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CHEMICAL AND LOW-EXPANSION TREATMENTS FOR PURIFYING NATURAL GRAPHITE POWDER

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Fine natural graphite powder shows good properties in heat resistance, heat expansion and electric conductivity, and has been used as the materials for high-efficient secondary batteries, lubrication, etc. Graphite powder, as a high-tech material, is made through purifying and surface control processes. Developed countries produce high functional graphite powders by additional intercalation processes and sub-micronizing. This study is conducted to utilize low grade natural graphite powders as nano-material resources. Prior to production of the ultrafine graphite powder, studies on its pretreatments were performed. Typical acid/alkali treatments with expansion process were conducted. Expanding temperature for gasification process is set low compared to those of the traditional processes. This will make possible to give appropriate expansion ratio for effective chemical treatments and grinding processes. Expansion ratios were controlled as 20~30% of the original volume at 200~250 °C, since excessive expansion of graphite powder by traditional approach at high temperature leads to a low grinding efficiency.

Key words: graphite, purification, chemical treatment

INTRODUCTION

There are many methods of purification of graphite powders (KORES, 2007; Kim, 2001). Most of them involve acid or alkali treatments while several involve either expansion processes or physical treatments. There are many studies on the expansion of graphite powder at high temperatures under conventional expansion conditions (Lee, 2000; Jung et al., 1991). This could help purify graphite (Bouvard et al., 1988), but it does not help grind the powder. Graphite expanded at high temperatures has very low bulk density, indicating very large volume. Therefore, this is regarded as an inappropriate process for grinding the powder.

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The final objective of this study is to produce raw materials for making nano-sized graphite powder of high purity. In the literature, some experiments were conducted to determine the expansion conditions appropriate for removing impurities from the powder while maintaining or improving grinding characteristics of graphite powder (Bouvard et al., 1988).

EXPERIMENTAL

Figure 1 shows the graphite powders expand at high temperatures. As one can see in the pictures, the expanded graphite has string-like shape, expanding along c-axis. The SEM image shows the graphite powder expanded in a cluster range. It means that the expanded graphite powders could be ground effectively in cluster range compared to natural powders. Figure 2 provides the XRD patterns showing the changes in crystallinity of the expanded graphite powder. The graphite powders show different crystallinities, and various graphite samples having different crystallinities could be produced by the expanding procedure. The difference in crystallinity may affect the purifying property or grinding characteristics of the graphite powder.

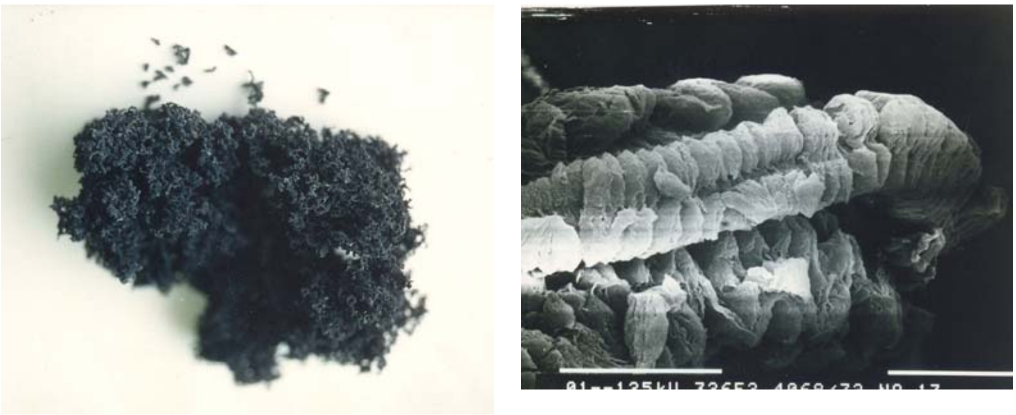


Fig. 1. Photos of expanded graphite powders: (a) optical image, (b) SEM image (x1,000)

In all experiments, two different sizes of graphite powder were used. One is the natural flake-shape graphite powder having a size ranging from 150 to 300 μm and a 90% fixed carbon content. This was used as the sample for preliminary tests to determine optimum expanding conditions. The other is also natural flake-shape graphite powder having an size of under -45 μm (average size of about 20 μm) and 85% fixed carbon. The latter was used in the main tests for purification with acid and alkali reagents and expansion by gasification.

