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DIP COATING OF SOL-GELS*

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Dip coating is the primary means of depositing sol-gel films for precision optical coatings. Sols are typically multicomponent systems consisting of an inorganic phase dispersed in a solvent mixture, with each component differing in volatility and surface tension. This, together with slow coating speeds (< 1 cm/s), makes analysis of the coating process complicated; unlike most high-speed coating methods, solvent evaporation, evolving rheology, and surface tension gradients alter significantly the fluid mechanics of the deposition stage. We set out to understand these phenomena with computer-aided predictions of the flow and species transport fields. The underlying theory involves mass, momentum, and species transport on a domain of unknown shape, with models and constitutive equations for vapor-liquid equilibria and surface tension. Due accounting is made for the unknown position of the free surface, which locates according to the capillary hydrodynamic forces and solvent loss by evaporation. Predictions of the effects of mass transfer, hydrodynamics, and surface tension gradients on final film thickness are compared with ellipsometry measurements of film thickness on a laboratory pilot coater. Although quantitative agreement is still lacking, both experiment and theory reveal that the film profile near the drying line takes on a parabolic shape.

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INTRODUCTION

Dip coating (Figure 1) is commonly used to apply thin films of sol-gel to rigid substrates. This case study involves the application of thin films of sol-gel materials, or solutions from which glasses or ceramics are synthesized at room temperature by a polymerization process. Sols are typically multicomponent systems consisting of an inorganic phase dispersed in a solvent mixture, with each component differing in volatility and surface tension. They start at viscosities around 1 cp and harden into a gelatin-like material. This, together with slow coating speeds (< 1 cm/s), makes analysis of the coating process complicated; unlike most high-speed coating methods, solvent evaporation, evolving rheology, and surface tension gradients alter significantly the fluid mechanics of the deposition stage. Many applications rely on coating such solutions in thin layers and hence invite development of sol-gel processing.

Dip coating is the simplest way of getting a precisely uniform film[1]. In the absence of mass transfer, or evaporation, the faster the surface is withdrawn from the coating bath, the thicker the film that is formed, up to a limit. Conversely, the thinner the film desired, the slower the surface must be withdrawn. Consequently, dip coating is today seldom encountered outside the laboratory. Because sol-gel processes are relatively underdeveloped, however, dip coating serves as a useful prototype on which to build an understanding of the physics involved.

The first step in this research is to understand the coating of the carrier (solvent) alone. In this paper experimental measurements of film formation are substantiated by theoretical predictions of dip coating water-ethanol mixtures, one of the most common carriers.

BASIC THEORY

The coating of water-ethanol solutions is not without mass-transfer. Although water in an open environment will evaporate when the liquid is exposed to air, ethanol does so much faster, being far more volatile. The governing principles must then include not only conservation of mass and conservation of momentum, but also conservation of volatile species, with models and constitutive equations for vapor-liquid equilibria and surface tension. Due accounting must also be made for the unknown position of the free surface, which locates according to the capillary hydrodynamic forces and ethanol loss by evaporation. For now, thermal effects induced by latent heat of evaporation and convection that diffusion can drive are neglected, and water is assumed to be relatively involatile.

The complete convective-diffusion problem includes mass-transfer in both the liquid and the gas. Here the theory of convection and diffusion in the liquid is considered together with a lumped-parameter (or mass transfer) model in the gas. This avoids the seemingly intensive problem of dealing with simultaneous momentum and mass transfer in both phases, but at the expense of having to derive a mass transfer coefficient for the flux of ethanol at the interface. Such a coefficient depends on, among other things, the diffusivity of ethanol in air and the gas flow near the liquid surface. In this work a simple boundary layer theory is used to approximate the latter, and, assuming no convection induced in the gas by the evaporating solvent, a mass transfer coefficient is derived as a function of the Reynolds number of the gas flow and the Schmidt number in the gas.

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The foregoing principles lead to nonlinear differential equations. Those equations are transformed to algebraic ones by subdomaining and the Galerkin/finite element method. The set is then solved with Newton's method. Special attention is given to the disparate boundary layers of concentration. The problem is that these boundary layers are roughly 30 times narrower than the momentum boundary layers because the diffusivity of the ethanol is much smaller than the kinematic viscosity of the liquid. By designing a fine mesh to represent the concentration and to fit into the coarse mesh which suffices for the rest of the flow, both fields can be represented adequately without squandering computational effort on unnecessary resolution.

