CHANGES IN PARAMAGNETIC CHARACTERISTICS OF PITCH AND PITCH FIBER DURING THEIR OXIDATION IN LOW TEMPERATURE OXYGEN PLASMA

A.A. Bliznyuk[1)], V.P. Berveno[2)], V.G. Grigoriev[2)], S.Yu. Lurshchikov[2)]

[1)] Institute of Solid State Chemistry & Mechanochemistry, SB RAS, 18, Kutateladze, Novosibirsk, 630128, Russia
[2)] Institute of Solid State Chemistry & Mechanochemistry, Kemerovo Division, SB RAS 18 Sovetsky Ave., Kemerovo 650099, Russia; carbnanof@kemnet.ru

Introduction

Carbon-based adsorbents are used in various fields of human activities, from domestic filters for drinking water purification to molecular sieve filters for separation of gases. To create scientific bases for preparation of carbon adsorbents with controlled properties, comprehensive studies of pore formation processes in carbon materials (CMs) are required. For this purpose, we have employed a method of low temperature oxygen plasma oxidation (LTOP) of CMs. From kinetic data of mass losses during this process, it has been established that a time-dependent curve of fiber-forming pitch oxidation consists of three oxidation stages – two linear ones and a non-linear stage that can be rectified in semi-logarithmic coordinates [1]. The first stage is ended at about 33-40% of burnoff, and the second – at 65-70% of burnoff, i.e. after 1/3 and 2/3 carbon material burnoffs, respectively. For detailed studies of the samples obtained during the LTOP process, an ESR technique was used.

Experimental

Fiber-forming pitch (its softening point was of 245°C) and pitch fiber samples were prepared by a method described in [2-4]. According to elemental analysis data, coal tar pitch used in this study contained, mass. %: carbon (C) 92.15, hydrogen (H) 4.42 and oxygen (O) 3.50. Prior to fiber spinning, pitch was heated to a temperature being by 30-40°C higher than its melting point value. The melt was pushed by a plunger through a spinneret. Then pitch melt stream was twisted onto a bobbin. During the spinning, a diameter of melt stream decreases from 0.3 to 0.03 mm to form monofiber. By varying a winding velocity, pitch fibers having different diameters and differently ordered elementary textural fragments (ETFs) of pitch matrix along the fiber axis can be obtained. On average, pitch and pitch fiber ETFs consist of three aromatic molecules [5,6]. As-received fiber-forming pitch and thin pitch fibers of *ca*. 30 mcm in diameter were analyzed by ESR method. ESR spectra were recorded using a SE 1344 instrument (RadioPAN, Poland) with a maximal power of electromagnetic irradiation of 35 mW. An rectangular resonator of H102 type was used in this study. All the measurements were carried out at room temperature . Mn^{2+} ions dissolved in MgO are used for magnetic field calibration. Copper chloride dehydrate ($CuCl_2 \cdot 2H_2O$) was the reference standard for measure of spectrum amplitudes (due to the fact that resonance transitions of unpaired electrons in copper chloride are not saturated at maximal MF power of the spectrometer used). The ESR spectra obtained were processed with a WinEPR program package (Bruker, Germany).

The CM sample masses after LTOP oxidation steps up to 80% burnoff were of 1-2 mg. This resulted in rather high relative errors (± 20%) during the ESR line amplitude and ESR integrated intensity measurements. An ESR spectrum is a first derivative of an absorption line. The ESR line width, H_{pp} (a distance between maximal curvature points of the ESR absorption line), and ESR line amplitude, I_{pp} (a distance between extremums of the first derivative of the ESR absorption line), were fixed during the ESR measurements.

Results and Discussion

Pitch and pitch samples had not any significant macrostructure defects after oxidation. A microphotograph of oxidized fiber is shown in Fig. 1.

