

DENSIFICATION OF C/C COMPOSITES USING PULSED CHEMICAL VAPOR INFILTRATION

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SUMMARY: Pulsed chemical vapor infiltration, PCVI, is a modification to traditional CVI that has been suggested to reduce internal porosity while also decreasing manufacturing time and costs. The basic difference between these processes is a cyclic interruption in the precursor gas flow into, and out of, the furnace during processing. To test this prediction, a CVD reactor has been modified to allow low frequency pulsing, and carbon fiber preforms have been infiltrated under various pulsing conditions. Specimens are evaluated using quantitative optical microscopy to map the amount of deposition within the preform at varying depths. The primary results observed include a significant increase in the rate of deposition near the preform surface for specimens densified using pulsed flow and improved deposition with time throughout the thickness for these same specimens. Further, the additional amount of deposition that PCVI provides, along with reduced amounts of gas used, increases the gas utilization efficiency of the process.

KEYWORDS: CVI, Carbon/Carbon, Pulsed Mode Deposition, Precursor Gas Efficiency

INTRODUCTION

Recent developments in technology have driven the need for materials able to withstand high temperatures while maintaining structural rigidity. Carbon/carbon, C/C, composites show promising abilities in many structural applications and are already used in volume in aircraft disk brake systems, but the manufacture of these materials remains difficult and expensive. The most popular method of manufacture of C/C composites is chemical vapor infiltration (CVI). Carbonizing a thermosetting polymer that has been impregnated into a fibrous preform and Chemical Vapor Infiltration (CVI) are methods that have traditionally been costly [1]. In addition, traditional constant flow CVI methods require long process durations and produce parts that are often high in porosity resulting in mechanical property degradation. While there is interest in the development of totally new manufacturing technologies, the enhancement of the Chemical Vapor Infiltration process remains an important approach to improving the cost of C/C composites and enabling more widespread use in commercial applications.

Chemical Vapor Deposition/Infiltration

Chemical vapor deposition is a process in which a substrate upon which a coating is to be applied is heated to an elevated temperature while in a vacuum. During CVD of C/C composites a hydrocarbon gas is introduced into a high temperature reactor where the hydrocarbon reacts and carbon is deposited onto the carbon substrate. In addition to allowing the deposition of surface coatings, the process of CVD can also be used to densify spaces within a fibrous preform. The densification of such a preform is described as chemical vapor infiltration or CVI. In CVI processes the carbon atoms penetrate into the pores and densify the interior structure in addition to depositing on the surface. This allows the development of the matrix in the C/C composite. These processes require durations of 10's of hours to 10's of days depending on process kinetics and the desired coating thickness or the required amount of densification. Process duration also varies with the specimen geometry and reactor parameters. Most of the C/C composites produced using CVI techniques have strengths on the order of 175 MPa which falls short of the 450 MPa theoretical strength due to poor densification [2]. However, even at these performance levels C/C composites produced by CVI usually yield higher performance than C/C composites produced using other techniques.

Efforts to reduce the porosity in C/C composites are typically costly and time consuming. Traditional CVI methods inject a constant flow of gas into the reactor while using a vacuum pump adjusted to remove the same amount of gas to maintain constant pressure [1]. This method, using a conventional hot wall reactor, usually concentrates the reaction at the surface of the preform closing off internal pores prior to complete densification. A variation of CVI called pulsed chemical vapor infiltration (PCVI) was described in 1975 and research suggested that reduced sealing of internal pores and increased overall deposition resulted [3].

PCVI introduces pulses of gas into the reactor followed by a dwell time during which the pressure is held constant with no further gas flowing. This dwell allows the gas in the chamber to react and deposition to occur. The vacuum port is then opened and the pressure rapidly drops to below 1 torr. This process cycle is repeated for the duration of the production operation. Because few studies have investigated the deposition resulting from PCVI, accessibility to literature on the subject is limited. Available research results do suggest an improvement in the infiltration over that of constant flow CVI [4]. This may be attributed to the increased process efficiency resulting from increased residence times of the gas in the chamber and the increased time the reaction gas is allowed to diffuse into the preform. During PCVI the gas is held, almost stagnant in the reactor which, theoretically, allows the gas to heat, react and diffuse into the preform without the effects of flowing precursor gas. This is suggested to result in enhanced infiltration. Since PCVI uses less gas than CVI during a given period of time, increased deposition using this method would further suggest higher gas utilization efficiency. Thus, PCVI is one method suggested to help alleviate extremely long run times and reduce porosity encountered during constant flow CVI.

