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Engineering of magnetic properties of amorphous and nanocrystalline microwires

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Abstract

We present an overview of the factors affecting soft magnetic properties and giant magnetoimpedance (GMI) effect in thin amorphous wires. Low coercivity and high Gaint magnetoimpedance (GMI) effect have been observed in as-prepared Co-rich microwires. We showed that the magnetoelastic anisotropy is one of the most important parameters that determine magnetic softness and GMI effect of glass-coated microwires and annealing can be very effective for manipulation the magnetic properties of amorphous ferromagnetic glass-coated microwires.
After annealing of Co-rich we can observe transformation of inclined hysteresis loops to rectangular and coexistence of fast magnetization switching and GMI effect in the same sample. We demonstrated that the switching field value of microwires can be tailored by annealing in the range from 4 to 200 A/m.

Keywords: Magnetic anisotropy; magnetic permeability; soft magnetic material; magnetoelastic anisotropy; magnetoimpedance.

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1. Introduction

Recent technological and industrial advances are greatly affected by the development of novel advanced functional materials with improved physical properties. Magnetic materials form important part of functional materials. Many industrial sectors, such as magnetic sensors, microelectronics, security, automobile, energy-efficient refrigerators, medicine, aerospace, energy harvesting and conversion, informatics, electrical engineering, magnetic recording, electronic surveillance and other demand cost-effective magnetic materials with improved magnetic characteristics.

One of most promising families of soft magnetic materials are amorphous magnetic materials introduced few decades ago (Jiles, 2003; Durand, 1983; González & Zhukov, 2006). The main interest in amorphous soft magnetic materials is related to their liquid-like structure characterized by the absence of long range atomic ordering. Particularly the absence of magneto-crystalline anisotropy is the main reason of extremely soft magnetic properties exhibited by amorphous magnetic materials (Jiles, 2003; Durand, 1983; González & Zhukov, 2006).

Amorphous magnetic materials are presently used in many areas, including transformers for electric power distribution, power electronics for small and large-scale power management, pulse power devices, telecommunication devices, and sensors (Jiles, 2003; González & Zhukov, 2006). The use of amorphous metal-based electrical transformers is becoming increasingly significant. Therefore the development of soft magnetic materials in different forms such as ribbons, wires, microwires, and multilayered thin films with amorphous and nanocrystalline structure continue to attract considerable attention of the scientific community.

One of the recent tendencies related with development of industrial applications in the field of magnetic sensors is the miniaturization of the magnetic sensors. Certain progress has been recently achieved in fabrication of novel amorphous magnetic materials (amorphous ribbons, amorphous wires, sintered materials) exhibiting excellent soft magnetic properties (Jiles, 2003; Durand, 1983; González & Zhukov, 2006). On the other hand, most industrial sectors, like magnetic sensors, microelectronics, security etc, need less expensive materials with reduced dimensionality and simultaneously with high soft magnetic properties. This tendency stimulated progress in technology for preparation of novel magnetic materials with reduced dimensionality, such as thin films and thin wires (González & Zhukov, 2006).

One of the most attractive properties from the viewpoint of magnetic sensors applications is the so-called giant magnetoimpedance effect, GMI. Since 1994 the GMI effect became o topic on intensive research and the GMI phenomenology is extensively de- scribed in few reviews and original papers (Beach & Berkowitz, 1994; Panina & Mohri, 1994).

The GMI effect was interpreted assuming scalar character for the magnetic permeability, as a consequence of the change in the penetration depth of the alternating current caused by the applied static magnetic field. The electrical impedance, Z, of a magnetic conductor presenting cylindrical symmetry is given by (Beach & Berkowitz, 1994; Panina & Mohri, 1994):

$$Z = R_{dc} kr J_0(kr)/2J_1(kr) \quad (1)$$

where k = (1 + i)/δ, J = 0 and J1 are the Bessel functions, r - wire's radius and δ the penetration depth given by:

$$\delta = 1/\sqrt{\pi\sigma\mu_{\phi} f} \quad (2)$$

where σ is the electrical conductivity, f the frequency of the current flowing trough the conductor, and μ_{f} the circular magnetic permeability assumed to be scalar. An external static magnetic field H_E applied along the conductor axis introduces significant changes in the circular permeability μ_{ϕ}. Therefore, the penetration depth also changes and, finally, results in a change of impedance Z (Beach & Berkowitz, 1994; Panina & Mohri, 1994). Usually for quantification of the MI effect the MI ratio, $\Delta Z/Z$, is used:

$$\Delta Z/Z = [Z(H_E) - Z(H_{max})]/Z(H_{max}) \quad (3)$$

where H_{max} is the maximum field applied in the experiment, usually up to a few kA/m. This interpretation of the GMI effect in terms of classic skin effect in magnetically soft conductor is suitable for explain the most of observed dependencies and is commonly used by a great majority of published research papers on GMI effect.

The most technological interest in GMI effect is related to the extraordinary high magnetic field sensitivity (few hundred percent change of impedance under low external magnetic field) quite interesting for application in magnetic sensors and magnetometers. Presently the most extended technologies employed for the magnetic field sensing are Hall-effect, Magnetoresistance and Fluxgate techniques. Quite recently Giant magneto-impedance effect (GMI) technology allowing achievement of extremely high magnetic field sensitivity has been developed and proposed for various applications in magnetic sensors (Uchiyama et al., 2011; Honkura, 2002; Gudoshnikov et al., 2014). Presently magnetic compass and acceleration sensors utilizing the GMI effect of thin amorphous FeCoSiB wires integrated in CMOS circuit are employed by Aichi Steels in Japan for a cell phones . Last magnetic field MI sensor generations are characterized by quite interesting sensitivity of about 1 pT (Uchiyama et al., 2011; Honkura, 2002, Gudoshnikov et al., 2014). These advanced features of the GMI sensors attracted attention for the detection of a biomagnetic field in small musculature samples with spontaneous electric activity, using a GMI sensor with the pico-Tesla sensitivity (Nakayama et al., 2011).

