프로판과 에탄올 그리고 혼합가스로부터 **C/C** 복합재 **TG-CVI** 제조공정 연구

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Studies on the preparation of C/C Composites from the TG-CVI of propane, ethanol, and mixture gas

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ABSTRACT

Annulus carbon fiber preforms were infiltrated with TG-CVI of propane, ethane, and mixture of these two gases. Amounts of deposition in the preform were estimated with mathematical modeling and compared with experimental data. The overall deposition rate constant of carbon with propane precursor obtained in these processes was 2.2 times bigger than that reported by Vaidyaraman. That with ethanol precursor was obtained by multiplying 0.018 to the gas phase decomposition reaction rate constant reported by Li et al. When a mixture gas of propane and ethanol was used, the amounts of deposition in each part of the preform were more uniform in our system because of the different temperature dependencies of the deposition rate constants of propane and ethanol. It could be shown in this research that a more uniform deposition throughout the preform can be obtained with a mixture precursor gas and a proper temperature gradient in the preform.

INTRODUCTION

Deposition rate can vary depending on temperature in the preform therefore non-uniform depositions in the preform can occur due to a non-uniformity of temperature. This non-uniformity of temperature differences can be counteracted by the concentration gradient. For example, a temperature gradient such as a high temperature at a low concentration region and a low temperature at a high concentration region in the preform can give a uniform deposition in the preform. This method is called TG-CVI which would be used in the following research.

There are many precursor gases which are used for carbon deposition such as, methane, ethane, propane, and ethanol, etc. Yan reported $1.67 g/cm^3$ of C/C composite with ethanol precursor after 114 h infiltration. Mixture of gases are also used as precursor gas. Junniie Ren et al. reported $1.82 g/cm^3$ of C/C composite with CVI of 120 h methane and 85 h mixture gas of methane and ethanol.

Even if the hydroxyl group in ethanol was known to oxidize the carbon before. But in a recent paper reported by Ren et al. The advantage of the oxygen contained in the ethanol has been noticed.

The textures of pyrolytic carbon were grouped as high texture (HT), medium texture (MT), low texture (LT), and isotrope. HT carbon was reported to have excellent wear resistance and friction properties than the other of the deposited carbon. Ren et al., the mixture gas of ethanol and methane was used as the precursor to make carbon/carbon composites and reported that the average bulk density was raised up to $1.8 g/cm^3$ after 85 h infiltration. They used the mixture gas to enhance the production efficiency of the carbon/carbon composite and HT.

The mixture gas of propane and ethanol was used similarly in this research. carbon/carbon composites were prepared with CVI of propane, ethanol, and propane-ethanol mixture gas. After infiltrations, the preform was cut in 5 pieces and measured weight. The amount of deposition in each piece was obtained with this measured weight. Then the amounts of deposition in all parts of preform were compared with modeling results. In these processes the overall deposition rate constants could be decided.

EXPERIMENTAL

Annulus preform was used for C/C composite preparation. The shape and dimensions of carbon

fiber preform used in the experiment are shown at Fig. 1. Before infiltrate, the preform was dehydrated in the oven. Schematic diagram of the system is shown in Fig. 2. The system consist of temperature controller, pressure controller, the gas inlet and outlet. The gas used in the experiment is nitrogen, argon, propane and ethanol. The thermo-controllers were positioned inside and outside the preform to heat the system. The thermocouple was positioned at the same positon where the thermo-controllers to measure the temperature.

Propane, ethanol and mixture gas were used as the precursor. Nitrogen was used as the carrier gas. Before the experiment, the dehydrated preform was weighted. After fixing the preform to the holder, assemble the reactor. The reactor was evacuated. Then argon gas was injected into the reactor to create inert atmosphere and to heat the system. The temperature of the system rises to a target temperature, the argon gas injection was stopped and the precursor and the carrier gas was injected. After the experiment, the precursor and the carrier gas injection was stopped and the argon gas was injected in order to cool the reactor. When infiltration is completed, the bulk density of the preform was measured and the preform was cut in 5 pieces in the r-direction. Then density at each part is measured.
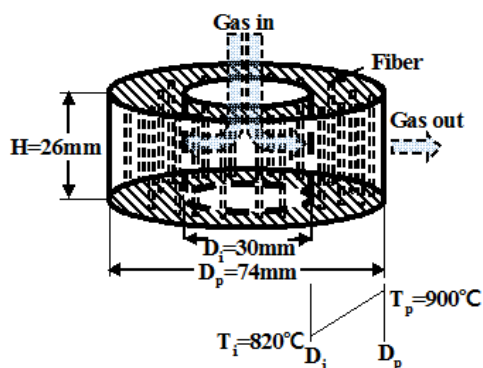

