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SURFACES, INTERFACES, AND THIN FILMS

Raman Scattering in Self-Formed Nanoporous Carbon Produced on the Basis of Silicon Carbide

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Abstract—The Raman spectra of nanoporous carbon materials produced from silicon carbide are studied. The experimental data considered in comparison with the data obtained from other types of measurements are used to analyze the processes of self-formation of the material. Changes in the Raman spectra are observed in the material subjected to extra treatment with hydrogen. The effect is interpreted as a result of transformation of graphene-like carbon clusters into hydrocarbon derivatives, graphenes.

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1. INTRODUCTION

Nanoporous coals produced by chlorinating metal carbides are materials of interest for both fundamental and applied research. The materials of this family feature high purity (99.9% carbon content) and high degree of porosity (≈70%). The size distribution of pores exhibits a narrow peak in the region of a few nanometers. Different technological methods make it possible to vary the parameters of the materials to optimize the parameters for specific applications.

Materials with such unique parameters are needed for many applications. The materials are used as selective adsorbers and catalyst carriers [1]. Nanoporous carbons are especially promising for the fabrication of supercapacitors. It is possible to produce supercapacitors with an accumulated energy density up to 150 J g^{-1} on the basis of these materials. This makes such supercapacitors competitive to other types of energy-storage devices [2].

The chemical process used for production of nanoporous coals is rather well understood and was described as early as the end of the 1950s [3]. Carbon materials of this type are produced by high-temperature treatment of crystalline metal carbides (SiC, TiC, B_4C, etc.) with chlorine in accordance with the reaction

$$\mathrm{Me}_x\mathrm{C}_y + \frac{xm}{2n}\mathrm{Cl}_2 = \frac{x}{n}\mathrm{Me}_n\mathrm{Cl}_m + y\mathrm{C}. \qquad (1)$$

Here, Me = B, Al, Si, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W.

In contrast, the physical processes that provide formation of nanoporous material remain unclear in many respects. One of the specific features of the process described by reaction (1) is that the samples of the material retain their macroscopic shape, whereas their crystal structure is completely lost. In other words, when subjected to chemical and heat treatment, carbide grains (crystal fragments) transform into carbon, but their external appearance remains almost the same. At the same time, such a structural characteristic as the crystal lattice completely disappears on chemical and heat treatment. As follows from X-ray diffraction (XRD) analysis, carbon produced in the initial stage of the above process is amorphous (see, e.g., [4]); i.e., the long-range order in the atomic arrangement is not retained. Such a process, which results in the complete loss of the initial structure and in conservation of the external shape, almost never occurs. It is likely that one of the few natural analogues of the above process is the formation of fossils.

As far as we know, only one study concerned with the mechanism of formation of the porous structure of carbon materials has been reported [5]. However, in [5], the consideration was based on general concepts and the results were not correlated with experimental observations.

In this study, we experimentally investigate Raman scattering in nanoporous carbon materials produced from silicon carbide. The choice of silicon carbide is governed by the fact that silicon carbide forms various polytypes, so that it is possible to compare the properties of materials produced from chemically identical initial materials different in crystal structure. On the basis of the experimental results and data obtained by other authors, we consider the processes of formation of the porous structure of nanoporous carbon produced from silicon carbide.

2. EXPERIMENTAL

The Raman spectra were recorded with the use of a Horiba Jobin-Yvon MRS 320 micro-Raman spectrometer with a resolution better than 0.5 cm^{-1}. The

