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Studies of Fe–Cu microwires with nanogranular structure*

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Abstract

We report on the fabrication, and structural and magnetic characterization of $Cu_{63}Fe_{37}$ microwires with granular structure produced by rapid quenching, using the Tailor–Ulitovsky method, from the immiscible alloys. X-ray diffraction study demonstrated that the structure consists of small (6–45 nm) crystallites of Cu and body centred cubic α-Fe. Magnetic properties have been measured in the range of 5–300 K using a SQUID (superconducting quantum interference device) magnetometer. The temperature dependences of the magnetization measured in a cooling regime when no external magnetic field is applied (zero-field cooling) and in the presence of the field (field cooling) show considerable difference below 20 K. This difference could be related to the presence of small α-Fe grains embedded in the Cu matrix. Those α-Fe grains appear to be blocked at temperatures below that at which the maximum of the magnetization is observed in the low temperature range. Significant magnetoresistance (about 7%) has been found in the samples studied. The shape of the observed dependences is typical of a giant magnetoresistance effect.

1. Introduction

Since their discovery in 1988, granular alloys based on immiscible (Co, Fe, Ni)–(Cu, Pt, Au, Ag) elements have been intensively studied owing to their potential technological applications. These alloys have a number of outstanding magnetic properties including giant magnetoresistance (GMR), which makes them promising for magnetic recording and sensing [1–3]. Initially the GMR effect was observed in thin multilayered films, but later similar properties were found for so called 'granular' alloys consisting of small ferromagnetic grains (usually of Co or Fe) embedded in paramagnetic matrix (typically Cu, Ag or Au) [3]. A rapid quenching technique such as melt spinning has been employed recently for fabrication of Co–Cu ribbons. In this method a high quenching rate typical for the melt spinning method is used for fabrication of metastable crystalline materials when the crystalline phases, stable at high temperature, can be quenched in at room temperature. The granular structure and the GMR effect were obtained after recrystallization of such metastable phases [4].

The GMR effect has been interpreted through the scattering of the electrons at grain boundaries separating the ferromagnetic nanograins from the paramagnetic matrix. At zero applied field, when magnetic moments of the particles are not aligned (e.g. oriented randomly), the resistivity of the material is high, and when an external magnetic field aligns these moments, the resistivity decreases, as in the previously discovered GMR multilayered materials [1]. This

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effect is large and almost independent of the magnetic field direction [2, 3]. The maximum GMR ratio of around 60% under ambient conditions was obtained for sputtered polycrystalline Co/Cu multilayers with (1, 1, 1) texture [4].

Recently thin glass-coated microwires produced by the Taylor–Ulitovsky technique received much interest mostly due to their small dimension and excellent soft magnetic properties [5]. Such a technique allows the fabrication of continuous glass-coated metallic microwires a few km long with the typical radius of the metallic nucleus ranging from 1 to 10 μm and the thickness of the insulating glass coating between 2 and 10 μm. This method allows achieving a high quenching rate and fabricating microwires with amorphous, nanocrystalline, microcrystalline or granular structure [5]. Few attempts have been made to prepare microwires with granular structure exhibiting semi-hard magnetic properties (coercivities of the order of 700 Oe) and GMR (up to 18%) for Fe–Ni–Cu and Co–Cu [6].

In this paper, microwires with granular structure based on Cu–Fe alloy have been studied, placing emphasis on the relation between microstructure, magnetic behaviour and wire geometry.

2. Experimental details

The master alloy of $Cu_{63}Fe_{37}$ composition was prepared by arc melting of the pure elements in Ar atmosphere. Molten metallic alloy inside the glass tube was simultaneously drawn, quenched with the water jet and wound onto a rotating bobbin. The samples obtained are thin composite wires consisting of an inner core covered by a glass layer. The metal core size was controlled during the fabrication process by means of non-contact electrical resistance measurements and this was further confirmed by optical microscopy. The sample geometry is characterized by the ratio, ρ, of the metallic core diameter and the total microwire diameter. The total microwire diameter was about 16 μm, while the metallic nucleus diameter was varied from 1 μm ($\rho = 0.063$) to 7.6 μm ($\rho = 0.46$).

