===== **PRODUCTION, STRUCTURE, PROPERTIES** =====

Special Features of the Heat Capacity of Detonation Nanocrystalline Diamond

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Abstract—The heat capacity of detonation nanocrystalline diamond has been studied by adiabatic calorimetry in the 60–300 K temperature range. It has been found that the heat capacity of commercial samples of nanodiamond exceeds that of bulk diamond by more than 30%. It has been shown that this excess is only partially caused by the impurities and for an impurity-free nanodiamond it is more than 15%. It has been proposed to explain this feature of the heat capacity by a contribution of surface carbon atoms into a low energy density of diamond phonon states. Based on the experimentally obtained temperature dependences of the heat capacity, the standard values of the enthalpy, entropy, and reduced Gibbs free energy of commercial and impurity-free nanodiamond have been calculated.

1. INTRODUCTION

It is known that detonation nanocrystalline diamond (from here on nanodiamond, ND) is the carbon nanostructured modification most promising for industrial applications since it may be comparatively easily produced with high purity in quantum satis [1]. There are various applications of nanodiamonds: additives to motor oils and electrolytic coatings; a number of areas in biology and medicine [2–5]; in growing diamond films by chemical deposition from a gas phase [6]; strengthening fillers in plastics, rubbers, metals, alloys, glass, and ceramics [7–9], etc.

For the thermodynamic calculations of the equilibria in reactions with the participation of nanodiamond one should have reliable values of its thermodynamic parameters. The use of corresponding values inherent in bulk diamond in this case is incorrect, as here the effect of the size factor on the material properties, including thermodynamic ones, is not allowed for. Investigations of the heat capacities of nanostructural modifications of other compounds indicate that their heat capacities exceed (and hence, variations of other thermodynamic parameters) the corresponding values for bulk compounds [10–13]. It is likely that a similar effect may be observed in diamond as well. From the point of view of the fundamental science the differences in values of thermodynamic parameters of various substances in the bulk state and in nanostate will make it possible to estimate an increment of the intrinsic energy during the transition to the nanostate. In both cases the admissible solution is an experimental study of the heat capacity of nanodiamond samples different in characteristics caused by a size factor, and determination of their values deviations from a certain comparative basis that is independent of particle sizes or other factors (e.g., impurities).

The aim of this work was the experimental study of the temperature dependences of the heat capacity of detonation nanocrystalline diamonds and their special features as compared to the heat capacity of the diamond ideal crystal lattice and its bulk form.

2. MATERIALS AND METHODS

We used samples of detonation diamond produced by Altay SPA (town of Biysk, RF) and Sinta NVP (Kharkiv, Ukraine). For convenience of discussion the samples were designated as NA1 (a commercial sample of Altay SPA), ND1VTT—the same sample after vacuum thermal treatment, and ND2 (a commercial sample of Sinta NVP).

Samples of ND1 and ND2 (fine-grained gray powders) were the products of detonation synthesis of diamond from toluene and hexogen after removal of a graphite component. According to the X-ray diffraction analysis, the samples have the diamond crystal structures with lattice constants of 0.357 and 0.356 nm, respectively. The broadening of diffraction lines compared to the corresponding micron powders made it possible to calculate sizes of the coherent-scattering regions, which is known to characterize the size (average diameter) of nanoparticles and according to the analysis, are 4.8 ± 0.5 nm for ND1 and 5.7 ± 0.5 nm for ND2. The samples specific surfaces defined by the BET method were 220 and 340 m^2/g, respectively. The results of studying the concentrations of gas-forming elements (H, N, O) using the reductional extraction by carbon in a helium flow followed by gas chromatography separation and determination of the restoration products (H_2, N_2, CO) as well as the samples phase compositions are given in Table 1.

Table 1. Phase and chemical compositions of the studied samples

Sample	Gas-forming impurities, wt %				Phase compositions, wt %		
	H	N	O	C	Diamond	Carbon	Ash content
ND1	0.36	2.30	7.71	> 88	> 98	< 1	< 1
ND1VTT	0.10	1.30	3.44	*	*	*	*
ND2	0.46	2.17	7.02	> 89	> 98	< 1	< 1

* The values were not defined as the results of the X-ray diffraction are similar to those of ND1, i.e., the phase composition remained unchanged.

