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# Effect of heating rate, temperature, and residence time during graphitization on the mechanical and electrical properties of isotropic graphite blocks

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|---|--|--|--|--|
| Keywords:<br>Isotropic<br>Graphite block<br>Graphitization<br>Temperature<br>Heating rate<br>Shrinkage rate<br>Isotropic coke | The present study aimed to determine the correlation between graphitization parameters during the manufacturing of isotropic graphite blocks, including temperature, residence time, and heating rate, and the physical properties of the obtained graphite blocks. It was found that during graphitization, nitrogen- and sulfur-containing gases were generated, and the isotropic graphite blocks exhibited volume shrinkage, and their apparent density and bulk density increased, regardless of any changes in the process parameters, due to the intrinsic microstructure of the isotropic coke. Graphite blocks with varying graphitization temperatures and residence time exhibited increased bulk density and open porosity but decreased flexural strength and electrical resistivity compared to carbonized blocks. It was also confirmed that the heating rate process parameter was related to gas release rates and crystallization. In addition, it was observed that micron-sized pores were created around the developed ergender of the superdestructure with increasing graphitization degree |  |  |  |

# 1. Introduction

Isotropic graphite blocks are widely used in various applications where high strength is required, such as nuclear reactors, aerospace components, and mechanical parts [1-4]. Isotropic graphite blocks are produced by mixing isotropic fillers and binders and then subjecting them to a series of processes, including forming, carbonization, impregnation, and graphitization [5].

The graphitization process inevitably involves heat treatment at 2200 °C or higher temperature to make sure that graphite blocks have high heat and chemical resistance and high electrical conductivity [6,7]. The blocks undergo volume shrinkage and densification while being heat-treated at graphitization temperatures, as the (002) d-spacing of the hexagonal structure decreases, leading to an increased degree of crystallinity [8]. In the meantime, however, hetero atoms (sulfur and nitrogen) contained in the carbon-based materials are released in a gaseous form, resulting in the formation of pores and cracks inside the graphite blocks by irreversible expansion. This phenomenon is called puffing [9]. The release of nitrogen is known to start at around 1400 °C, followed by the release of sulfur at around 1600 °C [8–11].

The degree of expansion caused by puffing is related to the arrangement, domain size, and pore structure of the coke [12]. Unlike

needle coke with a lamellar microstructure, isotropic coke has a mosaic structure and thus is less affected by puffing because the release of nitrogen- and sulfur-containing gases can be more effectively facilitated [13]. Accordingly, the coefficient of thermal expansion (CTE) is higher in isotropic coke than in needle coke, while the effect of puffing is larger in needle coke than in isotropic coke.

In a previous study, K. I. Fujimoto et al. prepared green bodies with a diameter of 20 mm by mixing needle coke and mosaic coke with binder pitch. The obtained bodies were then subjected to graphitization while being heated up to 2500 °C, and puffing curves were measured over the entire temperature range. In the needle-coke specimen, the diameter changes rate ( $\Delta$ L/L) sharply increased in the temperature range between 1600 and 2500 °C. During cooling, the extruded material was found to contract, but its volume was larger than its initial level. In contrast, with the mosaic-coke specimen, the expansion rate started to increase at 1500 °C, but the degree of expansion was significantly smaller than in the needle-coke specimen. Furthermore, the shrinkage rate during cooling was higher in the mosaic-coke specimen than in the needle-coke specimen, and thus the final volume of the extruded material was smaller than its initial volume [8].

The process parameters for graphitization include the final (graphitization) temperature, residence time, and heating rate. The final

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temperature and residence time are closely related to the level of densification, which results from an increase in the degree of crystallinity of the graphite blocks. The heating rate is related to the formation of pores and cracks accompanied by the generation of volatile gases [6, 8,14]. Consequently, the physical properties of isotropic graphite blocks can be improved by adjusting these graphitization process parameters.

