UDC 66-978

A.V. Sybir [a], S.M. Hubynskyi [b], S.S. Fedorov [a], K.M. Sukhyy [c], M.V. Hubynskyi [d], T.Y. Vvedenska [e]

PECULIARITIES OF HIGH-TEMPERATURE REFINING OF CARBON MATERIALS

[a] **Z.I. Nekrasov Iron and Steel Institute of National Academy of Sciences of Ukraine, Dnipro, Ukraine**
[b] **Ukrainian State University of Science and Technologies, Dnipro, Ukraine**
[c] **Ukrainian State University of Chemical Technology, Dnipro, Ukraine**
[d] **Thermal & Material Engineering Center SP. Z O. O., Opole, Poland**
[e] **Dnipro University of Technology, Dnipro, Ukraine**

The purpose of the study was to determine the influence of the main following factors on the efficiency of the process of high-temperature refining of natural and artificial graphite: processing temperature, distribution of metal oxides, and changes in the aggregate state of ash impurities. Thermal processing of natural graphite from Ukrainian deposits and anthracite from Donetsk coal basin was carried out in a chamber furnace at a holding time of $10-20$ minutes in a temperature range of $1500-3000^0C$. The quality of refining was carried out by ICP-OES and XRF analysis methods. It was established that the refining process may be divided into three following periods: $0-1600^0C$ (removal of moisture, volatiles, and decomposition of carbonates); $1600-2600^0C$ (evaporation of main ash-forming metals Fe, Si, Al, Ca, Mg in the form of oxides, silicides, and carbides); and $2600-3000^0C$ (evaporation of refractory compounds Ti, V, Mo, the content of which in the initial raw material determines the processing temperature and the quality of the final product). The distribution of metal oxides in the initial carbon material is not uniform, which complicates the use of equilibrium state models. The transition of ash into the liquid and then gaseous state has a significant impact on the result of heat treatment. This is what determines the choice of the process scheme. Intermittent process is the heating by an external heater in an inert gas environment. Continuous process is the heating of the material in moving containers or processing in an electrothermal fluidized bed.

Keywords: thermal refining, refractory metal oxide, ash distribution, aggregate state, external heater, electrothermal fluidized bed.

Introduction

Technological development has determined high requirements for the quality of carbon materials. This applies to synthetic and natural graphite for making batteries, graphitized products for nuclear reactors, electrode products, and carburetors for metallurgical processes. For finely dispersed graphite materials, the main quality indicators are chemical composition and crystal structure. They largely determine the performance properties of materials (electrical conductivity, thermal conductivity, etc.).

Purification of carbon materials is usually a multistage process [1−3] including flotation, which allows producing concentrate with carbon content of $90-98\%$. The subsequent stage may comprise chemical purification (acid-base method and acid method), high-temperature purification and high-temperature purification using halogen-containing gases. This article focuses on the second stage of purification of carbon materials: high-temperature treatment of the material without the use of acid and halogens. This refining option makes it possible to obtain a finished product

that meets the requirements for the production of lithium-ion battery anodes and carburetors with carbon content of 99.95% and higher.

The thermal purification of carbon materials consists in their heating to temperatures around 3000^0C and removing ash from the material in the form of vapor. In the process of heating, metal oxides contained the ash melt are evaporated and removed with effluent gases. This process also involves chemical interactions between carbon and elements of the ash. Thus, purification is a complex physical and chemical process that brings about change in the aggregate state of the reagents.

Qiu et al. [4] focused on the study of graphitization of anthracite with the ash content of 2.85% at Taixi Coal Preparation Plant (Ningxia, China). The ash contained SiO_2 (25.21%), Al_2O_3 (17.33%), Fe_2O_3 (20.01%), CaO (25.65%), and MgO (10.16%). In high-temperature research, the effect of heating rate ($5-20^0$C/min) and holding time ($1-4$ hours) on the reduction of ash content was determined. The processing temperature was 3000^0C. The studied samples of anthracite were parallelepipeds (2×1 cm). It was found that the heating rate does not affect purification of anthracite, and the duration of exposure allows reducing the ash content from 0.89% (1 hour of exposure) to 0.17% (3 hours of exposure). A further increase in the duration of exposure did not lead to a decrease in the ash content. Thus, the carbon content in graphitized anthracite after long processing at 3000^0C was 98.87%, considering the presence of volatile products at 0.96%. Their presence was not explained by the authors of the article. In addition, the authors observed an increase in macrocracks with increasing temperature of anthracite processing, which seems to be associated with formation of the liquid phase and fumes of ash elements.

