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Cobalt nanoparticles processed by thermal decomposition of metal-containing monomers

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Polymer matrix ferromagnetic nanocomposites, containing Co nanocrystallites, were processed by an innovative fabrication method that uses the frontal polymerisation of cobalt acrylamid complexes, followed by subsequent thermolysis at 873 and 1073 K. The thermolysis products were in the form of irregular powder particles, with a broad size distribution, from 10 up to 300 μm. The powder particles contained nanocrystallites of Co with a mean size in the range 12–15 nm, depending on the thermolysis temperature. The hysteresis loops recorded for materials processed at 873 and 1073 K proved that coercivity depends on the processing temperature and very slightly on the measurement temperature. The thermolysis product, processed at 873 K, showed soft magnetic properties. The particles were randomly distributed and their size and agglomeration could be controlled by the processing variables.

Key words: cobalt nanoparticles; ferromagnetic nanocomposite; magnetic nanostructure

1. Introduction

Nanoparticles exhibit unique physical properties due to surface or quantum-size effects. Particular attention has recently been focused on magnetic nanoparticles and substantial progress has been achieved in this field. This is mainly due to advances in processing methods and the development of characterization techniques. Substantial achievements in the field made it possible to produce metallic or oxide particles embedded in various organic or inorganic matrices. In those systems, such phenomena as

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giant magnetoresistance, a strong magnetocaloric effect and many others have been found. The composites containing cobalt nanoparticles focus particular attention due to their potential applications in high-density digital magnetic recording. As a principle, the magnetic recording material should combine ferromagnetic particles of sufficiently high coercivity to prevent demagnetisation, uniformly distributed in a non-magnetic matrix. Magnetic Co nanoparticles have been investigated in a number of works [1–10]. A general conclusion, however, is that their properties strongly depend on the processing method and parameters applied.

Generally, all processing techniques base on the idea of encapsulating metallic nanoparticles in a protective stabilising preventing their oxidation. The material most often employed is carbon, however polymeric insulating layers are also very common. Recently, spherical cobalt nanoparticles, encapsulated in carbon shells with the sizes of 10–100 nm, were prepared using arc discharge between carbon electrodes in a He atmosphere, with the anode filled with cobalt [11]. Boron and cobalt powders were exposed to a mixture of H_2 and NH_3 gases at 1073 K for 3 hours in order to prepare 20–60 nm Co particles, covered with 5 nm thick BN layers [12]. Widely used is also the deposition of Co nanoparticles on substrates. An example of this method is low--energy cluster beam deposition (LECBD), which was applied for the preparation of 3 nm Co nanoparticles on niobium foil [13]. One of the most promising routes for processing nanomaterials with stable structures and properties is nanoparticle synthesis in various matrices. Using this method, self-aggregated nanoparticles of Co in perfluorinated sulfo-cation membrane were prepared by the ion-exchange method. The Co crystallites had a mean radius of 3.8 nm and exhibited superparamagnetic properties with a blocking temperature between 800 and 300 K, depending on the Co concentration [14]. Particles 4 nm in radius were also obtained by thermal decomposition of Co formate in a polyethylene melt in mineral oil. In this case, the blocking temperature was above 600 K [15]. This fact points to a substantial influence of the processing method and resulting concentration of particles, their shape, agglomeration, etc. on physical magnetic properties. An extended review of the processing methods used for Co nanoparticles can be found in [16].

In the current study, nanocomposites containing Co nanoparticles were prepared by frontal polymerisation of acrylamide (AAm) monomers and subsequent thermolysis. This process generally comprises three stages: (i) the formation of an AAm metal nitrate complex by replacing the water of crystallization in crystal hydrates by AAm molecules, (ii) frontal polymerisation of acrylamide monomers, (iii) conversion of the polymer into a nanocomposite by thermolysis. In the last stage, nanoparticles of metals or their oxides, embedded in a stabilizing polymer matrix, are formed.

2. Experimental

The acrylamide metal nitride complex, $[Co(CH_2{=}CHCONH_2)_4(H_2O)_2]^{2+}$, was obtained by a substitution reaction of crystalline inorganic hydrate by acrylamide. Frontal polymerisation of the Co acrylamide complex was carried out at atmospheric pressure and in air. The initiation temperature was 433 K, and further polymerisation occurred at 483 K, with the front velocity equal to $4.8 \cdot 10^{-2}$ cm/s. The process of frontal polymerisation is accompanied by melting of the monomer. The melting and formation of the polymer matrix promote the encapsulation of nitrite groups and prevent their further decay.