In fact, extensive research has focused on puffing inhibitors and ways of changing the properties of graphite blocks during graphitization, in efforts to determine how puffing affects the graphitization process when fabricating electrodes using needle coke [8–12]. However, little research has considered how graphitization process parameters affect the graphitization behavior of isotropic graphite blocks fabricated using isotropic coke, which is relatively less affected by puffing. Most studies on isotropic graphite blocks have compared the mechanical properties and chemical resistance of different commercial isotropic graphite blocks for nuclear applications [15,16] or ways of improving their strength using ultra-fine particles [4,17].

In the present study, isotropic graphite blocks were prepared using isotropic coke and coal tar-based binder pitch, and the obtained blocks were then subjected to graphitization while varying the final temperature, residence time, and heating rate. Their shrinkage rate, density, mechanical strength, and electrical resistivity were also measured to determine how these properties were correlated with the graphitization process conditions.

# 2. Experimental procedure

#### 2.1. Forming and carbonization

Isotropic coke was pulverized into powder with a particle size of 10  $\mu$ m or less, and the obtained powder was mixed and kneaded with coal tar-based binder pitch. The mixture was then subjected to uniaxial compression molding to obtain green bodies with dimensions of 10  $\times$  10  $\times$  50 mm<sup>3</sup>. Carbonization was then performed in a tube furnace filled with nitrogen gas, in which the green bodies were heated at a rate of 2 °C/min to 1000 °C and kept at the temperature for 1 h.

#### 2.2. Graphitization

The calcined isotropic coke and isotropic carbonized blocks were heat-treated using a resistance-heating vacuum graphitization furnace. Graphitization conditions about process parameters are summarized in Table 1. Table 2 shows photo of heat-treated graphite blocks for various graphitization conditions. Visual observation did not show any peculiarities, such as cracks, on the surface after graphitization.

#### 2.3. X-ray diffraction of graphitized isotropic coke

Changes in the crystallinity of the calcined isotropic coke were analyzed for the applied graphitization temperature, residence time, and heating rate using an X-ray diffractometer (XRD, Smartlab, Rigaku). Cu-K<sub> $\alpha$ 1</sub> with a wavelength of 1.5406 Å was used as an X-ray target source, and all XRD spectra were measured in the scanning range of 5–60° and at a scanning rate of 1°/min. Afterward, d-spacings were calculated from

# Table 1

## Process conditions for graphitization.

| Graphitization process parameters | Values taken                                 | Fixed conditions                              |  |  |
|-----------------------------------|--|---|--|--|
| 1. Temperature                    | 1-1. 2400 °C<br>1-2. 2600 °C<br>1-3. 2800 °C | Heating rate: 2 °C/min<br>Residence time: 1 h |  |  |
| 2. Residence time                 | 2-1. 1 hr<br>2-2. 2 hr                       | Heating rate: 2 °C/min<br>Temp.: 2800 °C      |  |  |
| 3. Heating rate                   | 3-1. 2 °C/min<br>3-2. 20 °C/min              | Temp.: 2800 °C<br>Residence time: 1 h         |  |  |

the  $2\theta$  values obtained from each peak using the Bragg equation, and the Lc and La were also estimated based on the full width at half maximum (FWHM) values using the Scherrer equation.  $L_a$  size of calcined isotropic coke was calculated with FWHM of (10*l*), and graphitized isotropic coke was calculated with (100). XRD analysis was measured four times for each sample and expressed as average value and dispersion.

The degree of graphitization of the graphite blocks can be calculated using Equation (1) according to the applied graphitization conditions [18,19].

$$G(\%) = \{(3.440 - d_{002}) / (3.440 - 3.354)\} * 100$$
(1)

G(%): Degree of graphitization.

3.440: Interlayer spacing of fully non-graphitized carbon (Å) 3.354: Interlayer spacing of the ideal graphite crystallite (Å)  $d_{002}$ : Interlayer spacing obtained from the XRD spectra (Å)

# 2.4. Apparent density

The dimensions and weights of the carbonized blocks obtained at 1000  $^{\circ}$ C and the graphite blocks heat-treated according to the graphitization process conditions were measured to determine changes in the apparent density of the graphite blocks compared to the carbonized blocks. Three carbonized blocks were graphitized for each process condition, and their dimensions were determined by measuring the width, length, and height three times using vernier calipers and averaging them.

