Russian Journal of Applied Chemistry, Vol. 78, No. 4, 2005, pp. 559–564. Translated from Zhurnal Prikladnoi Khimii, Vol. 78, No. 4, 2005, pp. 566–571.

Synthesis of Metallofullerenes by Electric-Arc Method with a Surface-Modified Electrode

S. M. Kuz'min, N. Yu. Borovkov, A. M. Kolker, and V. L. Brazhyunas

Institute of Chemistry of Solutions, Russian Academy of Sciences, Ivanovo, Russia
Ivanovo State University of Chemical Technology, Ivanovo, Russia

Received September 30, 2004; in final form, February 2005

Abstract—A method for synthesis of metallofullerenes by electric-arc sputtering of graphite, in which lanthanum compounds are deposited on the surface of a graphite electrode, was suggested. The influence exerted by the amount of deposited lanthanum on the yield of lanthanum was studied.

At present, endohedral complexes of fullerenes [1] and higher fullerenes attract researchers' attention as potential objects of nanotechnologies [2], which possess nonlinear optical characteristics [3] and unique physicochemical properties [4]. Synthesis and identification of new forms of endofullerenes (various isomers, bi- and trinuclear complexes in encapsulation of the whole variety of the available elements in the void in the fullerene molecule) have been extensively studied [5–18]. The known methods for synthesis of metallofullerenes consist in bombardment of a fullerene-containing substrate with metal ions [19] or in evaporation of a metal–carbon composite in the atmosphere of an inert gas [16–23]. The composites are evaporated with lasers [21, 22] or by electric-arc sputtering [16, 22, 23].

Commonly, the composite is prepared as follows. A hole bored in a graphite rod is filled with a mixture of a metal oxide, powdered graphite, and binder resins. Then the rod (electrode) is annealed in a vacuum at a temperature of about 2000°C. As a result, the carbide of the starting metal is formed and fixed in the bulk of the electrode.

It should be noted that C_{60} and C_{70} are formed in synthesis of metallofullerenes. There is evidence [16, 21, 23] that the amount of a metal oxide introduced into the electrode affects the total yield of fullerenes. The ratio of yields of hollow fullerenes and metallofullerenes [16, 21, 24] suggests that the formation of an endocomplex is, in fact, the side process in synthesis of hollow fullerenes.

Use of a combined electrode results in that metal atoms are introduced into the discharge zone in sputtering of the electrode. Having a low ionization potential, metal atoms markedly change the discharge parameters, and, primarily, make lower the temperature of electrons in the arc and of the gas [25]. Using a combined electrode, as a rule, leads to a decrease in the yield of fullerenes [16, 25, 26].

The yield of metallofullerenes in synthesis is low and the procedure for preparing a composite is prolonged and complicated. This results in that the problem of obtaining industrial samples of metallofullerenes remains unsolved. The efficiency of synthesis of metallofullerenes is raised by varying the composition of the composite [22] and by improving the design of the reactors used for this purpose [23].

The aim of this study was to examine specific features of synthesis of metallofullerenes with a surface-modified electrode.

EXPERIMENTAL

The experimental installation for synthesis of fullerenes by electric-arc sputtering of graphite is shown schematically in Fig. 1. A combined electrode was fabricated from 10-cm-long rectangular graphite rods with a cross-section of 2×4 to 4×6 mm. The electrode was prepared by depositing an aqueous suspension of lanthanum carbonate on its surface. The deposited layer was dried in air to constant mass and then the electrode mounted into the reactor was an-