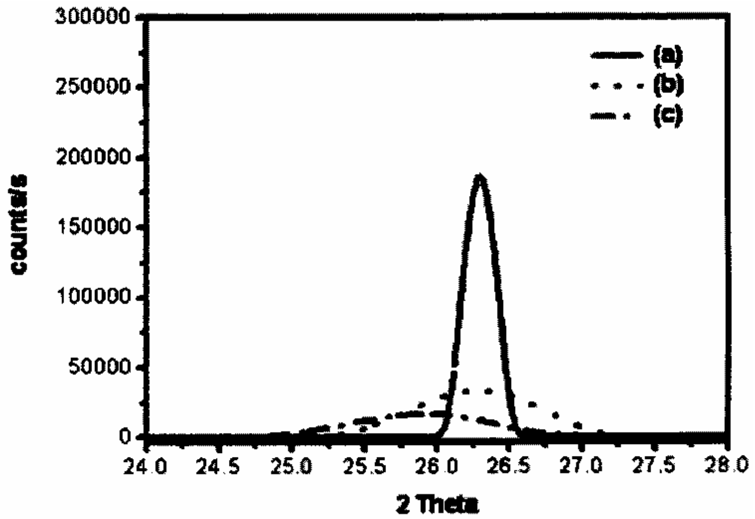


Fig. 2. XRD patterns for graphite powder: (a) raw material, (b) expanded in cluster range, and (c) expanded in layer, stack and cluster

Table 1. Acid treatment and gasification of 100-150 μm graphite powder for XRD pattern analysis

# of sample	Reagents	Expanding temp.	Treatment
13			Raw materials
3	H_2SO_4 600g+H_2O_2 14g	Room temperature	Acid treatment
3-1			Duplicate of #3
4	H_2SO_4 1,200g+H_2O_2 14g		H_2SO_4 added
5	H_2SO_4 600g+H_2O_2 14g		Acid treatment
6			Duplicate of #5
10	H_2SO_4 267g+CH_3COOH 133g	600 °C	Acid treatment
11	H_2SO_4 267g+CH_3COOH 267g		CH_3COOH added
19	H_2SO_4 600g+H_2O_2 14g	1,000 °C	Gasification
20		400 °C	
21		450 °C	
22		500 °C	
23		600 °C	
24		650 °C	

CHANGES IN CRYSTALLINITY OF GRAPHITE POWDER BY ACID TREATMENT AND GASIFICATION

General conditions in these tests were given in Table 1. After the acid treatment and gasification, samples were analyzed by XRD. All reagents used were a mixture of hydrogen peroxide and sulfuric acid, or sulfuric acid and acetic acid. In all the tests the amount of graphite sample was 100g and time of treatment was 3 hours. Samples treated with acid mixture were rinsed with enough amount of clean warm deionized water, filtered and dried. These dried samples underwent gasification at various expanding temperatures. The gap between each layer of was analyzed by XRD pattern analyzer.

PREPARATION OF EXPANDED GRAPHITE SAMPLES AND PURIFYING PROCESS

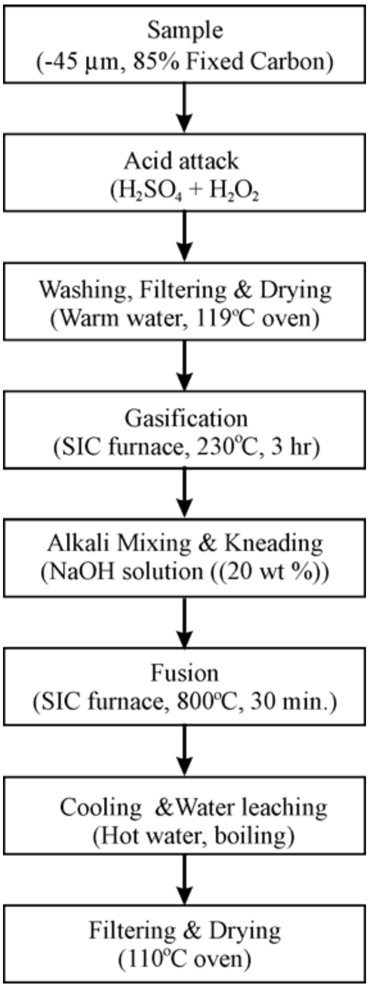


Fig. 3. Treatment procedure for processing graphite powder

In the tests samples smaller than 45μm were used. Reacting agents for acid treatments were the mixture of 600g of sulfuric acid and 14g of hydrogen peroxide. Reacting time was about 2 hours and reaction was performed at room temperature. After the acid treatment, samples were rinsed with 50 °C clean water, filtered and dried. These samples were used as acid treated samples.

