EXCIMER LASER-INDUCED CVD OF CARBON ENCAPSULATED COBALT NANOPARTICLES

Radek FAJGAR, Miroslav MARYŠKO, Vladislav DŘÍNEK, Jaroslav KUPČÍK, Jan ŠUBRT,

aInstitute of Chemical Process Fundamentals, 165 02 Prague, Czech Republic, fajgar@icpf.cas.cz
bInstitute of Physics, 160 00 Prague, Czech Republic, marysko@fzu.cz
cInstitute of Inorganic Chemistry, 250 68 Husinec-Řež, Czech Republic, subrt@iic.cas.cz

Abstract
Decomposition of acetylene / Co(NO)(CO)₃ mixtures induced by excimer ArF laser pulses is an efficient technique for preparation of amorphous cobalt nanoparticles encapsulated in carbon. Vacuum heating up to 900°C leads to crystallization the metal core. The cobalt core crystallizes in a face-centered cubic (β) form as revealed by X-ray and electron diffraction techniques and carbon affords graphite outer part. Properties of the Co(core) - carbon(shell) nanocomposites were examined by spectroscopy and microscopy techniques. Magnetization studies revealed paramagnetic behaviour of the as-prepared amorphous deposit and superparamagnetic behavior of the annealed samples.

Keywords: amorphous cobalt nanoparticles, carbon encapsulation, magnetic properties

INTRODUCTION
There is a considerable interest in research and production of magnetic nanoparticles in the last two decades. Encapsulation of the magnetic nanoparticles is an important issue for their potential nanomagnetic applications like magnetic recording media, biomedicine or electrodes in batteries. Various techniques have been applied for preparation of the carbon encapsulated magnetic nanoparticles [1]. In this paper we present excimer laser-induced process for preparation of amorphous paramagnetic cobalt/carbon nanoparticles. Their annealing to 600 and 900°C leads to crystalline superparamagnetic Co/C nanoparticles.

EXPERIMENTAL
Carbon encapsulated cobalt nanoparticles were prepared in a 1l glass reactor equipped with a PTFE stopcock and a quartz window. The nanoparticles were deposited on a tantalum substrate (Aldrich) and collected from inner walls of the reactor. Cobalt nitrosyl tricarbonyl Co(NO)(CO)₃ (Strem Chemicals) and acetylene C₂H₂ (Linde) were used as precursors after distillation on a vacuum line. Reaction mixture was prepared using standard vacuum line evacuated by rotation pump to a base pressure 3 Pa. Mixture of 300 Pa of Co(NO)(CO)₃ and 4600 Pa of C₂H₂ was prepared and the ArF laser (193 nm, 60 mJ/pulse, Semento Estonia) was used to initiate the decomposition.

Analyses of the gaseous products were conducted by GC-MS technique (GCMS 5050, Shimadzu). FTIR spectroscopy was used to measure depletion of the reactants and analyse the gaseous products (Impact 400, Thermo Nicolet). FTIR spectra of the deposit on tantalum foil with resolution 2 cm⁻¹ were collected using specular reflectance technique. Raman spectra were collected using Nicolet Almega XR spectrometer (Thermo Electron) with excitation line 473 nm.

Thermogravimetry was used to study a thermal stability of the deposit up to 900°C in a stream of argon (Cahn D-200 recording microbalances). Thermal treatment was performed in a Tube furnace 21100 (Thermolyne). A quartz tube with the deposit was evacuated by a turbostation (Pfeiffer Vacuum TCP 380) and temperature ramp
was set at 10°C/min. The samples were maintained at desired temperatures (600 and 900°C) for 90 min. and then were slowly cooled to the room temperature.

X-ray diffraction data were collected at ambient pressure and temperature by a Bruker D8 system using Cu Kα line ($\lambda = 0.15418$ nm, angular range from $2\theta = 20°$ - $100°$). EDX measurements were performed on XL 30 CP instrument (Philips) equipped with an EDX detector PV 9760; the accelerating voltage was selected in range from 5 to 25 kV. The chemical composition was measured on a beryllium substrate. The X-ray photoelectron spectra of the deposited nanoparticles were measured in an ESCA 310 (Scienta) electron spectrometer using Al-Kα radiation (1486.6 eV). The superficial compositions were calculated from integrated spectral intensities corrected for subshell photoionization cross sections.

Transmission electron microscopy and selected area electron diffraction was measured using a Philips EM 201 microscope. ProcessDiffraction V 4.3.8.B software was used to solve the diffraction patterns [2]. The magnetic measurements were carried out in the temperature region 5 – 300 K using a SQUID magnetometer MPMS-5S (Quantum Design).

RESULTS AND DISCUSSION

Cobalt nitrosyl tricarbonyl Co(NO)(CO)₃ and acetylene C₂H₂ were used as gaseous precursors. The focused ArF laser pulses decompose the reaction mixture which results in formation of solid deposit along with gaseous products. Conversion of the reactants was calculated from the FTIR spectra measured before and after the reaction using analytical stretching and bending vibrations of Co(NO)(CO)₃ (2047 and 565 cm⁻¹) and acetylene (3308 and 729 cm⁻¹). Cobalt precursor decomposed to metal nanoparticles as solids together with CO, NO as the main gaseous products. Acetylene converted to encapsulating carbon and mainly hydrogen as the gaseous product is formed. Minor products (vinylacetylene, diacetylene) are formed as a result of acetylene dimerization/hydrogenation.

1.1 Characterization of the nanoparticles

The as-prepared sample deposited on the Ta substrate and the bottom of the reactor was deeply black and its adhesion was loose. The chemical composition was studied by EDX and XPS techniques. The bulk composition found by EDX is Co₁.₀C₇.₇ for the as-prepared sample. This result is in a good agreement with the composition calculated from depletion of reactants (Co₁.₀₀C₈.₃₃). Low content of nitrogen and oxygen was also observed. Heating to 600 and 900°C at pressure 10⁻³ Pa has an influence on sample stoichiometry. Carbon content is lower due to evaporation of adsorbed gases, formed in the course of the reaction. Surface composition calculated from intensities of photoemission lines of Co 2p and C 1s electrons is Co₁.₀ₐC₆.₆. The composition calculated from XP spectra shows similar contents of both cobalt and carbon atoms in the superficial layer. The measured binding energy (BE) 778.₄ eV of the Co 2p₃/₂ electrons is characteristic for metallic cobalt. No carbides or oxides were detected in the samples.

Thermal stability of the sample was studied in the argon atmosphere by the thermogravimetry and the volatiles were analyzed by mass spectrometry. The analysis shows that the sample is stable up to 300 °C and then the weight of the sample decreases by 24% due to desorption of the volatile products of the reaction from the sample surface. Among decomposition products also hydrogen was detected.

The annealed samples show much higher carbon content in the superficial layer as found by XPS. (Co₁.₀₀C₁₁.₄) at 600°C and Co₁.₀₀C₂₀.₄ at 900°C). Higher carbon surface content is a consequence of the encapsulation of the metallic core, better carbon organizing and formation of more compact carbon layer. Also in the annealed samples no carbide is detected in the interface between metallic core and carbon. Small content of oxygen is also present in both the as-prepared and annealed samples (BE of O 1s electrons 531.₅ eV).
The FTIR spectra of the collected nanoparticles were measured in the range of 400 - 4000 cm\(^{-1}\). Very weak and broad bands centered at 2962 and 2875 cm\(^{-1}\) were observed and they are assignable to valence C-H vibrations. Both \(\nu\) (Co-CO) centered to 2165 cm\(^{-1}\) and \(\nu\) (Co-NO), 1874 and 1798 cm\(^{-1}\) bands were revealed in the solid material, which means that some metal - ligand bonds are preserved in the deposit. The annealed deposits show no peaks in the FTIR spectra.

Raman spectrum of the as-prepared material, acquired with the lowest excitation energy reveals two broad bands centered at 1358 (D-band) and 1570 cm\(^{-1}\) (G-band). The D-band is associated with disordered carbon structure in amorphous and quasi-crystalline form of carbon. The G-band corresponds to the \(E_{2g}\) mode (stretching vibrations) in the basal plane of the crystalline graphite. The FWHM (full width at half maximum) of the G-band of the as-prepared sample is 113 cm\(^{-1}\) which proves presence of turbostratic carbon forms. After annealing at 900\(^0\)C, when both D- and G- bands are much sharper, we obtain the FWHM value 97 cm\(^{-1}\). It shows, that heating of the sample contributed to the higher degree of graphitization, but turbostratic structures are still prevailing.

The Raman spectra of the nanoparticles were measured with the lowest excitation energy to avoid oxidation of the samples and formation of metal oxides. However, the as-prepared sample is sensitive to heating on air and its beginning oxidation initiated by focused laser beam was detected in the spectrum as weak band at 683 cm\(^{-1}\).

**Fig. 1** TEM images of the (a) as-prepared sample and the (b) the sample annealed to 600\(^0\)C. Insets: corresponding electron diffraction patterns.

TEM image shows ball-shaped nanoparticles (Fig. 1a). The size of the as-prepared nanoparticles is about 40 nm with a relatively narrow size distribution. Electron diffraction analysis of this sample affords a diffuse pattern, consistent with an amorphous cobalt and carbon (Fig.1a, inset). The sample after annealing possess also ball-shaped structure (Fig. 1b). The nanoparticles crystallize as evidenced by the electron diffraction pattern (Fig 1b, inset). Discrete rings are consistent with presence of cubic fcc crystal lattice of cobalt.

