1 of 1

CHEMICAL VAPOR INFILTRATION OF NON-OXIDE CERAMIC MATRIX COMPOSITES

THEODORE M. BESMANN, DAVID P. STINTON, AND RICHARD A. LOWDEN
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6063

ABSTRACT

Continuous fiber ceramic composites are enabling new, high temperature structural applications. Chemical vapor infiltration methods for producing these composites are being investigated, with the complexity of filament weaves and deposition chemistry merged with standard heat and mass transport relationships. Silicon carbide-based materials are, by far, the most mature, and are already being used in aerospace applications. This paper addresses the state-of-the art of the technology and outlines current issues.

INTRODUCTION

Chemical vapor infiltration (CVI) has been particularly successful in the preparation of continuous fiber-reinforced, non-oxide ceramic matrix composites (CMCs), most notably SiC matrix materials. 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[®] suffers degradation at processing temperatures above 1100°C [1,2], a temperature which is well below that for sintering SiC. The high modulus, small diameter (15 μ m) 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 process, leading to what has become a group of techniques known as CVI.

This paper is a brief overview of the CVI field, focussing on processing and resultant material properties, and enumerating the material systems which have been investigated. Included is consideration of the composite materials system, its microstructure, and the resultant mechanical properties.

THE CVI PROCESS

In CVI, gaseous reactants infiltrate a porous (typically fibrous) preform held at elevated temperature, depositing matrix material on the substrate structure via a standard chemical vapor deposition (CVD) reaction. The 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. A typical reaction is the deposition of

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

SiC from methyltrichlorosilane:

which occurs efficiently at temperatures as low as 950 C.

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.

During CVI, the primary objective is to maximize the rate of matrix deposition and minimize density gradients. Unfortunately, there is an inherent competition between the deposition reaction and the mass transport of the gaseous species. Deposition reactions which are too rapid usually result in severe density gradients, where there is complete densification near the external surfaces and much lower densities in the interior regions. Alternatively, exceptionally slow deposition reactions require uneconomically long times to densify components. The series of photos in Fig. 1 illustrates this progression during the infiltration of Nicalon fibers with SiC matrix.

ORNL-PHOTO 7374R-90

**EVOLUTION OF MICROSTRUCTURE IN FORCED CVI OF
SiC/NICALON SHOWS EARLY SEALING OF FIBER BUNDLES
(40 vol % NICALON)**

ornl

Fig. 1: Polarized light optical photos of polished specimens of Nicalon/SiC composites illustrating pore filling at different stages of the CVI process.

CVI TECHNIQUES

There are five general classes of CVI techniques which rely on diffusion and/or forced flow for transport of gaseous species and thermal control of the reaction rate. (Fig. 2) The most

oml

Fig. 2: The five general classes of CVI techniques.

widely used commercial process is isothermal/isobaric CVI (ICVI) [3-5], 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 of parts 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 at least several-week infiltration times and machining times. 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, in order to deposit significant amounts of material in these larger volumes within a reasonable time. In ICVI the conditions (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 only

contact 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 more rapidly fill the coarser porosity. During these interruptions of the process surface-grinding can be performed in order 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, and, for example, in cloth layup preforms the theoretical lower limit of the void fraction is $\sim 10\%$.

The 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 due to the dependency on diffusion. In a new development for this technique, there have been some exploratory efforts in using microwave heating to produce the thermal gradient [6-10]. 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, due to the dependency on diffusion. Initial difficulties appear to relate to the initial and changing electric and dielectric properties of the composite materials [9].

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 also 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 [11]. The 3M Company's SICONEX[®] 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 times of the order of hours [12-14]. Unlike the ICVI method, however, significantly greater fixturing is required in order 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 the directed 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 with a diffuse densification front moving from the hot surface towards the cooled entrance surface. For the volume near the cooled surface the deposition rate is limited by the low temperature, whereas nearer the hot surface it is forced to small values by depletion of reactants, thus preventing premature sealing and poor densification.

As the finer porosity is filled and the density of the part increases, its thermal conductivity increases and the thermal gradient decreases. Temperatures across the part are generally higher, increasing the deposition rate 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 [15-18]. The technique has not been widely investigated, although some modeling calculations indicate it can significantly improve infiltration rates over those experienced in isothermal CVI [17].

MATERIALS

The materials systems of CMCs fabricated by CVI 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.

Fibers/Preforms

Although an advantage of CVI processing is prevention of damage to relatively sensitive fibers, the fibers must still be able to withstand the CVI 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 which are stable with respect to most CVI environments. Yet, there is substantial motivation to replace carbon with more oxidation resistant fibers since many applications are in high temperature, oxidative ambients.

There is great interest in SiC fibers because of the high oxidation resistance of the phase. A chemical vapor deposited, large diameter ($\sim 150 \mu\text{m}$) SiC filament produced by Textron Specialty Materials has been used in CVI, 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[®], 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 - 1100°C due to reactions with residual oxygen and carbon, and recrystallization [1,2].

As in most CMCs, preform geometries can be tailored to the application in order to maximize strength and toughness in the direction of maximum stresses. The demands of the CVI 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 which 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 [4].

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, there are the additional phenomena of 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 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 which are flat and smooth with no evidence of fiber pull-out and result in little toughening. (Fig. 3) To control the

Fig. 3: Flexure curve and fracture surface of a Nicalon/SiC composite prepared with no interfacial layer.

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 [19, 20]. Thus the coating results in an increase in the toughness and ultimate strength of the composite material.