According to the result of preliminary experiments, expanding temperature was set at 200~250 °C. In this range, the samples showed about 30% of expansion ratio in volume. So various expanded graphite samples were produced at various temperature and expansion time.

Alkali treatments were also conducted for raw material, basic acid treated sample, and expanded sample with acid treatment. 5N sodium hydroxide solution (20 wt%) was used as the reagent for these tests. 10g of each graphite sample was mixed with 25g of alkali solution and kneaded during 12 hours. After that, the samples were dried about 10 hours and fusion process was followed at 800 °C using a SiC furnace. Fused samples were cooled and rinsed several times with hot clean water. Final samples were obtained after neutralization with 12 wt% HCl solution, re-rinsing and drying. Overall procedure was given in Fig. 3.

ANALYSIS OF VARIOUS SAMPLES

Samples produced in each step underwent several analyzing procedures to establish such properties as ash content, expansion ratio, particle shape and size. Table 2 shows the major test conditions and properties analyzed by the test. Especially, expansion ratios were determined using samples produced at 230 °C with different treating times. According to the result of expanding tests at 210 °C, 230 °C and 250 °C, graphite powders expanded properly at 230 °C without excessive expansion.

Table 2. Acidic, gasification and alkaline treatment of -45 μm graphite powder at different times and temperatures

Treatment	Temp., °C	Sample No.	Time	Wt., g
Gasification	230	4	1 min	6 ~ 7
		5	2 min	
		6	4 min	
		7	8 min	
		8	15 min	
		9	30 min	
		10	60 min	
		11	120 min	
		12	240 min	
	210	13	240 min	60
	230	14		
	250	15		
Alkali	800	27	180 min	50
		28	180 min	

Analyses for ash contents were conducted basing on KSL 3412:2002 “Test methods for ash in graphite,” using SIC furnace and alumina crucibles (KSIC, 2002). SEM images were taken using JEOL JSM-6380 at 20kV of acceleration voltage. Expansion ratios were calculated by ‘tapping method’ based on volume.

RESULTS AND DISCUSSION

CHANGES IN CRYSTALLINITY OF GRAPHITE POWDER

Figure 4 shows the XRD patterns and gap of layer of treated graphite powder under various conditions, respectively. Sample numbers are based on Table 1. As shown in the figure, crystallinity of raw material was best with 3.37Å of layer gap. #3, #3-1 (repeated analysis of #3), #5, and #6 were the patterns of powder treated under the same conditions and so they show similar trend. On the other hand, #4 shows less crystallinity and larger layer gap compared to other samples. #10 and #11 is the XRD patterns of samples treated with acetic acid mixture and show higher crystallinity and larger layer gap. It means that graphite powder could be treated with less damage in crystallinity when acetic acid is used as acid treatment reagent.

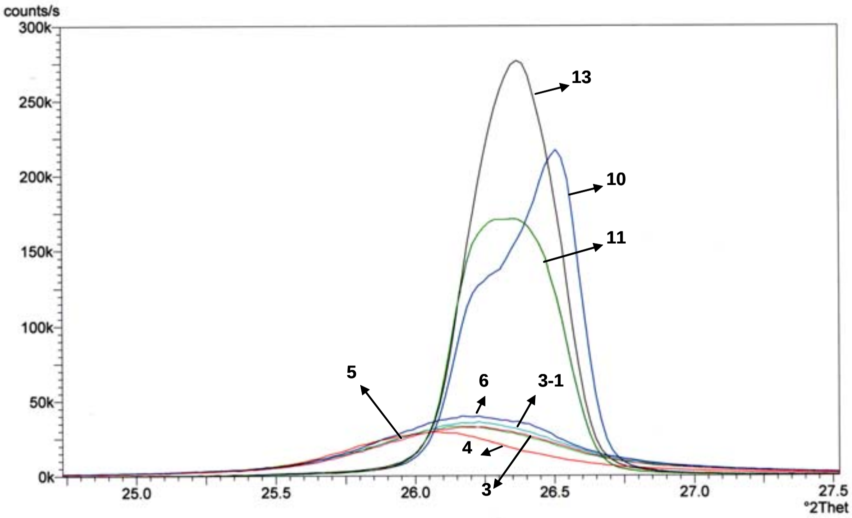


Fig. 4. XRD patterns of various graphite powders at various treating conditions (No. are based on Table 1)

