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

August 15, 2003

Report Prepared by

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under

UT-Battelle subcontract 4000016368

for

OAK RIDGE NATIONAL LABORATORY

Oak Ridge, Tennessee 37831

Managed by

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for the

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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. With air plasma spray (APS) it is difficult to produce uniform coatings 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 suffers from high capital cost and its line-of-sight nature limits coating uniformity and the ability to coat large and complex shapes.

The chemical vapor deposition (CVD) process 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. A previous report¹ described initial efforts toward developing a model for the process and for ORNL's bench-scale reactor. The 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. This report describes continuing progress over the period October 1, 2002 to September 30, 2003 toward two milestones: increasing the CVD coating rate and coating of complex turbine blade geometries.

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TECHNICAL APPROACH

Our previous work demonstrated that detailed modeling of the CVD process can provide insight into the fundamental mechanisms that control the deposition process. The research effort described in this report involves using the model to identify methods for increasing the coating deposition rate and to design a prototype reactor for uniform coating of a turbine blade shape. Since increasing the coating deposition rate like will require evaluation of different organo-metallic precursors, we also developed an experimental method to investigate the vaporization behavior of these materials

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. Initial experiments at ORNL used $Zr(tmhd)_4$ and $Y(tmhd)_3$ dissolved in tetrahydrofuran (THF). The maximum deposition rate observed at ORNL with this combination precursors and solvent was approximately 7 $\mu\text{m/hr}$, which is considered too low for application of relatively thick (50-200 μm) thermal barrier coatings.

Our approach to increasing the deposition rate is to use the CVD model to test the effect of changes in process parameters – such as pressure, temperature and gas flow rate – prior to experimental evaluation at ORNL. By identifying the most promising approaches experimental development of the process can proceed more quickly. Since our initial modeling results identified precursor vapor pressure as a critical element in controlling the deposition rate, we added an experimental effort to measure this property for YSZ precursors.

The ultimate goal of this research program is development of a process that will economically and effectively coat complex three-dimensional shapes such as gas turbine blades and vanes. Initial

experimental efforts at ORNL demonstrated uniform coating over a flat substrate with a simple impinging jet inlet. Extension of this result to more complex shapes likely will require careful control and positioning of vapor inlet and outlet. Our CVD model was used to explore design options for a turbine blade geometry and to identify coating thickness variations for these designs.

RESULTS

This section discusses results of modeling investigation of methods to increase the CVD coating rate, development of a method for measuring precursor vapor pressure and preliminary design of a turbine blade coating system.

INCREASING YSZ DEPOSITION RATE

In general, CVD processes are controlled by substrate temperature, reactor pressure and inlet gas flow rate and composition. Prior experimental results at ORNL indicated rapid increase in deposition rate as temperature increased up to approximately 1000 °C². Beyond this, the deposition rate increased only slowly and eventually decreased. Model results show this effect as a transition from a surface reaction limit to a mass transport limit. At high temperature the deposition rate is limited by the rate at which the precursor molecules diffuse to the surface from the bulk gas phase. This diffusion rate increase only slowly with increasing temperature. Also, at the high temperature the precursor starts to decompose in the gas phase, reducing the deposition rate. Experiment also shows that increasing the system pressure increases the low temperature deposition rate, however, it does not increase the rate in the high temperature, “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. These effects combine to limit the effectiveness of increasing pressure as a means for increasing the deposition rate.

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 1)

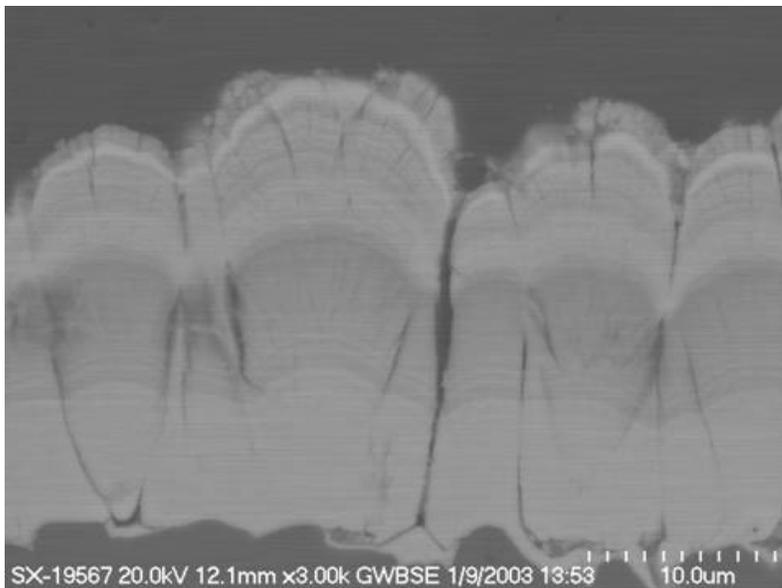


Figure 1. Initial experiment with alkoxide precursor yielded good quality coating and high deposition rate.

