



(11)

EP 2 148 338 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:

08.03.2017 Bulletin 2017/10

(21) Application number: **06807882.3**

(22) Date of filing: **25.08.2006**

(51) Int Cl.:

H01F 1/153 ^(2006.01)

(86) International application number:

PCT/ES2006/000434

(87) International publication number:

WO 2008/023079 (28.02.2008 Gazette 2008/09)

(54) **ULTRA-THIN GLASS-COATED AMORPHOUS WIRES WITH GMI EFFECT AT ELEVATED FREQUENCIES**

ULTRADÜNNNE GLASBESCHICHTETE AMORPHE DRÄHTE MIT GMI-EFFEKT
(RIESEN-MAGNET-IMPEDANZ) BEI HOHEN FREQUENZEN

FILS AMORPHES ULTRAFINS RECOUVERTS D'UN REVÊTEMENT VITREUX PRÉSENTANT UN
EFFET DE MAGNÉTO-IMPÉDANCE GÉANTE (GMI) À DES FRÉQUENCES ÉLEVÉES

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR**

(43) Date of publication of application:
27.01.2010 Bulletin 2010/04

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Description

[0001] - The invention consists of the fabrication of thin (metallic nucleus diameter below 10 μm) microwires with determined chemical composition containing Co, Fe, Si, B, C with additions of Ni, Mo, Cr, Zr, Hf with determined relation between metallic nucleus diameter and glass coating thickness.

The subject of the patent

[0002] - The present patent, as expressed in its title of the present description, consists of a method of fabrication of thin (metallic nucleus diameter below 20 μm) microwires with determined chemical composition containing Co, Fe, Si, B, C with additions of Ni, Mo, Cr, Zr, Hf, C with determined relation between metallic nucleus diameter and glass coating thickness.

Background of the invention

[0003] The scientific aspects forming a base of the invention can be found in the following scientific issues:

[1] L.V. Panina and K. Mohri, Appl. Phys. Lett. 65 (1994) 1189.

[2] V. Zhukova, A. Chizhik, A. Zhukov, A. Torcunov, V. Larin and J. Gonzalez, IEEE Trans. Magn. 38, 5, part1, (2002) 3090.

[3] Spanish patent "Amorphous glass-coated microwires as an element of magnetic sensors based on the magnetic bistability, magneto-impedance and as material for the protection from the radiation." (Ref. P200202248)

[4] V. S. Larin, A. V. Torcunov, A. Zhukov, J. González, M. Vazquez, L. Panina "Preparation and properties of glass-coated microwires" J. Magn. Magn. Mater. 249/1-2 (2002) 39-45

[0004] The present patent is closely related with previous Spanish patent "Amorphous glass-coated microwires as an element of magnetic sensors based on the magnetic bistability, magneto-impedance and as material for the protection from the radiation." (Ref. P200202248) [3], but paying special attention to the GMI effect (absolute value and tensor components) in thin wires (with diameter of metallic nucleus below 20 μm).

[0005] Microwires are manufactured by means of a modified Taylor-Ulitovsky process [3,4] based on direct casting from the melt, as schematically depicted in Fig. 1. In the laboratory process, a few grams of the master alloy with the desired composition is put into a Pyrex-like glass tube and placed within a high frequency inductor heater. The alloy is heated up to its melting point, forming a droplet. While the metal melts, the portion of the glass tube adjacent to the melting metal softens, enveloping the metal droplet. A glass capillary is then drawn from the softened glass portion and wound on a rotating coil. At suitable drawing conditions, the molten metal fills the glass capillary and a microwire is thus formed where the metal core is completely coated by a glass shell. The amount of glass used in the process is balanced by the continuous feeding of the glass tube through the inductor zone, whereas the formation of the metallic core is restricted by the initial quantity of the master alloy droplet. The microstructure of a microwire (and hence, its properties) depends mainly on the cooling rate, which can be controlled by a cooling mechanism when the metal-filled capillary enters into a stream of cooling liquid (water or oil) on its way to the receiving coil.

[0006] The main advantages of this method of microwire fabrication are:

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

[0007] The giant magneto-impedance, GMI, attracted great attention for the sensor applications owing to the large sensitivity (up to 600%) of the electrical impedance to the DC magnetic field of soft magnetic conductor [1]. The recent tendency in miniaturization of the magnetic sensors requires the development of extremely thin composite wires produced by the Taylor-Ulitovsky method (1 ÷ 30 μm in diameter) consisting of metallic nucleus coated by glass. Recent significant progress in tailoring of magnetically soft Co-rich glass coated microwires with metallic nucleus diameter of about 20 μm fabricated by this method enabled to enhance significantly the GMI ratio (up to about 600%) [2].

The AC current frequency should be high enough (usually above 100 kHz) in order to observe significant change of the electrical impedance. On the other hand special care is needed in order to study GMI effect at frequencies above 10 MHz. Particularly, the sample holder should have special design and the electrical cables should be as shorter as possible

and should possess special HF specifications.

As has been mentioned, initially the GMI effect was interpreted in terms of the classical skin effect in a magnetic conductor assuming scalar character for the magnetic permeability, as a consequence of the change in the penetration depth of the *ac* current caused by the *dc* applied magnetic field. The electrical impedance, *Z*, of a magnetic conductor in this case is given by [1,5,6]:

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

with $k = (1+j)/\delta$, where J_0 and J_1 are the Bessel functions, *r* -wire's radius and δ the penetration depth given by:

$$\delta = (\pi \sigma \mu \phi f)^{-1/2} \quad (2)$$

where σ is the electrical conductivity, *f* the frequency of the current along the sample, and $\mu\phi$ the circular magnetic permeability assumed to be scalar. The *dc* applied magnetic field introduces significant changes in the circular permeability, $\mu\phi$. Therefore, the penetration depth also changes through and finally results in a change of *Z* [1, 5,6].

[0008] From aforementioned on the GMI effect for optimization of the GMI effect the materials must present high magnetic permeability, $\mu\phi$.

[0009] In the absence of the magnetocrystalline anisotropy (that is the case of amorphous materials) the magnetoelastic anisotropy plays the most important role and must be minimized.

The magnetoelastic anisotropy is essentially determined by the magnetostriction coefficient, λ_s and internal stresses, σ_i :

$$K_{me} \approx 3/2 \lambda_s \sigma_i, \quad (3)$$

The magnetostriction constant depends mostly on the chemical composition and is vanishing in amorphous Fe-Co based alloys with the content of Co/Fe $\approx 70/5$ [2].

