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Chemical Vapor Infiltration of TiB₂ Composites

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Metals and Ceramics Division

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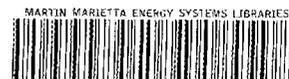


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CHEMICAL VAPOR INFILTRATION OF TiB_2 COMPOSITES*

Theodore M. Besmann, James H. Miller, Kevin C. Cooley,
Richard A. Lowden, and Thomas L. Starr†

ABSTRACT

The efficiency of the Hall-Heroult electrolytic reduction of aluminum can be substantially improved by the use of a TiB_2 cathode surface. The use of TiB_2 , however, has been hampered by the brittle nature of the material and the grain-boundary attack of sintering-aid phases by molten aluminum. In the current work, TiB_2 is toughened through the use of reinforcing fibers, with chemical vapor infiltration (CVI) used to produce pure TiB_2 . It has been observed, however, that the formation of TiB_2 from chloride precursors at fabrication temperatures below 900 to 1000° C allows the retention of destructive levels of chlorine in the material. At higher fabrication temperatures and under appropriate infiltration conditions, as determined from the use of a process model, a TiB_2 /THORNEL P-25 fiber composite, 45 mm in diam and 6 mm thick, has been fabricated in 20 h. The material has been demonstrated to be stable in molten aluminum in short-duration tests.

1. INTRODUCTION

The development of TiB_2 Hall-Heroult cell cathodes for aluminum smelting has seen substantial interest due to the high electrical conductivity of TiB_2 and its wettability by aluminum. The carbon cathodes in current use require significant anode-to-cathode spacing in order to prevent back reaction, causing significant electrical inefficiencies. Aluminum's inability to wet carbon causes instability in the cathodic aluminum pad. Prevention of back

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reaction is best achieved using a wettable, drained cathode because this prevents magnetohydrodynamic stirring of a thick layer of molten aluminum.

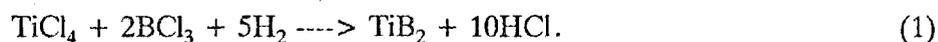
The primary aluminum industry has an installed capacity of approximately 5 million tons/year, which implies a power requirement of 7.5×10^{10} kWh/yr (ref. 1). Todd² estimates that between 10 and 18% of that power could be saved by the use of TiB₂ electrodes. In addition, there is the potential for greater throughput because TiB₂ can handle greater power levels. Single-phase TiB₂ appears to be unacceptable, however, due to its brittleness and low thermal shock resistance.³ In addition, sintering aids necessary for the preparation of TiB₂ bodies make the material susceptible to grain-boundary attack.^{4,5} Composite materials containing TiB₂ have been investigated as a means of overcoming these difficulties, with particular emphasis on TiB₂-carbon particulate composites. Martin Marietta Aluminum Corporation has reported mixed results with such a system.⁶

The current work is designed to develop a Hall-Heroult aluminum-smelting cathode with substantially improved properties. It is suggested that a fiber-reinforced-TiB₂ matrix composite would have the requisite wettability, strength, strain to failure, cost, and lifetime to solve this problem. The approach selected to fabricate such a cathode material is chemical vapor infiltration (CVI). This process produces high-purity matrix TiB₂ without damaging the relatively fragile fibers. The overall program is designed to evaluate potential fiber reinforcements, fabricate test specimens, and test the materials in a static bath and lab-scale Hall cell. The work reported here will cover the TiB₂ matrix infiltration process development and the results of aluminum soak-tests of specimens.

2. CVI OF TiB₂

In CVI, gaseous reactants infiltrate a porous (typically fibrous) preform held at elevated temperature, depositing matrix material on the substrate structure by means of a

standard chemical vapor deposition (CVD) reaction. Continued deposition of this CVD coating forms the composite matrix. CVD reactions are attractive in that they permit the use of 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 the one of interest in this work, TiB_2 , which has a melting point of 3225°C but which can be easily deposited at 900°C by means of:



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 between fiber and matrix, results in a composite 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 that are too rapid usually result in severe density gradients, where there is essentially complete densification near the external surfaces and much lower densities in the interior regions. Alternatively, exceptionally slow deposition reactions require an uneconomically long time to densify the part. The object is to balance mass and heat transport and chemical kinetics to properly infiltrate a preform.

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

widely used commercial process is isothermal/isobaric CVI (ICVI), which depends only on diffusion for species transport.⁷⁻⁹ ICVI generally operates at reduced pressure (1 to 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 infiltration times of at least several weeks.

A forced CVI (FCVI) process has been developed at Oak Ridge National Laboratory (ORNL) that is self-optimizing and which has allowed for much shorter infiltration times and less difficulty in obtaining uniform infiltration.^{10,11} The furnace is configured to apply a thermal gradient across the preform, in part by actively cooling the reactant gas entrance surface (Fig. 1). Because CVD reactions are generally thermally activated and follow an Arrhenius temperature dependence, the preform is infiltrated most rapidly near the hot surface. As the density of the part increases, its thermal conductivity increases and the thermal gradient decreases, with the increasing temperatures causing locally greater deposition. A diffuse densification front thus moves from the hot surface toward the cooled entrance surface. Infiltration is typically assumed to be complete when permeability is diminished so that the pressure drop across the part becomes prohibitive (70 to 140 kPa). Unlike ICVI, intermediate surface grinding is not necessary, and the process can continue, uninterrupted, to final density. Some finishing may be necessary, however, to remove pieces of fixturing or to smooth surfaces.

