COMPOSITES OBTAINED FROM Cu AND Fe_3O_4 NANOPOWDERS

Andrei PREDESCU[1], Petru MOLDOVAN[2]

Un nanocompozit cu baza cupru armat cu nanoparticule de magnetită a fost obţinut şi caracterizat Pulberile nanometrice de cupru şi respectiv magnetită, au fost obţinute prin metode chimice. Aceste pulberi caracterizate prin XRD, SEM, TEM, s-au folosit pentru obţinerea unui nanocompozit Cu-Fe_3O_4, prin metodele clasice ale metalurgiei pulberilor (presare şi 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-Fe_3O_4 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 Fe_3O_4-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

[1] Ph. D. Student, Materials Science and Engineering Faculty, Politehnica University of Bucharest, Romania, e-mail: andrei.predescu@ecomet.pub.ro
[2] Prof., Materials Science and Engineering Faculty, Politehnica University of Bucharest, Romania

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_3O_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_3O_4, containing 5%, 15% and 20% Fe_3O_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^o and 800^o 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_3O_4 powders has shown that the particles size was of an order 5-10 nm. The magnetite nanoparticles were preapared 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 sferical particles with low sizes, well dispersed. Fig. 1b represents an electron diffraction image that shows the interplanar distances coresponding 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.

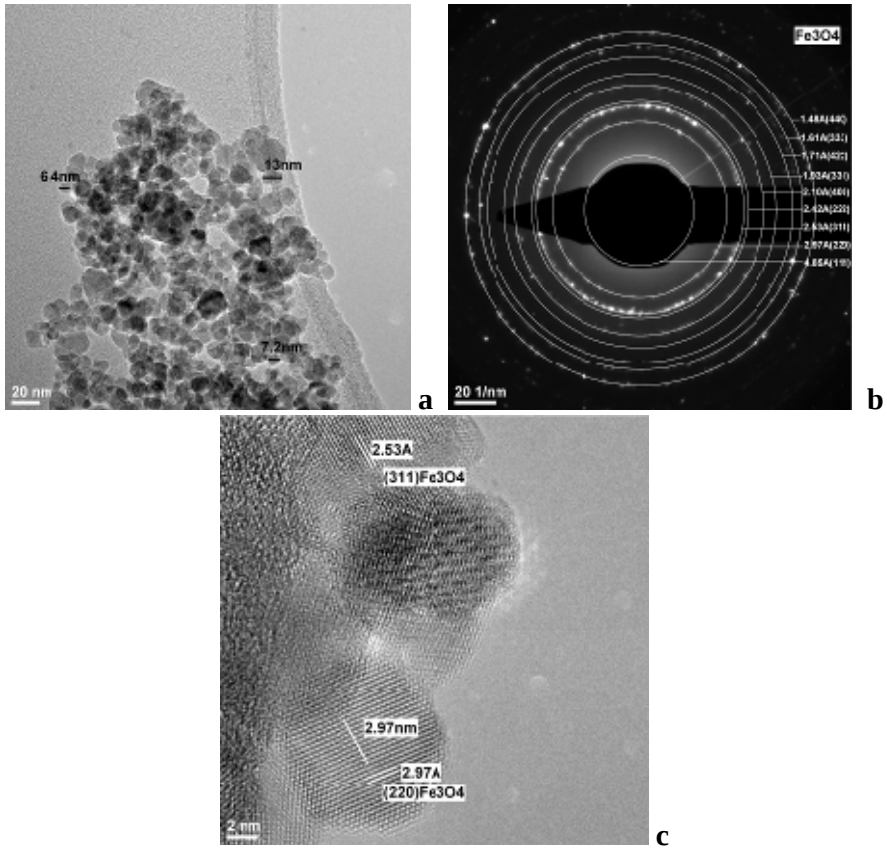


Fig. 1 a) TEM micrography of Fe_3O_4 particles; b) Electron diffraction pattern; c) HRTEM image with interplanar distances

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

Technological properties of powder mixtures of Cu-Fe3O4

Content Fe_3O_4 in Cu [%]	Theoretical Density [ρ_m g/cm^3]	Apparent density [ρ_a g/cm^3]	Compacted fill C_u %	Pore filling P %	Density shaking [ρ_t g/cm^3]	Flow rate [sec.]
5	8,753	1,2141	13,870	86,130	1,4570	not flowing
10	8,566	1,1886	13,876	86,120	1,4382	not flowing
15	8,379	1,1631	13,881	86,119	1,4099	not flowing
20	8,192	1,1375	13,885	86,115	1,3878	not flowing

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.

