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The Effect of Chemically Active Media on the Structure and Properties of Cubic Boron Nitride

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Properties of cubic boron nitride (cBN) powders from 2 to 200 mm particle size have been studied before and after chemical treatment. Impurity compositions of the bulk and surface, density, magnetic, electrophysical, physicochemical, and radiospectroscopic characteristics are considered. Structural changes in samples and the origin of the observed effects are discussed.

INTRODUCTION

Cubic boron nitride (cBN) is the most thermostable material and is applied as a rule in cases where diamond cannot be used (at heavy loadings and high temperatures). At present, properties of disperse superhard materials that are widely used in industry are being intensely studied. Among these is powdered cBN. It is commonly supposed that cBN is a chemically inert substance. Due to surface imperfection, however, chemically active media might affect properties of finely disperse samples. Similar effects of strong oxidizers have been reported on diamond (1). The influence of size factors on substance properties via the surface is well known.

The present paper deals with the physicochemical, magnetic, electrophysical, and radiospectroscopic properties of cBN powders versus chemical media and particle size before and after chemical treatment with respect to impurity and elemental compositions (including surface composition).

EXPERIMENTAL

KP grits and KM micron[1] powders with various particle sizes in the initial state and as-treated by chemical reagents were the subjects of our investigation. The samples were made of hexagonal boron nitride (hBN) at high pressures and temperatures at the Institute for Superhard Materials of the National Academy of Sciences of Ukraine. To stimulate the process, magnesium was added. The recovery was performed by a chemical method; i.e., the samples obtained were subjected to a treatment with the following chemically active substances: (i) a concentrated sulfuric acid with addition of calcium sulfate (the samples were boiled in the acid for 5–6 h); (ii) a potassium hydroxide melt, where the samples were kept for 3–4 h; (iii) a chlorine flow at 950–1050°C for 1.5 h up to the termination of a chloride precipitation. The first treatment is called acid, the second alkaline, and the third chlorination.

Sample impurities were determined by spark mass spectroscopy and the surface composition by Auger spectroscopy. The specific surface was defined by the method of Brunauer, Emmet, and Teller (BET) using isotherms obtained by low-temperature nitrogen adsorption in a Coultronics Acusorb 2100 device (1). EPR was used as a structural-sensitive method, which allows the structure of defects to be studied at the microlevel both in the bulk and at the surface (2). In particular, by analyzing variations of EPR spectra under various external effects (temperatures, gases, irradiation, etc.) one can conclude on the model of surface defects and on their corresponding structure variations. The measurements were performed on a 3-cm-range EPR radiospectrometer at room temperature. To compare EPR signal intensities, they were taken from equal volume amounts of powders.

RESULTS

The use of the spark mass spectroscopy method revealed that all three methods of chemical treatment are sufficient in clearing powders from accompanied impurities. The total basic impurity contents of grits and micron powders (Si, Al, Mg, Ca, Fe, Ti) range from 0.98 to 0.53 and from 0.37 to 0.20 relative %, respectively, the basic impurity being Mg. The impurity composition of the surface found by Auger spectroscopy and basic physicochemical and electrophysical characteristics of samples (specific surface (S_{BET}),

[1] Cubic boron nitride grits are powders of cBN with particle size above 60 μm and micron powders are powders with particle size below 60 μm.

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TABLE 1
The Surface Composition and Basic Characteristics of cBN Powders

