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Kondo-like behavior and GMR effect in granular Cu$_{90}$Co$_{10}$ microwires

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We observed a significant increase of the giant magnetoresistance (GMR) effect (up to 32% after the adequate annealing) and Kondo-like behavior in Cu$_{90}$Co$_{10}$ glass-coated microwires. Observed enhancement of the GMR effect can be interpreted considering the formation of the fine Co grains inside the Cu matrix as well as appearance of lamellar nanostructures allowing enhancement of the MR effect after annealing. Observed experimental data are discussed considering the regions with higher Co-ions content responsible for the presence of Co inhomogeneities or clusters and the regions with lower Co-ions content behaving as the magnetic impurities in the metallic host. Observed resistivity minimum on temperature dependence can be described considering Kondo effect mechanism involving magnetic impurities in metals. But the other mechanisms responsible for the resistivity minimum have been considered. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4973291]

I. INTRODUCTION

Rapid quenching from the melt is quite fast and an effective method for preparation of novel metastable materials with crystalline, amorphous, nanocrystalline or granular structures with a new combination of physical properties (mechanical, magnetic, electrochemical...). Most attention has been paid to studies of amorphous soft magnets presenting excellent magnetic softness. This magnetic softness is originated from the absence of magnetocrystalline anisotropy in amorphous alloys.

On the other hand, granular or inhomogeneous materials typically formed by immiscible elements (Co, Fe, Ni)-(Cu, Pt, Au, Ag) attracted considerable attention since the beginning of 1990s. The main interest in granular materials is related to giant magnetoresistance (GMR), previously discovered in magnetic multilayered films. A substantial economic difference between multilayered thin films and granular materials is the preparation cost: multilayered materials must be fabricated with multisource MBE and sputtering. The high fabrication cost is an obstacle. On the other hand, granular materials can be fabricated with much simpler technology.

The origin of the GMR effect in granular materials has been attributed to spin-dependent scattering of conduction electrons within the magnetic granules, as well as at the interfaces between magnetic and nonmagnetic regions. These granular inhomogeneous solids can be prepared by different techniques including mechanical alloying and rapid quenching techniques.

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Conventional route for optimization of the GMR effect in granular inhomogeneous materials involves appropriate recrystallization of the prepared metastable alloys through the annealing allowing formation of a structure consisting of magnetic nano-sized precipitations into conductive metallic matrix.\textsuperscript{9,10} Formation of such structure is related to the phase diagram of the immiscible elements. Typically, at room temperature the ferromagnetic metals present quite low solubility in the metallic matrix. Consequently, rapidly quenched immiscible alloys at room temperature usually form a supersaturated solid solution.\textsuperscript{9,10}

During last few years studies of glass-coated magnetic microwires prepared using Taylor-Ulitovsky technique involving rapid quenching from the melt gained considerable attention.\textsuperscript{4,11} This inexpensive and fast preparation process method allows preparation of long uniform microwires (up to 10km) with few grams of the master alloy.\textsuperscript{4} The diameter of metallic nucleus typically ranges from 1 up to 70 µm, although preparation of nanowires using almost the same technique is reported.\textsuperscript{12}

Amorphous magnetic microwires can present excellent magnetic properties (giant magnetoimpedance effect and fast magnetization switching).\textsuperscript{4,13} Moreover the developed technology is suitable for mass production.\textsuperscript{4}

On the other hand, strong internal stresses may be induced during the simultaneous rapid solidification of the metallic wire surrounded by the glass coating. The origin of these stresses is related to different thermal expansion coefficients of metal and glass-coating. The strength of these stresses depends on thickness of the glass coating and metallic nucleus diameter, which provides another control mechanism of the magnetoelastic anisotropy in the metallic nucleus.\textsuperscript{14–16}

Essentially the same fabrication method can be employed for preparation of Co-Cu and Fe-Cu microwires exhibiting granular structure and GMR effect.\textsuperscript{11,17} But as-prepared microwires Co-Cu and Fe-Cu generally present GMR effect below 10%.