Co-containing nanocomposites are formed in the process of thermolysis of the polymeric matrix. The thermolysis was carried out in a self-generated atmosphere at temperatures of 873 K and 1073 K. The procedures applied to the specimens are summarized in Table 1. The thermolysis products were cooled slowly in the reactor to room temperature. The solid products, formed during thermolysis, consisted of cobalt nanoparticles and an amorphous matrix which protected the metal crystallites from oxidation. EDS analysis of the amorphous matrix revealed the presence of carbon, nitrogen, and oxygen atoms. Further studies of this product are in progress. A more detailed description of the processing route, as well as the products, can be found in [17].

Table 1. Characteristics of the studied specimens

Specimen number	Processing history
1	acrylamide complex formation – monomer
2	acrylamide complex formation – monomers; frontal polymerisation of the monomer
3	acrylamide complex formation – monomers; frontal polymerisation of the monomer thermolysis of the polymer at 873 K for 95 min
4	acrylamide complex formation – monomers; frontal polymerisation of the monomer thermolysis of the polymer at 1073 K for 120 min

The structures of the materials after all processing stages were studied using X-ray diffraction (Philips X-pert, Cu-Kα). The crystallite size was evaluated from the line broadening of the X-ray peaks using the Scherrer method. The microstructure was studied with a Hitachi S-3500N scanning electron microscope and high resolution JEM 3010 transmission electron microscope. The hysteresis loops were recorded at temperatures of 50, 100 and 250 K using a Faraday balance. Zero-field-cooled (ZFC) and field-cooled (FC) magnetisation curves were studied versus temperature in the field of 5×10^{-3} T.

3. Results and discussion

Acrylamide monomers of Co (II) exhibit a complex crystalline structure (Fig. 1a), composed of octahedral cations $[\mathrm{Co(CH_2{=}CHCONH_2)_4(H_2O)_2}]^{2+}$ of $\bar{1}$ symmetry and $\mathrm{NO_3^-}$ anions interconnected by a system of hydrogen bonds [19].

After frontal polymerisation, the colour of the specimen changed from pink to dark cherry. The process led to the decomposition of the crystalline structure and amorphisation of the material (Fig. 1b), accompanied by a mass loss. It is believed that the starting monomers initially lose one water molecule, leading to the hydrate. The loss of a second water molecule promotes the formation of the anhydrous phase and finally the polymerisation of the material [17].

