Final Technical Report to:

NASA LEWIS RESEARCH CENTER
Cleveland, OH 44135

Attention:
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Subject:

Research on Chemical Vapor Deposition Processes for Advanced Ceramic Coatings

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Research on Chemical Vapor Deposition Processes for Advanced Ceramic Coatings

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1. INTRODUCTION, BACKGROUND

Our interdisciplinary background and fundamentally-oriented studies of the laws governing multi-component chemical vapor deposition (VD), particle deposition (PD), and their interactions, (ca. 72 refereed experimental and theoretical publications since 1979, supported first by NASA, then also by DOE-METC, DOE-PETC and AFOSR) put the Yale University HTCRE Laboratory in a unique position to significantly advance the 'state-of-the-art' of chemical vapor deposition (CVD) R&D. With NASA-Lewis RC financial support, we initiated a program in March of 1988 that has led to the advances described in this report (Section 2) in predicting chemical vapor transport in high temperature systems relevant to the fabrication of refractory ceramic coatings for turbine engine components. This Final Report covers our principal results and activities for the total NASA grant of $190,000. over the 4.67 year period: 1 March 1988-1 November 1992. Since our methods and the technical details are contained in the publications listed in Section 5.2 (9 Abstracts are given as Appendices (Section 6)) our emphasis here is on broad conclusions/implications (Section 2) and administrative data (Section 3), including personnel, talks, interactions with industry, and some known applications of our work.

2. RESEARCH ACCOMPLISHMENTS

Our principal results may be conveniently subdivided into the following generic categories:


In the presence of interfacial kinetic barriers the onset of vapor phase chemistry in the immediate vicinity of hot CVD surfaces is often associated with a dramatic reduction in CVD-rates and film quality (cf. the early investigations of Ghoshtagore et.al., 1970). To understand when vapor phase reactions will be "ignited", we carried out a high activation energy asymptotic analysis (Castillo and Rosner, Castillo, 1992, 1993), and have begun to apply it to predict threshold conditions for the success of CFBL predictions (eg. transport-shifted CVD phase diagrams (Rosner and Collins, 1989, 1990, 1991). In AFOSR-supported laboratory experiments aimed at verifying and exploiting this theory, graduate student (NASA-Training Grant fellowship holder) Joshua Collins observed "vapor phase ignition" (VPI) in the deposition of TiO$_2$(s) films from TTIP. These films were partially characterized, based on visits to NASA-Lewis. We developed and applied the asymptotic approach of Rosner et.al. 1990, and Collins et.al. 1991, to predict rational onset conditions for vapor phase reactions in the CVD of TiO$_2$(s) and closely related oxides, and partially validated this approach in a prototypical case (eg, TiO$_2$(s) via TTIP) using a CVD stagnation flow reactor of our own design (Rosner, Collins and Castillo, 1993). This sets the stage for future use of the theory to design optimal CVD reactors, and infer homogeneous kinetic parameters based on well-defined VPI-threshold CVD-rate measurements in "new" (eg, Hf-, and/or, Zr-containing) systems. This combined theoretical and experimental CVD work formed the basis of the Yale U. PhD dissertation of Joshua Collins, who was supported for 4 years by NASA Training Grant: 50377.
2.2 Prediction of Transport-'Shifted' CVD Phase Diagrams; Theory of Deposit Composition

Valuable guidance for complex CVD processes has in the past been provided by 'phase diagrams' which, on purely thermophysical equilibrium grounds, display the 'fields' of stability of various eligible surface compounds (see, eg., Spear, 1984) in terms of reactor feed conditions (eg. elements ratios) and surface temperature. However, as we discovered and documented for the CVD of Na$_2$SO$_4$(l) (turbine "hot corrosion" applications) and W(s) (halogen-cycle lamps) (Rosner and Nagarajan, 1985; Rosner, Nagarajan, Gokoglu and Kori, 1987; Rosner, 1988, Rosner and Tandon, 1991), significant transport-induced 'shifts' in the boundaries of these 'fields' occur due to chemical element segregation ('enrichment') phenomena within the nonisothermal vapor boundary layers adjacent to the deposit surface. Using our asymptotic CFBL multicomponent transport methods (Rosner, Chen, Fryburg and Kohl, 1979) including updated algorithms for more accurately computing the Soret effect, in this program we compared transport-shifted and 'purely LTCE' CVD-diagrams for a prototypical ceramic coating system of special interest to NASA: viz., the titanium/boron system, for the case of a coaxial filament flow reactor configuration. Our results show how such diagrams can be used to select CVD conditions which will deposit the required stoichiometry at the highest possible rate. Indeed, based on recent contacts with US Air Force contractors (eg. Amercom, CA) this work can be used to guide the optimum choice of operating conditions of CVD reactors for synthesizing near-stoichiometric SiC(s) fibers, as well as TiB$_2$(s) coatings. Our efficient CFBL computational methods for multicomponent (>40 vapor species) CVD systems which employ an excess of inert 'carrier' gas can now be exercised in many new CVD situations of practical interest.

In the deposition of doped glass for ultimate use as an optical waveguide, combustion products heavily laden with SiO$_2$-rich submicron droplets are passed over a slowly rotating surface which thermophoretically captures the microdroplets. The dopant (eg., GeO$_2$, P$_2$O$_5$, B$_2$O$_3$-) content of these microdroplets, in turn, dictates the local refractive index of the ultimate waveguide product, and hence, must be carefully controlled and understood theoretically. We recently developed a fully coupled, pseudo-single phase laminar boundary layer theory to predict deposit compositions as a function of the mainstream loading of silicon and the dopant (here, Ge), as well as substrate temperature (Park and Rosner, 1989). We have shown that it is not permissible to neglect the effects of silica particle mass loading or even the heat of GeO$_2$ condensation. As a byproduct of our mathematical model and calculations, we have obtained the structure of the dopant vapor boundary layer, and, hence, the decisive ratio of dopant vapor number density established at the wall to that in the equilibrium mainstream. The capability of predicting both the rate of glass microparticle deposition and deposit composition (eg., dopant/Si element ratio) for each feed condition and wall/combustion gas temperature ratio should provide valuable insight into the optimization and improvement of this process, and generically related PD/VD processes. Moreover, while illustrated in this paper for the case of a single dopant (eg., Ge), our methods are readily extended to multi-element ceramic deposition. In principle, such information could also be superimposed on our transport-shifted CVD-phase diagrams (Rosner and Collins, 1989, 1990; discussed above).

