

Inverse Problem for the Chemical Vapor Infiltration Process*

ANDREW D. JONES JR.
Florida A&M University
Department of Mathematics
Tallahassee, FLorida 32307
USA

PIERRE NGNEPIEBA
Florida A&M University
Department of Mathematics
Tallahassee, FLorida 32307
USA

Abstract: A model for Chemical Vapor Infiltration is analyzed and developed. Consider a cylindrical pore with a reacting and carrier gas flowing in from the left. The gas reacts with the interior of the pore and the result is a solid matrix. The model assumes that the flux due to binary diffusion is negligible. The model also assumes that the reactions are first order.

There is little data containing gas-solid reaction rates between hydrocarbons and graphite. The inverse problem includes comparing the model to experimental data and using optimal control to estimate gas-solid reaction rates. Numerically, we look at how the void and the concentration of reacting gas change as a function of space and time. We use data on how the void changes with time to estimate the flux of the reactant out of the preform.

Key-Words: Composites, CVI, Process Modeling, Optimal Control

1 Introduction

1.1 Overview

Consider a porous preform, (*e.g.* fibers, or particles) and a vapor flowing into the preform on one side. The fluid consists of a carrier gas that is non-reacting and a reactant that bonds with the interior surfaces of the preform. The result of the reaction is the deposition of a solid matrix phase that decreases the void of the preform. The void of the preform may continuously decrease until the void at the inlet is zero and no more fluid can enter the solid. At this time the process ends. It is usually desirable that the voids in the preform are minimized and the solid is uniform before the process ends. Since Chemical Vapor Infiltration (CVI) often takes an extremely long time, it is also important to choose parameters that achieve the requisite amount of solid formation in the minimum amount of time.

The process involves several parameters: temperature, pressure, initial void of the preform, chemical composition, chemical concentration, etc. An accurate mathematical model is necessary to inexpensively and effectively optimize the process.

A process is successful if the remaining voids in

the matrix are within some tolerance. The tolerance is determined by the application of the material. The conclusions that follow can be used to choose the values of the parameters that will yield a successful process. Specifically, these results can be used to adjust the controls on a CVI reactor and produce a successful product.

In the research presented here, the parameters α^2 (proportional to the reaction rate divided by the diffusion rate) and β (proportional to the reaction rate) are constant during each process. Because they are assumed to be functions of temperature and pressure, this corresponds to an isothermal-isobaric process.

There is little data containing gas-solid reaction rates, k , between hydrocarbons and graphite. We assume that the flux of reactants out of the solid is proportional to the concentration of reactants. However, the constant of proportionality, A , is not known. The inverse problem involves comparing the model to experimental data using optimal control to estimate k and A .

The formulation yields a coupled system of Partial Differential Equations (PDEs) for the void fraction of the preform and the concentration of the reacting gas. Finite Difference Methods are used to give approximate solutions to the PDEs as a function of space and time. The approximate solutions of the void

*This research is supported by Army Research Laboratory

fraction and the concentration are used to determine conditions of a successful process and how α^2 and A (proportional to the flux of reactants out of the solid) effect the process.

1.2 Formulation

A mathematical description of infiltration requires one or more partial differential equations which describe the evolution of the matrix (i.e., the solid phase), and at least one additional partial differential equation for each chemical species in the fluid phase. For a simple pore structure, the continuity equation for species i is

$$-\frac{\partial(\varepsilon C_i)}{\partial t} = \nabla \cdot N_i - \sum_r^{n_r} \nu_{ir} R_r \quad (1.2.1)$$

where t is time, ε is the void fraction of the media, C_i is the concentration of species i , n_r is the number of the gaseous species, ν_{ir} is the stoichiometric coefficients for the i th gaseous species in the r th reaction, and R_r represents the volumetric reaction rate of reaction r .

