Manufacturability of Very Thin Zirconia Tapes In An ISO 9001 Environment

A.H. Feingold, M.A. Stein, R.L.Wahlers, M. Heinz, E. Twiname,
Z. Topka
ESL Electro-Science
416 E. Church Rd.
King of Prussia, PA, 19406
Email: afeingold@electroscience.com

Abstract

Zirconia is a unique ceramic. Its strength, flexibility and wear resistance have been advantageous in milling media, diaphragms and implants. Its electrical properties make it a prime candidate for solid oxide fuel cells and gas sensors, where high temperature ionic conductors are needed. While building functional devices is critical, success of these technologies depends on providing economic advantage to the market and profit to manufacturers of materials, cells and sensors. Tape casting, a well-established technique, is currently used to provide materials for several electronic ceramic development programs. Tapes for these applications are manufactured in laboratory and prototype volumes on an ongoing basis. In most cases, laboratory materials are not representative of those used in production.

Zirconia for electrolytic applications must fire to form dense, crack-free films and provide the high ionic conductance required for cells or sensors to function. Performance efficiency is related to ionic resistivity and thickness of the active zirconia layer. It is therefore desirable to obtain the thinnest zirconia tape capable of meeting overall system requirements. This technological advantage, however, presents a manufacturing challenge. This paper discusses the ability to cast YSZ tapes at 17µm that can be fired to full density in thicknesses of 10-12µm and the equipment and procedures required to reliably make measurements in this size range in both prototype and full scale manufacturing environments.

Manufacturing tapes under ISO 9001 conditions results in reproducible materials in the laboratory and eases scale-up. SPC charts will be presented showing data used to ensure consistency of raw material properties such as powder particle morphology and surface area. Slurry viscosity, and casting parameter limits are set to control green tape properties. Results are confirmed with measurements of green and fired thickness, and fired density.

Introduction

Zirconia electrolytic devices such as planar oxygen sensors and solid oxide fuel cells are being developed in laboratories all over the world. As new formulations are evaluated, it is important to know that the good ones can be reproduced. An ISO 9001 documented system is aimed at ensuring that this will happen. Unfortunately, ISO 9001 does not exist in most laboratories. Formulas and process procedures are part of the ISO 9001 system. In a manufacturing environment where ISO 9001 certification is in place, it is required that these documentation procedures are followed. This starts with the initial development of any new product or process. Changes that are made as the development progresses are tracked and documented.

The process starts with characterization of the raw materials. Intermediates and final product properties are monitored as part of the process. Control charts are maintained for each measurement. Measurement techniques are documented and gauge repeatability and reproducibility (Gauge R&R or GRR) studies are performed. Statistical Gage R&R studies determine the within-system and between-system measurement variation for a given measurement technique. Gauge R&R studies enable us to minimize measurement variation and ensure that measurements are meaningful.

The tapes used for planar oxygen sensors and solid oxide fuel cells can be manufactured economically under these conditions. Since formulations and processes are reproducible, waste is correspondingly minimized. Scale-up issues are also minimized (1) and economies of scale can apply to larger lots of materials required for prototyping cells and stacks.

The tapes used for the electrolyte function present an unusual challenge. Sensor and cell efficiency depends on the properties of this tape, since a small tape defect may harm or destroy the devices. Internal resistance determines the ionic conductance and consequently the efficiency of electron production (2). Since resistance is a product of ionic resistivity and thickness, these properties are the focus of many development programs (3). A variety of chemical formulations have been evaluated in efforts to increase conductivity at lower temperatures, which would lower the cost of materials. Although a variety of electrolytic compositions have been cast at ESL, the focus of work is on tape thickness. Fired thicknesses as low as 6 to 8μm have been attained with these tapes. The tapes described in this paper are cast in the range of 10 to 20μm green (unfired). ESL has routinely manufactured tapes in this thickness range and ISO 9001 manufacturing documentation has been established to ensure control consistency from lot to lot and with scale-up.

The techniques used to cast these tapes and the procedures used to characterize and document the raw materials, intermediates and final product will be described.

