EXAFS Studies and Magnetic Behavior of FeCuZr Ball-Milled Alloys

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Metastable alloys of nominal composition $(Fe_{0.5}Cu_{0.5})_{100-x}Zr_x$ $(x = 0 - 17$ at.%) have been synthesized by high energy ball milling. In spite of the high and positive enthalpy of mixing between Fe and Cu, nanocrystalline or amorphous alloys have been obtained depending on the Zr content. Alloys exhibit a ferromagnetic behavior with a Curie temperature below room temperature. The thermal dependence of the thermorremanence shows a anomalous increase above the Curie temperature. This behavior seems to be related with a magnetovolume effect. Extended X-ray absorption fine structure (EXAFS) measurements have been performed to explain this effect. Preliminary results seem to indicate an almost negligible thermal expansion at temperatures below Tc, while normal thermal expansion takes place at higher temperatures.

***Index Terms*—Amorphous alloys, Curie's temperature, extended X-ray absorption fine structure (EXAFS), high energy ball milling (HEBM), thermoremanence.**

I. Introduction

IN RECENT years, there has been a new interest on alloys with high enthalpy of mixing. In order to overcome the immiscibility, nonequilibrium processing techniques are required for producing mixing at an atomic level. Among them, high energy ball milling (HEMB) has emerged as a powerful technique since it can extend regions of metastable solubility of immiscible elements to obtain solid solution of elements with high enthalpy of mixing [1]. HEBM is a technique commonly used to obtain supersaturated solid solutions, alloys with high energy of mixing and alloys of combinations of elements which do not show appreciable solubility in their equilibrium phase diagrams [2]–[5]. The FeCu system is an example of a binary system with a very low solid miscibility at room temperature. The FeCu equilibrium phase diagram indicates a small miscibility at room temperature, only Fe_4Cu_{96} and $Fe_{90}Cu_{10}$ has been obtained [6], however, by means of HEBM FeCu solid solutions have been obtained in almost all the compositional range. Fe_xCu_{100-x} alloys with $x < 60$ (at.%) exhibit a face centred cubic (fcc) structure while for higher Fe content the alloys exhibit a body centred cubic (bcc) structure. It is worth to mention that equiatomic fcc-FeCu alloys are ferromagnetic, with a Curie temperature (Tc) of around 500 K, in spite of fcc-Cu and fcc-Fe not being ferromagnetic at their ground state. The ferromagnetic character observed in $Fe_{50}Cu_{50}$ alloys seems to be related with magnetovolume effects, since the fcc lattice is expanded with respect to fcc-Cu and fcc-Fe [7].

Amorphous FeCu alloys have been not synthesized up to present date by high energy ball milling or by any other nonequilibrium technique. Amorphization of 3-D transition metals has been, traditionally, induced by adding metalloids such as boron or by high atomic volume elements such as Zr. Normally, amorphous alloys with around 80 at.% of 3-D metal can be obtained by HEBM. In this paper, amorphization of equiatomic fcc-FeCu alloys has been induced by adding Zr [8].

In this paper, the influence of Zr alloying on the magnetic properties of $Fe_{50}Cu_{50}$ alloys is studied. Binary FeZr on the Fe rich side exhibit anomalous magnetic behavior at low temperature, as well as invar and re-entrant spin glass behavior. The magnetic properties are strongly dependent of the Fe content as well as on the local atomic order. Amorphous FeZr alloys have been produce by melt spinning up to an Fe concentration range of 90 at.%. By using other non equilibrium processing techniques, such as sputtering or mechanical alloying, different amorphization ranges are observed. For instance, by mechanical alloying amorphous alloys can be obtained for Fe concentrations ranging between 30–70 at.%. It will be shown that the magnetic properties change drastically with respect to $Fe_{50}Cu_{50}$ alloys upon Zr addition. In particular, the alloys exhibit an anomalous magnetic behavior for temperatures above Curie temperature characterized by an spontaneous increase of the magnetization above Tc that seems to be associated with a change of the thermal expansion behavior in the ferromagnetic-paramagnetic transition temperature [9], [10]. In order to account for such behavior the temperature dependence of the nearest-neighbor distance has been studied by means of EXAFS in the K-edge of iron.