The GMI sensor simultaneously realizes highly sensitivity, micro-size, low cost and cover the required frequency range starting from dc fields (Uchiyama et al., 2011; Honkura, 2002). On the other hand, the GMI technology already compares well with other high sensitivity magnetometers exhibiting one of the lowest noise levels between the non-cryogenic magnetometers (Uchiyama et al., 2011; Honkura, 2002; Gudoshnikov et al., 2014). So, GMI magnetic sensors already achieved mature enough development stage allowing to enter in the relevant area of extremely sensitive magnetic field sensoring. On the other hand, the GMI effect interpretation requires a deep understanding of the micromagnetic features of soft magnetic materials. Consequently the GMI is actually opening a new branch of research combining the micromagnetics of soft magnets with the classical electrodynamics. The highest GMI effect is reported for magnetic wires presenting high circumferential magnetic anisotropy (Pirota et al., 2000; Zhukova et al., 2002).

On the other hand studies of fast and controllable domain wall (DW) propagation in thin magnetic wires attracted considerable attention due to promising applications in micro- and nanotechnology (Zhukov & Zhukova, 2014). From the point of view of applications the speed of controllable DW propagation is one of the most relevant parameters (Varga et al., 1976; Ekstrom & Zhukov, 2010).

In the case of cylindrical microwires exhibiting spontaneous magnetic bistability the DW speed above1 km/s has been reported (Varga et al., 1976; Ekstrom & Zhukov, 2010). Therefore studies of DW dynamics in amorphous glass-coated microwires are quite important for understanding of the origin of fast DW propagation and ways to enhance the DW velocity in other materials.
The technology for the thinnest magnetic wires - Taylor-Ulitovky method involves simultaneous rapid quenching of metallic nucleus inside the glass coating. Considerable difference of the thermal expansion coefficients of the glass and the metal results in appearance of considerable internal stresses (Velázquez et al., 1996; Chiriac et al., 2003). Therefore, in the absence of magnetocrystalline anisotropy the magnetoelastic anisotropy is main factor determining magnetic properties of glass-coated microwires and DW propagation (Velázquez et al., 1996; Chiriac et al., 2003; Zhukova et al., 2009).

Consequently the aim of the present review is to update the experimental data on the tailoring of magnetic softness, giant magnetoimpedance effect and domain wall dynamics of glass-coated microwires.

2. Tailoring of the GMI effect and magnetic properties

As already mentioned in the previous section, until now the highest GMI effect is reported for soft magnetic wires with high circumferential permeability that is typical for amorphous wires with vanishing magnetostriction coefficient (Zhukova et al., 2009).

Additionally value of GMI ratio, Z/Z, and features of magnetic field dependence of the GMI ratio are intrinsically related to the magnetic anisotropy of the material. Thus for the wires with circumferential magnetic anisotropy the magnetic field dependence of $\Delta Z/Z$ presents double-peak shape. For axial magnetic anisotropy the maximum value of the GMI ratio corresponds to zero magnetic fields (Usov et al., 1998), i.e. results in a monotonic decay of the GMI ratio with the axial magnetic field.

Consequently GMI effect (its value and magnetic field dependence) depends on fabrication method, material chemical composition internal stresses and also can be modified by the annealing (Zhukova et al., 2009). Moreover the GMI effect usually observed in extremely soft magnetic materials, therefore optimization of magnetic softness is the way of the GMI effect optimization.

As mentioned in the introduction one of the recent main trends for optimization of magnetic softness of magnetic materials is preparation of magnetic materials with amorphous structure. The main source of magnetic softening of amorphous materials is the absence of magneto-crystalline anisotropy (Jiles, 2003; Durand, 1983; González & Zhukov, 2006).

On the other hand there are various factors affecting soft magnetic behavior of amorphous materials. At least five pinning effects have been identified and discussed by H. Kronmüller et al. (1979) as contributing to the total coercivity, Hc:

1. Intrinsic fluctuations of exchange energies and local anisotropies (10^{-3}–1 me), $H_c(i)$
2. Clusters and chemical short ordered regions (< 1 me), $H_c(SO)$
3. Surface irregularities (< 5 Me), $H_c(surf)$
4. Relaxation effects due to local structural rearrangements (0.1-10 me), $H_c(rel)$
5. Volume pinning of domain walls by defect structures in magnetostrictive alloys (10-100 Me), $H_c(\sigma)$.

A detailed analysis of each term can be found in literature (Kronmüller et al., 1979).

Consequently the problem of the optimization of the GMI effect is intrinsically related to the problem of the optimization of soft magnetic properties of various magnetic materials. Some of them (such as surface irregularities, volume pinning centers) are related to proper fabrication process and preparation conditions. The other factors (i.e., clusters and chemical short ordered regions relaxation effects due to local structural rearrangements, magnetostriction coefficient, *etc*.) can be tailored by the post-fabrication processing, i.e. by heat treatment, glass-removal etc.

Below we will shortly review the fabrication techniques allowing preparation of soft magnetic glass-coated microwires promising from the view point of achievement of high GMI effect.

