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Improvement of Graphitization of Isotropic Carbon by Al_2O_3 Formed from Aluminium Chelate Compound

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Abstract

For improving the graphitization of isotropic carbon, ethyl acetoacetate aluminium diisopropoxide and aluminium oxide were used as catalysts. Their effect was investigated and the corresponding mechanism was discussed. The results showed that the isotropic carbon was graphitized greatly by the addition of ethyl acetoacetate aluminium diisopropoxide when the heat-treatment temperature was over 1850°C, and slightly by the addition of aluminium oxide at 1900°C. The mechanism is considered to be that the aluminium compound formed from ethyl acetoacetate aluminium diisopropoxide reacted with C to give Al_4C_3 *and with increasing temperature the* Al_4C_3 *decomposed to form Al(g) and* C_{Gr} *which was graphitized. Additionally, Al-containing gases and* $CO_2(g)$ *were the reactants of the reaction between aluminium oxide and C. This showed only a little effect on the graphitization of isotropic carbon when the heat-treating temperature was 1900°C. © 1999 Elsevier Science Ltd. All rights reserved*

Keywords: graphitization, microstructure-final, Al_2O_3, carbon, precursors-organic.

1 Introduction

For enhancing the graphitization of isotropic carbon, the processes of catalytic graphitization of the carbon have been extensively studied in recent years. As catalysts, metals such as Fe, Si, Ti, Ca, Mg and Al, and oxides such as Al_2O_3 and MgO were used[1–3]. The graphitization of the carbon was improved by using some catalysts, however, there were some problems in the processes. For example, (i) completed graphitization of carbon was not obtained, (ii) the degree of crystallization of graphitized carbon was lower and (iii) after the process of catalytic graphitization, the catalyst could not be removed from the graphitizited carbon. In other words, the effect of catalysts on the graphitization of isotropic carbon was not obvious, and the graphitizited carbon was contaminated as well.

In the present paper, a new method for the graphitization of isotropic carbon by using aluminium chelate compound is presented and the corresponding catalystic mechanism is discussed briefly.

2 Experimental Procedure

The raw materials used in the present study were liquid phenolic resin (fixed carbon: about 50%), ethyl acetoacetate aluminium diisopropoxide (hereafter referred to as ALCH, Al_2O_3 content: 18·6 mass%) and aluminium oxide (purity: 99·9%).

The phenolic resin was mixed with various amounts of ALCH (ALCH was pre-diluted with ethanol) and aluminium oxide to form resin/ALCH and resin/aluminium oxide admixture. The admixtures were dried at 110°C for 12 h and then carbonized at 600°C in Ar atmosphere for 1 h. The obtained isotropic carbons with and without Al-containing catalyst were heated at 1800, 1850 and 1900°C for 2 h in a flowing Ar atmosphere at a rate of 0·4 l/min.

The Al-containing catalyst formed after carbonization was investigated by X-ray diffraction (XRD) and infrared spectroscopy (IR). The samples after heat-treatment were observed by scanning electron microscopy (SEM) and analyzed by X-ray diffraction. The Al content in the samples was analyzed by ICP.

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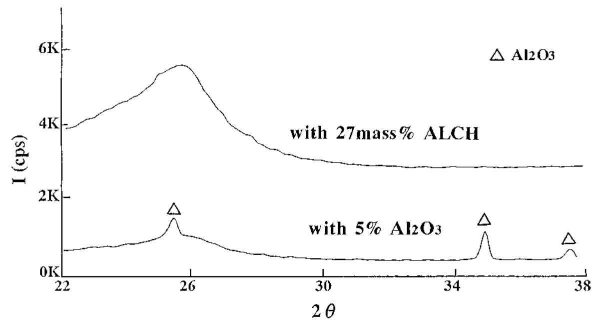

Fig. 1. X-ray diffraction patterns of the samples obtained by carbonizing the admixtures of resin/ALCH and resin/aluminium oxide at 600°C.