The FCVI process has been exclusively used in this work. Figure 2 is a schematic of the TiB_2 infiltration system indicating the flow control, sensor, furnace, and scrubber

FORCED CVI PROCESS

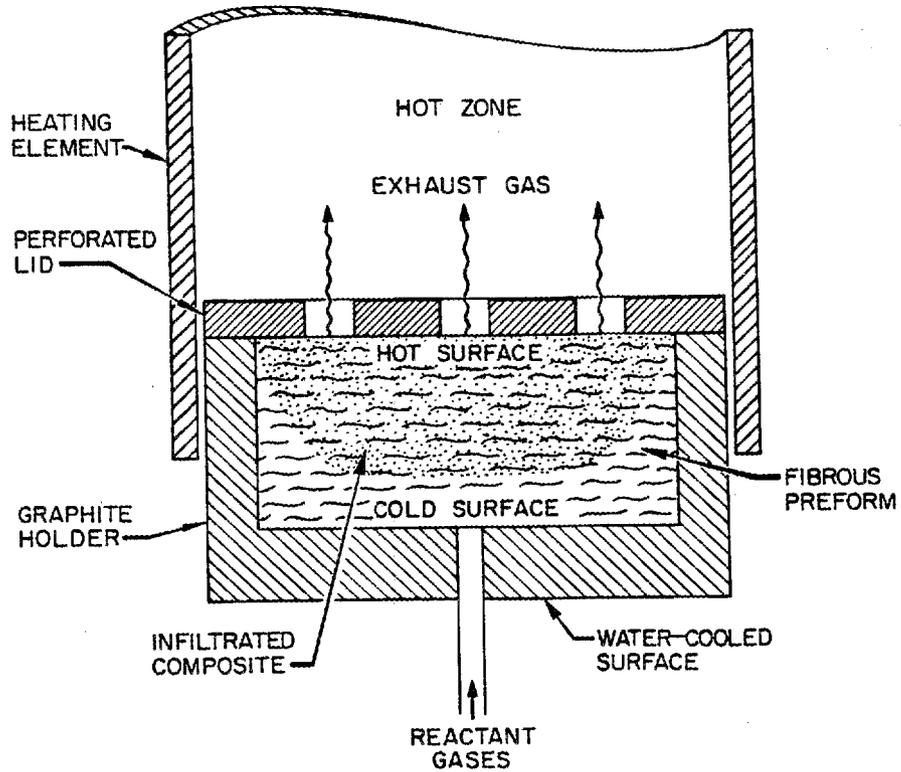


Fig. 1. Schematic of the preform holder in position in an FCVI reactor.

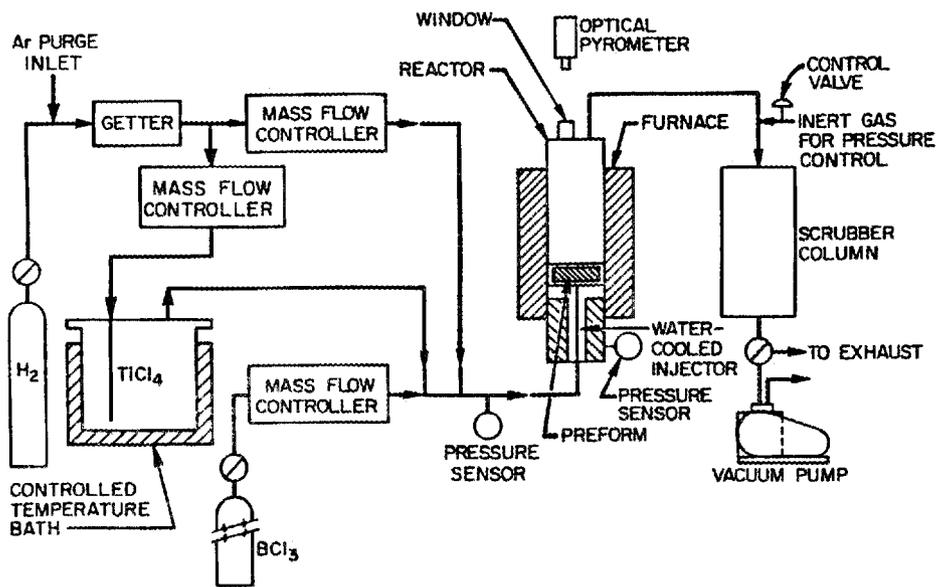


Fig. 2. Flow diagram of the FCVI system for the infiltration of TiB_2 from chloride precursors.

systems. Hydrogen and BCl_3 are metered using mass flow controllers. The TiCl_4 vapor is carried by hydrogen bubbled through a heated vessel of liquid TiCl_4 . The rate of vaporization of TiCl_4 is determined through calibration utilizing hydrogen flow through the vessel and determination of vessel weight loss. The furnace is resistively heated, and the hot-side temperature is measured optically. The pressure drop across a part being infiltrated is used as a measure of infiltration; when the permeability of the composite causes an ~ 70 kPa differential, further densification is unlikely, and the run is considered completed.

3. TiB_2 MATRIX STABILITY

Initial studies of fiber-reinforced TiB_2 materials were performed utilizing single layers of a 16 by 16 plain-weave Nicalon* (a 15- to 20- μm -diam, amorphous SiC-based fiber) cloth constrained in a graphite holder that forces reactant gases to flow through the cloth. In this configuration, the system utilized forced flow, yet the thin, single-layer cloth did not allow a significant thermal gradient to be established. The furnace side of the cloth was exposed to 1200°C . The result of this simple experiment was a moderately infiltrated layer of cloth that could be used for a scoping aluminum soak-test.

Specimens were provided to C. Schilling of Pacific Northwest Laboratories (PNL) for aluminum soak-testing as part of their "Inert Electrode Program." Figures 3 and 4 are metallographic sections of the material before and after 4-, 10-, and 20-week exposures to aluminum. Their evaluation of the results was that the TiB_2 matrix is unaffected by the aluminum; however, exposures of 10 weeks or more resulted in heavy attack of the Nicalon fibers.¹²

*Nippon Carbon, Tokyo, Japan.

