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Exfoliation of Graphite via Residue Compounds with Sulfuric Acid

硫酸残留化合物を経由する黒鉛の膨張化

Michio INAGAKI*, Ryuichi TASHIRO* and Taisuke SUWA*

稲垣道夫，田代隆一，諏訪泰亮

Abstract Exfoliation of graphite via its residue compounds with sulfuric acid was followed by measuring the bulk density of resultant exfoliated graphite and analyzing the pore structure inside of the worm-like particles. Rapid heating above 800 °C gave the exfoliated graphite with the bulk density as low as 7-10 kg/m^3, which corresponds to become the volume roughly 300 times larger, and with the average cross-sectional area and sizes of inside pores of 320 μm^2 and 31 x 11 μm^2, respectively.

1. Introduction

Exfoliated graphite is an important industrial raw material for flexible graphite sheets which are widely used as gaskets, seals and packings, because it is flexible, compactable, resilient and possible to form into a various shapes, in addition to the fundamental properties of graphite; lubricious, chemically inert, electrically and thermally conductive, and resistant to heat and corrosion [1,2]. It is produced by rapid heating of residue compounds of natural graphite flakes with sulfuric acid, which are prepared through intercalation compounds, to about 1000 °C. It consists of fragile worm-like particles formed by exfoliation preferentially along the normal to the basal plane of graphite.

Recently, it attracted our attention because of its very high sorption capacity of spilled heavy oils and easy recovery [3-15] and also of biological proteins and body fluids [16]. These new applications, which are using pores formed in exfoliated graphite, promoted detailed studies on its pore structure; pore structure analysis inside of worm-like particles using image processing [17], clivages on the surface of worm-like particles [18], careful mercury porosimetry to evaluate the large pores among particles [19], together with the measurement of bulk density or exfoliation volume as a function of preparation conditions [18, 20].

In the present work, exfoliation process was revisited to determine the exfoliation condition more exactly by combining the measurement of bulk density of exfoliated graphite to the pore structure analysis with image processing.

* 愛知工業大学　工学部　応用化学科

2. Experimental

Two kinds of raw materials A and B, residue compounds of natural graphite with sulfuric acid, were the ones used in industrial production of exfoliated graphite. They had a little different contents of volatile matters measured at 1000 °C. Residue compounds of about 0.10 g was placed at the bottom of ceramic crucible and then inserted into the furnace where the temperature was kept constant. After 1 minute, the crucible was pulled out from the furnace and cooled down to room temperature. The exfoliated graphite thus obtained was transferred into a glass cylinder in order to measure its volume and then its bulk density.

Representative SEM micrograph of exfoliated graphite prepared at 1000 °C was shown in Fig. 1a), showing worm-like particles.

By selecting three exfoliated graphite samples which had been prepared at 600, 800 and 1000 °C, pore structure inside the worm-like particles was determined by image processing, according to the same procedure as reported before [17], except that the image was converted to binary one through tracing the pore walls by hand after recording the SEM image on fractured cross-section of the particles by a scanner with the resolution of 600 dpi. SEM micrographs on fractured cross-sections were observed with an acceleration voltage of 10 kV and the magnification of 200 times. In Fig. 1b), an example of fractured cross-section of the particle is shown.

3. Experimental Results

3.1. Bulk density of exfoliation graphite

In Fig. 2, bulk density in logarithmic scale is plot-

ted against exfoliation temperature on two runs of experiments on residue compounds A and on another B.

With increasing exfoliation temperature, bulk density decreases rapidly. After exfoliation at 1000 °C, bulk density of the resultant exfoliated graphite is about 7 kg/m^3, which is almost the same as commercially available ones. Two experimental runs for residue compounds A give almost the same bulk density dependence on exfoliation temperature. Residue compounds B also gave the same dependence.

3.2. Pore structure inside of the particles

In Fig. 3a) to e), cross-sectional area and its cumulative curve, lengths along the major and minor axes, and aspect ratio of pores observed in the cross-sections of worm-like particles, respectively, are shown in histograms. Also averaged values of these pore parameters are listed in Table 1, together with the number of pores used and also with fractal dimension calculated.