Sample number	Sample grade and grit size (μm)	Mode of treatment[a]	Surface composition (at.%)					Powder basic characteristics				
			B	N	C	O	B/N	ρ (Mg/m^3)	S_{BET} (m^2/g)	χ (10^{-8} m^3/kg)	ρ' (10^{13} Ohm·m)	tg(δ) (10^{-4})
1	KP 200/160	i	20.5	16.8	42.9	19.8	1.22	3.52	0.014	8.2	6.6	1066
2	KP 200/160	a	41.5	28.1	20.4	10.0	1.48	—	0.101	1.3	4.5	—-
3	KP 200/160	al	22.5	18.4	51.9	7.2	1.22	—	0.043	1.6	7.0	1027
4	KP 100/80	i	27.6	9.5	41.6	11.2	1.41	3.51	0.018	3.3	2.2	1307
5	KP 100/80	a	30.3	23.4	41.8	4.5	1.29	—	0.044	1.4	3.2	428
6	KM 20/14	i	37.9	25.7	30.9	5.5	1.47	3.50	0.167	0.9	3.6	443
7	KM 20/14	a	37.5	22.9	43.3	6.3	1.20	—	0.452	− 0.4	8.2	401
8	KM 7/5	i	31.5	25.5	36.3	6.8	1.24	3.49	1.127	2.5	2.8	224
9	KM 7/5	a	39.9	26.3	28.9	4.9	1.51	—	0.925	− 0.3	1.9	284
10	KM 7/5	al	39.5	27.1	27.3	6.1	1.46	—	0.377	− 0.3	3.8	294
11	KM 5/3	i	47.3	29.5	17.1	6.1	1.60	3.53	1.431	2.5	3.3	341
12	KM 5/3	a	7.3	29.5	17.1	6.1	1.60	—	1.575	− 0.3	1.1	303
13	KM 3/2	i	47.0	30.9	15.8	6.3	1.52	3.54	1.816	1.9	2.6	363
14	KM 3/2	ch	44.7	31.3	14.8	8.4	1.43	—	1.435	− 0.5	$2.5 \cdot 10^{-6}$	496

[a] i, initial; a, acid; al, alkali; ch, chlorination.

pycnometric density (ρ), specific magnetic susceptibility (χ), specific electrical resistance (ρ'), and dielectric loss tangent (tg(δ))) are listed in Table 1.

Typical EPR spectra from the samples of cBN grits and micron powders under study are shown separately in Figs. 1 and 2 as they have qualitative differences. The parameters of the L_1 and L_2 lines of the EPR spectra are given in Table 2.

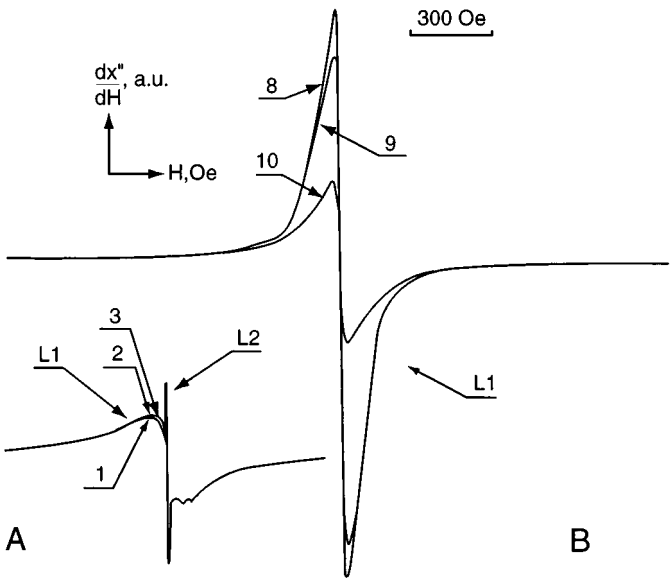

FIG. 1. Lines L_1 and L_2 of EPR spectra from cubic boron nitride after various treatments of (A) grits and (B) micron powders. (the sample definitions are given in Table 1).

In the general case, the EPR spectrum of each sample is a superposition of lines of three types: line L_1 with the g factor of about 2 and width (a spacing between curvature peaks) ΔH from 40 up to 120 Oe, line L_2, a narrow line with $g = 2$ and ΔH of about 6 Oe, and line L_3, which is observed in the wide region of resonance magnetic fields (from 0 up to 6000), with the ΔH value on the order of several thousand oersted. Some of the L_1 and L_2 lines have multicomponent structures. The lengths of lines L_1 and L_2 in the EPR spectrum is rather small (hundreds of oersteds) as compared with the region occupied by line L_3 (thousands of oersteds), while the peak intensities of lines L_1 and L_2 are by about one order of magnitude higher than that of line L_3. Therefore the spectra corresponding to them are given separately and to different scales along the coordinate axes.

