Synthesis and characterization of cobalt nanoparticles, nanowires and their composites

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Abstract

Cobalt (Co) nanoparticles in amorphous and crystalline state were synthesized at room temperature and atmospheric pressure by chemical reduction in aqueous solutions of Co salts with NaBH₄. Two types of reactors were used ensuring various hydrodynamic conditions of mixing for both solutions (CoSO₄·7H₂O solution and NaBH₄ solution). From the synthesized Co nanoparticles and micronized AlN powder (10-30 mass %) were prepared composites by pressing and sintering in the temperature range from 550 °C to 750 °C for a potential application as getters or catalysts. Co nanowires were synthesized also by reduction in the presence of SiO₂, SiMCM, and AlMCM supports. The content of B, H₂, and O₂ by elemental analysis of nanoparticles and their specific surface area by BET method were determined. Some physical-mechanical properties such as density and electroconductivity of nanoparticles and their composites with AlN heat treated in 200 °C to 850 °C range were measured. IR spectroscopic studies of synthesized nanostructures were carried out by FTIR in 4000 to 400 cm⁻¹ frequency range, as well as SEM micrographs of the Co nanowires were made which allow determining their diameters.

Key words: chemical reduction with NaNH₄, Co nanoparticles, Co nanowires, supports, AlN nanocomposites, BET method, IR spectroscopy, SEM.

1. Introduction

The preparation of nanosized materials and their characterization corresponds to the expectation of the 21-th century to join up the macro-, micro- and nanotechnologies for the reason of the higher integration of the electronic components. Nanoparticles, nanowires, nanotubes, nanorods of various materials exhibit interesting and remarkable properties (optical, electric, magnetic and mechanical) due to their quantum size resulting of quantum-size effects which differ from the bulk materials properties. This determines the world tendencies for the intensive development of methods for synthesis of nanostructural materials and their characterization [1,2].

The aim of the paper is to synthesize metal amorphous and metal nanoparticles in aqueous solutions and metal nanowires using various supports [3,4], as well as to characterize the structure, the specific surface area (SSA), the composition and some parameters of the nanostructures using SEM [3,5], BET [8], XRD [3], XPS [5], IR spectroscopy in 4000 to 400 cm⁻¹ frequency range [4,6] from a point of view for an application of these nanomaterials as getters and catalysts using the nanostructures higher developed SSA.

2. Experimental details

Co nanoparticles are prepared by chemical reduction in aqueous solutions of CoSO₄·7H₂O with NaBH₄. Two types of reactors performing at different hydrodynamic conditions are used for mixing CoSO₄·7H₂O and NaBH₄ solutions. Amorphous Co nanoparticles in a reactor of ideal mixing conditions (T-method) and Co nanoparticles with crystalline structure in a reactor ensuring an ideal displacement regime (A method) are synthesized at room temperature and atmospheric pressure.

The nanoparticles are pressed at loading pressure P = 10 MPa and sintered at low (200 to 400 °C) and high temperatures (500 to 850 °C) in a quartz reactor in a pure N₂ stream (5N). Composites with amorphous and crystalline nanoparticles and micronized AlN as 10 to 30 mass % additions are pressed and sintered at temperatures higher than 550 °C. The pressing was done with an automatic press with a diameter of the press form 6 mm at a loading pressure of 1000 kg/cm² for the amorphous nanoparticles and 300 kg/cm² for the crystalline nanoparticles.

IR spectra of amorphous and crystalline nanoparticles and their composites with 10 to 30 mass % micronized AlN – powder are recorded. The FTIR spectroscopic investigations were carried out with EQUINOX 55 spectrophotometer with Fourier transformation of “Brucker”, Germany in 4000 to 400 cm⁻¹ frequency range. The samples are prepared in the form of tablets with a diameter of 13 mm mixing 1 mg of the specimen and 200 mg KBr (“Spectral purity”) in a special press-matrix under vacuum and a pressing load at 8 tons/cm².

SSA of the amorphous and crystalline nanoparticles is determined by the BET method using AREA meter, Strohlein in a stream of nitrogen at temperature of 78 K. The boron content (mass %) in the samples is titrimetrically determined, and those of hydrogen and oxygen are determined by vacuum melting with “Exhalograph -EA1”.

Co nanowires are obtained using various ceramic supports (SiO₂, SiMCM, and AlMCM) with different SSA (SSA (SiO₂) = 189 m²/g, SSA
The synthesized Co nanowires are characterized by SEM and AFM. To determine the morphology and the size of the nanowires SEM micrographs were made using scanning electron microscope TEM JEM 200 CX JEOL - Japan with a scanning appliance ASID 3D. The image was recorded under conditions of secondary emissions under vacuum 10⁻⁷ Torr and accelerating voltage 100 kV. AFM characterization of the nanowires is a non contact force mode (NCF).