The Need For Thin Tape

The electrolytic functionality of zirconia is based on the conductivity of ionic oxygen at elevated temperatures. In a fuel cell, oxygen ions pass from the air side to the fuel side to complete a circuit. On the air side $\frac{1}{2}\ O_2 + 2e \rightarrow O^{2-}$. On the fuel side, $H_2 \rightarrow 2H^+ + 2e^-$ and $2H^+ + O^{2-} \rightarrow H_2O$. In a sensor, the oxygen gradient between the reference side and the sensed side of the zirconia membrane causes oxygen ions to diffuse, thus setting up a potential difference which is related to the onygen concentration on the sensed side. Therefore functionality depends on ionic conduction of O^{2-} through the zirconia. If electrons penetrate the membrane (electrical conductivity), the flow of electrons through the external circuit would be short-circuited. Therefore the zirconia must permit high ionic conductivity and minimize electrical conductivity. Furthermore, for high efficiency the fired zirconia must have a dense microstructure to minimize penetration of un-ionized gases, which would reduce efficiency.

The fired zirconia requirements can be summarized as follows.

- Compositional integrity and thinness for highest ionic conductivity with minimal electronic conductivity
- Density to minimize gas penetration
- Large area to maximize current capacity
- Strength to resist thermal and mechanical shock

The composition of the zirconia will determine the ionic conductivity. Although yttria stabilized zirconia is not the most conductive composition reported, its high electrical resistivity at operating temperatures of 600 to 1000°C contributes to its usefulness. It is desirable, however, to operate fuel cells in the lower end of this temperature range to extend cell life, reduce thermal stress, improve reliability and reduce cost. For example lower cost metallic interconnect structures can be used below 800°C. This creates an additional burden on the zirconia, since ionic conductivity (σ) decreases exponentially with decreasing temperatures (T). (4)

$$\sigma \sim (1/T)\ e^{(-E/RT)} \qquad [1]$$

where E is the activation energy for ionic diffusion. While membrane thicknesses of 50 to 250μm are useable at temperatures above 800°C, thickness must be reduced to the 5 to 20μm range in order to operate efficiently at temperatures below 800°C. (5). This follows from the fact that, ionic resistance (R) can be reduced by reducing membrane thickness (t).

$$R = (1/\sigma)\ t \qquad [2]$$

It is therefore desirable to economically and reproducibly use the thinnest tape feasible.

Making Thin Tape Reliably

Methods of casting ceramic tape depend on whether the tape is to be thick, intermediate or thin. Each method has similarities with the others but also involves specific techniques, formulations and equipment. These three thicknesses are generally understood to be; < 50μm, 50 to 1000μm and >1000μm (6). Tapes in the middle range include multi-layer ceramic packages, electrode-supported SOFC and low temperature co-fire ceramic (LTCC), while thick tapes are more commonly used for armor, substrates or other structural applications. Manufacture of thin tapes (~< 50μm) has until recent years been the realm of passive components alone; multi-layer ceramic capacitors (MLCC), multi-layer ceramic inductors(MLCI), etc. The manufacture of these thin tapes entails manufacturing and handling challenges. Casting variables such as dispersion and thickness variation become magnified in importance.

Thin tapes require greater dispersion of inorganic particles. While this is true of most wet ceramic processes, this need becomes more critical as tape thickness decreases in order to minimize structure defects stemming from even low levels of agglomeration. Achieving excellent dispersion becomes more difficult due to the need for extremely fine particles, with correspondingly high surface area (7), in thin tapes. Submicron or “nano-scale” powders are known for their tendency to agglomerate. Particle size must decrease to ensure a packed particle bed. This is necessary to increase structure uniformity in both green and fired states, minimize or negate through-layer defects, homogenize densification shrinkage and increase the strength of the layer after sintering (8).

Thin tape requires enough green strength per unit of cross-sectional area to maintain integrity through device assembly. Building this strength into a high surface area particle bed requires a delicate balance between dispersion, strength, green density and viscosity. Controls must be established and maintained for consistency.