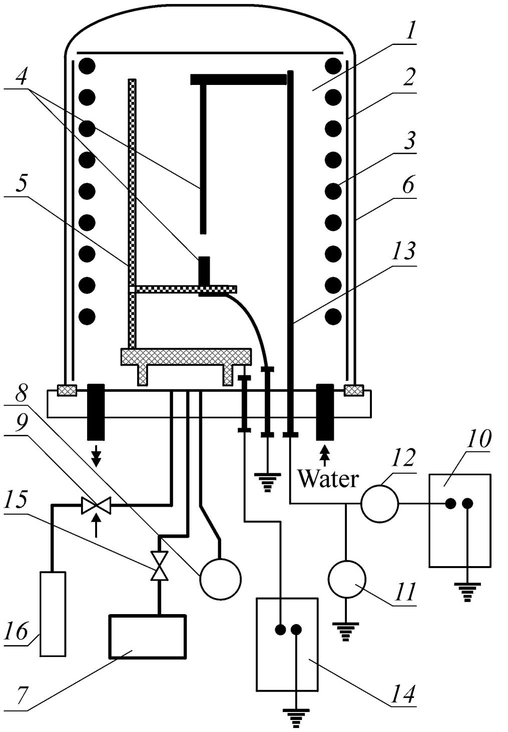

Fig. 1. Schematic of the experimental installation for electricarc synthesis of fullerenes: (*1*) reactor, (*2*) reflector, (*3*) cooling circuit, (*4*) graphite rods, (*5*) microlift, (*6*) bell-jar, (*7*) vacuum station, (*8*) vacuum gage, (*9*) leak valve, (*10*) discharge feeding unit, (*11*) voltmeter, (*12*) ammeter, (*13*) current-carrying bar, (*14*) microlift-feeding unit, (*15*) vacuum cock, and (*16*) cylinder with helium.

nealed by passing a dc current of 50–70 A through short-circuited electrodes at a residual pressure in the reactor of 10^{-2} Pa or in the atmosphere of helium.

The cycle of reactor preparation to synthesis included the following stages: (1) mounting of graphite electrodes in the reactor, with their mass preliminarily determined; (2) evacuation of the reactor to a pressure of about 10^{-3} Pa; (3) heating of the electrode by passing an electric current; (4) filling of the reactor with helium to the working pressure and heating of the electrodes in this atmosphere; (5) repeated evacuation of the reactor to a pressure of 10^{-3} Pa; and (6) letting-in helium to a working pressure of 2×10^4 Pa.

The working pressure in synthesis of metallofullerenes has been experimentally determined previously [27]. This pressure corresponds to the maximum yield of hollow fullerenes.

To sputter the combined electrode, a voltage sufficient for arc initiation was applied across the electrodes and microlift displacement at a preliminarily adjusted velocity was switched on. In the course of sputtering, the arc current was 100–150 A at a voltage across the discharge gap equal to 20–25 V. The completion of the sputtering process was judged by visual inspection.

After the sputtering of the electrode, the carbon black obtained in the course of synthesis was collected and its mass was determined. Also weighed were the residue of the electrode being sputtered and the cathode deposit (carbon layer formed on the cathode in synthesis).

The fullerenes contained in the carbon black were extracted with *ortho*-xylene at a temperature of 40°C under agitation for 24 h. Then the solution was filtered on a glass filter and the carbon black was additionally washed with *ortho*-xylene to a colorless extract. The resulting filtrate was brought to a mark of 100 ml in the volumetric flask with *ortho*-xylene.

The concentration of individual fullerenes in solution was analyzed by HPLC and spectrophotometry. Chromatograms were obtained on a LIQUOCHROME 2010 chromatograph with a UV detector (analytical wavelength 330 nm), with hexane as eluent (residual content of water $\leq 6 \times 10^{-3}$%) and a column packed with SGX Separon adsorbent (grain size 7 μm). The chromatograms of reference solutions and those being analyzed were processed using Multichrom 1.5 software. The spectra were recorded with a Hitachi U2001 spectrometer.

A theoretical description of the synthesis of fullerenes has resulted in model concepts of the assembly of a carbon skeleton [28–31]. Also represented in the literature are the results of quantum-chemical calculations of the stability of various endocomplexes [32, 33]. An analysis of published data made it possible to maintain that both the C_{60} fullerene and the endocomplex are formed in the jet of a carbon vapor produced by sputtering in the electric-arc synthesis of fullerenes [30].