From the histograms on pore parameters (area, major and minor axis, and aspect ratio) and cumulative frequency curves of pore area, pore structures in the worm-like particles of 600°C- and 800 °C-exfoliated samples were difficult to differentiate, only slight shifts of these maxima, though their bulk density decreases markedly from 40 to less than 10 kg/m^3. On the other hand, exfoliated graphite prepared at 1000 °C has broadened histograms of each pore parameters and much larger average pore parameters, larger lengths of major and minor axes, and consequently larger area, than those prepared at low temperatures, though change in bulk density from 800 to 1000 °C is not so pronounced.

Fractal dimension calculated from periphery of the pores is very close to 1.00, revealing the smooth pore walls in worm-like particles of exfoliated graphite. This is reasonable because exfoliated graphite was prepared from natural graphite flakes.

4. Discussion

The present results on the dependence of bulk density of the resultant exfoliated graphite on exfoliation temperature show that for complete exfoliation of graphite flakes rapid heating up to 1000°C is required. Although bulk density, in other words, exfoliation volume, is an important parameter to characterize exfoliated graphite, its pore structure inside the worm-like particles has also to be defined. Two samples exfoliated at 600 and 800 °C have similar pore parameters, similar distributions in cross-sectional area and lengths along the major and minor axes and also similar averaged values of these parameters, though bulk density values are quite different from each other. On the other hand, the 1000°C-exfoliated sample has quite different pore parameters from the 800°C-exfoliated one, though bulk densities for these two samples showed only a slight difference.

The present results suggest the following exfoliation process. In the beginning of exfoliation the spaces among the particles increase markedly mainly due to the exfoliation of graphite flakes and complicated entanglement among the resultant worm-like particles, which is suggested by similar pore structure but quite different bulk density (*i.e.* exfoliation volume) between 600°C- and 800°C-exfoliated graphite. The last step of exfoliation is the development of pores in worm-like particles, because the increase in exfoliation temperature from 800 °C to 1000 °C causes only the growth of pores, increases in cross-sectional area and the lengths along the major and minor axes, but no pronounced decrease in bulk density (*i.e.* increase in exfoliation volume).

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References

1. D. D. L. Chung: *J.Mater.Sci.*, 22, 4190-4198, 1987.
2. G. Furdin: *Fuel*, 77, 475-485, 1998.
3. M. Toyoda, J. Aizawa, and M. Inagaki, *Desalination,* **115,**199-201, 1998,.
4. M. Toyoda, J. Aizawa, and M. Inagaki, *Nihon Kagaku Kaishi* **1998**. 563-565, 1998.
5. M. Toyoda, K. Moriya, J. Aizawa, and M. Inagaki, *Nihon Kagaku Kaishi,* **1999**, 193-198, 1999.
6. M. Toyoda, K. Moriya, and M. Inagaki, *TANSO,* **1999** [No.187], 96-100, 1999.
7. M. Toyoda, K. Moriya, and M. Inagaki, *Nihon Kagaku Kaishi* **2000** [No.3], 217-220, 2000.
8. M. Toyoda, K. Moriya, J. Aizawa, H. Konno, M. Inagaki, *Desalination,* **128**, 205-211, 2000.
9. M. Inagaki, H. Konno, M. Toyoda, K. Moriya, and T. Kihara, T.; *Desalination,* **128**, 213-218, 2000.
10. M. Inagaki, K. Shibata, S. Setou, M. Toyoda, J. Aizawa,*Desalination,* **128**, 219-222, 2000.
11. M. Toyoda, and M. Inagaki, *Carbon,* **38**, 199-210,

2000,.
12. M. Toyoda, K. Moriya, and M. Inagaki, *Sekiyu Gakkai Shi,* **44**, 169-172, 2001.
13. M. Inagaki, M. Toyoda, and Y. Nishi, *Kagaku Kougaku,* **64**(4), 179-182, 2001.
14. M. Inagaki, M. Toyoda, N. Iwashita, and Y. Nishi, H. Konno, *Carbon Science, Korea,* **2**, 1-8, 2001.
15. 稲垣道夫; 豊田昌宏; 岩下哲雄; 西陽子; 金野英隆; 藤田淳; 木原勉; *炭素*, **2002**(No.201), 16-25, 2002.
16. W. E. Shen, S. Z. Wen, N. Z. Cao, L. Zheng, W. Zhou, Y. G. Liu, and J. L. Gu, *Carbon,* **37**, 351-358, 1999,.
17. M. Inagaki, and T. Suwa, T.; *Carbon,* **39**, 915-920, 2001.
18. F. Y. Kang, Y. Leng, T. Y. Zhang, and M. Inagaki, *Carbon* (in press).
19. 西陽子，岩下哲雄，澤田吉裕，稲垣道夫，*炭素*, **2002**(No.201), 31-34,2002.
20. B. Tryba, R. J. Kalenczuk, F. Y. Kang, M. Inagaki, and A.W. Morawski, *Mol. Cryst. Liq. Cryst.*, **340**, 113-119, 2000.