EPR spectra of cBN grits and micron powders differ qualitatively, while spectra of powders of the same grade are superficially similar and differ only in the width and intensity. Thus, spectra of grits contain lines L_1 and L_2 and in this case, line L exhibits a weakly expressed structure, the width of the envelope of which is 100 ± 10 Oe in all the cases. In the case of micron powders, line L_2 is not observed and line L_1 is structureless.

DISCUSSION AND CONCLUSIONS

The EPR method was used earlier to examine both hexagonal and cubic boron nitride. EPR spectra or their basic parameters (g factor and DH) reported in (3–5) are close to those given for our lines L_1 and L_2 (Table 2). The existing discrepancies, essential in a number of cases, are evidently

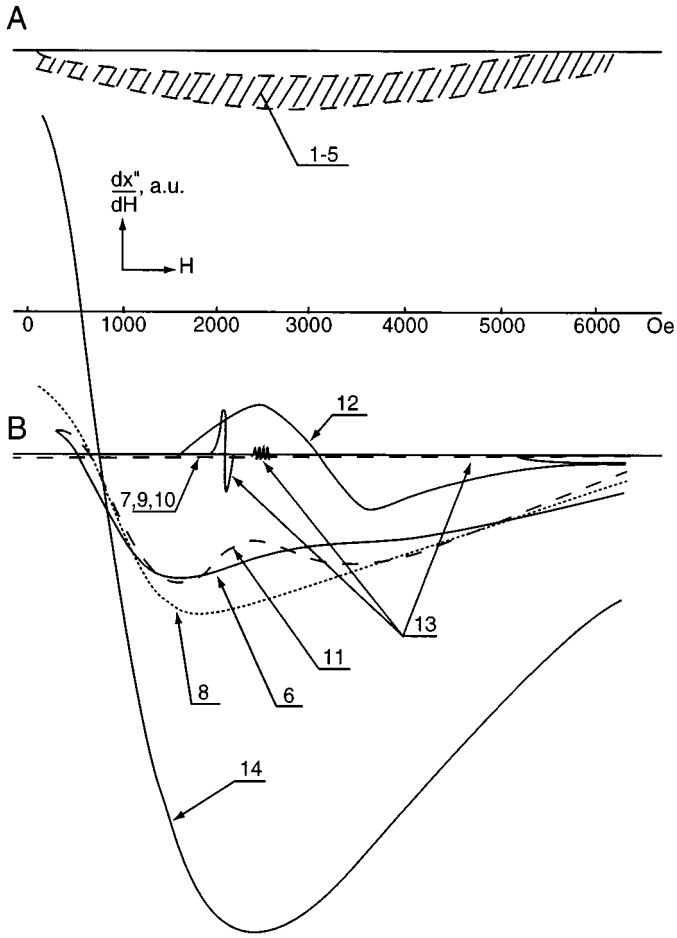

FIG. 2. Lines L_3 of EPR spectra from cubic boron nitride after various treatments of (A) grits and (B) micron powders (the sample definitions are given in Table 1). The shaded region covers all the curves of the given samples.

associated with the difference in particle size, usually not reported.

The most typical defects of hexagonal BN are the so-called one- and three-boron centers, in which an unpaired electron reacts hyperfinely with either one or three nuclei of boron atoms (^{10}B, ^{11}B). Up to now only a model of the three-boron center has been established: a positively charged nitrogen vacancy trapped an electron (the analogy to F centers in alkali-haloid crystals). By analogy with this model, a four-boron center for cBN has been suggested (3): a positively charged nitrogen vacancy, which trapped an electron, is in a tetrahedral surrounding of four boron atoms. This center is supposed to be responsible for lines similar to our narrow line L_2. Although the line hyperfine structure is not resolved (as opposed to the centers in hexagonal BN), the model is convincing because of the fact that in cubic BN, nitrogen also is negatively charged (6). Obviously, the final model might be established by experiments on double electron-nuclear resonance. A model of the center responsible for a wide line (analogy to line L_1) is unknown up to now. It can be assumed only that it is due to combined defects (groups of F centers combined with impurities), the nature of which as demonstrated by experiments depends on the sample preparation and their subsequent exposure to the external factors.