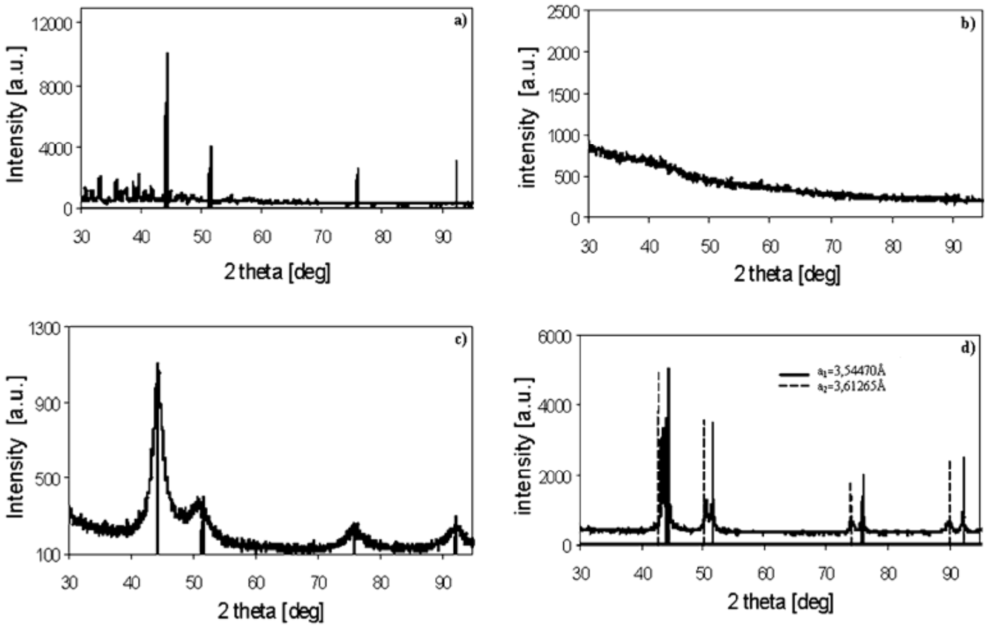

Fig. 1. X-ray patterns of: a) $[Co(CH_2{=}CHCONH_2)_4(H_2O)_2]^{2+}$ complex, (specimen 1), b) the material after frontal polymerisation (specimen 2), c) the material after thermolysis at 873 K (specimen 3), d) the material after thermolysis at 1073 K (specimen 4)

The thermolysis dramatically changes the structure of the material. Distinct crystalline reflections appeared in the pattern. The spectra obtained at various thermolysis temperatures were somewhat different, however. The diffraction pattern for the specimen thermolysed at 873 K matched well the FCC cobalt lines, with the lattice parameter a_1 = 3.54470 Å (Fig. 1c). The material thermolysed at 1073 K showed two coexisting types of metallic cobalt, both having a FCC structure, with lattice parameters a_1 = 3.54470 Å and a_2 = 3.61265 Å, respectively (Fig. 1d). The formation of FCC cobalt nanocrystallites has been reported by several authors [20, 21].

Thermolysis products were in the form of irregular powder particles exhibiting high porosity and a broad distribution of sizes, ranging from 10 to 300 μm (Fig. 2).

TEM images gave a more detailed insight into the microstructure and morphology of the nanocomposites (Fig. 3). The crystallites obtained at the thermolysis temperature of 873 K showed individual spherical particles with a quite uniform size distribution between 12 and 15 nm. Increasing thermolysis temperature resulted in a partial coarsening of the microstructure, which led to the appearance of some amount of large crystallites (over 20 nm) present together with small 12 nm particles.

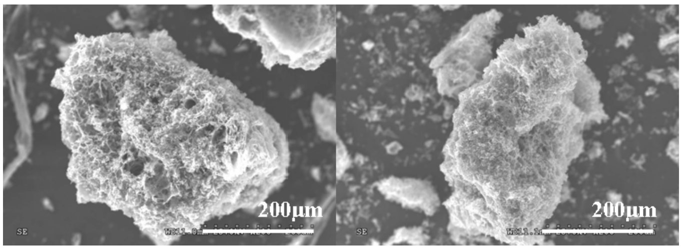

Fig. 2. SEM microstructures of powder particles obtained by thermolysis of frontally polymerised monomers (specimen 3)

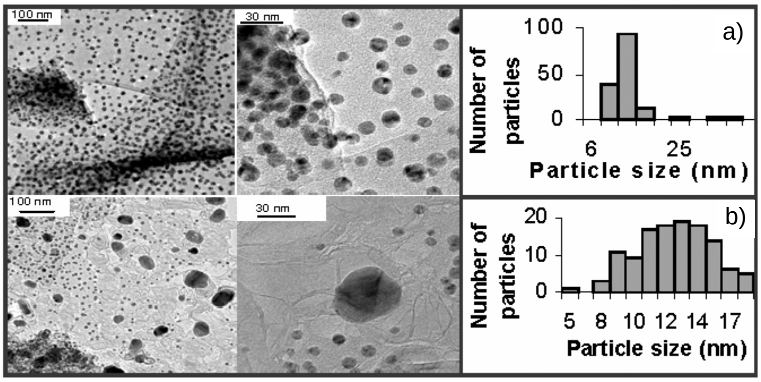

Fig. 3. TEM microstructures of nanocomposites obtained by thermolysis of frontally polymerised material at different temperatures: a) 873 K (specimen 3) and b) 1073 K (specimen 4)

The crystallites are embedded in a matrix consisting mostly of carbon which protects them from oxidation. The structure of the matrix is currently under investigation.

