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Development of technology for production and application of graphite from hydrolytic lignin

Olga V. Popova · Mikhail Yu. Serbinovskiy · Anna G. Abramova

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Abstract The fine-dispersed artificial graphite is produced from hydrolytic lignin by thermolysis followed by graphitization. The article describes the influence of grinding and thermolysis on the granulometric composition of hydrolytic lignin powders, the carbon-base material, produced by thermolysis from lignin and artificial graphite. This research develops the rational technology of producing artificial graphite from lignin, defines its structural and physical characteristics. Graphite consists of particles with a size less than 45 μ for more than 80 %. The degree of graphitization of the graphite from lignin is not less than 94 %. The possibility of application of graphite to synthesis of intercalation compounds and thermally expanded graphite production is described.

1 Introduction

Nowadays, fine-dispersed graphites are highly demanded in electrochemical and other technologies. However, the production of fine-dispersed fractions from natural graphites is connected to well-known problems caused by the structure and antifriction properties of graphite. As a result, the possibility of the production of artificial graphite attracts attention if the dispersion of the raw materials poses no technological difficulties.

O. V. Popova (✉) · A. G. Abramova
Department of technospheric safety, ecology and chemistry, Southern Federal University, Nekrasovsky 44, Taganrog 347922, Russia
e-mail: ovpopova@sfedu.ru

M. Yu. Serbinovskiy
Department of the aircrafts, Southern Federal University, Nekrasovsky 44, Taganrog 347922, Russia

Research related to the graphitization lignin or biomass is scarce. The publication by Kubo et al. (2003) on catalytic graphitization of hardwood acetic acid lignin with nickel acetate additions at temperatures up to 1,000 °C needs to be mentioned. There is research on the production of carbon fibers from lignin, including temperatures up to 2,000 °C (Kadla et al. 2002). Baker and Rials (2013) reported in a review on recent advances in the field of carbon fiber from lignin.

It was assumed that the hydrolytic lignin (HL), which is a large-tonnage waste after wood percolation with diluted sulfuric acid, can be the raw material for artificial graphite. The percolation hydrolysis is usually carried out at elevated pressures (0.6–0.9 MPa) and temperatures up to 200 °C (Khol'kin 1989). It is significant that processes of condensation, oxidation, demethylation etc. take place in acidic medium (Lai and Sarkanen 1971). As a result, the acid lignin molecule largely consists of linked benzene rings unlike the natural lignin structure. Furthermore, it is known that pyrolysis of the organic macromolecular compounds is accompanied by condensation reactions. Therefore, the formation of condensed aromatic structures should be continued with increasing temperature of lignin pyrolysis without air access. Indeed, Kaplunova et al. (1990), Mohan et al. (2006) and Nassar and Mackay (1984) found that there is no significant opening of the benzenes structures in the process of lignin thermolysis in the absence of oxygen. Presumably, after hydrolysis and pyrolysis processes condensed structure for the formation of the artificial graphite is obtained.

According to Fialkov (1965) the artificial carbon materials produced from various raw materials and according to different technologies can be graphitized, not graphitized or have different degrees of graphitization. It has been found that the carbon material from lignin is liable to the

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graphitization process. Thus, the authors' assumption was experimentally confirmed, and as a result, the artificial graphite was produced from the hydrolytic lignin (AGL).

This publication contains the research of the process of obtaining the graphite from lignin, and also includes characteristics of the bisulphate graphite and the thermally expanded graphite.

2 Materials and methods

For thermal modification of lignin, hydrolytic industrial waste, characterized by Rabinovich (2010), was used. Namely the hydrolytic lignin of corncobs (HLCC), hydrolytic lignin of softwood (HLSW) and hydrolytic lignin of cotton hulls (HLCH) were used. The content of the typical components for different hydrolytic lignin are shown in Table 1. The weight ratio of C, H, O is calculated in the Klason lignin.