Quite recently we reported on considerable improvement of the GMR effect after annealing of Cu-Co microwires and on observation of Kondo-like behavior in Cu\textsubscript{95}Co\textsubscript{5} microwires.\textsuperscript{17,18} On the other hand, there are still open questions as regarding the origin of the GMR effect in materials prepared from immiscible elements. Thus Co particles embedded in Cu matrix, small Co clusters within a Cu matrix, homogeneous spinodal decomposition characterized by long parallel Co-excess stripes are considered by various authors.\textsuperscript{9,19,20} Moreover Kondo-like behavior reported for Cu\textsubscript{95}Co\textsubscript{5} microwires is quite unusual even for alloys containing 5% Co. Indeed, classical Kondo-effect is usually observed in alloys with quite low content of magnetic impurities (0.002-0.02 %).\textsuperscript{21}

Consequently, in this paper, we present our last experimental results on the influence of annealing conditions on magnetic, transport and structural properties of Cu\textsubscript{90}Co\textsubscript{10} glass-coated microwires.

II. EXPERIMENTAL METHOD

Studied Cu\textsubscript{90}Co\textsubscript{10} glass-coated microwires (total diameters, $D \approx 20.2$ µm, metallic nucleus diameter, $d \approx 14.7$ µm have been prepared using the Taylor-Ulitovsky technique.\textsuperscript{4,12–16} A Co\textsubscript{10}Cu\textsubscript{90} master alloy has been prepared by arc melting of the pure elements in Ar atmosphere. The master alloy ingot was first placed into a Pyrex tube inside an inductive coil. Once the composite material was melted (metallic alloy and Pyrex glass coating), it was drawn and wound onto a motorized cylinder shaped spool. A water jet has been applied to the moving wire for enhancing the quenching rate. Thin metallic wires ($D \approx 20.2$ µm, $d \approx 14.7$ µm) covered by a Pyrex glass have been obtained using aforementioned technique.

Structure and phase composition have been studied using a BRUKER (D8 Advance) X-ray diffractometer with Cu Kα ($\lambda = 1.54$ Å) radiation.

Magnetic and transport properties have been measured using a Quantum Design PPMS device (with applied magnetic field up to 90 kOe) in the temperature range 5 - 300 K. For magnetic and transport measurements we used 4-5 mm long samples. Electrical contacts were prepared by mechanically removing the insulating glass coating at the very end of microwires. The electrical resistance has been measured using four probe method.

The magnetoresistance ratio (MR) is defined as:

$$\frac{\Delta R}{R}(\%) = \left( R(H) - R(0) \right) \times 100 / R(0)$$ (1)
Where $R(H)$ is resistance at given magnetic field, $H$, $R(0)$ is the resistance at $H = 0$. Because of thin diameters the sample resistance is not small (a few Ohms). Consequently, observed resistivity changes are of the order from 0.2 to 1 Ohms.

Samples have been annealed in conventional furnace at annealing temperatures, $T_{\text{ann}} = 400^\circ$C varying the annealing time, $t_{\text{ann}}$. Since all the samples are coated by the insulating glass coating the annealing has been performed on air (without any inert gas or vacuum).

III. EXPERIMENTAL RESULTS AND DISCUSSION

The magnetization curves, $M(H)$, of studied Cu$_{90}$Co$_{10}$ microwires measured at temperatures 5 -150 K are shown in Fig. 1. $M(H)$ of as-prepared sample measured at 5 K exhibits saturation (see Fig. 1). For higher temperature (above 75 K) $M(H)$ dependences are almost linear. After annealing the saturation has been observed at least up to 80 K in the same sample (Fig. 1(b)).

As-prepared Cu$_{90}$Co$_{10}$ samples present magnetoresistance, $\Delta R/R$, of about 5% similarly to that reported previously$^{11}$ (see Fig. 2(a)). After annealing we observed gradual increasing of $\Delta R/R$ (see comparison of $\Delta R/R(H)$ for as-prepared and annealed at 400$^\circ$C for $t_{\text{ann}} = 1$ h and 5 h). After long enough annealing we observed increasing of $\Delta R/R$ up to 32% (see Fig. 2(b)). This behavior is similar to that recently reported by us for Cu$_{95}$Co$_5$ and Cu$_{80}$Co$_{20}$ microwires.$^{17,18}$ But $\Delta R/R$ values observed in studied Cu$_{90}$Co$_{10}$ microwires ($\Delta R/R \approx 32\%$) are higher.

