

# STRUCTURE AND PROPERTIES OF MAGNETIC NANOPARTICLES PROCESSED BY PYROLYSIS OF POLYMERS CONTAINING Co AND Fe

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**Abstract.** Nanocomposites consisting of ferromagnetic nanoparticles embedded in an inorganic matrix were fabricated by a method comprising frontal polymerisation of cobalt or iron acrylamide complexes, followed by pyrolysis of the polymers at a temperature 873K. The pyrolysis products are in a form of irregular powder particles containing embedded nanocrystallites of elementary cobalt and iron carbide for the pyrolysed polymers containing cobalt and iron, respectively. The particles were randomly distributed and their size and agglomeration can be controlled by the processing variables. The particles exhibited ferromagnetic properties. Their room temperature coercivity depends on the composition and pyrolysis temperature. The material does not exhibit a superparamagnetic behaviour.

## 1. INTRODUCTION

Several methods have been developed for the processing of nanoparticles in a polymeric matrix. Among them a method which comprises processing of a monomer complex, followed by frontal polymerisation and subsequent pyrolysis of the polymer seems especially promising. Frontal polymerisation, which enables conversion of monomer to polymer in the localized reaction zone, was first described in 1970-ties [1]. Currently application of the frontal polymerisation and study of its kinetics, and dynamics is widely exploited [2]. Among the advantages of frontal polymerisation one can mention: high reaction rate, short reaction time, low energy consumption and the possibility of conducting polymerisation in an ecologically friendly way, without additional solvent.

In the current study the nanocomposites were prepared by frontal polymerisation of cobalt and iron acrylamides followed by subsequent pyrolysis. Structure and magnetic properties of the nanocomposites were evaluated and discussed.

## 2. EXPERIMENTAL

The acrylamide metal nitrate complexes:  $\text{Co}(\text{NO}_3)_2(\text{AAm})_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_2(\text{AAm})_4 \cdot 2\text{H}_2\text{O}$  were obtained by substitution reaction of crystalline inorganic hydrates by the appropriate acrylamides. The complexes were subjected to frontal polymerisation. The metal containing nanocomposites were formed in the process of pyrolysis of the polymeric matrix. The pyrolysis was carried out at 873K. More detailed description of the processing route can be found in [3]. Structure

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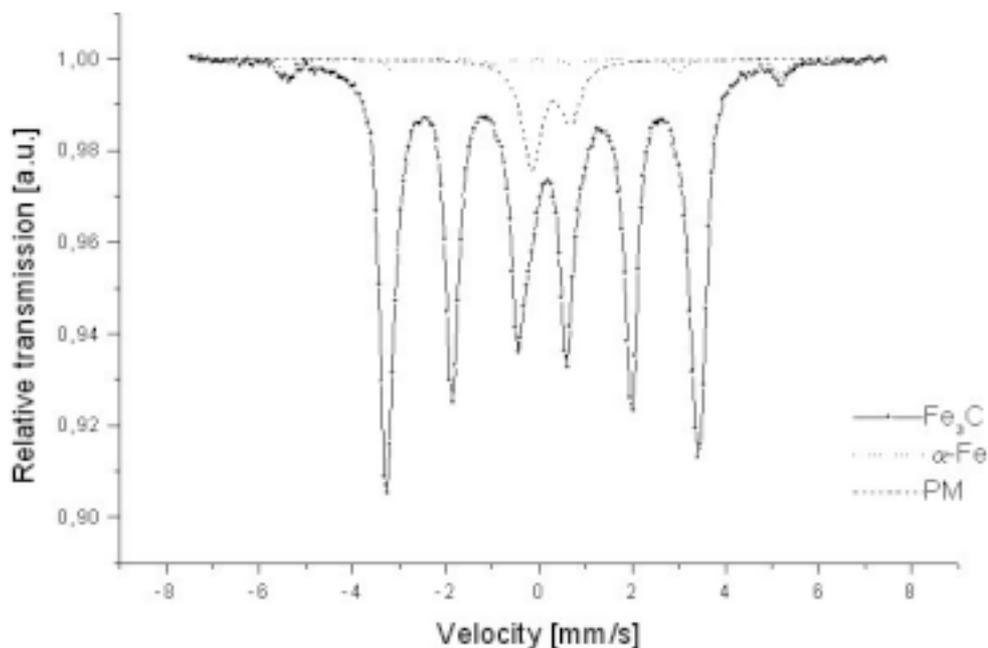


Fig. 1. Mössbauer spectra for the pyrolysed material containing Fe<sub>3</sub>C and Fe.

