

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

Thomas L. Starr

Chemical Engineering Department, University of Louisville, Louisville, KY 40292
E-mail: tom.starr@louisville.edu; Telephone: (502) 852-1073; Fax (502)852-6355

Weijie Xu

Chemical Engineering Department, University of Louisville, Louisville, KY 40292
E-mail: wjx243@yahoo.com; Telephone: (502) 852-2648; Fax (502)852-6355

Shenghong Qiu

Chemical Engineering Department, University of Louisville, Louisville, KY 40292
E-mail: qshenghong@yahoo.com; Telephone: (502) 852-2648; Fax (502)852-6355

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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. 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. Last year's report described our initial efforts toward developing a model for the process and for ORNL's bench-scale reactor. This model provides an understanding of the transport and kinetics phenomena that control the deposition process and ultimately will provide a tool for full-scale reactor design and optimization. Our overall research approach is: validate the 3-D computer model using experimental results at ORNL, use the model to identify and evaluate potential process improvements and design a reactor for large and complex substrates. This report describes the modeling effort at the University of Louisville which supports the experimental work at ORNL.

DISCUSSION OF CURRENT ACTIVITIES

Progress over the past year includes refinement of the computer model to match experimental results at ORNL over the full range of process temperatures and pressures. This refined model provides understanding of the factors that limit the deposition rate in the direct-liquid-injection CVD process. With this understanding we identified a new precursor solution and this was used at ORNL to produce high quality coating and high coating deposition rate. Finally, we initiated design of a reactor for uniform coating of a full-scale turbine blade.

MODEL REFINEMENT

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. Details of the reactor geometry and reactor simulation model were given in the previous report¹. Figure 1 shows a schematic of the reactor and model.

Many variables in the model are determined by experimental parameters of the reactor. Vapor composition and gas flow rate, substrate and nozzle temperatures, pressure and geometry are experimentally set and determine the boundary conditions for the model. Physical parameters of the materials and fluids in the model, such as viscosity, thermal conductivity and species diffusion