It is known that [34], in synthesis of the fullerene, the ions bombarding the cathode do not sputter it, but, conversely, are incorporated into its structure to give a cathode deposit. In this case, both the amount of the deposit formed and its structural features depend on the composition and energy of ions bombarding the cathode. Under the conditions of the synthesis performed, three sources are responsible for the composition of the near-cathode layer of plasma: buffer gas, sputtered graphite, and sputtered lanthanum. The lower the ionization energy, the larger the fraction of an ionized component. The ionization energy of helium is 24.587 eV [35]; that for components of the carbon vapor: C 11.260, C_2 12.10, C_3 11.65, and C_4 11.28 eV [36]; the energies of successive ionization for lanthanum ions are 5.577, 11.06, and 19.17 eV [35]. It should be noted that the existence of high-energy metastable states of helium leads to ionization of easily ionized components of plasma by the Penning mechanism [36]:

$$A^* + B \rightarrow A + B^+ + e,$$

where A^* stands for helium in excited state, and B, for the easily ionized component.

Thus, it would be expected that the ionic composition of plasma is mainly represented by C_n^+ and La^+ ions. As the discharge current in the cathode region is carried by positive ions, the mass of the deposit is proportional to the quantity of electricity consumed in the process and to the accommodation coefficient of the incident ion. The amount of graphite being evaporated is also proportional to the charge passed [37]. As a result, the ratio of the mass of sputtered graphite to that of the deposit can be used to characterize an experiment.

The shape of the deposit obtained in the experiment (Figs. 2a and 2b) corresponds to that of the electrode being sputtered. The cross-section of the cathode deposit exceeds that of the initial electrode and a crater is always present in the central part of the cathode deposit. Use of both graphite and surface-modified electrodes leads to the same distribution of sputtered graphite among the fullerene black and the cathode deposit (Fig. 3). The lanthanum being evaporated does not change the nature of the ion flow toward the cathode surface and, consequently, does not enter into the near-cathode zone of the discharge. In the authors' opinion, this is an indication of the separate evaporation of graphite and lanthanum.

The decrease in the amount of the cathode deposit with respect to the amount of sputtered graphite on making smaller the cross-section of the electrode is understandable. There exists a considerable temperature gradient at the cathode from the axis of the arc toward its periphery, as well as a temperature gradient in the gas phase [37, 38]. As a result, the gas phase contains larger carbon clusters in the peripheral parts of the near-cathode region; the lower surface temperature leads to a higher accommodation coefficient, compared with that in the central parts of the cathode. Apparently, the area of the peripheral regions of the electrodes increases in proportion to a squared characteristic size (equivalent electrode diameter). The factors mentioned lead to an increase in the fraction of the cathode deposit on raising the cross-section area of the electrode being sputtered and provide the observed shape of the cathode deposit.

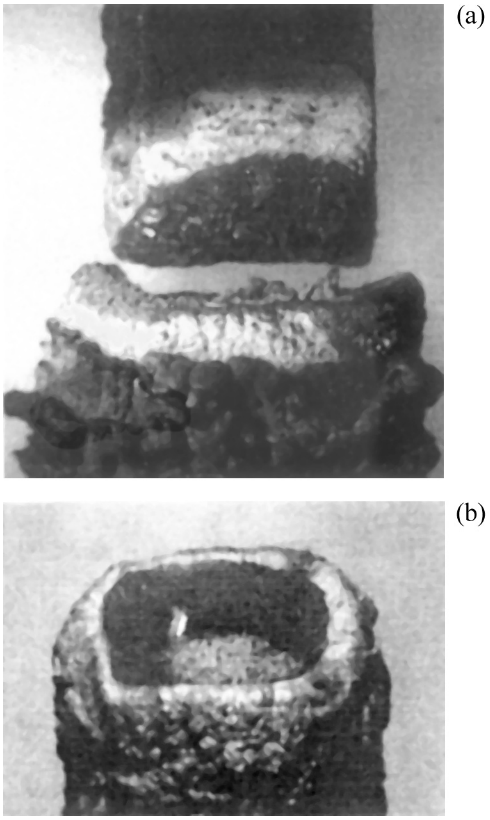

Fig. 2. Photographs of a typical cathode deposit upon completion of the synthesis. (a) Correspondence between the electrode being sputtered and the deposit formed, and (b) characteristic crater at the center of the deposit.