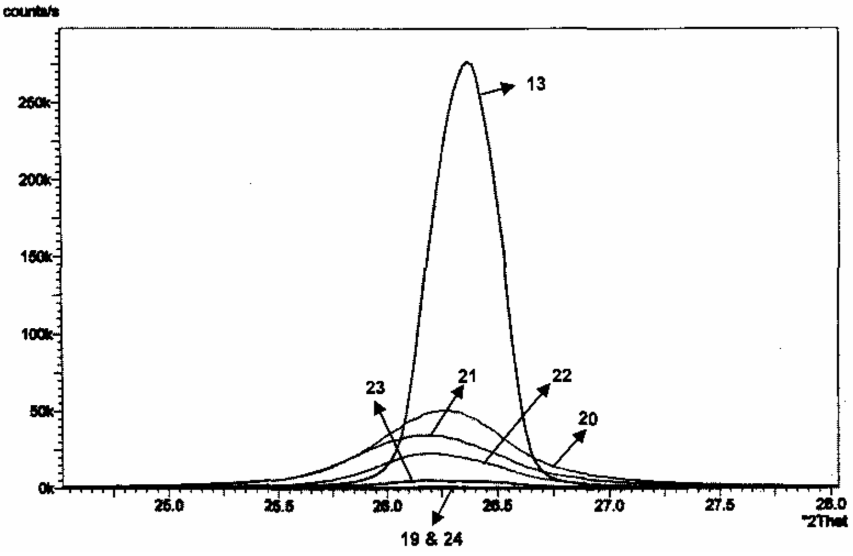
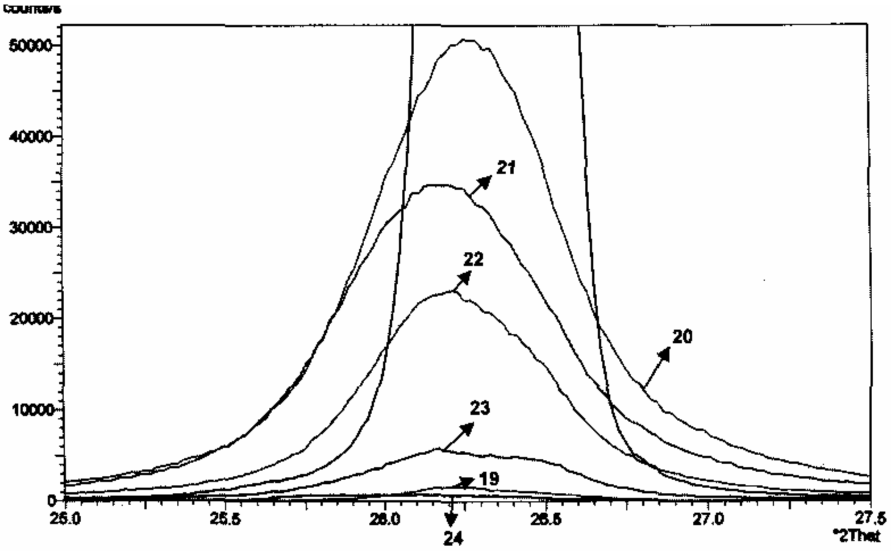


Fig 5. **a)**



b)

Fig. 5. XRD patterns of various graphite powders at various temperatures (No. are based on Table 1)

Figure 5 shows the XRD patterns of the graphite samples expanded after acid treatment. Sample numbers were based on Table 1, and Figure 5(b) is the image enlarging the major part of Figure 5(a). Crystallinity of graphite powders decreased significantly according to the increase of treating temperature and powders lost their crystalline properties at over 650 °C. On the other hand, the layer gaps were staying at 3.36~3.38Å. This implies that high expanding temperature makes the graphite powders losing their crystalline properties. So, it is important to search the optimum conditions for maintaining the crystallinity of graphite and improving the efficiency of purification or grinding simultaneously.

BULK DENSITIES AND EXPANSION RATIOS

Table 3 shows bulk densities and expansion ratio of -45μm graphite powders in various treating. Sample numbers were based on Table 2. The expansion ratio was calculated from the expanded volume percent compared to initial volume in %. The results show that expansion ratio changed from 9% to 28% with the increase of the treating time at 230 °C, and there were no changes of volume after 2 hours. At 210 °C and 250 °C, 31% and 26% of volume increases were observed. Decreasing from 31% to 26% according to the increase of temperature was because of the experimental errors or nonuniform expansions.

