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The atomic scale structure of glass-like carbon obtained from fullerene extract via spark plasma sintering

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ABSTRACT

The spark plasma sintering technique was successfully used to transform fullerene extract into glass-like carbon. The sintered sample was characterized via thermogravimetry, scanning electron microscopy, X-ray photoelectron spectroscopy, the X-ray and neutron diffraction. To reconstruct the atomic scale structure the diffraction results were combined with computer simulations. The comparative analysis was performed in the form of the structure factor and the pair correlation function in the reciprocal and direct space. In the first approach the two different concepts of graphite-based models have been verified. For such constructed models the pair correlation functions maxima positions indicate the strong differences in comparison with the experimental data. In the second approach the proposed models were constructed successively on the icosahedral from C_{960} up to C_{3840} fullerenes fragments. The final model consists of triple layer fullerene C_{3840}-like fragments in which the isolated pentagon presence guaranties the stronger curvature. The calculated pair correlation function fits the experimental data well and therefore proves that the atomic structure of sintered glass-like materials originated from C_{60}/C_{70} fullerene extract consists of defected fullerene C_{3840}-like fragments. The curvature was assured by isolated pentagon, but the disorder of surrounded hexagonal lattice was modeled and properly reconstructed by the Stone-Thrower-Wales topological defects.

1. Introduction

Glass-like carbon often called glassy carbon (GC) or vitreous carbon belongs to a non-graphitizing carbon group, which is very stable and extremely resistive to temperature up to around 3000 °C and also to the aggressive chemicals [1–3]. Thus, such highly resistant material is very useful and widely implemented in industry as chemical utensil, element for emission electronics, and even material for prosthetic and cardiological appliances due its biocompatibilty.

These application possibilities are directly linked with its structural properties basing on macroisotropic microcrystallinity with large number of closed pores. There are several atomistic models of GC that coexist in the data interpretations. Among them the most popular models of GC crystallites are consist: of stacks of narrow graphite-like layers in the shape of ribbons suggested by Jenkins and Kawamura [3], of “crumpled sheets” suggested by Oberlin [4], of closed pores introduced by Shiraishi [5] and of fullerene-related structure by Harris [6]. Up till now there are many detailed studies carried out using high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, neutron and X-ray diffraction on various non-graphitizing carbons that provide evidence for non-hexagonal rings in curved carbon sheets [2,7–9].

In the present paper the glassy carbon was synthesized via spark plasma sintering (SPS) technique from the fullerene C_{60}/C_{70} extract. To verify the chemical composition of the fullerene extract and subsequently sintered glassy carbon the X-ray photoelectron spectroscopy measurements were performed. The microstructural information was provided by scanning electron microscopy observations. Thermogravimetric analysis was done to evaluate the thermal stability in the context of sample homogeneity. In order to reconstruct the atomic-scale structure the detailed real space

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representation analysis of the neutron and X-ray diffraction data combined with computer simulations data were adapted. Such analysis was previously successfully used to build the atomistic models of various disordered carbons, in which the topological point defects induced the local structure curvature [10–12]. The aim of this work was to examine the glassy carbon atomic structure, i.e. to test the two hypotheses on the graphite-based and fullerene-based models.

2. Experimental

2.1. Sample preparation

The fullerene extract in the form of powder was obtained from SES Research with its catalog number: 300–6070. According to the material specification the extract contents in approximately 70% of C_{60} fullerenes, 28% of C_{70} fullerenes and 2% of higher fullerenes. The Spark Plasma Sintering (SPS) process of fullerene extract powder was carried out at Spark Plasma Sintering system (model HP D 5/2 FCT Systeme GmbH, Rauenstein, Germany). The Spark Plasma Sintering is a non-conventional sintering technique based on the simultaneous use of pulsed current, enabling fast heating (up to 600 °C)/cooling rates and mechanical pressing. Hence lower sintering temperatures are often observed in comparison with conventional sintering techniques. Typical SPS cycle consists of sparking, densifying and cooling stages. The applied electric current and mechanical load may be constant throughout the sintering cycle or may vary during the selected densification stages. The automatic controller adjusts the current parameters to achieve the defined temperature. The SPS process is performed on powder poured in cylindrical graphitic die as a conductive container and two (top and bottom) graphitic pistons as a current electrodes (more details on SPS technique is provided in Ref. [13]). In the present study a 20 mm graphitic die lined with graphite foil was employed. The samples were slowly heated to 450 °C, then heated from 450 °C with rate of 100 °C/min up to 1500 °C with 100 °C/min ramp and held for 20 min. The temperature was controlled by optical pyrometer focused on the upper plunger 3 mm above the sample. The heating was conducted by use of 12 ms pulses separated by 2 ms pauses. During the sintering process, pressing force of 16 kN was applied. The vacuum equals to 0.1 mbar was maintained in the furnace chamber during the whole process.

