

## A New Method of the Preparation of Composite Materials Containing Nano-Sized Particles of Transition Metals

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### Abstract

The vacuum calcination of layered intercalation compounds of aluminium hydroxide containing copper, cobalt, and nickel complexes with ethylenediaminetetraacetic acid (EDTA) is demonstrated to result in the formation of composite materials containing nano-sized metal particles stable towards oxidation. The morphology of the formed products is studied by means of high-resolution electron microscopy, X-ray phase analysis and small-angle scattering; their magnetic properties are studied by means of magnetic weighing.

### INTRODUCTION

Materials containing nano-sized particles (NPs) are widely used in diverse areas of science and technology. The preparation of ultra-small metal particles and composite materials with NPs of transition metals intercalated into the matrix is of a special interest [1–6]. However, their synthesis and investigation cause the questions connected both with the control of their dimensions and with the stabilization of the resulting highly reactive NPs. We proposed the method to prepare the systems composed of the amorphous oxide matrix of lithium and aluminium containing NPs of cobalt, nickel and copper and their alloys that are thus screened from further oxidation.

The precursors used in our study were the intercalation compounds based on layered aluminium-lithium double hydroxide (LADH) containing in the interlayer space the complexes of transition metals Ni, Co and Cu with organic ligand EDTA. These intercalation compounds were synthesized for the first time. The distance between the nearest transition metal cations in the structure of these compounds is about 7–15 Å which causes diffusion hindrance

when the metal phase is formed during thermolysis. Formation of carbon in the samples during the pyrolysis of complexones helps to passivate the resulting metal NPs. The goal of the present study was the investigation of the state of metal formed during thermal decomposition of the mentioned intercalates.

### EXPERIMENTAL

Initial intercalation compounds of the composition  $[\text{LiAl}_2(\text{OH})_6]_2[\text{Medta}] \cdot p\text{H}_2\text{O}$  (further referred to as LADH-Medta where M is  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ; edta is a tetracharged anion of ethylenediaminetetraacetic acid) were obtained by the anion-exchange synthesis from  $[\text{LiAl}_2(\text{OH})_6]\text{Cl} \cdot 1.5\text{H}_2\text{O}$  according to the technique described in [7]. Final samples were obtained by the calcination of LADH-Medta compounds in vacuum at different temperatures for 2 h. X-ray diffraction patterns of powders were recorded with a DRON-4 diffractometer with  $\text{CoK}_\alpha$  radiation. Small-angle scattering was measured at the Diffraction Movies Station of the VEPP-3 accumulator ring of the Budker Institute of Nuclear Physics, SB RAS [8]. X-ray wavelength was 1.497 Å. Diffraction patterns

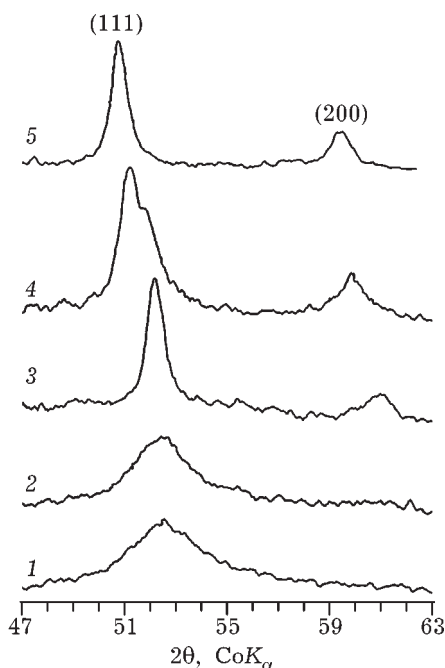


Fig. 1. X-ray diffraction patterns of LADH-Medta after calcination in vacuum at 450 °C. M = Ni (1), Ni<sub>0.56</sub>/Co<sub>0.44</sub> (2), Co (3), Co<sub>0.55</sub>/Cu<sub>0.45</sub> (4), Cu (5).

were recorded with a single-coordinate detector OD-2. The data on small-angle scattering were processed according to the technique described in [9]. Electron microscopic studies of the samples calcined at 400 and 450 °C were carried out using high-resolution electron microscopes JEM-400 and JEM-2000FXII with the scanning unit ASID-20. Magnetic properties of the products after calcination within the temperature range 300–450 °C were studied using the Faraday balance. To characterize these properties, we used the ratio of sample weight in the magnetic field of 4600 E to that in

the absence of field under strictly fixed conditions, normalized per metal content.