Composite Densification

The process of PCVI has been suggested to enhance infiltration over that of standard continuous flow CVI methods [3,4,5,6]. The locations within the specimen nearest to the core with the finest porosity must be densified first in order to achieve full densification. If these areas are not densified first, the larger pore areas will seal off and full densification will never be achieved. A quick pulse of gas into the chamber may reduce the nonuniformity of the gas species along the length of the reactor and allow for a more uniform density throughout the specimen [3,6]. Using standard CVI techniques the flow of gas past the specimen causes the

reaction to primarily occur on the surface, or in the large pores of the specimen, since diffusion into the smaller pores of the sample requires more time. Further deposition increases the thickness on the surface and seals off smaller internal pores. PCVI has been suggested as a possible technique to eliminate this problem since the evacuation step of the cycle may remove the byproducts from the fine pores of the sample without the interference of fresh gas flowing into the chamber. With more byproducts removed, more fresh reaction gas is allowed to enter the chamber and infiltrate the specimen during the next step of the cycle. The combination of pulsing and CVI is suggested to be highly effective when infiltrating porous preforms and densifying fibrous preforms and may help reduce the density gradients that exist in C/C created using constant flow methods [3,4,6]. Thus, to investigate the PCVI process, this research measures the effects of varying the pulsing frequency on the densification profile and reaction gas utilization efficiency during the infiltration of unidirectional carbon fiber preforms.

PULSED CVI EXPERIMENTS

Overview of Experimental Procedure

Unidirectional carbon fiber preforms were produced by pyrolysis of carbon fiber/epoxy specimens. These specimens were then densified by reacting methane in the CVD furnace at 1100°C, using various pulsing conditions, for times of 10, 30 and 50 hours. The resulting C/C composites were evaluated, using quantitative optical microscopy, to determine the amounts of carbon deposited at locations through the preform thickness. This data was then used to generate deposition profiles within the composites for process parameter comparison.

PCVI Apparatus

To investigate the effects of pulsing on the deposition rate and profile, special modifications were made to a laboratory CVD furnace. These modifications enabled computer control of the precursor gas and of the vacuum ports of the furnace, allowing the computer to control both the opening and closing sequence and the open and closed dwell times. Thus, the furnace could be operated in conventional constant flow mode by forcing the computer to leave both the precursor gas and vacuum valves open continuously. In PCVI mode the controls enable a furnace cycle which involves precursor gas flow into an isolated furnace until a preset pressure is achieved. An upper pressure reaction dwell can then be implemented and, with the precursor gas inlet still closed, the furnace can be evacuated and, if desired, a lower dwell may be implemented.

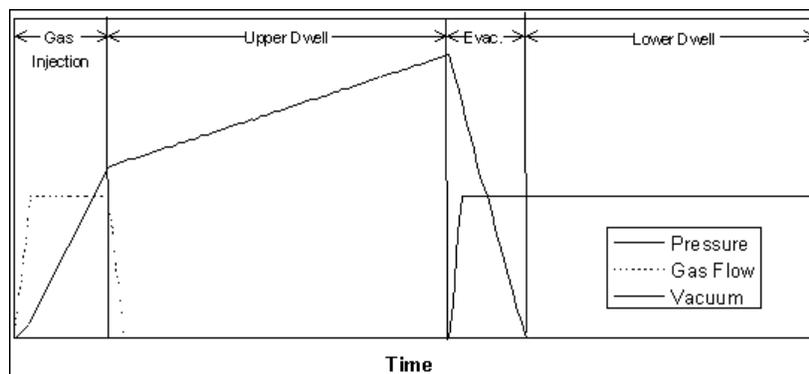


Figure 1 Components of a PCVI furnace cycle.

