

GRAPHITIZABILITY OF CARBONS UNDER 5 KBARS PRESSURE

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Introduction

Most of carbons have been classified into either graphitizing or non-graphitizing carbons. This classification of carbons is rather rough, but very convenient to explain and understand the graphitization behaviour of carbons at high temperatures under normal pressure.

We have heat-treated different kinds of carbons under a pressure of 5 kbars. The non-graphitizing carbons, phenol resin char [1], glassy carbon[2] and carbon beads[3,4], are graphitized completely under 5 kbars at the relatively low temperature as 1600°C. On the graphitizing carbons, however, the different results are obtained; on the polyvinylchloride coke carbonized up to 700°C the complete graphitization through heterogeneous process is observed[5,6], but on the same coke heat-treated at high temperature the graphitization retards remarkably[7].

Here, we will show the graphitizability of carbons under high pressure quite different from that under normal pressure: the carbons non-graphitizing under normal pressure are graphitizing under high pressure.

Experimental

Different carbons were used as the starting materials. These carbons were heat-treated under a solid pressure of 5 kbars at various temperatures for 1 hour. The piston cylinder type apparatus was used. The temperature of heat treatment was determined from electric power input by using the relation between temperature and power input which was established beforehand with the aid of a chromel-alumel thermocouple.

On the specimen heat-treated, the X-ray diffraction profiles were measured by using Ni-filtered Cu K α radiation and a recording goniometer. The average interlayer spacing d_{002} was determined from 002 and 004 profiles referring to an inner standard of silicon.

Results

In Figs. 1 a) and b), the changes of 004 diffraction profile with HTT under 5 kbars are shown on two different petroleum cokes calcined up to 1400°C. The former is graphitized completely, as has been observed on the polyvinylchloride coke [5]. The latter, however, shows only partial graphitization even after the heat treatment at 1900°C under 5 kbars. It appears to consist of two component profiles, the component at high angle side having the d_{002} -spacing of 3.36 Å (graphitic component). We found a similar partial graphitization on various petroleum cokes calcined, the amount of the

graphitic component depending on the coke.

In Figs. 2 a) and b), the changes of 004 diffraction profile are also shown on the mesophase spherules which have been separated from an asphalt by quinoline. The as-separated spherules show partial graphitization, but on the same spherules pre-heated at 2200°C no graphitic component detected. The retardation effect of pre-heat-treatment on graphitization under 5 kbars was observed on other kinds of mesophase spherules[8]. A similar retardation of graphitization under 5 kbars was observed on the fluid coke [9] and gilsonite coke[10].

In Figs. 3 a) and b), the change of 002 diffraction profile are shown on the carbon beads. They are made from pitches and are non-graphitizing under normal pressure. The carbon beads carbonized up to 1000°C are graphitized abruptly at about 1600°C. The same abrupt graphitization was observed on the phenol resin char[1] and glassy carbon spheres[2]. The retardation effect of pre-heat-treatment is again observed on the carbon beads. In this case, however, it is not so remarkable as the cases described above. Large amount of graphitic component seems to be formed after the heat treatment at 1800°C under 5 kbars.

Discussion

From this series of experiments, we understand the importance of the microstructure of the starting materials on the graphitization under 5 kbars. The isotropic random microstructure is favorable for graphitization under pressure, though it does not give graphite structure under normal pressure. Therefore, we would say that the non-graphitizing carbons are graphitizing under high pressure. The carbons with anisotropic microstructure show a wide range of graphitizability, from complete graphitization to almost no graphitization at 1900°C under 5 kbars. According to the detailed observations by high resolution electron microscopy[11], the sizes of the elemental domains of carbon layers are 10 - 30 Å for both graphitizing and non-graphitizing carbons. These carbons are graphitized under 5 kbars. By the heat treatment under normal pressure, elemental domains grow remarkably in graphitizing carbons, but only little in non-graphitizing carbons. The sizes of the domains, in other words, are probably responsible for retardation effect of pre-heat-treatment on graphitization under 5 kbars, for graphitizing carbons the effect being remarkable and for non-graphitizing carbons not so remarkable.

