

Thermal processing of multilayer PLZT actuators

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Cofired multilayer actuators (MLAs) can suffer from reliability problems due to internal cracking, resulting from imperfections formed during binder extraction or sintering. Thermal processing methodology was developed to optimize manufacturing output of defect-free multilayer actuators. Rate-controlled thermogravimetry (RCT), in which furnace power is adjusted to maintain a constant specimen weight loss rates, was used for organic binder burnout in MLAs. The effectiveness of the various thermal schedules in eliminating MLA damage was determined through image analysis of depth profiles, ground perpendicular to the layers. The damage resulting from RCT schedules were compared to those produced using conventional temperature-controlled thermogravimetry (TCT). Specimens heat-treated with mass loss rates of 0.003 to 0.03 wt%/min showed fewer microstructural defects than all evaluated TCT schedules. Under RCT, furnace power was adjusted to mitigate the effects of rapid burnout of the multicomponent binder, which surged at specific temperature ranges. The effect of introducing a modified atmosphere of MLAs was also investigated using thermogravimetry in conjunction with mass spectrometry. © 2001 Kluwer Academic Publishers

1. Introduction

Actuators are devices which convert an electrical signal into a mechanical displacement. Piezoelectric ceramic multilayer actuators are capable of ultramicroscopic displacement control, rapid electromechanical energy conversion, and good displacement reproducibility. Compared to monolithic actuators, MLAs permit equivalent displacement at significantly lower voltages.

Conventionally, there are two methods of fabricating multilayer actuators (MLAs), stacked disk and cofiring. Stacked disk fabrication, though fairly reliable, is usually done by hand, and thus is very expensive, as well as inappropriate for large-scale production. Cofired multilayer ceramic actuators, made by a tape-casting technology, have been developed, facilitating large-volume production. However, cofired actuators suffer from reliability problems due to internal cracking, resulting in part from stress concentrations at electrode/ceramic interfaces. Of crucial importance is control of the concentration, size, shape, and distribution of the pores and fissures in a fired body. A high concentration of these defects in fired specimens result in property degradation. A common green MLA is composed of lanthanum-modified lead zirconum titanate (PLZT) calcined powder, organic binder, plasticizer, solvent, and platinum electrodes. In the green electrode layers, platinum particles are also suspended in plasticizer, binder, etc.

For industries producing MLAs, a binder burnout process which avoids pore/fissure formation typically requires several days. Because many of the reactions

during organic removal are exothermic in nature [1], they may generate enough heat for uncontrolled, self-feeding burnout. The associated rapid escape of gaseous phases form bubbles in the green body, as well as fluctuations in green body density, resulting in non-uniform shrinkage. Multicomponent organic systems aid in the burnout process by distributing gas evolution over a broad temperature range. Self-combustion processes are eliminated by removing oxygen from the surrounding atmosphere. Hence, the use of a modified atmosphere can be employed for controlling organic removal. Residual species such as carbon may be left behind which must be removed by a second extraction heat treatment in an oxidizing atmosphere.

Optimization of the burnout process would result in time-efficient heat-treatment schedules which still form defect-free MLA's. The rate-controlled binder burnout technique originally developed by Verweij and Bruggink [2] is based on adjustment of furnace power in order to maintain a constant weight loss rate. The merit of rate-controlled binder extraction is that the control algorithm eliminates self-ignition by sensing an increase in weight loss rate, and in response, lowers the temperature of the specimen or decreases its rate of increase by decreasing furnace power. The temperature profile that results from a specified extraction rate can then be programmed into a conventional temperature controlled furnace, forming defect-free actuators on a production scale. This would allow organic constituent extraction in a matter of hours, rather than several days.