2.1. Melt spinning methods

Amorphous metallic alloys can be produced by a variety of rapid solidification techniques, including splat quenching, melt spinning, gas atomization and condensation from the gas phase. Among the existing techniques, the melt spinning technique has been most widely used to produce amorphous metallic alloys. Amorphous materials can be produced using rapid solidification process if the cooling rates achieved by given fabrication process is high enough to produce liquid-like structure at room temperature (typically cooling rate must be of the order of 10^4–10^6 K/s) (Jiles, 2003; Durand, 1983; González & Zhukov, 2006).

Usually amorphous metallic alloys are synthesized by rapid solidification techniques in alloy systems where the liquid phase remains stable to low temperature and there are competing crystalline phases below the liquidus, i.e. systems with deep eutectics.

Common feature of rapid solidification techniques is that it consists of a rapid quenching of a molten alloy. The method employed for achievement of high enough cooling rate for each particular technique are different.

The fabrication method denominated in most of modern publications as a modified Taylor-Ulitovsky and/or quenching-and-drawing method (Jiles, 2003; González & Zhukov, 2006) is actually well-known since 60-th (Badinter et al., 1973; Larin et al., 2002; Ulitovski & Avernin, 1964; Ulitovsky et al., 1960). Initially this method has been used mostly for fabrication of non-magnetic microwires (for example Cu), but the casting method is essentially the same. This method is based essentially on direct casting from the melt of the composite thin wire consisting of metallic nucleus surrounding by glass coating through the quenching liquid (water or oil) jet onto rotating bobbins (Larin et al., 2002).

The main advantages of this method of microwire fabrication are (Larin et al., 2002):

- repeatability of microwire properties at mass-production;
- extended range of variation in parameters (geometrical and physical);
- fabrication of continuous long pieces of microwire up to 10,000 m;
- control and adjustment of geometrical parameters (inner core diameter and glass thickness) during the fabrication process.

In spite of many advantages this method meets some complexities related with peculiarities of metallurgical processes in rapidly quenching of the composite material and effect of electromagnetic field of inductor on alloy ingot and stability of the process. Moreover recently formation of the interface layer between the metallic nucleus and glass-coating with typical thickness of about 0.5 μm is reported (Zhukov et al., 2014).). But the main peculiarity of this method is the simultaneous rapid quenching of metallic nucleus surrounding by the glass coating. These materials present quite different thermal expansion coefficients and therefore the fabrication process gives rise to strong internal stresses appeared during fast quenching from the melt. All these peculiarities affect magnetic and structural properties of cast microwires.

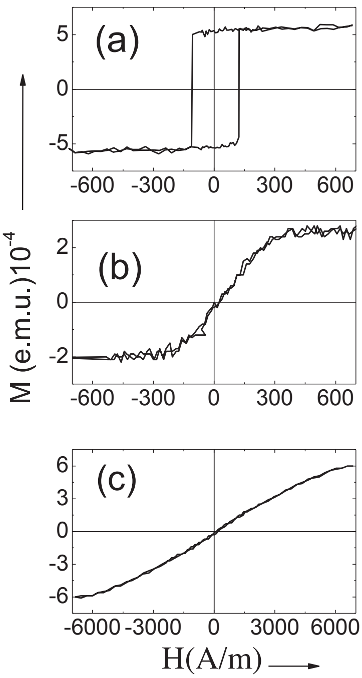

Fig. 1. Typical hysteresis loops of Fe-rich (a), Fe-Co-rich (b) and Co-rich (c) glass coated microwires.

2.2. Effect of composition and magnetoelastic anisotropy on GMI of amorphous wires

As mentioned above the highest GMI effect is usually observed in magnetically soft wires presenting cylindrical shape and high circumferential permeability. Therefore we´ll overview different ways of optimization of the GMI effect in amorphous wires.

As a rule, better soft magnetic properties are observed for nearly-zero magnetostrictive compositions. It is worth mentioning, that the magnetostriction constant, λs, in system $(Co_xFe_{1-x})_{75}Si_{15}B_{10}$ changes with x from $-5x10^{-6}$ at x= 1, to $\lambda s \approx 35\ x10^{-6}$ at x≈0.2, achieving nearly-zero values at Co/Fe about 70/5 (Konno & Mohri, 1989; Zhukov et al.,2003).

In this way, three main groups of amorphous microwires can be distinguished:

- Fe-based wires with positive (of the order of 10^{-5}) magnetostriction constant
- Co-based wires with negative (of the order of 10^{-6}) magnetostriction constant
- Co-based wires with vanishing magnetostriction constant.

Magnetic properties of glass-coated microwires are affected by their composite origin and therefore they present rather different magnetic properties from the other families of magnetic wires. The main difference is that Co-rich microwires with negative magnetostriction coefficient present almost non-hysteretic magnetization curves with quite low coercivity in contrast to Co-rich conventional wires which exhibit rectangular hysteresis loop. Fe-rich microwires present perfectly rectangular hysteresis loops (Fig.1a). Additionally apart of the magnetostriction sign and value the strength of internal stresses is an additional factor affecting the magnetic properties (Zhukova et al., 2009).

For glass-coated magnetic microwires it is commonly assumed, that the magnetic field dependence of GMI effect and overall magnetic properties are determined by the magnetoelastic anisotropy, K_{me}. This magnetoelastic anisotropy, K_{me}, is affected by internal stresses σ_i, and magnetostriction coefficient, λ_s (Zhukova et al., 2009):

$$K_{me} = 3/2 \lambda_S \sigma_i \quad (4)$$

where λ_S is the saturation magnetostriction and σ_i is the internal stress.

In particular, loops of nearly-zero magnetostrictive compositions exhibit very low coercivities and quite large initial susceptibility. Figs 1b and 2 show examples of such a hysteresis loops with vanishing magnetostriction coefficient.