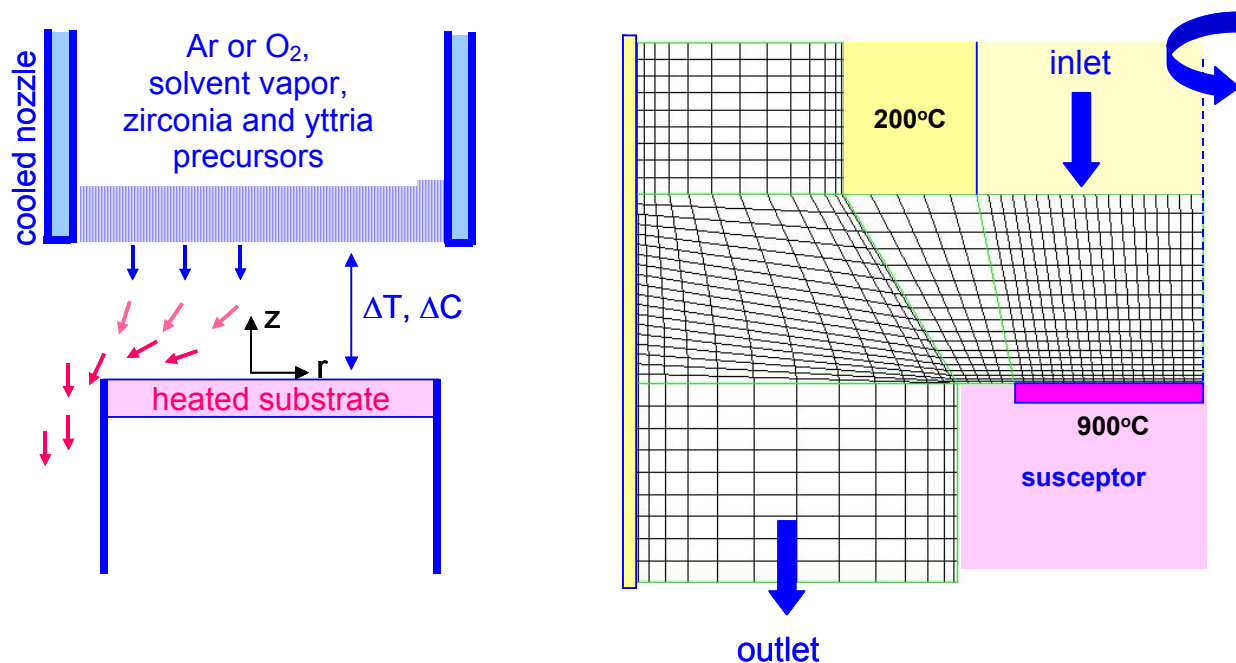


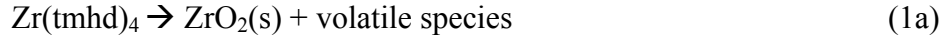
Figure 1. ORNL reactor (left) uses a stagnation point flow configuration. CVD model for this reactor uses a variable mesh and boundary conditions as shown (right).

coefficients, are known from measurement or from well-established estimation methods. The principal uncertainty in the model is specification of the chemical reactions that lead to deposition of solid YSZ on the substrate.

Initial experimental efforts at ORNL used metal-organic zirconia and yttria precursors where the organic part is tetramethylheptanedionate (tmhd). These precursors are commonly used in CVD processing because of their good stability in the vapor phase. They can produce good quality metal oxide coatings but control of the coating composition and maintenance of high coating rate is difficult due to difficulty in controlling the vaporization rates of the solid precursors. The direct-liquid-injection CVD process avoids this difficulty by dissolving the precursors in the correct proportion in a compatible solvent and metering this liquid solution into the reactor. Experiments at ORNL used $Zr(tmhd)_4$ and $Y(tmhd)_3$ dissolved in tetrahydrofuran (THF).

Chemical reactions important for this process may include gas-phase and gas-surface reactions. As previously reported¹ a simple gas-surface reaction model matches experimental results at low temperature but overestimates the reaction rate at higher temperatures where the deposition rate is limited by transport from the gas phase to the surface. Also, more recent experimental results at higher pressure show a decrease in deposition rate at high temperature which cannot be matched by a simple gas-surface reaction model.

Our refined model includes three types of reactions. At the solid surface zirconia and yttria deposition rates are given by Arrhenius-type reactions, first-order with respect to the concentration of the precursor species at the surface.

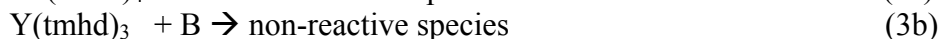
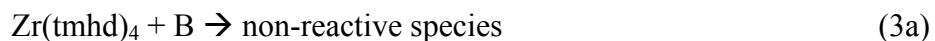


A second type of reaction involves pyrolysis of the solvent at the substrate surface, again represented by an Arrhenius-type reaction, first-order with respect to the concentration of the solvent at the surface.



While the actual pyrolysis of THF is certainly more complex than (2) the essential feature of this reaction is the production of three moles of gas from one mole of THF. Other possible pyrolysis reactions will produce similar numbers of moles of gas. This additional gas production at the surface has the effect of diluting the precursor concentration and reducing the deposition rate.

A third type of reaction is gas phase decomposition of the precursor to form non-reactive species. This reaction is pressure dependent since it depends on collisions with other gas-phase species (B).



Rate constants and activation energies for these reactions are selected to best fit the experimental results.

Experiment and refined model results are shown in Figures 2 and 3. Model boundary conditions are set to match ORNL experimental conditions for YSZ with nozzle temperature of 200°C, a range of substrate temperatures, oxygen flow of 100 sccm, solution flow of 0.87 ml/min, solution of tetrahydrofuran (THF) with 0.040 g/ml precursor with $Y/(Y+Zr)=0.165$.

Model results show that, 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 axial 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 near 90% depletion of the precursors at the surface for temperatures above approximately 930°C. Under these conditions, the deposition rate is controlled by the rate of diffusion across a mass-transport pseudo-boundary that is approximately 0.6 cm wide.

