MODELING OF CHEMICAL VAPOR DEPOSITED ZIRCONIA FOR THERMAL BARRIER AND ENVIRONMENTAL BARRIER COATINGS

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INTRODUCTION

Thermal and environmental barrier coatings are important components of current and future energy systems. Such coatings – applied to hot, metallic surfaces in combustors, heat exchanger and turbines – increase the allowable operating temperature and increase the efficiency of the energy system. Because of its low thermal conductivity and high thermal expansion yttria-stabilized zirconia (YSZ) is the material of choice for protection of structural components in many high temperature applications. Current coating application methods have their drawbacks, however. Air plasma spray (APS) is a relatively low-cost process and is suitable for large and relatively complex shapes. It is difficult to produce uniform, relatively thin coatings with this process, however, and the coatings do not exhibit the columnar microstructure that is needed for reliable, long-term performance. The electron-beam physical vapor deposition (EB-PVD) process does produce the desirable microstructure, however, the capital cost of these systems is very high and the line-of-sight nature of the process limits coating uniformity and the ability to coat large and complex shapes.

The chemical vapor deposition (CVD) process also produces the desirable columnar microstructure and – under proper conditions – can produce uniform coatings over complex shapes. CVD has been used for many materials but is relatively undeveloped for oxides, in general, and for zirconia, in particular. The overall goal of this project – a joint effort of the University of Louisville and Oak Ridge National Laboratory (ORNL) – is to develop the YSZ CVD process for application of thermal barrier coatings for fossil energy systems. This report describes the modeling effort at the University of Louisville, which supports the experimental work at ORNL.

DISCUSSION OF CURRENT ACTIVITIES

Experimental investigation of the CVD process at ORNL uses a stagnation flow reactor, which is shown schematically in Figure 1and described in greater detail elsewhere in these proceedings. While the initial investigation used metal chloride precursors efforts over the past year have focused on metal-organic complexes of zirconium and yttrium as precursors for YSZ. These precursors offer the advantages of low gas-phase reactivity (They form films, not powders!), easy handling, commercial availability and documented success for deposition of a variety of oxide films. In particular, $Zr(tmhd)_4$ and $Y(tmhd)_3$, where tmhd = tetramethylheptanedionate, have been used to produce one-component

and multi-component oxides using a variety of reactor configurations. Control of precursor transport into the reactor is always an issue with these low volatility materials. At ORNL this is overcome by using direct liquid delivery of a solution of the mixed metal organic precursors in an organic solvent.

MODEL DESCRIPTION

Computer modeling research at the University of Louisville is being performed in order to provide understanding of transport and kinetics factors that control the deposition process and to develop a tool for reactor design and optimization. This research uses a commercial fluid dynamics code (CFD-ACE from CFD Research Corporation, Huntsville, AL) with an axisymmetric 3-D model for heat, momentum and mass transport throughout the reactor. Detailed reactor geometry and boundary conditions are set to match experiments at ORNL. Kinetics and transport parameters are derived from literature and from comparison to experiments at ORNL.

Figure 1 shows the reactor model used to simulate the ORNL reactor. The axisymmetric computational region includes the volume from the outer surfaces of the nozzle (inlet) to a position several centimeters downstream from the substrate surface. In the radial direction the model volume extends from the centerline of the reactor to the inner wall of the quartz reactor tube. All dimensions are set to match ORNL reactor dimensions. The computational volume is divided into 974 elements with a variable mesh as illustrated.