## RESULTS

X-ray diffraction patterns of the products of LADH-Medta thermolysis shown in Fig. 1 suggest that thermal decomposition leads to the appearance of reflections corresponding to the metals with face-centred cubic lattice including the case for cobalt (its usual structure under normal conditions is the tightest hexagonal packing). Final products were analysed by means of small-angle scattering in order to obtain the function of the distribution over distance  $p(r)$  (Fig. 2). The latter characterizes both the maximal size of the scattering centres and their shape. The distance  $r$  at which  $p(r)$  becomes zero characterizes the maximum size of the scattering centre (particle or pore). For the case of spherical scattering centre, the position of the maximum in the curve defines the radius of the centre. The peak of the finely dispersed samples observed in the  $p(r)$  curve characterizes electron density non-uniformities with maximum dimensions of about 40–50 nm. However, for the case of nickel samples, also the formation of smaller scattering centres with a characteristic size of about 5 nm is observed.

The data of electron microscopic studies are the evidence that rounded nickel NPs are formed. They are uniformly spread over the matrix volume (Fig. 3, *a*). Well-ordered strips of the grid are observed on nickel particles at a high

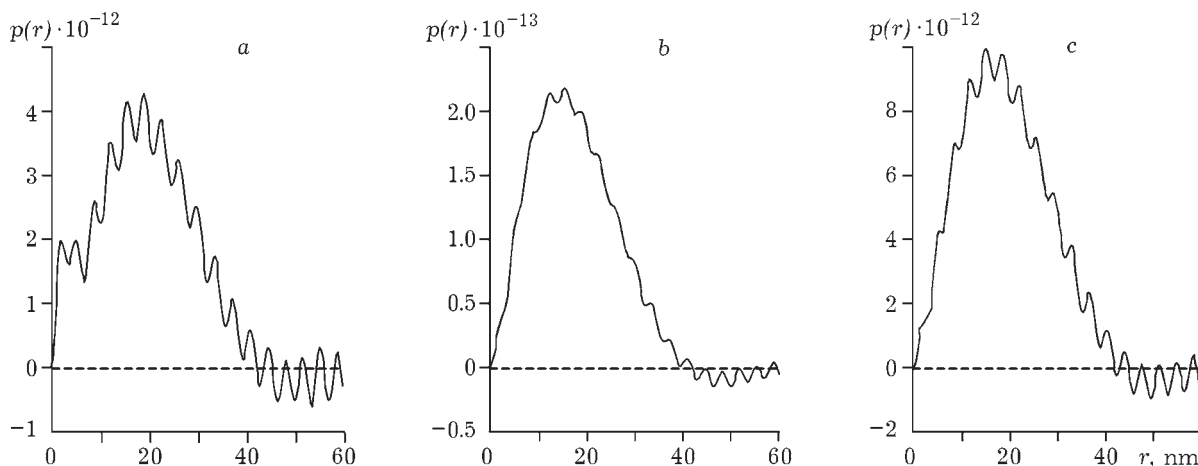


Fig. 2. Distribution functions  $p(r)$  for the LADH-Medta compounds calcined in vacuum at 400 °C. M = Ni (*a*), Cu (*b*), and Co (*c*).

resolution. The mean diameter of these particles is close to 5 nm with very narrow size distribution. The estimates of the size of coherent scattering region (CSR) made for the broadened reflection with the (111) indices (see Fig. 1) gives 3–4 nm for nickel particles. These data allow us to assume that characteristic dimensions of scattering centres, observed in the experiments on small-angle scattering at about 5 nm, are related to nickel particles. Practical coincidence between the size obtained from CSR estimates and that determined by means of electron microscopy is the evidence of the fact that the particles are well crystallized and have no internal defects. Characteristic size 40–50 nm observed in the experiments on small-angle scattering are likely to be connected with the non-uniformities of the matrix that contains X-ray amorphous aluminate and a carbon-containing product.

