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AGEING EFFECT IN CARBON-COATED COBALT NANOPARTICLES EMBEDDED IN A CEMENT MATRIX STUDIED BY FMR

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Abstract. Samples containing agglomerated cobalt magnetic nanoparticles coated with carbon and dispersed in a cement matrix have been prepared. The samples with (25/75 wt.%) carbon/cobalt content dispersed at low concentration in cement (about 0.5%) have been studied using the ferromagnetic resonance (FMR) method at room temperature (RT). Very intense and broad FMR lines have been recorded in the fresh samples, more intense than those obtained from the same agglomerates dispersed in a paraffin matrix. The FMR spectrum of the cement matrix sample consisted of three different magnetic resonance components: (a) a very broad FMR line attributed to iron oxide, (b) an EPR line arising from trivalent iron ions in a crystal field of low symmetry, and (c) a line from divalent manganese ions. After two months the FMR spectra of cobalt nanoparticles dispersed in cement has changed drastically, while the same agglomerates dispersed in paraffin has shown only weak time dependence. Magnetic interaction between magnetic nanofillers could be more intense in the case of a cement matrix for two reasons: one is due to the porous state of this material and the other is owing to the chemical and physical reactions of agglomerates with various cement constituents. Applications of the obtained results could lead to the production of cement with much better mechanical properties.

1. INTRODUCTION

Magnetic nanoparticles introduced in different matrixes have shown many interesting physical properties [1-9]. The magnetic interactions between them were investigated successfully by using the FMR (ferromagnetic resonance) method. The type of matrix has played a very important role. For a low concentration of magnetic nanoparticles embedded in a polymer matrix it has been shown that the size of agglomerates influenced essentially the FMR spectra [8]. The temperature dependence of the FMR spectra has revealed the presence of critical points of the matrix [9]. A porous material as a

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matrix for magnetic nanoparticles could be a very interesting medium as it is expected to display the so-called "pillow" phenomenon [10]. A very promising material for such matrix is Portland cement (concrete) because of its widespread application [11]. Finely dispersed metallic particles in the mineral composition and microstructure of clinker minerals have been used successfully for a positive change of its technological parameters [12]. To broaden the beneficial reuse of sewage sludge, small amounts of nanomaterial were considered as additives to evaluate the influence of nanomaterials on the microstructure of sludge cement paste. Moreover, nanomaterial additives could make crystallizations denser, pore sizes smaller, and decrease the number of pores [13]. The equivalent performance of Portland cement materials is one target for these cements which are broadly used and modified and thus may provide the basis for advanced and efficient construction techniques [14].

The aim of this report is the EPR (electron paramagnetic resonance)/FMR (ferromagnetic resonance) study of a low concentration of cobalt nanoparticles in the agglomerated state, dispersed in the Portland cement produced in Szczecin Cement Plant (Poland).

2. EXPERIMENTAL

The nanocrystalline carbon-cobalt has been prepared by using a method, which has been presented previously [15]. Small amount of Al_2O_3 and CaO were used as structural promoters to stabilize the cobalt nanoparticles at elevated temperatures at subsequent preparation steps (reduction and carburization). Cobalt (II), calcium and aluminium nitrates were used in the preparation of the hydroxides. The salts were dissolved in water and the solution of 25% NH_4OH had been continuously added to obtain *p*H=8. The metal hydroxides were precipitated from the solution and the obtained deposit was washed with water, filtered and next dried at 70 °C. The next preparation step was the calcination at 500 °C for one hour to obtain the precursor of nanocrystalline cobalt - cobalt oxide (with small amount of structural promoters – CaO and Al_2O_3). The chemical composition of the samples was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, JY 238 Ultrace equipment from Jobin Yvon). The sample of cobalt precursor contained 0.2% CaO and 1.5% Al_2O_3. The cobalt oxide powder was pressed, crushed and sieved to obtain a grain size fraction in the range of 1.2 – 1.5 mm. The process of cobalt oxide reduction and cobalt carburization was carried in a differential reactor with thermogravimetric mass measurement. The sample of cobalt oxide of 0.5 g was placed as a single layer of grains in a platinum basket. The reduction process was carried out in the temperature range of 25 – 500 °C at the heating rate of 10 °C/min, under pure hydrogen (99.999%) flow (20 dm^3/h).

After the reduction process the hydrogen flow was replaced by ethylene flow. The carburisation process was performed under pure ethylene (99.9%) flow (20 dm^3/h) in the temperature range of 340 – 500 °C. After the carburisation process, the samples were cooled under helium (99.9996%) flow. The phase composition of the samples was determined using the XRD technique (CoK_α radiation). The samples after carburisation were also characterized using High Resolution Transmission Electron Microscopy (HRTEM) (Jeol JEM 3010). The HRTEM method was used to study the morphology of the samples. For the matrix standard Portland cement produced by Szczecin Cement Plant, Poland, has been used.