The structural characteristics of the samples were determined using wide angle x-ray scattering (WAXS) in a powder diffractometer provided with an automatic divergence slit and graphite monochromator using Cu Kα radiation (λ = 1.54 Å). The measurements were carried out using the step scanning technique using 40°–80° (2θ) units in steps of 0.02° (2θ) with accumulation times of 3 s for each point. Note that 2θ is the scattering angle and the region of measurement is the one where these compositions show their more significant crystalline peaks with Cu Kα wavelength.

All magnetic measurements were performed using a Quantum Design physical property measurement system model 6000. The magnetic field was applied along the wire axis. In this way, shape magnetic anisotropy has been avoided, since the sample length was above 5 mm.

The hysteresis loops $M(H)$ of these samples were measured in the temperature range from 10 to 300 K and for a maximum field of 10 kOe. Two types of the temperature plots were studied. Zero-field cooling (ZFC) curves were measured while cooling the samples down to 5 K in zero magnetic field and heating them in the presence of the field. Field cooling (FC) curves were measured with the magnetic field on during both cooling and heating regimes.

The magnetoresistance (MR) was measured using the Quantum Design physical property measurement system PPMS 9.

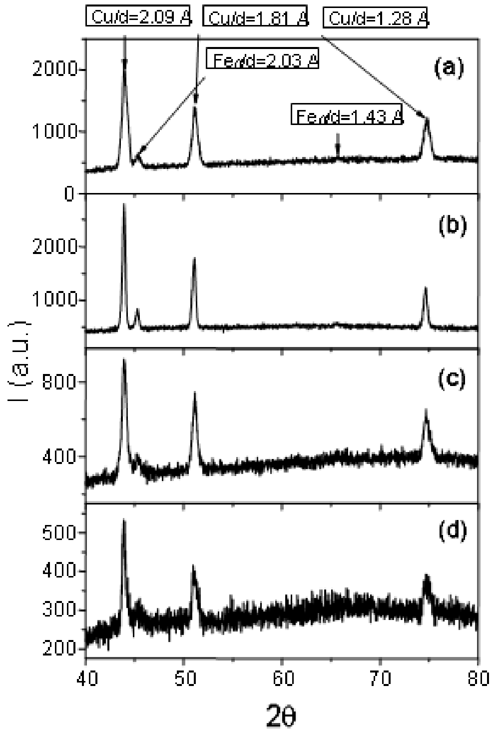

Figure 1. WAXS patterns for $Cu_{63}Fe_{37}$ microwires with different ρ values: 0.46 (a), 0.31 (b), 0.16 (c), 0.063 (d).

3. Results and discussion

Three clearly observed x-ray diffraction peaks are characteristic of the Cu phase (face centred cubic, FCC, lattice parameter: 3.61 Å with atomic spacings of 2.09, 1.81 and 1.28 Å). The other two peaks are related to the α-Fe phase (body centred cubic, BCC, lattice parameter: 2.87 Å corresponding to atomic spacings of 2.03 and 1.43 Å). Note that the peak corresponding to 1.43 Å (α-Fe) is rather small and hardly observed.

The observed x-ray peaks have been identified by means of Bragg's law, $2d\sin(\theta) = \lambda$, within an accuracy of 0.01 Å. The influence of the wire geometry on the x-ray patterns was then studied. It is easy to see in figures 1(a)–(d) that with increasing ratio ρ the intensity of x-ray peaks increases and its shape becomes more regular.

The structural information for the microwires is extracted once the crystalline peaks of each pattern are identified and the background contribution of the amorphous phase in the microwires (mainly from the glass coating) subtracted. An average grain size of the crystals formed in each case is derived from Scherrer's equation:

$$D = \frac{K\lambda}{\varepsilon\cos\theta_m} \quad (1)$$

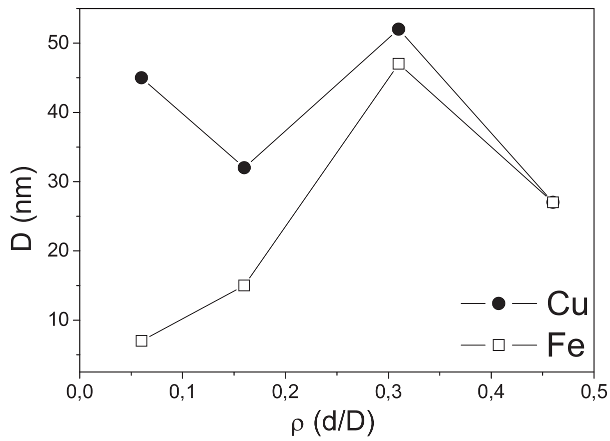

Figure 2. Size of Cu and α-Fe crystallites plotted versus ρ ratio for $Cu_{63}Fe_{37}$ microwires.

where $2\theta_m$ is the scattering angle corresponding to the maximum of the peak and ε is its half-height width [7]. The parameter K is assumed to be around 0.9 (or almost 1) in most cases [8]. Figure 2 shows the size of the Cu and α-Fe grains obtained for $Fe_{37}Cu_{63}$ microwires. As is seen, Cu nanograins with the average grain size of 40 nm are roughly independent of the sample geometry (represented by the ratio ρ), as found elsewhere [9]. On the other hand, the average size of Fe nanocrystals depends on the geometrical parameter varying between 6 and 45 nm, exhibiting a maximum at intermediate ρ ratio.

It should be indicated that x-ray diffraction allows estimating only the average grain size. The details of grain size morphology and grain size distribution might be obtained by means of high resolution SEM or TEM. Unfortunately, TEM experiments on microwires require special experimental techniques for the sample preparation. These studies are now in progress.

Magnetization curves measured at different temperatures are shown in figures 3(a) and (b). At room temperature the coercivity is of the order of 30 Oe. Significant dependence of the hysteresis loops on the geometrical parameter has been found. All curves display both superparamagnetic and ferromagnetic features. A small hysteresis area of the measured loops and the absence of saturation indicate the presence of a superparamagnetic phase, especially significant for $\rho = 0.06$. The ferromagnetic behaviour is evidenced by the values of remanence and coercivity, which are indeed rather low. Such behaviour can be attributed to the combined superparamagnetic–ferromagnetic phases due to coexistence of the ferromagnetic and superparamagnetic particles. Such coexistence occurs due to a wide size distribution of Fe grains and/or concentration distribution of Fe in Cu. At the same time, temperature dependences of the saturation magnetization, $M_s(T)$, shown in the insets of figures 3(a) and (b), exhibit decrease with temperature but did not present well defined Curie temperature typical for ferromagnetic materials. This probably related to the Fe nanocrystal size distribution and inhomogeneity of the ferromagnetic phase.