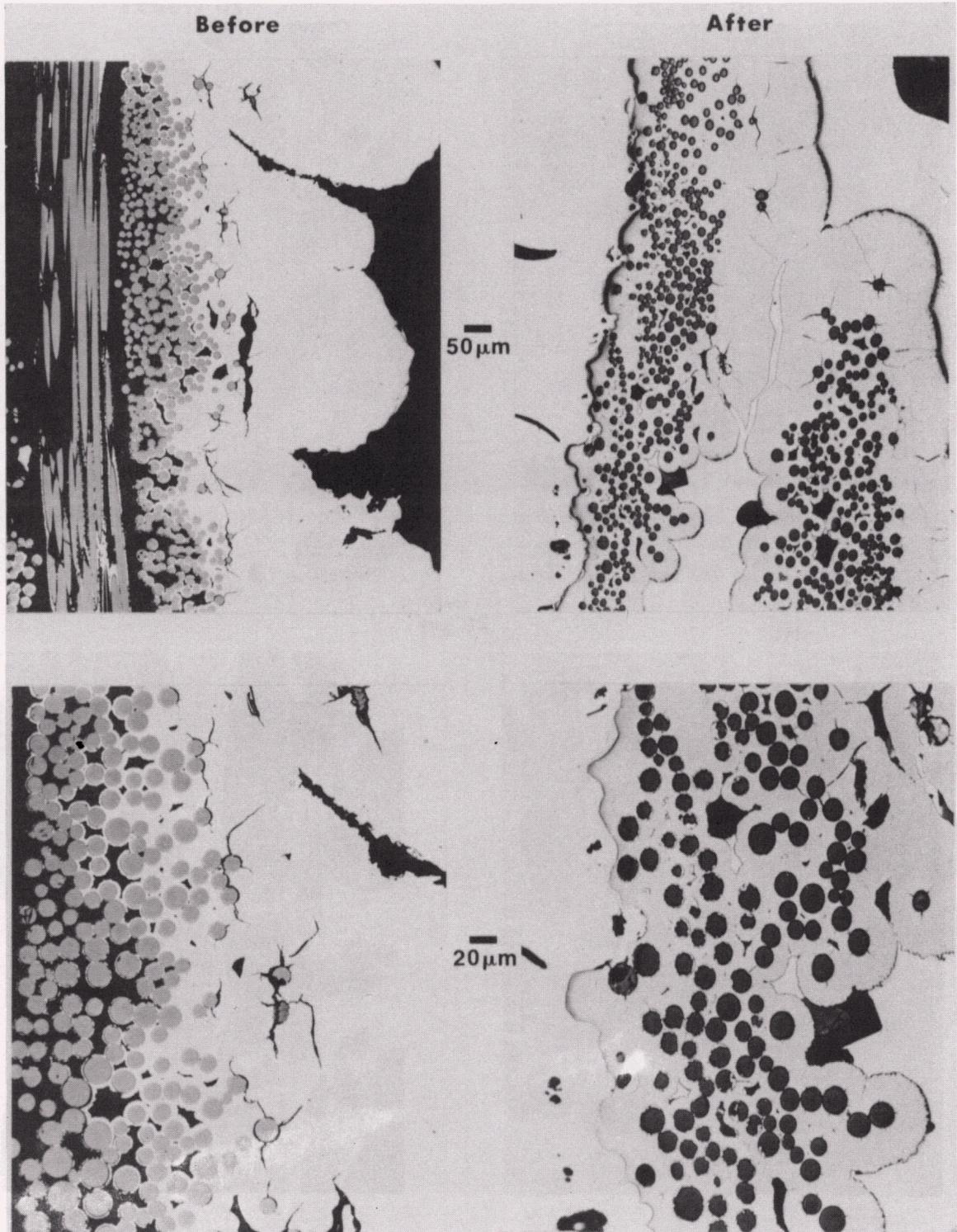


Fig. 3. Metallographic sections of the single-cloth layer TiB₂/Nicalon composites as fabricated and after exposure to molten aluminum for 4 weeks at 970°C. The material appears unaffected after this period.¹³ Source: Pacific Northwest Laboratories, Hanford, Washington.