2. Experimental procedure

The microbalance used for thermogravimetric analysis (TG, model TGS-2 analyzer and balance control unit, Perkin-Elmer, Norwalk, CT) was computer interfaced (Innovative Thermal System, Atlanta, GA) for furnace power control and data acquisition. A platinum specimen pan was suspended by a thin platinum wire into the hot zone of a small Pt-wound furnace. Flowing argon or CO₂ atmospheres in the thermogravimetric analyzer were preceded by repeated mechanical pump evacuations, followed by argon or CO₂ backfills. Multilayer PLZT ceramic actuators were used (TRS600, TRS Ceramics, State College, PA), which consisted of 0.5 μm piezoelectric ceramic calcined powder, organic binder, plasticizer, solvent, and platinum electrode layers (1.88 mm × 4.75 mm × 4.80 mm with 16 electrode layers per mm). The average specimen weight was 236 mg. The organic content consisted of $\sim\frac{2}{3}$ resin (polyvinyl butyral), $\sim\frac{1}{3}$ plasticiser (butyl benzyl phthalate) and a small concentration of belt release agent (polyethylene glycol). The total organic content was 9.2 weight percent, based on thermogravimetric analysis. All organic material was removed by 450°C under a heating rate of 0.75°C/min.

The thermal behavior of actuators was investigated by using a heat-flux differential scanning calorimeter (DSC model 2910, TA Instruments, New Castle, DE) with a data acquisition and control interface (Innovative Thermal System, Atlanta, GA) in air and argon atmospheres. Open aluminum specimen pans were used with a powdered alumina reference. Specimen and reference weights (6.5 mg) were measured and adjusted to be nearly the same (differences were less than 0.4 mg). The heating rate was 5°C/min and maximum temperatures were set to be less than 600°C in air and 625°C in argon. The purge flow rate of air (desiccated compressed air) and inert (ultra high purity argon) gases were 45 cm³/min.

A quadrupole mass spectrometer (Dycor M200M, Ametek, Inc., Pittsburgh, PA) was used for analyzing combustion and volatilization products during binder burnout. Quantitative information of weight loss and the vapor surrounding the specimen during binder burnout could be simultaneously elucidated through a computer interface. The gas emitted from the specimen was captured by a 0.2 mm diameter fused silica capillary whose intake was set just above the specimen in the TG analyzer. Gas samples were continuously drawn into the mass spectrometer via a turbomolecular pump. Intensity traces were based on collection of the most intense AMU for the selected species over time.

The weight loss rate-controlled thermogravimetric analyzer (RCT) and the temperature-controlled thermogravimetric analyzer were the same instrument, used with different software. The setpoint weight loss rate in mg/min was user-specified, along with a limit temperature which was the maximum allowed temperature under weight loss rate control. Both temperature and weight loss control were based on a proportional-integral-derivative algorithm [3]. A terminal weight loss was also user-specified so that the program could calculate the time at which to switch back to tem-

perature control. After setup specifications were provided by the user, the computer began the initial heating ramp schedule, nominally 5°C/min to specified switchover temperature, at which point weight loss control took over. RCT rates were varied from -0.03%/min to -0.005%/min. After binder burnout, specimens were exposed to a sintering heat-treatment of 10°C/min to 1000°C, and 5°C/min to 1300°C with a 1 h hold. These specimens were fired in alumina enclosures (65591 and 65616, Coors Ceramics Co., Golden, CO) with lead oxide overpressure maintained using 1.5 g of PbZrO₃ powder.

An optical microscope (REICHERT MeF3A, Leica, Wein, Austria) was used to analyze the cross-sections of fired MLA specimens for damage. Three penetration depths surfaces (~1.2 mm, ~2.2 mm, and ~3.0 mm, ground from the surface) were chosen for each specimen. Software, written in Microsoft Visual Basic 4.0, was developed to quantify the percent of damage based on counting pixels associated with deformed regions. Microscope pictures were digitally scanned and then the image of pixels was segregated by gray level (Fig. 1) and others by hand-adjustment using Adobe Photoshop 5.0. Calculation of the ratio of the damaged area to the total area was made based on the ratio of counted pixels. The results from the three evaluated depths are shown in damage evaluation figures.