3 Results

3.1 Al-containing catalyst formed after carbonization

Figure 1 shows the X-ray diffraction patterns of the samples obtained from carbonizing the admixtures of phenolic resin/ALCH and phenolic resin/aluminium oxide at 600°C. The Al-containing catalyst in the sample with aluminium oxide addition was identified to be Al_2O_3, which did not change in the carbonization. However, any crystalline phase was not found in the sample with ALCH addition.

Figure 2 shows the infrared spectra patterns of the samples obtained from carbonizing the admixtures of phenolic resin/ALCH and phenolic resin/aluminium oxide at 600°C. Compared with the infrared spectra pattern of the sample with aluminium oxide addition, which showed Al–O bounds in the range about 1000–450 cm^{-1}, the difference was observed in the infrared spectra pattern of the sample with ALCH addition, in which Al–O bound was not found.

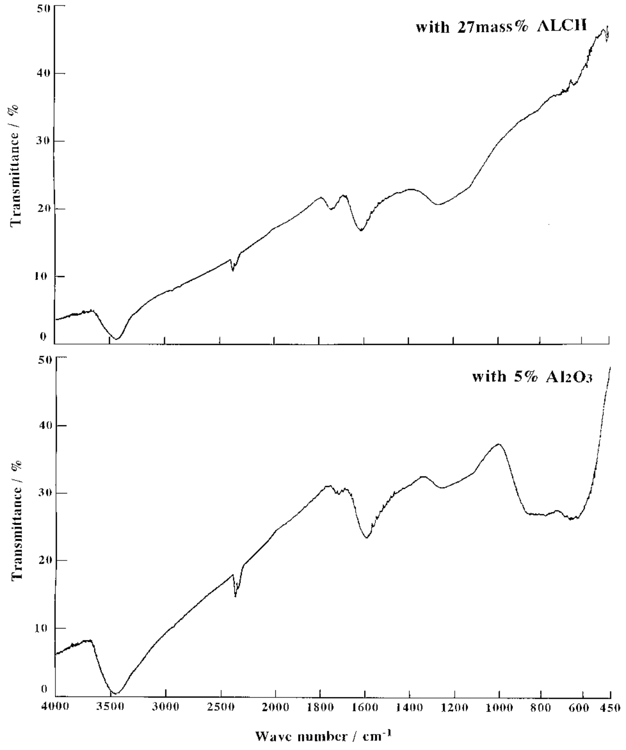

Fig. 2. IR spectra of the samples obtained by carbonizing the admixtures of resin/ALCH and resin/aluminium oxide at 600°C.

3.2 Effect of heat-treating temperature on the graphitization of the carbon

Figure 3 shows the X-ray diffraction patterns of the samples obtained from different admixtures and heated at various temperatures. With increasing the temperature, the intensity of the (002) diffraction peak of the carbon without addition increased a little and the peak shifted to a higher angle gradually [Fig. 3(a)]. However, with the addition of ALCH, the intensity of the (002) diffraction peak of the carbon increased obviously when heat-treating temperature was above 1800°C, and the peak shifted towards $2\theta = 26{\cdot}5°$ and at 1900°C 2θ was 26·48° [Fig. 3(b)]. Figure 3(c) shows X-ray diffraction patterns of the samples with aluminium oxide powder. Compared with the result without addition, there were no changes in the intensity and angle of the (002) diffraction peak of the carbon when the heat-treating temperature was below 1850°C. However, at 1900°C the intensity

