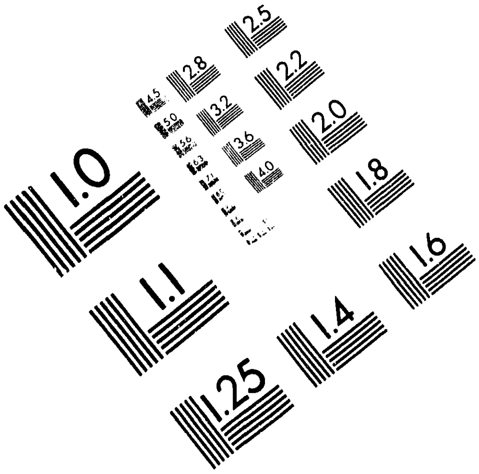

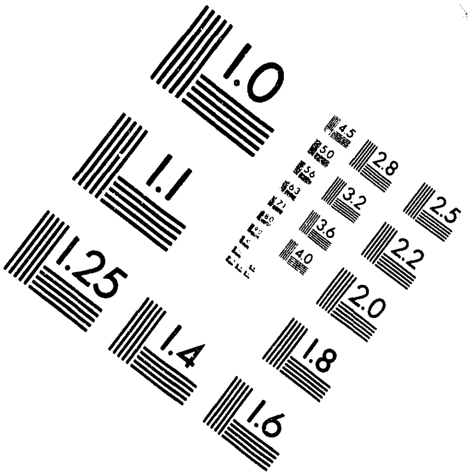

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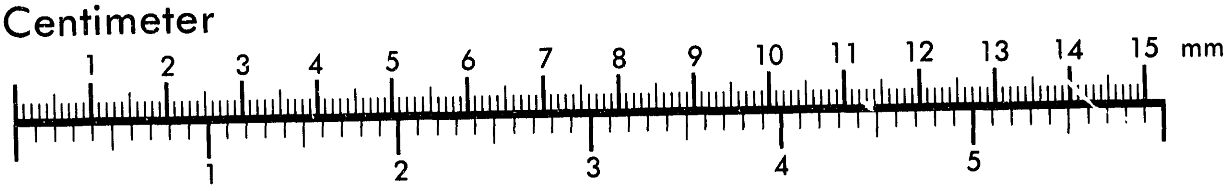

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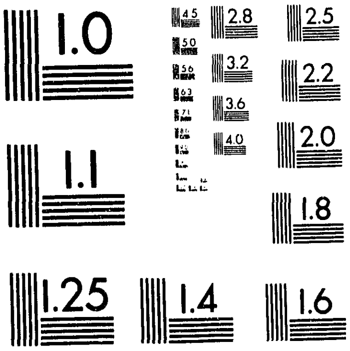

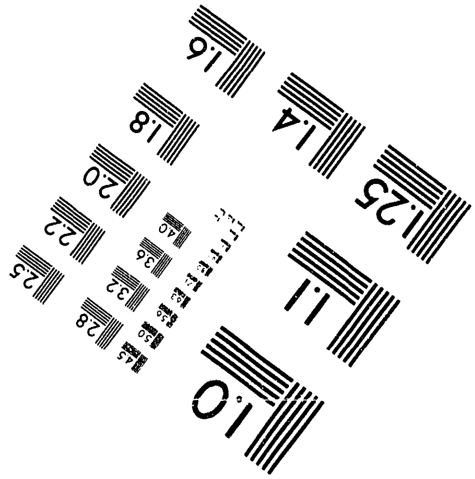

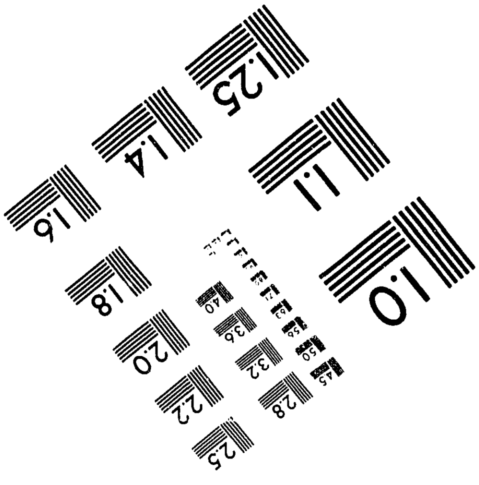

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OVERVIEW OF CHEMICAL VAPOR INFILTRATION

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ABSTRACT

Chemical vapor infiltration (CVI) is developing into a commercially important method for the fabrication of continuous filament ceramic composites. Current efforts are focused on the development of an improved understanding of the various processes in CVI and its modeling. New approaches to CVI are being explored, including pressure pulse infiltration and microwave heating. Material development is also proceeding with emphasis on improving the oxidation resistance of the interfacial layer between the fiber and matrix. This paper briefly reviews these subjects, indicating the current state of the science and technology.

INTRODUCTION

Chemical vapor infiltration (CVI) for the preparation of near-net-shape, continuous fiber ceramic matrix composites (CMCs) is emerging from the laboratory and pilot plant to commercial production. Interestingly, while a number of industrial companies are developing manufacturing capability, a simultaneous surge in activity is occurring in basic and applied research in CVI. These efforts range from fundamental kinetics and mass transport studies to investigations of the microchemistry and micromechanics of fiber-matrix interfaces and development of elaborate, predictive process models. Significant activity is ongoing in at least five nations, and the work of several are represented in this volume. This rich and diverse research is being performed at a number of institutions and has resulted in significant advances in understanding CVI, substantial development and optimization of its processes, and development of new material systems.

