JOURNAL OF MATERIALS SCIENCE 20 (1985) 643–647

A study on the deposition rate of pyrolytic carbon in a tumbling bed

J. H. JE, JAI-YOUNG LEE
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, PO Box 131, Cheongryang, Seoul, Korea

The factors on which the deposition rate of isotropic carbon is dependent are deduced from a suggested deposition mechanism and compared with experimental results. The deposition rate of isotropic carbon increases with the increase in the number of gas-borne nuclei, with the increase in the amount of carbon source available for the deposition as a surface carbon in the gas phase, and with the increase in the number of the gas-borne particles colliding with the substrate which is dependent on the gas flow conditions around it.

1. Introduction

Pyrolytic carbon is the quasicrystalline carbon material that is deposited on a substrate by the thermal pyrolysis of a carbon-bearing vapour [1]. Pyrolytic carbon coatings have been used on resistors [2], rocket nose cones and nozzles [3], for coating nuclear fuel particles [4], matrices of carbon fibre composite materials [5] and biomaterials [6].

The deposition rate of pyrolytic carbon has not been well analysed in terms of the deposition mechanism in spite of it being closely related to the deposition mechanism. Many mechanisms have been suggested. Recently Je and Lee [7] suggested a new formation mechanism of pyrolytic carbon applying a tumbling bed process. In particular they were able to explain why the isotropic or laminar carbon was easily formed in the dynamic system of the fluidized bed. The purpose of this work is to deduce the factors on which the deposition rate of isotropic carbon is dependent from Je and Lee's deposition mechanism of isotropic carbon [7] and to compare them with the experimental results of the deposition rate of isotropic carbon deposited in a tumbling bed.

2. Discussion of deposition rate and deposition mechanism

Isotropic pyrolytic carbon is formed at deposition conditions where homogeneous nucleation occurs in the gas phase and at the gas flow conditions where gas-borne droplets collide with the substrate [7–9].

Kaae *et al.* [10, 11] have examined the structure of pyrolytic carbon and found that isotropic carbon is composed of growth features of micrometer-order in size. They claimed that the droplets which are homogeneously nucleated in the gas phase, deposit on the substrate to form the growth feature. Lee *et al.* [12] suggested that each set of four bright spots observed in the microstructure of isotropic carbon is caused by a Maltese-cross pattern within a growth feature. Operating in the tumbling bed without any bed particles, the substrate periodically experiences static-state and tumbling-state [9]. During the static-state, a columnar growth can occur and a growth cone is formed. Kaae [10] had already observed the growth cone from transmission electron microscopy of an isotropic pyrolytic carbon and suggested that carbon continues to be deposited on the gas-borne particle as long as access to the gas is not blocked by the deposition of the other particles even after the gas-borne particle is deposited on the substrate. Therefore it is expected that the deposition rate of isotropic carbon is proportional to the number of gas-borne nuclei existing in the gas phase, the amount of carbon source available for deposition as surface carbon in the gas phase, and the number of gas-borne particles colliding with the substrate which depends on the gas flow conditions around it.