3. Results

Fig. 2 shows a TG trace of a green coarse-grained MLA, heated up to 800°C in flowing Ar, showing two distinct regions of weight loss, and then a weight gain during a second heating in air. When heating a sample in air to 800°C, more extensive weight loss occurred in the range 170–460°C, and a second weight loss region is not observed. Fig. 3 shows TG traces during binder extraction in flowing air or argon under various heating rates. Slower binder extraction rates and higher weight loss termination temperatures were reached in argon than in air. Specimens were also exposed to a two-step binder extraction (Fig. 4), the first in an argon atmosphere at a specified heating rate (e.g. 0.5°C/min) to 600°C, then cooled to 100°C at 5°C/min, and then reheated at the same heating rate in air to 500°C. During secondary heat treatments, specimens initially slightly gained weight (~0.12%) and then lost weight (~0.83%).

Fig. 5 shows TG and DTG traces of specimens heated in air, argon, or carbon dioxide purge flow atmospheres at 0.75°C/min. DTG peaks at 225, 300, and 385°C in air do not match with the major DTG peak at 270°C in argon. Similar thermal behavior was apparent in a TG trace at 5°C/min, though shifted to higher temperatures. Fig. 6 shows the DSC profiles of MLAs in purge flow air or argon gas. In air, the three superimposed DTG peaks in Fig. 5 show corresponding superimposed DSC exotherms. In argon, superimposed exothermic and endothermic transformations result in ill-defined trends in the DSC trace.

A mass spectrometer was used to analyze the gases released from MLA specimens during TCT. Many of

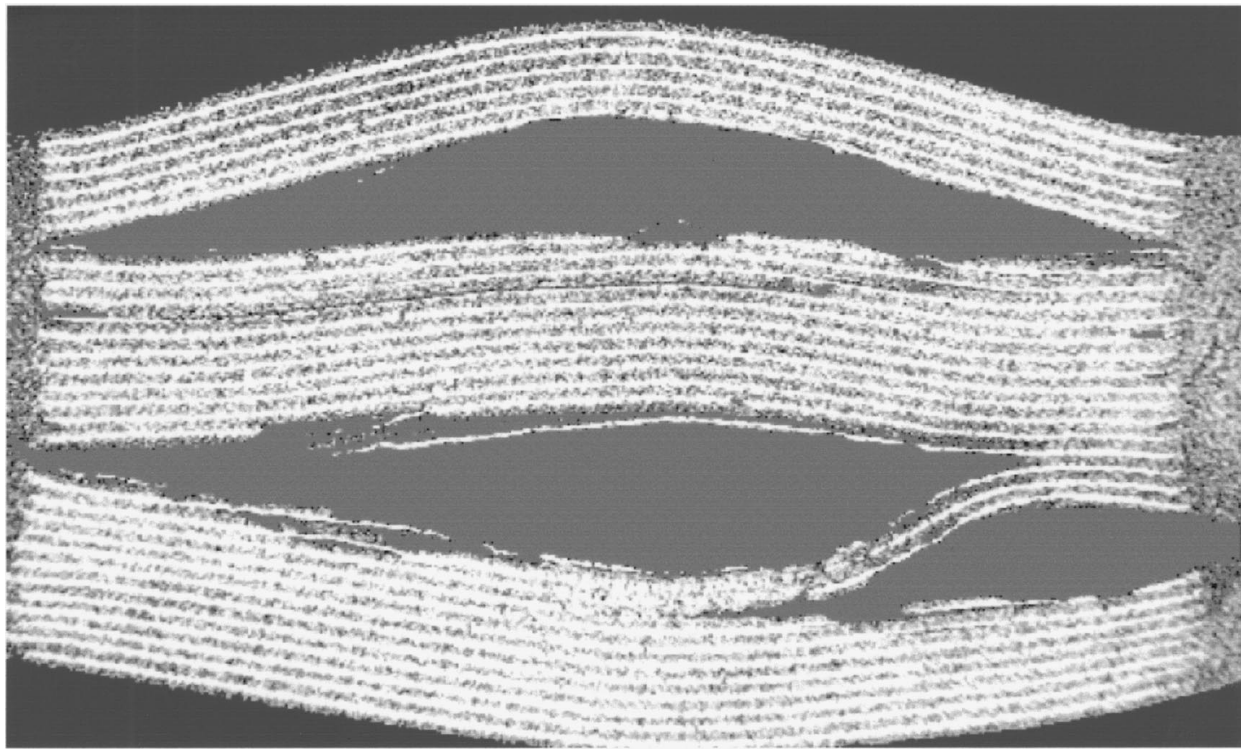


Figure 1 MLA damage percent determined based on scanned image pixel analysis: damaged (grey) area relative to crosssection (non-black) area.