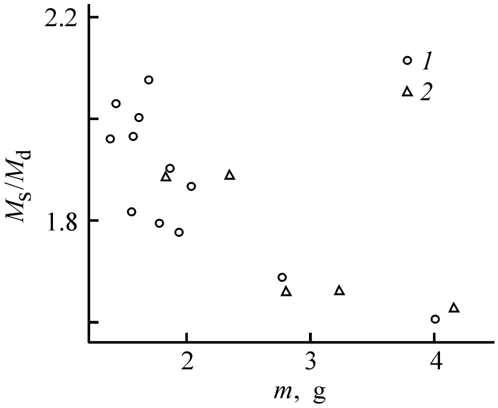

Fig. 3. Influence exerted by the mass *m* of the electrode being sputtered on the ratio M_s/M_d of the mass of the sputtered graphite to that of the cathode deposit for (*1*) graphite and (*2*) combined electrodes.

The flow of evaporated lanthanum is virtually not involved in the formation of the plasma composition in the arc, but affects the synthesis of fullerenes in the carbon vapor jet. This influence is primarily manifested in a change in the composition of the

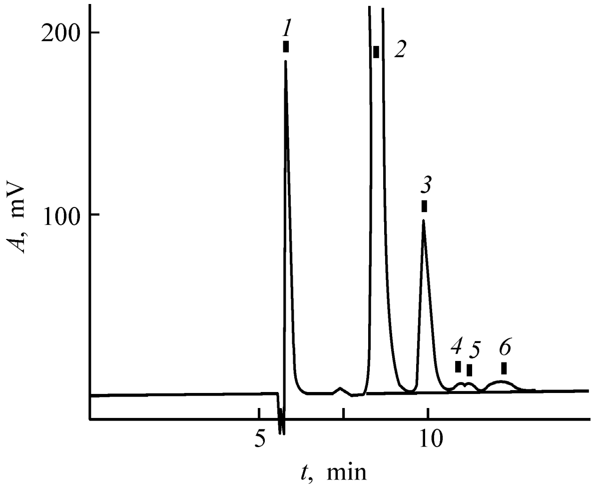

Fig. 4. Typical chromatogram of an extract of the carbon black synthesized. (*A*) Signal from the UV detector and (*t*) time. Peak assignment: (*1*) *ortho*-xylene, (*2*) C_{60}, (*3*) C_{70}, (*4, 5*) C_{72}–C_{86}, and (*6*) La@C_n.

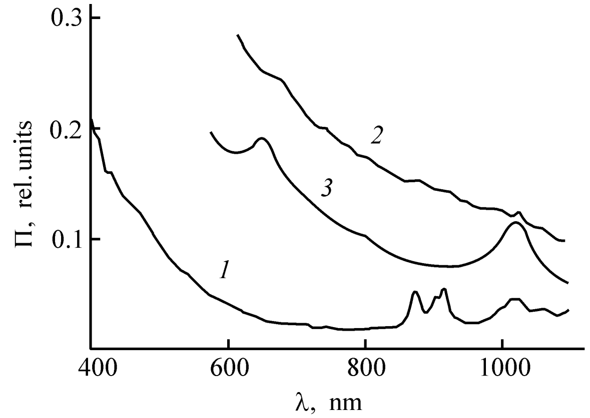

Fig. 5. Typical absorption spectrum of the extract. (Π) Absorption and (λ) wavelength. Extraction with (*1*) *ortho*-xylene and (*2*) DMFA; (*3*) published La@C_{82} spectrum.