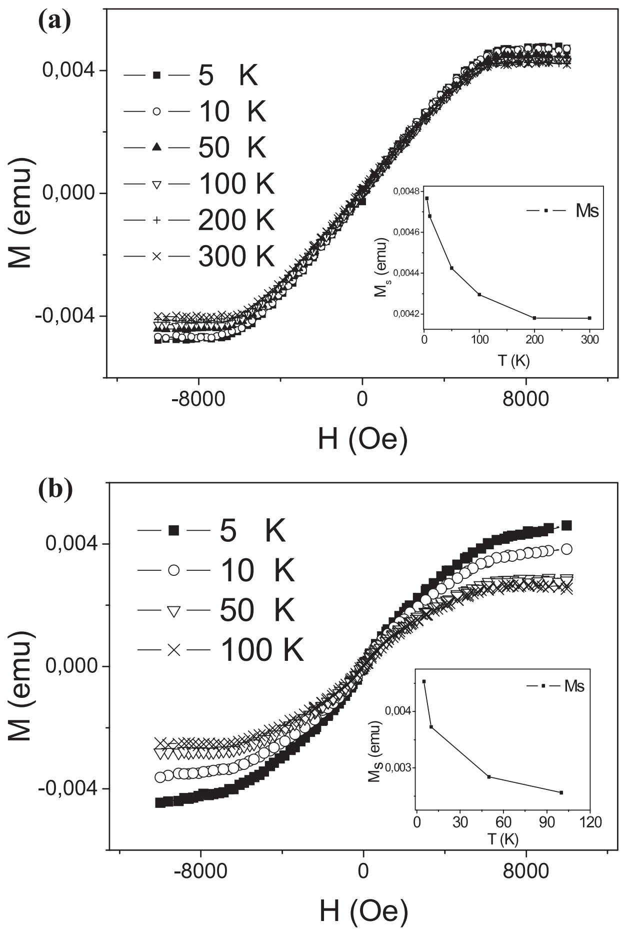

Figure 3. Hysteresis loop for the $Cu_{63}Fe_{37}$ as-cast sample at different temperatures with different ratio ρ values: (a) 0.46, (b) 0.063. The evolution of the magnetization at saturation is shown at the inset.

The magnetizations measured under an applied magnetic field (FC) and without a magnetic field (ZFC) exhibit a significant difference (see figure 4). From the comparison between the two curves seen in figures 4(a) and (b) it is possible to roughly determine the average blocking temperature and distribution $f(T_B)$ following a standard procedure [10]. The $f(T_B) = \frac{d(M_{ZFC}-M_{FC})}{dT}$ obtained confirms the inhomogeneous magnetic structure assumed from analysing the magnetization curves, consistently with previous works [11]. It follows from the analysis of figure 4(a), corresponding to $Cu_{63}Fe_{37}$ microwires with the geometrical parameter $\rho = 0.46$, that a large number of small particles exist with a diameter less than 30 nm and that there are just a few large particles. On the other hand, for figure 4(b) ($Cu_{63}Fe_{37}$ microwires with a geometrical parameter $\rho = 0.06$) the estimated averaged crystal size is around 5 nm. ZFC/FC measurements performed on microwires with different geometrical parameters exhibit an intermediate behaviour. However, it is worth noting that ZFC/FC analysis in this case is only indicative, and it gives a rather rough perspective on the nanostructure. In fact, the observed ZFC/FC behaviour resembles that expected for a rather narrow distribution of grain sizes. This apparently contradictory result was previously observed for several granular samples (see, for example, [12]). In fact dipolar interactions and

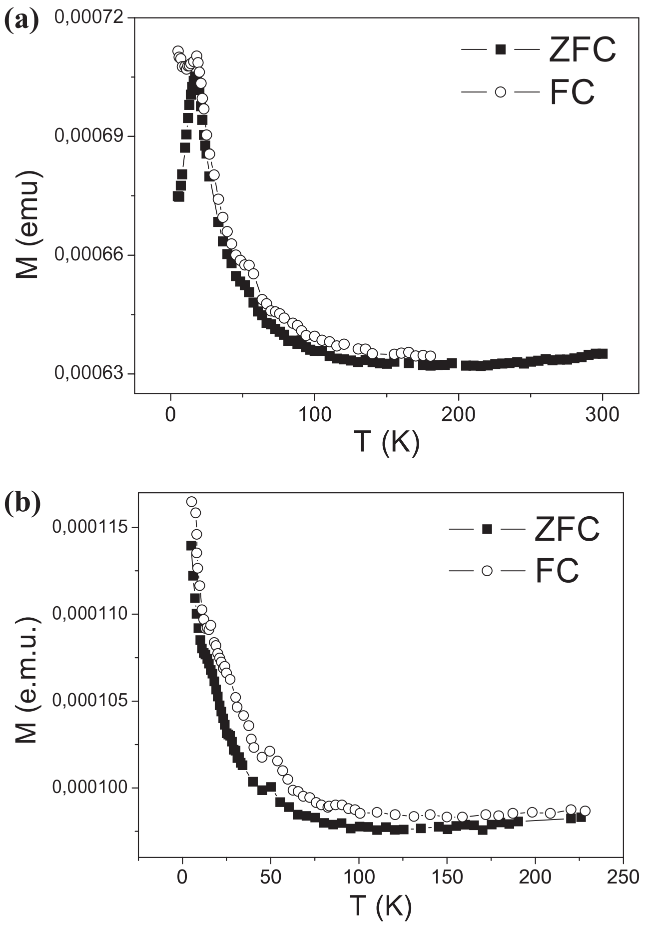

Figure 4. Zero-field cooled and field cooled curves for the as-cast $Cu_{63}Fe_{37}$, measured at $H_{DC} = 100$ Oe, up to 300 K with different ratio ρ values: (a) 0.46, (b) 0.063.

