Effect of the Heat Treatment Temperature on the Compressive Strength of Coal Powder Compacts

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Abstract

This study considered the effect of the heat treatment temperature on the compressive strength of coal powder compacts affected by density, porosity, and crystallinity. Coal powder compacts were made by pressing of milled coal powder and were heat treated at 200, 400, 600, 800, and 1000°C. The density and porosity of the heat treated specimens at each temperature were measured using the Archimedes method and changes in crystallinity were analyzed using Raman spectroscopy. Increases in compressive strength at 600°C or higher temperatures were proportionally related to increases in the density and the degree of crystallinity.

Key words: coal powder compacts, heat treatment, compressive strength, density and porosity, crystallinity

1. Introduction

Coke is a solid mainly composed of carbon produced from coal or petroleum. In a broad sense, it is a generic term for carbonaceous substances left after volatile matters are taken out when organic matters have been heated while being cut off from air supply. In a narrow sense, this refers to lump carbon substances generated through coal heating. Coke manufacturing methods include high temperature heat treatment and low temperature heat treatment. Low temperature heat treatment refers to processes up to the primary decomposition temperature of coal at around 600°C; the coke generated in such processes is called low temperature coke. High temperature heat treatment refers to processes up to the secondary decomposition of coal at around 1000°C; such processes produce high temperature coke. In general, heat treatment refers to processes up to high temperature heat treatment until the secondary decomposition of coal. Low temperature coke is hardly used these days [1].

Coal, which is the raw material of coke, is a cheap resource that has been widely used as a fuel for homes, power production, and industrial uses such as iron making. Coal is mostly composed of various substances such as ash, moisture and volatile matter in addition to its main component fixed carbon. These diverse constitutive substances are removed as volatile components such as water, hydrogen, hydrocarbon, and tar are generated during heat treatment for coke manufacturing. Simultaneously with the removal of volatile matters, new pores are formed and the pores undergo growing processes [2,3].

Among the qualities of coke, strength is an important element. Many researchers have reported factors that affect the strength of coke. Nishioka and Yoshida [4] indicated that coke strength relies on coal grades, cracks generated in the process of carbonization, and matrix strength and porosity. Patrick et al. [5] reported study results regarding the relationship between the microstructures of coke observed through an optical microscope (OM) and coke strength. They explained that although simple correlations between porosity and strength were insignificant, the correlations increased when the number of pores, the pore sizes and pore shapes, etc., were considered together. Hartwell et al. [6] studied the relationship be-

Fig. 1. Result of TGA analysis of raw coal.

Fig. 2. Result of XRD measurement of raw coal.

tween porosity and tensile strength. In general, as porosity increased, tensile strength showed a decreasing tendency. They reported, however, that there were cases in which porosity differed by around 10% even when tensile strength remained the same.

There have been lots of studies on the effects of density, porosity, and cracks on the compressive strength of bulk coal, however it is difficult to find the relationship among such changes and the crystallinity. Therefore we analyze the relationship between the compressive strength and the changes in the porosity, density, and crystallinity of coal powder compacts as a function of the heat treatment temperatures.

2. Experimental Procedure

2.1. Raw material

The raw material used in this study is a coking coal powder for metallurgical cokes. Coking coal undergoes the process of softening-melting-solidifying during heat treatment. Fig. 1 shows the results of thermo gravimetric analysis (TGA) of the raw coal used in this study. TGA measurement was conducted

Fig. 3. Graphite jig for heat treatment.

in air atmosphere under a heating rate of 5°C/min. According to the results, volatile components were 3.5%, ash was 9.5%, and fixed carbon was 87%. Fig. 2 shows an X-ray diffraction (XRD) profile of raw coal. According to the results of the XRD analysis, the main components of the ash were $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ and SiO_2 .

2.2. Green compacts and heat treatments

Before it was used in the experiment, raw coal was made into powder consisting of 38~52 μm sized particles by classifying after grinding by ball milling. A 10 mm diameter cylindrical mold was used to make the green compacts with 10 mm height under a load of 62.5 MPa. The green compacts were heat treated in a nitrogen atmosphere at a temperature heating rate of 10°C/min. The final heat treatment temperatures were 200°C, 400°C, 600°C, 800°C, and 1000°C. The coal compacts were cooled after being maintained for 30 min at each temperature.

Since the process of softening-melting-solidifying, which is a characteristic unique to coal, occurs in the range of 400~600°C during heat treatment, the green compacts were heat treated using graphite jigs to prevent changes in shape.

Fig. 3 shows the graphite jig for heat treatment. The internal space is where specimens are located; it was made into a cylindrical shape to maintain the shapes of specimens during heat treatment. In addition, to ensure the smooth discharge of the gases that are products during thermal reactions, gas outlets were made in the front and rear of the specimen space.

2.3. Analysis

The density and porosity of the specimens were measured using the Archimedeian method after heat treatment. Three specimens fabricated in the same conditions were measured and the average value was used. The microstructures of the specimens were observed using an OM and the crystallinity of the specimens was measured using micro-Raman spectroscopy.

