Nanostructured MP-Iron compounds. Properties and applications

A. M. Bondar, Elena Enescu*,C. Banciu**, G. Stoian*, *B. Rand**,*
*Ioan Stamatin****
**Research Institute for Electrical Engineering – Advanced Research, 313 Splaiul Unirii, 030138, Bucharest,*
** Institute for Materials Research ,School of Process, Environmental and Materials Engineering University of Leeds, Leeds, LS2 9JT, UK
****University of Bucharest, Faculty of Physics, 3Nano-SAE Research Centre, Bucharest, MG-11, 77125, Romania*
Corresponding author e-mail address: abondar@icpe-ca.ro

1. Introduction

The composites where a carbon phase contains metal nanoparticles dispersed have large studied due to they exhibit outstanding properties and used as electric, electronic, absorbent, antibacterial and catalyst materials. There is lot of methods to induce nanometric metal particles in a carbon matrix using different precursors with a further heat treatment up to 1000^0C. In many cases, the metallic phase looses their initial properties and uncontrolled reactions take place. To avoid these inconvenients composites based on MP with iron compound are developed in our contribution.

A series of composites, MP (mesophase pitch) with nanoiron/coated carbon, iron oxide (Fe_2O_3, Fe_3O_4), ranged from microscale to nanoscale, have been studied related to magnetically, electrical and structural properties. The magnetic properties can be accommodated from materials with memory to materials for EMI- shielding depending on the dispersion method and structural feature induced by thermal treatment up to 450^0C. The composites MP-Iron compounds can be developed as materials with extremely large applications from memory materials to EMI using a large spectrum in concentrations bellow and over percolation threshold. The aim of this paper concerns with methods for processing of these materials related to physical properties induced

2. Experimental

Raw materials:

- Mesophase and Carbon matrix precursor: petroleum pitch with softening point 70°C and high solubility to quinoline (99,55).
- Nanoiron carbon coated (*NCFe*): synthesized by Laser pyrolysis in a mixture ethylene /$Fe(CO)_5$ conform with procedure described in [1]. Grain size, 6-10 nm, measured with HRTEM. These nanoparticles are a complex compound iron-iron oxides-coated with nanocarbon.
- Iron oxide (Fe_2O_3) micron powder, obtained by an usual alkaline reduction chemical process with Fisher diameter 0.1 μm,

Mixtures and thermal treatment

- MP-NCFe were prepared conform with methods described elsewhere [3], in series of 0.05 - 1.5 % weight for iron coated nanocarbon and 1 - 7 % for iron oxide (*MPIrox*)

- The composites were treated at 460°C (previously established as an optimum temperature for mesophase nucleation in the presence of foreign particles),

Analysis:

- DC resistivity: home made Piston cylinder (PC) high pressure apparatus with teflon die and HSS anvils. The samples were compressed at ~0.1 GPa. The electrical resistance was measured with digital multimeter.
- AC measurements: loss tangent with Q-meter, model FERISOL, in range 0.2- 25 MHz
- Thermal analysis: DTA model Q 1500D in argon atmosphere.
- Optical microscopy: Carl Zeiss NU 2 microscope with digital camera
- Coercivity and the saturation magnetization: Vibrating Sample Magnetometer (VSM, 7300).
- Raman spectroscopy: model S-2000, Ocean optics

3. Results and discussions

Raman spectra on samples MP-NCFe and MP-Irox show the characteristics for iron oxides positioned to 500 - 550cm^{-1}, that being the evidence the oxides are not reduced or transformed.

The electrical resistivity of the composites (table 1) has distinctive features and give a rough idea of the dimension dependence when micro and nanoparticles are added.

Table1. Electrical resistivities for composites NC/Fe and Fe_2O_3

MPNCFe (% wt)	Resistivity (ohm *cm)	MPIrox Fe_2O_3 (% wt)	Resistivity (ohm cm)
0.05	36.3*10^5	1	8.21*10^5
0.1	31.5*10^5	3	5.78*10^5
1	43.8*10^5	5	6.52*10^5
1.5	137*10^5	7	14.6*10^5

By comparison, the two series of composites have a threshold at 1% and 5% respectively, where the resistivity increases several times. Under these thresholds, no any changes are induced. Optical microscopy inspection shows that MP in presence of micro and nanopartilces is much more fragmented in all the volume and seemingly is not dependent of the particle size.

