COAL TAR PITCH-BASED MOLECULAR SIEVE CARBON FIBER: SYNTHESIS, PROPERTIES AND NANOTEXTURE CHARACTERIZATION

Victor P. Berveno[1], Lyudmila V. Bryukhovetskaya[1], Tatiana M. Naimushina[1], Sergey A. Sozinov[1], Mikhail Y. Klimovich[2], Vadim G. Dodonov[3], Valery M. Pugachev[3], Lev I. Shchukin[2], Ivan Y. Petrov[2]

[1] *Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Kemerovo Division, Kemerovo 650099, Russia*

[2] *Institute of Coal and Coal Chemistry, SB RAS, Kemerovo 650099, Russia*

[3] *Kemerovo State University, Kemerovo 650043, Russia*

Corresponding author e-mail address: carbnanof@kemnet.ru

Introduction

Pitch-based carbon fibers (CF) are well known as multi-functional materials for various applications. They can used as high-modulus and reinforcing fillers for carbon and polymer composites [1], as molecular sieves for separation of vapors and gases [2,3], as adsorbents for methane and hydrogen storage [4,5], as electrodes for lithium re-chargeable batteries [6] or electrolytic supercapacitors [7], and as catalysts or catalyst supports [8].

Multi-functionality of CFs is connected with increased possibility for controlling their chemical composition and carbon matrix properties, as well as texture and pore characteristics. Depending on the type of fiber, CF textural elements have sizes ranging from several parts to tens nanometers. These elements can be oriented along or across the fiber, or in a random manner. In the CF adsorbents pore sizes range from <1 nm to ~1 μm. Various functional groups, heteroatoms, and metal ions can be introduced into the carbon matrix of pore walls surfaces. The CF matrix is built by carbon nanoparticles, and most of unique properties exhibited by carbon nanoparticles is also characteristic for CFs [4-8]. On the other hand, the possibilities to organize large-tonnage production of CF materials are considerably greater and the prices are substantially lower than those for fullerenes, nanotubes, nanocoils, and related nanomaterials.

Adsorptive properties of CFs are determined by the chemical composition and sizes of textural blocks (sizes and numbers of arene molecules in block units), type of their packing and distances between these blocks. Diameters of pores formed between disordered textural blocks are close to their sizes. Molecular pores ranging from decimal fractions of nanometer to several nanometers are situated between subnanometer blocks.

The present communicartion is aimed at establishing regularities of isotropic pitch-based CF nanotexture formation and to discuss some properties of texturally homogenious and inhomogenious CFs.

Experimental

Fiber-forming isotropic pitch was prepared from middle-temperature coal tar pitch. Arenes of ~ 0.5 nm in size (with 5-7 aromatic rings) were obtained as follows. Arenes containing less than 7-9 aromatic rings were prepared by dissolving the initial coal tar pitch in coal tar absorbing oil - coal tar fractions. The insoluble precipitate was separated by centrifugation and subsequent filtration of pitch dissolved in coal tar absorbing oil. Then solvent and arenes containing less than 4 aromatic rings were distilled in vacuo up to 300°C. Pitch purity was controlled by changes in its softening point, T_p (it was varied from 180 to 240°C; the content of quinoline insolubles was varied from 0.1 to 2 wt.%).

Fiber was obtained from pitch melt by spinning combined with mechanical pulling, followed by ruling on a bobbin, or by electrostatic field-forced spinning with packing on a metallic net. Pitch melt temperature was by 40-70°C higher than pitch softening point. As a result, fibers of 15-20 μm in diameter were prepared. They were stabilized (transfor med into non-melting form) by oxidation with oxygen (in air) at 220-330°C.

Fibers were carbonized at 500 -1000 °C and then activated by water steam treatment at 500 – 800 °C. The reactivity of CF textural fragments was estimated by their mass loss during cool oxygen plasma treatment [9]. Some CF samples were further treated with ultrasound in water. Benzene and water adsorption measurements were carried out ar room temperature in the desiccator. The molecular sieve properties of CFs were evaluated from a comparison of gas substitution rates (using probe gases of different molecule sizes). The substitution rates were calculated from the changes in amplitudes of the ESR spectra of CFs occurring during the substitution of probe gases (helium, nitrogen, methane, argon) with oxygen [10]. The sizes of textural elements were evaluated from small angle X-ray scattering (SAXS) diffraction patterns obtained with a DRON-2.0 difractometer (Russia). ESR spectra were recorded with a Radiopan SE/X 2540 ESR spectrometer (Poland). The processing of gas substitution kinetic curves was conducted using a computer WIN-EPR program (Bruker, Germany). CF texture was analyzed with a scanning electron microscope BS-340 (Tesla, Chechia).