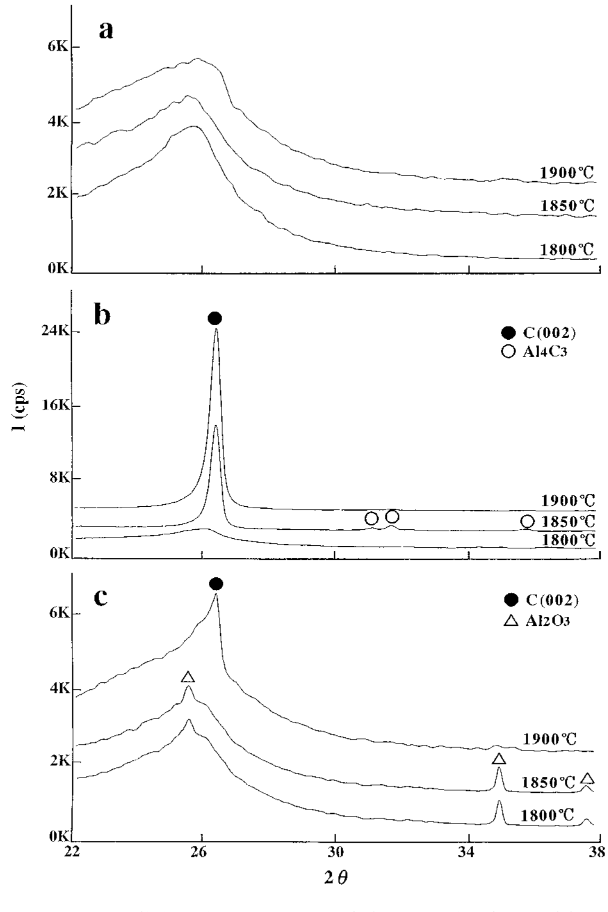

Fig. 3. X-ray diffraction patterns of the samples formed by (a) carbonization of resin, (b) resin/ALCH and (c) resin/aluminium oxide after heat-treating at 1800, 1850 and 1900°C for 2 h, respectively (a: without Al_2O_3 addition; b: with 27 mass% ALCH; c: with 5 mass% aluminium oxide).

was increased and the peak shifted to $2\theta = 26{\cdot}5°$. The variation of d_{002} values of the different carbons obtained with temperatures is illustrated in Fig. 4. The graphitization process of the carbon was accelerated greatly with the addition of ALCH and the d_{002} value of the carbon was close to 0·3354 nm at 1900°C.

In addition, the phases also changed with heat-treating temperatures and the Al-resource. Al_2O_3 phase was not confirmed in the samples added with ALCH after heat-treated at a temperature up to 1800°C. However, Al_4C_3 phase was observed at 1850°C, but decreased with increasing temperatures and disappeared at 1900°C. Al_2O_3 phase was observed in the sample when aluminium oxide powder was added. However, the peaks of Al_2O_3 decreased with increasing temperatures and disappeared at 1900°C.

3.3 Effect of the amount of ALCH addition on the graphitization of carbon

Figure 5 shows X-ray diffraction patterns of samples with various ALCH addition after carbonized at 600°C, and then heat-treated at 1900°C for 2 h. With increasing amount of ALCH, the intensity of the (002) diffraction peak of carbon increased and the peak shifted to 26.5°. When the amount of ALCH was 27 mass%, the 2θ was equal to 26·48°.

3.4 Change in microstructure of the carbon

Figure 6 shows SEM micrographs of the samples heat-treated at 1900°C for 2 h. The graphitized carbon was not observed in the sample without addition, while a small amount of carbon was graphitized in the sample added with 5 mass% aluminium oxide.

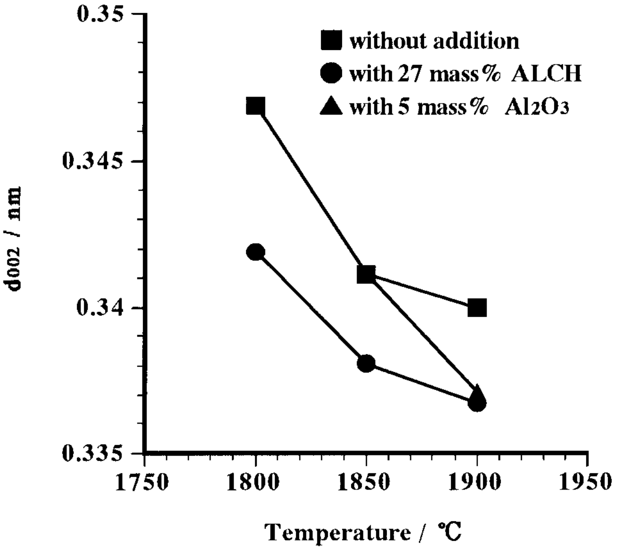

Fig. 4. Changes of interlayer spacing (d_{002}) with heat-treatment temperatures.