SAMPLE RESULTS

High interest attaches to being able to predict the best processing conditions, i.e., those which give the most uniform film. The analysis here is just a start. Figure 2 shows a sample prediction of the pattern of streamlines and the concentration contours of ethanol at a typical coating speed of 0.5 cm/s. At the inlet the composition is 60 wt. percent ethanol in water.

Liquid is drawn out of the bath on the right by the moving substrate and enforced by continuity to enter the bath at an equal rate along the substrate through the bottom. This makes the process steady, although in reality it is unsteady because the level of the bath falls with time. The large, counterclockwise recirculation in the bath is noteworthy. Rapid evaporation bends the streamlines upwards. On the surface appears two stagnation points lying on either side of the recirculation. Near the downstream stagnation point the liquid jets downwards, drawing ethanol-lean solution into the bath and thus creating an internal concentration boundary layer. Further downstream there is an apparent drying line, up to which the film thins rapidly by evaporation. The meniscus takes on a parabolic-like shape in accord with measurements of film profiles for the same system.

EXPERIMENTAL PROGRAM

Experimental validation of the forgoing predictions is underway. Through ellipsometric imaging [2], the thickness profile of entrained solvent during dip coating has been measured. For now we use only pure solvent, without the complicating aspects of suspended solids. In the experiments, a 1 cm-wide strip of optically polished silicon was drawn from a solvent reservoir at a speed of 0.5 cm/s. The region of entrained liquid film was illuminated at an incident angle of 67.5° with monochromatic light through a polarizer-compensator-sample-analyzer arrangement, and the polarizers were adjusted so that fringes could be seen at every quarter wavelength of optical thickness. First, the resulting film profiles for pure ethanol were compared to a simple lubrication theory, augmented to account for evaporation. Agreement was excellent over a wide range of operating conditions. Quantitative agreement with the predictions for multicomponent systems, for which the theory is described above, is still lacking.

REFERENCES

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[2] A. J. Hurd and C J. Brinker 1988 *J. Phys. France* **49** 1017.