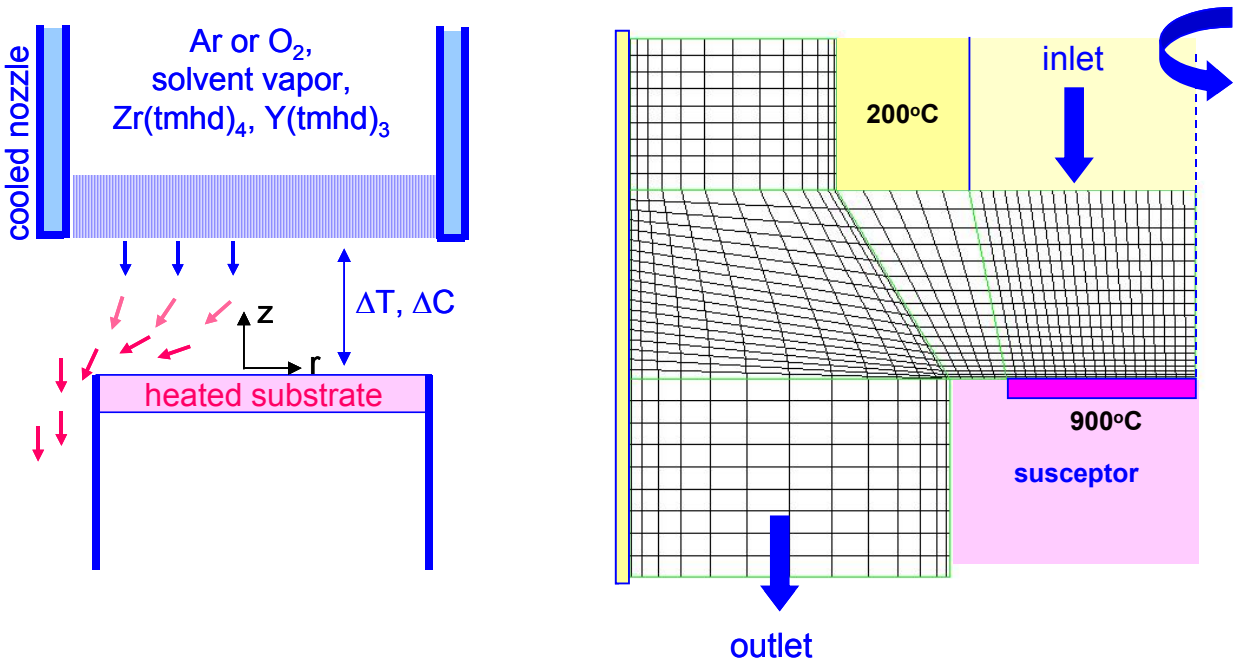

Figure 1. ORNL reactor (left) uses a stagnation point flow configuration. CVD model for this reactor uses a variable mesh and boundary conditions as shown (right).

Constant temperature conditions are used at all boundaries. The nozzle surfaces are set at 200°C, the controlled temperature of the oil-jacketed nozzle. The substrate and susceptor surfaces are set to the pyrometer-controlled temperature reported for a particular experiment. The outer wall temperature is 100°C, an estimate of actual temperature during a run.

Mass flow boundary conditions are "no-slip" at all solid surfaces, constant velocity across the inlet and "outflow" at the outlet boundary. Species transport boundary conditions are "zero-transport" for all species at the nozzle wall and outer wall, and constant concentration at the inlet. At the hot substrate and susceptor surfaces, the species transport in/out of the surface is determined by Arrhenius-type reactions, first-order with respect to the concentration of the precursor species at the surface.

$$Zr(tmhd)_4 \rightarrow ZrO_2(s) + \text{volatile species } (CO, C_2H_2)$$

$$2\ Y(tmhd)_3 \rightarrow Y_2O_3(s) + \text{volatile species } (CO, C_2H_2)$$

Rate constants and activation energies for both reactions are set to match literature[3] results by Pulver et al. for deposition of zirconia using low temperature (500-600°C) results.

Fluid properties - viscosity and thermal conductivity - are set using Sutherland's law constants and Prandtl number for oxygen provided in the CFD-ACE properties database. Mass diffusivities for all gas-phase species, except the precursors, are calculated using Chapman-Enskog theory from Lennard-Jones parameters in the database. Precursor diffusivities are based on values for the Lennard-Jones parameters that were determined from vaporization rate data[4].