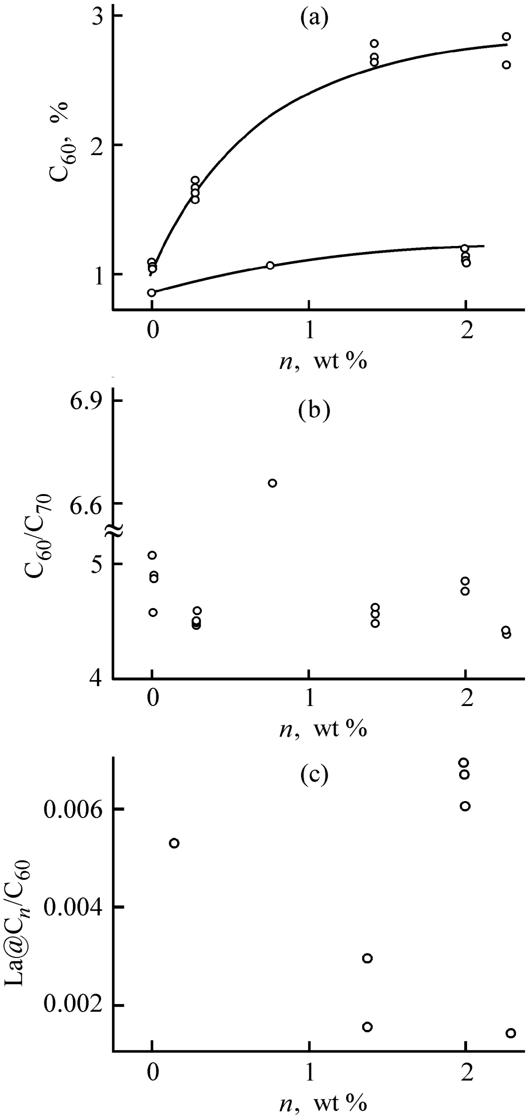

Fig. 6. Effect of the content *n* of lanthanum carbonate in the electrode on (a) yield of C_{60} and yield ratios, (b) C_{60}/C_{70}, and (c) La@C_n/C_{60}.

carbon black being synthesized and extracts obtained (Figs. 4–6).

A typical chromatogram of an extract of the carbon black obtained using the combined electrode under study differs from chromatograms of samples obtained with a graphite electrode in that peak *6* appears (Fig. 4). The spectrum of the extract obtained with the combined electrode contains absorption bands coinciding with the characteristic absorption bands of metallofullerenes [39] (Fig. 5). The yields of the substance (Fig. 6c), calculated from the absorption band at around 1000 nm and from peak *6* of the chromatogram (Fig. 4) are in a good agreement for all syntheses, which makes it possible to attribute peak *6* in the chromatogram to metallofullerenes. The shapes of the chromatographic peak *6* and optical absorption peak at around 1000 nm indicate that several forms of endohedral fullerenes exist in the substrate synthesized.

The yield of the fullerene C_{60} increases as the fraction of lanthanum in the combined electrode becomes higher (Fig. 6a). It is noteworthy that a similar tendency has been observed previously in synthesis of metallofullerenes by electric-arc sputtering of a combined electrode [24]. The maximum total yield of fullerenes was observed at a C/La ratio in the combined electrode equal to 50. Surprisingly, the maximum yield of La@C_{82} has been observed at the same C/La ratio in synthesis of metallofullerenes by laser evaporation of a combined electrode [21], although the influence exerted by lanthanum-doping of the electrode on the yield of hollow fullerenes was quite the opposite. It may be assumed that this is due to the existence of a temperature gradient in the carbon vapor jet. It has been shown in a study of how the synthesis temperature affects the yield of fullerenes that the yield of La@C_{82} is the highest at 1200 K, whereas the maximum yield of C_{60} is obtained at lower temperatures. Apparently, the optimal conditions for stabilization of a certain structure of the carbon cluster can be satisfied in an expanding carbon vapor jet only locally.

The relative yield of C_{60} (Fig. 6b) remained virtually unchanged in a set of experiments, with the exception of that with a mass fraction of lanthanum carbonate equal to 0.75% (C_{60}/C_{70} of about 6.6). At the same time, the yield of metallofullerenes shows a significant scatter (Fig. 6c). This scatter is possibly due, as mentioned above, to presence of a mixture of various forms of metallofullerenes in a sample being analyzed, with the concentration of any particular form of metallofullerenes in the extract being low.

Experiments with a mass fraction of lanthanum carbonate equal to 0.75 and 2% (Fig. 6) cannot be explained in the same way as other experiments. Of a similar nature are the data of [16, 21, 23]. The possible reason for this phenomenon is that different steady states of the arc and structures of the gas-dynamic flows in the reactor are possible in the course of synthesis, even if the synthesis procedure is strictly observed. In the case under study, there exist at least two different dependences of the yield of fullerenes on the mass fraction of lanthanum in the combined electrode (Fig. 6a).