The heat capacities of commercial samples ND1 and ND2 were studied without a pretreatment and preparation. To study the effect of light elements impurities (gas-forming impurities) on the nanocrystalline diamond heat capacity, the ND1 sample was subjected to a vacuum thermal treatment, whose procedure and analysis of the results are given in [14]. The main results that are needed for discussion in the present work are shown in Table 1.

For comparison when analyzing the results of the study of a heat capacity we used the data of the calculation of the total heat capacity of diamond based on reliable data on the elastodynamic characteristics of a diamond crystal [15]. The procedure of the calculation, its results and discussion are given in [16].

Experimental studies of the heat capacities of all samples were carried out by the adiabatic method using the low-temperature thermophysical model setting in the temperature range from 60 to 300 K and in a vacuum not below 2×10^{-3} Pa. The design and calibration of the plant are described in detail in [17]. Based on the derived temperature dependences of the heat capacities of ND1 and ND1VTT, we calculated the heat capacity of the impurity-free nanocrystalline diamond using the linear extrapolation to zero concentration of gas-forming impurities.

To define the values of basic thermodynamic functions (enthalpy, entropy, and reduced Gibbs energy) of nanocrystalline diamond at standard conditions, the derived experimental temperature dependences of the heat capacity were processed with the aim to extrapolate them to 0 K. The resulting temperature dependences of the heat capacity in the 0–300 K range were used to calculate the above thermodynamic functions by the classic thermodynamic relations.
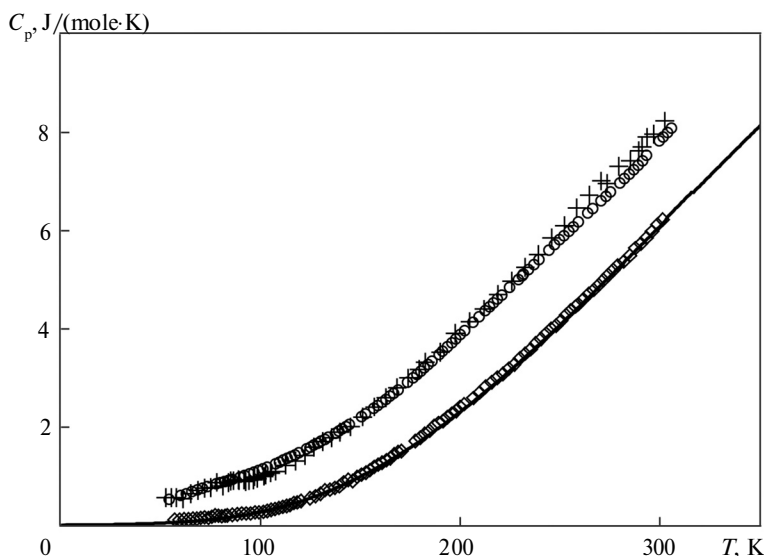
3. RESULTS

3.1. Heat Capacity of Bulk Diamond

The preparatory stage of the investigation into the heat capacity of detonation nanocrystalline diamond was the search for reliable data, which is possible to use as the basic one, i.e., such, with which may be compared the results obtained for nanocrystalline diamond. As in this sense the reasonable data are the heat capacity values of bulk diamond, we worked up the literature data on its low-temperature heat capacity, experimentally studied the isobaric heat capacity of synthetic diamond produced by the General Electric with averaged crystal sizes of 400–500 μm, and calculated its phonon heat capacity based on the vibration characteristics of crystals defined from the first principles [16].

The temperature dependence of the diamond heat capacity (Fig. 1) has certain features, to which much attention should be given. To the temperature ~ 100 K the heat capacity values are very low, close to zero. With increasing temperature an active excitation of the diamond phonon spectrum takes place, as a result of which the diamond heat capacity gradually increases and attains 6.1 J/(mole·K) at 298.15 K. Full excitation of the phonon spectrum occurs at temperatures above 1500 K. The literature data and results of our experiment and

calculation agree well despite the probable enhanced imperfection of synthetic diamond. The calculation results were considered to be the most suitable as the comparative basis since in this case the temperature dependence is continuous unlike discrete literature data and experimental results. That's why just they were used in discussing the results in this study.