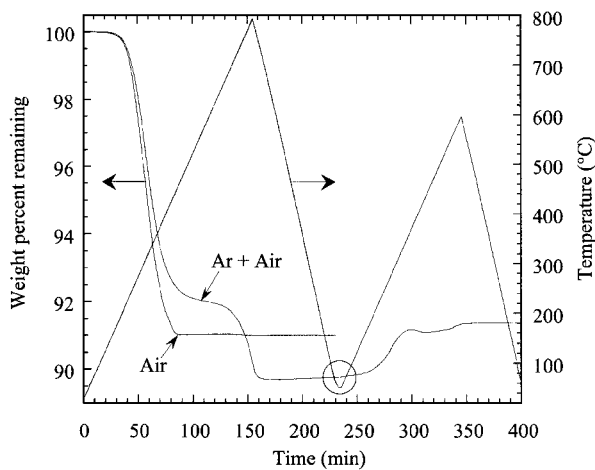


Figure 2 TG of binder extraction for green multilayer actuators. Circle marker indicates switch from flowing argon to air atmospheres. Heating/rate: 5°C/min.

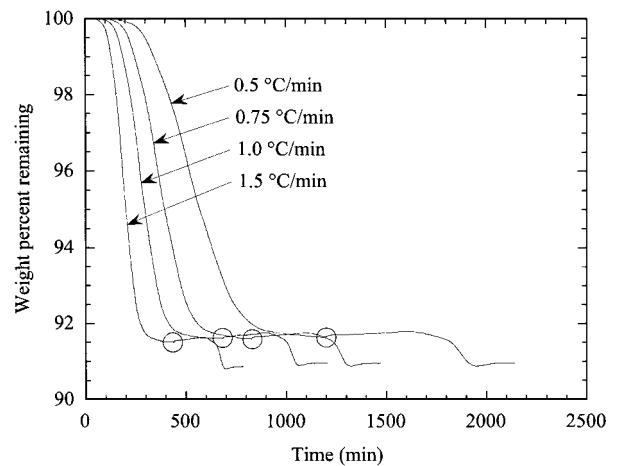


Figure 4 TG traces of binder burnout in MLAs. Circle markers indicate switch from flowing argon to air atmospheres. Specimens were heated at the specified heating rates to 600°C, cooled at 5°C/min to 100°C, and after switching atmospheres, heated at 5°C/min to 500°C.

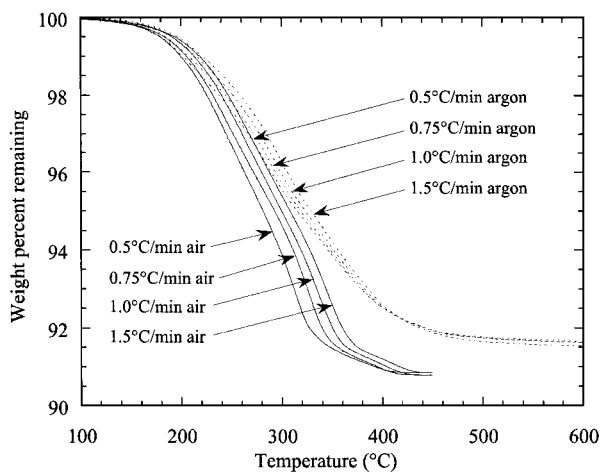


Figure 3 TG traces of binder burnout during heating of MLAs under various rates in an air or argon purge flow (45 cm³/min).

the detected species corresponded to those expected in an air atmosphere. Fig. 7 shows a comparison of H₂O⁺ and CO₂⁺ traces in air and argon atmospheres. Surges in CO₂ and H₂O content correspond to regions of rapid weight loss (correcting for differences in heating rate).

