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Study of coke microstructure by combination of XRD analysis and SEM

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Abstract

The article is devoted to research of microstructure of coke. Coke is the main most suitable component for the production of anode masses and baked anodes due to its availability in large volumes, chemical purity and ability to acquire electrical conductivity during heat treatment of coke. The properties of the anodes are largely determined by the properties of coke. Investigation was carried out by mean of complex methods of XRD analysis and SEM. In the work, a number of industrial samples of needle cokes of various manufacturers were studied by mean of complex of structural methods: X-ray diffraction and analytical scanning electron microscopy. The main characteristics of the crystal structure of the samples, that is the interplanar spacing (d00l), the dimensions of the structural components (La and Lc), and the degree of ordering, were obtained. To describe the morphology of the coke samples results on SEM analysis were used, the obtained data are compared with the crystallographic data from XRD analysis. Their structural parameters were determined, and the features of their microstructure were investigated, in result, their interrelations were revealed. The consistency of the conclusions obtained by the results of two independent methods makes it possible to consider X-ray structural analysis in combination with analytical electron microscopy as the necessary complementary tools for the evaluation of cokes with a view to their possible application in various technological processes.

References

- [1] M.W. Meier. Cracking Behavior of Anodes. PhD Thesis. Federal Institute of Technology (ETH). Zurich, Switzerland. 1996. 122p.
- [2] M.M. Akhmetov, S.A. Zaitseva, R.N. Gimaev. Production and use of calcined needle coke. *Moscow:* TSNIITEneftekhim. 1983. 56p. (russian)
- [3] P.X. Niu, Y.L. Wang, L. Zhan. Electrochemical Performance of Needle Coke and Pitch Coke Used as Anode Material for Li-ion Battery. J. Mater. Sci. Eng. 2011. No.29. P.204-209.
- [4] S. Hume. The Reactivity of the anode. *Krasnoyarsk: Classic Center LLC*. 2003. 457p. (russian)
- [5] W.K. Fisher, R.C. Perruchoud. Influence of Coke Calcining Parameters on Petroleum Coke Quality. Light Metals. 1985. P.811-824.
- [6] H.P. Halim, J.S. Im, C.W. Lee. Preparation of needle coke from petroleum by-products. *CarbonLett.* 2013. No.14(152).
- [7] H. Predel. Petroleum coke. Bohnet M, ed. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, Weinheim. 2012. 361p.
- [8] Y. Cheng, Q. Zhang, Ch. Fang, Y. Ouyang, D. Liu. Co-Carbonization Behaviors of Petroleum Pitch. Waste SBS: Influence on Morphology and Structure of Resultant Cokes. J Anal Appl Pyrol. 2018. No.129. P.154-164.
- [9] Ch.N. Barnakov, G.P. Khokhlova, A.N. Popova, A.I. Romanenko, Y.A. Bryantsev. Structure and conductivity of carbon materials produced from coal pitch with carbon additives. Coke and Chemistry. 2017. Vol.60. No.7. P.278-284. (russian)
- [10] Ch.N. Barnakov, V.Yu. Malysheva, A.N. Popova, G.P. Khokhlova, Z.R. Ismagilov. Assessment of the relationship between the structure of graphite-like materials according to the data of the Russian Federation and the electrical properties of graphite materials - anodes for LIA. Kuzbass State Technical University Bulletin. 2013. No.5. P.70-73. (russian)

