

# SYNTHESIS AND MAGNETIC PROPERTIES OF NANODIAMOND AGGREGATES DECORATED BY COBALTCONTAINING NANOPARTICLES

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**Abstract.** Conglomerates formed out of aggregated nanodiamond particles have been successfully covered with magnetic Co-containing nanoparticles by means of thermal destruction of metal-containing compounds in a hot mixture of mineral oil and detonation nanodiamonds. The samples produced were studied using TEM, XRD, and element analysis. The average sizes of the cobalt-containing particles are 5-7 nm. Magnetic studies of Co-containing samples have been performed. In order to detect if metallic cobalt phase really existed in the material, we used "NMR-in-magnetic" technique also known as the "spin-echo" method. The main peak of NMR spectra at ca. 227 MHz can be ascribed to the hcp form of metallic cobalt and confirms unambiguously the presence of metallic core in the nanoparticles. There is no clear evidence of signals which may correspond to the fcc metallic cobalt phase. The room temperature magnetization curves demonstrate high magnetization and large coercivity of the material confirming presence of metallic Co nanoparticles.

## 1. INTRODUCTION

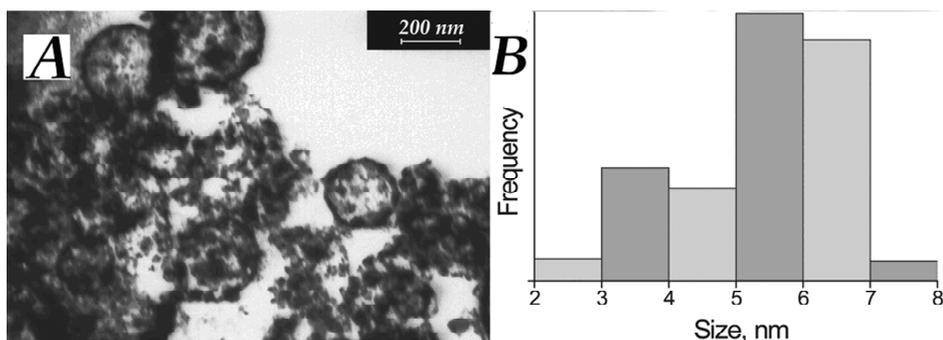
Detonation nanodiamond (ND) exhibits a number of interesting properties, including biological activity [1,2], and it is prospective for a wide range of applications. Hence fabrication of materials based on nanodiamond is of great interest. In particular, being combined with magnetic particles, ND may be controlled by means of magnetic fields, which gives it new prospective applications.

Nanodiamond which was formed during explosion of high explosives with negative oxygen balance [3] consists of tiny diamond particles of several nm in size, and a considerable number of them are aggregated into larger structures which are reported

to be up to hundreds nm in size [4]. Due to the treatment of detonation nanodiamond with oxidizing acids during the purification process, its particles are densely covered with various oxygen-containing functional groups, which are expected to facilitate adhesion of metal-containing nanoparticles to detonation nanodiamond.

This work is a part of the series of works devoted to fixation of metal-containing nanoparticles on the surface of various microgranules. Previously, a method for stabilization of nanoparticles on the surface of ultradispersed polytetrafluoroethylene microgranules has been developed in our laboratory [5]. This work is dedicated to nanometallization of aggregates of detonation nanodiamond (ADND),

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**Fig. 1.** Micrographs and size distribution graphs given for a Co-containing nanocomposite based on detonation nanodiamond (ADND).

which is further called microgranules, with magnetic Co-containing nanoparticles.

## 2. EXPERIMENTAL

The nanodiamond was used in the form of a gray water-based slurry which had been purified by means of treatment with oxidizing acids; the slurry contained 55 wt.% of water. The metal-containing reagents were used as received; their purity was 95–98 wt.%. The argon was de-oxygenized. The used mineral oil had been preliminarily treated with sulphuric acid and heated to 350 °C in argon in order to remove its most volatile fractions.

Thermal stability of ADND was sufficient to implement the already approved method for preparation of metal-containing nanoparticles [5]. According to the preliminary experiment which involved heating of the ADND/oil mixture in the argon atmosphere, intense removal of the absorbed water takes place at 130–170 °C. Upon complete water desorption, the reaction mass is visually uniform. Consequent heating up to 350 °C does not result in any visible changes.