Figure 7 shows SEM micrographs of the sample with 27 mass% ALCH after carbonized at 600°C and then heat-treated at 1800, 1850 and 1900°C for 2 h, respectively. At 1800°C, the graphitized carbon was not observed and the microstructure of the carbon was nearly the same as that of the carbon without addition (Fig. 6). However, when heat-treating at 1850 and 1900°C, the carbon was graphitized completely, and the size of the carbon graphitized at 1900°C was larger than that of at 1850°C.

Figure 8 shows SEM micrographs of the samples with 2·7, 8·1 and 13·5 mass% ALCH after carbonized 600°C, and then heat-treated at 1900°C. Compared with the carbon without addition (Fig. 6), the shape of carbon was developed with the ALCH addition, and with increasing the amount of the ALCH, the flake shape became obvious and clear. When the amount of the ALCH was 13·5 mass%, the graphitized carbon was observed.

3.5 Al content of the samples after heat-treatment

Figure 9 shows Al content of the samples heat-treated at 1800, 1850 and 1900°C, respectively. With increasing the heating temperature, Al content in the samples added with ALCH and aluminium oxide decreased and approached to zero at 1900°C.

4 Discussion

From the results as stated above, it was clear that the graphitization of isotropic carbon depended on the type of Al-containing catalyst. This might be attributed to the reaction between the Al-containing catalyst and C.

After carbonization of the phenolic resin/ALCH and phenolic resin/aluminium oxide admixture, Al_2O_3 was not change in the sample with aluminium oxide addition, however aluminium compound formed in the sample with ALCH addition was not determined to be any Al-containing compound by X-ray diffraction and infrared spectra investigation. When heating the samples

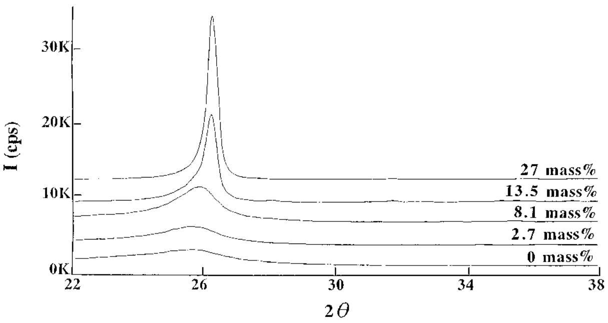

Fig. 5. X-ray diffraction patterns of the samples with 0–27 mass% ALCH after carbonized at 600°C and then heat-treated at 1900°C for 2 h.

obtained from the carbonization of phenolic resin/ALCH and phenolic resin/aluminium oxide at high temperature, reaction between the Al-containing catalyst and isotropic C is supposed to occur and affect the graphitization of the carbon.

In the case of with aluminium compound formed from ALCH, the Al_4C_3 phase formed when heated at 1850°C (Fig. 3). The Al_4C_3 phase might be considered to form according to the eqn (1).

