

# FERROMAGNETIC RESONANCE AND COMPRESSIVE STRENGTH STUDY OF CEMENT MORTARS CONTAINING CARBON ENCAPSULATED NICKEL AND IRON NANOPARTICLES

N. Guskos<sup>1,2</sup>, G. Zolnierkiewicz<sup>2</sup>, J. Typek<sup>2</sup>, J. Blyszko<sup>3</sup>, W. Kiernozycki<sup>3</sup>  
and U. Narkiewicz<sup>4</sup>

<sup>1</sup>Solid State Section, Department of Physics, University of Athens, Panepistimiopolis, 15 784 Zografou, Athens, Greece

<sup>2</sup>Institute of Physics, West Pomeranian University of Technology, Al. Piastów 48, 70-311 Szczecin, Poland

<sup>3</sup>Faculty of Civil Engineering and Architecture, West Pomeranian University of Technology, Al. Piastow 50, 70-311 Szczecin, Poland

<sup>4</sup>Institute of Chemical and Environment Engineering, West Pomeranian University of Technology, Pułaskiego 10, 70-332 Szczecin, Poland

Received: December 10, 2009

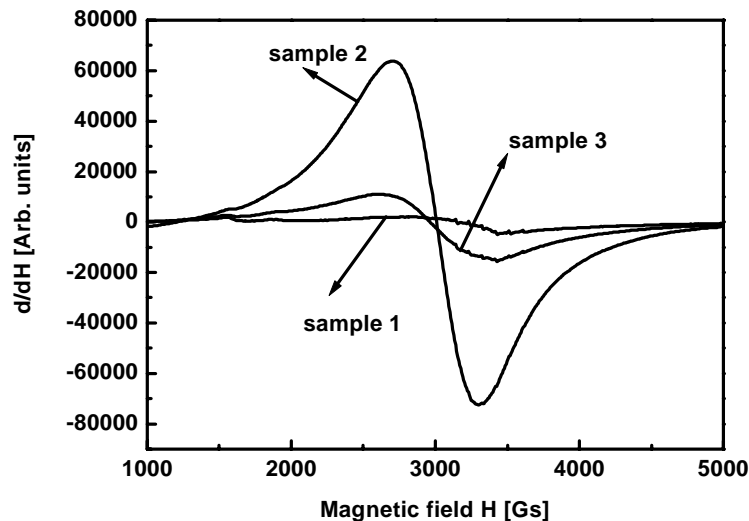
**Abstract.** Four types of cement mortars without and with a small amount of magnetic nanoparticles of fcc-nickel and  $\alpha$ -iron encapsulated in carbon were prepared. The samples were investigated by the ferromagnetic resonance (FMR) and compressive strength methods. The FMR spectra of the following samples were recorded: cement mortar in powder form, cement mortar powder/nanoparticles and cement mortar powder/nanoparticles/water. No difference was observed in the FMR spectra in the two former types. Samples containing magnetic nanoparticles showed a wide and intense almost symmetrical FMR line, while a sample with additional water molecules displayed an essentially lower intensity spectrum. A compressive strength study of samples with and without carbon encapsulated nickel nanoparticles showed an increase of over 15% for the former sample while an opposite effect was observed for concrete with  $\alpha$ -iron nanoparticles. The presence and interaction of magnetic nanoparticles embedded in non-magnetic materials could significantly change some of their physical properties. A possible explanation for the obtained results is discussed. The role of the size of nanoparticles agglomerates in enhancing the mechanical properties of cement mortars is emphasized.

## 1. 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 numerous applications. Among various ferromagnetic metals it is the nickel nanoparticles that have attracted much attention because of their unique magnetic properties promising potential applications, see e.g. [1-6]. Nanocomposite materials have found many applications because of their functionality [7].

The mineral composition and microstructure of clinker minerals with finely dispersed magnetic metallic particles (at a low concentration) have been successfully used 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. Small amounts of nanomaterials used as additives could make crystallizations denser, pore sizes smaller, and the number of pores decrease [10]

Corresponding author: G. Zolnierkiewicz, e-mail: grzegorz.zolnierkiewicz@ps.pl



**Fig. 1.** Room temperature FMR spectra of cement mortar with and without magnetic nickel nanoparticles: (1) without magnetic nanoparticles, (2) with nanoparticles and without water, (3) with nanoparticles and with water.

where the metallurgical slag is often used for partial Portland cement replacement [11,12]. A study of cement mortar with a small amount of magnetic nanoparticles 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 (magnetic moments are aligned antiparallel in the ground state) if magnetic nanoparticles are dispersed at a small concentration.