After binder burnout, specimens were exposed to a sintering heat treatment. Specimens lost an average of 2.37% in weight during the sintering step. Damage percentages determined from image analyses of cross-sections MLAs after various 2-step argon/air TCT schedules are shown in Fig. 8. Slower heating rates resulted in less damage.

RCT rates of -0.03, -0.02, -0.015, -0.01, -0.0075, -0.006, -0.005, and -0.003%/min were used on specimens under flowing air. Fig. 9 shows that actual weight loss profiles matched well with corresponding setpoint

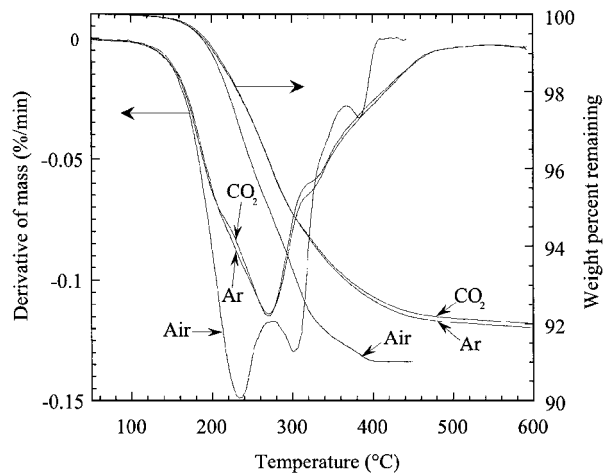


Figure 5 TG and derivative thermogravimetric analyses at 0.75°C/min of green multilayer actuators in purge flow compressed air, argon, or carbon dioxide.

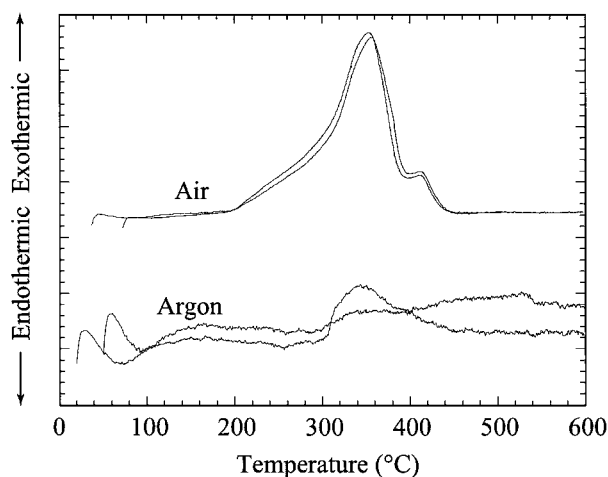


Figure 6 DSC profiles of MLAs, at 5.0°C/min in purge flow air or argon gas. The flow rate was 45 cm³/min. Two specimen scans are shown for each atmosphere.

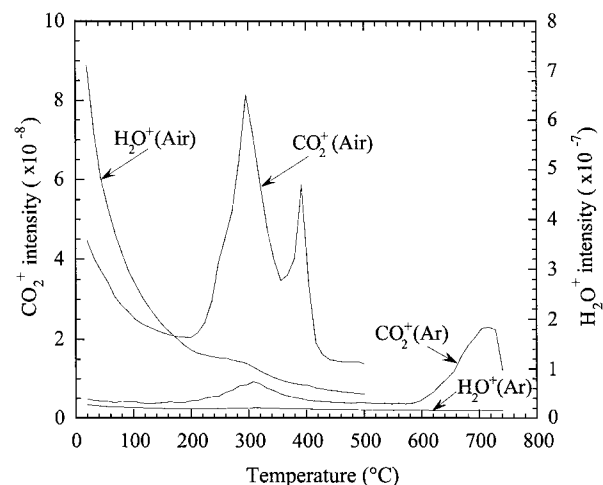


Figure 7 Comparison of air and argon atmosphere for mass spectra intensity changes in H₂O⁺ and CO₂⁺ from MLAs, when heating at 5°C/min.