The impetus for the development of CVI has been the inability of more conventional ceramic fabrication techniques to yield high-quality CMCs. Techniques such as hot-pressing (where a ceramic body is simultaneously subjected to high temperatures and pressures) involve fiber-damaging extremes of temperature and mechanical stress. For example, the popular SiC-based fiber Nicalon[a] suffers degradation at processing temperatures above 1100°C /1,2/, a temperature that is well below that for sintering SiC. The high-modulus, small-diameter (15-μm) Nicalon fibers are also susceptible to mechanical damage from high pressure consolidation methods. Thus novel approaches to densification are required and have largely involved impregnation of fibrous preforms with vapor or liquid matrix precursors. By far the most success has been with vapor sources, leading to what has become a group of techniques known as CVI.

CVI originated in efforts to densify porous graphite bodies by infiltration with carbon /3/. The technique has developed commercially such that half of the carbon-carbon composites currently produced are made by CVI (the remainder are fabricated by curing polymer-impregnated fiber layups). The earliest report of CVI for ceramics was a 1964 patent for infiltrating fibrous alumina with chromium carbides /4/. During the last two decades much of the development of CVI techniques has taken place at the University of Karlsruhe /5/, the University of Bordeaux /6,7/, and Oak Ridge National Laboratory /8,9/.

This paper provides a brief overview of the CVI field, largely focussing on processing considerations and enumerating the material systems that have been investigated. Included is a discussion of the fundamental phenomena of CVI and its parent process, chemical vapor deposition (CVD). A number of highly sophisticated efforts to model CVI are described. Details of issues such as interfaces, mechanical properties, and service behavior of CMCs are discussed at length by other contributions to this volume.

1. FUNDAMENTALS OF CVI

In CVI gaseous reactants infiltrate a porous (typically fibrous) preform held at elevated temperature, depositing matrix material on the substrate structure via a standard CVD reaction. This CVD coating grows with continued deposition to form the composite matrix. CVD reactions are attractive in that it is possible to deposit a wide variety of ceramic matrix materials including silicides, borides, carbides, nitrides, and oxides. Another advantage of CVD is that it allows the formation of very-high temperature materials at relatively low temperatures, sparing the fibers from degradation. An excellent example of a high temperature matrix material is TiB_2, which has a melting point of 3225°C but which can be easily deposited at 900°C via:

$$TiCl_4 + 2BCl_3 + 5H_2 \text{ ----> } TiB_2 + 10HCl. \qquad (1)$$

Vapor infiltration also imposes little mechanical stress on the fibers; and proper tailoring of the fiber-interface-matrix system, together with only modest differences in thermal expansion coefficients, results in a CMC with minimal residual stress.

The fundamental mass transport and kinetic steps in CVD are:

1. transport of reactant species to the vicinity of the substrate,
2. diffusion of reactant species to the substrate surface,
3. adsorption of reactant species,
4. surface diffusion, dissociation, inclusion of coating atoms into the growing surface, and formation of byproduct species,
5. desorption of byproduct species,
6. diffusion of byproduct species to the bulk gas, and
7. transport of byproduct species away from the substrate (exhaust).

During CVI the primary objective is to maximize the rate of matrix deposition and minimize density gradients. Unfortunately, an inherent competition exists between the deposition reaction and the mass transport of the gaseous species. Deposition reactions that are too rapid usually result in severe density gradients, where complete densification occurs near the external surfaces and much lower densities in the interior regions. Alternatively, exceptionally slow deposition reactions require uneconomically long times to densify components.

Describing the deposition of matrix material in a porous structure is, in principle, a simple matter. The process is accurately represented by the well-known partial differential equations that describe mass and heat transfer in conjunction with relationships that accurately describe the chemical kinetics and the evolution of the microstructure during infiltration. Because of the practicalities involved with obtaining these specific relationships, the development of fully predictive models, however, has been a significant challenge.

The simplest models treat CVI as a pore diffusion problem, using cylindrical pores and a first-order deposition reaction /10-13/. This treatment illustrates how undesirable density gradients are created during infiltration. It is convenient to compare the relative kinetic and mass transport rates in CVI using a dimensionless number, the Thiele modulus (Φ), which represents the ratio between the chemical kinetic deposition rate, k, and the gas-phase mass transport rate. The primary difficulty with applying the Thiele modulus to infiltration is that its value changes during the process owing to changes in pore size. It is therefore convenient to characterize CVI with the initial value of the Thiele modulus, Φ_o /14/. For a first-order deposition reaction in a cylindrical pore,

$$\Phi_o^2 = 2kL^2/r_oD_o, \qquad (2)$$

where r_o and D_o are the pore radius and the gas diffusivity in the initial preform, respectively, and L is the length of the pore (i.e., the characteristic thickness of the preform).

