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Tailoring of Magnetic Properties of Glass coated Microwires

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ABSTRACT

The magnetic behaviour of the glass-covered metallic microwires with a wide compositional range of composition with soft and hard magnetic character is presented. The effect of conventional furnace and *dc* current annealing under *dc* axial magnetic field or without it as well as of a chemical etching on the magnetic properties of Co and Fe-based glass coated microwires has been studied. Such treatments modify the magnetic parameters. In particular, annealing under applied magnetic field (field annealing) can improve significantly such magnetic parameters as permeability. Such phenomenology can be interpreted considering the noticeable magnetic anisotropy induced by the combined effects of the magnetic field and strong internal stresses arising from the coating. Giant magnetoimpedance (GMI) effect was observed in nearly-zero magnetostrictive amorphous microwires. Upon careful heat treatment, FeCuNbSiB amorphous microwires devitrificate into nanocrystalline structure with large variety of magnetic parameters. Hard magnetic materials with coercivity up to 800 Oe were obtained as a result of decomposition of metastable phases in Co-Ni-Cu microwires as well as after crystallization process of FeCuNbSiB amorphous microwires.

1. INTRODUCTION

Studies of ferromagnetic amorphous wires obtained by in-rotating-water quenching technique with a typical diameter of around 120 μm has become a classic topic of applied magnetism owing to their very particular magnetization properties. Large Barkhausen jump between two stable remanent states (so-called magnetic bistability, MB) and Giant Magneto-Impedance (GMI) effect have been observed and intensively studied in the last few years [1].

An alternative technology, the Taylor-Ulitovsky method, was recently employed to produce continuous microwire (0.4 Km/min) with a metallic nucleus (typically from about 1 μm to 20 μm in diameter) covered by insulating Pyrex-type glass coating sheath (with the thickness of 1- 10 μm). A number of outstanding magnetic properties, such as magnetic bistability, enhanced magnetic softness and GMI effect (up to 130%) have been found recently in such microwires [2-5]. The magnetic properties of microwires are correlated with their microstructure, composition and internal stresses originated from the difference of thermal expansion coefficients of the metal and the glass. Consequently, the magnetic properties could be improved by adequate treatment: heat treatment or chemical etching of the glass coating or by the selection of adequate chemical composition of the metallic nucleus.

The aim of this paper is to present novel results on compositional dependence and processing of glass-coated microwires in order to design their magnetic properties.

2. EXPERIMENTAL DETAILS

Microwires of different Fe- and Co-rich composition were obtained by the Taylor-Ulitovsky technique.

Varying the fabrication parameters, the microwires were fabricated with a different ratios, ρ , of the glass coating thickness, t , to the total radius, R , of the wire. The axial $M_z - H_z$ hysteresis loop of the samples was obtained by conventional induction method at 50 Hz. Chemical etching of the external glass coating was produced in diluted (10% or 20%) solution of hydrofluoric acid (HF). The evolution of the structure after the annealing was observed using X-ray diffraction with $\text{CuK}\alpha$ radiation. Furnace and current annealing treatments were used. Such treatments were carried out under the presence of a magnetic field (FA) and without field (CA).

The electrical impedance of the microwire was evaluated by means of the four-point technique. The magnetoimpedance ratio, $\Delta Z/Z$, has been defined as:

$$\Delta Z/Z = [Z(H) - Z(H_{\max})]/Z(H_{\max}) \quad (1)$$

A maximum direct current longitudinal magnetic field, H_{\max} , up to 2400 A/m was applied by a long solenoid.

3. EXPERIMENTAL RESULTS AND DISCUSSION

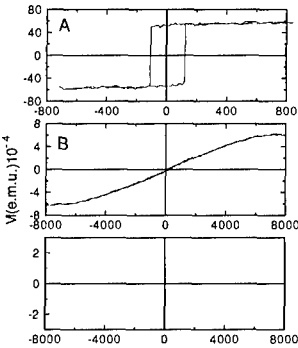


Figure 1. Hysteresis loops of $\text{Fe}_{70}\text{B}_{15}\text{Si}_{10}\text{C}_5$ ($\lambda_s > 0$), $\text{Co}_{75}\text{Si}_{10}\text{B}_{15}$ ($\lambda_s < 0$) and $\text{Co}_{68}\text{Mn}_7\text{Si}_{10}\text{B}_{15}$ ($\lambda_s \approx 0$) microwires.