Powder XRD pattern (figure 1) shows a sharper (002) for NCFe, and that with Iron oxide an excess of iron released ought to oxide reduction in the carbon presence. Large but well defined (10) and (004) peaks with NCFe is associated with the catalyst role of iron.

Thermo-differential analysis confirm the structural modification in composites

The composites with Iron oxides add-on have same behavior as MP. The mass loss is not influenced by iron oxide microparticles. Thermal decompositions have three temperature ranges and total loss is around of 41-42%.

The NCFe has an other influence: the volatiles being adsorbed by nanoparticles the first peak is shadowed.

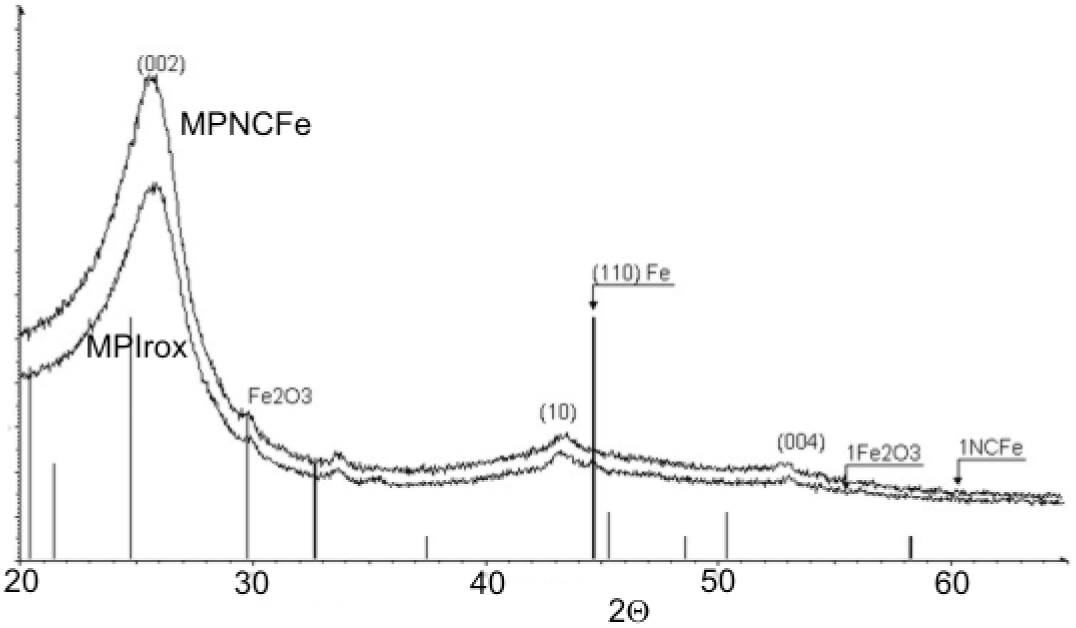

Figure 1- PXRD, for MP with 1% NCFe and MP with 1% Iron oxide microparticles.

The second peak is assigned to volatile desorption with a slow conversion to carbon. The third peak is assigned to massive residual volatile desorption ought to regular pyrolysis in MP. The catalyst effect of the iron nanoparticles being more slow than desorption phenomena do not give a significant contribution to carbon conversion. Significant is that the kinetics (V_{max}) is large decreased when nanoparticles are present in initial raw materials (petroleum coal tar pitch).

Tabel2. TG- analysis on MP, MPNCFe 1% and MPIrox 1%

Material	%Δm	$T_I\,^{o}C$	$T_{II}\,^{o}C$	$T_{III}\,^{o}C$	$\%\Delta m_{330^{o}C}$	V_{max}
MP	41.5	140-200	362	402-418	20.5	0.256
1% Fe_2O_3	42.1	160	326-342	400	22.6	0.276
1% NCFe	37.8	-	345	360-390	18.3	0.209

The dielectric losses are more sensitive with the frequency range. At low frequency the dielectric losses are more important in samples where NCFe are added. At higher range the effects are similar due to the both materials added in MP have more magnetic behavior, (table 3).

