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CHARACTERISATION OF A NEW Cu-Fe_3O_4 NANOCOMPOSITE

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Cu-Fe_3O_4 nanocomposites obtained by compacting and sintering nanometric copper and magnetite powders, were characterised from the point of view of their structure and main physical and magnetic properties. The structure and morphology of nanocomposites was determined by X-ray diffraction (XRD), bright field transmission electron microscopy (TEMBF) and scanning electron microscopy (SEM). Thermal and electrical conductivities of nanocomposites were also determined as well as certain magnetic properties.

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1. Introduction

At global level there is a tendency to increase the use of functional and structural materials, DSC (dispersion –strengthened copper). They could be used as electrical contact materials in relay, contactors, switches, circuit breaks, resistance-welding tips, continuous casting moulds and so on, where combination of high electrical or/and thermal conductivity with high strength at room and elevated temperatures is required. Within this group of materials particular attention is drawn to those with nanometric grain size of a copper matrix, which exhibit higher mechanical properties than microcrystalline copper.

During high-temperature processes there is the risk to destabilize the nanometric structure, which can be prevented by dispersing into the copper matrix of copper oxides or carbides. The efficiency of the stabilization of the nanostructure is given by the volume fraction of the phases and the dispersion degree [1]. The literature contains references related to obtaining copper nanostructures reinforced with yttrium oxides [1], or aluminium microstructures reinforced with Fe_3O_4, used very efficiently in aviation and electronics [2]. There is very few information in literature about the Cu-Fe_3O_4 nanocomposites. Preliminary attempts to obtain nanocomposites with copper matrix reinforced with Fe_3O_4, are presented in [3], and consist of direct grinding in vibratory mill of a mixture of Cu and Fe_3O_4.

The purpose of this paper is to determine the structure and physical, mechanical and magnetic properties of Cu-Fe_3O_4 composites obtained by methods specific to powder metallurgy (compacting –sintering), from nanometric copper and magnetite powders.

2. Experimental and methods of characterisation of Cu-Fe_3O_4 nanocomposites

Nanocomposites with copper matrix reinforced with particles of Fe_3O_4 were obtained from nanometric copper (35-45 nm) and magnetite (5-10 nm) powders through compacting-sintering. Mixtures of copper and magnetite nanopowders, and variable compacting pressures and sintering temperatures were used. The samples were obtained by co-precipitation method.

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The obtained nanocomposites were characterised in terms of morphostructure and of thermal, electrical, mechanical and magnetic properties.

The structure and morphology of nanocomposites were determined using:

- the standard X-ray diffraction (XRD) method, on a PANalytical X'PERT PRO MPD diffractometer, using a CuK_{α} characteristic X-ray beam with a wavelength of 1.54065 A;
- the energy-dispersive X-ray quality microanalysis performed with an EDAX detector with a resolution of 133eV;
- microscopic investigations: Bright Field Transmission Electron Microscopy (TEMBF) made with a high resolution transmission electron microscope (HRTEM) type TECNAI F30 G^2 with a linear resolution of 1Å and a punctual resolution of 1.4 Å and Scanning Electron Microscopy (SEM).

The thermal conductivity of λ *nanocomposites* was determined by measurements performed on a Laser Flash Analyzer device from Netzsch (2009) model LFA457 within the range of the room temperature and at the temperature of 900^0C. The thermal diffusivity was measured directly and the specific heat differentially against a commercial copper gauge. Based on them and taking into account the relation between the thermal conductivity, the thermal diffusivity, the material density and the heat capacity $\lambda = \frac{c.a}{\rho}$ where: λ - is the thermal conductivity [W/m.K]; c - the heat capacity of the material [J/g.K]; a - the thermal diffusivity [mm^2/s]; ρ - the material density [g/cm^3] [4,5], the thermal conductibility of the nanometric copper and of the nanocomposite Cu-Fe_3O_4 was determined.

The electric conductivity of σ *nanocomposites* was determined by heating the sample into a helium atmosphere in temperature range the room termerature-900^0C, with the help of a KEITHLEY 6517A electrometer.