This study on the influence of grinding of hydrolytic lignin on its granulometric composition was carried out in a laboratory mill with porcelain cylinders with a capacity of 2 and 5 l. As grinding objects three types of cylpebs were used: (1) cylindrical ones with a diameter of 30–35 and 35–40 mm high; (2) cylindrical ones with a diameter of 22–30 and 25–35 mm high; (3) round cylpebs with a diameter of 15–25 mm. The time of grinding, the relative volume of a lignin and the relative volume of grinding objects was varied. The density of grinding objects was 3.02 g/cm^3.

To produce a carbon material the lignin powder was heated at 600 °C without access of air in the graphite container or the stainless steel container. To produce artificial graphite (AGL), carbon material was graphitized at a temperature of 2,500–2,800 °C. The synthesis of graphite bisulphate from AGL (BGL) was carried out according to Yakovlev et al. (2006). The thermally expanded graphite (TEGL) was produced from bisulphate graphite by thermal shock at 750–900 °C for 5–15 s. A set of three bolters with a cell size of 100, 75 and 45 μ was used for particle-size analysis or sieving of lignin, carbon material and graphite powders.

Table 1 Characteristics of the hydrolytic lignins

Content, (%)	HLSW	HLCH	HLCC
Klason lignin	72.4	81.5	73.5
Moisture	5	4	5
Ash	2.5	2.3	2.3
Wood tar	6.4	3.4	3.1
H_2SO_4	1.1	1.3	1.4
Cellulose	12.6	7.5	14.7
Carbon	63.5	64.5	66.6
Hydrogen	5.0	5.3	6.1
Oxygen	31.5	30.2	27.3

The diffraction spectra for the powder samples after pyrolyse and graphitisation were obtained with X-ray diffractometer DRON-1.5 using nickel filtered CuKα radiation.

The microscopic investigations were conducted with a scanning electron microscope probe Quanta 200 (FEI) equipped with energy dispersive X-ray EDAX facility for elemental analysis.

3 Results and discussion

3.1 Features of producing graphite from lignin and characteristics of the material

It is known that the hydrolytic lignin is decomposed by heating forming activated carbon, gaseous fraction, fluid fraction vapors and tarry residue (Amutio et al. 2013; Caballero et al. 1996; Kaplunova et al. 1990). All main thermal reactions of a lignin, according to differential thermal analysis, are completed within temperature ranges of 400–600 °C (Kaplunova et al. 1990; Nassar and Mackay 1984; Wang et al. 2009). The thermal reactions of lignin destruction can be completed at higher or lower temperatures, which are considerably determined by the lignin heating rate and gas medium (Bilbao et al. 1990; Caballero et al. 1996; Ferdous et al. 2002; Várhegyi et al. 1997). Based on the aforementioned, separate heat treatment at 600 °C was performed prior to HL graphitization.

The vital point of rational technology is when and how to make a material dispersion for producing the necessary granulometric composition and that is why granulometric composition of HL powders of various factories was studied. The powders of a carbon material and graphite produced from the HL, received by various grinding modes, were also investigated. The first order plans of the three-factorial experiment (Table 2) were used. Response functions are the content of fractions of a particular size.

Experiments have shown that the grinding of the hydrolytic lignin of various plants happens with different intensity, but the obtained relations are very close (Figs. 1, 2, 3). The differences do not exceed 10–12 % in recommended parameters for a fraction content less than 45 μ.

In equations:

$X_1 = (x_1 - 100)/50$, where x_1—grinding time, min;

$X_2 = (x_2 - 60)/20$, where x_2—the relative volume of a lignin, %;

$X_3 = (x_3 - 9.5)/3.2$, where x_3—the relative volume of grinding subjects, %.

