Powders with superparamagnetic Fe₃C particles studied with Mössbauer spectrometry

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Abstract. Two nanopowders with superparamagnetic Fe₃C particles were synthesised by the method of laser-induced pyrolysis of gaseous precursors. Both were characterised by X-ray diffraction, Mössbauer spectrometry and standard magnetic measurements. The mean crystallite size of Fe₃C was 3 nm for the first sample and 10 nm for the second sample (Scherrer formula), i.e. it was lower than in our previously studied ferromagnetic Fe₃C-based sample. Fe₃C phase in both present samples exhibited by ~20 K reduced Curie temperature which is interpreted as a nanosize effect. After annealing of the samples at 1073 K for 30 minutes the Curie temperature of the Fe₃C phase in both samples matched its standard bulk value. Beside Fe₃C phase also Fe₃O₄ and carbon black were present in the synthesised samples.

1. Introduction

Magnetic nanoparticles (MNPs) attract the attention of the materials science community because of their unique magnetic and electronic properties [1,2]. Among MNPs gained high attention iron-based nanoparticles [3], especially for their prospective medical applications. α-Fe, γ-Fe and Fe₃C nanoparticles were studied predominantly as the catalysts for growing carbon nanotubes (CNTs).

Of all the gas phase synthesis methods, the laser-induced homogeneous pyrolysis (LIHP) is a powerful and versatile tool for the creation of nanoparticles with various chemical compositions and diameters ranging from a few nanometers to about 50 nm [4]. It has been demonstrated in our previous reports that this method can provide nanopowders with a dominant Fe₃C content [5-7].

In the present paper we study samples containing superparamagnetic Fe₃C particles, i.e. with thermally fluctuating orientation of the particle magnetic moment (superspin) at room temperature.

2. Experimental

Two types of Fe₃C-based nanopowders were synthesised by the method of laser-induced pyrolysis of gaseous precursors. The focused continuous-wave CO₂ laser radiation was orthogonally crossed with the reactant gas mixture stream that was admitted to the center of the reaction cell through the inner nozzle of the concentric two wall injector [4]. The outer nozzle was used for the argon coflow which confined the reactive gases stream to the flow axis. SF₆ was employed as the only laser radiation absorber. Fe(CO)₅ vapors served as an iron source, acetylene as a carbon donor and ammonia as a nitrogen precursor. The main parameters of the two experiments are resumed in Tab. 1.
The composition of the synthesised nanopowders was examined by X-ray diffraction (XRD). The XRD pattern fitting was done with the TOPAS software using the ICSD database of crystal structures and it yielded weight fraction \( F \) and mean crystallite size \( d_{\text{XRD}} \) for a given phase [8,9]. Mössbauer spectra were obtained at standard transmission geometry with \(^{57}\text{Co}\) in Rh matrix. Spectra were fitted with the CONFIT programme using transmission integral and we obtained the values of relative spectrum area \( A \) for a given phase and spectral component parameters: hyperfine magnetic induction \( B_{\text{HF}} \), quadrupole shift \( \varepsilon_Q \), quadrupole splitting \( \Delta E_Q \) and isomer shift \( \delta \) (against \( \alpha\)-Fe) [10]. Vibrating sample magnetometer (VSM) was employed for standard magnetic measurements.

### Table 1. Experimental data for the synthesis

| Sample  | \( P_{\text{laer}} \) after absorption (W) | Central nozzle flows (sccm) | Ar coflow (sccm) | Pressure (mbar) | Powder productivity (mg/min) |
|---------|---------------------------------|----------------------------|----------------|----------------|-------------------------------|
| FCB1    | 50                              | 34                         | 175            | 10             | 1100                          | 360                           | 55                            |
| FCB3N   | 40                              | 31                         | 140            | 10             | 1000                          | 350                           | 57                            |