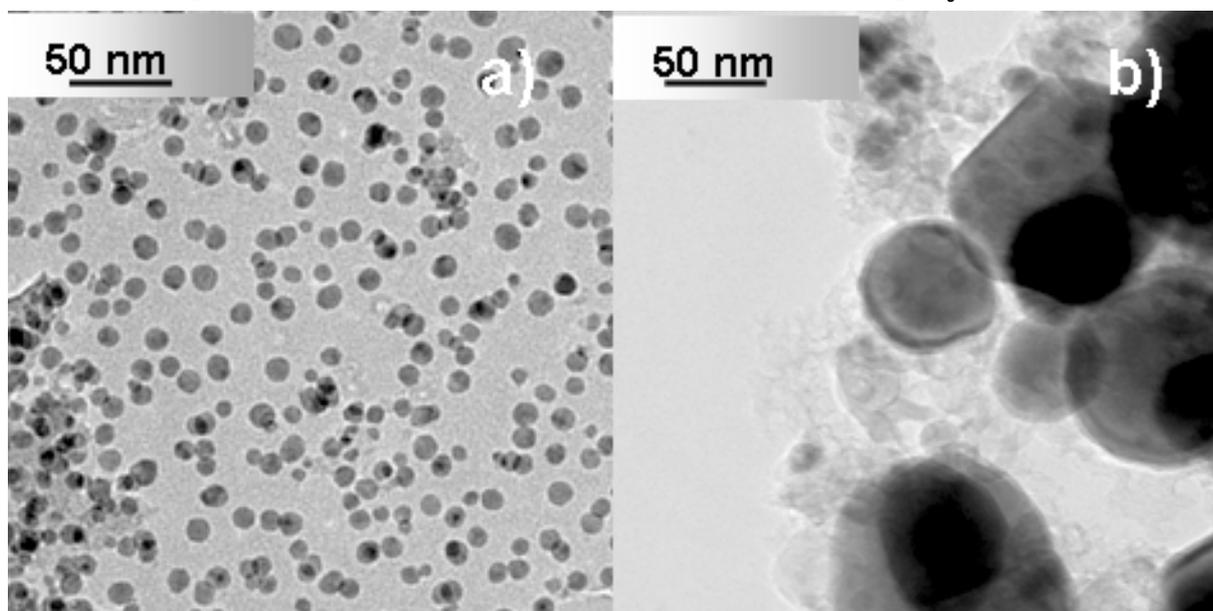


Fig. 2. TEM microstructure of the pyrolysed material containing cobalt – (a) and iron carbide - (b).

of the materials was studied using X-ray diffraction. The TEM observations were applied for microstructural analysis. Phase transformations temperatures were evaluated using a Perkin Elmer microcalorimeter at a heating rate of 10 deg/min. The hysteresis loops were recorded within temperature range of 5 - 300K, in external magnetic fields  $\pm 1.1$  T.

### 3. RESULTS AND DISCUSSION

The starting acrylamide cobalt and iron complexes exhibit different structure. The former had a complex crystalline structure, which, however, did not contain cobalt crystallites, whereas the latter showed amorphous structure. After polymerisation both materials have amorphous structure.