The vacuum chamber that these experiments were performed in uses a mullite tube with a 6.35 mm wall thickness and stainless steel end caps. A schematic of the reactor geometry is shown in figure 2. The chamber of the reactor is 920 mm long and 95 mm ID giving a total volume of approximately 6 liters. On the stainless steel end cap door of the gas inlet side of the reactor is a sapphire window to allow an optical pyrometer to be used to monitor specimen temperature. The pressure is measured through a port located on the end cap on the vacuum side of the reactor. The furnace is capable of 1300°C for short durations and 1250°C continuously. It has three separately controlled heating zones resulting in a combined hot zone of 457mm with a temperature variance of only 5% over the center 304mm. Thermocouples are provided for each zone and are in contact with the outer surface of the mullite tube. To calibrate the temperature of a specimen inside the reactor, a thermocouple was mounted on a graphite test substrate. It was found that a furnace thermocouple indicated wall temperature of 1000°C provides a graphite substrate temperature of roughly 1050°C.

As stated, there are three parameters that can be controlled in the reactor: temperature, pressure, and gas flow rate. The temperature is controlled directly based on thermocouple readings. Reactor pressure control is based on the number of molecules in the chamber. To control the number of molecules in the reactor, mass flow rate both into and out of the chamber may be changed. Thus, pressure and flow rate are controlled together to achieve the required experimental parameters. While performing steady state runs, the flow into the chamber is fixed and the pressure is controlled by throttling the vacuum system and therefore, changing the flow rate out of the chamber. In pulsed mode operation, pressure is varied by controlling the flow into and out of the chamber using valves on the precursor gas inlet system and on the vacuum port as shown in figure 3.

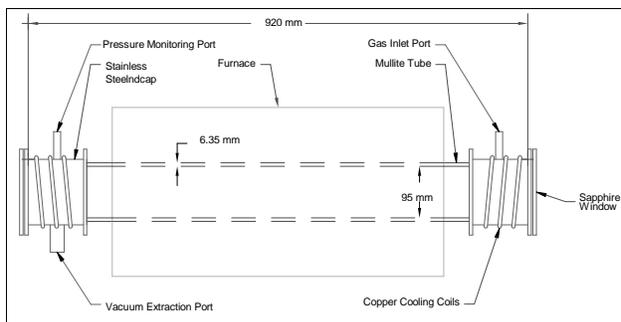


Figure 2 CVD Furnace Schematic

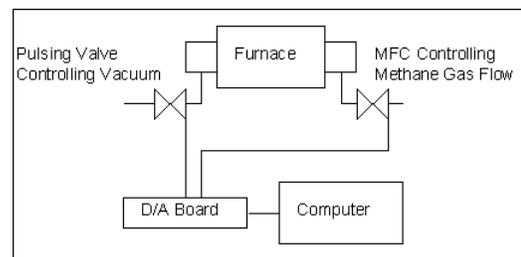


Figure 3 Pulsing Control Schematic

Specimen Preparation

Unidirectional carbon fiber preforms were used for all densification experiments. These preforms provide a geometry with capillary-like pores of irregular radii. While, a commercial preform would be more open, this approach more precisely models a large fiber bundle and, therefore, is sensitive to surface deposition blockage. Further the unidirectional geometry of the preform simplifies micrographic density analysis. Finally, the densification of these specimens can be readily compared to commercial applications and information can be transferred to a finished part so that optimization can be accomplished.

Composite Specimen Geometry

The C/C composite preform was produced from 48 layers of unidirectional carbon fiber/epoxy prepreg tape. The prepreg was first cut into 305 mm lengths and 102 mm widths with the fibers running along the length of the layers. The uncured panel was placed into an autoclave

and cured according to the recommended process at 121°C and 690 kPa. This resulted in a cured panel that was 6.35 mm thick. The panel was then cut into 48 test specimens, each approximately 6.35 mm wide and 89 mm long. This resulted in test specimens that were effectively 6.35 mm square rods, 89 mm long. After cutting to shape, the sides of the specimens were wet sanded to final size. These polymer matrix composite specimens were then pyrolyzed in special tooling to generate porous, unidirectional carbon fiber preforms. To hold the preforms perpendicular to the reactor tube axis and the gas flow, and to keep them centered in the reactor during densification, graphite tooling rings were fabricated.