The two kinetic limiting cases for isothermal-isobaric conditions are illustrated in Fig. 2. Under reaction-rate-controlling conditions ($\Phi_o^2 << 1$) gas transport is rapid, and the initial reactant concentration, C_o, is essentially uniform throughout the pore volume. As a result, uniform deposition takes place down the length of the pore causing no gradient in composite density. For diffusion-rate-controlling conditions ($\Phi_o^2 >> 1$), however, the deposition reaction is fast causing a depletion of reactants down the pore length with a proportional decrease in the formation of matrix material and a significant composite density gradient. Mixed control occurs when the two rates are comparable ($\Phi_o^2 \sim 1$).

Describing CVI with cylindrical pores does not accurately reflect the often complex microstructures that are present in real preforms. The most common reinforcements in composites formed by CVI are fibers with a relatively small diameter (~10 μm). Bundles of these are woven into cloth layers, which are then stacked to form a preform. In some cases three-dimensional weaves are also used. All of these preforms have multimodal porosity distributions that range from micrometer scale within fiber bundles to hundreds of micrometers between bundles and cloth layers. The porosity and fiber architecture, which are typically anisotropic, govern the gas permeability and the thermal properties. As densification proceeds, the dimensions and distribution of the porosity change nonuniformly with attendant changes in the preform's physical properties. For CVI to be successful, the reactant gases must initially reach the finest porosity (i.e., the interfilament volume), react, and fill those pores. When this volume is relatively well-infiltrated, the larger interbundle and interply porosity should then be filled. The series of photographs in Fig. 3 illustrate this progression during the infiltration of Nicalon fibers with SiC matrix.

2. CVI TECHNIQUES

The five general classes of CVI techniques rely on diffusion and/or forced flow for transport of gaseous species and thermal control of the reaction rate (Fig. 4). The most widely used commercial process is isothermal-isobaric CVI (ICVI) /5,7,15/, which depends only on diffusion for species transport. This process generally operates at reduced pressure (1-10 kPa) for deposition rate control. Density gradients are minimized by a low reaction temperature; although in order to get economical densification rates, deposition is often sufficiently rapid to overcoat the outer surface before infiltration is complete. Interruption of the CVI process for periodic machining is thus necessary for all but the thinnest parts to open diffusion paths from the surface. Regardless, this diffusion-dependent process is still slow requiring infiltration times of at least several weeks. It is commercially attractive, however, because large numbers of parts of varying dimensions are easily accommodated in a single reactor.

In CVI it may be most efficient to use different conditions to infiltrate the coarser porosity in a preform, after the finer porosity is filled, to deposit significant amounts of material in these larger volumes within a reasonable time. In ICVI the conditions (i.e., temperature or gas concentration) can be explicitly changed, and as a result, the process can occur in several steps. For large reactors the initial infiltration is likely achieved by placing the preform in the region of the furnace, which is at a lower temperature and/or where it will contact only significantly depleted reactant gases (downstream regions) so that deposition is slow and reactants can penetrate to the finest pores. As this finer porosity becomes filled, the parts may be moved to regions of higher temperature and/or lower gas depletion to fill the coarser porosity more rapidly. During these interruptions of the process, surface-grinding can be performed to reopen channels for diffusion. Although the coarser pores will eventually become fine (and unless the infiltration rate is once again slowed, they will neck and seal in voids), their larger size still allows infiltration of a significant volume of matrix material. It is not possible, however, to produce fully dense material using any CVI technique (e.g., in cloth layup preforms the lower limit of the void fraction is ~10%).

The isobaric-thermal gradient process may have advantages under certain circumstances. It, too, depends on diffusion; however, sealing of the entrance surface is prevented by maintaining it at low temperature. As densification approaches completion, the cooler surface rises in temperature as a result of the greater conductivity of the denser preform, causing infiltration of the entire volume. This is still a slow process, however, because of the dependency on diffusion. In a new development for this technique, some exploratory efforts have been made using microwave heating to produce the thermal gradient /16-20/. The outer regions of a relatively low thermal conductivity preform will be radiatively cooled, while the central volume rises to temperatures up to several hundred degrees centigrade higher. This may still be a slow process, however, because of the dependency on diffusion. Initial difficulties appear to relate to the initial and changing electric and dielectric properties of the composite materials /19/.

The potentially more rapid isothermal-forced flow process, which uses forced convection, can suffer from density gradients and loss of permeability at the entrance surface as is seen in the isothermal process. It is particularly useful for the very rapid infiltration of thin preforms, often no more than a single cloth layer in thickness /21/. The 3M Company's SICONEX[b] series of products are produced via this technique.

The forced-flow-thermal gradient technique (FCVI) overcomes the problems of slow diffusion and restricted permeability and has demonstrated a capability to produce thick-walled, simple-shaped components in hours /8,9,22/. Unlike the ICVI method, however, significantly greater fixturing is required to both allow for the imposition of the thermal gradient and appropriate seals to force reactants to flow through the preform. Densification times are directly related to the preform thickness in the direction of reactant flow. Typical rates of 0.5-1 mm/h have been achieved.

The FCVI process is self-optimizing, which has allowed for much shorter infiltration times and less difficulty in obtaining uniform infiltration. The furnace is configured to apply a thermal gradient across the preform, in part by actively cooling the reactant gas entrance surface. As expected, the preform is infiltrated most rapidly near the hot surface: a diffuse densification front moves from the hot surface toward the cooled entrance surface. Infiltration of the finer porosity must, again, occur during the initial infiltration period under conditions where $\Phi << 1$ for the micrometer-scale radii. For the volume near the cooled surface, Φ is minimized by the low temperature, while nearer the hot surface, it is forced to small values by depletion of reactants.