II. Experimental Details

Metastable alloys of nominal composition $(Fe_{0.5}Cu_{0.5})_{100-x}$ Zr_x $(x = 0-17$ at. %) have been synthesized by high energy ball milling (HEBM) in a planetary mill with hardened steel vials. To avoid oxidation of the powder upon the milling process, the vials were sealed under nitrogen atmosphere prior to the milling. The starting materials were Fe, Cu, and Zr in powder form, with

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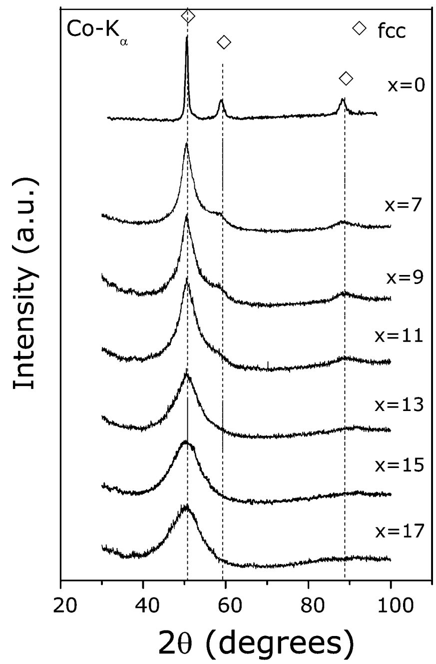

Fig. 1. XRD patterns of as milled samples.

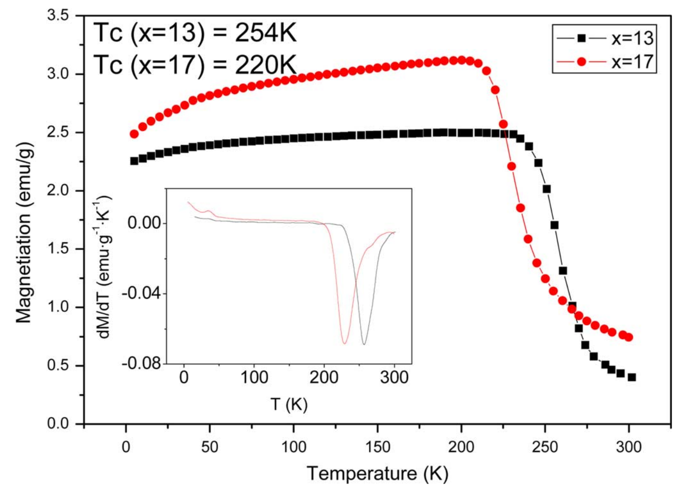

Fig. 2. Thermal dependence of the magnetization for $x = 13$ and $x = 17$ at.%. The inset shows the derivative of the M versus T curves used for determining the Tc.

a purity of 99.9%. The final milling time was 120 h. The final composition of the powder was determined by using scanning electron microscopy (SEM) equipped with an energy dispersive X-ray analysis (EDX). A maximum value of 2 at.% of additional Fe has been determined through this analysis, although no traces of Ni or Cr coming from the milling media have been detected.

In spite of the high and positive enthalpy of mixing between Fe and Cu for $Fe_{0.5}Cu_{0.5}$ composition, nanocrystalline (with a face cubic centred (fcc) structure) or amorphous alloys have been obtained depending on the Zr content.

The alloy formation has been confirmed by XRD, Mössbauer spectroscopy and by means of extended X-ray absorption fine spectra (EXAFS). The latter is a powerful technique for studying nearest-neighbor distances in these type of alloys for the different elements, since the energy of the radiation can be tuned for studying a particular element [11]. EXAFS measurements, as a function of temperature, have been performed in the Sp-line at ESRF in Grenoble and at the Center for Microwave Magnetic Materials and Integrated Circuits (Northeastern University, Boston, MA).

III. Estructural and Magnetic Characterization

Fig. 1 shows the X-ray diffraction (XRD) pattern of the alloys after 120-h milling time. For the sake of comparison, the spectrum corresponding to the equiatomic fcc-FeCu alloys is also included.

XRD patterns suggest the formation of single phase FeCuZr alloys. Depending on the Zr content, the alloys exhibit an fcc structure, the same structure as obtained for equiatomic FeCu alloys, or an amorphous one. In addition, the average crystallite size drops from 18 nm, for x $=$ 0, to around 7 nm for the nanocrystalline samples.

Mössbauer spectra recorded at room temperature exhibit a broad, 0.7 mm/s FWHM, and asymmetric single line centered around zero velocity. The spectra are characteristic of a disordered alloy paramagnetic at room temperature. No differences are observed between fcc and amorphous alloys, indicating that the local environment for the Fe atoms are similar in the disordered solid solution and in the fcc-alloys [12]. Alloying with Zr produces a decrease of the magnetic ordering temperature of the alloys, that lie below room temperature, together with a reduction of the Fe magnetic moment, which drops down to a value similar to that found on Fe-rich, FeZr alloys. Hyperfine splitting of bcc-Fe ferromagnetic particles is absent in all cases.