Apparently, it is necessary to take into account, in determining the yield of fullerenes and in comparing the results obtained with published experimental data, that studies of extracts provide only a limited knowledge of the structure and composition of the carbon black. It is known that the carbon substrate obtained by electric-arc sputtering of graphite contains a large amount of fullerene-like fragments [40]. In the course of extraction, the imperfect carbon structures are separated from the fullerenes synthesized. The aggregation susceptibility of fullerenes, including that with incomplete fullerene fragments, hinders extraction of fullerenes from the substrate. Therefore, the yield of the target product can be raised severalfold by changing the solvent used for extraction and the method for recovery of fullerenes from the substrate [42, 43].

CONCLUSIONS

(1) Use of a surface-modified electrode simplifies the electrode preparation procedure and makes it possible to synthesize by electric-arc sputtering a mixture of metallofullerenes in amounts comparable with those reported by other authors.

(2) Raising the amount of lanthanum carbonate contained in the electrode does not change the C_{60}/C_{70} ratio in the samples synthesized and leads to an increase in the total amount of fullerenes obtained at a mass fraction of lanthanum within the range studied. In addition, use of the electrodes suggested leaves unchanged the amount of graphite utilized into the cathode deposit. This fact supports the assumption that lanthanum and carbon evaporate separately in the case when surface-modified electrodes are used.

REFERENCES

1. Chai, Y., Guo, T., Jin, C., *et al.*, *J. Phys. Chem.*, 1991, vol. 95, pp. 7560–7564.
2. Neeb, M., Klingeler, R., Bechthold, P.S., *et al.*, *Appl. Phys. A*, 2001, vol. 72, pp. 289–295.
3. Gu, G., Huang, H., Yang, S., *et al.*, *Chem. Phys. Lett.*, 1998, vol. 289, pp. 167–173.
4. Liu, S. and Sun, S., *J. Organomet. Chem.*, 2000, vol. 599, pp. 74–86.
5. Wang, C.R., Inakuma, M., and Shinohara, H., *Chem. Phys. Lett.*, 1999, vol. 300, pp. 379–384.
6. Nishibori, E., Takata, M., Inakuma, M., and Shinohara, H., *Chem. Phys. Lett.*, 1998, vol. 298, pp. 79–84.
7. Wang, C.R., Kai, T., Tomiyama, T., *et al.*, *Nature*, 2000, vol. 408, pp. 426–427.
8. Takata, M., Nishibori, E., Sakata, M., *et al.*, *Phys. Rev. Lett.*, 1999, vol. 83, pp. 2214–2216.
9. Yamamoto, K., Saunders, M., Khong, A., *et al.*, *J. Am. Chem. Soc.*, 1999, vol. 121, pp. 1591–1603.
10. Murphy, T.A., Pawlik, T., Weidinger, A., *et al.*, *Phys. Rev. Lett.*, 1996, vol. 77, pp. 1075–1078.
11. Knapp, C., Dinse, K.-P., Piezak, B., *et al.*, *Chem. Phys. Lett.*, 1997, vol. 272, pp. 433–437.
12. Stevenson, S., Rice, G., Glass, T., *et al.*, *Nature*, 1999, vol. 401, pp. 55–57.
13. Olmstead, M.M., de Bettencourt-Dias, A., Duchamp, J.C., *et al.*, *J. Am. Chem. Soc.*, 2000, vol. 122, pp. 12 200–12 206.
14. Olmstead, M.M., de Bettencourt-Dias, A., Duchamp, J.C., *et al.*, *Angew. Chem. Int. Ed.*, 2001, vol. 40, pp. 1223–1225.
15. Wang, C.R., Kai, T., Tomiyama, T., *et al.*, *Angew. Chem. Int. Ed.*, 2001, vol. 40, pp. 397–399.

