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POROUS STRUCTURE OF CARBON NANOPARTICLES PREPARED BY CHLORINATION OF NANOPARTICLES OF SILICON CARBID

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Specific features of the structure of nanoporous carbon, prepared by chlorinating silicon carbide nanoparticles followed by treatment thereof by hydrogenation have been studied. A considerable number of microscopic pores in carbon nanoparticles have been shown.

Keywords: nanoporous carbon, carbon nanoparticles.

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1. Introduction

Properties of carbon materials with effective surface are attributable both to the quantity of specific surface, and to their structure, including morphology, size, and porous structure of nanoparticles.

Carbon materials with high surface area having micro-, meso-, and macropores based on particles of micron and submicron dimensions are known and widely applied.

The synthesis of new substances, based on highly-porous carbon opens promising prospects for the use of these materials and carbon-based nanocomposites as sorbents and gas accumulators, catalysts in producing super-condensers, electrodes for electric-chemical generators, etc. One of the promising classes of porous carbon materials is based on nanoporous carbon prepared by high-temperature chlorination of carbides [1, 2]. In papers devoted to the synthesis and study of nanoporous carbon, carbide powders of micron or submicron dimensions were chlorinated [1-4].

The study of the porous structure of carbon nanoparticles synthesized by chlorinating carbide powders is of interest. This article analyzes the porous structure of carbon nanoparticles synthesized by high-temperature chlorination of silicon carbide nanoparticles of cubic modification (SiC).

2. Experimental

For the synthesis of carbon nanoparticles, silicon carbide nanopowder primarily consisting of particles SiC (maximum content of amorphous phase 3-15%), with specific gravity 3.22 g/cm^3, spherical shape, 45–55 nm in diameter produced by Aldrich (USA) was employed. Silicon carbide was chlorinated in a Tamman furnace under chlorine atmosphere at 700 to 1000°C for 10 and 60 minutes. To remove chlorine impurities from the sample according to the procedure described in [3], after chlorination, the sample was exposed to thermal hydrogenation at 800°C for 60 minutes.

Reliable data on the structure of nanoscale objects can only be obtained by employing a comprehensive approach [5]. This requirement also applies to the analysis of the formed materials' porous structure. Therefore, to define the structure and dimensions of nanoparticles, as well as parameters for their porous structure, a variety of techniques were employed.

Parameters for the crystal structure of the sample were determined based on powder X-Ray diffraction data using a Shimadzu XRD-7000. Crystallites dimensions were calculated according to Scherrer formula based on data from X-Ray diffraction line broadening.

Pycnometric specific gravity of powders was measured using a helium pycnometer AccuPyc 1330 (Micromeritics, USA).

Adsorption and structural analysis of powders were carried out using an analyzer ASAP 2020 (Micromeritics, USA). Specific gravity of nanoparticles, cumulative pore volume, and distribution of pores by dimensions were calculated according to the model BET using DFT method [6], included in the analyzer software. These methods, like others, suggest that the pores have a particular shape. Therefore, the results obtained for spherical, cylindrical, and slot-like pores or pore space of mixed type may vary widely [7].

This paper suggested that slot-like pores are most prevalent. Despite ambiguity, this model was chosen following the results of papers [2-4].

3. Results and discussion

Diffraction patterns of the samples under investigation (Fig. 1) show that for the initial silicon carbide, consisting of nanocrystals SiC with diameters of d=20±2 nm (Table 1), the carbon synthesized by high-temperature chlorination will be amorphous. On the contrary, for the carbon prepared by chlorination of macrocrystalline σSiC, the diffraction patterns show the broadened lines similar in position to the graphite pattern lines [4].

Table 2 provides elemental composition of samples of nanoporous carbon prepared by chlorination of nanopowder SiC under different conditions. The data obtained show that the samples contain insignificant quantities of oxygen and chlorine. In the sample chlorinated at 700°C, low silicon content was observed. Silicon is apparently present as SiO_2. The presence of silicon dioxide is likely attributable to the presence of impurities of silicon dioxide in the initial sample, and to the stability of SiO_2 under a chlorine atmosphere at 700°C. To remove chlorine impurities, the samples were treated under hydrogen atmosphere. The treatment ensured almost complete chlorine removal, see Table 2. Then, the nanoporous carbon samples, once dechlorinated via hydrogenation, were then analyzed.

Table 3 gives the values for the specific surface area and parameters of porous structure for nanoporous carbon samples prepared under different conditions for the chlorination of SiC nanopowder. It should be noted that the results of the structural and adsorption analysis obtained for models BET and DFT vary widely (Table 3). The difference is most pronounced in nanoporous carbon samples synthesized at higher temperatures, i.e. at 850 and 1000°C. This can be proved by the data on micropore volumes and cumulative pore volumes provided in Table 3, as well as the by the data on distribution of pores by dimensions in nanoporous carbon prepared at different temperatures. Note that the presence of pores with dimensions of 37 nm is apparently attributable to interparticle porosity. The pores share dimensions for all chlorination conditions, because initial nanoparticles SiC were of 50–60 nm in size (Table 1), chlorination did not cause considerable change in the dimensions of the carbon particles as compared to the particles of the initial silicon carbide [7].

