

CVI DENSIFICATION OF CARBON-CARBON COMPOSITES

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INTRODUCTION

Most carbon-carbon (C-C) composites are fabricated by using methods that combine the preforming and chemical vapor infiltration (CVI) processes. C-C preforms are generally made by molding preimpregnated fiber tows, followed by carbonization and graphitization treatments [1,2]. Alternatively, C-C preforms can be made by textiling methods that produce various types of dry fibrous architecture. Following preforming, the CVI technique is used to densify porous preforms. A large-scale CVI process is influenced by gas flow characteristics, gas phase reaction, gaseous diffusion and deposition reaction. In laboratory-scale CVI, where gas composition over a preform is well-defined, the process is primarily governed by the competition between diffusion and reaction [3]. As a result, the CVI process is generally dependent upon temperature, pressure, source gas composition, gas flow rate, porosity size, porosity distribution, etc. Among these variables, the effects of temperature and gas composition were studied in this research.

EXPERIMENTAL

CVI experiments were conducted using an inductively heated furnace with a hot zone of 6 inches in diameter and 12 inches in height [4]. Temperature, pressure and gas flow rate were automatically controlled and logged. In-situ weight gain measurement and exhaust gas analysis were also performed for each experiment. All CVI experiments were conducted at 15 torrs of chamber pressure. Preforms used in this study were made of randomly-oriented pitch fiber towpreg which was preimpregnated with phenolic resin. The size of the preforms was 3"x3"x5/8". Initial density and open porosity were about 1.25 g/cm³ and 38 volume percent, respectively. Methane (CH₄) gas was used as the primary precursor gas due to its abundance as the major constituent in natural gas. The flow rate of methane was kept at 400 standard centimeter cube per minute (sccm) for all experiments. Hydrogen (H₂) was used as dilute gas. The flow rate of hydrogen was fixed at 100 sccm.

The processing variables of this study include temperature and propylene addition. A set of experiments was performed at temperatures ranging from 1000 to 1150 °C. In addition to the temperature-series experiments, small amounts of propylene (C₃H₆) were also added to the primary methane gas in 1050 °C experiments. The propylene added in these experiments was in the range of 0 to 75 sccm.

RESULTS AND DISCUSSION

During each experiment, the weight gain of the sample as well as the details of experimental conditions were monitored and recorded by a personal computer. Weight gain data were then extracted from the data file and plotted as weight gain percentage versus CVI processing time. The results are shown in figures 1 and 2. Generally, all weight gain curves show similar trends. At the early stage of these CVI experiments, the infiltration rate was fast and the weight gain was linear with time. Initially, the porosity in the preform was open and relatively large. This results in a large internal surface area, which remains relatively constant during early stages. Several hours into the experiments, weight gain curves began to level off and the infiltration rates started to decrease. During this period, open porosity decreased, internal surface area decreased, porosity size shrank, and closed porosity evolved. These effects, compounded with reduced diffusion efficiency, resulted in premature pore closure and, eventually, non-uniform deposition through the thickness.

The effect of temperature on CVI at 15 torr with 35 sccm propylene added is shown in Fig. 1. It was apparent from the figure that CVI was not effective at either low (1000 °C) or high (1150 °C) temperatures. Low temperature required a long processing time to achieve a given density; whereas high temperature resulted in a low final density and non-uniform infiltration due to premature pore closure. At intermediate temperatures (1050 and 1100 °C), the results were better, both in terms of final density and in terms of short processing time. The highest final density was obtained at 1100 °C.

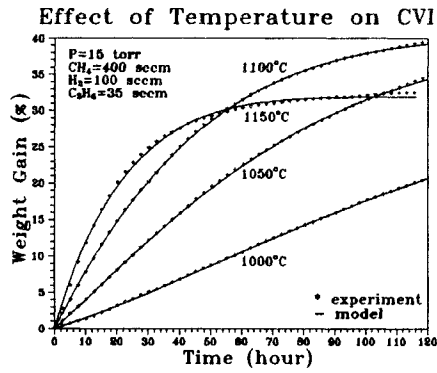


Fig. 1 Weight gain curves showing the effect of temperature on CVI.

