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СПЕЦИФИКА НА НАНОДИАМАНТЕНА ПОВЪРХНОСТ В ЗАВИСИМОСТ ОТ МЕТОДИТЕ НА ПРЕЧИСТВАНЕ

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**Ключови думи: детонационни диаманти, окислителна среда, функционални
групи**

Резюме. Различни методи, включващи термично окисление с въздух в поток или в тънък слой и окисление в течна фаза при използване на водороден пероксид като окислител, са приложени за характеризирание повърхностните свойства на диамантени частици получени чрез детонация. Методи като инфрачервена спектроскопия, окислително титруване и рН-метрия са използвани за сравняване на повърхностните функционалните групи на диамантените частици, формирани при различните методи на отделянето им от диамантената шихта.

При нагряване на диамантите до температури от 600°C се наблюдава наличие на повърхностните хидроксилни групи. Предполага се, че те се формират в резултат от последователна дисоциация на сорбирани водни молекули и са здраво свързани към повърхността на диамантените частици. Съотношението между основните повърхностни функционални групи се променя драстично с температурните обработки. Първоначалното окисление с пероксид в течна фаза модифицира функционалните групи на диамантената повърхност и ги прави значително по-устойчива към последващи температурни обработки.

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FTIR STUDY OF THE SURFACE STRUCTURE OF DETONATION DIAMOND POWDER

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Abstract. *A variety of post-treatments of diamond powders, as thermal oxidation in shallow bed or in a flow of air and of liquid phase oxidation using H₂O₂ as oxidant, had been used to determine the surface properties of the diamond powders with nano-sized particles, synthesized by detonation. The methods of IR spectroscopy, oxidative titration and pH values were applied for comparing the surface functional groups of diamond particles shell in dependence of the methods for their separation, purification and stabilization.*

The heating at 600°C in static air did not remove all the physically adsorbed water. Thus, it was assumed that, due to the process of dissociation of the sorbed water, free hydroxyl species were formed and strongly attached on diamond particles surface. The main functional groups were preserved, but due to the thermal treatments their proportion was changed. The liquid phase oxidation with H₂O₂, even at room temperature, modified diamond oxygen containing surface groups and thus influenced samples specific surface area and the pH. The surface functional groups, generated during diamond particles liquid oxidation, prevent its structure from further oxidative attack during thermal treatments in air.

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1. INTRODUCTION

The synthesis of ultra dispersed diamonds (UDDs), based on detonation mainly of carbon explosive materials, is a perspective method, since high diamond content (up to 75 wt. %) in the detonation semi-product (a mixture of diamond and non-diamond forms of carbon – so called diamond soot) is obtained [1]. Various targets have been successfully used, including a pure carbon materials as well as carbon containing mixtures (classically a mixture of trinitrotoluene and hexogene). Further, a variety of methods for separation of UDDs from the detonation soot, its purification and stabilization are applied [2, 3, 4, 5]. Depending on the detonation charge shape and on the purification method, the amount of

diamond phase as well as the surface functional groups formed and heteroatoms attached on the diamond particles varies. The quantity, the type and the similarity between diamond particles surface functional groups are of great importance, since they are the main factor contributing in the diamonds aggregation, especially when dried [6, 7, 8]. Therefore, the knowledge of the surface chemistry of UDD is of fundamental importance for UDDs application. In the paper we tried to contribute to the determination of diamond particles surface properties by applying thermal treatments of diamond powders in shallow bed or in a flow of air and of liquid phase oxidation using H_2O_2 as oxidant. The methods of IR spectroscopy, pH measurements and oxidative titration were applied for comparing the surface functional groups of the diamond particles.

2. EXPERIMENTAL

2.1 Samples

The detonation synthesis was carried out from carbon-containing explosives with cylindrical and conical shape (mixture of 2-methyl-1,3,5-trinitrobenzene (TNT) and hexogen) in a spherical camera with a volume of 3 m^3 , under conditions of negative oxygen balance in the Department of Space Materials of SPI-BAS [9]. The detonation products were cooled in water ice medium. The carbon yield was about 15-18 % of the explosive weight. The semi-product of detonation synthesis contained about 40 of diamond phase when used cylindrical charge and about 7% when used conical charge.