Recently this "scalar" model was significantly modified taking into account the tensor origin of the magnetic permeability and magneto impedance [7,8]. For instance, it was theoretically shown in [7], that the axial dependence of the GMI spectra is mainly determined by the type of magnetic anisotropy. It was shown particularly, that the circumferential anisotropy leads to the observation of the maximum of the real component of wire impedance (and consequently of the GMI ratio) as a function of the external magnetic field. In contrast, in the case of axial magnetic anisotropy the maximum value of the GMI ratio corresponds at zero magnetic field [8], i.e. results in a monotonic decay of the GMI ratio with the axial magnetic field. Consequently, non-diagonal components of the magnetic permeability tensor and impedance tensor were introduced in [6,7] in order to describe such circumferential anisotropy. In order to achieve highest GMI effect the magnetic anisotropy should be as smaller as possible.

The aim of this patent is to introduce a novel family of thin wires exhibiting high GMI effect including non-diagonal components at high enough frequencies (above 10 MHz).

References:

[0010]

[1] L.V. Panina and K. Mohri, Appl. Phys. Lett. 65 (1994) 1189.

[2] V. Zhukova, A. Chizhik, A. Zhukov, A. Torcunov, V. Larin and J. Gonzalez, IEEE Trans. Magn. 38, 5, partI, (2002) 3090.

[3] Spanish patent "Amorphous glass-coated microwires as an element of magnetic sensors based on the magnetic bistability, magneto-impedance and as material for the protection from the radiation." (Ref. P200202248)

[4] V. S. Larin, A. V. Torcunov, A. Zhukov, J. González, M. Vazquez, L. Panina "Preparation and properties of glass-coated microwires" J. Magn. Magn. Mater. 249/1-2 (2002) 39-45

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General description of the invention

[0011] In this patent deals with the method of fabrication of thin glass-coated microwires with elevated GMI effect at frequencies between 10 MHz and 500 MHz.

[0012] At 10 MHz the GMI of thin microwires is smaller than in thicker conventional wires, but increasing the frequency GMI effect significantly increases, exhibiting much higher GMI effect at high frequencies and the shape of the $Z(H)$ dependence at least for Co-rich materials is typical for the materials with circular magnetic anisotropy, i.e. with the a maximum at certain dc axial magnetic field (Fig. 2,3).

Besides, the glass-coating technology gives rise to the internal stresses due to the difference in the thermal expansion coefficients of the glass coating and metallic nucleus. This difference in the fabrication technique results in the different magnetic anisotropy in the surface and in different frequency dependence of the GMI effect.

[0013] The present patent deals with a method of a method of fabrication of thin (metallic nucleus diameter below 20 μm) microwires with determined chemical composition containing Co, Fe, Si, B, C with additions of Ni, Mo, Cr, Zr, Hf with determined relation between metallic nucleus diameter and glass coating thickness.

[0014] The GMI effect is related intrinsically with the hysteresis loops of the samples. In fact the hysteresis loops depend on many factors, such as the metallic nucleus composition which is closely related with the magnetostriction constant, the geometrical parameters (diameter of the metallic nucleus, total diameter of microwires). Effect of the metallic nucleus composition on hysteresis loops of microwires is reflected in Figs.4. On the other hand Fig. 5 shows the effect of the metallic nucleus diameter on hysteresis loop of the microwire with the same composition. As can be observed, the magnetic softness deteriorates when the metallic nucleus diameter becomes thinner. On the other hand best magnet softness (combination of high magnetic permeability with low coercivity) is observed in Co-rich composition with nearly-zero magnetostriction constant (Fig.4). GMI effect is also higher in Co-Fe-rich samples with nearly-zero magnetostrictive compositions. (Fig.3). Therefore further we concentrate on thin microwires with nearly-zero magnetostrictive compositions.

[0015] Axial hysteresis loops of studied $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$ microwire with metallic diameter of 8.5 μm is presented in Fig.6. As can be noted from Fig.6, excellent magnetic softness with coercivity of the order of 4 A/m has been achieved in this microwire in spite of its reduced diameter (only 8.5 μm).

[0016] The GMI effect of as-prepared $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$ measured at frequencies, f , up to 500 MHz is shown in Fig.7. As can be observed, considerable GMI ratio is achieved at higher frequencies, although at conventional frequency $f = 10$ MHz, the GMI ratio is about 60%. The shape of the DC magnetic field dependence of the GMI ratio is typical for the samples with small and negative magnetostriction constant with circular magnetic anisotropy, i.e. with a maximum at certain DC axial magnetic field, H_m . A maximum value of the GMI ratio, $\Delta Z/Z_{\text{max}}$, achieves about 180% at about 200 MHz. Frequency dependence of the $\Delta Z/Z_{\text{max}}$ is shown in Fig.8.

[0017] As it was shown, imaginary part of the impedance is quite useful for the use in magnetic sensors. Fig.9 shows the imaginary part the impedance, X , measured at different frequencies.

[0018] It is worth underlining high enough GMI effect in such thin microwires.

[0019] Fig.10 shows, that heat treatment conditions (annealing temperature in this concrete sample) play an important role for tailoring of the GMI effect in glass coated wires. In this particular case stress annealing for 40 min at different temperatures (as indicated in Fig.12: 1- 265°C; 2- 275°C and 3- 400°C) strongly affects the GMI ratio of $\text{Fe}_{74}\text{B}_{13}\text{Si}_{11}\text{C}_2$ microwire, measured at the same conditions (11 MHz).

[0020] Finally, even for the same composition, the GMI ratio depends on the samples geometry, as shown in Fig.11 for $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$. Samples with metallic nucleus diameter from 8.96 till 9.89 μm and total diameter from 10.29 till 11.94 μm are studied. Samples geometry affects not only GMI ratio but also imaginary part the impedance, X , measured at the same frequency (300 MHz) through the effect of the internal stresses on the magnetic anisotropy. Such dependences for the same samples as in Fig.11 are shown in Fig.12.

[0021] The steps of the realisation of the invention are:

- Selection of the sample alloy composition for obtaining better GMI properties
- Selection of the sample geometry for concrete application
- Fabrication of amorphous microwires with thin diameter of the metallic nucleus of determined composition.
- Tailoring of the magnetic properties b y means of heat treatment (without magnetic field, without stress or under magnetic field and/or applied stress)

[0022] The advantages of the present invention are:

- high corrosion resistance owing to the insulation coating;
- small size owing to the smaller microwire diameter and therefore smaller demagnetizing factor of short enough samples;
- flexibility of the samples which permits its use in the flexible objects.

Brief description of the figures

[0023] To complete this description and in order to help the understanding of the invention the present description includes figures:

Figure 1.

The schematic picture of the glass-coating microwires fabrication process, where 1- glass tube, 2-molten alloy, 3- glass cone, 4- HF inductor, 5- water jet, 6- solidified glass-coated microwire.

Figure 2.

