COMPOSITES OBTAINED FROM Cu AND Fe₃O₄
NANOPowDERS

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Un nanocompozit cu baza cupru armat cu nanoparticule de magnetită a fost
obținut și caracterizat Pulberile nanometric de cupru și respectiv magnetită, au
 fost obținute prin metode chimice. Aceste pulberi caracterizate prin XRD, SEM,
TEM, s-au folosit pentru obținerea unui nanocompozit Cu-Fe₃O₄, prin metodele
clasice ale metalurgiei pulberilor (presare și sinterizare).

A copper-based nanocomposite reinforced with nanoparticles of magnetite
has been obtained and characterized. Nanoscale powders of copper, respectively
magnetite, were obtained by chemical methods. These powders are characterized by
XRD, SEM, TEM and were used to obtain a Cu-Fe₃O₄ nanocomposite by
conventional methods of powder metallurgy (compacting and sintering).

Keywords: intermetallic composite, nanomaterials, powder metallurgy, magnetite

1. Introduction

In modern industry, more and more interest is given to the development of
new composites, such as high resistant, alternative materials of low density in
order to obtain multifunctional pieces. The powder metallurgy components are
being widely used for sophisticated industrial applications [1]. The worldwide
popularity of powder metallurgy is the ability of this technique to produce such
complex shapes with exact dimensions at a very high production rate and low
cost.

These materials show good thermal conductivity and wear resistance and
also low thermal expansion, all of which makes them high, multifunctional, light
weight materials. Additionally, it is a very attractive way to add Fe₃O₄-iron oxide
reinforcement to improve the magnetic permeability of these composites and by
this way, good synchronization between thermal and electrical conductivities and
magnetic permeability.

Besides high mechanical properties, high electrical and thermal
conductivity properties are more required [2]. Within this group of materials
particularly promising are those of nano - metric size of the matrix hardening

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phase grains. This paper is focused on this problem. Investigations on fabrication, properties and microstructure of a copper matrix - hardened with magnetite - microcomposites are presented.

2. Experimental procedures

The obtaining of the Fe$_3$O$_4$ nanopowders was made by the coprecipitation method [3]. Chemical coprecipitation is a simple and economical method of obtaining the magnetite nanoparticles. One can use cheap iron salts with different precipitation agents (NaOH, NH$_3$, urea, mixtures of precipitation). It results nanosize particles of iron oxides in relatively large quantities in a short reaction time, important aspects from economically point. The copper powder was obtained using the polyol reduction process [4].

Nanocomposites with Cu – Fe$_3$O$_4$, containing 5%, 15% and 20% Fe$_3$O$_4$ were obtained. These were obtained by the powder metallurgy technique [5], by compacting and sintering. The mixtures of powders were compacted at 500 and 700 MPa at room temperature and then sintering in vacuum at 650$^\circ$ and 800$^\circ$ C for 1 hour. The compacting was realized using a unidirectional press in an antimagnetic matrix. The resulted nanocomposites was examined using SEM, XRD and EDS. The paper presents also the resulted values for the technological properties of nanoscale powder mixtures. In the same time was performed a cold rolling in order to check the maximum degree of deformation [6].

3. Results and discussion

Examination of the microstructure of the Fe$_3$O$_4$ powders has shown that the particles size was of an order 5-10 nm. The magnetite nanoparticles were prepared by coprecipitation of ferrous ion (Fe$^{2+}$) and ferric ion (Fe$^{3+}$) with NaOH solution. The agglomeration of particles should be properly controlled. Fig. 1a represents a transmission electron microscope bright field (TEMBF) image. The image shows spherical particles with low sizes, well dispersed. Fig. 1b represents an electron diffraction image that shows the interplanar distances corresponding to the magnetite nanoparticles [7].

In Fig. 1c (HRTEM image), in a selected area of the sample, the interplanar distances (311) si (220), corresponding to magnetite could be identified. The obtained magnetite has a crystalline structure belonging to the face-centered cubic lattice.

The copper powder was obtained by the polyol reduction process. The size of the particles is between 10-30 nm and has a concentrations of 99,9% copper.

Mixtures of copper and magnetite nanopowders, obtained by chemical synthesis [8] are subjected to pressing process in order to obtain stable tablet form and size, and sufficient mechanical strength for the subsequent manipulation.
The obtained powders at different compaction pressures were characterized in terms of technological properties (density, compactness, porosity), and morphological structure assessed by high-performance electron microscopy. The resulted values for the technological properties of nanoscale powder mixtures are shown in Table 1.

**Table 1**

<table>
<thead>
<tr>
<th>Content Fe₂O₃ in Cu [%]</th>
<th>Theoretical Density ( \rho_m ) g/cm³</th>
<th>Apparent density ( \rho_a ) g/cm³</th>
<th>Compacted fill Cu %</th>
<th>Pore filling P %</th>
<th>Density shaking ( \rho_f ) g/cm³</th>
<th>Flow rate [sec.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>8.753</td>
<td>1,2141</td>
<td>13,870</td>
<td>86,130</td>
<td>1,4570</td>
<td>not flowing</td>
</tr>
<tr>
<td>10</td>
<td>8.566</td>
<td>1,1886</td>
<td>13,876</td>
<td>86,120</td>
<td>1,4382</td>
<td>not flowing</td>
</tr>
<tr>
<td>15</td>
<td>8.379</td>
<td>1,1631</td>
<td>13,881</td>
<td>86,119</td>
<td>1,4099</td>
<td>not flowing</td>
</tr>
<tr>
<td>20</td>
<td>8.192</td>
<td>1,1375</td>
<td>13,885</td>
<td>86,115</td>
<td>1,3878</td>
<td>not flowing</td>
</tr>
</tbody>
</table>
The table data are the arithmetic average of three determinations. Note that after pressing, there are initial particle rearrangement and particle welding, resulting in particle size between 300-600 nm.