produces mainly small changes in the coercive field, ascribed to the relaxation of internal stresses. Nevertheless, if the thermal treatment was carried out under the presence of an axial magnetic field (field annealing, FA), significant changes of the hysteresis loop were detected (figure 2). This change produces an increase of the initial permeability, μ_i , coercivity, H_c , remanent magnetization, $\mu_0 M_r$, and a decrease of the anisotropy field, H_K (see figure 3). The changes of the shape of the hysteresis loop with FA should be connected to the induction of magnetic anisotropy with an easy axis along the longitudinal direction of the microwire. The field of induced anisotropy, ΔH_k has been calculated as the difference between the

Hysteresis loops of three of studied microwires: Fe-rich (positive magnetostriction constant, λ_s), Co-rich (negative λ_s) and Co-Mn (nearly-zero λ_s) are shown in figures 1 (a-c) respectively. As can be seen, the shape of the hysteresis loops as well as main magnetic properties (coercivity, H_c , magnetic anisotropy field, magnetic permeability) depend on the composition of the sample. The conventional annealing (CA) in the range of 100 - 200 °C

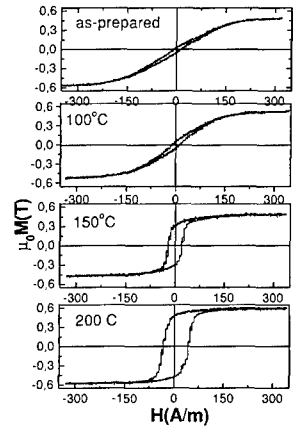


Figure 2. Effect of magnetic field annealing (FA) on hysteresis loops of $(\text{Co}_{0.92}\text{Mn}_{0.8})_{75}\text{Si}_{10}\text{B}_{15}$ microwire at different annealing temperatures.

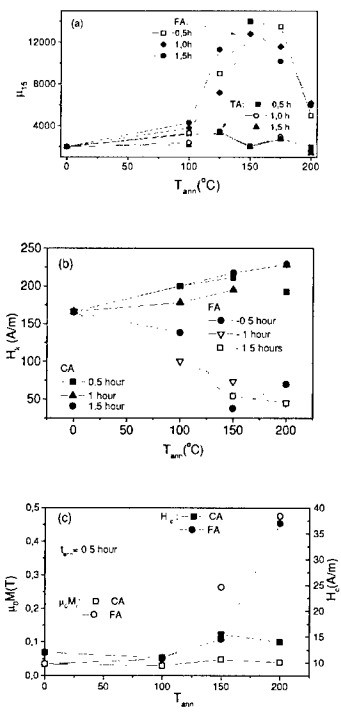


Figure 3. Effect of annealing on magnetic properties of $\text{Co}_{69}\text{Mn}_6\text{Si}_{10}\text{B}_{15}$ microwires: initial magnetic permeability, μ_{15} (a), anisotropy field, H_k (b), coercivity and remanent magnetization (c)

In the case of the sample $\text{Fe}_{70}\text{B}_{15}\text{Si}_{10}\text{C}_5$, both treatments (CA, FA) at 30 mA ($j=227 \text{ A/mm}^2$) caused a decrease of H_c with the t_{ann} . In the case of FA such decrease of coercivity is more significant.

In contrast, in the case of $\text{Co}_{56,5}\text{Fe}_{6,5}\text{Ni}_{10}\text{B}_{16}\text{Si}_{11}$ samples, both treatments result with opposite effects. CA treatment gives rise to roughly monotonic decrease of the coercivity, while FA results in an increase of H_c , with a broad maximum at $t_{ann} \approx 10$ min. Similarly with $\text{Fe}_{70}\text{B}_{15}\text{Si}_{10}\text{C}_5$ samples, a monotonic decrease of H_c has been observed for $\text{Co}_{68}\text{Mn}_7\text{Si}_{10}\text{B}_{15}$ sample after both CA and FA treatments. Besides, as in the case of the $\text{Co}_{56,5}\text{Fe}_{6,5}\text{Ni}_{10}\text{B}_{16}\text{Si}_{11}$ sample, the FA treatment results in higher H_c , as comparing with the CA treatment.

Like in the case of conventional annealing (figures 3 and 4) we can explain the observed difference between the CA and FA as the effect of the stress+longitudinal field induced magnetic anisotropy in the last case, where the strong internal stresses contribute as the reinforcing factor.

anisotropy field before and after treatments. In case of FA treatment ΔH_k is of around 120 A/m. It must be noted that the moderate values of the annealing temperature cannot assume the pair ordering mechanism. We believe that this anisotropy is developed by the combine effect of the high internal stress and the magnetic field applied during the treatment [5].