DC magnetic field dependence of the impedance of $\text{Fe}_{75.5}\text{B}_{13}\text{Si}_{11}\text{Mo}_{0.5}$ (a), $\text{Fe}_{3.7}\text{Co}_{69.8}\text{Ni}_1\text{Si}_{11}\text{B}_{13}\text{Mo}_{1.5}$ (b) and $\text{Co}_{77.5}\text{Si}_{7.5}\text{B}_{15}$ (c) glass-coated amorphous microwires with metallic nucleus diameter of about 15-20 μm

It represents the DC magnetic field dependence of the absolute value of the electrical impedance of glass-coated microwires of 3 different compositions as $\text{Fe}_{75.5}\text{B}_{13}\text{Si}_{11}\text{Mo}_{0.5}$ (a), $\text{Fe}_{3.7}\text{Co}_{69.8}\text{Ni}_1\text{Si}_{11}\text{B}_{13}\text{Mo}_{1.5}$ (b) and $\text{Co}_{77.5}\text{Si}_{7.5}\text{B}_{15}$ (c) measured at 3 different frequencies of AC driving current: 10, 100 and 500 MHz.

Figure 3.

It represents the frequency dependence of the absolute value of the GMI ratio, $\Delta Z/Z_{\text{max}}$ for different glass-coated thin amorphous wires: (a)- $\text{Fe}_{76}\text{Si}_{11}\text{B}_{13}$; (b)- $\text{Co}_{77.5}\text{Si}_{7.5}\text{B}_{15}$ and (c)- $\text{Co}_{68.5}\text{Fe}_{3.5}\text{Cr}_3\text{Si}_{11}\text{B}_{14}$ compositions.

Figure 4.

It represents the axial hysteresis loops of $\text{Fe}_{75.5}\text{B}_{13}\text{Si}_{11}\text{Mo}_{0.5}$, $\text{Co}_{77.5}\text{Si}_{7.5}\text{B}_{15}$ and $\text{Fe}_{3.7}\text{Co}_{69.8}\text{Ni}_1\text{Si}_{11}\text{B}_{13}\text{Mo}_{1.5}$ glass-coated microwires respectively with different magnetostriction constant.

Figure 5.

It represents the hysteresis loops of FeBSiC microwires with metallic nucleus Diameter of 15 μm (a), 13.5 μm (b); 11 μm (c); 6 μm (d) and 4 μm (e).

Figure 6.

It represents the axial hysteresis loop of $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$ microwire with diameter of 8.5 μm .

Figure 7.

It represents the GMI ratio of as-prepared $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$ with diameter of 8.5 μm measured at frequencies up to 500 MHz.

Figure 8.

It represents the frequency dependence of the $\Delta Z/Z_{\text{max}}$ of as-prepared $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$ with diameter of 8.5 μm measured at frequencies up to 500 MHz.

Figure 9.

It represents the imaginary part the impedance, X, of as-prepared $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$ with diameter of 8.5 μm measured at frequencies up to 500 MHz measured at different frequencies.

Figure 10.

Represents GMI effect of stress annealed of $\text{Fe}_{74}\text{B}_{13}\text{Si}_{11}\text{C}_2$ glass-coated microwire subjected to stress annealing for 40 min at different temperatures: 1- 265°C, 2- 275°C and 3- 400°C

Figure 11

It represents the GMI ratio of $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$ microwires with metallic nucleus, d, and total diameter, D as 1- d=8,96 μm , D=10.29 μm ; 2- d=9,17 μm , D=11.94 μm ; 3- d=9,64 μm , D=10.66 μm ; 4- d=9,78 μm , D=11,74 μm

Figure 12.

It represents the imaginary part the impedance, X, of as-prepared $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$ with metallic nucleus, d, and total diameter, D as: 1- d=8,96 μm , D=10.29 μm ; 2- d=9,17 μm , D=11.94 μm ; 3- d=9,64 μm , D=10.66 μm ; 4- d=9,78 μm , D=11,74 μm

Mode of the realization of the invention

Example 1.

- 5 **[0024]** The values of the GMI ratio, $\Delta Z/Z_{\max}$ and the hysteresis loop depend on the microwires dimensions: metallic nucleus diameters and thickness of glass coating, as presented in Fig.5 and Fig.11.

Example 2.

- 10 **[0025]** The values of the GMI ratio, $\Delta Z/Z_{\max}$ and the hysteresis loop depend on the microwires composition, such as presented in Figs.2-4

Example 3

- 15 **[0026]** The values of the GMI tensor components and its imaginary part depend on the microwires composition, such as presented in Figs.2, 7

Example 4

- 20 **[0027]** The values of the GMI tensor components and its imaginary part depend on the microwires geometry, such as presented in Fig.11, 12

Example 5.

- 25 **[0028]** The absolute value of the GMI ratio of stress annealed of $\text{Fe}_{74}\text{B}_{13}\text{Si}_{11}\text{C}_2$ glass-coated microwire subjected to stress annealing for 40 min depends on annealing temperature (between 265°C and 400°C), such as presented in Fig. 10.

Claims

- 30 **1.** The method of fabrication of glass-coated microwires with enhanced GMI effect at frequencies above 10 MHz wherein the microwires are manufactured by means of a modified Taylor-Ulitovsky process based on direct casting from the melt:
- 35 a few grams of the master alloy with the desired composition is put into a Pyrex-like glass tube and placed within a high frequency inductor heater. The alloy is heated up to its melting point, forming a droplet. While the metal melts, the portion of the glass tube adjacent to the melting metal softens, enveloping the metal droplet. A glass capillary is then drawn from the softened glass portion and wound on a rotating coil. The enhanced GMI effect is achieved in thin (metallic nucleus diameter below 20 μm) microwires with determined chemical composition containing Co, Fe, Si, B, with additions of Ni, Mo, Cr, Zr, Hf, C with determined relation between metallic nucleus diameter and glass coating thickness. The composition of the glass-coated microwires exhibiting the GMI effect is based on transition metal (between 65-85 at%) with metalloid additions between 15-35%. The total microwire diameter (D) is related with the metallic nucleus diameter (d) within the following limits: $0.2 < d/D_{\text{tot}} < 0.95$.
- 40 **2.** The method of fabrication of glass-coated microwires as claimed in claim 1 wherein obtained microwire possess enhanced non-diagonal components of the GMI effect at frequencies above 10 MHz.
- 45 **3.** The method of fabrication of glass-coated microwires as claimed in claim 1 wherein obtained microwire possess enhanced real and imaginary components of the GMI effect at frequencies above 10 MHz
- 50 **4.** The method of fabrication of glass-coated microwires as claimed in claim 1 wherein obtained microwire with reduced diameter with enhanced absolute value of the GMI ratio at frequencies above 10 MHz
- 55 **5.** The method of fabrication of glass-coated microwires as claimed in claim 1 wherein both hysteresis loops and GMI effect at frequencies above 10 MHz depend on microwires geometry.
6. The method of fabrication of glass-coated microwires as claimed in claim 1 wherein both hysteresis loops and GMI

effect at frequencies above 10 MHz depend on metallic nucleus composition of glass-coated microwires.