Preparation of cobalt-containing particles and their fixation on the surface of ADND microgranules was performed as follows. A mixture of ADND slurry and oil was heated under stirring in the argon atmosphere to give a visually uniform mass. As the desired temperature was achieved, a solution of a metal-containing precursor (cobalt formate) in water was introduced into the system dropwise at a constant temperature. The calculated Co in ADND mass were 66 wt.%, 50 wt.%, and 33 wt.%.

The metal-containing compounds were taken in excess in order to compensate incomplete attachment of the forming nanoparticles to the nanodiamond. Upon complete addition of a precursor solution to the reaction mass, the reaction mass was cooled down to the room temperature still being

stirred in the argon atmosphere. The obtained black masses were rinsed with hexane. All thus produced samples were black powders attractable by a magnet. The samples were stored in air; some of the studies were performed several months after the preparation of the samples.

TEM micrographs were taken on a JEOL JEM 100B electronic microscope; the samples were dispersed in alcohol by sonication, and drops of the formed suspensions were applied onto carbon-coated copper grids.

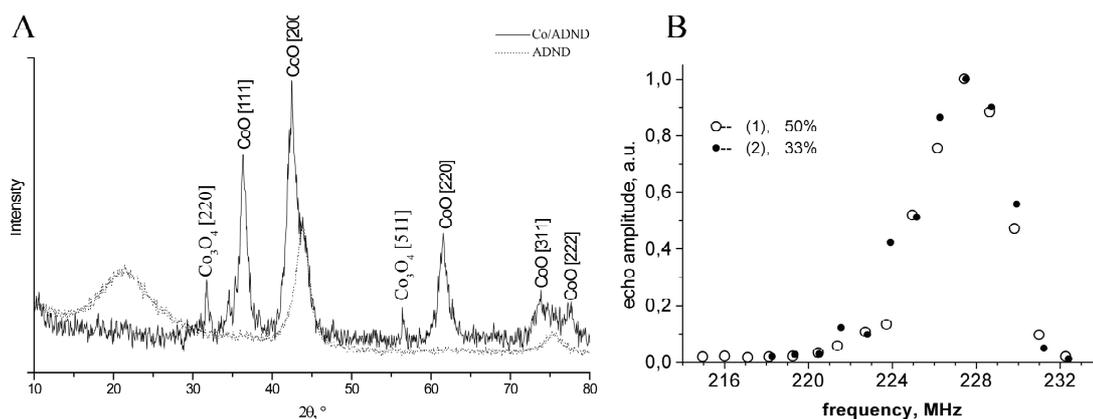
X-ray diffraction (XRD) studies were performed with a DRON3 diffractometer (CuK $\alpha$  radiation,  $\lambda = 1.54056 \text{ \AA}$ , graphite monochromator).

The NMR spectra were measured in an incoherently detected spin-echo spectrometer using 1 MHz frequency sweeping at 77K. At each frequency the echo amplitude was measured using conventional p1–s–p2 sequence with equal p1 and p2 pulses, 1.75 ls and s = 6 ls. In order to increase a signal-to-noise ratio by means of signal accumulation, pulse responses were recorded 1000 times for each spectrum (the repetition time was 10 ms).

Electron magnetic resonance (EMR) spectra were recorded with the help of computerized Varian E-4 spectrometer at X-band (9.15 GHz). The macroscopic magnetic properties were studied at room temperature in magnetic fields up to 5 kOe using EG&G vibrating sample magnetometer.

## 3. RESULTS AND DISCUSSION

TEM micrographs of the pristine ADND used for this work indicate that the aggregates formed out of diamond particles are mainly 300–350 nm in size. However, the granules are smaller (~150 nm) and less distinct in the TEM micrographs of the heated ADND. Possibly, it was caused by partial



**Fig. 2.** XRD pattern of the used nanocrystalline diamond and a typical Co/ADND sample (A);  $^{59}\text{Co}$  NMR spin-echo amplitude as a function of frequency measured for the sample with 50 wt.% Co (circles) and sample 33 wt.% of Co (bullets) at 77K (B).

disintegration of ADND conglomerates during heating.