Micro-Raman spectrometry (in Via System, Renishaw, France) uses an Ar laser (514.5 nm) as the light source. Magnification of x500 was used to select a point on which to focus the laser beam spot on the sample surface. The spot size of the laser beam was about 1 μm in diameter. Extended scans from 1000 to 2000 cm^{-1} were performed to obtain the 1st-order Raman bands of the specimens [7].

The Raman spectra changed significantly for disordered carbons and showed a D band at around 1350 cm^{-1} . Therefore, the characteristic Raman spectra show peaks at around 1350 cm^{-1} for the disordered carbon (D band) and at 1580 cm^{-1} for the or-

Table 1. Changes in the physical properties as a function of heat treatment temperatures

Temperature (°C)		R.T.	200	400	600	800	1000
Size	Diameter (mm)	10.0	10.0	10.0	9.0	8.5	8.0
	Length (mm)	17.0	17.0	17.0	16.0	15.0	14.0
Archimedeian method	Density (g/cm ³)	1.34	1.34	1.40	1.51	1.76	1.85
	Porosity (%)	29.6	30.2	32.1	28.2	23.3	26.2

R.T.: room temperature.

dered carbon (G band) [8]. Relative intensity between the G and D bands could be changed by heat treatment, crystallite size of the disordered carbon, and crystallinity. We introduce the intensity ratio (R) values from the 1st order Raman bands that were calculated by $R=I_d/I_g$. The average value of crystallinity was achieved after measuring at 10 different positions except during the ash phase on the specimen surface following heat treatments.

The compressive strength of the specimens was measured using a universal test machine (Instron 4468) at a cross head speed of 1 mm/min. During high temperature heat treatment at 600°C or higher temperatures, the specimens underwent the process of softening-melting-solidifying and volatile matters were removed; thus, the surfaces of the specimens were rough with bumpy dents and protrusions. Therefore, the surfaces of the specimens were fine-ground (1 µm) before compressive strength tests were conducted on the specimens.

3. Results and Discussion

Table 1 shows the changes in the sizes (diameter and height) of the specimens as a function of heat treatment temperatures measured by the Archimedeian method. The sizes of the specimens did not change when heat treatment temperatures were lower than 400°C. No change in size means that only volatile matters were removed from the specimens, as can be seen in the TGA results shown in Fig. 1. When the heat treatment temperatures had reached 600°C, the sizes of the specimens began to decrease because the specimens underwent a process of softening-melting-solidifying at 600°C or higher temperatures due to the coking property of coal. At higher temperatures, the sizes of the specimens decreased further as heat treatment continued.

3.1. Density and porosity

Table 1 and Fig. 4 show changes in the density and porosity as functions of heat treatment temperatures. The density increased as the temperatures increased and the increment of the density began to increase remarkably at temperatures over 600°C. This is because the specimens underwent the process of softening-melting-solidifying and shrank during the heat treatment process due to the coal properties. The porosity increased by 2.5% compared to that of the green compact when the temperatures were below 400°C, which is a temperature range in which volatile matters are removed. The porosity began to decrease when the temperatures went over 600°C becoming 23.3% at 800°C. However, the porosity increased to 26% at 1000°C. This is in

Fig. 4. Changes in the density and porosity as a function of heat treatment temperatures.

agreement with the results from Yoon's study in which it was found that the process speed of coal into coke at over 1000°C is too high and thus pores develop in the coke due to the rapid volatilizing of volatile matters [9].

3.2. Surface microstructure

Images (x200) of the change of the surface microstructure following the heat treatment of specimens are shown in Fig. 5. It was observed that pore sizes increased and the number of pores increased at 200°C and 400°C. The specimens showed the lowest porosity at 800°C. The vitreous phase observed at 600°C or higher temperatures is considered to be the result of the process of softening-melting-solidifying during the coal heat treatment process.

3.3. Crystallinity

Fig. 6 and Table 2 show intensity ratio (R) values of D- (around 1357 cm⁻¹) and G-bands (around 1581 cm⁻¹) as functions of heat treatment temperatures, obtained through Raman analysis.

In Fig. 6 it can be observed that the G peak became sharper as the heat treatment temperatures increased. In particular, this tendency is clear at 1000°C. The intensity ratio was 0.75 in the green compact and changed slightly up to 800°C to become 0.70. However this value became 0.59 at 1000°C, and thus the decrement is quite large. This indicates that the degree of crystallinity of the samples suddenly increased at 1000°C. This is in agreement with previous reports showing that the degree of crystallinity increased during coke manufacturing at high temperatures [10].

Fig. 5. Changes in microstructures as a function of heat treatment temperatures.

Fig. 6. Raman spectra as a function of heat treatment temperature.

Sharma et al., using high resolution transmission electron microscope, reported that the crystallinity increased at temperatures over 1000°C by heat treatment for many kinds of coal. They also obtained results showing that the increment of the crystallinity decreased when the carbon contents were over 90% [11]. The carbon content of raw coal was 87% in this study. Therefore, it is expected that the crystallinity will be increased when the coal samples are heat treated at high temperatures over 1000°C.