Dependencies of the coercivity on the annealing time, t_{ann} , for current annealing CA and FA with current density 227 for three microwires is shown in Figure 4.

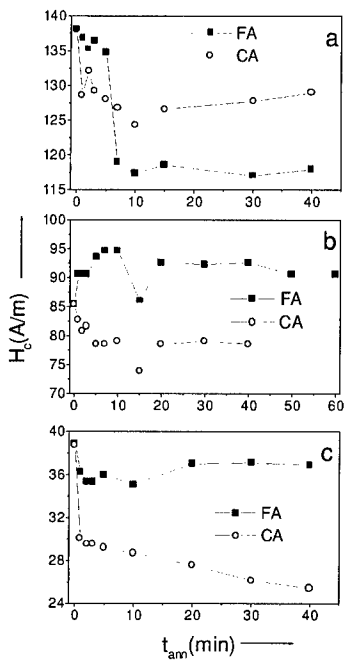


Figure 4. Comparative evolution of H_c with annealing time for CA and FA of $\text{Fe}_{70}\text{B}_{15}\text{Si}_{10}\text{C}_5$ (a), $\text{Co}_{56,5}\text{Fe}_{6,5}\text{Ni}_{10}\text{B}_{16}\text{Si}_{11}$ and $\text{Co}_{68}\text{Mn}_7\text{Si}_{10}\text{B}_{15}$ (c) microwires annealed at $j=227 \text{ A/mm}^2$ with the annealing time, t_{ann} , as a parameter.

A chemical etching treatment can also significantly change the magnetic properties. The effect of the chemical etching time, t , on coercivity, H_c , and remanence, $\mu_0 M_r$; is presented in figure 5. These observed experimental dependencies could be understood taking into account additional magnetoelastic energy arising from the glass coating. Strong internal stresses (up to 10^3 MPa) can even modify value and sign of the magnetostriction constant, especially if the magnetostriction constant is quite low. Consequently, removing of the glass coating gives rise to the stress relaxation.

The very soft magnetic behaviour found in $\text{Co}_{68.5}\text{Mn}_{6.5}\text{Si}_{10}\text{B}_{15}$ microwires with small negative magnetostriction constant makes them very attractive to investigate the magnetoimpedance effect. A really high GMI has been observed in $\text{Co}_{68.5}\text{Mn}_{6.5}\text{Si}_{10}\text{B}_{15}$ microwire annealed at 100 °C for 1 hour (see figure 6). A maximum

maximum, H_m , increase with frequency of driving current, f (see figure 6). This GMI effect is extremely sensitive to the application of external tensile stresses (figure 6b). The origin of this dependence is related with the magnetoelastic anisotropy induced by the tensile stress. It is remarkable to mention that the position of the DC axial field that corresponds to the maximum GMI ratio, H_m , should be attributed to the static circular anisotropy field, H_k . This allows us to estimate the magnetostriction constant using the well-known expression for the stress dependence of anisotropy field:

$$\lambda_s = (\mu_0 M_s / 3) (dH_k / d\sigma) \quad (2)$$

The $H_m(\sigma)$ dependence is roughly linear with a slope of around 0.7 A/(m×MPa), that gives $\lambda_{s,0} \approx -2 \times 10^{-7}$, which is reasonable in comparison with the recently reported values estimated for the similar composition ($\lambda_{s,0} \approx -3 \times 10^{-7}$) [6]

Annealing temperature, T_{ann} , dependence of the coercivity, H_c , for the $\text{Fe}_{71.8}\text{Cu}_{1.0}\text{Nb}_{3.1}\text{Si}_{15.0}\text{B}_{9.1}$ alloy with the geometric characteristics as parameter is shown in the figure 7. Generally a decrease of H_c has been observed at T_{ann} below 400 °C. Weak local minimum of H_c has been observed at about 400-450 °C with the temperature of that minimum depending on both alloy composition and geometry. Such decrease of H_c could be ascribed to the structural relaxation of the material remaining the amorphous character such as has been widely reported in metallic glass alloys. A small relative hardening (increase of coercivity) can be observed after annealing around 450-500 °C, which could be ascribed to the very beginning of first stage of devitrification. It is interesting to note the effect of the sample's geometry on this increase of the coercivity. A deeper softening (optimum softness) with rather low value of H_c is obtained in the samples treated at $T_{\text{ann}} = 500-600$ °C. Finally, abrupt increase of H_c is shown by the samples treated at T_{ann} above 600 °C, indicating the