The model-predicted deposition rate matches experimental results reasonably well over the full range of temperature and pressure. At low temperature the surface reactions, (1a) and (1b), control the deposition rate. At higher temperature the rate is controlled by transport and solvent pyrolysis dilutes the gas phase concentration of precursor. At higher pressure gas phase reactions deplete the precursor and produce a decreasing deposition rate with increasing temperature.

Pyrolysis of the THF solvent has a significant effect on the maximum achievable deposition rate. This “solvent effect” on CVD rate in direct liquid injection has not been recognized previously. The exact decomposition path likely involves many gas-phase and surface reactions, and is unknown. Our assumption represents a limiting case for solvent pyrolysis. It

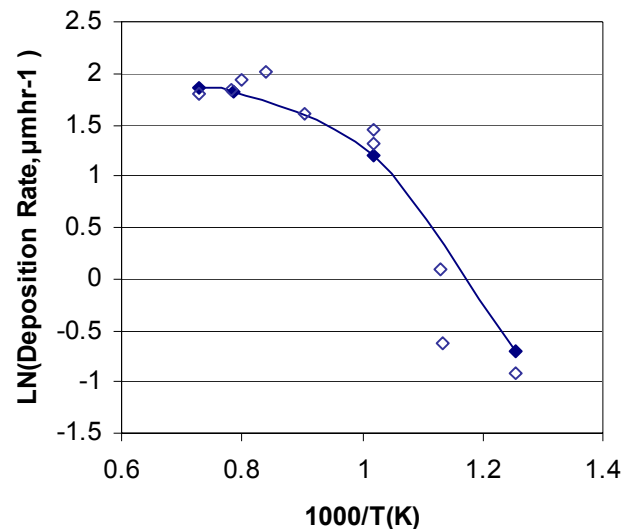


Figure 2. Experiment (solid symbol) and model (open symbol) deposition rate at low pressure (7 torr).

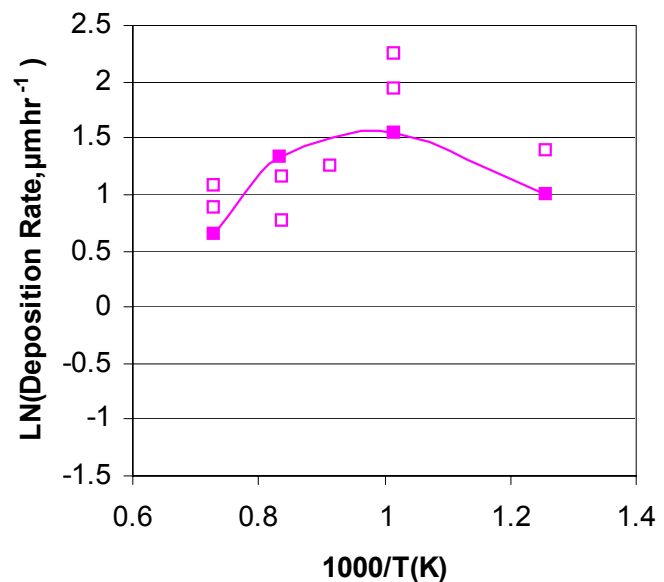


Figure 3. Experiment (solid symbol) and model (open symbol) deposition rate at high pressure (70 torr).

assumes that ALL solvent molecules reaching the surface react to form small, stable products. Again, neither the exact mechanisms of this reaction nor the distribution of products is known. However, stoichiometry places limits on the **total** moles of gaseous product that can be produced from one mole of solvent. For THF this limit is three and equation (2) builds this limit into the model.

INCREASING YSZ DEPOSITION RATE

The maximum deposition rate observed with the combination of tmhd precursors and THF solvent is approximately 7 $\mu\text{m/hr}$. While increasing pressure increases the low temperature deposition rate, it does not increase the rate in the transport limited regime. The model shows that this is due to two effects. First, increasing the pressure (with constant volumetric flow) reduces the linear velocity of the gas and increases the width of the mass transport boundary layer. Second, increasing pressure increases gas phase reactions with the precursors, (3a) and (3b).