Using similar methods, molten salt compositions (which determine corrosion potential and melting point) have recently been predicted in chlorine-containing environments of interest in proposed stationary power plants using coal-derived fuel (Rosner and Tandon, 1991).

2.3 Role of Vapor Phase Chemistry in Determining CVD-Rates;

Vapor phase chemical reactions can play a significant role in dictating deposition rates, and important properties of the resulting deposit. In a previous program, using both (stagnant) "film" theory and laminar boundary layer (convective-diffusion) theory, we developed and illustrated a tractable 'asymptotic approach' to predict multicomponent CVD-rates and dew points in high temperature vapor/condensate systems (see, eg. Rosner, Nagarajan, Gokoglu and Kori, 1987).
We calculated and systematically compared these quantities in two 'extremes' of vapor-phase chemical kinetics — one in which the gas-layer is taken to be in local thermochemical equilibrium (LTCE) everywhere along the diffusion path; the other in which the gas-layer is assumed to be chemically frozen (CF) everywhere. Based on this 'asymptotic' approach, we recently illustrated for laminar boundary layer alkali sulfate transport (Rosner and Tandon, 1991, and Gokoglu of NASA-Lewis RC, 1988) when CVD-rates will become sensitive to vapor phase chemical kinetics, and when, in the absence of interface kinetic barriers, a simple "chemically frozen" vapor phase analysis will be adequate for engineering purposes. This line of research appears to have had an impact on other US Govt. contractors concerned with the hot corrosion of combustion turbine parts (see, eg. Luthra, 1989). We anticipate that our ability to calculate CVT-rates in the LTCE-layer limit (also useful in halogen lamp applications, Rosner, 1988) will be useful in evaluating metal coatings for high pressure chemical rocket engine applications (eg., Ir(s), and Re(s)) of interest to NASA.

2.4 Scavenging of Vapors by Suspended Particulate Matter Within Boundary Layers (Castillo and Rosner, 1989; Rosner and Tandon, 1991)

In our earlier (DOE-supported) work we experimentally examined the mass transfer consequences of nonequilibrium scavenging of condensible vapor (Na2SO4) by suspended solid particles (MgO) within combustion gas boundary layers (BLs) (Rosner and Liang, 1988) using an extension of our 'flash-evaporation' technique (Rosner, 1989; Rosner and Liang, 1986) and laser light scattering methods. Both nonequilibrium laminar BL-theory (Castillo and Rosner, 1989) and our flash-evaporation light scattering experiments revealed that the alkali mass transfer rate reduction factor could be correlated with the scavenging particle cloud external surface area per unit volume. This body of experiments, and boundary layer theory (Castillo and Rosner, 1988), combined with our recent work on the coupling between particle inertia and thermophoresis (Konstandopoulos and Rosner, 1991) and current theoretical studies of vapor "scavenging" by log-normal populations of suspended particles (see, eg. Rosner and Tandon, 1991) can now be used to analyze and improve recent work on aerosol-assisted CVD and particle precipitation-aided CVD (PPCVD) (see, eg. Shimiogaki and Komiyama, 1987 and Hurt and Allendorf, 1991) for the rapid growth of ceramic films.

Incidentally, in the vapor/condensate equilibrium limit, our earlier theoretical model (Castillo and Rosner, 1989) has recently been successfully used to explain the rates of frost formation on cryosurfaces in moist air (Epstein, et. al., 1991).

2.5 Morphological Stability of Growing Deposits; Transport and Kinetic Phenomena Governing CVD-Coating Surface Topography and Deposit Microstructure

To gain insight into the conditions governing surface roughness, especially when thermophoretic (or Soret-) transport is dominant, we carried out a linear stability theory in the (dilute) limit of low growth Peclet number and negligible interfacial energy (Castillo, Garcia-Ybarra and Rosner, 1990, 1991). In this way, we identified a new type of morphological instability for the commonly encountered case when the deposit thermal conductivity exceeds that of the growth fluid medium.

In general, it will be necessary to consider molecular transport and chemical reactions on a scale much smaller than that of the overall vapor diffusion boundary layer to understand the surface morphology and microstructure of coatings of even prescribed stoichiometry.

By exploiting plausible hypotheses, and making use of extensive available experimental data for some CVD materials (eg. pyrolytic graphite and boron nitride) we have also begun to develop, test, and hope to ultimately recommend, a rational general "theory" for the density (and
other density-related properties) of CVD materials as a function of deposition conditions. One promising hypothesis is that a suitably normalized density should be a universal function of a surface-diffusion based Damkohler number governing the adatom's search for a "crystalline" site. The present program provided the opportunity to demonstrate a preliminary version of this type of correlation, as well as extend our capability to establish mechanism/microstructure interrelations (Tassopoulos and Rosner, 1991).

The abovementioned concepts are now being confronted with TiO$_2$(s) deposit roughness and microstructural data recently obtained by J. Collins, using the Yale-HTCRE stagnation flow CVD reactor. These observations will be contained in his dissertation and reported in part at the 1993 AIChE annual meeting.

The present program also helped us initiate the development of what we believe will be a fruitful approach to predicting the important influence of deposition mechanism on resulting deposit density and microstructure. We introduced a Monte-Carlo (stochastic simulation) approach to describe particle incorporation events at the 'base' of the mass transfer boundary layers (Tassopoulos and Rosner, 1991; Tassopoulos, O'Brien and Rosner, 1989). In this way, we were able to predict particulate deposit microstructure for each condition of particle arrival (mechanism of arrival, particle size distribution, particle orientation distribution, particle sticking behavior, etc.). This work, which was made possible by our access to the NASA-Lewis Supercomputer, could soon be extended to describe the microstructure of deposits formed from vapor mixtures containing suspended particles, say, by "PPCVD", setting the stage for analogous treatments of CVD-coating microstructures using molecular level simulations.

2.6 Breakdown of Validity of "No-Slip" Boundary Conditions and Navier-Stokes Gas Dynamics in CVD and PVD Applications

Based, in part, on work carried out under this NASA Grant (and NAG3-898) we have also identified the importance of hitherto neglected gas-kinetic phenomena---e.g., thermal gas "creep" along non-isothermal surfaces and "thermal stress convection" in PVD and CVD applications (Rosner, 1989). We demonstrated that these "non-classical" transport phenomena, predicted by "higher-order" gas kinetic theories but now known to be important in highly non-isothermal low Reynolds number flows, would be especially noticeable (and amenable to study) under microgravity conditions.