The basic partial differential equation(s) which describe reaction and mass transport in porous media (i.e., the fluid phase) are well established (Aris (1975) [3]; Dullien (1979) [4]). The Dusty-Gas model (see Mason and Malinauskas (1983) [5]) describes multicomponent diffusion and convection. Neglecting thermal diffusion, the relationship between the molar fluxes, N_i , is given by (see Jackson (1977) [6]):

$$\frac{N_i}{D_{K_i}} + \frac{RT}{P} \sum_{j \neq i} \frac{C_j N_i - C_i N_j}{\mathcal{D}_{M_{ij}}} = -\nabla C_i - \frac{C_i B_e}{\mu D_{K_i}} \nabla P \quad (1.1.2)$$

where B_e is the permeability of the porous media, μ is the viscosity of the mixture, and P is the total pressure. $\mathcal{D}_{M_{ij}}$ and D_{K_i} are the effective binary diffusivity for species i and j and the effective Knudsen diffusivity of species i , respectively.

The change in the solid structure is equivalent to considering the change in the void fraction, ε (i.e., the volume fraction of gas inside of the porous solid). The evolution of ε is given by:

$$\frac{\partial \varepsilon}{\partial t} = -u S_v(\varepsilon) \quad (1.2.3)$$

where u is the rate at which the solid product grows (volume/area/time) and $S_v(\varepsilon)$ is the surface area per unit volume of the porous solid.

The simplest formulation for the fluid phase is obtained by considering one reacting species and no pressure gradient. That is, we assume $i = j$ and $\nabla P = 0$ in (1.1.2). Thus, for highly diluted reactant systems in one dimension, the Dusty-Gas model can be simplified to give the following approximate expression for the flux:

$$N = -D_K \frac{\partial C_i}{\partial Z} \quad (1.2.4)$$

where C is the concentration of diluted species and Z is the distance into the preform. The effective diffusivity of the diluted species, D , can be expressed as

$$D = \frac{\varepsilon}{\theta} D_{Mm} [1 + N_k(\varepsilon)]^{-1} \quad (1.2.5)$$

where m refers to the bulk species, D_{Mm} is the binary diffusion coefficient for M in m , N_k is the ratio of the Knudsen diffusion coefficient and D_{Mm} , and θ is the tortuosity factor. For a diffusion-limited process in one spatial dimension, using Eq. (1.2.4), Eq. (1.2.1) becomes:

$$\frac{\partial(\varepsilon C_i)}{\partial t} = \frac{\partial}{\partial Z} \left[D_K \frac{\partial C}{\partial Z} \right] - \frac{u S_v(\varepsilon)}{V_M} \quad (1.2.6)$$

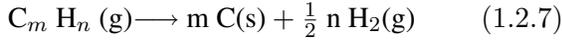
where V_M is the molar volume of the solid product. The last term in Eq. (1.2.6)

$$\frac{u S_v(\varepsilon)}{V_M} = \sum_r^{n_r} \nu_{ir} R_r$$

describes the rate at which the gas-phase precursor is consumed or created by chemical reactions inside of the pores with the assumption that there are no homogeneous gas-phase reactions.

Are assumption, that there are no gas phase reactions is based on the following. If the gas inlet is a large distant from the sample many gas phase reactions will occur before the gas reaches the first pore. We assume that the gas that reaches the pore is in equilibrium with 44 species of hydrocarbons. The reaction rate of the gas with the surface is taken to be the average of the reaction rates of 44 gasses.

A specific CVI model requires expressions for u , S_v , and D . Our objective in this work is to use simple formulations for each, as a basis for assessing the general behavior of infiltration problems. As an example, consider the formation of carbon matrix composites using a hydrocarbon in an argon carrier gas, where the following net reaction occurs:



The form of Eq. (1.2.6) is based on the assumption that the hydrocarbon concentration, C_r , is dilute (i.e., the reactant concentration is much smaller than the carrier gas concentration). If the carbon growth rate is proportional to the precursor concentration, then:

$$u = kC_r \quad (1.2.8)$$

where k is the reaction rate constant.

