

THE EFFECT OF HEAT TREATMENT ON THE SURFACE CONDITION OF NANODIAMOND

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Our interest is in studying factors that favour the variation of the chemical activity of nanodiamond powders which produced by detonation of explosives in a medium with negative oxygen balance. For this purpose we have investigated the effects of the method of the powder chemical cleaning as well as of the heat treatment in the protective argon atmosphere on the surface activity of diamond particles. The peculiarities of adsorption and ion-exchange processes proceeding at the nanoparticle surface have been studied. Diamond particles have been found to be of hypomolecular structure of variable activity that depends on the nature and quantity of functional groups, which were adsorbed during the diamond synthesis and powder manufacture. Carbonyl, carboxyl and hydroxyl groups are most important of them. OH-groups exert the highest effect on variations of the particle surface activity. Our findings show that detonation-synthesised diamond is a material having specific surface properties, which can be changed by chemical and heat treatments.

Keywords: Nanodiamond, Surface activity, Heat treatment

1. Introduction

Synthesis of nanodiamond by detonation of explosives with a negative oxygen balance is one of the most interesting ways of producing diamond powders, which is being intensively developed in Russia, Ukraine, Belarus [1, 2, 3], and other countries.

A high dispersity (4 to 10 nm) of particles of this diamond and a considerable specific surface of them ($\sim 200 \text{ m}^2/\text{g}$) as well as high chemical and adsorption activities attract attention of researchers and technologists.

Chemical composition of a diamond powder is known to depend on the way of the synthesis product purification and is defined by the constitutions of functional groups on the surface of diamond particles. The amount and quality of functional groups are responsible for the ion exchange and adsorption properties of nanodiamond as well.

We have studied factors that facilitate variations in surface activity of a nanodiamond powder. For this purpose the powder that was obtained by purification of the synthesis product with an acid has been subjected to additional purification following two procedures and a subsequent heat treatment in a protective atmosphere.

2. Experimental

The synthesis product, that incorporated in addition to the diamond phase, nanodiamond forms of carbon, metallic and non-metallic impurities, was treated with chromium anhydride, nitric, and sulphuric acids. At the final stage of purification, the powder was divided into two lots and treated with a melt and a solution of the NaOH and KOH mixture in the ratio 1:1. Then the mass was neutralised with hydrochloric acid and washed with distilled water. As a result, we obtained two lots

of powders (UDA₁ and UDA₂), that have been characterised by 0.8 and 1.2 % of combustion residue, respectively.

Using the low-temperature nitrogen adsorption (the BET method) on an Acusorb-2100 device (Coultronics), IR and Auger spectrometers, we have studied adsorption and structural characteristics of powders as well as compositions of functional groups on the particle surfaces. The stability of the characteristics and properties of UDA₁ and UDA₂ powders in heat treatment from 200 to 700 °C have been also examined.

As the nanodiamond oxidises in air at about 450 °C, it has been heat-treated in a protective argon atmosphere. The powders have been annealed for 30 min in a furnace heated up to the required temperature and allowed to cool with the furnace.

3. Results

Our studies of the nitrogen adsorption have shown that the initial UDA₁ and UDA₂ powders are characterised by isotherms of the II type, equal specific surface (166 m²/g) and different weighted means of the adsorption potential (419 and 595 J/g, respectively).

IR spectroscopy shows the presence of, mainly, carbonyl, carboxyl and hydroxyl groups on the surface of powder particles, and the amount of the groups is higher on the surface of UDA₂ particles. The contents of –CH₂ and –CH₃ groups of the powders are low. According to Auger spectroscopy data, the initial powders contain 0.5 % nitrogen, 5.4 % (UDA₁) and 6.0 % (UDA₂) oxygen, the balance being carbon.

It is seen from Fig. 1 that the heat treatment of the UDA₁ and UDA₂ powders results in changing the shape of the nitrogen adsorption isotherms. This affects the rated adsorption and structural characteristics (specific surface S_s , specific volume of a monolayer of adsorbed nitrogen V_m , adsorption potential A , and specific adsorption potential A').