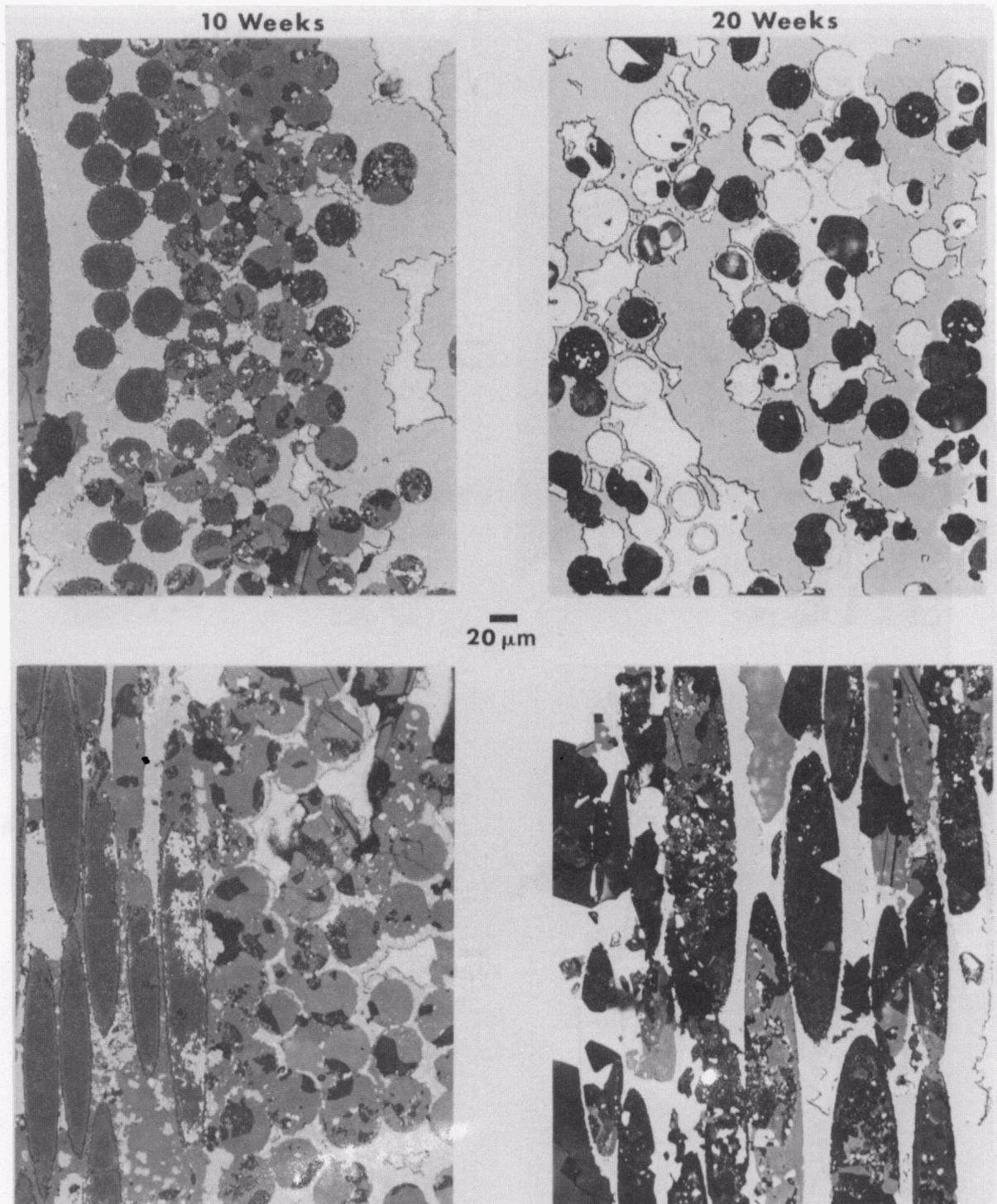


Fig. 4. Metallographic sections of the single-cloth layer TiB_2 /Nicalon composites after exposure to molten aluminum for 10 and 20 weeks at 970°C . Although the TiB_2 matrix still remains unaffected, the Nicalon fibers are degraded.¹³ *Source:* Pacific Northwest Laboratories, Hanford, Washington.

The encouraging preliminary results led to efforts to prepare multi-layer specimens that would have sufficient thickness to be of interest as cathodes. Disk-shaped, Nicalon cloth layup preforms were prepared containing 52 plies, yielding a part 12.5 mm in thickness and 45 mm in diam. These were infiltrated at a hot-surface temperature of 900°C. Such a low temperature maintained the cool-surface temperature sufficiently low so as to prevent premature sealing by deposited TiB_2 . The resulting specimens appeared to be well infiltrated and were cut into specimens for aluminum soak-testing at ORNL.

The results of the aluminum soak-tests of the thick FCVI material were problematic. Exposures as short as 24 h resulted in heavy attack of the TiB_2 and catastrophic delamination of the composite. Specimens stored in air also degraded with time and delaminated over a period of several weeks (Fig. 5).

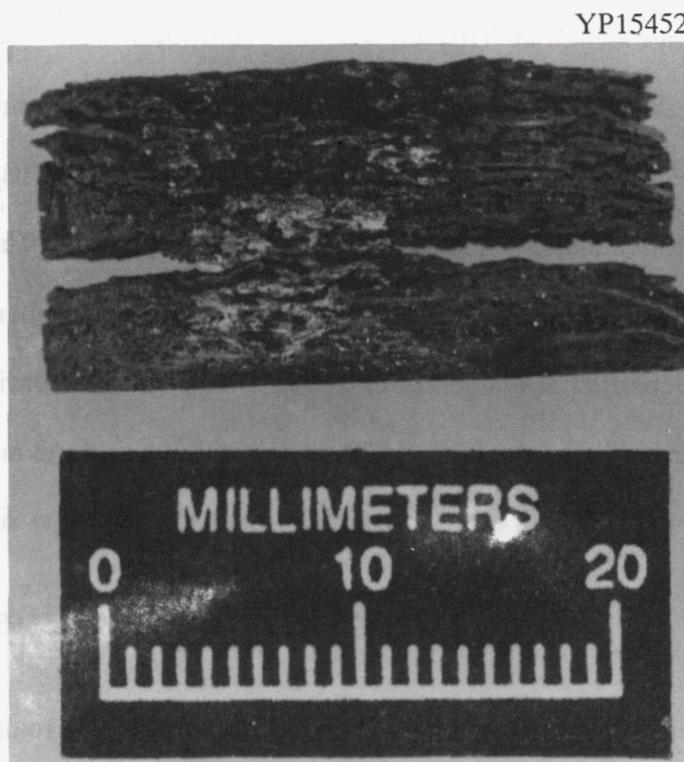


Fig. 5. Photograph of part of a 12-mm-thick TiB_2 /Nicalon composite prepared at low temperatures after exposure to air for several months.

The only significant difference in the conditions used for preparing the single-cloth layer composite and those used for the thicker preform was temperature. For the thicker preform, the highest temperature seen in the specimen was 900°C, as compared to the single-cloth layer, which was processed at 1200°C. Previous work on the CVD of TiB₂ determined that at lower temperatures, TiB₂ deposited from the chlorides retained significant levels of chlorine. It was thus postulated that chlorine retained in the TiB₂ destabilized the phase with respect to molten aluminum and promoted TiB₂ oxidation in moist air. Such an effect may be the cause of the premature dissolution of the CVD TiB₂ observed by Becker and Banks,¹³ who deposited the material at 900 to 1000°C.