The preforms used for CVI typically have a complex porous structure. However, a cylindrical pore is often used to formulate simple models. This leads to the following expression for S_v :

$S_v(\varepsilon)$ in terms of ε is given by [1],

$$S_v(\varepsilon) = \frac{2\sqrt{\varepsilon_0}\sqrt{\varepsilon}}{r_0} \quad (1.2.9)$$

where r_0 is the initial pore radius and ε_0 is the initial void fraction of the preform.

We neglect the change in the number of molecules in the gas phase

$$\frac{\partial(\varepsilon C_i)}{\partial t}$$

This is assumed because solids are much denser than gases, so that the time-scale for changes in the gas profile is much shorter than the time scale associated with changes in the solid structure. The temporal change is given by (1.2.3). For gas-solid reaction processes such as CVI, this is sometimes referred to as the pseudo-steady-state approximation (Chang (1995) [7]). Transforming ε to η simplifies equation (1.2.10). Since η is proportional to S_v , it is also possible to view η as a dimensionless surface area per volume.

Substituting Eqs. (1.2.8) and (1.2.9) into Eqs. (1.2.3) and (1.2.6) gives the following forms:

$$\frac{\partial \eta}{\partial t} = -\frac{1}{2}\beta c \quad (1.2.10)$$

$$\frac{\partial}{\partial z} \left[\frac{\eta^2}{\theta} [1 + N_k(\eta)]^{-1} \frac{\partial c}{\partial z} \right] = \alpha^2 \eta c \quad (1.2.11)$$

where:

$$\eta = \sqrt{\varepsilon} \quad (1.2.12)$$

$$c = \frac{C_r}{C_0} \quad (1.2.13)$$

$$z = \frac{Z}{L} \quad (1.2.14)$$

$$\alpha^2 = \frac{2k\sqrt{\varepsilon_0}L^2}{V_M r_0 D_{Mm}} \quad (1.2.15)$$

$$\beta = \frac{2k\sqrt{\varepsilon_0}C_0}{r_0} = \alpha^2 \frac{V_M C_0 D_{Mm}}{L^2} \quad (1.2.16)$$

where L is the thickness of the preform and C_0 is the concentration of the reactant species in the bulk gas-phase (i.e., outside of the preform). The expression for α (1.15) is based on the assumption that u is determined by a first order reaction, where k is the rate constant (i.e., $u = kC_r$). Note that α^2 is dimensionless and that β has units of inverse time.

The parameters α^2 and β depend on the three key process variables: T (temperature), P (pressure), and C_0 (initial concentration). T , P do not appear explicitly in Eqs. (1.2.15) and (1.2.16), however, k typically obeys an Arrhenius-type exponential temperature dependence, and D_{Mm} varies with both temperature and pressure.

The boundary conditions that are most often used for CVI models are to fix the concentration at the left surface (the inlet) of the preform at C_0 :

$$c(0, t) = 1 \quad (1.2.17)$$

and to assume that the flux at the right surface (i.e., at $z = 1$) is proportional to the concentration:

$$c_z(1, t) = -Ac(1, t) \quad (1.2.18)$$

where A is the constant of proportionality. The initial condition is given by:

$$\varepsilon(z, 0) = \varepsilon_0 \quad (1.2.19)$$

During CVI, the infiltration kinetics are controlled by diffusion and the deposition reaction. To achieve relatively uniform infiltration, diffusion must be fast relative to the deposition rate. This is typically accomplished by choosing processing conditions that result in a slow deposition rate, which usually leads to long infiltration times. Thus, a key processing objective is to obtain the desired amount of infiltration in the shortest possible time. The total amount of infiltration in the preform is given by integrating over z :

$$\bar{\varepsilon}(t) = \int_0^1 \varepsilon(z, t) dz \quad (1.2.20)$$

Since it is important to obtain the desired density (i.e., void fraction), ε_f , in the shortest possible time, the optimization problem of interest corresponds to determining the shortest time where $\varepsilon(t) = \varepsilon_f$, for values of ε_f that are significantly smaller than ε_0 .