The model suggests two methods for increasing the maximum deposition rate: increasing the volumetric flow rate and increasing the gas phase concentration. Increasing the flow is not recommended. First, there is a square root relationship between flow rate and deposition rate, i.e. doubling the deposition will require quadrupling the flow. Also, increasing the flow will reduce the mass efficiency of the process, i.e. a smaller fraction of the precursor will be used to produce coating.

The second method for increasing the deposition rate is to increase the gas phase concentration of precursor. With liquid injection CVD the solvent vapor is the major gas phase species and the concentration of precursor in the gas phase is directly related to the concentration in the liquid solution and to the pyrolysis characteristics of the solvent. The THF solution used in the previous experimental work is near the solubility limit for tmhd precursors and higher deposition rate cannot be achieved with this combination of precursor and solvent.

The recommended method for increasing deposition rate is to increase the liquid solution precursor concentration. As a demonstration of this approach we proposed a demonstration experiment using commercially available solutions of zirconium n-butoxide in butanol (76%) and yttrium n-butoxide in toluene (0.5M). A initial deposition run at ORNL using a mixture of these two solutions yielded a deposition rate of approximately 30 $\mu\text{m/hr}$ and good columnar grain structure (Figure 4) even though there was significantly clogging of the nozzle during the run. This initial experiment confirms the value of this approach and future efforts will include

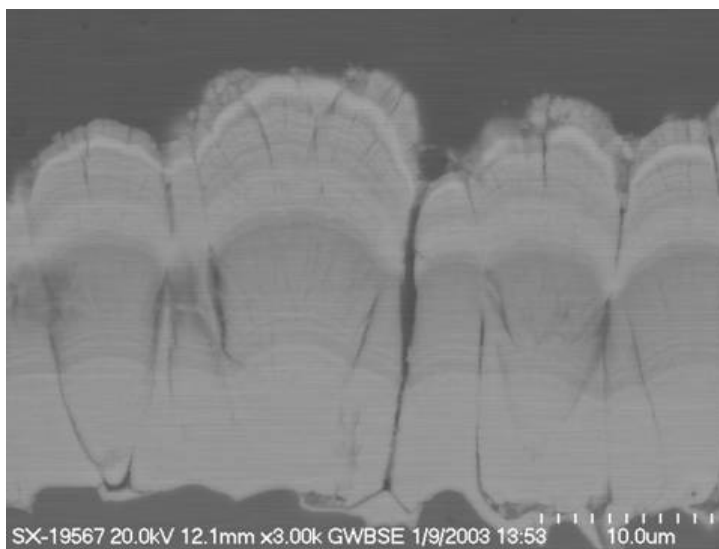


Figure 4. Initial experiment with alkoxide precursor yielded good quality coating and high deposition rate.

systematic review of other solvents and precursors to achieve the optimum combination. The use of liquid injection method offers the potential for using precursors that may not be suitable for vapor phase precursor delivery.

FULL-SCALE TURBINE BLADE

The geometry of a blade for a typical industrial gas turbine is shown in Figure 5. The overall length and width of such a blade is approximately 40 cm by 12 cm. At high deposition rates modeling shows that coating uniformity cannot be controlled simply by controlling substrate temperature but also depends on the gas flow pattern from inlet to outlet. The refined model can be used to investigate alternative CVD reactor designs and compare them based on predicted coating. An example of this use

is shown below. Figure 6 shows cross-sectional views of two possible reactor designs with somewhat different inlet configurations. The top design has a relatively narrow inlet nozzle with equal flows impinging onto the top and bottom blade surfaces similar to that in the ORNL bench-scale reactor. The second design is similar but includes a three-part inlet nozzle, top and bottom, with different flow rates. Model predicted deposition rates (Figure 7) for the two designs are different. The initial design yield large variations in deposition across both surfaces and from top to bottom. The second inlet design produces significantly better uniformity. This example illustrates how the model will be used for in future reactor design.

