Nanotexture of a Carbon Fibre from Pitch*

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Abstract

The uniformly disoriented carbon fibre with textural blocks about 0.5 nm in size is produced from the pitchy fibre that was moulded in an electrostatic field from a melt with a moulding temperature T_m that exceeded the softening point T_s by 70 °C. The layered carbon fibre with the ordered shell and disoriented nucleus is produced from a pitchy fibre through its mechanical draft at T_m that exceeds T_s by 40 °C. The average size of textural blocks in it is of about 1.0 nm.

INTRODUCTION

Carbon fibre (CF) from pitch is a multipurpose material, which is in use as a catalyst carrier [1], high-modulus, strong reinforcing filler of composites, a molecular sieve for separation of vapours, gases [2, 3], for accumulation of methane, hydrogen [4, 5], in lithium current supplies [6], and electrolytic capacitors [7]. Multifunctionality of CF is determined by a large potential for adjusting of texture, composition, and properties of carbon matrix and of a surface of pore walls. Depending on the fibre type, the size of CF textural elements vary from several nanometres to tens of microns. Textural elements can be oriented along, across a fibre axis, or in random order. In sorption CF, pores can amount from several fractions to hundreds of nanometres in size. Various functional groups, heteroatoms, ions of metals can be introduced within the matrix on the surface of pore walls. The CF matrix is constructed from blocks of nanoparticles; therefore, a substantial part of unique properties of carbon nanoparticles is characteristic for the CF too [1, 4–7]. Potentials for large-tonnage production of CF-materials are much wider and the cost of these materials is many times lower as compared to fullerenes, nanopipes, and nanofibres.

Properties of CF-sorbents are controlled by composition and size of textural blocks (by size and quantity of arene molecules in the unit block), by their packing type, and distances between them. Pore sizes between the disordered textural blocks correlate with the dimensions of the last-mentioned. Located between subnanometre blocks are molecular pores from several tenth to nanometre in size.

The purpose of the present communication is to study the process of CF nanotexture formation from isotropic pitch and some properties of texture-homogeneous and non-uniform CF.

EXPERIMENTAL

Fibre-forming isotropic pitch was produced from medium-temperature coal pitch. Arenes with an average size about 0.5 nm with 5–7

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aromatic nuclei were isolated as follows. Arenes containing less than 7–8 aromatic nuclei were dissolved in methyl-, ethylnaphthalenes (absorption fraction of coal tar) from the initial coal pitch. An insoluble residue was separated by centrifugation followed by filtering the solution of pitch in scrubbing oil. In the subsequent process, the solvent and arenes containing less than four aromatic nuclei were separated through elimination in vacuum in a thin-film rotary evaporator at a temperature lower than 300 °C. The decontamination degree was controlled by variation in softening point T_s of pitch. Fibre-forming isotropic pitch was obtained with T_s from 180 to 230 °C, and with the content of quinoline-insoluble fraction from 0.1 to 2 %. A fibre from a melt of pitch was moulded through mechanical draft (with winding on the bobbin) or in an electrostatic field (with packing on a mesh). Melt temperature exceeded the softening point of pitch by 40–70 °C. Resulting was a fibre of diameter 15–20 μm, which was stabilised (transformed to the infusible form) by (air) oxygen oxidation at 220–330 °C. Then the fibre was activated with water vapour at 500–800 °C. Reactivity of CF textural fragments was determined from decrease of its weight upon interaction with low-temperature oxygen plasma [8].

Adsorption of benzene and water from saturated air vapours at ambient temperature was determined by the exsiccator method.

Molecular-sieve properties of CF were estimated from comparison of substitution rates for gases with various sizes of molecules on the basis of variation in amplitude of EPR spectra of CF upon replacement of gases by oxygen [9].

