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EFFECT OF PARAMETERS OF THE ANTHRACITE HEAT TREATMENT ON THE PROPERTIES OF CARBON MATERIALS DURING SHOCK HEATING

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The aim of the study was to experimentally determine the effect of the heat treatment parameters of anthracites from Donetsk basin on the properties of carbon materials when using shock heating, typical of furnaces with a fluidized electrothermal bed. Anthracite was treated in an electric thermal furnace at the heating rate of 1000 K/min and the holding time of 10–20 min. The processing temperature range was 1500–3000^{0}C. For processing, we used initial anthracites and anthracites after calcination at 1100–1200^{0}C. The properties of the carbon material were investigated by X-ray radiographic analysis, XRF analysis and diffuse reflectance infrared Fourier transform. It was found that pre-calcination did not produce any effect on the properties of anthracite carbon materials during shock heating and holding time less than 1 hour. Based on the results of studies of anthracite heat treatment while changing the holding time, the following kinetic characteristics of transformations during shock heating were determined: the pre-exponential coefficient of 1.79 and the apparent activation energy of 103.85 kJ/mol. Thermal processing of anthracite from Donetsk coal basin in electric furnaces with the fluidized bed at the temperature 3000^{0}C for 55–60 min allows obtaining the crystalline structure characteristic of artificial graphite with necessary electroconductivity and element composition.

Keywords: anthracite, heat treatment, shock heating, electrothermal fluidized bed, X-ray analysis, infrared spectroscopy, kinetic dependence.

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Introduction

The mandatory properties of graphitized carbon materials generally include electrical conductivity, density, mechanical properties, special chemical composition (carbon content and residual ash content). All these properties are largely determined by the crystal structure of the carbon material, which, during heat treatment, undergoes rearrangement approaching the graphite structure. Simultaneously with restructuring, complex physical and chemical processes occur that influence both the chemical composition and the ordering of the carbon atoms. These can include:

– polymerization processes at 1000–1200^{0}C (calcination) and removal of volatiles,

– solid-phase reactions of carbide formations and their decomposition with the temperature increase, which is one of the probable mechanisms of ash elements catalytic effect on the carbon material structure and, accordingly, its properties.

The aim of this study was to determine the effect of anthracite pre-calcination and ash elements on the properties of carbon materials during high-temperature heat treatment. Changes in the indicators

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of their structure were chosen as an integral characteristic of the influence of physical and chemical processes on the properties of carbon materials.

Over the past two decades, three main groups of scientists can be distinguished who have been systematically engaged in the study of graphite production from anthracite. They include the following research groups: University of Mining and Technology, China [1–3]; Pennsylvania State University, USA [4–8]; and Instituto de Ciencia y Tecnologia del Carbono, Spain [9–11]. Interest in anthracite is associated with the idea of replacing the known precursors in obtaining artificial graphite (petroleum coke, etc.). It is connected, first of all, with the lower price of anthracite.

The research of Instituto de Ciencia y Tecnologia del Carbono is based on the process of high-temperature thermal treatment of Spanish anthracite from the Villablino zone: semianthracite AF with the ash content of 19.74% and anthracite ATO with the ash content of 10.12%. The main components of ash were Al, Fe, K and Si. Thermal treatment was carried out both with and without pre-calcination of anthracite during heating to 1000°C. The studies were conducted in the temperature range of 2000–2800°C with holding time of 1–4 hours. Heating was carried out at the rate of 10–20°C/min. As a result, a significant influence of temperature on the process of crystal structure rearrangement was shown, with two stages associated with the kinetics of the process indicated: the first stage at 2000–2400°C, which is characterized by an intensive increase in the crystallinity of anthracite; and the second stage at temperatures >2400°C, which leads to a significant slowdown of the graphitization process. The duration of holding in the studied temperature range insignificantly influenced the final result of the treatment.

The effect of calcination on the final result of graphitization was pronounced for anthracites with an insufficiently high degree of metamorphism. The main result of the studies confirmed the possibility to obtain artificial graphite from anthracite corresponding to the crystallinity indices for the known grades of artificial graphite based on traditional precursors. In these works, the possible influence of ash composition on the final result of treatment was indicated, but the graphite purification indicators after treatment were absent.