After the mechanical removal of the detonation admixtures, the extraction and purification of the diamond powder from the detonation soot was carried out in different paths:

1. Chemical purification - the soot was first cleaned with boiled mixture of sulfuric acid and potassium bichromate ($K_2Cr_2O_7+H_2SO_4$) (heating up to $100-115^\circ\text{C}$) followed by moderate thermal oxidation with HNO_3 ($80-100^\circ$) in a glass technological vessels for removing the metal impurities. After washing with water until pH 7 and dried, a hydrophilic diamond powder was obtained, denoted as **DP1** (from cylindrical charge) and **DP2** (from conical charge)
2. Low temperature burning in air and in presence of vanadium catalysis, followed by a removal of the metal impurities as described above. A formation of hydrophobic diamond powder denoted as **DP3** (from conical charge) was obtained.

All diamond samples were gray powders. Some of the properties were given in Table 1 and its IR spectra were presented in Figure 1.

2.2. Measurements of pH value: The determination of the pH value was carried out as followed. A 20-ml portion of boiled de-ionized water was added to 0.2 g of the corresponding sample in a flask equipped with a reflux condenser. The mixture was heated to a boil on a hot plate, boiled gently for 10 min and filtered after cooling below $50 \pm 5^\circ\text{C}$. The pH values

were determined at room temperature. The obtained results were given in Table 1, columns 3.

2.3. Thermal treatment in shallow bed. An amount of 0.2 g of the as-received DP sample was placed in laboratory pottery vessel and heated till constant weight at 630°C in a furnace (shallow bed). The weight of the initial and heated samples was determined with accuracy $\pm 0.0005\text{g}$. The diamond carbon (wt. C %) was estimated, using the following equation: $C\% = (M2-M) \times 100 / (M1-M)$, where M – weight of the pottery vessel after heating, g; M1 - weight of the pottery vessel with initial sample, g; M2 - weight of the pottery vessel with the diamond residue, g. The results are presented in Table 1, column 4. The obtained diamond powders were denoted as DP1t, DP2t and DP3t. Its IR spectra were compared in Figure 2.

2.3. Thermal treatment in flow conditions. An amount of 0.2 g of the as-received DP sample was placed in a flow type reactor. The temperature was raised with 10°/min from ambient up to 400°C in atmospheres of air or argon (Ar) and kept for 2 h. The samples were denoted in the text as DP1_{air} and DP1_{Ar} and its IR spectra were presented in Figure 3.

2.4. Chemical oxidation. 0.2 g of the as-received DP sample were put in a flask and stirred with a magnetic stirrer at room or at 60°C temperature with a 30 ml aqueous H₂O₂ (26-wt %). After 2 h, the powder was filtered, washed with water and dried. The investigated samples were denoted as DP1_{rt}; DP1₆₀ and the IR spectra were given in Figure 4. Further on, both samples were heat-treated inside a horizontal furnace in shallow bed in air up to 400°C for an hour.

2.5. Determination of the oxidized part of carbon through titration.

The part of carbon, which was easily oxidized, was determined performing standard titration. 0.1 g of the sample, 8.3 ml deionized water and 10 ml 0.25N K₂Cr₂O₇ were put in a flask and stirred with a magnetic stirrer at room temperature. Further on, 20 ml of H₂SO₄ and trace of Ag₂SO₄ were added. The flask was heated in reflux condenser for 2 hours at 90°C. After hot filtration and cooling of the filtrate, the titration was carried out with 0.25n Moor salt in presence of 0.2% N-phenylantranilic acid as buffer/indicator. The equilibrium transition of the indicator is from violet to green. The results are presented in Table 1, columns 5 and 6.