Fig. 1. Schematic diagram of the annular preform. The precursor and carrier gas are introduced from the inside into the outside of the preform.
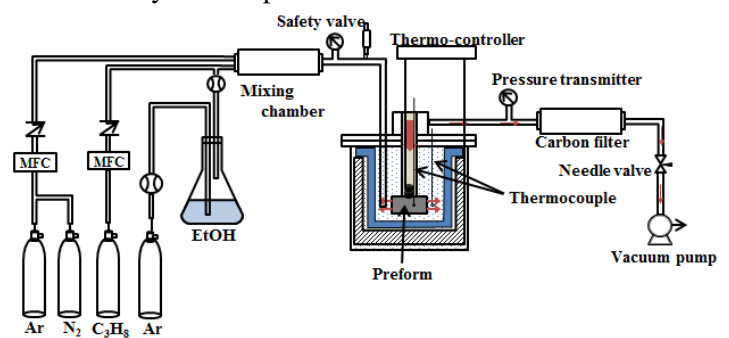

Fig. 2. Schematic diagram of Forced flow-Thermal Gradient-Chemical Vapor Infiltration system.

MODEL DEVELOPMENT

The mass balance equation for propane in the system is as follows.

$$\text{(1)}$$

Terms of r [cm] and z [cm] are the radial- directional coordinate and the axial-directional coordinate in the preform. $k_{s\text{-Prop}}$ [cm/s] the first order rate constant for carbon deposition from propane, N_f [/cm^2] is the number of fibers per unit cross-sectional area of the preform, r_f [cm] the radius of fiber, $q_{C\text{-prop}}$ is the number of moles of deposited carbon per one mole of propane, C_{Prop} [mol/cm^3] the concentration of propane, v_r [cm/s] is the gas velocity in r-direction, $J_{r\text{-Prop}}$ and $J_{r\text{-Prop}}$ [mol/cm^2·s] are the z- and r-directional diffusion fluxes of propane. R_i and R_P [cm] the inner and outer radius of annulus preform, H the height of preform.

The mass balance equation for the pure ethanol precursor CVI was also made in the same way as Eq. (1) using $k_{s\text{-EtOH}}$, C_{EtOH}, $J_{r\text{-EtOH}}$, $J_{z\text{-EtOH}}$ and $q_{C\text{-prop}}$ in place of $k_{s\text{-Prop}}$, C_{Prop}, $J_{r\text{-Prop}}$, $J_{z\text{-Prop}}$ and $q_{C\text{-Prop}}$.

RESULTS AND DISCUSSION

1. CVI of propane precursor

Changes of the amount of carbon deposition with time in the whole preform from pure propane precursor are in Fig. 3. Dots in Fig. 3 are experimental results. The amount of deposition increases with time as expected. In addition, the rate of deposition increases with time in spite of the decreasing porosity. That's because the surface area for deposition around cylindrical fibers increases due to the increasing radius of carbon fibers.

As explained in the introduction section, Vaidyaraman et al. suggested k_{s-Prop}, the overall surface carbon deposition rate constant from the pure propane precursor. When 2.2 times of k_{s-Prop} was used in our modeling, the modeling results of the amount of deposition per unit volume vs. time (curves) fitted the experimental data (dots) well. Hence, 2.2 k_{s-Prop} was used in all of the following modeling calculations. Even if experimental data which were obtained in our laboratory are only up to 120 h, modeling results of the total amount of deposition per unit volume in the whole preform could be calculated up to the time of surface-pore plugging (1,093 h) as shown in Fig. 4.
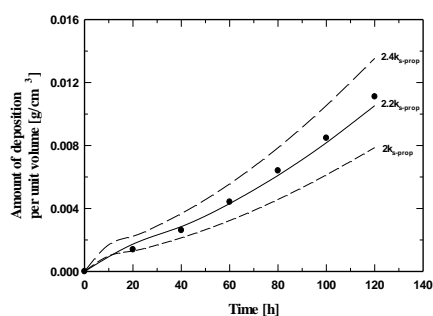

Fig. 3. Deposition conditions were 10% propane, 30 torr, and 100 sccm. Dots are experimental data and lines are results of numerical modelling.
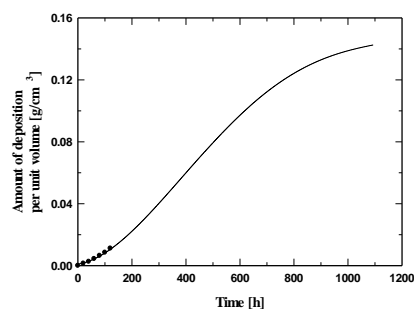
Fig. 4. It was calculated with 2.2ks. Deposition conditions were 10% propane, 30 torr, and 100 sccm.