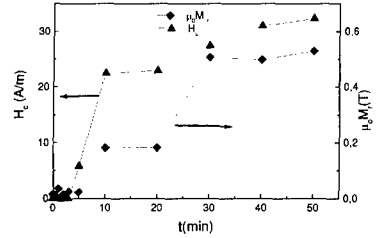


Figure 5. Effect of chemical etching on the magnetic parameters of the $\text{Co}_{68}\text{Mn}_7\text{Si}_{10}\text{B}_{15}$ amorphous microwire.

GMI ratio, $(\Delta Z/Z)_m$, as well as a field of

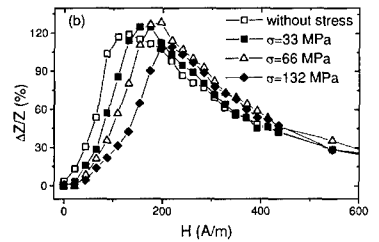
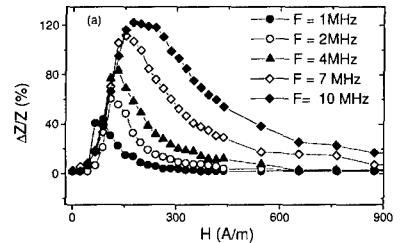


Figure 6. Effect of the frequency, f , (a) and applied stresses (b) on $\Delta Z/Z$ ratio of $\text{Co}_{68.5}\text{Mn}_{6.5}\text{Si}_{10}\text{B}_{15}$ amorphous microwire

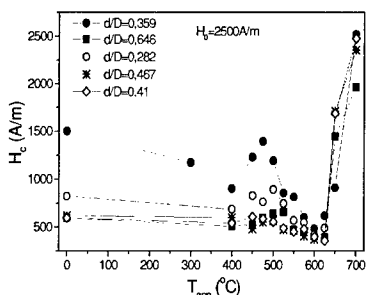


Figure 7. Dependence of coercivity on the annealing temperature, T_{ann} , for $Fe_{71.8}Cu_1Nb_{3.1}Si_{15}B_{9.1}$ with the ratio d/D ranging from 0,282 to 0.646

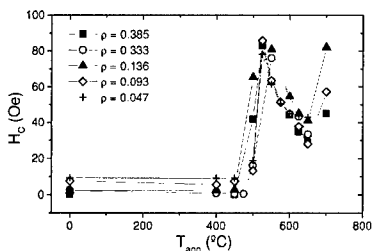


Figure 8. Dependence of the coercivity on the annealing temperature, T_{ann} , of the $Fe_{72.3}Cu_1Nb_{3.1}Si_{14.5}B_{9.1}$ microwires with the ratio d/D as the parameter.

nanocrystalline structure consists of small α -Fe(Si) grains embedded in a residual amorphous matrix with vanishing magnetostriction constant. Probably, a small change in the composition of the metallic nucleus does not permit to achieve the vanishing magnetostriction constant. In addition, strong internal stresses due to the glass coating can result in a change of structure of the precipitates (it is well known that internal strains of different nature can be as the origin of a martensitic-type transformation in Fe alloys). Probably, the strong internal stresses in the metallic nucleus could induce a precipitation of γ -Fe fine grains during the first stage of the crystallization process. Particularly, the presence of γ -Fe crystallites could be attributed the magnetic hardening observed in this microwire. To clarify this point new studies actually are in progress.

Figure 9 shows the $H_c(T_{ann})$ behaviour for the crystalline $Co_{29}Ni_{25}Cu_{45}Mn$ microwires. The as-prepared sample shows a relatively low coercivity (50 —100 Oe). Raising the annealing temperature until 973 K a strong increase in H_c is obtained,

beginning of the precipitation of iron borides (with grain size larger than 50 nm). Such beginning of the increase of H_c varies depending mainly on sample composition as well as on geometry. It must be noted that for the thickest glass coating the increase of H_c appears at lower temperature, which could be related with the fact that the internal stresses induce some ordering to hinder the crystallization.

Slight change of the chemical composition results in drastic change of $H_c(T_{ann})$ dependence. Effect of the annealing temperature on the coercivity, H_c , of the $Fe_{72.3}Cu_1Nb_{3.1}Si_{14.5}B_{9.1}$ alloy with the ratio ρ as parameter is shown in the figure 8. A sharp magnetic hardening (significant increase of the coercivity) can be observed after annealing (500 – 550 °C during 1 hour).

