The cobalt and nickel-containing polyethylene prepared by using metal-vapor synthesis

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Abstract. Cobalt and nickel-containing low-pressure polyethylene samples (HDPE) were prepared by metal-vapor synthesis (MVS) of unstable bisarene complexes of Ni and Co type \( \text{C}_6\text{H}_5\text{C}_3\text{H}_3\text{M} \) and their further decomposition at a temperature of 178 K in the volume of HDPE. The Faraday method shows that Ni and Co nanometer particles are stabilized by the polyethylene matrix up to \( T = 370 \) K. When the Ni-HDPE material is heated above 420 K, irreversible processes of interaction of Ni clusters with the polyethylene matrix occur with the formation of a less magnetic phase. When the Co-HDPE material is heated above 420 K, Co clusters coalesce to form a more magnetic phase. At temperatures above 520 K, the magnetization of the Co/HDPE system begins to increase rapidly and approaches the value characteristic of massive cobalt. Changing the conditions of cryosynthesis significantly influences the properties of the resulting products. The sample of 2.5% Co-HDPE obtained at a temperature of 185 K is characterized by weak magnetic properties. Its magnetization at room temperature is lower than that of the samples with a similar metal content by 30-40 times. The XPS shows that nickel atoms are in the form of \( \text{Ni(OH)}_2 \).

1. Introduction

The production of hybrid materials based on polyethylene and metal nanometer particles has long attracted researchers. This is due to the fact that, firstly, the resulting hybrid materials, along with the characteristics inherent in polyethylene, such as high chemical resistance, dielectric properties, low sensitivity to shock (good shock absorber), extremely low adhesion, softening when heated (80 – 120°C) acquire additional valuable qualities possessed by metal nanometer particles and primarily their special magnetic and conductive properties. Secondly, polyethylene due to its chemical inertness can be considered as a convenient matrix for stabilizing highly active and unstable metal nanoparticles.

There are several main ways to produce hybrid materials based on polymers containing metal nanoparticles. It is possible to introduce directly metal nanoparticles or their oxides into the polymer matrix. In [1], a nanometer ZnO sol-gel powder was first obtained by the method of zinc acetate \( \text{Zn(\( \text{CH}_3\text{COO}\))}_2 \cdot \text{H}_2\text{O} \) using isopropanol and diethanolamine. Most of the particles had a size in the range of 40-75 nm. The resulting ZnO powder was then mixed with high density polyethylene (HDPE) powder and was driven through a two-roll mill heated to 140°C, and then pressed in a hydraulic press at a pressure of 30 bar at a temperature of 160°C. In the material, along with nanometer particles,
particles exceeding micron sizes were found in a small amount, which is due to the negative influence of heating and pressing in the process of manufacturing nanocomposites.

Introduction of metal nanoparticles into the polymer matrix is possible by reduction of various metal salts. For example, polyethylene fibers containing Ag nanoparticles were produced by chemically reducing AgNO$_3$ using ultrasonic irradiation. Ethylene glycol, ethanolamine (EA) and n-propanol were used as reducing agents. The smallest average size of silver nanoparticles was obtained using EA and amounted to 48 nm [2].

A common method is the destruction of metal-containing compounds in the polymer volume. An original version of this method was reported in [3], where elastic wave pulses were used to decompose iron sulfate, cobalt and nickel chlorides in a volume of high-pressure polyethylene (HPPE). The result was a HPPE containing Fe, Co, Ni particles with dimensions of 10-100 nm.

More often use thermolysis of metal-containing precursors, such as inorganic and organic salts and organometallic compounds [4]. For example, in [5, 6], a solution of Li acetate together with Mn, Co and Ni acetates in acetic acid was introduced into the molten polyethylene-hydrocarbon oil solution. HPPE was used as a polymer matrix. The average sizes of nanoparticles were: for the sample Li-Co-HPPE – 1,8±0,4, Li-Mn-HPPE – 2,0±0,3, Li-Ni-HPPE – 1,4±0,3 and Li-Ni-Mn-Co-HPPE – 2,3±0,4 nm.

It is of interest to use the method of the destruction of metal-containing compounds in the polymer volume under milder conditions, for example at temperatures not exceeding room temperature or even lower. This is possible with the use of organometallic compounds that are unstable at room temperature. In our work [7], a method of obtaining metal polymers by MVS of unstable bisarene complexes of nickel and cobalt type $(\text{C}_8\text{H}_{12})_2\text{M}$ and their further decomposition at a temperature of 178 K in the volume of HDPE $(M = 2\cdot10^5)$ was described.