1.3 The Equations

If $f(\eta) = \frac{\eta^2}{\theta} [1 + N_k(\eta)]^{-1}$ then equations (1.2.10) and (1.2.11) become

$$\frac{\partial \eta(z, t)}{\partial t} = -\frac{\beta}{2} c(z, t) \quad (1.3.1)$$

$$\frac{\partial}{\partial z} \left\{ f[\eta(z, t)] \frac{\partial c(z, t)}{\partial z} \right\} = \alpha^2 \eta(z, t) c(z, t) \quad (1.3.2)$$

We subject (1.3.1) and (1.3.2) to the boundary conditions

$$c(0, t) = 1 \quad (1.3.3)$$

$$\frac{\partial c}{\partial z}(1, t) = -Ac(1, t) \quad (1.3.4)$$

and the initial condition

$$\eta(z, 0) = \eta_0 \quad (1.3.5)$$

Where η_0 , the initial value of the square root of the void fraction, is constant in space and

$$f[\eta(z, t)] = \frac{\eta^2}{\theta} [1 + N_k(\eta)]^{-1}$$

and

$$\frac{f(\eta)}{\eta}$$

are both C^∞ monotonically increasing functions of η , and $\eta(z, t)$ is positive. For a cylindrical pore

$$\theta = 1 \quad \text{and} \quad f(\eta) = \frac{1}{3} \frac{\eta^3}{\eta + \tau}$$

where $\tau = \frac{1.54 \cdot 10^{-5} T}{p}$ where T and p are temperature and pressure respectively

Throughout the process the concentration of the reactants will be held constant on the left-hand surface of the matrix, i.e. $c(0, t) = 1$.

$$\frac{\partial c}{\partial z}(1, t)$$

is proportional to the flux of reactants out of the porous solid. η_0^2 is the initial void of the preform. The void function, $\eta(z, t)$ is the square root of the void fraction of the preform.

2 Computational Analysis

2.1 The Scheme

In the following section we analyze the system (1.3.1-1.3.5) numerically and compare the results with the asymptotic solution. We begin by developing a numerical scheme.

We discretized the spatial equation (1.3.2) by using a finite central difference approximation and used equation (1.3.1) to step forward in time with the Euler Forward Method.

First, consider equation (1.3.2).

Let $f(\eta) = \frac{\eta^2}{\theta} [1 + N_k(\eta)]^{-1}$ and use the product rule so that (1.3.2) becomes

$$f[\eta(z, t)] \frac{\partial^2 c(z, t)}{\partial z^2} + \frac{\partial f[\eta(z, t)]}{\partial z} \frac{\partial c(z, t)}{\partial z} - \alpha^2 \eta(z, t) c(z, t) = 0 \quad (2.1.1)$$

Since, as $\Delta z \rightarrow 0$

$$f(z_0, t_0) \frac{\partial^2 c(z_0, t_0)}{\partial z^2} = f(z_0, t_0) \times \left\{ \frac{c(z_0 + \Delta z, t_0) - 2c(z_0, t_0) + c(z_0 - \Delta z, t_0)}{(\Delta z)^2} \right\} = f_j^m \frac{c_{j+1}^m - 2c_j^m + c_{j-1}^m}{(\Delta z)^2}$$

and

$$\frac{\partial f[\eta(z_0, t_0)]}{\partial z} \frac{\partial c(z_0, t_0)}{\partial z} = \frac{f(z_0 + \Delta z, t_0) - f(z_0 - \Delta z, t_0)}{2\Delta z} \times \left\{ \frac{c(z_0 + \Delta z, t_0) - c(z_0 - \Delta z, t_0)}{2\Delta z} \right\} = \frac{(f_{j+1}^m - f_{j-1}^m)(c_{j+1}^m - c_{j-1}^m)}{(2\Delta z)^2}$$

Thus, the equivalent discretized equation is

$$f_j^m \frac{c_{j+1}^m - 2c_j^m + c_{j-1}^m}{(\Delta z)^2} + \frac{(f_{j+1}^m - f_{j-1}^m)(c_{j+1}^m - c_{j-1}^m)}{(2\Delta z)^2} + -\alpha^2 \eta_j^m c_j^m = 0$$

Rearrangement yields

$$c_{j+1}^m = u_j^m c_j^m + v_j^m c_{j-1}^m$$

difference will be used to approximate the gradient of the cost function J as follow

$$\nabla_A J = \frac{J(A + \zeta, k) - J(A, k)}{\zeta}$$

$$\nabla_k J = \frac{J(A, k + \zeta) - J(A, k)}{\zeta}$$

The exact gradient of the cost function J can be obtained by using an adjoint equation (see Le Dimet and Talagrand [9]).

