Changes and Migration of Coal-Derived Minerals on the Graphitization Process of Anthracite

Lipeng Wang, Tian Qiu, Zhimin Guo, Xiaofeng Shen, Jianguo Yang,* and Yuling Wang

1. INTRODUCTION

Graphite materials are considered as a type of revolutionary materials that have excellent characteristics of corrosion resistance, self-lubricity, thermal conductivity, and electrical conductivity. Therefore, graphite materials have many practical applications in various fields.1−5 Due to the limited natural graphite resources and poor quality, synthetic graphite has attracted more attention in recent years.6−11 In specific conditions (e.g., with catalyst, high temperature, or high pressure), most carbon-containing materials such as needle coke, carbon fibers, and petroleum pitch coke could be transformed into graphite.12−16 Not only does anthracite have a high carbon content, but it also has abundant resources and low production cost compared with natural graphite and petroleum-based graphite.17,18 Anthracite could be employed as the raw material for producing synthetic graphite, but there are a lot of minerals in coal, which restricts the development of coal-based graphite.

The influence of silicon on the graphitization of anthracite has been discussed in the previous work.19 However, coal-derived minerals include not only silicate and quartz but also carbonates, sulfides, metal oxides, sulfates, phosphates, etc.20−23 Many reports have been done on the influence of minerals on coal gasification and pyrolysis24−27 but little on the graphitization process.1,6 At present, the most commonly used method to evaluate the effect of mineral components in the gasification process is to compare the difference between original coking coal and demineralized coking coal. However, the influence of the change of coal molecular structure after acid and alkali treatment on gasification is usually ignored.28−31 Other researchers have compared raw coal with demineralized coal added with metal oxides to explain the effect of mineral composition. However, metal oxides do not dominate at high temperatures, nor does it take into account the effect of interactions between minerals.32−34 These experimental designs are one-sided. Therefore, it is necessary to conduct research on the influence of various minerals and the features of minerals on the graphitization process of coal35−39 so that it can provide a theory for the removal of minerals in the process of graphitization and the production of high-purity graphite.

In the present work, the Taixi anthracite, Ningxia, China, was employed to investigate the changes and migration of coal-derived minerals in the graphitization based on the classical theory of the graphitization transition mechanism.35−36 First, the Taixi anthracite was treated with a low-temperature ashing instrument, and the type and content of the residues were...
analyzed by X-ray diffraction (XRD). XRD can also reflect the crystal structure of the residues at different heat-treatment temperatures. Subsequently, the features of minerals in raw coal are explored, and the fusibility of pure minerals and mixed minerals is characterized by an ash fusion instrument. The microstructure of the Taixi anthracite during the heat-treatment process was observed by scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy—energy-dispersive X-ray spectroscopy (SEM–EDS) were used to analyze the microstructure and mineral composition of the escapes in experimental and industrial ultrahigh-temperature graphitization furnace. Finally, changes and migration mechanism of the coal-derived minerals during the graphitization process of anthracite was obtained by combining with the features of minerals in anthracite, the microstructural changes of anthracite during the heat-treatment process, and the analysis of the residues and escapes compositions.

2. EXPERIMENTAL SECTION

2.1. Materials. Anthracite samples were provided by Taixi Coal Preparation Plant (Ningxia, China). Industrial analysis and elemental analysis of the Taixi anthracite sample are based on GB/T 212—2008 and ash composition analysis is according to GB/T 1574—2007. The instruments for industrial analysis and elemental analysis are 5E-MAG6700 and EA 2400II, respectively. Proximate analysis results and ash compositions of the sample are shown in Tables 1 and 2.

| proximate analysis | ultimate analysis (daf) |
|-------------------|-------------------------|
| Mdaf              | Adf                     |
| Vdaf              | C                       |
| H                 | O                       |
| N                 | S                       |
| 1.33              | 2.85                    |
| 8.63              | 96.81                   |
| 1.17              | 1.35                    |
| 0.59              | 0.08                    |

Table 2. Ash Compositions of the Taixi Anthracite Sample, wt %

| SiO2       | Al2O3  | Fe2O3 | CaO   | MgO   | Na2O + K2O |
|-----------|--------|-------|-------|-------|------------|
| 25.21%    | 17.33% | 20.01%| 25.65%| 10.16%| 0.82%      |

It can be seen from Table 1 that the Taixi anthracite has low impurity (moisture, ash) content and high fixed carbon content. It can be seen from Table 2 that the ash content of the Taixi anthracite is mainly SiO2, Al2O3, Fe2O3, and CaO.