mass loss rates. The corresponding temperature profiles are shown in Fig. 10. Fig. 11 shows cross sections of typical microstructures after various RCT schedules, followed by sintering heat treatments. The dam-

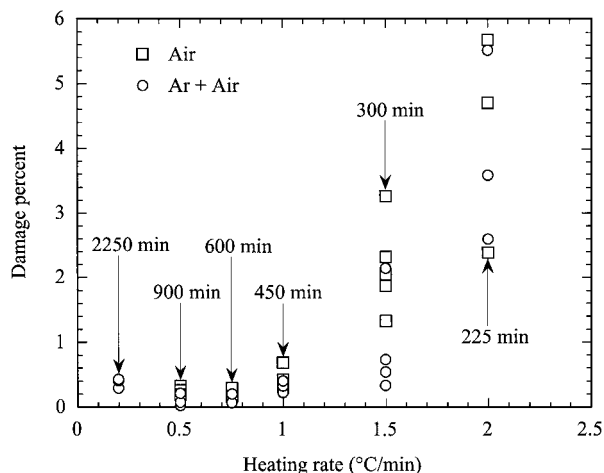


Figure 8 Damage evaluation of MLAs after varying TCT binder extraction schedules in air and argon followed by air atmospheres. Marked are the times to completion of the heat treatment schedules.

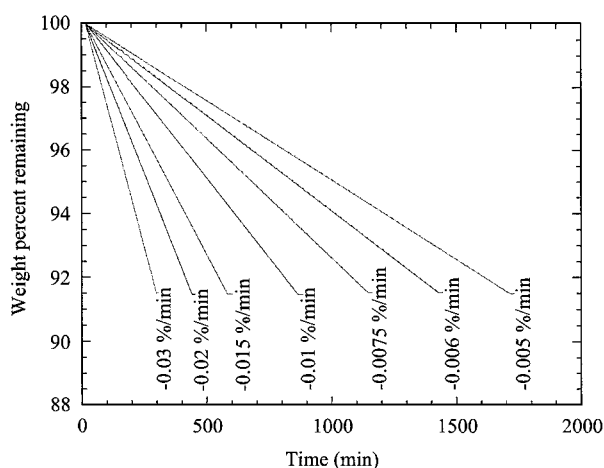


Figure 9 Weight loss (solid lines) and RCT schedules (dotted lines) during binder burnout of MLAs in an air purge flow.

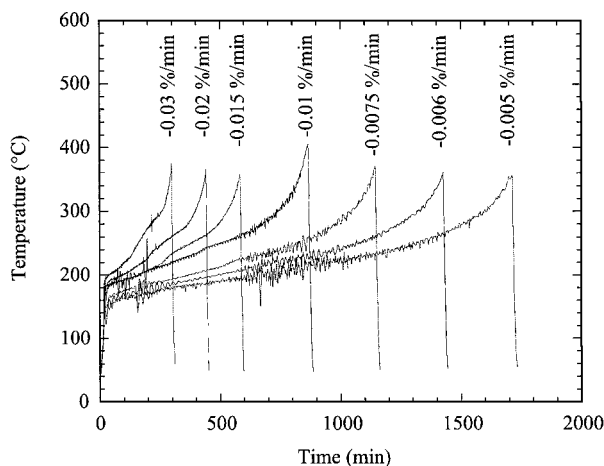


Figure 10 RCT temperature profiles corresponding to Fig. 9

age percent evaluations after RCT schedules are shown in Fig. 12. Comparing Figs 8 and 12 shows that a damage-free specimen was formed after a RCT schedule of $-0.01\%/min$ to -9.22 wt% (922 min), while TCT specimens still retained $\sim 0.2\%$ damage after a heating schedule of $0.5^\circ C/min$ to $375^\circ C$ (900 min).

