

C. Processing and Characterization of Structural and Functional Materials for Heavy Vehicle Applications

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Objectives

- Produce yttria-stabilized zirconia (YSZ) thin films using combustion chemical vapor deposition technique for solid oxide fuel cells.
- Investigate the nucleation of YSZ and its controlling parameters.
- Study the evolution of the thin film microstructure.
- Enhance the film deposition rate.

Approach

- Deposit YSZ thin films using combustion chemical vapor deposition (CCVD).
- Characterize the films using scanning electron microscopy (SEM) and X-ray diffraction.
- Study the effects of substrate temperature and metal concentration on the nucleation density.
- Examine the evolution of the thin film microstructure by experiments and stochastic simulation.
- Optimize the operation parameters of the CCVD system.

Accomplishments

- Enhanced the nucleation density
- Developed a stochastic model to simulate the evolution of the thin film microstructure.
- Established a set of conditions for high film growth rates.

Future Direction

- Study YSZ film deposition on porous electrodes.
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Introduction

YSZ is an oxygen-ion-conductive material that has conventionally been used as an electrolyte in solid oxide fuel cells (SOFCs) and in oxygen sensors for pollution and safety monitoring, control, and automation of industrial processes, and energy conservation.¹ Because of the relatively low electrical conductivity of YSZ (about $0.1 \text{ S}\cdot\text{cm}^{-1}$ at 1000°C), most of the ohmic loss is due to the resistance of the electrolyte. To reduce the ohmic loss and increase the power generating efficiency of the fuel cell, it is desirable to use a thin film electrolyte. On the other hand, a temperature of as high as 1000°C is usually employed to obtain reasonable ion conductivity for YSZ material. This high temperature makes material selection difficult and increases the product cost greatly. Reducing the thickness of the electrolyte would increase the conductivity at lower temperatures.

YSZ thin films usually have been synthesized by CCVD or electrochemical vapor deposition (EVD).^{2,5} [Should this ref callout be 2–5? No callouts found for refs. 3 and 4.] The vacuum systems used by these techniques limit the sizes of the parts and increase the cost of the products. Liquid fuel CCVD is a promising technique to produce YSZ thin films for industrial applications because CCVD works in an open atmosphere and offers the potential for conformal deposition of films on non-flat surfaces. Moreover, because no vacuum chamber is needed for the process, there is no size restriction on parts on which the film can be deposited. Because of the relatively high precursor concentration in liquid fuel compared with the fuel usually used for low-pressure CVD processes, CCVD is expected to have a higher deposition rate. Therefore, CCVD is a promising technique for producing YSZ thin films for industrial SOFC applications at a lower cost than any other CVD/EVD technique.

Electrolytes for SOFCs must be highly dense to avoid any cross flow of oxygen or fuel. The main purpose of this research is to produce dense YSZ thin films through the study of nucleation and microstructure evolution. Reducing the cost of fuel cell manufacturing by using thin film technology and a high film growth rate is of great interest. Methods to enhance the growth rate of YSZ have been studied.

Approach

Thin films of YSZ to be used as electrolytes for SOFCs have been deposited using CCVD. The deposition system was developed at North Carolina A&T State University. Metal-organic reagents were dissolved in an organic solvent (toluene). The solution was atomized into small aerosols with a nebulizer, mixed with oxygen, and then ignited by a pilot flame. Thin films then were deposited on substrates placed downstream of the aerosol flame.

Nucleation study of YSZ was performed by varying the substrate temperature and metal concentration in the solvent. At design conditions, depositions were conducted for different lengths of time. The microstructures of these depositions were observed and analyzed, and the grain growth was studied with stochastic modeling. Efforts to enhance the film growth rate were carried out through study of the effects of thermophoresis and metal concentration. All the present depositions were performed on mirror-polished single-crystal silicon substrates. The phases of the deposited films were examined with X-ray diffraction, and their morphology was characterized by SEM.

Results

Nucleation

Effect of substrate temperature. The temperature of the substrate is an important factor that controls the nucleation density, defined as the number of aggregates created per unit area. To be able to use the image analysis software Image Pro to compute the nucleation density, the nucleation time of the YSZ particles was set for 130 s. The depositions were conducted at substrate temperatures of 800, 900, 1000, 1100, and 1200°C and a metal concentration of $1.25\text{E-}03 \text{ M}$. The as-grown samples were characterized with SEM as shown in Figure 1.