7. The method of fabrication of glass-coated microwires as claimed in claim 1 wherein both hysteresis loops and GMI effect at frequencies above 10 MHz depend on heat treatment conditions, such as temperature of heat treatment, application of magnetic field and/or stress during heat treatment of glass-coated microwires.

8. The method of fabrication of glass-coated microwires as claimed in claim 1 wherein the composition of the glass-coated microwires exhibiting the GMI effect is:

Mandatory elements are

Fe : $0 < \%Fe \leq 85.0$ at%

B: 5.0-20.0 at%

Si: 5.0-15.0 at%

Co : $0 < \%Co \leq 85.0$ at%

Optional elements are

C: 0-15.0 at%

Ni: 0-60 at%

Mn : 0-7.5 at%

Cr: 0-20 at%

Mo: 0-10 at%

9. The method of fabrication of glass-coated microwires as claimed in claim 1 wherein the metallic nucleus diameter is within 0.6 and 20 μm and the glass coating thickness is within 0.1- 20 μm .

Patentansprüche

1. Das Verfahren zur Herstellung von glasbeschichteten Mikrodrähten mit verbessertem GMI-Effekt (Riesen-Magneto-Impedanz-Effekt) bei Frequenzen über 10 MHz. Mikrodrähte werden durch ein modifiziertes Taylor- Ulitovsky-Verfahren auf Basis des Direktgusses aus der Schmelze hergestellt. Im Laborverfahren werden einige Gramm der Vorlegierung mit der gewünschten Zusammensetzung in ein Pyrex-Glasrohr gegeben und in eine Hochfrequenz-Induktionsheizung gelegt. Die Legierung wird bis zu ihrem Schmelzpunkt erhitzt, wobei ein Tröpfchen gebildet wird. Während das Metall schmilzt, erweicht der an das schmelzflüssiges Metall angrenzende Teil des Glasrohres, der das Metalltröpfchen umhüllt. Eine Glaskapillare wird dann aus dem erweichten Glasteil gezogen und auf eine rotierende Bobine gewickelt. Der verbesserte GMI-Effekt wird in dünnen (Metallkerndurchmesser unter 20 μm) Mikrodrähten mit einer bestimmten chemischen Zusammensetzung, die Co, Fe, Si, B enthält, unter Zugabe von Ni, Mo, Cr, Zr, Hf, C mit einer bestimmten Beziehung zwischen Metallkerndurchmesser und Glasbeschichtungsdicke, erreicht. Die Zusammensetzung der glasbeschichteten Mikrodrähte, die den GMI-Effekt aufweisen, wird auf Übergangsmetall (zwischen 65-85%) mit Metalloidzugabe zwischen 15-35% basiert. Der gesamte Durchmesser des Mikrodrahtes (D) hängt mit dem Metallkerndurchmesser (d) innerhalb folgender Grenzen zusammen: $0.2 < d / D_{\text{tot}} < 0.95$. Die metallische Kernzusammensetzung und die Geometrie (Metallkerndurchmesser, d, Glasbeschichtungsdicke, T und ihre Beziehung) bestimmen sowohl die magnetischen Eigenschaften als auch den GMI-Effekt (Absolutwert, Tensorkomponenten, Magnetfeldabhängigkeit von GMI).

2. Das Verfahren zur Herstellung von glasbeschichteten Mikrodrähten nach Anspruch 1, wobei der erhaltene Mikrodraht verbesserte nicht-diagonale Komponenten des GMI-Effekts bei Frequenzen über 10 MHz besitzt.

3. Das Verfahren zur Herstellung von glasbeschichteten Mikrodrähten nach Anspruch 1, wobei der erhaltene Mikrodraht verbesserte Real-und Imaginärkomponenten des GMI-Effekts bei Frequenzen über 10 MHz besitzt.

4. Das Verfahren zur Herstellung von glasbeschichteten Mikrodrähten nach Anspruch 1, wobei der Mikrodraht mit reduziertem Durchmesser und mit einem erhöhten Absolutwert des GMI-Verhältnisses bei Frequenzen über 10 MHz erhalten wurde.

5. Das Verfahren zur Herstellung von glasbeschichteten Mikrodrähten nach Anspruch 1, wobei sowohl Hysterese-

schleifen als auch GMI-Effekt bei Frequenzen über 10 MHz von der Geometrie des Mikrodrahtes abhängen.

6. Das Verfahren zur Herstellung von glasbeschichteten Mikrodrähten nach Anspruch 1, wobei sowohl Hystereseschleifen als auch GMI-Effekt bei Frequenzen über 10 MHz von der metallischen Kernzusammensetzung der glasbeschichteten Mikrodrähte abhängen.

7. Das Verfahren zur Herstellung von glasbeschichteten Mikrodrähten nach Anspruch 1, wobei sowohl Hystereseschleifen als auch GMI-Effekt bei Frequenzen über 10 MHz von Wärmebehandlungsbedingungen, wie Temperatur der Wärmebehandlung, Anwendung des Magnetfeldes und/oder der Spannung während der Wärmebehandlung von glasbeschichteten Mikrodrähten abhängen.

8. Das Verfahren zur Herstellung von glasbeschichteten Mikrodrähten nach Anspruch 1, wobei die Zusammensetzung der glasbeschichteten Mikrodrähte, die den GMI-Effekt zeigen, ist:

Obligatorische Elemente sind

Fe : $0 < \%Fe \leq 85.0\%$

B: 5.0-20.0 %

Si: 5.0-15.0 %

Co: $0 < \%Co \leq 85.0\%$

Optionale Elemente sind

C: 0-15.0 %

Ni: 0-60 %

Mn: 0-7.5 %

Cr: 0-20 %

Mo: 0-10 %

9. Das Verfahren zur Herstellung von glasbeschichteten Mikrodrähten nach Anspruch 1, wobei der metallische Kerndurchmesser innerhalb von 0.6 und 20 μm liegt und die Glasbeschichtungsstärke innerhalb von 0,1-20 μm liegt.