3. Results and discussion

3.1. X-ray diffraction

Wide and overlapping diffraction peaks appeared in the X-ray diffractograms. The XRD patterns of the samples were fitted with orthorombic cementite \( \theta\)-Fe\(_3\)C (ICSD No. 16593) and magnetite Fe\(_3\)O\(_4\) (ICSD No. 43001). The Rietveld refinement yielded in the case of the FCB1 sample for Fe\(_3\)C values \( d_{\text{XRD}} = 3 \text{ nm}, \) \( F = 74 \text{ wt.\%}, \) and for Fe\(_3\)O\(_4\) values \( d_{\text{XRD}} = 4 \text{ nm}, \) \( F = 26 \text{ wt.\%}; \) in the case of the FCB3N sample for Fe\(_3\)C values \( d_{\text{XRD}} = 10 \text{ nm}, \) \( F = 33 \text{ wt.\%}, \) and for Fe\(_3\)O\(_4\) values \( d_{\text{XRD}} = 3 \text{ nm}, \) \( F = 67 \text{ wt.\%}. \) The presence of maghemite \( \gamma\)-Fe\(_2\)O\(_3\) could not be excluded because \( \gamma\)-Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\) have similar XRD patterns. Compared with our previously studied Fe\(_3\)C-based sample [5], the \( d_{\text{XRD}}(\text{Fe}_3\text{C}) \) values in present samples are considerably lower. The presence of carbon black in both samples was confirmed by Raman spectroscopy (well pronounced D peak at \(~1360 \text{ cm}^{-1}\) and G peak at \(~1580 \text{ cm}^{-1}\)).

3.2. Mössbauer spectrometry

The Mössbauer spectrum (MS) of the FCB1 sample measured at 293 K (Fig. 1) was fitted with three components: a narrow doublet probably of superparamagnetic Fe\(_3\)C (\( \delta = 0.18 \text{ mm s}^{-1}, \) \( \Delta E_Q = 0.42 \text{ mm s}^{-1}, A = 0.36; \) dashed line), a broad doublet of superparamagnetic Fe\(_3\)O\(_4\) (\( \delta = 0.30 \text{ mm s}^{-1}, \) \( \Delta E_Q = 0.91 \text{ mm s}^{-1}, A = 0.53; \) full line) and a superposition of three sextets (\( B_{\text{HF}} = 19.2 \text{ T}, 12.3 \text{ T}, 15.9 \text{ T}, A = 0.11; \) dark gray filler). In the MS measured at 60 K the sextet characteristic for ferromagnetic Fe\(_3\)C (\( B_{\text{HF}} = 23.9 \text{ T}, \) \( \varepsilon_Q = 0.04 \text{ mm s}^{-1}, \) \( \delta = 0.31 \text{ mm s}^{-1}, A = 0.30; \) light gray filler) was clearly identified [7]. In this spectrum also the superparamagnetic Fe\(_3\)O\(_4\) doublet (\( \delta = 0.40 \text{ mm s}^{-1}, \) \( \Delta E_Q = 1.07 \text{ mm s}^{-1}, A = 0.40 \) was found. In the MS measured at 27 K the sextet of ferromagnetic Fe\(_3\)C (\( B_{\text{HF}} = 24.5 \text{ T}, \) \( \varepsilon_Q = 0.07 \text{ mm s}^{-1}, \) \( \delta = 0.36 \text{ mm s}^{-1}, A = 0.74; \) light gray filler) dominated. The absence of the characteristic ferromagnetic Fe\(_3\)C sextet at 293 K and its appearance at lower temperatures is the consequence of the superparamagnetism of Fe\(_3\)C nanoparticles at 293 K.

In the case of the FCB3N sample the MS measured at 293 K (Fig. 1) exhibits very low absorption. This spectrum was fitted with the ferromagnetic Fe\(_3\)C sextet (\( B_{\text{HF}} = 20.5 \text{ T}, \) \( \varepsilon_Q = 0.01 \text{ mm s}^{-1}, \) \( \delta = 0.19 \text{ mm s}^{-1}, A = 0.28; \) dark gray filler) [5], a doublet (\( \delta = 0.19 \text{ mm s}^{-1}, \) \( \Delta E_Q = 0.51 \text{ mm s}^{-1}, A = 0.64; \) dashed line) and the superparamagnetic Fe\(_3\)O\(_4\) doublet (\( \delta = 0.68 \text{ mm s}^{-1}, \) \( \Delta E_Q = 0.70 \text{ mm s}^{-1}, A = 0.08; \) full
line). In the MS measured at 60 K again the ferromagnetic Fe$_3$C sextet ($B_{HF} = 24.9$ T, $\epsilon_Q = -0.05$ mm s$^{-1}$, $\delta = 0.32$ mm s$^{-1}$, $A = 0.32$; light gray filler) was found as well as in the spectrum measured at 27 K ($B_{HF} = 25.0$ T, $\epsilon_Q = 0.01$ mm s$^{-1}$, $\delta = 0.32$ mm s$^{-1}$, $A = 0.42$; light gray filler). The intense outer lines in the MS measured at 27 K correspond to a high fraction of Fe$_3$O$_4$ in the FCB3N sample. Iron nitrides were not found.

