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Effect of Nano-Sized Powder Additions of Complex Alloy Fe-Si-Al-Ca-Ti in the Electrode Charge on Graphitization Process and Enhancement of Graphitized Products Properties

M.I. Gasik /D.Sc. (Eng.)/, M.M. Gasik /D.Sc. (Eng.)/, E.I. Tsybulya, A.G. Grinshpunt /D.Sc. (Eng.)/¹, S.V. Kutuzov /Ph.D. (Eng.)/, O.Yu. Urazlina, V.M. Golchanskaya, V.P. Gnezdilova²

¹National Metallurgical Academy of Ukraine
4 Gagarin Ave., Dnipropetrovsk 49600, Ukraine

²JSC "Ukrgrafit"
20 Severnoye Shosse, Zaporizhzhya 69600, Ukraine

Abstract

The results of investigation of the effect of disperse ferrosilicon additions in charge mixture "pitch coke + coal-tar pitch" on properties of graphitized samples after high-temperature annealing at 1800 °C, 2200 °C and 2600 °C are stated. Ferrosilicon addition in quantity of 1 % provides commensurable parameters by degree of graphitization, specific electrical resistance and physical and mechanical characteristics at 2200 °C as compared to the samples annealed at 2600 °C.

Keywords: graphitized products, graphitization methods, catalyzing additions, annealing temperature, physical and mechanical properties, electrical properties

Statement of research purpose

Making of graphitized products (electrodes for arc steel-smelting and ferroalloy furnaces, lining blocks and electrolytic-cell anodes) is characterized by a great specific energy consumption at the technological stage of graphitization of carbon raw materials preliminary annealed at 1000-1200 °C [1]. In this respect, decrease in specific energy consumption at maintenance of proper quality is one of primary scientific and technological problems in the complex multistage technological scheme of graphitized products making.

The literature analysis of the papers related to research of the processes that occur during graphitization of carbon raw materials preliminary annealed proves that one of the key factors influencing operational characteristics of graphitized electrodes is a high quality of raw solid carbon materials (oil, needle or pitch cokes) and carbonaceous binder. Raw materials should have, first of all, stably low content of sulfur, ashes and to be characterized as follows: cokes – by a number of high coke and chemical parameters of quality, while

binding agent – by a definite group content and required flow characteristics. At the same time, although quality of raw materials from various suppliers is decreasing, the consumer requirements to graphitized products are constantly increasing. Hence, scientific and technological research related to improvement of quality and decrease in specific energy consumption at making of graphitized carbon products is still urgent.

One of priorities is a development of compositions of additions in basic charge mixtures for obtaining graphitized products and study of catalytic agents effect on graphitization processes. Thus, temperature-time parameters of graphitization are the key parameters at which the required criteria of products quality are reached at smaller specific energy consumption and, consequently, at the increase in performance of graphitization electric furnaces.

Analysis of literature and patents related to the subject of research

A number of research works on the effect of various additions in the basic mixtures of solid

carbon components and carbonaceous (or oil) binder (pitch) on intensification of the process of products graphitization has been carried out lately. As a consequence, the quality of graphitized products is determined both by initial components and parameters of obtaining untreated raw materials for their subsequent graphitization. To our point of view, among a lot of scientific papers of not only Ukrainian and Russian but also of foreign authors, the results of scientifically-grounded mechanism of processes that occur at the stage of untreated raw materials annealing are of interest.

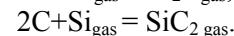
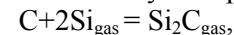
According to T. White's data [2], carbonized binding agent exists in the form of a liquid crystal or so-called *mezophase* (anisotropic melt) in the process of heat treatment of raw materials for graphitized products making. Fine insoluble particles are segregated during mezophase transformations whereas the effect of larger graphitic particles consists in arrangement of mezophase layers in parallel to the basic mass. M.V.Averin and others [3] observed that the particles of coal pitch mezophase and similar types of raw material have a regular spherical shape in the moment of their formation. This shape of particles is the same in the annealed and graphitized samples. Their sizes in the plane of graphitized layers (a-axis) – do not change considerably whereas between layers (c-axis) – decrease significantly.

