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Effect of heat shock on graphitization of Donbass anthracite

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Abstract

Purpose. The aim is to conduct experimental research into graphitization process of anthracites from the Donbass basin using shock heating, which is characteristic of furnaces with electrothermal fluidized bed.

Methods. Graphitization was carried out in an electrothermal furnace at the heating rate of 1000 K/min and exposure time of 10 minutes. The temperature range of the studies was 1973-2873 K. The structure of the material was studied by X-ray diffraction and the electrical conductivity of the coal particles layer was determined using a CamScan 4DV scanning electron microscope with Link760 attachment. The changes in ash and sulfur content were determined.

Findings. It was found that with an increase in the processing temperature, the interlayer distance d_{002} decreased from 0.350 to 0.341 nm, the ash content decreased from 3.46 to 0.4%, and the relative electrical conductivity increased by 4 times. The absolute value of anthracite graphitization degree significantly differed from the values characteristic of artificial graphite. This may be due to insufficient exposure at the studied temperatures, as well as the production of a porous, insufficiently densified coal structure during high-speed heating to 1573 K.

Originality. The principal possibility of obtaining graphitized anthracite using shock heating in furnaces with electrothermal fluidized bed and the possibility of assessing anthracite graphitization degree by the value of the relative conductivity of coal particles layer are shown.

Practical implications. The practical implementation of the new technology is possible after determining the optimal parameters for graphitization of anthracites, which provide a deep structural adjustment characteristic of artificial graphites. First of all, this concerns the preliminary heating of anthracite to the temperature of 1273-1373 K, as well as choosing the temperature and exposure during graphitization. Determination of these parameters will allow to evaluate the technical and economic indicators of the new technology and to adjust the design parameters of furnaces with electrothermal fluidized bed.

Keywords: *graphitization, anthracite, shock heating, electrothermal fluidized bed, X-ray analysis, electrical conductivity*

1. Introduction

Coal is one of the most important energy resources, whose share in global energy consumption is 28%, and the share in Ukraine's electricity generation is about 44%. That is, coal is a resource that ensures the country's energy security. However, one of the main trends in the development of the coal industry in the world is reduction in the production and consumption of coal. This is happening due both to the economic crisis and increased competition in the energy market, as well as to the decarbonization of the economy and the fulfilment of obligations to reduce greenhouse gas emissions. Thus, the volume of emissions by 2050 should not exceed 1000 Gt CO_2, and this can only be realized if 88% of the world's proven coal reserves remain in the ground. This applies both to the energy industry, where solar and wind power plants are being actively commissioned, and to metallurgy developing hydrogen-free coke technologies. Pilot projects aimed at replacing coke with hydrogen are already being implemented in a number of European countries.

In this situation, the development of coal consumption as a raw material resource for the chemical industry and a carbon source for producing carbon materials and artificial graphite is of particular importance for the coal industry. The integrated development of the coal industry, on the one hand, ensures the stability of its functioning, on the other hand, it allows the production of products with added value, which will positively affect the economic performance of the coal industry.

In recent years, markets for electric batteries have been actively developing, consumers of which are power plants based on renewable energy sources, electric vehicles, gadgets, etc. The forecast of graphite consumption for anodes of lithium-ion batteries will be about 1600 thousand tons per

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year by 2027 [1]. The increase in the share of electric steel production among traditional metallurgical technologies requires an increase in the production of electrode products [2]-[4]. The development of metallurgical technologies involves the use of a large number of carburizers – pure carbon materials for carburizing steel and synthetic cast iron [5].

The most promising material for producing graphitized products is anthracite. The issues of its heat treatment for the purpose of graphitization have remained relevant for several decades [4], [6]-[8]. The purpose of the present research was to determine the influence of processing parameters (temperature, processing time, composition of the gas atmosphere, pressure) and the initial structure of the graphitized material on the formation of the structure and properties of artificial graphites, as well as the mechanisms and kinetics of anthracite restructuring.