2.2. Graphitization Processes. The anthracite with a size range of 10–20 mm was used as the sample of this work. The anthracite samples were put into a graphite pot, which was subsequently covered and placed in a vertical ultrahigh-temperature-graphitized furnace (model: IGBT). Because the anthracite samples are low-ash coal, the volume of the coal used is about 2/3 of the furnace chamber volume to collect enough escapes. The pressure in the furnace chamber was 20–30 kPa (relative pressure), with high-purity argon as the protective gas used during the heat-treatment process. The furnace was heated at a rising rate of 10 °C/min up to a specified temperature and heat-preserved for 3 h. Afterward, the furnace was naturally cooled down to room temperature to obtain the coal-based graphite products and the gas generated in the heating.

2.3. Characterization of Materials. The morphology of the coal-based graphite samples was obtained using a scanning electron microscope (SIGMA, Carl Zeiss). The coal-based graphite samples were immobilized onto a layer of conductive adhesive and sputter-coated with a layer of gold before the measurement.

The samples are treated by a low-temperature ashing instrument (EMS1050, Electron Microscopy Sciences company) to ash them prior to elemental analysis. Pulverize the coal sample below 200 meshes, subsequently, weigh the coal sample about 3 g in a glass dish. Place the glass dish 5–10 cm below the working coil. Then, the airtightness of the device is checked. The whole system is pumped to approach a single vacuum, and the pressure of the whole system is kept below 0.267 kPa by adding proper oxygen.

The ash fusibility of the sample was obtained by the ash fusion instrument (HKHR-4000, Heng Ke company, China). The main reference index was the special temperature of the coal ash in the melting process (e.g., deformation temperature, softening temperature, hemisphere temperature, and flowing temperature).

X-ray diffraction (XRD) spectra were obtained on a PANalytical B.V. XPert3 Powder diffractometer. Using the copper target and potassium radiation (λ = 0.154056 nm), 40 kV tube voltages, 100 mA tube currents, in 50–60 °C scanning, scanning range 10–80°, high-purity silicon as the internal standard. To prepare the LTA ashes for XRD, the blocky samples need to be ground to below 300 mesh, that is, the particle size is around 48 μm before the measurement.

X-ray photoelectron spectroscopy (XPS) spectra were obtained using a multifunctional X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Fisher) with the pass energy of 18.05 eV and an Al Kα line excitation source. To take into account the charging effects on the measured binding energy, all spectra have been referred to the C 1s line (E_B = 284.8 eV).

3. RESULTS AND DISCUSSION

3.1. Mineral Compositions. Figure 1 shows the XRD spectra of the products of the low-temperature ashing treatment.

Figure 1. XRD spectra of the low-temperature ashing product from the Taixi anthracite (Q, quartz; I, illite; K, kaolinite; P, pyrite; C, calcite; B, bassanite).

As can be seen from Figure 1, the minerals in the Taixi anthracite are mainly oxides, clay minerals, sulfides, carbonates, and sulfates, including quartz, kaolinite, illite, pyrite, calcite, and bassanite. Pyrite is not only the main occurrence form of iron but also the main occurrence status of inorganic sulfur in coal. Table 3 shows the quantitative analysis of the XRD spectra of the...
anthracite using X’Pert High Score phase analysis software and PDF2-2004 database.

**Table 3. Mineral Compositions and Content of the Taixi Anthracite Sample**

| mineral    | content  |
|------------|----------|
| quartz     | 31%      |
| illite     | 46.48%   |
| kaolinite  | 8.52%    |
| pyrite     | 4%       |
| calcite    | 2%       |
| bassanite  | 8%       |

From the data in Table 3, it can be concluded that clay minerals (illite, kaolinite) and oxides (quartz) are the main minerals in the Taixi anthracite; sulfides (pyrite), carbonates (calcite), and sulfates (bassanite) content is less. Through the analysis of the sulfur forms of the Taixi anthracite, bassanite content increases after low-temperature ashing, and bassanite actually accounts for 3.5% of the mineral compositions of the Taixi anthracite.

