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# Effects of pressure on the pore formation of carbon/carbon composites during carbonization

I. S. OH
*Department of Fire Safety Engineering, Chongyang Provincial College, Chongyang, Chungchongnam-Do, Korea, 345-800*
*E-mail: isoh@chongyang.ac.kr*

J. I. KIM, J. K. KIM, K. W. KIM, H. J. JOO
*Department of Polymer Science and Engineering, Chungnam National University, Taejon, Korea, 305-764*
*E-mail: joohj@hanbat.chungnam.ac.kr*

In this study, porosity and graphitizability of coal tar pitch with the treatment pressure were investigated. 4-directional carbon/carbon composites (4D C/C) were made from the matrix precursor of coal tar pitch through the process of impregnation and carbonization. Then the effects of applied pressure during the densification on the composites were observed. The matrix pitch which had 600 bar applied during the carbonization process had one and a half times less pore area ratio than that treated at 1 bar. When the pitch was heat treated up to 2300 °C after the high pressure carbonization, the degree of graphitization was improved on a small scale and the crystal size tended to reduce. As the applied pressures to 4D C/C composites increased from 1 to 600 bar, the densification ratio was greatly improved. In the pore size distribution of the 4D C/C composites, the macropore portion was decreased while the mesopore portion increased, when high pressures were applied. *© 1999 Kluwer Academic Publishers*

## 1. Introduction

The C/C composites, consisting of carbon matrix reinforced with carbon fiber, have high toughness and specific strength and retain their mechanical properties even at elevated temperatures [1, 2]. They are known as the most advanced high temperature materials. Due to the high thermal conductivity and the coefficient of thermal expansion, they can be used as the rocket nozzle, the nose cone of the space shuttle, the plasma facing components of the nuclear fusion reactor, etc [3]. However, since they suffer from serious drawbacks from oxidation at high temperatures in oxidizing environments. In order to overcome this weakness, currently-used technologies providing the oxidation inhibition of C/C composites are coated with ceramics as a protection surface layer and treatment with phosphoric acid, for example [4]. As a matrix precursor of C/C composites, phenolic resin, furfuryls and pitch are used. Among them, pitch has high wettability, permeability, low melt viscosity and superior graphitizability [5, 6]. The impregnated matrix precursor within C/C composites forms many pores and cracks due to the formation of decomposed materials and the increase of volume shrinkage during the carbonization process [7]. These pores and cracks exert a negative influence on the properties. Consequently, the impregnation process should be performed many times [8]. Even though the density can be increased by repeating the impregnation/carbonization, this repetition is time-consuming and cost-ineffective. The problem can be solved by raising carbon yields and impregnation efficiency of C/C composites [9–12]. When using pitch as a matrix precursor, the pore size within the matrix is affected by the pressure applied. When a low pressure was applied, volatile materials were discharged readily, pushing the pitch that had occupied the pores and the cracks out of them, reducing the overall carbon yield [13]. In contrast, when a high pressure was applied, the pressure not only inhibited the efflux of pitch and the gasification of volatile materials but also forced the matrix into the fine pores, which made the efficiency high [14]. High-pressure may also reduce the size of individual bubble and may produce a little disoriented matrix by suppressing flow-induced bubble coalescence and mesophase distortion [15]. It was reported that pressure carbonization with pitch resulted in the improvement of mechanical properties of C/C composites, making it possible to improve the carbon yield and to reduce the porosity [16]. In preparing multi-directional C/C composites, the fabrication procedure of preform should be studied, yet the microstructure examination, impregnation mechanism and the way of obtaining maximum impregnation efficiency are the most important aspects to be studied.

In this study, the porosity and the graphitizability of the coal tar pitch with carbonization pressures were investigated. The microstructures of C/C composites were examined to determine the influence of pressure on the densification, where coal tar pitch was

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TABLE I Properties of carbon fiber used for fabrication of the 4D CFRC as a reinforcement

| Fiber type | Filament no. | Diameter ($\mu$m) | T.S. (MPa) | T.M. (GPa) | U.E. (%) | Yield (kg/1000 m) | Density (kg/m$^3$) |
|---|---|---|---|---|---|---|---|
| TZ-307 | 12,000 | 6.85 | 3528 | 245 | 1.4 | 0.8 | 1800 |

T.S.: Tensile Strength, T.M.: Tensile Modulus, U.E.: Ultimate Elongation

TABLE II Properties of coal tar pitch used for fabrication of the 4D CFRC as a matrix impregnant

| Pitch type | Q.I. (wt %) | B.I. (wt %) | S.P. (wt %) | C (%) | H (%) | N (%) | S (%) | C/H | Carbon yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| Coal tar pitch | 6.31 | 29.30 | 114.7 | 92.61 | 4.44 | 1.20 | 0.49 | 1.738 | 39.52 |

Q.I.: Qunoline insouble, B.I.: Benzene insoluble, S.P.: Softening point

impregnated to the 4D weaving preforms by applying the different pressures of 1, 100, and 600 bar, respectively.

## 2. Experimental

The carbon fiber used as a reinforcement for fabrication of C/C composites were PAN-based high strength fiber (TZ-307), sized with 1.5 wt % epoxy resin. It was manufactured by Taekwang Industry Co. in Korea. Coal tar pitch was used as a matrix precursor and has a carbon yield of approximately 39%, manufactured by Jungwoo Ltd. in Korea. The properties of these materials are shown in Tables I and II.

In order to understand the effect of the pressure on the composites, three types of coal tar pitch were heat treated up to 650 °C with the pressure of 1, 100, and 600 bar, respectively. As shown in Fig. 1, the 4D preform took a hexagonal form ($\varphi$: 100 mm, $h$: 100 mm) where the X, Y, U axes of adjacent layers are set at an angle of 60° to one another. Then, Z-direction fiber bundle was set at right angles to the X, Y, U layers [17].

Then, after putting the powdered pitch and the 4D preform into a high pressure reactor, a vacuum state was maintained for three hours at the temperature of 300 °C in order to readily allow the molten pitch to infiltrate into the preform and to obtain a high carbon yield by promoting the discharge of volatile materials. Then, the pressure of 1, 100, and 600 bar was applied to three different specimens, respectively, for five hours at the temperature of 300 °C. This process, facilitating the infiltration of pitch into the preform, was followed by the coking process to obtain cokes, which was performed for 10 h at the temperature of 650 °C. The carbonization of the specimen was carried out inside a furnace up to 1000 °C, then graphitization up to 2300 °C at the rate of 100 °C/h was performed. The graphitization process is to form open pores and to make the carbon well graphitized. The C/C composites were densified by repeating the impregnation, carbonization and graphitization process several times.