Industrial technology for the thermal treatment of anthracite includes two stages:

– the first stage – preliminary heat treatment (calcination) to obtain thermoanthracite. When processing in fuel furnaces (rotary, retort), the heating is carried out to a temperature of 1173-1473 K. This is accompanied by the removal of volatiles and partially sulfur, the beginning of a change in the structure of the material and a sharp decrease in electrical resistance. In the case of processing in an electrocalcinator, the material is heated due to the heat of the exhaust gases to a temperature of 1173-1473 K, and then by direct electric heating in a dense layer to temperatures of 1873-2073 K [3]. When heated to 1873-2073 K, sulfur removal is completed and the process of structural adjustment of the material continues, its density increases, while the electrical resistance of the material changes slightly.

– the second stage – graphitization process at temperatures up to 3273 K in the Acheson furnace, Castner furnace or LWG furnace. Final processing at high temperatures is characterized by a decrease in the ash content and electrical conductivity of the material, by ordering its structure, approaching that of a natural graphite [9]. The duration of anthracite treatment at all stages is from an hour to several dozens of hours, including the time of heating the material to the exposure temperature. The choice of heat treatment modes in the study of anthracite graphitization corresponded to practical modes.

Table 1 are the heat treatment modes used to study the graphitization processes of anthracites from various deposits [6], [10]-[19]. Analysis of these modes shows that the heating rates in the experiments were 2-10 K/min, and the exposure time was 60-240 min. In [10], [11], the exposure time was lower, but the low heating rate of the material, in fact, leveled this indicator.

Table 1. Anthracite graphitization modes used in the research

Material	Calcination			Graphitization				References
	t, K	*τ*, min	*V*, K/min	*t*, K	*τ*, min	*V*, K/min	Gas	
Anthracite of the Gorlovsky basin	–	–	–	1473-2273	0-240	–	–	[10]
Anthracite of the Nazarailok deposit, Kazakhstan	–	–	–	up to 1473	120	5	–	[12]
Low metamorphosed anthracites, samples from particles 0.03-2.5 mm with a binder from coal tar pitch	1273	240	1.7	1473-2773	180	5	nitrogen	[6]
Donbass anthracite	–	–	–	up to 2273	0-240	10	argon	[11]
Taixi anthracite, China, sample 2×1 cm	–	–	–	up to 3273	180	10	argon	[13]
AF Anthracite from Villablino, Spain	1273	60	2	2273-3073	60-240	10	argon	[14]
Taixi anthracite, China, sample 2-3 cm	–	–	–	2273-3273	180	10	argon	[15]
Taixi anthracite, China, after grinding in a ball mill	–	–	–	1673-3073	180	2.5	argon	[16]
PSOC1515 semi-anthracite and DECS21 anthracite, Pennsylvania, USA, 250 μm samples, chemical demineralization	1693	60	4	3273	1440	–	argon	[17]
Anthracite from Pennsylvania, USA, -60 mesh samples	–	–	–	2273-2873	60	10	argon	[8]
AF and ATO Anthracite from Villablino, Spain, 200 μm samples	1273	60	2	2273-3073	60	10	–	[18]
Anthracite grade A according to ISO 11760 from Douro basin, Portugal, and Alto Chicama, Peru, grade C anthracite from Peñarroya Belmez-Espiel basin, Spain	1273	60	2	1773-2773	60	10	argon	[19]

In contrast to traditional graphitization process in Acheson or Castner furnaces, heat treatment in furnaces with electrothermal fluidized bed (EFB) provides fast heating of carbon materials and does not require pressing the workpiece using pitch and other binders [20]-[22]. Studies of the thermal treatment of oil coke in furnaces with electrothermal fluidized bed [22] showed that the influence of the heating rate affects the formation of the material structure during the first stage of heating associated with the release of volatiles. In these experiments, the formation of a closed porous structure was observed. In this case, XRD showed that the degree of graphitization, according to [23], for cokes of different initial structures was g = 72-86%. However, the authors do not indicate the temperature of the treatment and the duration of exposure. At the same time, it is known that the heat treatment process in EFB furnaces does not exceed 30 minutes, and the average temperature of the layer is 2773-3273 K.

Thus, the heating rate and the short exposure time are factors which significantly affect the results of the graphitization process. This effect on anthracites graphitization has been insufficiently studied. The present article aims to analyze the above issue, which, in our opinion, will allow to approach the development of technology for the thermal treatment of anthracite in electro-fluidized bed.