Thus, the certain types of additions – catalytic agents can influence coke formation whereas the others affect the process of crystal-structure transformations at high-temperature formation of graphite.

In the early 20s of 20th century, S.I. Telnyi noticed a positive effect of ferrous oxides on degree of graphitization. He studied catalytic effect of small additions of scale in electrode charges and managed to explain the positive results he reached by intermediate compound formation (ferric carbide), from which graphite precipitates during heat treatment. According to I.Natsume's report [4], in Japan 1-2 % of ferric oxides was added into electrode charge and such an operation has a positive effect on improvement of electrodes quality. It is noted that ferric oxides prevent bloating at the initial stage of graphitization of needle coke (1400-2000 °C) containing a large amount of sulfur. The Japanese experts explained the effect of natural siderite FeCO_3 on graphitization process not by catalytic effect due to formation and decomposition of carbides at 2000 °C but by increase in mobility of carbon crystalline particles

caused by recrystallization processes of carbides formed on the coke surface [4].

Prediscovery on intensification of graphitization of carbon electrode untreated raw materials with the use of silica in electrode charges is carried out. It is demonstrated that silicon carbide SiC is formed under condition of temperatures prior to the stage of graphite recrystallization. This silicon carbide dissociates at high temperatures of graphitization. According to G.Sherer's [5], a positive effect of silica on the process of carbon materials (products) graphitization has no well-defined interpretation but, as he believes, growth of graphite crystals is caused by transport reactions



I.M.Yurkovskiy and D.S.Konstantinova [6] established that with obtaining graphitized materials, 1-2 % addition of silicon and iron as catalysts accelerates the processes of structural transformations and allows lowering the treatment temperature from 2700 °C without addition down to 2400 °C, i.e. by 11.1 %. The authors [6, 7] accepted an interlayer distance d_{002} (nm) related to degree of graphitization as a criterion of structural transformation of carbon-pitchy composition using the formula by I. Marie and I. Mering [8]

$$g = \frac{0,344 - d_{002}}{0,344 - 0,3354}.$$

Further development of complex structural transformations is observed during annealing of test samples at temperatures above 1200 °C [6]. Formation of graphitized phase at rather low temperature (1600 °C) in samples with 1-2 % of silicon and iron is proved by means of experiments [6]. The comparative data of sample with addition of 10 % catalyst containing Si+ Fe are presented in Figure 1 to demonstrate splitting of profile (002) on the line of graphite and non-graphitic carbon. When the temperature of samples heating raises from 1600 up to 2400 °C, amount of graphitized phase calculated by the area of (002) line profile increased from 36 up to 62 %, while at 2400 °C the experimental mixtures transformed into graphite.

The mechanism of graphite phase formation from structurally disordered carbon is related to the process of formation and decomposition of carbides, since it has been established earlier [6] that carbides can participate *repeatedly* in carbon transfer from disordered state into crystal graphite phase. According to the subject of Japanese patent [9], obtaining of graphitized material with a high

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degree of graphitization is reached via high-temperature treatment of mezocarbon spherulins and/or products of carbon materials heat treatment with iron and silicon in quantity of 0.1-25 wt. % to quantity of raw materials at the ratio Fe / (Fe + Si) equal to 30-90 %.

A.V. Dyomin et al. [10] analyzed the results of many authors concerning the effect of Si, Zr, B, Ti, carbides of these elements and aluminum silicates on the process of carbon raw materials graphitization when obtaining graphitized products. For example, titanium powder (from 7.5 up to 20 % by weight) and titanium carbide TiC (2.5 % by weight) of 0.044 mm size were added to carbon mixture (oil coke + 20 % of medium temperature coal pitch). Annealing of original pressed charge was carried out at 1200 °C, and graphitization - at 2200 and 2800 °C. It is established that specific electrical resistance (SER) of obtained graphitized electrodes decreases with increase of titanium added and raise of graphitization temperature. And SER of samples with no titanium was 30 m Ω ·m (2200 °C) and 12 m Ω ·m (2800 °C).