Fig. 1. Heat capacity of coarse crystalline diamond and commercial samples of detonation nanodiamond: calculation (——), diamond produced by GE ($\diamond$), ND1 ($\bigcirc$), ND2 (+).

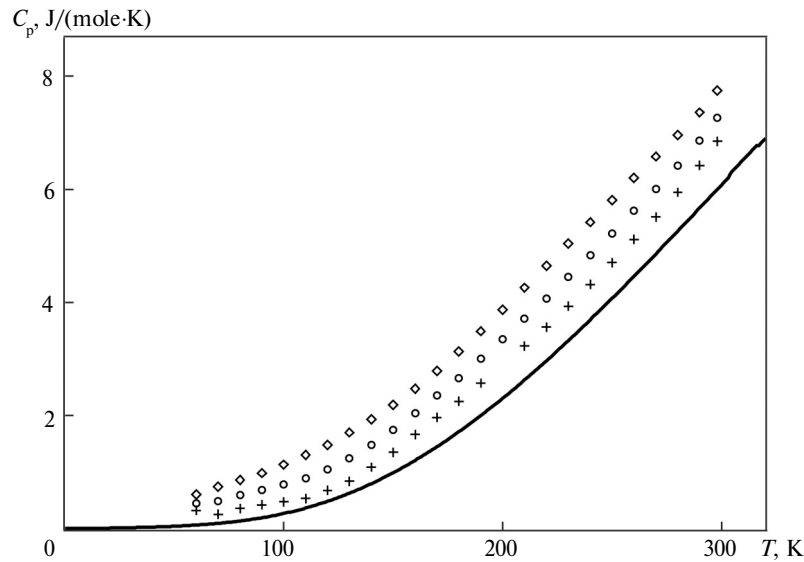### 3.2. Heat Capacity of Nanocrystalline Diamond

The data of the experimental studies of the nanocrystalline diamond heat capacity essentially exceed corresponding values of the bulk diamond (Fig. 1). The differences are so substantial that doubts come to mind about the structure identity of the samples studied, as the heat capacity is a representation of the energy spectrum of vibrations of atoms of the crystal lattice and vibrations in a diamond phonon spectrum, which may lead to an increase of the heat capacity even at low temperature, are absent. However, at the temperature ~ 55 K the nanodiamond heat capacity exceeds the corresponding values of the bulk diamond almost by a factor of 4 and at 300 K by 30%. A similar superiority is observed for both commercial samples of nanodiamond produced by different manufacturers.

Commercial samples of nanocrystalline diamond are characterized by well agreed values of heat capacity in the whole temperature range under study (60–300 K). Some differences that, however, do not exceed the errors of measuring, are observed at temperatures above 250 K, which may be caused by the special features of operation of the adiabatic systems of the low-temperature thermophysical model plant at a low bulk weight of studied substances and especially near upper boundary of the measurement range.

Commercial samples of nanocrystalline diamond contain a great deal of gas-forming impurities (generated by light elements H, O, N). The studied samples contained in total more than 10% impurities each (Table 1). Therefore, the ND heat capacity was also examined after the vacuum thermal treatment (VTT) of the initial sample in order to reveal the effect of impurities [14]. The results of this study are shown in Fig. 2, from which it is seen that as because of the cleaning and decreasing the number of gas-forming impurities to values listed in Table 1, the heat capacity of nanodiamond decreased: at the temperatures of the onset of the experiment by 11%, at 300 K by 6.5%, increasing in the absolute value with the temperature. This clearly indicates that at least a part of the excess of the nanodiamond heat capacity over that of the bulk diamond is caused by the effect of gas-forming impurities.

Using the linear extrapolation of the experimental data on the ND1 and ND1VTT heat capacity to zero concentration of gas-forming impurities, we obtained the heat capacity value of impurity-free nanocrystalline diamond. The calculation results (see Fig. 2) characterize the differences in heat capacity value between nano- and bulk diamonds, which are caused by factors, other than effect of gas-forming impurities.

