Benefits for Our Industries and Our Nation

- Reduced energy consumption for glass coating
- Reduced solid waste generation

Applications in Our Nation's Industries

The process optimization strategies developed here are specific to the glass coating industry. However, the principles employed are general and can be easily adapted to other energy-intensive processes involving high-temperature reactions on surfaces

Project Partners

Sandia National Laboratories
Livermore, CA

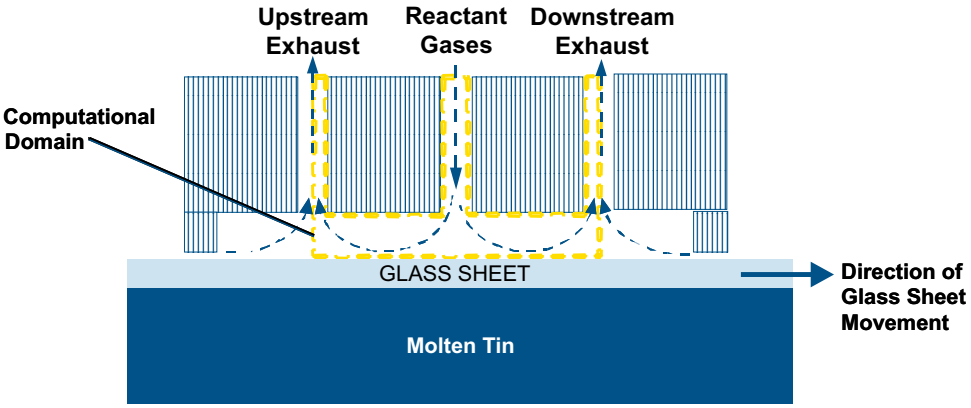
PPG Industries Glass Technology Center
Pittsburgh, PA

On-Line Coating of Glass with Tin Oxide by Atmospheric Pressure Chemical Vapor Deposition

Summary

Atmospheric pressure chemical vapor deposition (APCVD) of tin oxide (SnO_2) is a very important manufacturing technique used in the production of low-emissivity architectural glass. It is also the primary method used to provide wear-resistant coatings on glass containers and is employed in the manufacture of high-tech products such as solar cells. The complexity of on-line APCVD systems, which involve chemical reactions in both the gas phase and on the deposition surface, as well as complex fluid dynamics, makes process optimization and design of new coating reactors a very difficult task. APCVD processes in the flat-glass industry can be as little as 10% efficient (i.e., only 10% of the incoming precursor chemicals are converted to coating), resulting in annual production and waste-treatment disposal costs to the industry of nearly $23 million. In addition, remelting of glass with defective coatings results in over 1.1 x 10^{11} Btu/year of unproductive energy usage.

In 2001 the U.S. Department of Energy Industrial Technologies Program Glass Industry of the Future Team funded a project to improve the energy and production efficiency of on-line APCVD coating processes. Specifically, the need for more accurate process-related data for tin oxide APCVD was recognized as a critical barrier to developing strategies for reducing energy consumption and minimizing waste. Sandia National Laboratories in Livermore, CA, and the PPG Industries Glass Technology Center in Pittsburgh, PA formed a team to address this need. This project developed a generalized methodology for understanding APCVD processes, combining laboratory measurements with computational modeling, which can be applied to any CVD-based glass coating process, including containers as well as flat glass. In the broadest context, it can be used to optimize coating processes for materials other than tin oxide as well.



Schematic of on-line atmospheric pressure chemical vapor deposition (APCVD) float glass coater (computational domain shown as dashed yellow line).

Project objectives

1. Identify modifications to existing APCVD coating processes and/or new coater designs that will double the efficiency of reactant utilization, thereby substantially reducing waste emissions and purchases of raw materials.

2. Develop validated computational models to predict defects due to thickness nonuniformity and haze; use these to reduce defect frequency and improve the overall energy efficiency of the process by reducing the amount of rejected glass that must be remelted.

3. Generate a database of fundamental thermodynamic and kinetic information for APCVD.

4. Provide enhanced understanding of the underlying chemical reactions that control APCVD, which will enable the development of improved process models and control strategies for float- glass coating and other types of glass, such as containers, that use APCVD coatings.