The unconstrained minimization algorithm of the quasi-Newton limited memory type [8] with the convergence criterion either on the number of iterations or the gradient norm of the cost function is used to determine the optimal parameters A^* and k^* .

We compared the model with experiments by Huttinger [10]. First, we compared the model with the experiment at a pressure $P = 12\text{kPa}$ and a temperature $T = 1273\text{K}$.

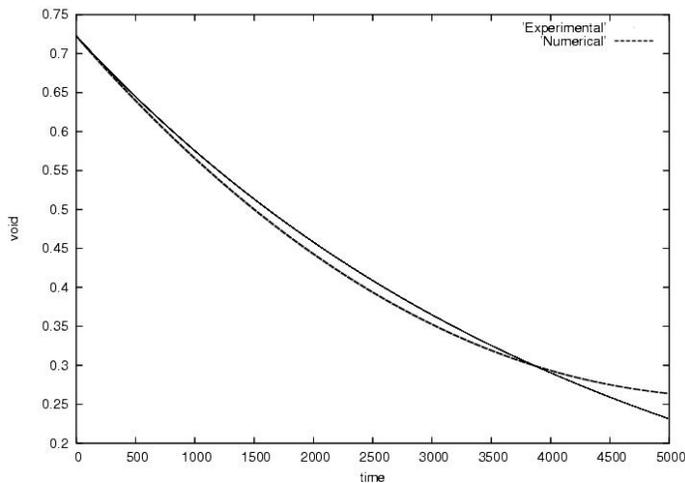


Figure 1: Void vs. time at 12kPa

We then used experimental data at higher pressures, $P = 15\text{kPa}$ and $P = 20\text{kPa}$ Pa shown in figure 2 and figure 3 respectively.

From the above figures we see that the model matches the experimental data qualitatively and is close quantitatively.