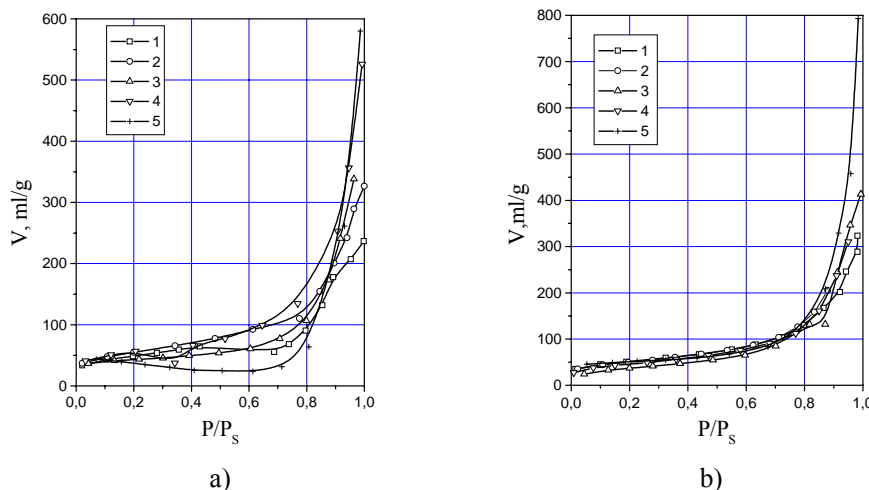


Fig. 1. Isotherms of the initial and heat-treated UDA₁ (a) and UDA₂ (b) powders: initial (1), treated at 200 (2), 300 (3), 400 (4), and 700 (5) °C.

The calculations of the isotherms have shown that the heat treatment of powders causes their specific surface to vary up to 40 %. In accordance with the change in the specific surface, the specific volume of a monolayer of adsorbed nitrogen varies in the range from 44 to 34 ml/g and from 43 to 29 ml/g for UDA₁ and UDA₂, respectively (Table 1).

The heat treatment affects essentially the adsorption potential. Thus, the treatment of UDA₁ and UDA₂ powders at 700 °C increases the weighted means of A by factors of ~ 4.5 and ~ 3.5 , respectively (Table 1). Due to the heat treatment, not only the highest A values increase, but their range extends too (Fig. 2). The highest A values observed in a function of distribution run as high as

2600 and 3300 J/g for UDA₁ and UDA₂, respectively. It is seen from the Table that there is a certain anomaly in the ordinal dependence of the weighted means of the adsorption potential (A) and specific adsorption potential (A') on the treatment temperature in the regions of 400 and 500 °C.

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Table 1. Surface characteristics of the powders.

Adsorption characteristics	Powder	The initial powder	Annealing temperature, °C					
			200	300	400	500	600	700
$S_{уд.}, m^2/g$	УДА ₁	167	156	135	163	173	148	96
	УДА ₂	166	158	123	121	170	113	156
$V_m, ml/g$	УДА ₁	42	39	34	41	44	37	24
	УДА ₂	42	40	31	30	43	29	39
A, J/g	УДА ₁	419	498	857	1019	957	952	1892
	УДА ₂	595	634	865	805	940	1204	2143
$A_{max}, J/g$	УДА ₁	960	640	1400	1600	1600	1500	2600
	УДА ₂	1040	1120	1500	1200	1300	1800	3300
$A', J/m^2$	УДА ₁	2.5	3.2	6.3		5.5	6.4	19.7
	УДА ₂	3.6	4.0	7.0	6.6		10.6	13.7