Quasi non-hysteresis behaviour can be observed for Co-rich microwires with a well-defined transverse circular anisotropy. For the Co-rich microwires with low and negative magnetostriction coefficient coercivities of the order of 4 A/m have been reported elsewhere (Zhukova et al., 2009). For fixed Co-rich metallic nucleus composition the field of magnetic anisotropy is a function of the strength on internal stresses induced by the glass coating. The strength of internal stresses is mostly determined by the ratio, ρ, between the metallic nucleus diameter, d, and total composite wire diameter, D, (ρ = d/D).

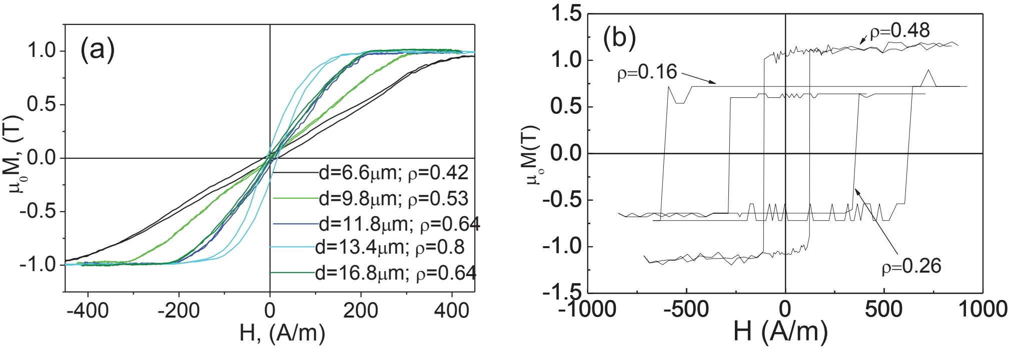

Fig. 2. Hysteresis loops of $Co_{67.1}Fe_{3.8}Ni_{1.4}Si_{14.5}B_{11.5}Mo_{1.7}$ microwires with different geometry (a) and of $Fe_{70}B_{15}Si_{10}C_5$ amorphous microwires with with ρ = 0.63; d=15 μm (a); ρ= 0,48; d= 10,8 μm (b); ρ =0,26; d= 6 μm (c); ρ =0,16; d= 3 μm (d).

In this particular case the magnetisation process takes place by quasi-reversible magnetisation rotation from the circumferential to the axial direction as increasing the axial applied magnetic field.

Hysteresis loops of Fe-rich microwires ($Fe_{70}B_{15}Si_{10}C_5$ with different metallic nucleus diameters are shown in Fig. 2b. As can be appreciated, considerable increasing of switching filed (from about 80 A/m till 700 A/m, i.e. almost one order) is observed when ferromagnetic metallic nucleus diameter decreases from 15 till 3 μm . At the same time, rectangular hysteresis loop shape is maintained even for smallest microwires diameters.

The main interest of the GMI effect is related with the high sensitivity of the impedance to an applied magnetic field, easy achieving up to 300% relative change of impedance in different families of amorphous wires with vanishing magnetostriction (see Fig. 3 for the $(Co_{0.94}Fe_{0.06})_{72.5}B_{15}Si_{12.5}$ conventional amorphous wire). Circular domain structure with high
Fig. 2. Hysteresis loops of $Co_{67.1}Fe_{3.8}Ni_{1.4}Si_{14.5}B_{11.5}Mo_{1.7}$ microwires with different geometry (a) and of $Fe_{70}B_{15}Si_{10}C_5$ amorphous microwires with with ρ = 0.63; d=15 μm (a); ρ= 0,48; d= 10,8 μm (b); ρ =0,26; d= 6 μm (c); ρ =0,16; d= 3 μm (d).

Circumferential permeability proved to be very favorable for highest GMI effect (Beach & Berkowitz, 1994; Panina & Mohri, 1994). Such domain configuration is typical for the nearly-zero magnetostrictive amorphous wires and microwires (Kabanov et al., 2005)

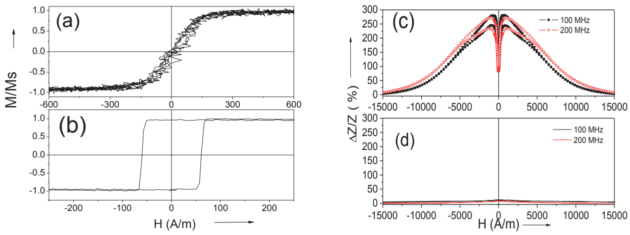

Fig. 3. Hysteresis loops (a,b) and GMI ratio measured in as-prepared $Co_{69.2}Fe_{4.1}B_{11.8}Si_{13.8}C_{1.1}$ and in $Fe_{73.8}Cu_1Nb_{3.1}B_{9.1}Si_{13}$ microwire respectively.

Rather high GMI effect ($\Delta Z/Z \approx 300\%$) is observed in as-prepared Co-rich ($Co_{69.2}Fe_{4.1}B_{11.8}Si_{13.8}C_{1.1}$) microwires, although quite low ($\Delta Z/Z < 10\%$) GMI effect is observed for as-prepared Fe-rich ($Fe_{73.8}Cu_1Nb_{3.1}B_{9.1}Si_{13}$) (see Fig. 3).