**3.2. Occurrence Status of Minerals.** The primary maceral in the Taixi anthracite is vitrinite in which dispersed, disseminated, and nodular clay minerals occur. Figure 2 shows the main occurrence status of clay minerals in the Taixi anthracite. Coal-derived minerals are distributed in the form of filled cells, dispersed, nodular, etc. In the Taixi anthracite, the sulfides are mainly pyrite, which is distributed in two forms: cell filling and dispersion (Figure 2a); the oxides are mainly quartz, mostly existing in the form of particles independently and a few are distributed in the form of particles in the degradation of the Taixi anthracite (Figure 2c). In the Taixi anthracite, pyrite is mostly distributed in high-density components.

**3.3. Changes and Migration of Minerals.** Although the programmed heating rate is set to 10 °C/min, there is a certain difference between the measured temperature detected by the infrared temperature probe and the set temperature during the heat-treatment process. Figure 3 shows the actual heating curve drawn with the relationship between the measured temperature and time.

It can be seen from Figure 3 that the actually measured heating rate curve is not a smooth straight line with a slope of 10, but multiple thermal equilibria and temperature fluctuations occur during the heating process. This is because in this temperature range, the noncarbon impurities in the system appear to melt, decompose, escape, etc., and the fine ash generated interferes with the infrared probe, resulting in a difference between the measured temperature and the actual temperature in the furnace.

Based on the above experimental phenomena, the temperature at which the temperature fluctuation occurs is taken as the heat-treatment temperature during subsequent research, namely, 1200, 1500, 1800, 2200, and 2700 °C.

The fusibility results of pure and mixed minerals are presented in Table 4. The flow temperature of mixed minerals is lower than that of any pure minerals except pyrite. This may be caused by the fact that various minerals react with each other at high temperature to form a low-temperature eutectic. Both quartz and kaolinite ultimately exist in the form of silica at high temperatures, and their melting point is about 1670 °C, which exceeds the detection limit of the ash fusion instrument.

To study the thermal transformation of mixed minerals, the six minerals of quartz, illite, kaolinite, pyrite, calcite, and bassanite were mixed according to the proportion of minerals in the anthracite sample, placed in a 100 mL graphite pot, and a high-temperature graphitization furnace was used. Five heat-treatment residues are obtained with this method at a heating rate of 10 °C/min, in a high-purity argon atmosphere, under slight positive pressure conditions (20–30 kPa), the temperature raised to 1200, 1500, 1800, and 2200 °C, and kept warm for 3 h after naturally cooling to room temperature. The five heat-treatment residues obtained are shown in Figures 4 and 5 shows the XRD spectra.

As can be seen from Figure 5, when heated above 1500 °C, the mixed mineral basically exists in the form of aluminosilicate. When heated above 2700 °C, the remainder of the heat treatment consists of silica and a small amount of silicon carbide formed by the reaction of silica with the graphite pot.

**Figure 3.** Actual heating rate curve of the graphitization process of the anthracite.

**Table 4. High-Temperature Fusibility Data of Pure Minerals and Mixed Minerals (°C)**

| sample            | DT      | ST      | HT      | FT      |
|-------------------|---------|---------|---------|---------|
| illite            | 1400    | 1420    | 1460    | 1480    |
| quartz            | >1500   | >1500   | >1500   | >1500   |
| kaolinite         | >1500   | >1500   | >1500   | >1500   |
| pyrite            | 1090    | 1100    | 1110    | 1120    |
| calcite           | 1220    | 1260    | 1280    | 1320    |
| bassanite         | 1440    | 1450    | 1460    | 1470    |
| mixed minerals    | 1260    | 1270    | 1280    | 1300    |
observed that a lot of mineral crystal particles accumulated in the crack due to recrystallization after cooling. At 1800 °C, the number of mineral crystal particles in the crack is significantly reduced. Beyond 2200 °C, the minerals almost disappear. Since the minerals in solid form cannot migrate in the anthracite, the conclusion is reached that within this temperature range (1500−2200 °C), the minerals begin to migrate from the interior of the anthracite to the fissures in the form of gas or liquid phase and escape out of the reaction system.