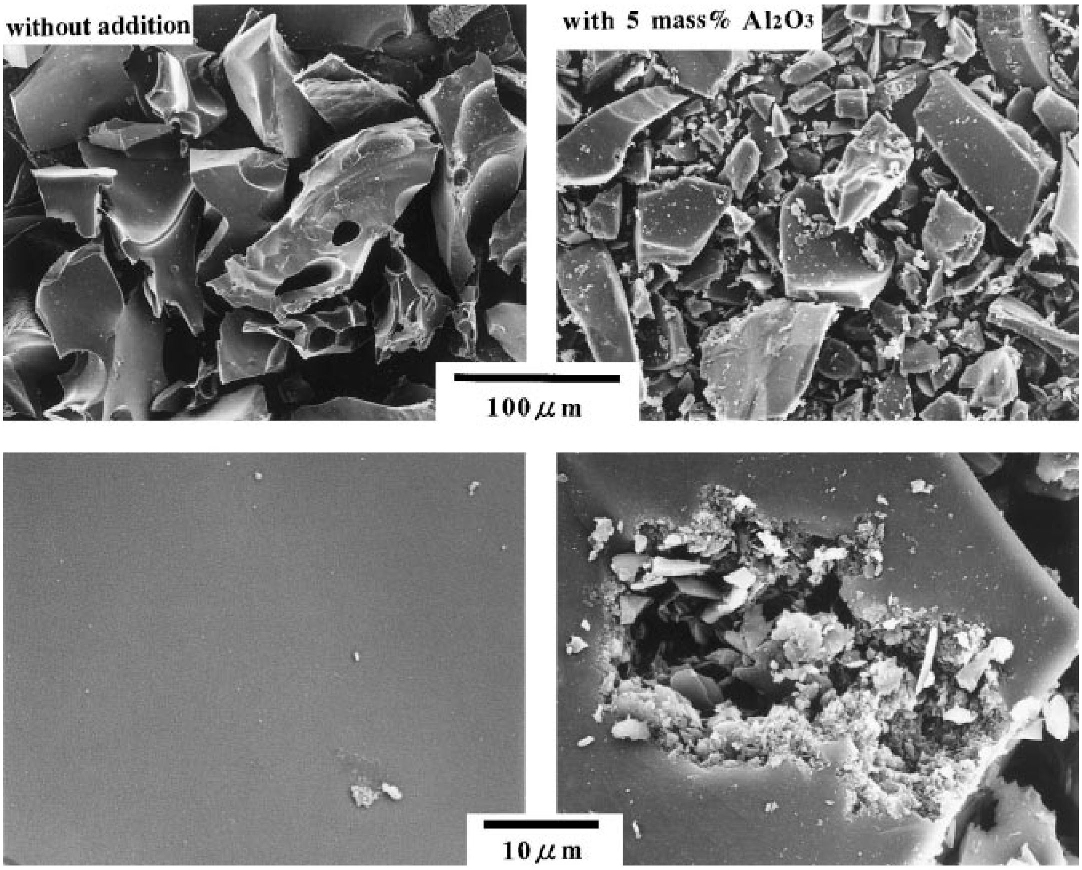

Fig. 6. SEM micrographs of the samples without addition and with 5 mass% aluminium oxide after carbonized at 600°C and then heat-treated at 1900°C for 2 h.