At pressure of 700 MPa, there is a sliding of the formed agglomerates and partial filling holes deeper than at compaction pressure of 500 Mpa. Electron microscopy images obtained at magnifications of x160000 show that agglomerates are actually composed of nanoparticles with sizes between 23 - 47nm (Fig.2a and b). Thus the obtained particles have a nanostructure, similar to the initial powder mixture subjected to pressing.

Fig. 2. SEM micrographs of pressed powders at 700Mpa
a). agglomerated powder b). agglomerated detail

The mixtures of pressed powders were sintered in vacuum. The technological parameters for this process were the following: sintering temperature 650°C respectively 800°C and sintering time, one hour.

In Fig. 3 it can be seen the sintering installation that was used to perform the above operations.
The sintering curve of a sample containing 15% Fe3O4, performed at a temperature of 800°C is shown in Figure 4.

After compacting and sintering, the obtained nanocomposite was examined by SEM, EDAX and XRD. In Fig. 5 is shown the SEM microstructure of the nanocomposite with 15% Fe3O4 (before and after sintering in vacuum at 650°C).
The images shows that after sintering the nanocomposites are more compact, but the investigations have shown that it is difficult to compact to high densities, avoiding retained porosity, and at the same time ensuring good powder particle bonding. Agglomeration is a definite problem in consolidated nanopowders.

The X-ray diffraction pattern of the Cu-Fe$_3$O$_4$ with 20% Fe$_3$O$_4$ nanocomposite is shown in Fig.6. The X-ray powder diffraction patterns of the materials proved its crystalline nature.

All the detected diffraction peaks that were indexed in Fig. 6 indicate that the particles correspond to magnetite, copper and a newly formed compound
Composites obtained from Cu and Fe₃O₄ nanopowders during sintering, CuFeO₂ (corresponding to natural mineral compound known as delafossite). The figure includes the distribution of the identified compounds according to the XRD semiquantitative analysis. The newly determined compound has 8% in the nanocomposite matrix.

The diffraction patterns showed very broad diffraction lines, in accordance with the small particle size and high specific surface area.

The EDS analysis (Fig. 7) of the nanocomposite Cu-Fe₃O₄ with 15% Fe₃O₄ represents the distribution of the elements which forms the matrix. The image shows an irregular dispersion of the magnetite which confirms the tendency to agglomerate of the nanoparticles.

![Fig. 7. EDS distribution in the nanocomposite Cu-Fe₃O₄](image)

The nanostructure of the sintered sample was examined using the transmission electron microscopy of high resolution (HRTEM) TECNAI F30 G² type. Crystalline magnetite nanoparticles are located both inside the larger copper grain and on the interface between them. Fig. 8 points to the existence of the nanocrystallite precipitates, which confirms the possibility to obtain nanostructures after pressing and sintering.
The obtained nanocomposite, was subjected to plastic deformation. Cold rolling was performed on a Mario di Maio reversible type LQR 120 (diameter cylinders support / work: 118/53 mm, figure9). The rolling speed was 3 m / min.

The rolling process was continued until the appearance on the surface of the samples of the first cracks (visible to the naked eye close observation). The maximum degree of deformation that can be supported by sample "A" (containing 5% Fe3O4) was 39.70%. The maximum degree of deformation that it can be supported by sample "B" (containing 15% Fe3O4) was 24.16%. The degree of deformation before mentioned are significant for a composite material. The quality of the rolling surface was good, there were no detachments or flaking.
Composites obtained from Cu and Fe3O4 nanopowders

Material. Increased content of magnetite results in decreased ability of plastic deformation of the material analyzed. Tests were performed with the hardness of nanocomposite reinforced with magnetite. The composite has a Vickers hardness higher than that of bulk copper, by approximately two times.

4. Conclusions

Results of the experiments show the possibility to obtained a Cu-Fe3O4 nanocomposites by conventional methods of powder metallurgy (pressing and sintering). The originality of the paper consists in using copper and magnetite nanopowders obtained by chemical methods (solvothermal method for Cu and coprecipitation method for Fe3O4). A new composite with a nano-size structure was obtained. After pressing and sintering, a new intermetallic compound CuFeO2 was identified. This intermetallic composite reinforced with iron oxide (Fe3O4) can be used essentially in electronic industry and robotics. First of all, certain parameters such as sintering time and sintering temperature, percentage of the reinforcement, compacting pressure, etc. were evaluated. A very important fact is that samples kept their nanostructure after the pressing and sintering process. Mechanical properties of the nanocomposite studied to date, exceeds the bulk material.

REFERENCES