The ratio of the pore area of cokes, obtained by heat treatment of the pitch at the various pressures, was evaluated by analyzing the SEM photos with an image analyzer. For the investigation of pore ratio and the distribution of 4D C/C composites, an Autopore II 9220 mercury porosimeter (Micromeritics Co.) was employed, applying 4,136 bar for the mercury filling pressure. In order to examine the variation in crystallinity with the pressure and the temperature of pitch, JDX-8030 X-ray spectroscopy (JEOL Co.) was used, with a Ni-filtered Cu$K_\alpha$ ($\lambda = 0.1542$ nm) ray. The pores and the impregnation behaviors of 4D C/C composites with the pressures of matrix pitch were examined using a JSM-840A scanning electron microscopy (JEOL Co.).

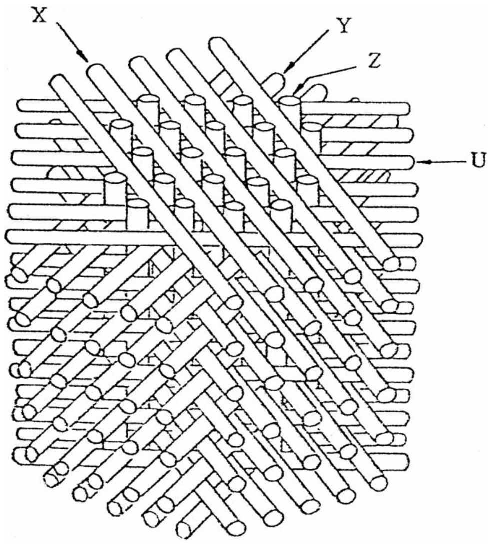


*Figure 1* Schematic diagram of hexagonal type 4D preform.

## 3. Results and discussion

### 3.1. Pore distribution of matrix pitch

The samples that had been carbonized at the temperature of 650 °C and at pressures of 1, 100, and 600 bar respectively, were investigated with a SEM and image analyzer. The results are as follows. Fig. 2a is SEM of carbonized pitch formed at atmospheric pressure. As no pressure was applied to the pitch, volatile materials were easily discharged from inside of the pitch, which facilitated the formation of bubbles. This resulted in the free movement of the pores, making them significantly large. As shown in Fig. 2b, however, when 100 bar was applied to the pitch, the size of pore area was drastically reduced compared with Fig. 2a. When treated with 600 bar, the pressure carbonized pitch contained very fine uniform pores in comparison with those of 1 and 100 bar, as can be seen in Fig. 2c. This phenomenon seems to due to the inhibition of discharge of pyrolyzed gases, originated during heat treatment of pitch.

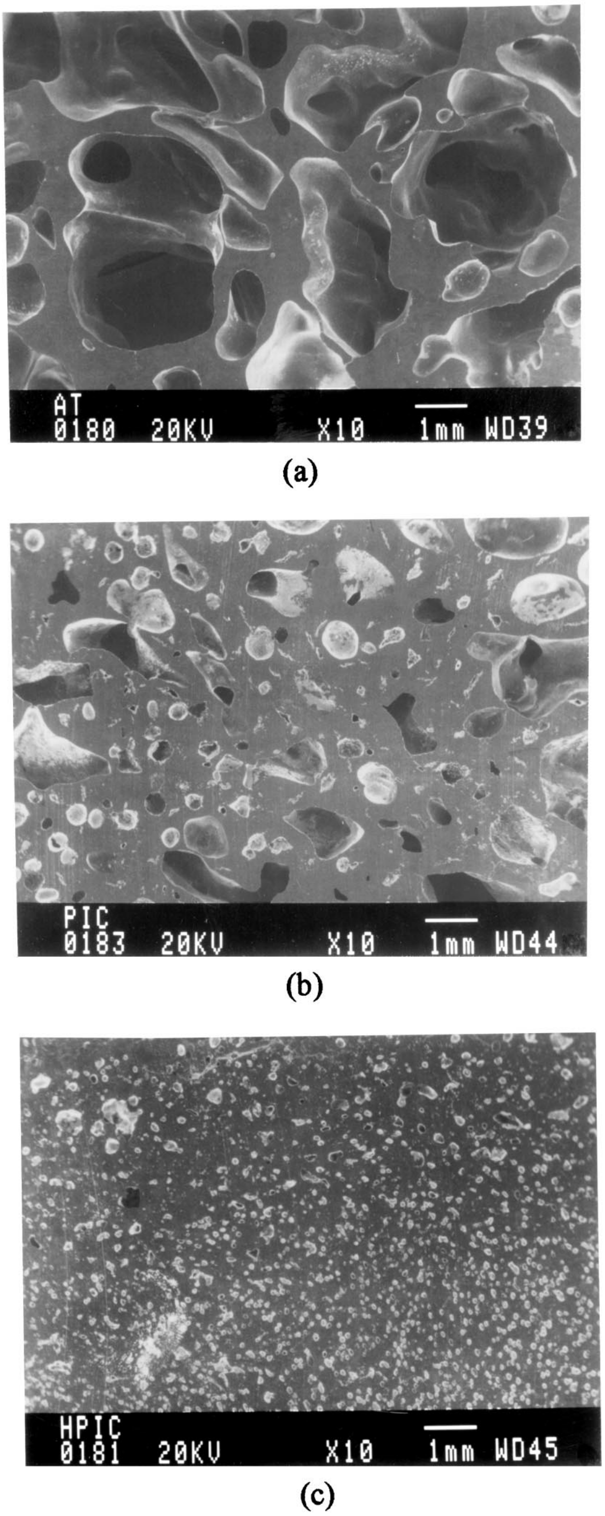


*Figure 2* SEM photographs of coal tar pitch, heat-treated up to 650 °C under various pressures; (a) 1 bar, (b) 100 bar, and (c) 600 bar.

Fig. 2 is the image obtained from the image analyzer to determine the size of pore area distribution with applied pressures. The result is presented in Fig. 3. As shown in the figure, the distribution was reduced as high pressures were applied. Fig. 3a illustrates the coal tar pitch, treated with the 1 bar pressure, had the pore distribution of $1.275 \times 10^3$–$2.535 \times 10^7$ $\mu m^2$, and most of the pore diameter was 2.3–5.6 mm. When 100 bar was applied as can be seen in Fig. 3b, pores bigger than $4.230 \times 10^6$ $\mu m^2$, in other words, pores above $4.301 \times 10^6$ $\mu m^2$ in Fig. 3a almost disappeared. When 600 bar was applied to the specimen, the pore distribution of below $1.886 \times 10^4$ $\mu m^2$ (diameter : 0.154 mm) appeared, as shown in Fig. 3c.