Many equipment-related demands also accompany the manufacture of micron scale tapes. Simple tasks such as tape thickness measurement as an in-process control check must be performed on more sensitive and accurate equipment than is typically found in a production area. For green tape thickness in the range of 12.5µm, production floor measuring equipment must have accuracies in the single micron range. Commercially available precision milled or surface ground casting heads (doctor blades) often have flatness tolerances no better than 2.5µm and up to 5µm after use. Solid granite precision casting surfaces may only be certified flat to 8 µm. Polymer carrier films claimed to have been processed in clean rooms have been seen to include static related debris larger than 8µm. These mechanical factors and additional factors such as web speed uniformity, head pressure repeatability, slip homogeneity, lot to lot repeatability of casting slips and in-depth operator training become key process variables as layer thickness decreases to <50µm. (9)

Procedure And Results

The procedures and controls described above were put to use to cast very thin (10-20µm) zirconia tape. YSZ powders were obtained from several sources to determine the parameters required to cast consistent tapes. Incoming powders were characterized by measuring surface area, particle size distribution and other parameters. Powder lot records were maintained so that cast and fired tape properties could be traced back to the original lots of powders and their properties. The submicron YSZ powders used had surface areas in the range of 8-10 m^2/gm.

Slurries were formulated using phosphate free dispersants and solvents that could be used safely in manufacture. This precluded the use of toluene. PVB binder systems were chosen which provide good strength for handling thin green tapes. Formulations included enough binder to ensure adequate laminating characteristics. The YSZ powders were dispersed for 24-48 hours before binder was added. Dissolution milling followed for an additional 24-48 hours. Viscosity of the dispersed powder slurry was monitored to determine that agglomerates of the high surface area powders were adequately broken up. After complete dissolution of the binder, viscosity was adjusted to a range, which is consistent with practical casting parameters.

The casting slurry was then de-aired to remove dissolved bubbles and finally filtered before it is fed into the doctor blade reservoir . An initial set-up of the doctor blade height was adjusted after the dry green tape came off the caster and was measured to assure that the thickness was within the control range. The leading part of the cast was discarded after this adjustment is made. Drying parameters and casting rate were optimized for the slurry composition to maximize throughput. The tape was periodically monitored for thickness along the length and across the width of the cast. Figure 1 shows thickness data taken on a 250 meter (~800 feet) cast of zirconia tape. Each point represents the average of four points taken across the 8 inch width of the cast. This lot (number 8 in figure 2) is typical of the data obtained on all the thin tape casts shown in figures 2 and 3. The dried tape was then taken onto rolls at the end of the caster. Each cast was re-rolled on a light table for visual inspection and additional thickness measurements.

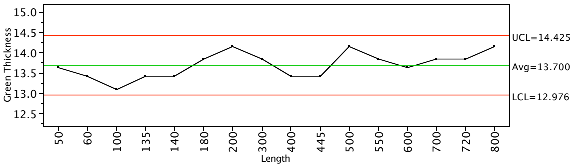

Figure 1

Control Chart of Green Thickness(µm) vs. Length

Figures 2 and 3 are charts of green tape thickness obtained for two thicknesses of green tape. Figure 2 shows data obtained from nine separate lots of tape cast to a target green thickness of 14.5 µm. The target thickness for the five lots of tape shown in Figure 3 is 12 µm.

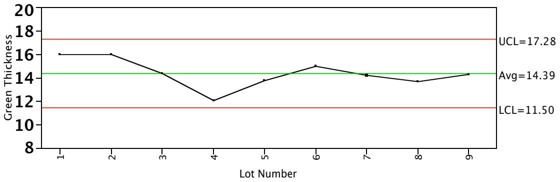

Figure 2

Control Chart of Green Thickness if 14.5µm Tape

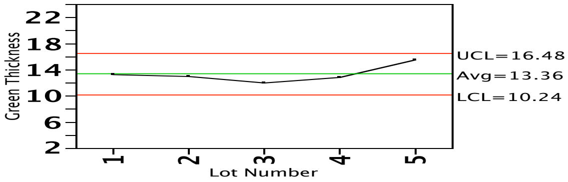

Figure 3

Control Chart of Green Thickness of12µm Tape

Figure 4 shows data obtained for green density for the five lots of electrolyte tape shown in figure 3.