The aim of this report is to study the influence of a small amount of carbon encapsulated fcc-nickels and  $\alpha$ -irons nanoparticles in cement mortar on its mechanical properties using the FMR and compressive strength methods.

## 2. Experimental

Magnetic nanocarbons containing fcc-nickels and  $\alpha$ -iron were prepared by a presented previously method [15,16]. Samples of fcc-nickel and  $\alpha$ -iron nanomaterials were prepared by carburisation of nanocrystalline nickel/iron with ethylene. An average size of carbon encapsulated Ni and Fe nanoparticles was 80 nm and 50 nm, respectively.

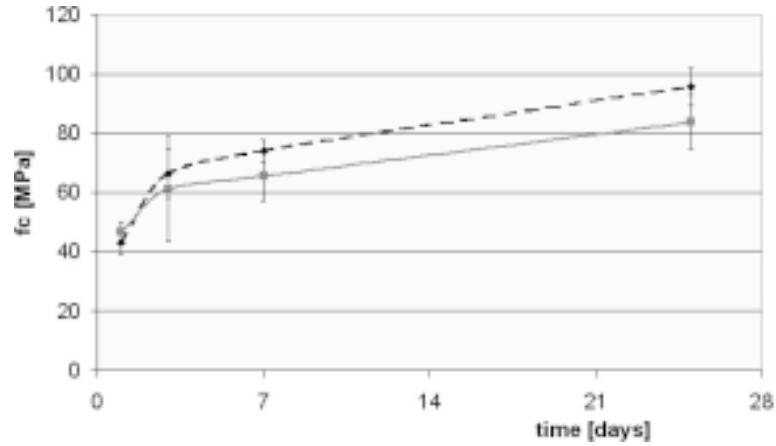
The matrix used was a standard silica fume and cement produced by Gorazdze, Poland. Agglomerated fcc-nickel/carbon and  $\alpha$ -iron/carbon magnetic about 0.6 %wt dispersed in a mixed cement matrix was formed [9]. This particular amount of

nanoparticles (0.6 wt.%) is the lowest that causes observable changes in the mechanical properties of cement. Samples with lower concentrations (0.2 wt.% and 0.4 wt.%) of nanoparticles did not have any measurable effect on the mechanical properties. Cement mortar specimens of a polyhedron shape 40x40x160 mm in size were manufactured and cured in wet air regimes. Both types of samples were prepared in the same conditions. The water-cement ratio  $w/c$  was 0.33. The same kinds of concrete and sand were used in all measurements. The compressive strength measurements were done according to the Polish standard PN-88/B-06250 on automatic TONI-TROL strength apparatus manufactured in Germany. The strength assessments were done after 1, 3, 7, and 28 days from the samples fabrication.

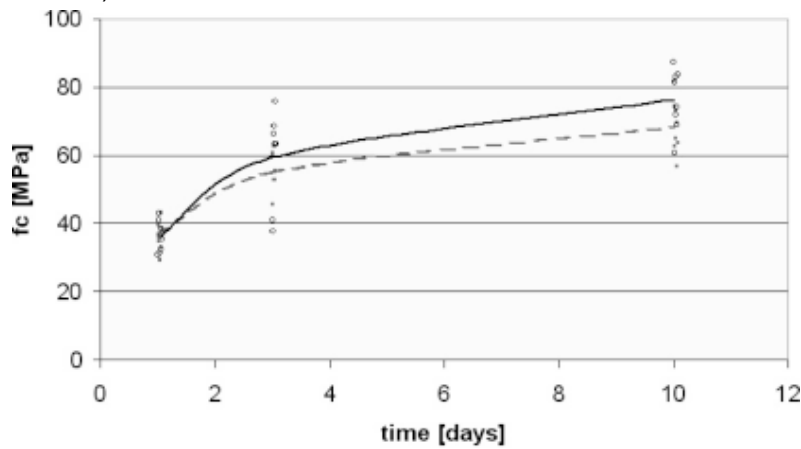
The FMR spectra were recorded using a standard X-band Bruker E 500 ( $\nu = 9.4$  GHz) spectrometer with a magnetic field modulation of 100 kHz at room temperature. The magnetic field was scaled with an NMR magnetometer. Samples containing ~20 mg of the investigated material in form of fine powder were sealed into quartz tubes 4 mm in diameter.

## 3. RESULTS AND DISCUSSION

Samples of cement mortar with magnetic nanoparticles were subjected several times to a high magnetic field (~1.6 T) before FMR measurements. After this treatment the obtained spectra were iden-



**Fig. 2.** Room temperature compressive strength of cement mortar without (solid line) and with nickel nanoparticles (dashed line).