We have the regression equations for the content of separate fractions HLCC (%) taking into account the

Table 2 Conditions of lignin grinding

Plan characteristics	Grinding time x_1, min	Relative volume of lignin x_2, (%)	Relative volume of grinding bodies x_3, (%)
Zero level	100 ($X_1 = 0$)	60 ($X_2 = 0$)	9.5 ($X_3 = 0$)
Interval of variation	50	20	3.2
Top level ≪+≫	150 ($X_1 = +1$)	80 ($X_2 = +1$)	12.7 ($X_3 = +1$)
Bottom level ≪–≫	50 ($X_1 = -1$)	40 ($X_2 = -1$)	6.3 ($X_3 = -1$)

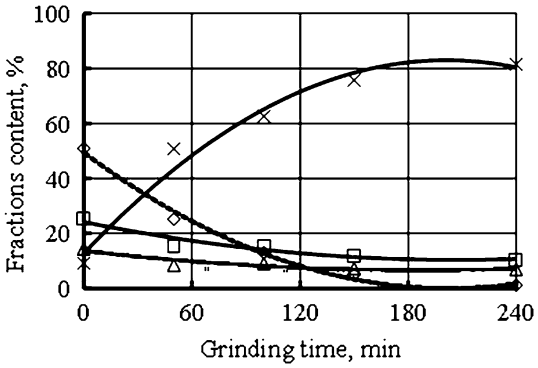

Fig. 1 Content of HLCC fractions depending on the grinding time: *open diamond* more than 100, *open square* 75–100, *open triangle* 45–75, *cross symbol* less than 45 μ

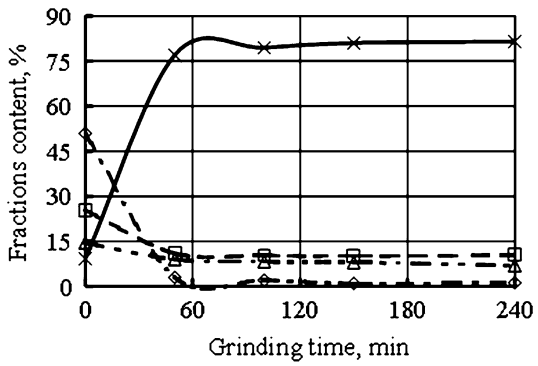

Fig. 2 Content of HLCC fractions depending on grinding time at the optimal mass lignin and grinding bodies: *open diamond* more than 100, *open square* 75–100, *open triangle* 45–75, *cross symbol* less than 45 μ

significance coefficients for a confidence interval of 95 %. They are:

– for fraction >100 μ:

$$m_1 = 15.125 - 10.125X_1 + 7.875X_2 - 4.375X_3 - 5.875X_1X_2 + 2.375X_1X_3,$$

value of Fischer's variance ratio $F = 2.625 < F_{tab} = 3.6$, the equation is adequate;

– for fraction 75–100 and 45–75 μ the equations are inadequate as there are no significant coefficients ($F > F_{tab}$);

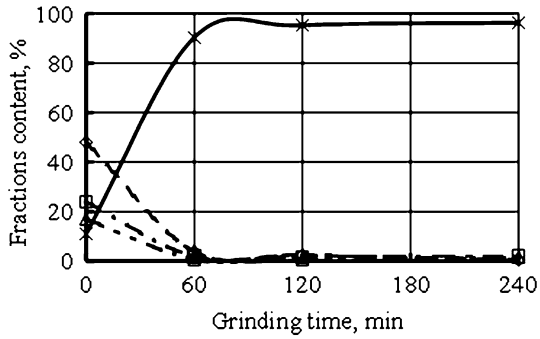

Fig. 3 Content of HLSW fractions depending on grinding time at the best yield of small fraction for: *open diamond* more than 100, *open square* 75–100, *open triangle* 45–75, *cross symbol* less than 45 μ

– for fraction <45 μ: $m_4 = 63.25 + 12.5X_1 - 8.75X_2 + 5.25X_3 + 7X_1X_2$.
value of Fischer's variance ratio $F = 3.518 < F_{tab} = 3.8$, the equation is adequate.