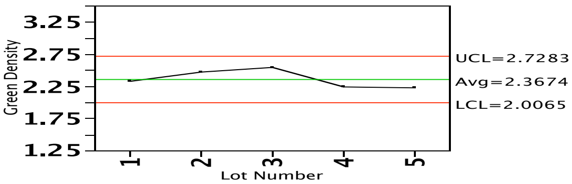

Figure 4
Control Chart of Green Density (gms/cc)

Green density is an indication of solids loading and powder dispersion in the casting slurry. High green density led to lower shrinkage and a more consistent fired tape. All measurements were done using procedures, which had been certified to pass gauge R&R. This ensured acceptable measurement variation among operators.

These zirconia tapes attained >97% of theoretical density when fired at 1450°C for 2 hours. For anode-supported cells, the zirconia electrolyte tape was typically laminated to the anode support structure and co-fired with the anode tape. Our customers reported that the resulting fired electrolyte tape was free of leaks when subjected to helium leak detection. Figures 5 and 6 are a photomicrographs of fired zirconia tape.

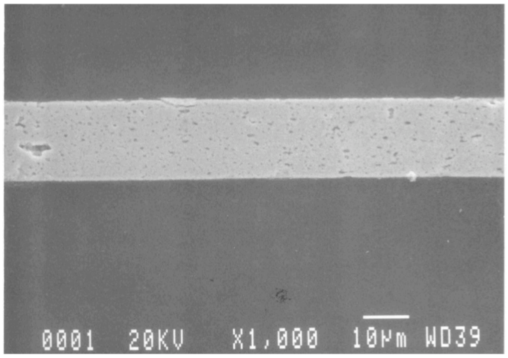

Figure 5

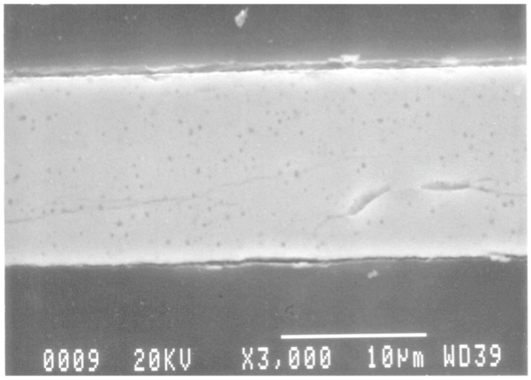

Figure 6
Zirconia Tape Fired at 1450°C for 2 Hours

Conclusion

The ability to consistently cast very thin zirconia tape in a documented prototype and production environment has been demonstrated. This allows the developers of zirconia electrolyte devices such as sensors and solid oxide fuel cells to do experiments with consistent materials. The data presented in this paper is for YSZ tapes. Other tape materials have been cast with similar controls and specifications. ISO 9001 compliance ensured consistency from incoming inspection of raw materials to final tape and device properties.

References

1. R.S. Webb, A.H. Feingold, Z.J. Topka, and E. Twiname: Fuel Cell Science, Engineering and Technology-2004 , June 14-16, 2004, Rochester, New York, pp. 477-481
2. T.I. Ishihara, N.M. Sammes and O. Yamamoto, in High Temperature Solid Oxide Fuel Cells; S.C. Singhal and K. Kendall, Editors, pg 103, Elsevier, 2003
3. T.I. Ishihara, N.M. Sammes and O. Yamamoto, in High Temperature Solid Oxide Fuel Cells; S.C. Singhal and K. Kendall, Editors, pg 96, Elsevier, 2003
4. S.C. Singhal, in Solid Oxide Fuel Cells VII, eds H. Yokokawa and S.C. Singhal, The Electrochemical Society Proceedings, Pennington, NJ, PV2001-16, 2001, p. 85
5. S.C. Singhal, in Solid Oxide Fuel Cells VII, eds H. Yokokawa and S.C. Singhal, The Electrochemical Society Proceedings, Pennington, NJ, PV2001-16, 2001, p. 166
6. R.E. Mistler, and E. Twiname, Tape Casting Theory and Practice, p. 96, American Ceramic Society, Ohio, 2000
7. R.E. Mistler, and E. Twiname, Tape Casting Theory and Practice, p. 13, American Ceramic Society, Ohio, 2000
8. R.E. Mistler, and E. Twiname, Tape Casting Theory and Practice, p.214, American Ceramic Society, Ohio, 2000
9. R.E. Mistler, and E. Twiname, Tape Casting Theory and Practice, pp. 83-151 American Ceramic Society, Ohio, 2000