We were the first to record lines L_3 in BN. Similar lines were observed earlier in studying synthetic diamond (10, 11). They were attributed to ferromagnetic inclusions that had been added to the initial mixture as a crystallization medium in diamond synthesis. Based on a superficial resemblance of the spectra shown in Fig. 2 to the spectra given in (7, 8), we conclude that the L_3 lines we observed are caused by ferromagnetic metal inclusions.

It is seen from Figs. 1 and 2 and Table 2 that in the general case, EPR spectra of variously sized samples differ greatly from one another regardless of the method of treatment. Thus, the intensity of line L_1 is maximal near $d = 6$ μm, while its width, which is almost constant at low d values, drastically increases with d. EPR spectra from ferromagnetic inclusions of variously sized samples differ greatly, too (Fig. 2). Three groups of lines can be separated here: lines from KP grade samples 1 through 5, from KM grade samples 6 through 12 and 14, and from sample 13. Inside each group, the spectra are qualitatively similar. Parameters of line L_2 are less dependent on the sample size. The fact that lines L_2 are virtually not observed with small sizes of particles is practically caused by the decrease in the number of corresponding centers with the particle size along with the increase in the number of centers responsible for line L_1. Hence, it can be concluded that lines L_2 are associated with paramagnetic centers located in the bulk, while lines L_1 and L_3 are associated with the centers located near the surface.

Chemical treatment results in a decrease in the intensities of lines L_1 from KM grade and of lines L_2 from KP grade powder, thus pointing to the different nature of these two types of powders. It is seen from Fig. 2b that line L_3 from KM is heavily affected and from KP slightly affected by chemical treatment. A particularly strong effect is exerted by chlorination, which unlike other types of treatment induces an increase in the EPR line intensity.

EPR data correlate with the results obtained by other methods. Thus, large values of dielectric loss tangent are indicative of a great imperfection of crystals. In EPR spectra, this corresponds to great widths and low intensities of the lines. It should be noted that the maximum of line L_1 correlates with the lowest $\mathrm{tg}\, d$ (except for sample 14). Large specific surfaces $S_{Я}$ favor the increase in the number of free bonds, which results in the increase in the amount of unpaired electrons and as a consequence in an increase in the line L_1 intensity observed with the decrease in d. Finally, it should be noted that an abrupt change in the EPR

TABLE 2
Parameters of Lines L_1 and L_2 of EPR Spectra[a]

Sample	ΔH_1(Oe)	ΔH_2(Oe)	I_1 (arb.un)	I_2 (arb.un)	S_1 (arb.un)	g_1	g_2
1	108 ± 10	5.6 ± 0.5	33	67	80	$2.0026 \pm \delta$	$2.0030 \pm \gamma$
2	107 ± 10	5.6 ± 0.5	32	35	78	$2.0050 \pm \delta$	$2.0035 \pm \gamma$
3	120 ± 10	5.6 ± 0.5	33	46	85	$2.0047 \pm \delta$	$2.0032 \pm \gamma$
4	114 ± 10	5.6 ± 0.5	36	39	78	$2.0051 \pm \delta$	$2.0032 \pm \gamma$
5	113 ± 10	5.6 ± 0.5	35	26	75	$2.0063 \pm \delta$	$2.0035 \pm \gamma$
6	45 ± 5	—	72	—	97	$2.0061 \pm \delta$	—
7	58 ± 5	—	72	—	105	$2.0065 \pm \delta$	—
8	41 ± 5	—	100	—	100	$2.0062 \pm \delta$	—
9	46 ± 5	—	87	—	85	$2.0070 \pm \delta$	—
10	46 ± 5	—	68	—	88	$2.0058 \pm \delta$	—
11	40 ± 5	—	91	—	71	$2.0060 \pm \delta$	—
12	43 ± 5	—	82	—	77	$2.0039 \pm \delta$	—
13	42 ± 5	—	58	—	46	$2.0057 \pm \delta$	—
14	40 ± 5	—	101	—	91	$2.0053 \pm \delta$	—

[a] I_1 values correspond to peak intensities of lines L_1 and S_1 to integral intensity of line L_1; $\delta = 0.0010$; $\gamma = 0.0005$.

spectrum of metal inclusions (Fig. 2, samples 7, 9, 10) correlates with the severe variation in magnetic susceptibility c (Table 1). At the same time this fact is additional evidence supporting the magnetic origin of line L_3.

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