Sine excessive expansion generated by gasification at high temperature could cause lowering of the efficiency of grinding process, it was expected that about 30% of volume expansion could help improve the purifying and grinding efficiency.

Table 3. Bulk densities and expansion ratios of -45 μm graphite powders

Sample no.	Bulk density, g/cm^3				Expansion ratio, %
	test 1	test 2	average	variation	
1	0.375	0.349	0.362	7.1%	100.0
2	0.358	0.354	0.356	1.1%	101.5
4	0.334	0.330	0.332	1.3%	109.0
5	0.330	0.323	0.326	2.1%	110.9
6	0.302	0.310	0.306	2.6%	118.2
7	0.302	0.293	0.297	3.2%	121.7
8	0.295	0.296	0.295	0.3%	122.5
9	0.297	0.287	0.292	3.2%	124.0
10	0.286	0.290	0.288	1.3%	125.7
11	0.282	0.281	0.281	0.3%	128.6
12	0.287	0.283	0.285	1.5%	127.1
13	0.273	0.279	0.276	2.0%	131.2
14	0.265	0.299	0.282	13.1%	128.3
15	0.292	0.282	0.287	3.7%	126.1

Table 4. Ash contents of each graphite samples

Sample no.†	Ash content‡	Average ash content	Treatments
1	14.09%	14.15%	Raw materials
	14.20%		
2	11.02%	11.10%	Acid treated only
	11.19%		
27	23.58%	23.70%	Acid/alkali treated
	23.81%		
28	14.55%	14.54%	Acid/gasification/alkali treated
	14.54%		
27-2	16.94%	16.85%	Acid/alkali treated (2nd rinsing)
	16.77%		
28-2	11.39%	11.43%	Acid/gasification/alkali treated (2nd rinsing)
	11.48%		
27-3	4.30%	4.44%	Acid/alkali treated (3rd rinsing with HCl)
	4.58%		
28-3	3.84%	3.91%	Acid/gasification/alkali treated (3rd rinsing with HCl)
	3.99%		

Sample no.† is based on Table 2.

Ash content‡ is determined according KS L 3412:2002

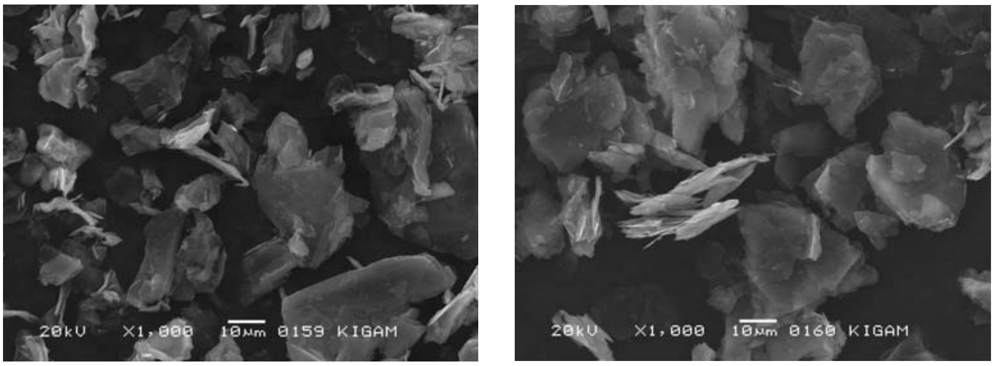
ANALYSES OF ASH CONTENTS FOR -45 μm SAMPLES

Table 4 shows the result of ash analyses for raw material (#1), basic acid treated sample (#2), acid and alkali treated sample (#27), and the sample treated by alkali after acid treatment and gasification (# 28).

The ash content of raw material was about 14%, and after the acid treatment the ash content was about 11%, 20% lower than the raw material. It is believed that metallic impurities including iron were removed. The ash content of #27 and #28 appeared higher than #2 because of the incomplete removal of soluble silica formed by the alkali treatment. But the ash content of #27 and #28 proved that the gasification was helpful for removing the impurities by showing low ash content in #27. #27-2 and #28-2 were the samples rinsed 5 additional times with clean water. The ash contents achieved lower level, but not sufficient. In general, soluble silica could remain when alkali reagent was not removed completely. So, additional rinsing was performed using a small dose of hydrochloric acid aqueous solution. Finally, less than 5% of ash content was obtained.