Further research into graphitization of anthracite at Taixi Coal Preparation Plant (Ningxia, China) is presented in ref. [5], which was devoted to the processes of change in the ash component during high-temperature treatment. Studies were carried out on similar samples [5] at heating temperatures up to 2700^0C. Compositions of anthracite ashes were modeled and investigated by XRD analysis, starting from the initial point and at the processing temperatures of 1200^0C, 1500^0C, 1800^0C, 2200^0C, and 2700^0C. This allowed the authors to determine a sequence of changes in the chemical composition of ash depending on temperature. The transition of ash inclusions into the liquid state is assumed to take place at $1200-1500^0$C. The decomposition of mineral complexes into oxides and their sublimation with the formation of porosity is associated with further heating (1800^0C). Small portions of silicon and aluminum

form carbides, which decompose to form graphite. At graphitization temperature of 2700^0C, traces of carbides decomposition are observed on the surface of anthracite particles, and porosity visibly decreases. Particles of ash elements in anthracite samples are uniformly distributed and look like inclusions (filled voids and knots).

The issues of natural graphite thermal refining were studied in detail in ref. [2], which discusses purification of graphite-6 from flake graphite (FG) deposits and microcrystalline graphite-4 deposits in China. The composition of graphite ash part is very similar to the composition of anthracite ash. The main ash-forming elements of graphites are Al, Si, Fe, K, and Ca. Thermal treatment of FG at 3000^0C with a holding time of 30 minutes and a heating rate of 10^0C/min showed that the ash content decreased while the carbon content reached $99.95-99.99\%$. The main residual impurities include elements with high boiling point: carbides of B, Ti, Ta, V, W and Mo. Gravimetric studies, investigation of gas atmosphere composition, XRD analysis of ash at different processing temperatures allowed the authors to determine the main features of high-temperature graphite refining. Removal of the main ash-forming elements is associated with reduction of oxides and evaporation of metals or carbides. After reduction, Fe forms Fe_3Si and is removed during further heating at 2700^0C, by passing the formation of iron carbide. As in previous papers, the issues of purification kinetics and organization of gas removal processes were not considered. However, the authors gave two possible schemes of continuous graphite purification: horizontal with a feed screw and vertical with separate moving containers.

Early studies of high-temperature refining reported in ref. [6] confirmed the general approach to thermal purification: evaporation of ash inclusions or their compounds with carbon. The authors studied the kinetics of the refining process and stated that the main factor determining the refining kinetics is the rate of the material heating to a given temperature. First of all, the authors consider refining processes in Achenson furnaces, where the composition of the initial graphite and the ash content of the backfill significantly affect the final result, which can lead to the process of reverse condensation. The mechanism of purification is based on the reduction of oxides at temperatures around 1800^0C and the partial formation of carbides, which decompose and evaporate upon further heating. In this case, the processing temperatures do not exceed the boiling point of carbides and oxides.

Analysis of literature showed that researchers consider only the general approach to thermal treatment, defining the main process associated with

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evaporation of ash elements and their removal from graphite with waste gases. Possible processes of graphite impurities condensation and removal of gases are not considered but are taken as a given. In addition, the refining quality is largely determined by removal of impurities, which may be insignificant in ash composition, but at thermal treatment, their influence significantly increases, and the issues of their removal become decisive for obtaining a product of the required quality. In refining studies, it is usually assumed that ash distribution is uniform, which is a rough assumption that can affect the final refining result. These issues will be addressed in this paper.

Experimental

Materials and thermal treatment regimes

Natural graphites from Ukrainian deposits were investigated in the present research. The initial composition is shown in Table 1, with a total ash content of $A^d=6.38\%$. In addition, the purification process of anthracite from Donetsk coal basin with ash content of $A^d=3.32\%$ was studied. Based on the X-ray phase analysis of the initial anthracite, the content of the main components of its ash was determined as follows: Al 29.6%, Si 49.0%, Mg 5.5%, Fe 12.0%, and Ca 3.9%.

Natural graphite was refined in a laboratory furnace [7] with external heating of the material at a high rate up to 1000^0C/min. Heating was carried out in the temperature range of $1600-3000^0$C. Preliminary studies have shown that the duration of exposure, providing full heating of the load, is 10 min. A decrease in the holding time led to an increase in the ash content, which confirms the idea reported in ref. [7] that the refining kinetics is determined by the heating rate of carbon material. After cooling, the ash content of the material was determined and elemental analysis was carried out using the ICP-OES method after treatment at temperatures of 1600^0C, 2600^0C, and 3000^0C.

The anthracite was treated in the same furnace at temperatures of 1500^0C, 1800^0C, 2100^0C, 2400^0C, 2700^0C, and 3000^0C. The holding time was 20 minutes. The samples were examined by XRF analysis, which allowed investigating the distribution of ash inclusions and their removal during the heat treatment.