Fig. 4 shows the porosity (the ratio of total pore area) and the density of each cokes. In case of the atmospheric carbonization, the porosity was 75%, but in the case of 100 and 600 bar, it was 48 and 31%, respectively. With these results, it was understood that the porosity was reduced continually as the applying pressure increased. The density was 500 kg/m$^3$ at atmospheric pressure, while it was 1310 kg/m$^3$ at 600 bar. Thus, in preparing C/C composites, high pressure reduced pore size during the densification process.

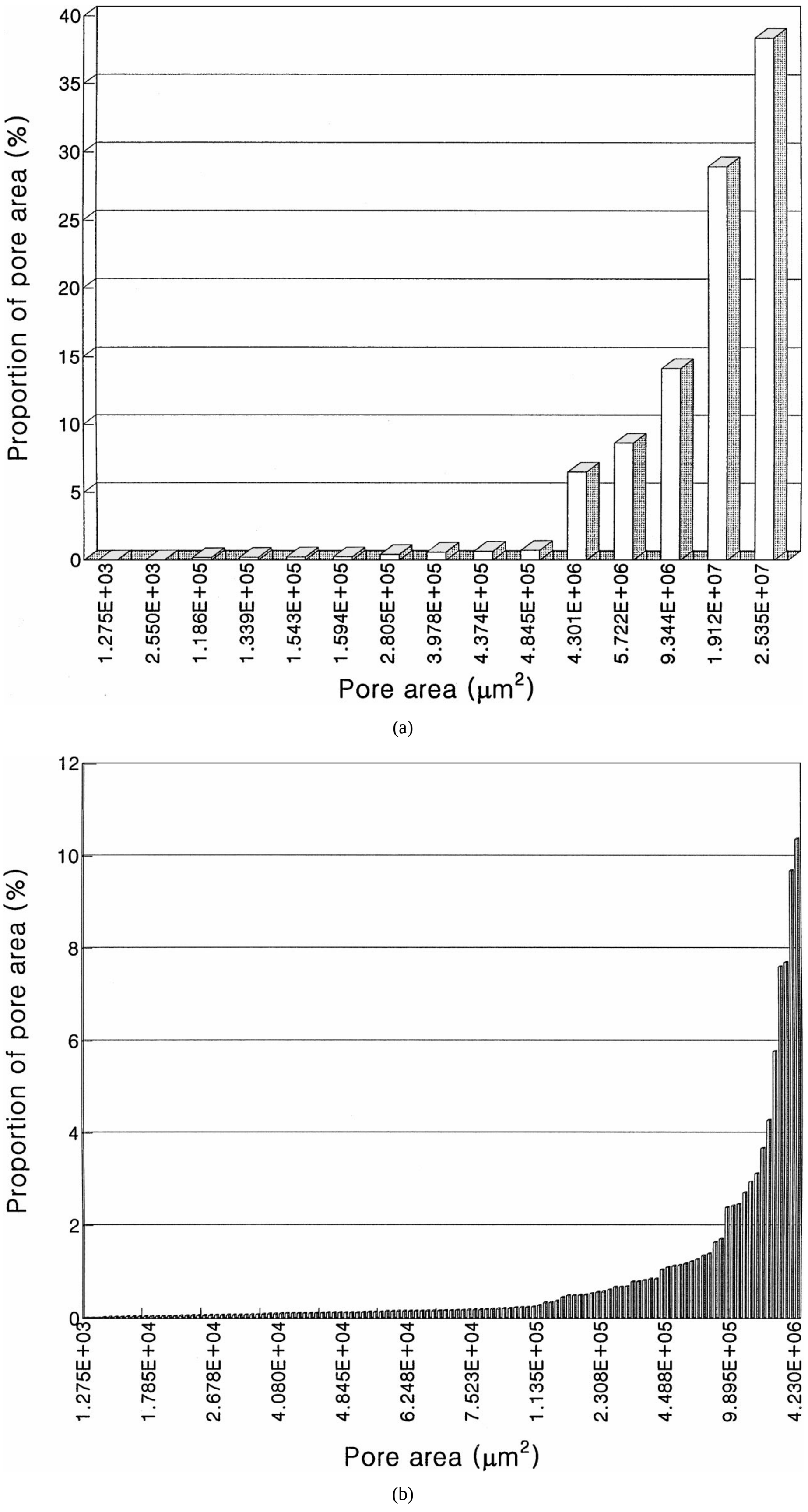
## 3.2. Crystallinity of matrix pitch

To investigate the effects of the temperature and the pressure on crystallinity, X-ray diffraction was performed to the coal tar pitch. The results are shown in Table III.

It has been known that pitch shows a good graphitizability as the temperature rises due to the development of mesophase flow texture. In other words, the mesophase, appearing during the liquid phase carbonization process, determines the graphitizability according to the treatment conditions. A raw pitch has the interlayer spacing of 0.3651 nm and the crystal size of 0.7700 nm, while the pitch treated 650 °C at atmosphere has 0.3433 and 1.905 nm, respectively. After being treated up to 2300 °C, its crystals gradually increased in size to become the interlayer spacing of 0.3388 nm and the crystal size of 20.41 nm, which shows a good graphitizability. At the pressure of 100 bar, the pitch appeared to have a more or less good graphitizability. However, at the pressure of 600 bar, the interlayer spacing changed little (0.3393 nm), but the crystal size decreased to 17.01 nm. Thus, excessive pressure seems to be rather a negative factor to the graphitizability, which corresponds the results of Fitzer and Terwiesch [14]; i.e. the pressure treatment gives little effect on the graphitization. This result is considered to be due to the inhibition of crystal growth and orientation at the formation step of the mesophase, which is caused by high pressures. During the mesophase step, the mobility of pitch is restricted by the pressure, forming a fine grain mosaic phase. In this condition, it is not easy for the pitch to form a flow phase to develop graphite structure. However, as a matrix

TABLE III X-ray diffraction data of coal tar pitch, heat-treated under various pressures

| Pressure (bar) | Temperature (°C) | Interlayer spacing $d_{002}$ (nm) | Crystal size $L_c$ (nm) |
|---|---|---|---|
| 1 | *RT* | 0.3651 | 0.7700 |
| | 650 | 0.3433 | 1.905 |
| | 2300 | 0.3388 | 20.41 |
| 100 | 650 | 0.3424 | 1.863 |
| | 2300 | 0.3378 | 20.42 |
| 600 | 650 | 0.3424 | 2.193 |
| | 2300 | 0.3393 | 17.01 |