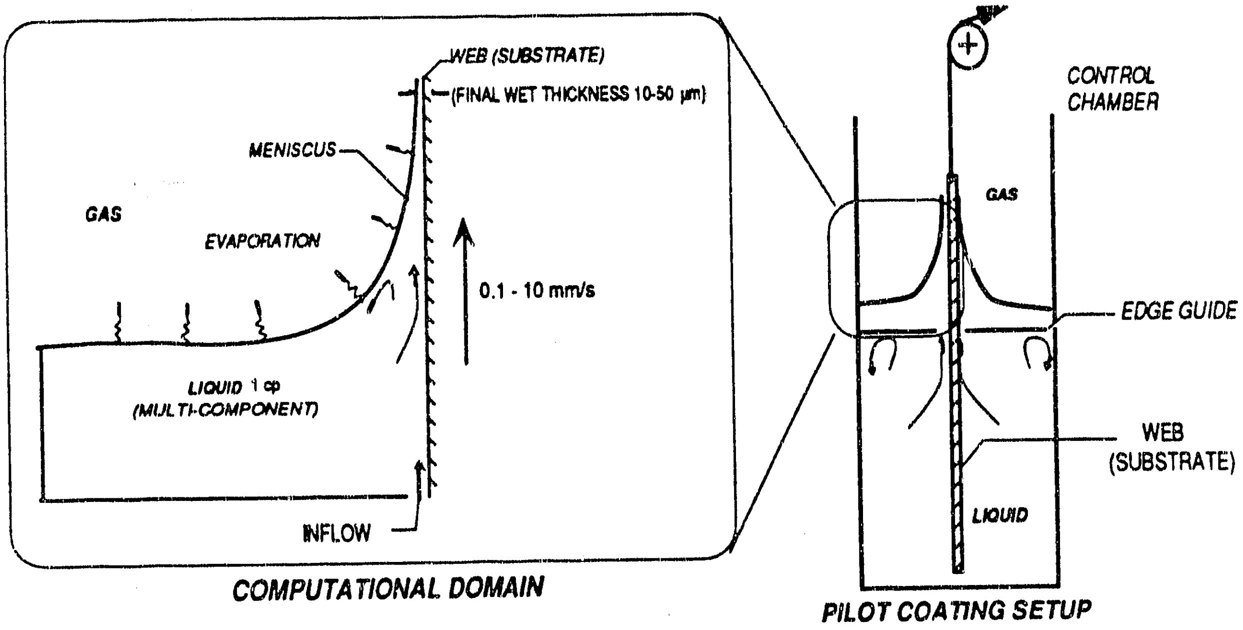

Figure 1

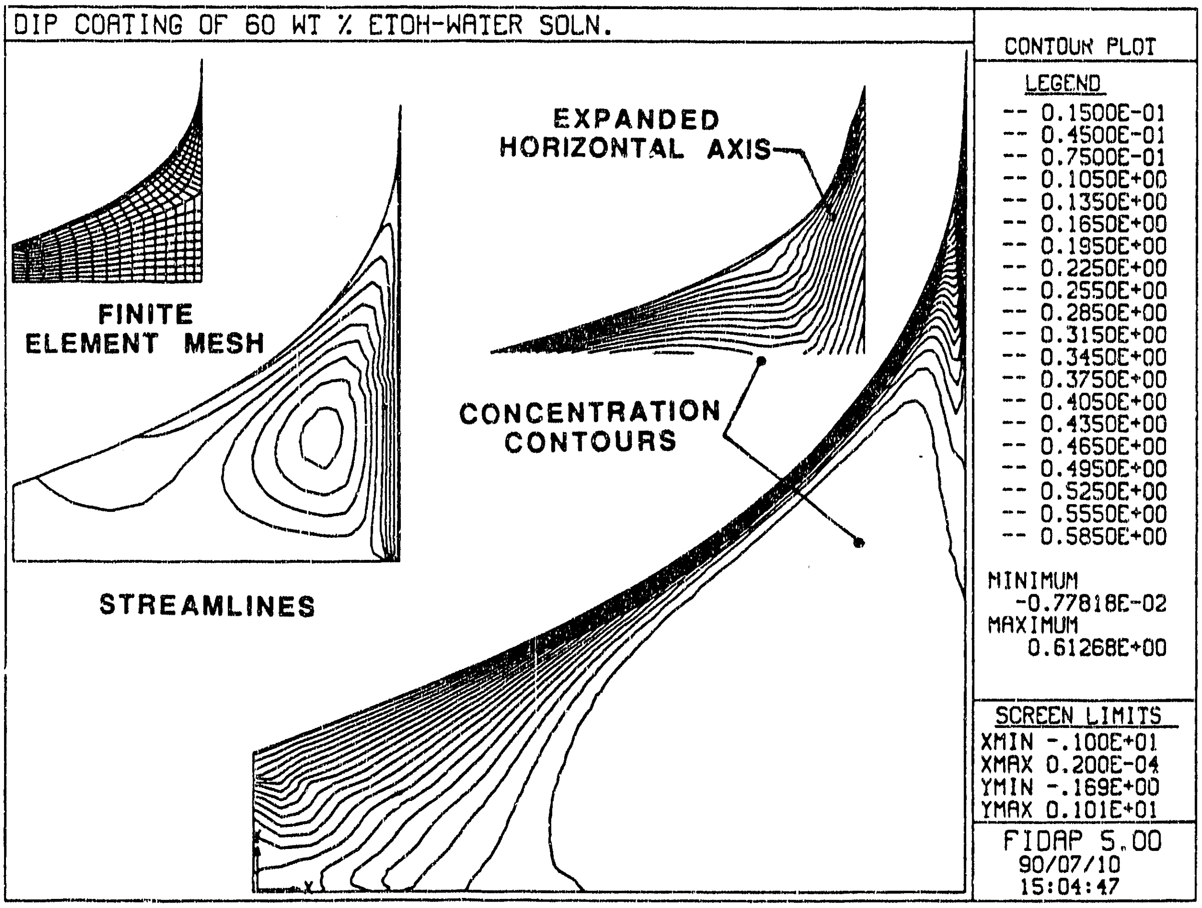

Figure 2

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