Studies conducted at Pennsylvania State University are aimed at replacing coke in the manufacture of synthetic graphite products. The studies determined the effect of temperature on the graphitization process. Two sets of anthracites were investigated: the first anthracites are from the Lykens Valley (DECS 21), Mammoth (PSOC 1461), and Buck Mountain (PSOC 1468) seams in Pennsylvania with the ash content of 11.16; 24.18; and 6.83% respectively [7]; and the second anthracites from Buck Mountein, Jeddo, LSNN, Sammit, Trevorton, UAE with the ash content of 6.7–17.6% [6]. The studies were carried out in the temperature range of 2000–2900°C with the holding time of 1–5 hours. As a result, a significant effect of temperature on the properties of carbon materials was confirmed. The graphitization degree reached 0.942 and more. Ash content of anthracite of LSNN grade was 0.001%, which corresponds to the requirements for battery graphite.

Particular attention was paid to the influence of ash on the properties of carbon materials. The results of treatment with the same parameters of initial anthracite and demineralized ones are given [7]. At the same time, the degree of graphitization slightly increased according to X-ray diffraction analysis. It was stated [4] that after the treatment, the initial anthracite had a three-dimensional structure confirmed by the appearance of reflex (112) on X-ray diffractogram, while in the case of demineralized anthracite it was absent on X-ray diffractograms. The reappearance of reflex (112) was observed after artificial increase in ash content. Thus, it is impossible to assert the positive effect of ash as a catalyst on the graphitization process definitively.

Research of Chinese scientists is based on experimental studies of heat treatment of anthracite at Taixi Coal Preparation Plant (Ningxia, Chaina) with the ash content of 2.85%. The samples with the size 2×2×1 cm were heated in a neutral atmosphere. Parametric studies of the heating rate effects of the furnace (5–20°C/min), holding time (1–4 hours) and processing temperature (1500–3000°C) were carried out. As a result of the studies, it was determined that the heating rate in this range had little effect on the final result of treatment: the final ash content changed only by 0.81–0.86%, and the degree of graphitization reached 94.9–95.5%. In further studies, the heating rate was assumed to be 10°C/min. The selected time of exposure at a constant temperature was 3 hours, which corresponds to the maximum value of graphitization degree. With a further increase in the processing time, the degree of graphitization when the material was heated up to 3000°C practically did not change. The peculiarity of these studies was that the residual ash content (A^d 0.17%) significantly exceeded the standard requirements for graphite of lithium-ion batteries,

which is apparently due to the large size of the investigated samples.

As a result of thermodynamic studies of the graphitization process similar to work [12], based on the analysis of changes in heat capacity, heat of combustion and entropy, a three-stage mechanism of anthracite graphitization was proposed:

– the first stage, up to 1500^{0}C – removal of moisture and volatiles, formation of cracks, polycondensation reaction, decomposition of carbonates and removal of sulfur;

– the second stage, 1500–2200^{0}C – ordering of the structure, reduction of the inter-layer distance, transition of oxides to the liquid phase and their evaporation, which is accompanied by chemical interactions and the formation of eutectics;

– the third stage, 2200–3000^{0}C – recrystallization and elimination of lattice defects, formation and decomposition of carbides. In this case, most of the silicon is removed in the form of oxides, and only a small part is involved in the formation of carbides and may affect the graphitization of anthracite.

The latter is confirmed by direct studies of the amount of silicon in the heat treatment, which showed little effect of silicon content on the degree of graphitization. At the same time, its influence of graphite structure was shown [3].

Summarizing the results of previous studies, we can formulate the following. It is possible to obtain anthracite-based artificial graphite with structural characteristics corresponding to those of traditional grades based on petroleum coke. To obtain the necessary indicators, it is preferable to use highly metamorphic coal grades. The positive influence of pre-calcination on the process of anthracite structure rearrangement is not conclusively proved, neither is the catalytic effect of ash elements. At the same time, the research parameters (heating rate and holding time), as a rule, correspond to the technologies of processing materials in Acheson furnaces or chamber furnaces with indirect material heating.

