Carbon/iron composites

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The objective of our investigations was to establish the electrical and magnetically behavior of composites when structural changes are induced by different types of additives and different temperatures of processing. The composites based on conductive matrix are obtained by additivation of a fractionated coal tar pitch with nanoiron with a carbon shell (NCFe) and iron oxides (Fe_2O_3). The additivated fractionated coal tar pitch was heat treated at mesophase condensation (460°C) and coke formation (900°C) temperatures. The structural and physical changes have been investigated.

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1. Introduction

The composites with a carbon phase containing dispersed metal nanoparticles have been extensively studied because they exhibit outstanding properties and they can be widely used as electronic, electrical and magnetic devices, adsorbents, antibacterial agents and oxidation/reduction catalysts, electromagnetic inference shielding [1]. There are lots of methods of inducing nanometric metal particles in a carbon matrix using different precursors with a further heat treatment, up to 1000°C: from a petroleum residue by heating at 420°C with ferrocene under pressure [2], from a furan resin or polyfurfuryl alcohol and ferrocene [3] or by a sol-gel technique [4]. In many cases the metallic phases lose their initial properties and uncontrolled reactions take place. To avoid these inconvenient, we have developed composites based on MP (mesophase pitch) with iron compounds [5].

A series of composites, MP with carbon-coated nanoiron (NCFe) and with iron oxide (Fe_2O_3), ranging from micro scale to nano scale, have been studied relating to their structural, electrical and magnetic properties [6-9]. The magnetic properties depend on the dispersion method and the structural feature induced by the thermal treatment at 460°C and 900°C. The MP-iron composites can be developed as materials with extremely large applications from memory materials to EMI shielding using a large spectrum in concentrations below and over percolation threshold. The aim of this paper concerns with methods for processing of these materials related to induced physical properties.

2. Experimental

Raw materials:

- Mesophase and carbon matrix precursor: petroleum pitch with softening point 70°C and high solubility to quinoline (99.55).
- Carbon-coated nanoiron (NCFe): synthesized by laser pyrolysis in a mixture ethylene/$Fe(CO)_5$ in concordance with procedure described in [10]. Grain size, of about 6-10 nm, was measured with HRTEM technique. These nanoparticles are a complex compound iron-iron oxides-coated with carbon.
- Iron oxide (Fe_2O_3) micron powder, obtained by a usual alkaline reduction chemical process with Fisher diameter 0.1 μm.

Mixtures and thermal treatment:

- The carbon matrix precursor (mesophase) was a petroleum pitch with softening point 70°C and high solubility to quinoline (99.55).
- MPNCFe and MPIrox were prepared in concordance with methods described elsewhere [7], in series of 0.05 - 1.5 % weight for carbon-coated nanoiron and 1 - 10 % for iron oxide.
- The composites were heat treated, at a rate of 1°C/minute, up to 460°C and 900°C, in an inert atmosphere (argon), with a soaking time of 3 hours at each final temperature.

3. Results

The composites, MPNCFe and MPIrox, were structural characterized using optical microscopy. The optical properties were studied by using a Carl Zeiss Jena NU 2 microscope with digital camera attached.

The electrical DC resistivity was performed with a 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.

The coercivity and the saturation magnetization were performed with a Vibrating Sample Magnetometer (VSM, 7300).