Results and discussion

The results of experimental research into natural graphite thermal refining are shown in Figs. 1 and 2. The whole refining process can be conditionally divided into following three stages in terms of temperature:

$0-1600^0$C (28.6% reduction in ash content) − removal of moisture, volatiles, decomposition of carbonates, partial removal (evaporation and reduction) of K, Mg, Fe, and Na oxides;

$1600-2600^0$C (69.9% of ash content reduction) − evaporation of the main ash-forming metals in the form of oxides, silicides, carbides of Fe, Si, Al, Ca, Mg, as well as Mo, Cu, V, Cr, W impurities;

$2600-3000^0$C (1.3% of ash content reduction) − evaporation of Ti, V compounds.
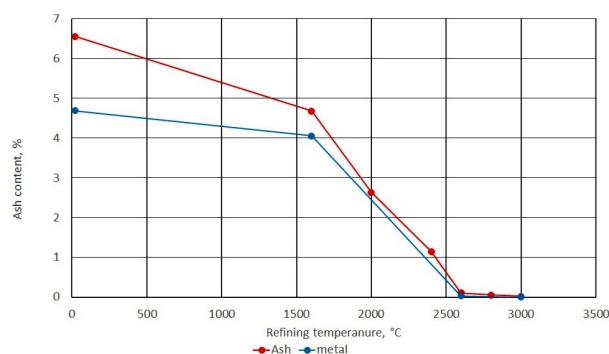

Fig. 1. Decrease in ash and ash-forming metal content depending on refining temperature

It is the third refining period that allows obtaining the carbon content in graphite corresponding to the requirements for the anode material of lithium-ion batteries (99.95−99.98%). Analysis of boiling temperatures of Ti, its oxides and carbides (Table 2) shows that it is possible to remove titanium from graphite by evaporating reduced titanium or its oxides. If titanium carbides are formed, its evaporation at refining temperature is impossible.

Thus, during thermal purification, the initial composition of graphite should contain only minimum amount of Ti, W, and V.

To clarify the processes of graphite thermal purification, we studied the possibility of using the TERRA computational complex, which allows simulating the chemical equilibrium of multicomponent systems, considering the aggregate state of substances at given thermodynamic parameters [8]. The condition of the system equilibrium corresponds to the maximum of its entropy: $dS=0$ and $d^2S<0$. Simulation was carried out for experimental conditions of thermal refining of graphite. The simulation results were compared with the results of experimental data obtained after

Table 1

Graphite a composition, ppm

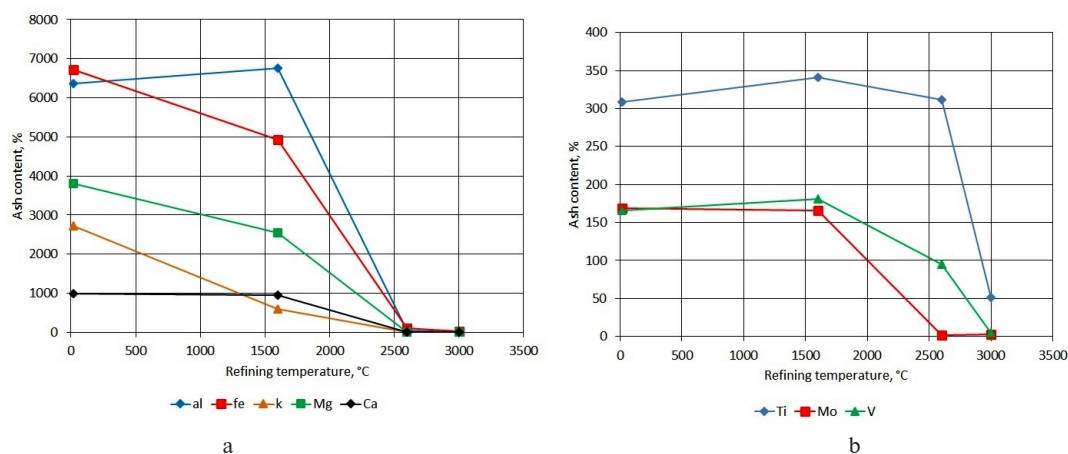| Si	Fe	Al	Mg	K	Ca	Na	Ti	Mo	V	V
12723	6921	6285	4011	2738	986	415	325	182	171	171

Fig. 2. Change of metal content in natural graphite during thermal refining:
a − initial anthracite; and b − after thermal treatment at 3000⁰C

full heating of the material in the furnace and stabilization of its chemical composition (exposure time being 10 minutes). The simulation results are shown in Fig. 3. It follows that the experimental data on the ash-forming elements content are close to the calculated ones at the temperature of 1600⁰C (the beginning of refining) and at 3000⁰C (the end of refining). The process of purification of the main ash-forming elements differs considerably from the equilibrium one, which does not allow using thermodynamic models for investigation of the refining process. The reasons for this, in our opinion, are the following factors, which can determine the dynamics of refining: uneven distribution of ash elements, the presence of physical processes of melting and evaporation of melts, the yield of melts on the surface of particles.

