FMR and compression strength studies of cement with nickel nanoparticles

N. Guskos[1,2], G. Zolnierkiewicz[2,*], M. Orlowski[2], J. Typek[2], J. Blyszko[3], W. Kiernozycki[3], U. Narkiewicz[4], and M. Podsiadly[4]

[1]Solid State Section, Department of Physics, University of Athens, Panepistimiopolis, 15 784 Zografos, Athens, Greece;
[2]Institute of Physics, Szczecin University of Technology, Al.Piastow 17, 70-310 Szczecin, Poland;
[3]Faculty of Civil Engineering and Architecture, Szczecin University of Technology, Al. Piastow 50, 70-311 Szczecin, Poland;
[4]Institute of Chemical and Environment Engineering, Szczecin University of Technology, Pułaskiego 10, 70-332 Szczecin, Poland

Abstract

Four types of concrete samples without and with a small concentration of magnetic nanoparticles of fcc-nickel and α-iron covered with graphite layer have been prepared. The samples have been investigated by ferromagnetic resonance (FMR) and compression strength methods. The FMR spectra of the following samples have been recorded: cement in powder, cement powder/water form, cement powder/nanoparticles, and cement powder/nanoparticles/water. For the two former types no difference is observed in the FMR spectra. Samples containing magnetic nanoparticles showed a wide and intense, almost symmetrical FMR line, while sample with additional water molecules displayed essentially lower intensity spectrum. These differences are arising from the presence of water molecules having a high value of the dielectric constant. The compression strength study of samples with and without Ni/C nanoparticles has shown over 15 % of increase of strength while an opposite effect was observed for concrete with α-iron. Interaction of magnetic nanoparticles in non-magnetic materials could essentially change their physical properties and the kind of used nanoparticles is also very important.

Introduction

During the last twenty years a great deal of interest has been devoted to magnetic metal nanoparticles due to their unusual behavior and prospects of applications. Among various ferromagnetic metals nickel at the nano-scaled level has attracted much attention because of its unique magnetic properties promising potential applications, see e.g [1-6]. The nanocomposite materials have found numerous applications because of their functionality [7]. The mineral composition and microstructure of clinker minerals with finely dispersed magnetic metallic particles (at low concentration) have been used successfully for a desired change of technological parameters [8,9]. The magnetic nanoparticles can hold a promise in building materials, especially cement (concrete) applied in magnetic shielding. The small amounts of nanomaterials as additives could make crystallizations denser, pore sizes smaller, and the number of pores decreased [10] where the metallurgical slag is often used for a partial Portland cement replacement [11,12]. The study of low concentration of magnetic nanoparticles in concrete by using FMR/EPR (ferromagnetic/electron paramagnetic resonance) methods has shown that the freezing processes are more intense and that in turn could influence essentially their mechanical properties [9,13,14]. The magnetic interaction could form an additional attracting force (in the ground state the magnetic moments are align antiparallel) if magnetic nanoparticles are dispersed at small concentration.
The aim of this report is to study the influence of small concentration of fcc-nickels and α-irons nanoparticles in concrete on its mechanical properties using the FMR and compression strength methods.

Experimental

The magnetic nanocarbons containing fcc-nickels and α-iron were prepared by a method presented previously [15,16]. The samples of fcc-nickel and α-iron nanomaterials were prepared by carburisation of nanocrystalline nickel/iron with ethylene.

The matrix which has been used was a standard cement produced by Gorazdze Factory, Poland. Agglomerated fcc-nickel/carbon and α-iron/carbon magnetic nanoparticles were dispersed in mixed cement matrix (0.5 wt.% of additive) [9]. Concrete samples of cylindrical shape sized Q=30 mm, h=30 mm were manufactured and cured in wet air regimes. Both types of samples were prepared in the same conditions. The value of water-cement index was w/c=0,33. The same kinds of cement has been used in all measurements. The measurements of the compression strength have been done according of subject index PN-88/B-06250 on automatic, German produced strength apparatus TONI-TROL. The strength assessments have been done after 1, 3, 7 and 28 days of samples fabrication.