**Fig. 3.** Room temperature compressive strength of cement mortar without (solid line) and with  $\alpha$ -iron nanoparticles (dashed line)

tical in repetitive measurements. The magnetic nanoparticles were dispersed almost homogeneously in the concrete matrix because the FMR spectra from different parts of a bulk material were the same.

Fig. 1 shows the FMR spectra of cement mortar with a small concentration (0.6 wt.%) of magnetic nanoparticles of 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 the sample without magnetic nanoparticles is similar to that obtained in [14]. The spectrum of cement mortar with a mixture of magnetic fcc-nickel/carbon nanoparticles with and without water presents a symmetrical and intense FMR line with a resonance field centred at  $H_r = 3008$  Gs ( $g_{\text{eff}} = 2.23(1)$ ) with linewidth  $\Delta H_{pp} = 610(5)$  Gs and  $H_r = 2964$  Gs ( $g_{\text{eff}} = 2.27(1)$ ) with linewidth  $\Delta H_{pp} = 780(5)$  Gs, respectively. The relative integrated intensity of both samples with nanoparticles is the following:  $I_3 \Delta H_3^2 / I_2 \Delta H_2^2 = 1.6$ ,

where  $I$  is the line amplitude and  $\Delta H$  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 cement mortar in which the magnetic nanoparticles could 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,  $\nu$  - the resonance frequency,  $\mu_B$  - 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  $\alpha$ -iron magnetic nanoparticles is similar to that observed for these aggregates embedded in other non-magnetic matrices [15].

Figs. 2 and 3 present the compressive strength action on the cement mortar samples with fcc-nickel/carbon and  $\alpha$ -iron/carbon nanoparticles, respectively. The shape of the samples and the procedure of measurements has been described in [9]. The figures show the time dependence of mechanical parameters of the cement mortar during the most important period of 28 days. The compressive strength increased about 15% for the specimen with fcc-nickel/carbon while an opposite effect of decreasing of about 9% for sample with  $\alpha$ -iron/carbon was observed. The compressive strength for cement mortar with a small concentration of magnetic nanoparticles of  $\alpha$ -iron/carbon displayed a similar trend as registered for samples with carbide iron and cobalt nanoparticles [9]. Opposite behaviour of bcc-nickel/carbon could be connected with a smaller size of nanoparticle aggregates.

Cement mortar is composed of small grains of hydrated calcium silicate gels and large crystals of hydrated products, with nanosized pores and capillary pores distributed among them. There is room for nanoparticles to improve the plain cement mortar properties. However, as the nanoparticles easily aggregate due to their great surface energy, a large quantity of these particles could not be uniformly dispersed. In this case the aggregating nanoparticles will create a weak zone, in form of voids, and the mechanical properties of cement mortars will be degraded.

The cement mortar matrix system of pores offers a possibility for greater mobility of fcc-nickel nanoparticles with small-sized agglomerates. 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 nanoparticles could participate in the so called "pillow" phenomenon which would increase the compressive strength of the cement mortar. There are three other possible nonmagnetic routes to increase the compressive strength. Firstly, the nanoparticles act as a nucleus to tightly bind with the cement hydrate promoting cement hydration. Secondly, nanoparticles will prevent large crystals such as  $\text{Ca}(\text{OH})_2$  from growing. Thirdly, nanoparticles and small agglomerates could fill the cement pores, thus increasing the strength, as the silica fume does. It is very probable that these nonmagnetic mechanisms play a leading role in changing the compressive strength of the investigated specimens and the magnetic interactions could be crucial in case of a larger amount of used nanoparticles.

It is already known that an addition of a small amount of magnetic nanoparticles to a polymer matrix changes essentially such critical parameters of the polymer as crystallization or melting temperatures [17,18]. An increase in the melting point of a matrix containing a small concentration of magnetic nanoparticles suggests an increase in the attraction force. The freezing processes influenced by the relaxation phenomena and connected with increased internal stress with decreasing temperature could induce the reorientation processes and increase the magnetic momentum of agglomerates [19-21]. A similar effect could be accomplished in concrete materials by dehydration processes. The time dependence of the compressive strength parameter for both samples with different magnetic nanoparticles shows an opposite effect (Figs. 2 and 3). The critical factor here is the different size of agglomerated nanoparticles: nickel nanoparticle agglomerates are much smaller than iron agglomerates. Complicated magnetic interactions in this situation depend on the sizes of magnetic agglomerates. We have to deal with an 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 fabrication of magnetic shielding for radiation.