2. Experiment

2.1. Materials and graphitization process

In the experiment, we used Donbass anthracite with the ash content of 6.61%. The sulfur content was 1.27%. XRD pattern of the initial anthracite showed the presence of a turbostratic structure (Fig. 1). Material with particle sizes less than 0.5-2.0 mm was studied.

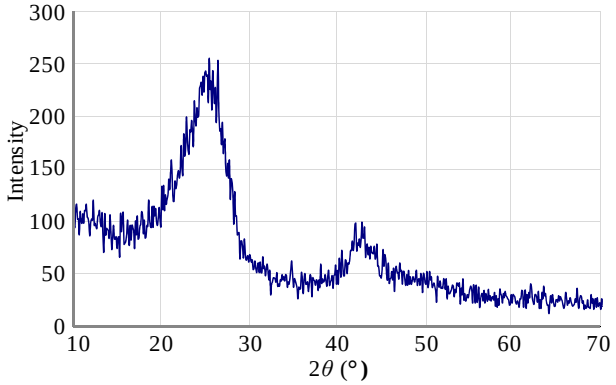

Figure 1. XRD of original anthracite

Thermal treatment of anthracite was carried out in a special electrothermal furnace, allowing heating at a high speed close to the heating rate in EFB furnaces [24]. 15-20 g of the original material was placed in the cavity of the heater (Fig. 2) to be heated to a temperature of 573-673 K at a speed of about 100 K/min to remove moisture.

Further, heating was carried out to predetermined temperatures of 1973, 2273, 2573 and 2873 K at a speed of about 1000 K/min. The exposure time at these temperatures was 10 minutes. Processing was carried out in argon atmosphere.

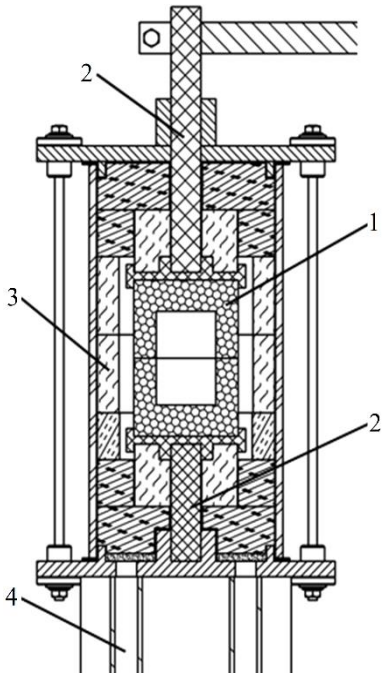

Figure 2. Scheme of a laboratory electrothermal furnace: 1 – heater; 2 – current leads; 3 – thermal insulation; 4 – inert gas supply

2.2. Analysis and testing

XRD spectra were obtained on a DRON-3M diffractometer equipped with a computer system for fixing the diffraction pattern and a graphite monochromator. The power parameters of the x-ray tube with a copper anode were 20 mA and 30 kV. Scanning of samples was carried out in increments of 0.05 degrees. with exposure at each point for 4 s. Ash content and sulfur content were determined using a Cam-Scan 4DV scanning electron microscope with Link760 attachment. The electrical resistance of the powder material after heat treatment was determined on a stand according to GOST 4668-75 with axial compression of the sample 9.6 MPa.

Changes in the structure of anthracite during graphitization were assessed by the value of interlayer spacing d_{002} calculated according to the Wulff-Bragg's law and the crystallite sizes L_c calculated by the 002 reflection and the Scherrer equation with a value of $k = 0.9$. In addition to this, an indirect characteristic of the change in the structure of the material is the dependence of its electrical conductivity; this approach was successfully demonstrated in [25]. Studies of the electrical conductivity of a dispersed carbon material [3]-[5], [26] show that its specific electrical conductivity Ω is determined by several factors: the size of particles in the layer, the pressure compressing them, the electrical conductivity of the particle material Ω_0. It is the latter indicator that can indirectly characterize the change in the structure of the graphitized material. The general view of the dependence of electrical conductivity has the form:

$$\Omega = \Omega_0 \cdot A, \quad (1)$$

where complex A includes the particle size distribution, compression pressure, and other characteristics of the dispersed material.