Revendications

1. Procédé de fabrication de micro-fils revêtus de verre avec effet GMI amélioré à des fréquences supérieures à 10 MHz. Les micro-fils sont fabriqués au moyen d'un procédé modifié Taylor-Ulitovsky basé sur la coulée directe à partir de la masse fondue. Dans le procédé de laboratoire, quelques grammes de l'alliage principal avec la composition souhaitée sont placés dans un tube en verre de type pyrex et placés dans un dispositif de chauffage à inductance haute fréquence. L'alliage est chauffé jusqu'à son point de fusion, formant une gouttelette. Pendant que le métal fond, la partie du tube de verre adjacente au métal de fusion se ramollit, enveloppant la goutte métallique. Un capillaire en verre est alors tiré de la partie de verre ramollie et enroulé sur une bobine tournante. L'effet de GMI amélioré est obtenu dans des micromètres minces (diamètre de noyau métallique inférieur à 20 μm) avec une composition chimique déterminée contenant Co, Fe, Si, B, C avec des additions de Ni, Mo, Cr, Zr, Hf, C avec une relation déterminée entre le diamètre du noyau métallique et l'épaisseur du revêtement de verre. La composition des micro-fils revêtus de verre présentant l'effet GMI est basée sur le métal de transition (entre 65-85% at.) avec des additions de métalloïdes entre 15-35%. Le diamètre total du micro-fil (D) est lié au diamètre du noyau métallique (d) dans les limites suivantes: $0.2 < d / D_{\text{tot}} < 0.95$.

La composition du noyau métallique et la géométrie (diamètre du noyau métallique, d, épaisseur du revêtement de verre, T et leur relation) déterminent à la fois les propriétés magnétiques et l'effet GMI (valeur absolue, composantes tenseurs, dépendance champ magnétique de GMI).

2. Procédé de fabrication de micro-fils revêtus de verre selon la revendication 1, dans lequel les micro-fils obtenus possèdent des composantes non diagonales améliorées de l'effet GMI à des fréquences supérieures à 10 MHz.

3. Procédé de fabrication de micro-fils revêtus de verre selon la revendication 1, dans lequel les micro-fils obtenus possèdent des composantes réelles et imaginaires améliorées de l'effet GMI à des fréquences supérieures à 10 MHz.

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4. Procédé de fabrication de micro-fils revêtus de verre selon la revendication 1, dans lequel le micro-fil obtenu avec un diamètre réduit avec une valeur absolue accrue du rapport GMI à des fréquences supérieures à 10 MHz
5. Le procédé de fabrication de micro-fils revêtus de verre selon la revendication 1, dans lequel les deux boucles d'hystéresse et l'effet GMI à des fréquences supérieures à 10 MHz dépendent de la géométrie des micro-fils.
6. Procédé de fabrication de micro-fils revêtus de verre selon la revendication 1, dans lequel les deux boucles d'hystéresse et l'effet GMI à des fréquences supérieures à 10 MHz dépendent de la composition de noyau métallique de micro-fils revêtus de verre.
7. Procédé de fabrication de micro-fils revêtus de verre selon la revendication 1, dans lequel les deux boucles d'hystéresse et l'effet GMI à des fréquences supérieures à 10 MHz dépendent des conditions de traitement, telles que la température de traitement thermique, l'application de champ magnétique et / ou le stress pendant le traitement thermique des micro-fils revêtus de verre.
8. Procédé de fabrication de micro-fils revêtus de verre selon la revendication 1, dans lequel la composition des micro-fils revêtus de verre présentant l'effet GMI est:

Les éléments obligatoires sont

Fe: $0 < \% \text{ Fe} < 85.0$ à %
B: 5.0-20.0 à %
Spi: 5.0-15.0 à %
Co: $0 < \% \text{ Co} \leq 85.0$ à %

Les éléments facultatifs sont

C: 0-15.0 à %
Ni: 0-60 at %
Mn: 0-7.5 à %
Cr: 0-20 à %
Mo: 0-10 à %

9. Procédé de fabrication de micro-fils revêtus de verre selon la revendication 1, dans lequel le diamètre du noyau métallique est compris entre 0.6 et 20 μm et l'épaisseur du revêtement de verre est comprise entre 0.1 et 20 μm .

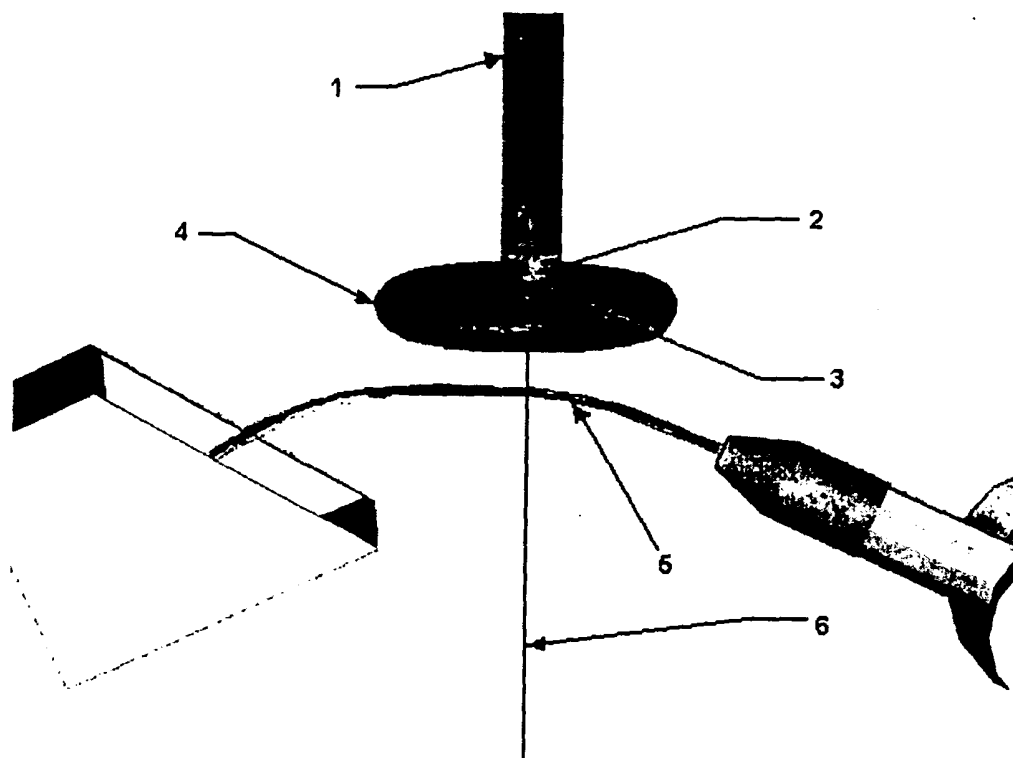


Fig.1. The schematic picture of the glass-coating microwires fabrication process, where 1- glass tube, 2-molten alloy, 3- glass cone, 4- HF inductor, 5- water jet, 6- solidified glass-coated microwire.