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 systematic review of other solvents and precursors to achieve the optimum combination.

MEASURING PRECURSOR VAPOR PRESSURE

The use of liquid injection method offers the potential for using precursors that may not be suitable for vapor phase precursor delivery. Even with liquid delivery the precursor vapor pressure must be high enough to avoid condensation in the inlet nozzle prior to transport to the substrate. Vapor pressure data for many potential precursors is unavailable and must be measured.

Our method for measuring precursor vapor pressure is based on thermogravimetric (TGA) detection of vaporization (boiling or sublimation) temperature at a series of pressures^{3,4}. The TGA method uses a sample of material placed in a sealed capsule with a laser-drilled hole in the top. Rapid weight loss occurs when the material reaches its boiling or sublimation temperature. This temperature is determined at a range of pressures. The extrapolated onset temperature for rapid weight loss is taken as the temperature at which the equilibrium vapor pressure of the material corresponds to the pressure maintained by the TGA system. The accuracy of this method has been confirmed over the pressure range from 40 to 760 torr (5.3 to 101 kPa) by comparison with previously published data^{5,6}.

This method was implemented using a TA Instruments Model 2950. A simple vacuum system (Figure 2) produced sub-ambient pressures. An argon purge flow was maintained by the mass flow controller (MKS type 259B) at 150 sccm, following TA Instruments recommendations. A pressure transducer (MKS Baratron model 225A) was employed to monitor the system pressure. The laser-drilled aluminum capsules were obtained from Perkin-Elmer (Part No. B016-9316). The drilled holes were approximately 0.05 mm diameter. Typically, 5-8 mg samples were sealed in the 50 μ L pans. The pressure was maintained at the desired pressure ± 1.0 torr by the manually controlled needle valve. The heating rate was set at 30°C/min.

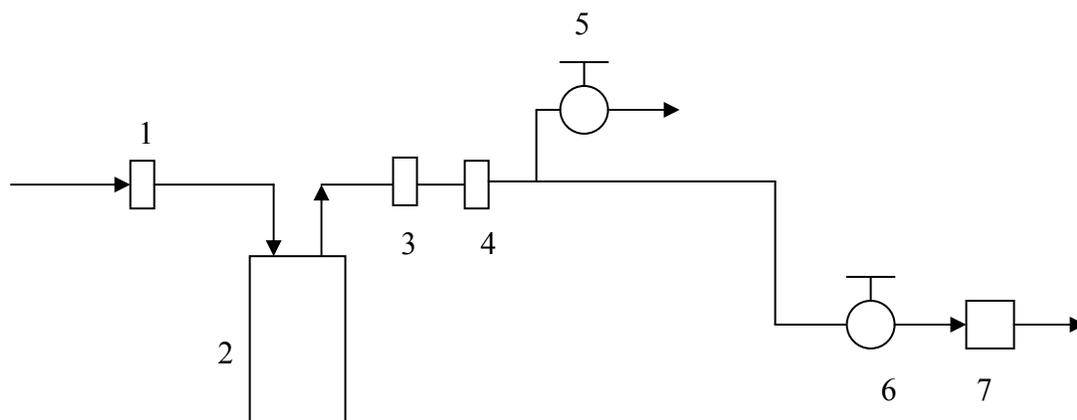


Figure 2. Schematic of Vacuum System. (1) Mass Flow Controller, (2) TGA, (3) Cold Trap, (4) Pressure gage, (5) Valve, (6) Needle Valve, (7) Mechanical Pump

To check the accuracy of this method, myristic acid (C₁₄H₂₈O₂) was employed as a reference material.

Figure 3 shows a typical TGA plot.

The onset temperature was estimated by extrapolating the tangent of the beginning part of derivative curve.

The initial base line was steady which suggests that there was no

decomposition before the vaporization

point was reached. Vaporization temperatures for myristic acid at three different pressures by the TGA method are shown in Table 1. Also shown are values extrapolated from reference sources^{7, 8, 9} using the Clausius-Clapeyron equation:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap} (T_2 - T_1)}{R T_2 T_1}$$

where P is the pressure and T is the temperature in Kelvin.