As mentioned above one of the main peculiarities of glass-coated microwires is the existence of internal stresses. The principle source of the internal stresses arising in glass-coated microwires is the difference in the thermal expansion coefficients between the glass coating and the ferromagnetic nucleus (Velázquez et al., 1996; Chiriac et al., 2003). Consequently these internal stresses are the source of additional magnetoelastic energy negatively affecting magnetic softness of glass-coated microwires. Therefore additional efforts for optimization of magnetic softness of glass-coated microwires are needed. This was the reason why an inferior GMI effect has been initially observed in as-prepared glass-coated Co-rich microwires without special treatment (Vázquez et al., 1998).

Accordingly, coercivity, magnetic anisotropy field as well as magnetic field dependence of GMI effect, $\Delta Z/Z(H)$ can be tailored by modification of the strength of internal stresses by the aforementioned ρ-ratio between the metallic nucleus diameter, d, and total composite wire diameter, D, ($\rho = d/D$).

General features of observed $\Delta Z/Z(H)$ dependences in Co-rich microwires are existence of two maximums and shift of the magnetic field of maximum, H_m, to the higher field region decreasing the ρ-ratio. The magnetic field of maximum, H_m, has been attributed to the magnetic anisotropy field (Beach & Berkowitz, 1994; Panina & Mohri, 1994).

It must be underlined that the diameter reduction achieved in the case of glass-coated microwires must be associated with the increasing of the optimal GMI frequency range: a tradeoff between dimension and frequency is required in order to obtain a maximum effect (Ménard et al., 1998). Consequently for Fe and Co-rich glass-coated microwires considerable $\Delta Z/Z_m$ values have been obtained at elevated frequencies (see Figs. 4, 5). Thus for Fe-rich $Fe_{75.5}B_{13}Si_{11}Mo_{0.5}$ microwire with metallic nucleus diameter of about 18 μm (Fig. 4a, b) increase of $\Delta Z/Z_m$ up to 500 MHz has been observed ($\Delta Z/Z_m \approx 45\%$ at f= 500 MHz). General feauture of both Co-rich and Fe-rich microwires is the increasing of the magnetic field of GMI maximum, H_m, with frequency, *f*.

Co-rich microwires generally present higher GMI effect (Fig. 5). For the case of $Fe_{3.7}Co_{69.8}Ni_1Si_{11}B_{13}Mo_{1.5}$ glass-coated microwire (d≈19 μm) optimum $\Delta Z/Z_m$≈140% achieved at about 300 MHz (Fig. 5b), while Hm incrases with f (Fig. 5c).

Recenly observation of quite high GMI effect at GHz frequencies is reported elsewhere (Zhukov et al., 2014). It is worth mentioning that the magnetic fields corresponding to the impedance maximum, H_m, at GHz frequencies are much higher than the magnetic anisotropy field. At elevated frequencies the magnetic field of *Z* maximum, H_m, (1-10 kA/m) while the magnetic anisotropy field, H_k, observed in quasi-static hysteresis loops are about 0.1 kA/m., i.e. all the studied samples are magnetically saturated when exhibit an impedance maximum at GHz frequency range (Zhukov et al., 2014).

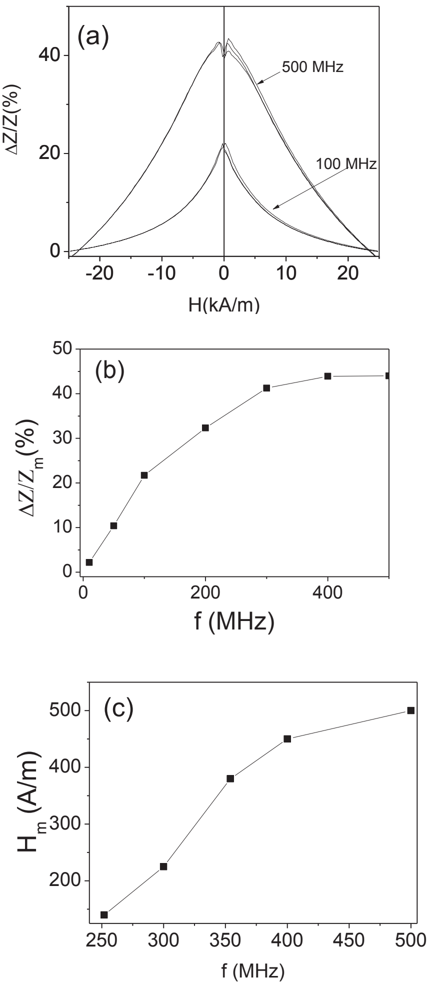

Fig. 4. GMI effect measured in $Fe_{75.5}B_{13}Si_{11}Mo_{0.5}$ glass-coated microwire (d≈18 μm) at different frequencies of AC current (a), dependence of *ΔZ/Zm (b)* and H_m (c) on f.

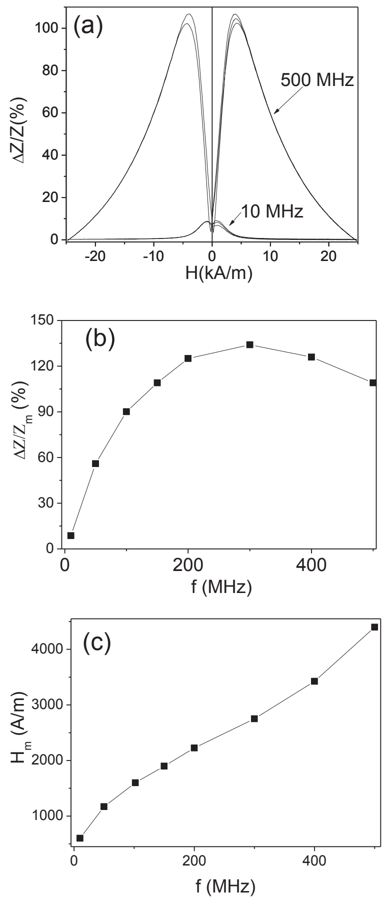

Fig. 5. GMI effect measured in $Fe_{3.7}Co_{69.8}Ni_1Si_{11}B_{13}Mo_{1.5}$ glass-coated microwire (d≈19 μm) at different frequencies of AC current (a), dependence of *ΔZ/Zm (b)* and H_m (c) on f.

