

Reduction of Hazardous Waste

The reclamation of BaTiO₃ tape cast trimmings

Submitted by Heidi Schulze
9/30/05

Advisor: Dr. Steve Pilgrim

Funded by a CEER Fellowship Grant

Summary

The purpose of the following research was to develop a reclamation process for scrap BaTiO₃ tape cast material used in the production of capacitors from a local company. Two compositions were supplied, 833 and 402, in three different forms: the virgin, the reclaimed from a partner plant, and the scrap trimmings. The 402 composition was the primary focus of the tests. A major initial step was construction of a rotary calciner at AU. This allowed for a range of optimal calcining temperatures to be identified that could produce reclaimed powder with close to the same weight loss as the virgin, pristine powder. TGA results showed a 0.1-0.2% weight loss in the powders calcined between 450°C-675°C, while the virgin showed a 0.25-0.35% weight loss. EDS analysis showed qualitatively that there is as much carbon present in the reclaimed powders as there is in the virgin. SEM imaging has shown that the reclaimed powder before ball milling contains many agglomerates and has poor particle size distribution. Ball milling has a dramatic effect on improving the particle size distribution of the reclaimed powder.

Introduction

The object of this study is to reuse the BaTiO₃ based dielectric material found in the clean trimmings of the tape used in the production of multi-layer capacitors. Depending on specific fabrication techniques, this can approach 50% of the total dielectric powder. The scrap trimmings are considered hazardous to the environment and have to be disposed of according to EPA regulations. This means they occupy space in landfills and are a possible source of Ba leach. The reclaiming process must cause a minimum change in the powder as determined by the final properties of capacitors made with the reclaimed material.

The local company produces many tons of scrap ceramic tape, which represents a significant loss in productivity and disposal changes. Currently the company is able to reuse about 10% of the scrap by shipping it to a partner branch for reclamation. However, the color and some properties are changed in this material.

Two compositions, 402 and 833, in three forms of BaTiO₃ material were to be studied for this project. The first form is their virgin powder. This is the ideal BaTiO₃ powder that produces the best capacitors and meets customers' expectations. The second is the reclaimed powder from the partner company. This powder produces capacitors that have the same electrical properties, but are slightly darker in color. The color difference is cause for customers to complain and question the product. The third material provided is the scrap trimming. Both 402 and 833 are BaTiO₃ based powders, but differ slightly in specific composition. The scrap tape of 402 and 833 use the same binder systems. Both compositions were examined by basic characterization, but the majority of the experiments were only conducted using the 402 because of time constraints.

Objectives of Project

- Successfully eliminate the organics from the scrap via pyrolysis with the least possible alterations in particle morphology
- Identify the source of the color in the capacitor when reclaimed powder is used
- Ultimately to reduce the waste that the local company produces each year

Experimental Procedures

A small rotary calciner was constructed and connected to a vibratory feeder to create a continuous flow process for the reclamation of powder. A 5cm by 121cm silica tube was used because of its transparency allowing the powder to be observed during its travel through the tube. Before the scrap entered the vibratory feeder, it was chopped using a small electric coffee grinder. Chopping the large tape cast pieces of scrap before entering the kiln allows for more surface area to be exposed to the air. The "coffee ground" scrap has the same visual appearance as the reclaimed powder from the partner plant. Both have millimeter sized unground chunks present.

Thermal gravitational analysis (TGA) was used to measure the loss of organics during the reclamation of the scrap material. TGA is able to indicate the quantity, rate, and temperature over which the organics are removed.

The 402 scrap powder was run through the rotary calciner at a series of different temperatures ranging from 350°C-675°C and then tested by TGA. The 402 virgin powder was analyzed by TGA to obtain the optimal weight loss that the reclaimed powder should achieve to ensure no organics are present. The virgin powder was treated as the standard. The 833 scrap

was also tested. It displayed the same results as the 402 because they both contained the same binder system.

The SEM (scanning electron microscope) was used to view the different powders' particle morphology. The virgin, the reclaimed, and the newly reclaimed powders were all compared. Once again the virgin was used as the "ideal" or standard during comparison. EDS (energy dispersive spectrometry) analysis was performed to identify the chemical compositions of the powders. The carbon content was examined closely because of the color changes that exist when the reclaimed powder is used to make a capacitor.

Zeta potential testing was performed to determine the ideal pH at which a BaTiO₃ solution would remain suspended, i.e., the isoelectric point. Problems were encountered with rapid settling of the powder even with the addition of a dispersant. Therefore a study of zeta potential was done to determine why the powder would not disperse.

ICP (inductively coupled plasma) was used to measure the amount of barium ions that leach into solution. BaTiO₃ is known for its lack of stability in an aqueous solution. It is possible that the loss of Ba ions while in the aqueous tape casting slurry could cause some change in composition and properties for the reclaimed powder. Also the loss of ions could explain the unexpected results obtained from the zeta potential tests.

TGA results provided the ideal calcination temperatures for the least amount of weight loss. Three of these temperatures were chosen (450°C, 550°C, and 675°C) and large amounts of 402 scrap were ground and calcined.

The ball-milled powders were then pressed into pellets in order to test for electrical properties. Half-inch pellets were pressed and then sent to the local company for firing.