Size and size distribution of cobalt-containing particles were determined via analysis of TEM micrographs (Fig. 1a). Metal-containing particles were distinguished from the diamond ones due to the difference in contrast. The average sizes of the cobalt-containing particles are 5–7 nm. Size distribution graphs, as well as sample TEM micrographs, are given in Fig. 1b. It should be noted that there are a few large ( $\geq 10$  nm) Co-containing particles on many micrographs, but their quantity is very small and is not displayed in the distribution graphs.

Large spherical formations can be clearly seen in many micrographs of Co-containing samples. The formations are mainly 150–350 nm in size, so we assume they were formed on the basis of ADND aggregates. In a number of cases, the contrast of such formations allows to assume that they contain ADND within them. Prior to the TEM studies, all the samples were subject to sonication, so the presence of those structures in the TEM micrographs indicates that the adhesion of metal-containing nanoparticles to nanodiamond is sufficiently strong.

Characteristic XRD patterns of all the Co-containing samples are shown in Fig. 2. They have one broad signal attributable to the amorphous carbon (JCPDS card 22-1069), and two peaks which corre-

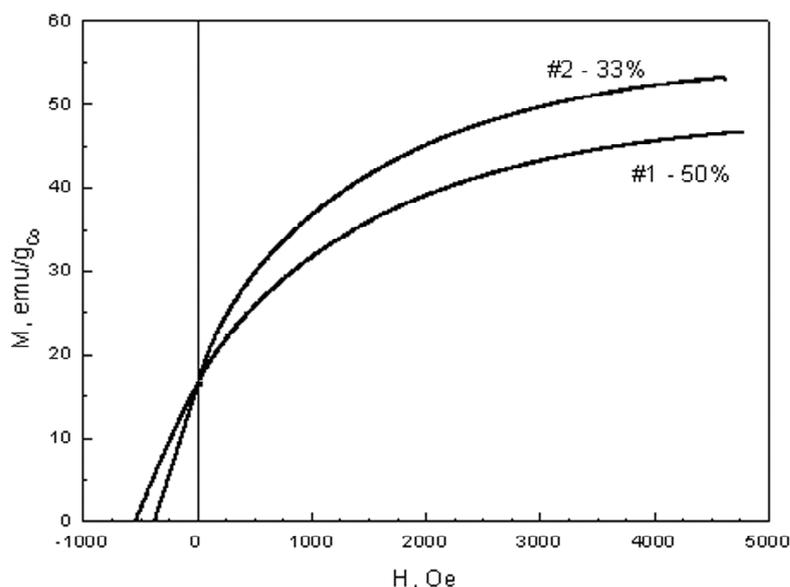
spond to the (111) and (220) atomic planes of ADND, respectively (JCPDS card 791467). Among the signals which arise from ADND, they include the peaks which can be ascribed to the CoO (Fm3m; JCPDS 2004: 780431) and  $\text{Co}_3\text{O}_4$  (Fm3m; JCPDS 2004: 43-1003). There is no clear evidence of presence of signals which may correspond to a metallic cobalt phase. However, such signals may be masked by noise.

In order to detect if metallic cobalt phase actually exists in the material, we used the “NMR-in-magnetic” technique also known as the “spin-echo” method [6]. The technique is an effective tool for investigation of different magnetic materials including cobalt clusters [7] and has been successfully used before for characterization of cobalt nanoparticles bound to the surface of UPTFE granules [8].

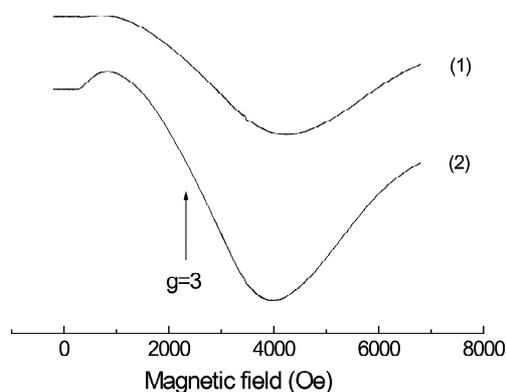
Characteristic NMR spectra of both (33 and 50 wt.%) samples are similar (Fig. 2a) and differ only in the amplitude (see the table 1). The main peak at ca. 227 MHz can be ascribed to the hcp form of metallic cobalt [6–9] and confirms unambiguously the presence of metallic core in the nanoparticles. There is no clear evidence of signals which may correspond to the fcc metallic cobalt phase. Therefore the NMR spectra allow one to conclude that cobalt-containing material based on ND matrix is similar to the materials based on the UPTFE nanogranules and contain metallic cobalt core