Table 2

Melting/boiling temperatures of titanium and its compounds

Ti compounds	Melting temperature, ⁰C	Boiling temperature, ⁰C
Ti	1670	3560
TiO₂	1843	2972
TiC	3260	4300

The distribution of ash in carbon materials was thoroughly studied by scientists who investigated the formation of fly ash during combustion of pulverized fuel in boilers [9−11]. The detailed study of the mineral content distribution [11], carried out on 18 kinds of coal from Australia, North America and Great Britain, showed that the ashes are distributed between the particles of coal after milling in the following way:

− particles containing mainly carbon (no more than 10% ash in a particle) are 88% to 35%, with the proportion of such particles decreasing with increase in ash content;

− particles with carbon and mineral part (from 10% to 90% of ash in a particle) make from 9% to 53% of the total ash content in coal. With increasing ash content, the share of such particles increases;

− particles containing mainly the mineral part (more than 90% of ash in a particle) make up 3% to 19%, while the effect of the total ash content on the share of such particles is of random nature.

Studies of the particle size distribution of particles containing different amounts of mineral part showed that particles containing mainly mineral part were significantly smaller in size than the rest, within the range of 4−40 microns; while particles containing carbon were 10−200 microns. A similar result was confirmed in ref. [10] when an increase in ash content was observed alongside a decrease in grain size distribution.

Experimental research into the distribution of the mineral part in coal and distribution of the main ash-forming elements was carried out during thermal refining of anthracite from the Donetsk deposit. Heating of samples was carried out at temperatures of 2100⁰C, 2400⁰C, 2700⁰C, and 3000⁰C. XRF analysis of the initial anthracite samples (Fig. 4) showed that ash distribution corresponds to the classification given elsewhere [11]. The distribution of Al, Si, and Mg is determined by significant concentrations associated with particles containing mainly mineral part. The distribution of Fe is more uniform. Thus, the distribution of ash-forming elements is uneven, which is confirmed by the data in Fig. 5.

Mineral inclusions after heat treatment at 2100−2400⁰C are point like shown in Fig. 6. It can be seen that the inclusions are in the molten state in the shape of a sphere.

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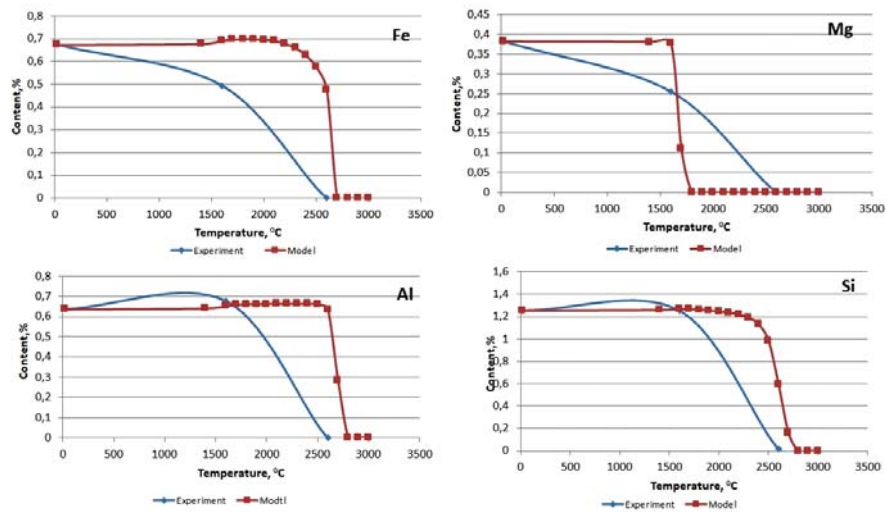
Fig. 3. Comparison of calculated and experimental data of Si, Fe, Mg, and Al content in graphite depending on the processing temperature
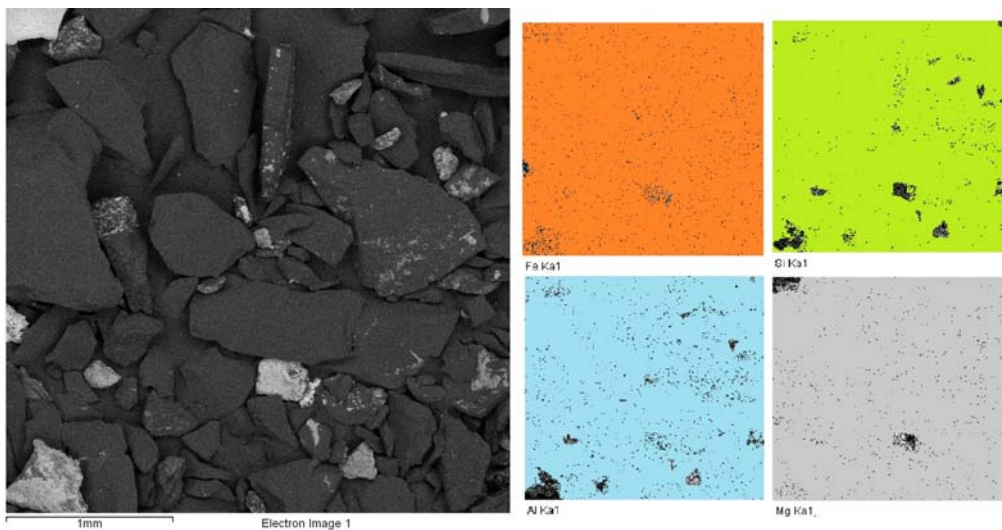