The relations between the average content of separate fractions of HLCC and grinding time (averaging was carried out for the fixed value of one of the parameters) are presented in Figs. 1 and 2. The listed parameters have little influence on fractions content 75–100 and 45–75, what mathematical processing of the experiments results has confirmed. The intensively powdering of large fraction and some powdering of fractions less than 100 μ takes place during the first 50–60 min of the grinding process. At the same time the increasing lignin weight and the weight of milling subjects in a cylinder promote intensification of the grinding process. However, the increase of lignin mass over 400–450 g and grinding subjects mass over 520–570 g and duration of grinding over 60–100 min does not lead to significant increase of the content of fraction smaller than 45 μ.

When the masses of the lignin and grinding subjects are optimum, the influence of grinding time on the content of fractions can be seen in Fig. 2.

The content of the separate fractions depends on grinding time when optimum masses of lignin and grinding subjects for the HLSW are used (Fig. 3). The duration of efficient grinding of lignin takes 1 h.

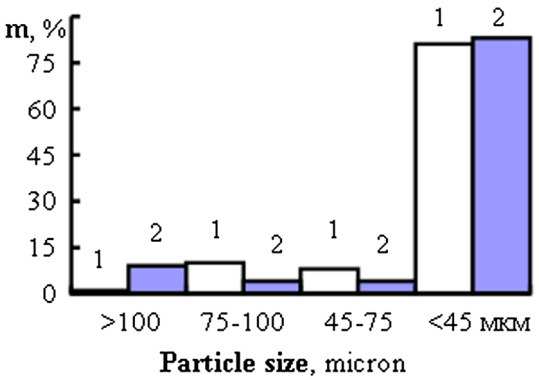

Fig. 4 Histogram of granulometric composition of HLCC after grinding for 2.5 h (*1*) and a carbon material from HLCC without grinding (*2*)

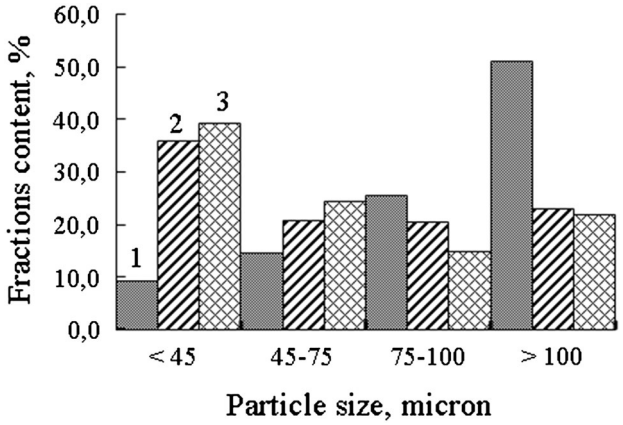

Fig. 5 Histogram of granulometric composition: *1* HLCH, *2* carbon material from HLCH, *3* graphite from HLCH

The powdered hydrolytic lignin is the raw material in the chemical and electrochemical modification processes. The fine fractions are used as fillers and composite ingredients. But there is the question: what sizes of fractions are required for pyrolysis?

As a result, the fractional composition of the carbon material produced from the hydrolytic lignin of various fractional compositions was identified. The experimental results showed that grinding of large fractions takes place during the process of pyrolysis. So the granulometric composition of a carbon material practically does not depend on the composition of the initial lignin. The comparative histogram of granulometric composition of HLCC powder and of the powder of a carbon material from HLCC is depicted in Fig. 4. The HLCC powder was produced after grinding for 2.5 h. The powder of a carbon material produced from HLCC was not ground. The carbon material has larger fractions than lignin. It is probably due to the fact that some agglomerates stay mechanically connected; however, they are very fragile as they disappear after a short-term grinding.

In this study it was found that the granulometric composition of carbon materials depends on the nature of initial lignin. Carbon materials with a high content of fine fractions are produced from the lignin of wood (HLSW). A more large-dispersed composition of fractions has the carbon material produced from the lignin HLCH (Fig. 5).