0022–2461/85 $03.00 + .12

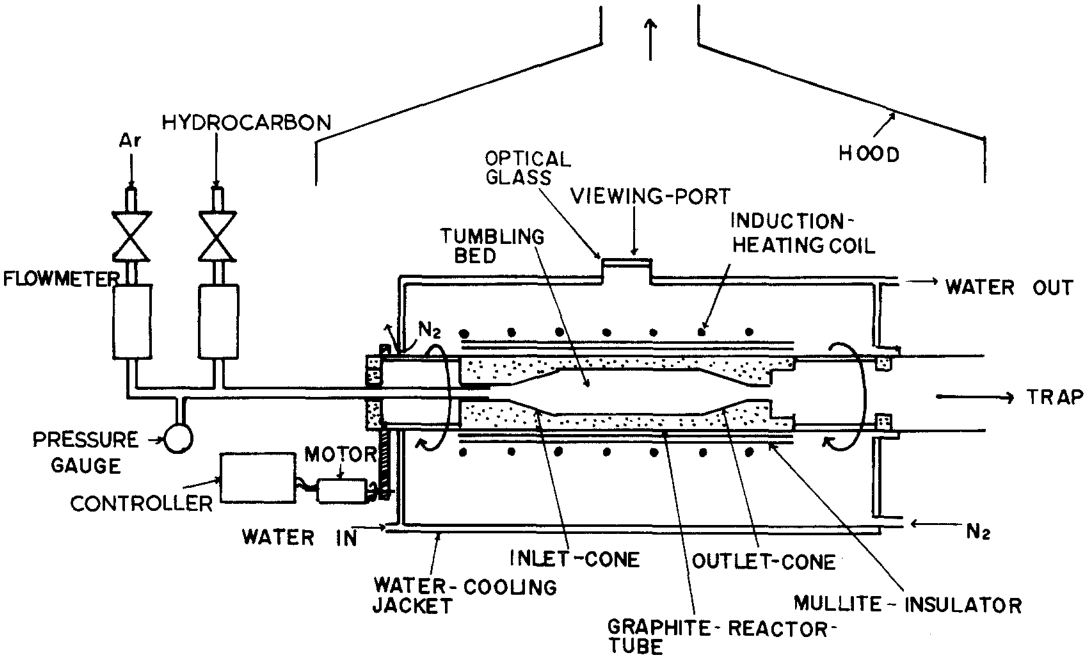

Figure 1 Schematic diagram of the coating apparatus.

3. Experiments

Fig. 1 is a schematic diagram of the tumbling bed apparatus [13, 14] used to deposit the pyrolytic carbon on the disc-shaped graphite substrates. The reaction tube was rotated by a variable-speed motor. The inside diameter of the reaction was 3 cm, the inlet and outlet cone angle was 15°, and the length of the hot zone was 5 cm. On the inner wall of the tumbling bed were imbedded 5 grooves, parallel with the tube axis, to promote the tumbling action of the substrate.

All deposits were made on a graphite disc of 18 mm in diameter and 2.54 mm in thickness. Propane was used as the carbon source in all experiments, with argon as the carrier gas. The total pressure was 760 torr and the total flow in all experiments was 1.4×10^3 cm^3 min^{-1}. The deposition temperature was varied from 1050 to 1200° C. The concentration of propane ranged from 10 to 70%. The bed surface area was varied by changing the amount of silica particles from 1.0 to 7.5 g. And the rotational speed of the reaction tube ranged from 10 to 100 rpm. The average deposition rate was determined by measuring the thickness of the deposit on the substrate and dividing by the total deposition time.

4. Comparison of proposed model with experimental results

The structure of the deposits obtained from propane in all experiments was the isotropic carbon [12].

4.1. Effect of the propane concentration on deposition rate of pyrolytic carbon

Fig. 2 shows the variation of the deposition rate of pyrolytic carbon with propane concentration at 40 rpm, no bed particles, and a temperature of 1150° C. The deposition rate increases linearly as the propane concentration increases. The amount of carbon source available for the deposition of pyrolytic carbon increases as propane concentration increases, promoting the deposition rate.

However, Lahaye and Prado [15, 16] showed that the number of gas-borne droplets formed depended only on the supersaturation and on temperature. At a given temperature, the supersaturation does not depend on the initial hydrocarbon concentration. Thus, the number of droplets formed must not vary with hydrocarbon concentration in the thermal decomposition system. Therefore, it is believed that the increase in the deposition rate, on increasing propane