Counting the particle number in the specific area with the application software showed that the nucleation rates ranged over an order of magnitude, from 10^{10} to 10^{11} cm^{-2} , in the tested temperature range. The nucleation rate variation versus the substrate temperature is illustrated in Figure 2. The variation of the nucleation rate with the substrate temperature is characterized by two tendencies: When the substrate temperature is between 1000 and 1200°C , the nucleation rate decreases with the

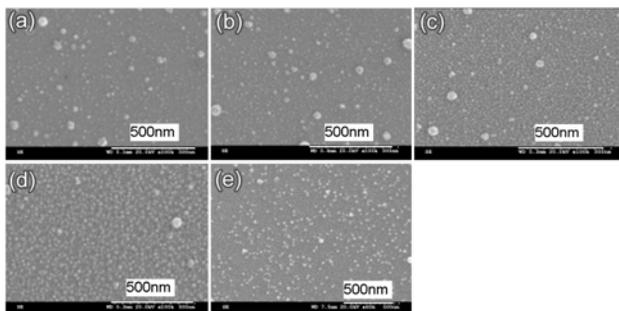


Figure 1. Micrographs of YSZ nuclei nucleated at various substrate temperatures: (a) 800°C, (b) 900°C, (c) 1000°C, (d) 1100°C, and (e) 1200°C under conditions of nucleation time of 130 sec and total metal concentration of 1.25×10^{-3} M.

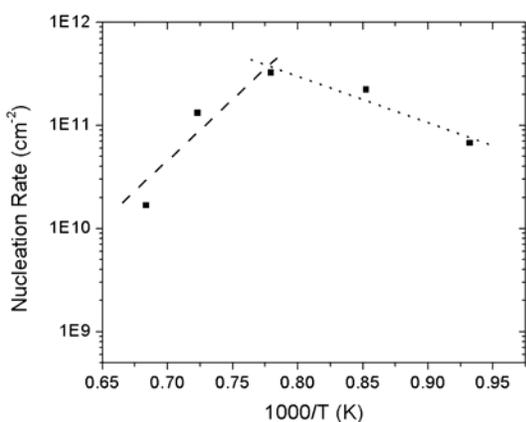


Figure 2. YSZ nucleation rate as a function of the substrate temperature according to the information in Figure 1.

substrate temperature; in the substrate temperature range of 800 to 1000°C, the nucleation rate increases with the substrate temperature. The former nucleation rate tendency was well accepted. As far as the author knows, the latter tendency has not been reported. It is proposed that at low substrate temperatures, the material species in the gas phase condense into a solid phase and coagulate into particles. They rebound from the surface instead of becoming adsorbed when they hit the substrate surface. This process also leads to depletion of species in the gas phase that is needed for CVD and then results in a decrease in the nucleation rate. The images in Figure 1 also reveal that on samples nucleated at low temperatures, there are many large nodular particles that support the above statement.

Effect of metal concentration. Another method used to enhance the nucleation rate was to increase the deposition flux, i.e., the metal concentration, for our experimental system. At low concentrations of 5×10^{-4} and 1.25×10^{-3} , only isolated particles presented on the substrate surface after depositions of 130 s, whereas almost continuous films were obtained when the concentration was increased to 3×10^{-3} M and up. At high total metal concentrations, the particle size reached 30–50 nm. From this set of experiments, it can be concluded that the lowest metal concentration, 5.5×10^{-4} M, is not suitable if a high nucleation rate is demanded.

Structural Evolution

Experimental study. To grasp the physics of the evolution process of the YSZ thin film, the grain sizes at various stages of the processing time were measured for statistical post-processing. Figure 3 shows the micrographs of YSZ particles/crystallites at different processing times. In Figure 3(a), the nuclei can hardly be seen after only 70 s of processing, except some large particles that are assumed to be contamination. From Figures 3(b) to (d), with the increase of processing time, the sizes of the particles increase; however, the number of particles is reduced. This phenomenon can be interpreted by the mechanisms of coarsening and coalescence of the growing particles. With increased processing time, the sizes of the particles increase. Some secondary nucleation and growth on the large particles can be noticed. It is also reasonable to assume that the secondary nucleation should take place on the substrate before all the surface of the substrate is covered with particles. The film consists of both (111) and (100) oriented crystals. The difference in orientation originated at the stage when the particles were very small.