2. Experimental setup and characterization techniques

A 5 liter MVS reactor [8-11] has a vacuumed. Cobalt or nickel shards (0.25-0.6 g) are evaporated in $10^{-2}$ Pa vacuum by a evaporator in the form of a tungsten spiral. Metal vapors are allowed to condense on the walls of the reactor cooled down to 77 K simultaneously with toluene (80-130 ml). Before the synthesis, toluene was distilled over sodium under Ar and further degassed in vacuum by several successive freeze-pump-thaw cycles. After the synthesis, the reactor walls are allowed to heat up and the metal-toluene ice is transferred right upon melting into jelly-like HDPE-toluene mixture. Metal-polymer composites have been prepared in two ways I and II (Fig. 1), the relevant conditions are presented in Table 1.

| Sample | Metal | Amount of metal, wt % | Means of influence$^3$ (temperature, K) | Way |
|--------|-------|-----------------------|----------------------------------------|-----|
| 1, 2   | Co    | 3.5, 4.6              | MS (363)                               | I   |
| 3, 4   | Ni    | 1.4, 4.3              | MS (363)                               | I   |
| 5      | Co    | 2.5                   | US (185)                               | II  |

$^3$ stirring of suspensions with a magnetic stirrer (MS) or under ultrasonication (US)

Magnetization measurements were carried in vacuum or in Ar by the Faraday method [12] in the temperature range of 77-573 K at magnetic field of 500-3200 Oe.

The X-ray photoelectron spectra were recorded using a XSAM-800 spectrometer (Kratos, UK) with Al K$_\alpha$ radiation in the fixed analyzer transmission mode. The spectra were measured with step size of 0.1 eV at ~20 °C and a pressure in the analytical chamber of $5\cdot10^{-8}$ Pa. The photoelectron spectra were approximated by Gauss function or the sum of Gauss functions, and the background caused by secondary electrons and photoelectrons that lost energy, was approximated by the straight line. The energy scale of spectrometer was calibrated according to the standard procedure taking into account the following binding energies: 932.7, 368.3 and 84.0 eV for Cu 2p$_{1/2}$, Ag 3d$_{5/2}$, and Au 4f$_{7/2}$.
respectively. Quantification was performed using atomic sensitivity factors (ASF) included in the software of the spectrometer. Sample charging was corrected by referencing to the C-C/C-H peak in the C 1s spectrum (284.8 eV).

![Diagram of the preparation of Ni-HDPE and Co-HDPE hybrid materials](image)

**Figure 1.** Scheme for preparation of Ni-HDPE and Co-HDPE hybrid materials.

3. Results and discussion
In both ways, at the initial stage of MVS, thermally labile bisarene complexes of Ni or Co are formed by interaction of metal vapors with toluene (Fig. 1). Resultant toluene solutions of these complexes just after the synthesis were transferred into the jelly-like HDPE-toluene mixtures prepared by boiling polyethylene in toluene under argon followed by cooling of the mixtures down to 363 and 185 K.

The synthetic way I initiates rapid thermal decomposition of the complexes in the bulk of the polymer at a temperature by far exceeding the decomposition point. Metal nanoparticles formed fill in cavities and defects present in the polymer and are immobilized therein due to sterical or other factors.

Effects of temperature on the properties of the composites were controlled by magnetostatic measurements. Thermomagnetic curves for Ni-HDPE hybrid materials (Fig. 2) demonstrate reversible behavior over 80-370 K, which suggests that Ni particles are stabilized by the polyethylene matrix at these temperatures.

An increase in the temperature of Ni-containing polyethylene to 420-430 K is accompanied by an irreversible decrease in magnetization and the appearance of new thermomagnetic curves, which also demonstrate reversible behavior over 300-420 K. This behavior of the samples may indicate that at temperatures above 370 K in the system there are irreversible processes of interaction of Ni clusters with the polyethylene matrix to form a less magnetic phase. This effect was observed for the Ni-nonadecan system [13].
The influence of the nature of metal on the properties of metal polymers was studied using cobalt-containing polyethylene as an example. Co-HDPE samples manifest substantially different magnetic properties. Fig. 3 shows thermomagnetic curves of some representative Co-containing samples. A 3.5% Co-HDPE composite exhibits a reversible thermomagnetic curve up to 370 K and demonstrates a 1.5-fold decrease in magnetization upon cooling to 80 K.