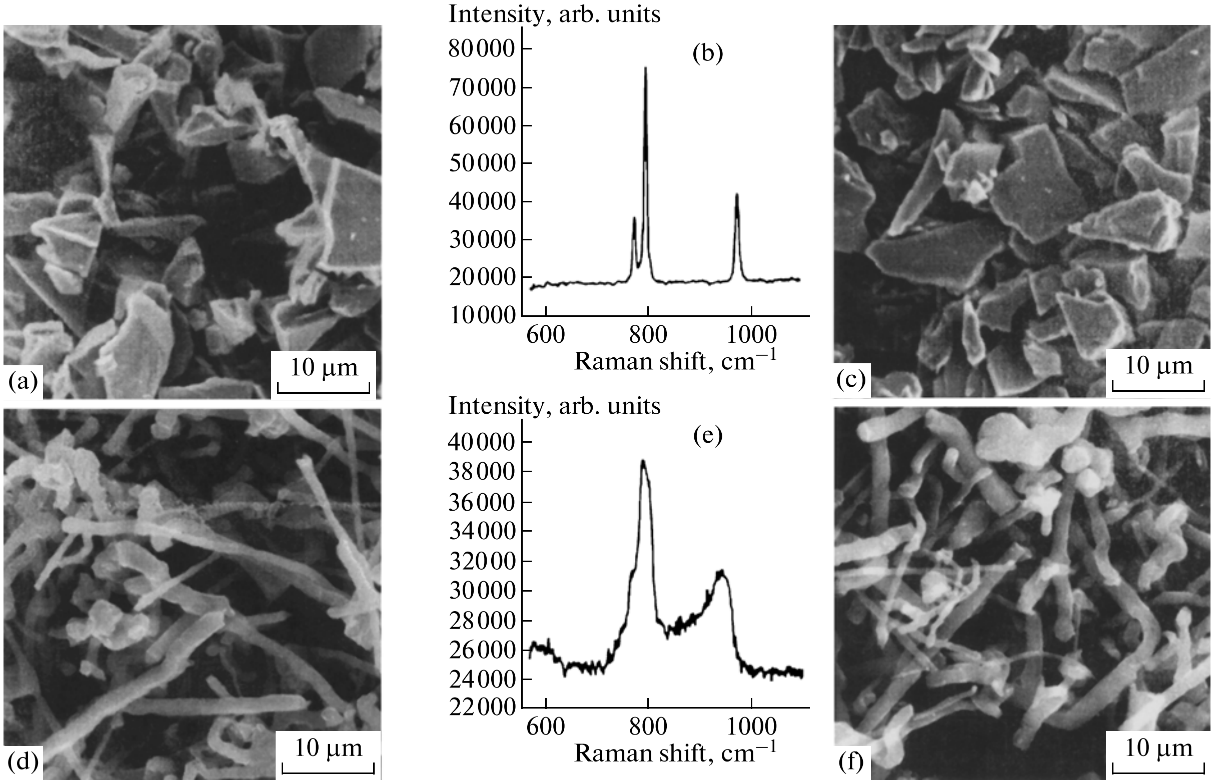

Fig. 1. (a) An external view of hexagonal silicon carbide microcrystals, (b) their Raman spectrum, and (c) an external view of nanoporous carbon particles produced from silicon carbide of this type. (d, e, f) The same in the case of cubic silicon carbide.

position of lines in the spectra was corrected with reference to the emission lines of gaseous Ne. The spectra were excited with He–Ne laser radiation at the wavelength 632.8 nm. The excitation power in the focus of the microscope was lower than 2 mW. The experiments were conducted at room temperature.

The samples to be studied were fabricated by means of technology described elsewhere [3, 6]. The material was a fine-dispersed powder. The spectra were recorded for both separate carbon particles of the corresponding series and for pored continuous layers. No systematic distinctions between the spectra of separate particles and layers were observed.

3. RESULTS

In experiments, the Raman spectra were recorded for several series of samples. One group of the samples was produced from the hexagonal silicon carbide powder, and the other group was obtained from cubic silicon carbide (whisker β-SiC crystals).

Figure 1 illustrates the initial shape of carbide particles and the morphology of the resulting porous carbon particles. Figures 1a–1c show the external view of the initial hexagonal silicon carbide crystals, the Raman spectra of this material, and the external view of the resulting carbon particles, respectively. The corresponding data obtained in the case of whisker cubic silicon carbide crystals are shown in Figs. 1d, 1e, and 1f. It can be clearly seen that the nanoporous carbon particles inherit the morphology of the initial carbide particles.