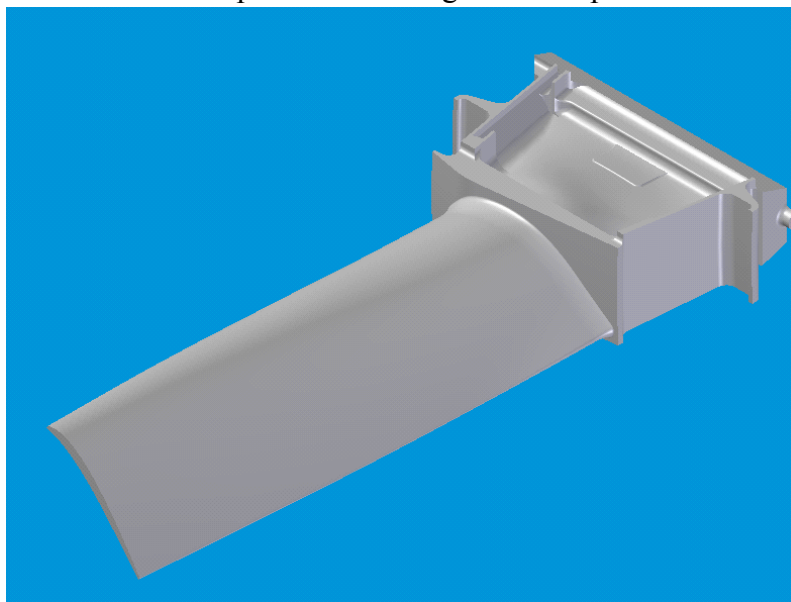


Figure 5. Actual gas turbine blade has complex, 3-D curvature.

CONCLUSIONS

The refined CVD model matches experimental results over a range of temperature and pressure conditions. Experimental work at ORNL confirms the model prediction of improved deposition rate using an alkoxide precursor solution. Future work will included detailed review of precursor and solvent options and selection of an optimum combination. With success in modeling the ORNL 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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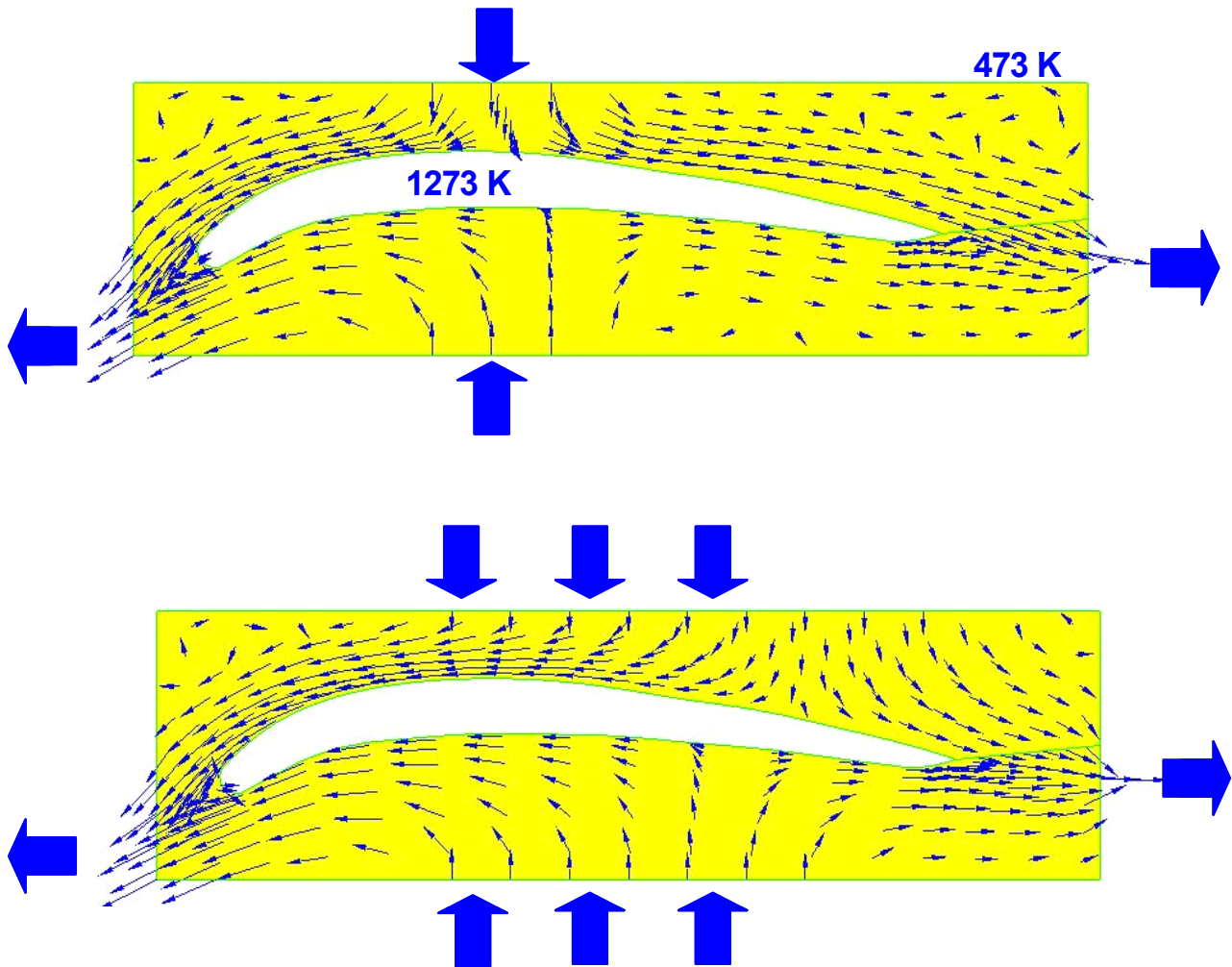