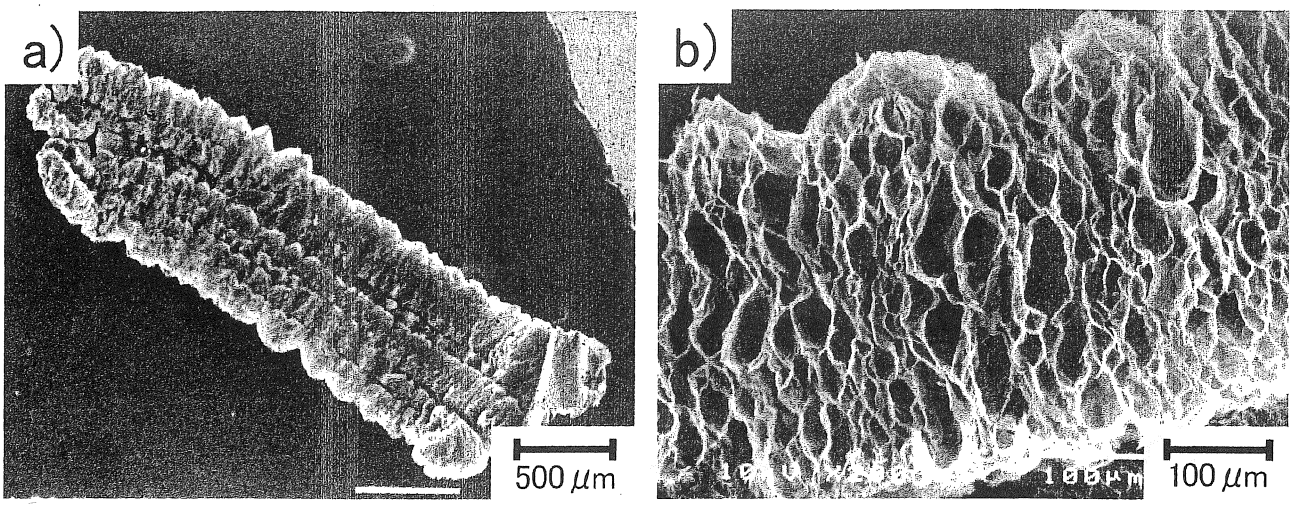

Fig. 1 SEM micrographs of worm-like particle of exfoliated graphite.
a) Appearance and b) its fractured cross-section.

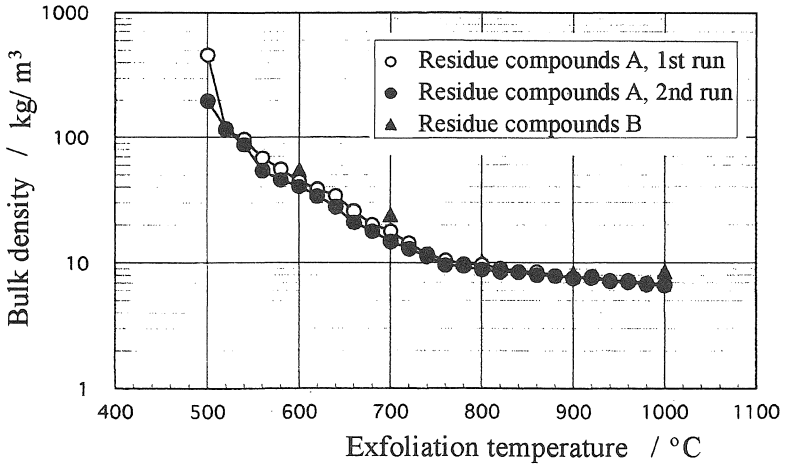

Fig. 2 Changes in bulk density of exfoliated graphite with exfoliation temperature.