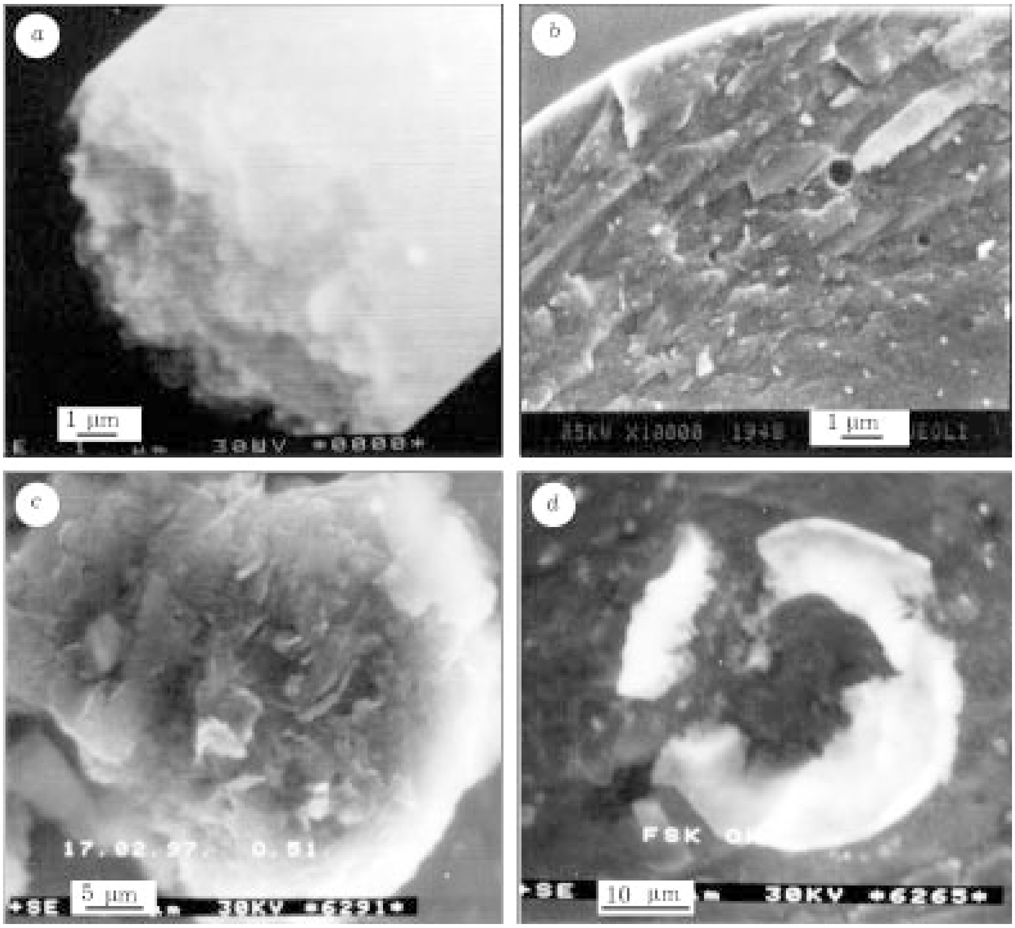

Fig. 1. Microtexture of CF: a – CF moulded in an electrostatic field ($T_m > T_s$ by ~70 °C) and activated in water vapour at 800 °C; b–d - upon mechanical draft ($T_m > T_s$ by 40 °C) (b), CF oxidized in low-temperature oxygen plasma during 7 h (c) and processed in water in ultrasound (d).

EPR spectrometer Radiopan SE/X registered variation in amplitude of EPR spectra of CF 2540 (Poland). Processing of the kinetic curves for substitution of gases was conducted with the use of WIN-EPR code of Bruker Corporation (Germany).

The sizes of textural elements were estimated from diffractograms of a small-angle scattering of X-rays by means of DRON-2.0 diffractometer.

CF texture was analysed by means of BS-340 electronic scanning microscope of TESLA Company.

RESULTS AND DISCUSSION

In the electrostatic field, a fibre was moulded from a melt with the temperature that exceeded the softening point of pitch by (70±5) °C. The CF activated in water vapour at 800 °C shows homogeneous structure across a section (Fig. 1, *a*).

From evidence of small-angle scattering of X-rays, the sizes of textural elements can amount from 0.5 to 1.5 nm (see Fig. 1, *b*). Textural blocks of CF-500 are made up on average from two or three graphene layers about 0.7–1.0 nm in height. The produced CF adsorbs 90 mg/g of water and 120 mg/g of benzene. The size of molecular pores is of about 0.35 nm.