2.2. X-ray photoelectron spectroscopy (XPS)

The XPS analyses were performed with monochromatized Al Kα radiation ($h\omega = 1486.6$ eV) at room temperature using two spectrometers - a VGScienta/Prevac and PHI 5700 from Physical Electronics. The analysed region of raw fullerene extract powder before and after SPS process was a rectangle 0.3 × 2 mm and about 20–40 Å in depth due inelastic mean free path of photoelectrons. Atomic concentration of the detected elements was calculated from the XPS core levels and the analysis of the spectra was performed with the use of Multipak programme from Physical Electronics.

2.3. Scanning electron microscopy (SEM)

The SEM observations of the fullerene extract and glassy carbon after SPS process were performed on LEO GEMINI 1525 electron microscope.

2.4. Thermogravimetry (TG)

The TG measurements of obtained samples were performed with use of STA 449 F3 Jupiter (Netzsch, Germany) thermal analyser. Samples were heated up to 1000 °C with the 5 °C/min ramp using Al_2O_3 plate.

2.5. X-ray diffraction (XRD)

The X-ray diffraction experiment was performed at room temperature using the Rigaku-Denki D/MAX RAPID II-R diffractometer (Rigaku Corporation, Tokyo, Japan) with a rotating anode Ag Kα tube ($\lambda = 0.5608$ Å), an incident beam (002) graphite monochromator and an image plate in the Debye–Scherrer geometry as a detector. The pixel size was 100 μm × 100 μm. The powdered sample was placed inside glass capillaries (1.5 mm in diameter). The measurements were performed for the sample filled and empty capillaries and then the intensity for the empty capillary was subtracted. The beam width at the sample was 0.3 mm. The two-dimensional diffraction pattern was then converted into one-dimensional intensity data using suitable software. The intensity was measured as a function of the scattering vector Q ($Q = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength) up to $Q_{max} = 20$ Å^{-1}. The intensity was corrected and normalized using the data processing procedure developed for high energy X-rays [14–16] and then the structure factor $S(Q)$ was computed as:

$$S(Q) = \frac{I(Q)}{f^2(Q)} \tag{1}$$

where $I(Q)$ is the coherent intensity and $f(Q)$ is the atomic scattering factor of carbon. For further analysis, a real space representation of the diffraction data in the form of the pair correlation function (PCF) was calculated converting the structure factor by the sine Fourier transform as follows:

$$PCF = \frac{2}{\pi} \int_0^{Q_{max}} Q[S(Q) - 1] \sin(Qr) \frac{\sin\left(\frac{\pi Q}{Q_{max}}\right)}{\frac{\pi Q}{Q_{max}}} dQ \tag{2}$$

where Q_{max} is the maximum value of the scattering vector available in the experiment (in the present experiment $Q_{max} = 20$ Å^{-1}) and the last term denotes the Lorch modification function that reduces effects arising from the finite value of the upper Q-limit.

2.6. Neutron diffraction (ND)

The neutron diffraction measurements were performed at the Institut Laue–Langevin in Grenoble, France. The D4 diffractometer, optimized for disordered materials, was employed [17]. A sealed cylindrical vanadium can of diameter 7 mm was used as a sample holder. The measurements were performed at ambient temperature, under vacuum conditions. The wavelength was $\lambda = 0.4989$ Å, the monochromator face was Cu 220 and a λ/2 Rh filter was used. The diffraction patterns for the empty bell jar and empty can were measured in order to subtract the background. Thereafter, to normalize the sample's diffraction intensity to an absolute scale, a vanadium rod was also measured. The data analysis and the corrections on multiple scattering and absorption were made using the CORRECT program [18]. The corrected normalized intensity was presented as a function of the scattering vector magnitude Q. The structure factor was calculated as:

$$S(Q) = 1 + \frac{I(Q) - \overline{b^2}}{\overline{b}^2} \tag{3}$$

where $I(Q)$ is the corrected intensity, b is the scattering length of carbon, and $\overline{b^2}$ and $\overline{b}^2$ are defined as follows: