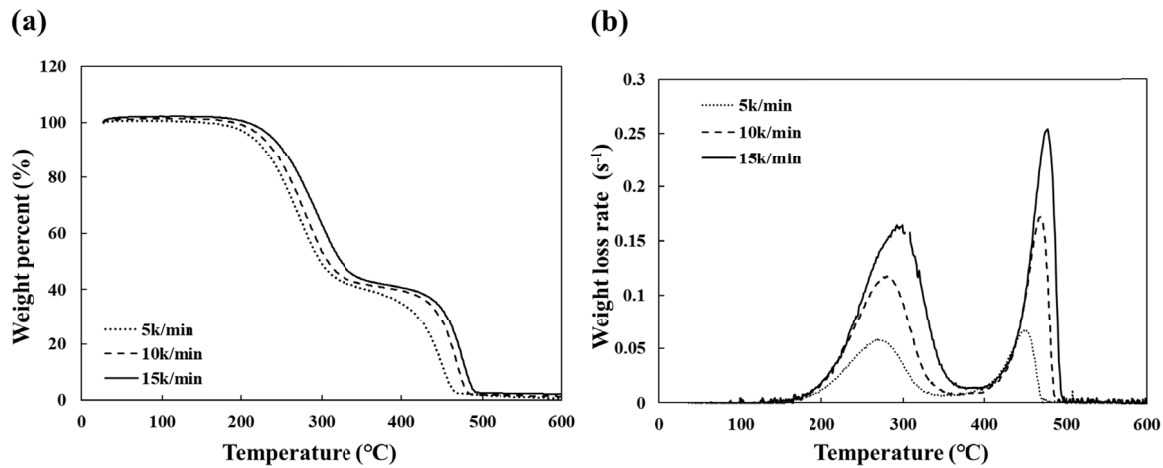


Fig. 2. Thermal decomposition behavior of pre-mixed feedstock: (a) weight percent, (b) weight loss rate

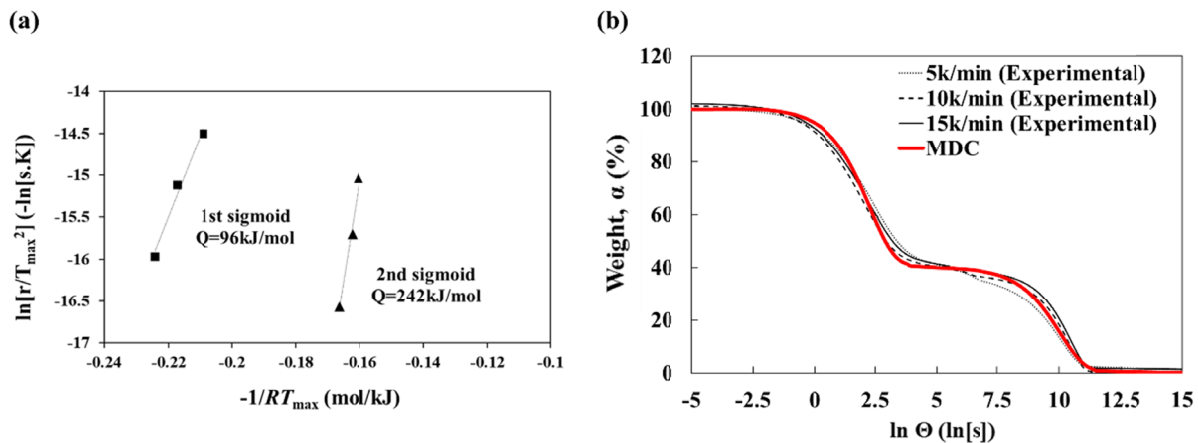


Fig. 3. Master debinding curve construction: (a) apparent activation energy calculation, (b) two-stage sigmoid MDC plot

binder showed higher apparent activation energy for thermal decomposition. Constructed decomposition curve can be used to following applications. Firstly, it can be used for the process parameter optimization. Based on constructed MDC, process parameters can be optimized under constructed. For example, MDC can be used as an efficient technique to analyze effects of binder system in PIM process development.

3.2. Master sintering curve

Similar to MDC, densification behavior of PZT ceramics was modeled based on the MSC theory. Densification related term and sintering cycle related term can be separately summarized and representative densification curve can be plotted using master curve analysis. MSC model started from combined-stage sintering model [19]. Equation (8) explains instantaneous linear shrinkage.

$$-\frac{dL}{Ldt} = \frac{\gamma\Omega}{kT} \left[\frac{\Gamma_V D_V}{G^3} + \frac{\Gamma_b \delta D_b}{G^4} \right] \quad (8)$$

where γ is surface energy, Ω is the atomic volume, k is the Boltzmann constant, T is the absolute temperature, δ is the width

of the grain boundary, G is the mean grain diameter, D_V and D_b are the coefficients for volume and grain boundary diffusion, Γ is the lumped scaling parameter.