The spectra of the carbon materials produced from the above-mentioned types of carbides do not exhibit any systematic distinctions. Below in the paper, the experimental results are presented without indication of the initial material from which the particular carbon sample was produced.

The Raman lines characteristic of the spectrum of silicon carbide become unobservable in the spectra of the samples chlorinated at temperatures of 300–400°C and higher. A similar observation was reported previously [3]. The lines characteristic of amorphous carbon become evident for the samples chlorinated at temperatures higher than ~500°C. As the temperature of the chemical and heat treatment was elevated, the Raman spectra of the resulting samples change and, finally, approach the spectra of crystal graphite. Figure 2 gives an insight into the character of these changes. The last-recorded spectrum of the material produced by treating at 2000°C exhibits a high-intensity narrow line (the so-called G line) at about 1580 cm^{-1} and a rather low-intensity D line observed in this study at about 1320 cm^{-1}. This position of the D line is close to the typical position of the D line for crystal graph-

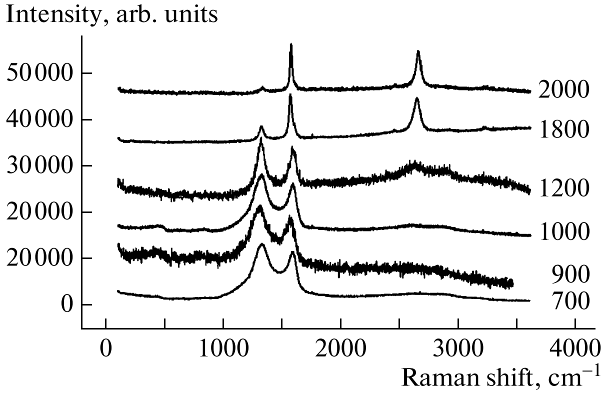

Fig. 2. Raman spectra of nanoporous carbon produced at different temperatures. The temperatures (°C) corresponding to each of curves are indicated. Curves are shifted along the vertical axis.

ite [7]. The differences between the positions of the D lines are discussed below.

The dependences of the parameters of the spectra on the temperature of chemical and heat treatment are shown in Fig. 3. Figure 3a shows the positions and half-widths of the G and D lines versus the temperature of treatment of the initial carbide with chlorine. Figure 3b shows the corresponding dependence for the ratio between the intensities of the D and G bands. Below, in discussing the results, we relate the experimentally observed dependences to the proposed mechanism of formation of the coals.

Figure 4 shows the Raman spectrum of one of the series of coals produced by chlorinating silicon carbide at 1800°C and then subjected to extra treatment with hydrogen. The spectrum substantially differs from the spectra of other series of materials produced at the same temperature, but replicates in detail the spectra of a recently produced new carbon material, graphene [8]. Along with the possibility of observing graphene traces in such system, the fact that the above result can be used to draw some inferences relative to the structure of the coals is of interest.

4. DISCUSSION

The Raman spectra of nanoporous coals are often reported in papers devoted to studies of this type of materials. However, most publications are only illustrative. As a rule, authors only detect the transformation of amorphous carbon to graphite-like carbon with elevation of the temperature of chemical and heat treatment. In this case, some specific features of the spectra and their correlation with the process of self-formation of the nanoporous carbon material remain poorly understood. For example, no explanation was given to the maximum of the ratio I_D/I_G at 1100°C–1200°C. One more distinction of the results obtained in this study from the data reported by other researchers is the difference in the position of the D line. According to publications, the position of the D line corresponds to 1350 cm^{-1}. However, in the experiments conducted here, we systematically recorded the D line at 1315–1320 cm^{-1}.