Usually the magnetic field of maximum is attributed to the magnetic anisotropy field (Beach & Berkowitz, 1994; Panina & Mohri, 1994). This considerable growth of H_m with increasing of the frequency can be explained considering decreasing of the skin depth with increasing of the frequency. Consequently magnetic anisotropy of the surface area can be rather different from the bulk magnetic anisotropy. Indeed recently we reported on the formation of the interface layer between the metallic nucleus and glass-coating (Zhukov et al., 2014). This interfacial layer can have different from the bulk magnetic anisotropy.

2.3. Effect of annealing on magnetic properties and GMI effect of glass-coated microwires

Before annealing studied samples present inclined hysteresis loop with low coercivity typical for Co-rich microwires with low and negative magnetostriction coefficient (Figs 1b, 2b, 6). As we observed, annealing even for quite short time and at low temperature leads to significant changing of the magnetic properties (Figs 6b-d).

In spite of considerable magnetic hardening (increasing of coercivity from 4 to 200 A/m), both as-prepared and annealed microwires present considerable GMI effect as shown in Fig 7. The main difference of observed ΔZ/Z (H) dependences for as-prepared and annealed samples is the value of the magnetic field, H_m, at which ΔZ/Z maximum takes place: for annealed samples H_m –values are much lower than for as-prepared samples for all measured frequences.

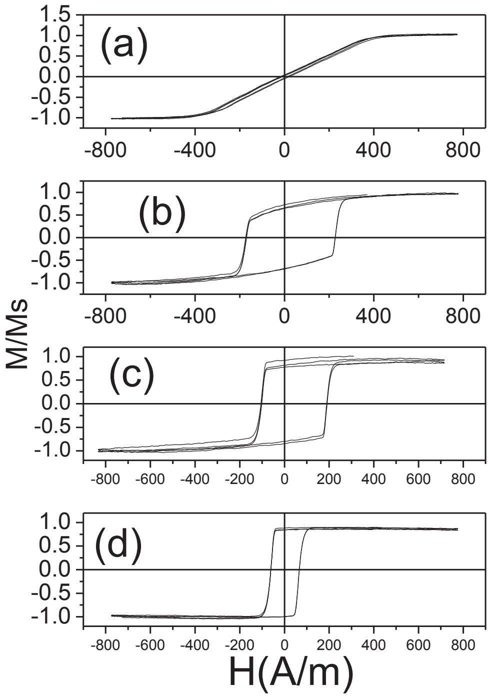

Fig. 6. Hysteresis loops of as-prepared (a) and annealed for 5 min at 200 ºC (b), 250 ºC (c), and 300 ºC (d) $Fe_{8,13}Co_{50,69}Ni_{17,55}B_{13,29}Si_{10,34}$ microwires.

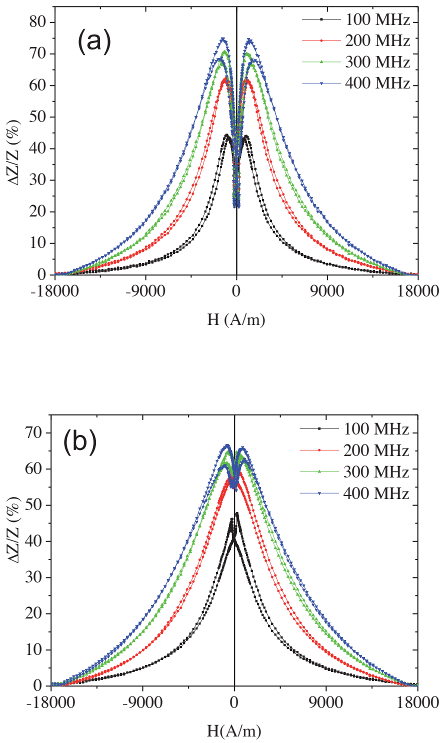

Fig. 7. ΔZ/Z (H) dependences of as-prepared (a) and annealed at 200 °C for 5 min (b) $Fe_{8,13}Co_{50,69}Ni_{17,55}B_{13,29}Si_{10,34}$ microwires measured at different frequencies.

For an interpretation of the unusual magnetic hardening observed after annealing (Fig. 6) we must consider not only the stress relaxation (that usually results in coercivity decreasing) but also the change of the character of the remagnetization process induced by the heat treatment. The observed tendency allow us to assume that annealing induces an axial magnetic anisotropy, which is confirmed by the perfectly rectangular hysteresis loops exhibited by the annealed microwire and that are typical for microwires with a positive magnetostriction constant presenting an axial easy magnetization axis. To explain this unusual dependence of the magnetic properties upon the annealing temperature, we must consider that the stress relaxation affects the magnetostriction coefficient, as also recently described for other Co-rich microwires (Barandiaran et al., 1987):

$$\lambda_{S,\sigma} = \lambda_{S,0} - B\sigma \quad (5)$$

where $\lambda_{S,\sigma}$ is the magnetostriction coefficient under stress, $\lambda_{S,0}$ is the zero-stress the magnetostriction coefficient and B is a positive coefficient of order 10^{-10} MPa. This stress dependence of the magnetostriction coefficient is expected to be relevant for nearly zero magnetostriction microwires compositions, i.e. for Co-rich microwires. Similarly to recently observed changes induced by annealing we can assume that the stress relaxation induced by annealing can change the sign of the magnetostriction constant. Indeed reported internal stresses values inside the metallic nucleus are between 200 MPa and 5 GPa (Velázquez et al., 1996; Chiriac et al., 2003). Experimentally measured B - coefficient values of expression (5) reported for similar $(Co_{0.94}Fe_{0.06})_{75}Si_{15}B_{10}$ amorphous alloy are about 1.8 10-10 MPa^{-1}(Barandiaran et al.,1987). Moreover recently we confirmed this assumption by direct measurements of the magnetostriction coefficient in as-prepared and annealed Co-rich microwires (Zhukov et al., 2015).