Pyrolysis 873 K

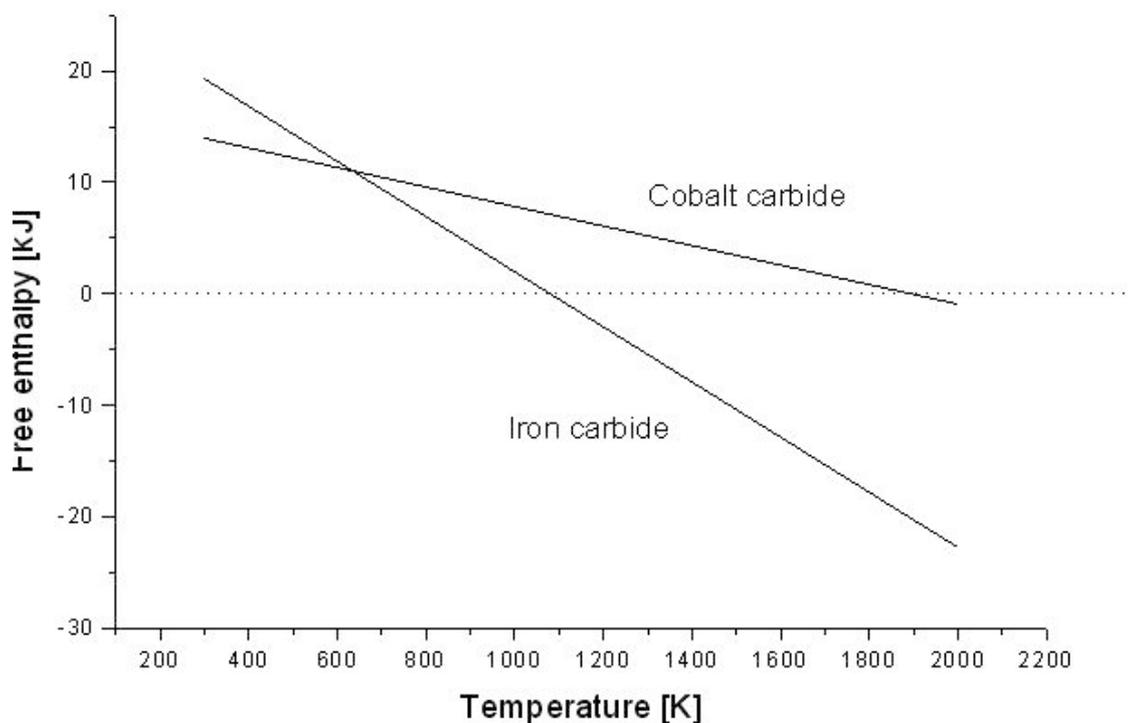


Fig. 3. Ellingham plots of cobalt and iron carbides formation.

The pyrolysis products were in a form of coarse, irregular powder particles exhibiting broad size distribution, ranging from 50 to 500  $\mu\text{m}$  and high porosity with pores size within a range 5-50  $\mu\text{m}$ . The nanocrystallites were embedded in the volume of the powder particles. Their formation was confirmed by the X-ray phase analysis, Mössbauer spectroscopy (Fig. 1), TEM observations (Fig. 2) and magnetic measurements.

The distinct crystalline reflections, which appeared in the pattern processed by pyrolysis of the cobalt containing polymer, matched well the characteristic lines of metallic cobalt. The broad spectra suggested nanocrystalline structure.

A coarser microstructure was obtained for the pyrolysed iron containing polymer. Moreover, the stoichiometry of the nanocrystallites was found to match iron carbide ( $\text{Fe}_3\text{C}$ ).

More detailed study of the phase constitution, using Mössbauer spectroscopy, for the pyrolysed material containing iron, revealed that, apart from the major phase – iron carbide, which occupied

86.87%, some amount of  $\alpha\text{-Fe}$ , at a level of 3.17% was also present (some remains of the paramagnetic phase, PM, was also found). The Mössbauer spectra for the pyrolysed material are shown in Fig. 1.

The TEM studies for the pyrolysed cobalt containing polymer showed individual, spherical particles having uniform mean size 12 nm (Fig. 2a).

The iron carbide crystallites, obtained by the thermolysis of iron containing polymer, were partly agglomerated and had broad range of sizes, from 10 up to 80 nm (Fig. 2b). Closer look at their surface showed few nanometers thick amorphous surface layer. The EDS analysis of the amorphous matrix revealed the presence in it of carbon, nitrogen and oxygen atoms.

The difference in the phase constitution of the nanocrystallites can be explained on a basis of Ellingham plots of the average free enthalpy for cobalt carbide and iron carbide formation (Fig. 3). Although the average values shown in the figure are located within a wide gap of error one can con-

clude from these plots that, at the equilibrium conditions, the formation of iron carbide occurs at lower temperatures than of the cobalt carbide. In fact, in our studies not shown here, we found that the elevation of the pyrolysis temperature can also form a thin surface layer of cobalt carbide in the pyrolysed polymer containing cobalt atoms. In our case all of the temperatures of carbides formation seem to be shifted towards lower values.

The hysteresis loops recorded at room temperature were closed and symmetrical versus origin of the coordinate system. Shape of the loops evidenced the ferromagnetic character of the material. At the room temperature the material containing cobalt nanoparticles showed soft magnetic properties with coercivity 0.01 T. Somewhat higher coercivity, 0.06 T, was observed for the material containing Fe<sub>3</sub>C nanocrystallites. This was caused by a higher anisotropy of the iron carbide when compared with elementary cobalt. No evidence for a superparamagnetic behaviour was found.

#### 4. CONCLUSIONS

Pyrolysis of polymers containing cobalt and iron showed individual, spherical particles of Co (12 nm) and Fe<sub>3</sub>C (10-80 nm) for the former and latter, respectively.

At the room temperature the material containing cobalt nanoparticles showed soft magnetic properties with coercivity 0.01 T. Somewhat higher coercivity, 0.06 T, was observed for the material containing Fe<sub>3</sub>C nanocrystallites.

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