3. ADMINISTRATIVE INFORMATION

The following sub-sections summarize some pertinent 'non-technical' facets of the abovementioned Yale HTCRE Lab/NASA-Lewis research program:

3.1 Personnel

The present results (Sections 2 and 5) are due to the contributions of the individuals listed in Table 3.1-1, which also indicates the role of each researcher and the relevant time interval of their main activity. It will be noted that, in addition to the results themselves, this program has simultaneously contributed to the research training (Section 3.2) of a number of students and recent PhDs, who will now be in an excellent position to make future contributions to CVD technologies oriented toward ceramic coatings.
Table 3.1-1 Summary of Research Participants* on NASA Grant: NAG 3-8834
Research on Chemical Vapor Deposition Processes for Advanced Ceramic Coatings

<table>
<thead>
<tr>
<th>Name</th>
<th>Status</th>
<th>Date(s)</th>
<th>Principal Research Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castillo, J.L.</td>
<td>VS</td>
<td>Summers '88,'89</td>
<td>Asymp theory of vapor phase ignition</td>
</tr>
<tr>
<td>Collins, J.</td>
<td>GRA</td>
<td>'88-'92</td>
<td>CVD of ceramic coatings</td>
</tr>
<tr>
<td>Garcia-Ybarra, P.</td>
<td>VS</td>
<td>Summers '88,'89</td>
<td>Kinetic theory of Soret coeff.</td>
</tr>
<tr>
<td>Kho, T.</td>
<td>GRA</td>
<td>'92</td>
<td>chemical vapor infiltration (coatings)</td>
</tr>
<tr>
<td>Rosner, D.E.</td>
<td>PI</td>
<td>'88-'92-'93</td>
<td>program direction-dep. theory/exp</td>
</tr>
<tr>
<td>Tandon, P.</td>
<td>GRA</td>
<td>'91-'92</td>
<td>transport phenomena in BLs and CDFs</td>
</tr>
<tr>
<td>Tassopoulos, M.</td>
<td>GRA</td>
<td>'88-'91</td>
<td>deposit microstructure simulations</td>
</tr>
</tbody>
</table>

* PDRA = Post-doctoral Research Asst  GRA = Graduate Research Assistant
  PI = Principal Investigator  VS = Visiting Scholar

b See Section 5 for specific references cited in text (Section 2);

3.2 Presentations and Research Training
Apart from the publications itemized in Section 5, our results have also been presented at annual or topical conferences of the following professional organizations:

American Assoc. Aerosol Research (6/90)
ASME-Engineering Foundation (3/14/91)
AIChE (11/9/89, 11/6/90, 11/3/92)
CVD XI-Seattle (10/90)
CVD XII-Hawaii (to occur 5/93)
Electrochemical Soc., Symposium on Lamp Chemistry (5/88)
Int. Heat Transfer Conference (Jerusalem) (8/89)
Materials Research Soc. (11/29/89, 12/4/91
Physicochemical Hydrodynamics (PCH) at MIT 6/27/89

In addition, during the period: 3/1/88-1/1/92, the PI presented seminars at the following Universities:

Athens (NTU) 10/18/91  Auckland (11/88)
Brown 9/22/92  Brisbane 10/91
Christ Church . (10/91)  KTH-Stockholm (9/91)
Leeds (5/29/92)  J. Hopkins U.
Limoges (10/10/91)
Notre Dame (10/27/92)  Oslo (9/18/91)
Penn State (7/28/92)  Princeton (9/90)
Sydney (10/11/88)  Surrey (9/91)
Technion (Haifa) 10/27/91  Toulouse (9/91)
Trondheim (9/17/91)  UNED-Madrid (89)
Waterloo (7/11/91)  Wisconsin (4/91)

In all, a total of some 32 external talks were given based, in part, on the results of this NASA research program.

This program has involved the PhD dissertation research of three Yale graduate students (J. Collins, M. Tassopoulos and P. Tandon; cf. Table 3.1-1). Indeed, J. Collins, who was supported for 4 years on a related NASA Training Grant, is expected to complete his Yale U. PhD degree requirements in Fall '93.
Moreover, a Yale Undergraduate ChE major, Jim Tsang (Yale BChE '93), also completed a summer ('91) research project on this CVD reactor.
3.3 Interaction With US Industry

The research summarized here was supported by NASA under Grant NAG 3-884 between 3/1/88 and 11/1/92. During this same period the Yale HTCRE Laboratory has also been the beneficiary of continuing smaller grants from U.S. industrial corporations, including Union Carbide, SCM-Chemicals, GE-Schenectady, DuPont, and Shell, as well as the feedback and advice of principal scientists/engineers from each of these corporations and Combustion Engineering-ABB and AVCO-Textron-Lycoming. We appreciate this level of collaboration, and expect that it will accelerate inevitable applications of our results in areas relevant to their technological objectives in the area of high temperature coatings.

3.4 Impact/Applications

It has been particularly gratifying to see direct applications of some of this generic NASA-supported CVD research in more applications-oriented investigations reported in recent years. Indeed, the writer would appreciate it if further examples known to the reader can be brought to his attention.

In the area of multicomponent vapor deposition in combustion systems additional applications of our predictive methods (for "chemically frozen" (Rosner et al., 1979) and LTCE multicomponent laminar boundary layers) continue to be made by British Coal Corporation-Power Generation Branch (I. Fantom, contact) in connection with their topping cycles which run gas turbines on the products of fluidized bed coal combustors/gasifiers. The writer has also proposed applications of our computational methods to Aerojet Propulsion Div. (D.M. Jassowski) in connection with predicting the chemical stability of iridium rocket nozzle coatings.