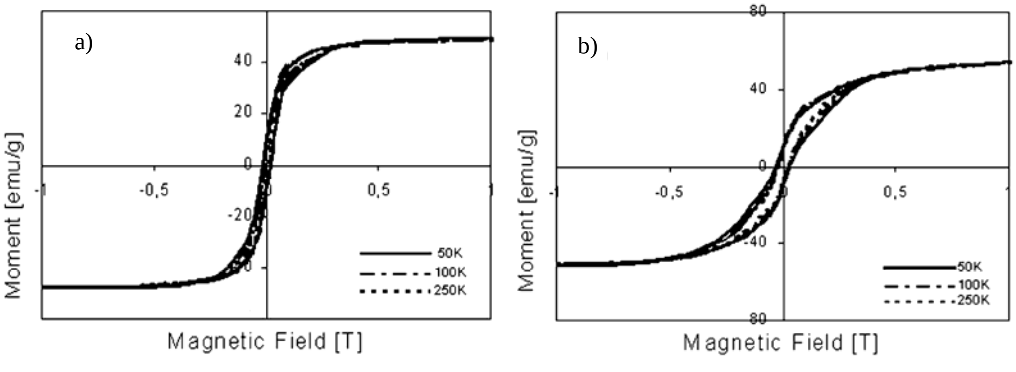

Fig. 4. Hysteresis loops of the nanocomposites after frontal polymerisation and thermolysis at: a) 873 K (specimen 3), b) 1083 K (specimen 4)

The hysteresis loops recorded at 50, 100, and 250 K are shown in Figure 4. The loops are closed and symmetrical with respect to the origin of the coordinate system. The shape of the loops evidences the ferromagnetic character of the material. No evidence of superparamagnetism was observed. The coercivity depends on the measurement temperature and very slightly decreases with increasing temperature. At room temperature, the material thermolysed at 873 K showed soft magnetic properties with a coercivity of 0.01 T. A somewhat higher coercivity was observed for the material thermolysed at 1023 K. This may be related to the formation of two crystallographic forms of cobalt, differing in their lattice constants and magnetic anisotropy field. The remanence could not be measured accurately, because the specimens were compacted with additional resin.

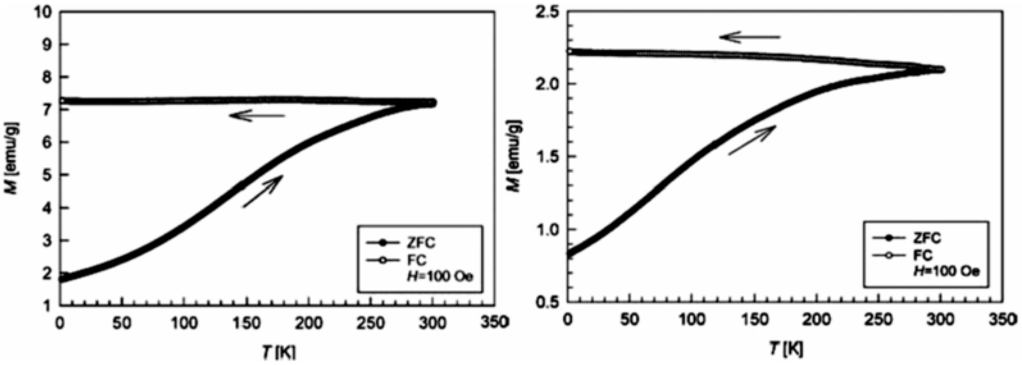

Fig. 5. ZFC and FC curves versus temperature for nanocomposites obtained by thermolysis of frontally polymerised material at different temperatures: a) 873 K (specimen 3), b) 1073 K (specimen 4)

In Figure 5, the zero-field-cooled (ZFC) and field-cooled (FC) magnetisation curves as a function of temperature, taken in the field of 5×10^{-3} T, are presented. Both dependences look similar and the magnetisations of the FC curves are almost independent of temperature. The magnetisation of the ZFC curves increases with increasing temperature, however no distinct maximum representing a blocking temperature is seen. The ZFC and FC magnetisation curves show irreversibility up to 300 K, but their shapes are characteristic of a system dominated by interparticle interactions rather than superparamagnetism.

4. Conclusions

Cobalt nanoparticles with a mean size in the range 12–15 nm can be prepared by the frontal polymerisation and thermolysis of acrylamid cobalt nitrate complex. The particle size strongly depends on the thermolysis temperature. The application of this procedure stabilizes the nanostructure, enables spherical nanoparticles to be processed within a narrow window of sizes, and protects the crystallites from oxidation. The particles exhibit ferromagnetic properties. Their room temperature coercivity depends on the thermolysis temperature, and higher temperatures result in higher coercivity. The magnetic behaviour of the nanocomposites is dominated by interparticle dipolar interactions.

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