Carbon Products Prepared from Variant Pitch Materials. VIII. The Preparation of Isotropic Pitch Carbon with a High Density

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The present works were undertaken in order to prepare the isotropic Pitch Carbon with a high density and with a desired degree of graphitization. The tablets were prepared by pressing some kinds of variant pitch materials and were then heat-treated below 2600°C in N_2 gas. Isotropic Pitch Carbon with a high density and with a low degree of graphitization can be readily prepared by pressing the non-graphitizable variant pitch material under high pressure. On the other hand, for the purpose of preparating isotropic Pitch Carbon with a high density and with a high degree of graphitization, a graphitizable variant pitch material with a low softening point, —in other words, with a good ability of sintering— was pressed into tablets under low pressure. The typical properties of the Pitch Carbon thus obtained (H.T.T. 2600°C) were as follows: Bacon Anisotropic Factor: 1.01; Bulk density: 1.79 g/cc; d_{002}: 3.40 Å; *Lc*: 210 Å.

The high-temperature gas-cooled reactor (HTGR) has lately attracted considerable attention, simultaneously, the isotropic carbon products with a high density have been required as one of the most important materials for the reactor.[1,2]

It was previously reported by the present authors that carbon rods or tablets could be prepared from specific variant pitch materials instead of coke powder and pitch binder. The carbon articles prepared by this method were referred to as Pitch Carbon.[3] From the previous results, it was been found that the properties of Pitch Carbon can be changed greatly by choosing variant pitch materials and/or conditions of heat-treatment. These facts suggest the possibility of thus preparing a carbon product for the reactor use.

The present experiments were undertaken to prepare an isotropic Pitch Carbon with a high density and with various degrees of graphitization.

Experimental

In order to prepare the variant pitch materials, coal tar pitch was distilled at 500°C for 30 min by bubbling N_2 gas through it. The resulting variant pitch materials (to be referred to as variant pitch material-N) did not clearly exhibit its softening point (S.P.) by the penetration method[4] (heating rate: 30°C/min), but it was sintered to an appreciable extent after the measurement. This variant pitch material was crushed to under 100 mesh and was used in preparing the Pitch Carbon. This variant pitch material was then pressed into tablets 10 mm in diameter and about 10 mm thick. The tablets were pre-heated in air up to 300°C at about 1.5°C/min to prevent their deformation at the subsequent heating stage, and were then heat-treated in N_2 gas at a temperature below 2600°C for 10 min. In addition, four kinds of variant pitch materials (A,[5] C,[6] L,[7] Al[8]) were used in preparing Pitch Carbons with various degree of graphitizability. The details of their methods of preparation have been reported elsewhere. Unless otherwise noted, however, the variant pitch material used was variant pitch material-N.

As first, the relationships between the preferred orientation of graphite crystallite in Pitch Carbon and the following factors were examined: the graphitizability, the particle size of the variant pitch material, the heat-treatment temperature (H.T.T.), and the addition of natural graphite or needle cokes. Furthermore, the preferred orientation of Pitch Carbon was compared with those of the other carbon materials. For the representation of the preferred orientation of graphite crystallite, the Bacon Anisotropic Factor (BAF)[9] was measured from the orientation diagram which was obtained by using the X-ray transmission technique reported by Noda and Inagaki.[10] The value of BAF is 1.00 for the completely isotropic carbon product, and it increases with a lowering of its isotropy. Carbon sections about 0.5 mm thick were cut with their planes parallel to or vertical to the pressing direction of Pitch Carbon.

The interlayer spacing, d_{002}, and the crystallite thickness, *Lc*, of carbon specimens were calculated according to a method previously described.[4] Some carbon specimens gave composite (002) diffraction profiles. These profiles were separated into two symmetrical components, and the X-ray parameters of each component were calculated. Moreover, the properties such as the density and the porosity were measured, and the internal structure was observed according to a method previously described.[4]

Results and Discussion

1. *The Preferred Orientation of the Graphite Crystallite in the Pitch Carbon.*

For all the carbon sections cut with their planes vertical to the pressing direction, the values of BAF were nearly 1.00. Therefore, the values for these sections will not be presented in this report; only the values for sections cut with their planes parallel to the pressing direction will be shown.