Based on the temperature dependences of the heat capacity of ND1 and impurity-free ND, we calculated their enthalpy, entropy, and reduced Gibbs free energy, whose standard values are shown in Table 2.

Fig. 2. Heat capacities of nanocrystalline diamonds with different concentrations of gas-forming impurities: calculation (—), ND1 ($\diamond$), ND1VTT ($\bigcirc$), impurity-free ND (+).

Table 2. Standard values of the enthalpy, heat capacity, entropy, and reduced Gibbs energy of commercial and impurity-free nanodiamond

Structure	$H^0(298.15\ K) - H^0(0\ K)$	$C_p^0(298.15K)$	$S^0(298.15\ K)$	$\Phi^0(298.15\ K)$
	J·mole^{-1}	J·mole^{-1}·K^{-1}		
ND1	823.4	7.75	3.83	1.07
Impurity-free ND	631.8	6.90	3.08	0.96
Diamond*	515.61	6.00	2.35	0.62

* The calculated data on diamond are given for comparison.

4. DISCUSSION

The data of the experimental study of the ND heat capacity essentially differ from the values of the heat capacity of bulk diamond, which may be due to the following: effect of the light elements impurities, specific surface area, peculiarities of the surface structure of nanoparticles.

Gas-forming impurities in nanocrystalline diamond are mainly located on the particle surface as various functional groups [18]. These groups are weaker connected with diamond crystal lattice than with carbon atoms, which form the structure itself that should lead to an increase of the occupancy of low-energy regions of the phonon spectrum. Therefore, the excitation of their vibrations and, as a consequence, increasing of the heat capacity is possible even at low temperatures. In addition, they have a larger number of degrees of freedom and this increases its contribution to the heat capacity. The above results of our study indicate that excess of the heat capacity of the nanocrystalline diamond over the heat capacity of the bulk diamond is really largely caused by the effect of gas-forming impurities, which corresponds to this assumption. But the cleaning removed more than 50% impurities, and maximum decrease of the heat capacity is only 11%, i.e., the difference in the heat capacity values of the nanocrystalline diamond before and after vacuum thermal treatment remains considerable and much exceeds a proportional decrease of the heat capacity in the case of a hypothetical decrease of the concentrations of gas-forming impurities to zero (see Table 2). This is the evidence of the existence of an additional mechanism of the heat absorption by nanodiamond.

A simple calculation shows that depending on the particle model taken for calculation in the composition of detonation nanodiamond 20−25% carbon atoms are on the surface. There are solid argumentations to state that just they may be the reason for the excess of the heat capacity of nanodiamond over that of bulk diamond [19]. Therefore, the experimentally defined excess of the nanodiamond heat capacity may be of the integral mode: to be the result of the effects of both gas-forming impurities and carbon surface atoms. It should be noted that, depending on the production technology, detonation nanodiamonds may have different specific surface areas. If we assume that there is a correlation between the specific surface areas of the nanodiamonds

and the number of carbon surface atoms, then the increment of the heat capacity caused by the carbon atoms, may be defined by measuring the heat capacities of samples, whose characteristics are similar and differ only in specific surface area.

For this purpose we chose a sample of nanocrystalline diamond ND2, whose chemical composition coincided with the composition of the ND1 sample within 1% deviation at the total number of gas-forming impurities with retention of the relationship between the components. On the other hand its specific surface area is larger than the specific surface area of the ND1 by more than 50%.

It is seen from the results of studying the heat capacities of ND1 and ND2 (see Fig. 1) that despite the essential difference in the specific surface area between the nanodiamonds samples their heat capacities are virtually identical (the differences are within the errors of the experiment). This result contradicts the stated assumption about the effect of the specific surface area and is probably caused by the peculiarities of the nature of ND powders, namely, anomalously strong agglomeration of nanoparticles.