Fig. 4. SEM of the initial anthracite from Donetsk deposit

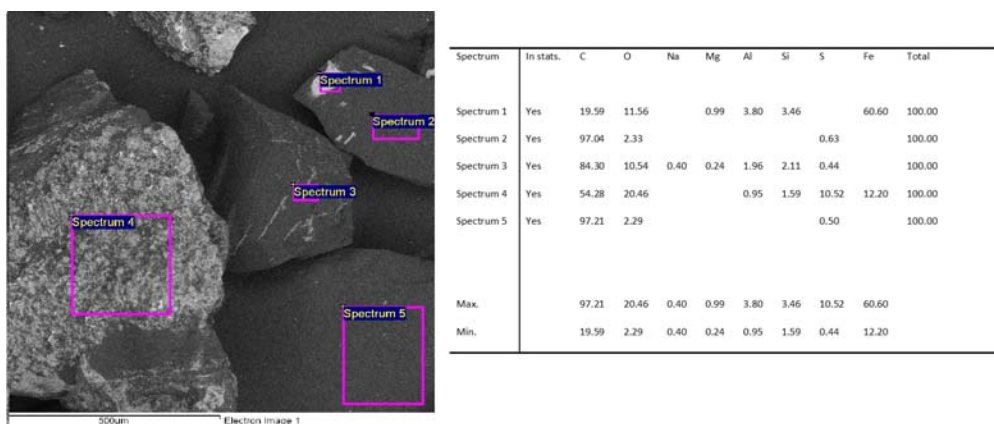| Spectrum	In stats.	C	O	Na	Mg	Al	Si	S	Fe	Total
Spectrum 1	Yes	19.59	11.56		0.99	3.80	3.46		60.60	100.00
Spectrum 2	Yes	97.04	2.33					0.63		100.00
Spectrum 3	Yes	84.30	10.54	0.40	0.24	1.96	2.11	0.44		100.00
Spectrum 4	Yes	54.28	20.46			0.95	1.59	10.52	12.20	100.00
Spectrum 5	Yes	97.21	2.29					0.50		100.00
Max.		97.21	20.46	0.40	0.99	3.80	3.46	10.52	60.60	
Min.		19.59	2.29	0.40	0.24	0.95	1.59	0.44	12.20	

Fig. 5. Values of ash-forming elements based on the results of XRF analysis

With an increase in the temperature, the value of inclusions decreases. The XRF analysis data show that at 2100^0C, the silicon is present in the mineral inclusions, but at 2400^0C and above, it is not detected. Similarly, there is no aluminum at $2700-3000^0C$. The main part of graphite particles represents carbon.

The obtained results allow us to describe the mechanism of carbon material purification during thermal refining and the influence of physical processes involved in changing the aggregate state of the precursors mineral part on this process.

As was reported by Qiu et al. [4], the transition of the mineral part of carbon materials into the liquid state occurs at temperatures of $1260-1500^0C$. This has not been experimentally recorded during thermal treatment. At the same time, the results of thermal treatment of fine-grained graphite to the temperature of 1500^0C given in ref. [12] are very indicative. Significant areas of particles covered by a bed of molten ash can be clearly seen on microphotographs (Fig. 7).

The formation of ash on the surface of the melt particles leads to their agglomeration (sticking) and the impossibility of their independent movement relative to each other, which significantly reduces the fluidity of carbon material. At further heating at 2100^0C, the main part of the melt evaporates, and the flowability of the material is restored. Thus, the processes of the mineral component melting and evaporation are determined by the heating temperature of the carbon material, which depends on the heating modes and the design of the thermal refining reactor. Several heating options and the related advantages and disadvantages of the reactors are discussed below.

Reactors with batch treatment process

The material is loaded into a dense bed of the heating chamber, where it is heated by an external heater while inert gas is supplied into the working space. Heating starts from the bed surface and ends when the bed is fully heated. Then the material is cooled down in the inert medium. Subsequently, the cycle repeats. The scheme of material processing in the batch reactor is shown in Fig. 8.

Sublimations of the carbon material mineral part move from the low-temperature zone to the high-temperature zone, which excludes their recondensation, and are evacuated from the furnace together with the inert gas. The high temperature zone gradually advances to the material axis and ensures a quality refining.

This is not the case in batch furnaces with direct electrical heating – Achenson and Kastner furnaces, where heating takes place directly in the material to be cleaned (Kastner furnace) or in the charge which is in direct contact with the material to be cleaned. In practice, we observe the phenomenon of backward

condensation: contamination of the carbon material by condensation of subcarbons coming from the backfill when cooling the furnace. In addition, the processing temperature produces the main influence on the refining quality. The heating irregularity in Achenson and Kastner furnaces reaches $200-400^0C$ during exposure at the maximum temperature [2,6,13]. This can lead to an uneven carbon content in the finished material from 99.87% to 99.96%. To eliminate such a phenomenon, halogen-containing gases are used, which provides the required quality of purification [6].