During mechanical draft of a fibre, the temperature of pitch melt is 40 °C higher than its softening temperature. An oriented shell is formed near the CF surface (see Fig. 1, *b–d*); this shell is more stable against oxidation by low-temperature oxygen plasma (oxidation rate is 6.5 % per hour at 80 °C). Textural blocks in a disordered nucleus are oxidized quicker (9 % per hour). Adsorption of benzene and water in CF activated by water at 500 °C comprises 110 and 91 mg/g, respectively. There is no substantial difference from adsorption values of these vapours in homogeneously-disordered activated CF. The average size of textural blocks (Fig. 2) on average is 2 times more (about 1.0 nm) than for the disordered one.

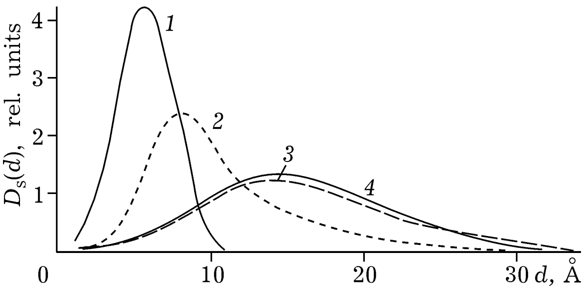

Fig. 2. Distribution of inhomogeneities within the samples of carbon fibre (*d* is a plate diameter): *1* – homogeneous textured sample activated at 500 °C; *2* – the same at 600 °C, layered structure; *3*, *4* – the sample of oxidized pitchy fibre before carbonization and activation, oriented perpendicular (*3*) and parallel (*4*) with the registration plane.

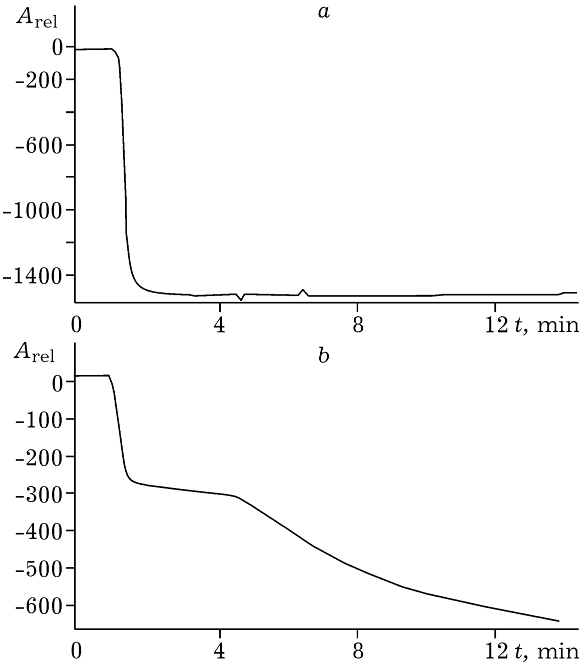

Fig. 3. Kinetic curves of methane replacement by oxygen in CF-sorbent: *a* – homogeneous-porous sorbent moulded in an electrostatic field, *b* – biporous sorbent moulded through a mechanical draft.

Kinetic curves of methane replacement by oxygen in homogeneous and layered CF are presented in Fig. 3. In homogeneous CF, methane is mostly displaced by oxygen in 2 min (see Fig. 3, curve *1*). In the layered CF, this process is longer and takes more than 14 min. The kinetic curve has a stepped structure (see Fig. 3, curve *2*). Layered texture of CF is responsible for two-stage diffusion of gas in its pores.

CONCLUSION

A texture disordered across the CF section is formed upon moulding a fibre from a melt of isotropic pitch with a temperature that exceeds by 70 °C the temperature of its softening, whereas the layered texture with the ordered shell is formed when the difference of temperatures is 40 °C. Average sizes of textural blocks in the disordered CF from isotropic pitch comprise 0.5 nm, and do about 1.0 nm in the layered CF.

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