According to the obtained mean particle radii, particle growth rate can be estimated by plotting the mean diameter versus the growing time, as shown in Figure 4. The particle growth rate is approximately linear during the time period studied (130 to 430 s). The intercept of the line on the time axis is about 33.3 s, which shows the incubation time for nucleation. With prolonged deposition time, continuous thin films can be obtained.

Stochastic simulation. The number and size of the particles were obtained with the image processing software. After statistical post-

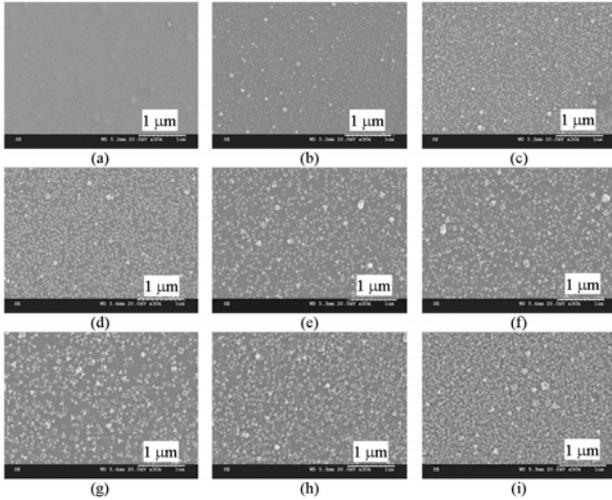


Figure 3. Microstructure of the YSZ particles/crystallites at different processing times: (a) 70 s, (b) 130 s, (c) 190 s, (d) 250 s, (e) 310 s, (f) 370 s, (g) 430 s, (h) 490 s, and (i) 550 s on Si(100) substrates, at a substrate temperature of about 1200°C, metal concentration of 1.25×10^{-3} M.

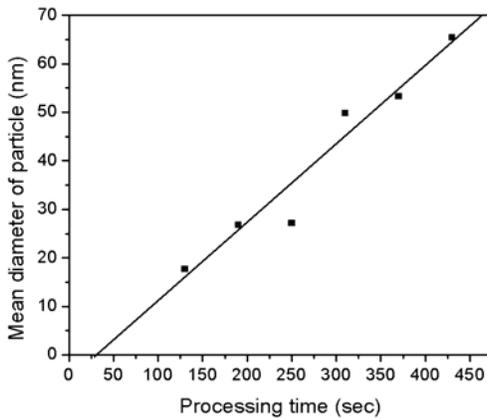


Figure 4. Particle growth rate vs. processing time from the data obtained from the micrographs as shown in Figure 3.

processing, a comparison of cumulative distribution functions (CDFs) of grain radius normalized by the mean radii is given in Figure 5. As can be seen from Figure 5, there is a distinct dispersion among these CDFs plotted in the normalized space. Thus the use of a normal grain growth model cannot accurately capture the evolution process of grains in YSZ thin films. The deviation from the normal grain growth model is mainly attributed to the orientation-dependent grain boundary energies and mobility.

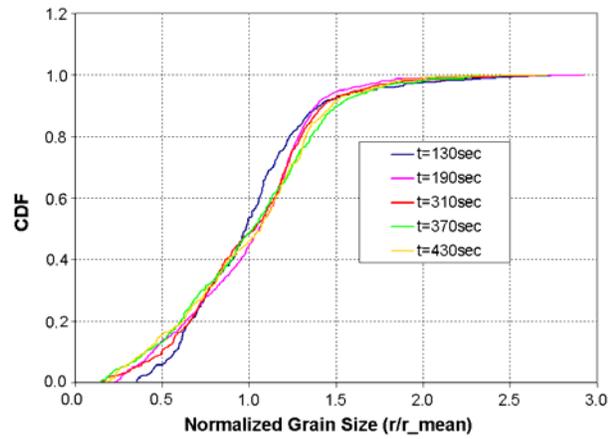


Figure 5. Comparison of CDFs of grain radius in normalized space.

