F-CVI 반응기 내의 C/C 복합재료 제조공정에서 프리폼 뒤집는 증착공정 연구

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Modeling studies on the infiltration process with overturning of the preform for the preparation of C/C composites in the F-CVI reactor

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Abstract

The modeling for the actual processes including overturning the preform in the middle of the deposition process was carried out. Changes of the distribution of porosity and effects of the interval and the number of overturning processes were observed.

The deposition process could be continued longer by overturning the preform. Additionally, confirmed that a low concentration and a slow reaction rate are necessary for a uniform infiltration even when the preform is overturned in the middle of the process.

Key words: C/C composites, CVI, Propane, Numerical modeling, Overturning

INTRODUCTION

In the CVI process, the precursor gas diffuses into a porous preform, reacts at pore walls, and deposits matrix materials [1]. Here, deposition of pyrolytic carbon in a well defined manner is required. Hence the modeling of the real deposition process such as overturning the preform in the middle of the process is important [2]. The numerical simulations were usually used to optimize parameter values of the CVI process [3].

The kinetic mechanisms of the heterogeneous carbon deposition have been proposed [4, 5]. And modeling based on the detailed surface kinetic mechanism [6-8] and the active surface sites [9] were also proposed. For the visualization of the deposition profile in the preform, the modeling based on the overall deposition reaction kinetics proposed by Vaidyaraman [10] was developed in this work.

The objective of this work is modeling the preparation of fiber reinforced C/C composites by F-CVI of C from propane. Time changes of pore size, porosity, and amount of deposition, etc. could be estimated. The main interest is focused on the effects of overturning the preform in the middle of the deposition process.

MODEL DEVELOPMENT

The same modeling as used in our previous work [11] was used in this research. The only difference was the inclusion of overturning the sample after a certain reaction time. For the inclusions of the overturning process, additional mathematical equations were not necessary. Only the numberings of the calculated parameter values were exchanged in the following way that the entrance parameter values become the exit parameter values and vice versa. Since the following explanations for the model equations are almost same as reported in our previous work [11], it will be mentioned briefly.

The cylindrical preform is composed of fibers which are assumed nonporous. Reactant gas, propane, flows from one side of the preform to another by z-directional forced convection in the isothermal reactor. It is supposed that carbon infiltration reaction is a first order reaction of propane by which 1 mole propane produces 3 mole carbon and 4 mole hydrogen.

$$C_3H_8 \longrightarrow 3C+4H_2 \quad (1)$$

Following the reaction equation, the mole balance of each ingredient was made.

$$\frac{1}{A}\frac{\partial QC_A}{\partial z} - 2v_A \pi W k_s r_f C_A = 0 \quad (2)$$

Here, the second item is the deposition on the outside lateral surface of fibers in the preform. The deposition rate constant (ks)reported by Vaidyaraman[10] was used.

$$\ln(k_s)=2.2-23{,}610/RT \quad (3)$$

Here, R is the gas constant and T the reaction temperature. The momentum balance equation for the packed column was used. The equation for the changes of fiber radius, the amount of deposition per unit cross-sectional area, and porosity are as follows.

$$\frac{\partial r_{fz}}{\partial t} = \frac{qM_m}{\rho_m} kC_{A,z} \quad (4)$$

$$D_z = \pi \sum_{z=0}^{L}\left(r_{fz}^2 - r_{f0}^2\right)\Delta z W \rho_m \quad (5)$$

$$\epsilon_z = 1 - \pi r_{fz}^2 W \quad (6)$$

The above equations were changed into dimensionless form and solved in a finite difference method. Porosity, fiber radius, and the amount of infiltration were calculated. As explained above, the overturning process was included in the following way. After a certain time of deposition, the numberings of the calculated parameter values were exchanged so that the entrance parameter values become the exit parameter values and vice versa.

RESULTS AND DISCUSSION

Mathematical modeling was carried out with the parameter values listed in Table 1. Dimensions of the preform were taken from a sample used in the experiments done in our laboratory. This adjusted reaction rate constant was used in the following work.

Table 1. Dimensions of the preform and deposition conditions used in the modeling.