The EPR/FMR spectra were recorded using a standard X-band spectrometer (Bruker E500 ν=9.5 GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with a NMR magnetometer. The measurements were performed at room temperature. The powder sample, containing about 10 mg of cement with magnetic nanoparticles, was placed into 5 mm diameter quartz tubes.

3. RESULTS AND DISCUSSION

Before measurements have been carried out, the sample containing cobalt nanoparticles had been subjected to a high magnetic field and subsequently the FMR spectra did not depend on the direction of magnetic field sweep. The cobalt agglomerates were dispersed homogenously in the cement matrix because the FMR spectra from different parts of the prepared bulk material were the same.

Fig. 1 shows the FMR/EPR spectra of the investigated Portland cement sample. The spectrum consists of an EPR line centered at g_{eff}=4.3(1) with linewidth ΔB=16(1) mT, an FMR line centered at magnetic field B_r = 274(1) mT with linewidth ΔB = 94(1) mT and another EPR line centered at g_{eff}~2, with six hyperfine lines with the hyperfine constant A = 9(1) mT. The first EPR component is arising

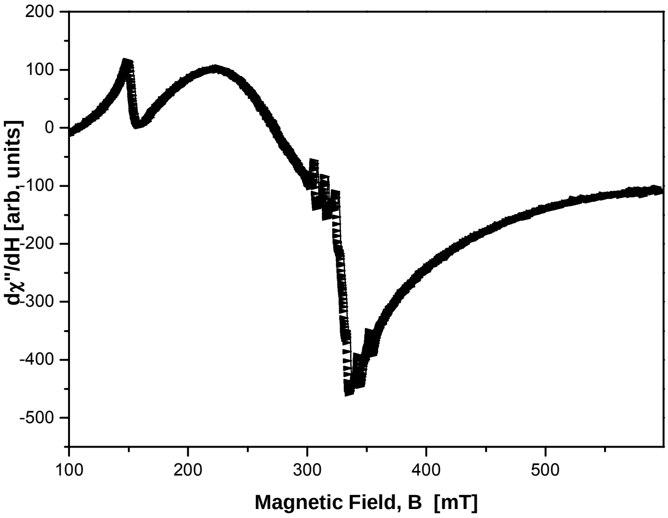

Fig. 1. The EPR spectra of cement at room temperature.

from trivalent iron ions in the high spin state in a crystal field with a low symmetry. The second spectral FMR component is due to iron oxide compound subjected to a strong internal magnetic field, which changes the resonance condition. The third EPR constituent is produced by Mn^{2+} ions with the ground state ^6S.

Fig. 2 presents the FMR spectra of cobalt nanoparticles in paraffin (1) and cement (2) matrixes. For the description of the FMR spectrum of cobalt nanoparicles three parameters are introduced: B_0 - the position of the FMR line at zero intensity, I_r - the intensity of the line right extreme feature, and ΔB – the difference between line position of the extreme and zero intensity [16]. The above parameters have the following values: B_0 = 182(1) mT, ΔB = 256(1) mT for paraffin matrix sample and B_0 = 177(1) mT, ΔB = 270(1) mT for cement matrix sample. The ratio of the cement/paraffin intensity was calculated to be 1.7. As the cement matrix forms a system of pores, which allows for much greater mobility of the cobalt nanoparticles, this might be the reason for a large change of the spectral parameters in comparison with the paraffin matrix.

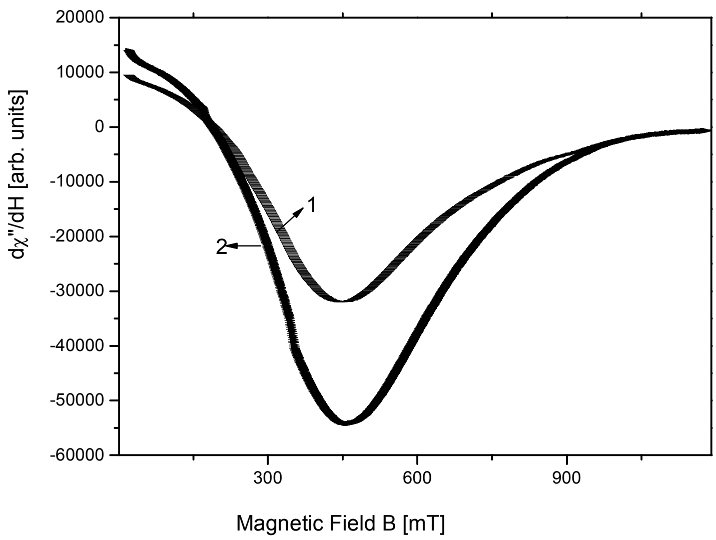

Fig. 2. The FMR spectra of cobalt magnetic nanoparticles in paraffin (1) and in cement (2) registered shortly after preparation.