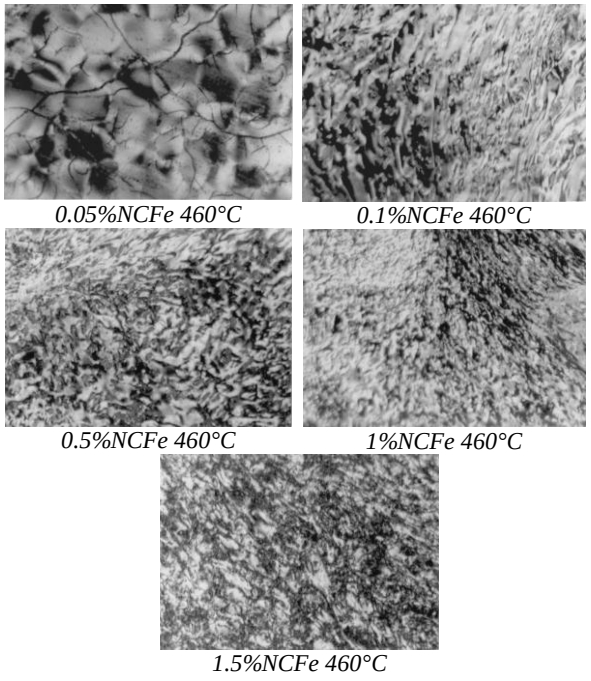


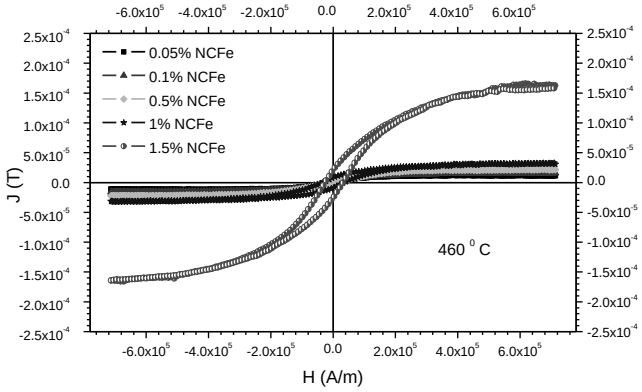
Fig. 1. Optical micrographs of MPNCFe and MPIrox samples heat treated at 460°C and 900°C (300X).

Table 1. Electrical resistivity for composites MPNCFe and MPIrox.

MPNCFe			**MPIrox**		
NCFe (% wt)	**Resistivity (ohm·cm)**		**Fe_2O_3 (% wt)**	**Resistivity (ohm·cm)**	
	460°C	**900°C**		**460°C**	**900°C**
0	$29.1 \cdot 10^5$	0.256	0	$29.1 \cdot 10^5$	0.256
0.05	$36.3 \cdot 10^5$	0.566	1	$8.21 \cdot 10^5$	0.262
0.1	$31.5 \cdot 10^5$	0.437	3	$5.78 \cdot 10^5$	0.448
0.5	$50.3 \cdot 10^5$	0.430	5	$6.52 \cdot 10^5$	1.070
1	$43.8 \cdot 10^5$	0.589	7	$14.6 \cdot 10^5$	0.383
1.5	$137 \cdot 10^5$	0.996	10	$2.12 \cdot 10^5$	0.510

Table 2. Magnetic properties for composites NCFe and Fe_2O_3.

MPNCFe				MPIrox		
T [°C]	NCFe % wt	Hc [A/m]	Jr [T]	Fe_2O_3 % wt	Hc [A/m]	Jr [T]
460	0.05	16000	2.40E-06	1	18000	2.01E-05
	0.1	22000	3.15E-06	3	25000	1.72E-04
	0.5	25400	4.05E-06	5	22900	7.90E-04
	1	34600	8.62E-06	7	25400	1.04 E-03
	1.5	28500	2.25E-05	10	25900	3.01 E-03
900	0.05	65255	4.39E-08	1	19895	2.34E-07
	0.1	23078	6.74E-08	3	23078	6.23E-07
	0.5	14324	4.70E-08	5	18304	1.18E-06
	1	21487	8.36E-08	7	21487	6.73E-07
	1.5	19099	1.17E-07	10	20691	3.51E-06



a)