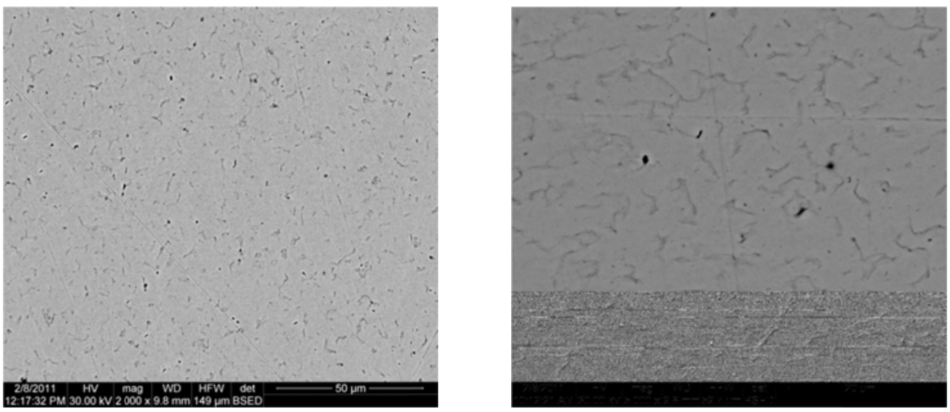
The magnetic properties of Cu-Fe_3O_4 nanocomposites consisted in determining the *magnetisation of* nanocomposites, according to the intensity of the magnetic field (M vs.H), for H $\in$ [-10000, +10000] Gauss. The results obtained are given below.

3. Results and discussions

3.1 Structural properties

The aspect of Cu-Fe_3O_4 nanocomposite was highlighted by SEM electron microscopy.

We can observe a good distribution of magnetite nanoparticles in the copper matrix (figures 1a and 1b).



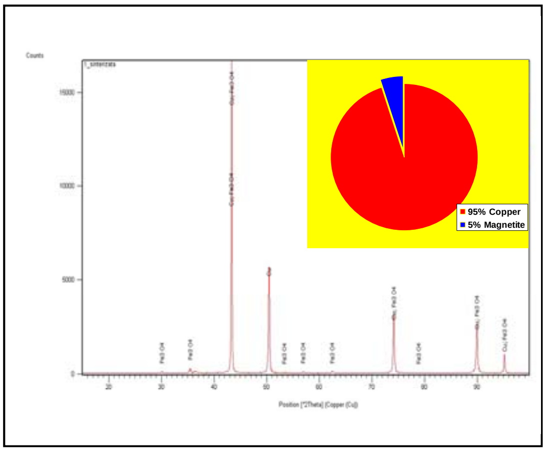
a b

Fig. 1. SEM microscopy image a). Cu-5%Fe_3O_4 nanocomposite.; b). Cu-15%Fe_3O_4 nanocomposite.

X-ray diffraction investigations performed on the samples of nanocomposites with copper matrix reinforced with 15-20%Fe_3O_4, obtained by sintering at temperatures of 800^0C, highlight the emergence of a new $CuFeO_2$ compound that is not present in the case of nanocomposites with contents under 10% Fe_3O_4 or sintered at temperatures of 650^0C .

Figures 2a and 2b present peaks characteristics to the compounds highlighted by X-ray diffraction for Cu-5%Fe_3O_4 and Cu-15%Fe_3O_4 nanocomposites sintered at 800^0C. Figure 2b presents the emergence of the $CuFeO_2$, compound, referred to as delafossite in the field literature [6], a compound creating reduced porosities and higher compactness to nanocomposites.

a)



b)