Table 3- dielectric losses (tgδ) and dielectric constant (k)

Frequency range, kHz	1% Fe_2O_3	1%NC/Fe tgδ	1% Fe_2O_3 k	1%NC/Fe k
200-2800	0.1583	0.0845	1.1542	1.1143
3200-5000	0.0739	0.0345	1.1429	1.3280
5500-8500	0.0528	0.0338	0.9396	0.9419
9000-11500	0.0517	0.0533	0.9969	0.9933

The magnetic properties in special the hysteresis is much more different in that two samples.(figure 2). The MPNCFe has a hysteresis more tight than iron oxide

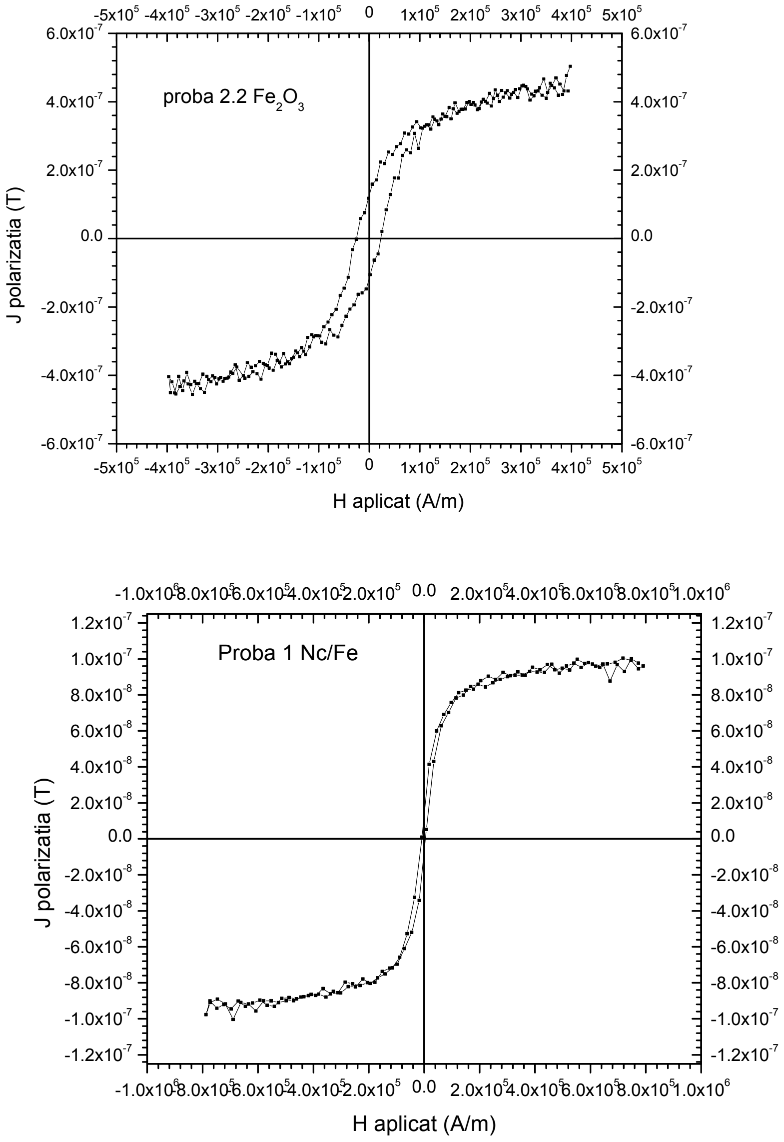

Figure 2- Hysteresis cycle for Iron oxide and NCFe samples

4. Conclusions

The insertion of the micro and nanoparticles with magnetic properties in raw materials, petroleum coal tar pitch, with thermal treatment in range where MP is developed induce morpho-structural transformations giving materials with large area of applications in electromagnetic interference shielding. The accommodation of the particle size this materials can be shaped to have a residual magnetic memory.

References

1. Project NATO-SfP 974214, Carbon ceramic materials, 2000-2004
2. F. Dumitrache, I. Morjan, et all, *“Laser-induced single step preparation of carbon encapsulated iron nanoparticles”,* Int. Conf on Carbon CARBON’03, Oviedo, Spain, 6-10 July, 2003