Materials and research methods

The research purpose of present work is to investigate the effect of additions in charge mixtures on obtaining graphitized electrodes EG400, brand new intensifier (catalyst) in the form of disperse powder of collected dust formed at rectification of ingots of industrial ferrosilicon of grade FS65 (DSTU 4127-2002). As solid carbon materials the following mixture was used: pitch coke (6 % volatile, 0.6 % ash, 0.5 % S, density 2.10 g/cm³, 77 wt. %), graphite (15 %) and filter dust (8 %). Coal pitch of B grade was added in quantity of 23±1 % from weight of solid ingredients.

It must be noted that collected ferrosilicon dust is enriched with impurity elements Ca, Al, Ti, etc. The impurity elements concentrate in a mother melt and enrich it gradually during the mechanized casting of ferrosilicon with the use of conveyor machines with cast-iron casting molds under crystallization. The impurity elements form microvolumes with silicon crystallizing under eutectic mechanism on the border "solid-liquid". When ratifying ferrosilicon ingots, the eutectic phases partially transform into offgrade fractions (fines less than 6 mm), and some of them go in bag filters.

The impurity elements (Ca, Al and Ti) coupled with silicon and iron are supposed to take part in the intensification of graphitization of electrode raw materials.

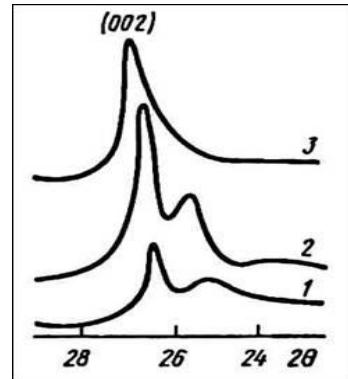


Figure 1. Splitting of line (002) in the process of graphitic phase growth in carbon-pitchy mixture with addition of 10 % (Fe+Si) heat treated with 1 hour holding time at, °C: 1 – 1600; 2 – 2000; 3 – 2400

The test samples of pressed raw materials were subjected to preliminary annealing at 1000 °C. The characteristics of test samples after annealing at 1000 °C are presented in Table 1.

Table 1. Apparent density (ρ_a), shrinkage and burn-off loss of laboratory samples after annealing at 1000 °C

No. of mix formula	ρ_a , g/cm ³		Σ Shrinkage, %		Burn-off loss , %
	untreated	annealed	\emptyset	L	
No.1 (production sample)	1.72	1.60	0.95	1.66	9.91
No.2 (1 % of catalyst)	1.71	1.60	0.64	1.49	9.65
No.3 (5 % of catalyst)	1.74	1.61	0.34	1.13	9.33

To estimate the effect of catalyst upon graphitization process and properties of material obtained, the laboratory samples were graphitized in Tamman's furnace at temperatures of 1800 °C, 2200 °C, 2600 °C during 1 hour.

The results of research and their analysis

The presence of iron silicides FeSi₂, FeSi and phases of pure silicon is proved by means of X-ray structure analysis of FS65 ferrosilicon fines carried out in Central Scientific Research Laboratory of JSC "Ukrgrafit". This phenomenon is in agreement with phase research results of lump ferrosilicon (grade FS65, industrial smelting).

The microstructure was studied using electronic microscopy, X-ray phase analysis and X-ray spectrum microanalysis. It is established that matrix phases are presented mainly as

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nonstoichiometric silicide Fe_xSi_2 (ξ -phase, leboit) $\rightarrow \text{FeSi}_2 + \text{Si}$ -phase and partially as a phase of primary silicon. X-ray spectrum microanalysis of superfluous phases was carried out on the "fresh" fractures of FS65 ferrosilicon samples. The spectrograms of two eutectics are presented in Figure 2. The chemical composition of superfluous phases formed on grain boundaries of matrix phases is presented in Table 2.

The results of X-ray structure analysis of samples annealed at 1800 °C (Figure 3) and 2200 °C (Figure 4) demonstrate that at 1800 °C the disordered form of carbon and formed silicon carbide (the sample with 5 % of catalyst) are partially preserved in laboratory samples. The structure of samples is presented by graphite during annealing at 2200 °C.

