The analysis of thermal stability of detonation nanodiamond

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Abstract. The detonation nanodiamond is a new perspective material. Ammunition recycling with use of high explosives and obtaining nanodiamond as the result of the detonation synthesis have given a new motivation for searching of their application areas. In this work nanodiamond powder has been investigated by the method of synchronous thermal analysis. Experiments have been carried out at atmospheric pressure in the environment of argon. Nanodiamond powder has been heated in the closed corundum crucible at the temperature range of 30–1500 °C. The heating rates were varied from 2 K/min to 20 K/min. After the heat treatment, the samples have been studied by the x-ray diffraction and the electron microscopy. As one of the results of this work, it has been found that the detonation nanodiamond has not started the transition into graphite at the temperature below 800 °C.

1. Introduction

At the present time, detonation nanodiamonds (DND) are synthesized in the industry with the using of the carbon explosives with the negative oxygen balance. Often explosive ammunition utilization is used for the obtaining of nanodiamonds [1, 2]. It has increased the interest to possible applications of this nanosized compounds. There are already some technologies with the applications of the detonation nanodiamonds [3–5]. Mainly it concerns the production of composite materials [6–8], electrochemistry and biomedicine [9]. There are a lot of investigation directions with possible the nanodiamonds application [1]. However, we have a very small part of detonation nanodiamond used in the real industry [4]. So, the general market of application has not been found yet.

Despite the fact that nanodiamonds are being obtained a long time, their thermal properties are not determined exactly. In particular the beginning of phase transition diamond–graphite which has important value for the application in the composite materials. This process can be referred to the reconstructive phase transition. At such the transition a large number of the interatomic bonds breaks up and a new bonds are formed. This process is slow and has very high energy of activation. Therefore, it is expedient to speak about the beginning and the end of such transition. Numerous works have been devoted to the graphitization of nanodiamond powder under various conditions. Unfortunately data of the graphitization beginning are in the broad range of temperatures from 670 to 927 °C (table 1). Therefore, the present study was carried out to refine this value at the various treatment conditions of nanodiamonds.
Table 1. Temperature of the graphitization beginning in according to literary data.

| Temperature of the beginning of graphitization $T$ $^\circ C$ | References |
|------------------------------------------------------------|------------|
| 670                                                        | The nanodiamond powder was produced from graphite by an explosion method. Measurements were made by the differential scanning calorimetry in the inert environment (argon) at the atmospheric pressure [10]. |
| 927                                                        | The nanodiamond powder was produced from mixture of TNT and RDX (60/40) by explosion. The detonation nanodiamonds were investigated by thermal analysis in argon ambient under atmospheric pressure [4]. |
| 800                                                        | The nanodiamond powder was produced from graphite by the explosion method. The powder was annealed for an hour in pure argon ambient under atmospheric pressure at each of the following temperatures: 300, 600, 800, 1000, and 1150 $^\circ C$. After each annealing process, the structure and composition of the sample were analyzed by using XRD and RS techniques [11]. |
| 927                                                        | The nanodiamond powder was produced from mixture of TNT and RDX (60/40) by the explosion method. The powder was annealed for a three hours in pure argon ambient under atmospheric pressure in the range of temperatures 720–1400 K (447–1127 $^\circ C$). The samples after annealing were analyzed by using XRD and RS techniques [12]. |

2. Experiment

In this work investigated nanodiamond powder has been produced from mixture of TNT and RDX (50/50) by the explosion method [2]. Diamond blend (the condensed product of detonation synthesis) has been subjected to the acid treatment and chemical cleaning. The metal impurities have been removed from the blend by the method of the acidizing. The carbon impurities containing the carbon-like phase have been removed by the thermal oxidation at 350 $^\circ C$ for 4 hours. The chemical cleaning of the diamond blend has been performed by the barothermal method in the reactor with the nitric acid at the temperature of 240 $^\circ C$ and the pressure of several tens of atmospheres. The purified product has been washed and dried in the thermostat at the temperature of 100 $^\circ C$. The elemental composition of the DND after the purification is presented in table 2. The purity of carbon is over 98%, as it was determined by the x-ray diffraction (table 2).
Table 2. Element compound of the cleared DND.

|   | C  | Fe | Cr | Ti | Ba | Cl | S  | Si | Al | Cu | Ca | K  | Mg | Na |
|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
|   | 98.6 | 0.30 | 0.22 | 0.20 | 0.04 | 0.02 | 0.02 | 0.03 | 0.32 | 0.02 | 0.03 | 0.04 | 0.13 |

Figure 1. Size distribution of detonation nanodiamond particles [13]. Point 1—the size of detonation nanodiamonds is 2.2 nm; point 2—the size of detonation nanodiamonds is 6.6 nm.

The study of detonation nanodiamonds by the transmission electron microscopy showed that the particles have diameter from 4 nm to 6.6 nm [2]. This range corresponds to the size distribution of the nanodiamond particle (figure 1) [13].

Nanodiamond powder properties have been investigated by the thermoanalyzer Netzsch STA 409 PC [14] which includes thermogravimetric measurements (TG) and the differential scanning calorimetry (DSC).

Prior to the sample investigation the basic line has been measured. It allows to except the instrument readings not connected with thermal behavior of the sample. Measurement lines have been recorded under absolutely the same conditions (heating rate, holding time, gas supplying rate, etc.), as the subsequent measurements of the sample. In known works, the authors use only single first annealing. In this work two-step heating of the detonation nanodiamond powder has been suggested. The first heating of the sample was carried out up to the temperature of 800 °C with the rate of 10 K/min. The final temperature of the first heating has been selected to avoid the beginning of graphitization of powder. The x-ray diffraction analysis of our sample after the heating to 800 °C has not found the presence of the graphite phase. It corresponds to the data from [11]. The secondary heating of the sample was carried out up to the temperature 1500 °C with the rates of 2, 5, 10, 20 K/min.

