

INFLUENCE OF ACETYLENE DOPING IN THE CHEMICAL VAPOR INFILTRATION OF PYROCARBON IN POROUS CARBON SUBSTRATES

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Introduction

Chemical vapor infiltration (CVI) is the core as well as the rate limiting process in the manufacture of carbon-carbon composites for aircraft brakes. Modest increases in infiltration rates while achieving the required final properties and performance have potentially large benefits in cycle time reduction and therefore on throughput. To achieve this goal, a fundamental understanding of the correlation of structures and properties of pyrocarbon with the deposition conditions is required.

Early studies by Bokros and coworkers [1-3] focused on pyrocarbon deposition from methane in fluidized bed reactors at temperatures between 1000 and 2400°C and partial pressures between 30 and 300 torr. At medium to low temperatures and high partial pressures, isotropic carbon was deposited while at high temperature and low partial pressures rough laminar carbon was deposited.

Similar investigations were performed by Pierson and Lieberman [4] for the deposition on carbon fibers from methane/hydrogen mixtures in a tubular reactor between 1200 and 1450 °C. To explain their results based on thermodynamic calculations, the following correlation of possible growth species with the observed microstructures was developed. Smooth laminar pyrocarbon was formed at acetylene/benzene ratios less than 5 (low temperatures and high partial pressures); rough laminar at acetylene/benzene ratios between 5 and 20 (medium temperatures and partial pressures); isotropic at acetylene/benzene ratios greater than 20 (high temperatures and low partial pressures).

Huttinger and coworkers [5] further extended this analysis with thermodynamic calculations of equilibrium partial pressures of the various gas components as a function of temperature as well as a thorough kinetic analysis of the possible reaction pathways for pyrocarbon deposition. They assumed that methane does not form pyrocarbon directly and concluded that aromatics are the dominating species for pyrocarbon growth in the low temperature regime. With increasing temperature, the influence of acetylene should dominate especially at

higher hydrogen concentrations suppressing formation of condensed aromatics as intermediates. In the present study we use acetylene/hydrogen mixtures as dopants to simulate these conditions of higher acetylene/benzene ratios during CVI of natural gas.

Experimental

The preform samples are contained in a 2" OD quartz tube located in a single zone furnace. The heated section of the furnace is 12" long. The precursor gas flows are controlled by electronic mass flow controllers. All process parameters (temperature, pressure and gas flow) are controlled and monitored by a laboratory computer. The pressure was maintained at a constant value of P1 less than 50 torr. The center preform was maintained at a fixed temperature of T1°C above 800°C. The flow was set at a fixed value of Q1 above 500 SCCM.

The infiltration reactor was loaded with 5 preform samples held along the center axis of the reactor tube with a quartz sample holder. The preform centers are spaced 2" apart and the central preform is located at the center of the furnace hot zone. A quartz capillary tube extends along the reactor axis, passing through the center of each preform. Temperature profiles of the reactor were obtained by inserting a shielded thermocouple into the capillary tube.

All experiments consist of measuring the preform weight before and after a fixed infiltration time to determine the amount of carbon deposited in the preform per infiltration interval. Since the preform weight change is a critical measurement, virgin preform material was baked out under vacuum to determine any weight change caused by outgassing of water or other weight loss mechanisms during heat up prior to initiation of the infiltration cycle. Bake-out weight changes were found to be less than 0.04%.

Three infiltrations for 5 hours each, were run with the above configuration using the natural gas mixture to generate a baseline infiltration rate for natural gas, and to provide statistic on the reproducibility of the infiltration rate measurement. The center preform was maintained at a

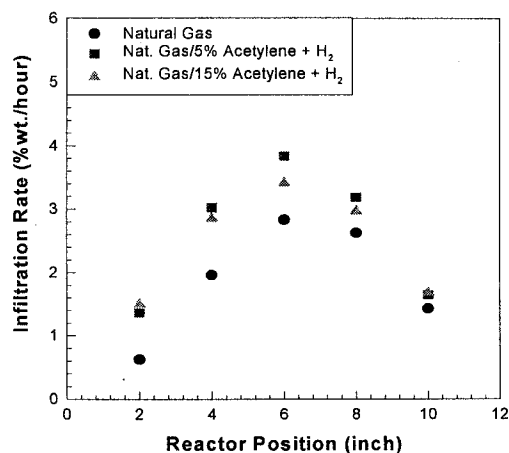
temperature of $T1 \pm 0.5$ °C for each of the three runs which resulted in an average infiltration rate of 2.80 ± 0.05 wt. increase/hour. The experimental reproducibility represents a 2% variation in the rate measurement. The preforms on either side of the center location are at a lower temperature due to a thermal gradient in the reactor. The average temperatures at each preform position of the reactor taken during several infiltration runs are shown in the table below:

Furnace Position	Temperature (°C)
2"	T1-75
4"	T1-18
6"	T1
8"	T1-8
10"	T1-55

Sufficiently long deposition runs were subsequently done for the natural gas and natural gas/5% acetylene + 15% H₂ mixtures to reach a limiting preform density. Final preform volumes are determined by diameter and length measurements of the preform cylinders which gives an estimated accuracy in determining densities of $\pm 2.5\%$. After densification, the preforms were sectioned and polished for the infiltrated carbon microstructure analysis by optical microscopy.

Results and Discussion

In order to determine the potential acceleration of the infiltration process by acetylene additions to natural gas, infiltration rates for natural gas, natural gas/5% acetylene + 15% H₂, and natural gas/15% acetylene + 45% H₂ were measured. The results are summarized in the figure below:



Several conclusions are apparent from the above plot. The addition of 5% acetylene, with 3-fold associated hydrogen, to the natural gas mixture increases the

infiltration rate by about 50% at the center. Surprisingly, the addition of 15% acetylene + 45% hydrogen to natural gas shows less of an enhancement than the 5% acetylene addition. This result probably reflects the large excess of hydrogen present (45% of the precursor mixture) which reduces the carbon deposition rates for both the acetylene and natural gas components.

As expected, the infiltration rates are a function of the preform temperature and hence the location in the reactor furnace. The acetylene infiltration rate enhancement is 2.2 times that of natural gas at the reactor entrance, but is reduced to 1.2 times at the reactor exit. The formation of acetylene from methane appears to be a slow step. This explains the overall reaction rate enhancement at the inlet and center upon acetylene doping. In the case of undoped natural gas, acetylene forms as the gas flows through the preforms causing higher rates at the exit. At the 15% level of addition of acetylene with hydrogen to natural gas, the lower increase in the infiltration rate may be due to the high associated hydrogen concentrations driving the dehydrogenation reaction equilibrium in the unfavorable direction for carbon deposition.

For the long deposition runs, the 5% acetylene-doped mixture was found to reach the asymptotic weight gain value more quickly than the natural gas mixture. The initial infiltration rate was almost 2-fold higher than natural gas alone. Within experimental error the final preform densities for the two mixtures were equal. Both gas mixtures produce rough laminar carbon microstructure throughout the preform sample.

Conclusions

Although, the addition of 5% acetylene with a 3-fold hydrogen excess to natural gas increases the infiltration rate by 50% compared to natural gas alone, the final asymptotic final preform densities are comparable. A 15% addition of acetylene with hydrogen to natural gas increases the infiltration rate somewhat less than the 5% addition. Both the natural gas and 5% acetylene plus hydrogen natural gas mixtures infiltrate carbon fiber preforms with rough laminar carbon.

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