Lignin heat treatment at a temperature of 600 °C leads to destruction of large agglomerates. As a result more than 75 % of particles have a size less than 100 μ, but more than 50 % of particles of initial lignin powder have a size of more than 100 μ (Fig. 5). After graphitization of the carbon material, the granulometric composition of powder was practically not changed though the quantity of particles of fine fractions (less than 45 and 45–75 μ) was little increased.

Thus, using the results of the research it can be confirmed, that there is no need to grind the hydrolytic lignin prior to pyrolysis, moreover, granulometric composition of the received carbon material allows its use in the production of various materials and artificial graphite without additional grinding.

The XRD of carbon material and graphite from HLCC were measured (Fig. 6). The (0002), (1011), (1013) diffraction peaks of carbon material refer to the diffraction of graphite. The other defined peaks were not identified. Apparently, these peaks correspond to structural units of the residual lignin or products of their interaction with oxygen and nitrogen of air (pyrolysis container contains a small amount of air).

The diffractogram of the graphitized carbon material reveals the structural change in carbon material from disordered carbon to crystalline graphite. The d_{0002}, d_{1011}, d_{1013} of the carbon material become better defined. Furthermore, there are other peaks typical for hexagonal structure of graphite, that allow to characterize the quality of the obtained graphite (Fialkov 1965). Based on these data, it can be assumed that the initial carbon material is graphitized almost completely. Calculated on Bragg relation interlayer distances are: $d_{0002} = 0.3360$ nm, $d_{0004} = 0.3358$ nm, $d_{0006} = 0.3356$ nm. Relation $I_{1122}/I_{1120} = 1.06$. The degree of graphitization of the produced material is not less than 94 %. Table 3 summarizes the principal characteristics of the carbon material and graphite obtained from HLCC.

3.2 Application of graphite from HLCC for synthesis of intercalated graphite compounds and thermally expanded graphite

Nowadays, the intercalated compounds of graphite are widely applied to many fields of technology. So the graphite from lignin was investigated as a matrix for synthesis of intercalated compounds.

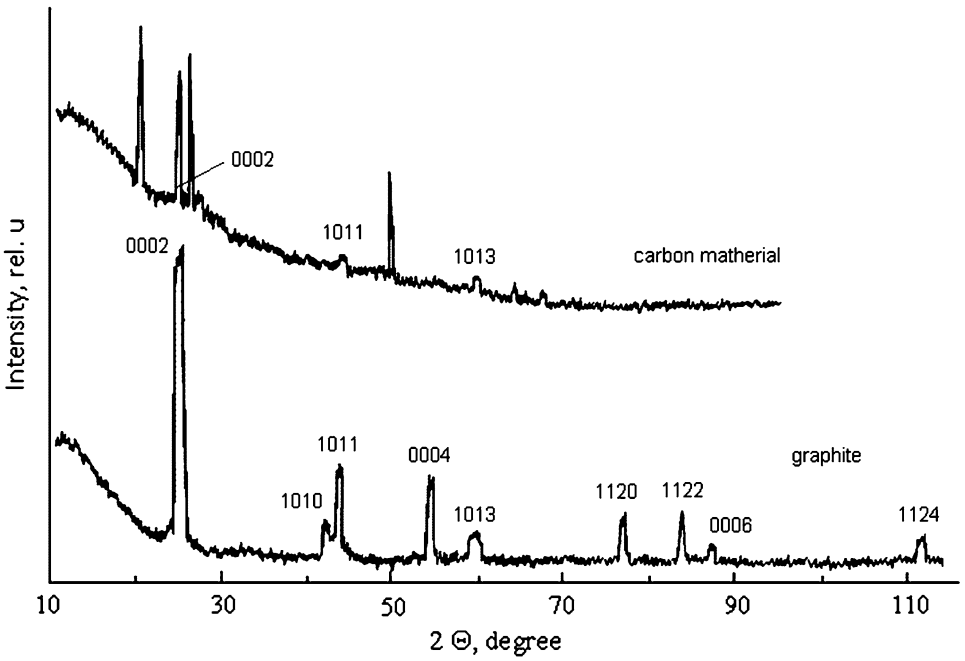

Fig. 6 X-ray diffractograms of the carbon material and the graphitized carbon material from HLCC