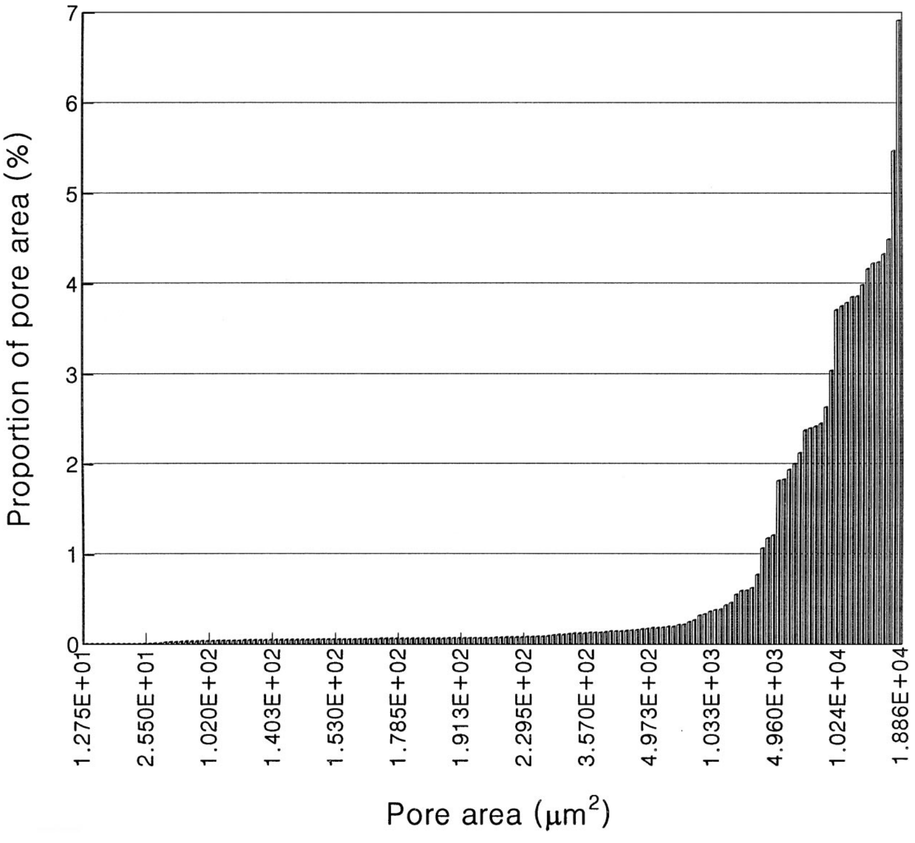


(a)

(b)

*Figure 3* Pore distributions of coal tar pitch, heat-treated up to 650 °C under various pressures; (a) 1 bar, (b) 100 bar, and (c) 600 bar. (*Continued*)

precursor needs superior erosion resistance property, the fine grain mosaic type is favored due to its small crystal size and excellent impregnation efficiency. $d_{002}$ and $L_c$ data reveal that the crystal state of composites after 2300 °C is on its way from two-dimensional turbostratic crystal structure to three-dimensional crystal structure. The temperature of 2300 °C cannot complete the graphitization of the pitch because its interlayer spacing does not amount to 0.3354 nm of the natural graphite.



(c)

*Figure 3* (*Continued*).

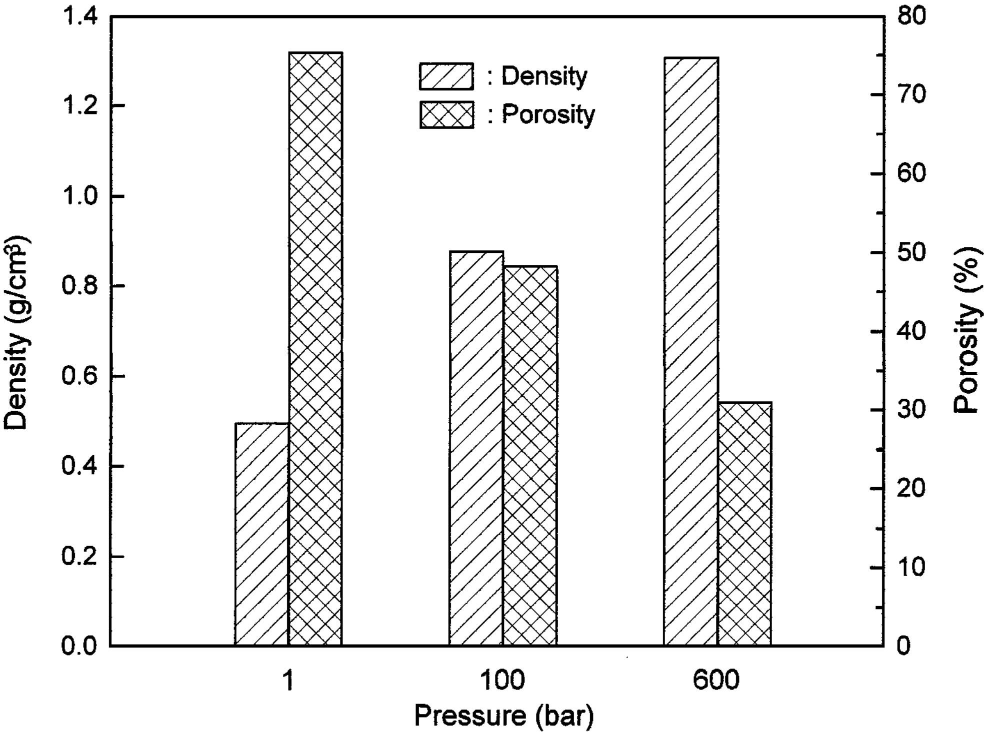


*Figure 4* Density and porosity change of coal tar pitch, heat-treated up to 650 °C under various pressure.

### 3.3. Density change of C/C composites

4D preforms, the densities of 800–850 kg/m$^3$, experienced the impregnation/carbonization processes with the coal tar pitch at the pressure of 1, 100, and 600 bar. The resulting densities of this process are shown in Fig. 5.