The FMR spectra were recorded using a standard X-band Bruker E 500 (=9.455 GHz) spectrometer with magnetic field modulation of 100kHz at room temperature. The magnetic field was scaled with a NMR magnetometer. Samples, containing ~20 mg of investigated material in form of fine powder were sealed into 4 mm in diameter quartz tubes.

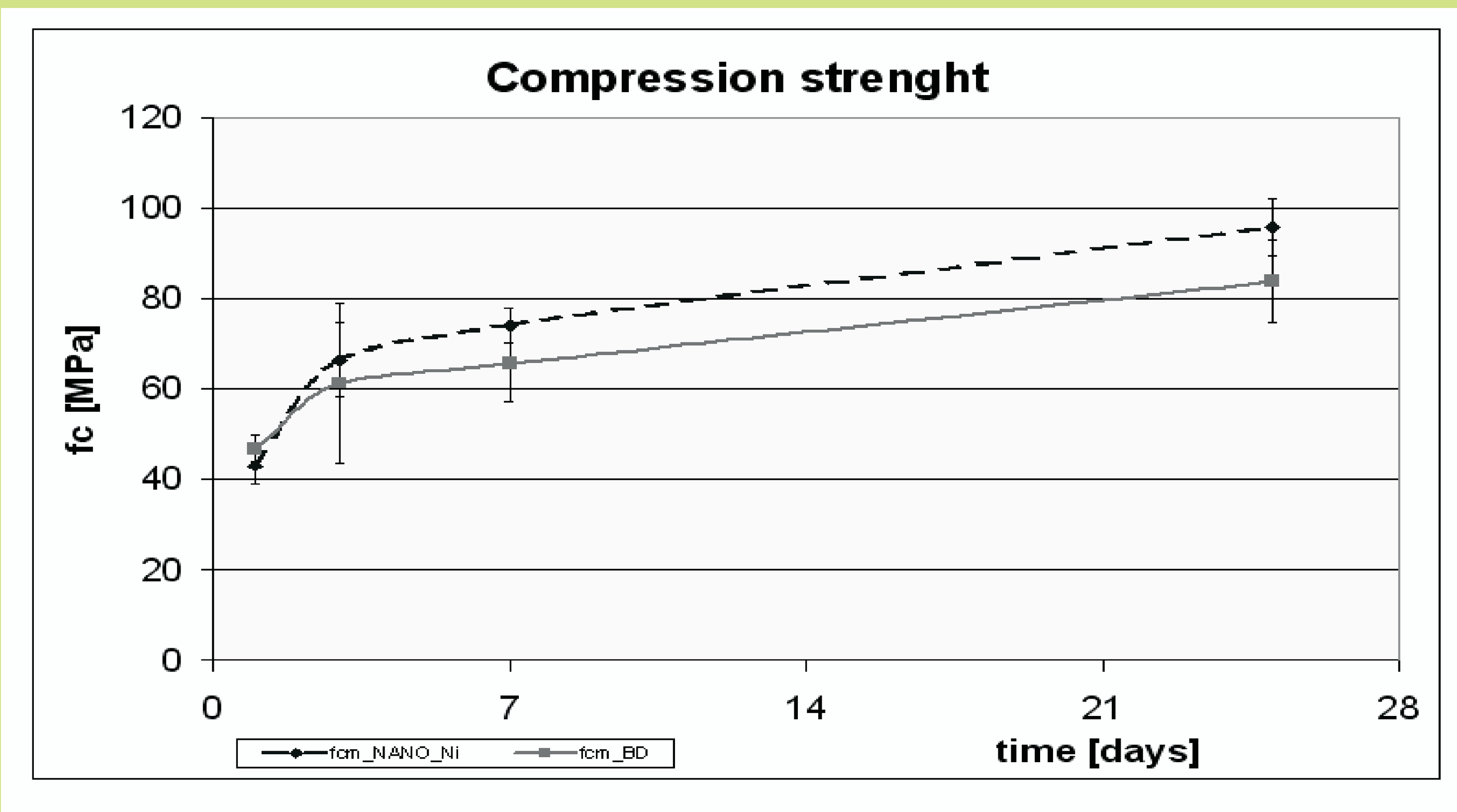

Figure 2. Room temperature compression strength of concrete without solid line and with nickel magnetic nanoparticles dashed line.