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- [11] S.A. Sozinov, L.V. Sotnikova, A.N. Popova, and R.P. Kolmikov. Study of the film of *n*-hexane insoluble asphaltene produced from coal-tar pitch. Butlerov Communications. 2017. Vol.51. No.7. P.75-80. DOI: 10.37952/ROI-jbc-01/17-51-7-75
- [12] T. Tano, T. Oyama, T. Oda, I. Fujinaga, H. Hashisaka. Process for producing needle coke for graphite electrode and stock oil composition for use in the process. European Patent EP2336267 A1. 2011.
- GOST 26132-84 Oil and pitch coke. Microstructure evaluation method. (russian) [13]
- [14] V.G. Zelenkin, N.P. Molotok. Graphite electrodes for high power electric steel furnaces. *Moscow:* TSNIItsvetmet economy and information. 1982. 48p. (russian)
- [15] R.C. Perruchoud, M.W. Meier and W.K. Fischer. Coke Characteristics from the Refiners to the Smelters. Light Metals. 2000. P.459-465.
- [16] B. Vitchus, F. Cannova, H. Childs. Calcined Coke from Crude Oil to Customer Silo. *Light Metals*. 2001. P.589-596.
- [17] S. Song, X. Cheng. The influence of alkyl group on needle coke formation. *AdvMaterRes.* 2011. No.1433. P.335-336.
- [18] M.M. Akhmetov. To the mechanism of formation of the structure of needle cokes. *World of Oil* Products. 2015. No.4. P.29-35. (russian)
- [19] B.A. Sadler, B.J. Welch. Anode Cosumption Mechanisms -a Practical Review of the Theory and Anode Property Consideration. Seventh Australasian Aluminium Smelting Technology Conference and Workshop. 2001. 41p.
- [20] P.X. Niu, Y.L. Wang, L. Zhan. Electrochemical Performance of Needle Coke and Pitch Coke Used as Anode Material for Li-ion Battery. J. Mater. Sci. Eng. 2011. No.29. P.204-209.
- [21] B. Zhang, H. Guo, X. Li, Z. Wang, W. Peng. Mechanism for effects of structure and properties of carbon on its electrochemical characteristics as anode of lithium ion battery. J.Cent.SouthUniv. (Sci. Technol.) 2007. No.38. P.454-460.
- [22] K. Hulse. Anode production. Krasnoyarsk: Classic Center LLC. 2004. 452p. (russian)
- [23] G.P. Khokhlova, Ch.N. Barnakov, V.Yu. Malysheva, A.N. Popova, Z.R. Ismagilov. Effect of heat treatment conditions on the catalytic graphitization of coal-tar pitch. Solid Fuel Chemistry. 2015. Vol.49. No.2. P.66-72. (russian)
- [24] G.P. Khokhlova, V.Yu. Malysheva, CH.N. Barnakov, A.N. Popova, Z.R. Ismagilov. Influence of the nature and amount of catalyst on the phase structure of carbon material obtained by low-temperature catalytic graphite coal tar pitch. Kuzbass State Technical University Bulletin. 2013. No.5. P.21-24. (russian)
- [25] G.P. Khokhlova, C.N. Barnakov, A.N. Popova, L.M. Khitsova. Influence of carbon additives on the thermal transformation of coal pitch. Coke and Chemistry. 2015. Vol.58. No.7. P.68-274. (russian)
- [26] G.P. Khokhlova, C.N. Barnakov, A.N. Popova. Carbonization of coal pitch with graphite additives. Coke and Chemistry. 2016. Vol.59. No.1. P.27-34. (russian)
- [27] Ch.N. Barnakov, G.P. Khokhlova, A.N. Popova, S.A. Sozinov, Z.R. Ismagilov. XRD characterization of the structure of graphites and carbon materials obtained by the low-temperature graphitization of coal tar pitch. Eurasian Chemico-Technological Journal. 2015. Vol.17. No.2. P.87-93.
- [28] H. Shi, J.N. Reimers, J.R. Dahn. Structure-refinement program for disordered carbon. J. Appl. Cryst. 1993. No.26. P.827-836.
- [29] M. Inagaki, M. Shiraishi. The evaluation of graphitization degree. Carbon Tech. 1951. No.5. P.165-175.
- [30] H.J. Wang, H.F. Wang. The effect of graphitization temperature on the microstructure and mechanical properties of carbon fibers. New Carbon Mater. 2005. No.20. P.158-163.
- [31] Sh. Zhao, B. Wang, Q. Sun. Effect of physical disturbance on the structure of needle coke. *ChinPhysB*. **2010**. No.19(10). P.108101.
- [32] I.C. Popovici, S. Birghila, G. Voicu, V. Ionescu, V. Ciupina, G. Prodan. Morphological and microstructural characterization of some petroleum cokes as potential anode materials in lithium ion batteries. JOptoelectronAdvM. 2010. No.12(9). P.1903-1908.
- [33] I.J. Kim, S. Yang, M.-J. Jeon, S.-I. Moon, H.-S. Kim. Structures and electrochemical performances of pyrolized carbons from graphite oxides for electric double-layer capacitor. J Power Sources. 2007. No.173(1). P.621-625.
- [34] B.J. Monaghan, R. Nightingale, V. Daly, E. Fitzpatrick. Determination of the thermal histories of coke in a blast furnace through x-ray analysis. Ironmaking and Steelmaking. 2008. Vol.35. P.38-42.
- [35] Ph. Ouzilleau, A.E. Gheribi, G. Eriksson, D.K. Lindberg, P. Chartrand. A size-dependent thermodynamic model for coke crystallites: The carbon-hydrogen system up to 2500K. Carbon. 2015. Vol.85. P.99-118.

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- [36] ICDD, PDF-2 (Database), edited by Dr. Surya Kalakkodu, International Centre for Diffraction Data. Newtown Square, PA, USA. 2011.
- [37] A.N. Popova. Crystallographic analysis of graphite by x-ray diffraction. *Coke and Chemistry*. 2017. Vol.60. No.9. P.361-365. (russian)
- [38] Ch.N. Barnakov, G.P. Khokhlova, V.Yu. Malysheva, A.N. Popova, Z.R. Ismagilov. X-ray diffraction analysis of the crystal structures of different graphites. Solid Fuel Chemistry. 2015. Vol.49. No.1. P.25-29. (russian)
- [39] A.N. Popova. The method of calculation of crystallographic characteristics of graphite. *Butlerov* Communications. 2017. Vol.51. No.7. P.86-90. DOI: 10.37952/ROI-jbc-01/17-51-7-86
- [40] H. Marsh. A tribute to Philip L Walker. *Carbon.* **1991**. Vol.29(6). P.703-704.