ANALYSES OF SEM IMAGES OF GRAPHITE SAMPLES

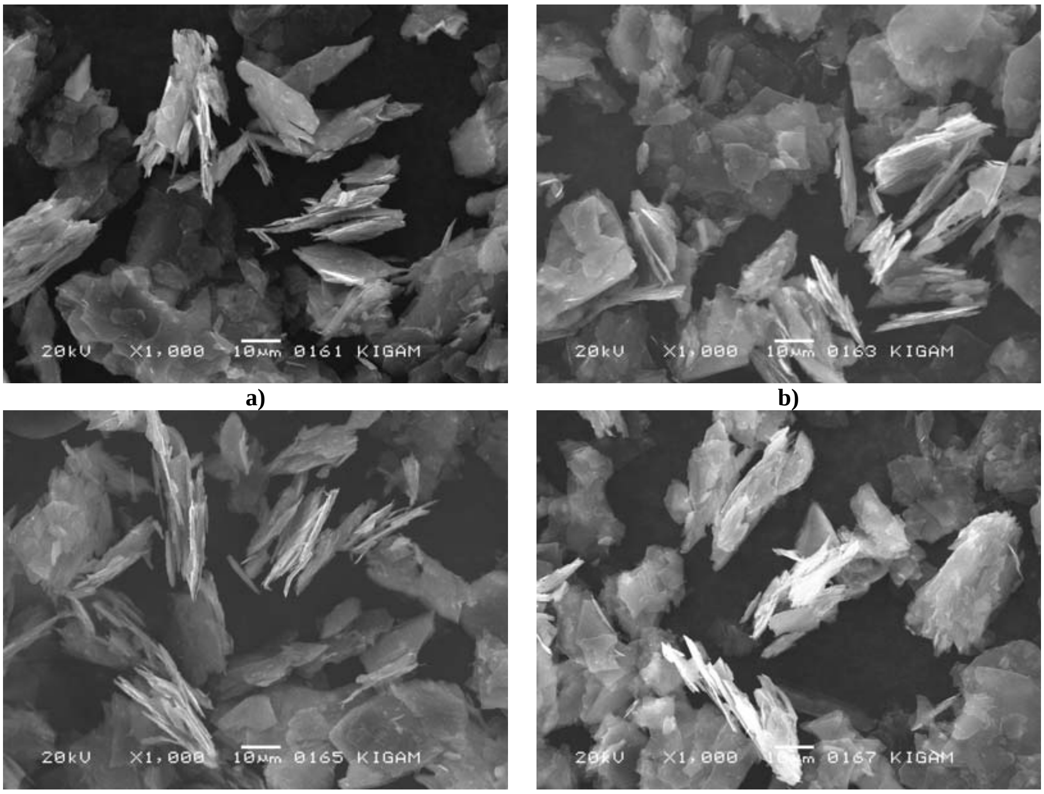
Figure 6 shows the SEM images of raw graphite powders and powders after the acid treatment. Image of raw materials shows wide size range of particles showing flake-shape. Image of acid treated powders shows some aggregates created during rinsing and drying, and several particles show somewhat expanded shape in spite being prior to gasification process.



a) **b)**

Fig. 6. SEM images of graphite powders; (a) raw materials (#1 in Table 2) and (b) acid treated (#2 in Table 2)

Figure 7 gives the SEM image of graphite powders treated in SIC furnace at 230 °C with various treating time. Expanded powders were observed more frequent in samples treated with long expanding time, but there was little difference in shape between expanded particles. It was not observed the excessive expansion in this temperature condition. It implies that temperature is proper to produce the low-expanded powders.