Thus, to analyze the change in the structure of the particle material, we used the relative value of the specific electrical conductivity referred to the electrical conductivity of anthracite after heat treatment at the temperatures of 1273-1473 K – Ω / Ω_{1000}. The choice of the base temperature of 1273-1473 K is associated with the type of dependence of anthracite electrical conductivity on temperature. Figure 3 shows the results of measuring the electrical conductivity of the anthracite layer at different temperatures and compression pressures [27], from which it follows that when heated to 1273-1473 K, the electrical conductivity increases by three orders of magnitude. With further heating, the electrical conductivity continues to grow, but the growth rate decreases sharply. This fact is well known from numerous experimental works [4], [11], [28].

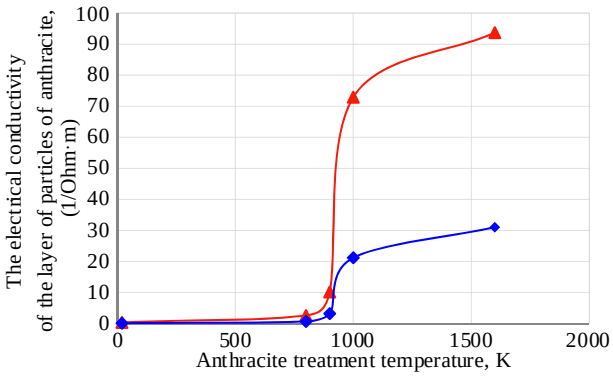

Figure 3. Dependence of anthracite electrical conductivity on the processing temperature: 1 – compression pressure 62 KPa; 2 – compression pressure 2 KPa

3. Results and discussion

The XRD analysis – XRD curves, the interlayer spacing d_{002} and the crystallite sizes L_c – are presented in Table 2 and Figures 4-6. As expected, the results show that an increase in the anthracite treatment temperature causes structural ordering, decrease in the interlayer spacing and an increase in crystallite sizes. At the same time, comparison of these dependences with the known experimental data (Figs. 5 and 6) shows that an increase in the heating rate to 1000 K/min and a decrease in the duration of exposure to 10 min negatively affect the structural rearrangement of anthracite. Dependence 6 (Fig. 5) is significantly higher than analogues, regardless of the initial structure of the studied anthracites and their chemical composition. However, the value of crystallites L_c obtained in our studies is lower than the results presented in the literature [10], [14], [18] (Fig. 6).

Table 2. The results of Donbass anthracite graphitization

Graphitization temperature, K	d_{002}, nm	L_c, nm	C, %	S, %	Ω/Ω_{1000}, relative units
1973	0.350	2.91	96.54	0.96	1.09
2273	0.349	4.29	97.00	0.6	1.41
2573	0.345	10.19	98.85	0.22	2.18
2873	0.341	10.19	99.60	0.02	4.00

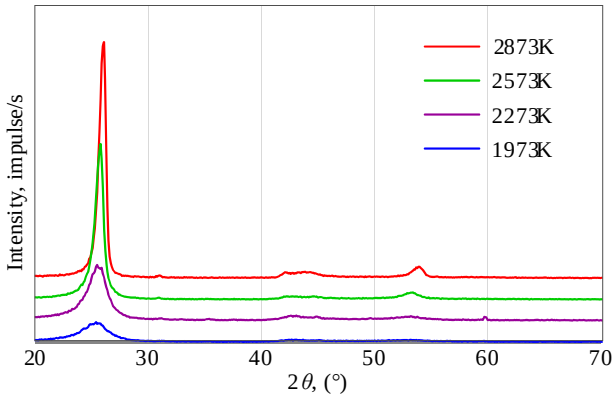

Figure 4. XRD curves of anthracite after heat treatment at temperatures of 1973, 2273, 2573 and 2873 K with exposure of 10 min and speed of about 1000 K/min