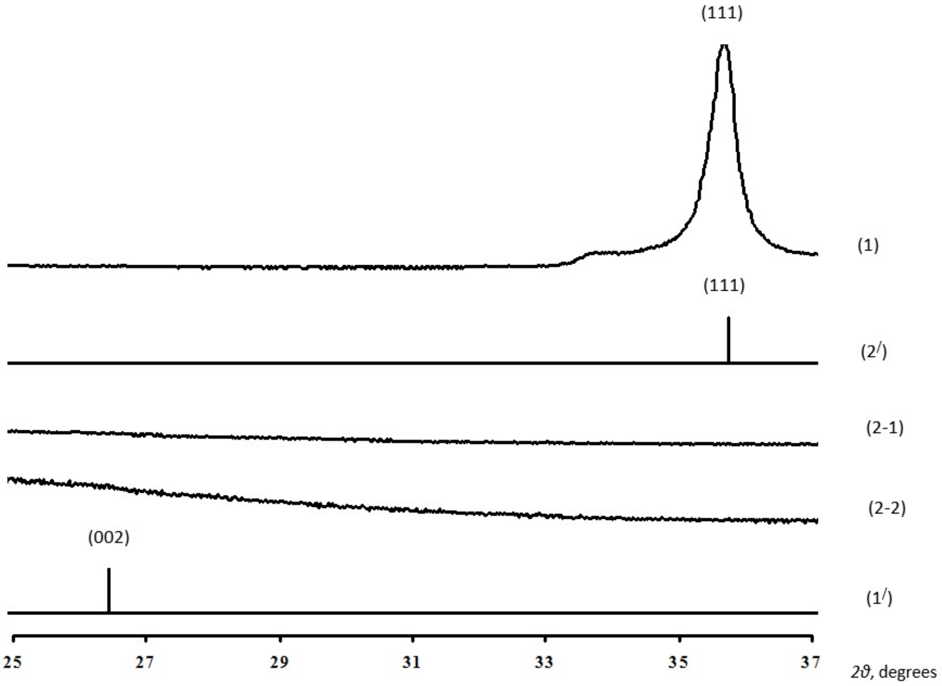

FIG. 1. X-Ray diffraction patterns of silicon carbide (1), carbon prepared by chlorination (2-1), and carbon sample treated in vacuum (2-2). Line diagrams of powder patterns show the peaks corresponding to phases -SiC (1´) and graphite (2´)

TABLE 1. Characteristics of silicon carbide nanopowder

Substance	Crystal structure	Specific density, g/cm^3		size (d), nm		Specific surface	
		X-Ray	Pycnometric	Crystallites	Particles	Per unit of volume, m^2/cm^3	Per unit of weight, m^2/g
Silicon carbide	Cubic, primarily -phase (3-15% of amorphous one)	3.219	3.220 (1) 3.217 (2)	d_{111}=20±2	45-50 (1) 59 (3)	100.7 (3)	70-90 (1) 31.3 (3)

Notes:

(1) characteristics of the powder provided by company Aldrich, USA (CAS Number 409-21-2);

(2) helium pycnometry data;

(3) following the data of adsorption and structural analysis

TABLE 2. Elemental analysis of nanoporous carbon synthesized from -SiC

Chlorination conditions	Elemental composition, At. %	
	After chlorination	After treatment in hydrogen flow
1,000°C, 10 min	C – 96.99 O – 1.58 Cl – 1.43	C – 97.31 O – 2.69
850°C, 60 min	C – 94.22 O – 2.68 Cl – 3.10	C – 98.42 O – 1.58
700°C, 100 min	C – 91.67 O – 3.36 Si – 0.77 Cl – 4.20	C – 98.68 O – 1.05 Si – 0.24 Cl – 0.03

TABLE 3. Specific surface and porous structure of carbon synthesized from nanoparticles β-SiC

Chlorination conditions	Pycnometric density g/cm^3	Pore volume (<2 nm), cm^3/g	Cumulative pore volume (DFT), cm^3/g	Specific surface (BET), m^2/g	Specific surface (DFT), m^2/g	Size in the peak points of the size distribution curve, nm
1000°C, 10 min	2.17	0.403	Pores sizes $\leqslant$86 nm 0.564	1472	1126	<0.45 0.68 0.8 1.3 37
850°C, 60 min	2.11	0.470	Pores sizes $\leqslant$93 nm 0.599	1529	1270	0.5 0.66 0.8 1.3 37
700°C, 100 min	1.98	0.527	Pores sizes $\leqslant$86 nm 0.612	1538	1550	0.54 0.8 1.3 37

4. Conclusion

The results obtained show great potential for the synthesis of nanoporous carbon from nanoparticles of silicon carbide, as the prepared carbon nanopowder had effective specific surface areas and high micropore content.

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