As the finer porosity is filled and as the density of the part increases, its thermal conductivity increases and the thermal gradient decreases. Temperatures across the part are generally higher, increasing Φ and allowing coarser porosity to be efficiently filled with matrix. Thus, in a self-controlled manner the various scales of porosity are progressively filled. Infiltration is typically assumed to be complete when permeability is diminished such that the pressure drop across the part becomes prohibitive (70 - 140 kPa). Unlike ICVI, intermediate surface grinding is not necessary, and the process can continue to final density uninterrupted. Some finishing may be necessary, however, to remove pieces of fixturing or to smooth surfaces.

Pulsed-flow CVI utilizes alternate introduction of reactant gases and evacuation of the CVI reactor to rapidly transport reactant species into, and product gases out of, the preform /23-26/. The technique has not been widely investigated, although some modeling calculations indicate that it can significantly improve infiltration rates over those experienced in ICVI /25/.

3. MODELING CVI

Accurately modeling CVI is a substantial task, requiring representation of the complex fiber architecture noted above and expressions for mass and heat transfer (in nonisothermal systems) coupled to chemical kinetic rate expressions. In addition, the pore size distribution changes with time, albeit slowly, such that a model must be iterated in time to describe component densification.

Several CVI models have used descriptions of the porosity that are based on the nearly cylindrical shape of the fibers that are actually used for CVI /14,27-32/. Recent efforts to describe the evolving porosity in fibrous preforms are based on Avrami's /33/ model for phase transformations /14,30/. Models other than CVI have also been developed for reacting porous solids that undergo pore closure. These more accurately describe the inevitable formation of trapped porosity by using percolation theory /34-36/. The approaches describe mass transport with percolation in a Bethe lattice /37/ and can easily be modified to describe CVI /14/. The primary shortcoming of all of these continuum and percolation based models is that they fail to describe the multimodal nature of the porosity in real preforms. Recently, however, several modeling efforts have begun to employ multimodal descriptions of the porosity /32,38/.

Although work is continuing at several of laboratories to develop more extensive CVI models, most of these have not been successfully applied to experimental results. Thermogravimetric experiments of the reaction-controlled infiltration of fiber bundles with carbon /39/ agree generally with Currier's model. Sheldon and Besmann /14/ compared isothermal data for the infiltration of individual fiber bundles with SiC from methyltrichlorosilane, to modeling results that were based on a first order reaction and a wide variety of different descriptions of diffusion. The results of this comparison imply that a multistep reaction leads to poor infiltration compared with the predictions for a first-order reaction. It is theoretically possible, however, that other complex reaction kinetics can lead to infiltration that is more uniform than the first-order predictions. A relatively simple description of ICVI with a sequence of two first-order reactions has been used to demonstrate this possibility /40,41/. These experimental and calculated results suggest that a greater understanding of complex reaction sequences can lead to significant improvements in existing ICVI techniques.

Several ICVI modeling efforts have described non-isothermal processes /16,17,27,28,38/. In these systems additional complexities are associated with heat transfer and forced convection as infiltration proceeds and the structure of the material changes. For models such as these to describe infiltration behavior accurately, appropriate descriptions of the complexities associated with these transport processes will have to be combined with the complex microstructure evolution and chemical kinetics that have already been discussed in connection with ICVI.

Regardless of these complexities and the current inability to describe them fully, understanding the general relationships between the relevant kinetic processes has led to the practical solution of many ICVI problems. Control of temperature is critical because chemical reactions exhibit Arrhenius behavior such that the rates increase exponentially with temperature. Therefore, relatively low temperatures slow the deposition rate substantially more than they do diffusion, which reduces Φ /5/. Simple reactant gas depletion within the ICVI reactor or etching of the deposit by reaction by-products (e.g., HCl in the ICVI of SiC from methyltrichlorosilane) also reduces the deposition rate /42/. In non-isothermal processes, controlling the temperature gradient prevents the gas entrance surfaces from becoming sealed until after the interior of the component has reached an acceptable density.

The model developed by Starr and coworkers /43/ has been successful in fully describing macroscopic densification during ICVI and FCVI. One of the applications for such models is the optimization of the densification process, often focused on reducing processing time and improving density and uniformity. Their model has resulted in full densification by FICVI of a 12.5-mm-thick disk within 19h. In addition, the density proved to be fairly uniform both axially and radially (Fig. 5).

4. MATERIALS

The materials systems of CMCs fabricated by ICVI typically consist of fibers fashioned into a preform, often an interface coating applied to the fibers either before or after preparation of the preform, and the infiltrated matrix. The properties of each of these components are fundamental to the ultimate behavior of the composite, and even the nature of the technique by which the interface or matrix is deposited can influence its properties.

4.1 Fibers/Preforms

Several carbon, oxide, carbide, and nitride fibers have been used in ICVI materials with mixed success, and this review will only briefly mention some of the most popular. Although an advantage of ICVI processing is prevention of damage to relatively sensitive fibers, the fibers must still be able to withstand the ICVI environment. This generally entails elevated temperatures of the order of 1000°C and corrosive matrix precursors.

The greatest effort and success has been with carbon fibers that are stable with respect to most ICVI environments. Motivation to replace carbon with more oxidation-resistant fibers is substantial since many applications are in high-temperature, oxidative ambients environments.