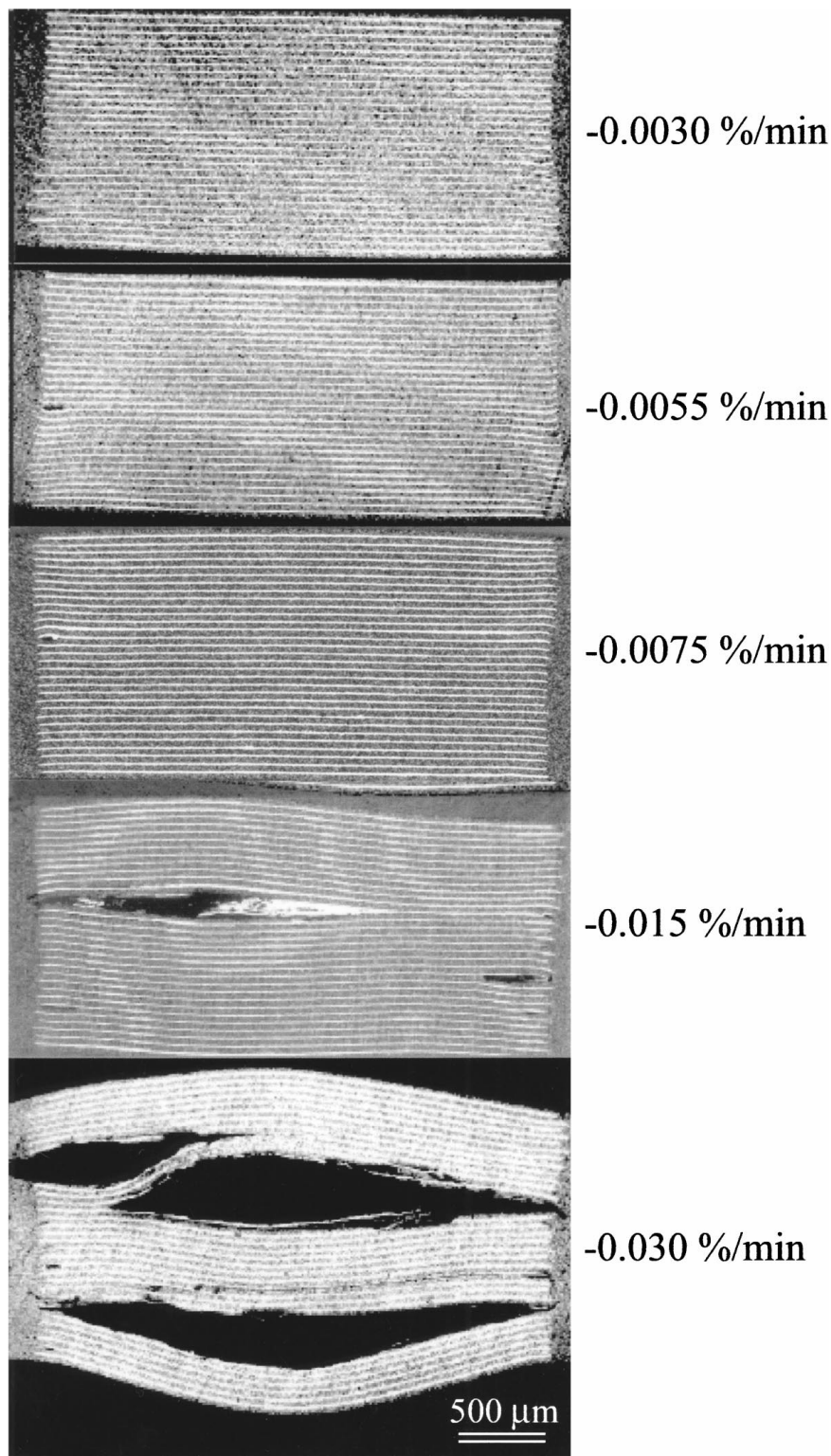


Figure 11 Appearance of coarse-grained MLAs after varying RCT heat treatments, after mounting in epoxy and grinding from the surface, using an optical microscope.