The IR spectroscopy measurements were done on a Bruker Vector 22 FTIR spectrometer in the region of framework vibrations by using KBr pellet technique. A portion of 0.5 – 1 mg of DP to 100-150 mg KBr depending on sample type was used.

Table 1. Sample characteristics:

Diamond sample	BET, m ² /g	pH	diamond carbon, wt. C% ^a	Oxidized carbon of initial sample, wt. % ^b	Oxidized carbon after annealing wt. % ^b
1	2	3	4	5	6
DP1	250	4.5	47	16	3

DP2	330	6.1	30	8	3
DP3	50	6.8	85	6	2

^a determined by thermal treatment in shallow bed

^b as determined by titration method

3. RESULTS AND DISCUSSION

It is well proved that a single particle of DP consists of chemically inert diamond core (about 4 nm in size) and a shell [10]. On figure 1, the IR spectra of the initial DP samples were presented.

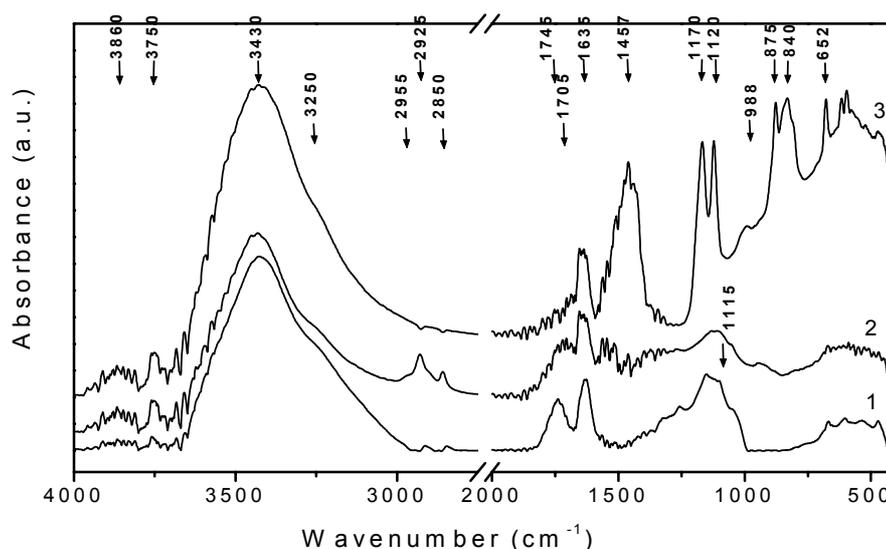


Figure 1: IR spectra of as-received diamond powders: line 1 – DP1; line2 – DP2; Line 3 – DP3

A broad band centered around 600 cm^{-1} , was observed in the spectra of samples DP1 and DP2, while identifiable overlapping bands at 573 , 625 and 652 cm^{-1} were present in the spectrum of sample DP3. The latter could be assigned to C-O bond, as it was established for the meteoritic diamonds [11], while the other should be related to contamination with N-O, Cl-O bonds or impurities of free element or oxide [12,13]. Strong bands in the region $750\text{-}1000\text{ cm}^{-1}$, assigned to the existence of graphite sp^2 carbon and well resolved strong bands in the region $1000\text{-}1250\text{ cm}^{-1}$ (generally assigned to C-O-H and C=C vibrations), [14], were also seen in the spectrum of DP3.

The existence of C=O bond, belonging to organic compounds of different classes was determined at 1705 (acidic C=O, curve 2), at 1745 (C=O lactone type, curve 1). Strong bands at 1457 cm^{-1} (C-O) and at 1635 cm^{-1} (C-OH) vibration were observed on curves 3.

The spectra of all samples exhibited the characteristic IR bands of crystalline diamond in the region $2000\text{-}3000\text{ cm}^{-1}$ [15]. Absorption bands at 2890 , 2925 , 2960 cm^{-1} corresponded to diamond associated CH, CH₂, CH₃ groups and consequently to vacancies [16]. A

dominant absorption band centered at 3430 cm^{-1} with shoulder at 3250 cm^{-1} (OH stretching vibrations) was observed.