The results of X-ray structure analysis of graphitized samples at 1800°C, 2200°C and 2600 °C are summarized in Table 3. In accordance with this table data, the degree of graphitization and value of specific electrical resistance of samples annealed at 2200 °C are comparable to data for production samples (without ferrosilicon) graphitized at 2600 °C.

Physical and mechanical properties of production sample and sample with 1 % and 5 % of catalyst regulated by DSTU 4494-2005 regarding the parameters of true and apparent density, heat conductivity, temperature coefficient of linear expansion, breaking strength and bend strength, accessible porosity.

Thus, addition of disperse ferrosilicon dust

Table 2. Chemical composition of superfluous phases (wt.%)

Si	Ca	P	Al	Fe	As	Cu	Zr
35.70	34.69	15.93	10.37	2.60	0.49	0.23	-
36.30	38.70	5.91	15.21	2.61	-	-	0.15

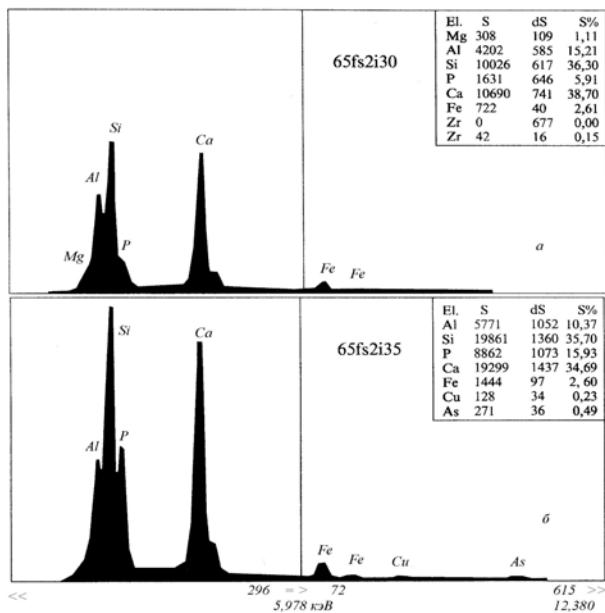


Figure 2. Energy spectra of elements in superfluous precipitated phases in the plane of "fresh" failure of 65 % ferrosilicon-based sample

in coke-pitch mixture for manufacture of graphitized products allows obtaining the equal values of almost all quality parameters reached for production samples at 2600 °C.

Table 3. Structure parameters of graphite of laboratory samples

Parameter	1800 °C			2200 °C			2600 °C		
	Prod.	+1 %	+5 %	Prod.	+1 %	+5 %	Prod.	+1 %	+5 %
<i>a</i> , nm	0.2451	0.2455	0.2458	0.246	0.246	0.246	0.246	0.246	0.246
<i>c</i> , nm	0.6858	0.6851	0.6849	0.6760	0.6737	0.6737	0.6735	0.6735	0.6735
<i>g</i>	0.13	0.17	0.18	0.7	0.83	0.83	0.84	0.84	0.84
L _c , nm	18	22	20	32	29	34	30	35	40
L _a , nm	7	9	7	23	20	20	14	14	19
SER, mkOhm·m	42.8	39.6	39.1	19.0	14.0	11.2	12.4	11.1	11.4
ρ_a , g/cm ³	1.53	1.56	1.56	1.50	1.51	1.50	1.53	1.52	1.47

a and *c* – the parameters of hexagonal crystal lattice of graphite;

g – the degree of graphitization;

L_c and *L_a* – the estimations of thickness and diameter of carbon components, respectively;

