

Magnetic nanoparticles fixed on the surface of detonation nanodiamond microgranules

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Abstract

Conglomerates formed out of aggregated nanodiamond particles have been successfully covered with magnetic Fe- and Co-containing nanoparticles by means of thermal destruction of metal-containing compounds in a hot mixture of mineral oil and detonation nanodiamond. Thus produced samples were characterized by TEM, XRD, and element analysis. Magnetic studies of the Co-containing samples have been performed. © 2007 Published by Elsevier B.V.

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1. Introduction

Detonation nanodiamond (ND) exhibits a number of interesting properties, including biological activity [1,2], and it is a prospective material 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 [3,4] 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 [5]. 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 should 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 stabilizing nanoparti-

cles on the surface of ultradispersed polytetrafluoroethylene microgranules has been developed in our laboratory [6]. This work is dedicated to nanometallization of detonation nanodiamond conglomerates, which are further called microgranules, with magnetic Fe- and Co-containing nanoparticles.

2. Experimental

The nanodiamond was used in the form of gray water-based slurry formed after the treatment of the soot with oxidizing acids (it should be noted that the ND was not extracted in the dry form); 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 ND was sufficient to implement an already approved method for preparation of metal-containing nanoparticles [6]. According to the preliminary experiment which involved heating of the ND/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.

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Table 1
Reagents and synthesis conditions

Precursor/solvent	Calculated metal:ND weight ratio	Temperature, °C
Co(HCOO) ₂ /H ₂ O	2:1, 1:1, 1:2	300–340
Fe(CO) ₅ /hexane	1:2	260

Preparation of metal-containing particles and their fixation on the surface of ND microgranules was performed as follows. A mixture of ND 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 was introduced into the system dropwise at a constant temperature. The used precursors and conditions are given in Table 1. 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 (via decantation), which resulted in separation of light particles from the main product. All thus produced samples were black powders attractable by a magnet. The samples were stored in closed vessels filled with 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 thus formed suspensions were applied onto carbon-coated copper grids. X-ray diffraction (XRD) studies were performed with a DRON-3 diffractometer (CuK α radiation, $\lambda=1.54056$ Å, graphite monochromator). Electron magnetic resonance (EMR) spectra were recorded with the help of computerized Varian E-4 spectrometer at X-band (9.15 GHz). Differential thermal analysis (DTA) was performed on a Mettler Toledo TGA/SDTA 851° using Mettler Toledo Star SW 7.01 software. Element analysis was performed in the Microanalysis Laboratory of Nesmeyanov Institute of Organoelement Chemistry, Moscow.

3. Results and discussion

TEM micrographs of the used ND, both treated by heating to 350 °C in oil and not, are given in Fig. 1. According to the Scherrer equation, diamond particles are 2–3 nm in size, and the granules formed out of them are mainly 300–350 nm in size in the untreated sample. At the micrographs of the specimen of the ND which underwent heating in oil, the granules are smaller (≈ 150 nm) and are less distinct. Possibly it was caused by partial disintegration of ND conglomerates during heating.

XRD patterns of the used ND, both the treated and untreated by heating, are virtually the same (Fig. 2). They have one broad signal attributable to the amorphous carbon (JCPDS card 22-1069), and two peaks which correspond to the (111) and (220) atomic planes of diamond, respectively (JCPDS card 79-1467). It should be noted that the signal which can be ascribed to the amorphous carbon is relatively weak at the XRD patterns of the metallization products.

For ND powder, DTA revealed a weight loss of only 4% at 400 °C with endothermic effect during heating in nitrogen. The powder had been prepared by drying of the available slurry with consequent grinding of the formed mass.

The size distribution graphs for metal-containing particles were calculated manually based on TEM micrographs, and the counts for the smaller particles (<4 nm) may be erroneous due to the insufficient image resolution and sharpness. Average particle sizes were calculated on the basis of XRD patterns according to the Scherrer formula. Metal-containing particles were distinguished from the diamond ones due to the difference in contrast. The average sizes of the metal-containing particles are 5–7 nm for the Co-containing samples and 11–13 nm for the Fe-containing ones. Size distribution graphs, as well as sample TEM micrographs, are given in Fig. 3. Please note that there are a few large (>10 nm) Co- or Fe-containing particles on many micrographs, but their quantity is negligible and is not displayed in the distribution graphs.