The vaporization temperatures obtained from the TGA method are somewhat higher than those calculated from the references. This may be due to error in extracting the onset temperature from the differential weight loss curve. The onset of weight loss is not perfectly sharp (Figure 3) and the linear extrapolation method will tend to overestimate the onset temperature. Also, the difference in temperatures from different reference sources indicates some uncertainty in the reference values.

ΔH_{vap} is calculated from a linear fit to the log-pressure vs. 1/T plot. The enthalpy of vaporization is in good agreement with the reference values.

Table 1. TGA and reference data for myristic acid

Pressure (torr)	Boiling temperature (°C)		
	Ref. 7	Ref. 8,9	TGA
760	297	304	318
105	244	251	262
58.5	229	237	235
ΔH_{vap} (kJ/mol)	86	94	89

Sample: M-Acid
Size: 70.0420 mg

TGA

File: D:\Data\TGA\qiu8.008
Operator: Shenghong Qiu
Run Date: 1-May-03 15:45

Comment: Ramp 80°C to 500°C, Iso 10 min,

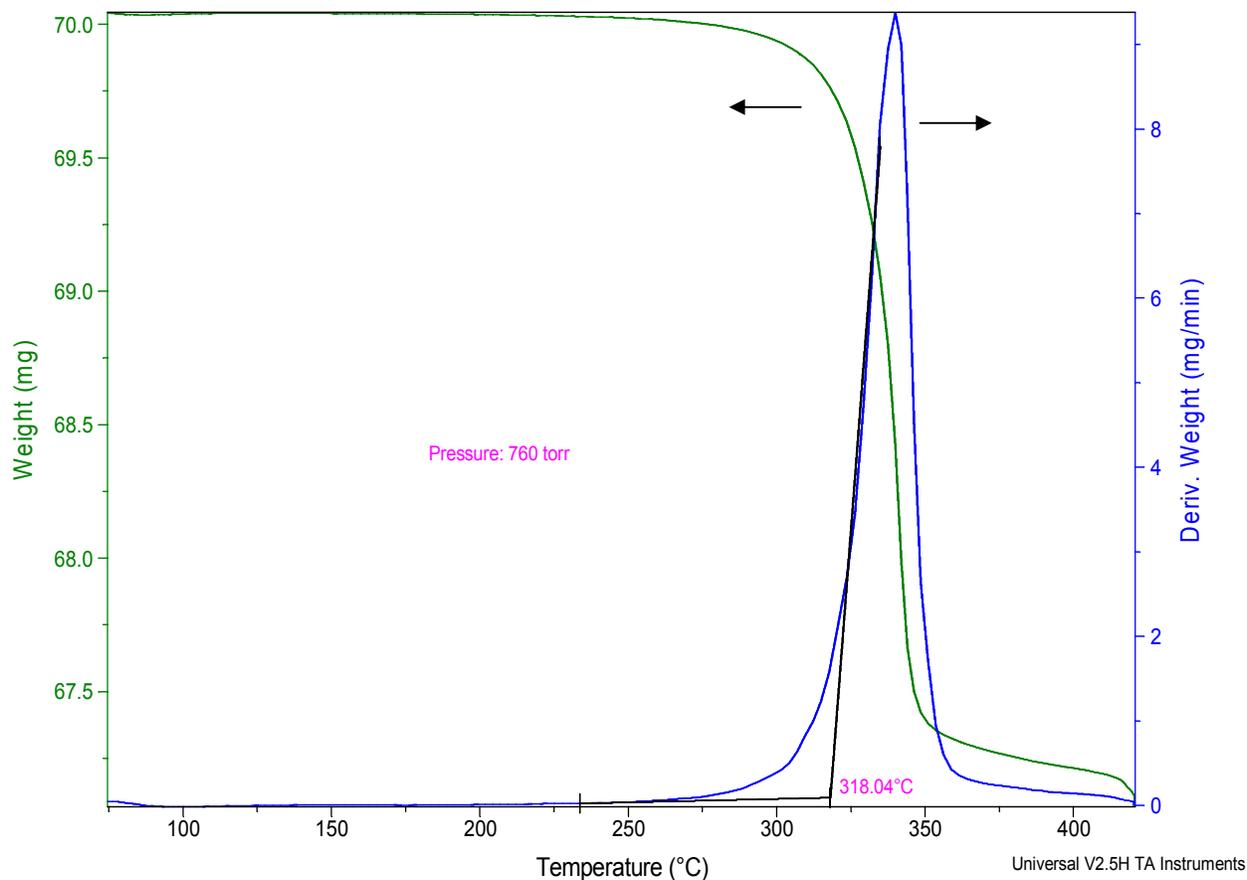


Figure 3. DTA curve for myristic acid at 760 torr system pressure.