At the first impregnation process, the incremental rate of densities were great in all specimens at different pressures. However, from the second impregnation process, the higher the applied pressure, the higher the incremental rate of density. This can be related with the fact that raw pitch has the carbon yield of approximately 40% at 1 bar pressure, while it was as high as 90% at the pressure of above 100 bar [11, 16]. During the initial stage, the pressure has a significant effect on the density due to many open pores within the pitch. On the

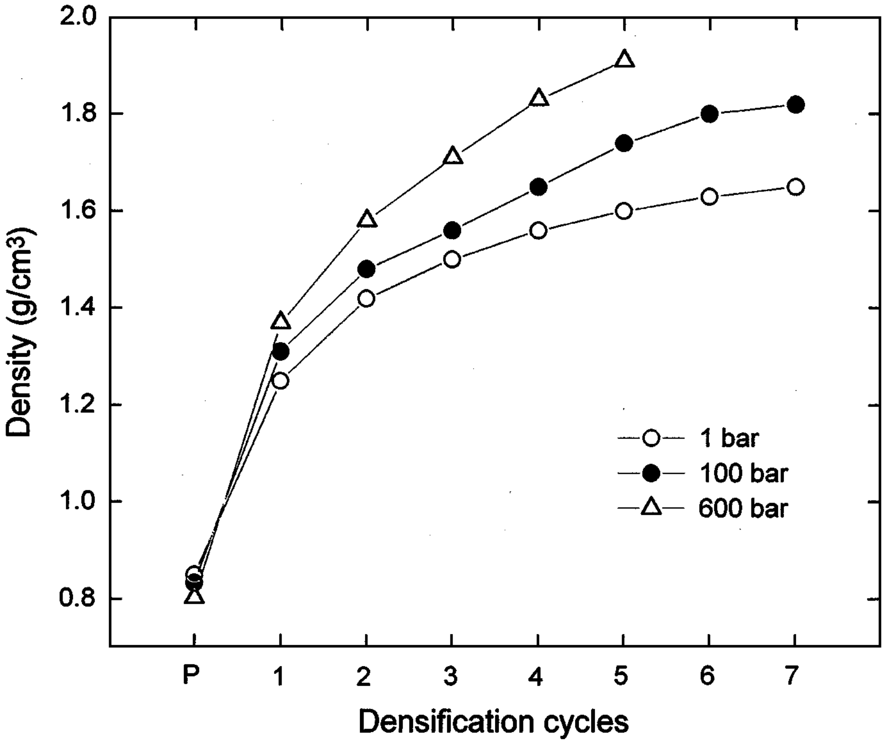
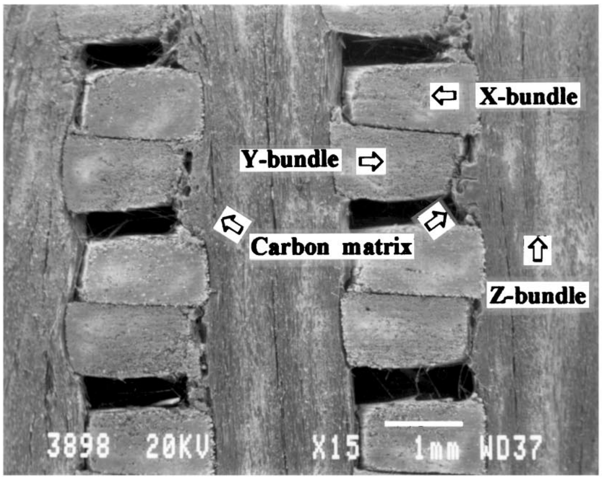


*Figure 5* Density change of 4D C/C composites with densification cycles.

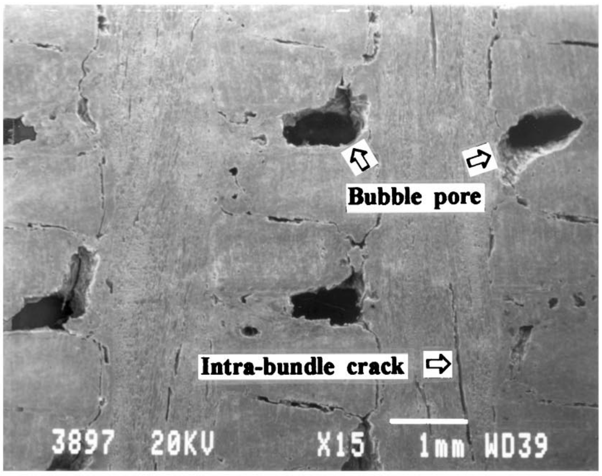
other hand, if the pitch has high density, densification is seldom affected by the pressure because of the small number of open pores. In other words, the incremental rate of density of the 1 bar pressure was intensive up to the 2nd impregnation process, but as the process was repeated, that of density was subdued. Thus, after the 7th densification process, the very last process, the density of the specimen reached 1620 kg/m$^3$. In the initial stage, a great amount of molten pitch was induced into the open pores. This is because the pores were large enough to be filled by the pitch even at low pressures. However, from the 2nd impregnation, the pore size decreased and more closed pores were generated than those at the initial stage, which reduced the incremental rate of density. Thus, it is not easy to induce the molten pitch into the pores without pressure application. On the other hand, the efficiency was improved at the pressure of 100 bar. When the specimen was impregnated at the pressure of 600 bar, as shown in the 5th densification step at 1940 kg/m$^3$, the incremental rate of density was higher than at other pressures. As can be seen in Fig. 5, significantly high pressure—as high as 600 bar—helps the induction of molten pitch into the fine pores within the C/C composites in spite of the high density owing to the excessive molten pitch. From these results, it is clearly understood that high pressure should be applied to cut down the repeating times of densification process.

### 3.4. Impregnation behavior of C/C composites

In order to investigate the impregnation behavior of the C/C composites with applied pressures, open pores at the intersection part of X, Y, U bundle layers were observed extensively. The 4D C/C composite which was



(a)



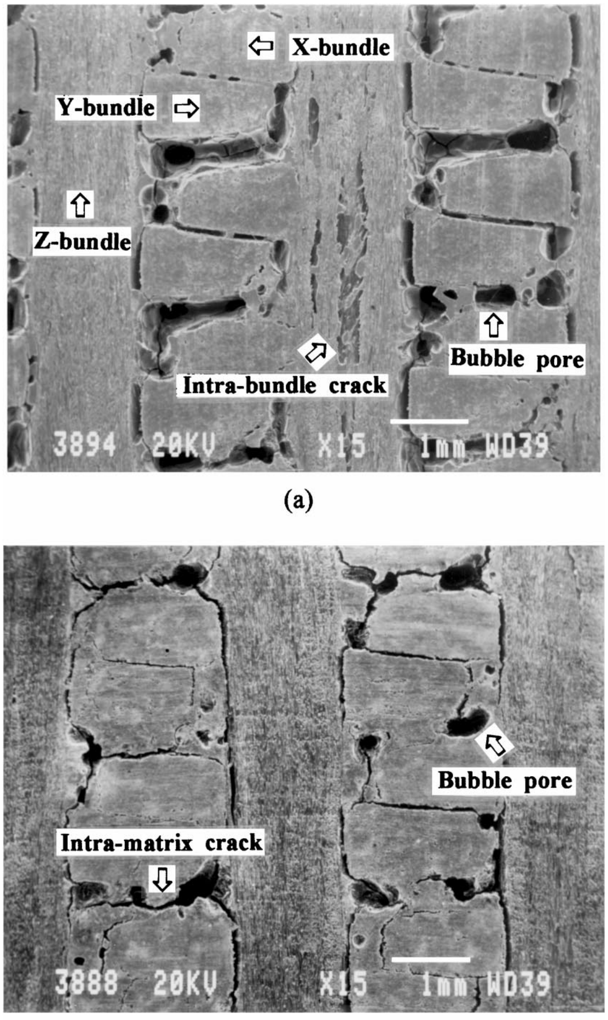
(b)

*Figure 6* SEM photographs of 4D C/C composites impregnated with coal tar pitch under the pressure of 1 bar (a) 1st densification, and (b) 7th densification.

prepared after the first atmospheric carbonization at the temperatures up to 650 °C is shown in Fig. 6a. In the figure, there are fiber bundles in X, Y, U directions and empty space not being filled with matrix. Although molten pitch filled into the pores during the impregnation process, it flowed out during the heat-treatment process.