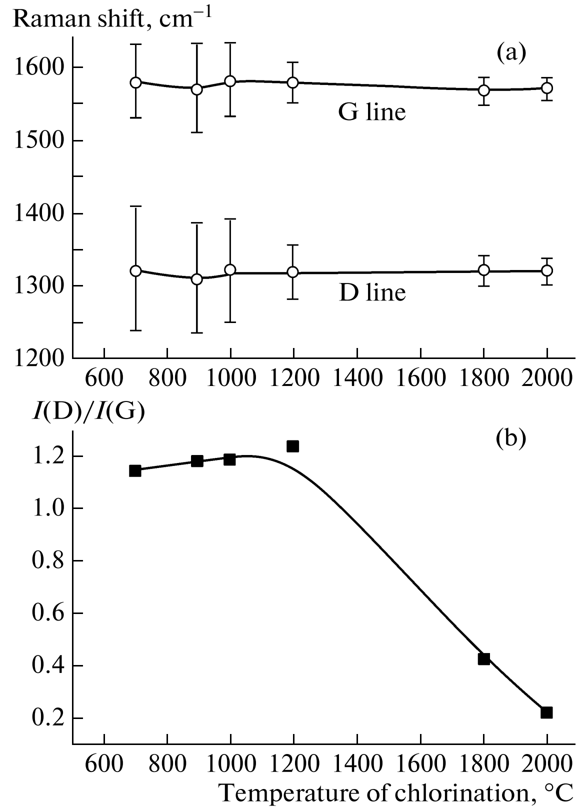

Fig. 3. (a) The position and half-width of the basic lines in the Raman spectrum of nanoporous carbon materials and (b) the ratio between the intensities of the D and G lines vs. the temperature of production of the materials.

Let us now try to combine these facts and, on this basis, to formulate a general concept of self-formation

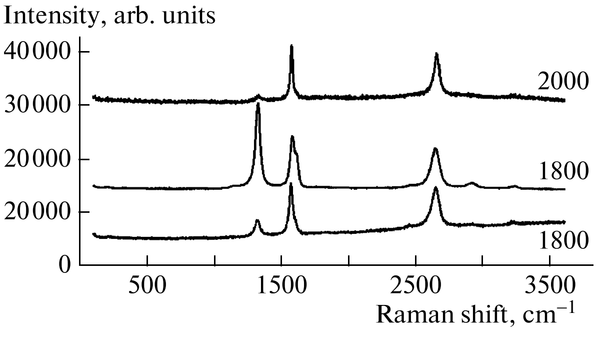

Fig. 4. Raman spectra of nanoporous carbon produced (upper and lower curves) with and (middle curve) without supplementary treatment with hydrogen. The temperatures of production of the carbon materials (°C) are indicated. Curves are shifted along the vertical axis for convenience of comparison.

of nanoporous carbon materials. First of all, in contrast to [5], we believe that pores are not formed in the initial carbide crystal. One of the arguments in favor of this statement is that the carbide traces disappear at treatment temperatures lower than the treatment temperatures at which the amorphous carbon traces become observable. As noted above, this conclusion agrees also with the conclusion of [3]. The initial stage of the process must, apparently, be considered to be the destruction of the carbide crystal.

Gaseous chlorine interacting with silicon atoms and forming a volatile product (the boiling temperature t_b of $SiCl_4$ is 57°C) leaves the atoms of the carbon sublattice with completely unbalanced interatomic forces. However, it would seem to be incorrect to consider this intermediate state of the material as a specific gas of carbon atoms. It should be taken into consideration that the material retains its external shape and, hence, some interatomic bonding still exists. It is apparently correct to believe that, during the release of $SiCl_4$, carbon atoms retain some fraction of bonds. Since the C–C distances in silicon carbide (1.85 Å) and, especially, the average spacing between C atoms in this material (2.8 Å) are larger than the lengths of the C–C sp^3 bonds in diamond (1.54 Å) and the C–C sp^2 bonds in graphite (1.41 Å), it can be expected that new bonds will be formed between the neighboring carbon atoms, which accidentally become close to each other during degradation of the crystal lattice. In the initial stage (the results of which can be conceived from the results of low-temperature treatment), an unstable material somewhat similar to an air gel is formed of carbon atoms. Because of the relatively low temperature, no substantial transformation of the material can occur. The Raman spectra reflect the formation of amorphous carbon with random bonds only. Nevertheless, a sparse network of random bonds makes it possible to retain the rough spatial arrangement of the ensemble of carbon atoms without external forces.