The assumption about the necessity of the interpretation of the heat capacity of ND having different values of the specific surfaces areas (the BET method) with allowance made for the agglomeration of diamond nanoparticles is verified by the results of calculation of average sizes of particles according to X-ray powder diffraction data. The average sizes of particles calculated from the area of the special surface using the BET method (in approximation of spherical particles) are 7.8 and 5.0 for ND1 and ND2, respectively, while the average diameters of particles defined from broadening of diamond diffraction lines are 4.8(5) and 5.7(5) nm. If we allow for the errors and assume that the average particle size is the same (5.3 nm), then the specific surfaces areas of these samples are equal (near 320 m^2/g). If nanodiamond particles generate strong agglomerates, whose sizes attain 200 nm, as is described in [20], then in samples of nanocrystalline diamond the formation of a large number of pores closed for the nitrogen penetration is possible. In this case the results of measuring the specific surface area of such a sample using the BET method will be underestimated but the boundary between the crystallites remains sufficient to define it as a defect of a continuous structure. In such a case, the surface contributions to heat capacities of ND1 and ND2 are uniform and, accordingly, the absolute values of their heat capacities are equal, which agrees with the results of the experiment.

This situation allows a conclusion that to define the real sizes of particles and surface area of nanocrystalline diamond the investigations using only one method is not enough. In particular, the difference in the specific surface area between different ND samples according to BET probably characterizes the measure of the nanoparticles agglomeration and does not affect the ND basic physicochemical properties, e.g., thermodynamic ones.

On the condition that the real specific surface areas of studied samples of nanocrystalline diamond are equal, the most acceptable reason of the revealed excess of the impurity-free ND heat capacity over the heat capacity of bulk diamond is the peculiarities of the diamond crystallites structures, i.e., the structure of their surface and physicochemical state of atoms on it and in the immediate vicinity of it. According to the ascertained notions, a crystallite of a nanocrystalline diamond is a diamond nucleus, which approaching the surface transforms into a layer of amorphized carbon. The layer is formed by atoms with a decreased number of the nearest neighbors, i.e., a changed type of hybridization from sp^3 to sp^2 and sp or its loss (atom stops to be hybridized). The loss of the nearest neighbors by atoms on the surface is partially compensated through joining heteroatoms (gas-forming impurities). The loss of the nearest neighbors and a change of the hybridization type of carbon atoms lead to the possibility of low energy excitation of atoms oscillations in the directions that are free from restrictions of the chemical bonds, i.e., to an additional occupation of low energy regions of the phonon spectrum. Since the number of surface atoms (as is mentioned above) may attain 25%, this value is the maximum in the amount of low-energy oscillators, i.e., such would be the excess of heat capacity provided the above atoms passed to the state of the ideal gas. Carbon atoms on the nanocrystallite surface remain bound with the structure to one or another degree; therefore, one should expect that the excess of the heat capacity will be lower. According to the results of the simulation [19], the excess is ~20%, and according to the assessment based on the experimental data obtained by the linear extrapolation of the results of studying samples having different concentrations of gas-forming impurities to zero impurity concentration, the excess is more than 15%.

Thus, in thermodynamic calculations and assessments of processes with nanodiamond participations the use of the values of heat capacity and thermodynamic functions of ND, which take into account at least 15% excess of the heat capacity values of this nanoform over the heat capacity values of bulk diamond at standard conditions, is reasonable.

5. CONCLUSIONS

— It has been found that the heat capacity of nanocrystalline diamond at 50−300 K essentially, at least by 15%, exceeds corresponding values for bulk diamond, which is mainly caused by contributions of impurities components (gas-forming impurities) and probably by peculiarities of the structure of near-surface layers of nanocrystalline diamond nanoparticles.

— The specific surface area of nanocrystalline diamond that has been defined by the BET method can't be a measure of the assessment of sizes of the initial crystal of nanocrystalline diamond, as its values may essentially depend on the agglomeration of nanodiamond crystallites. Correct estimate of particles sizes of nanocrystalline diamond requires the examinations by various methods, especially with the use of X-ray diffraction.

— The established differences of the heat capacity of nanocrystalline diamond from that of bulk diamond together with the peculiarities detected by other researchers for nanostructural forms of different substances allow us to speak of their fundamental nature. Establishing the regularities that describe these differences requires further systematic investigations into bulk substances and their nanocrystalline forms with allowance made for the peculiarities of real nanostructures and state of the nanoparticles surfaces.

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