MODEL RESULTS

Representative model results are shown in Figure 2. Boundary conditions are set to match ORNL experimental conditions for YSZ with 960°C substrate temperature, oxygen flow of 100 sccm, solution flow of 0.87 ml/min, solution of tetrahydrofuran (THF) with 0.040 g/ml precursor with Y/(Y+Zr) = 0.165. In the region between the inlet and substrate, fluid flow and temperature profiles closely match those expected for ideal stagnation point flow, i.e. temperature and x-velocity are independent of radial position and depend only on height above the substrate surface. Near the outlet, the flow approaches fully developed, parabolic flow. Very slight recirculation zones are formed in the annular region outside of the nozzle.

Precursor concentrations above the substrate are independent of radial position and show nearly complete depletion of the precursors at the surface for temperatures above approximately 650°C. Under these conditions, the deposition rate is controlled by the rate of diffusion across a mass-transport pseudo-boundary that is approximately 0.35 cm wide. Figure 3 shows the model-calculated deposition rate as a function of radial position. The rate is constant (+/- 0.7%) from the center of the substrate to a radius of about 1.0 cm. Beyond this radial position the deposition rate rises as the flow turns downward at the edge of the substrate holder. The yttria concentration in the film matches that in the mixed precursor solution. The average deposition rate predicted by the model is about twice that observed experimentally.

Figure 4 shows model results for deposition rate as a function of temperature for two different reactors: the ORNL reactor and the reactor used in reference 3. The latter is a cold-wall reactor with a heated substrate, similar to the ORNL reactor. The inlet gas is $Zr(tmhd)_4$ vapor carried by a mixture of argon and oxygen that impinges upon the flat substrate. For modeling this reactor, model boundary

conditions are based on reported process conditions and two assumptions about the velocity distribution at the inlet lead to somewhat different model predictions at higher temperatures.

DISCUSSION

The model-predicted deposition rate for both reactors increases with increasing temperature. The very good agreement between the model and the Pulver results at low temperature is a consequence of using those results to determine the surface reaction rate constants. There is a distinct change in slope at higher temperatures, which corresponds to the transition from surface-kinetics-limited to transport-limited conditions. For the Pulver results, the model-predicted rate is somewhat lower than experiment at higher temperatures. Pulver reports a maximum in deposition rate at 650^{o}C with a slight decrease at 680^{o}C, attributed to mass transport resistance and gas phase reactions.

For the ORNL reactor the experimental deposition rate is less than half that predicted by the model and 25% of the Pulver maximum deposition rate. The reason for these differences is not clear. The concentration of precursor in the gas phase is higher in the ORNL reactor than in the Pulver reactor. At the ORNL temperature (960^{o}C) the surface kinetics are very fast. However, at this temperature the precursor may pyrolyze in the gas phase forming non-reactive species and/or powders. Additional investigation of these discrepancies is needed.

FUTURE WORK

The YSZ model shows reasonably good match to experimental results for this simple reactor and substrate geometry. Future work will include refinement of the model to improve prediction of deposition rate, exploration of methods to increase the experimental deposition rate and incorporation of realistic turbine vane geometry into the model.

For reactor conditions that produce high deposition rates, gas phase transport – rather than surface kinetics – is always the limiting and controlling factor. While the present model includes full, multi-component transport there is some uncertainty about the values of key diffusion constants, particularly for the precursor species. Also, gas phase reactions are not included in the current model and these may be important at high temperature. Model refinements will be evaluated by comparison to future experiments at ORNL. Current results for YSZ are limited to one set of process conditions. Additional runs with different temperatures, precursor concentrations and flow conditions will guide model development.

High deposition rate is desirable for a commercial CVD process. Previous studies and these modeling results clearly show that gas phase mass transport is the limiting factor at high deposition rates. Under these conditions the gas phase concentration of the precursor at the inlet and the mass diffusivity of the precursor are rate-controlling factors. With the ORNL reactor the gas phase concentration is limited by the choice of precursor and its solubility in the selected solvent for the direct liquid delivery system. Additional precursor-solvent combinations will be evaluated to identify combinations that will provide increased gas phase precursor concentration in the reactor. The gas phase mass diffusivity of a molecular species depends on its molecular weight and size and on the characteristics of the other species in the mixture. Candidate precursor-solvent combinations will be evaluated with respect to increasing the diffusion rate of precursor to the surface.