A 3.5% Co-HDPE hybrid materials is thermally stable to 370 K, which follows from the reversibility of the thermomagnetic curve (curve 1). When the temperature decreases to 80 K, a 1.5-fold decrease in magnetization is observed, apparently due to the anisotropy of the Co particle shape. An increase in the sample temperature to 470 K leads to an irreversible increase in magnetization and the appearance of a new, also reversible in this temperature range, thermomagnetic curve (curve 1'). This is due to the enlargement of Co particles, which, apparently, is due to a decrease in the stiffness of the matrix during the transition of polyethylene to the viscous state. At the same time, the anisotropy of the Co particle forms is still partially preserved, as indicated by the preserved decrease in magnetization when the temperature drops to 80 K. When the cobalt content in the polyethylene matrix increases, the initial magnetization value $\sigma_{Co}$ increases (curve 2). The 4.6% Co-HDPE sample also demonstrates a decrease in magnetization when the temperature drops to 80 K, although not to the same extent as the 3.5% Co-HDPE sample. An increase in temperature to 470 K, as well as in the sample of 3.5% Co, leads to an irreversible increase in magnetization and the appearance of a new thermomagnetic curve (curve 2'). Further stepwise temperature increase to 585 K leads to the formation of a series of reversible thermomagnetic curves, each of which corresponds to the temperature dependence of the magnetization of cobalt particles, stable in these temperature ranges (curve 2''). At temperatures above 520 K, the magnetization of the Co-HDPE system begins to increase rapidly and approaches the value characteristic of massive cobalt.

Variations of cryosynthesis conditions strongly affect properties of the resultant products. A 2.5% Co-HDPE hybrid materials maintained at cryogenic temperatures (way II) is characterized by weak magnetic properties. Its magnetization at room temperature is lower than that of samples with a similar metal content synthesized via the route I by a factor of 30-40 (Fig. 3, spot 3). Furthermore it is characterized by a very weak ferromagnetic resonance signal.
The MVS synthesis of non-ferromagnetic Ni powders upon interaction of metal particles with alkanes has been described earlier. At the same time, cobalt blacks demonstrate totally different behavior [14]. Probably, the application of a lower temperature in the case of the toluene+HDPE system coupled with ultrasonication effectively encapsulate very small Co nanoparticles within the polymer shell.

Ni-HDPE hybrid materials was studied by XPS. XPS quantification based on ASF gives composition C_{88.5}O_{8.1}Ni_{2.4}. The Ni 2p spectrum consists of a spin-orbit doublet and two satellites (Fig. 4).

![Ni 2p and O 1s photoelectron spectra of Ni-HDPE samples.](image)

The binding energies of the main Ni 2p_{3/2} and Ni 2p_{1/2} peaks are 856.7 and 874.4 eV, and the corresponding satellites are at 862.3 and 830.8 eV. The O 1s spectrum shows a wide peak at 531.4 eV, which can be equipped with three Gaussian peaks at 531.0, 532.3 and 533.3 eV with a width of 2.14 eV and relative intensities of 46:49:5. The peak at 531.0 eV represents the bound hydroxyl groups OH, and the peaks at 532.5 and 533.3 eV represents O-C bonds and water. Taking into account the characteristics of photoelectron spectra given in Table 2, such as binding energies (E_b) of the main and satellite peaks, satellite shifts (∆E_b = E_b(Ni 2p_{3/2}) - E_b(Ni 2p_{1/2})) and ∆E_s = E_b(Ni 2p_{3/2}) - E_b(Ni 2p_{1/2}), spin-orbit splitting (∆E_1 = E_b(Ni 2p_{1/2}) - E_b(O 1s)), an energy interval between Ni 2p_{3/2} and O 1s peaks (∆E_4 = E_b(Ni 2p_{3/2}) - E_b(O 1s)) we assigned the Ni 2p_{3/2} spectrum to the Ni(OH)_{2} phase [15-27].

In case of NiO, according to NIST XPS Database, the peak position of Ni 2p_{3/2} is in the range of 853.4 - 856.5 eV [28], while the position of O 1s is in the range 528.9-530.7 eV. It should be noted that for a reliable destination, we have collected only data containing satellite peak shifts.

To distinguish between Ni(OH)_{2} and NiO we also compared the shape of Ni 2p line [29-31]. The Ni 2p binding energies of the Ni-HDPE samples compared to those in Table 2 show a positive shift relative to the original data. For the Ni/SiO_{2} sample obtained by a similar method, the chemical shift was less by 0.8 eV [32, 33].