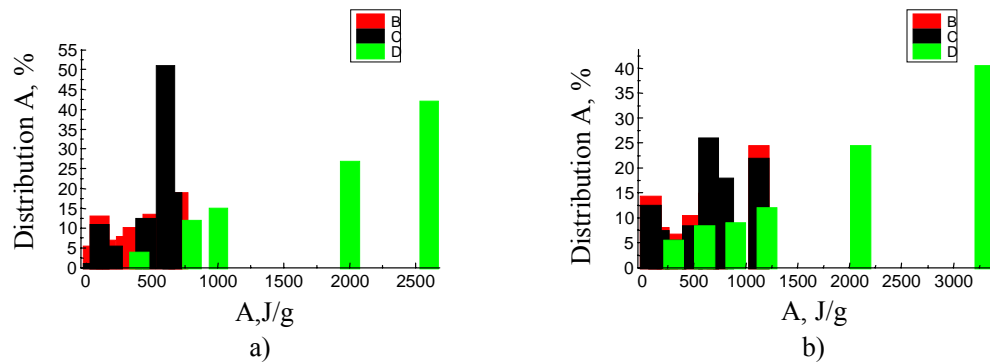


Fig. 2. Functions of distribution of adsorption potentials of the initial and heat-treated UDA₁ (a) and UDA₂ (b) powders: initial (B), treated at 200 (C) and 700 (D) °C.

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anomaly in the ordinal dependence of the weighted means of the adsorption potential (A) and specific adsorption potential (A') on the treatment temperature in the regions of 400 and 500 °C.

IR spectra from the initial (Fig. 3) and heat-treated samples differ only slightly in the range of 1000-1500 cm^{-1} wavenumbers. The only exception is an absorption band with a maximum at 1055

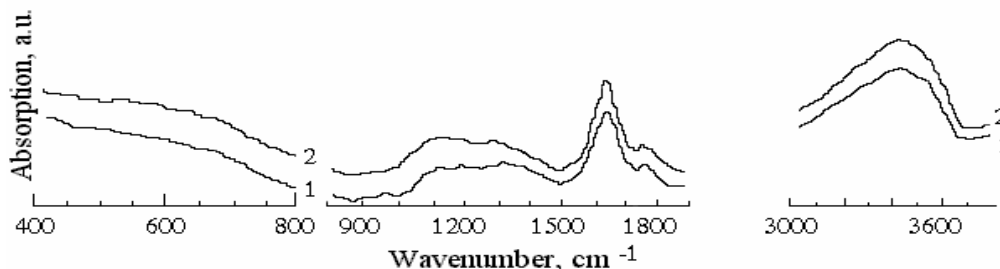


Fig. 3. IR absorption spectra of the initial UDA_1 and UDA_2 powders.

cm^{-1} in the spectrum from UDA_1 treated at 300 °C. We have failed to establish the origin of the maximum.

A notable result of the heat treatment is a monotone change of the band at 1750 cm^{-1} and a relative increase in the absorption intensity at 3580 cm^{-1} as demonstrated in Figs. 4a, b.

4. Discussion

The analysis of our data shows that in the process of additional purification the surfaces of particles of the UDA_1 and UDA_2 powders acquire different superstructures. It can be assumed that in result of a more aggressive treatment by melting with a mixture of alkalis, the surface of a diamond particle loses a portion of active centres and has a lower amount of oxygen-containing functional groups. The data of IR and Auger spectroscopies provide support for this view. The purification of powders with an alkali solution is softer and as a result the amount of combustion residue and the surface activity of the UDA_2 powder are by 0.4 % and by a factor of 1.5 higher than those of the UDA_1 powder. Thus, from the same synthesis product, we have obtained powders having different characteristics.

A heat treatment of the UDA_1 and UDA_2 powders in an argon atmosphere causes a progressive desorption of functional groups. Due to this, the surface activity of diamond particles increases, which is supported by an increase in the A and A' values of the heat-treated powders, found by the low-temperature adsorption nitrogen (see Table 1). We should note the effect of some decrease in the rise of the surface activity of the UDA_1 powder that has been treated at 500 and 600 °C and of the UDA_2 powder that has been treated at 400 and 500 °C.