Scanning Auger spectroscopy was used to determine if significant levels of chlorine were retained in the TiB₂ composites. Measurements performed on surfaces fractured within the high vacuum of the instrument did indeed reveal the presence of chlorine.

Coatings of CVD TiB₂ on graphite substrates were prepared over a range of temperatures (800, 900, 1000, and 1100°C) in order to obtain a direct determination of the effect of deposition temperature on the stability of deposited TiB₂. These were then soaked in molten aluminum and examined metallographically. The results shown in Fig. 6 reveal that coatings produced at temperatures equal to or higher than 1000°C are stable, yet those deposited at temperatures of 900°C or lower are heavily attacked by aluminum. The conclusion is that the CVI of TiB₂ matrix within a preform must occur at temperatures above 900 to 1000°C in order to maintain retained chlorine at sufficiently low levels.

4. CHOICE OF FIBER REINFORCEMENT

In ceramic matrix materials, the continuous filament reinforcement largely acts to toughen the material rather than to strengthen it.¹⁰ Thus, the reinforcing fibers must have

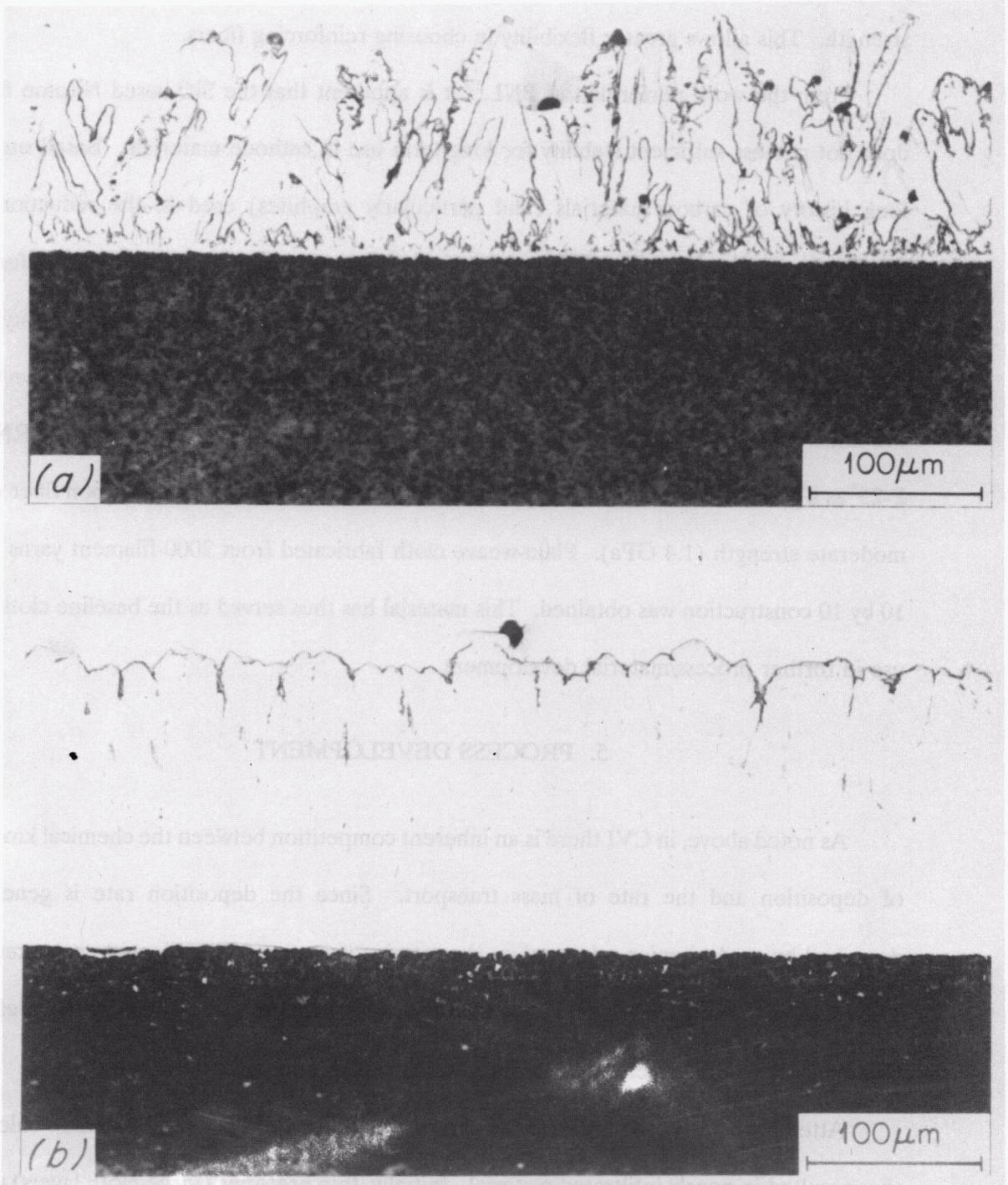


Fig. 6. TiB₂ coatings on graphite prepared at: (a) 900°C and (b) 1000°C after exposure to molten aluminum.

reasonably high strengths but are not relied upon for increasing the material's ultimate strength. This allows greater flexibility in choosing reinforcing fibers.

From the work performed at PNL,¹² it is apparent that the SiC-based Nicalon fiber does not possess sufficient stability for long-term use in cathode materials. Based on the long history of carbon materials (and particularly graphites) used in the reduction of aluminum, efforts were undertaken to identify appropriate carbon fibers for use in preforms.

A large variety of carbon fibers are commercially available; however, the majority are less than 10 μm in diam. This is problematical for FCVI because experience has shown that the infiltration of bundles of such small fibers is difficult. We have identified THORNEL P-25* as a good candidate for use in preforms because it is an 11- μm -diam. carbon fiber with moderate strength (1.4 GPa). Plain-weave cloth fabricated from 2000-filament yarns in a 10 by 10 construction was obtained. This material has thus served as the baseline cloth for use in further process/material development.