Weight gain curves in Fig. 1 were fitted against an analytical model which was based on the geometrical consideration of the evolution of open and closed porosity. The solution of the model:

$$\%wt\ gain = (100\%) \frac{\rho_{CVD}}{\rho_i} \left(\frac{1}{k} \right) \ln \left[1 + \frac{1}{a} \left(\exp^{-bt} - ct^2 - 1 \right) \right]$$

where t is CVI time and k , a , b and c are constants, appeared to be an excellent fit with experimental data.

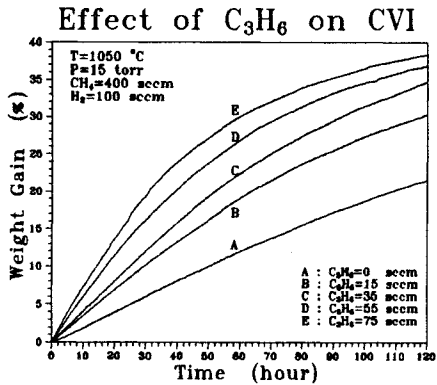


Fig. 2 Weight gain curves of CVI with various propylene addition.

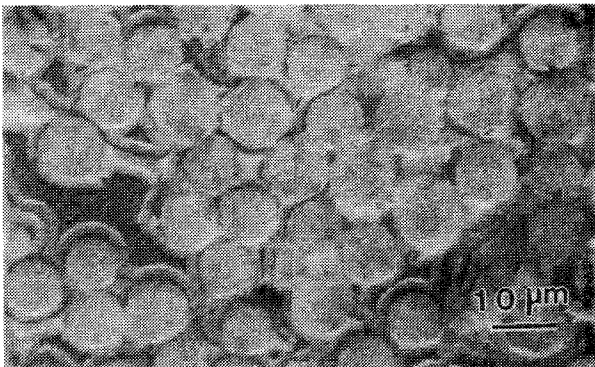


Fig. 3. Optical micrograph of the specimen densified at 1050 °C without propylene addition.

Figure 2 shows the effect of propylene addition on CVI. In these experiments, the temperature was fixed at 1050 °C while the flow rate of propylene was varied from 0 to 75 sccm. The results clearly indicated that adding small amount of propylene dramatically increased both initial deposition rate and overall weight gain. Addition of propylene not only significantly increased CVI weight gain, but also drastically influenced the microstructure of the deposited carbon. Figs. 3 and 4 show the optical micrographs of samples densified at 1050 °C without propylene addition and with addition at 35 sccm, respectively. It was obvious that without propylene, the deposited carbon was isotropic. With 35 sccm of propylene added, the carbon changed to a highly anisotropic microstructure.

CONCLUSION

Temperature has a strong effect on CVI processing. Moderate temperature is preferred when final density, density uniformity, and processing time are considered. Adding a small amount of propylene to the primary methane precursor improves the deposition rate and the overall weight gain resulting from a CVI process. Additionally, propylene addition promotes anisotropic carbon deposition, which is generally favorable for obtaining improved composite properties.

REFERENCE

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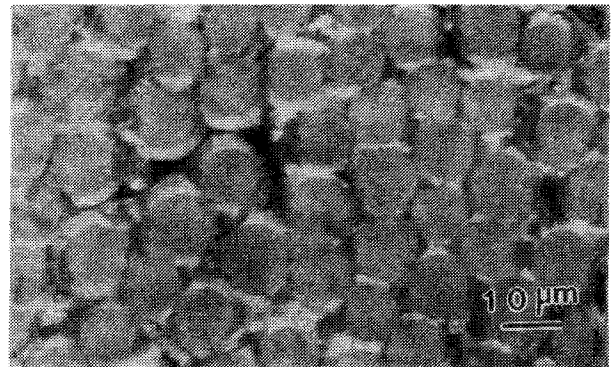


Fig. 4. Optical micrograph showing anisotropic CVD carbon obtained with 35 sccm propylene addition.