Experimental Evaluation Procedure

To gain insight into the deposition rate, tests were performed for durations of 10, 30, and 50 hours for each set of parameters. At the onset all three samples were placed into the chamber. After 10 hours the first was removed from the chamber while the remaining two stayed in the chamber for another 20 hours. After a total of 30 hours at temperature, the second specimen is removed and the final specimen reheated for a final 20 hours of deposition, to yield a total run of the 50 hours. While this technique reduced the overall experimental test program duration, it also increased the microcracking in the specimens due to the multiple heating and cooling cycles.

The deposition evaluation approach involved the application of quantitative optical microscopy. Densified specimens were sectioned, mounted and polished. Each specimen was then examined to determine the thickness of deposition on individual fibers at various depths. Three separate profiles were taken for each specimen, with five deposition thicknesses recorded at each of eight positions through the specimen thickness. (figure 5) The micrograph of figure 6 indicates five fibers measured in a single field of view for the deposition thickness measurement and shows a representative section of the partially densified composite.

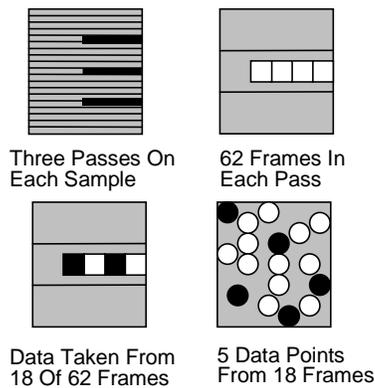


Figure 5 Procedure for Data Collection

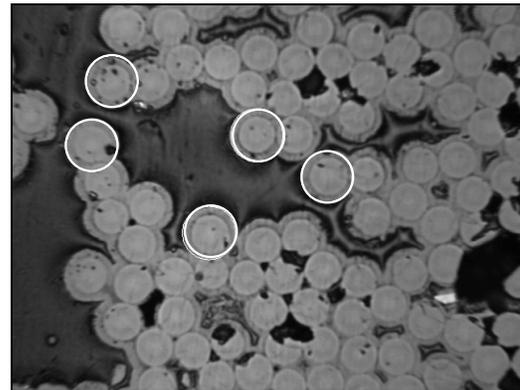


Figure 6 Representative Cross-section

Pulsed Chemical Vapor Infiltration Parameters Studied

The parameters were chosen not only to correlate with the included constant flow CVI runs but also to provide adequate amounts of soot-free deposition to successfully measure. The residence time for the PCVI runs (t_{RP}) is approximated by adding half the time it takes to fill the reactor (t_F) plus the upper dwell time (t_{UD}) as shown in equation (1).

$$t_{RP} = \frac{1}{2}t_F + t_{UD} \quad (1)$$

Reactor fill time was halved to account for average molecule residence time in the reactor during the fill cycle because the specimens were placed halfway down the length of the reactor. The amount of gas used in each PCVI experiment is calculated by finding the percentage of the time the gas is flowing during each cycle then multiplying that by the total time and also by the volume flow rate. The parameters for the 10 second upper pressure dwell PCVI runs were chosen so that the residence times of the gas in the reactor matched the residence time of the gas in the continuous flow experiments. The gas used for the PCVI experiments was only 33% of that used for the corresponding constant flow runs. The 20 second upper dwell PCVI runs double the residence times of the first, and thus use just more than half the amount of gas as the 10 second dwell case. Finally, the 40 second upper dwell again doubled the residence times. The parameters for the PCVI runs are summarized in Table 1. Three runs, 10, 30 and 50 hours, were performed for each of the listed parameters.

Table 1 : Pulsed Chemical Vapor Infiltration Parameters.

Temperature (° C)	Upper Pressure (torr)	Flow Rate (1/min)	Upper Dwell (seconds)	Lower Dwell (seconds)	Residence Time (seconds)	Gas Used (1/hr)
1100	5	0.5	Continuous	0	12.5	30.0
1100	5	0.5	10	0	12.75	10.31
1100	5	0.5	20	0	22.75	6.34
1100	5	0.5	40	0	42.75	3.59
1100	5	0.5	10	10	12.75	6.34
1100	5	0.5	20	20	22.75	3.59

RESULTS AND DISCUSSION

Deposition profiles were determined, by quantitative microscopy, for gas flow rates, furnace run durations, and dwell conditions listed in Table 1. Figure 7 shows the measured deposition thickness versus the depth within the preform. The line for each set of parameters represents 18 different depths, ranging from the surface to the center of the specimen. In each case the measured deposition thickness shows some undulation which can be related to the layered nature of the preform. This layering plus microcracking which occurred during the cooldowns required to remove the 10 and 30 hour specimens, results in preferred paths for gas flow and deposition. To better represent the deposition profile and remove the undulations related to morphology variations, a power series approximation was applied. Not only does a power series best represent the data, with the lowest measured error, but also the deposition profile is expected to follow this type of relationship based on the governing mechanisms.