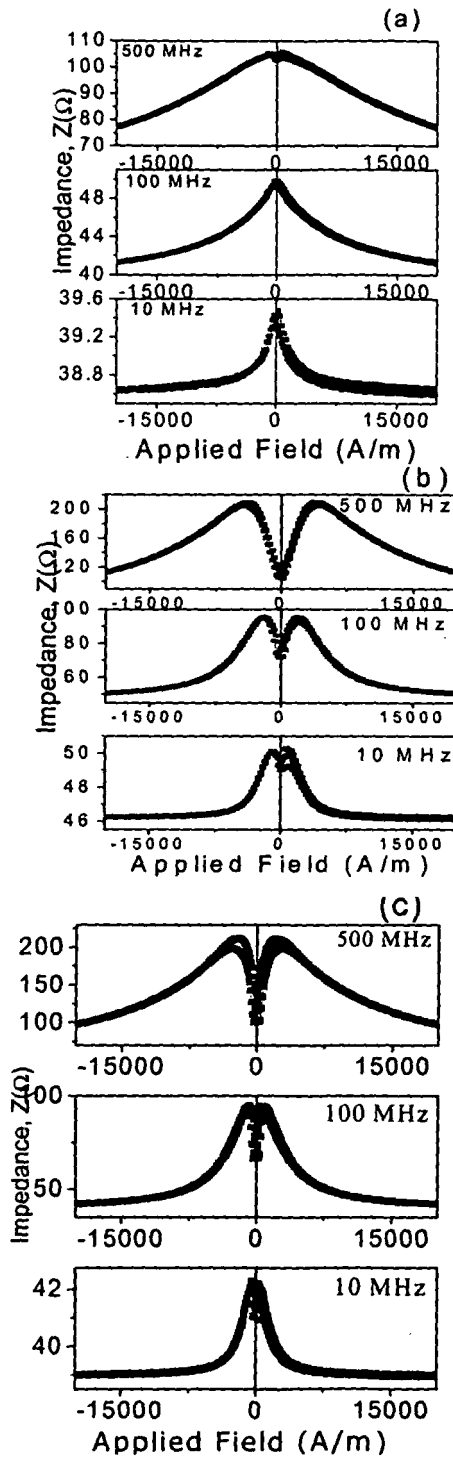


Fig.2. DC magnetic field dependence of the impedance of $\text{Fe}_{75.5}\text{B}_{13}\text{Si}_{11}\text{Mo}_{0.5}$ (a), $\text{Fe}_{3.7}\text{Co}_{69.8}\text{Ni}_1\text{Si}_{11}\text{B}_{13}\text{Mo}_{1.5}$ (b) and $\text{Co}_{77.5}\text{Si}_{7.5}\text{B}_{15}$ (c) glass-coated amorphous microwires with metallic nucleus diameter of about 15-20 μm

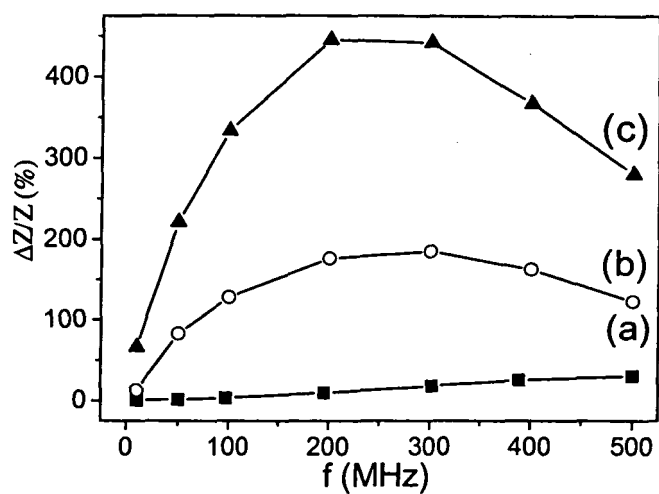


Fig.3 Frequency dependence of the $\Delta Z/Z_{\max}$ for different glass-coated thin amorphous wires:
 (a)- $\text{Fe}_{76}\text{Si}_{11}\text{B}_{13}$; (b)- $\text{Co}_{77.5}\text{Si}_{7.5}\text{B}_{15}$ and
 (c)- $\text{Co}_{68.5}\text{Fe}_{3.5}\text{Cr}_3\text{Si}_{11}\text{B}_{14}$ compositions.

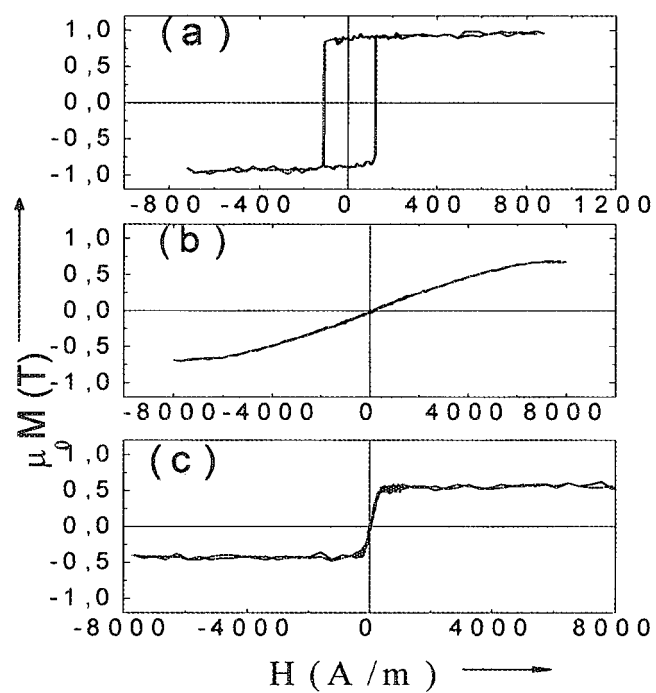


Fig.4. Axial hysteresis loops of $\text{Fe}_{75.5}\text{B}_{13}\text{Si}_{11}\text{Mo}_{0.5}$, $\text{Co}_{77.5}\text{Si}_{7.5}\text{B}_{15}$ and $\text{Fe}_{3.7}\text{Co}_{69.8}\text{Ni}_1\text{Si}_{11}\text{B}_{13}\text{Mo}_{1.5}$ glass-coated microwires respectively with different magnetostriction constant.