The Curie temperature of the alloys has been determined from the inflection point of the thermal dependence of the magnetization measured with an applied field of 0.01 T, after cooling the sample down to 5 K under a zero magnetic field. As an example, Fig. 2 shows the magnetization versus temperature for $x = 13$ and $x = 17$ at.%. As mentioned previously, the Curie temperature lies below room temperature, decreasing from 285 K for $x = 7$ at.% down to 220 K for $x = 17$ at.%.

From the thermal dependence of the magnetization curves, the thermal evolution of the coercive field (Hc) has been determined. As an example, hysteresis loops measured at different temperatures for the sample $x = 13$ at.% are shown in Fig. 3. In the inset, the thermal evolution of Hc is shown. In all cases, an anomalous magnetic hardening of the material is observed for temperature above Tc. A similar anomalous behavior is observed concerning the temperature dependence of the thermoremanece (TRM). TRM measurements are performed by cooling the sample under the presence of an applied magnetic field down to 5 K. Then, the field is removed and the remanence is measured while heating up the sample. TRM decreases with increasing temperature until it reaches a minimum value for temperatures close to the Tc calculated from Fig. 2. However, further increase in temperature promotes a spontaneous increase of the magnetization that is observed up to 300 K, see Fig. 4. This behavior is reversible, meaning that no irreversible structural changes take place in the alloys.

This increase of the spontaneous magnetization with the temperature and in absence of an applied field, could be related

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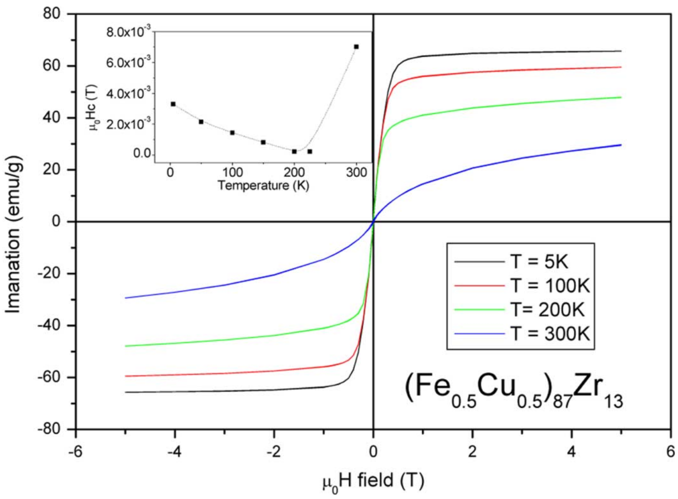

Fig. 3. Hysteresis loop of the sample $(Fe_{0.5}Cu_{0.5})_{87}Zr_{13}$ and the evolution of the coercive field with the temperature.

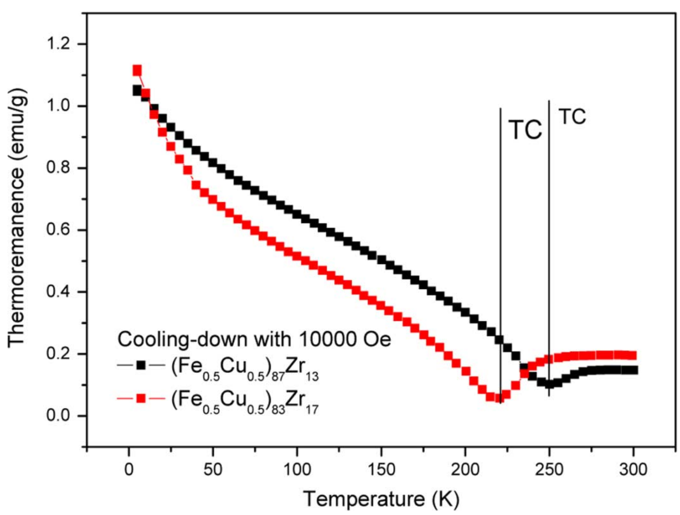

Fig. 4. Thermoremanence measurements on $(Fe_{0.5}Cu_{0.5})_{100-x}Zr_x$ ($x = 13$, 17 at.%), performed after cooling down under a magnetic field of 1 T.

with changes in the interatomic distances with temperature, as occurs in invar alloys. Magnetovolume effects have been reported in FeCu solid solution obtained [7]. In addition, neutron-diffraction measurements performed in Fe-Zr(B,Cu) soft magnetic glasses indicate that a true enhancement of the average local magnetic moment seems to occurs above Tc Such enhancement has been tentatively attributed to the increasing volume expansion that takes place beyond the Curie temperature and reinforces ferromagnetism in some low-density clusters [13].

For determining whether a similar mechanism is the responsible for the TRM anomaly observed in the FeCuZr alloys, EXAFS measurements have been performed with temperature. EXAFS is a powerful technique for studying nearest-neighbor distances in amorphous and nanocrystalline alloys for the different elements, since the energy of the radiation can be tuned for studying a particular element.