The above-mentioned features of refining are also typical for *continuous processes* of carbon materials purification. The presented variants of continuous graphitization processes [2], horizontal and vertical, have fundamental differences which complicate implementation of the process. The vertical variant of continuous technology is, in fact, a realization of a periodic process with containers moving from top to bottom, and realization of this process is possible at removal of gases and sublimations directly in each position of the container, while gases move in the same direction as the material. The material itself does not move relative to the container. The horizontal scheme proposed by the authors of work [2] raises doubts about its implementation, because when heated to the outlet temperature of liquid mineral components, particles of the carbon material will agglomerate, and the screw operation will be difficult.

In contrast to the mentioned variants of continuous refining processes, the technology of carbon materials purification in the electrothermal fluidized bed provides all necessary conditions of purification and uniform heating of the precursor (Fig. 9).

Electrothermal fluidized bed [14] is heated due to heat release when current passes through the fluidized bed of graphite particles between the central and external electrodes. Fluidization of graphite particles is provided by inert gas supply. The bed is heated to the temperature 3000^0C. The precursor is continuously fed into the bed, and, at the same time, the purified product is removed from it. Particles of carbon material entering the bed are intensively heated and its mineral part enters in the form of sublimations into the flow of inert gas and is removed together with it from the working space of the furnace. Condensation of substrates takes place in the effluent gas cleaning system from the reactor. Mixing of the fluidized bed ensures uniform heating of the particles, and the temperature difference in the bed does not exceed $25-50^0C$ [14]. Thus, the refining of carbon materials in the electrothermal fluidized bed provides all the necessary conditions for their purification in the continuous operation mode.
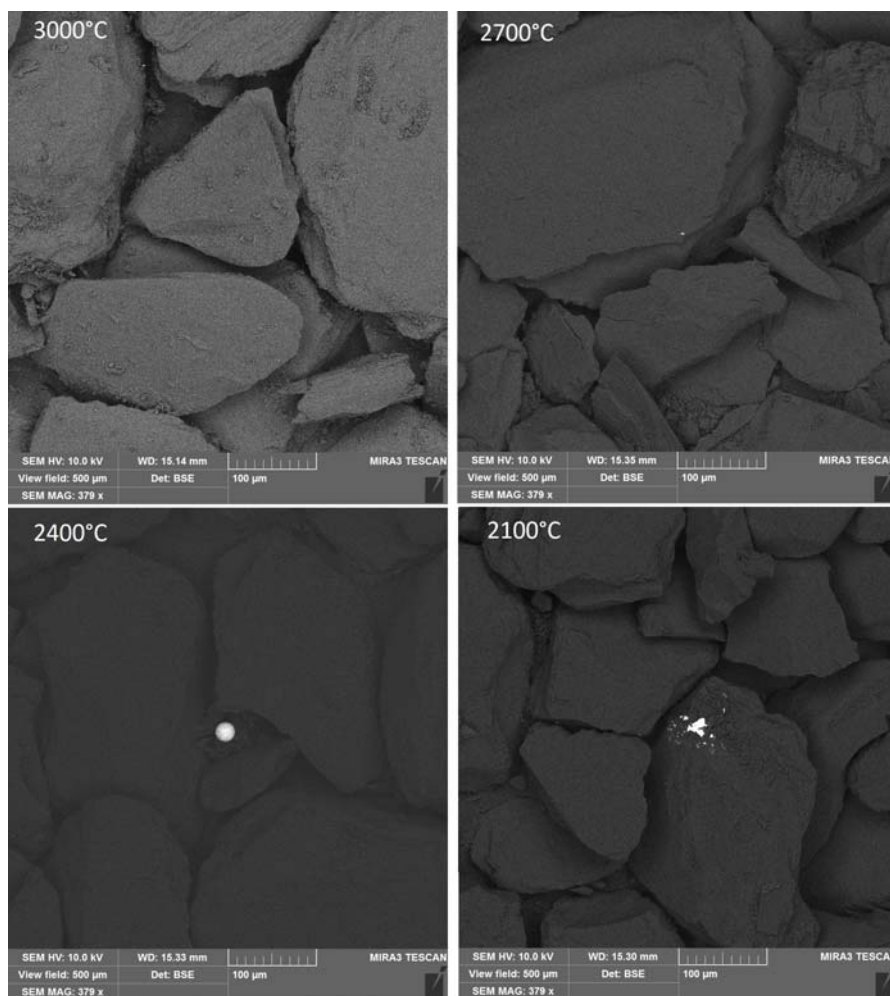
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Fig. 6. SEM of anthracite from Donetsk deposit after heat treatment at the temperatures of 2100⁰C, 2400⁰C, 2700⁰C, and 3000⁰C
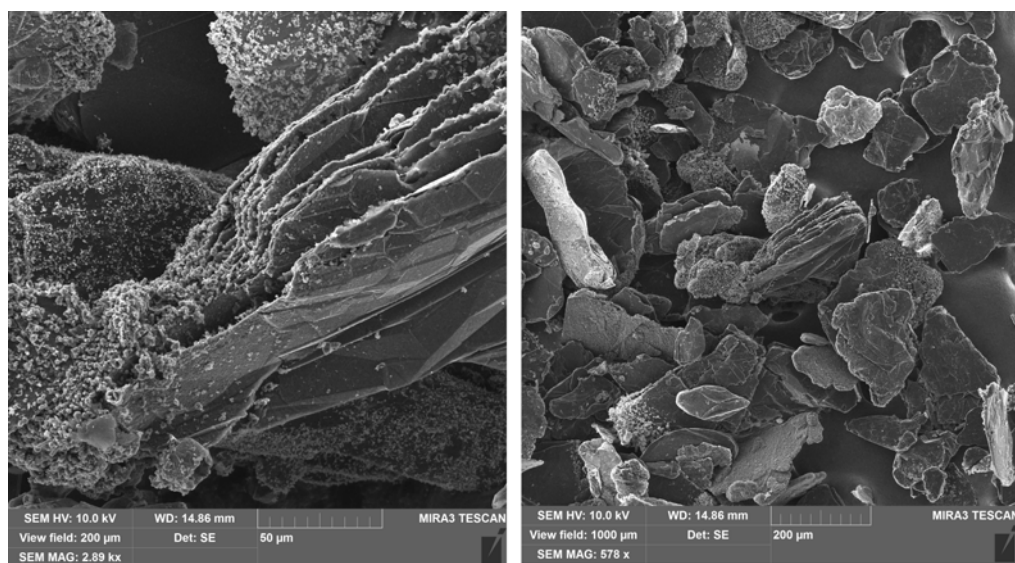