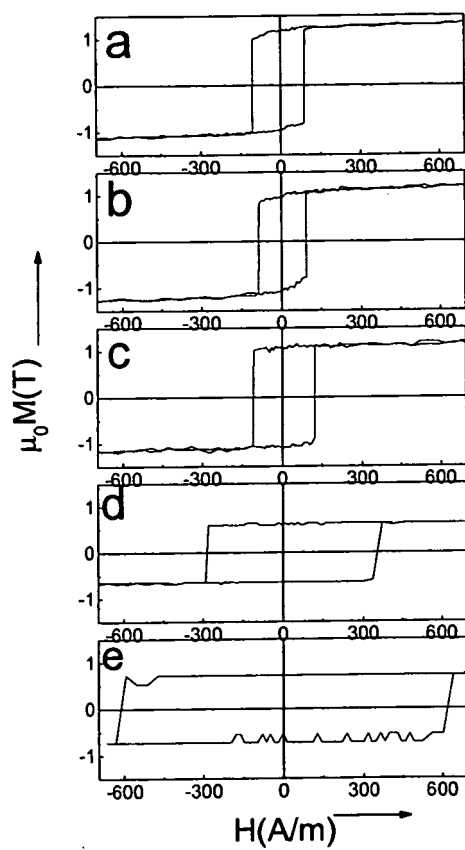


Fig.5. Hysteresis loops of FeBSiC microwires with metallic nucleus
Diameter of 15 μm (a), 13.5 μm (b); 11 μm (c); 6 μm (d) and 4 μm (e)

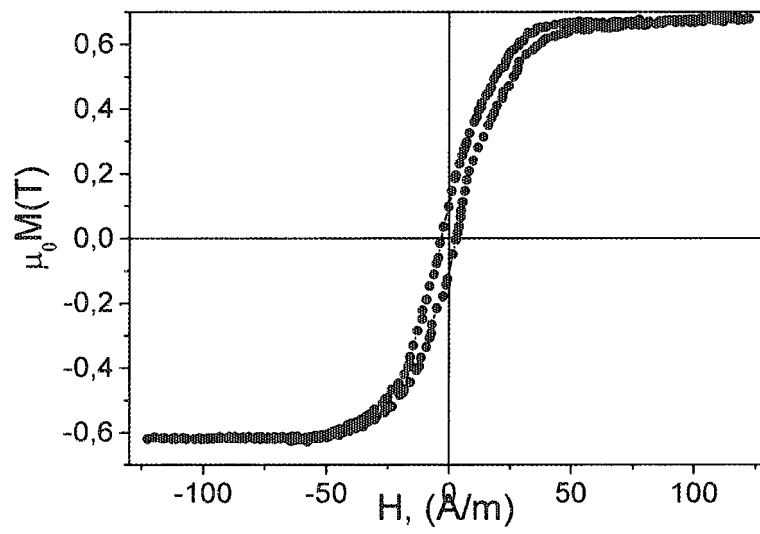


Fig. 6. Hysteresis loops of $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$ microwire.

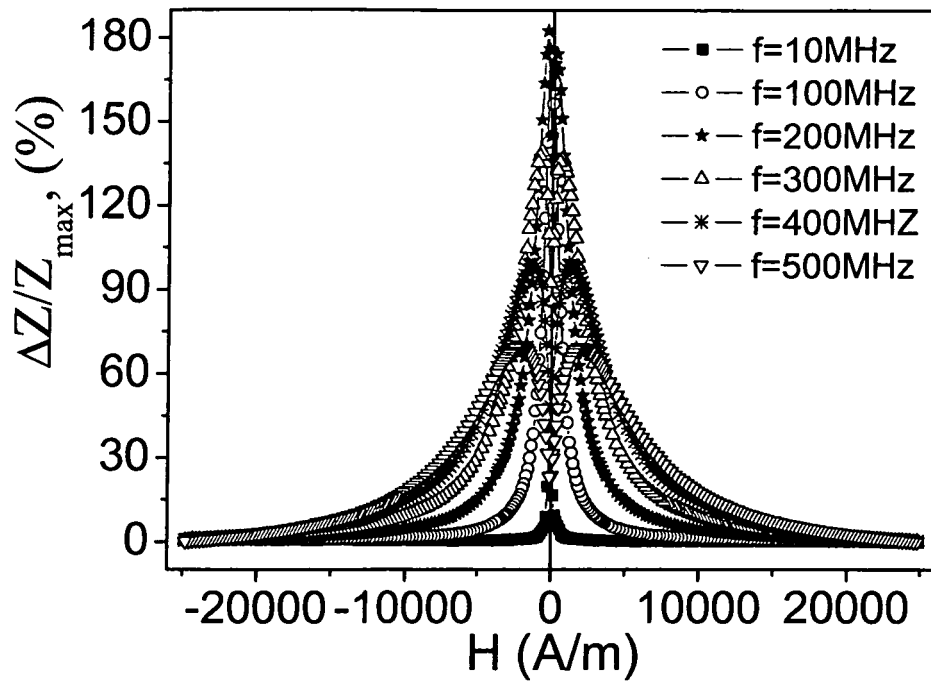


Fig. 7. GMI ratio of as-prepared $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$ measured at frequencies up to 500 MHz

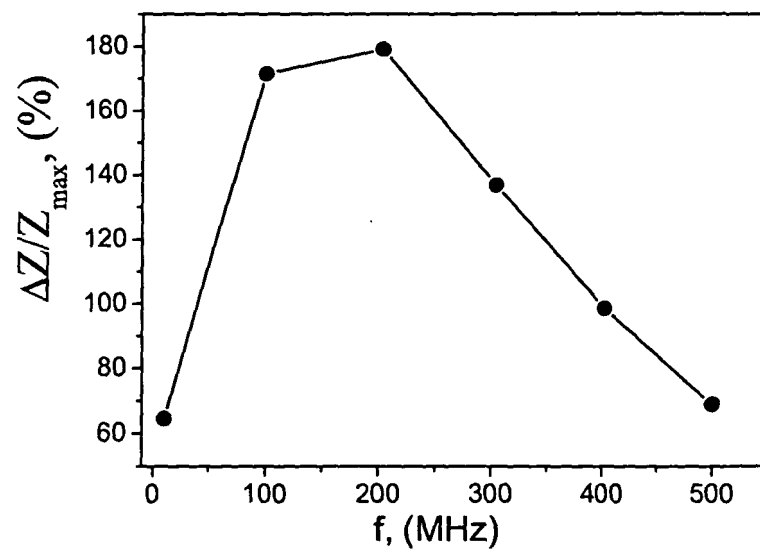


Fig. 8. Frequency dependence of the $\Delta Z/Z_{\max}$.