5. PROCESS DEVELOPMENT

As noted above, in CVI there is an inherent competition between the chemical kinetics of deposition and the rate of mass transport. Since the deposition rate is generally described by an Arrhenius relationship, the rate increases exponentially with temperature. The result is that higher temperatures tend to cause sealing of the volume in the preform that is closer to the gas entrance surface, which causes nonuniform densification.

Attempts to raise the preform temperature in order to exclude contaminant chlorine thus resulted in poorly infiltrated material. Initially, thin preforms (three-cloth layers) were used to empirically determine an appropriate hot-surface temperature. The reactant flows

*Amoco, Marietta, Georgia.

used were: 25 cm³/min TiCl₄, 100 cm³/min BCl₃, and 500 cm³/min hydrogen. (The FCVI furnace system used was configured to accept disk-shaped preforms 45 mm in diam and up to 25 mm in thickness.) When the hot-side temperature was too high, infiltration was incomplete due to sealing within the body of the preform. The result was one or more layers of cloth on the hot side of the part having little or no TiB₂ deposited on the fibers, with the parts often delaminating upon removal from the graphite holder. The minimum hot-side temperature that resulted in TiB₂ matrix material relatively uniformly infiltrated, and also stable in molten aluminum, was found to be approximately 1100°C.

As a result of the success with three-cloth layer preforms, efforts were made to infiltrate more practical, 14-cloth layer parts (6 mm in thickness). In addition, the carbon fibers were precoated in the FCVI unit with an ~0.2- μ m thickness of graphitic carbon through the pyrolysis of propylene: 25 cm³/min C₃H₆ for 2 h at a uniform temperature of 1100°C. Earlier work with SiC/Nicalon composites indicated that improved mechanical properties are obtained with the use of a carbon precoat.¹¹

The infiltration temperature and flow conditions described for the three-cloth layer preform were used for the 14-cloth layer part. Initially, early sealing near the entrance surface was observed. Reduced hot-surface temperature (1050°C) and significantly halied dilution (including reduced BCl₃/TiCl₄ ratios), were found to improve infiltration: 4 cm³/min TiCl₄, 10 cm³/min BCl₃, and 940 cm³/min hydrogen. Relatively complete densification occurred through the thickness of parts near the axis; however, the circumferential region was poorly infiltrated. The graphite holder was then modified to allow the reactant gas to flow to the periphery of the part, improving densification in that area. Low-density areas were found, however, in the axial region near the hot surface. Figure 7 is an exploded view of the preform and holder assembly.

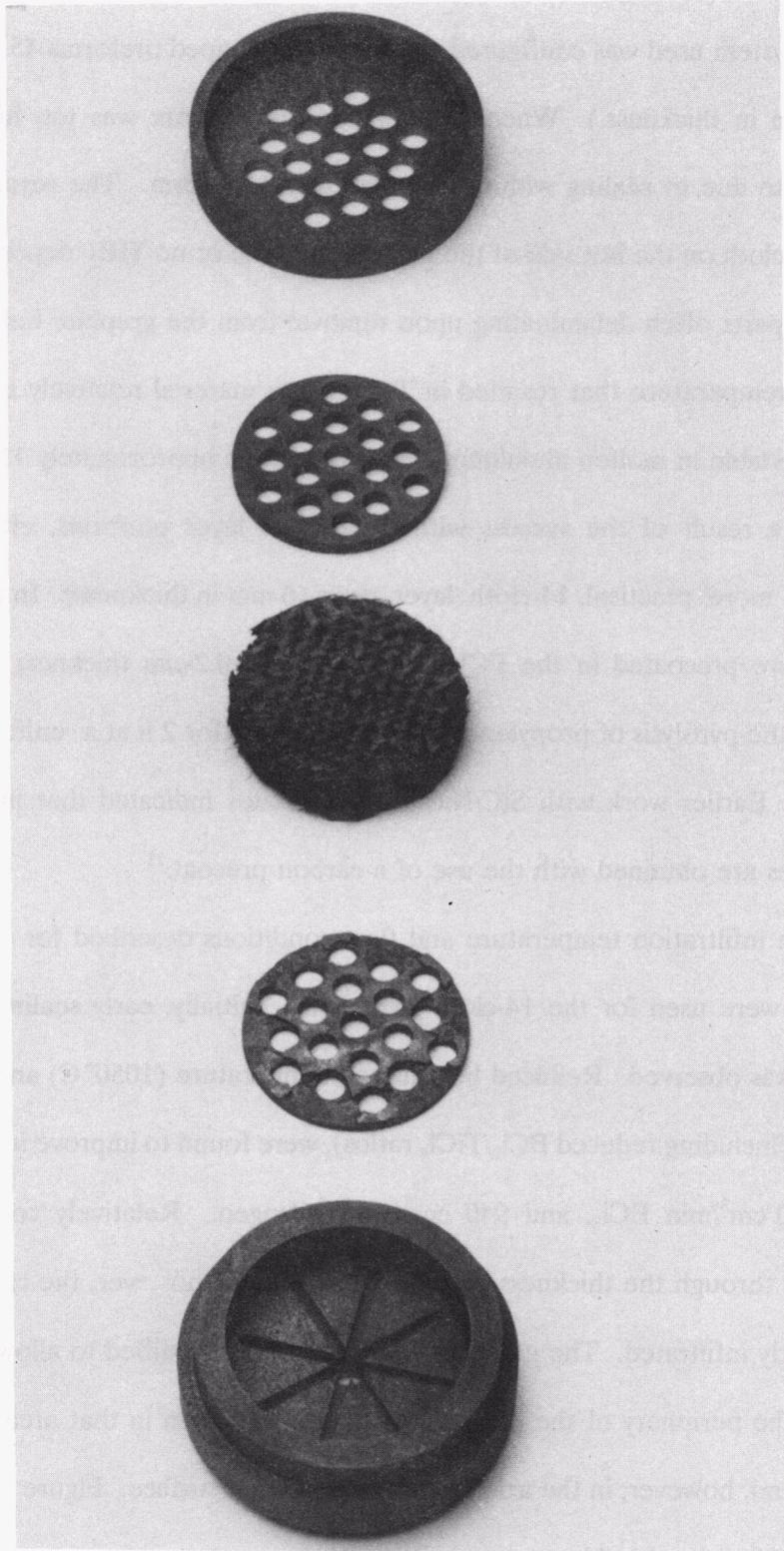


Fig. 7. Exploded view of the preform and holder developed for uniform infiltration of 6-mm-thick parts.