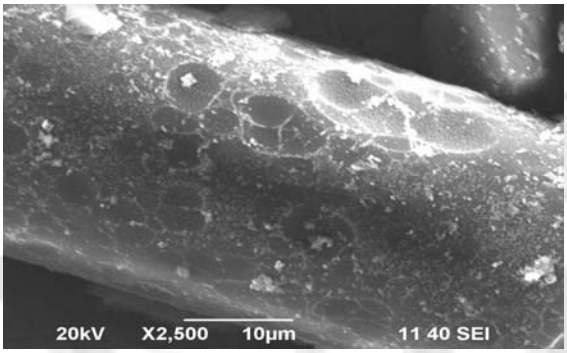

Fig.1 Pitch fiber with a 80% burnoff in LTOP. (JEOL- JSM 6390LA scanning electron microscope)

The absence of any changes in fiber diameter even after their 80% mass losses allows one to suppose that pore formation processes take place in these fibers.

The relative amplitudes of the first derivatives of ESR absorption lines for the samples with different masses, recorded in air, are in the range of measurement errors, while ESR line amplitude values for pitch samples, oxidized to 39 and 85% burnoffs and also recorded in air, markedly differ from amplitude values for other samples (Fig. 2). In case of insignificant changes of line shapes, this fact points to a twice decrease of the amount of paramagnetic centers. Such a result may be caused by partial or complete destruction of elementary textural fragments, comprising pitch matrix, at the expense of combusting one of three aromatic molecules, namely, a central molecule. At higher mass losses, an ESR line amplitude value was recovered. Probably, a shift of π-electrons observed in the central molecule due to interactions with lateral molecules disappears with central molecules removal after their complete combustion. Unpaired electrons are in only the ETF central molecules but they are absent in the ETF lateral molecules. This predetermines a drop of unpaired electron concentration. At further steps of the burnoff

process, the second ETF molecule is removed. Due to a relatively weak bonds between ETFs in pitches and their high mobilities, pitch matrix, after achieving some critical number of defects (voids), is, probably, reconstructed to form another equilibrium spatial state, more friable than the initial state, including other three-molecule ETFs. This results in recovering of unpaired electron concentration.

It should be noted that for the sample with 95% burnoff, the ESR line amplitude value does not differ from amplitude values for other samples; this fact indicates that the ESR signal is not related to impurities present in fiber-forming pitch.

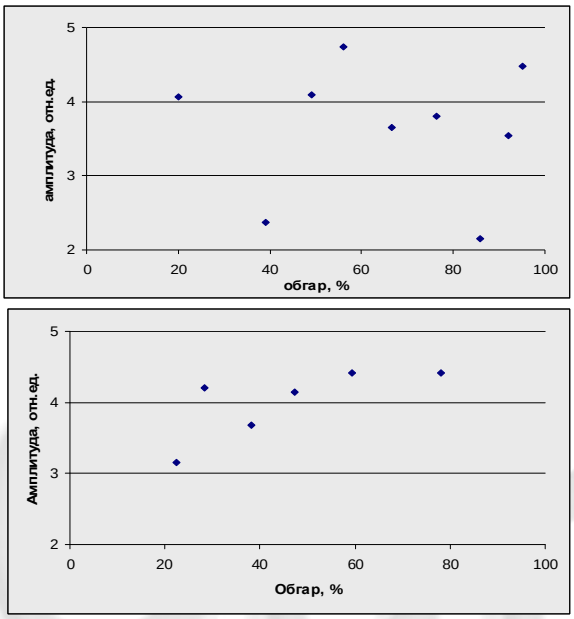

Fig. 2 Changes in ESR spectrum line relative amplitudes as functions of burnoff extents of fiber-forming pitch (up) and pitch finer (down) during their LTOP oxidation. (The MF irradiation power in an resonator was of 1.7 mW).

The similar studies for pitch fiber samples in air did not give the same results: no minimums of unpaired electron concentrations at 35-40 and 70-80% burnoffs were observed.