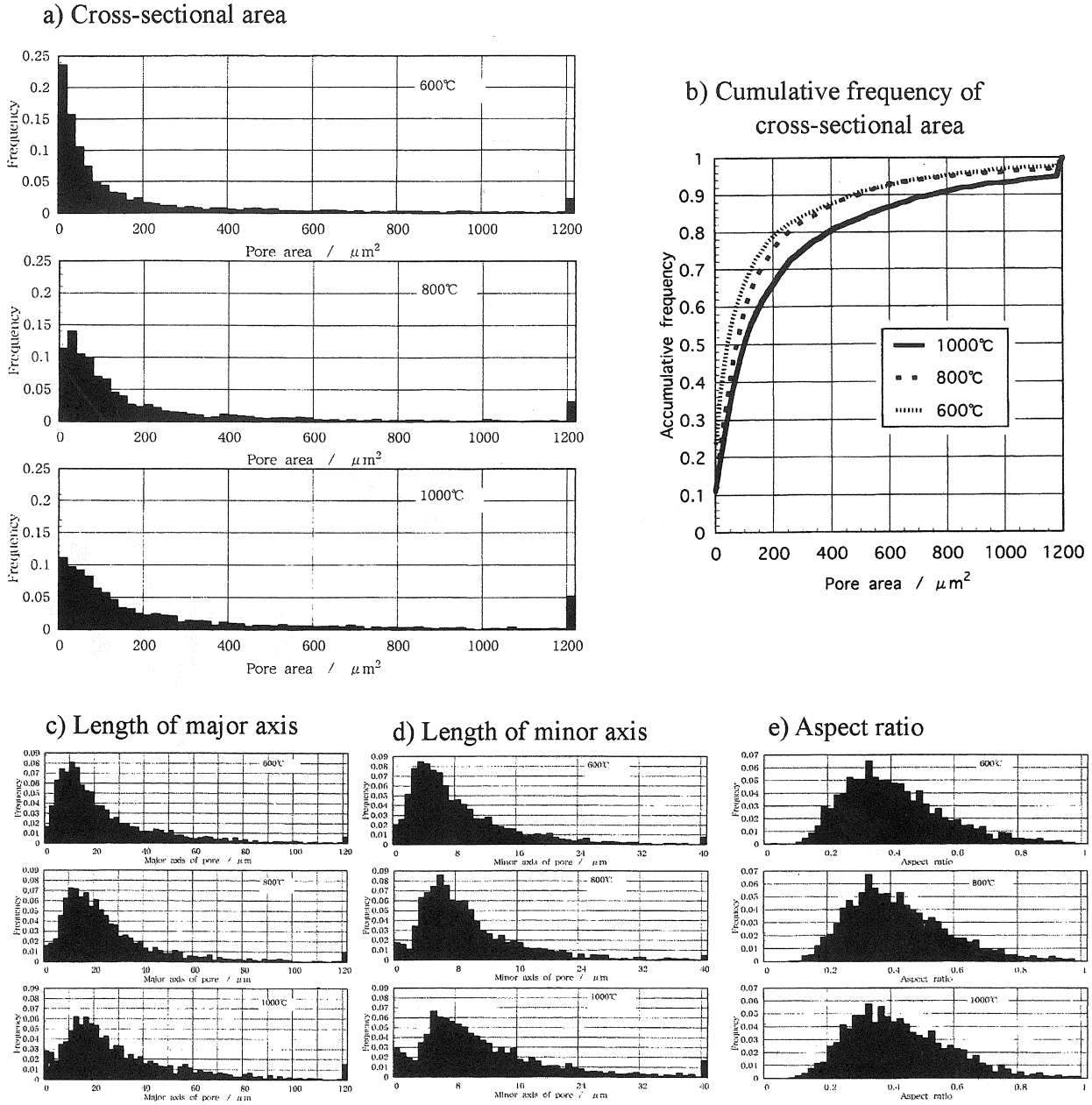

Fig. 3 Distribution histograms for parameters of pores inside of worm-like particles.

Table 1 Averaged values of pore parameters for exfoliated graphite prepared at different temperatures from the raw materials A

Exfoliation temperature		600 °C	800 °C	1000 °C
Bulk desity (kg/m^3)		40.3	8.8	6.6
Number of pores used		2583	2161	2059
Averaged pore parameters	Area (μm^2)	193	217	321
	Major axis (μm)	24.4	26.0	31.2
	Minor axis (μm)	8.8	9.7	11.2
	Aspect ratio	0.412	0.424	0.412
	Fractal dimension	1.09	1.10	1.09

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