The lognormal distribution has been used extensively as the initial distribution of grain size.^{6,7} To validate the use of the lognormal model, a comparison of the initial CDF of grain radius at $t=130s$ with its equivalent lognormal distribution is shown in Figure 6. As shown in Figure 6, the equivalent lognormal distribution can accurately capture the true initial grain size distribution. A stochastic model was developed by taking the radii of the neighboring grains and the orientation-dependent constants into consideration. The computational efforts were greatly reduced by dividing the entire population of grains into several sub-groups based on the level of their percentiles. It was assumed that all grains within each sub-group have identical grain growth behavior. The orientation-dependent grain growth constants were determined from curve fitting of the experimental data. An example of comparing model prediction with the experimental observations is shown in Figure 7.

Growth Rate

Thermophoresis is a thermal-gradient-directed flow of material from high-temperature to low-temperature regions. Thermophoresis has been found to be a strong factor in some CVD environments.⁸ A temperature gradient across a diffusion boundary layer causes a thermophoresis effect. In this case, if the flame were hotter than the substrate, on average, the gas molecules from the substrate would have a smaller velocity than the gas molecules traveling toward the substrate. This creates a driving force for YSZ clusters formed in

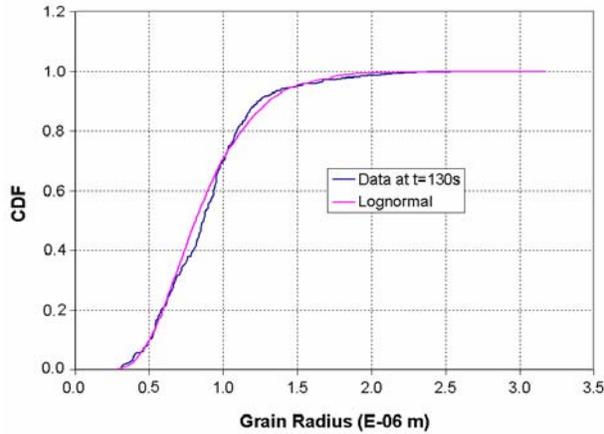


Figure 6. Illustration of accuracy of using an equivalent lognormal distribution for statistical characterization of initial grain size distribution.

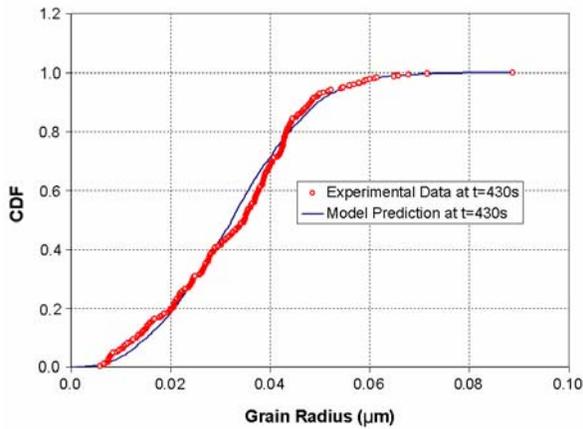


Figure 7. Comparison of model prediction with measured CDF data of grain radius at $t=430s$.

the direction toward the substrate. A larger temperature gradient adjacent to the substrate increases the thermophoresis effect. The study of the effect of thermophoresis was carried out by film depositions at different substrate-to-nuzzle distances from 51 mm (far into the flame) to 83 mm (out of the visible end of the flame). The film thickness measured on SEM images is plotted versus the substrate-to-nozzle distance in Figure 8 on a solid line. The data can be fit by an exponential equation. With an increase in the substrate-to-nozzle distance, precursor concentration in the flame will be attenuated because of the expansion of the flame. Normalization was done to eliminate the effect of concentration dilution on the film growth rate. The normalized thickness data were again plotted in the

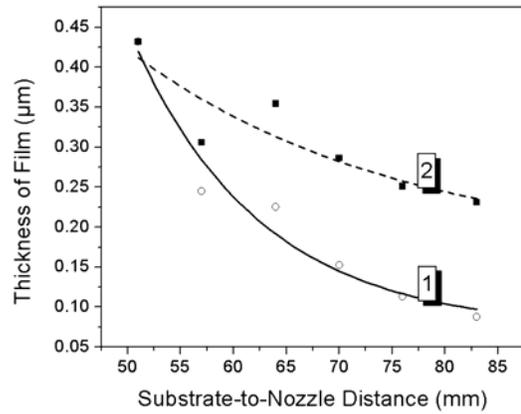


Figure 8. Film thickness as a function of the substrate-to-nozzle distance, line 1 for the original measured data, line 2 for the normalized data.

same graph of the originally measured data, as is shown in Figure 1 by curve 2 in the dashed line. It is apparently noticeable that after normalization, the growth rate of the film still follows the exponentially decaying mode with the substrate-to-nozzle distance. In other words, the parameter substrate-to-nozzle distance does play a role in film growth.