Interest in SiC fibers is high because of their high oxidation resistance. A chemical-vapor-deposited, large-diameter (~150 μm) SiC filament produced by Textron Specialty Materials has been used in ICVI, although such a large filament is difficult to form into other than very simple shapes.

Some of the most commonly used SiC-based fibers are Nicalon and Tyranno[c], which are polymer-derived microcrystalline/amorphous material containing significant amounts of silica. Unfortunately, these fibers lose their high strength when exposed to temperatures approaching 1000 to 1100°C because of reactions with residual oxygen and carbon, along with recrystallization /1,2/.

Oxides are inherently oxidation-resistant, yet sol-gel-derived, amorphous/microcrystalline oxide fibers generally do not retain adequate properties after infiltration. Recent work, however, has demonstrated an ability to stabilize oxide fibers such as Nextel 440[d], offering the possibility of a composite with similar properties to Nicalon but at lower cost and greater oxidation resistance /44/. Single-crystal and polycrystalline oxide fibers with very high temperature capabilities have been produced, but their very high modulus makes preform manufacture difficult. In addition, they are generally not available in sufficient quantities at reasonable prices.

As in most CMCs, preform geometries can be tailored to the application to maximize strength and toughness in the direction of maximum stresses. The demands of the ICVI process, however, place restrictions on the fiber architectures. Sufficient permeability is necessary to allow the precursor species to transport to all fiber surfaces. Practically, multimodal porosity is required so that adequate numbers of larger pores will permit reactants to reach the fiber bundles that typically make up woven or braided preforms. The negative result, however, is that these larger pores, either between tows or between cloth layers, are not fully infiltrated and can act as incipient cracks /7/.

4.2 Fiber-Matrix Interface

In single-phase materials the energy absorbed during fracture is determined by the applied forces and the strain and surface energies of that material. In composites, however, additional phenomena include the strain energy of the fibers and the work done in debonding and pulling the fibers from the matrix. These additional factors will contribute to increasing the stress at which the matrix in a composite will begin to crack and increase the energy necessary to cause material failure.

Experience has shown that Nicalon, and most other fibers, require precoating before infiltration to avoid strong interfacial bonding with resultant low flexure strength and brittle fracture. Composites with uncoated fibers exhibit fracture surfaces that are flat and smooth and have no evidence of fiber pull-out;

these result in little toughening (Fig. 6). To control the mechanical properties of Nicalon-SiC composites, a thin pyrolytic carbon layer is deposited on fibrous preforms prior to densification to provide a controlled and uniform interface with the matrix. The carbon deposition conditions are chosen to produce a graphitic coating with a laminar structure. The coating has been found to prevent chemical damage of the fibers during processing, as well as appropriately weakening the fiber-matrix interface, enhancing fiber debonding and slip /45,46/. Thus the coating results in an increase in the toughness and ultimate strength of the composite material.

The current limitation on the use of ICVI materials in oxidizing environments, however, is due to the susceptibility of the interface material to oxidation. Although under certain conditions the flaws on composite surfaces can seal via the formation of silica and protect the carbon interface /7/, under most oxidizing and stress environments this would not adequately occur. Recent, substantial efforts to replace carbon with somewhat more oxidation-resistant hexagonal BN have been successful (Fig. 7). The capability of the phase to absorb residual stresses in a manner similar to graphitic carbon appears to be the result of the highly aligned hexagonal basal planes that are observed near the fiber surface /7,47,48/. In addition, BN can interact with the silica oxidation product to form a borosilicate glass with a sufficiently low viscosity so that it might flow and seal cracks and openings. Still, BN will likely provide only marginal improvement over carbon with respect to oxidation; therefore, significant efforts to identify truly oxidation-resistant interfaces, such as oxide coatings, are important.

4.3 Matrix Materials

ICVI in all its variants has been used to produce many matrices including SiC, B_4C, TiC, HfC, BN, Si_3N_4 (amorphous), TiB_2, Al_2O_3, and ZrO_2. These systems uniformly use metal halide precursors and processing temperatures of 900 to 1200°C. Almost any other ceramic that can be deposited using a CVD reaction can be produced as a ICVI matrix. These may include even complex systems such as the new, high-temperature superconductors. Also, the matrix need not be single-phase, since composite coatings by CVD have been demonstrated and thus multiple phase matrices are theoretically possible. With such composite matrices, CMC toughness may be further enhanced.

CONCLUSIONS

Significant efforts in understanding and modeling ICVI processes for the production of CMCs have resulted in workable models. These efforts promise to yield an even closer understanding of ICVI with concomitant improvements in processing. Ultimately, model-based, real-time control of ICVI should be realized.

Material development in ICVI is accelerating and emphasis is on alternative fibers and interfaces. Specifically, improvement of the oxidation resistance of interface coatings in CMCs is needed so that the true, high-temperature potential of these materials can be realized. Finally, the long-term interest in CMCs, and in ICVI, is in the development of oxide matrix-oxide fiber systems that would thus be inherently oxidation resistant and compatible in a variety of applications.