3. Experimental results

The prepared by the T–method Co nanoparticles are black on a view and amorphous, while the nanoparticles prepared by the A-method are gray on a view and crystalline [8].

Data referring to the content of B, H₂ and O₂ in Co nanoparticles and their SSA are presented in Table 1.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Amorphous nanoparticles</th>
<th>Crystal nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>B, mass %</td>
<td>5.50 - 7.50</td>
<td>6.90 - 8.20</td>
</tr>
<tr>
<td>H₂, mass %</td>
<td>0.20 - 0.53</td>
<td>0.26 - 0.63</td>
</tr>
<tr>
<td>O₂, mass %</td>
<td>5.60 - 13.70</td>
<td>7.32 - 10.8</td>
</tr>
<tr>
<td>SSA, m²/g</td>
<td>8 - 14</td>
<td>2.25 - 2.50</td>
</tr>
</tbody>
</table>

The amorphous nanoparticles are characterized with higher developed SSA and smaller size respectively compared to the crystalline nanoparticles which results from different conditions in the synthesis reactors used.

After the treatment at constant temperature (200 to 850°C) the volume of the amorphous nanoparticles samples decreases as a result from packing during the sintering due to the occurrence of solid phase crystallization processes of conversion and new phases (Co₂B, Co₂B and Co) formation (density increases from 2.75 to 5.50 g/cm³).

In the same temperature range the crystalline nanoparticles vary their densities diversely. From 200 to 500°C they do not change their volumes (the density is with an almost constant value of 1, 80 g/cm³). Above 500°C the density increases reaching a maximal value at 550°C (2, 50 g/cm³). At temperatures from 600 to 850°C the density decrease resulting from solid phase recrystallization processes of the type:

\[ Co₂B + Co \rightarrow Co₃B. \]

After thermal treatment at constant temperature the AlN composites with amorphous or crystalline nanoparticles change their density diversely depending on the content of the AlN.

In Table 2 are presented data of some physical parameters of AlN composites of amorphous nanoparticles heat treated at 700°C. Their density decrease and they become more porous after thermal treatment from 550 to 850°C when AlN mass % increase (Table 2).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>10 mass % AlN</th>
<th>20 mass % AlN</th>
<th>30 mass % AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>4.304</td>
<td>4.030</td>
<td>3.726</td>
</tr>
<tr>
<td>Resistance, mΩ</td>
<td>28</td>
<td>30</td>
<td>28.5</td>
</tr>
<tr>
<td>Specific resistance, mΩ.mm</td>
<td>0.0347</td>
<td>0.0354</td>
<td>0.0285</td>
</tr>
</tbody>
</table>

The density of the AlN composites of crystalline nanoparticles treated at the same temperatures increases with the content of AlN too and is due to a change in the lattice parameters and samples shrinkage resulting from the occurring recrystallization processes.

Such a variation of the properties of amorphous and crystalline nanoparticles and their composites with AlN during the heat treatment by reason of the occurring physical-chemical processes and their structural variation are confirmed by XRD analysis in previously published papers [5].

3.1. IR spectroscopic studies of the amorphous and crystalline nanoparticles and their composites with AlN

IR spectra of the amorphous nanoparticles treated from 200 to 500°C are characterized with not clear determined or broad bands of absorption in 1500 - 500 cm⁻¹ frequency range [5, 10]. Above 500°C sharp absorption bands with distinctly outlined peaks appear defined by the stretching vibrations of B-O bonds in BO₃ and BO₄ groups or in B-O radicals as boroxol rings, di-, three-, and tetraborate units [8-10].

In IR spectra of AlN composites of amorphous nanoparticles heat treated from 550 to 700°C at lower frequencies (950-650 cm⁻¹) appear absorption bands characteristic for the stretching vibrations of Al-O bonds in Al₂O₃ tetrahedra and AlO₆ octahedra.

IR spectra of crystalline nanoparticles and their AlN composites treated at 200 to 700°C are shown in Figures 1-6.

The absorption bands are well outlined – broad at low temperatures from 200 to 500°C with peaks at 1150, 750, and 480 cm⁻¹ (Fig.1), but sharper at higher temperatures (above 500°C) with bands more intensive and peaks shifted towards the higher frequencies at 1200, 800 and 500 cm⁻¹ (Fig.2).