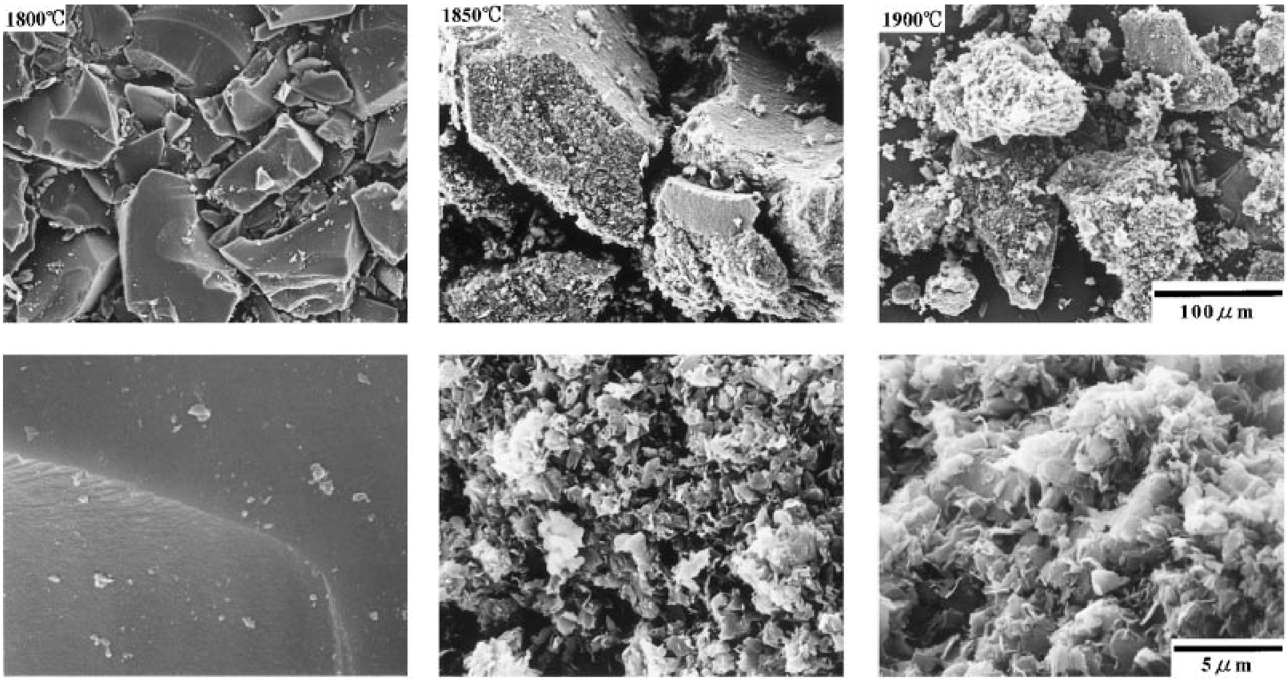

Fig. 7. SEM micrographs of the sample with 27 mass% ALCH after carbonized at 600°C and then heat-treated at 1800, 1850 and 1900°C for 2 h, respectively.