The vapor pressures for $\text{Zr}(\text{tmhd})_4$ and $\text{Y}(\text{tmhd})_3$ were measured using the TGA method. All the weight-loss curves were simple and sharp with no second thermal transitions, i.e. no thermal decomposition was observed prior to complete vaporization. The Table 2 shows the experimental vaporization temperatures and derived ΔH_{vap} . Review of the literature reveals limited vapor pressure data for $\text{Zr}(\text{tmhd})_4$ and $\text{Y}(\text{tmhd})_3$. A recent paper¹⁰ compiles results from several studies and for materials from different suppliers over the temperature range 160 to 250 °C. These data are plotted with TGA-method results in Figure 4. Although all of the TGA data is take at significantly higher

temperature, these results are consistent with the lower temperature literature results. This agreement confirms both the TGA method and the good stability of tmhd precursors at relatively high temperatures. Future work will include determination of vapor pressure data for the zirconium and yttrium n-butoxides use in recent ORNL runs. These measurements should clarify whether nozzle clogging problems experienced with these precursors is due to low vapor pressure or to premature decomposition. Vapor pressure data will be measured for other precursors as these are evaluated in the future.

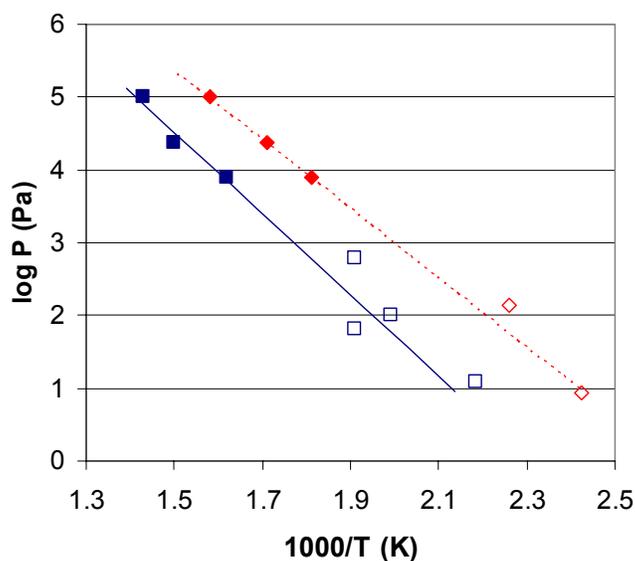


Figure 5. TGA-method vapor pressure data are consistent with ref. 10. Squares are Zr(tmhd)4 and diamonds are Y(tmhd)3. Filled symbols are TGA data. Open symbols are from reference. Lines are best fit to TGA data.

Table 2. Vapor pressures data for Zr(tmhd)4 and Y(tmhd)3

Pressure (torr)	Vaporization Temperature (°C)	
	Zr(tmhd)4	Y(tmhd)3
760	427	360
182	394	312
61	345	279
ΔH_{vap} (kJ/mol)	100	90

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 rate, 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

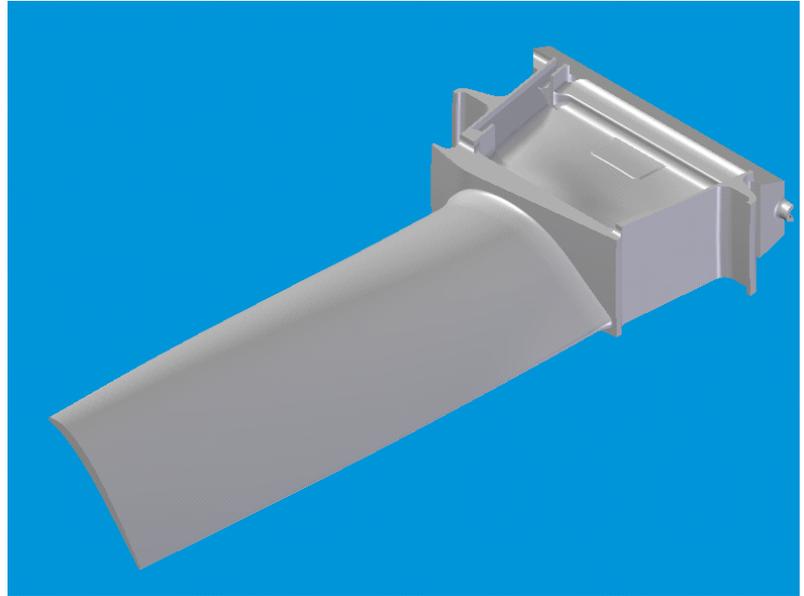


Figure 5. Actual gas turbine blade has complex, 3-D curvature.