1.1. *The Effect of the Graphitizability of Variant Pitch Materials (Table 1).*

Pitch Carbons were prepared from several kinds of variant pitch materials with various degree of graphitizability. As the degrees of

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[1] H. Suzuki, *Ceramics*, **4**, (4) 306 (1969).
[2] T. Sasaki, *Tanso*, No. 64, 14 (1971).
[3] S. Otani, A. Oya, and Y. Kitazume, *Nippon Kagaku Kaishi*, **1972**, 727.
[4] S. Otani, A. Oya, and T. Fukabori, *Kogyo Kagaku Zasshi*, **72**, 317 (1969).
[5] S. Otani, A. Oya, I. Nakagawa, and T. Fukabori, *ibid.*, **72**, 323 (1969).
[6] S. Otani, A. Oya, and T. Nagashima, *ibid.*, **73**, 2095 (1970).
[7] S. Otani and A. Oya, This Bulletin, **44**, 3181 (1971).
[8] S. Otani and A. Oya, *Kogyo Kagaku Zasshi*, **73**, 1110 (1970).
[9] G. E. Bacon, *J. Appl. Chem.* (London), **6**, 477 (1959).
[10] T. Nada and M. Inagaki, *Kogyo Kagaku Zasshi*, **62**, 1300 (1959).

TABLE 1. THE EFFECT OF THE GRAPHITIZABILITY OF VARIANT PITCH MATERIALS

Variant pitch materials	Moulding pressure (kg/cm^2)	HTT (°C)	d_{002} (Å)	*Lc* (Å)	BAF
Al[8]	400	2600	3.39	370	1.13
N	400	2600	3.41	270	1.11
A[5]	400	2600	3.41	220	1.06
C[6]	400	2600	3.41 3.45	200 43	1.05
L[7]	400	2600	3.42 3.45	150 30	1.00

graphitization of Pitch Carbon which were represented by d_{002} and *Lc* decreased, the values of BAF gradually decreased also. The Pitch Carbon which was prepared from the variant pitch material-L was completely isotropic; that is, the value of BAF was 1.00. From these results, it was found that the isotropic Pitch Carbon could easily be prepared from non-graphitizable variant pitch materials.

TABLE 2. THE EFFECT OF THE MOULDING PRESSURE

Variant pitch materials	Moulding pressure (kg/cm^2)	HTT (°C)	d_{002} (Å)	*Lc* (Å)	BAF
N	100	2600	3.41	270	1.07
N	400	2600	3.41	270	1.11
N	1600	2600	3.41	250	1.18

1.2. The Effect of the Moulding Pressure (Table 2). The values of BAF were remarkably increased with an increase in the moulding pressure. However, such a relation was not observed for the Pitch Carbon prepared from non-graphitizable variant pitch materials.

TABLE 3. THE EFFECT OF THE PARTICLE SIZE OF VARIANT PITCH MATERIAL

Variant pitch materials	Moulding pressure (kg/cm^2)	HTT (°C)	d_{002} (Å)	*Lc* (Å)	BAF
N	100	2600	3.41	270	1.07
N[a]	100	2600	3.39	270	1.05
N	400	2600	3.41	270	1.11
N[a]	400	2600	3.39	280	1.06

a) Crushed by ball mill for 8 hr.

1.3. The Effect of the Particle Size of Variant Pitch Materials (Table 3). The variant pitch material-N (under 100 mesh) was further crushed by the use of a ball mill for 8 hr and was then pressed into tablets. The tablets were then heat-treated in the way described above. It seems that the preferred orientation of Pitch Carbon generally falls off as the particle size of the variant pitch material decreases. However, the preferred orientation of the Pitch Carbon which was prepared from such fine pitch powder was scarcely affected by the moulding pressure.

1.4. The Effect of Heat-treatment Temperature (Table 4). The degree of the graphitization of Pitch Carbon was gradually increased by raising the temperature between 1400 and 2400°C. The values of BAF, on the whole, increased with the increase of H.T.T.