Figure 6. Two possible designs for blade coating system are shown. Top design includes single inlets top and bottom. Bottom design has three-part inlets with different flow rates.

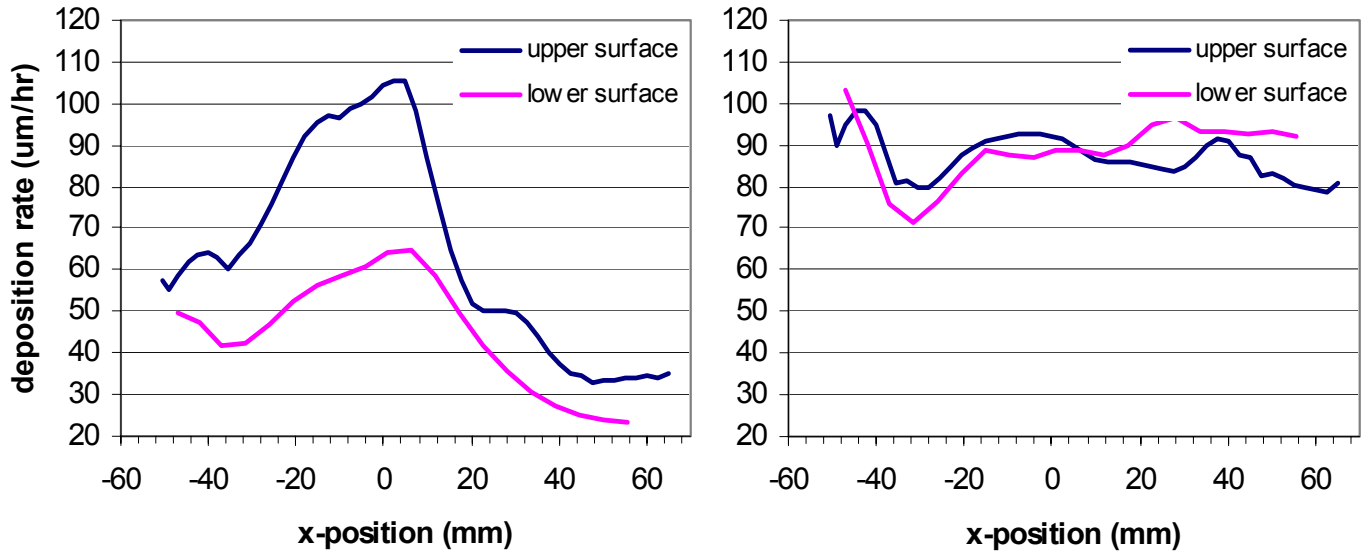


Figure 7. Model-predicted deposition rate for simple inlet (left) and three-part inlet (right) designs show strong effect of gas flow pattern on coating uniformity.