Kinetic Modeling of Isothermal CVI Process

W.C. Choi, I.H. Oh and K.S. Kim
Aerospace R&D center, Daewoo Heavy Ind. Ltd. 24, Sungju-Dong, Changwon, Korea

1. Introduction

Carbon fiber reinforced carbon composites (C/C) are of considerable interest beacuse of their unique properties such as high heat of ablation, outstanding strength retention at very high temperature and high thermal shock resistence. C/C composites can be. produced from fiber preforms by liquid impregnation using resin, by chemical vapor infiltration(CVI), or by mixed process in which liquid impregnation is generally followed by CVI process. In mixed process, uniform and fast infiltration of pyrolytic carbon to the low density substrate is dependent on the hydrocarbon gas as process parameters, and substrate surface morphology. This paper describes the kinetic modeling of isothermal CVI process and shows good correlation between the predictions and experimental data. Macro-kinetic approach is used to calculate the deposition rate of pyrolytic carbon derived from methane and propane. Assuming that the decomposition reaction of hydrocarbon gas as shown in Fig. 1[1] occurs at the pore surface of substrate, both methane and propane have very similar kinetic characteristics. CVI experiments with propane were performed to prove the accuracy of kinetic model, in which the input data are specific surface, effective diffusion coefficient, geometry of sample and furnace volume, gas flowrate, and the known values of kinetic for the decomposition of the hydrocarbon gas[2].

2. Experimental

In this experiment, C/C composites were processed using a two stage process involving an initial stabilization of a carbon fiber preform followed by CVI densification. The semi-random chopped PAN based carbon fabric prepreg as surface layers were laid-up on the autoclave to make a green body into a size of 340mm x 340mm x 20mm. This green body was carbonization at 1000°C and 3 times impregnation and carbonization to have a density of about 1.6g/cc. Further densification of this carbon preform was preformed in the CVI furnace; The diameter and height of furnace's hot zone were 200mm and 380mm, respectively.

Five different CVI process conditions were investigated as in Table 1. In CVI furnace, the gas flow was plug type ; Hydrocarbon gas was flowing upward from bottom of the furnace. The flowrate at certain temperature was regulated with a view to prevent gas phase reaction caused by the increase of gas temperature.

3. Results and discussions

The pore size of the carbon preform after 3rd carbonization, as shown in Fig. 3, indicates that the porosity is about 17 vol% and the range of pore size is from 0.5 nm to 10^4 nm. The substrate is considered to have two dominant pore size distributions : the pore radius of 70 ~ 130 nm (~11vol%) with the specific surface of 2.8×10^6 m^{-1} and 10^3 ~ 3.5×10^3 nm (~6 vol%) with the specific surface of 0.14×10^6 m^{-1}. The pore with the order of radius of 10^2 nm overwhelmingly contributes to the densification of this carbon preform. The densification process by CVI was predicted by kinetic model and compared with experimental data as in Fig. 3. The weight gain decreased as process time increased. This densification behavior can be explained from the fact that the accessible inner surface of small pore decreased as process time increased because of pore closure, especially, near the surface region.

It can be concluded that the kinetic modeling developed here gives good prediction of weight gain as a function of process time.

Acknowledgment

The authors wish to thank the Agency for Defense Development in Korea for the support of this study.

Reference

1. K. T. Muckarov, V. K. Petchik ; "The kinetic study of thermal transformatin of methane", kinetics and catalysis, vol. XVI, 6, 1975
2. P. A. Tesner ; "Kintics of pyrolytic carbon formation", Chemistry and Physics of Carbon, Vol. 19, pp 65~162, 1984

Table 1 The experimental condition of specimen and CVI process.

Class No.	Initial Weight (g)	Dimension of specimen	CVI condition
#1	61.61	OD=80mm, t=8mm	T=760°C, Q=450sccm
#2	64.03	ditto	T=810°C, Q=450sccm
#3	51.02	OD=75mm, ID=48mm, t=14mm	T=835°C, Q=300sccm
#4	52.82	ditto	T=860°C, Q=250sccm
#5	52.44	ditto	T=875°C, Q=250sccm

(a) Assumed reactions ;

$$CH_4 \xrightarrow{k_1} C_{(s)} + 2H_2, \qquad CH_4 + H_2 \xrightarrow{k_2} R\,C_{(s)} + M\,H_2$$

(Hydrogen retardation)

(b) Decomposition kinetics ;

$$W = \frac{k_1 k_2 \chi^2_{CH_4}}{\chi_{CH_4} + \chi_{H_2}} \left(\frac{S}{V}\right)$$

$$k_1 = P_1 \exp\left(-\frac{E_1}{RT}\right), k_2 = P_2 \exp\left(-\frac{E_2}{RT}\right)$$

Fig. 1 The assumed reactions and the kinetics of decomposition of methane using kinetic modeling..