We can also assume that the outer domain shell of the annealed Co-rich microwire that exhibits both rectangular hysteresis loop and a GMI effect has high circumferential magnetic permeability. This assumption is deduced by observing the much higher GMI ratio of Co-rich microwires that exhibit a rectangular hysteresis loop after annealing than that of the Fe-rich amorphous microwires also exhibiting similar bulk hysteresis loop characteristics but much lower GMI effect (usually about 1-5%).

2.4. Effect of nanocrystallization on soft magnetic propertiesand GMI effect of glass-coated microwires

As mentioned above amorphous materials usually present excellent soft magnetic properties. On the other hand, it is well known that, the so-called “nanocrystalline materials”, that is, two-phase systems consisting of nanocrystalline grains randomly distributed in a soft magnetic amorphous matrix attracted great attention mostly owing to their soft magnetic behavior and higher saturation magnetization (Yoshizawa & Yamauchi, 1990; Herzer, 2005). After the first crystallization process, such material consists of small (around 10-20 nm grain size) nanocrystallites embedded in the residual amorphous matrix. In addition, the devitrification process of these amorphous alloys (with trademark FINEMET) leads to the possibility of obtaining rather different microstructures depending on the annealing parameters as well as on the chemical composition. These features are the basis for the excellent soft magnetic properties indicated by high values of permeability about ($1x10^5$) and correspondingly, low coercivity. Such soft magnetic character is supposed to be originated because the magnetocrystalline anisotropy vanishes and a very small magnetostriction value arises when the grain size approaches 10 nm (Yoshizawa & Yamauchi, 1990; Herzer, 2005).

Vanishing effective magnetocrystalline anisotropy is explained due the size of crystals below the exchange length which is around 35 nm for pure iron (Yoshizawa & Yamauchi, 1990; Herzer, 2005). In such a case, the magnetocrystalline anisotropy of single grains is averaged out and the material behaves like a soft magnet. Also the average magnetostriction constant takes nearly- zero values (Yoshizawa & Yamauchi, 1990; Herzer, 2005), thanks to the control of a crystalline volume fraction:

$$\lambda_{s,eff} = V_{cr}\,\lambda_{s,cr} + (1 - V_{cr})\,\lambda_{s,am} \qquad (6)$$

Consequently enhancement of the GMI effect is reported after nanocrystallization of amorphous precursor (Guo et al., 2001).

Nanocrystalline materials have been introduced by Yoshizawa et al. (1988) and later have been intensively studied by a number of research groups (Herzer, 2001; McHenry et al., 1999; Yoshizawa & Yamauchi, 1990; Herzer, 2005; Dudek et al., 2007; Arcas et al., 1996; Guo et al., 2001).

Recently considerable magnetic softening and great enhancement of GMI effect has been observed after devitrification of Finmet-type glass-coated microwires (Talaat et al., 2014; Zhukov et al., 2014).

Usually, the basic method to obtain a nanocrystalline structure from the amorphous state is achieving the crystallization of amorphous matrix by an appropriate heat treatment. The evolution of structural and magnetic properties has been studied for each sample at different annealing temperature in the range between 400-650 °C for 1 hour (Fig. 8).

Starting from 550 °C to 650 °C a main crystalline peak is appearing in the range between 42 °C to 45 °C which correspond to the existence of α-Fe (Si) BCC crystal structure, as well as another two weak peaks appearing in the range between 65 °C to 85 °C (Fig. 8).

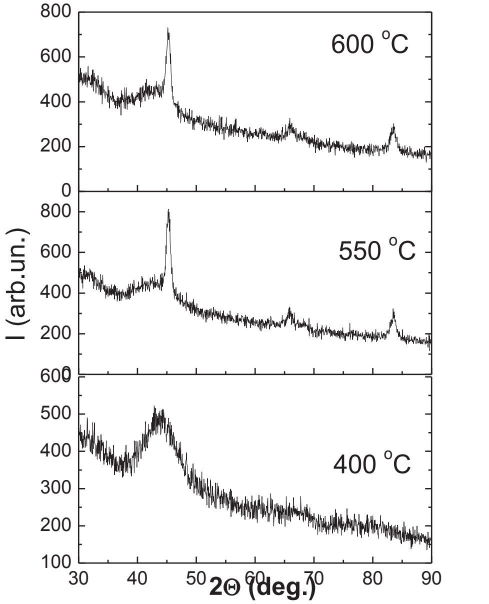

Fig. 8 XRD patterns of annealed microwires $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ with ρ = 0.81, Annealing temperatures are indicated within each pattern.

It is worth mentioning, that the coercivity decreases upon increasing the annealing temperature, while the rectangular character of hysteresis loops is observed for T_{ann} < 600 °C.

In Fig. 9 the hysteresis loops of as-prepared and annealed $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ microwires and coercivity dependence on annealing temperature for $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ glass-coated microwire with different ρ – ratio is presented.