In case of ESR spectra of pitch fibers recorded in hydrogen atmosphere, a drastic decrease in line amplitude is observed for the sample with 47% burnoff (Fig. 3). This is explained by substitution of sorbed gases by hydrogen. In other words, the sample with 47% burnoff contains some amount of paramagnetic centers that can be formed due to the presence of gases sorbed by pitch matrix, and hydrogen can replace these gases from pores. ESR line amplitudes of the samples with burnoffs other than 47% increase in hydrogen atmosphere, compared to their amplitudes in air; some rises in ESR line widths for them in hydrogen atmosphere are also observed. The increase in ESR line amplitude is due to the increase in the amount of paramagnetic centers; here hydrogen can be considered as a donor of electrons, and it can substitute sorbed acceptor molecules (mostly, oxygen molecules). As a result of this, ETF molecules that did not contain unpaired electrons, become paramagnetic species and give ESR signals. These new paramagnetic molecules may have ESR characteristics different from those recorded in air medium; therefore, the line width in their ESR spectra may increase.

It is worth to notice that, in contrast to ESR spectra of pitch fibers, neither in hydrogen atmosphere nor in air we could not find any minimums in ESR line amplitude dependences for similar spectra of fiber-forming pitch samples oxidized to various extents of burnoff. This fact permits one to conclude that pore structure formed during the oxidation of pitch-based samples is unstable.

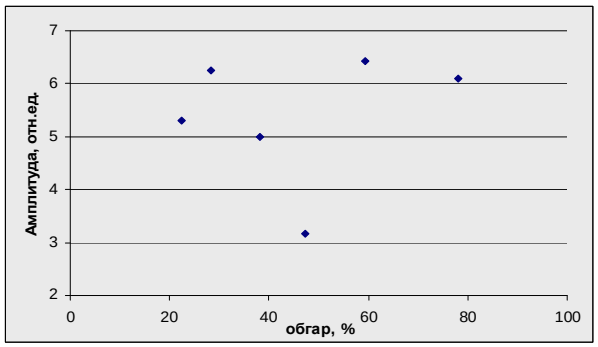

Fig. 3 The dependence of the ESR line relative amplitude on the burnoff extent in LTOP for pitch fiber in hydrogen atmosphere. (The MF irradiation power in an ESR spectrometer resonator was of 1.7 mW).

Conclusions

1. ESR line amplitude minimums have been discovered in pitch and pitch fiber samples oxidized to 40% burnoff and in pitch samples oxidized to 80% burnoff;
2. Pores formed during oxidation of pitch-based samples have sizes appropriate for sorption of light gases;
3. It has been established that pore structure formed in pitch during its oxidation is unstable; the pores formed are progressively collapsed with time as a result of elementary textural fragments restoration caused by thermal motion of molecules.

References

[1] Grigoriev V.M., Berveno V.P., Kornievich M.V., Shchukin L.I. Oxidation of aromatic molecules in isotropic pitch-based fiber nanofragments in low temperature oxygen plasma // Polzunov Bulletin. 2008. N 3. P. 121-125 (in Russian). Joo L.A. City J. McKee J.A. US Patent 3595946, 1971.

[2] McKee J.A. Joo L.A. New carbon monofilament substrate for chemical vapor deposition.// In Proc. Ann. Tech.Conf. of RP/Composites Inst., The Society of Plastic Ind. New York 1972;27:536-551

[3] Derbyshire F. Andrews R. Jacques D. Jagtoyen M. Kimber G. Rantell T. Synthesis of isotropic carbon fibers and activated carbon fibers from pitch precursors.// Fuel 2001;80:345-356.

[4] H. L. Riley, H. E. Blayden, J. Gibson An X-Ray study of the structure of coals, cokes and chars// «The ultra-fine structure coals and cokes» Proceeding of a conference. London: The British coal utilization research association, 1944

[5] P. B. Hirsch Proc. Roy. Soc.,A226,143,1956 цит. по W. Francis Coal its formation and composition/ London: Edward Arnold (publishers)LTD 1961 p. 806