Specimens prepared under the conditions described above were soak-tested in molten aluminum for 24 h at 700°C. Metallographic examination revealed no attack of the TiB₂ by the aluminum (Fig. 8). Longer duration soak-tests are currently in progress.

6. PROCESS OPTIMIZATION

Under the low-flow conditions described above, relatively successful infiltration is accomplished with the exception of the axial area near the hot surface. In addition, infiltration of a 6-mm-thick part requires approximately 60 h, which is an impractically long time. As a result, a newly developed model of the FCVI process was applied to the infiltration of TiB₂ in order to further optimize the process.

The finite-volume model of Starr¹⁴ was applied to the FCVI system and temperature and flow rates varied to determine a relatively optimum set of conditions. Besides the physical properties of the material system and the geometric configuration, chemical kinetic data from Besmann and Spear¹⁵ were used to obtain deposition rates.

Some of the results of the modeling effort are shown in Figs. 9 and 10. The main conclusions of the optimization effort are that the hot-surface temperature cannot be further lowered without reaching temperatures that will likely cause destructive retention of chlorine. However, it was also recognized that the axial, hot-side region was not being densified due to high depletion of the reactants. The model demonstrated that significantly increasing the total flow rate, while maintaining the relative reactant concentrations, would improve densification uniformity. Although the model indicated that a TiCl₄ flow rate as high as 50 cm³/min would be appropriate, such a rate was not practical. At a TiCl₄ vessel temperature of 50°C and a hydrogen flow rate of 300 cm³/min, the TiCl₄ vaporized at only 16 cm³/min. Initial experimental efforts, however, have demonstrated that this fourfold

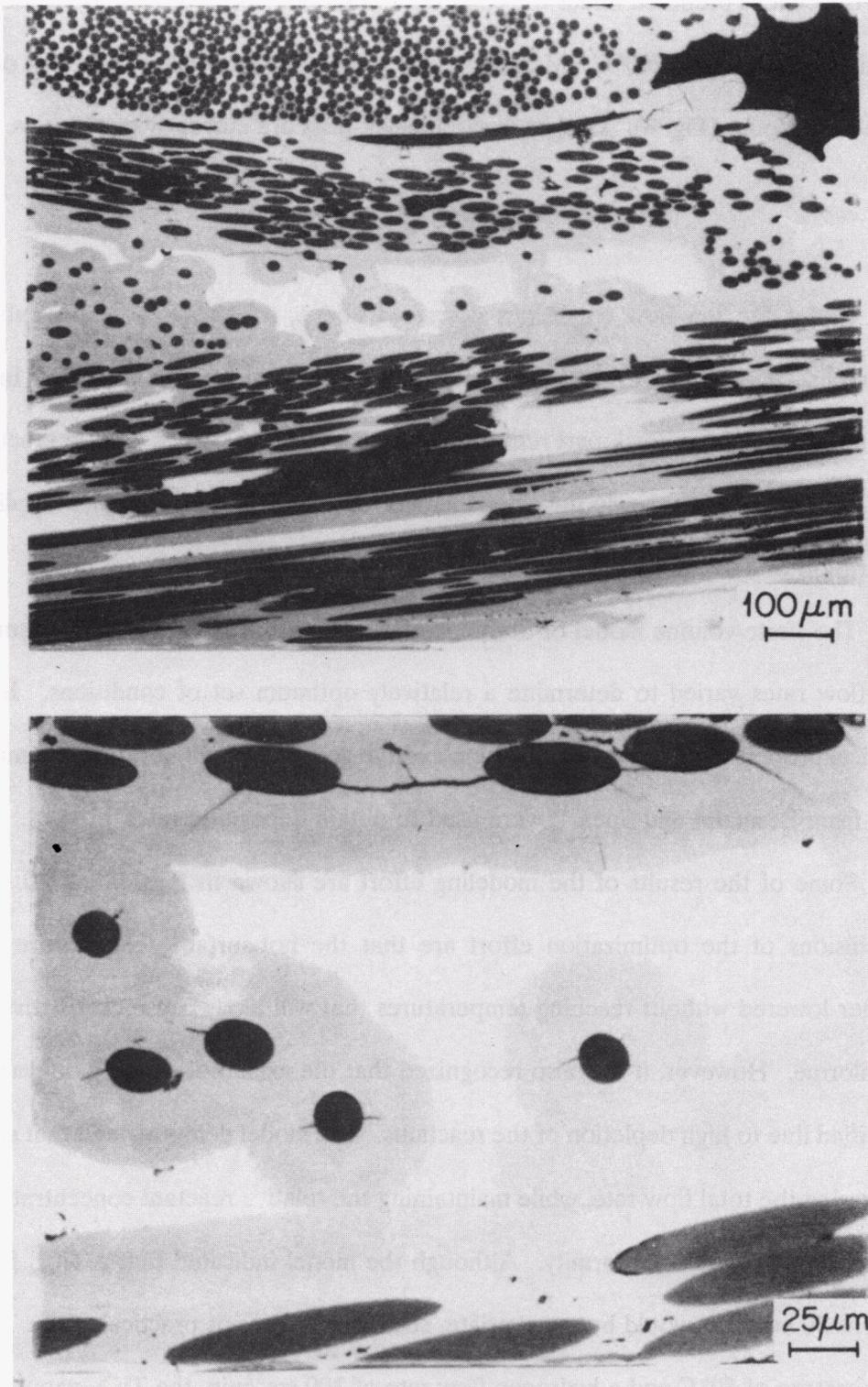


Fig. 8. Metallographic cross sections of TiB₂/P-25 composites after a 24-h soak-test in molten aluminum. The dark grey circles and lines are the P-25 fibers, the grey phase is TiB₂, the white phase is aluminum, and the black areas are voids filled with mounting material.