According to these data, a tendency towards decreasing H_c values is observed at the range of 500-550 °C. Similar behavior associated with devitrification and magnetic softening has been previously reported in other Finemet-type microwires (Arcas et al., 1996).

Consequently magnetic softening with lowest value of coercivity and switching field is obtained in the samples treated at 500–600 °C which could be ascribed to the fact that the first crystallization process has been developed, leading to fine α-Fe (Si) nanocrystals with grain size around 10-20 nm (compare Figs. 8, 9). This behavior is similar to that one widely reported for FINEMET ribbons (Yoshizawa & Yamauchi, 1990; Herzer, 2005).

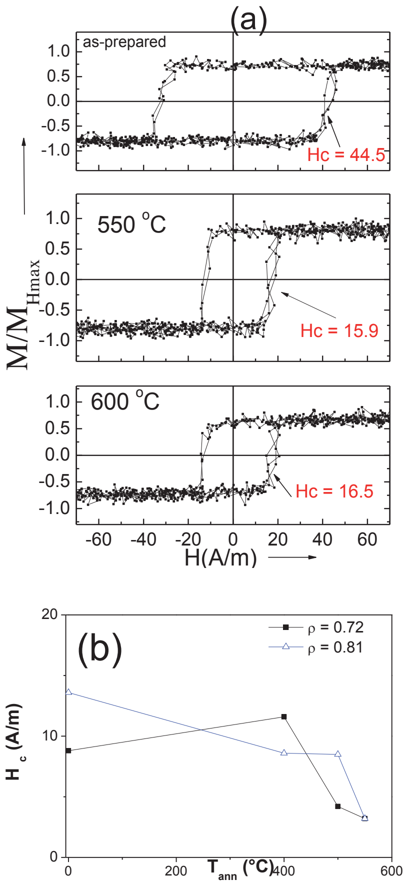

Fig. 9. Hysteresis loops of as-prepared and annealed $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ microwires, with ρ=0.81, at different temperatures measured at fixed magnetic field amplitude of 225 A/m (a) and dependence of the coercivity, H_c, for the $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ glass-coated microwire with selected ρ-ratio on annealing temperature (b).

Consequently, as-prepared microwires with amorphous structure exhibit a rather small GMI effect (below 5% see Fig. 10) similar to other Fe- based glass-coated microwires with positive magnetostriction. In contrast, nanocrystalline $Fe_{70.8}Cu_1Nb_{3.1}Si_{16}B_{9.1}$ microwires annealed at 550 °C exhibit higher GMI effect ($\Delta Z/Z \approx 90\%$, see Fig. 10).

Observed double peak *ΔZ/Z(H)* in nanocrystalline microwire is typical for the samples with low negative magnetostriction constant. Therefore, we can assume that annealing results in formation of double-phase structure with vanishing magnetostriction constant.

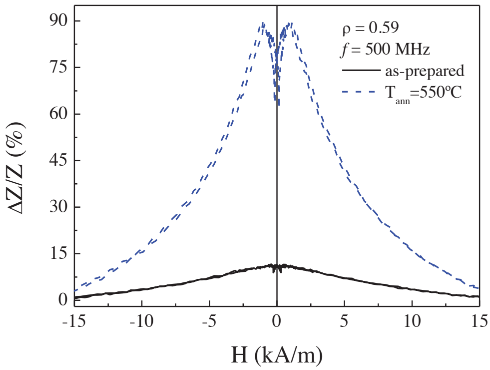

Fig.10. Effect of annealing at 550°C for 1 hour on ΔZ/Z (H) dependence of $Fe_{70.8}Cu_1Nb_{3.1}Si_{16}B_{9.1}$ microwire with ρ = 0.59 measured at 500 MHz in comparison with the GMI response of the as-prepared sample.

As discussed elsewhere, after the nanocrystallization the average magnetostriction constant takes nearly-zero values (Yoshizawa & Yamauchi, 1990; Herzer, 2005, Talaat et al., 2014; Zhukov et al., 2014), thanks to the control of the crystalline volume fraction (see eq. (16)) As discussed elsewhere GMI effect is affected by the magnetic anisotropy (Beach & Berkowitz, 1994; Panina & Mohri, 1994; Usov et al., 1998). Consequently, the shape of ΔZ/Z (H) dependence and maximum GMI ratio $\Delta Z/Z_{max}$ are considerably affected by annealing (Usov et al., 1998) and considerable increase of $\Delta Z/Z_m$ is observed after the devitrification of Finemet-type glass-coated microwires.

3. Conclusions

We overviewed of the factors affecting soft magnetic properties and giant magnetoimpedance (GMI) effect in thin amorphous wires paying attention on the possibility to tailor the magnetic properties of amorphous ferromagnetic microwires Low coercivity and high Gaint magnetoimpedance (GMI) effect have been observed in as-prepared Co-rich microwires. We showed that the magnetoelastic anisotropy is one of the most important parameters that determine magnetic softness and GMI effect of glass-coated microwires and annealing can be very effective for manipulation the magnetic properties of amorphous ferromagnetic glass-coated microwires.

We demonstrated that annealing conditions drastically affect the magnetic properties. The annealing of amorphous Co-rich microwire considerably affects its hysteresis loop, GMI effect and allows the simultaneous observation of a GMI effect and magnetic bistability in the microwire. We demonstrated that the coercivity value of microwires can be tailored by annealing in the range from 4 to 200 A/m. The observed dependences of these characteristics are attributed to stress relaxation and changes in the magnetostriction after sample annealing.

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