In 1300 - 1000 frequency range the bands are characteristic for stretching asymmetric vibrations ν₃(BO₃) mode of B-O bond in BO₃ groups forming a boroxol ring (BO₃)x, with three non-bridging oxygen atoms. In 900 - 500 cm⁻¹ frequency range the bands characterize stretching vibrations of B-O bonds in BO₄ groups connected by oxygen to BO₃ groups or forming borate rings. The vibrations at 750 cm⁻¹ are symmetric stretching ν₁(BO₄) mode of B-O bonds, while at 480 - 430 cm⁻¹ they are deformation

\[ ν₁(BO₄). \]
vibrations of B-O-B bonds $\nu_4(BO_4)$ mode in various borate groups.

Fig. 1. IR spectra of crystalline nanoparticles at 30 °C

In Figs. 3-4 IR spectra of crystalline nanoparticles and their AlN composites treated at 550 °C are presented, while in Figs. 5-6 IR spectra of the same crystalline nanoparticles and their composites are shown but heat-treated at 700 °C.

Fig. 3. IR spectrum of crystalline nanoparticles at 550°C

When the content of AlN grows the absorption bands at higher frequencies become less defined and with not clear outlined peaks. The absorption band of the crystalline nanoparticles (Fig.3) and composites containing 10 mass % AlN (Fig.4,a) at 750 cm$^{-1}$ is with a lower intensity and completely disappears for 20 and 30 mass % AlN composites (Fig. 4, b). This band at 750 cm$^{-1}$ characterizes the symmetric stretching vibrations of B-O bonds in triborate unit with one BO$_4$ group.

Such a behavior of the composites at 550°C is completely logical. AlN contains 0.20-0.26 mass % H$_2$ [10]. At 550°C H$_2$ desorbs and Al remains bonded to N$_2$. This temperature is insufficient for Al to be in oxidized form as AlO$_4$ tetrahedra or AlO$_6$ octahedra. H$_2$ desorbed reduces BO$_4$ groups to BO$_3$ groups, which is confirmed by IR spectra in Fig. 4.

AlN has bands in 800 – 600 cm$^{-1}$ frequency range with a peak at 740 cm$^{-1}$ characterizing the stretching vibrations of Al-N bond. At lower frequencies the composites treated at 550°C independent on the AlN quantity show weak bands which are related to the stretching vibrations of B-O bonds in BO$_3$ groups.

IR spectra in Figs. 5-6 of nanoparticles and their composites treated at 700°C are characterized with sharp bands and well outlined peaks. The observed bands are typical for the stretching vibrations of B-O bonds in BO$_3$ groups (at 1300 - 1200 cm$^{-1}$, 750 -650 cm$^{-1}$) and in BO$_4$ groups (1000 – 750 cm$^{-1}$ and 650 – 400 cm$^{-1}$).

The bands in 800 to 650 cm$^{-1}$ range are related to stretching vibrations of Al-O bonds in AlO$_4$ tetrahedra, while those in 650 to 500 cm$^{-1}$ range are typical for stretching vibrations in AlO$_6$ oktahedra (at 700°C Al is oxidized in the form of AlO$_4$ or AlO$_6$).

The higher content of AlN increases AlO$_4$ and AlO$_6$ groups respectively, whose absorption bands overlay the absorption bands of BO$_4$ groups at lower frequencies, and a variation of boron coordination occurs from 3(BO$_3$) to 4(BO$_4$) with active asymmetric stretching $\nu_3(BO_3)$ vibrations.

The higher content of AlN increases AlO$_4$ and AlO$_6$ groups respectively, whose absorption bands
wires and similar anisotropic by shape formations respectively obtained by using the above mentioned supports.

The application of various supports with higher developed SSA at equal metal/support ratio predetermines the preparation of nanowires with increasing diameter respectively for SiO₂ supports 80 nm by SEM and in the range from 80 to 100 nm by AFM, for SiMCM supports 115 nm by SEM and from 115 to 140 nm by AFM, and for AlMCM supports 142 nm by SEM and 132 nm by AFM.

Conclusion

The variation of the physical and mechanical parameters of Co amorphous and crystalline nanoparticles and their AlN composites as a function of temperature and AlN quantity are investigated in terms of their application as getters and catalysts. By using the suitable technological regime of thermal treatment at constant temperature the density and the relation of surface/volume could be optimized for application of the nanomaterials in preparing of getters mixing with AlN powder.

IR spectroscopic studies of these nanostructures allow optimizing the chemical composition of the getters after the thermal treatment.

Co nanomaterials anisotropic by shape are not suitable for use as catalysts because of their less SSA in comparison with the SSA of spherical nanoparticles with the same composition.

SEM and AFM investigation methods for these nanozised materials anisotropic by shape are comparable and give the relative and near results measured for the diameter of nanowires.

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References