Such a concept of the intermediate form of the material agrees also with the well-known fact that the specific surface area of the carbon material produced by low-temperature treatment (600°C) is still relatively small (800–1000 $m^2 g^{-1}$) [9], as is consistent with the data obtained in this study as well. This is apparently due to the fact that, in the ensemble of weakly bonded carbon atoms, low-density regions are yet too small in dimensions (the dimensions on the order of atomic displacements during the primary transformation). The low-density regions are of about several angstroms in dimensions and, hence, undetectable experimentally in the measurements of the surface area of pores.

As the temperature of chlorination is elevated, the mobility of atoms increases; specifically, the atoms can travel longer distances and find energetically more favorable sites and configurations. Finally, such stable configurations are bound to correspond to clusters of the stable forms of carbon. The Raman spectra of materials produced at the highest temperatures of treatment unambiguously suggest that the materials are graphite-like in structure. The same conclusion was drawn by the authors of [4] from the X-ray photoelectron spectroscopy (XPS) data.

The formation of clusters seems to be understandable on the basis of general considerations. In fact, the centers of formation of stable atomic configurations can appear at many randomly located sites in the carbon array. Using the small-angle X-ray scattering (SAXS) method, Kyutt et al. [10] estimated the dimensions (radii of inertia) of such clusters. For nanoporous carbon produced from silicon carbide, the estimation yields ~4.5 Å. From the Raman data obtained in this study, we can also estimate the size of graphite-like clusters. This can be done by the method suggested in [7], if it is assumed that the D line observed in this study at 1320 cm^{-1} corresponds to the 1350 cm^{-1} line observed in [7]). Specifically, for the material produced by treating at 1000°C, such estimation yields the cluster dimension of about 40 Å. The difference between the estimates is substantial (of about an order of magnitude). However, we must take into account that the materials studied here and in [9] were produced from different series of materials and, in addition, the methods used in [7] and [10] exploit different types of interaction of external fields with the material.

The specific surface area of the material produced by chemical and heat treatment at temperatures higher than 900°C–1100°C becomes again smaller as the temperature is increased [9]. The physical cause of this effect also seems clear. At high temperatures, the mobility of atoms is high and individual clusters transform into larger crystallites, including bulk graphite crystallites with a large number of carbon sheets. Obviously, such carbon is bound to exhibit a small specific surface area. The electron micrograph of the material in this stage of treatment unambiguously shows parallel carbon sheets similar to those in graphite [11].

After treatment at intermediate temperatures, the material exhibits the maximum specific surface area. For the material produced from silicon carbide in this study, the maximum specific surface area is attained in the material produced at about 900°C. In that case, the specific surface area was 1300–1500 $m^2 g^{-1}$.

It is interesting to correlate this result with the features of the Raman spectra and the process of self-assembling of atoms in the material under study. As noted above, one of such features is the maximum of the ratio between the intensities of the D and G bands, I_D/I_G, for the material produced at 1100–1200°C. Such maximum was observed in most studies concerned with the Raman spectra of nanoporous coals produced from carbides.

The position of the D line is close to that of the Raman band in diamond and is often attributed to the sp^3 hybridized bonds in the material. An explanation for this may inevitably come to mind that because of the larger length of the sp^3 bonds compared to the length of the sp^2 bonds, the sp^3 bonds have some advantage over the sp^2 bonds in kinetics of formation at intermediate temperatures and, at first, the sp^3 bonds are formed for the most part. As the temperature is increased further, the structural transformation continues to occur, and carbon atoms are rearranged into more stable sp^2-bound graphite sheets.