As explained above, it increased at first because of the increasing surface area around cylindrical fibers in the preform. Then, it deceased later. That's because the speed of precursor gas became fast due the decreasing porosity. Hence, the time for deposition became short. The final plugging time of pores among fibers in the preform was 1093 h.

2. CVI of ethanol precursor

Changes of the amount of carbon deposition per unit volume with time in the whole preform from pure ethanol precursor are in Fig. 5. Dots are experimental results. The rate of deposition increased with time in spite of the decreasing porosity in the same way as for the propane precursor. That's because the surface area for deposition around cylindrical fibers increases due to the increasing radius of carbon fibers.

k_{EtOH}, the overall surface carbon deposition rate constant from the pure ethanol precursor, was used. When 0.018 was multiplied to the pre-exponential factor of the gas phase reaction rate constant, k_{EtOH}, the modeling results of the amount of deposition vs. time fitted the experimental results (dots) well as in Fig. 5. Hence, 0.018k_{EtOH} was used in all of the following modeling results. So modeling results of the total amount of deposition in the whole preform, calculated with that k_{EtOH} up to 934h, the time of surface pore plugging, are in Fig. 6. The rate of surface deposition increased at first because of the increasing surface area around cylindrical fibers in the preform. Then, it deceased later, because the speed of precursor gas became fast due the decreasing porosity. Hence, the time for deposition became
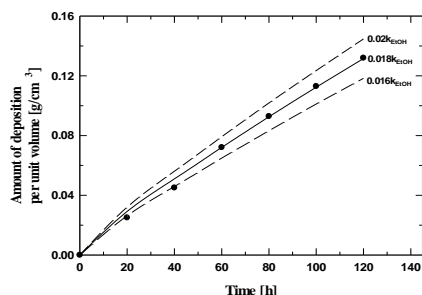

Fig. 5. Deposition conditions were 10% ethanol, 30 torr, and 100 sccm. Dots are experimental data and curves are results of numerical modelling.
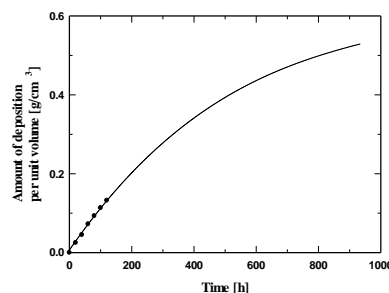
Fig. 6. Deposition conditions were 10% ethanol, 30 torr, and 100 sccm. Dots are experimental data

and   the   curve   is   the   result   of   numerical   modelling.
short. The final plugging time of pores among fibers in the preform was 934 h.

3. CVI of mixture of ethanol and propane precursors

   Time changes of carbon deposition per unit volume are in Fig. 7. Dots are experimental data and the curve is a modeling result. Modeling result fits the experimental data very well. This is one proof that the estimated carbon deposition rate constants of $0.018k_{EtOH}$ for the ethanol precursor and $2.2k_{s-Prop}$ for the propane precursor are reasonable.
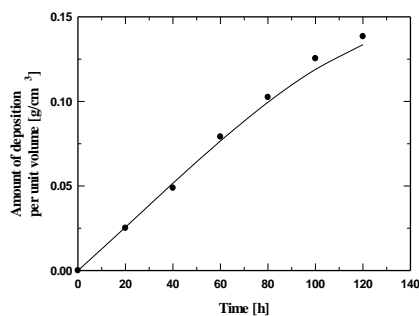

Fig. 7. Deposition conditions were 10% ethanol, 10% propane, 30 torr, and 100 sccm. Dots are experimental data
   and the curve is the result of numerical modelling.

CONCLUSIONS

   Experimental and modeling studies on the preparation of C/C composites by the TG-CVI were carried out using propane precursor, ethanol precursor, and the mixture precursor of propane and ethanol. The amounts of deposition in each part of the annulus carbon fiber preform were calculated by the mathematical modeling, and compared with experimental data. The following conclusions were obtained.

   1. The average density of a preform increased about 3 times from 0.38 to 1.15 g/cm^3 after 60 h deposition with a thermal gradient under the conditions of 10% propane in nitrogen and 840^oC to 900^oC.
   2. The overall deposition rate constant of carbon with propane precursor obtained in these processes was 2.2 times bigger than that reported by Vaidyaraman.
   3. The overall deposition rate constant of carbon with ethanol precursor was obtained by multiplying 0.018 to the gas phase decomposition reaction rate constant reported by Li et al.
   4. When a mixture gas of propane and ethanol was used, the amounts of deposition in each part of the preform were more uniform in our system because of the different temperature dependencies of the deposition rate constants of propane and ethanol.
   5. It could be shown in this research that a more uniform deposition throughout the preform can be obtained with a mixture precursor gas and a proper temperature gradient in the preform.