EXAFS measures at room temperature have been performed at the Center for Microwave Magnetic Materials and Integrated Circuits. Northeastern University (Boston, MA). These results confirm the disordered nature of the samples. In particular, EXAFS performed at the K-edge of Fe, indicate a dramatic decrease in peak amplitude as well as a shift to lower values in the nearest Fe-Fe distances for Zr contents above 13 at.% that indicates a transition to an amorphous structure.

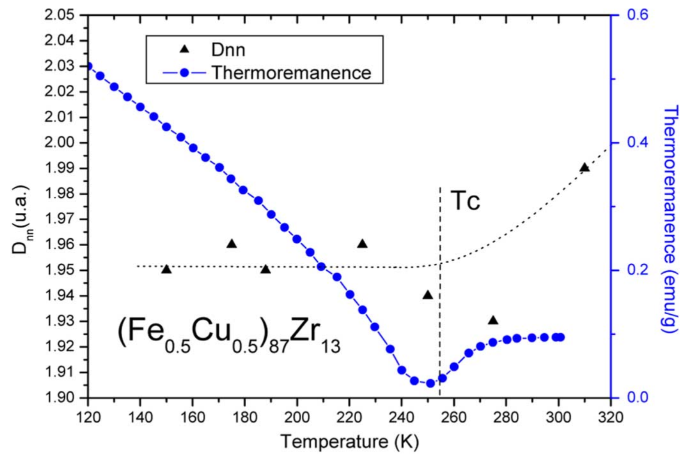

Fig. 5. Comparison of EXAFS and TMR measures on $(Fe_{0.5}Cu_{0.5})_{87}Zr_{13}$ sample.

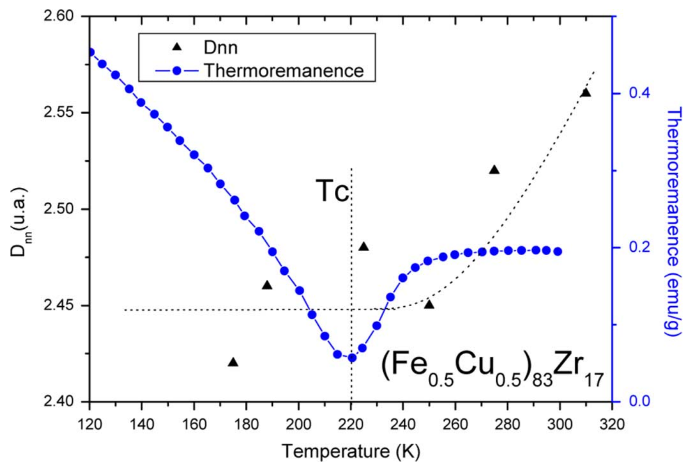

Fig. 6. Comparison of EXAFS and TMR measures on $(Fe_{0.5}Cu_{0.5})_{83}Zr_{17}$ sample.

Also EXAFS measurements have been performed at the Sp-line at ESRF in Grenoble, as a function of temperature. Figs. 5 and 6 show the nearest-neighbor (D_{nn}) (in arbitrary units) distances of iron atoms in $(Fe_{0.5}Cu_{0.5})_{87}Zr_{13}$ and $(Fe_{0.5}Cu_{0.5})_{83}Zr_{17}$ samples. It should be remarked that the D_{nn} distances are nearly temperature invariant for temperatures below Tc, as corresponding to the proposed invar effect. On the other hand, at temperatures over Tc the normal thermal expansion is evident. As it can be seen in Fig. 5 and 6, an abrupt change in the slope takes place at temperatures around Tc.

Figs. 5 and 6 also compare the evolution of the nearest-neighbor (D_{nn}) distances of iron atoms with the thermoremanence measurements obtained after cooling the sample with a magnetic field of 1 T. The thermal expansion is accompanied by an increase of the magnetic signal on the thermoremanence measurements. The increase of first near-neighbor's distances

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with temperature produced by thermal expansion, can yield to and enhancement of the density of the states at Fermi level that could promote the appearance of a new magnetic order above Tc [13].

IV. Conclusion

$(Fe_{0.5}Cu_{0.5})_{100-x}Zr_x$ alloys have been obtained by HEBM. Zr contents over 15 at.% produce amorphous samples, whereas samples with $x < 13$ at.% exhibit a nanocrystalline FCC structure.

In all samples, an anomalous increase of thermoremanence signal and coercive field has been observed at temperatures above Tc of the sample.

Preliminary EXAFS measurements performed with temperature indicates that iron interatomic distances remain almost invariant with temperature for T < Tc, while over Tc the normal thermal expansion takes place. This thermal expansion could produce an increment of the density of states in Fermi's level, that it could promote the appearance of a new ferromagnetic order on the sample.

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