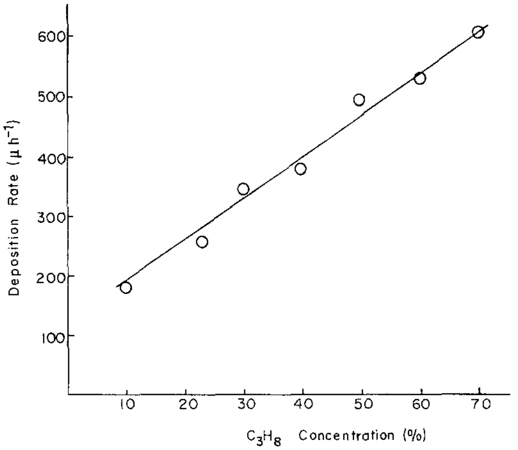

Figure 2 Effect of propane concentration on the deposition rate of pyrolytic carbon in a tumbling bed at a speed of rotation of 40 rpm, no bed particles, and a temperature of 1150° C.

concentration, is dependent of the number of gas-borne nuclei.

4.2. Effect of the deposition temperature on the deposition rate of pyrolytic carbon

Fig. 3 shows the variation of the deposition rate with deposition temperature at 40 rpm, a propane concentration of 23% and no bed particles. The deposition rate increases as the deposition temperature increases. As deposition temperature increases, the number of gas-borne nuclei increases [15, 16], increasing the deposition rate.

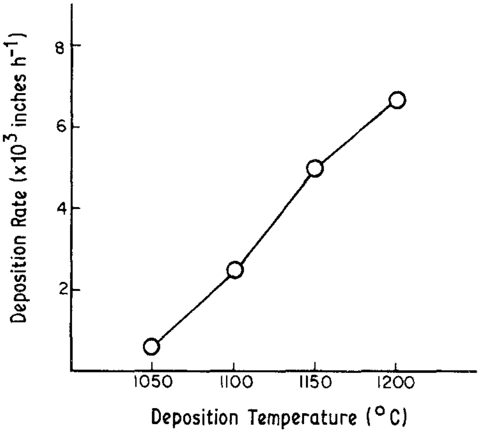

Figure 3 Effect of deposition temperature on the deposition rate of pyrolytic carbon in a tumbling bed at a speed of rotation of 40 rpm, a propane concentration of 23%, and no bed particles.

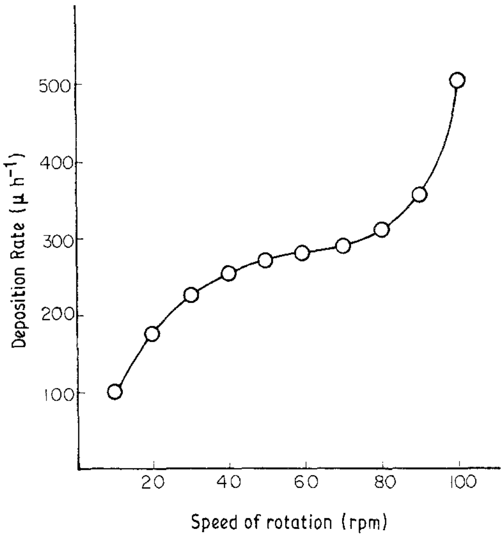

Figure 4 Effect of the speed of rotation of the reaction tube on the deposition rate of pyrolytic carbon in a tumbling bed at 1150° C, a propane concentration of 23%, and no bed particles.

4.3. Effect of the speed of rotation on the deposition rate of pyrolytic carbon

Fig. 4 shows the plot of the deposition rate of pyrolytic carbon as a function of the speed of rotation of reaction tube between 10 and 100 rpm at 1150° C, with a propane concentration of 23%, and no bed particles. The rate increases drastically with increasing speed up to 40 rpm and increases slowly between 40 and 80 rpm, and then again increases drastically above 80 rpm. The tumbling action of the substrate in a tumbling bed can produce gas-circulation on the rear part of the tumbling substrate. The change of tumbling speed makes the number of gas-borne particles colliding with the rear surface of the tumbling substrate change. During the deposition of pyrolytic carbon in a tumbling bed, the total tumbling number of a disc substrate can be expressed as follows:

$$\begin{aligned}&(\text{total tumbling number})\\&= 5\,tf(\text{speed of rotation})\end{aligned} \qquad (1)$$

where 5 represents the 5 grooves on the bed wall, t is the deposition time, and f is the tumbling factor. The tumbling number of the disc substrate per unit rotation of reactor in the tumbling bed having 5 grooves on the bed wall is 5. But as the speed of rotation increases, the actual tumbling number of the substrate per unit rotation decreases. Thus the tumbling factor, f, is defined as follows:

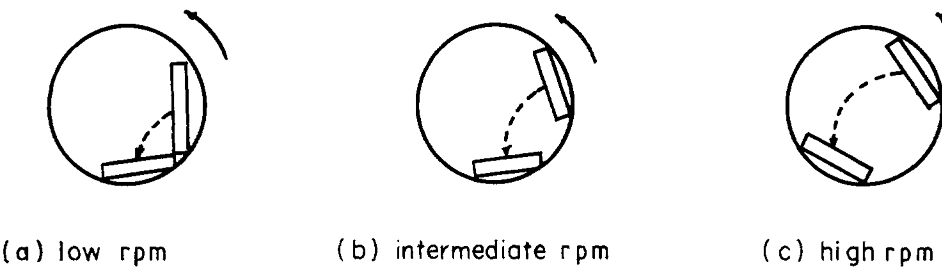

Figure 5 Variation in the movement of a tumbling disc substrate with increasing rotational speed of reaction tube.

$$\text{(the actual tumbling number of the substrate per unit rotation)} = 5f \quad (2)$$

As the speed of rotation increases, the total tumbling number of the substrate increases at a given deposition time according to Equation 1. Thus the number of gas-borne particles colliding with the substrate increases, increasing the deposition rate. The rate of increase of the deposition rate decreases with speed in the low speed range. This is due to the decrease of the tumbling factor with the increase in speed of rotation as shown in Fig. 5. Although the tumbling factor decreases with speed in the high speed range, the tumbling distance of the substrate is lengthened and the tumbling velocity of the substrate increases. These factors make the number of gas-borne particles colliding with the rear surface of the tumbling substrate increase, drastically increasing the deposition rate in the high rotational speed range.

4.4. Effect of the bed surface area on the deposition rate of pyrolytic carbon

Fig. 6 shows the variation of the deposition rate of pyrolytic carbon with bed particles at a speed of rotation of 40 rpm, a propane concentration of 23 %, and a temperature of 1150° C. Silica particles of 15 to 20 mesh were used as bed particles. As the number of bed particles increases, the surface area on which the pyrolytic carbon can be deposited increases. The rate of deposition decreases slowly with increasing bed particle weight up to 4.0 g, and then decreases drastically at above 4.0 g. In the case where bed particles are added during the deposition process of pyrolytic carbon in a tumbling bed, the bed surface area increases. Thus the deposition rate of isotropic carbon on the disc substrate decreases as the number of bed particles increases [12]. The drastic decrease in deposition rate above 4.0 g, is due to two factors; one is the decreased tumbling number of the substrate due to the hindering of the tumbling action by bed particles and the other is the decreased exposure time of the substrate to the gas phase because the substrate is surrounded by bed particles when a large number of bed particles are present. With a small number of bed particles these factors can be neglected; the decrease in the deposition rate with the amount of bed particles being due only to the increase of bed surface area.

The above experimental results show that the proposed model for the deposition rate of isotropic carbon is closely related to the deposition mechanism in which isotropic carbon is required for homogeneous nucleation and growth and for the recirculation of gas flow.