#### 2.5. Bulk density and open porosity measurement

The bulk density and open porosity of the carbonized and graphite blocks were measured using Archimedes' method [20,21]. Three specimens were prepared for each process condition, and their dry weight, underwater weight, and saturated weight were measured. The specimen was dried in an oven at 100 °C for 24 h and the dry weight was measured. Then, the specimen was soaked in boiling water for more than 3 h and cooled down to room temperature, and only the water on the specimen surface was removed with wet gauze to measure the saturated weight. Finally, the underwater weight of the specimen soaked in distilled water was measured. Based on the results, their bulk density and open porosity were calculated using Equation (2) and Equation (3), respectively.

Bulk density 
$$(g/cm^3) = Weight_{Dry} / (Weight_{Saturated} - Weight_{Underwater})$$
 (2)

Open porosity (%) = {(Weight<sub>Saturated</sub> - Weight<sub>Dry</sub>) / (Weight<sub>Saturated</sub> - Weight<sub>Underwater</sub>)} \* 100 (3)

## 2.6. Flexural strength measurement

The flexural strengths of each specimen were measured using a universal testing machine (UTM) according to ASTM D 7972. Three specimens were prepared for each process condition. During the tests, the upper loading point was placed right at the center of each specimen, in both the longitudinal and transverse directions. Each of the two lower loading points was placed 20 mm away from the center. All measurements were performed at a loading rate of 0.5 mm/min, and the flexural strengths of each specimen were calculated using Equation (4).

$$S_{b} = 3WI / 2bt^{2}$$
<sup>(4)</sup>

 $S_b$ : Flexural strength (N/cm<sup>2</sup>), I: Distance between the two points (cm), W: Maximum load

b: Specimen width (cm), and t: Specimen thickness (cm)

Table 2

# Photo images of graphite blocks. Conditions **Top views** Side views Carbonized block (1000 °C) 1cm 2400°C for 1hr (2 °C/min) 2600°C for 1hr (2 °C/min) 2800°C for 1hr (2 °C/min) 2800°C for 2hr (2 °C/min) 2800°C for 1hr (20 °C/min)

# 2.7. Electrical resistivity measurement

Electrical resistivity measurements were conducted according to the potential drop method described in ASTM C 611. Three graphite block specimens were prepared for each process condition, and the corresponding potential drop between the voltage terminals, their cross-sectional area, current level, and the distance between the voltage terminals was measured, and based on the results, the electrical resistivity of each specimen was calculated using Equation (5).

$$\rho = eS / il \tag{5}$$

 $\rho \text{:}$  Electrical resistivity ( $\Omega \text{cm})\text{,}$  e: Potential drop between the terminals (V),

S: Cross-sectional area of the specimen (cm<sup>2</sup>), i: Current (A), and l: Distance between the terminals (cm)

# 2.8. Observation of microstructure

The Microstructure of the isotropic graphite block with respect to the graphitization conditions was observed by using an optical microscope (OM, Nikon ECLIPSE, LV150) and a scanning electron microscope (SEM, JEOL, JSM6500). In Table 2, the top face of the graphite block was micro-polished to 0.25  $\mu$ m without mounting. After acquiring 48 bright field images while moving the position at a magnification of 50, OM images obtained an image with an area of about 10  $\times$  10 mm<sup>2</sup> by world mapping. SEM images were observed at 100x and 500x magnification.

#### 3. Results and discussion

#### 3.1. X-ray diffraction of graphitized isotropic coke

Fig. 1 is the XRD spectra of isotropic coke with respect to the graphitization conditions. In Fig. 1(a), the  $2\theta$  position of (002) shifted to the right as the graphitization temperature and residence time increased. However,  $2\theta$  of graphitized isotropic coke at 20 °C/min shifted the position of  $2\theta$  to the left compared to that at 2 °C/min. In Fig. 1(b), the calcined coke showed a (10*l*) peak, and as the graphitization temperature increased, the (100) and (101) peaks gradually decomposed.