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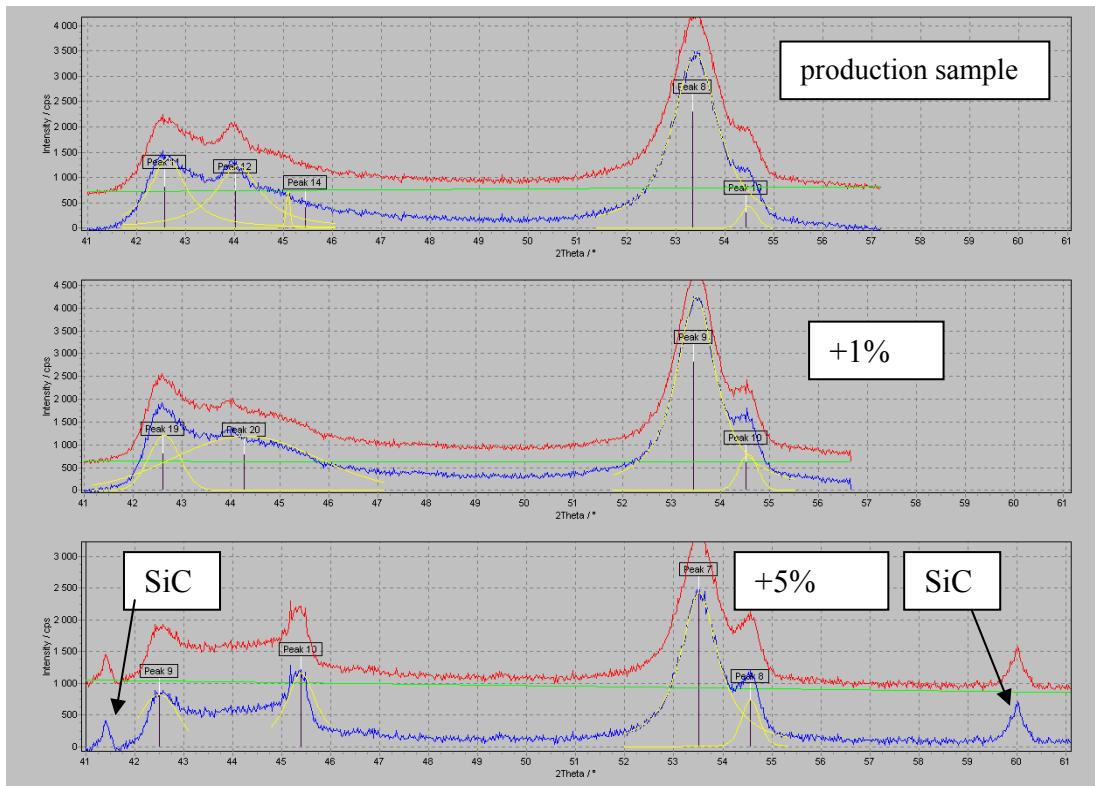