ACKNOWLEDGEMENTS

The authors thank A. E. Pasto and G. R. Romanoski for their thoughtful reviews of the manuscript, J. W. Turner and S. M. Monday for assistance in manuscript in preparation and H. R. Livesey for graphic design. Research sponsored by the U. S. Department of Energy, Office of Fossil Energy, Advanced Research and Technology Development Materials Program, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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[a] A trademark of Nippon Carbon, Tokyo, Japan.
[b] A trademark of the 3M Company, St. Paul, MN.
[c] A trademark of Ube Industries, Tokyo, Japan.
[d] A trademark of the 3M Company, St. Paul, MN.

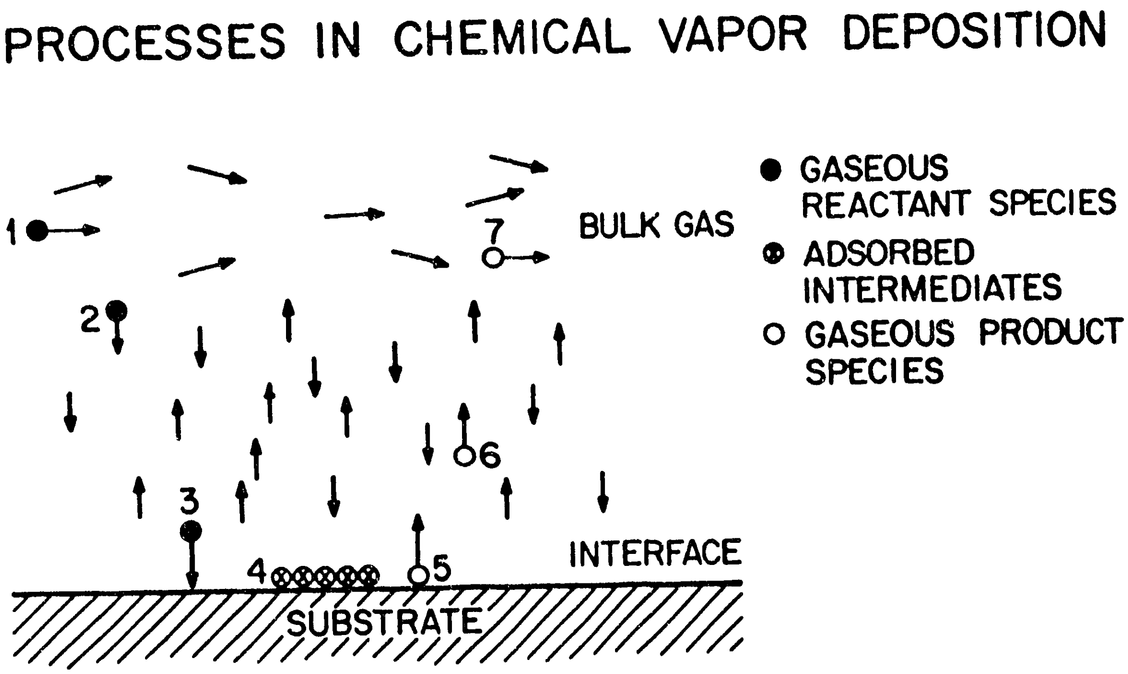

Fig 1: The processes in chemical vapor deposition.

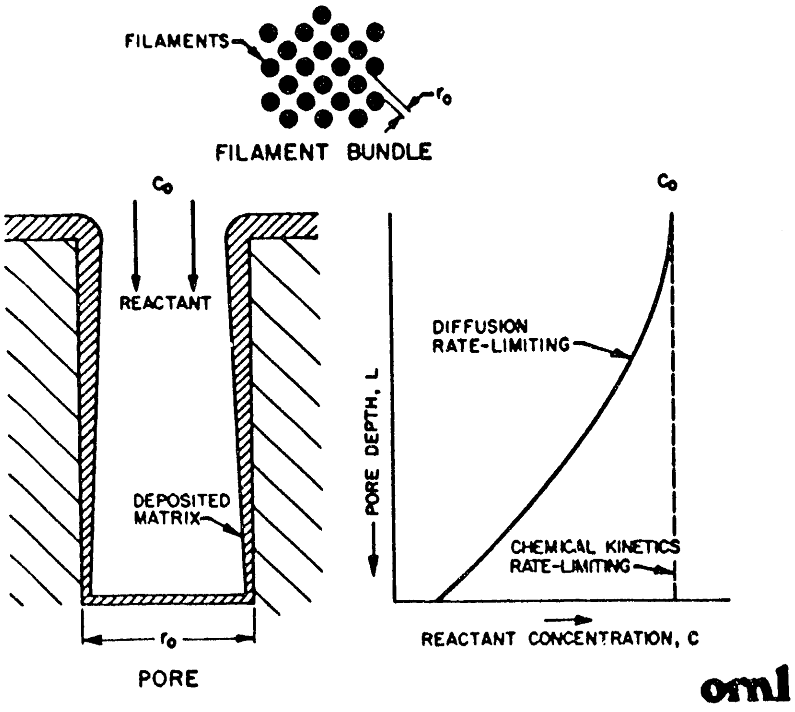

Fig 2: Reactant gas concentrations as a function of axial position down a cylindrical pore under diffusion and chemical kinetic rate-limiting conditions.