Fig. 2 and Table 3 present changes in the XRD parameters of the isotropic coke with respect to the graphitization process conditions. The (002) d-spacing of the calcined coke (at about 1400 °C) was measured and found to be 3.465 Å, and the crystallite sizes  $L_c$  and  $L_a$  were 27.0 Å and 56.8 Å, respectively.

As the graphitization temperature and residence time increased, the (002) d-spacing continued to decrease while the crystallite size continued to increase. Thus, at the graphitization temperature of 2800 °C, the (002) d-spacing was 3.366 Å,  $L_c$  was 258.1 Å, and  $L_a$  was 383.8 Å when the residence time was 2 h. It was also found that the crystallinity was higher when the residence time at 2800 °C was 2 h than when it was 1 h. The degree of graphitization, which was 66.0% at 2400 °C, continued to increase with increasing graphitization temperature and residence time; when the residence time at 2800 °C was 2 h, the degree of graphitization was 85.7%.



Fig. 1. XRD spectra of isotropic coke with respect to the graphitization conditions. (A colour version of this figure can be viewed online.)



**Fig. 2.** Changes in the XRD parameters of the isotropic coke with respect to the graphitization conditions: (a)  $d_{002}$ , (b)  $L_c$ , (c)  $L_{a}$ , and (d) G (%). (A colour version of this figure can be viewed online.)

The heating rate during graphitization also affected the crystallinity. When 2800 °C for 1 h,  $d_{002}$  of isotropic coke graphitized at 2 °C/min was 3.368 Å,  $L_c$  was 248.0 Å,  $L_a$  was 373.5 Å, and the degree of graphitization was 83.7%. On the other hand, the isotropic coke graphitized at 20 °C/min decreased crystallinity.  $d_{002}$  was 3.371 Å,  $L_c$  was 242.9 Å,  $L_a$  was 359.5 Å, and the degree of graphitization was 80.5%.

# 3.2. Effect of temperature and residence time

As previously described, isotropic graphite blocks were produced at different graphitization temperatures of 2400 °C, 2600 °C, and 2800 °C; the heating rate was 2 °C/min, and the residence time at each graphitization temperature was 1 h. At the graphitization temperature of 2800 °C, however, the residence time was set to up to 2 h, unlike the

Table 3

Changes in the XRD parameters of the isotropic coke with respect to the graphitization conditions.

|                      | Calcined           | 2400 °C    | 2600 °C    | 2800 °C    | 2800 °C    | 2800 °C     |
|----------------------|--------------------|------------|------------|------------|------------|-------------|
|                      | (at about 1400 °C) | for 1hr    | for 1hr    | for 1hr    | for 2hr    | for 1hr     |
|                      |                    | (2 °C/min) | (2 °C/min) | (2 °C/min) | (2 °C/min) | (20 °C/min) |
| $2\theta$            | 25.69              | 26.32      | 26.42      | 26.44      | 26.46      | 26.42       |
| d <sub>002</sub> (Å) | 3.465              | 3.383      | 3.371      | 3.368      | 3.366      | 3.371       |
| $L_c$ (Å)            | 27.0               | 238.8      | 247.8      | 248.0      | 258.1      | 242.9       |
| L <sub>a</sub> (Å)   | 56.8               | 309.4      | 364.6      | 373.5      | 383.8      | 359.5       |
| G (%)                | -                  | 66.0       | 79.9       | 83.7       | 85.7       | 80.5        |

other cases, to examine the effect of the residence time. Changes in the volume, weight, and apparent density of the graphite blocks were examined with respect to the graphitization temperature and residence time, and the results were compared with those obtained from the carbonized blocks, as shown in Fig. 3.