Figure 3. X-ray structure analysis of laboratory samples annealed at 1800°C

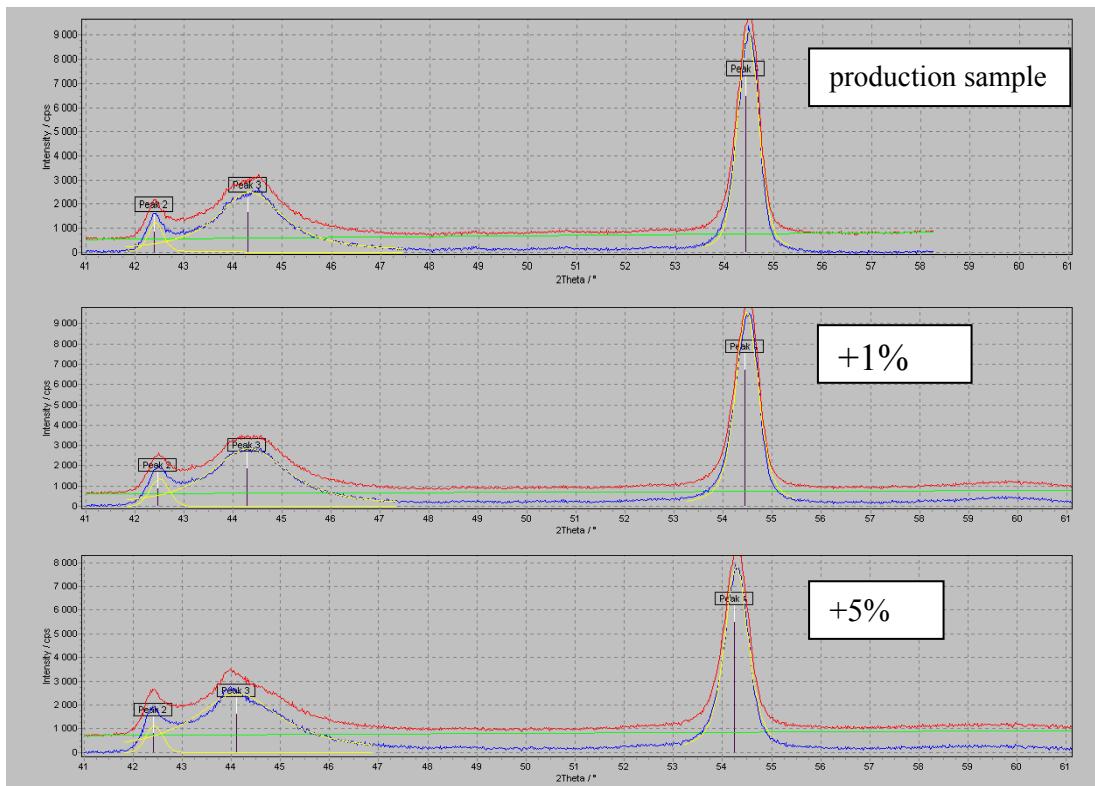


Figure 4. X-ray structure analysis of laboratory samples annealed at 2200°C

Table 4. Physical and mechanical properties of graphitized laboratory samples

No. of mix formula	Density		Accessible porosity, %	Total porosity, %	$\sigma_{\text{bend.}}$, MPa	Heat conductivity, W/mK (20°C)	SER, $\text{m}\Omega\cdot\text{m}$	$\sigma_{\text{break.}}$, MPa	Ash content, %	SiC content, %
	ρ_a , g/cm ³	ρ_m , g/cm ³								
1 (production)	1.49	2.23	30.0	33.2	4.2	63.2	10.0	2.2	0.1	-
2 (with 1 % of catalyst)	1.54	2.24	24.8	31.3	5.4	81.3	9.4	3.0	0.1	-
3 (with 5 % of catalyst)	1.47	2.25	31.3	34.9	3.0	58.6	8.1	1.5	0.1	0.055
Requirements of DSTU 4494-2005	not less 1.57	not less 2.20	-	no more 27.0	not less 6.5	100-130	no more 9.0	not less 3.0	no more 0.5	-

Conclusions

1. An analytical review of literature and patents related to one of priority trends of energy-saving technologies of industrial making of graphitized products in the area of intensification of high-temperature structure transformations of disordered carbon material into graphite by means of application of catalysts and choosing the rational temperature-time parameters of graphitization is carried out.

2. It is established that one of the most effective and rather cheap catalysts are mixtures of iron and silicon powders, addition of which in electrode charge ensures lowering the temperature of isothermal graphitization of products under otherwise equal conditions. The disadvantages of the known catalyst compositions, methods of their production and parameters of graphitization process are specified.

3. The phase composition of ferruginous alloy with content of silicon 65 % and impurity elements Ca, Al and Ti is studied experimentally with the application of electronic microscopy. It is confirmed that when the structure of ferrosilicon ingots is being formed, the impurity elements concentrate on the boundaries of matrix phases (iron silicides) in the form of eutectics having a complex chemical composition.

4. The laboratory research related to the effect of fine-dispersed ferrosilicon powder in the form of dust caught by fabric filters during rectification of ingots upon degree of graphitization of electrode mixture of charge materials with addition of catalyst in quantity of 1.0 and

5.0 wt.% is carried out.

5. Production and test samples (with 1 % and 5 % of catalyst) were annealed in the laboratory furnace according to the technology of annealing of electrode raw materials with 400 mm in diameter.