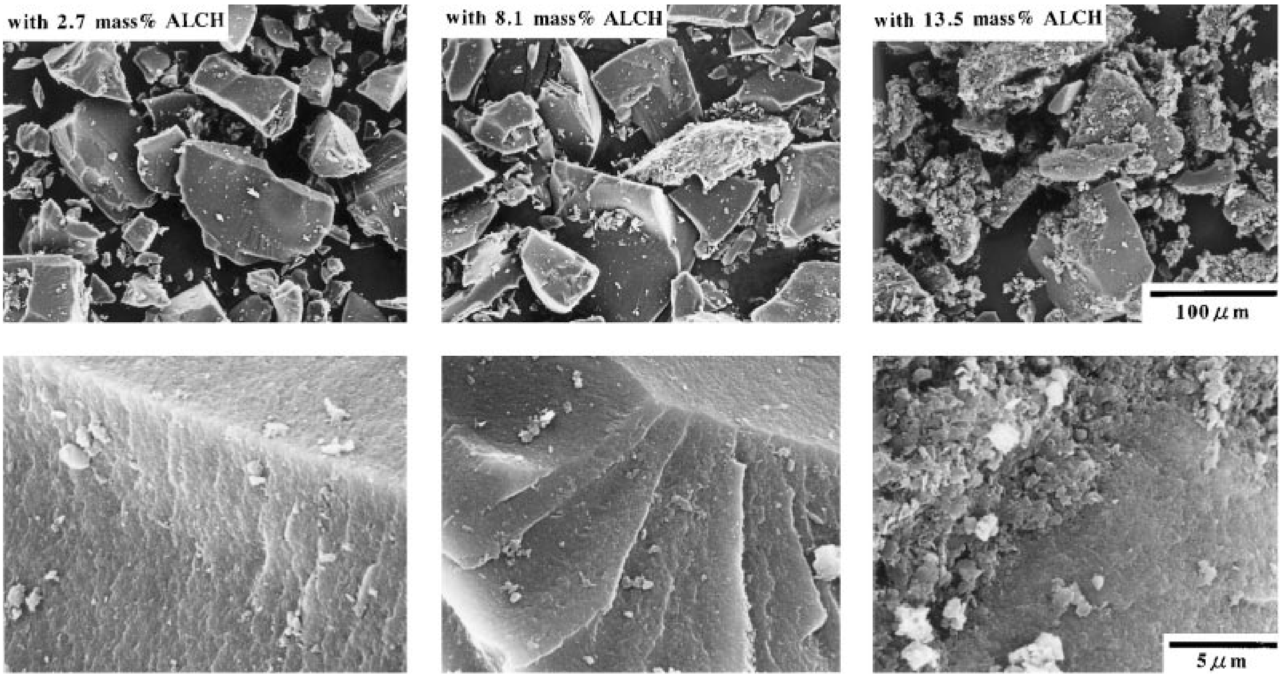

Fig. 8. SEM micrographs of the samples with 2·7, 8·1 and 13·5 mass% ALCH after carbonized at 600°C and then heat-treated at 1900°C for 2 h.

$$\begin{aligned}&\text{Aluminium compound(s)} + \text{C(s)}\\ &\qquad \rightarrow \text{Al}_4\text{C}_3\text{(s)} + \text{CO(g)}\end{aligned} \tag{1}$$

When the temperature increased further to 1900°C, this Al_4C_3 phase became thermodynamically unstable, the decomposition reaction occurred and formed Al(g) and C(s) as shown in the following equation.

$$\text{Al}_4\text{C}_3\text{(s)} = 4\text{Al(g)} + 3\text{C}_{\text{Gr}}\text{(s)} \tag{2}$$

According to Ref. 4, the carbon obtained from the above decomposition reaction should be graphitized. The Al(g) decomposed by the reaction (2) vaporized out from the sample and hardly remained in the sample.

In the case of aluminium oxide addition, according to thermodynamic data,[5] Al_4C_3 is a stable equibrium phase at relatively high temperature under a lower CO(g) partial pressure in the Al–O–C system as shown in Fig. 10. Because the samples were heat-treated in a flowing Ar atmosphere, the partial pressure of CO(g) inside the furnace was much lower and close to 10^{-6} atm according to calculation.[6] When the temperature was over 1600°C, the Al_4C_3 should form according to reaction (3).

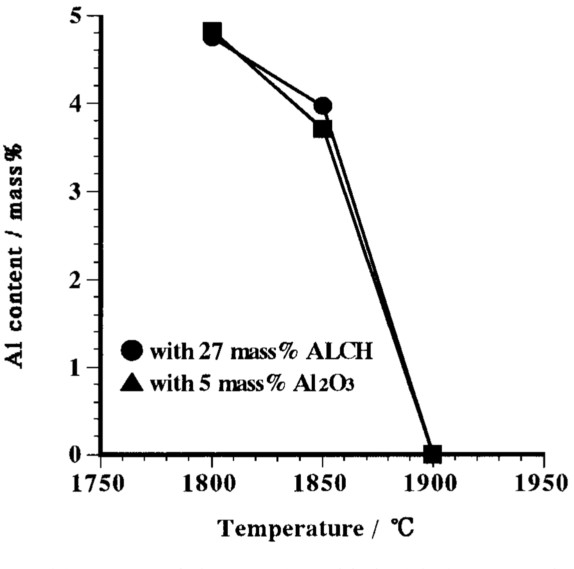

Fig. 9. Al content of the samples added with ALCH and aluminium oxide after carbonized at 600°C, and then heat-treated at 1800, 1850 and 1900°C for 2 h, respectively.