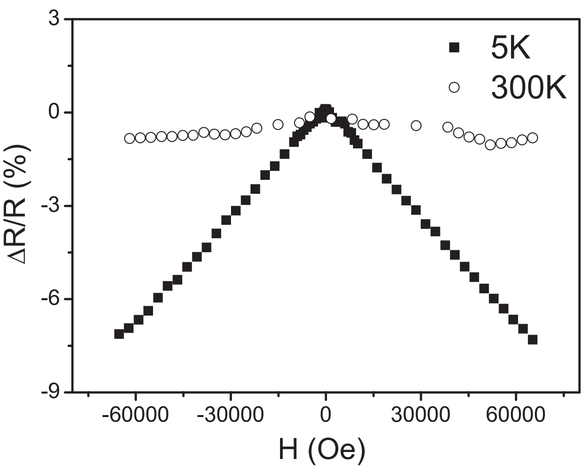

Figure 5. Magnetoresistance of the as-cast $Cu_{63}Fe_{37}$ microwire with $\rho = 0.46$ measured at 5 and 300 K for magnetic field from −7 to 7 T.

magnetic cluster formation can lead to spurious structural data being indirectly obtained from ZFC/FC curves, and thus such results are only valid when analysed together with direct structural data, such as in x-ray diffraction and TEM analysis. Furthermore, it is worth noting that the FC curve displays an additional peak at lower temperature, indicating a more complex magnetic behaviour, probably a re-entrant spin (or cluster) glass-like transition. This magnetic phase is usually present in complex granular systems, and can be related to both dipolar interactions and/or surface effects (see, for example, [13]). Although a careful analysis of this extra peak can lead to interesting results, it goes far beyond from the scope of the present work.

The behaviour of the main magnetic phase (α-Fe) is very important for such materials. Note that the content of α-Fe phase and the average grain size are lower for the sample $Cu_{73}Fe_{37}$ with $\rho = 0.063$. The content of α-Fe phase obtained varies around 1% for $\rho = 0.06$, 8% for $\rho = 0.16$ and 0.31, 7% for $\rho = 0.46$, as was deduced from figure 1 and can be found elsewhere [9]. It should be noted that following the previously proposed scheme for such samples [14], the loops show a superparamagnetic character for $\rho = 0.063$ and a ferromagnetic one for $\rho = 0.46$. This ferromagnetic character could be related to the aforementioned higher content of α-Fe phase and larger average grain size for this sample and, in a certain way, there is a correlation between magnetic measurements and structural results.

It should be noted also that the field at which the saturation is roughly achieved is quite large (around 6 kOe; see figure 3). But complete saturation of the sample with the lowest ratio ρ is not reached even at this magnetic field (figure 3(b)).

One of the possible explanations is that the axis of the microwires is the hard direction. But this assumption contradicts logic, since the demagnetizing factor of the sample with the lowest value of ρ when the applied magnetic field is along the microwire axis takes the lowest values. Additionally, from the experimental data on Fe nanowires, it is known that usually Fe nanowires have an easy axis along the nanowire axis [15]. We assume that the higher contribution of the superparamagnetic behaviour of the thinnest microwire related also to the dependence of the structure on the ratio ρ can be attributed to the higher internal stresses induced by the difference in thermal expansion coefficient of simultaneously solidifying glass and metal [5, 11]. In fact it is well established that the strength of the internal stresses, σ, is related to the glass coating thickness through the difference in thermal expansion coefficient of the metallic nucleus and outer glass coating solidifying simultaneously. The estimated values of the internal stresses in these glass-coated microwires arising from the difference in thermal expansion coefficient of the metallic nucleus and glass coating are of the order of 100–1000 MPa, depending strongly on the ratio between the glass coating thickness and the metallic core diameter [16–18], increasing with increasing glass coating thickness. These internal stresses can affect the grain size of Fe grains. Similar behaviour has been observed in Finemet-type microwires when the nanocrystallization process has been affected by the ratio ρ. To explain this, it was suggested [19] that the internal stresses in the metallic nucleus hinder the segregation of crystalline phases. It is also consistent with figure 2, where lowest Fe grain size is observed for the lowest ratio ρ.