Methodology for understanding APCVD processes

To reach these goals it was essential to use a methodology that includes experimental measurements as well as modeling, because the data available in the literature were insufficient to test and validate process models. A thermodynamic data generation component was also essential so that the extent of gas-phase precursor decomposition could be assessed. Thus, a methodology was developed that included the following elements:

1. Computer modeling was used to predict missing thermochemical and kinetic data for gas-phase tin oxide precursors.

2. Laboratory reactor designs were adopted that can be accurately modeled using reacting-flow codes. In this case, a stagnation-flow reactor with temperature-controlled walls was constructed, since this geometry can be approximated as one-dimensional and is computationally practical to simulate.

3. Comprehensive measurements of film growth rates under highly controlled experimental conditions were performed to generate data for model development and validation.

4. Computational fluid dynamics simulations were used to predict growth rates in pilot- and full-scale reactors under realistic processing conditions.

For this project, a widely used precursor system, monobutyltintrichloride (MBTC) with oxygen and water vapor, was used. However, the approach is extendable to other precursors systems.

Key results

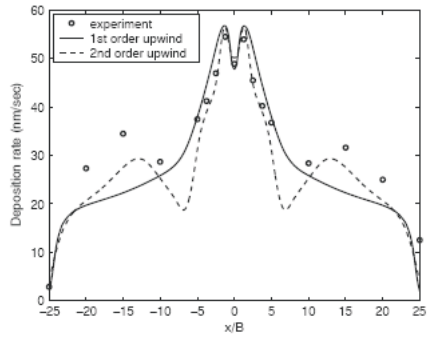
The combination of experiments and modeling conducted during this project resulted in the most comprehensive and thorough investigation of a tin-oxide CVD process ever performed. Results were fully documented in several publications (see list below). The key outcomes were:

1. An experimentally validated model of tin oxide CVD was developed that predicts growth rates as a function of process variables and is in excellent agreement with laboratory data. The model accurately predicts spatial growth-rate profiles in production APCVD reactors.

2. Demonstrated the functional dependence of tin oxide growth rates on all major process variables, including substrate temperature, reactor pressure, total gas flow rate, and reactant mixture composition.

3. Compiled the most extensive data base available of thermochemistry for gas-phase tin species. Data for more than 50 tin-containing molecules were generated, including species required to model the reaction of all precursors used industrially. These data are available at http://www.ca.sandia.gov/HiTempThermo/.

4. Demonstrated the effectiveness of computational fluid dynamics (CFD) for modeling full-scale APCVD reactors, including assessments of effects such as glass speed, inlet-outlet pressure differentials, and coater top-wall temperature.

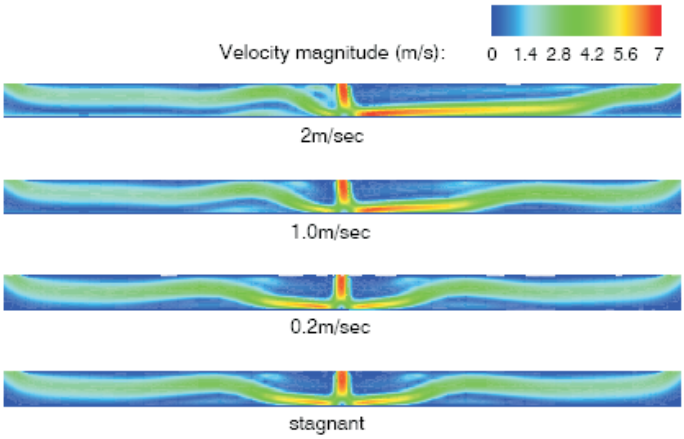


Comparison between measured growth rate profiles and two numerical schemes for modeling the fluid dynamics.

5. Showed that tin precursor conversion efficiencies can be dramatically increased (by a factor of 2 or more) using one of three methods: 1) increasing the temperature of the glass, 2) increasing the inlet water vapor concentration; and 3) increasing the coater inlet and outlet separation. The complete dependence of precursor conversion efficiency on these variables was modeled using kinetic expressions measured experimentally. Thus, the results are sufficiently general that they can be extended beyond the conditions and geometries of the reactors used here.