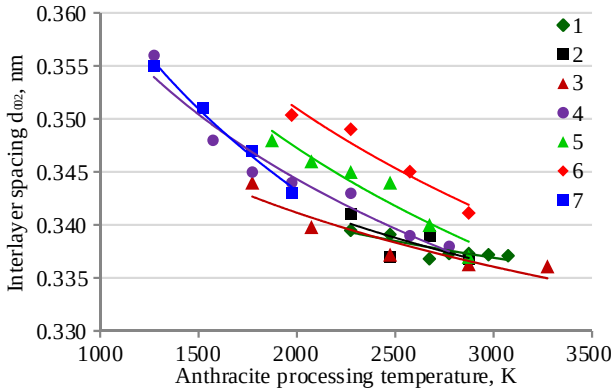

Figure 5. Dependences of the change in the interlayer spacing d_{002} on the treatment temperature of anthracites from various deposits: 1 – Anthracite AF Villablino [14]; 2 – Anthracite ATO [18]; 3 – Anthracite Pennsylvania [8]; 4 – Anthracite Taixi [13]; 5 – anthracite of the Donbass basin [2]; 6 – anthracite of the Gorlovsky basin [10]; 7 – experimental data (Table 2)

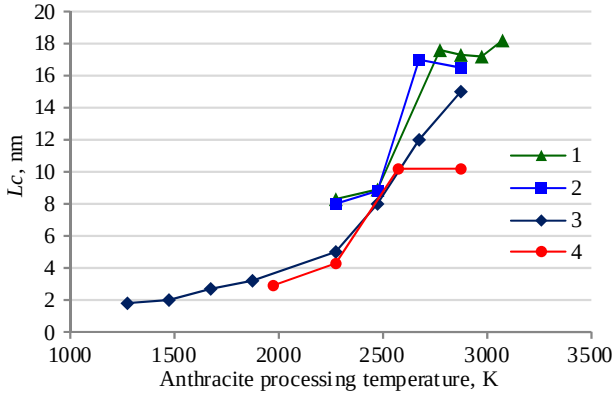

Figure 6. Dependences of changes in the crystallite height L_c on the treatment temperature of anthracites from various deposits: 1 – anthracite AF Villablino [14]; 2 – anthracite ATO [18]; 3 – anthracite of the Gorlovsky basin [10]; 4 – experimental data (Table 2)

First of all, the phenomena treated above can be explained by the kinetics of the graphitization process, which was studied in detail for petroleum coke and pyrolytic graphite [29]-[31]. The kinetic dependences of the decrease in the interlayer spacing d_{002} on the exposure time at various processing temperatures presented in these studies showed that, at a temperature of 2873 K, the graphitization process, depending on the initial structure of the graphitized material, ranged from 40 min (petroleum coke) [30] to dozens of hours for pyrocarbon [29]. Thus, graphitization of anthracite in the studied temperature range 1973-2873 K requires an increase in the exposure time or an increase in the anthracite treatment temperature to 3273 K when graphitization process is intensified.

This conclusion can also be confirmed by a change in the ash content during anthracite processing. It is known that one of the features of the anthracite graphitization process is the catalytic effect of ash inclusions (Si, Al, Fe, Ti), which form carbides during high-temperature treatment. Their decomposition results in the formation of active carbon which eliminates structural defects of the initial material [8], [19]. Changes in the carbon content of anthracite (Table 2) lead to a decrease in ash content with an increase in the processing temperature from 3.46% in the initial material to 0.4% in the material processed at 2873 K. It is known from [20]-[22], that increase in the processing temperature allows to reduce the ash content of the material to 0.05% and lower. To assess the temperature conditions for the formation and decomposition of carbides during the heat treatment of coal, the chemical composition of a multicomponent system was simulated. The initial composition of this system corresponds to the chemical composition of anthracite, at temperatures of 1300-3300 K and pressure p = 0.1 MPa. The simulation was carried out using the TERRA package [23], which allows to calculate the maximum equilibrium states and implements a method based on the maximum entropy of the system: $dS = 0$ and $d_2S < 0$. The simulation results showed that the formation of iron carbide Fe_3C is observed at 1450 K, while at 2450 K iron carbide in condensed form is absent in the chemical composition of anthracite. The presence of condensed titanium carbide TiC can be traced from 1500 to 3000 K.