Results and Discussion

In the case of electrostatic field-forced spinning experiments, pitch fiber was spinned from pitch melt at the temperature (T_s) by 70±5°C higher than pitch softening point (T_p). Cross-sections of CFs carbonized and activated in a water steam atmosphere at 500 °C have a homogenious cross-section structure (Fig. 1-1). The sizes of texture elements (from SAXS data) are about 0.5 nm (Fig. 2). Textural blocks of CFs treated at 500°C consist of 2-3 graphene layers (L_c ~ 0.7-1.0 nm). Such CFs adsorb 90-120 mg/g H_2O and 120-140 mg/g C_6H_6. According to probe gas chromatograhic measurements, molecular pores in these CFs are about 0.30 nm.
In the case of mechanically pulled and spinned pitch fibers, the temperature of pitch melt (T_s) was maintained by 40°C higher than T_p. This results in the formation of an ordered shell on the CF surface (see Figs. 1-2, 1-3, 1-4). Such a shell is more stable to oxidation with cool oxygen plasma (oxidation rate is of 6.5% per hour at 80°C). Textural

blocks formed in a disordered core are plasma oxidized more rapidly (9% per hour). Benzene and water adsorption capacities for such CFs carbonized, then activated in water steam medium at 600°C are of 110 and 91 mg/g, respectively. No substantial differences have been discovered between these values and those for activated CFs with homogeneously disordered textural blocks. An average size of textural blocks (from SAXS results presented in Fig. 2) in the shell-ordered CFs (~ 1.0 nm) is on the average twice as large as for the disordered ones.

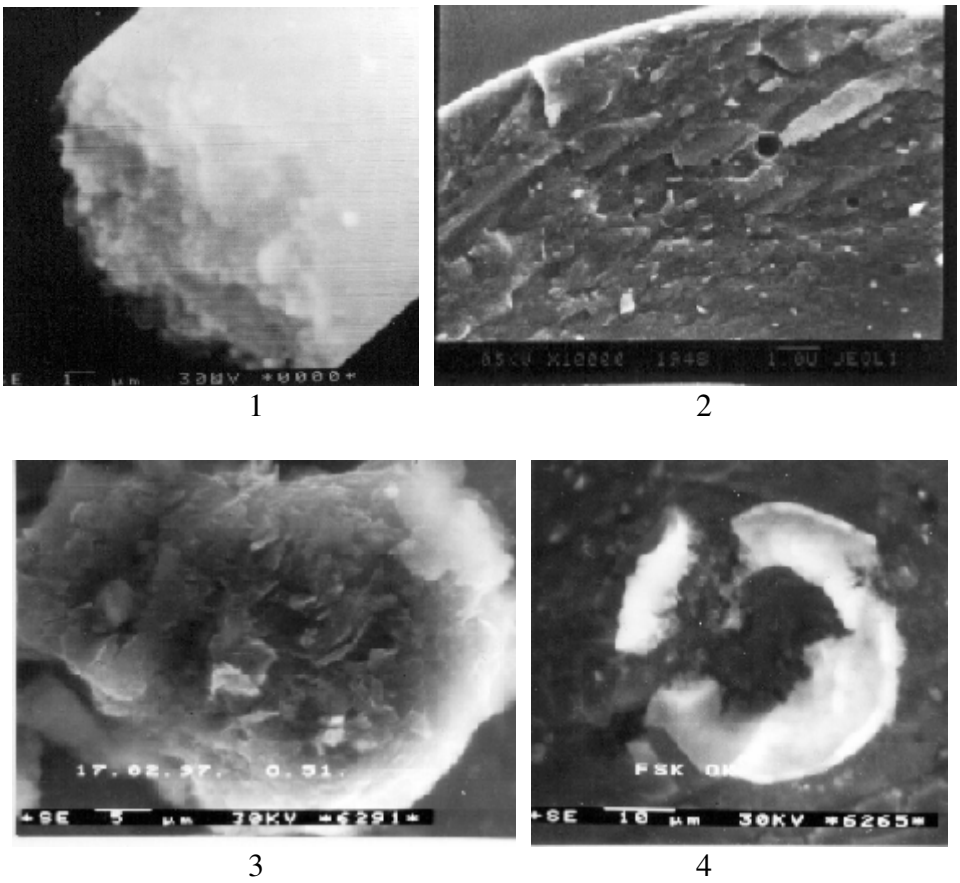

Figure 1. Microtexture of pitch-based CFs: 1 – prepared by electrostatic field-forced spinning ($T_s > T_p$ by 70 °C), followed by water steam treatment (500 °C, 2 h); 2,3,4 – prepared by spinning combined with mechanical pulling ($T_s > T_p$ by 40 °C), followed by N_2 treatment (1100 °C) (2), then oxidized with cool oxygen plasma (80 °C, 7 h) (3) and treated with ultrasound in water (4).