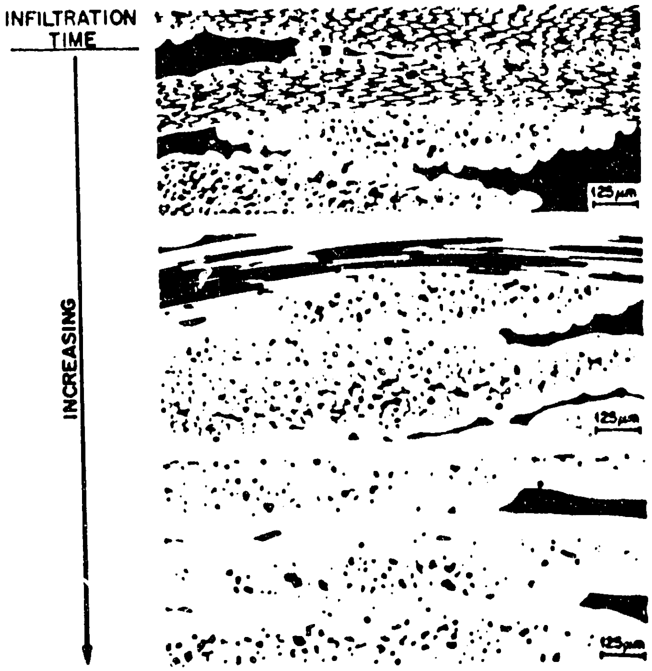

Fig. 3: Polarized light optical photo~~s~~graphs of polished specimens of Nicalon-SiC composites illustrating pore filling at different stages of the CVI process.

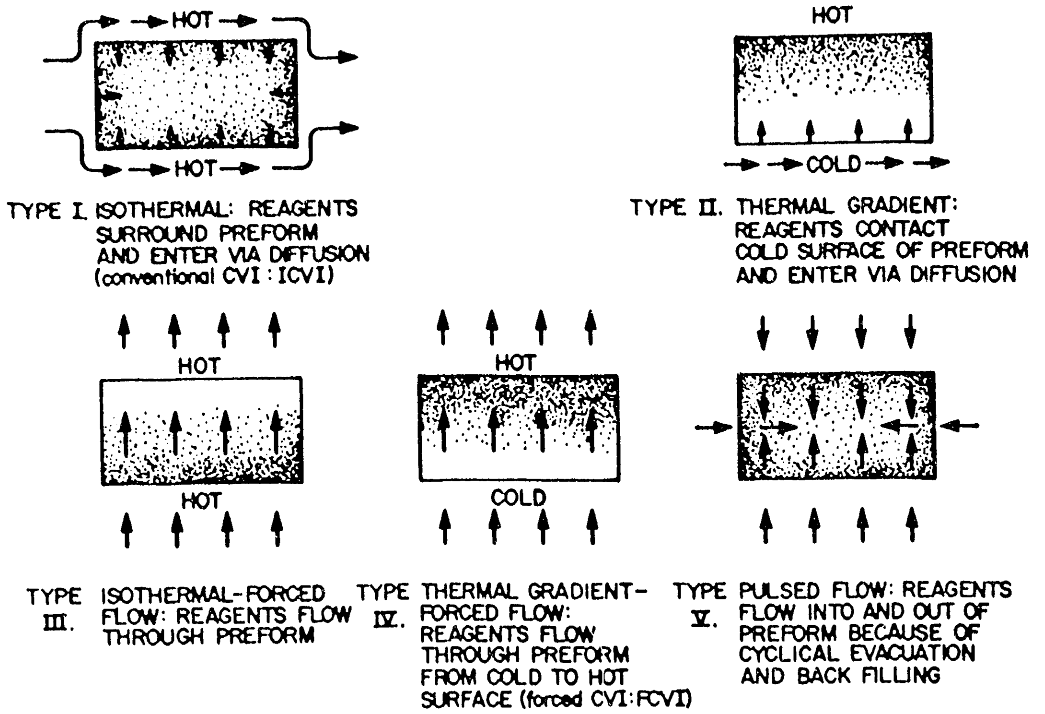

Fig. 4: The five general classes of CVI techniques.

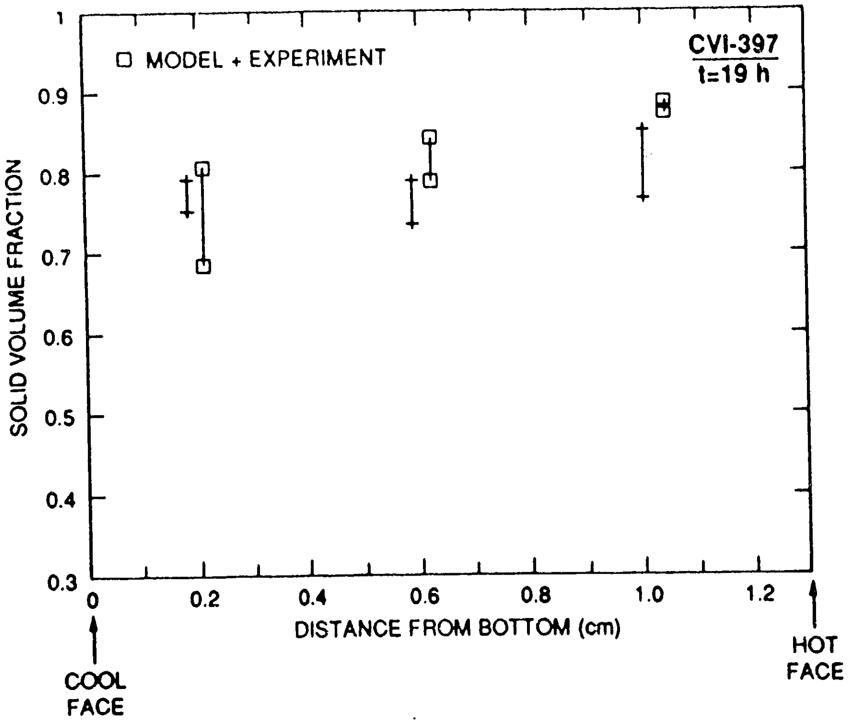

Fig. 5: Predicted and experimentally observed solid volume fraction in an FCVI sample illustrating optimized infiltration.