Figure 7 shows the XPS spectra of the two samples of escape from the IGBT vertical ultrahigh-temperature graphitization furnace at 2800 °C. The wide scan diagram of escape No. 1 is shown in Figure 7a; it is found that the sample contains C, O, N, Al, Si, Ca, Na, Fe, Mg, and K. This is consistent with the conclusion in Table 3. The Si (5.54%) and Al (15.9%) elements whose contents are second only to C (27.64%) and O (37.3%) are scanned and fitted by different peaks. In Figure 7b, the results of these fits for Si 2p spectra are reported. It can be observed that the aluminosilicate ($E_B = 102.4 \text{ eV}$), silica ($E_B = 103.7 \text{ eV}$), and
silicon carbide ($E_B = 100.2$ eV). Figure 7c shows the results of these fits for the Al 2p spectra. It is shown that the $E_B$ of aluminosilicate is 74.2 eV and that of alumina is 73.62 eV.

The wide scan spectra of escape No. 2 is shown in Figure 7d, it is found that the sample contains C, O, N, Al, Si, Ca, Na, and K. This is consistent with the conclusion in Table 3. The Si (17.88%) and Al (10.58%) elements whose contents are second only to C (33.56%) and O (28.18%) are scanned and fitted by different peaks. In Figure 7e, the results of these fits for Si 2p spectra are reported. It is shown that the aluminosilicate ($E_B = 102.4$ eV), silica ($E_B = 103.7$ eV), silicon carbide ($E_B = 100.2$ eV), and elemental silicon ($E_B = 99.8$ eV). Figure 7f shows the results of these fits for Al 2p spectra. It can be observed that the $E_B$ of aluminosilicate is 74.2 eV and that of alumina is 73.62 eV.

Figure 8 shows the SEM–EDS spectrum of the escapes from the Taixi industrial ultrahigh-temperature graphitization furnace at 2800 °C. This is consistent with the conclusion in Figure 7. This indicates that Si not only performs a catalytic function in
the conversion of amorphous carbon to graphite, it is carried out also by inert gas in the form of oxide.\textsuperscript{19} Aluminum is carried out also by inert gas in the form of oxide. These oxides, combined with basic metal oxides, escape to form aluminosilicate in the flue gas as seen in the examination of Figures 7 and 8.

Due to the existence of a large amount of the carbon skeleton in the coal, the probability of mutual contact of various minerals is reduced, consistent with the conclusion of the occurrence in the coal, the probability of mutual contact of various minerals (calcite), and sulfate minerals (bassanite), among which clay minerals have the highest content, accounting for 55%, and most of them are dispersed in vitrinite in which clay minerals have the highest content, accounting for 55%, and most of them are dispersed in vitrinite in the anthracite in different temperature ranges mainly react as follows.\textsuperscript{51—53}

Below 1200 °C:
\[
\begin{align*}
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 & \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O} \tag{1} \\
2(\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2) & \rightarrow 2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \text{ (Al–Si spinel)} + \text{SiO}_2 \text{ (tridymite)} \tag{2} \\
2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 & \rightarrow 2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \text{ (pseudomullite)} + \text{SiO}_2 \text{ (tridymite)} \tag{3} \\
\text{CaCO}_3 & \rightarrow \text{CaO} \text{ (quicklime)} + \text{CO}_2 \tag{4} \\
\text{Fe}_2\text{O}_3 & \rightarrow \text{Fe} + 2\text{S} \text{ (sulfur)} \tag{5} \\
2\text{Na}_2\text{SO}_3 \cdot \text{H}_2\text{O} & \rightarrow 2\text{Na}_2\text{SO}_4 \text{ (anhydrite)} + \text{H}_2\text{O} \tag{6} \\
2\text{KAl}_2\text{Si}_2\text{O}_8 \cdot \text{H}_2\text{O} & \rightarrow \text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 + 2\text{H}_2\text{O} \tag{7}
\end{align*}
\]

Kaolinite loses water at 600–650 °C to form metakaolin, which decomposes into the Al–Si spinel and tridymite at 925–1000 °C. As the temperature increases, the Al–Si spinel forms pseudomullite and tridymite. Calcite decomposes at about 650 °C to produce quicklime and carbon dioxide. Pyrite is decomposed into elemental iron and elemental sulfur, and elemental sulfur escapes from the anthracite in the form of gas at ultrahigh temperature. The bassanite gradually loses water from 300 °C and turns into anhydrite. Illite is the main clay mineral containing potassium silicate in coal, and dehydration, dihydroxylation, decomposition, and other reactions occur from 850 °C.