The use of high-capacity technology of anthracite processing in the electrothermal fluidized bed (EFB) [13,14] provides heating at a rate up to 1000^{0}C/min and holding time up to 30 minutes. This significantly differs from the experimental conditions given in the literature and requires additional research in order to confirm the possibility of using the EFB technology to produce carbon material of the required quality based on anthracite.

Experimental

Materials and graphitization process

Anthracite from Donetsk coal basin with the ash content Ad=3.32% was chosen for the study. Based on XRF analysis of the initial anthracite, the content of the main ash components was determined as follows: Al 29.6%, Si 49.0%, Mg 5.5%, Fe 12.0%, and Ca 3.9%. FTIR spectrum of ash from the initial anthracite showed asymmetric and symmetric valence as well as strain vibrations of metal oxygen bonds of various oxides: Si–O–Si(Al) 1042, 944, 915, 747, 610, 548, 489, 431 cm^{-1}; Fe–O–Fe 572, 519, 410 cm^{-1}; Ti–O–Ti 594, 395 cm^{-1} and others.

The grain size class of 1000–100 μm was used for the study.

Thermal treatment was carried out in an electric chamber furnace of special design [14], which provided a heating rate of up to 1000^{0}C/min. Exposure time was 10 and 20 minutes. Heating was carried out to temperatures of 1500^{0}C, 1800^{0}C, 2100^{0}C, 2400^{0}C, 2700^{0}C, and 3000^{0}C. Two series of research were carried out: the first for initial anthracite and the second for anthracite that was pre-calcinated at the temperatures of 1000–1100^{0}C for 1 hour.

Analysis and testing

XRD analysis was performed on a Rigaku UltimaIV Diffractometer at 23^{0}C; the scanning angle range was 5–90^0 with the scanning step of 0.02^0. The structure was evaluated by the interlayer spacing (d002) and the mean crystallite height (Lc). In addition, the degree of graphitization (DOG) was determined by the following well-known formula:

$$DOG = \frac{0.3440 - d_{002}}{0.3440 - 0.3354}, \quad (1)$$

where 0.3440 nm is the interlayer spacing of carbon with no graphitic order and 0.3354 nm is the interlayer spacing of graphite.

The process of graphite purification was observed using XRF analysis was conducted via a detector «Oxford X-max 80». The microscopic photos of graphite samples were obtained via a Tescan Mira 3 LMU microscope.

The content of heteronuclear bonds in the molecular structure of anthracite during heating was evaluated by diffuse reflectance FTIR spectrometry (DRIFT) using a Nicolet iS10 spectrometer (Thermo Scientific).

Results and discussion

The initial structure of anthracite belongs to turbostratic type, and pre-calcination has almost no effect on it (Fig. 1, Table). The ash is found both as individual rock particles and as inclusions in

anthracite particles. The distribution of ash inclusions has a point character and, apparently, cannot affect the uniform transformation of anthracite structure into graphite (Fig. 2,a).

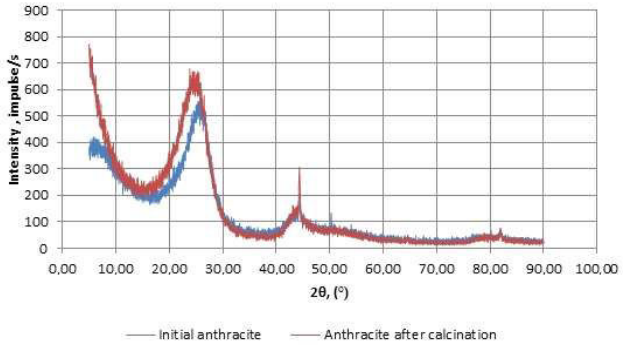
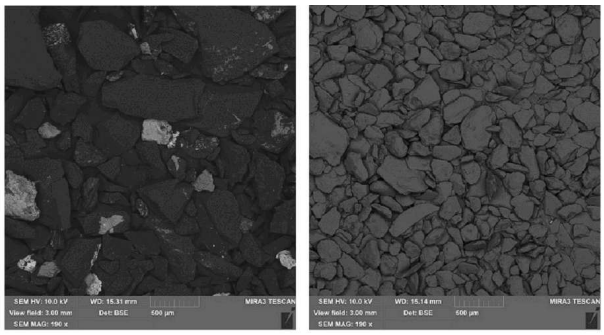