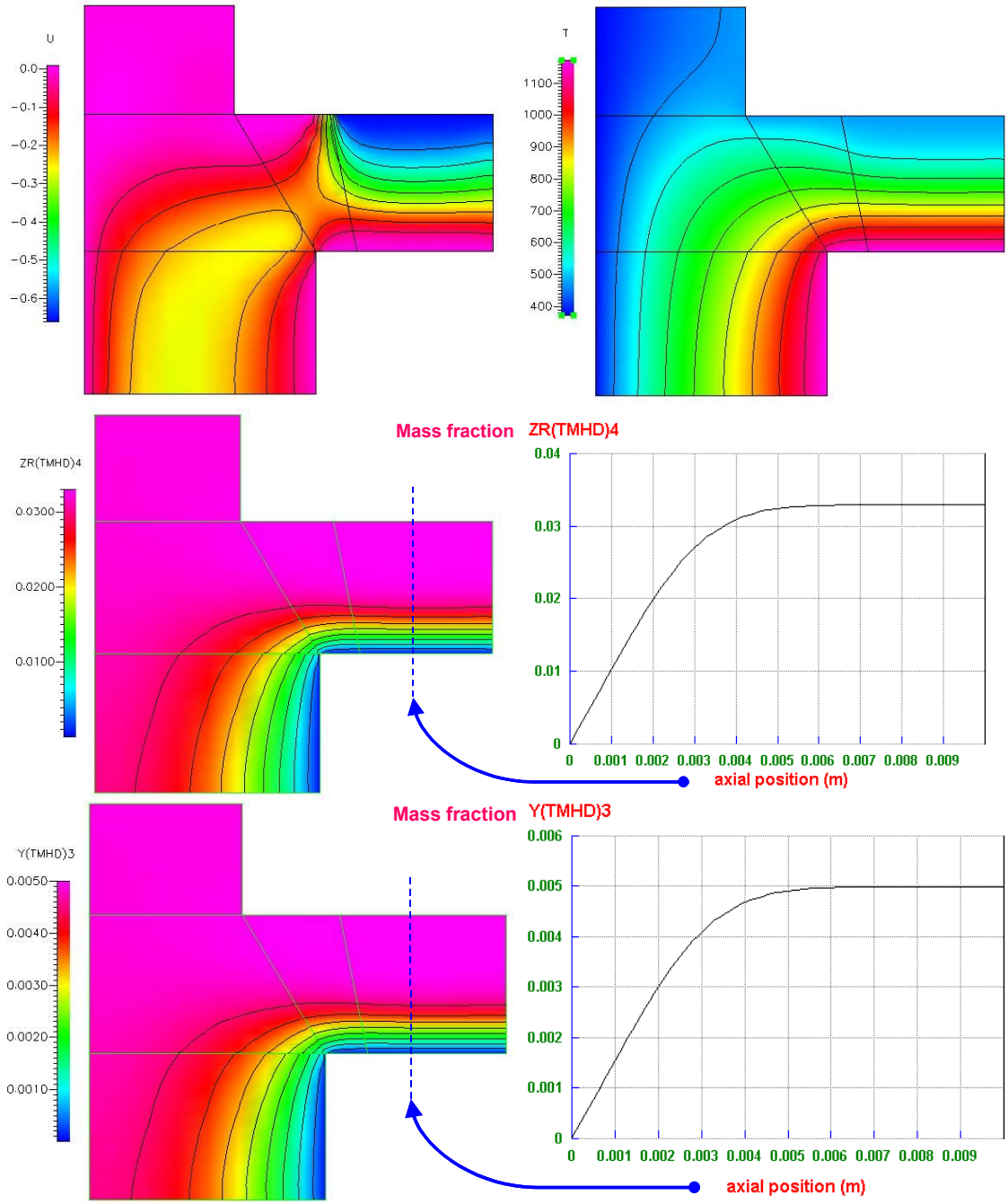

Figure 2. Axial velocity (top left) and temperature (top right) are independent of radial position near the center of the reactor. Depletion of $Zr(tmhd)_4$ (middle) and $Yr(tmhd)_3$ (bottom) at substrate indicates that deposition rate is limited by diffusion across a mass transfer boundary of approximately 3.5 mm width.