The volume shrinkage rate was found to increase with increasing graphitization temperature. At 2600 °C and 2800 °C, however, there was no significant difference in the shrinkage rate. There was also no significant trend found in the weight change over the entire graphitization temperature range. This was attributed to the fact that almost all impurities that had remained in the block after the carbonization process was released in the temperature range of 1500–2000 °C, resulting in no significant weight difference over the experimental temperature range.

Meanwhile, the shrinkage rate and apparent density were found to increase with increasing residence time. This was attributable to an increase in crystallinity. At 2800  $^{\circ}$ C, the (002) d-spacing was smaller when the residence time was 2 h than when it was 1 h, as previously discussed in the XRD analysis of the isotropic coke.

The physical properties of the graphitized blocks were examined and compared in relation to the graphitization temperature and residence time, as presented in Fig. 4. The bulk density and open porosity of the graphitized blocks were greater, regardless of the graphitization temperature, compared to the blocks carbonized at 1000  $^{\circ}$ C, but their flexural strength was lower. However, the graphitization temperature was found to have no significant effect on these physical properties. In contrast, the electrical resistivity tended to decrease with increasing graphitization temperature.

These property analysis results demonstrate that high-temperature graphitization is required to produce isotropic graphite blocks with low electrical resistivity. It was, however, determined that hightemperature graphitization is not necessarily required to produce



Fig. 3. Changes in apparent density with respect to the graphitization temperature and residence time. (A colour version of this figure can be viewed online.)

typical high-density, high-strength isotropic graphite blocks. The suitable graphitization temperature can be determined based on production costs, maximum operating temperature, and the particular field of industrial application.

There was no significant difference in the physical properties of the graphite blocks with respect to the residence time; all measurements were within the allowable error range.

D.B. Fischbach [22] analyzed the correlation of the graphitization temperature and residence time with the (002) d-spacing in pyrolytic carbon. During the tests, the residence time was increased on a log scale. At 2700 °C, the (002) d-spacing continued to decrease over time when the residence time remained in the range of  $10^{1}$ – $10^{2}$  min. At 2900 °C, however, there was no significant difference in the (002) d-spacing when the residence time was in the range of  $10^{1}$ – $10^{3}$  min. S.H. Chi et al. calculated the degree of graphitization of four commercial isotropic graphite blocks for nuclear applications by XRD analysis. According to the researchers, the isotropic graphite blocks exhibited a degree of graphitization ranging from 78.9 to 84.7% [15].

Accordingly, if one intends to achieve the desired decrease in the (002) d-spacing and the resultant increase in the degree of graphitization, it would be necessary to either increase the graphitization temperature to over 2800 °C or lengthen the residence time while maintaining the graphitization temperature.

# 3.3. Effect of heating rate

To examine the effect of the heating rate during graphitization on the physical properties of the obtained isotropic graphite blocks, the graphite blocks were heated to 2800 °C at different heating rates of 2 °C/ min and 20 °C/min, and changes in their volume and weight after the heat treatment were measured, as shown in Fig. 5. When the heating rate was 2 °C/min, the volume of the graphite block contracted by 6.8%, and its weight decreased by 1.8%, leading to a 5.4% increase in apparent density. At 20 °C/min, the volume of the graphite block contracted by 4.6%, and its weight decreased by 1.8%, leading to a 3.0% increase in apparent density.

Regardless of the heating rate, all of the graphite blocks tended to contract after graphitization, but the shrinkage rate was about 32.3% smaller when the graphitization heating rate was 20 °C/min than when it was 2 °C/min. This phenomenon can be explained by the following two reasons.

First, it can be attributed to the fact that an increasing heating rate sharply accelerates the release of nitrogen- and sulfur-containing gases in the temperature range of 1400–2000 °C. Indeed, Y. Kawano et al. reported that during the graphitization of coal tar-based needle coke, puffing was more pronounced when the heating rate was higher because nitrogen- and sulfur-containing gases could be activated in a shorter time [23]. Thus, the reduced shrinkage rate observed in the isotropic graphite blocks at a heating rate of 20 °C/min can be attributed to the rapid release of such gases during graphitization.