Except for its application to particle-modified CVD systems (e.g., Komiyama, 1987, and Hurt and Allendorf, 1991) particle deposition (PD) was not emphasized in the present NASA program. However, for completeness we should mention that explicit PD-examples are provided in ongoing work at MIT (Walsh et al., 1992), and Sandia CRF, both groups having incorporated our rational correlation of inertial particle impaction (e.g., a cylinder in cross-flow) in terms of an effective Stokes number. This PI was also pleased to confirm recent applications of our deposition research (on the correlation of inertial impaction by cylinders in crossflow) by the National Engineering Laboratory (NEL) of Glasgow Scotland (Contact: Dr. Andrew Jenkins). NEL is apparently collaborating with Marchwood Labs-CEGB on developing mass-transfer prediction methods applicable to waste-heat recovery systems in incinerators, as well as pulverized coal-fired boilers. These applications are somewhat similar to those reported by the Combustion Lab R&D group at MIT and Penn State U. Explicit use of our studies of self-regulated "capture" of incident impacting particles (Rosner and Nagaragan, 1987) is also being made in current work on impact separators and ceramic heat exchangers for coal-fired turbine systems in high performance stationary power plants. Related potential applications arise in connection with "candle filters" used to remove fines (sorbent particles,...) upstream of the turbines. A useful summary of work in these interrelated areas (Solar Turbines, Textron Defense Systems, Hague International,...) was presented at the Engineering Foundation Conference Inorganic Transformations and Ash Deposition During Combustion, the proceedings of which appeared during 1992.

* * * * * * *

Clearly, fruitful opportunities for the application of our recent inorganic vapor and/or particle deposition research now exist in many of the programs currently supported by NASA, as well as US industrial R&D.
4. CONCLUSIONS

Because of (i) the need for tractable predictive methods, instructive prototypical results, and rational correlation formulae suited to the needs of the CVD-coatings community, and (ii) our previous theoretical and experimental progress in the areas of vapor deposition (VD), particle deposition (PD), and their interactions, in March 1988 we embarked on a theoretical program embracing each of the fundamental topics:

* Role of High Activation Energy Homogeneous Reactions in Limiting CVD-Rates and Deposit Quality for Heated Surfaces
* Prediction of Transport-Shifted CVD-Phase Diagrams; Theory of Deposit Composition
* Role of Vapor Phase Chemistry in Controlling CVD-Rates (LTCE vs CF)
* Scavenging of Vapors by Suspended Particulate Matter
* Morphological Stability of Thermophoretically Growing Deposits; Transport and Kinetic Phenomena Governing CVD-Coating Surface Topography and Deposit Microstructure

and

* Breakdown of "No-Slip" Boundary Condition and Navier-Stokes Gas Dynamics in CVD and PVD Applications

Our contributions to the CVD-field in several of these areas (Sections 2, 5.2) were closely coupled with corresponding CVD-measurements and calculations at NASA-Lewis Research Center. Thus, new concepts and capabilities developed in this program guided the direction of closely-related CVD-investigations at NASA-Lewis Labs. This symbiosis benefitted both programs—eg., led to respected (and sometimes unforeseen) developments in the area of alkali sulfate CVD, some of which are already documented in the References (see, eg. Luthra, 1989). In each of the specific tasks, the most relevant background literature or precedent is cited (Section 5.1).

The cumulative results of this NASA-supported program, along with complementary studies at NASA-Lewis Labs, are expected to constitute a significant body of advances, allowing, for the first time, many rational predictions/optimizations for CVD-equipment. The emphasis of the fundamental studies described above was on obtaining and communicating an understanding of physicochemical phenomena occurring in CVD reactors. In each case we pointed out and explored the engineering implications of our findings in those areas of refractory coating synthesis vital to the international competitiveness of the U.S. combustion turbine/chemical rocket industry.

Based in part on the fruitfulness of the CVD program summarized in the present Final Technical Report (and the publications listed in Section 5 below) this laboratory is currently exploring opportunities for future collaboration with NASA-Lewis Lab research staff—especially in the area of combustion phenomena oriented toward materials synthesis.
5. REFERENCES

5.1 CITED BACKGROUND REFERENCES


5.2 PAPERS WHICH APPEARED BASED IN PART ON NASA NAG 3-884


- 11 -
5.3 RELATED PAPERS IN PREPARATION OR SUBMITTED FOR PUBLICATION


Rosner, D.E. and Tandon, P., "Diffusion and Heterogeneous Reaction in Large Multi-particle Aggregates; Calculation and Correlation of 'Accessible' Surface Area", (accepted; to appear AIChE J. Fall '93)


LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>BL</td>
<td>Boundary layer</td>
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<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<tr>
<td>LTCE</td>
<td>Local thermochemical equilibrium</td>
</tr>
<tr>
<td>TTIP</td>
<td>Titanium tetra-isopropoxide</td>
</tr>
<tr>
<td>VD</td>
<td>Vapor Deposition</td>
</tr>
<tr>
<td>VPI</td>
<td>Vapor Phase Ignition</td>
</tr>
<tr>
<td>CFBL</td>
<td>Chemically Frozen BL</td>
</tr>
<tr>
<td>PPCVD</td>
<td>Particle Precipitation (-Modified) CVD</td>
</tr>
<tr>
<td>PD</td>
<td>Particle Deposition</td>
</tr>
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</table>

6. APPENDICES (Abstracts of 9 Publications)
TRANSPORT PROCESSES AND CHEMICAL KINETICS IN HIGH TEMPERATURE LAMP MODELING

Daniel E. Rosner

Department of Chemical Engineering
High Temperature Chemical Reaction Engineering Laboratory, Yale University, New Haven, CT 06520, USA

Abstract

Trace (halogen-containing) additives and impurities, which counter quartz envelope blackening, 'regenerate' within halogen (reversive) cycle incandescent tungsten filament) lamps, rendering thermochemical equilibrium predictions 'alone' inaccurate. Rational, yet efficient computational methods are outlined which not only include the necessary multicomponent chemistry (e.g., tungsten transport by vapor species as simple as W(g) and as complex as WO3Br(g), or, say, (WO3)g), but also the relevant transport phenomena (Soret and Fick diffusion, and 'solute' convection) which cause trace chemical element (W, O, Br, H, C) to 'aggregation' (ionizing) within operating lamps, whatever the choice of background gas (N2, Ar, Kr, and/or Xe). While local thermochemical equilibrium (LTEC) everywhere within the vapor phase, and at vapor/solid interfaces (filaments, bulb) is often a useful and quite tractable first approximation, kinetic limitations on important chemical reactions (e.g., hydrogen and bromine atom recombination) in the vapor phase: W(g) gasification from the leads or envelope by mixtures of O2(g), Br(g), Br2(g), HBr(g), ...), etc.) can influence predicted lamp performance under conditions which can now be understood, if not yet evaluated (due to the absence of data under the relevant conditions). These considerations, combined with parallel developments on the numerical computation of laminar, nonreactive, momentum-, energy-, and mass-transport within enclosures of complex shape and orientation, set the stage for the realistic, yet economical, computer-aided design of halogen-cycle (and discharge) lamps.