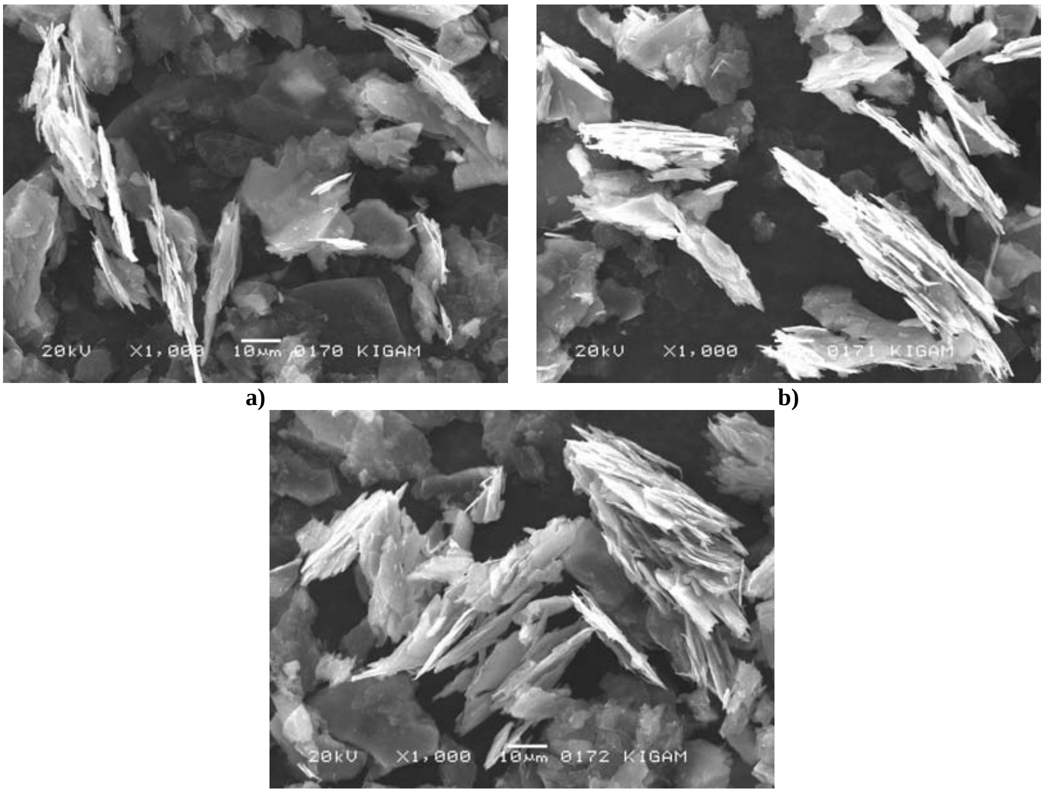
a) b)

c) d)

Fig. 7. SEM images of graphite samples expanded at 230℃ for; (a) 1 min (#4), (b) 4 min (#6), (c) 15 min (#8), and (d) 1 hour (#10) (# are based on Table 2)

Figure 8 is the SEM images of graphite samples treated at 210, 230, and 250 °C for 3 hours. Similarly to the previous cases, there was little difference in shape between samples but some difference in expansion ratio. Especially, in spite of enough expanding time, there were not expanded particles. It implies that there are other factors affecting expansion of graphite powders, such as the shape of particle, structure of layer system or reagents.

Figure 9 shows the shape of graphite particles treated by alkali reagent. There also existed expanded particles and no expanded particles together, and some white particles having indeterminate form were observed on the surface of large particles, or between particles. These untypical particles are very likely silica particles recrystallized by alkali treatment and drying. in Fig. 9(b) some peculiar shapes were observed. These are particles having damaged layer structures which might be caused by gasification and chemical treatments. This phenomenon was thought to be helpful to improve the efficiency of fine grinding process.