Thermal decomposition of the LADH-Coeda intercalate at 450 °C leads to the formation of larger cobalt NPs with the size as large as 100–150 nm (see Fig. 3, b). According to electron microscopic data, particle shapes are diverse,

depending on whether they are located on the surface of the solid phase or inside it. Metal particles located within the matrix are shaped as a lens while the particles at the surface look like triangles or hexagons when viewed from above. The estimates of CSR give ~14 nm. This is the evidence that the formed cobalt particles, as a rule, are composed of separate blocks. The presence of these blocks is also observed in transmission electron microscopic images.

Thermal decomposition of LADH-Cuedta leads to the formation of rounded copper particles (see Fig. 3, c). Their dimensions vary within rather broad range from 2–30 nm inside the X-ray amorphous matrix till 100 nm at its surface. CSR estimates give 15 nm which is close to that of cobalt and also is the evidence of the block character of coarse copper particles. This is confirmed by electron microscopic data. Similar character of small-angle scattering observed for the thermolysis products of cobalt- and copper-containing intercalates allows us to assume the similarity of size distribution for both the copper and nickel particles, and for their X-ray amorphous matrices.

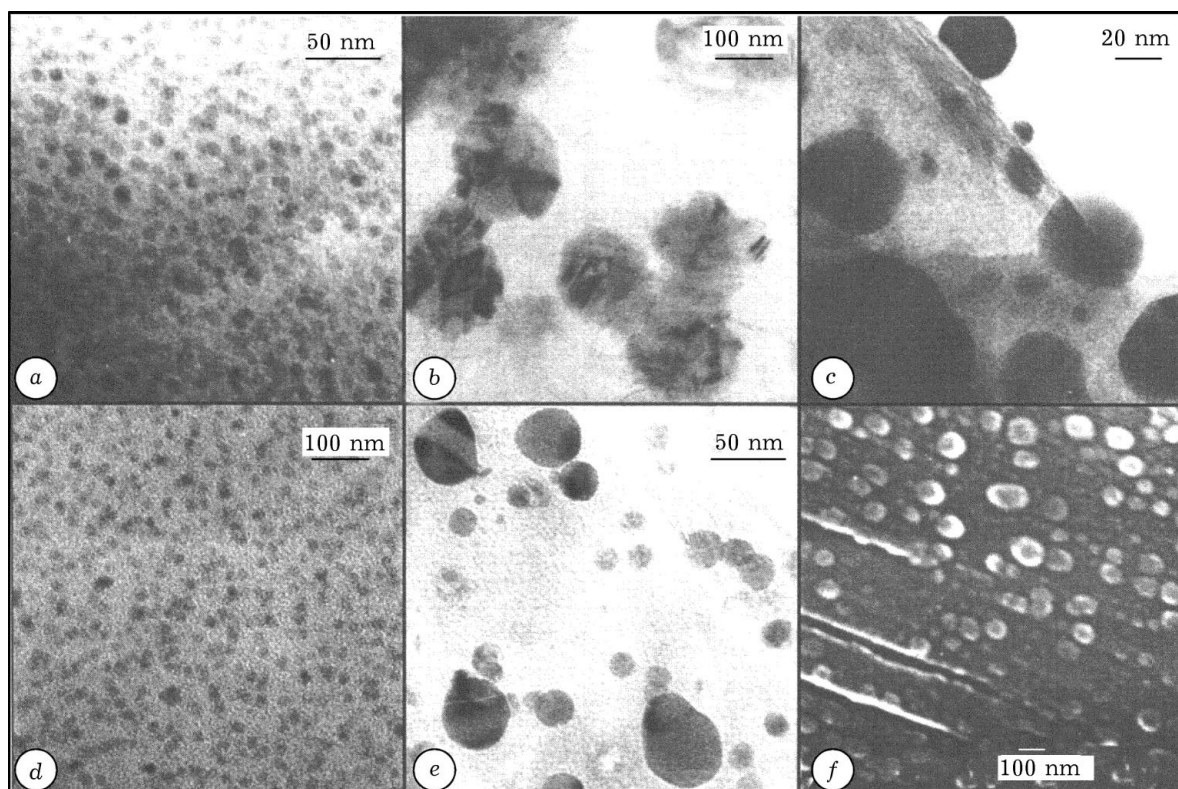


Fig. 3. Electron microscopic photographs of the products of thermal decomposition in vacuum, for the compounds LADH-Medta. M = Ni (a), Co (b), Cu (c),  $\text{Ni}_{0.56}/\text{Co}_{0.44}$  (d),  $\text{Co}_{0.55}/\text{Cu}_{0.45}$  (e and f). Treatment temperature, °C: 400 (a and c), 450 (b, d, e, and f). The image f was obtained under scanning regime.

Thermal decomposition of LADH-Cu<sub>0.45</sub>Co<sub>0.55</sub>edta and LADH-Ni<sub>0.56</sub>Co<sub>0.44</sub>edta compounds incorporating two transition metals also leads to the formation of NPs. The size of the rounded particles of the copper-cobalt product is 5–35 nm inside the matrix and up to 100 nm on its surface (see Fig. 3, *d* and *e*). Most probably, these particles are not a solid solution of these metals that have a positive heat of mixing but are formed by individual