Results and Discussion

The TGA runs of the newly reclaimed 402 scrap were compared with the runs done on the 402 virgin powder. The 402 virgin powder had a 0.25-0.35% weight loss while the powders calcined between 450°C-675°C displayed a 0.1-0.2% weight loss. The runs calcined at 350°C and 400°C had a much larger weight loss, indicating organics were still present. These powders also were not as white as the higher temperature powders. They were slightly gray, hinting at the presence of residual carbon.

The reclaimed powder showed a much larger range in particle size than the virgin powder when viewed in the SEM. Agglomerates are present in abundance in the reclaimed powder and the "coffee ground" scrap. After a ball-milling step, the particle size distribution was reduced and the reclaimed powder appears much finer like the virgin.

EDS analysis was performed to test for residual carbon that may not have been removed in the calcining. The lower temperature powders are darker in appearance than the higher temperature powders. The virgin powder is a milky white while the reclaimed powder is gray in color. Reclaimed powder, newly reclaimed powder, and virgin powder were dispersed on aluminum stubs and viewed for carbon content. None of the peaks were noticeably higher than the virgin powder, meaning there most likely is no residual carbon causing the color change.

A second possibility for the color change is the oxidation state of Ti changing from 4+ to 3+ because of reduction or the creation of oxygen vacancies [1]. Semiconducting BaTiO₃ can be made either by reduction (the formation of oxygen vacancies) or by donor doping of a trivalent ion on the Ba²⁺ site or with a pentavalent ion on the Ti⁴⁺ site. The charge compensation from a substitution is made by a valency shift of the Ti: e⁻ + Ti⁴⁺ --> Ti³⁺

The oxidation state change of Ti provides a donor level from which electrons can be excited into the 3d conduction band. This alteration in the electron configuration of Ti allows for a limited amount of conduction, but it also causes a change in color of the BaTiO₃. The electrical property change cannot be seen initially, but the color change is noticeable quite readily. The reduction of BaTiO₃ could occur during the heat treatment if not enough oxygen is present [1].

Barium titanate has a wide range of isoelectric points (IEP) and this is probably why it is difficult to disperse. Its true IEP is around pH 6-7. When the concentration of Ba²⁺ ions increases in an aqueous solution, an IEP value greater than pH 7 can occur. Fully dehydrated BaTiO₃ can have IEP values as low as pH 4 [2]. Zeta-potential tests were run to find the IEP value or optimal suspension pH. The resulting double-step curve brought about more questions because no single IEP value was identified.

ICP tests were run on the BaTiO₃ powder to see approximately the concentration of Ba ions seeping out in an aqueous suspension that may be causing the strange zeta potential curve. The 402 powder shows around 27-30ppm in solution. A second ICP test was run to find an optimal pH value where the least amount of Ba ions and others would go into solution. The solutions were tested for the presence of Ba, Ti, and Zr ions. A pH 10.4 showed the lowest concentrations of the three ions.

To determine dissolution in solvents, the 833 scrap was mixed on a stir plate in DI water, acetone, toluene, isopropynol, and methanol. None of the listed solvents were able to dissolve the scrap. To confirm no organics were dissolved, the mixture was dried, ground, and run through the TGA where the results showed weight loss matching scrap with no calcining and soak time in DI water.

Conclusions/Future Work

The research performed has determined that the scrap trimmings can be successfully pyrolyzed to remove the known binder organics at temperatures between 450°C and 675°C. This has been confirmed by TGA results showing 0.1-0.2% weight loss after heat treatment at these temperatures.

The organics have successfully been removed, but the electrical properties must be tested to confirm no major composition and property changes have occurred. Currently the pellets are being tested for electrical properties.

Qualitatively it can be confirmed that there is no unnecessary residual carbon remaining in the calcined powders between 450°C and 675°C. The EDS peaks of the calcined powder compared to those of the virgin powder all show relatively the same small amount of carbon being present.

The ball-milling step has proved to be important in reducing the particle size distribution. Between 4 and 18 hours on the ball mill will produce powder with a similar morphology as to the virgin.

The ICP and zeta potential tests have proved that there are small changes in the specific composition of the reclaimed powder compared to the virgin. BaTiO₃ powder being in the presence of water loses a fair amount of Ba ions into solution. The effects of this change will be determined once the electrical properties are tested.

There is the possibility of a reducing environment during the heat treatment of the scrap. A future test on the reclaimed powder would be to test the oxidation states of the Ti ions.

The attempt at dissolving the scrap trimming in different solvents failed. The scrap is similar to latex paint in that the dried acrylic binder has most likely cross-linked to form an insoluble mass.

References

[1] Capurso, Joseph S. Aspects of piezoresistivity in semiconducting barium titanate ceramics. Ph.D. Thesis, NYSCC, Alfred NY, 1996.

[2] Lopez, M.C. Blanco, Rand , B., Riley, F.L. The isoelectric point of BaTiO₃. Journal of the European Ceramic Society, Volume 20, Issue 2, February 2000, Pages 107-118.

[3] Chiang, Chia-Wen, and Jean , Jau-Ho. Effects of barium dissolution on dispersing aqueous barium titanate suspensions. Materials Chemistry and Physics, Volume 18, Issue 3, 26 June 2003, Pages 647-655.

[4] Lopez, M.C. Blanco, Rand , B., Riley, F.L. The Properties of Aqueous Phase Suspensions of Barium Titanate. Journal of the European Ceramic Society, Volume 17, 1997, Pages 281-287.