#### 4. CONCLUSIONS

The FMR study of a small amount of fcc-nickel/carbon and  $\alpha$ -iron magnetic nanoparticles as additives to concrete showed an observable influence of the magnetic interaction on the process of concrete formation for a concentration of nanoparticles greater than 0.4 wt.%. The compressive strength increased by 15% for the concrete with the fcc-nickel/carbon nanoparticles in form of small aggregates while an opposite effect was observed (decrease by 9%) for concrete with  $\alpha$ -iron/carbon nanoparticles forming large aggregates. The magnetic mechanism of influencing the compressive strength could be important in case of a large concentration of nanoparticles. Thus, the amount of nanoparticles and the size of agglomerates seems to play a critical role in enhancing the mechanical performance of cement mortars.

#### REFERENCES

- [1] B. Heinrich, S. T. Purcell, J. R. Dutcher, K. B. Urquhart, J. F. Cochran and A. S. Arrot // *Phys. Rev. B* **38** (1988) 12879.

- [2] N. B. Brookes, A. A. Clarke and P. D. Johnson // *Phys. Rev. B* **46** (1992) 237.
- [3] V. F. Puentes, K. M. Krishan and A. P. Alivisatos // *Science* **291** (2001) 2115.
- [4] L. F. Yin, D. H. Wei, N. Lei, L. H. Zhou, C. S. Tian, G. S. Dong, X. F. Jin, L. P. Guo, Q. J. Jia and R. Q. Wu // *Phys. Rev. Lett.* **97** (2006) 067203.
- [5] P. Yu, X. F. Jin, J. Kudrnovsky, D. S. Wang and P. Bruno // *Phys. Rev. B* **77** (2008) 054431.
- [6] T. Nagao, Y. Kubo, A. Koizumi, H. Kobayashi, M. Itou and N. Sakai // *J. Phys.: Condens. Matter* **20** (2008) 055201.
- [7] P. C. Aitcin // *Cem. Concr. Res.* **30** (2000) 1349.
- [8] J. O. Odigure // *Cem. Concr. Res.* **26** (1996) 1171; **29** (1999) 303; **31** (2001) 51.
- [9] J. Blyszko, W. Kiernozycki, N. Guskos, G. Zolnierkiewicz, J. Typek, U. Narkiewicz and M. Podsiadly // *J. Non-Cryst. Solids* **354** (2008) 4515.
- [10] D. F. Lin and M. C. Tsai // *J. of the Air & Waste Manag. Assoc.* **56** (2006) 1146.
- [11] C. Shi and J. Qian // *Resources, Conservation and Recycling* **29** (2000) 195.
- [12] S. Kourounis, S. Tsivilis, P. E. Tsakiridis, G. D. Papadimitriou and Z. Tsibouki // *Cem. Concr. Res.* **37** (2007) 815.
- [13] M. Sobon, E. Lipinski, J. Typek, A. Guskos, U. Narkiewicz and A. Podsiadly // *Solid State Phenomena* **128** (2007) 193.
- [14] N. Guskos, G. Zolnierkiewicz, A. Guskos, J. Typek, J. Blaszkowski, W. Kiernozycki, U. Narkiewicz and M. Podsiadly // *J. Non-Cryst. Solids* **354** (2008) 4510.
- [15] N. Guskos, E. A. Anagnostakis, G. Gasiorek, J. Typek, T. Bodzionny, U. Narkiewicz, W. Arabczyk and W. Konicki // *Mol. Phys. Rep.* **39** (2004) 58.
- [16] D. Sibera, U. Narkiewicz, N. Guskos and G. Zolnierkiewicz // *J. Phys. (Conference Series)* **146** (2009) 012014.
- [17] J. Majszyk, N. Guskos, J. Typek, V. Likodimos, M. Maryniak, Z. Roslaniec, M. Kwiatkowska and D. Petridis // *J. Non-Cryst. Solids* **352** (2006) 4279.
- [18] M. Maryniak, N. Guskos, J. Typek, D. Petridis, A. Szymczyk, A. Guskos, K. Goracy, Z. Roslaniec and M. Kwiatkowska // *Polimery (Poland)* **54** (2009) 546.
- [19] N. Guskos, V. Likodimos, S. Glenis, J. Typek, M. Maryniak, Z. Roslaniec, M. Baran, R. Szymczak, D. Petridis and M. Kwiatkowska // *J. Appl. Phys.* **99** (2006) 084307.
- [20] N. Guskos, V. Likodimos, S. Glenis, M. Maryniak, Z. Roslaniec, M. Baran, R. Szymczak, D. Petridis and M. Kwiatkowska // *J. Nanoscience and Nanotechnology* **8** (2008) 2127.
- [21] N. Guskos, J. Typek and M. Maryniak // *phys. stat. sol. (b)* **244** (2007) 859.