The current limitation on the use of CVI 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 [4], 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. 4) 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

Fig. 4: Flexure curve and fracture surface for a Nicalon/SiC composite fabricated with an $\sim 0.3 \mu\text{m}$ BN interface layer.

hexagonal, basal planes which are observed near the fiber surface [4, 21, 22]. 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 and therefore significant efforts to identify truly oxidation resistant interfaces, such as oxide coatings are important.

Matrix Materials

CVI in all its variants has been used to produce a number of non-oxide matrices, including SiC, B_4C , TiC, HfC, BN, Si_3N_4 (amorphous), and TiB_2 . These systems uniformly use metal halide precursors and processing temperatures of 900 - 1200°C. Almost any other ceramic that can be deposited using a CVD reaction can be produced as a CVI matrix. These may include even complex systems such as the new, high temperature superconductors. There is also no reason why the matrix must be single-phase, since composite coatings by CVD have been demonstrated and thus multiple phase matrices are theoretically possible. With such composite matrices the CMC toughness may be further enhanced.

CONCLUSIONS

Process and material development by CVI is accelerating, with the emphasis on increasing densification rates and alternate fibers and interfaces. Specifically, there is a significant need to improve the oxidation resistance of interface coatings in CMCs so that the true, high temperature potential of these materials can be realized. Finally, the long term interest in CMCs, and in CVI, is in the development of improved matrices and interfaces for a variety of applications that would be inherently tougher with possibly higher temperature capability.

ACKNOWLEDGEMENTS

This research was sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Concepts (AIC) Materials Program, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. The authors wish to thank L.L. Snead and M.A. Karnitz for their thoughtful reviews of the manuscript. J. Z. Palmer aided in manuscript preparation and H.R. Livesey produced the drawings.

REFERENCES

1. G. Simon and A. R. Bunsell, *J. Mater. Sci.* **19**, 3658 (1984).
2. P. J. Lamicq, G. A. Bernhart, M. M. Dauchier, and J. G. Mace, *Am. Ceram. Soc. Bull.*, **65** 336 (1986).
3. E. Fitzer and R. Gadow, *Ceram. Bull.* **65**, 326 (1986).
4. R. Naslain, *J. Alloys and Compounds*, **188**, 42 (1992).
5. J.Y. Rossignol, F. Langlais, and R. Naslain, in Proc. 9th Int'l. Conf. CVD, edited by McD. Robinson et al., (The Electrochemical Society, Pennington, New Jersey, 1984) pp. 596-614.
6. D. Gupta and J.W. Evans, *J. Mater. Res.* **6**, 810 (1991).
7. J.I. Morell, D.J. Economou, N.R. Amundson, *J. Mater. Res.* **7**, 2447 (1992).
8. D.J. Devlin, R.P. Currier, R.S. Barbero, B.F. Espinoza, and N. Elliott, in Chemical Vapor Deposition of Metals and Ceramics II, edited by T.M. Besmann, B. M. Gallois, and J.W. Warren (*Mat. Res. Soc. Proc.* **250**, Pittsburgh, PA, 1992) pp. 207-219.
9. D.J. Devlin, R.P. Currier, R.S. Barbero, and B.F. Espinoza, *Ceram. Eng. Sci. Proc.* **14**, 761 (1993).
10. M.S. Spatz, D.J. Skamser, P.S. Day, H.M. Jennings, and D.L. Johnson, *Ceram. Eng. Sci. Proc.* **14**, 753 (1993).
11. Y. G. Roman, C. Steijsiger, J. Gerretsen, and R. Metselaar, *Ceram. Eng. Sci. Proc.* **14**, 1190 (1993).
12. D.P. Stinton, A. J. Caputo, and R.A. Lowden, *Ceram. Bull.* **65**, 347 (1986).
13. T.M. Besmann, B.W. Sheldon, R.A. Lowden, and D.P. Stinton, *Science* **253**, 1104 (1991).
14. T.D. Gulden, J.L. Kaae, K.P. Norton, and L.D. Thompson, in Proc. 11th Int'l. Conf. CVD, edited by G.W. Cullen and K.E. Spear (The Electrochemical Society, Pennington, New Jersey, 1990), pp. 546-552.
15. R.L. Beatty and D.V. Kiplinger, *Nuc. Appl. Tech.*, **8**, 488 (1970).
16. K. Sugiyama and E. Yamamoto, *J. Mater. Sci.* **24**, 3756 (1989).

17. S.V. Sotirchos and M.M. Tomadakis, in Chemical Vapor Deposition of Metals and Ceramics, edited by T.M. Besmann and B. M Gallois (Mat. Res. Soc. Proc. 168, Pittsburgh, PA, 1990) pp. 73-78.
 18. K.Itoh, M. Imuta, J. Gotoh, and K. Sugiyama, J. Mat. Sci. 27 , 6022 (1992).
 19. R.A. Lowden, Ceram. Trans. 19 , 619 (1991).
 20. N. Fretty and M. Boussuge, Composites Science and Technology 37, 177 (1990).
 21. R.A. Lowden and K.L. More, in Interfaces in Composites, edited by C.G. Pantano and E.J.H. Chen (Mat. Res. Soc. Proc. 170, Pittsburgh, PA, 1990) pp. 205-214.
 22. R. Naslain, O. Dugne, and A. Guette, J. Am. Ceram. Soc. 74, 2482 (1991).
- ^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.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**DATE
FILMED**

9/29/94

END