**Table 1.** Gaussian fit parameters for the data of samples #1 and 2.

Sample #	Center, MHz	Width, MHz	Relative signal intensity
1 (50 wt.% Co)	227.4 $\pm$ 0.1	3.8 $\pm$ 0.2	100%
2 (33 wt.% Co)	227.4 $\pm$ 0.2	4.2 $\pm$ 0.4	50%



**Fig. 3.** Room temperature demagnetization curves for samples with with 50 wt.% (1) and 33 wt.% (2) of Co. Magnetization is per Co mass.



**Fig. 4.** EMR spectra of the samples with 50 wt.% (1) and 33 wt.% (2) of Co.

mainly in the form of the hcp phase. Unfortunately, the obtained  $^{59}\text{Co}$  NMR spectra cannot reveal information on a cobalt oxide phase as (i) the signals for both  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$  compounds have their resonance frequencies very far from the metallic cobalt range and (ii) amplitude of the antiferromagnetic signals are very low as compare to FM ones.

Average particle sizes estimated using the Scherer equation comply with the size-relevant data obtained from TEM images.

Elemental analysis of several Co-containing samples was performed. The revealed metal:ND ratios indicate that the weight loss of ADND is negligible. The elemental analysis also revealed high concentrations of oxygen in all the samples. Unfortunately, reliable determination of the metal/metal oxide ratios is not possible due to the presence of unpredictable amounts of oxygen in nanodiamond

particles themselves. In one of the Co-containing samples, the observed oxygen concentration is so high that it can't be only due to the presence of cobalt oxides. We assume that some of the observed oxygen is contained within the ADND, in this case its concentration is higher than in the dried original ADND. That indicates that during the synthesis, ND is probably subject to oxidation.

Investigation of the Co-containing samples by means of static magnetometry and EMR revealed their marked magnetic properties even at the room temperature. Room temperature demagnetization curves for samples with 33 wt.% and 50 wt.% Co concentration are shown in Fig. 3. Both samples demonstrate high magnetization and large coercivity. The value of magnetization is near one third of bulk Co value. The ferromagnetic metallic Co nanoparticles often have close value of magnetization since large portion of material is in magnetically dead surface layer. Most likely Co in our samples forms metallic nanoparticles. Large coercivity at room temperature show relatively large size of these particles.

EMR spectra are very broad curves with the peak-to-peak linewidth  $\approx 3$  kOe and the effective g-factor near to 3 (Fig. 4). It should be noted that the revealed relatively high value of saturation magnetization is not specific for the antiferromagnetic cobalt oxide, even in case of uncompensated magnetic lattices. Presence of metallic cobalt (ferromagnetic) and cobalt oxide (antiferromagnetic) phases usually leads to a shift of the hysteresis loop off the zero

magnetic field value, this effect was not found. According to the work [9], CoO nanoparticles with the diameter of 7 nm must experience a paramagnetic-antiferromagnetic transition at 291K. However, the temperature dependences of the magnetic resonance spectra did not reveal any noticeable anomalies at that temperature. Hence, the results of magnetic and EMR studies indicate rather to metallic nature of cobalt nanoparticles in contrast to the XRD data.

In accordance with the results of XRD, NMR, and magnetic studies, the Co-containing nanoparticles must contain both cobalt oxide and metallic cobalt (most probably the hcp form). In this case the Co-containing particles should have the structure identical to the structure, i.e. metallic cores covered by oxide shells.

#### 4. CONCLUSION

A simple reproducible method for nanometallization of nanodiamond aggregates has been developed. The method has been successfully used for preparation and fixation of Co-containing nanoparticles. In all the prepared samples, metal-containing particles contain both metallic and metal oxide forms of Co. Magnetic properties of Co-containing samples have been studied.

#### ACKNOWLEDGEMENTS

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