The ultimate goal of this research program is to develop a precise tool for design of a CVD reactor for applying a thermal barrier coating to fossil energy system components. With success in modeling the simple ORNL stagnation point flow reactor, the next step is to incorporate realistic turbine vane geometry into the model and use the model to explore reactor modifications that produce desirably uniform YSZ coatings.

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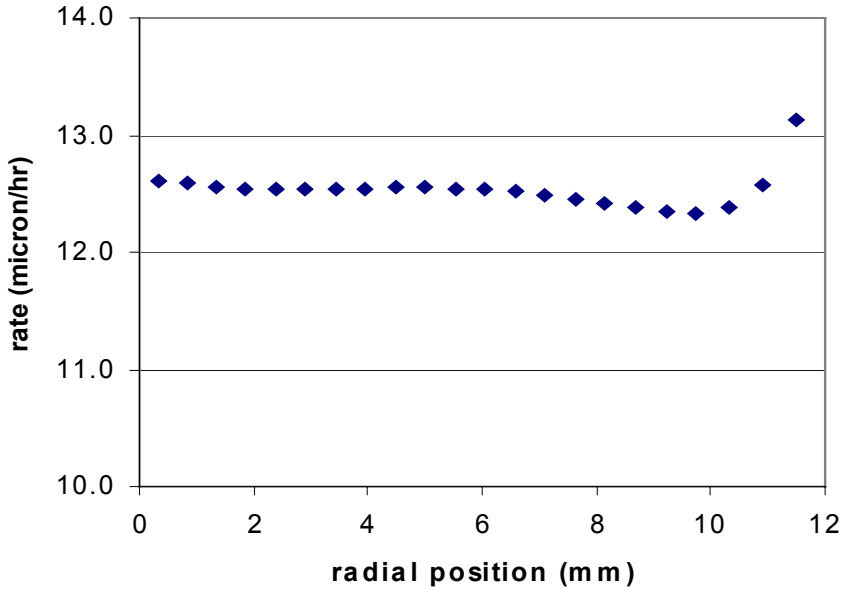

Figure 3. Model predicts uniform deposition rate (+/- 0.7%) within 1.0 cm of the center of the substrate. For these conditions, ORNL observed a deposition rate of 4.7 micron/hr.

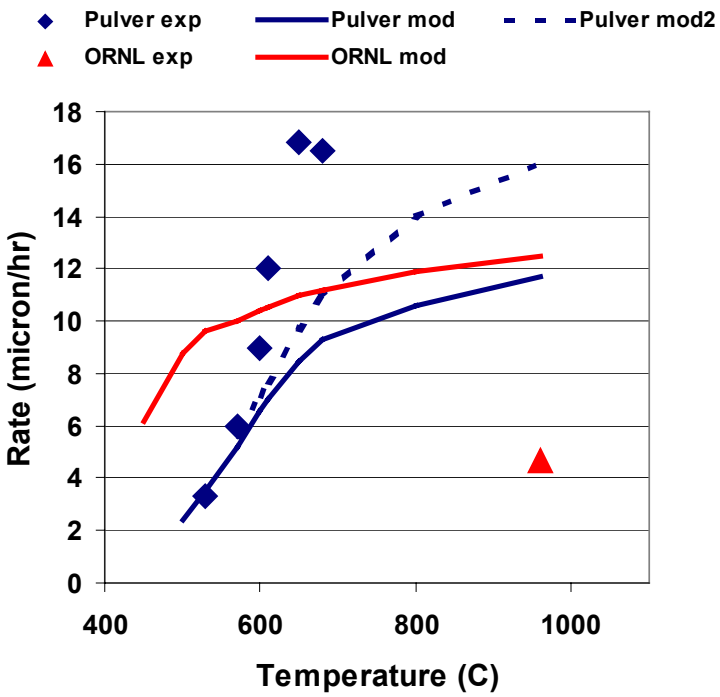

Figure 4. Surface reaction rate is based on Pulver (reference 3) low temperature results. At high temperature, deposition is limited by mass transport.