3.4. Compressive strength

Fig. 7 shows the compressive strength at different heat treatment temperatures. The compressive strengths of specimens heat treated at 200°C and 400°C did not increase remarkably

Fig. 7. Compressive strength-strain profiles.

but the strain increased around 2~2.5 times compared to that of the green state specimens. The compressive strength of the specimens heat treated at 600°C and 800°C increased more than

Table 2. Results of intensity ratio (R) values using Raman spectroscopy

Temperature (°C)	R. T.	200	400	600	800	1000
Intensity ratio (I _d /I _g)	0.75	0.74	0.74	0.71	0.70	0.59

R.T.: room temperature.

Table 3. Results of compressive strength measurement

Temperature (°C)	R.T.	200	400	600	800	1000
Compressive strength (kgf/mm ²)	0.22	0.18	0.36	2.21	2.84	4.48

R.T.: room temperature.

Fig. 8. Relationship between the compressive strength and the density as a function of heat treatment temperatures.

10 times compared to that of the green state specimen and the strain increased around 5.5 times. The compressive strength of the specimens that were heat treated at 1000°C increased more than 20 times and the highest strength in the present study was obtained. However, the strain was shown to be similar to that of the specimen heat treated at 200°C. Table 3 provides a summary of the results of the compressive strength measurement.

3.5. Relationship between density, porosity, crystallinity, and compressive strength

Fig. 8 shows the relationship between the compressive strength and the density. It was shown that the changes in density between the green specimen and the specimens that were heat treated at 200°C and 400°C had a tendency similar to that of the compressive strength change. The density was in a range of 1.34–1.40 g/cm³ and the compressive strength was in a range of 0.18–0.36 kgf/mm². There was no remarkable difference in the values that were obtained at temperatures under 400°C.

However, the density and compressive strength of the specimens that were heat treated at over 400°C showed a rapidly increasing tendency. As heat treatment temperatures increased to 600°C, 800°C, and 1000°C, the density increased to 1.51, 1.76, and 1.85 g/cm³, respectively, and the compressive strength rapidly increased to 2.21, 2.84, and 4.48 kgf/mm², respectively. Therefore, it can be considered that increases in the density directly affect increases in the compressive strength of the specimens.

Fig. 9 shows the relationship between the porosity and the compressive strength. The porosity decreased and the compressive strength increased as heat treatment temperatures increased over 400°C. As can be seen in Tables 1 and 3, the porosity increased to 26.2% at 1000°C; however, the compressive strength still increased, showing its highest value of 4.48 kgf/mm² in this

Fig. 9. Relationship between the compressive strength and the porosity as a function of heat treatment temperatures. **Fig. 10.** Relationship between the compressive strength and intensity ratios (I_d/I_g) as a function of heat treatment temperatures.

study. Therefore, it is difficult to explain the relationship between the compressive strength of a specimen made at 1000°C and the porosity, as shown in Fig. 9.

As explained above, the process speed of changing coal into coke at over 1000°C is too high and thus pores develop in the coke due to the rapid volatilizing of the volatile matter (in Section 3.1). Furthermore, Yoon et al. [9] reported that low strength (Drum Index 67) was shown when the final temperature to make coke was lower than 900°C, while high strength (Drum Index 75) was shown when the temperature was over 900°C. Although there have been cases in which increases in porosity and increases in strength separately resulted from increases in temperatures, it is difficult to find studies that have analyzed the relationship between increases in porosity and increases in strength.

The increase in compressive strength, even when porosity in-

creases at high temperature (1000°C), can be explained with the relationship between the increase and changes in the degree of crystallinity, as shown in Fig. 10.

In Fig. 10, intensity ratios (I_d/I_g) that indicate the degree of crystallinity gradually decrease as heat treatment temperatures increase. This means that the degree of crystallinity of coal also increases as the heat treatment temperatures increase. The degree of crystallinity rapidly increases and the compressive strength also keeps increasing at 1000°C.

Considering Figs. 8 and 10 together, it could be asserted that the density increases as crystallization occurs rapidly at high temperatures over 1000°C, and this brings about increases in the strength. The strength of specimens should be considered not only in terms of the density and porosity but also in terms of the crystallinity.

4. Conclusions

The effects of changes in the density, porosity, and degree of crystallinity of coal powder compact on the compressive strength as functions of heat treatment temperatures were studied and the following conclusions can be drawn from the results.

The density, degree of crystallinity, and compressive strength of specimens heat treated below 400°C were not much different from those in the green compact; however, all of those characteristics increased at temperatures over 600°C. The porosity kept decreasing in the range of 400–800°C, while it increased at 1000°C.

The compressive strength did not show any significant change at temperatures below 400°C. Increases in the compressive strength showed a tendency to be proportional to increases in the density and the degree of crystallinity at temperatures over 600°C.

Density increases when crystallization occurs rapidly at high temperatures over 1000°C, and this brings about increases in the strength. The strength of specimens should be considered not only in terms of the density and porosity but also in terms of the crystallinity.

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