The second reason for the decrease in the efficiency of anthracite graphitization during shock heating is the influence of the first stage of heat treatment associated with the

removal of volatile components, increasing density and formation of the coke residue structure. In industrial processes, the speed of preliminary firing of electrode products or graphite blocks is limited by the need to minimize the formation of cracks in finished products. In experimental studies (Table 1), either preliminary firing is performed at a temperature of at least 1273 K with a heating rate of 2-4 K/min, or the initial anthracite is heated at a low speed. In this case, pyrolytic carbon is deposited in a dense layer in the pores and on the surface of the calcinated material. Thus, its strength and density increases, while the porosity decreases. It is known that low heating rates contribute to the formation of the microporous structure of anthracite, and high heating rates result in meso- and macro- porosity [32]. So, heating anthracite in a fluidized bed at a rate of 1000 K/s led to doubling of porosity. Similar effects were confirmed in [22] during the rapid heating of petroleum coke in electrothermal fluidized bed.

As an indirect estimate of the change in the material structure during graphitization, the dependence of the relative specific conductivity of the anthracite particle layer on the decrease in the interlayer spacing d_{002} was studied (Table 1). Figure 7 presents the data from Table 1 and [10], which clearly shows the correlation between the change in the interlayer spacing and the relative electrical conductivity of the anthracite layer obtained at different processing temperatures (1573-2873 K) for Donbass and Gorlovsky anthracites, with different exposure times (10-240 min). The graph is approximated by an exponential dependence with a correlation coefficient $R^2 = 0.94$. Similar results were obtained by the authors of experimental works [25], [31]. They present empirical dependences that relate the increase in the electrical conductivity of a carbon material to an increase in the crystallite size L_a [31] and a decrease in the interlayer spacing d_{002} [25]. Thus, measurement of the electrical conductivity of anthracite particle layer can fairly accurately characterize the degree of anthracite structure ordering during graphitization in fluidized bed.

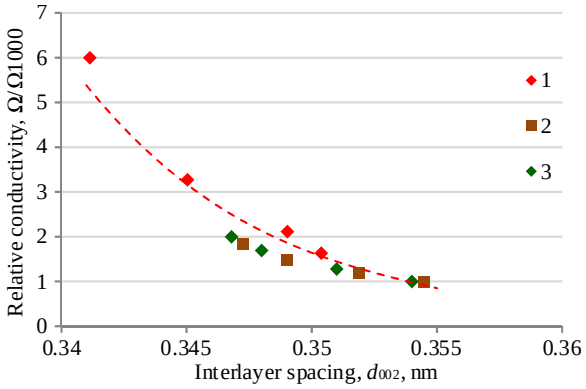

Figure 7. Dependence of the relative conductivity Ω/Ω_{1000} on the interlayer spacing d_{002} for anthracites of the Donbass and Gorlovsky deposits: 1 – anthracite of the Donbass basin, exposure 10 min (Table 1); 2 – anthracite of the Gorlovsky basin, exposure 60 min [10]; 3 – Gorlovsky basin anthracite, exposure 240 min [10]

The results showed a fundamental possibility of obtaining graphitized anthracite using shock heating in furnaces with electrothermal fluidized bed. The use of these furnaces will improve the uniformity of heat treatment and the quality of thermoanthracite due to an increase in the processing temperature compared to electric calcinators. In this case, the energy intensity of the process will remain at the same level. This will improve the quality of the electrode products used in steel and aluminum production.

The practical implementation of the new technology is possible after determining the optimal parameters of anthracite graphitization, which will provide a deep restructuring characteristic of artificial graphites. First of all, this concerns the preliminary firing of anthracite to the temperatures of 1273-1373 K, as well as the choice of temperature and exposure during graphitization. The determination of these parameters will allow to evaluate the technical and economic indicators of the new technology and to adjust the design parameters of furnaces with electrothermal fluidized bed.

4. Conclusions

The research into graphitization of Donbass anthracite was carried out at a heating rate close to heating in electrothermal fluidized bed and a short exposure time. It was found that the dynamics of changes in the structure of coal corresponds to the known dependences on the processing temperature, but the absolute value of graphitization degree (the value of the interlayer spacing d_{002}) is significantly higher than that of artificial graphites. The main factors determining the rearrangement of coal structure are:

– short exposure, which for the studied temperature range should be at least 30-40 minutes, or the processing temperature should be increased;

– intense heating of anthracite in the temperature range up to 1573 K leads to the formation of a porous coal structure, which prevents its compaction and impedes further graphitization.

The research has shown that it is possible to assess the degree of anthracite graphitization by the value of relative electrical conductivity of a coal particles layer.