6. Glass line speed has little effect on the overall growth rate at the speeds used in typical on-line APCVD processes. Similarly, changing the temperature of the coater top wall (opposite the glass surface) does not significantly influence the growth rate or precursor utilization. Finally, varying the distance between the glass and the coater top wall affects the flow pattern in the reactor. If this distance becomes too large, boundary-layer separation may occur, causing the growth rate to drop to zero over a portion of the reactor zone downstream of the precursor inlet.

Using the kinetic and thermodynamic data provided by Sandia National Laboratories, PPG developed a CFD process model that is able to approximate the local deposition profile and the average deposition rate of tin oxide at pilot-scale. As a result of the improved insight into the reaction mechanism and parameters controlling APCVD deposition of tin oxide, an enhanced real-world process model was enabled that is contributing to process improvement and cost reduction.



Influence of glass line speed on velocity flow field. Note that typical glass lines speeds are 0.1 – 0.3 m/s.

Lessons learned

The approach developed here, which integrates controlled laboratory experiments with computational modeling of both precursor chemistry and reactor fluid dynamics, proved to be an effective route to optimization strategies for APCVD tin oxide coating of flat glass. However, because this approach separates the underlying phenomena controlling growth from the specifics of reactor design, its use is not limited to flat glass. Rather, the robust computational models developed here can be used to model any APCVD tin oxide coating process, including both flat-glass and container coating. It is important to note, however, that in the absence of growth-rate data obtained from well characterized and controlled reactor environments, the benefits of such models are severely curtailed, requiring major assumptions or simplifications. In this project, the investment in a laboratory investigation of tin oxide growth kinetics lead to a quantitative understanding of the effects of important process variables, including temperature, reactant concentrations, total flow rate, and glass temperature, and ribbon speed, on coating rate. With this information it became possible to quickly evaluate a wide range of process optimization strategies that would otherwise be extremely costly and time consuming to test experimentally. As a result, the number of tests required in pilot- and full-scale coating reactors to validate the strategies was considerably reduced.

It is also clear that accurate thermodynamic data are absolutely essential for meaningful process modeling. While this project concerned itself primarily with the tin oxide precursor MBTC, the development of a thermodynamic data base that includes a broad range of tin compounds enables equilibrium, chemical kinetic, and CFD modeling to be extended to many other APCVD systems (there are at least four major precursor systems used by industry today). This conclusion is equally valid when considering the optimization of other high-temperature materials manufacturing processes. Thus, the generation of thermodynamic relevant information, either through data mining or, as done here, through computational methods (required because data were not available otherwise), should be included as a key project element.

Key Publications

1. Y. Chae, W. G. Houf, A. H. McDaniel, M. D. Allendorf "Mechanisms for the Chemical Vapor Deposition of Tin Oxide from Monobutyltintrichloride," J. Electrochem. Soc., 153 (2006), C309.
2. A.M.B. van Mol; Y. Chae; A.H. McDaniel; M.D. Allendorf "Chemical vapor deposition of tin oxide: Fundamentals and applications," Thin Solid Films, 502 (2006), 72.
3. M. D. Allendorf, C. F. Melius "BAC-MP4 Predictions of Thermochemistry for Gas-Phase Tin Compounds in the Sn-H-C-Cl System," J. Phys. Chem. A., 109, 4939 (2005).
4. Y. Chae, A. H. McDaniel, W. G. Houf, M. D. Allendorf "Stagnation-Flow Reactor Investigation of the Deposition of Tin Oxide from Monobutyltintrichloride," J. Electrochem. Soc., 151 (2004), C527.
5. M. D. Allendorf, A. M. B. van Mol, "Gas-Phase Thermochemistry and Mechanism of Organometallic Tin Oxide Precursors," Topics in Organometallic Chem., Springer (Berlin) vol. 9, p. 1, 2005.
6. Mingheng Li, John F. Sopko, James W. McCamy "Computational fluid dynamic modeling of tin oxide deposition in an impinging chemical vapor deposition reactor," Thin Solid Films, in press, 2006.

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