Synthesis of ultra dispersed graphite-like structures doped with nitrogen in supersonic carbon plasma flow

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Abstract. In this paper the synthesis of ultra dispersed graphite-like structures doped with nitrogen by using a magneto plasma accelerator is shown. The synthesis of such structures is realized during supersonic carbon plasma jet flowing into the chamber filled with the nitrogen atmosphere. Plasma jet is generated by coaxial magneto plasma accelerator (CMPA) based on graphite electrode system. The CMPA is supplied from the pulsed capacitive energy storage with the maximum value of stored energy of 360 kJ. Electrical and energy parameters of plasma flow are recorded during experiment. According to X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) methods obtained particles with well seen triangle sectors are graphite-like carbon structures doped with nitrogen atoms. This is confirmed by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy analyses in which carbon-nitrogen bonding configurations have been identified.

1. Introduction
The first introduction of the material with the stoichiometry $\text{C}_3\text{N}_4$ was made in 1922 [1]. After more than sixty years this material ran into renaissance and has become widespread, due at least partly to the paper published by Marvin L. Cohen [2]. The author made an assumption about a hypothetical phase of the carbon-nitrogen material which is isostructural to $\beta$-Si$_3$N$_4$, with the bulk modulus comparable to that of diamond. In 1996 Teter and Hemley predicted several carbon nitride polymorphs such as cubic, graphitic, pseudocubic etc. based on first-principles calculations [3]. In spite of numerous attempts concerning the synthesis of C$_3$N$_4$ [4], there is no unambiguous evidence about successful synthesis of ultra-hard crystalline carbon nitride solids [5]. At the same time graphitic carbon nitride with different stoichiometries has already been experimentally obtained. Up to now, several methods such as direct dynamic synthesis [6], synthesis using dynamic pressures [7], mechanochemical synthesis [8], solvothermal method [9], pyrolysis [10], are widely used. Also it has been claimed that the carbon nitride compound could be formed in thin amorphous films [11]. In the past few years there has been an increasing interest to graphitic carbon nitride materials due to their photocatalytic properties [12, 13]. Because of good prospects of carbon nitride as a promising complement to carbon materials, the synthesis process in the C-N system by using high-current coaxial magneto plasma accelerator was realized [14, 15]. In this paper the possibility of synthesis of ultra dispersed graphite-like structures doped with nitrogen via this versatile technique is presented.
2. Experimental

A sketch map of the system used for magnetoplasmadynamic synthesis is shown in figure 1. It consists of three main elements such as capacitive energy storage, coaxial magnetoplasma accelerator (1-7) and working chamber. Capacitive energy storage is divided into 24 sections with 1,2 mF capacitor banks (8). Maximum charging voltage of capacitor banks is 5 kV. Sectioning is made for varying the value of input energy. Such a way by using sectioning capacitive energy storage it’s possible to supply the system with energy up to 360 kJ.

The z-pinch discharge current and the voltage between z-axis pinch accelerator electrodes were measured using a Rogowski coil (R) and a resistive voltage divider (VD). The signals were registered in real time by a two-channel Tektronix TDS1012 oscilloscope (OSC). The photoregistration system triggering is realized with pushing a button in the camera software PC suit. Camera generates a TTL signal, which by the way of the cascade amplification closes keys in the power circuit. Oscillographic testing is started with an appearance of the current signal front from the Rogowski coil.

![Figure 1. Sketch map of system: 1 – metal case of central electrode; 2 – insulator; 3 – metal case; 4 – graphite insert; 5 – plasma formation zone; 6 – inductor; 7 – graphite accelerating channel; 8 – capacitive energy storage; R -Rogowski coil; VD – voltage divider; HSC – high-speed camera.](image)

Such a way powder sample was synthesized in the superhighspeed carbon plasma jet flowing into the chamber filled up with nitrogen atmosphere (N\textsubscript{2}) at normal conditions. Before experiment working chamber was evacuated. The total capacity of energy storage was 6,0 mF (5 sections). The charging voltage was 3,5 kV. The precursor powder (a carbon black with purity of 99%) of 0.5 g was put into the plasma formation zone. Besides extra carbon ions are involved into the plasma flow due to erosion of accelerating channel. The typical work cycle of the system was up to 0.5 ms. The chamber was opened and the powder product was collected after an hour.

The final product (mass of 0.5 g) was analyzed by X-ray diffraction (XRD) with a Shimadzu XRD7000 diffractometer with a Cu \textit{K}α radiation, high resolution transmitting electron microscopy (HRTEM) via JEOL JEM 2100F high resolution transmission electron microscope, X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific ESCALAB 250 spectroscope and Raman spectroscopy using a Thermo Scientific Nikolet NXR 9650 Raman spectrometer.

3. Results and discussion

Figure 2 shows the electrical (a) and energy (b) discharge parameters during the working cycle. The discharge current and voltage were registered with using the Rogowski coil and resistive voltage divider, respectively. It’s clearly seen that process time is about 270 µs and during this time the current maximum is over 150 kA. The presence of residual voltage (~ 400 V) can be connected with the recharge of capacitors. Using obtained current and voltage data the instantaneous power and energy were calculated.
The XRD pattern of the synthesized powder (1) and initial carbon black (2) used as a precursor is shown in figure 3. It can be noticed positions of diffraction peaks are typical for graphite-like structure. An analysis of XRD pattern was carried out by using database PDF2+.

**Figure 2.** Electrical and energy discharge parameters: a) Current and voltage oscilloscope traces; b) Instantaneous power and energy.