The behavior of $\Delta R/R(H)$ curves is typical for GMR effect showing decreasing with magnetic field, $H$, increasing (Fig. 2(a)).

In order to analyze the origin of the GMR effect we compared the temperature dependence of $\Delta R/R$ and $M^2$ for studied as-prepared and annealed Cu$_{90}$Co$_{10}$ microwire (see Fig. 3). We observed qualitative correlation for all temperature range.

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**FIG. 1.** Magnetization curves, $M(H)$, in as-prepared (a) and annealed at 400$^\circ$C for 10 h (b) Cu$_{90}$Co$_{10}$ sample measured at different temperatures.
As described elsewhere, a number of magnetic systems exhibit large negative MR. In multilayers and granular systems, the MRs can be saturated under a sufficiently large magnetic field when ferromagnetic alignment is achieved. In our case we did not observe the saturation even at high magnetic field (see Figs. 2(a) and 2(b)). This behavior is typical for spin glasses and alloys containing small magnetic clusters, where the large negative MRs cannot be readily saturated by the field due to the inability to accomplish ferromagnetic alignment of all the moments. Consequently, we can only assume that studied samples are magnetically inhomogeneous or disordered on the scale of the mean-free path.

The other peculiarity of studied as-prepared Cu$_{90}$Co$_{10}$ samples is that surprisingly they present well-defined resistivity minimum at rather high temperature (about 50K, see Fig. 4). This minimum is affected by applied magnetic field, but in as-prepared sample can be totally suppressed by rather strong magnetic field (about 70 kOe). After annealing the resistivity minimum on $R(T)$ dependence still persists, but this minimum can be suppressed by much lower magnetic field, i.e. by $H = 10$ kOe (Fig. 4(b)).

Usually the resistivity minimum is attributed to the Kondo effect related to the magnetic impurities in metals. But, as mentioned above, classical Kondo-effect is usually observed in alloys with quite low content of magnetic impurities (0.002-0.02 %) and the scattering processes on these magnetic impurities could give rise to a resistivity minimum on $R(T)$ dependence.

Typically in the case of classical Kondo effect the magnetic field suppresses the resistivity minimum. The temperature of $R(T)$ minimum is usually much lower, but relatively high Co content can be the reason of the higher minimum temperature. Considering high Co content we can expect the interaction between magnetic Co-ions and therefore suppression of the Kondo effect. The existence of Co inhomogeneities or clusters can be assumed from the magnetic saturation observed at low temperatures (see Fig. 1).
The other feature of the classical Kondo effect is a resistivity contribution behaving as $\ln(T)$. In order to prove it we re-plotted $R(T)$ dependences in a semi-logarithmic scale (see Fig. 5). As can be observed, the $R - R_{\text{min}}(\ln T)$ dependence is not perfectly linear, although for annealed Cu$_{90}$Co$_{10}$ sample linear dependence fits better.

Consequently, after annealing magnetic and transport properties are rather different from as-prepared Cu$_{90}$Co$_{10}$ microwires.

More detailed structural studies can provide additional information on origin of $R(T)$ minima. Consequently, we employed the X-ray diffraction (XRD). The structure of the metallic core can be interpreted as granular with two phases: the main one, fcc Cu phase (lattice parameter 3.61 Å), found in all samples and small amount of hcp Co phase (lattice parameters 2.51 Å and 4.07 Å), obtaining an evaluation of the grain size between 20 and 40 nm. The grain size, $D_g$, of the crystals formed in each case can derived from Scherrer’s equation:

\[
D_g = \frac{K \lambda}{\varepsilon \cos 2\theta}
\]  

where, $K$ is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. $\varepsilon$, is the half height width of the crystalline peak, and $2\theta$ is the angular position of the maximum crystalline peak.

The Co phase shows a diffraction peak which is very close to the Cu one and, in fact, on those compositions with low Co concentrations, the Co peak is only seen as a shoulder in the high angle side of the Cu peak.\(^{23}\) The diffraction peaks of both phases in observed XRD scans are quite close to each other and even overlapped (see Fig. 6(b)) and only a shoulder in the single peak corresponding to a small amount of the Co phase (presenting also small average grain size) can be observed in the main Cu peak. This fact is only observed when the peak in Fig. 6(b) is seen at very precise scale. The simple view of Fig. 6(b), where the annealed sample shows a wider peak than the as cast one in the high angle 20 side, leads to deduce the existence of the peak corresponding to the Co phase.