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.

FUTURE WORK

The ultimate goal of this research effort is experimental demonstration of the CVD process for deposition of thermal barrier coating on a full-scale gas turbine blade. In order to reach this goal additional research is needed to identify an optimized precursor solution, to investigate the relation between coating microstructure and process conditions, and to complete design and testing of a full-scale turbine blade coating system.

As discussed above the composition of the YSZ precursor solution is the critical factor in producing high deposition rate with a liquid-delivery CVD process. The use of a liquid solvent carrier offers several advantages for CVD processing: simple and reliable metering of precursor delivery, precise control of zirconia/yttria ratio and use of a wide variety of precursor compounds, i.e. compounds that are not stable under vapor-delivery conditions. While the combination of zirconia n-butoxide and yttria n-butoxide yielded good YSZ coating and an improved deposition rate, many other combinations of precursor and solvent are possible. Full-scale commercial adoption of this process will require an optimized combination based on consideration of many factors, including process performance, handling characteristics, safety, waste, cost and availability.

The microstructure of thermal barrier coatings is critical to their success. Previous research and industrial practice suggest that this microstructure should include oriented grain boundaries or other “defects” that will inhibit heat flow through the coating and an overall columnar structure that can accommodate thermal strains parallel to the coating. While initial coatings at ORNL show reasonably “good” microstructure it is not clear if this is optimized or how the microstructure relates to process conditions. Better understanding of microstructure/processing relationships is needed for scale-up of the CVD process.

Current design and modeling work has demonstrated the feasibility of controlling deposition rate on a turbine blade geometry through control of inlet and outlet locations and variation of gas flow rates. A detailed design for a full-scale turbine blade must incorporate additional system details and full 3-D geometry.

ACKNOWLEDGEMENT

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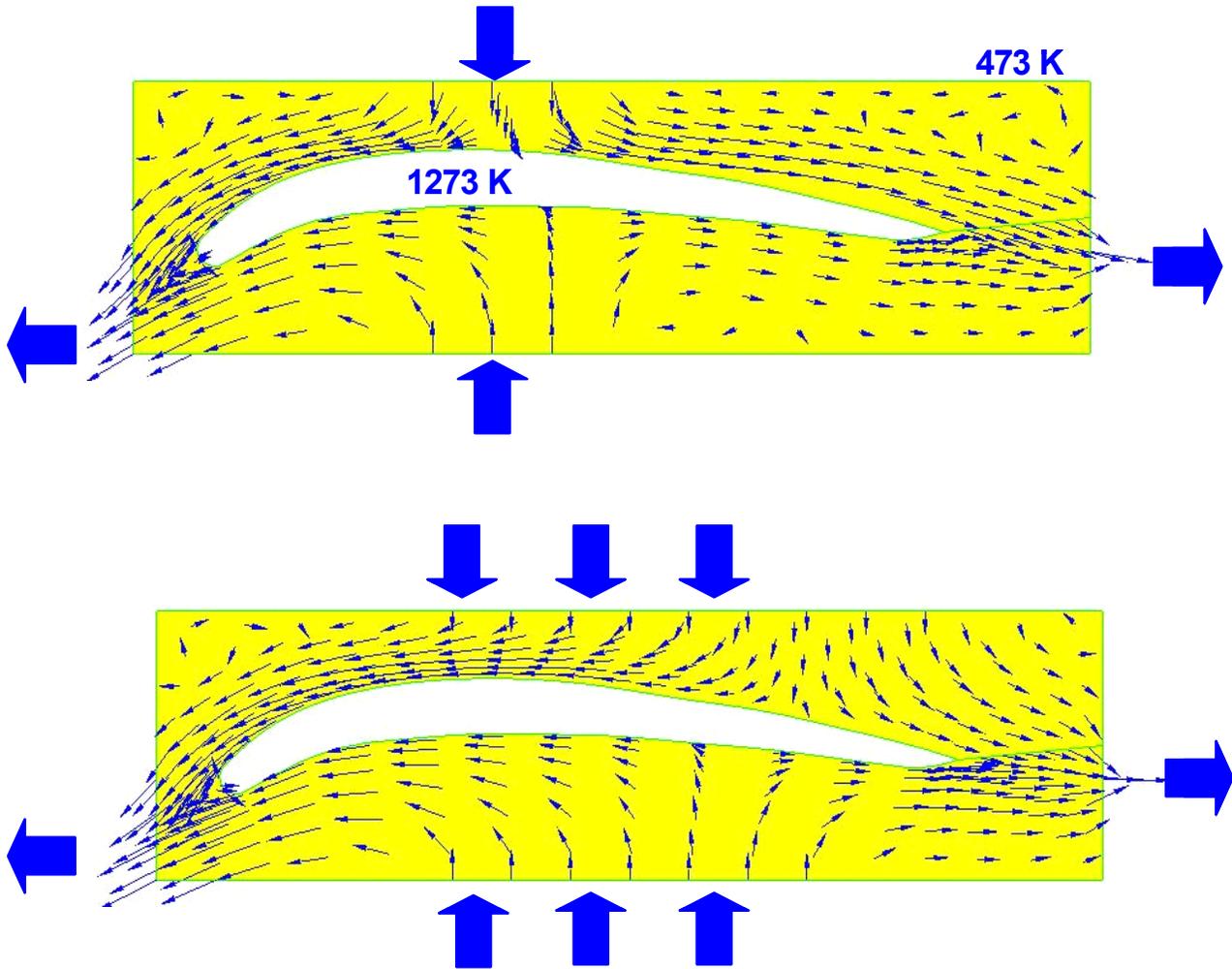