Fig. 1. XRD of the initial anthracite

Influence of pre-calcination

Intense heating of anthracite particles in the electrothermal fluidized bed could cause a significant change in the porosity and density of graphite due to the intense yield of volatiles, as well as have a corresponding effect on the rearrangement of the crystal structure of the material [13,15]. However, the results of direct experiments with anthracite from Donetsk basin, which we carried out, showed that the effect of pre-calcination on the graphitization process is practically absent. A decrease in the value of interlayer distance d002 and a growth of crystallite height Lc coincided both in magnitude and in the dynamics of the process when treating anthracite without calcination and with pre-calcination (Fig. 3). Moreover, calcination led to some decrease in crystallite height.



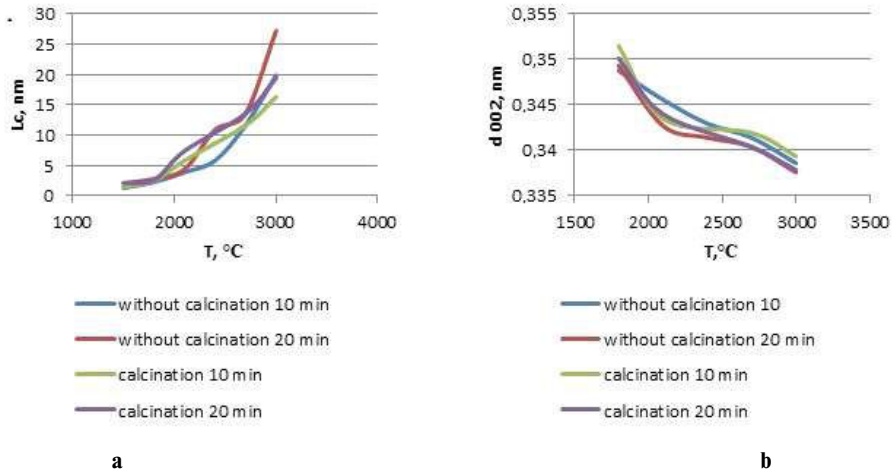
a **b**

Fig. 2. Microphotographs of graphite samples obtained with Tescan Mira 3 LMU microscope: a – initial anthracite, b – after thermal treatment at 3000°C

The dynamics of changes in the interlayer distance d002 (Fig. 3,b) allows us to distinguish three stages of the graphitization process at intensive heating and short holding time. The first stage, at <2000–2100°C, formation of two-dimensional

The results of anthracite graphitization

Source material	Graphitization temperature, °C	Exposure time, min	d002, nm	Lc, nm	DOG, %
No calcination	1500	10	3.490	13.137	–
		20	3.497	20.619	–
	1800	10	3.488	22.626	–
		20	3.493	28.086	–
	2100	10	3.456	38.806	–
		20	3.427	44.070	15.24
	2400	10	3.429	58.233	12.22
		20	3.414	108.728	27.26
	2700	10	3.414	116.494	28.76
		20	3.404	135.932	42.19
	3000	10	3.386	198.981	62.89
		20	3.376	271.985	74.62
Calcination at the temperature of 1000–1100°C	1500	10	3.501	15.081	–
		20	3.531	20.873	–
	1800	10	3.515	24.673	–
		20	3.501	26.270	–
	2100	10	3.435	58.228	–
		20	3.440	74.103	6.18
	2700	10	3.419	116.484	24.27
		20	3.404	135.932	42.19
	3000	10	3.394	163.144	54.04
		20	3.378	194.267	71.69



a b

Fig. 3. Change of crystallite height Lc (a) and interlayer distance d002 (b) as a function of processing temperature and exposure time

structure and high dynamics of d002 decrease; the second stage, 2100–2700°C, decrease in the rate of interlayer distance change, removal of most ash elements and formation of carbides; and the third stage, 2700–3000°C, formation of three-dimensional graphite structure and its improvement, which is confirmed by appearance of hkl (110, 112, 006) reflections (Fig. 4). Thus, the catalytic effect of ash elements through the formation of carbides during shock heating was not confirmed.

