Formation of Onion-like Structures from Pitch Coke under Pressure

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Carbon structures containing oxygen are promising in regard to their industrial application. In this work, we studied coke pitch produced on the basis of melted coal tar pitch mixed with thermally expanded graphite. A mixture of pitch and foamed graphite was fired and then subjected to high pressure in a diamond anvil cell. The obtained samples were studied by Raman spectroscopy, and scanning and transmission electron microscopy. Two types of onion-like structures were found: dense and loose structures. It is established that the concentration of oxygen in the loose structures reaches 5 atomic percent.

Keywords: pressure; carbon onions; carbon-oxygen compounds.

Processing of various carbon materials in a high-pressure shearing diamond anvil cell has revealed some interesting experimental data. It has been shown that it is possible to obtain a wide range of carbon structures known today, depending on the initial carbon material and treatment conditions: diamond, lonsdaleite, onions, and onion-like structures [1–6]. For further research, carbon structures containing oxygen are of particular interest. Such materials are interesting from the point of view of their industrial application. They have high heat resistance...
and strength, they do not become brittle even at high temperatures and have high resistance to temperature changes. Their additional advantages include low density, low level of heat absorption, and low coefficient of thermal expansion [7]. This study focused on the material intended for obtaining structural graphite. The starting material was a pitch coke obtained from a molten coal tar pitch that was mixed with thermally expanded graphite to obtain a uniform mass. To oxidize the pitch, we applied heating in the 250–300 °C temperature range during 5-6 hours. The mixture of pitch and expanded graphite after oxidation was ground and the resulting powder was used to press the workpieces. This was followed by firing in a non-oxidizing atmosphere at 1100–1300 °C and graphitization at a temperature of at least 2500 °C [8]. A high-pressure shearing diamond anvil cell was used for pressure treatment of the samples. The pressure was measured by piezospectroscopy of the stressed anvil top [9]. The working surface diameter of the diamond anvils was 200 μm. The sample was placed in a tungsten gasket and then pressure was applied. NaCl was used as the pressure-transferring medium. Electron microscopy was carried out on a JSM-7600F scanning electron microscope equipped with EDS and WDS X-ray spectroscopy attachments, as well as on a JEM-2010 transmission electron microscope (TEM) with electron energy loss spectroscopy (EELS) and EDS attachments. The Raman spectra were determined using a Renishaw inVia Raman microscope with a 532 nm wavelength. Samples for the TEM studies were prepared by a standard procedure. Fig. 1 provides the photographs of the source material. Fig. 1a shows the image obtained with a scanning microscope, whereas Fig. 1b is an image taken by a transmission electron microscope. The curved graphite planes are clearly visible. The WDS method revealed that the material contains an average of 0.4 atomic percent oxygen. In this case, oxygen is distributed uniformly over the sample.

Fig. 1. Images of the source material: a) a scanning electron microscope photograph; b) a TEM image, the curved graphite planes are clearly visible

Fig. 2 illustrates the photographs of the material processed in a diamond cell: a) onion-like structures consisting of graphite layers densely adjacent to each other; b) onion-like structures consisting of curved graphite layers. While the distances between the graphite layers in Fig. 2a are close to the interplanar distance for (002) graphite planes which is usually equal to 0.335 nm, the corresponding distances in Fig. 2b reach the values of 0.36–0.37 nm. A distinctive feature of the
two onion-like structures presented in Fig. 2 is the concentration of oxygen. The concentration of oxygen in the EELS spectra corresponding to Fig. 2a is at a background level, while the concentration of oxygen on the EELS spectrum of the structure shown in Fig. 2b, as it follows from Fig. 3, reaches 5 atomic percent. Thus, the effect of pressure and shear on the source pitch coke material leads to the formation of two types of onion-like structures: dense and loose, the latter containing oxygen in sufficiently large amounts.

Fig. 2. Images of the material processed in a diamond cell: a) onion-like structures consisting of graphite layers densely adjacent to each other; b) onion-like structures consisting of curved graphite layers

Fig. 3. EELS spectrum of the onion-like structures depicted in Fig. 2. The arrow shows a 532 eV peak of oxygen. The concentration of oxygen is about 5 atomic percent

The Raman spectra of the sample before and after the pressure treatment (the maximum pressure was 76 GPa) are shown in Fig. 4(a). Two bands are observed in the spectra: a D-band (1347 cm\(^{-1}\) before pressure treatment and 1360 cm\(^{-1}\) after) and a G-band (1581 cm\(^{-1}\) before pressure treatment and 1584 cm\(^{-1}\) after). The relative intensities of the D- and G-bands before and after the pressure treatment changed slightly. Intensity ratio ID/IG for the disorder-
induced D-band and the Raman-allowed first-order G-band is 1.1 for the initial sample and 1.2 for the pressure-treated sample which appeared for the average distance between the defects in graphene of 1.4 and 1.5 nm, accordingly (in-plane correlation length), as follows from Ref. [10]. The observed shift of the D- and G-bands indicates some possible structural changes in the sample, which is confirmed by the peculiarities of the G-band position dependence on pressure.

Fig. 4. a) — Raman spectrum of a pitch coke sample before and after the pressure treatment (the maximum pressure was 76 GPa); b) — the G band dependence on pressure

The pitch coke sample G-band dependence on pressure is depicted in Fig. 4 (b). The dependence shown in Fig. 4 is similar to the dependence for graphite [11] and multi-walled carbon nanotubes [3]. When the pressure reaches about 30 GPa, there is a broadening of the G-band. The dependences shown in Fig. 4 demonstrate the instability of sp$^2$-bonding: a typical so-called Raman mode softening (pressure increasing does not lead to Raman frequency increasing) is observed at pressure above 30 GPa [12]. The mentioned instability of the Raman mode at pressures above 30 GPa, along with the shift of the Raman bands in the sample after the pressure treatment, indicates a phase transition that starts at a 30 GPa pressure.

## Conclusion

As a result of processing a sample of pitch coke containing about 0.4 atomic percent oxygen in a high-pressure chamber, two types of onion-like structures have been found: dense and loose structures. It is established that the concentration of oxygen in loose structures reaches 5 atomic percent. The oxidation temperature of graphite in air is about 400 °C [13]. Since the pressure treatment was carried out at room temperature, the increase in oxygen concentration in onion-like structures is apparently due to its redistribution during treatment.

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References


Образование онионоподобных структур из пекового кокса под давлением

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Углеродные структуры, содержащие кислород, интересны с точки зрения их промышленного применения. В работе исследовали пековый кокс, полученный на основе расплавленного каменноугольного пека, который смешивали с терморасширенным графитом. Смесь пека и пенографита проходила обжиг и затем подвергалась высокому давлению в камере с алмазными наковальнями. Полученные образцы исследовались методами Рамановской спектроскопии, сканирующей и просвечивающей электронной микроскопии. Были обнаружены два типа онионоподобных структур: плотные и рыхлые. Установлено, что концентрация кислорода в рыхлых структурах достигает 5 атомных процентов.

Ключевые слова: высокое давление, углеродные луковичные структуры, соединения углерода с кислородом.