6. The analysis of experimental data about change of physical and mechanical properties of graphitized samples with 1 % of catalyst at 2600 °C demonstrates that the following characteristics are improved as compared to the production sample:

- SER decreases from 10.0 down to 9.4 $\text{m}\Omega\cdot\text{m}$ or by 6.0 %;
- heat conductivity raises from 63.2 up to 81.3 Watt / (m•K) or by 28.6 %;
- apparent density of sample increases from 1.49 up to 1.54 g/cm³ or by 3.4 %;
- accessible porosity decreases from 30.0 down to 24.8 % or by 17.3 %;
- total porosity decreases from 33.2 down to 31.3 % or by 5.7 %;
- bend strength increases from 4.2 up to 5.4 MPa or by 28.6 %.

7. X-ray structure analysis demonstrates that predetermined degree of graphitization of test sample with 1 % of catalyst at 2200 °C is reached in the production sample at 2600 °C.

8. The results of research confirmed a positive effect of catalyst on improvement of qualitative characteristics of graphitized products and therefore are the precondition for carrying out further industrial experiments on development of energy-saving technology of annealed raw materials graphitization.

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References

1. E.N. Panov, S.V. Kutuzov, I.L. Shylovich, S.V. Leleka, M.F. Bozhenko Otsenka energeticheskoy effektivnosti pechey grafitaytsii postoyannogo toka (*Energy Efficiency Estimation of Direct Current Graphitization Furnaces*) // Energetika: economika technologii, ekologiya. – 2006. – No. 2. – P. 60-65.
2. T. White – Industri Heating, 1970. – Sept. – P. 1801-1802.
3. M.V. Averina, I.A. Kondratyev, I.M. Rozenman Izmeneniye formy sfericheskikh chasits mezofazy pri termoobrabotke (*Shape Change of Mezophase Spherical Particles During Heat Treatment*) // Khimiya tverdogo topliva. – 1974. – No. 4. – P. 70-73.
4. Natsume Isamu. Electrodes from artificial graphite / “Tanso”. – 1970. –No. 60. – pp. 30-38 (Japanese). (RZhM, 1971, 5Б50).
5. G. Sherer Khimicheskiye transportnyye reaktsii (*Chemical Transport Reactions*) / Translation from German. – M.: Mir, 1964. – 189 p.
6. I.M. Yurkovskiy, D.S. Konstantinova Grafitatsiya uglerodnykh materialov s katalizatorami (*Graphitization of Carbon Materials with Catalysts*) // Tsvetnyye metally, 1988. – No. 6. – P. 62-63.
7. I.M. Jurkovskiy, L.S. Strelchenko Kataliticheskaya grafitatsiya uglerodnykh materialov pod deistviem bornykh soedineniy (*Catalytical Graphitization of Carbon Materials under Influence of Boric Compounds*) // Reports of Academy of Sciences of USSR, 1980, v. 251, No. 6. –P.1444
8. I. Marie, I. Mering. Ind. Carbon and Grafite, London, 1958, P. 204.
9. JP Patent 2007031233. Method for producing graphitematerial / Sakai Minoru, Hatano Hitomi; published 08.02.2007, priority: JP20050219339 28.07.2005.
10. A.V. Demin, A.V. Rakcheeva, G.A. Perkova, N.N. Shipkov Novyi class iskusstvennykh grafitov (*The New Class of Artificial Graphites*)// Tsvetnyye metally. - 1970. – No. 4. – P. 61-62.

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Исследование влияния добавок в электродную шихту наноразмерного порошка комплексного сплава системы Fe-Si-Al-Ca-Ti на процесс графитации и повышение комплекса свойств графитированных изделий

*Гасик М.И. /д.т.н./, Гасик М.М. /д.т.н./,
Цыбуля Е.И., Гринишпунт А.Г. /д.т.н./,
Кутузов С.В. /к.т.н./, Уразлина О.Ю.,
Гольчанская В.М., Гнездилова В.П.*

Изложены результаты исследования влияния присадок дисперсного ферросилиция в шихтовую композицию смоляной кокс+каменноугольный пек на свойства графитированных образцов после высокотемпературного обжига при 1800, 2200 и 2600 °C. Добавка ферросилиция в количестве 1 % обеспечивает при 2200 °C соизмеримые показатели по степени графитации, УЭС и физико-механическим характеристикам в сравнении с образцами, обожженными при температуре 2600 °C.