Analysis of IR spectra from samples of the UDA_1 and UDA_2 powders has shown that the band in the 1750 cm^{-1} , which is associated with the vibrations of the carbonyl group, changes monotonically. The position of the band maximum is known to change depending on the degree of conjugation of the $=\text{C}=\text{O}=\text{}$ groups. Thus, in the spectrum from the UDA_1 powder treated at 700 °C (Fig. 4a), the shift of the maximum is 40 cm^{-1} . This increase in the frequency of valence vibrations is, evidently, due to a decrease both in the conjugation degree of the bond multiplicity and in the nonsaturation of the double bond that come to being in desorption of the surface groups. In addition to the shift of the absorption band at 1750 cm^{-1} , a change in the shape of the maximum is also observed. The abrupt change in the shape of the maximum is just characteristic of the UDA_1 sample treated at 500 °C. From our point of view, this effect calls for further investigation.

Changes in the behaviour of carbonyl bonds agree with the changes in the manifestations of intermolecular hydrogen bonds (Fig. 4b). The absorption spectra exhibit a deformed curve due to a

relative increase in the intensity of absorption at 3580 cm^{-1} , which can be attributed to the breaking of hydrogen bonds.

As to the interpretation of a broad low-intensity band between 1000 and 1500 cm^{-1} (Fig. 4a), it cannot be unambiguously interpreted since the majority of active-in-the-IR-absorption functional groups manifests itself in this spectrum region. The absorption at 1640 cm^{-1} is caused by deformation

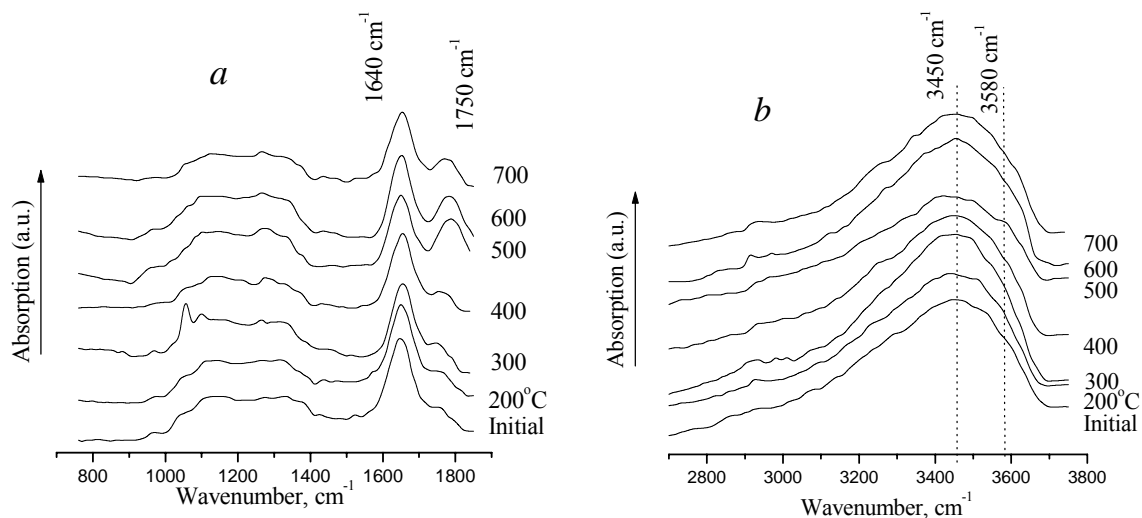


Fig. 4. IR absorption spectra of heat-treated UDA_1 samples.

vibrations of water both bonded and free. A comparison between IR spectra from the initial UDA_1 and UDA_2 powders shows that the heat treatment results in the higher loss of OH-groups (1640 cm^{-1}) from the UDA_2 samples. The fact is also supported by Auger spectroscopy studies. For instance, the oxygen content of the UDA_1 sample treated at $700\text{ }^\circ\text{C}$ decreased from 5.4 to 5.3 at. %, while the oxygen content of the UDA_2 sample decreases from 6.0 to 5.7 at. %.

5. Conclusions

Our findings show that detonation-synthesised diamond is a material having specific surface properties, which can be changed by chemical and heat treatments.

The methods of additional purification of nanodiamonds we used in our experiments have allowed us to produce powders, whose surface activities differ by a factor of 1.5.

The heat treatment of powders has increased their surface activity by a factor of 4.5.

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