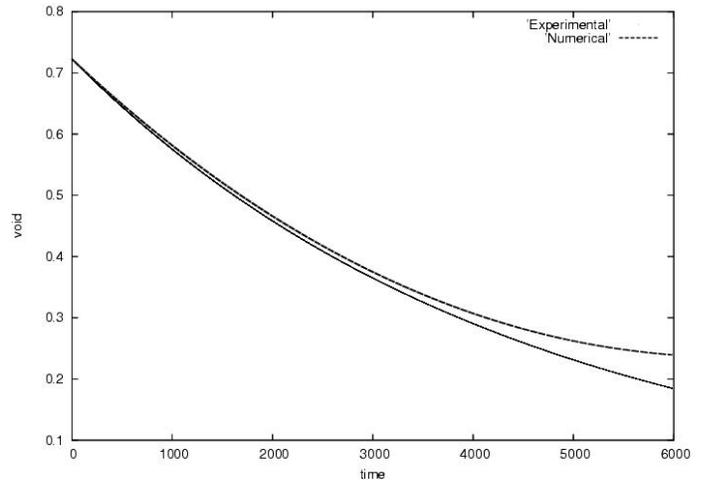


Figure 2: Void vs. time at 15kPa

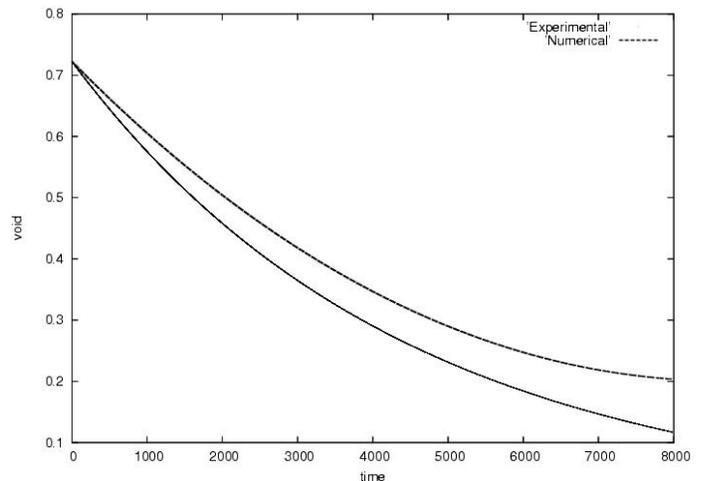


Figure 3: Void vs. time at 20kPa

3 Conclusion

This model assumes simple reaction kinetics. Specifically, we assume that the molecules in the gas don't react with each other gasses and bond to the surface on contact. Since the temperatures and pressures that promote gas-solid reactions also cause gas-gas reactions, this assumption is does not fit all process. However, if the sample is sufficiently far away from the gas inlet so that gas-gas reactions occur before the gas reaches the sample, then this model yields a good approximation to the experiment. The research presented here accurately models the CVI process for

some process as a function of time.

Again, if the gas is in the reaction chamber for some time before it reaches the preform, radicals and large molecules are formed chemically and equilibrium is established. These large molecules and radicals react at the pore inlet and in the interior of the pores. In this case, the deposition profile decreases with pore depth. With this model it can be shown (see [1]) that the void increases with space. This process causes the pore inlet to close before densification is complete or "choking".

Some researchers [11] have created a process where the gas enters the pore before it reaches reaction temperatures so that the radicals and large molecules formed inside the pore. This process can be used so that densification increases with space. This model does approximate a void that decreases with space.

We plan to model the CVI process considering the chemistry of the gas and with fewer simplifying assumptions. This will produce a model that is accurate for different CVI processes in space and time.

References:

- [1] A. Jones, Profile of Unsuccessful Process and the Criteria for a Successful Process for the Chemical Vapor Infiltration Process, *Applied Mathematical Modeling* No.7604, 2005
- [2] H.-C. Gottlieb, Chang, M. Marion, and B. W. Sheldon, Mathematical Analysis and Optimization of Infiltration processes, *Scientific Computing* 13, 3, (1998).
- [3] R. Aris, *The Mathematical Theory of the Diffusion and Reaction in Permeable Catalysts*, – Oxford University Press, London 1975.
- [4] F. A. L. Dullien, *Porous Media: Fluid Transport and Pore Structure*, Academic Press, New York, 1979.
- [5] E. A. Mason and A. P. Malinauskas, *Gas Transport in Porous Media: The Dusty-Gas Model*, Elsevier Science Publisher 1983.
- [6] R. Jackson, *Transport in Porous Catalysts*, Elsevier Science Publisher 1977.
- [7] H.C. Chang, *Minimizing Infiltration Time during Isothermal Chemical Vapor Infiltration* Ph.D. Thesis, Brown University 1995.
- [8] J. C. Gilbert and C. Lemarchal, Some numerical experiments with variable-storage quasi-Newton algorithms, *Math. Program.* 45, pp. 407-435, (1989).
- [9] F. X. Le Dimet and O. Talagrand, Variational algorithms for analysis and assimilation of meteorological observations: theoretical aspects, *Tellus* 38A, pp.97-110,(1986).
- [10] A. Becker and K. -J. Huttinger, Chemistry and kinetics of chemical vapor deposition of procarbon-III procarbon deposition from propylene and benzene in the low temperature regime *Carbon* 36, (3) pp.201-211, (1998).
- [11] T. A. Langhoff, T.-A. Schnack *Modelling chemical vapor infiltration of pyrolytic carbon*, Lecture Notes in Applied and Computational Mechanics (Editor s: Wendland, W.L., Efendiev, M.) 12, pp 149-154, Springer. (2003).