CHARACTERISATION OF A NEW Cu-Fe$_3$O$_4$ NANOCOMPOSITE

A. PREDESCU*, L. M. VLĂDUŢIU, P. MOLDOVAN, C. PREDESCU
Faculty of Materials Science and Engineering, Politehnica University of Bucharest, Romania

Cu-Fe$_3$O$_4$ 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.

(Received August 10, 2012; Accepted August 27, 2012)

Keywords: Nanostructures, Thermal conductivity, Electrical conductivity, Magnetization

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$_3$O$_4$, used very efficiently in aviation and electronics [2]. There is very few information in literature about the Cu-Fe$_3$O$_4$ nanocomposites. Preliminary attempts to obtain nanocomposites with copper matrix reinforced with Fe$_3$O$_4$, are presented in [3], and consist of direct grinding in vibratory mill of a mixture of Cu and Fe$_3$O$_4$.

The purpose of this paper is to determine the structure and physical, mechanical and magnetic properties of Cu-Fe$_3$O$_4$ 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$_3$O$_4$ nanocomposites

Nanocomposites with copper matrix reinforced with particles of Fe$_3$O$_4$ 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.

* Corresponding author: a_predescu@yahoo.com
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 CuKα characteristic X-ray beam with a wavelength of 1.54065 Å;
- 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 G² with a linear resolution of 1Å and a punctual resolution of 1.4 Å and Scanning Electron Microscopy (SEM).

The thermal conductivity of \( \lambda \) 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°C. 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: \( \lambda \) - is the thermal conductivity [W/m.K];
\( c \) - the heat capacity of the material [J/g.K]; \( a \) - the thermal diffusivity [mm²/s]; \( \rho \) - the material density [g/cm³] [4,5], the thermal conductibility of the nanometric copper and of the nanocomposite Cu-Fe₃O₄ was determined.

The electric conductivity of \( \sigma \) nanocomposites was determined by heating the sample into a helium atmosphere in temperature range the room temperature-900°C, with the help of a KEITHLEY 6517A electrometer.

The magnetic properties of Cu-Fe₃O₄ 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-Fe₃O₄ nanocomposite was highlighted by SEM electron microscopy. We can observe a good distribution of magnetite nanoparticles in the copper matrix (figures 1a and 1b).

![Fig. 1. SEM microscopy image a). Cu-5%Fe₃O₄ nanocomposite; b). Cu-15%Fe₃O₄ nanocomposite.](image)
X-ray diffraction investigations performed on the samples of nanocomposites with copper matrix reinforced with 15-20% Fe₃O₄, obtained by sintering at temperatures of 800°C, highlight the emergence of a new CuFeO₂ compound that is not present in the case of nanocomposites with contents under 10% Fe₃O₄ or sintered at temperatures of 650°C.

Figures 2a and 2b present peaks characteristics to the compounds highlighted by X-ray diffraction for Cu-5%Fe₃O₄ and Cu-15%Fe₃O₄ nanocomposites sintered at 800°C. Figure 2b presents the emergence of the CuFeO₂ compound, referred to as delafossite in the field literature [6], a compound creating reduced porosities and higher compactness to nanocomposites.

The electron microscopy images obtained through bright field (TEMBF), and presented in figures 3a, 3b, 3c, 3d highlight: (a) the nanostructure of the Cu-Fe₃O₄ 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).
Fig. 3. Bright field electron microscopy images (TEMBF) a). composite nanostructure; b). Cu nanoparticles; c). Fe₃O₄ 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.

![Image 1](image1.png)  ![Image 2](image2.png)

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

![Image 3](image3.png)

**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-Fe₃O₄ 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°C 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°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].

Fig.6. The determination of the thermal properties of Cu-Fe₃O₄ nanocomposites: a). thermal diffusivity; b). Specific heat, c). thermal conductivity
3.3 Electrical properties

The specific conductivity $\sigma$ of the Cu-Fe$_3$O$_4$ nanocomposites generally decreases, with the temperature increase (fig. 7).

From the figure we can see how the conductivities of the two analysed nanocomposite samples (Cu-5%Fe$_3$O$_4$ and Cu-15%Fe$_3$O$_4$), grow around the temperature of 100°C, probably due to the surface water desorption, then the specific conductivity decreases with the temperature increase. However, in the case of Cu-5%Fe$_3$O$_4$ 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$_3$O$_4$ and Cu-15%Fe$_3$O$_4$ nanocomposite samples was determined (fig. 8).
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.

![Graph](image)

**Fig.9. Saturation magnetization of the nanocomposites a). Cu-5%Fe₃O₄; b). Cu-15%Fe₃O₄**

**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-Fe₃O₄ structure have a metallic nature, are electrical conductors but have magnetic properties as well.

**References**