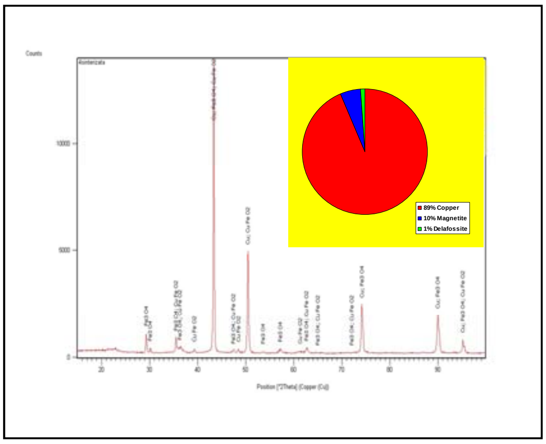


Fig.2. XRD images of Cu-Fe_3O_4 nanocomposites
obtained by sintering at 800^0C a). Cu-5% Fe_3O_4 nanocomposite; b). Cu-15%Fe_3O_4 nanocomposite

The electron microscopy images obtained through bright field (TEMBF), and presented in figures 3a, 3b, 3c, 3d highlight: (a) the nanostructure of the Cu-Fe_3O_4 composite, (b) copper nanoparticles in the nanocomposite matrix, and (c) an agglomeration of magnetite nanoparticles embedded in a copper matrix. We can also notice magnetite precipitates at the bigger copper granule edges, and the existence of magnetite precipitates inside copper granules (figure 3d).

a).

b)

c).

d).

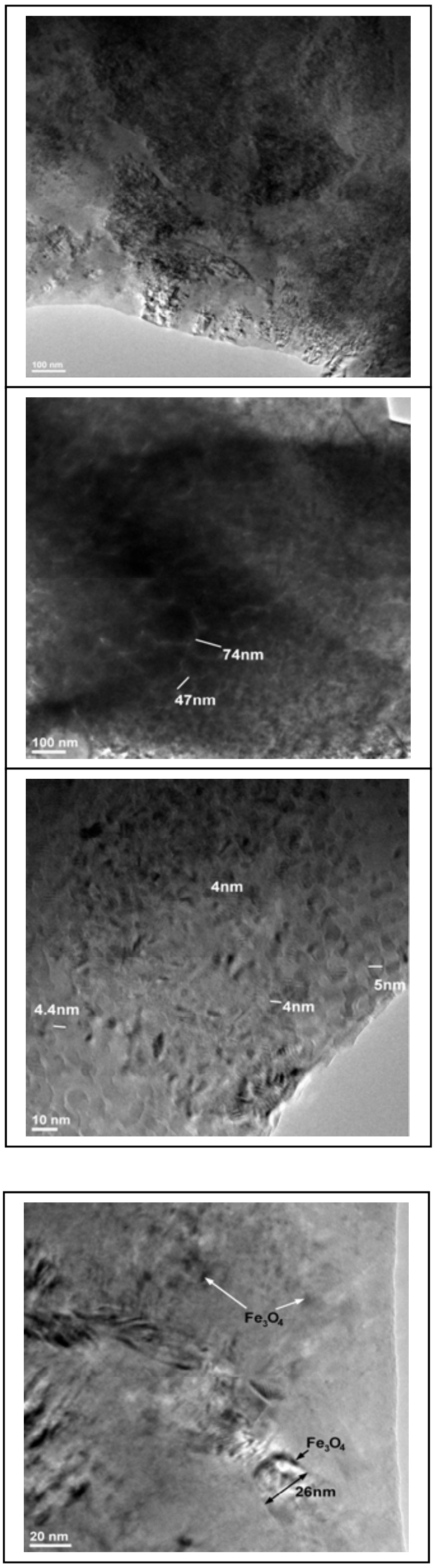
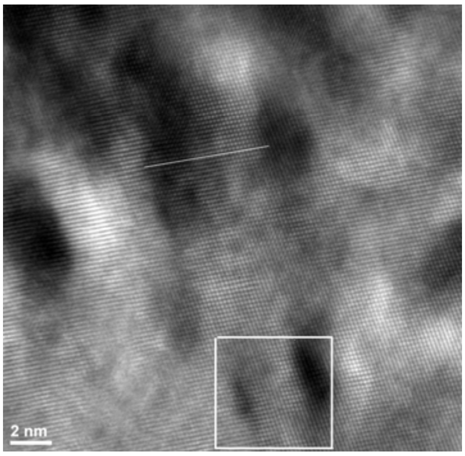
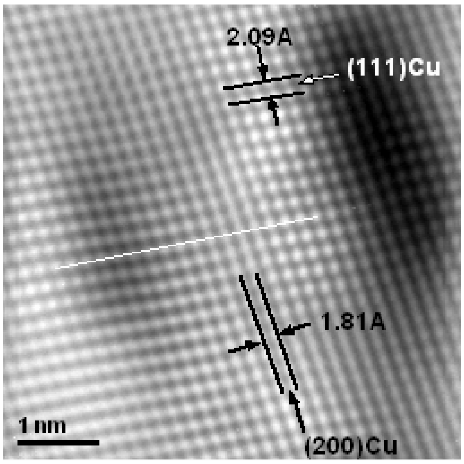