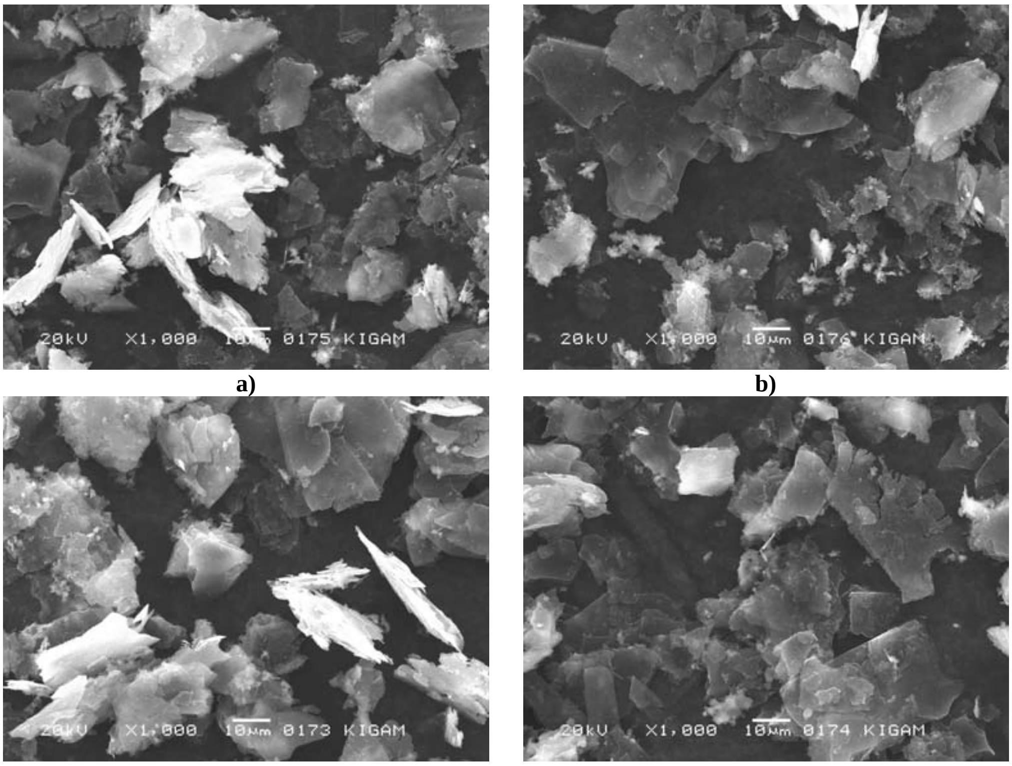
a) **b)**

c)

Fig. 8. SEM images of graphite samples expanded for 3 hours at; (a) 210 (#13), (b) 230 (#14) and (c) 250℃ (#15) (No. are based on Table 2)

CONCLUSIONS

Several set of tests were conducted to make the high-grade graphite samples suitable for producing high-value fine graphite powders. To do this, typical acid/alkali treatment and low-expansion process were used. After the acid treatment and gasification at low temperature, the crystallinity of graphite particle decreased and only small change of the layer gap was observed. By acid treatment, using the mixture of sulfuric acid and hydrogen peroxide, about 20% of impurities, most likely metallic impurity, were removed. Gasification at low temperature (about 230°C) could help produce low-expanded graphite powders. After the gasification, we observed about 30% volume increase for 3 hours heating. Despite more or less non-homogeneous expansion, there were not excessively expanded particles which were unfavorable to the grinding process. Final samples, produced by acid treatment, gasification and alkali treatment, showed 3.91% of ash contents, and some damaged-layer structures were observed.



a) **b)**

c) **d)**

Fig. 9. SEM images of graphite samples; (a) treated with acid and alkali reagent without gasification (#27) and (b) treated with alkali reagent after acid treatment and expansion in SIC furnace for 3 hours at 230 C (#28) (No. are based on Table 2)

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Jeongyun Kim, Byounggon Kim, *Oczyszczanie naturalnego grafitu metodami chemicznymi oraz ograniczonej ekspansji,* Physicochemical Problems of Mineral Processing, 41 (2007), 37-49 (w jęz. ang.).

Naturalny rozdrobniony grafit wykazuje dobrą odporność na ogrzewanie, niską rozszerzalność oraz małe przewodnictwo i jest używany do jako materiał wysoko wydajnych baterii, do smarowania, itd. Proszek grafitowy, aby mógł być zastosowany jako materiał zaawansowanych technologii, jest oczyszczany i modyfikowany powierzchniowo. Kraje rozwinięte produkują wysokiej jakości proszek grafitowy metodą interkalacji i sub-mikronowego rozdrabniania. Obecnie badania zostały przeprowadzone dla wykorzystania niskiej jakości naturalnego grafitu jako źródło nano-materiału. Dla produkcji ultradrobnego proszku grafitowego przeprowadzono badania dotyczące wstępnej modyfikacji stosując typowy proces ekspansji i modyfikacji „kwas/zasad”. Zastosowano niską temperaturę gazyfikacji w porównaniu do tradycyjnego procesu, co pozwala uzyskać odpowiedni stopień ekspansji w celu efektywnej obróbki chemicznej i rozdrabniania. Proces ekspansji prowadzono w temperaturze 200~250℃ dla uzyskania 20~30% wzrostu objętości ponieważ ekspansja proszku grafitowego, stosując tradycyjne podejście, tj. wysokie temperatury, prowadzi do słabej efektywności rozdrabniania.