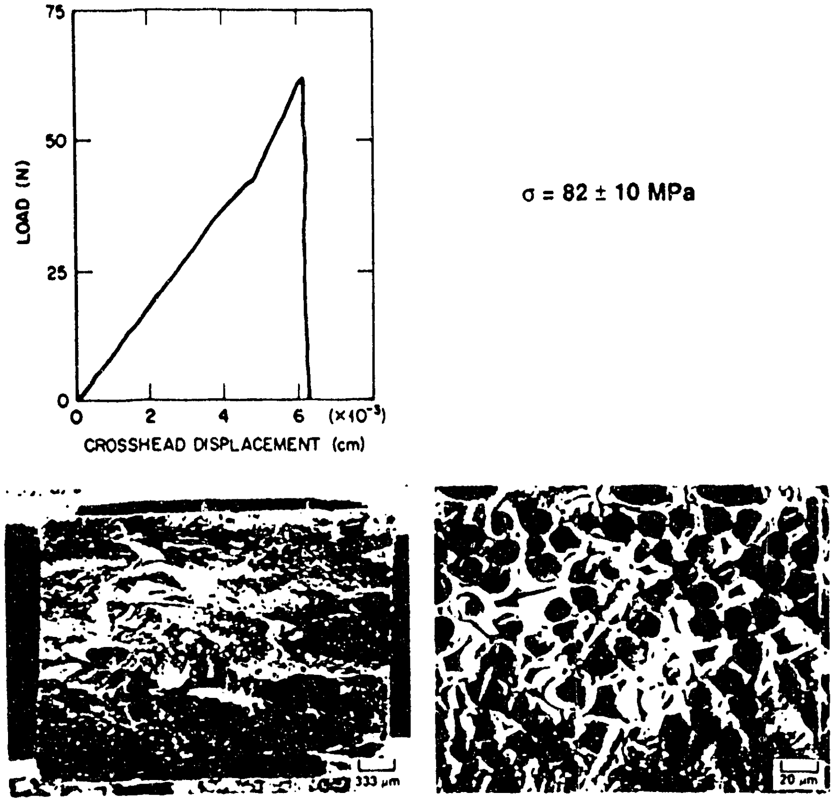

Fig. 6: Flexure curve and fracture surface of a Nicalon/SiC composite prepared with no interfacial layer.

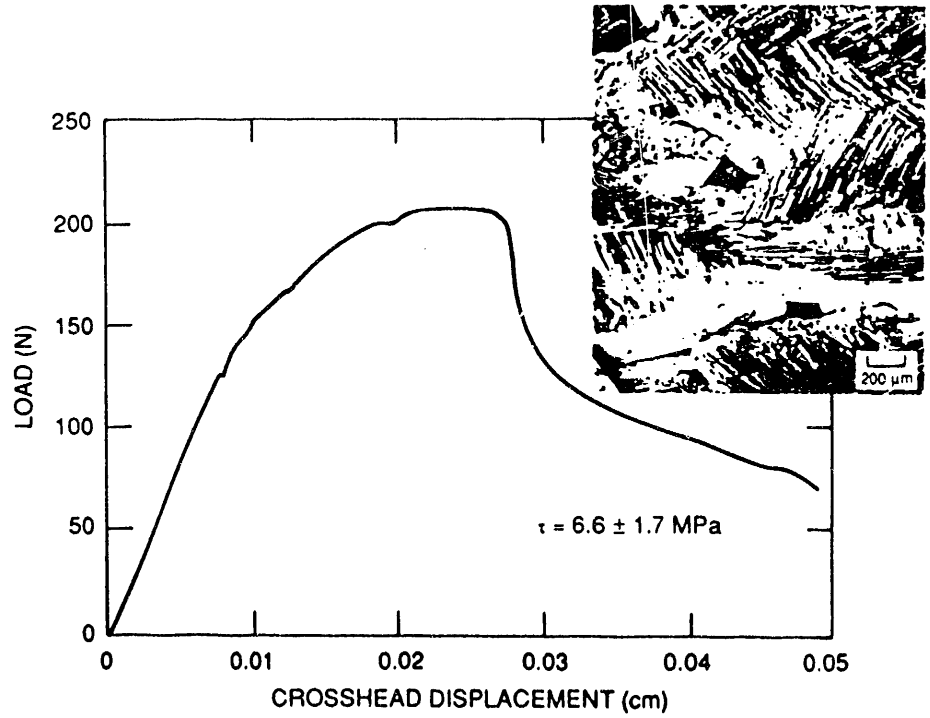

Fig. 7: Flexure curve and fracture surface for a Nicalon/SiC composite fabricated with an ~0.3 μm BN interface layer.

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