Second, when the heating rate was higher, the processing time at each temperature was shorter, and this may lead to a decrease in the crystallinity. At a heating rate of 2 °C/min, it took about 14.2 h to reach 2800 °C. At a rate of 20 °C/min, it took about 2.3 h. Therefore, the



Fig. 4. Physical properties of the graphite blocks with respect to the graphitization temperature and residence time: (a) Bulk density & porosity, (b) Flexural strength, and (c) Electrical resistivity. (A colour version of this figure can be viewed online.)



**Fig. 5.** Variation (%) in volume and weight with respect to the graphitization heating rate. (A colour version of this figure can be viewed online.)

observed difference in the degree of graphitization is caused by a sixtime shortening of the graphitization duration.

The physical properties of the graphitized blocks were examined and compared concerning the graphitization heating rate, as presented in Fig. 6. Regardless of the heating rate, these graphitized blocks exhibited increased bulk density and open porosity but decreased flexural strength and increased electrical resistivity compared to carbonized blocks. The increased bulk density was attributed to a decrease in the (002) d-spacing of the graphite blocks after graphitization, while the increased porosity was considered to be due to the removal of remaining impurities.

The decrease in the flexural strength and the electrical resistivity was attributable to the increased degree of graphitization and the increased porosity. Notably, at a low heating rate of 2 °C/min, all physical properties of the graphite blocks were found to be excellent. At a heating rate of 20 °C/min, there was a large deviation in the flexural strength measurement of the graphite blocks. This was attributed to the non-steady and rapid release of gases occurring at high heating rates, which caused the graphite blocks to have an irregular microstructure.

The apparent density and physical properties of the graphite blocks with respect to the graphitization parameters in the present study are summarized in Table 4.



Fig. 6. Physical properties of the graphite blocks with respect to the graphitization heating rate: (a) Bulk density & porosity, (b) Flexural strength, and (c) Electrical resistivity. (A colour version of this figure can be viewed online.)

#### Table 4

Apparent density and physical properties of the graphite blocks with respect to the graphitization parameters.

| Temp. (°C)   | Residence time (hr) | Heating rate (°C/min) | Variation (%) |        |                  | te (°C/min) Variation (%) Physical properties |              |          |             |  |  |
|--------------|---------------------|-----------------------|---------------|--------|------------------|---|--------------|----------|-------------|--|--|
|              |                     |                       | Volume        | Weight | Apparent density | Bulk  | Porosity (%) | Flexural | Electrical  |  |  |
|              |                     |                       |               |        |                  | density                                       |              | strength | Resistivity |  |  |
|              |                     |                       |               |        |                  | (g/cm <sup>3</sup> )                          |              | (MPa)    | (μΩm)       |  |  |
| Carbonized ( | 1000°C)             |                       | -             | -      | -                | 1.70  | 9.7          | 38.0     | 45.8        |  |  |
| 2400         | 1                   | 2                     | -6.0          | -1.7   | +4.3             | 1.79  | 11.3         | 34.1     | 15.9        |  |  |
| 2600         | 1                   |                       | -6.9          | -1.9   | +5.3             | 1.80  | 11.0         | 30.9     | 12.9        |  |  |
| 2800         | 1                   |                       | -6.8          | -1.8   | +5.4             | 1.78  | 12.2         | 33.2     | 10.8        |  |  |
|              | 2                   |                       | -7.2          | -1.8   | +5.8             | 1.79  | 11.8         | 30.3     | 11.3        |  |  |
|              | 1                   | 20                    | -4.6          | -1.8   | +3.0             | 1.75  | 12.4         | 30.3     | 12.0        |  |  |

# 3.4. Microstructure

Fig. 7 shows OM and SEM images with respect to the graphitization conditions of isotropic graphite blocks. It can be confirmed in the SEM that the black areas in the OM image are pores. The difference in porosity in the OM world mapping images with respect to the graphitization conditions does not seem to be significant, and the measured porosity is in the range of 9.7–12.4% (Table 4), showing no dramatic difference. The reason why the number of pores observed in the image appears to be more than the measured value is that the polished surface

was focused on during the OM observation (i.e., the shallow focus at the pore). However, the surface morphology before and after graphitization can be clearly distinguished by enlarging the images, as shown in Fig. 8.