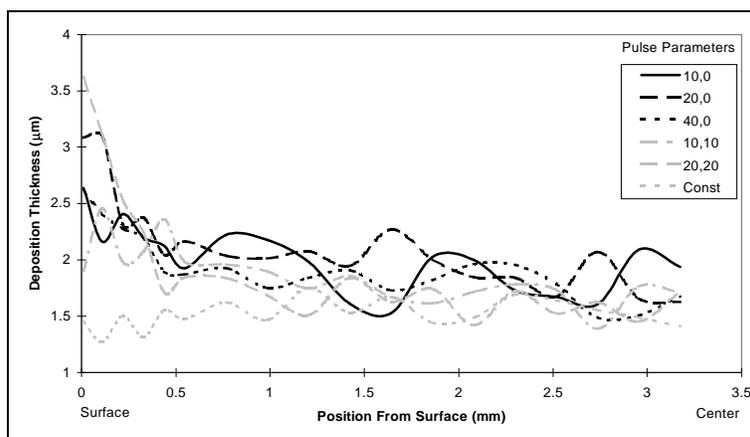


Figure 7 Measured Deposition Thickness of 0.5 l/min, 50 Hour Duration Tests.

Figure 8 shows the power curve smoothed deposition results after 10 hours and figure 9 displays the comparable level of deposition after 50 hours. The results of figures 7, 8, 9 show results for upper pressure reaction dwells of 10, 20 and 40 seconds with no lower pressure evacuation dwell, plus more complex dwells of 10 seconds for reaction and 10 seconds for evacuation and 20 seconds for reaction and 20 seconds for evacuation. Finally, the figures also show the results for the constant, 0.5 liter/minute, flow rate case at both 10 and 50 hours.