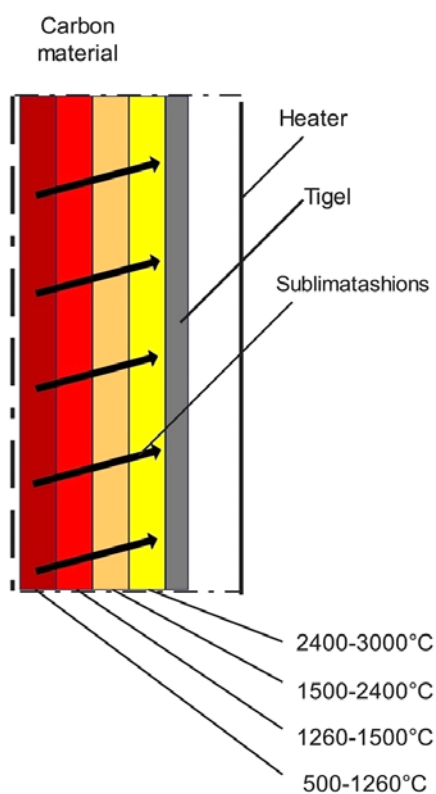Fig. 7. SEM of natural graphite after heating to 1500⁰C [12]

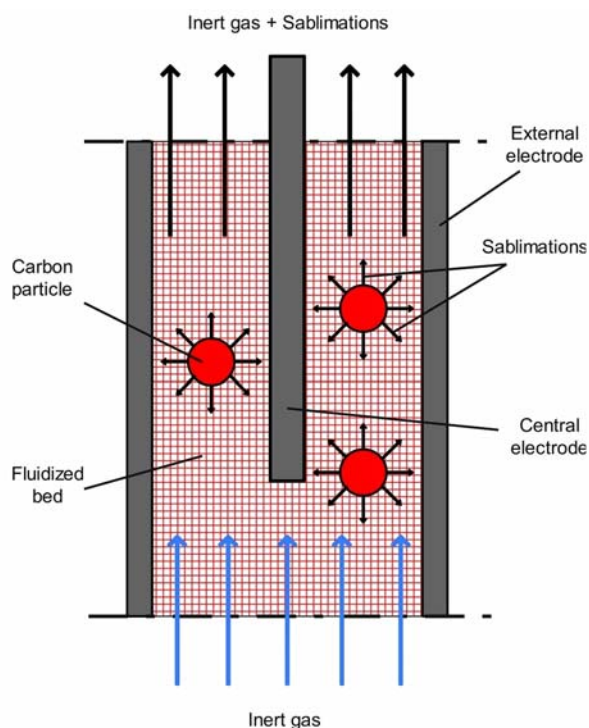Fig. 8. Diagram of carbon material refining
in a batch furnace

Fig. 9. Diagram of carbon material refining in the
electrothermal fluidized bed

Conclusions

1. Thermal refining of carbon materials is a complex physical and chemical process, the main factors of which, determining the quality of the finished product, are processing temperature, temperature difference in the reactor, removal of vapors of the precursors' mineral component.