Molten pitch was readily shoved by the gas, generated from the volatile materials on the C/C composites. Occasionally, dry zones existed which were never impregnated by molten pitch. The Fig. 6b represents the corss-section of C/C composites which experienced 7th densification process. Even after the 7th process, big bubble pores and interface cracks were still found between the fiber bundles. These bubble pores were large enough to be observed by the naked eye.

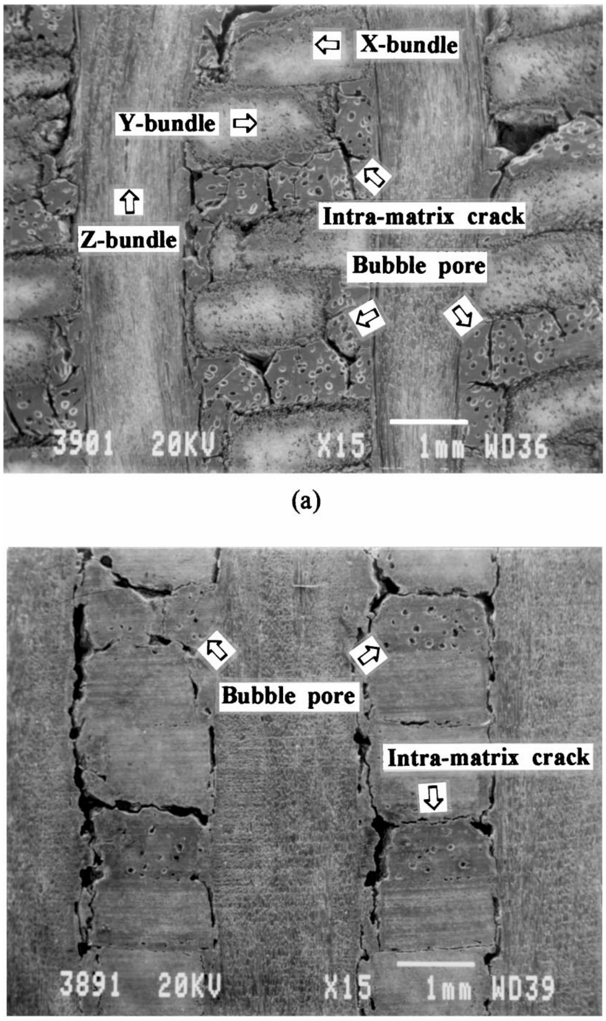
Fig. 7 illustrates 4D C/C composites, densified with 100 bar and graphitized at 2300 °C. Fig. 7a is the composite that underwent the first carbonization process. In the figure it is found that intra- and inter-X, Y bundles were filled with carbon derived from pitch, but its filling shapes were so sparse that they contained bubble pores in themselves. It was out of question that the bubble pore was smaller than that treated at the pressure of 1 bar. Fig. 7b is the picture of 4D C/C composite which experienced fifth densification process. In Fig. 7b, more carbon matrix was observed than in Fig. 7a, but still big bubble pores were shown in it. Also, many interface cracks were found in among differently oriented fiber bundles and between the interface of fiber bundle and carbon matrix.



(a)

(b)

*Figure 7* SEM photographs of 4D C/C composites impregnated with coal tar pitch under the pressure of 100 bar (a) 1st densification, and (b) 5th densification.

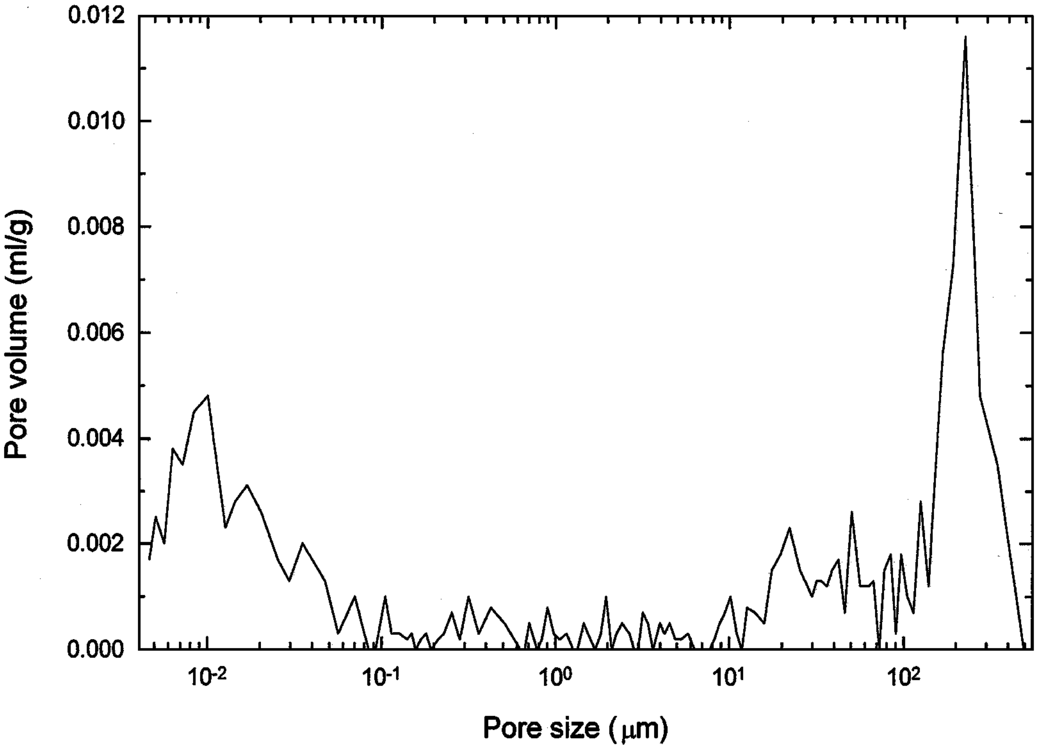


(a)