1. Introduction and Outline

High temperature lamps are "micro-chemical reactors" that can exhibit all of the complexities of multicomponent chemistry (e.g., involving the chemical elements W, Br, O, H and C) (10, 19, 32), molecular transport (Fick and Soret diffusion) (See Section 2) (20, 22) and (buoyancy-induced) convective flow of the local mixture (See Section 6 and Ref. (22)). Because of the existence of a broad spectrum of species molecular weights and large temperature gradients, even if the vapor phase chemical kinetics were adequate everywhere to achieve local thermochemical equilibrium (LTEC), it is not possible to predict accurately the performance of such devices based solely on equilibrium thermodynamics (so-called "zero-dimensional" models; see, Refs. (32, 33)). This is shown to be due to chemical element segregation (demixing) associated with the fact that each chemical element (e.g., W, H) finds itself in molecules of widely

2 Director, Yale HT CRE Laboratory; Professor of Chemical Engineering
A NONEQUILIBRIUM THEORY OF SURFACE DEPOSITION FROM PARTICLE-LADEN, DILUTE CONDENSIBLE VAPOR-CONTAINING LAMINAR BOUNDARY LAYERS

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(Received 1 January 1986; in revised form 27 June 1987)

Abstract—The deposition rate of a condensable substance from, say, flowing combustion products to "cold" solid surfaces can be strongly influenced by the simultaneous presence of a particulate aerosol since the particles can: (a) "scavenge" vapor, thereby influencing the vapor deposition rate, and (b) thermophoretically drift to the cold surface, carrying their inventory of scavenged condensate. A rational, yet quite tractable thermophoretic model of these nonequilibrium processes is developed here for high Reynolds number laminar stagnation region boundary layer flow, and implemented to the point of calculating and displaying the effects of mainstream particle loading, vapor loading and particle size on the deposition rate of condensable material at surface temperatures well below the vapor dew point. Despite the complexity of this multiphase flow situation, our theoretical model is quite general and is cast in terms of dimensionless parameters which dictate the importance of vapor-phase scavenging and particle thermophoresis, as well as the Kelvin (surface tension) effect in modifying the submicron particle (free-molecule) growth law. Illustrative numerical results are displayed for the deposition of alkali sulfate-like vapor from the combustion products of hydrocarbon fuel (or coal) with air, including the interesting "structure" of such nonequilibrium multiphase boundary layers. As a useful by-product, our results reveal which combinations of particle-phase parameters cause (a) previous "uncoupled" vapor-particle deposition rates to be approximately valid as well as (b) recent local vapor/condensate equilibrium limit results to be sufficiently accurate. We conclude with an outline of straightforward extensions of the present theory to include such factors as: (i) a nonuniform (polydispersed) particle size mainstream aerosol; and (ii) size-dependent particle thermophoretic diffusivity; which are likely to be important in current or future engineering applications.

I. INTRODUCTION—MOTIVATION

The performance of engineering equipment exposed to high-temperature gases containing both suspended particulate matter ("dust") and condensable vapors is determined, in part, by deposition phenomena, which can lead to fouling and/or corrosion (e.g. Rosner & Atkins 1983; Rothman 1985). Even relatively recent work in the areas of submicron particle deposition (e.g. Goren 1977; Walker et al. 1979; Gökoğlu & Rosner 1985; Rosner & Kim 1984) and vapor deposition (Rosner et al. 1979) has, for simplicity, imagined that these processes are separable, i.e. noninteractive. However, very recently we have developed a quantitative theoretical explanation of experimentally observed deposition rate reductions experienced by highly cooled surfaces due to near-equilibrium condensation processes occurring within the gas near the deposition surface (Castillo & Rosner 1988a–c; Liang et al. 1988). Actually, in most engineering applications it is not immediately evident whether vapor/condensate equilibrium (VCE) can be achieved within such two-phase boundary layers (BLs). A more comprehensive theory of such situations would not only yield explicit dimensionless criteria for "nearness to VCE", but would also enable the calculation of fully nonequilibrium vapor/particle transport situations—including the important effect of suspended aerosol particles on the rate at which condensable material arrives at the cooled surface (Rosner & Liang 1988). Our goal here is to develop a rational, but quite general and tractable mathematical model for accomplishing these seemingly ambitious goals.

1.1. Outline of the Present Paper

In this paper we present a tractable nonequilibrium theory of the deposition on "cold" surfaces of unary dilute vapors in high Reynolds number two-dimensional stagnation flow configurations.

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BOUNDARY LAYER COAGULATION EFFECTS ON
THE SIZE DISTRIBUTION OF THERMOPHORETICALLY
DEPOSITED PARTICLES

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Abstract In highly loaded aerosol flow systems of industrial interest, to what extent is the particle size distribution (PSD) in a deposit altered by inevitable coagulation events within the thin two-phase "boundary layer" adjacent to the collecting surface? As a timely example, under typical optical waveguide preform deposition conditions (which include thermophoretically dominated submicron particle deposition at high particle mass loadings), we predict that, while Brownian diffusion plays a negligible role in determining the total particle mass deposition rate, Brownian coagulation (along with gas shear) plays an important role in determining the size distribution of the depositing particles of doped silica. Since the size spectrum of the depositing particles, here assumed to be spherical, will strongly influence all thermophysical and structural properties of the porous deposited glass, our mathematical model/illustrative calculations can be used to circumvent the difficult problem of optically probing the thin laminar thermal boundary layer to infer this size spectrum information. Moreover, an understanding of "PSD shifts" induced by coagulation in the immediate vicinity of sampling probes/surfaces (including "thermophoretic sampling" recently applied in organic soot research) can be used to correct electron-microscope-inferred particle size/shape distributions for the systematic effects of coagulation within such boundary layers in systems with higher particle mass loadings.