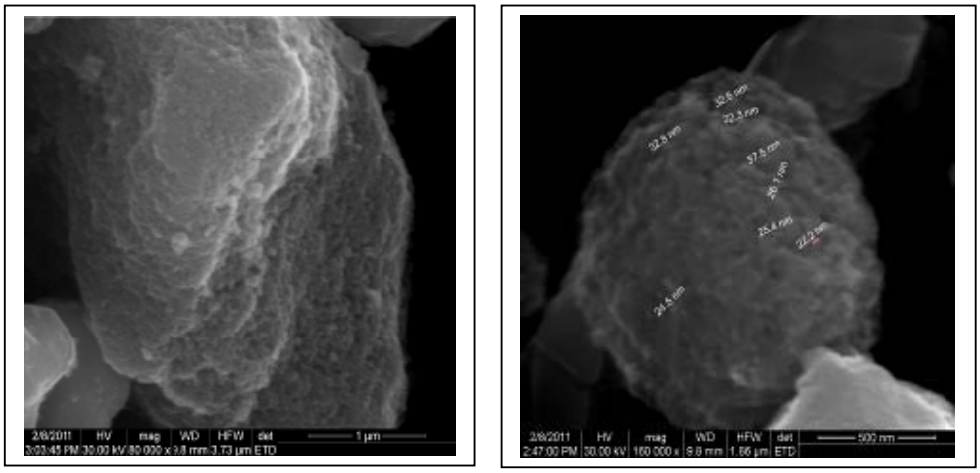


Fig. 2. SEM micrographs of pressed powders at 700Mpa
a). agglomerated powder b). agglomerated detail

The mixtures of pressed powders were sintered in vacuum. The technological parameters for this process were the following: sintering temperature 650^0C respectively 800^0C and sintering time, one hour.

In Fig. 3 it can be seen the sintering installation that was used to perform the above operations.

Fig. 3. Sintering Installation

The sintering curve of a sample containing 15% Fe3O4, performed at a temperature of 800^0C is shown in Figure 4.

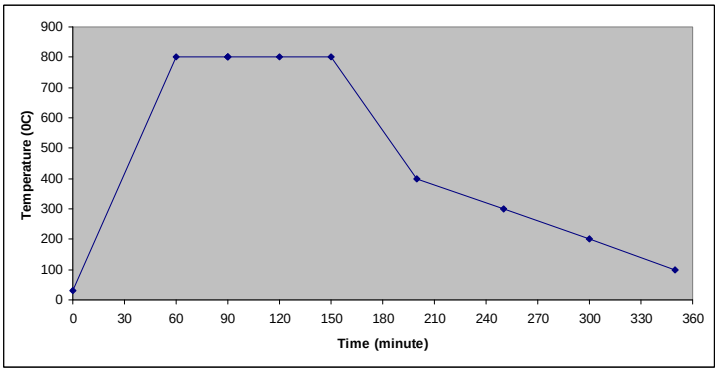
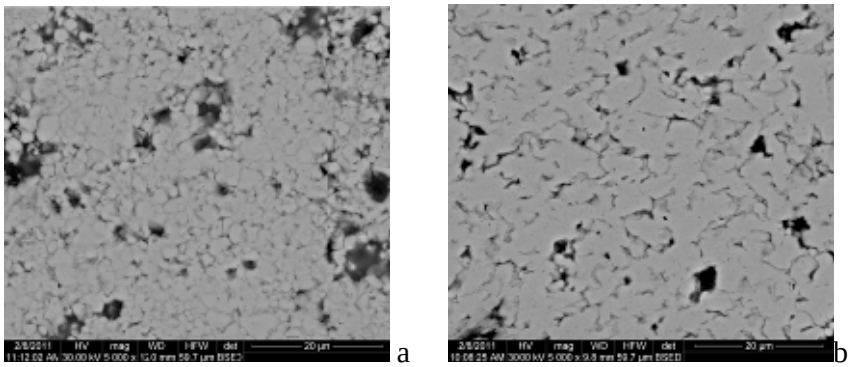


Fig.4. Sintering Curve Cu-15% Fe_3O_4

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% Fe_3O_4 (before and after sintering in vacuum at 650^oC).



a b

Fig. 5. SEM microstructure of the Cu-Fe_3O_4 nanocomposite: a) before sintering b) after sintering.

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_3O_4 with 20% Fe_3O_4 nanocomposite is shown in Fig.6. The X-ray powder diffraction patterns of the materials proved its crystalline nature.