This indicates the different nature of the interaction of Ni particles with SiO_{2} and polyethylene. A possible reason for this difference may be the presence of a large amount of O_{2} in SiO_{2} compared to polyethylene and the manifestation of differential charging. Another reason may be a large concentration of hydrogen in the polyethylene, which contributes to the predominant formation of Ni(OH)_{2}. The last hypothesis can be confirmed by the appearance of a signal at 282.8 eV in the C 1s spectrum, which can be attributed to Ni-C bond (Fig. 5).

The C 1s spectrum was provided with four states at 282.8, 285.0, 286.5 and 288.5 eV with Gaussian widths of 1.54, 1.81, 1.81 and 1.98 eV and relative intensities of 6:85:8:1, respectively (Fig. 5).

The peak at 285.0 eV represents the C-C/C-H bonds of polyethylene, while those at 265.5 and 288.5 eV represent C-O and C(O)O groups of oxidized carbon atoms. The peak at 282.8 eV is absent...
in the spectrum of the pristine polyethylene and may be assigned to formation of Ni-C bond and, therefore, indicates strong electronic interactions between Ni and C atoms.

Table 2. XPS characteristics of different Ni compounds: peak binding energies ($E_b$), satellite splitting ($\Delta E_{1,2}$), spin-orbit splitting ($\Delta E_3$) and $\Delta E_4 = E_b(\text{Ni 2p}_{3/2}) - E_b(\text{O 1s})$.

| Sample | Ni 2p$_{3/2}$ | Ni 2p$_{3/2}$ | $\Delta E_1$ | Ni 2p$_{3/2}$ | Ni 2p$_{3/2}$ | $\Delta E_2$ | Ni 2p$_{3/2}$ | $\Delta E_3$ | O 1s | $\Delta E_4$ | Assignments | Ref. |
|--------|---------------|---------------|--------------|---------------|---------------|--------------|---------------|--------------|------|--------------|--------------|------|
| NiO    | 853.6         | 860.7         | 7.1          | 529.2         |                |              |               |              |      |              |              | 15   |
| NiO    | 853.9         | 860.6         | 6.7          | 529.4         |                |              |               |              |      |              |              | 16   |
| NiO    | 854.1         | 861.6         | 7.5          | 529.6         |                |              |               |              |      |              |              | 17   |
| NiO    | 854.1         | 861.2         | 7.1          | 529.9         |                |              |               |              |      |              |              | 18   |
| NiO    | 854.4         | 860.9         | 6.5          | 530.9         |                |              |               |              |      |              |              | 19   |
| NiO    | 854.5         | 861.6         | 7.1          | 872.0         | 879.2          | 7.2          | 17.5          | 529.6        | 325.0 | Ni-O         | O-C          | 20   |
| NiO    | 856.6         | 864.2         | 7.6          | 873.9         | 881.9          | 8.0          |              | 531.6        |         |              |              | 19   |
| NiO    | 855.22        | 861.42        | 6.2          | 531.0         | 324.5          |              |              | 532.4        |         | Ni(OH)$_2$   | H$_2$O, O-C | 21   |
| NiO    | 857.13        |               |              | 529.3         | 326.2          |              |              | 530.8        |         | Ni$_2$O$_3$, Ni(OH)$_2$ | H$_2$O, O-C | 23   |
| Ni$_2$O$_3$·6H$_2$O | 855.5      | 861.3         | 5.8          | 873.1         | 879.7          | 6.6          | 17.6          | 531.0        | 324.7 | NiOOH        | H$_2$O, O-C | 24   |
| Ni$_2$O$_3$·6H$_2$O | 855.9      | 861.7         | 5.8          | 873.6         | 880.0          | 6.4          | 17.7          | 532.8        | 326.5 | Ni$_2$O$_3$, Ni(OH)$_2$ | H$_2$O, O-C | 25   |
| Ni$_2$O$_3$·6H$_2$O | 855.9      | 861.5         | 5.6          | 531.5         | 324.4          |              |              | 324.2        |         | Ni$_2$O$_3$·6H$_2$O | Ni-O | 26   |
| Ni$_2$O$_3$·6H$_2$O | 856.5      | 862.3         | 5.6          | 873.8         | 880.1          | 6.3          | 17.6          | 531.0        | 325.2 | Ni$_2$O$_3$·6H$_2$O | Ni-O | 27   |
| Ni$_2$O$_3$·6H$_2$O | 856.7      | 862.3         | 5.6          | 874.4         | 880.8          | 6.4          | 17.7          | 531.0        | 325.7 | Ni$_2$O$_3$·6H$_2$O | O-C | 28   |

