INTRODUCTION

In studies of fullerenes, great attention is now paid to their derivatives (heterofullerenes, endohedral complexes, metallofullerenes) [1, 2], because distortions of the symmetry of fullerenes produce new physical and chemical properties [1, 3, 4]. However, obtaining these unique materials in quantities sufficient for analysis is still a complicated task. We have undertaken an attempt to synthesize metallofullerenes containing nickel and cobalt.

MATERIALS AND METHODS

Earlier we described a plasmochemical reactor for the synthesis of fullerenes in a carbon plasma jet produced by an arc discharge between graphite electrodes at frequencies in the kilohertz range [5, 6].

In [7], a technique of synthesizing iron-containing fullerene complexes was described. The central electrode has an axial hole that was filled with carbonyl iron. In the present study, a similar technique was used, except that the hole in the central electrode was filled with nickel or cobalt. Carbon condensate was deposited on the chamber walls during synthesis, and the fullerenes extracted from this with benzoil and the growth on the outer electrode (thermolysis residue [6]) were investigated by electron paramagnetic resonance using Se/X-2544 and RE1308 spectrometers in the temperature range 77 to 500 K and by electron microscopy in a JEM-100C electron microscope with an EM-ASID-4 scanning attachment and image processing equipment.

RESULTS AND DISCUSSION

1. In electron microscopic studies of the carbon condensate, particles of nickel coated with a non-conducting material (both groups of particles and isolated particles of sizes $10^3$ to $10^4$ nm) have been detected (Fig. 1). The fact that the particles were nonconducting has been established by an indirect method. The particles were placed under a microscope on a conducting (metallic) surface and irradiated with an electron beam. As a charge accumulated on the particles, a discharge via the substrate occurred. The discharge of the particles was accompanied by visually-detected radiation.

2. EPR spectroscopy detected a magnetic resonance of the metallic particles in the soot and the thermolysis residue (Fig. 2):

\[
\begin{align*}
D_H^{\text{Ni}} &= 80 \text{ mT}, \\
g^{\text{Ni}} &= 2.20 \\
D_H^{\text{Co}} &= 150 \text{ mT}, \\
g^{\text{Co}} &= 2.23
\end{align*}
\]

Similar results ($D_H^{\text{Ni}} = 100 \text{ mT}$, $g^{\text{Ni}} = 2.22$ and $D_H^{\text{Co}} = 90 \text{ mT}$, $g^{\text{Co}} = 2.23$) were obtained earlier by Bagguley [8] in experiments on the ferromagnetic resonance of metallic particles synthesized by the aerosol method in an RF arc discharge in a hydrogen atmosphere at 1 atm pressure with subsequent spinning in paraffin. The diameter of the particles was assumed to be 5–10 nm. It is known for single-domain particles of a monocrystalline metal in the absence of the skin effect that $D_H^{\text{Co}} = 11 \text{ mT}$ and $D_H^{\text{Ni}} = 12 \text{ mT}$ [9]. The large width of the electron paramagnetic resonance line in our experiments (Figs. 2a, 2b) is explained by the fact that the particles of nickel and cobalt in the soot have sizes amounting to a few millimeters. The $g$-factor values coincide with the data in [8].

Lines of EPR spectrum of the fullerene extract (Fig. 3) grouped by the types of their variation with temperature

<table>
<thead>
<tr>
<th>Line No.</th>
<th>$g$</th>
<th>$\Delta H$, mT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.001</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>2.15</td>
<td>40</td>
</tr>
<tr>
<td>3'</td>
<td>2.6</td>
<td>15</td>
</tr>
<tr>
<td>3''</td>
<td>3.6</td>
<td>15</td>
</tr>
<tr>
<td>3'''</td>
<td>3.98</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>7.7</td>
<td>13</td>
</tr>
</tbody>
</table>
A study of the synthesis products

Line 1 for \( g = 2.001 \), as well as a narrower line 2 for \( g \approx 2.15 \) (Fig. 2), are observed not only in the spectrum of the nickel-containing soot but also in the thermolysis residue and in the fullerene extract, and are discussed below.

3. In the fullerene extract, the content of nickel according to the analysis of the X-ray luminescence data was 0.02\%. Lines in the EPR spectra of the extract fall into four groups according to their temperature behavior (see table).

A narrow line 1 (Fig. 3a) for \( g = 2.001 \) usually observed in the spectra of solid fullerene mixtures [10] is due to a \( C_{60}(70) \) radical. Its shift with temperature, typical of a paramagnetic center, can be seen in Fig. 4 (1).

At \( T = 293 \) K, parameters of line 2 are \( g = 2.15 \) and \( \Delta H = 40 \) mT (Fig. 3 (2)). Raising the temperature to 510 K causes gradual narrowing of this line down to 10 mT, an increase in its intensity and a shift to higher fields (\( g = 2.08 \)). At temperatures below 293 K, the line first broadens to 70 mT (at \( T = 250 \) K) and then splits into two narrower components (at \( T = 230 \) K). At still lower temperatures, three lines are seen in the spectrum, having effective \( g \)-factor values of 2.06, 2.12, and 2.27, and the line width ~ 20 mT. At 77 K, the spectrum consists of a single asymmetric line 4 (Fig. 3b).

Fig. 1. Nickel particles in a fullerene-containing soot.