Table 3 Characteristics of the carbon material and graphite from HLCC

Gaged parameter	Result	Normative document
Carbon material from HLCC		
Ash content, (%)	2.3	GOST (All Union State Standard) 11022-95 (ISO 1171-81)
Moisture of analytical test, (%)	2.3	GOST 27314-91 (ISO 589-81)
Total sulfur, (%)	0.6	GOST 8606-93 (ISO 334-92)
Highest combustion heat, (kcal/kg)	5512	GOST 147-95 (ISO 1928-76)
Graphite from HLCC		
Interlayer distance of d_{002}, (nm)	0.3360	–
Particle size[a], (μ)	less than 45	–
Density, (g/cm^3)	2.29–2.30	–
Specific surface area, (m^2/g)	not less than 85	–

[a] Fraction ≪−045≫

The results confirm that AGL can be successfully used for electrochemical synthesis of graphite bisulphate, and any degree of oxidation can be produced. The over-oxidized BGL are synthesized at high specific capacities (more than 200 mA h/g). The regularities of the processes of BGL electrochemical synthesis from AGL and other brands of graphite are similar (Yakovlev et al. 2006). The differences are connected with larger dispersion of AGL and that is why the expense of electricity for formation of the surface functional groups of the small particles of AGL is larger and the tendency to over-oxidation is larger. However, using the identical potentials of potentiostatic synthesis of graphite bisulphate from AGL, current densities are higher than the same one of graphite bisulphate synthesis from other brands of graphite (for example, high purity crystalline graphite (GC) with dispersion 200–300 μ). So intercalation process inside AGL goes faster. Therefore, the same step of oxidation at equal potentials is received slightly faster inside AGL than inside the other graphite with the larger particles.

The obtained TEGL has a density from 2.4 to 4.0 g/dm^3 depending on the expense of electricity for BGL synthesis (I and I + II steps). The essential advantage of graphite from lignin (in comparison with other graphites) is that the rather high impurities content in initial HL (ash content 2.0–2.6 % – Table 3) does not influence the density of the received thermally expanded graphite. This is probably due to the external character of impurities in HL and in the graphite obtained. The graphite particles by themselves have rather high purity and the content of impurities is decreased greatly during graphitization process. The elemental analysis which has been carried out with a precision of 0.1 % has revealed only carbon in the TEGL.

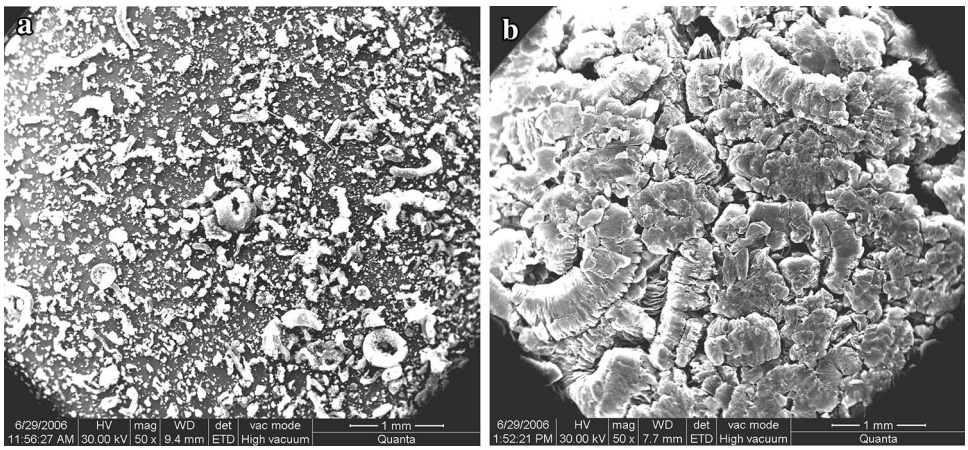

Fig. 7 **a** Microstructure of TEGL from HLCC in comparison with **b** TEG (×50)