The effect of the metal concentration on the film growth rate is shown in Figure 9. Within the range of the concentration employed in our experiments, a linear relationship was obtained between the film growth rate and the concentration. By observing the morphologies of the samples, the films had well-crystallized and faceted particles as long as the metal concentration was less than 4.25×10^{-3} M. Beyond this limitation, the film was in a cauliflower-like structure.

Conclusions

According to the investigations we have performed, the CCVD technique has been demonstrated to be a promising method for film processing of YSZ electrolyte. Nucleation density can be improved by controlling the substrate temperature and the metal concentration appropriately. The analysis of the grain growth demonstrated that after the initial stage, the grain growth does not follow the lognormal mode. A stochastic model has been developed to predict the grain size in the film at any deposition time. The experiments confirmed the enhancement of the film

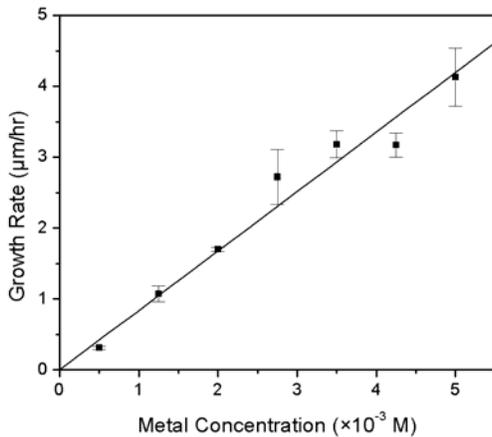


Figure 9. Film growth rate versus metal concentration in the liquid solution.

growth rates by employing the effect of thermophoresis and increasing the metal concentration.

References

1. S. P. S. Badwal, "Ceramic Superionic Conductors," p. 570 in *Materials Sciences and Technology, A Comprehensive Treatment*, R. W. Cahn, P. Haasen, and E. J. Kramer, eds., Vol. 11, 1994.
2. G. Garcia, J. Casado, J. Llibre, and A. Figueras, *J. Crystal Growth* **156**, 426 (1995).
3. S-C. Hwang and H-S. Shin, *J. Am. Ceram. Soc.* **82**(10), 2913 (1999).
4. U. B. Pal and S. C. Singhal, *J. Electrochem. Soc.* **137**, p. 937 (1990).
5. L. G. J. De Haart, Y. S. Lin, K. J. de Vries, and A. J. Burggraaf, *J. Eur. Ceram. Soc.* **8**(1), 59 (1991).
6. V. Y. Novikov, *Acta Mater.* **47**(18), 4507 (1999).
7. C. V. Thompson, *Annu. Rev. Mater. Sci.* **20**, 245 (1990).
8. W. Bai, K. L. Choy, N. H. J. Stelzer, and J. Schoonman, *Solid State Ionics* **116**, 225.

Publications

1. Z. Xu, J. Sankar, and S. Yarmorlenko, "Ytria-Stabilized Zirconia Coatings Produced Using Combustion Chemical Deposition," *Surface and Coating Tech.*, in print.
2. Z. Xu, C. Hilton, Bobby Watkins, Sergey Yarmolenko, and J. Sankar, "Thin YSZ Electrolyte Film Depositions on Dense and Porous Substrates", paper IMECE2003-43330, *2003 ASME International Mechanical Engineering Congress and RD&D Expo*, 2003.
3. Z. Xu, J. Sankar, S. Yarmolenko, and Q. Wei, "Nucleation And Growth of Ytria-Stabilized Zirconia Thin Films Using Combustion Chemical Vapor Deposition," pp. 509–514 in *Materials Research Society Symposium Proceedings*, Vol. 756, 2003.
4. Z. Xu, S. Yarmolenko, and J. Sankar, "Enhancement Of YSZ Thin Film Deposition Rate In CCVD," pp. 861–862 in *Proceedings of 10th International Conference on Composites Engineering*, New Orleans, July 20–26, 2003.