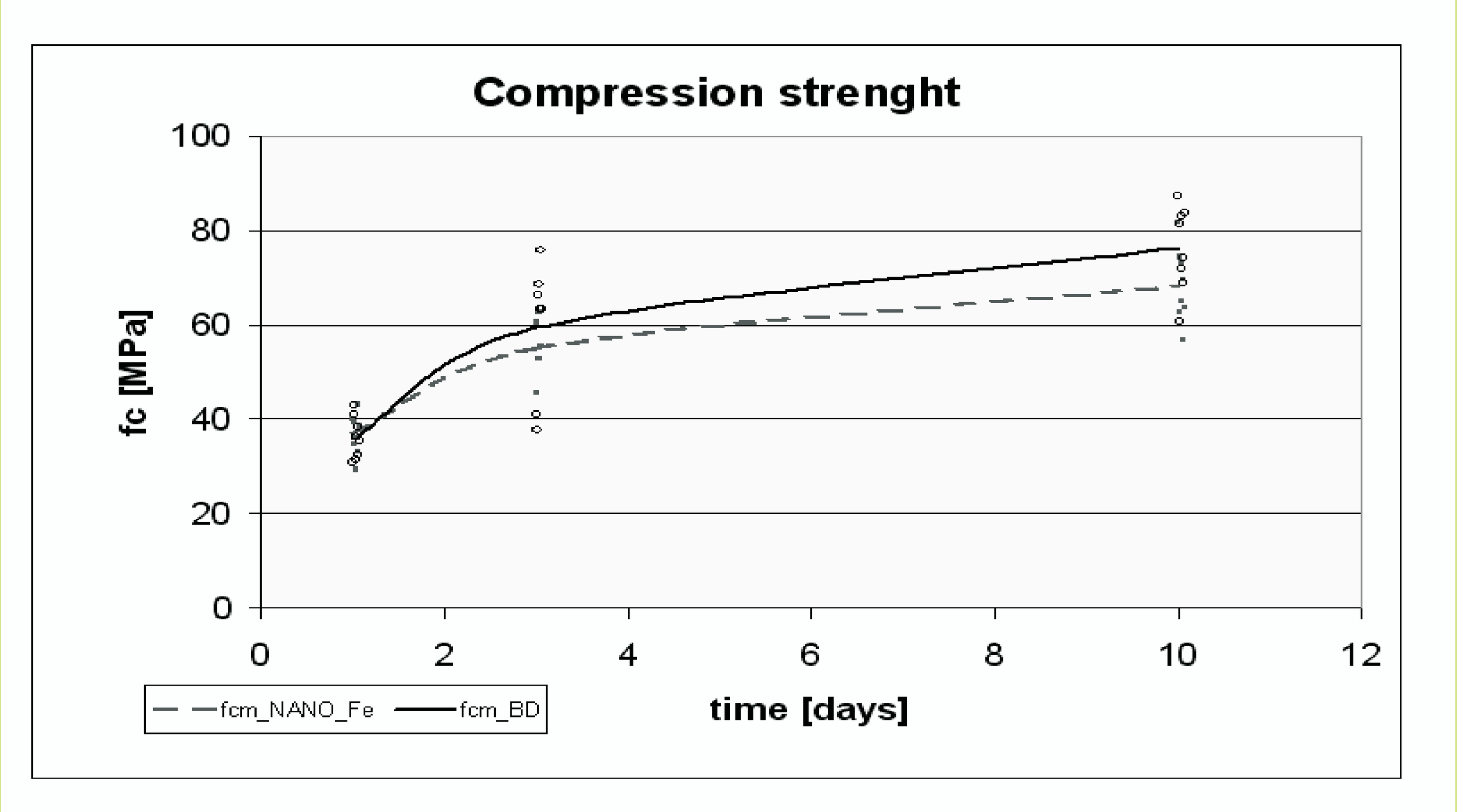

Figure 3. Room temperature compression strength of concrete without solid line and with α-iron magnetic nanoparticles dashed line.