3. Discussion of results

As the x-ray diffraction analysis (figure 2) shows, the content of the diamond phase in the sample decreases at the heating of the DND powder to 800 °C, but a new crystal structure does not form. This could mean that there is the destruction of the crystal lattice. It can be assumed
that the nanoparticles of the diamond have transformation to the amorphous state. So, by means of the first heating to 800 °C the sample was purified off the water and gas phase from the nanodiamond particles surface without the influence on the phase transition.

Table 3 shows the results of the secondary thermal heating of the nanodiamond powder. The first heating has been performed to the temperature 800 °C with the rate 10 K/min in argon ambient at the atmospheric pressure. The secondary heating has been carried out to the temperature 1500 °C with the different rates and holding time at the maximum temperature during 15 min. The secondary heating has been started after cooling of the crucible with investigated sample from 800 °C to room temperature.

The percentage of DND in the sample after the secondary heat treatment was determined from the ratio of the integral intensities of the diffraction peak (111) of the standard and the treated samples. The initial sample of the detonation nanodiamond before the heat treatment was taken for the standard for further calculation of the residual nanodiamond content.

The heat treatment of DND powder accompanied by a change of mass and thermal energy of the sample. The temperatures $T_1$ and $T_2$ in columns 6 and 7 in table 3 correspond to the characteristic bendings of TG curve in the heating thermogram. With the moment of the heating start and before achieving temperature $T_1$ the mass of the sample decreased by 3% only. Herewith in DSC curve is observed endothermic effect with the maximal heat absorption at the temperature of 65.1 °C. Mainly it is connected with the removal of water from the sample. After achieving $T_1$ the mass loss rate increases. We associate this with the active process desorption of the radicals from the surface of the DND particle. In the range of 400–600 °C there is an evolving of CO$_2$ and CO [15] at the destruction of the surface groups. It corresponds to sharp increasing of the mass loss rate of the sample. Above 600 °C CO$_2$ evolving is terminated. Consequently, the rate of the mass loss of the sample decreases, as being observed at the temperature $T_2$ on the TG curve. Along with the destruction of the surface groups of the particles there is a transition of detonation nanodiamond to the amorphous state. The x-ray diffraction analysis of the treated sample to the temperature 800 °C was carried out. It showed that the amount of the diamond has decreased by about 10% compared to their content in the initial sample, but a new crystalline phase (graphite) does not form. Thus, by heating the powder to 800 °C "gas

Figure 2. The XRD pattern of the powder detonation nanodiamond: 1—the initial simple; 2—the first heating to 800 °C with the rate of 10 K/min.
Table 3. Data on the thermal heating of nanodiamonds: $v$—the rate of heating; $m_1$, $m_2$—initial and final mass of the sample; $T_1$, $T_2$—temperatures of the characteristic bending of TG curve.

| Number | $v$, K/min | Exposure, min | $m_1$, mg | $m_2$, mg | $T_1$, °C | $T_2$, °C | Amount of ND after second heat treatment, % |
|--------|------------|--------------|-----------|------------|-----------|-----------|---------------------------------|
| 1      | 2          | 15           | 17.438    | 10.756     | 493.9     | 689.3     | 13                              |
| 2      | 2          | 15           | 16.48     | 9.57       | 518.3     | 689.5     | 17                              |
| 3      | 5          | 15           | 20.3      | 17.208     | 556.1     | 738.5     | 38                              |
| 4      | 10         | 15           | 17.5      | 9.73       | 546.7     | 717.6     | 7                               |
| 5      | 20         | 15           | 24.222    | 21.226     | 498.2     | 790.1     | 34                              |

coat” removed from the surface of nanodiamond particles and the partial transformation of the diamond cores in the amorphous state occurs.

The residual content of nanodiamond after the secondary heating of the sample with different rates is shown in the column 8 in table 3. The dependence of the residual content of nanodiamond in the treated powder on the rate of the heating has not been investigated at this stage. Perhaps one of the factors that influences on such a large dispersion of the diamond content in the final product, is the heterogeneity of the initial powder. This statement requires further investigation. However, one can definitely say that even by very low (2 K/min) and relatively fast (20 K/min) heating of the powder, diamond phase presents in the sample. Besides, we suppose that the gasification products of the investigated sample can contain nanodiamonds in these experiments. But in our experiment we did not analysis gasification products and it requires further investigation. These data do not provide the quantitative dependence on the heating rate. But it is necessary to note that after the secondary heating with the various rate up to 1500 °C and holding at this temperature during 15 min all saved samples contain the diamond phase. It indicates their high thermal “vitality” under these conditions [16].

4. Conclusions

In this work the heating of the detonation nanodiamond up to 1500 °C with the different rate was studied by the method synchronous thermal analysis. Novelty of the method was consisted in the two-step heating of the sample. The first heating of the samples has been conducted up to 800 °C with the rate 10 K/min. Then, the samples cooled down to the room temperature were heated up to 1500 °C with the different rate of 2–20 K/min. It was found that the graphitization of the DND sample was not observed at the heating up to 800 °C with the rate 10 K/min. But the content of the diamond phases in the sample was decreased. Maybe some part of the DND transited in the amorphous phase. It was found that part of the DND was presented in the sample even after the second treatment up to 1500 °C with the different rate. This indicates their high thermal vitality. Dependence of the utmost stability of the nanodiamond particles on the physical properties needs the additional study.

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