INTRODUCTION

In most previous particle deposition rate theories [see, for example, Friedlander (1977) and Rosner (1989) (who explicitly considered convection/Brownian diffusion); and Goren (1977), Rosner and Park (1988) and Park and Rosner (1986; 1987) (who considered thermophoretically driven submicron aerosol particle transport through nonisothermal combustion product gases)] it has been assumed that the suspended particles were spherical and remained constant in diameter up to the moment of deposition. However, as is well known, aerosols are unstable with respect to coagulation, and, especially in highly loaded aerosol systems, coagulation may exert an important influence on system or product performance. In previous investigations of thermophoretic deposition rates under conditions of high particle mass loading we could neglect particle coagulation phenomena by exploiting the fact that, since the thermophoretic diffusivity, \( \pi_T D_p \), remains nearly constant with respect to the particle Knudsen number for submicron particles in atmospheric pressure combustion products (Rosner, 1980), particle coagulation does not affect the resulting aerosol deposition rate (Rosner and Park, 1988). However, in many industrial applications, including the manufacture of "preforms" for optical waveguides, the size distribution of the depositing particles will exert a strong influence on the porosity and other important microstructural properties of the deposit (Tassopoulos et al., 1989), thereby affecting all subsequent processing (e.g. drying, spinning etc.) (Keiser, 1983). As a useful first step in the prediction of size distribution "shifts" for thermophoretically deposited particles we present here a simple mathematical model that describes particle coagulation behavior across nonisothermal highly-loaded "dusty-gas" laminar boundary layers (BLs).

THEORETICAL FORMULATION

Overall BL flow structure

If we neglect particle inertial drift [see Rosner and Park (1988, Appendix)], the Eulerian BL flow equations for highly particle mass loaded systems treated as a continuum are [see, for example, Fernandez de la Mora and Rosner (1982) and Rosner and Park (1988)] a mixture mass balance, x-momentum balance, mixture energy balance and total particle mass (irrespective of particle size) balance. In their similar forms these equations, combined with an appropriate mixture equation of state \( \rho = \rho_0 \exp[RT/\rho_0(T - T_0)^{1/2}] \) and boundary conditions, were derived and solved numerically by Rosner and Park (1988) to obtain the overall boundary layer structure and wall transfer rates of x-momentum, mass and energy, under parametric conditions relevant to optical waveguide processing. It was pointed out [Rosner and Park (1988, Appendix 5)] that, while the explicitly considered
Side-wall gas "creep" and "thermal stress convection" in microgravity experiments on film growth by vapor transport

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While "no-slip" boundary conditions and the Navier–Stokes equations of continuum fluid mechanics have served the (moderate-to-"high" pressure) vapor transport community well until now, it is pointed out that transport conditions within highly nonisothermal ampoules (e.g., those used to grow organic solid thin films in microgravity experiments) are such that the nonisothermal side walls "drive" (rather than damp) the dominant convective flow, and the familiar Stokes–Fourier–Fick laws governing the molecular fluxes of momentum, energy, and (species) mass in the "continuum" field equations will often prove to be inadequate, even at Knudsen numbers as small as $10^{-3}$. The implications of these interesting gas kinetic phenomena under microgravity conditions, and even under "Earth-bound" experimental conditions, are outlined here, along with a tractable approach to their systematic treatment.

It is well known that even in outwardly simple, closed ampoules, rather complex vapor motion can occur as a result of the effects of a body force (usually gravity) and/or induced by the net mass transfer itself (the so-called Stefan flow). Using familiar "no-slip" boundary conditions, these have been analyzed in simple situations (ampoule geometry and orientation with respect to gravity, small fractional change in mixture density, equal vapor diffusivities for the transport of momentum, energy and mass, no side-wall effects on energy and mass transfer, etc.), with a typical set of results reported by Miller. We recently completed a preliminary theoretical study whose goal was to converge on the simplest thermophysical model capable of accurately describing film growth conditions in sealed nonisothermal ampoules used to grow organic thin films under microgravity conditions (see, e.g., Refs. 5 and 6). In the course of this study, we discovered that, whereas the above-mentioned Stefan- and buoyancy-driven flows are likely to be negligible under the typical microgravity conditions employed, instead several previously neglected "gas kinetic" phenomena (consequences of the Boltzmann equation of low-density gasdynamics) become rather important "sources" of convection. These less familiar phenomena are discussed sequentially below. The importance of non-Fickian vapor diffusion via the Soret (thermal mass diffusion) effect is also briefly considered. We conclude with the future implications of these interesting departures from the conventional Navier–Stokes–Fourier–Fick convection–diffusion laws, with emphasis on developing a tractable approach to the systematic inclusion of these gas kinetic effects in the general field of physical vapor transport (PVT) and chemical vapor transport (CVT).

To the best of our knowledge, in all previous analyses of vapor transport ("chemical" or "physical") in nonisothermal ampoules, it has been explicitly or implicitly assumed that the (motionless) ampoule side walls will bring any local gas tangential motion to rest—a familiar hypothesis known as the "no-slip" condition. From this "classical" perspective the side walls "dump" any gas motions established as a result of gravity and/or the net vapor transfer process itself. However, the quantitative estimates below reveal that, in fact, the nonisothermal side walls will act like a "pump," producing a side-wall gas "creep," which would be present (indeed dominant) in the complete absence of gravity and/or Stefan flow! For this reason, we outline here the essential features of such nonisothermal side-wall gas "creep" and call attention to its implications for future vapor transport microgravity experiments and ancillary modeling efforts. Even in ground-based experiments on ampoules at the same pressure level, we estimate that side-wall-induced gas "creep" velocities can be within one order of magnitude of those associated with conventional buoyancy-induced gas velocities—convection known to strongly influence "solute" vapor transport rates, and film quality (uniformity, orientation, etc.).

Just over one century ago, and in the last year of his life, Maxwell pointed out that (unless gas/solid encounters were completely "specular," i.e., with no tangential momentum exchange) a nonuniform temperature surface would in...
PREDICTION AND USE OF TRANSPORT-SHIFTED CVD PHASE DIAGRAMS: TITANIUM DIBORIDE CVD FROM TiCl₄/BCl₃ MIXTURES

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ABSTRACT

An efficient method for predicting mass "transport-shifted" CVD phase diagrams is described. Prototypical results are presented revealing important systematic shifts in deposit phase/stoichiometry due to chemical element segregation in the mass transfer controlled CVD of TiB₂. Our convective-diffusive mass transfer model accounts for both multicomponent Fick and Soret transport of dilute species (18 for TiB₂ deposition) across the gaseous boundary layer, with local thermochemical equilibrium imposed at the deposition surface. Selected results of this analysis, which also yields loci of constant rates of deposition or etching, are compared with available experimental data within the predicted domain of self-consistency (i.e. under conditions such that neither homogeneous reactions nor heterogeneous kinetic barriers are expected to play a significant role).