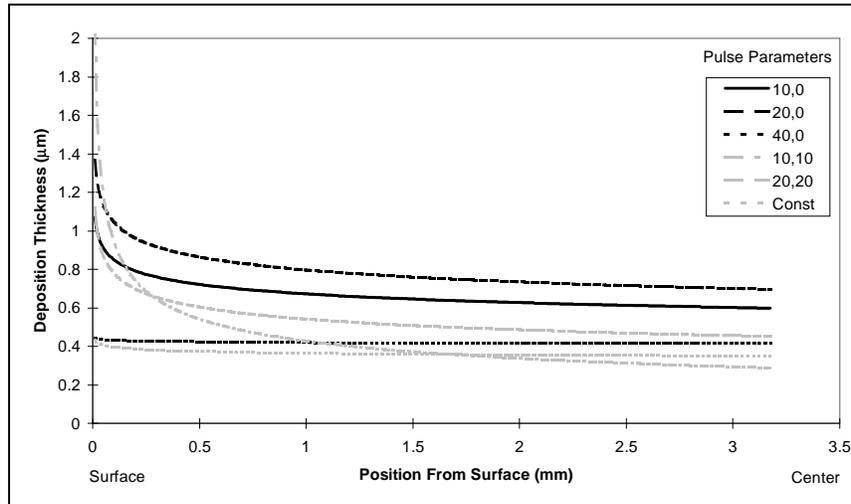


Figure 8 Power Fit of 10 Hour Deposition Thickness Data

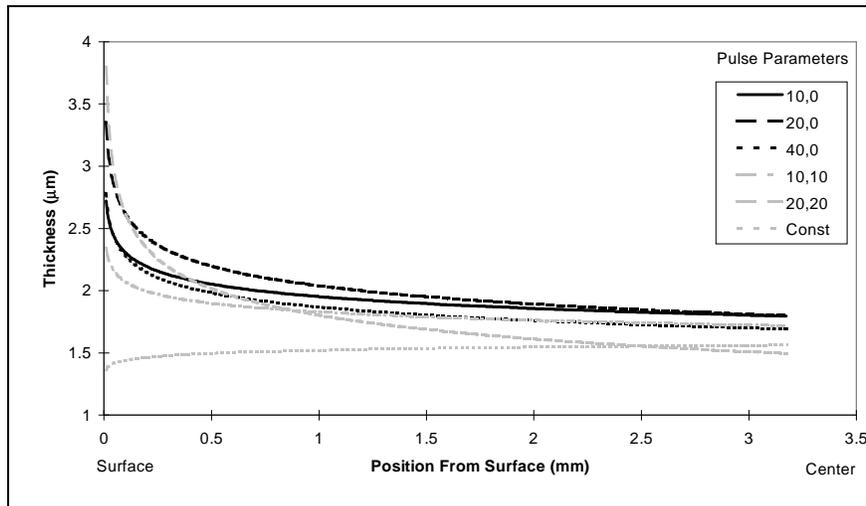


Figure 9 Power Fit of 50 Hour Deposition Thickness Data

Deposition Thickness

The results indicate that PCVI not only increases the amount of deposition at the surface but also increases deposition on fibers inside C/C specimen. The maximum surface deposition thickness achieved under the constant flow condition was 1.5 μm after 50 hours, while PCVI, using a 20 second upper dwell and no lower dwell, provided a deposition thickness of 4 μm after 50 hours. For the same constant flow and PCVI runs, the deposition thickness at the center of the preform was 1.5 μm and 2 μm respectively.

This increased deposition in the PCVI experiments can be attributed to several phenomena as suggested in literature. The first is the reduction of reaction byproducts left in the chamber when fresh gas is injected [3,4]. The pulsing cycle allows the reacted gas to exit the chamber unimpeded as only fresh gas is flowing during the first stage of the pulsing cycle. The reaction byproducts are not only extracted from the chamber but also from the small internal pores of the preform. The second phenomenon is caused by the different flow characteristics of gas in PCVI versus constant flow CVI [7,8]. A constant flow of gas past the preform causes reaction byproducts to be trapped in the boundary layer between the flow of gas and the preform. The boundary layer is caused by the reduction in gas velocity due to the shearing resistance at the preform surface [8]. This boundary layer may limit mass transport of the fresh gas into, and reaction byproducts out of, the preform. This traps the reaction byproducts in the pores of the substrate, blocking the infiltration of fresh reaction gas, and causes a higher concentration of reaction byproducts at the preform surface. PCVI has been suggested to reduce this problem by leaving the gas relatively stagnant during the upper dwell stage of the cycle. Without constant flow, the boundary layer is eliminated allowing improved removal of reaction byproducts, and thus minimizing the interference with infiltration.

Another reason for the increased deposition seen in PCVI is the difference in the temperature, and the final degree of reaction of the methane due to increased residence times. Since the furnace is at a very low pressure the gas is heated primarily through radiation heat transfer. As the gas molecules spend more time in the furnace with increased residence times, the gas temperature approaches the furnace wall temperature. The experiments with a 10 second upper dwell time have the same residence time as the constant flow runs with a flow rate of 0.5 l/min, yet PCVI still results in greater deposition. This may be attributed to the boundary layer effects. The PCVI experiments with 20 second upper dwell times show further increases in deposition and have roughly twice the residence time of the 10 second upper dwell experiments. This indicates a definite effect of residence time on deposition rate. However, there is a practical upper limit on the residence time since a compromise must be made between the degree of reaction completion and depletion of available unreacted gas. The 40 second upper dwell experiments show decreased deposition as the reaction gas is depleted and the final 20 seconds result in little deposition.

Deposition Profile

Investigating the deposition profile provides information about the ability of the process to eventually fully densify the preform. A steep profile would indicate deposition favored on the surface and limited infiltration while a flat profile shows that infiltration is just as probable as deposition on the surface. The tests performed in this study did not seal off the interior porosity of the preform, even in the case of the 50 hour PCVI runs. The deposition profiles of the samples directly correlate to the residence times and possibly to the reaction rates. The specimens with the steepest deposition profiles were the ones with the longest residence times and highest rates of deposition. The PCVI runs provided longer residence times than the corresponding constant flow experiments and thus, resulted in the steepest deposition profiles. The increased deposition rates provide steeper deposition profiles and increase the likelihood of skinning over the surface and sealing off the internal pores of the preform [9]. This suggests that PCVI should show greater surface deposition and skinning; however, the experiments indicate more deposition at all locations through the thickness than measured for the constant flow process, at this fraction of total densification.

