Hybrid technology for the synthesis of ultrafine carbon powder material in an amorphous state

V A Chaika¹, ⁴, V V Savin¹, I S Zherebcov¹, M E Boiko² and A M Boiko³

¹Immanuel-Kant Baltic-Federal University, Nevsky st., 14, 23616 Kaliningrad, Russia
²Ioffe Physical-Technical Institute of RAS, 26 Polytekhnicheskaya, 194021 Saint Petersburg, Russia
³Herzen Pedagogical University, embankment of the Moika River, 48, 191186 Saint Petersburg, Russia

⁴E-mail: v.chayka8@rambler.ru

Abstract. The results of using a hybrid technology for the synthesis of ultrafine carbon powder material in an amorphous state are considered. Different modes of hybrid technology are proposed, including mechanochemical synthesis in a ball mill and the process of self-propagating sustainable combustion in a natural atmosphere to produce carbon powder materials (CPM) in an amorphous state. Using X-ray diffraction methods: diffractometric, radiographic, and small-angle X-ray scattering, heterogeneities of the CPM structure were studied. Areas of structural heterogeneity having a flat shape and containing up to 10 graphene-like layers are revealed.

1. Introduction

There processing, abrupt changes in the lattice period and graphite properties are noted [4]. Intense changes in the macro- and microstructure of the material being processed alternate with relaxation processes, resulting structural inhomogeneities and defects.

The aim of this work was to obtain an amorphous state in carbon powder materials using the method of mechanochemical synthesis (MCS) during long-term processing in a planetary ball mill of MPG-7 graphite.

2. Results

MHS was carried out in a PM-100 planetary ball mill (manufactured by RetschGmbH) at 600 rpm in a steel can with steel balls in the atmosphere of residual air. The feedstock was particles of graphite MPG-7 fractions of less than 1 mm. The ratio of the mass of the balls to the mass of the charge charge corresponded to a ratio of 19: 1.

During the synthesis, 4 processing modes were used: 1) four times for 6 hours with stops for 18 hours; 2) six times for 4 hours with stops for 8 hours; 3) 12 times for 2 hours with stops at least 3 hours; 4) 24 times for 1 hour with stops for 0.5 hours.

After MCS, when glasses are opened in natural atmospheric conditions, the process of oxidation (burning) of the powder material occurs. The process is realized by the local occurrence of one or several centers (foci) of combustion and a propagating stable combustion front according to the type of self-propagating high-temperature synthesis (SHS). The most intense course of the combustion
process (according to the time of occurrence of the foci, their number, and the velocity of the combustion front) is observed in the powder material after MCS under conditions No. 3 and No. 4. Under conditions No. 1 and No. 2, combustion passed into the process of decaying decay of one or more local ignition centers.

Figure 1 shows a fragment (frame) of a video of the propagating stable combustion front of the MHS powder obtained in mode N3 in PM100 with a steel headset.

![Video image of powder decay after 24 hours of processing with stops every 2 hours in PM100 with a steel headset.](image)

Figure 1. Video image of powder decay after 24 hours of processing with stops every 2 hours in PM100 with a steel headset.

In the work, powder carbon materials obtained by the MCS method and subjected to combustion according to the SHS type were studied in detail, i.e. obtained by hybrid synthesis technology (MCS + SHS).

The resulting material is characterized by high dispersion. Figure 2 shows the results of metallographic studies of the shape and structure of the powder material synthesized by the hybrid (MCS + SHS) method. As can be seen from the data presented, all particles have a “fragmentation” shape. After hybrid processing, white and brown particles are present in the array of powders. It was experimentally established that powder material obtained according to regime N3 is prone to agglomeration.

To clarify the chemical composition of the powder material, detail the morphology and microstructure of the synthesized powder particles, scanning electron microscopy (SEM) studies were carried out on a JSM-6390LV instrument (JEOL, Japan) with an OxfordINCAEnergy energy dispersive analyzer (Oxford Instrument, England). The research results are shown in figure 3.

The bulk (up to 90%) of the synthesized powder material has a particle size of less than 10 microns. According to the chemical composition data, there are practically no impurities in the obtained material, except oxygen.

As shown by X-ray studies (DRON-3M diffractometer, Cu-K$_{\alpha}$ radiation) in all powder samples, the diffraction maxima of graphite in the amorphous type are weakened and broadened (figure 4). It is noteworthy that the center of gravity of the main peak is shifted nonlinearly.