X-ray diffraction pattern of the as-prepared sample, measured using Cu K\(_{\alpha}\)1 line shows very broad reflection with low intensity (Fig. 2, line a), evidencing for poor crystallization. There is an accordance between ED and XRD results. The electron diffraction technique confirmed also presence of amorphous material.
The sample, annealed at 600°C shows the pattern with strong reflections centered at $2\Theta = 44.32$, 51.68, 76.04, 92.44 and 98.24° (Fig. 2, line b). The pattern is consistent with cubic fcc crystal lattice of cobalt (PDF File No. 15-0806). At increased temperature (900°C, Fig. 2, line c) we observe the same pattern. Weak reflections at $2\Theta = 36.96$ and 42.00° were recognized as cobalt oxide Co$_3$O$_4$.

Neither peaks, ascribable to hcp metallic cobalt nor cobalt carbides were detected in the diffractogram. Absence of carbides is important for better magnetic behaviour, because carbide content is deleterious to the magnetic properties and their formation is therefore undesirable.

### 1.2 Magnetic properties

Magnetic hysteresis loops $M(H)$ were recorded in the temperature region 5-300 K. The $M(H)$ curves at $T = 5$ and 300 K for the as prepared (AP) and annealed samples are shown in Figs. 3 and 4 respectively. These measurements yield the basic magnetic parameters which are summarized in Table 1. For the (AP) sample (Fig.1a) the magnetization does not exhibit any saturation and the $M(H)$ dependence can be approximately expressed as

$$M = M_s + \chi_p H$$

where $M_s$ and $\chi_p$ are ferromagnetic and paramagnetic contributions respectively. The saturation magnetization $M_s$ corresponds to large nanoparticles which are in a blocked state and the paramagnetic contribution arises from small nanoparticles or clusters which are in a superparamagnetic state. The dependence $\chi_p(T)$ evaluated from the measured $M(H)$ loops at different temperatures (Fig.3b) can be well described by the Curie-Weiss law with a Curie constant $C = 0.00885 \text{emu.K}/\text{g.Oe}$. Taking the saturation magnetization in bulk Co 1.7 $\mu_B$ /atom, we may estimate that this value of the Curie temperature corresponds to the situation, where cobalt atoms are mostly (90 – 95%) in the paramagnetic or superparamagnetic (for Co clusters) state. In the case of the annealed materials, the $M(H)$ loops point to the ferromagnetic state characterized by a saturation magnetization $M_s$ and coercivity $H_c$.

### Table 1 Magnetic properties of Co-C powder samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_s$ (5K) (emu/g)</th>
<th>$M_s$ (300K) (emu/g)</th>
<th>$H_c$ (5K) (Oe)</th>
<th>$H_c$ (300K) (Oe)</th>
<th>$w_{FM}$ (5K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as prepared</td>
<td>9.2</td>
<td>4.96</td>
<td>300</td>
<td>100</td>
<td>0.058</td>
</tr>
<tr>
<td>ann.600°C</td>
<td>73.5</td>
<td>71.55</td>
<td>700</td>
<td>355</td>
<td>0.44</td>
</tr>
<tr>
<td>ann.900°C</td>
<td>129.3</td>
<td>127.6</td>
<td>900</td>
<td>475</td>
<td>0.80</td>
</tr>
</tbody>
</table>
The values of $M_s$ can be compared with the saturation magnetization of the bulk cobalt $M_s(5K) = 162.5$ emu/g. The fraction $w_{FM} = M_s / 162.5$ emu/g (Table 1) expresses then an apparent relative weight portion of Co in the material.

![Hysteresis loops](image1)

**Fig. 3** (a) Hysteresis loops at $T = 5$ and 300K for the AP sample, (b) paramagnetic susceptibility evaluated between $H = 15$ and 30 kOe.

**Fig. 4** Hysteresis loops of the annealed samples at (a) $T = 300$ K and (b) $T = 5$K.

For the as-prepared material $w_{FM}$ is very low because the most of cobalt atoms are present, as stated above, in the form of atoms encapsulated in carbon and contribute only to the total paramagnetic moment. In the case of the annealed samples the value $w_{FM}$ increases with increasing annealing temperature with regard to the fact that the annealing process leads to enlarging of Co nanoparticles [3]. For the sample annealed at 600 $^0$C the value $w_{FM}$ equals approximately to the cobalt weight portion deduced from the chemical composition of the deposit whereas for the 900$^0$ sample $w_{FM}$ is two times larger. We may also notice that for the both annealed samples the ratio $M_s(5K)/M_s(300 K)$ is nearly the value found for the bulk cobalt. In the materials studied here a wide distribution of the nanoparticle diameters is evident. This fact is manifested for the sample annealed at 600$^0$C. In this case an anomalous constricted form of the hysteresis loop was observed. It can be explained by presence of both single-domain (less than about 20 nm) and multi-domain (larger than about 20 nm) nanoparticles [4] in the annealed samples.

**CONCLUSION**

This work demonstrates the laser-induced CVD as an efficient technique for preparation of amorphous cobalt nanoparticles encapsulated in carbon. The as-prepared nanoparticles are paramagnetic. Vacuum annealing leads to crystallization of cobalt in a face-centered cubic ($\beta$) form and nanoparticles show paramagnetic behavior.
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LITERATURE