Figure 6. Two possible designs for blade coating system are shown. Top design includes single inlets top and bottom. Bottom design has three-part inlets with different flow rates.

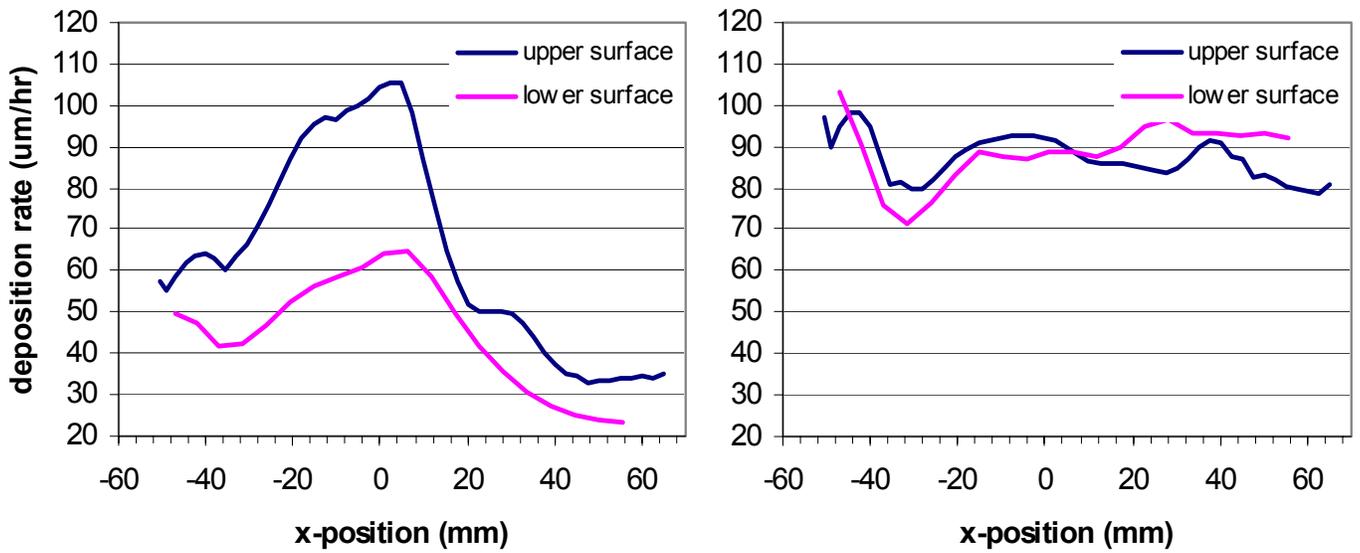


Figure 7. Model-predicted deposition rate for simple inlet (left) and three-part inlet (right) designs show strong effect of gas flow pattern on coating uniformity.