Estimation of the CSR size (D) and crystallite size along the crystallographic axis “a” (L$_{a}$) of the test material is presented in table 1. According to the data in table 1, ultrafine powder is obtained under processing conditions N2 and N3.
Figure 2. Optical image of the powder after 24 hours of processing in PM100 with a steel headset under processing conditions: N1 – (d); N2 – (c); N3 – (b) and N4 – (a).

Figure 3. SEM image of the powder after 24 hours of processing with stops every 1 hour (mode N4) in the PM100 with a steel headset.
Figure 4. X-ray powder diffraction patterns MCS.

Table 1. Estimation of the size of the CSR material after MCS synthesized by hybrid (MCS + SHS) technology.

| Parameters | Processing Modes |
|------------|-----------------|
|            | N4  | N3  | N2  | N1  |
| D, nm      | 96.4| 6.63| 6.65| 27.5|
| L, nm      | 4.7 | 1.37| 1.89| 4.56|

Based on the location of the (002) line, the average interatomic distance R1 in the material was estimated (see table 2).

Table 2. The concentration of heavy metals in the diets of feeding bulls of the black-and-white breed, mg.

| Parameters | Processing Modes |
|------------|-----------------|
|            | N4  | N3  | N2  | N1  |
| 2θ, degree | 26.06| 23.99| 26.66| 25.33|
| d/n, Å     | 3.415| 3.705| 3.339| 3.512|
| H          | 150  | 122  | 30  | 120  |
| FWHM, degree | 2.76| 8.2  | 3.36| 6.15  |
| R1, Å      | 4.2  | 4.557| 4.107| 4.32 |

When comparing the data of tables 1 and 2, we can conclude that the bulk of the material is a flat flakes with a thickness of about 3–10 atomic layers.

Figure 5 shows the radiographic image (MCS + SHS) of the powder material (modes No. 1 and No. 2). The image was obtained on a unique scientific facility (USI) – a scientific and educational multifunctional complex for preparing and conducting synchrotron studies “SynchrotronLike” (X-ray source ExcillumMetalJet D2 manufacturer – Excillum AB, Swedish corporation). The image shows transparent flakes of processed graphite, consisting of many small particles. Transparency indicates a small number of atomic layers in the particles.
Figure 5. Radiographic image of the material after a long MCS in PM100 with a steel headset with stops every 4 (a) and 6 (b) hours.

To clarify the grain size, small-angle X-ray scattering studies were performed [6] and FWHM = 0.102 was obtained for the material after the hybrid technology in regime N3 (see figure 6). The values of the Porod modulus (from left to right) were determined 2.7 – 2.4, which indicates that the shape of the particles is more gravitated to the shape of the membranes than to the shape of the particles of dense powder. The gyration radius (R giration) of graphite particles is determined in the range of 22– 34 nm, which is much larger than the CSR sizes and is explained by the flat shape of the particles.

Figure 6. An example of a small angle X-ray scattering curve for a powder material obtained by the hybrid (MCS + SHS) technology according to mode N3.
3. Conclusion
1. For the synthesis of carbon materials in an amorphous state, a hybrid technology has been applied, including mechanochemical synthesis (MCS) in a PM100 ball planetary mill with a steel headset and the process of self-propagating sustainable combustion in a natural atmosphere (SHS).
2. The modes of hybrid technology for the synthesis of powder ultrafine carbon powder materials in an X-ray amorphous state are proposed.
3. X-ray methods were used to determine the flat shape of material particles with a thickness of the order of 3-10 atomic layers.

Acknowledgments
The study was supported by a subsidy allocated for the implementation of the Competitiveness Program of the Immanuel Kant Baltic Federal University.

References
[1] Opalev SV and Belenkov E A 2004 An experimental study of changes in the structure of graphite during mechanical grinding Physical chemistry and technology of inorganic materials. Bulletin of the Chelyabinsk Scientific Center 3(24) 27–30
[2] Nikonova R M, Pozdeeva N S and Ladyanov V I 2011 The deformation behavior of copper during mechanical activation with carbon Chemic. physics and mesoscopy 1(13) 88–93
[3] Belenkov E A and Greshnyakov V A 2016 Structure, properties and possible mechanisms of the formation of diamond-like phases Solid State Physics 58(10) 2145–2154
[4] Borunova A B 2015 The effect of the dose of mechanical activation on the defective structure of artificial graphite Colloid. Journal 77 134–143
[5] Chaika V A, Savin V V, Savina L A, Osadchy A V and Zherebcov I S 2018 Structural-phase changes of graphite during mechanochemical treatment Key Engineering Materials 777 205–209
[6] RU patent. N2548601 C1: Method for X-ray spectral determination of the composition and size of nanoparticles in a sample. dated 11/20/2013