Drift spectra of initial anthracite and that after heat treatment at 3000°C for 20 minutes (Fig. 5) showed the reduction of heteronuclear bonds in the carbon matrix and intercalated molecules after heating. In particular, in the absorption bands of the valence and strain vibrations (3300±80 cm^{-1} and 1610 cm^{-1}), the content of hydroxyl groups of bound water decreased. The vibrations of SiO_2 (diffuse peak at 1100 cm^{-1}) and iron oxide (at 536 cm^{-1}) also decreased. There are vibrations of heteroatoms (O, S, and N) in the range of 400–1500 cm^{-1} included in the carbon matrix, whose intensity decreased significantly. Thus, the analysis of IR spectra confirmed the purification of the carbon matrix and the decrease in the entropy of the molecular structures of the initial anthracite resulted from the thermal treatment.

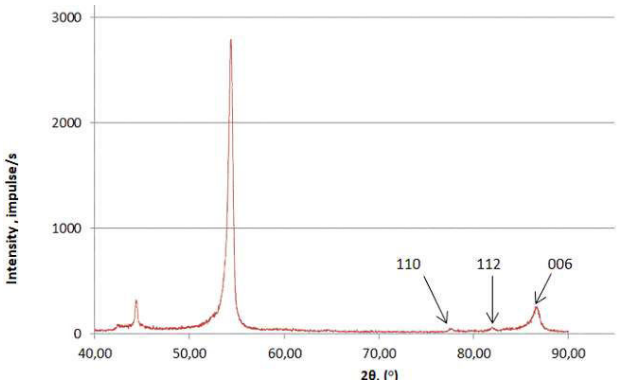


Fig. 4. X-ray diffractogram of anthracite after graphitization at 3000°C and the exposure time of 20 minutes

Kinetics of the graphitization process

As shown above, in addition to temperature, the duration of exposure has a significant influence on the final result of anthracite heat treatment, especially at the initial stage of the process [12,13]. Increasing the holding time from 10 to 20 minutes allowed reducing the interlayer distance d002 by about 10% as compared to the effect of temperature. Thus, the duration of processing can allow the degree of graphitization of anthracite to significantly approach the state of traditional artificial graphites having d_{002}=3.36–3.367 [9,11].

The kinetics of the graphitization process was investigated on the basis of the graphitization degree DOG, using the following monomolecular kinetic equation similar to [12]:

$$DOG = 1 - \exp(-K\tau), \quad (2)$$

where K is the rate constant of the graphitization process (min^{-1}), and τ is the duration of isothermal exposure (min).

The pre-exponential coefficient A=1.79 was determined based on the dependence of the process rate constant on temperature (Fig. 6) and the Arrhenius equation, with apparent activation energy E_a=103.85 kJ/mol.

Using the obtained kinetic characteristics, we evaluated the duration of exposure, which will provide the degree of anthracite graphitization, typical for

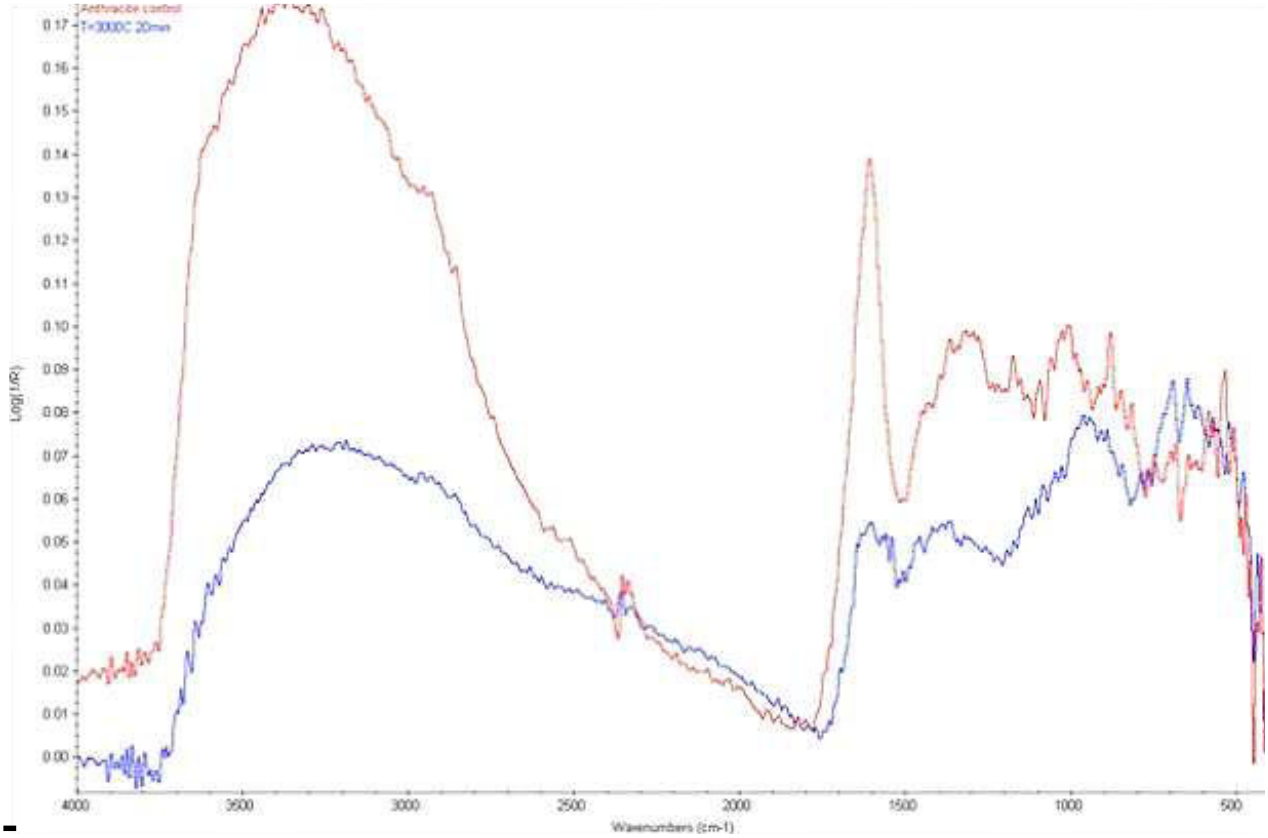


Fig. 5. Drift spectra of initial anthracite and that after heat treatment at 3000°C with a holding time of 20 minutes

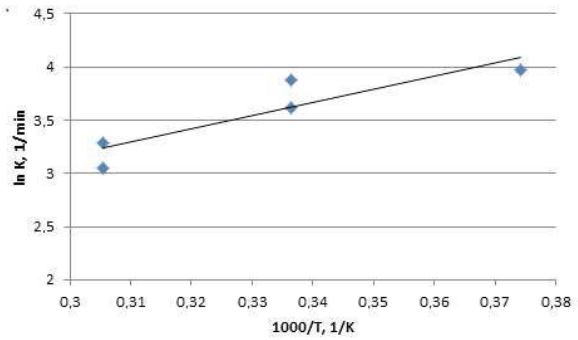


Fig. 6. Dependence lnK vs. reciprocal temperature according to Table

artificial graphite of traditional grades (DOG>93%). At the exposure temperature of 3000°C, its duration should be 50–60 minutes. Taking into account that increasing the holding time at the expense of anthracite staying in the fluidized bed significantly affects the increase in the size of EFB furnace and reduces its productivity, the possibility of holding the heated material in the dense bed after unloading from the working space of the furnace is promising.