4. Discussion of results

For a given heating rate, binder extraction occurred more rapidly in an air atmosphere as compared to argon and CO₂ atmospheres (Fig. 5), since at least a portion of the removal was via combustion of organic species with oxygen. In both air and argon, extraction was complete at lower temperatures for slower heating rates since more time was allotted for the process before elevated temperatures were reached. In an air atmosphere, the effect was more substantial (Fig. 3); since at least

a portion of the extraction in the presence of oxygen was due to an exothermic (Fig. 6) combustion process, faster heating rates contributed to more extensive self-feeding of the combustion reaction. In argon, the extraction took place by decomposition and volatilization reactions, which were a combination of individual endothermic and exothermic transformations. Applying an overpressure of 1 atm of CO₂ did not succeed in slowing or shifting the weight loss profile (as compared to Ar).

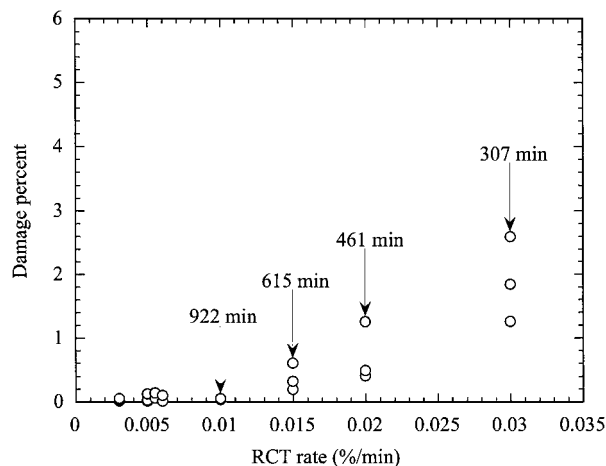


Figure 12 MLAs damage percentage under varying RCT schedules in flowing air.

After binder extraction in Ar, residual carbon was extracted during the second heating in air (Fig. 4). Heating in argon or CO₂ above 620°C caused additional weight loss, not observed when heating in air. This weight loss has a corresponding CO₂ mass spectrometer peak. It is interpreted that PbO was reduced to a sub-oxide (Pb₂O) or elemental lead, and the released oxygen reacted with residual carbon to form CO₂. This is corroborated by the weight gain during the reheat in air corresponding to oxygen uptake (e.g. $\text{Pb}_2\text{O} + \frac{1}{2}\text{O}_2 = 2\text{PbO}$), after heating in argon to 800°C (Fig. 2).

A number of superimposed DTG peaks are apparent in Fig. 3 under a heating rate of 0.75°C/min, corresponding to formation of gaseous species through oxidation of various constituents in the binder. In argon, a significant fraction of binder removal was by decomposition/volatilization processes, leaving residual carbon behind.

CO₂ gaseous product release peaks correspond to the regions of rapid weight loss. The correspondence

must be corrected for differences in heating rate (e.g. 0.75°C/min versus 5°C/min); faster heating rates shift peaks to higher temperatures. H₂O gas release was less clear since H₂O is a regular constituent in the atmosphere.

The more extensive damage with increasing TCT or RCT rates is attributable to gas pressure buildup within the specimen opening up fissures or bubbles in the specimen; slower rates allowed gas to diffuse out of the specimen rather than building up such pressure. The slowest RCT rates formed more fully damage-free specimens than the slowest TCT rates. This is attributed to the fact that under RCT, heating rates are slowed in regions of rapid weight loss (e.g. 225, 300, and 385°C), but no such adjustment is made under TCT.

5. Conclusion

Binder extraction via oxidation occurred more rapidly in air as compared to argon or CO₂ atmospheres via volatilization/decomposition. In Ar, residual carbon remained which had to be extracted in a second heating step in air. Rate-controlled thermogravimetry succeeded at maintaining specified mass loss rates of MLAs, ultimately forming more damage-free MLAs than with any tested TCT schedule.

References

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