It can be concluded that two effects strongly influenced the measured Mössbauer spectra (Fig. 1): superparamagnetic effect (sextet representing magnetically ordered phase collapses to doublet above the blocking temperature $T_B$) [11] and soft bonding of Fe-based particles to the pyrolytic carbon matrix (recoilless factor $f$ strongly increases with decreasing temperature, i.e. relative absorption at 27 K is higher than at 293 K) [12]. Therefore the direct assignment of $A$ values of Fe$_3$C or Fe$_3$O$_4$ spectral components to corresponding weight fractions at 293 K, 60 K and 27 K is not possible.

![Mössbauer spectra](image)

**Figure 1.** Mössbauer spectra for the as-synthesised samples measured at the indicated temperatures. Sextets with light grey filler correspond to Fe$_3$C.

3.3. Magnetic measurements

From the hysteresis loop of the **FCB1** sample measured at 293 K we obtained the values: $H_C = 1.2$ kA m$^{-1}$, $\sigma_R = 0.35$ A m$^2$ kg$^{-1}$, $\sigma_S = 22.1$ A m$^2$ kg$^{-1}$ (lower than previously reported in [6]). The shape of the hysteresis loop exhibited superparamagnetic character. The majority of Fe$_3$C and Fe$_3$O$_4$ nanoparticles were in superparamagnetic state at 293 K. By the same measurement of the **FCB3N** sample we obtained the values: $H_C = 17.1$ kA m$^{-1}$, $\sigma_R = 7.4$ A m$^2$ kg$^{-1}$, $\sigma_S = 40.2$ A m$^2$ kg$^{-1}$. In this case higher $H_C$ and $\sigma_R$ values reflected the presence of certain amount of Fe$_3$C nanoparticles in ferromagnetic state at 293 K whereby Fe$_3$O$_4$ particles were superparamagnetic.
By the thermomagnetic curve measurement (TM curve) a pellet was held in the evacuated cell (~1 Pa), heated up to 1073 K (hold time 30 minutes) at the rate of 4 K min\(^{-1}\) in the external field \(H_{\text{ext}} = 4\ \text{kA\ m}^{-1}\) and then cooled down to room temperature. The Curie temperatures \(T_C(\text{bulk-}\alpha-\text{Fe}) \approx 1040\ \text{K}\) and \(T_C(\text{bulk-Fe}_3\text{C}) \approx 483\ \text{K}\) [5,6] can be recognised on the TM curves of both samples (Fig. 2). However, \(T_C(\text{nano-Fe}_3\text{C})\) determined from the \(\sigma(T)\) measured with increasing temperature, i.e. for the as-synthesised mainly superparamagnetic \(\text{Fe}_3\text{C}\) nanoparticles, is evidently by \(\sim 20\ \text{K}\) lower than \(T_C(\text{bulk-Fe}_3\text{C})\) determined from the \(\sigma(T)\) measured with decreasing temperature (recrystallised sample). This effect has not been observed in our previous study dealing with a ferromagnetic \(\text{Fe}_3\text{C}\)-based nanopowder with \(d_{\text{XRD}}(\text{nano-Fe}_3\text{C}) = 12\ \text{nm}\) [5-7]. The decrease of \(T_C\) is well known as a nanosize effect and was described, for instance, by the authors of the articles [13,14].

![Figure 2. TM curves for the the as-synthesised samples.](image)

4. Conclusions

It can be summarised that in the studied samples the presence of the significant amount of \(\text{Fe}_3\text{C}\) particles superparamagnetic at room temperature was proved. According to our knowledge, such \(\text{Fe}_3\text{C}\)-based nanopowders were synthesised by the laser-induced pyrolysis method for the first time.

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