Large spherical formations can be clearly seen in many micrographs of Co-containing samples (Fig. 3A). Similar formations can be seen in micrographs of Fe-containing samples

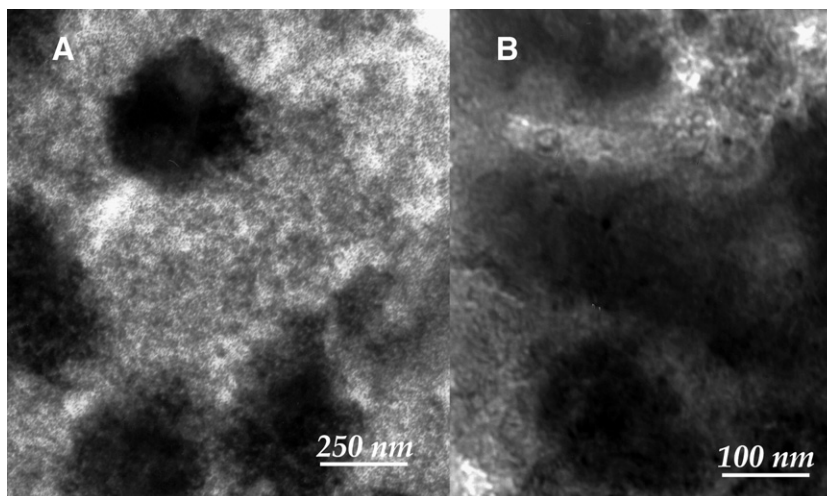


Fig. 1. TEM micrographs of a nanodiamond sample before heating (A) and after heating (B). The nanodiamond microgranules can be seen.

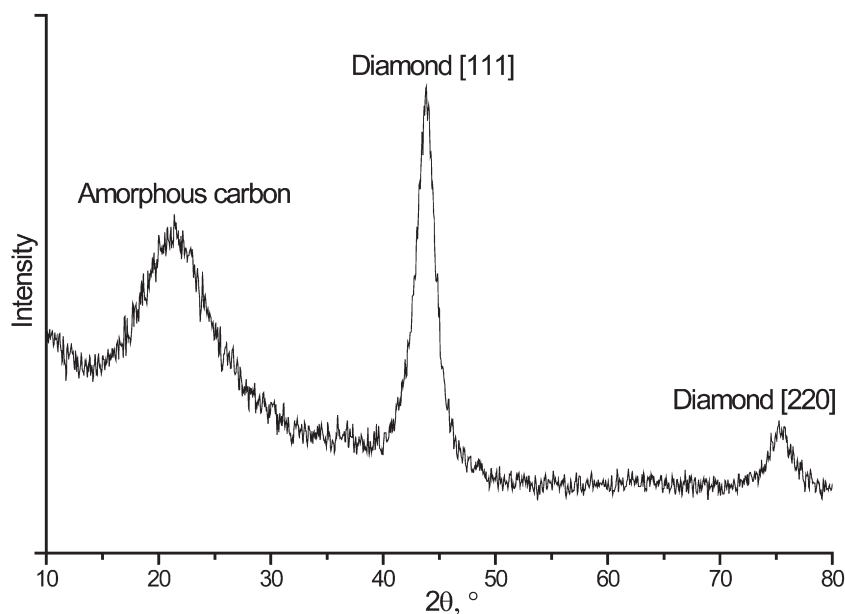


Fig. 2. An XRD pattern of the used nanocrystalline diamond.

(Fig. 3B). The formations are mainly 150–350 nm in size, so we assume them to be formed on the basis of ND microgranules. In a number of cases, the contrast of such formations allows to assume that they are not just separate ensembles of metal-containing nanoparticles but contain nanodiamond microgranules within themselves. Prior to the TEM studies, all the samples were subject to sonication, so the presence of those structures in the TEM micrographs indicate that the adhesion of metal-containing nanoparticles to nanodiamond is sufficiently strong.

XRD studies of the Fe-containing samples revealed presence of large amount of α -Fe (JCPDS card 85-1410), and a small amount of γ -Fe₂O₃ (JCPDS card 39-1346). The following peaks are present at the XRD patterns (Fig. 4): Fe₂O₃ (220) at $2\theta=30.15^\circ$, Fe₂O₃ (311) at $2\theta=35.5^\circ$, Fe₂O₃ (400) at $2\theta=43.25^\circ$, Fe (110) at $2\theta=44.7^\circ$, Fe₂O₃ (440) at $2\theta=62.75^\circ$, Fe (200) at $2\theta=64.9^\circ$. Hence we suppose the iron-containing particles to be represented by metallic cores covered by oxide shells.

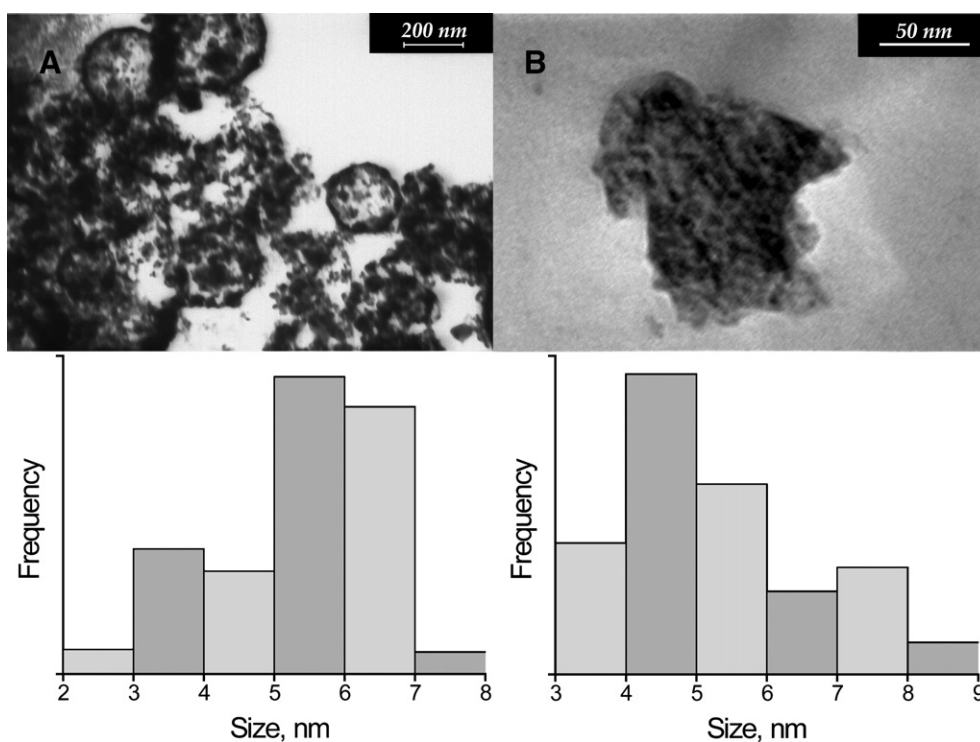


Fig. 3. Micrographs and size distribution graphs given for a Co-containing (A) and Fe-containing (B) samples.

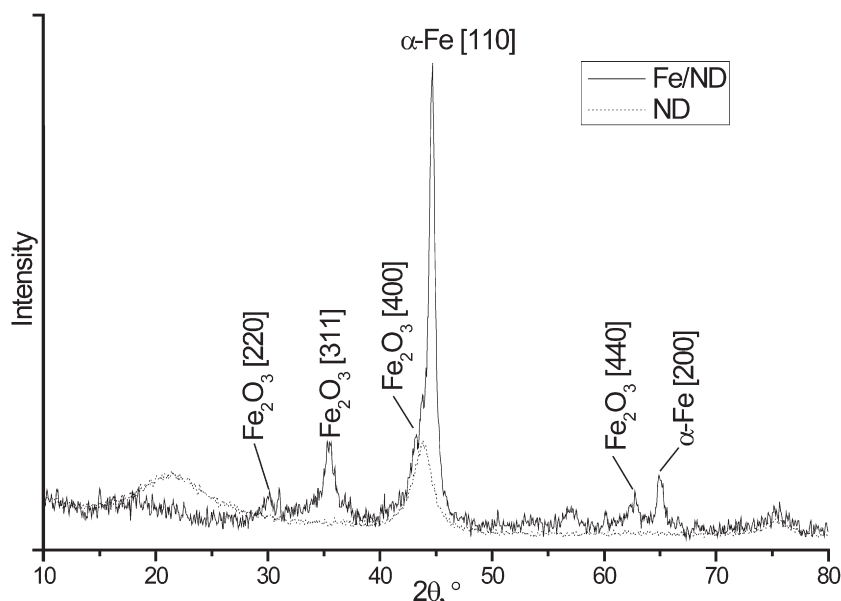


Fig. 4. An XRD pattern of a typical Fe-containing sample.

XRD patterns of all the Co-containing samples are similar (Fig. 5). Among the signals which arise from ND, they include the peaks which can be ascribed to the fcc form of CoO (JCPDS card 78-0431): (111) at $2\theta=36.3^\circ$, (200) at $2\theta=42.45^\circ$, (220) at $2\theta=61.55^\circ$, (311) at $2\theta=73.85^\circ$, and (222) at $2\theta=77.65^\circ$. There is no clear evidence of presence of the signals which may correspond to a metallic cobalt phase. However, such signals may be masked by the noise. Moreover, preliminary NMR studies of the Co-containing samples indicate presence of the hcp cobalt in the Co-containing particles.

Elemental analysis of several Co- and Fe-containing samples was performed. The revealed metal:ND ratios indicate that the weight loss of ND 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 ND, in this case its concentration is higher than in the dried original ND. 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. Samples 1 and 2, which differ in Co:ND ratios, have saturation magnetization of ≈ 16 emu/g in the field of 5 kOe and coercive force of 510 and

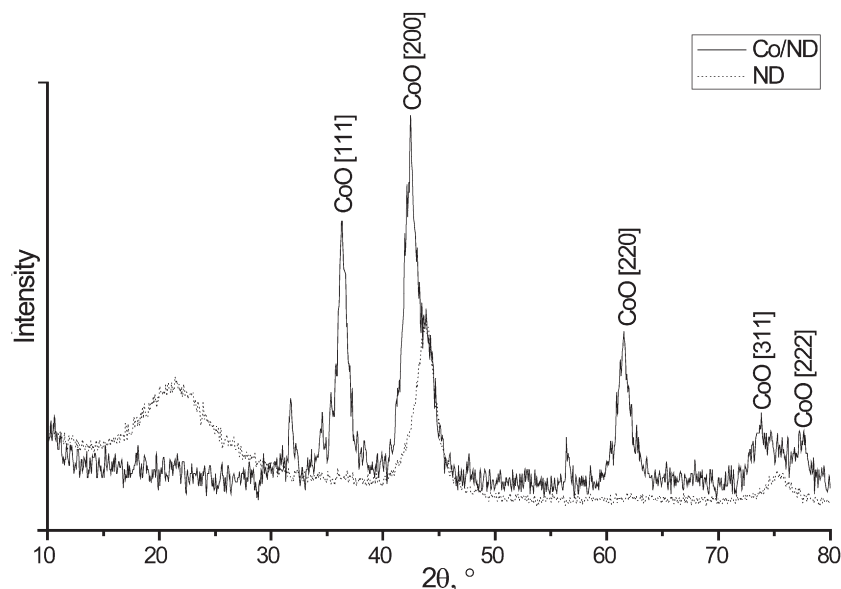


Fig. 5. An XRD pattern of a typical Co-containing sample.

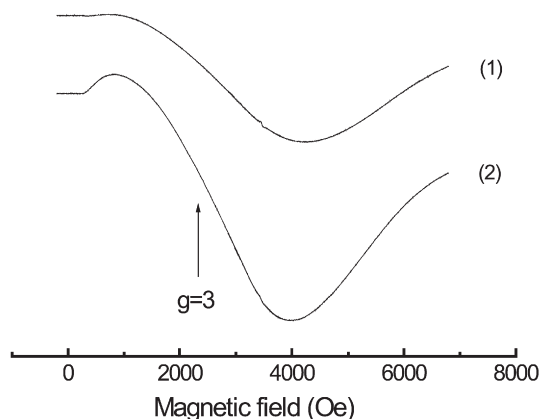


Fig. 6. EMR spectra of the samples with 53% wt. (1) and 31% wt. (2) of Co.

380 Oe, respectively. Assuming the Co:ND ratio to be 1:1 wt., the saturation magnetization will be 1.8 kOe, which is approximately 10 times less than the saturation magnetization of pure cobalt. EMR spectra are very broad curves with the peak-to-peak linewidth ≈ 3 kOe and the effective g -factor near to 3 (Fig. 6). It should be noted that the revealed relatively high value of saturation magnetization is not specific for the antiferromagnetic cobalt oxide, even in the 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 [7], CoO nanoparticles with the diameter of 7 nm must experience a paramagnetic–antiferromagnetic transition at 291 K. 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 should 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 of Fe-containing particles, i.e. metallic cores covered by oxide shells.

4. Conclusion

A reproducible method for nanometallization of granules formed by ultradispersed diamond has been developed. The method has been successfully used for preparation and fixation of Fe- and Co-containing nanoparticles. In all the prepared samples, metal-containing particles seem to contain both metallic and metal oxide forms of either Fe or Co (however, no peaks specific for a metallic cobalt phase were found in the XRD patterns). Magnetic properties of Co-containing samples have been studied.

Acknowledgements

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