The MR effect in the 7% range has been also observed for $\rho = 0.46$ and 0.31 $Cu_{73}Fe_{37}$ glass-coated microwires

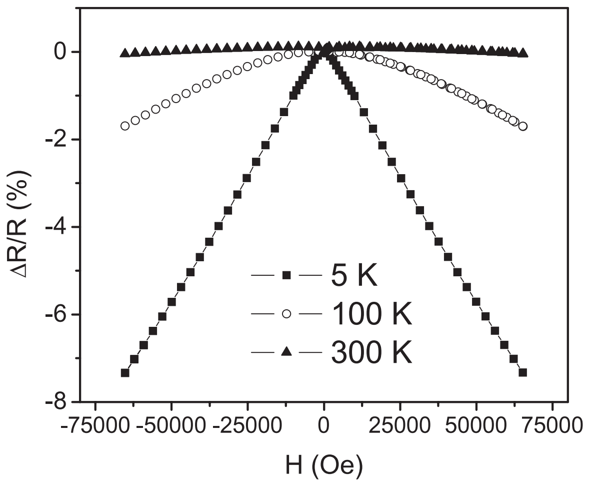

Figure 6. Magnetoresistance of the as-cast $Cu_{63}Fe_{37}$ microwire with $\rho = 0.31$ measured at 5, 100 and 300 K for magnetic field from −7 to 7 T.

(figures 5 and 6 respectively). The shape of the magnetic field dependence is typical for the GMR effect, when the resistance decreases with increasing magnetic field. Decreasing the temperature increases the MR (from 0.05% (300 K) to 7.6% (5 K) for the sample with $\rho = 0.31$ and from 1% to 7% for the sample with $\rho = 0.46$). In most systems exhibiting GMR the GMR ratio increases on decreasing the temperature [20, 21]. Usually this increase is attributed to the superparamagnetic origin of grains responsible for the GMR behaviour as well as being related to the temperature dependence of the resistivity [20, 21].

The field-dependent resistivity of granular materials is related to a spin-dependent scattering of conduction electrons within the magnetic particles as well as the interfaces between magnetic and non-magnetic regions (however, it is assumed that the interfacial effect contributes to a dominant extent to the GMR [1–4]). Because of the complex structure of the granular materials, the relationship between the microstructure and GMR is still not fully understood.

In the case of glass-coated microwires the internal stresses induced mostly by the difference in thermal expansion coefficient of glass and metal are quite significant [11]. Therefore studies of the aforementioned composition with different geometry could be interesting, in order to reveal the internal stress contribution in magnetic and magneto-transport properties. Similar studies on Co–Cu microwires allowed us to find that the crystalline structure and GMR effect are indeed affected by the glass coating thickness and metallic nucleus diameter [22]. These internal stresses can affect the structure and magnetism of small Fe grains inside the Cu matrix, as has been previously observed for the case of epitaxially grown Fe films on Cu(100), where BCC-like and FCC-like structures were observed, depending on the film thickness [23]. Such studies are in progress on Cu–Fe microwires.

4. Conclusions

The main conclusions that can be drawn from the structural and magnetic study described in this work are:

(1) $Cu_{63}Fe_{37}$ microwires with granular structure have been produced by rapid quenching using the Tailor–Ulitovsky method and characterized using x-ray diffraction and the SQUID magnetometer technique.
(2) The microwire structure consists of Cu nanograins with average grain size of around 40 nm and α-Fe nanocrystals with average grain size ranging between 6 and 45 nm, depending on the sample geometry. The resulting content of α-Fe phases also strongly depends on the sample geometry.
(3) Magnetic characterization has been performed and it was found that the temperature dependences of the magnetization (ZFC and FC curves) and hysteresis loop behaviour depend on the geometrical parameters.
(4) Experimental data are interpreted assuming mixed ferromagnetic–superparamagnetic behaviour of the fabricated samples.
(5) Significant magnetoresistance (about 7%) has been found in the samples studied. The shape of the observed dependences is typical for the GMR effect.

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