Results and discussion

Samples of concrete with fcc-nickel were subjected several times to high magnetic field (~1.6 T) before FMR measurements. After this treatment the obtained spectra were identical in repetitive measurements. The magnetic nanoparticles were dispersed almost homogenously in the concrete matrix because the FMR spectra from different parts of a bulk material were the same.

Figure 1 shows the FMR spectra of concrete with small concentration of magnetic nanoparticles fcc-nickel/carbon without water (sample 2) and with water (sample 3) in comparison with a sample without magnetic Ni (sample 1) nanoparticles. The FMR spectrum of sample without magnetic nanoparticles is similar to that obtained in [14]. The spectrum of concrete with mixture of magnetic nanoparticles fcc-nickel/carbon with and without water presents a symmetrical and intense FMR line with a resonance field centred at H_r=3008 Gs (g_{eff}=2.23(1) with linewidth ΔH_{pp}=610(5) Gs and H_r=2964 Gs (g_{eff}=2.27(1) with linewidth ΔH_{pp}=780(5) Gs, respectively. The relatively integrated intensity of both samples with nanopartilces is the following: $I_3\Delta H_3^2/I_2\Delta H_2^2=1.6$, where I is the line amplitude and ΔH is the linewidth. This result suggests that a more rigid matrix (containing water) is more susceptible for penetration of the microwave radiation. A more rigid matrix causes the position of the FMR resonance line to shift essentially and the linewidth to broaden significantly. It could be connected with the porous state of the concrete in which the magnetic nanoparticles could more freely reorganize what provides a more intense dipole-dipole interaction. The effective internal magnetic field produced by the magnetic dipoles changes the resonance condition, $h\nu = g\,\mu_B\,(H_o - H_i)$, where h- is the Planck constant, ν- the resonance frequency, μ_B- the Bohr magneton, H_o an applied external magnetic field and H_i – an internal magnetic field. The FMR spectra of low concentration of aggregated α-iron magnetic nanoparticles in concrete is similar to that for induced in the non-magnetic matrix [15].

Figures 2 and 3 present the compression strength action on concrete samples with fcc-nickel/carbon and α-iron/carbon nanoparticles, respectively. The procedure of measurements was described in [9]. The figures show the time dependence of mechanical parameters of the concrete during the most important period of 28 days. The compression strength has increased about 15 % for the sample with fcc-nickel/carbon while an opposite effect of decreasing of about 9 % for sample with α-iron/carbon has been observed. The compression strength for concrete with small concentration of magnetic nanoparticles α-iron/carbon has displayed a similar trend as registered for samples with carbide iron and cobalt nanoparticles [9]. An opposite behaviour of bcc-nickel/carbon could be connected with smaller size of nanoparticles aggregates. The concrete matrix is usually forming a porous system which for the bcc-nickel nanoparticles with lower sizes of agglomerates is offering a possibility for their greater mobility. The magnetic dipole interaction could make the antiparallel ordering more intense which could effectively form an attractive force producing a more complicated state. The carbon shell covering the nanoparticls could participate in the so called "pillow" phenomenon which would be increasing the compression strength.