16. Bubnov, V.P., Kol’tover, V.K., Laukhina, E.E., *et al.*, *Izv. Akad. Nauk, Ser. Khim.*, 1997, no. 2, pp. 254–258.
17. Tagmatarchis, N., Aslanis, E., Shinohara, H., and Prassides, K., *J. Phys. Chem. B*, 2000, vol. 104, pp. 11 010–11 012.
18. Okazaki, T., Lian, Y., Gu, Z., *et al.*, *Chem. Phys. Lett.*, 2000, vol. 320, pp. 435–440.
19. Hirata, T., Otomo, Y., and Hatakeyama, R., *Thin Solid Films*, 2002, vol. 407, pp. 32–37.
20. Ying, Z.C., Jin, C., Hettich, R.L., *et al.*, *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, vol. 1, Kadish, K. and Ruoff, R., Eds., Pennington: Electrochem. Soc., 1994, pp. 1402–1412.
21. Suganuma, T., Kasuya, D., Ishigaki, T., *et al.*, *Eur. Phys. J. D*, 1999, vol. 9, pp. 373–376.
22. Lian, Y.F., Shi, Z.J., Zhou, X.H., *et al.*, *J. Phys. Chem. Solids*, 2000, vol. 61, pp. 1037–1040.
23. Tran, N.E. and Lagowski, J.J., *Carbon*, 2002, vol. 40, pp. 939–948.
24. Sueki, K., Kikuchi, K., Akiyama, K., *et al.*, *Chem. Phys. Lett.*, 1999, vol. 300, pp. 140–144.
25. Lange, H., Huczko, A., Byszewski, P., *et al.*, *Chem. Phys. Lett.*, 1998, vol. 289, pp. 174–180.
26. Wilson, M.A., Moy, A., Rose, H., *et al.*, *Fuel*, 2000, vol. 79, pp. 47–56.
27. Kuz’min, S.M., Kozlov, A.V., and Leonov, A.A., Abstracts of Papers, *VII Mezhdunarodnaya konferentsiya “Problemy sol’vatatsii i kompleksoobrazovaniya v rastvorakh” Ivanovo, 8–11 okt. 2001 g*, (VII Int. Conf. “Problems of Solvation and Complexation in Solutions,” Ivanovo, October 8–11, 2001), p. 185.
28. Yamaguchi, Y. and Maruyama, S., *Chem. Phys. Lett.*, 1998, vol. 286, pp. 336–342.
29. Gao, X. and Gao, J., *J. Phys. Chem. B*, 1994, vol. 98, pp. 5618–5620.
30. Krestinin, A.V., Moravskii, A.P., and Tesner, P.A., *Khim. Fiz.*, 1998, vol. 17, no. 9, pp. 70–84.
31. Churilov, G.N., Novikov, P.V., Tarabanko, V.E., *et al.*, *Carbon*, 2002, vol. 40, pp. 891–896.
32. Mandziuk, M. and Bacic, Z., *J. Phys. Chem. B*, 1994, vol. 101, pp. 2126–2140.
33. Kobayashi, K., Nagase, S., and Akasaka, T., *Chem. Phys. Lett.*, 1996, vol. 261, pp. 502–506.
34. Ellacott, M.V., Pang, L.S.K., and Prochazka, L., *Carbon*, 1994, vol. 32, pp. 542–544.
35. *Fizicheskaya entsiklopediya* (Physical Encyclopedia), Prokhorov, A.M., Ed., Moscow: Bol’sh Sov. Entsikl., 1988, vol. 1; 1990, vol. 2.
36. Egorov, V.S., Tolmachev, V.A., Klyucharev, A.N., *et al.*, *Spravochnik konstant elementarnykh protsessov s uchastiem atomov, ionov, elektronov, fotonov* (Reference Book og Constants of Elementary Processes Involving Atoms, Ions, Electrons and Phonons), Zhiglinskii, A.G., Ed., St. Petersburg: SPb. Gos. Univ., 1994.
37. Byszewski, P., Lange, H., Huczko, A., and Behnke, J., *J. Phys. Chem. Solids*, 1997, vol. 58, pp. 1679–1683.
38. Lange, H., Huczko, A., and Starski, A., *J. Phys. Chem. A.*, 1997, vol. 101, pp. 1267–1269.
39. Shinohara, H., *Rep. Prog. Phys.*, 2000, vol. 63, pp. 843–892.
40. Kanowski, M., Vieth, H.-M., Luders, K., *et al.*, *Carbon*, 1997, vol. 35, pp. 685–695.
41. Nath, S., Pal, H., and Sapre, A.V., *Chem. Phys. Lett.*, 2000, vol. 327, pp. 143–148.
42. Sun, D., Liu, Z., Guo, X., *et al.*, *J. Phys. Chem. B*, 1997, vol. 101, pp. 3927–3930.
43. Sun, B., Feng, L., Shi, Z., and Gu, Z., *Carbon*, 2002, vol. 40, pp. 1591–1595.