Fig.3. Bright field electron microscopy images (TEMBF) a). composite nanostructure; b). Cu nanoparticles; c). Fe_3O_4 nanoparticles embedded into the Cu matrix, d). magnetite precipitates from the edges of and inside the Cu granules;

The existence of the magnetite nanometric precipitates inside the copper crystallite distorts the crystal lattice (the line marked on the image, shows the distortion of the crystal lattice), by local curving of the crystal plane along the line, as can be seen in figures 4a and 4b.



a)



b).

Fig. 4. Bright field electron microscopy images (TEMBF) a). nanometric precipitates embedded in a Cu crystallite; b). filtered image with the reverse Fourier attached to the square in fig. 3a.

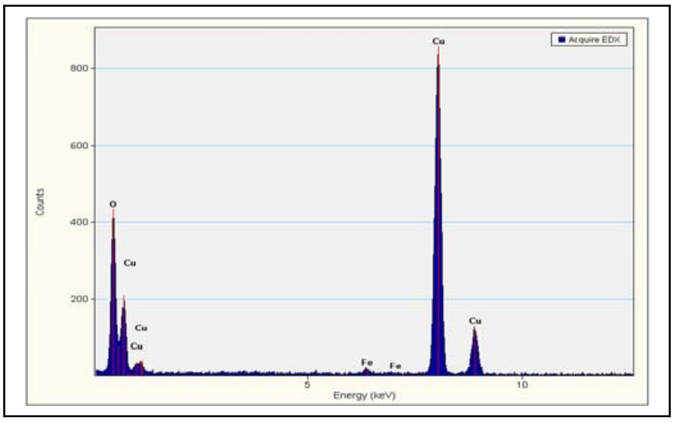


Fig. 5. Energy-dispersive X-ray spectrum – the area in fig. 3a

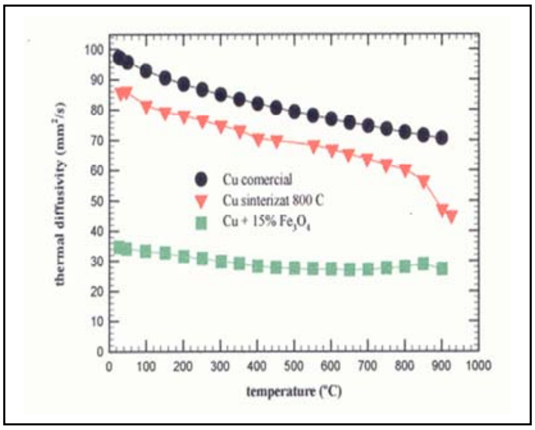
The precipitates can be very small magnetite crystallites, and their presence is confirmed by the energy-dispersive X-ray spectrum, obtained on the crystallite which includes this detail (figure 5). This spectrum shows the existence of Fe and O elements, in addition of Cu elements.
From the investigations performed, we can
conclude that the Cu-Fe_3O_4 nanocomposite obtained from copper and magnetite nanometric powders definitely has nanometric structure.