Note: $\Delta E_1 = E_b(\text{Ni 2p}_{3/2} \text{ sat}) - E_b(\text{Ni 2p}_{3/2})$, $\Delta E_2 = E_b(\text{Ni 2p}_{1/2} \text{ sat}) - E_b(\text{Ni 2p}_{1/2})$, $\Delta E_3 = E_b(\text{Ni 2p}_{1/2}) - E_b(\text{Ni 2p}_{3/2})$, $\Delta E_4 = E_b(\text{Ni 2p}_{3/2}) - E_b(\text{O 1s})$. The energies are in eV.

This Ni(OH)$_2$ - C interface is also an important factor for reflecting the magnetic properties of Ni-polyethylene system. It should be noted that the C 1s photoelectrons are more sensitive to the surface that Ni 2p photoelectrons due to the difference in kinetic energies determining the inelastic mean free path of the electrons. The analysis of the XPS data for the Ni-HDPE hybrid materials showed that along with the metal oxidation process, the polymer matrix is destroyed and the Ni-C state is formed. The probability of these processes increases significantly with increasing temperature. This can lead to the formation of a non-magnetic metal-carbon phase, the influence of which seems to be evident in the study of magnetic properties.

Co-HDPE hybrid materials was also analyzed by XPS. No peaks characteristic of cobalt were observed in the survey spectrum of the sample. This indicates the presence of metal particles at a depth greater than the sampling depth of Co 2p photoelectrons.
Figure 5. The C 1s photoelectron spectrum of Ni-HDPE samples.

The inelastic mean free path (λ) of Co 2p photoelectrons in pure Co is ~ 12 Å [35], while that in polyethylene is ~ 27 Å [36], the corresponding information depth 3 λ is ~ 81 Å. Since λ of the valence band and the C 1s photoelectrons is more than that of Co 2p photoelectrons they were analyzed also. The introduction of cobalt into polyethylene leads to a slight broadening of the C 1s peak, while significant changes in the spectrum of the valence band are observed (Figure 6). These changes reflect changes in the density of states near the Fermi level. Figure shows the spectra of C 1s and valence band of polyethylene and Co-HDPE.

Figure 6. The C 1s and valence band (VB) spectra of HDPE (1) and Co-HDPE samples (2).

Figure 6 shows the C 1s and valence band spectra of polyethylene and Co-HDPE hybrid materials. The C 1s spectrum of polyethylene can be provided by three Gaussian peaks at 285.0, 285.6 and 288.4 eV with a width of 1.98 eV and relative intensities of 93:4:3. This peaks are assigned to C-C/C-
H, C-O and C(=O)O groups, respectively. The C 1s spectrum of Co-HDPE can be provided by three Gaussian peaks at 285.0, 285.6 and 288.7 eV with a width of 2.04 eV and relative intensities of 91:5:4.

Figure 7 shows the O 1s spectrum equipped with three peaks at 529.4, 532.4 and 534.5 eV with a width of 2.14 eV and relative intensities of 4:87:9.

![Figure 7. The O 1s spectrum of Co-HDPE samples.](image)

The peak at 532.4 eV is for oxidized polyethylene carbon atoms, and the peak at 534.5 eV is for chemisorbed water. The peak at 529.4 eV can be attributed to physically absorbed water and/or Co-O bonds [23,29]. However, the latter assignment is less likely due to the small difference in the inelastic mean free paths of the Co 2p and O 1s electrons and great difference in ASF [30].

4. Conclusions

Ni and Co nanoparticles are stabilized by the HDPE matrix up to T=370 K. An XPS analysis of the Ni-HDPE hybrid materials showed formation of Ni-C bonds. When the Ni-HDPE nanocomposite is heated above 420 K, irreversible processes of interaction of Ni clusters with the polyethylene matrix occur with the formation of a less magnetic phase. The Co-HDPE hybrid materials behaves differently. When the Co-HDPE nanocomposite is heated above 420 K, the Co clusters fuse to form a more magnetic phase, which appears to be due to the coalescence of cobalt particles. At temperatures above 520 K, the magnetization of the Co-HDPE system begins to increase rapidly and approaches the value characteristic of massive cobalt.

The properties of nanocomposite materials with similar compositions are determined both by the synthesis conditions and post-synthesis factors. Thus, the 2.5% Co-HDPE sample obtained at a temperature of 185 K is characterized by weak magnetic properties.

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