Under isotropic shrinkage assumption, density can be represented as follows:

$$-\frac{dL}{Ldt} = \frac{d\rho}{3\rho dt} \quad (9)$$

Here ρ is relative density and L is the sample length. Using Equation (8) and Equation (9), following equation can be derived:

$$\frac{d\rho}{3\rho dt} = \frac{\gamma\Omega(\Gamma(\rho))D_0 k G^n}{kT(G(\rho))^n} \exp\left(-\frac{Q}{RT}\right) \quad (10)$$

Where Q is apparent activation energy, R is gas constant, D is the diffusion mechanism parameter. When the volume diffusion is dominant, it becomes $n = 3$, $D_0 = (D_V)_0$ and when the grain boundary diffusion is dominant, it becomes $n = 4$, $D_0 = (\delta D_b)_0$. Similar to MDC theory, as separating terms, following equation can be derived.

$$\int_{\rho_0}^{\rho} \frac{kG^n}{3\gamma\Omega\rho D_0\Gamma} d\rho = \int_{t_0}^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (11)$$

In above equation, left-side term is related with the density which means of densification and right hand side is related with the sintering cycle. Left side can be defined as Φ which represent material properties in densification. Right side can be defined as work of sintering which related with the densification behavior with respect to sintering cycle.

$$\Phi(\rho) \equiv \int_{\rho_0}^{\rho} \frac{kG^n}{3\gamma\Omega\rho D_0\Gamma} d\rho \quad (12)$$

$$\Theta(t, T) = \int_{t_0}^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (13)$$

In the MSC theory, the term apparent activation energy which represents the sensitivity of densification to temperature is generally obtained by calculating of linear fitting. Equation (14) describes normalized mean residual method to obtain apparent activation energy. Appropriate activation energy for densification can be estimated at the point where curve fitting error becomes smallest value. Using the defined activation energy,

the other material parameter can be obtained by curve fitting of dilatometer experiment.

$$R_m(Q_\rho) = \sqrt{\frac{1}{\rho_f - \rho_0} \int_{\rho_0}^{\rho_f} \frac{\sum_{i=1}^N \left(\frac{\Theta_i}{\Theta_{avg}} - 1 \right)^2}{N} d\rho} \quad (14)$$

where ρ_f is the final density, ρ_0 is the initial density, Θ_i is the work of sintering up to the density ρ of the i^{th} dilatometry experiment, Θ_{avg} is the average work of sintering up the density ρ for all experiments.

MSC represent sigmoid type density function. Equation 15 represent co-relation between density and work of sintering. In this equation, a and b represent parameters which define the types of sigmoid function.

$$\rho = \rho_0 + \frac{1 - \rho_0}{1 + \exp\left[-\frac{\ln \Theta - a}{b}\right]} \quad (15)$$