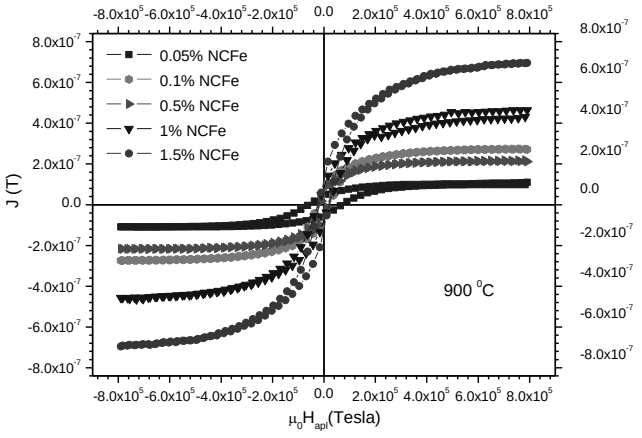


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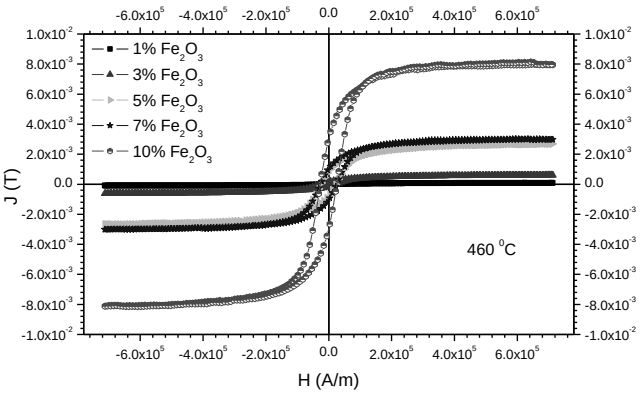
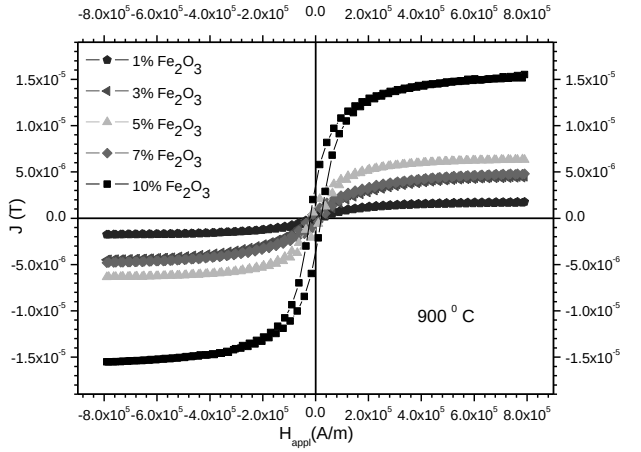
Fig. 2. Hysteresis cycles for MPNCFe samples heat treated at 460°C (a) and 900°C (b).



a)



b)

Fig. 3. Hysteresis cycles for MPIrox samples heat treated at 460°C (a) and 900°C (b).

4. Discussion

In Fig. 1 are presented optical micrographs of all the samples. Optical microscopy structures show that MP in presence of micro and nanoparticles is much more fragmented in all the volume and seemingly is not dependent of the particle size, but the structure depends on quantity of micro or nanoparticles added.

At the temperature of 460°C, the mesophase stage was surpassed and the structure is like a semicoke. We can observe the coalescence of mesophase spherules only for two samples heat treated at 460°C, added with 0.05% NCFe, respectively 1% Fe_2O_3.

The coke structure is more fragmented with the increasing of quantity of particles added. For the samples with 10% Fe_2O_3 added in pitch, the iron oxide appears agglomerated.

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

By comparison, the two series of composites heat treated at 460°C have a threshold at 0.5% and 7% respectively, when the resistivity increases several times.

For the samples MPNCFe at 460°C, resistivity increase with the increasing quantity of nanoparticles added, the resistivity depending on the matrix of the composites. For the samples MPIrox at 460°C, resistivity decrease with the increasing quantity of microparticles added. For the samples MPNCFe and MPIrox heat treated at 900°C, the resistivity decrease very much with approximate 10^6 due to matrix carbonization. At this temperature, low resistivity is given by the carbon matrix, which became more conductive because the structure is more ordered than in composites heat treated at 460°C.

From analyses of magnetic data we can conclude that the saturation increase with mass concentration of magnetic particles. The analysis of primary data plot of resistivity and magnetic properties depending on the mass concentration of particles, we can see that point of inflection coincides in all, and it indicates the percolation threshold. The samples MPNCFe in both cases of temperature, the percolation threshold is around 1%, while the samples with Fe_2O_3, it is observed at 7%. These data are validated by optical microscopy.

5. 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 and coke are developed induce morpho-structural and functional transformations. Taking into account the results of electrical and magnetic measurements, the resulting materials could be used for electromagnetic interference shielding applications conform to the safety and health legislative requirements regarding the workers exposure to the risks generated by electromagnetic fields [11, 12, 13].

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