TABLE 4. THE EFFECT OF HEAT-TREATMENT TEMPERATURE

Variant pitch materials	Moulding pressure (kg/cm^2)	HTT (°C)	d_{002} (Å)	*Lc* (Å)	BAF
N	400	2600	3.41	270	1.11
N	400	2200	3.42	120	1.07
N	400	1800	3.43	77	1.09
N	400	1400	3.46	25	1.05
N	400	1000	3.42	25	1.05

TABLE 5. THE EFFECT OF THE ADDITION OF NEEDLE COKES OR NATURAL GRAPHITE

Additives	Moulding pressure (kg/cm^2)	HTT (°C)	d_{002} (Å)	*Lc* (Å)	BAF
—	400	2600	3.41	270	1.11
25 wt% of needle cokes	400	2600	3.39	480	1.24
25 wt% of natural graphite	400	2600	3.35 3.40	1000 190	1.44
50 wt% of natural graphite	400	2600	3.35 3.40	1000 230	1.99

1.5. The Effect of the Addition of Needle Cokes or Natural Graphite (Table 5). The values of BAF were increased considerably by the addition of 25 wt% of natural graphite (under 100 mesh, Madacascar flaky graphite) or of needle cokes (under 100 mesh) which were very lamellar in shape. The further addition of natural graphite increased more remarkably the value of BAF for the resulting Pitch Carbon.

TABLE 6. THE COMPARISON WITH THE OTHER CARBON MATERIALS

Carbon materials	Moulding pressure (kg/cm^2)	HTT (°C)	d_{002} (Å)	*Lc* (Å)	BAF
Pitch carbon	400	2600	3.41	270	1.11
Carbon electrode	—	2600	3.38	480	1.18
Pyrolytic carbon	—		3.42	210	4.16
Vitro carbon	—	2600	3.45	27	1.02

1.6. The Comparison with Other Carbon Materials (Table 6). In order to evaluate the preferred orientation of the Pitch Carbon which was prepared from the variant pitch material-N, the values of BAF of the other carbon materials were measured. For the carbon electrode or Vitro Carbon,[11] the thin section was cut with its plane parallel to the pressing- or depositing-direction. Pyrolytic carbon exhibited an extremely remarkable preferred orientation, while, on the contrary, Vitro Carbon was almost isotropic. Pitch Carbon and the carbon electrode exhibited values of BAF intermediate between those of pyrolytic carbon and Vitro Carbon.

2. The Relationships between the Moulding Pressure and Some Properties of Pitch Carbon. Figure 1 shows microscopic photographs of Pitch Carbon which was

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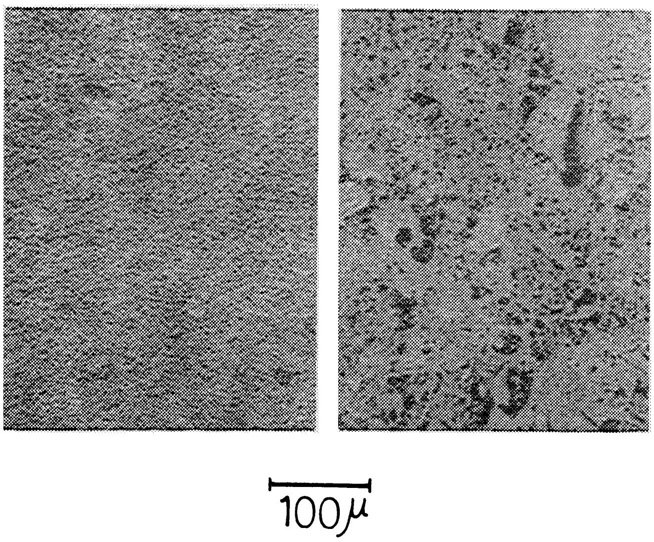
[11] H. Honda, Y. Sanada, and T. Furuta, *Tanso*, No. 46, 2 (1966).



(a) Before heating (b) After heating

Fig. 1. Internal structures of pitch carbon pressed at 1600 kg/cm^2 (variant pitch material-N)

prepared from the variant pitch material-N by pressing at 1600 kg/cm^2. Large pores or grains were not observed in the tablet before the heat treatment. After the tablet had been heat-treated at 2600°C, on the other hand, large pores or grains were developed in it. From the above photographs, it is clear that these changes were caused by the coalescence and/or shrinkage of variant pitch particles at the heating stage.[6] This fact shows that the variant pitch material-N has a good ability of sintering. The internal structures of the other tablets (moulding pressure: 100 and 400 kg/cm^2) before the heat treatment were similar to that shown in Fig. 1(a), and 2600°C-specimens gave less dense and less homogeneous structures than that shown in Fig. 1(b). Such differences are probably due to the difference in moulding pressure. The formation of cross-linkages among the molecules included in the pitch and the resulting elevation of the S.P. of pitch materials depended mainly on the progress of the oxidation reaction in the pre-heat treatment process in air. The oxygen is difficult to diffuse into closely-packed tablets. Therefore, these tablets tend to become semi-fused, thus having more mobility than in the solid state in this oxidation stage. As a result, a high moulding pressure accelerates sintering among particles of variant pitch materials.[6] A similar tendency of becoming semi-fused and accelerating the sintering can also be expected in the use of an oxidation temperature in the first stage lower than 300°C.[5]