It should be indicated that the maximum of H_c takes place at the same range of annealing temperature as first small increase of coercivity in $Fe_{71.8}Cu_{1.0}Nb_{3.1}Si_{15.0}B_{9.1}$ related with the first re-crystallization process (see figure 7).

X-ray analysis of as-prepared $Fe_{72.3}Cu_1Nb_{3.1}Si_{14.5}B_{9.1}$ microwire does not detect a presence of crystalline phases after annealing at 550 °C. Nevertheless, TEM diagram allowed to detect a small amount of fine grains of α -Fe, γ -Fe and α -Fe(Si) with the average grain size of such crystallites around 20-70 nm in annealed sample at 550 °C.

The difference in magnetic behaviour with respect to the conventional *finemet*-type microwires can be attributed to different composition as well as to high internal stresses. It is well known that the best magnetic softness is achieved when the

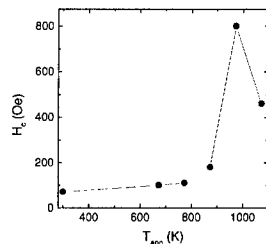


Figure 9. $H_c(T_{ann})$ dependence in $Co_{29}Ni_{25}Mn_1Cu_{45}$ microwire

reaching the maximum value of around 800 Oe. A further increase of the annealing temperature results in a decrease of the coercivity such as can be observed in figure 9. The largest reduced remanence ratio $M_r/M_s = 0.5$ is also found after annealing at 973 K and the estimated saturation magnetization is of about 3.6 KG.

In the as-prepared microwire, quenched from a high temperature, only a single phase, with a lattice parameter $a = 0.3573$ nm was found (figure 10a). When the sample was heated at high temperatures, this metastable phase started to decompose. This can be seen in the sample treated at 973 K, where the segregation is not yet complete (figure 10b). After annealing at 1073 K, the sample shows the equilibrium phases, consisting of a copper matrix ($a = 0.3591$ nm) with Cu-rich particles ($a = 0.3545$ nm) (figure 10c).

These results are in agreement with the magnetic hardening in bulk Co-Ni-Cu permanent magnet alloys, and the maximum value of coercivity obtained after annealing at 973 K during 1 hour agrees with that previously reported by Bozorth [7].

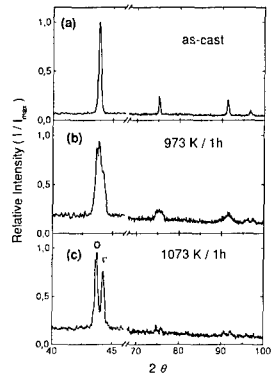


Figure 10. Effect of annealing on X-ray patterns of $\text{Co}_{29}\text{Ni}_{25}\text{Mn}_1\text{Cu}_{45}$ microwire

4. CONCLUSIONS

Magnetization process of glass-coated microwires determines by the magnetoelastic and shape anisotropy. Sign and value of the magnetostriction constant affect strongly the magnetization process. Significant changes of soft magnetic properties have been observed in Fe- and Co-rich microwires after different treatments (conventional and current annealing with or without axial magnetic field as well as chemical etching). The observed experimental results on the soft magnetic properties in Fe- and Co-rich microwires submitted to conventional and current annealing (with or without field) can be explained as a consequence of the induced magnetic anisotropy arising from the counterbalance between internal quenched-in stresses owing to the difference in thermal expansion coefficients of the metal and the glass. This induced anisotropy should be understood as originating from the simultaneous action of the large internal stresses and the axial applied magnetic field. Enhanced magnetic softness and GMI effect (up to 130%) has been observed after adequate thermal treatment. Significant stress dependence of this GMI effect has been found. The magnetostriction constant ($\lambda_{s,\theta} \approx -2 \times 10^{-7}$) is estimated from stress dependence of the GMI ratio.

It must be noted that the coercivity obtained by annealing Co-Ni-Cu-(Mn) microwire with a metastable single phase in the as-prepared state is enhanced up to 800 Oe by decomposition of the metastable phase. In the case of Fe-based (*finemet*-type) microwire, the strong magnetic hardening at low annealing temperature (around 550 °C) could be ascribed to the role of the internal stresses induced by the glass coating on the metallic nucleus.

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