Following main crystalline phases such as graphite gC (space group P6-3mc (186)) and silicon oxide SiO$_2$ (space group P24/mnm (136)) were identified. The presence of small amount of silicon oxide in the powder can be explained with the features of the plasma formation zone construction, in particular, due to the using of fiberglass-filled plastic insulator. It is worth noting positions of diffraction peaks of gC are significantly different from the etalon model. It can be connected with differences in lattice parameters between etalon (a=2,470 Å; c=6,790 Å) and calculated gC phases. Lattice parameters of calculated gC are follow: a=2,448 Å; c=6,854 Å. These differences in lattice parameters, shifts of positions and broadening of the peaks for calculated phase may be attributed to the disorder induced by N incorporation into the carbon network.

To confirm the assumption about nitrogen incorporation into carbon network, an XPS method was used for obtaining the information about the chemical bonding nature of the powdered product. The survey scan XPS spectrum is shown in figure 4. It indicates the presence of mainly C and small amounts
of O and N. The measured [N]/[C] ratio is 0.05. The presence of O may be due to surface absorption and oxidation [13].

The XPS spectra of C1s, N1s and O1s core level lines are also shown in figure 5. C1s consists of two main peaks with binding energy values at 284.4 and 285.2 eV, which are identified as sp² C-C and sp³ C-C bonding, respectively [16-20]. The low and broadened band centered at 286.7 eV can be interpreted as sp² C in a C-N bonding configuration [18,19]. The N1s spectra can be decomposed in five Gaussian peaks. Peak identification may be as follows [16-20]: the 1 component (at 398,3 eV) has been assigned to a sp³ C-N configuration; the component 2 (399,1 eV) correspond to C≡N bonding configuration; third component (399,8 eV) can be identified as C=N bonding configuration; 4 component (400,5 eV) assigned to a sp² C-N and the last one (402,5 eV) assigned to N=N type bonding. But it should be noted that there are some ambiguities in the literature concerning the structure and assignments of the binding energy of the N1s XPS spectra [21]. Deconvolution of O1s spectrum was carried out with using the NIST XPS database. According to it the first component (530,6 eV) is interpreted as C-O bindings and second one is Si-O bindings (532,4 eV). XPS results are in a good accordance with XRD data and confirm the presence of carbon, nitrogen and silicon oxide in the final product.

In figure 5 the Raman scattering spectrum of synthesized product in the 1000-2000 cm⁻¹ region is shown. It’s possible to see a series of sharp peaks in this region.
Two main peaks can be identified as the so-called D and G peaks, attributed to disordered sp² microdomains and graphite-like sp² microdomains, respectively [22]. It should be noted that D-peak is situated in the region of lower frequencies (1284 cm⁻¹), which is different from data in the literature, where D-peak is situated around 1350-1360 cm⁻¹ [22-24]. This may indicate the presence of high nitrogen concentration in the sample [25]. There exists good accordance in the $I_D/I_G$ ratio (~ 1.0), which is enhanced with increasing of nitrogen content [26]. According to the result that the intensity of D-peak is a little higher than that of G-peak, it is concluded that the symmetry in the sp² microdomains has been broken due to the incorporation of nitrogen into carbon network [25, 27]. The presence of three peaks in 1086 cm⁻¹, 1221 cm⁻¹ and 1310 cm⁻¹ is interesting. They are close to peaks of the calculated spectrum of graphitic C₃N₄: 1098 cm⁻¹, 1221 cm⁻¹ and 1316 cm⁻¹ [23], and may be assigned to nitrogen rich microdomains.

According to the HRTEM image (figure 6a) the typical particle has a natural faceted structure with inclusions of triangular sectors. Sectors are visible because the particle consists of crystalline and quasi-amorphous areas. The transition region between these areas in the radial direction is clearly visible in figure 6d. The set of these transitions forms triangular sectors. The measured interplanar distance in one of the sector is close to, but a little higher than that of graphite gC ($d_{101}=3.395 \text{ Å}$) probably due to nitrogen incorporation and is equal to 3.50 Å. In the SAED pattern (figure 6b) it’s possible to see that the first Debye ring consists of two closely spaced rings. It can be supposed that first ring is a superposition of diffraction maximums, which are attributed to families of gC–002 ($d=3.395 \text{ nm}$) planes and probably planes of areas doped with nitrogen ($d=3.550 \text{ nm}$). Also in dark-field TEM image (figure 6c) luminous triangle sectors corresponded to diffraction maximums of first Debye ring are clearly visible. So it can be assumed that these triangular sectors are nitrogen incorporated areas into the framework of crystalline graphite.

Figure 6. HRTEM-images of typical particle of synthesis product: a) Bright-field image; b) SAED; c) dark-field image; d) lattice image.
4. Conclusion
The ultra dispersed powder sample of graphite-like structures doped with nitrogen was synthesized in the supersonic carbon plasma jet flowing into the chamber filled up with the nitrogen atmosphere by using high current coaxial magneto plasma accelerator. The duration of pulsed power supply is 270 µs. During this time the value of energy equal to 35 kJ is supplied to z-pinch accelerator from the capacitive energy storage. According to HRTEM and XRD analysis the obtained particles with well seen triangle sectors are graphite-like carbon structures doped with nitrogen atoms. FT-IR, Raman and XPS analyses are in a good accordance with HRTEM and XRD data and confirmed the presence of carbon-nitrogen bonds in the powder.

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Acknowledgments
This work was supported in part by the State task to universities (no. 1998). We heartily thank Dr. Oleg Khasanov (Tomsk polytechnic University) for supporting HRTEM analysis.