The relationships between the bulk density of Pitch Carbons and the moulding pressure were as follows; 100 kg/cm^2: 1.60 g/cm^3, 400 kg/cm^2: 1.64 g/cm^3, 1600 kg/cm^2: 1.83 g/cm^3. For the Pitch Carbons pressed at 100 and 400 kg/cm^2, their bulk density were analogous in spite of the differences in the moulding pressure and in the values of BAF (r.f. 1.2).

3. *Possibility of Isotropic Pitch Carbon with a High Density and with Various Degree of Graphitization.*

According to the results described above, it seems that the preferred orientation of Pitch Carbon increases with a rise in the graphitizability of the variant pitch material used, but changes only slightly with an increase in the degree of graphitization upon heat treatment. These facts suggest that the preferred orientation of the final products is mainly determined at the moulding stage. In addition, the moulding pressure has scarcely no effect on the degree of graphitization of the resulting Pitch Carbon, but has a remarkable effect on the preferred orientation as well as the graphitizability of the variant pitch materials. The preferred orientation gradually became isotropic with a decrease in the moulding pressure. On the other hand, there were two methods for the preparation of Pitch Carbon with a high density. One is the use of the high moulding pressure described above, and the other is the acceleration of the sintering by using raw variant pitch materials with low S.P. and/or by applying a low oxidation temperature at the first stage.[6] The high-moulding-pressure-method is useful in the preparation of the isotropic Pitch Carbon with a low degree of graphitization which is prepared from non-graphitizable variant pitch materials such as chlorinated pitch.[6] It is clear that this method can not, however, be used for the preparation of isotropic Pitch Carbon with a high degree of graphitization, the other method would be better for this purpose. Since the degree of graphitization of Pitch Carbon is not affected by the moulding pressure, but is essentially affected by the graphitizability of the raw variant pitch, our purpose can be accomplished in the following manner. At first, graphitizable variant pitch materials with a low S.P. are moulded into tablets under a pressure lower than 100 kg/cm^2, and then the tablets are oxidized at as low temperature as possible within the limits required to prevent their deformation at the subsequent heating stage. By this treatment, the graphitizability of the product generally deteriorates to some extent. Therefore, even when this procedure is used, it is unavoidable that there is some limit to the improvement in the degree of graphitization of the resulting products.

4. *Attempt to Make Isotropic Pitch Carbon with a High Density and with a High Degree of Graphitization.*

When the tablet from material-N was heated under N_2 gas, it was deformed. From this fact, it seemed that the S.P. of the material-N was sufficiently low for this purpose. Therefore, the acceleration of the sintering was attempted by the control of the oxidation temperature in air. Moreover, for the improvement of the preferred orientation, a moulding pressure smaller than 100 kg/cm^2 was applied. The variant

Table 7. Typical properties of isotropic Pitch Carbon with high density

Pitch carbon	d_{002} (Å)	Lc (Å)	BAF
dia. 20 mm	3.39	210	1.02
dia. 40 mm	3.40	210	1.01

App. density (g/cm^3)	Bulk density (g/cm^3)	App. porosity (%)
2.12	1.75	17.3
2.12	1.79	15.4

pitch material-N (under 100 mesh) was pressed into tablets (diameter: 20 and 40 mm; thickness: about 10 mm) at 80 kg/cm^2. Then, the tablets were heated at the rate of 0.15°C/min up to 210°C in air, followed by heat-treatment at 2600°C in N_2 gas.

Some properties of the Pitch Carbon thus obtained are shown in Table 7. Both Pitch Carbons were almostly isotropic and were considerably improved in density in comparison with the other Pitch Carbons. In addition, their degrees of graphitization were considerably improved.

As a result, it seems reasonable to conclude that an isotropic carbon product with a high density, in addition to an improved degree of graphitization, can be prepared by the use of the method of preparing Pitch Carbon without any other techniques.