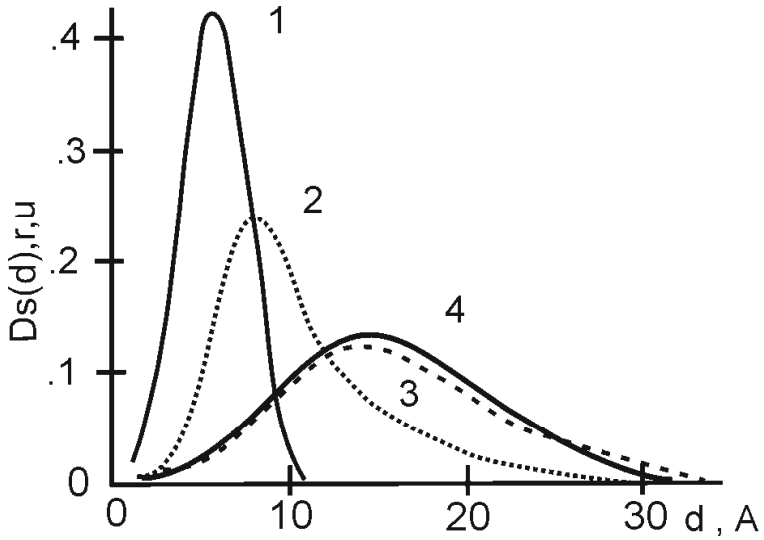

Figure 2. The distribution of inhomogeneities in the CF samples: 1 – CF with unimodal texture (activated by water steam at 500°C); 2 – CF with layered (bimodal) texture (treated by water steam at 600°C); 3,4 – oxidized pitch fibers (before carbonization and partial activation in water steam medium) oriented perpendicular and parallel to the X-ray beam, respectively.

Designations: *d* – diameter of graphene plates (L_a) (from SAXS measurements); Ds (d) – function of distribution of X-ray signal intensities.

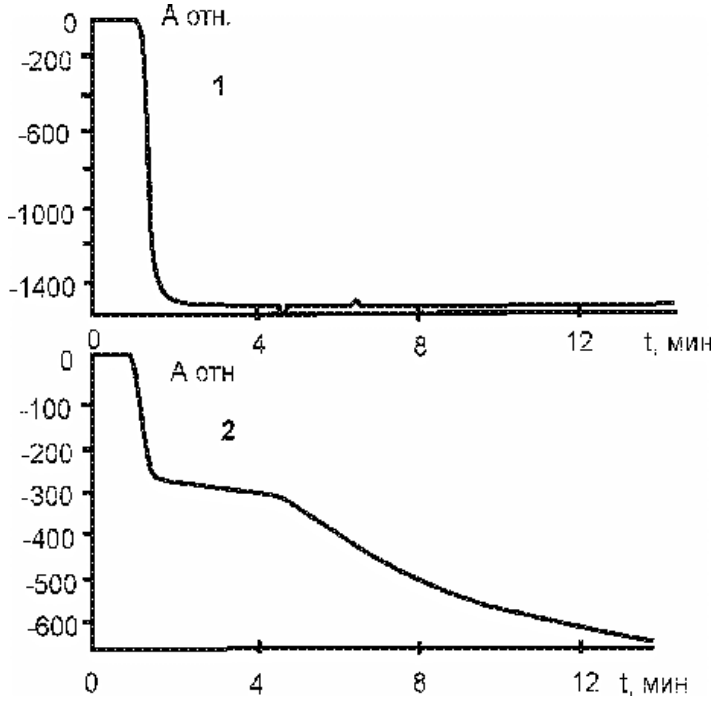

Figure 3. Methane substitution with oxygen in the unimodal (electrostatic field-forced spinning) (1) and bimodal (spinning combined with mechanical pulling) (2) CFs.

Designations: *t* – time-on-stream; *A* – intensity of ESR signal.

Kinetic curves of methane substitution with oxygen in homogenious (unimodal) and inhomogenious (layered, bimodal) CFs are shown in Fig. 3. In the homogenious CF methane is substituted with oxygen, as a rule, during 2 minutes (curve 1 in Fig. 3). In the layered CF the duration of this process is several times longer (more than 14 minutes), with a kinetic curve being stepwise (curve 2 in Fig. 3). Thus, a layered texture of CF results in the two-step diffusion of gases in fiber pores.

Conclusions

Summarizing the above results, texturally disordered (in cross-section) carbon fibers can be formed during simultaneous carbonization and partial activation (t = 500°C, H_2O steam) of coal tar pitch-based fiber prepared during fiber spinning from isotropic pitch melt at $T_s > T_p$ by 70°C. Layered carbon fibers having spatially shell-ordered and core-disordered textural blocks are formed at $T_s > T_p$ by 40°C. Average sizes of textural blocks in the disordered CFs prepared from isotropic pitch are of ~ 0.5 nm, and average sizes of these blocks in the layered CFs – about 1.0 nm.

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