3.2 Thermal properties

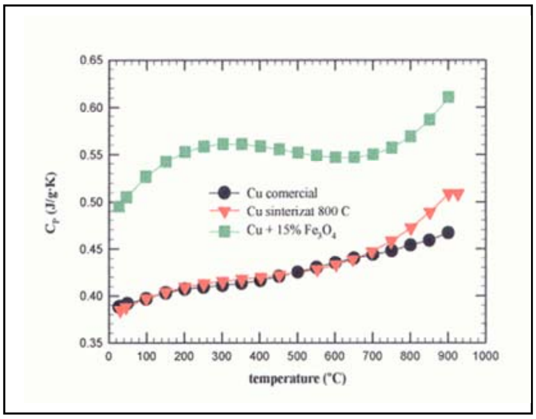
Nanometric Cu and Cu-15% Fe3O4 nanocomposite samples sintered at 800^0C were investigated. We can notice a slight decrease in the diffusivity in the nano-sintered Cu sample, as compared to the standard metal (probably due to a higher porosity of the sample), and a significant decrease in all the analysed temperature range for the nanocomposite sample with Cu-15% Fe3O4. At high temperatures (more than 650^0 C) a more significant diffusivity appears due to a possible grow of the granules. This can be correlated with an increase in the heat capacity in the same temperature range (figures 6a, 6b, 6c).

Based on the values of the thermal conductivities determined (83-100 W/m.K), we can say that the obtained nanocomposites have a metallic nature [4].

a)



b).



c)

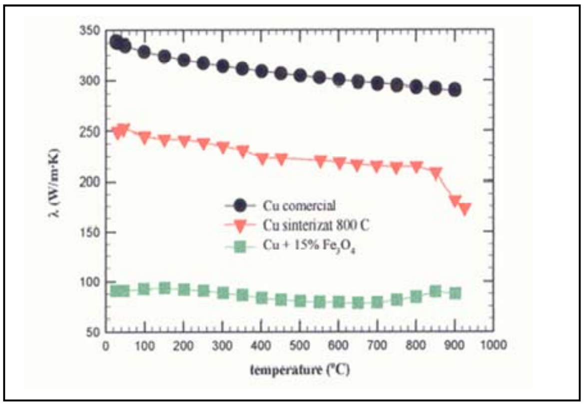


Fig.6. The determination of the thermal properties of Cu-Fe_3O_4 nanocomposites: a). thermal diffusivity; b). Specific heat, c). thermal conductivity

3.3Electrical properties

The specific conductivity σ of the Cu-Fe_3O_4 nanocomposites generally decreases, with the temperature increase (fig. 7).

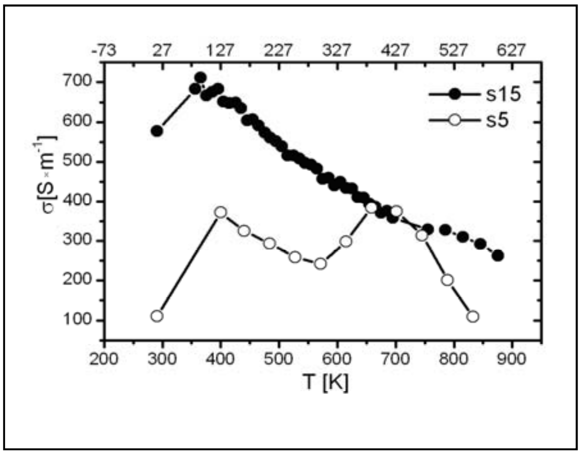


Fig.7. The specific conductivity (σ) of nanocomposites with 5% Fe_3O_4 (s5) and 15% Fe_3O_4(s15), sintered at 650^0C, according to the temperature

From the figure we can see how the conductivities of the two analysed nanocomposite samples (Cu-5%Fe_3O_4 and Cu-15%Fe_3O_4), grow around the temperature of 100^0C, probably due to the surface water desorption, then the specific conductivity decreases with the temperature increase. However, in the case of Cu-5%Fe_3O_4 nanocomposite, a different behaviour is noticed. With the temperature increase, in the 600-700K range the specific conductivity grows, and then decreases.