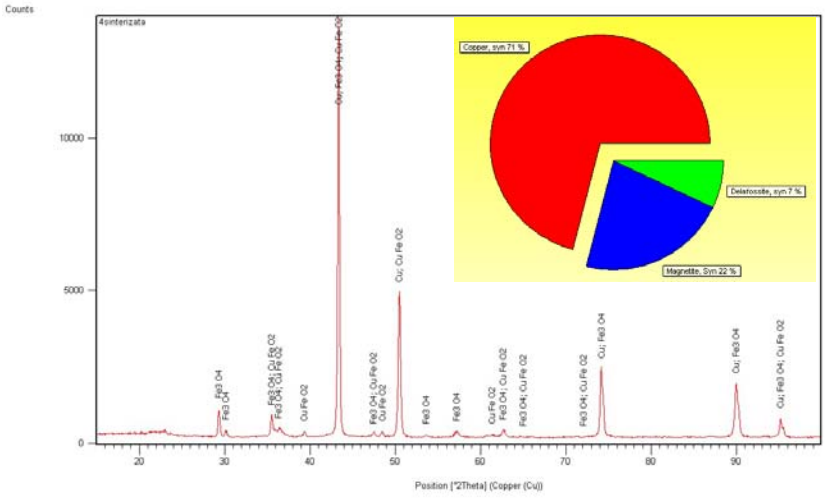


Fig. 6. XRD Pattern of the nanocomposite Cu-Fe_3O_4.

All the detected diffraction peaks that were indexed in Fig. 6 indicate that the particles correspond to magnetite, copper and a newly formed compound

during sintering, $CuFeO_2$ (coresponding 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-Fe_3O_4 with 15% Fe_3O_4 represents the distribution of the elements which forms the matrix. The image shows an irregular dispersion of the magnetite which confirms the tendancy to agglomerate of the nanoparticles.

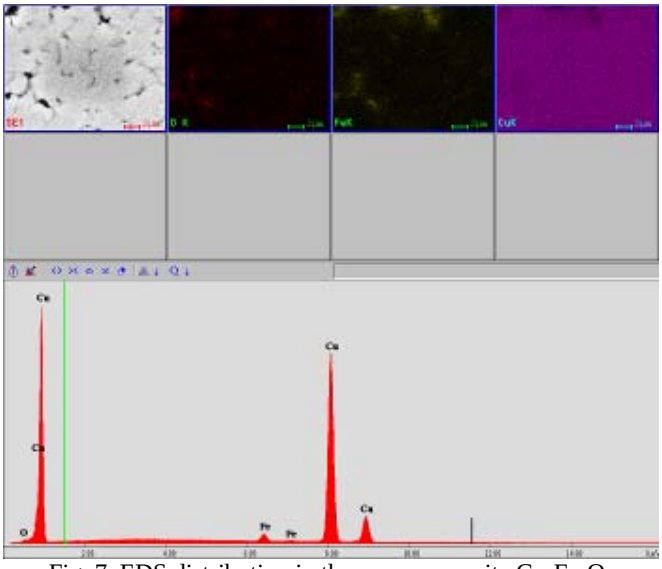


Fig. 7. EDS distribution in the nanocomposite Cu-Fe_3O_4

The nanostructure of the sintered sample was examined using the transmission electron microscopy of high resolution (HRTEM) TECNAI F30 G^2 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.

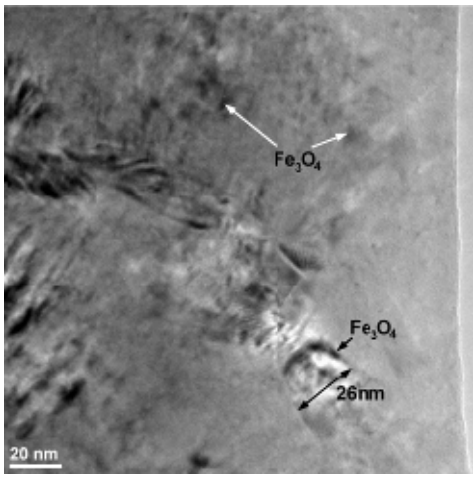


Fig. 8. Magnetite precipitates at grain boundaries of Cu and the existence of magnetite precipitates inside Cu grains

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.

Fig. 9. Cold rolling equipment

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% Fe_3O_4) 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

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-Fe_3O_4 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 Fe_3O_4). A new composite with a nano-size structure was obtained. After pressing and sintering, a new intermetallic compound $CuFeO_2$ 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.

R E F E R E N C E S

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