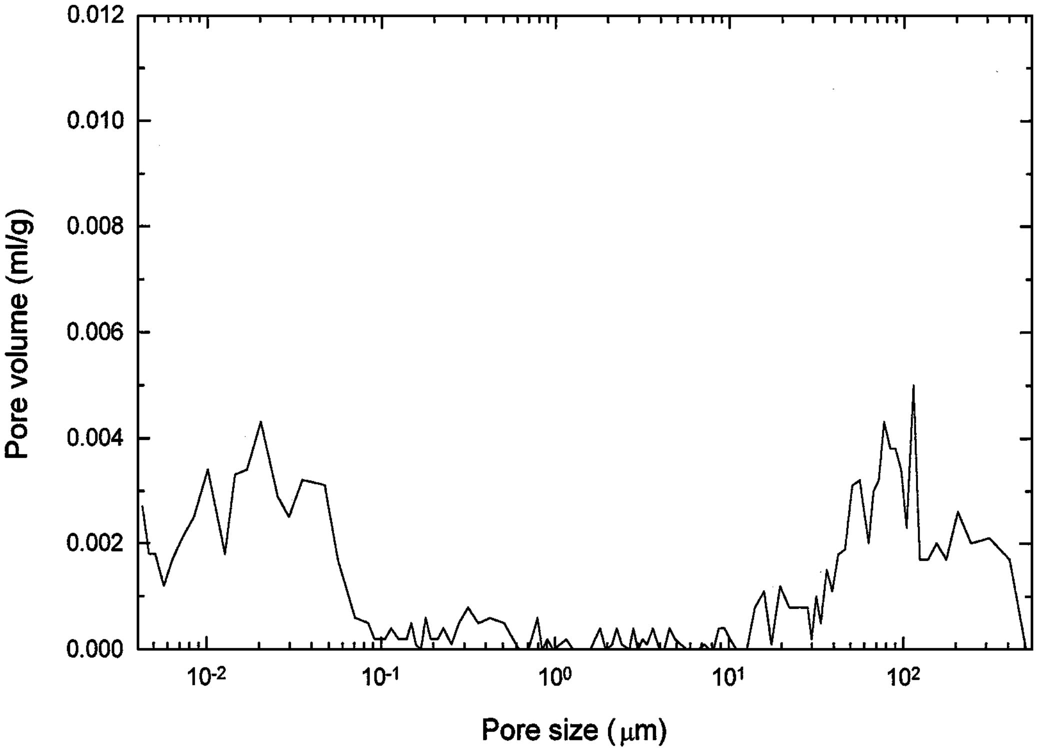
(b)

*Figure 8* SEM photographs of 4D C/C composites impregnated with coal tar pitch under the pressure of 600 bar (a) 1st densification, and (b) 3rd densification.

Fig. 8 shows the 4D C/C composite, densified one time with molten pitch at 600 bar and graphitized. In the Fig. 8a, small and regular bubble pores were observed in the formed matrix, but the pore sizes were much smaller than the pores obtained by 1 and 100 bar. This may be caused by the high pressure of 600 bar that inhibited not only the coalescence of pores, but also the outflow of impregnation pitch. Also, there are many intra-matrix cracks and interface cracks of matrix and fiber bundles. Fig. 8b represents the cross-section of C/C composite which experienced the third densification process. In Fig. 8b, bubble pores and intra-cracks inside of carbon matrix were almost filled up. However, a great deal of cracks still existed in the interface. When the above figures were compared, it became evident that the pore sizes depended an applied pressures. Therefore, the higher the pressure was applied, the smaller pores were formed. This result is in accordance with the tendency observed in the coking process of the coal tar pitch converting into the cokes. As for the densified C/C composites, almost all the pores were occupied by the carbon derived from pitch. Thus, cracking and debonding occurred on the interface, caused by the thermal mismatch of the fiber/matrix and the contraction of the matrix during the heat treatment. The C/C composites, prepared with the atmospheric carbonization process, were apt to be broken down by the mechanical loads and to exhibit inferior thermal behavior because of large pores in them. It seems that the