This non-linear variation of the specific conductivity with the temperature, correlated with its value, is specific to semiconductor materials [5].

3.4 Magnetic properties

For the magnetization of the copper matrix nanometric magnetite powder was used through the coprecipitation of Fe^{+3} and Fe^{+2} ions in an alkaline medium [8]. The saturation magnetization M_S of the Cu-5%Fe_3O_4 and Cu-15%Fe_3O_4 nanocomposite samples was determined (fig. 8).

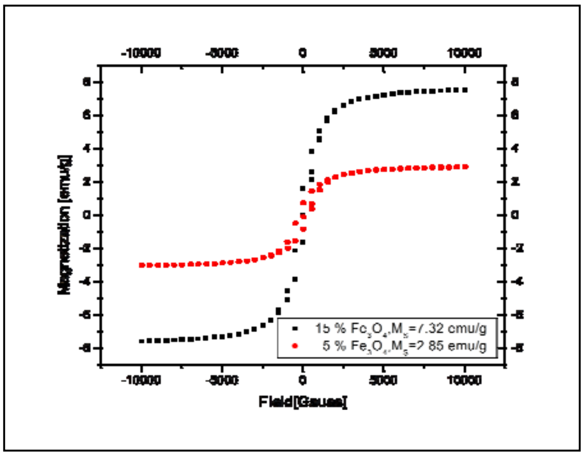
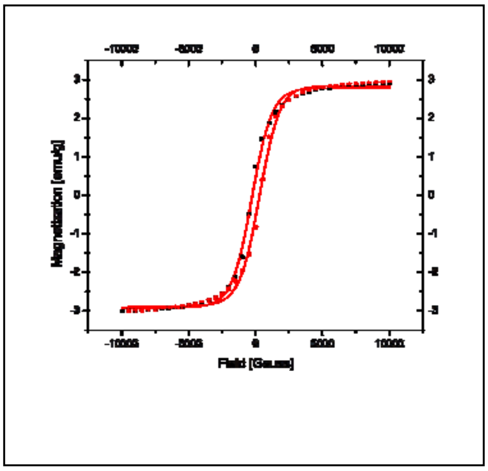


Fig. 8. The magnetization curves of the Cu-5%Fe_3O_4 and 15% Fe_3O_4 nanocomposites obtained at room temperatures.

Graphically represented with a better resolution (the curve fit was made with SIGMOID Boltzmann), the curves have hysteresis on areas other than zero, which highlights the anisotropy in the magnetic behaviour of the samples (figures 9a and 9b) [9].

In the analysed samples there is a decrease in the saturation magnetization from the known value of the nano-magnetite (55 emu/g). The values of the saturation magnetization of 2,85 emu/g and respectively 7,32 emu/g , represents in a first approximation even the percentages of 5% and respectively 15% of the value of 55 emu/g of the initial nano-powder.

a).



b).

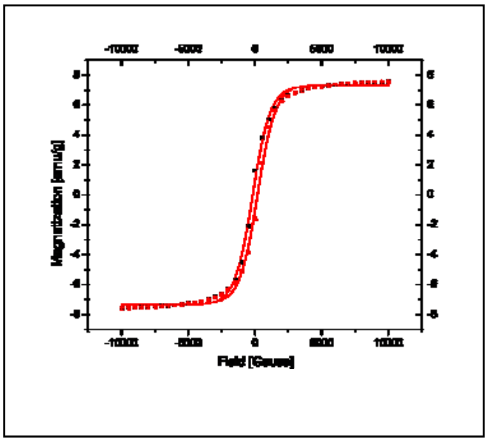


Fig.9. Saturation magnetization of the nanocomposites a). Cu-5%Fe_3O_4; b). Cu-15%Fe_3O_4

4. Conclusions

The nanocomposites obtained from copper and magnetite have a nanometric structure, proved by morphostructural investigations. The nanocomposites have thermal, electric and magnetic properties that were determined in this study. According to the obtained results, nanocomposites with a Cu-Fe_3O_4 structure have a metallic nature, are electrical conductors but have magnetic properties as well.

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