A series of composites, mesophase pitch with nanoiron/coated carbon, iron oxide, have been studied related to magnetically, electrical and structural properties. 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 below and over percolation threshold.

Key words: mesophase pitch, nanoiron, iron oxide, composites.

1. INTRODUCTION

The composites where a carbon phase contains metal nanoparticles dispersed have been largely studied due to the fact that they exhibit outstanding properties and are used as electric, electronic, absorbent, antibacterial and catalyst materials. There are a lot of methods to induce nanometric metal particles in a carbon matrix using different precursors with a further heat treatment up to 1000°C. In many cases, the metallic phase loses its initial properties and uncontrolled reactions take place. To avoid these inconvenient 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 (Fe₃O₄, Fe₃O₃), 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°C. 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 below 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 to procedure described in article [2]. Grain size, 6–10 nm, measured with HRTEM. These nanoparticles are a complex compound iron-iron oxides-coated with nanocarbon.
- Iron oxide (Fe₂O₃) micron powder, obtained by a usual alkaline reduction chemical process with Fisher diameter 0.1 µm.

Mixtures and thermal treatment

- MP-NCFe were prepared according to the methods described elsewhere [3], in series of 0.05–1.5% weight for iron coated nanocarbon and 1–7% weight for iron oxide (MP-Irox).
- 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).

3. RESULTS AND DISCUSSIONS

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

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
MP/NCFe [wt %] & Resistivity [Ω m] & MP/Irox [wt %] & Resistivity [Ω m] \\
\hline
0.05 & 36.3 \times 10^3 & 1 & 8.21 \times 10^3 \\
0.1 & 31.5 \times 10^3 & 3 & 5.78 \times 10^3 \\
1 & 43.8 \times 10^3 & 5 & 6.52 \times 10^3 \\
1.5 & 137 \times 10^3 & 7 & 14.6 \times 10^3 \\
\hline
\end{tabular}
\caption{Electrical resistivities for composites NC/Fe and Fe$_2$O$_3$, $T = 25$°C}
\end{table}

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 nanoparticles is much more fragmented in all the volume and seemingly is not dependent of the particle size.

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

![Fig. 1. – PXRD, for MP with 1% NCFe and MP with 1% Iron oxide microparticles.](image)

Thermo-differential analyses 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 another influence: the volatiles being adsorbed by nanoparticles the first peak is shadowed.

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 ($V_{\text{max}}$) is large decreased when nanoparticles are present in initial raw materials (petroleum coal tar pitch).

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).

The magnetic properties in special the hysteresis is much more different in that two samples (Fig. 2). The MP-NCFE has a hysteresis more tightly than iron oxide.

### Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>$%\Delta m$</th>
<th>$T_{\text{I}}$°C</th>
<th>$T_{\text{II}}$°C</th>
<th>$T_{\text{III}}$°C</th>
<th>$%\Delta m_{330°C}$</th>
<th>$V_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>41.5</td>
<td>140–200</td>
<td>362</td>
<td>402–418</td>
<td>20.5</td>
<td>0.256</td>
</tr>
<tr>
<td>1% Fe$_2$O$_3$</td>
<td>42.1</td>
<td>160</td>
<td>326–342</td>
<td>400</td>
<td>22.6</td>
<td>0.276</td>
</tr>
<tr>
<td>1% NCFE</td>
<td>37.8</td>
<td>–</td>
<td>345</td>
<td>360–390</td>
<td>18.3</td>
<td>0.209</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Frequency range, kHz</th>
<th>$\text{tg} \delta$</th>
<th>$k$ [F/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>200–2800</td>
<td>0.1583</td>
<td></td>
</tr>
<tr>
<td>3200–5000</td>
<td>0.0739</td>
<td>1.1542</td>
</tr>
<tr>
<td>5500–8500</td>
<td>0.0528</td>
<td>1.1429</td>
</tr>
<tr>
<td>9000–11500</td>
<td>0.0517</td>
<td>0.9969</td>
</tr>
</tbody>
</table>

### 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 these materials can be shaped to have a residual magnetic memory.
REFERENCES