1200 – 1500 °C:
\[
\begin{align*}
3(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) & \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \text{ (mullite)} + \text{SiO}_2 \text{ (cristobalite)} \tag{8} \\
\text{CaSO}_4 \text{ (anhydrite)} & \rightarrow \text{CaO} \text{ (quicklime)} + \text{SO}_2 \tag{9} \\
\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 & \rightarrow \text{K}_2\text{O} \uparrow + 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \text{ (mullite)} \tag{10} + 4\text{SiO}_2 \text{ (cristobalite)}
\end{align*}
\]

When the temperature is higher than 1200 °C, pseudomullite forms mullite and cristobalite. Illite also decomposes into mullite and cristobalite. In this process, anhydrite can be decomposed into quicklime and sulfur dioxide. The basic metal oxides escape in the form of gas at this temperature.

Most of the quartz (including primary quartz and the quartz obtained from the decomposition of clay minerals) is combined with basic metal oxides (Na\textsubscript{2}O, K\textsubscript{2}O, etc.) that have escaped and condurum to form aluminosilicate in the flue.

\[
\begin{align*}
4\text{SiO}_2 & + \text{Al}_2\text{O}_3 \rightarrow 2\text{NaAlSi}_2\text{O}_6 \tag{11} \\
4\text{SiO}_2 & + \text{Al}_2\text{O}_3 + \text{K}_2\text{O} \rightarrow 2\text{KAlSi}_2\text{O}_6 \tag{12} \\
1500 – 1800 °C \\
3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{CaO} & \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \text{ (anorthite)} \tag{13} \\
\text{CaO} + \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 & \rightarrow 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \tag{14} \text{ (gehlenite)}
\end{align*}
\]

As the temperature rises, a small amount of quicklime with higher activity reacts with other minerals to produce anorthite and gehlenite. However, these minerals are not stable and decompose into liquid oxides, which are discharged from the cracks of the coal and finally escape out of the furnace with inert gas. These oxides will react again in the flue gas during the escape process to form a glass phase. Quicklime is also a very effective flux for aluminosilicate, which can form a eutectic.

\[
\begin{align*}
1800 – 2200 °C \\
3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 & \rightarrow 3\text{Al}_2\text{O}_3 \text{ (corundum)} + 2\text{SiO}_2 \text{ (quartz)} \tag{15} \\
\text{SiO}_2 & + 2\text{C} & \rightarrow \text{SiC} + \text{CO}_2 \uparrow \tag{16} \\
\text{SiC} & \rightarrow \text{Si} + \text{C} \text{ (graphite)} \tag{17} \\
\text{Si} + \text{C} (\text{amorphous carbon}) & \rightarrow \text{SiC} \tag{18}
\end{align*}
\]

A small part of the quartz stays in the high-temperature furnace cavity. According to the theory of carbon conversion, quartz reacts with amorphous carbon to form silicon carbide, which then decomposes into graphite and then continues to combine with amorphous carbon, cyclically.

4. CONCLUSIONS

The research results show that the mineral components of the Taixi anthracite mainly include clay minerals (illite, kaolinite), oxide minerals (quartz), sulfide minerals (pyrite), carbonate minerals (calcite), and sulfate minerals (bassanite), among which clay minerals have the highest content, accounting for 55%, and most of them are dispersed in vitrinite in fine particles. The second is quartz, accounting for 31%, and the contents of other minerals are less. A series of reactions take place during the high-temperature graphitization. The majority of the minerals decompose at about 1500 °C and begin to migrate from the inside of the anthracite to the cracks in the form of gas or liquid and escape the furnace cavity with the inert gas. In fact, between 1800 and 2200 °C, the mullite decomposes into corundum and liquid quartz. Most of the Al and Si escape out of the furnace cavity in the form of oxides during the graphitization process of anthracite. After
reaching 2700 °C, only a small amount of silicon remains as a catalyst in the high-temperature system. These oxides (Al2O3, SiO2, etc.) react again in the flue to form a glass phase or aluminosilicate.

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L.W. performed the investigation and formal analysis and wrote the original draft. T.Q. and J.Y. did the investigation and formal analysis. Z.G. and X.S. did the investigation. L.W., T.Q., Z.G., X.S., J.Y., and Y.W. did the writing, reviewing, and editing. J.Y. performed conceptualization and supervision.

**Notes**

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