![Fig. 3. Temperature dependences of $\Delta R/R$ and $M^2$ for as-prepared (a) and annealed at 400°C (b) Cu$_{90}$Co$_{10}$ microwires.](image)
Then, we deduced considerable preferred orientation of the grains visible from the peak intensities. Usually the peaks at $2\Theta \approx 43.95^\circ$ in Co-Cu granular alloys without texture present the highest intensity.\textsuperscript{23}

After annealing, it can still be found a marked preferred orientation in the sample, although intensities of each peak change with the treatment. When we look into the details, we clearly observed a broadening of the peaks (especially for ones at $2\Theta \approx 50^\circ$, see Fig. 6(b)) that must be attributed to the Co precipitation from the solid solution of Co in Cu matrix. This broadening has been estimated as $0.3^\circ$ to $0.5^\circ$ (in the high angle side of the peak) and this means that the concentration of the Co phase is increased with the annealing.
Consequently, we can assume that, after annealing the precipitation of fine Co grains from the metastable structure of Co$_{10}$Cu$_{90}$ microwire takes place.

It is worth mentioning that the other possible reason of the observed changes can be related to appearance of the nanostructures typical for the spinodal decomposition.$^{21}$

On the other hand it is known that amorphous and disordered materials can exhibit a minimum on temperature dependence of resistivity or decreasing of the resistivity with temperature increasing.$^{24,25}$ Studied Cu$_{90}$Co$_{10}$ microwires present crystalline structure. But high degree of disorder related to the preparation method involving rapid quenching from the melt can be the origin of the unusual temperature dependence of resistivity.

Consequently, observed features of the resistivity minimum can be described considering Kondo effect mechanism involving magnetic impurities in metals. But, besides the classical Kondo effect, we must consider also the other mechanisms responsible for the $R(T)$ minimum, like weak localization, enhanced electron-electron interaction, scattering of conduction electrons by structural TLS, scattering of strongly spin-polarized charge carriers on diluted magnetic moments and disordered structure. The fact that $R(T)$ minimum is affected by the magnetic field supports the classical Kondo effect contribution. On the other hand, non-homogeneous and broad Co ions distribution and atomic disorder mentioned above can give rise to the other mechanisms.

It is worth mentioning that for similar Co content in Co-Ag system the non-monotonic resistivity temperature dependence was explained using the two-current model without involving a Kondo mechanism.$^{26}$ Additionally recently we reported on similar behavior in Co$_5$Cu$_{95}$ microwires with lower Co content.$^{17}$

The fact that the minimum on $R(T)$ dependence of annealed sample is suppressed by much lower magnetic field must be attributed to the redistribution of Co in the studied sample after annealing and formation of either Co grains or lamellar nanostructures.

FIG. 6. XRD patterns of as-prepared (a) and annealed at 400°C for 24 h (b) Cu$_{90}$Co$_{10}$ microwires.
The fine granular structure obtained after annealing allows also the enhancement of the MR effect in the studied Co$_{10}$Cu$_{90}$ microwire up to 32%.

IV. CONCLUSIONS

We prepared and studied magnetic properties and magnetoresistance of Cu$_{90}$Co$_{10}$ microwires. As-prepared microwires present MR of about 5%. After annealing we observed considerable enhancement of the MR effect from 5 up to 32%. We also observed resistivity minimum on temperature dependence. The temperature of minimum is affected by annealing. In both as-prepared and annealed samples $R(T)$ dependence is affected by external magnetic field.

The obtained results can be interpreted considering the formation of the fine Co grains inside the Cu matrix as well as appearance of lamellar nanostructures allowing enhancement of the MR effect after annealing. Observed resistivity minimum can be described considering Kondo effect mechanism involving magnetic impurities in metals. But, besides the classical Kondo effect, we must consider also the other mechanisms responsible for the $R(T)$ minimum, like weak localization, enhanced electron-electron interaction, scattering of conduction electrons by structural TLS, scattering of strongly spin-polarized charge carriers on diluted magnetic moments and disordered structure.

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