It is already known that addition of small amount of magnetic nanoparticles to a polymer matrix changes essentially such critical parameters of the polymer as crystallization or melting temperatures [17,18]. The increase of melting point of matrix containing small concentration of magnetic nanoparticles suggests an increase of the attract force. The freezing processes influenced by the relaxation phenomena and connected with increased internal stress with decreasing temperature could induce the reorientation processes and increased the magnetic momentum of agglomerates [19-21]. A similar effect could be accomplished in concrete materials by the dehydration processes. The time dependence of the strength parameter for compression in both samples with magnetic nanoparticles shows an opposite effect (**Figs. 2 and 3**). This is due to complicated magnetic interactions that depend on the sizes of magnetic agglomerates. We have to do with interplay of two important effects: an additional inter-agglomerate magnetic interaction and an essential influence of the matrix (concrete). The proper selection of magnetic nanoparticles could lead to applications of these materials in magnetic shielding for radiation.

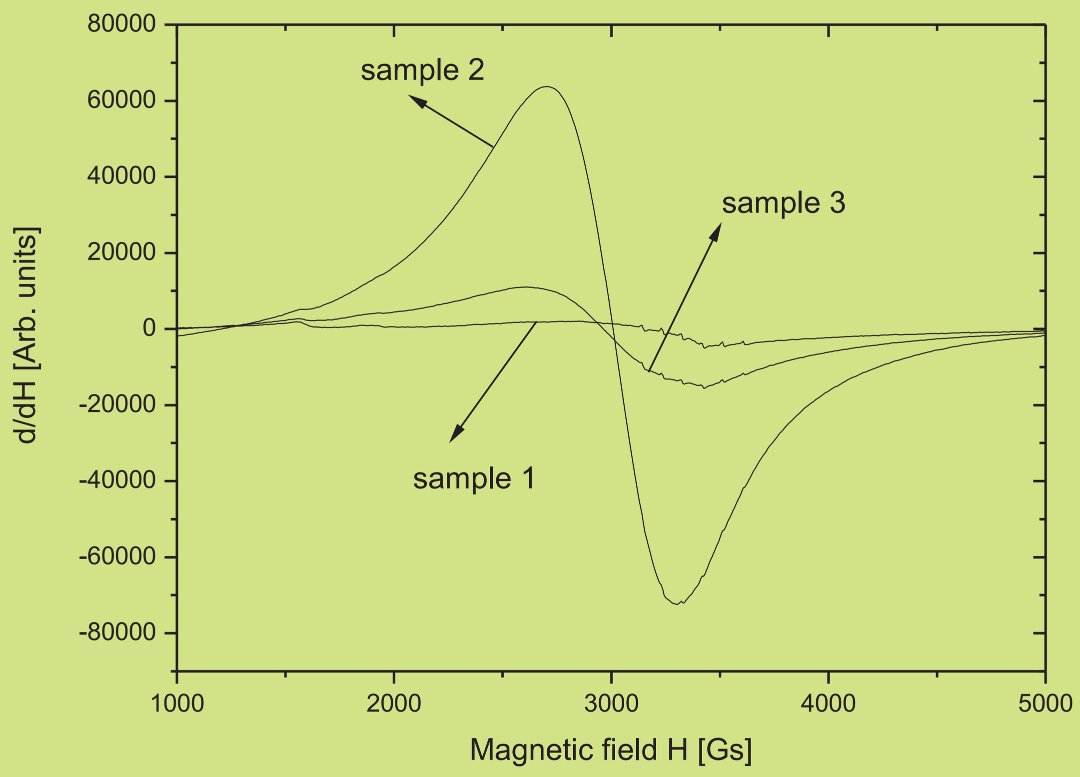

Figure 1. Room temperature FMR spectra of concrete with and without magnetic nanoparticles: (1) without magnetic nanoparticles, (2) with nanoparticles and without water, (3) with nanoparticles and with water.

Conclusions

The FMR study of small amount of fcc-nickel/carbon nanoparticles as additives to concrete has shown a significant influence of magnetic interaction on the process of concrete formation. The compression strength has increased essentially for the concrete with small concentration of the fcc-nickel/carbon nanoparticles while for concrete with α-iron/carbon nanoparticles an opposite effect was observed.

Corresponding author:
(G. Zolnierkiewicz) e-mail:
gzolnierkiewicz@ps.pl