However, such an inference would contradict the fact that materials produced at approximately these temperatures exhibit the maximum specific surface area. Since the sp^3 bonds are of three-dimensional (3D) character, this type of bond is bound to be responsible for the formation of 3D clusters and, hence, for a small specific surface area. The specific surface area of 1500 $m^2 g^{-1}$ attained in the case under consideration is close to the maximum possible specific surface area for one-sheet graphene (2630 $m^2 g^{-1}$).

An explanation based on previously reported results [12] of comparison between the Raman spectra of amorphous carbon and those of graphite seems to be more plausible. In [12], it was shown that the ratio between the intensities of the D and G bands, I_D/I_G, as a function of the cluster dimensions has a peak at the cluster dimensions of about 20 Å. This conclusion is based on the interpretation of the D line in the Raman spectra as the line associated with defects at the boundaries of graphite clusters (flakes). In the beginning of formation of the structure of the material from amorphous carbon, the number of flakes and their size increase. Then, during structural rearrangement at higher temperatures, large-sized clusters assimilate small-sized ones. In that case, the surface areas of clusters are bound to decrease, resulting in a decrease in the intensity of the D line. For the materials under study, the above inference is consistent also with the electron micrographs of the material produced at high temperatures [11]. In these micrographs, one can see large-sized and well-formed multilayered graphite structures.

Such an interpretation of the nature of the maximum of the quantity I_D/I_G agrees with all concepts of Raman scattering in carbon materials and with the data on the parameters of the porous structure of these materials. Nevertheless, it must be kept in mind that the materials studied in [12] and here are substantially different and, therefore, no quantitative agreement between the corresponding data can be expected.

Particular attention must be given to the nontrivial Raman spectrum of the material subjected to supplementary treatment with hydrogen. Undoubtedly, this spectrum differs from the spectra of the initial series of carbon samples and, at the same time, is similar to the spectrum of recently discovered graphene [8]. The fact that the modified material was produced from the initial carbon material by supplementary annealing in hydrogen only supports the inference that, in this experiment, we fabricated clusters similar to graphene. In the context of the considerations presented in this study, this result suggests that, in some cases, nanoporous carbon produced from carbides really presents a conglomerate of graphene-like clusters with a thickness below one sheet of carbon atoms. In the case of thicker flakes, adsorption of hydrogen at the surface cannot induce such a modification of Raman scattering [8].

Finally, special attention must be given to the substantial difference between the positions of the D line observed in this study and in other studies where this position was identified. In this study, we calibrated the positions of Raman lines with reference to the emission lines of gaseous Ne and the possibility of noticeable experimental error is ruled out. Moreover, the neighboring G line is detected at the same Raman shift, as in other studies. This sends us in search of physical causes of the differences between the experimental data.

In general, carbon materials exhibit a wide variety of structures and structural defects. Even with rather definite assumptions relating to the structure of the material in this study, some additional uncertain parameters and features remain. Among these are such as the shape or the degree of imperfectness of the constituent graphene clusters in the material and the possible adsorption at their surface. For example, in [12], it is noted that some disorder of bonding is bound to yield a shift of Raman lines to lower energies. Such disorder-induced shifts of Raman lines are known and observed also in other materials, e.g., in silicon. It is possible that the shift observed in this study can be controlled in part by this mechanism. However, the amorphization-induced shifts are usually accompanied by line broadenings, which is unobserved in the study.

One of the possible hypotheses that can be helpful in explaining the above-discussed anomaly is suggested in [13]. The authors of [13] calculated the possible Raman modes of graphene clusters that presented strips of finite width and different functional groups bound to the strips. It was shown that, in this case, the range of possible types of vibrations was substantially modified; specifically, new modes appeared in the vicinity of the D line. It is conceivable that this result provides a key to understanding the mechanism of the experimentally observed shift.

5. CONCLUSIONS

The Raman spectra of nanoporous carbon materials produced from silicon carbide of two modifications, hexagonal and cubic, are studied. On the basis of the experimental data obtained here and by other authors, the mechanism of self-formation of the nanoporous system and the specific features of the Raman spectra of the materials are interpreted.

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