Fig. 8 is an enlarged SEM image at the  $10 \ \mu m$  scales. In Fig. 8(a), the pore walls are smooth and round, and the surface around the pore is smooth. In comparison, Fig. 8(b) has a very complex shape. The pore wall is rough, and a zebra pattern can be found around the pore, and a layered plate can be easily observed inside the surface. These zebra patterns and layered plates are thought to be observed due to the development of a graphite layered structure, which can be said to be



Fig. 7. OM and SEM images of isotropic graphite blocks. SEM images were magnified from white boxes of OM images. (A colour version of this figure can be viewed online.)

evidence that the degree of graphitization increases.

In addition, it was observed that micron-sized pores were also generated around the developed graphitic layered structure. Although it is not yet clear, it is thought that if a graphitic structure develops within a certain volume, the shrinkage effect will leave pores.

After numerous discussions, we determined that this phenomenon is evidence that the flexural strength and electrical resistance decrease simultaneously with increasing graphitization degree.

### 4. Conclusions

In the present study, changes in the apparent density and physical

properties of isotropic graphite blocks were examined concerning graphitization process parameters, and the major findings are as follows.

All of the isotropic graphite blocks exhibited volume shrinkage, along with improved density and electrical properties, regardless of any changes in the graphitization process parameters.

It was confirmed that the graphitization temperature was the most significant process parameter affecting the properties of the graphite blocks. After the release of nitrogen- and sulfur-containing gases, the graphitization temperature had the most significant effect on the degrees of crystallinity and graphitization. As the graphitization temperature increased,  $d_{002}$  tended to decrease while the crystallite size increased, as a result the electrical conductivity increased.



Fig. 8. SEM images of isotropic graphite blocks (a) carbonized, (b) 2800  $^{\circ}$ C for 1hr (2  $^{\circ}$ C/min). The scale bar is 10  $\mu$ m. (A colour version of this figure can be viewed online.)

To determine the effect of residence time on the physical properties of isotropic graphite blocks, a longer residence time needs to be applied. In the present study, at a graphitization temperature of 2800  $^{\circ}$ C, an increase in residence time from 1 h to 2 h only led to a decrease in flexural strength; an expected dramatic decrease in electrical resistivity was not observed.

The graphitization heating rate was found to be closely related to the release rate of nitrogen- and sulfur-containing gases in the temperature range of 1400–2000 °C. Notably, as the heating rate increased, the release of gases sharply accelerated, which suppressed the volume shrinkage of the isotropic graphite blocks. The heating rate process parameter also determined the entire process time required for graphitization, thereby affecting the crystallization of the graphite blocks.

It was observed that micron-sized pores were created around the developed graphite layered structure through microstructure examination, which is determined as evidence that the flexural strength and electrical resistance simultaneously decrease with increasing graphitization degree.

In this experimental condition, the importance of parameters in the graphitization of isotropic graphite block can be listed as follows; Temperature > Heating rate and > Residence time.

In the present study, changes in the shrinkage rate and the physical properties of the isotropic graphite blocks were examined and compared for the graphitization process parameters. These results are expected to help with the selection of suitable process conditions for graphitization while considering production costs and fields of applications.

## CRediT authorship contribution statement

Sang-Hye Lee: Conceptualization, Investigation, Validation, Writing – original draft. Young-Min Hwang: Formal analysis, Resources. Tae-Sub Byun: Formal analysis, Methodology. Jong-Hwan Ko: Formal analysis. Jae-Seung Roh: Writing – review & editing, Project administration, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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