Fig. 3a) Carbon beads

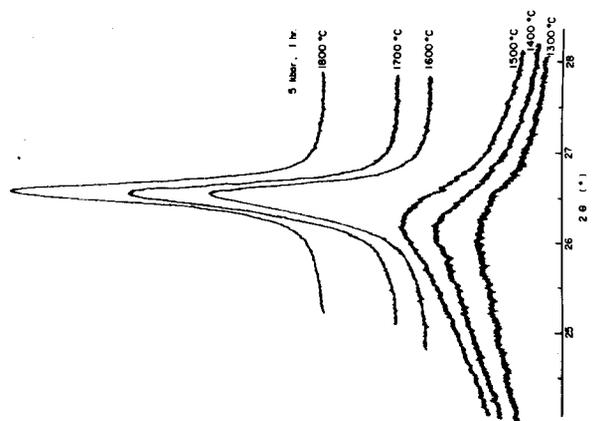


Fig. 3b) Carbon beads 2760°C-pre-heated

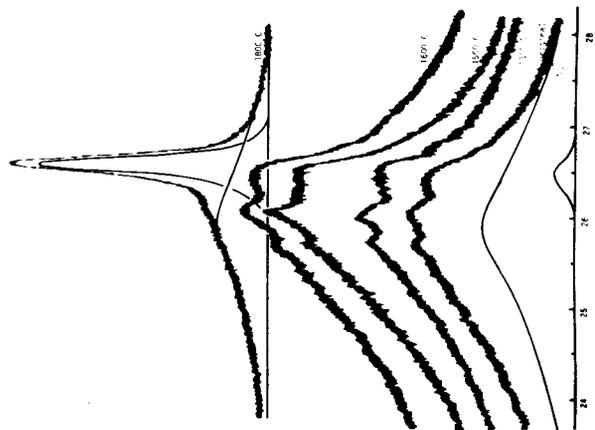


Fig. 2a) Mesophase spherules as-separated

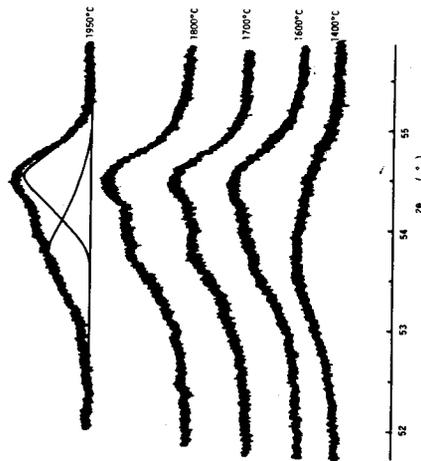


Fig. 2b) Mesophase spherules 2200°C-pre-heated

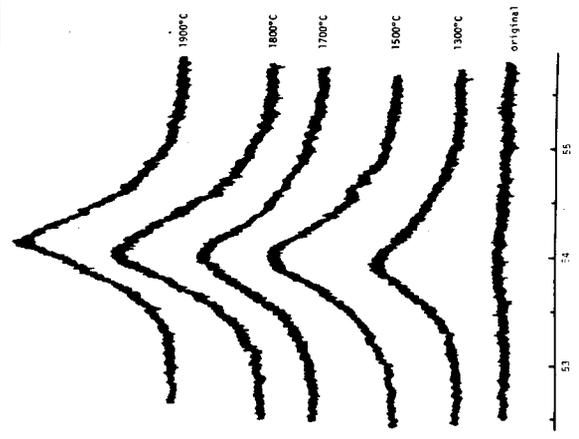


Fig. 1 a) Petroleum coke

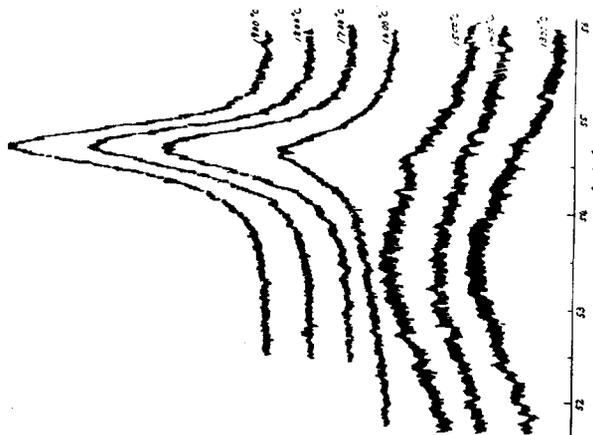
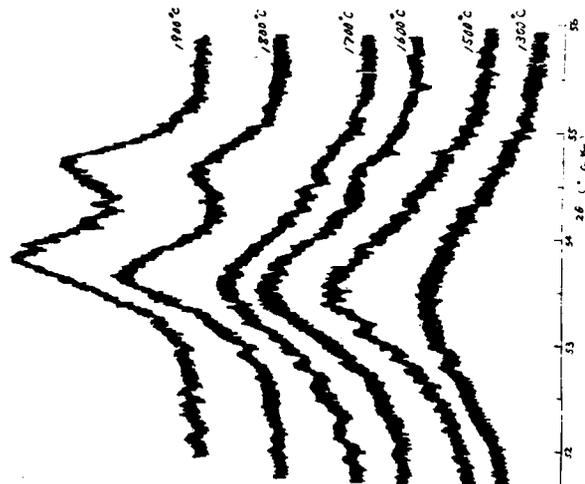


Fig. 1 b) Petroleum coke



References

1. K. Kamiya, M. Inagaki, M. Mizutani & T. Noda, *Bull. Chem. Soc. Japan* **41**, 2169 (1968)
2. M. Inagaki & S. Naka, *J. Mat. Sci.* **10**, 814 (1975)
3. M. Inagaki, Y. Tamai, S. Naka & K. Kamiya, *Ceram. Bull.* **52**, 856 (1973)
4. M. Inagaki, K. Horii & S. Naka, *Carbon* **13**, 97 (1975)
5. T. Noda, K. Kamiya & M. Inagaki, *Bull. Chem. Soc. Japan* **41**, 485 (1968)
6. K. Kamiya, M. Inagaki & T. Noda, *High Temp.-High Press.* **5**, 331 (1973)
7. K. Kamiya, M. Inagaki & T. Noda, *Bull. Chem. Soc. Japan* **43**, 926 (1970)
8. M. Inagaki, Y. Tamai, S. Naka, Y. Yamada & H. Honda, *Carbon* **14**, 203 (1976)
9. M. Inagaki, Y. Tamai, S. Naka & K. Kamiya, *Carbon* **12**, 639 (1974)
10. M. Inagaki, Y. Tamai & S. Naka, *Tanso* **1973** [No. 75], 118 (1973)
11. A. Oberlin, G. Terriere & J. L. Boulmier, *Tanso* **1975** [No. 80], 29 (1975)