2. The quality of the finished product is ensured by removal of not only the main ash-forming elements, Si, Fl, Fe, and Mg, but also metal oxides with a small content of Ti, W, and V in the ash. It is their content in the precursor that determines the final result of thermal refining.

3. The refining process differs greatly from the equilibrium one, and the use of thermodynamic calculation models of the system equilibrium states gives a considerable error in calculated and experimental data. The reason is uneven distribution of the mineral part elements of the precursor, physical processes of melting and evaporation of ash.

4. The refining process involves the appearance of the mineral part melts on the surface of particles which leads to their agglomeration and impossibility to move the dense bed of particles. In this regard, it is possible to implement a periodic refining process with external heating or heating of carbon material in moving containers. The implementation of all requirements for continuous thermal purification of carbon materials (uniform heating of the precursor, removal of sublimations from the working chamber without recondensation) is characteristic of electrothermal fluidized bed reactors.

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ОСОБЛИВОСТІ ВИСОКОТЕМПЕРАТУРНОГО РАФІНУВАННЯ ВУГЛЕЦЕВИХ МАТЕРІАЛІВ

Сибір А.В., Губинський С.М., Федоров С.С., Сухий К.М., Губинський М.В., Введенська Т.Ю.

Мета даного дослідження − визначення впливу основних факторів на ефективність процесу високотемпературного рафінування природних і штучних графітів: температури оброблення, розподілу оксидів металів, зміни агрегатного стану золових домішок. Термічне оброблення природного графіту українських родовищ і антрациту Донецького вугільного басейну виконувались в камерній печі за тривалості витримування 10−20 хвилин у температурному діапазоні 1500−3000⁰С. Якість рафінування проводилося методами ICP-OES і XRF аналізу. Встановлено, що процес очищення можна розділити на три періоди: 0−1600⁰С (видалення вологи, летких речовин, розкладання карбонатів); 1600−2600⁰С (випаровування основних золотоутворювальних металів Fe, Si, Al, Ca, Mg у вигляді оксидів, силіцидів, карбідів); 2600−3000⁰С (випаровування тугоплавких сполук Ti, V, Mo, вміст яких у вихідній сировині визначає температуру оброблення і якість готового продукту). Розподіл оксидів металів у вихідному вуглецевому матеріалі нерівномірний, що ускладнює використання моделей рівноважного стану. Значний вплив на результат термічного оброблення має перехід золи в рідкий і потім в газоподібний стан. Саме це визначає вибір схеми процесу. Періодичний процес − нагрівання зовнішнім нагрівачем у середовищі інертного газу. Безперервний процес − нагрівання матеріалу в переміщуваних контейнерах або оброблення в електротермічному киплячому шарі.

Ключові слова: термічне рафінування, оксиди тугоплавких металів, розподіл золи, агрегатний стан, зовнішній нагрівач, електротермічний киплячий шар.

PECULIARITIES OF HIGH-TEMPERATURE REFINING OF CARBON MATERIALS

*A.V. Sybir [a], S.M. Hubynskyi [b, *], S.S. Fedorov [a], K.M. Sukhyy [c], M.V. Hubynskyi [d], T.Y. Vvedenska [e]*

[a] **Z.I. Nekrasov Iron and Steel Institute of National Academy of Sciences of Ukraine, Dnipro, Ukraine**

[b] **Ukrainian State University of Science and Technologies, Dnipro, Ukraine**

[c] **Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

[d] **Thermal & Material Engineering Center SP. Z O. O., Opole, Poland**

[e] **Dnipro University of Technology, Dnipro, Ukraine**

[*] **e-mail: gubinm58@gmail.com**

The purpose of the study was to determine the influence of the main following factors on the efficiency of the process of high-temperature refining of natural and artificial graphite: processing temperature, distribution of metal oxides, and changes in the aggregate state of ash impurities. Thermal processing of natural graphite from Ukrainian deposits and anthracite from Donetsk coal basin was carried out in a chamber furnace at a holding time of 10−20 minutes in a temperature range of 1500−3000⁰C. The quality of refining was carried out by ICP-OES and XRF analysis methods. It was established that the refining process may be divided into three following periods: 0−1600⁰C (removal of moisture, volatiles, and decomposition of carbonates); 1600−2600⁰C (evaporation of main ash-forming metals Fe, Si, Al, Ca, Mg in the form of oxides, silicides, and carbides); and

2600−3000⁰C (evaporation of refractory compounds Ti, V, Mo, the content of which in the initial raw material determines the processing temperature and the quality of the final product). The distribution of metal oxides in the initial carbon material is not uniform, which complicates the use of equilibrium state models. The transition of ash into the liquid and then gaseous state has a significant impact on the result of heat treatment. This is what determines the choice of the process scheme. Intermittent process is the heating by an external heater in an inert gas environment. Continuous process is the heating of the material in moving containers or processing in an electrothermal fluidized bed.

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A.V. Sybir, S.M. Hubynskyi, S.S. Fedorov, K.M. Sukhyy, M.V. Hubynskyi, T.Y. Vvedenska