Conclusions

The study of the heat treatment of anthracite from Donetsk coal basin by shock heating in the temperature range of 1500–3000°C and holding time of 10–20 min allowed us to draw the following conclusions:

– pre-calcination of anthracite at 1000–1100°C has no effect on the change in its structure during heat treatment;

– the following kinetic characteristics of graphitization process at shock heating were established: the pre-exponential coefficient A=1.79 and the apparent activation energy E_a=103.85 kJ/mol.

Based on the obtained data, we determined the holding time 55–60 min at 3000°C, which would provide the graphitization degree typical for artificial graphite of traditional grades (DOG>93%).

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ВПЛИВ ПАРАМЕТРІВ ТЕРМІЧНОГО ОБРОБЛЕННЯ АНТРАЦИТУ НА ВЛАСТИВОСТІ ВУГЛЕЦЕВИХ МАТЕРІАЛІВ ПРИ ШОКОВОМУ НАГРІВІ

Сибір А.В., Губинський М.В., Балалаєв О.К., Бурчак А.В., Сухий К.М., Федоров С.С., Пінчук В.О., Губинський С.М., Введенська Т.Ю.

Мета дослідження – експериментальне визначення впливу параметрів теплового оброблення антрацитів Донецького басейну на властивості вуглецевих матеріалів при використанні шокового нагріву, характерного для печей з електротермічним киплячим шаром. Оброблення антрацитів здійснювалось в електротермічній печі при швидкості нагріву 1000 К/хв, тривалість витримки 10–20 х. Температурний діапазон досліджень 1500–3000^{0}С. При обробленні використані вихідні антрацити та антрацити після кальцинації при температурі 1100–1200^{0}С. Дослідження матеріалу проводилося методами рентгенографічного аналізу, XRF аналізу та дифузійного відображення в інфрачервонім світлі. Встановлено, що при шоковому нагріві та витримуванні менш 1 год вплив попередньої кальцинації на властивості вуглецевих матеріалів з антрациту не спостерігається. На основі досліджень термічного оброблення антрациту при зміні терміну витримування визначено кінетичні характеристики перетворень при шоковому нагріві: передекспоненційний коефіцієнт 1,79 та уявна енергія активації 103,85 кДж/моль. Визначено, що тривалість термічного оброблення антрациту Донецького вугільного басейну в електротермічних печах киплячого шару, що дорівнює 55–60 хв при температурі 3000^{0}С, забезпечує одержання кристалічної структури, характерної для штучних графітів з необхідною електропровідністю та елементним складом.

Ключові слова: антрацит, термічне оброблення, шоковий нагрів, електротермічний киплячий шар, рентгенографічний аналіз, інфрачервона спектроскопія, кінетичні залежності.

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The aim of the study was to experimentally determine the effect of the heat treatment parameters of anthracites from Donetsk basin on the properties of carbon materials when using shock heating, typical of furnaces with a fluidized electrothermal bed. Anthracite was treated in an electric thermal furnace at the heating rate of 1000 K/min and the holding time of 10–20 min. The processing temperature range was 1500–3000°C. For processing, we used initial anthracites and anthracites after calcination at 1100–1200°C. The properties of the carbon material were investigated by X-ray radiographic analysis, XRF analysis and diffuse reflectance infrared Fourier transform. It was found that pre-calcination did not produce any effect on the properties of anthracite carbon materials during shock heating and holding time less than 1 hour. Based on the results of studies of anthracite heat treatment while changing the holding time, the following kinetic characteristics of transformations during shock heating were determined: the preexponential coefficient of 1.79 and the apparent activation energy of 103.85 kJ/mol. Thermal processing of anthracite from Donetsk coal basin in electric furnaces with the fluidized bed at the temperature 3000°C for 55–60 min allows obtaining the crystalline structure characteristic of artificial graphite with necessary electroconductivity and element composition.

Keywords: anthracite; heat treatment; shock heating; electrothermal fluidized bed; X-ray analysis; infrared spectroscopy; kinetic dependence.

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