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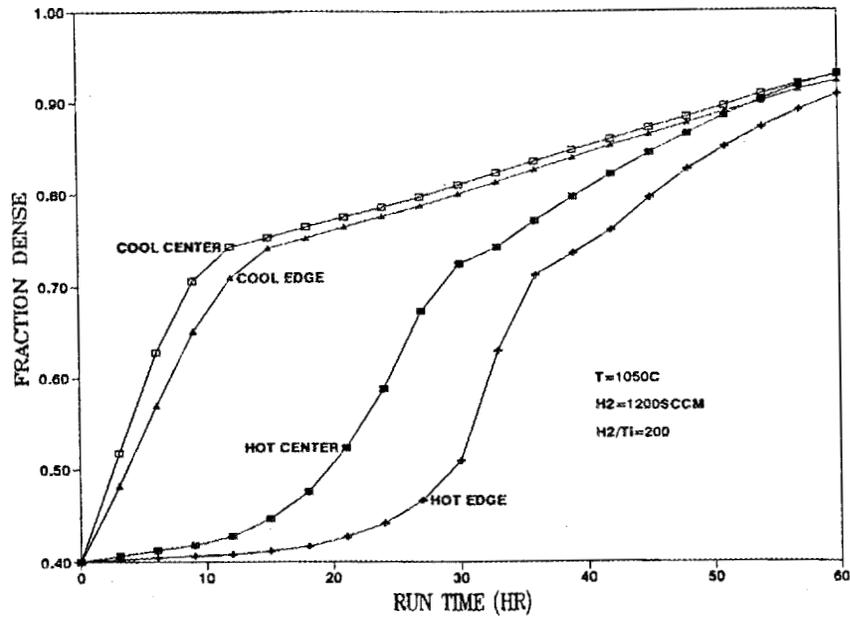


Fig. 9. Plots of the infiltration time versus fractional density, using the low chloride flow parameters, for the center and edge of a part on both the hot and cold sides as determined from the finite-volume model. Note that the predicted infiltration time is about 60 h.

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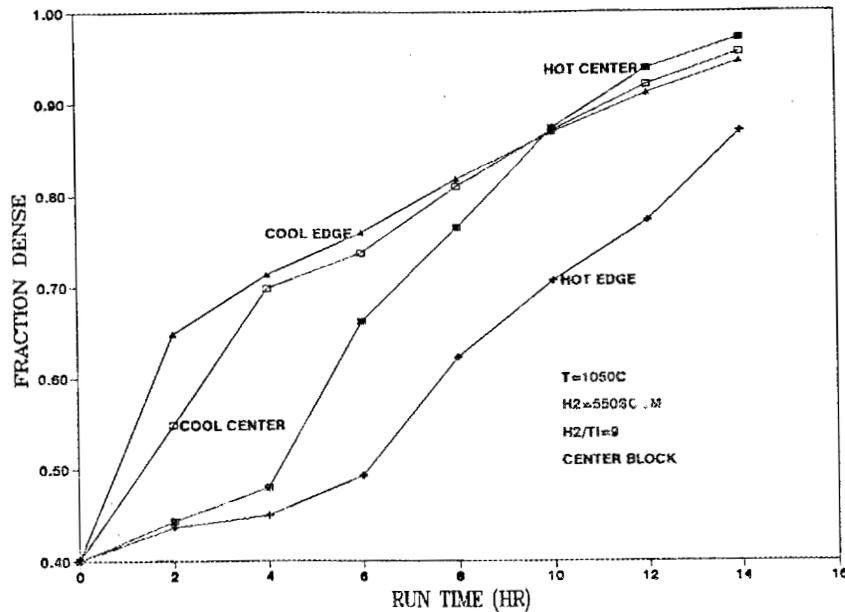


Fig. 10. Plots of the infiltration time versus fractional density, using the higher chloride flow parameters, for the center and edge of a part on both the hot and cold sides as determined from the finite-volume model. Note that the predicted infiltration time is about 14 h.

increase over the 4 cm³/min utilized previously did substantially improve the uniformity of densification and densification time. A 14-cloth layer preform can now be infiltrated in approximately 20 h utilizing the following flows: 16 cm³/min TiCl₄, 32 cm³/min BCl₃, and 300 cm³/min hydrogen.

7. CONCLUSIONS

Potential ceramic composite cathodes of TiB₂/carbon fibers can be effectively produced in 6-mm thicknesses by the FCVI process. More specific conclusions are:

1. Infiltrated TiB₂ has demonstrated stability in molten aluminum for periods up to 20 weeks.
2. SiC-based fibers (Nicalon) were shown to have inadequate long-term stability in molten aluminum.
3. THORNEL P-25 carbon fibers woven into plain-weave cloth appear to be appropriate reinforcements in composites for this application.
4. During infiltration, care must be taken that a deposition temperature in excess of 900 to 1000°C be used to prevent destructive levels of chlorine from being retained in the material.
5. Application of a finite-volume model to the FCVI of TiB₂ matrix indicated appropriate conditions for efficient infiltration so that the 6-mm-thick preform can be densified within 20 h.

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