1. INTRODUCTION

In chemical vapor deposition (CVD) systems the elemental composition established at the gas/solid interface is generally different from the feed stream elemental composition. Therefore, conventional CVD phase diagrams based on equilibrium calculations using feed stream element fractions cannot be expected to yield the equilibrium state corresponding to the temperature, pressure, and element fractions actually established at the gas/solid interface, where the decisive CVD chemical reactions occur.Indeed, mass transport induced shifts in elemental composition between the feed stream and the gas/solid interface in CVD systems have often been suggested as a qualitative explanation for experimentally observed shifts in CVD deposit phase boundaries, as in the SiBₓ deposition studies by Spear and Dirkx (1,2). However, we are unaware of any systematic treatment of the required multicomponent mass transfer problem.

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CALCULATION OF TRANSPORT-SHIFTED CVD PHASE DIAGRAMS

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ABSTRACT

A non-iterative method is presented for constructing CVD phase diagrams which include the systematic effects of chemical element segregation in mass-transfer controlled flow reactors. Element segregation is shown to substantially shift predicted deposit phase boundaries when the vapor/deposit interface equilibrium is calculated using the local element fractions instead of the feed gas elemental composition, as is usually done. The mass transfer analysis developed here accounts for both Fick and Soret multicomponent diffusion acting across a non-isothermal boundary layer. The gas phase is assumed to be chemically frozen, with local thermochemical equilibrium imposed only at the vapor/deposit interface (as in a cold wall reactor with a hot substrate). As a specific example, the model is applied to the chemical vapor deposition of titanium diboride from TiCl4(g), BC3(g) and H2(g) in an Ar(g) carrier gas for ceramic composite material applications. These calculations, which account for boron and titanium transport via 17 chemical species, are illustrated for a long cylindrical reactor with a resistively heated coaxial fiber deposition substrate and coaxial annular flow. However, the method presented here is general in that both the chemical system and CVD reactor geometry can be changed to any other system of interest, provided: i) adequate thermochemical and thermophysical data are available; ii) the deposition rate is vapor transport controlled; and iii) convective-diffusion heat and mass transfer coefficients are estimable.

1. INTRODUCTION

CVD phase diagrams, as illustrated by Spear and his research group1,2 are used to display equilibrium deposit phases as functions of temperature, pressure, and feed gas composition. These diagrams have become valuable tools for first estimates of CVD reactor performance when homogeneous chemical kinetic barriers do not cause local non-equilibrium at the deposition surface. However, even when it is reasonable to assume that local equilibrium exists at the gas/deposit interface, chemical element segregation due to unequal species mass transfer to and from this interface makes it necessary to calculate the wall equilibrium state based on the prevailing wall element fractions, not the element fractions in the feed gas3. The extent of chemical element segregation may also be influenced by homogeneous chemical reaction rates, particularly in systems with particle nucleation in the gas phase, but there is also a broad class of mass transfer (diffusion) limited CVD systems and conditions in which the effects of surface and gas phase kinetics may safely be ignored.

In this paper, mass transfer in steady-state diffusion controlled CVD systems is analyzed to reveal the extent of chemical element segregation between the free stream and the gas/solid interface (deposition surface). With this information CVD phase diagrams are generated using both feed gas and mass transfer corrected wall element fractions. This multicomponent mass transfer analysis also yields realistic deposition (and etching) rate estimates which can be included on transport-shifted CVD phase diagrams as constant deposition rate contours. The principal assumptions used in this analysis are:

A1) Local thermochemical equilibrium (LTCE) exists at the deposition surface.
A2) Deposition is mass transfer controlled, with Fick and Soret diffusion and convection acting across a vapor mass transfer boundary layer.
A3) There is negligible gas phase homogeneous reaction in the mass transfer boundary layer (i.e. a chemically frozen boundary layer (CFBL)) and free stream.

Due to the form of the diffusion flux equations used in this paper, a further restriction is made that all but one species must be dilute (by mass) in a carrier gas. This diluteness restriction may be relaxed if an additional factor in the diffusion flux equations (Poisson-diffuse) is included to...
Morphological instability of a thermophoretically growing deposit

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The stability of the planar interface of a structureless solid growing from a depositing component dilute in a carrier fluid is studied when the main solute transport mechanism is thermal (Soret) diffusion. A linear stability analysis, carried out in the limit of low growth Peclet number, leads to a dispersion relation which shows that the planar front is unstable either when the thermal diffusion factor of the condensing component is positive and the latent heat release is small or when the thermal diffusion factor is negative and the solid grows over a thermally-insulating substrate. Furthermore, the influence of interfacial energy effects and constitutional supersaturation in the vicinity of the moving interface is analyzed in the limit of very small Schmidt numbers (small solute Fickian diffusion). The analysis is relevant to physical vapor deposition of very massive species on cold surfaces, as in recent experiments of organic solid film growth under microgravity conditions.

1. Introduction

The growth of solid deposits from the vapor phase is a technique widely used for the fabrication of thin layers of metals, insulators, and semiconductor materials; see, for instance, the review papers by Stringfellow [1] and Bryant [2]. Even though crystal growth from melts may be a more "efficient" process (usually giving growth rates several orders of magnitude larger than vapor phase growth), the latter is often preferred because of film quality considerations. In particular, new pharmacological and electro-optical applications demand the production of crystalline films of organic and organometallic macromolecules. The optimal growth of these materials from the vapor phase is now under intense experimental investigation internationally, even in microgravity environments to avoid crystal imperfections induced by buoyancy-driven instabilities, see Wal- ter [3]. Especially since the pioneering work of Mullins and Sekerka [4,5] and the review by Langer [6], it is well known that planar crystal growth may be morphologically unstable during the solidification of a supercooled liquid (i.e., in the absence of capillarity, a forward-facing bulge in the interface steepens the thermal gradient in the fluid ahead of it, so that latent heat is more rapidly removed from the surface and the bulge amplifies unstably), and in the similar case of isothermal solidification of a liquid mixture (respectively, directional solidification of a binary liquid) due to the constitutional supersaturation (respectively, consti-
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ONSET CONDITIONS FOR GAS PHASE REACTION AND NUCLEATION IN THE CVD OF TRANSITION METAL OXIDES

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ABSTRACT

A combined experimental/theoretical study is presented of the onset conditions for gas phase reaction and particle nucleation in hot substrate/cold gas CVD of transition metal oxides. Homogeneous reaction onset conditions are predicted using a simple high activation energy reacting gas film theory. Experimental tests of the basic theory are underway using an axysymmetric impinging-jet CVD reactor. No vapor phase ignition has yet been observed in the TiCl_4 system under accessible operating conditions (below substrate temperature T_s = 1700 K) and further experiments are planned using more reactive feed materials. The goal of this research is to provide CVD reactor design and operation guidelines for achieving acceptable deposit microstructures at the maximum deposition rate while simultaneously avoiding homogeneous reaction/nucleation and diffusional limitations.