Diamond powders pH values are given in Table 1, column 3. We assumed that during purification different acidic functional groups and admixtures are occluded. During the procedure of pH measurement they were extracted.

Effect of the thermal treatment

Through a procedure of DPs annealing the non-diamond carbon was removed and yielded a DP consistent to diamond core [8, 17]. As was seen from Figure 2, significant differences in the IR-spectra of the diamond cores were obtained.

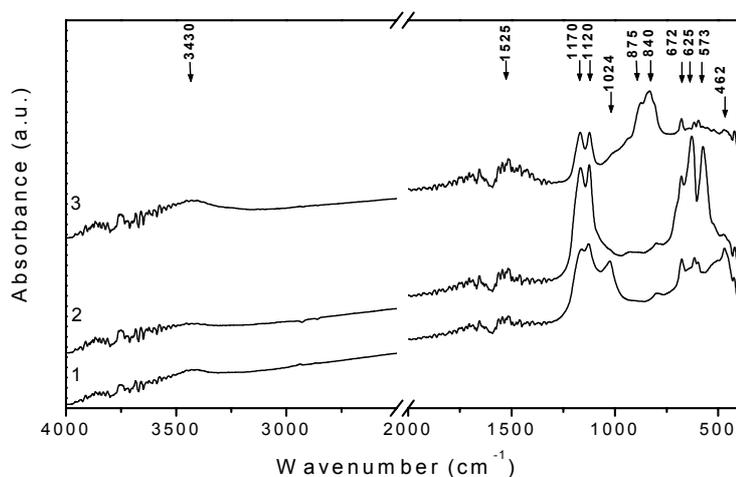


Figure 2: IR spectra of thermally treated in shallow bed at 630°C samples:

line 1 – DP1t;

line 2 – DP2t;

line 3 – DP3t

In the *spectral region* $500\text{ and }750\text{ cm}^{-1}$, strong and well defined bands were seen only in the spectrum of DP2 sample. They were associated with deformation O-N=O vibrations in nitroso-groups (R-O-NO) and in functional groups as R-O-NO or R-NO_2 (oxygen–nitrogen vibration in nitro-group). The quantity of such groups was less in DP1 and negligible in DP3 sample. So, it should be marked that the element composition of diamond cores differed and the effect should be **connected not only** with the different methods of samples purification but with detonation as well. The bands in this region seemed to be sensitive to the DPs preparation technique.

Spectral region $750\text{-}1000\text{ cm}^{-1}$ - After annealing the intensity of the bands in the spectrum of DP3 sample were increased. Thus, it could be marked that the purification

method with vanadium catalyst lead probably to the formation of the sp^2 allotrope of carbon strongly attached to the diamond core [18]. As a result, the measured BET surface area is strongly diminished in comparison with the other to samples (Table 1).

Spectral region 1000 - 1250 cm^{-1} - After annealing the absorption bands in this region did not change in character, although they become more distinct for sample DP1 and DP2. Well resolved peaks at 1024, 1120, 1170 cm^{-1} were observed. Based on the literature, they were attributed respectively to C-O single bonds, such as those in ethers [19], to deformation vibrations of OH group [20], and to stretching vibration of -C-OH (or C=S) bonds in alkanes.

The absorption bands in the spectral area of 2830–3000 cm^{-1} due to C-H bonds completely disappeared during annealing most probably because of the process of thermooxidative destruction of the sp^2 carbon.

The stretching vibrations of OH groups were supported and associated with the existence of wide absorption band at 3430 cm^{-1} . After annealing the intensity of band at 3430 cm^{-1} decreased to about 90% of the original. So, does the band at 1630 cm^{-1} , as shown in Figure 2. The amount of residual OH groups diminished in an order DP3t > DP1t > DP2t.