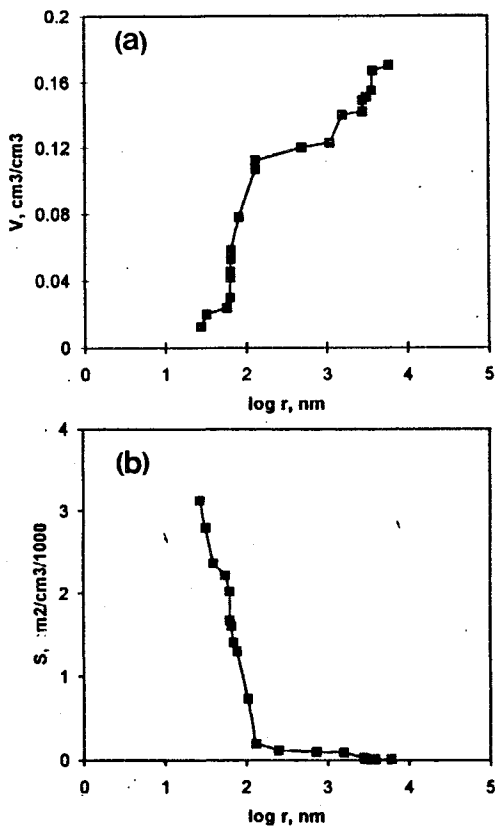

Fig. 2 The curves of integral volume (a) and surface (b) distribution in terms of their radii.

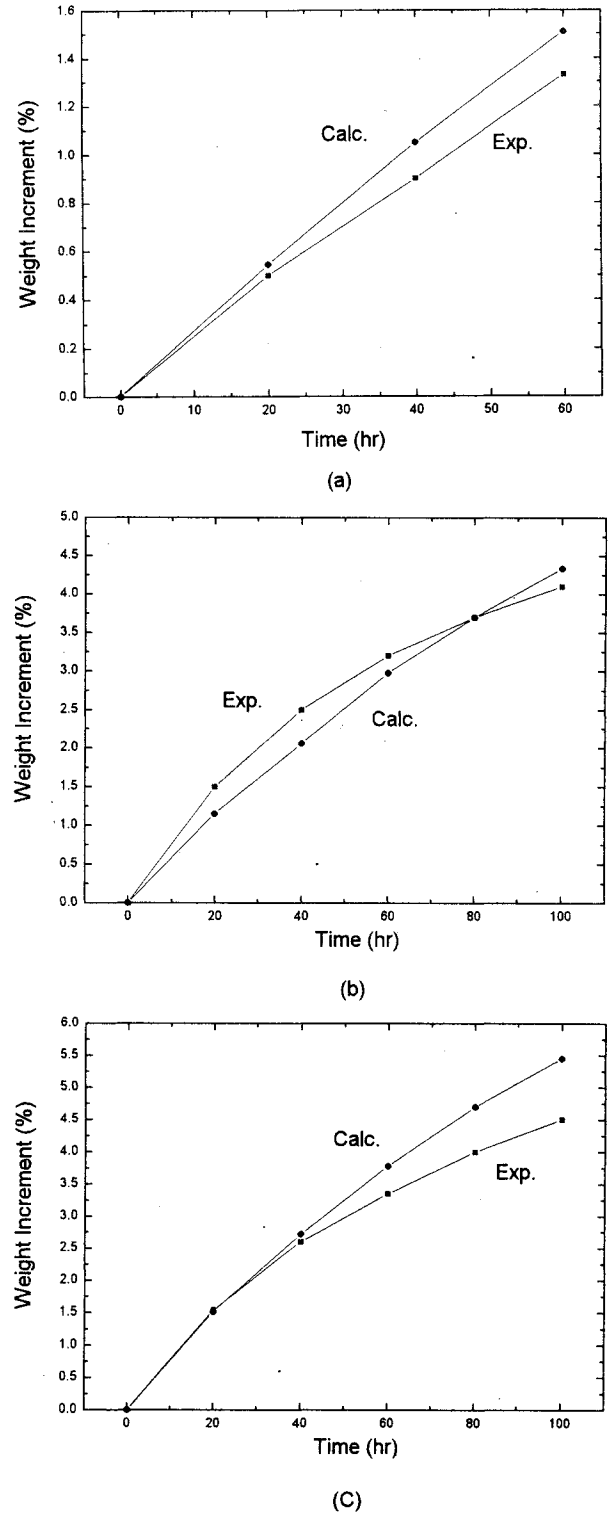

Fig. 3 The comparision of the results of experimental and calculated data ; (a), (b), (c), for class. No. #2, #4, #5, respectively.