metals. In the transmission-type photos one can see prolonged ovals that look like couples of particles soldered together. According to X-ray phase analysis data for the LADH-Cu<sub>0.45</sub>Co<sub>0.55</sub>edta calcined at 450 °C, the (111) is a compound reflection; its two summits are located between the corresponding reflections of pure cobalt and copper. An interesting result was obtained for the nickel-cobalt system in which the formed NPs of the solid solution of these metals have a size of about 10 nm and the morphology close to that of individual nickel but not cobalt (see Fig. 3, *d*). Estimated CSR size of the (111) reflection is 4 nm (see Fig. 1).

Preliminary experiments aimed at the investigation of the magnetic properties of nickel- and cobalt-containing products obtained at different temperatures revealed a correlation between the existence of ferromagnetic properties and the size of the observed metal particles. As Fig. 4 shows, with increasing calcination temperature, magnetic properties of metal-containing products increase. For example, calcination of cobalt-containing samples at temperatures up to 400 °C results in X-ray amorphous products exhibiting no ferromagnetic

properties, while the calcination at temperatures above 400 °C results in the products exhibiting metal cobalt in their X-ray diffraction patterns, and the force of the interaction with magnetic field increases sharply. The latter fact can be due to the increase in the size of cobalt particles. A similar picture is observed for the nickel-containing samples in which ferromagnetic properties are exhibited starting from 350 °C (a point at which metal nickel is registered by means of X-ray diffraction studies). An increase of calcination temperature does not cause a noticeable increase in the size of nickel particles: according to CSR data, their mean size increases from 3 to 4 nm, which is likely to be due to the improvement of their crystallinity. This may be also a possible reason of insignificant increase in ferromagnetic properties of the sample. As Fig. 4 shows, the products of LADH-Cu<sub>0.45</sub>Co<sub>0.55</sub>edta and LADH-Ni<sub>0.56</sub>Co<sub>0.44</sub>edta calcination at 450 °C also possess ferromagnetic properties.