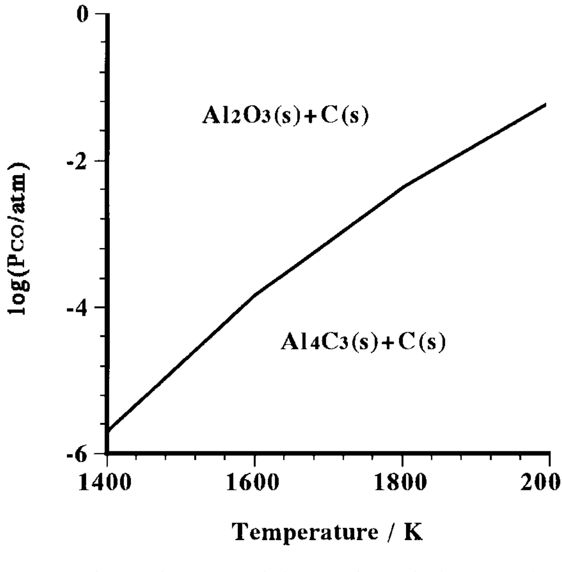

Fig. 10. Stability domains of the condensed phases in Al–O–C system.

$$2Al_2O_3(s) + 9C(s) = Al_4C_3(s) + 6CO(g) \qquad (3)$$

However, Al_4C_3 phase was not found in the sample. It suggest that reaction (3) occurred to limited extend, because the Al_2O_3 and C particles were separated from each other by an Al_4C_3 layer. The direct reaction between Al_2O_3 and C is hindered, so as a result the following reactions need to be considered.

$$C(s) + CO_2(g) = 2CO(g) \qquad (4)$$

$$Al_2O_3(s) + 2CO(g) = Al_2O(g) + 2CO_2(g) \qquad (5)$$

$$2Al_2O_3(s) + 6CO(g) = 4Al(g) + 6CO_2(g) \qquad (6)$$

$$Al_2O_3(s) + CO(g) = 2AlO(g) + CO_2(g) \qquad (7)$$

Because the partial pressures of $Al_2O(g)$, Al(g) and AlO(g) gas are rather high in the Al–O–C system,[5] the remaining alumina probably decomposed and was flushed by the argon flow.

From the experimental result (Fig. 3), it is clearly shown that the graphitization of the carbon added with aluminium oxide was improved a little when heated at 1900°C, although the graphitization was not as good as in the sample with ALCH. It might be considered that the $CO_2(g)$ formed by the reactions (5)–(7) affected the homogeneous graphitization of carbon.[4]

5 Conclusions

The effects of Al-containing catalyst added in the form of ALCH and aluminium oxide were investigated in detail, the conclusions are as follows:

1. Isotropic carbon was graphitized greatly by aluminium compound formed from aluminium chelate compound and the graphitization of the carbon was considered to be by the formation and decomposition of Al_4C_3 phase in heating.
2. When heat-treating the samples with aluminium compound formed from aluminium chelate compound over 1850°C, the d_{002} value of the graphitizated carbon was close to 0·3354 nm.
3. Isotropic carbon was graphitized slightly with addition of aluminium oxide when the heat-treating temperature was 1900°C, and the graphitization of the carbon was affected by the existence of $CO_2(g)$ formed by reactions between Al_2O_3 and C.

References

1. Oya, A., Yamashita, R. and Otani, S., Catalytic graphitization of carbons by gaseous species formed from various metals. *High Temp.-High Press.*, 1978, **10**, 511–520.
2. Oya, A., Yamazaki, T. and Otani, S., Catalytic graphitization of charcoal by gaseous species formed from calcium. *High Temp.-High Press.*, 1978, **10**, 521–526.
3. Yu, J. K. and Yamaguchi, A., Crystallization and oxidation behavior of carbon from phenolic resin in MgO-C and Al_2O_3-C refractories. *J. Ceram. Soc. Japan*, 1995, **103**, 274–277.
4. Oya, A. and March, H., Phenomena of catalytic graphitization. *J. Mater. Sci.*, 1982, **17**, 309–322.
5. Chase Jr, M. W., Davies, C. A., Downey Jr, J. R., Frurip, D. J., McDonald, R. A. and Syverud, A. N., JANAF Thermochemical Tables, 3rd edn. American Chemical Society and the American Institute of Physics for the National Bureau of Standards, Midland, MI, 1985.
6. Yu, J. K. and Ueno, S., Synthesis of β-sialon whiskers from pyrophyllite. *J. Ceram. Soc. Japan*, 1997, **105**, 821–823.