Process Efficiency

Based on greater deposition thickness and lower volumes of gas utilized, the PCVI experiments performed can be considered more efficient than the corresponding continuous flow experiments. For the purposes of this effort, efficiency is defined as the amount of deposition divided by the amount of gas used. The pulsed flow runs reduce the amount of gas used because the gas is only flowing during the gas injection stage of the pulsing cycle rather than continuously as in the constant flow runs. This indicates that more of the gas in the chamber reacts and results in deposition, leaving less unreacted gas extracted from the furnace and wasted. While this may seem less important than deposition rate, it is significant because substantially less gas can be used, further reducing cost. The three upper dwell times evaluated result in a maximum deposition thickness at the intermediate dwell duration of 20 seconds. A higher maximum deposition thickness may exist at a slightly different residence time, but it is clear that an optimum value does exist. Once the residence time is moved much away from the optimum value, either insufficient time is available for reaction or gas depletion occurs. The efficiencies, after 10 hours of deposition, are summarized in figure 10.

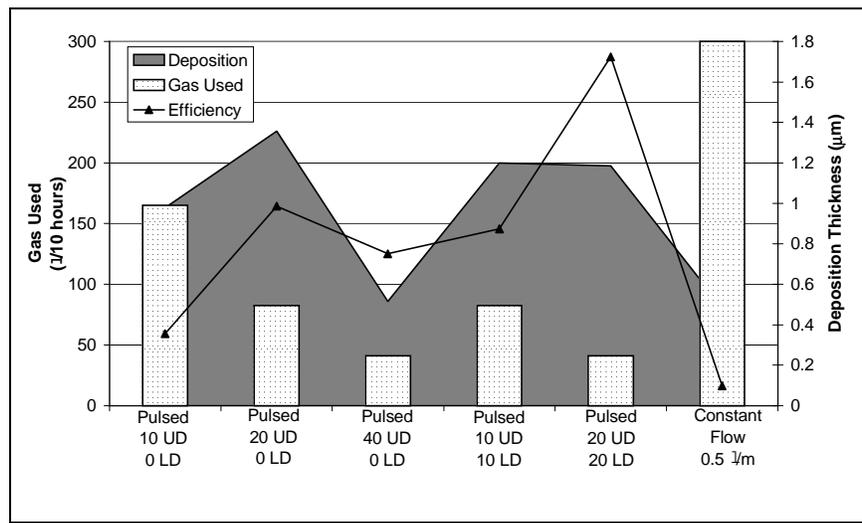


Figure 10 Efficiency for 10 Hour Tests Relating Deposition Thickness To Gas Used.

CONCLUSIONS

Pulsed Chemical Vapor Infiltration is a modification to the CVI process that may help reduce internal porosity while also decreasing manufacturing costs. This study has shown that PCVI significantly increases deposition at the surface when compared to the constant flow CVI process and at the same time increases deposition thickness on fiber surfaces at the center of the preform. The 20 second dwell time experiments increased the deposition thickness, at the preform surface, to almost 3 times the thickness deposited during the 50 hour baseline constant flow experiment. At the center of the preform this same set of pulsing parameters still generated 33% greater deposition than the baseline case. This increased deposition throughout the preform may be attributed to the increased residence times of PCVI. The increased residence times also allow more extensive heating of the gas in the chamber and provide more energy to drive the reaction, yielding enhanced deposition and deposition efficiency.

For industries that use expensive process gases during manufacture, the increases in efficiency of the PCVI process may be quite important. The increased residence times provided by PCVI allow more of the gas in the chamber to react and result in deposition. The additional amount of deposition that PCVI provides, along with reduced amounts of gas required, increases the efficiency of the process. Increased efficiency could further reduce manufacturing costs and help make C/C composites a more practical alternative in many industrial applications.

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