where $a \equiv \ln \Theta_{ref}$ and $b \equiv 1/n$

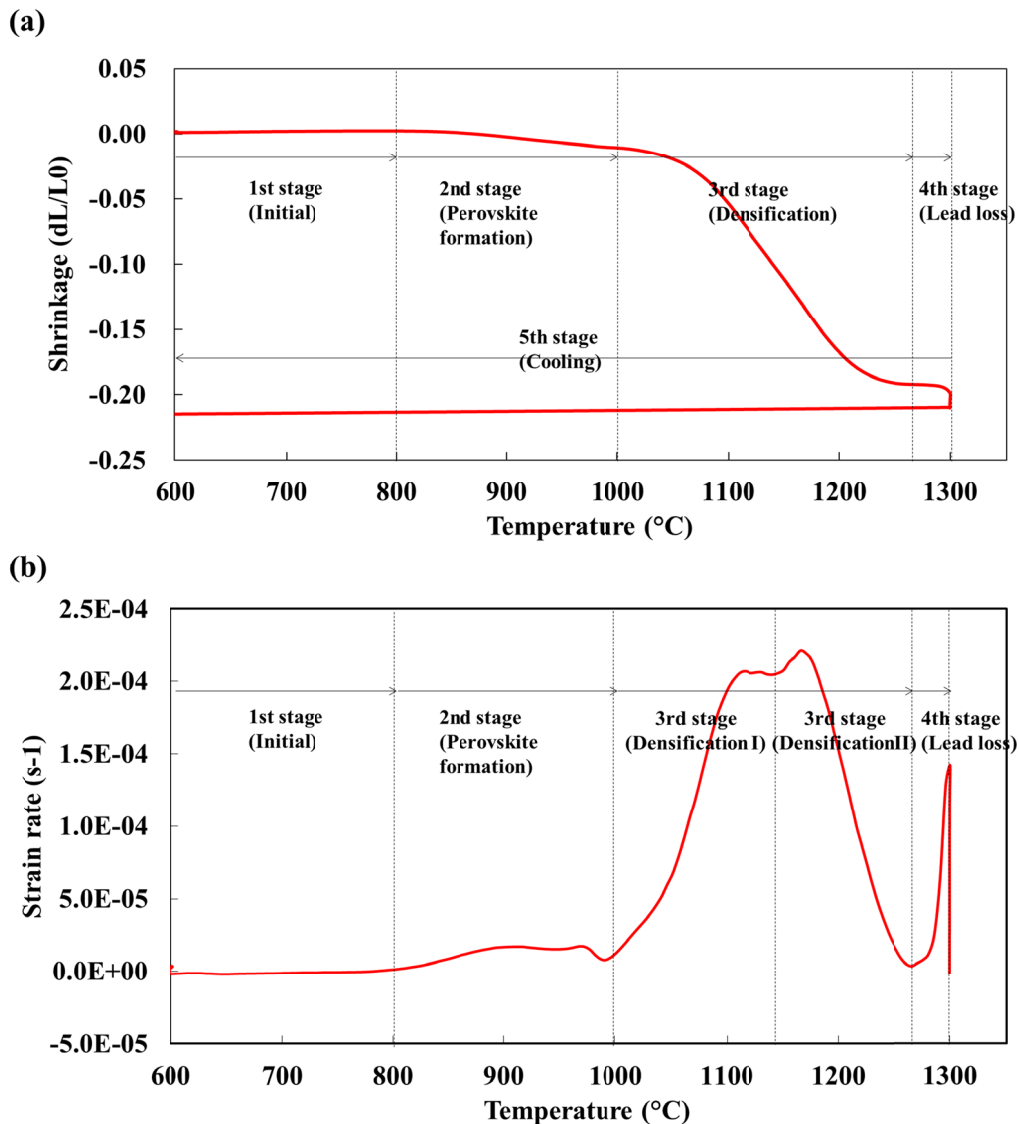


Fig. 4. In-situ densification behavior of PAN-PZT ceramics: (a) shrinkage, (b) strain rate

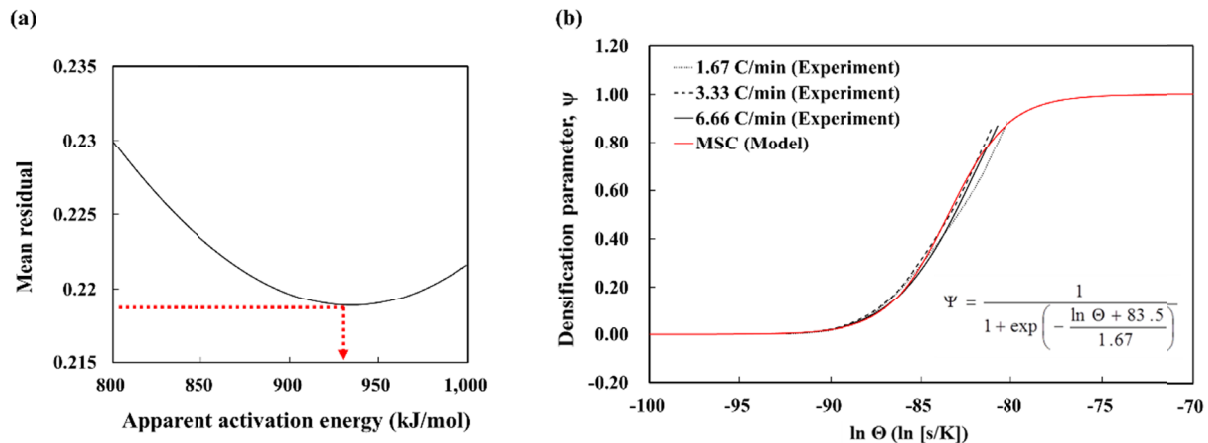


Fig. 5. Master sintering curve construction: (a) apparent activation energy calculation, (b) combined MSC plot

For sintering experiment, Pb rich atmosphere was maintained using extra PAN-PZT powder. Especially, closed type crucible was used to reduce Pb loss behavior in PZT sintering. Figure 4 shows *in-situ* dilatometer results. Figure 4(a) shows shrinkage behavior and Figure 4(b) shows strain rate behavior of PAN-PZT ceramics with respect to temperature. As heating rate increased, max strain was merged into one peak. Due to agglomeration behavior of micron size particles, it showed two-stage sintering curve in low heating rate region and one stage sintering curve was achieved in high heating rate region. Based on mean residual method, apparent activation energy was calculated as shown in Figure 5(a) and MSC was constructed as shown in Figure 5(b). Calculated apparent activation energy was around 928 kJ/mol. Constructed MSC matched well with the designed experiments. Similar to MDC theory, optimization of sintering cycle and material composition comparison can be conducted using constructed MSC model.

4. Conclusions

In this study, decomposition behavior and densification behavior of piezoelectric PAN-PZT ceramics were characterized based on master curve theory. Acquired apparent activation energy for first binder decomposition in MDC was 96 kJ/mol and second binder decomposition was 242 kJ/mol, respectively. Apparent activation energy for densification in MSC was 925 kJ/mol. Constructed curves matched well with experimental data. Process optimization and material development will be conducted based on derived master curve model.

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