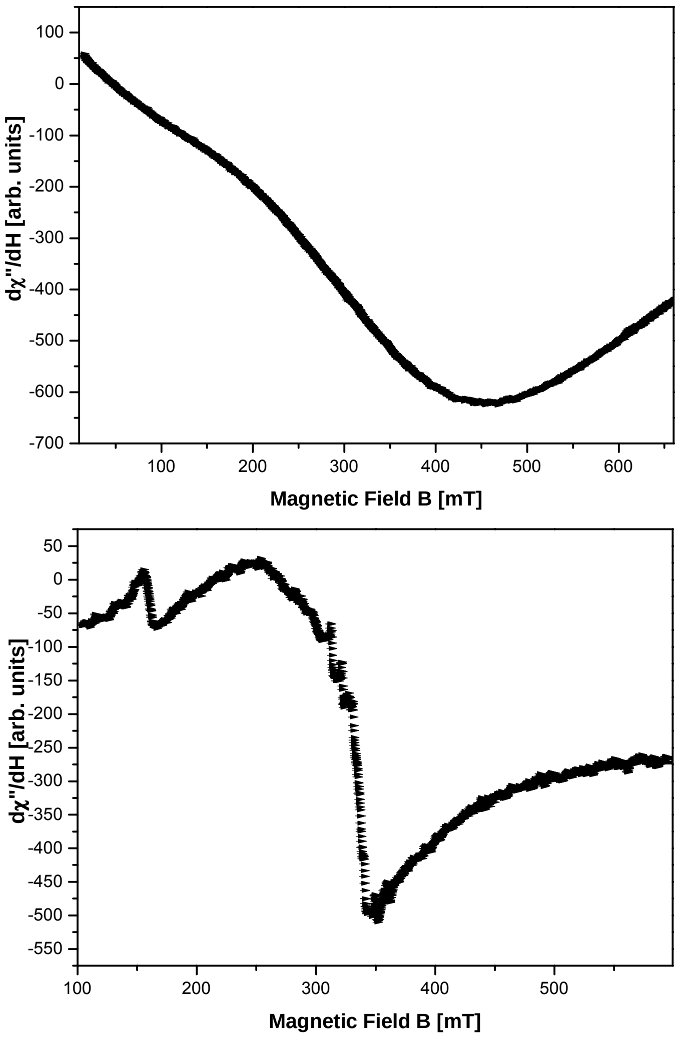

Fig. 3. The FMR/EPR spectra of cobalt nanoparticles in paraffin (a) and cement (b) matrix after 2 months.

Fig. 3 shows the FMR/EPR spectra of cobalt nanoparicles in paraffin (Fig. 3a) and cement (Fig. 3b) matrices registered after two months of the aging process. In both cases the spectra have changed significantly. For the paraffin sample the introduced parameters have the following values: B_0 = 41(1) mT and ΔB = 437(1) mT. It is suggested that the magnetic interactions inside the sample strongly increased and the zero position of the resonance line has shifted by dB_0 = 296 mT and the linewidth has increased by dΔB = 179 mT. For the cobalt nanoparticles in the cement the FMR spectrum has changed considerably (Fig. 3b). In the EPR spectra of iron(III) ions and manganium(II) ions the main change concerns their intensities - they have decreased. The FMR spectra of oxide iron is now centered at B_r = 268(1) mT and linewidth ΔB = 25(1) mT while the intensity decreased over two times. After the aging process the position of the FMR line of the iron oxide has changed essentially what could be explained by change of the resonance condition due to an internal magnetic field. The average internal field acting on the paramagnetic isolated centers produced by the introduction of magnetic nanoparticles or by already existing iron oxides is almost zero. These results suggest that the introduction of small amount of strong magnetic nanoparticles in the concrete could increase its elasto-mechanical properties [10], which in turn could improve its mechanical properties.

In conclusion, FMR study of a low concentration of cobalt nanoparticles in paraffin matrix and in concrete has revealed the effect of dynamical time dependent spin fluctuations, which were found to be stronger for aged than for fresh samples. In the case of cobalt nanoparticles in cement matrix the time dependence of the FMR spectra was stronger what was explained by the appearance of an internal magnetic field, changing effectively the EPR/FMR spectroscopic properties and magnetic interactions.

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