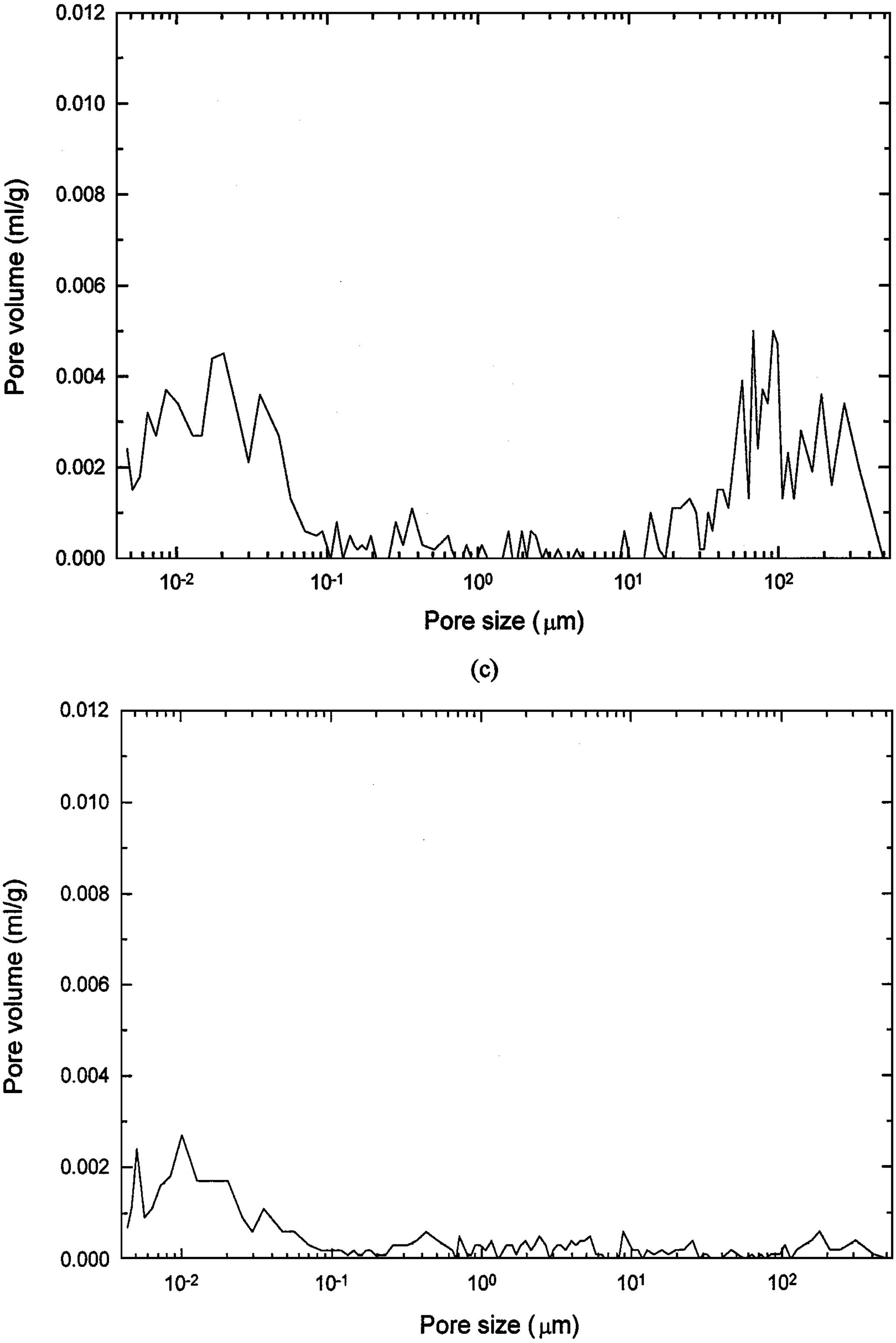


(a)



(b)

*Figure 9* Pore size distribution of 4D C/C composites impregnated with coal tar pitch under various pressures (a) 1 bar (1630 kg/m$^3$), (b) 100 bar (1620 kg/m$^3$), (c) 600 bar (1630 kg/m$^3$), and (d) 600 bar (1940 kg/m$^3$). (*Continued*)



(c)

(d)

*Figure 9* (*Continued*).

porosity should be reduced using the high pressure impregnation method and the high temperature treatment process should be performed with caution.

### 3.5. Pore distribution of C/C composites

The porosity of the 4D C/C composite was measured by the mercury porosimeter. The porosities of the specimens of similar densities, prepared in different pressures, are presented in Table IV.

The specimens of the density of about 1630 kg/m$^3$ had the same pore volume and porosity, but the portion of macropores was decreased as pressures increased. When treated with 600 bar, the specimen of the density of 1940 kg/m$^3$ had a low porosity of 8.30%. This is a very radical reduction compared with the specimen of 1630 kg/m$^3$ having the porosity of 20.4%. As for the pore distribution, the macropore portion was reduced significantly while the mesopore portion was increased. This tendency can be explained by the high

TABLE IV Pore characteristics of 4D C/C composites impregnated with coal tar pitch under various pressures

| | | | | Pore distribution (vol %) | | |
|---|---|---|---|---|---|---|
| Sample | Density (kg/m$^3$) | Pore volume (m$^3$/kg) | Porosity (vol %) | below $10^{-1}$ $\mu$m | $10^{-1}$–$10^1$ $\mu$m | over $10^1$ $\mu$m |
| 4D C/C-1 | 1630 | 128 | 20.8 | 32.2 | 12.9 | 54.9 |
| 4D C/C-100 | 1620 | 120 | 19.8 | 35.1 | 9.30 | 55.6 |
| 4D C/C-600 | 1630 | 126 | 20.4 | 38.7 | 8.50 | 52.8 |
| 4D C/C-600 | 1940 | 43 | 8.30 | 55.8 | 30.8 | 13.4 |

porosity of cokes, derived from the raw pitch by the heat treatment at atmospheric pressure. These large pores were generated by free discharge and bubbling of volatile materials in the impregnated pitch. However, high pressures prevented the volatile materials from being released so that a large number of small pores were created. When the porosity and the macropore volume, obtained by porosimeter (analysis range of 0.003–600 $\mu$m), were compared with SEM, there was an obvious presence of pores above 600 $\mu$m in size that were not able to be detected by the porosimeter. It thus can be expected that the porosity of the specimen, treated at low pressure, was higher than the results in Table IV.

Fig. 9 is the pore volume distribution analyzed by the porosimeter. Many of the pores were less than 0.1 $\mu$m and more than 10 $\mu$m in size. As the high pressure was applied, relatively small pores were increased rather than large ones. As shown in Table IV, the pores of 0.1–10 $\mu$m numbered very few in all specimens.

Some deductions can be made by this tendency. First, irrespective of the pressure, the pores of 0.1–10 $\mu$m in all the specimens were preferentially filled with the impregnated pitch because the pores in the range of 0.1–10 $\mu$m were abundant in the specimens. Secondly, as a large number of narrow and long tunnel type fine pores existed in the preform, the pores of 0.1–10 $\mu$m were filled with the molten pitch induced into the preform by capillary action. Thirdly, when the molten pitch wetted the inside of the pores, the optimum thickness of pitch wall it formed was 0.1–10 $\mu$m. Thus, the pores within this size range were filled almost completely with the molten pitch. On the other hand, it was hard for the pores less than 0.1 $\mu$m to be impregnated and the bubble pores of 0.1–10 $\mu$m remained as closed pores. Therefore, it can be expected that these pores are not able to be checked by the porosimeter. As for the big pores, above 10 $\mu$m, they were considered to be filled by the pitch preferentially, but the densification process should be performed many times in order to fill the pores completely due to the limit of the thickness of wetted wall. This tendency can be confirmed by the very last densified C/C composites (1940 kg/m$^3$). As shown in Fig. 9d, the pores of above 10 $\mu$m almost disappeared, while the mesopores of below 0.1 $\mu$m were not yet filled. Since the fine pores remained as closed pores at the density of 1600 kg/m$^3$, the intermediate graphitization process coupled with high impregnation pressure above 600 bar should be preformed in order to fill the residual fine pores, or by way of CVI method the residual pores also could be filled.

## 4. Conclusion

In this study, the effects of pressure on the porosity and graphitizability of the coal tar pitch used for C/C composites were investigated. The pressure effect on the densification of the 4D C/C composites, having experienced impregnation and carbonization with coal tar pitch, was also examined.

When the coal tar pitch was heat treated, the percentage of pore area at the pressure of 1 bar was 75% while at 600 bar it was 31%. This is because the pyrolized gases were prevented from discharging, which made the percentage reduced 1.5 times than that for 1 bar. When the pitch was graphitized up to 2300 °C after being carbonized with high pressure, the degree of graphitization was not significantly improved and the crystal size showed a tendency to reduce. In the densification of C/C composites, as the impregnation pressures increased, the incremental rate of density change was intensive and the impregnation efficiency improved. Additionally, in terms of the pore size distribution, the macropore portion reduced with rising pressure, while the mesopore portion had a tendency to increase. Also, all the specimens, irrespective of pressure, showed very low pore size distribution in the range of 0.1–10 $\mu$m.

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