INTRODUCTION

The onset of gas phase reaction and particle nucleation is a common problem in the CVD of transition metal oxides, often resulting in decreased deposition rates and reduced film quality [1-3]. This is particularly true in cold gaseous substrate CVD systems in which homogeneous reactions in the thermal boundary layer adjacent to the hot substrate produce particles which are thermophoretically repelled from the surface and, for most processes, do not deposit [4]. We call the sudden onset of significant reagent consumption by homogeneous reactions which result in non-depositing products (e.g., TiO_i particles) "vapor phase ignition" (VPI). Since the onset of homogeneous reactions can effectively starve the growing surface of reagent, it is often possible to detect vapor phase ignition by a sharp drop in deposition rates with increasing surface temperature. On the other hand, in hot gas/cool substrate systems the onset of homogeneous particle nucleation can lead to increased film growth rates due to surface roughening associated with thermophoretically driven particle/vapor co-deposition [5,6]. It must also be mentioned that high temperature deposition rate decreases may be due to other causes, such as reaction product thermodynamic instability [7]. Dramatic rate decreases attributed to VPI were first reported by Ghoshastri [4] for titania deposition from TiCl_4 in O_2. His early experimental studies may still be the most thorough. Unfortunately, it is difficult to use his data to predict conditions under which vapor phase ignition will occur in other reactions (let alone other chemical systems) because the transport conditions in his experiments were not well characterized.

We developed and are using an impinging-jet stagnation point reactor to experimentally study vapor phase ignition under well-defined transport conditions. In particular, we are inferring the onset of VPI in the thermal boundary adjacent to a hot substrate from observable decreases in deposition rates and changes in deposit microstructure. Future experiments will also include light scattering from particles nucleated in the boundary layer and non-intrusive measurements of local vapor species concentration. Experimental results are being used to assist in the development and eventual verification of a quantitative theory to predict the onset of vapor phase ignition in systems where high activation energy confines homogeneous reactions to a thin chemically reacting sublayer embedded within the thermal boundary layer adjacent to the hot deposition surface. Our objective is to develop a general theory which can be used with available homogeneous and heterogeneous chemical kinetics data to establish reactor design criteria and select optimal operating conditions which maximize deposition rates while avoiding both VPI and vapor reagent diffusional limitations. A potentially useful byproduct of the theory will be the ability to extract global homogeneous reaction kinetic parameters from deposition rate data taken under well-defined transport conditions, i.e., just as it is now common practice to extract heterogeneous kinetic parameters from experimentally increasing deposition rate data using an Arrhenius plot, with a more complete analysis of the type outlined here it should also be possible to
ONSET CONDITIONS FOR GAS PHASE REACTIONS AND PARTICLE NUCLEATION/GROWTH IN CVD BOUNDARY LAYERS.

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Literature CVD-rate data, and our recent experiments on TiO\textsubscript{2}(s) film growth from titanium (IV) tetra-isopropoxide (TTIP) vapor using a well-defined impinging jet reactor, reveal that the onset of vapor phase reactions near a hot deposition surface can lead to sharp reductions in CVD-rate and alterations in deposit microstructure. These observations have motivated our development of a thin chemical sublayer (CSL-) theory for predicting (using simple formulae) the interplay of heterogeneous kinetics, homogeneous kinetics and (Fick-, Soret-, convective-) transport phenomena in CVD reactors. CSL theory, only briefly outlined here, can be used to interrelate different CVD reactors/conditions and thereby guide the selection of reactor configurations/conditions that will lead to the maximum CVD-rate prior to the onset of vapor phase reactions and/or external transport limitations. Comparisons with our present TiO\textsubscript{2}(s) (via TTIP) data are used to suggest fruitful extensions of this work.

1. INTRODUCTION

To interpret our recent experimental observations on the CVD rate of TiO\textsubscript{2} films in an impinging jet reactor (1,5) and guide the design/operation of future CVD reactors, a rational asymptotic theory has been developed for the onset of homogeneous chemical reactions in the thermal boundary layer (BL) adjacent to a hot deposition surface, with emphasis on their effect on deposition rates and film quality (1,2). The analysis is tailored to systems in which a) gas phase reactions are confined to a thin chemical sublayer (CSL) embedded inside the thermal BL and b) the homogeneous reaction(s) of interest can be represented by a single high activation energy ($E_{\text{hom}}/(RT_e) \gg 1$) Arrhenius-type rate expression. In this limit one finds (2):

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predict the reduction in dust acquisition by heated surfaces (e.g., semiconductor wafers processed in a clean room or hot wall CVD surfaces).

**Transport phenomena in materials synthesis reactors.** Chemical reactors for producing valuable new materials (optical wave guides, ceramic precursors, thin films and components for the semiconductor electronics industry, pigments,...) operate under conditions for which the classical laws of energy, mass, and momentum transfer must be generalized to apply with accuracy, often because of the importance of new particle transport mechanisms. The HTCRE research group is using laboratory experiments and theoretical/computational techniques to develop rational yet tractable methods to design multiphase, non-isothermal reactors for synthesizing such materials.

**Kinetics of high temperature, gas/solid reactions.** At the high temperatures encountered in combustion and in the preparation or use of materials (e.g. the nose-cap and leading edges of the U.S. Space Shuttle), the important gas/solid reactions involve energetic species formed by dissociation of the gas molecules. We continue to develop novel chemical reactors to produce such free radicals and monitor their reactions with heated solid surfaces. These reactors, which often employ low pressure, transonic flow of the reactant gas through a microwave discharge, along with special, ancillary equipment (induction heaters, monochromators, etc.), permit us to examine the kinetics of surface reactions without complications from mass transport for efficient reactions occurring under the extreme conditions relevant to many emerging technologies.

**Selected Publications**