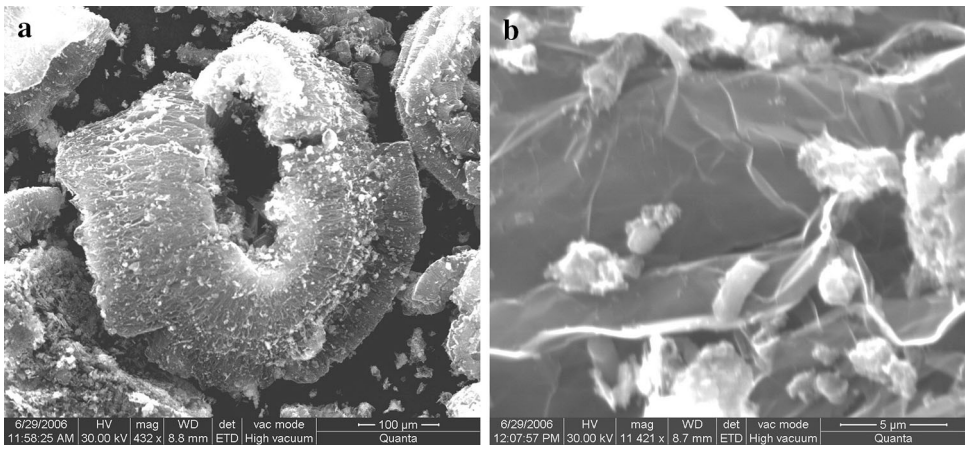

Fig. 8 **a** Microstructure of TEGL (×432) and **b** microstructure of TEGL (×11421)

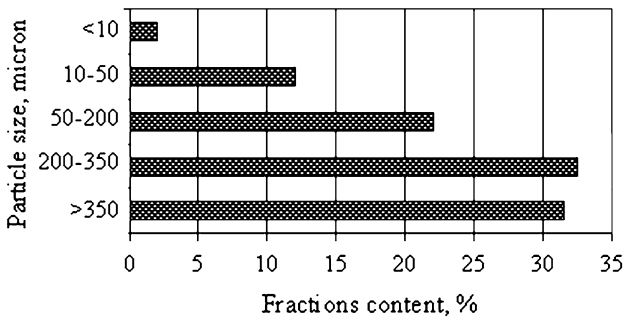

Fig. 9 Histogram of granulometric composition of TEGL

Comparative microscopic researches of TEGL and thermally expanded graphite obtained from graphite GC (TEG) with dispersion of 200–300 μ demonstrate considerable differences in their structures (Fig. 7).

TEG represents long fiber of relatively homogeneous material (Fig. 7b), on the contrary TEGL is the material with considerably smaller size of particles, which have a larger dimensional scatter (Figs. 7a, 8).

The histogram of particle distribution of TEGL according to their sizes is presented in Fig. 9. It is typical for TEGL that the particles have sizes less than 350 μ. For TEG it is typical that the particles are larger than 1,000 μ.

TEGL surpasses other graphite materials as the matrix for an intercalation of lithium (Popova et al. 2008). TEGL can be used to obtain graphite electrodes with high specific capacity (720 W h/kg) for lithium-ion accumulator.

4 Conclusion

The offered technology of producing artificial graphite from hydrolytic lignin allows to obtain the fine-dispersed graphite without grinding process.

The produced graphite consists of particles with a size less than 45 μ for more than 80 %, density of $\sim$2.3 g/cm^3, a specific surface area of more than 85 m^2/g, graphitization degree not less than 94 %. Graphite is suitable as a matrix for intercalation and can be successfully used for producing thermally expanded graphite of high quality.

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