Preform	**(a) Size**	**10mm×11mm×11mm**
	(b) Initial porosity (εo)	**61.7%**
Fiber	**(a) Number per unit cross sectional area (W)**	**995206**
	(b) Diameter (do)	**0.0007 cm**
	(c) Diameter at the time of plugging (dp, σp)	**0.00108 cm 1.539**
Deposition conditions	**(a) Temperature**	**900℃**
	(b) Inlet % of propane	**5%**

1. Effects of overturning the preform

During deposition, the porosity near pore entrances decreases fast because of a high propane concentration. On the other hand, the porosity near pore exits decreases slowly because of a low propane concentration. So it is necessary to overturn the preform during a deposition process in order to reduce the porosity differences. The porosity distributions in the preform are in Fig. 3 with overturning at every 30 hrs. The porosity differences between pore entrances and pore exits in the preform deposited without overturning are big. On the other hand, those porosity differences of the preform deposited by overturning many times decreased a lot. Furthermore, the differences between porosities at the entrance and at the exit become small when the time intervals of overturning the preform are small. as shown in Fig. 3, it can be seen again that porosity differences at pore entrances and at pore exits show little differences when the time-interval of overturning the preform is small.

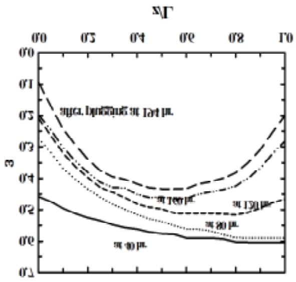


Fig. 3. Distributions of porosities in the preform at different reaction times for the different time intervals of overturning with the 30-hr-interval

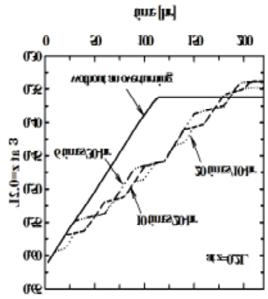
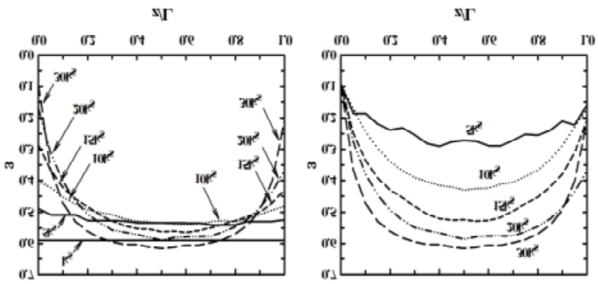


Fig. 5. Time changes of porosities at z=0.2L for the different time intervals of overturning such as 10, 20, 30, 60, and 90 hrs.

Time changes of the porosities at z=0.2L are shown in Fig. 5. As the time intervals of overturning the preform are different, the numbers of overturning are different in each case. The time of plugging pore entrances is extended as the time-intervals of overturning the preform become short. Additionally, the final porosities after plugging pore entrances become small.

2. Effects of other process parameters

Fig. 7 is the distributions of porosities in the preform (a) at 80-hr and (b) at the plugging time for the different reaction rate constants when the preforms were overturned at 30-hr-interval. Calculations were made at 900 oC for the 5% inlet propane concentration and 10ks. Are latively uniform deposition is obtained with a small reaction rate constant as expected.



(a) (b)

Fig. 7. Distributions of porosities in the preform for the different reaction rate constants (a) at 80-hr and (b) at the plugging time. Preforms were overturned at 30-hr-interval.

When the reaction rate constant is big, the differences between porosities at pore entrances and exits are big. Furthermore, the porosity at the center of the preform is very big compared with those at pore entrances and exits. In other words, a non-uniform deposition is obtained. In conclusion, it can be said that a uniform deposition is obtained at a slow reaction rate even when the preform is overturned in the middle of the deposition process.

Conclusions

The results were compared with those obtained without overturning the preform. Effects of parameters of the deposition process were also analyzed and the following conclusions were obtained.

1. When the preform is overturned in the middle of the deposition process, a relatively uniform deposition is obtained. The amount of deposition made with 10 times of 20-hr-interval overturning becomes twice of that done without overturning.
2. It was confirmed that a low concentration and a slow reaction rate are necessary for a uniform infiltration even when the preform is overturned in the middle of the process.
3. A small time-interval overturning results in a uniform deposition at the time of plugging pore entrances in the preform. And the time of plugging pore entrances is extended. As a result, the final porosities after plugging pore entrances become small.

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