During the thermal treatment in a flow reactor in oxygen atmosphere or in argon, we expected to free the DP particles from water and other volatile impurities. On the example of the IR spectra of DP1 sample, shown in Figure 3, the pronounced changes in the organic compounds of the diamond shell could be followed.

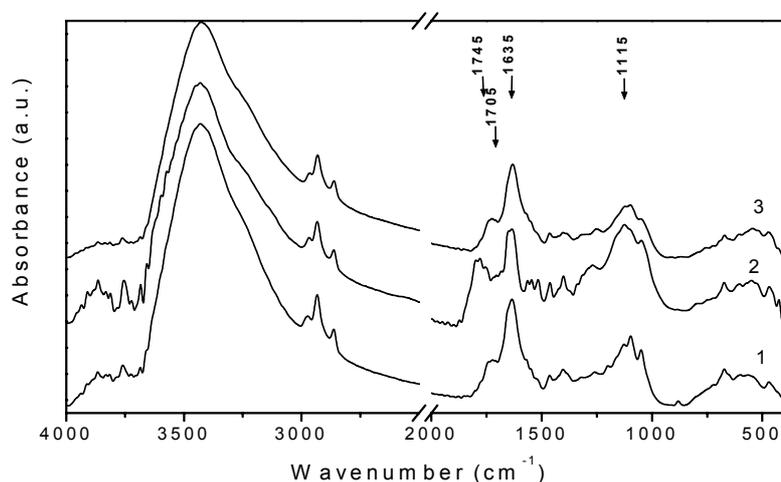
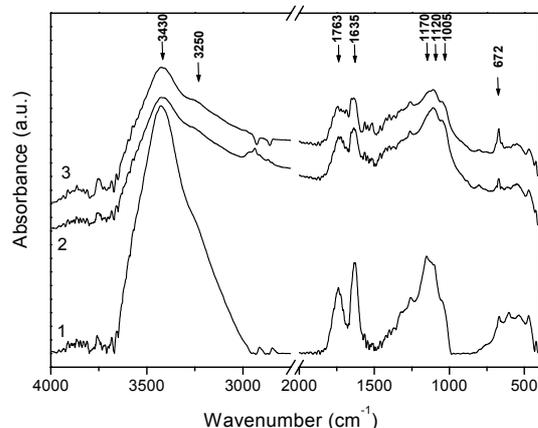


Figure 3: IR spectra of thermally treated in flow condition DP1 sample:
line 1 – DP1;
line 2 – DP1_{air};
line 3 – DP1_{Ar}

It was concluded that the main functional groups were preserved, but due to the



dehydration processes their ratio is changed. It should be marked that the absorption at 1745 cm^{-1} , connected with the carboxyl structures, increased considerably. Most probably, more carboxyl structures were formed as a result of thermal decomposition of ether structures during the oxidation processes.

Liquid phase oxidation

Comparing the spectra of sample DP1 (Figure 4) it could be stated that the liquid phase oxidation with H_2O_2 even at room temperature, modified the surface oxides groups and thus could influenced as the specific surface area as well as the pH value of the DP1.

The spectra showed general similar features with exception of the bands in the region $1500\text{-}1750\text{ cm}^{-1}$ connected with the structure of diamond particles. During the oxidative treatment in liquid phase by H_2O_2 the impurities (metals, carbides, salts metal oxides) as well as the main amount of the non-diamond carbon were removed. The surface generated during liquid oxidation prevents the diamond structure from attack during the following thermal treatment at 400°C .

Figure 4: IR spectra of DP1: 1 - as received; 2 - oxidized by H_2O_2 ; 3 - oxidized by H_2O_2 and heated in air at 400°C

CONCLUSIONS

By applying the method of FTIR spectroscopy, it was shown that the surface of nanodiamonds differed. It was confirmed that surface nitroso-groups were formed at a stage of its explosive synthesis. The methods of diamond chemical extraction and purification conditions from the detonation soot influenced its properties.

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