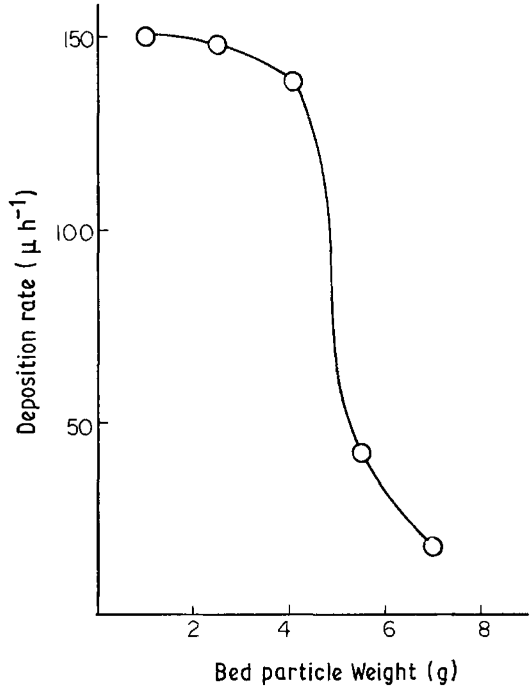

Figure 6 Effect of bed particle weight on the deposition rate of pyrolytic carbon in a tumbling bed at a speed of rotation of 40 rpm, a propane concentration of 23 % and a temperature of 1150° C.

5. Summary

The deposition rate of pyrolytic carbon is related to its deposition mechanism. The deposition rate of isotropic carbon can be explained by the factors suggested by the mechanism of Je and Lee [7–9]. The deposition rate increases with:

1. the increase in the number of gas-borne nuclei; i.e. the increase in the deposition temperature during the process,
2. the increase in the amount of carbon source available for deposition as surface carbon in the phase; i.e. the increase in hydrocarbon concentration and the decrease of bed surface area, and
3. the increase of the number of gas-borne particles colliding with the substrate which is dependent on the gas flow condition around it; i.e. the increase in the speed of rotation and the decrease of bed surface area during the process.

References

1. W. V. KOTLENSKY, in "Chemistry and Physics of Carbon" Vol. 9 edited by P. L. Walker Jr, (Marcel Dekker, New York, 1973) p. 174.
2. R. O. GRISDALE, A. C. PFISTER and W. VAN ROOSBROECK, *Bell System Tech. J.* **30** (1951) 271.
3. MARTIN C. HUGHES, JOSEPH P. COPELAND, RICHARD H. SINGLETON and KENNETH E. UNDERCOFFER, Vol. 1, Interim Report for Period Dec 1972–Jan 1974, AFRPL-TR-74-15.
4. R. L. R. LEFEVRE and M. S. T. PRICE, *Nucl. Techn.* **35** (1977) 263.
5. G. M. JENKINS, *Carbon* **15** (1977) 33.
6. J. C. BOKROS, *ibid.* **15** (1977) 355.
7. J. H. JE and J. Y. LEE, "A Study on the Deposition Mechanism of Pyrolytic Carbons from Hydrocarbons", *Carbon* (accepted).
8. *Idem.*, "A New Process of the Isotropic Pyrolytic Carbon Deposition", Proceedings of the 16th Biennial Conference on Carbon, University of California San Diego, July 18-22, 1983 p.455.
9. J. H. JE, "A Study on the Deposition Mechanism of Pyrolytic Carbons from Hydrocarbons", PhD Thesis, KAIST, Korea, 1983.
10. J. L. KAAE, *Carbon* **13** (1975) 55.
11. J. L. KAAE, T. D. GULDEN and S. LIANG, *ibid.* **10** (1972) 701.
12. J. Y. LEE, J. H. JE, W. S. RYU and H. J. KIM, *ibid.* **21** (1983) 523.
13. J. C. BOKROS, *ibid.* **3** (1965) 201.
14. J. LINKE, K. KOIZLIK and H. NICKEL, *Nucl. Techn.* **35** (1977) 257.
15. G. PRADO and J. LAHAYE, *J. Chim. Phys.* **70** (1973) 1678.
16. G. PRADO and J. LAHAYE, "Particulate Carbon Formation during Combustion" edited by Donald C. Seigla and George W. Smith (Plenum Publishing Corporation, New York 1981) p. 143.

Received 12 December 1983
and accepted 12 April 1984