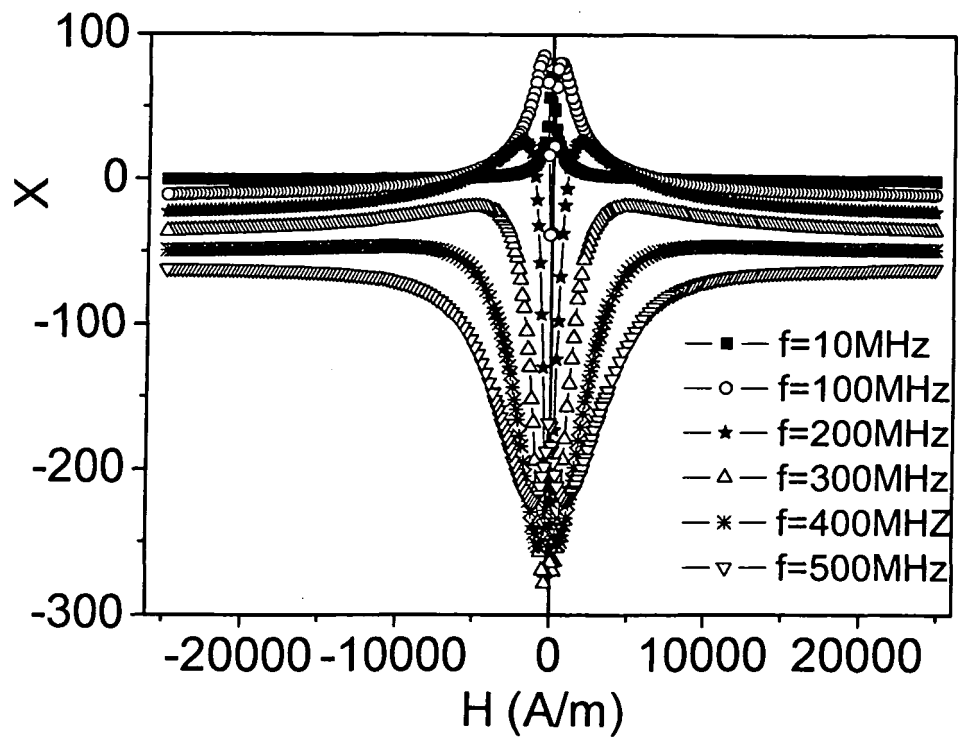


Fig. 9. Imaginary part the impedance, X , measured at different frequencies.

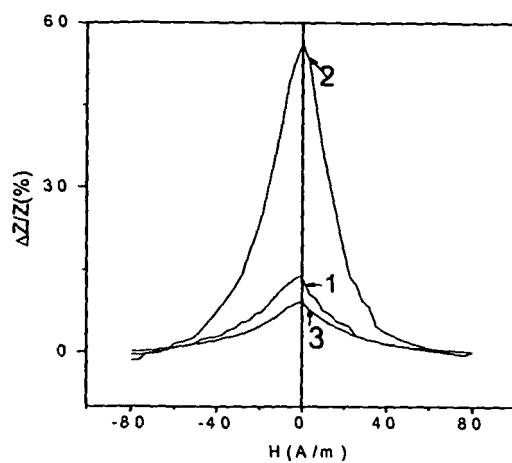


Fig.10. GMI effect of stress annealed of $Fe_{74}B_{13}Si_{11}C_2$ glass-coated microwire subjected to stress annealing for 40 min at different temperatures: 1- 265°C, 2- 275°C and 3- 400°C.

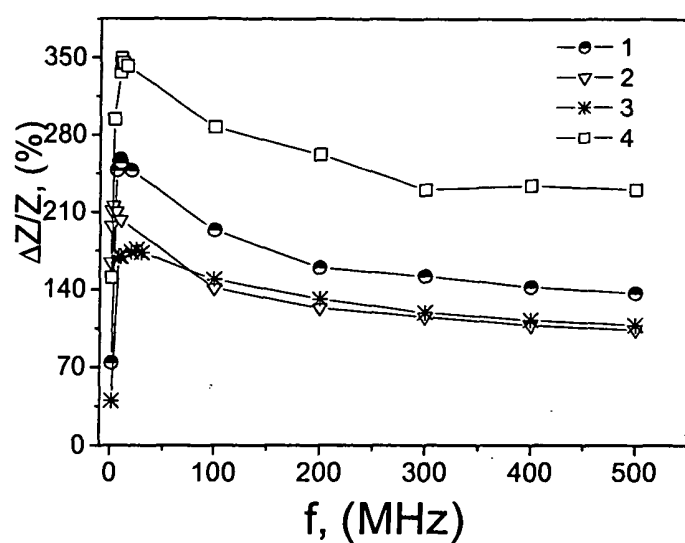


Fig.11. GMI ratio of $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$ microwires with metallic nucleus, d , and total diameter, D as: 1- $d=8,96\text{ }\mu\text{m}$, $D=10.29\text{ }\mu\text{m}$; 2- $d=9,17\text{ }\mu\text{m}$, $D=11.94\text{ }\mu\text{m}$; 3- $d=9,64\text{ }\mu\text{m}$, $D=10.66\text{ }\mu\text{m}$; 4- $d=9,78\text{ }\mu\text{m}$, $D=11,74\text{ }\mu\text{m}$

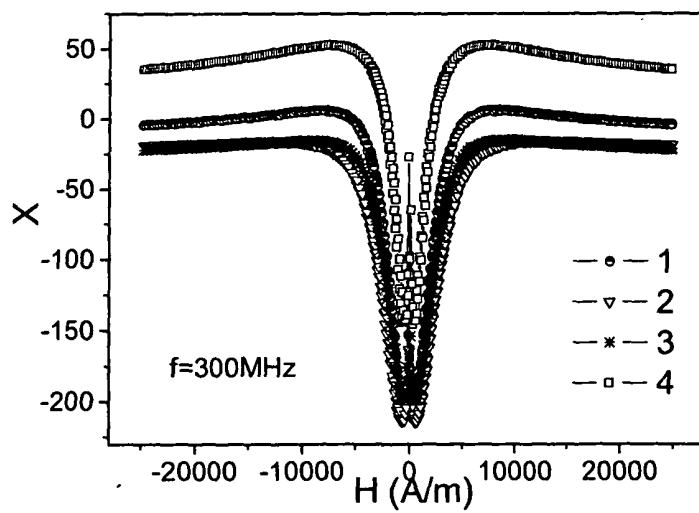


Fig.12. The imaginary part the impedance, X , of as-prepared $\text{Co}_{67.05}\text{Fe}_{3.84}\text{Ni}_{1.44}\text{Si}_{14.47}\text{B}_{11.51}\text{Mo}_{1.69}$ with metallic nucleus, d , and total diameter, D as 1- $d=8,96 \mu\text{m}$, $D=10.29 \mu\text{m}$; 2- $d=9,17 \mu\text{m}$, $D=11.94 \mu\text{m}$; 3- $d=9,64 \mu\text{m}$, $D=10.66 \mu\text{m}$; 4- $d=9,78 \mu\text{m}$, $D=11,74 \mu\text{m}$

REFERENCES CITED IN THE DESCRIPTION

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