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Вплив шокового нагріву на графітизацію антрациту Донбаського басейну

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Мета. Експериментальне дослідження процесу графітизації антрацитів Донбаського басейну при використанні шокового нагріву, характерного для печей з електротермічним киплячим шаром.

Методика. Графітизація проводилася в електротермічній печі при швидкості нагріву 1000 К/хв та часі витримки 10 хвилин. Температурний діапазон досліджень 1973-2873 К. Дослідження структури матеріалу проводилося методом рентгенографічного аналізу та визначення електропровідності шару частинок вугілля, із використанням скануючого електронного мікроскопа CamScan 4DV з приставкою Link760. Визначено зміни зольності й вмісту сірки.

Результати. Встановлено, що зі збільшенням температури обробки міжшарова відстань d_{002} зменшилася з 0.350 до 0.341 нм, зольність зменшилася з 3.46 до 0.40%, відносна електропровідність зросла в 4 рази. Абсолютне значення ступеня графітації антрацита значно відрізнялося від значень, характерних для штучного графіту. Однак абсолютне значення ступеня графітації антрациту значно відрізнялося від значень, характерних для штучного графіту. Це може бути пов'язано з недостатньою витримкою при досліджених температурах, а також отриманням пористої, недостатньо ущільненої структури вугілля при швидкісному нагріванні до 1573 К.

Наукова новизна. Показані принципова можливість отримання графітізованого антрациту з використанням шокового нагріву в печах з електротермічним киплячим шаром і можливість оцінки ступеня графітації антрацитів за величиною відносної питомої електропровідності шару частинок вугілля.

Практична значимість. Практична реалізація нової технології можлива після визначення оптимальних параметрів графітизації антрацитів, що забезпечують глибоку перебудову структури, характерну для штучних графітів. В першу чергу це стосується попереднього випалу антрациту до температури 1273-1373 К, а також вибору температури і витримки при графітації. Визначення цих параметрів дозволить оцінити техніко-економічні показники нової технології та скорегувати конструктивні параметри печей з електротермічним киплячим шаром.

Ключові слова: *графітизація, антрацит, шоковий нагрів, електротермічний киплячий шар, рентгенографічний аналіз, електропровідність*

Влияние шокового нагрева на графитизацию антрацита Донбасского бассейна

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Цель. Экспериментальное исследование процесса графитизации антрацитов Донбасского бассейна при использовании шокового нагрева, характерного для печей с электротермическим кипящим слоем.

Методика. Графитизация проводилась в электротермической печи при скорости нагрева 1000 К/мин и времени выдержки 10 минут. Температурный диапазон исследований 1973-2873 К. Исследование структуры материала проводилось методом рентгенографического анализа и определения электропроводности слоя частиц угля, с использованием сканирующего электронного микроскопа CamScan 4DV с приставкой Link760. Определены изменения зольности и содержания серы.

Результаты. Установлено, что с увеличением температуры обработки межслоевое расстояние d_{002} уменьшилось с 0.350 до 0.341 нм, зольность уменьшилась с 3.46 до 0.40%, относительная электропроводность выросла в 4 раза. Абсолютное значение степени графитации антрацита значительно отличалось от значений, характерных для искусственного графита. Однако абсолютное значение степени графитации антрацита значительно отличалось от значений, характерных для искусственного графита. Это может быть связано с недостаточной выдержкой при исследованных температурах, а также получением пористой, недостаточно уплотненной структуры угля при скоростном нагреве до 1573 К.

Научная новизна. Показан принципиальная возможность получения графитизированного антрацита с использованием шокового нагрева в печах с электротермическим кипящим слоем и возможность оценки степени графитации антрацитов по величине относительной удельной электропроводности слоя частиц угля.

Практическая значимость. Практическая реализация новой технологии возможна после определения оптимальных параметров графитизации антрацитов, обеспечивающих глубокую перестройку структуры, характерную для искусственных графитов. В первую очередь это касается предварительного обжига антрацита до температуры 1273-1373 К, а также выбора температуры и выдержки при графитации. Определение этих параметров позволит оценить технико-экономические показатели новой технологии и скорректировать конструктивные параметры печей с электротермическим кипящим слоем.

Ключевые слова: *графитизация, антрацит, шоковый нагрев, электротермический кипящий слой, рентгенографический анализ, электропроводность*

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