#### DISCUSSION OF THE RESULTS

These data allow us to present a possible scheme of the formation of nanoparticles of transition metals during the thermolysis of intercalation compounds. The structure of these compounds includes alternate layers composed of [LiAl<sub>2</sub>(OH)<sub>6</sub>]<sup>+</sup> and the layers containing [Medta]<sup>2-</sup> anions and 4 water molecules [10]. In the [Medta]<sup>2-</sup> complex anion, four oxygen atoms of carboxylic groups and two nitrogen atoms of the ethylenediaminetetraacetic acid anion form the nearest surroundings of the transition metal ions. The rest 10 carbon atoms, 4 oxygen atoms, and 10 hydrogen atoms of the complexone form a kind of shell around them. At the first stage of thermolysis at temperatures up to 200 °C, four water molecules are removed from the interlayer space of the intercalation compound [11]. This process is accompanied by the decrease of interlayer distance by about 2 Å which can be due to the re-orientation of [Medta]<sup>2-</sup> anions with respect to aluminium-hydroxide layers, or due to the removal of additional water sublayer from the interlayer space. Further increase of temperature leads to the destruction of hydroxide layers and

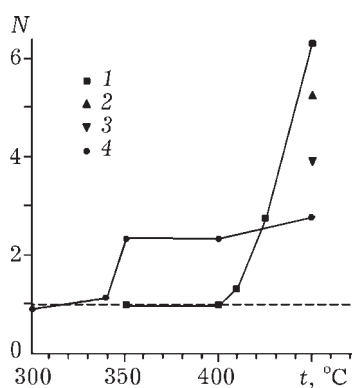


Fig. 4. Relative changes in the magnetic properties of LADH-Medta samples calcined in vacuum at different temperatures ( $N = m_2/m_1$  where  $m_1$  and  $m_2$  are the weight of the sample in the absence of magnetic field and in a field of 4600 E, respectively): 1 – Co, 2 – Co/Ni, 3 – Co/Cu, 4 – Ni.



to redox processes connected with the reduction of transition metal cations to metal atoms and decarboxylation of the complexonate keto-groups. The residual carbon atoms, as well as oxygen and nitrogen atoms, can surround metal atoms rather tightly, thus preventing them from aggregation into larger particles. The processes of metal coagulation are also inhibited by X-ray amorphous lithium aluminates formed during the decomposition of the matrix. Further increase of temperature leads both to the decomposition of the organic residue accompanied by the release of nitrogen in the form of ammonia, and to the increase in diffusion mobility of metal atoms, which helps increasing the size of metal particles.

The difference in particle size of intercalates is likely to be connected with the fact that decarboxylation in LADH-Cuedta and LADH-Coedta takes place simultaneously with the destruction of the hydroxide layer [11]. This circumstance is likely to simplify the aggregation of metal particles. In the case of LADH-Niedta, decarboxylation and reduction of the transition metal ions occur at higher temperatures (320–340 °C) than the start of hydroxide layer destruction (>200 °C). Dehydroxylation of the matrix and the recovery of metal occur at essentially different time moments, so the products of hydroxide packet destruction prevent nickel atoms from approaching each other. This is likely to result in the formation of smaller NPs. In order to explain the morphology of metal particles formed during the thermal decomposition of intercalates containing couples of metals, a more detailed study of these processes is necessary.

## CONCLUSION

Experimental data reported in the present paper are the evidence of the possibility to use

intercalation compounds of aluminium hydroxide containing the complexes of transition metals for the preparation of systems containing screened nano-sized particles of transition metals. The carbon-rich matrix provides a successful protection for NPs. This is confirmed by the fact that metals in final products are not oxidized by the oxygen of the air; even after being kept in nitric acid they exhibit the conservation of particles in the matrix volume and their removal from its surface. The morphology of the formed metal particles and their size distribution depend on the chemical composition of the initial intercalation compound. This allows one to govern the size of the resulting metal nanoparticles in a broad range which can be applied for practical purposes.

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